Performance Test on Copper (II) Removal by Using Fabricated Thin Layer Composite

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***Abstract*—The fabrication of thin film composite (TFC) membrane by casting the hybrid membrane on the surface hydrophobic support membrane provides a remarkable improvement to the mechanical and thermal properties of the TFC membrane. Nowadays, the pollution of copper metal is a critical problem for environment due to its persistence and toxicity. This research paper outlines the use of TFC composite as a new technology for removal of copper ions from wastewater obtained from electroplating industry. As for analysis purpose, polymer blend of PVA/chitosan was used for copper ions removal as well. The industrial wastewater was characterized in term of biochemical oxygen demand (BOD), chemical oxygen demand (COD), turbidity, total suspended solid (TSS), pH value and concentration. The performance testing only focus on the effect of pH to the percentage removal and flux rate. Therefore, the pH was varied at 2.35 (without adjustment), 7 and 10. The result shows that the highest removal achieved at pH 7 for both composite. While, in term of flux rate, both composite was decreased with time by increasing the pH of feed solution. Due to hybrid membrane shows a consistent in removal, therefore the hybrid membrane is more preferred.**

***Keywords*—characterize wastewater, heavy metal, performance testing and thin film composite (TFC) membrane.**

I. Introduction

This research is to study the performance on the removal of the copper metal from industrial wastewater by using fabricated thin film composite membrane. Nowadays, the copper metal is one of the heavy metal widely used in rapid development of industries such as electroplating industries, mining operation, fertilizer industries, batteries, paper industries and pesticides tend to heavy metal in wastewater (Fenglian Fu & Wang, 2011). Unlike organic contaminants, heavy metals tend to accumulate in living organisms due to it is non-biodegradable (Mohsen Arbabi & Golshani, 2016). Thus, the pollution of heavy metal is a critical problem for environment due to persistence and toxicity (Suat, Kiskan, Aksu, Balkis, & Yagci, 2016). Generally, heavy metals are considered those whose density exceeds 5g/cm^3 (Barakat, 2011).

Copper (Cu) is a naturally discovered from the earth's crust. It is remark as one of the earliest known toxic metals (Shrivatava, 2009). Mostly, copper originated from anthropogenic (industrial and domestic) discharges owing to the corrosion of copper at drainage system. Copper commonly exists in surface waters as the primary form copper ion (Cu^{2+}). Furthermore at low concentration, it becomes vital trace element to all plant and animals and mainly for human (Suat et al., 2016). For instance, copper is essential for human to proper functioning and metabolic processes and also for plant and animal where copper play a main role in various oxidation-reduction reaction. In contract, at high concentration it shift to highly toxic for aquatic organism such as fish and molluscs (Suat et al., 2016)

Therefore, various technique for the treatment of metal contaminated wastewater, for instances reverse osmosis, chemical precipitation, ion exchange, adsorption and photocatalysis (Jaros, Kaminski, Albinska, & Nowak, 2005). However, higher cost is the major drawback for all those method. Other limitation for those method are production of sludge that requires further treatment, incomplete metal removal from wastewater, unable to reduce the concentration of wastewater below the effluent limit and require of using higher energy. Thus the application of membrane technology in industrial wastewater treatment has become one of key solution in order to remove the copper metal in wastewater. However, the existing commercial membrane also has some limitations such as membrane fouling, lower efficiency at lower copper concentration and higher operating cost (M Arbabi & Golshani, 2016).

Thus, thin film composite (TFC) membrane which represent integrated complexation method is introduced as a new technology for heavy metal removal. The integrated complexation method for composite membrane is a new invention for the composite membrane technology. This method used similar principle separation method with complexation ultrafiltration method. However, this integrated method provides more efficient in separation owing to the combination of complexation of heavy metals and separation process in one equipment. TFC membrane is fabricated from film hybrid membrane as the barrier layer and polysulfone as porous membrane as shown in Figure 1.1(Barakat, 2011). According to (Rahman, Hafizh, & Fathel, 2016), the complexation occurs on hybrid membrane layer that consists of a polymer blend of polyvinyl alcohol (PVA) and chitosan as organic polymer and cross-linked with tetraethylorthosilicate(TEOS). Formulation of hybrid membrane and porous membrane is formulated by using sol-gel method and phase inversion method respectively (Rahman et al., 2016).

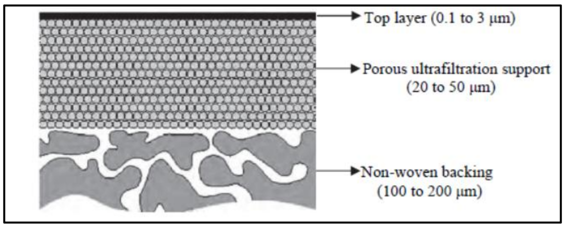


Figure 1.1: The structure of composite membrane (Mayur Ramesh Dalwani, 2011)

Chitosan is widely used in different industries sectors such as medical industry, textile industry and pharmaceutical. It is also used in wastewater treatment, food processing, cosmetic and also agriculture due to chitosan has a good coagulation properties, high permeability and tensile strength (He, Xu, & Li, 2015). Chitosan has reactive amino and hydroxyl functional groups, non toxic and environmental friendly as well as low-cost (El-hefian, Nasef, & Yahaya, 2010). Chitosan as a new biosorbent that able to performed highest sorption capacity for several metal ions to removal of heavy metal ions from industrial wastewater (He et al., 2015). Therefore the uses of chitosan for membrane preparation technology have become great interest because of its promising various remarkable advantage for heavy metal separation such as copper.

According to Li Yi Ye, Qing Lin Liu, Qiu Gen Zhang, Ai Mei Zhu, & Zhou (2007),polyvinyl alcohol (PVA) can be classified as hydrophilic materials. Mostly, PVA is used in the dehydration of organic solvent due to its unique properties, for instance it's have strong hydrophilicity, film-formation ability properties and good physical and chemical properties and also excellent in stability. Application of this polymer is widely used in biomaterial, drug delivery system, membrane preparation, recycling of polymer and packaging (Bahrami, Kordestani, Mirzadeh, & Mansoori, 2002). Formation of PVA is prepared by dissolving another polymer which is polyvinyl acetate (PVAc) in alcohol solution like methanol with the presence of alkaline catalyst such as sodium hydroxide or potassium hydroxide (Britannica, 2016)

Generally, sol-gel method is applied for the formulation of organic-inorganic hybrid materials (Sinica, Dhawade, & Jagtap, 2012) .Sol-gel method has been most appropriate method for formulation of hybrid membrane due to its simplicity and easy to handle. The most important thing, material blending is applicable to produce high purity homogenous hybrid materials through sol-gel method. Addition of TEOS with material blended provides hybrid membrane stability such as good mechanical strength and higher water selective permeability. While, formulation of polysulfone membrane act as porous support layer is formulated by phase inversion method. The phase inversion method can be defined as transformation of polymer form liquid phase to solid phase (Rahman et al., 2016). This is illustrated in Figure 1.2.

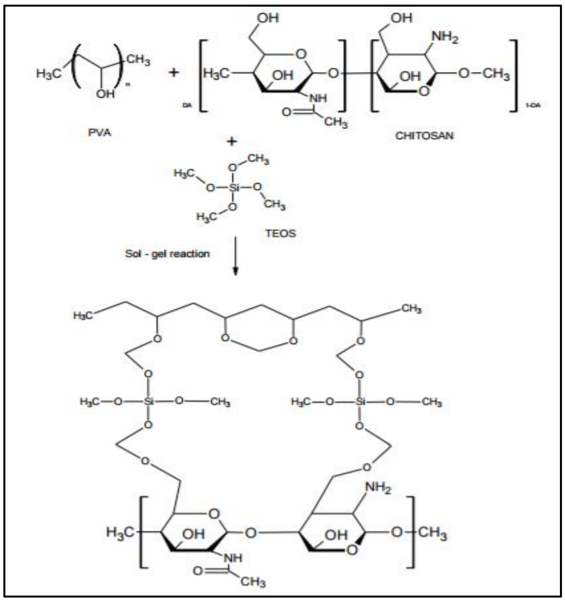


Figure 1.2: Interaction between polymers blending of PVA/Chitosan and cross linked with inorganic polymer, TEOS by the sol-gel method to form a hybrid membrane.

Two modes used for membrane filtration which are dead end filtration and cross-flow filtration. For this research dead end filtration is applied as mode of filtration which is known as batch filtration (Munir, 2006). The dead end filtration can be defined as the flow of water is perpendicular to the membrane surface. Dead end filtration was functioning by applied pressure will be used to push the water through the membrane. Furthermore, for this type of filtration, there is no rejected water because all the water at dead end cell will be passed through as the permeated. While, the accumulated particle on the membrane filter tend to increased resistance and decline permeate flux will inhibit the filtration process. Therefore, the filtration process needs to be stopped in order to remove particulates or replace the membrane (Munir, 2006).

The main objective of the research to characterize the wastewater that containing Cu (II) ions and to investigate on the percentage removal of Cu (II) ions using the fabricated thin film composite (TFC) membrane.

II. METHODOLOGY

A. Materials

To characterize the wastewater, the wastewater from Company Y that containing Cu (II) ion is used; deionized water and solvent used for BOD test such as Ferric Chloride, Magnesium Sulfate, Calcium Chloride, Phosphate buffer obtained from Faculty of Civil Engineering UITM Shah Alam; COD reagent as a digestion solution for COD with range 20-1500mg/L that obtained from HACH COMPANY WORLD HEADQUARTERS; nitric acid and distilled water. Materials used to formulate base support membrane is polysulfone resin pellet (MW: 44,000-53,000) and 1-methyl-2-pyrrolidone (NMP). 3% tetra-ortho silicate (TEOS) used as hybrid solution to formulate thin film composite membrane.

B. Formulation of Base Support Membrane

The support membrane is prepared through phase inversion technique. The 13g of polysulfone resin pellet was dissolve in the 87g solvent which is 1-methyl-2-pyrrolidone (NMP) in order to prepare 13wt% of polysulfone solution. Then, the solution mixture was stirred continuously for five hours, while the solution was heated at 60˚C to form homogenous mixture. Then, the homogenous solution was left to cool at room temperature in order to remove air bubbles. After the polysulfone was prepared, the solution was cast onto glass plate by using casting knife, while the thickness was adjusted to 90 µm. Then, the polysulfone membrane was keeping in the coagulation bath for about 24 hours and maintained at room temperature. Lastly, the membrane was placed in oven around 1 hour for completely dried (Rahman et al., 2016).

C. Production of Thin Film Composite Membrane

To prepare the thin film composite membrane, polysulfone that act as the base support membrane was placed on the glass plate. Then, a few drop of hybrid membrane solution that has been prepared previously was cast on the base support membrane (PSF). Then, thin layer hybrid membrane on top composite membrane was cast by using glass rod. After that, the prepared thin film composite membrane was left at room temperature for 24 hours for curing. Next, prior to the performance testing and characterization of the thin film composite membrane, the membrane was dried in an oven for 1 hours at 45˚C (Nurul Aida Sulaiman et al., 2016).

D. Characterization of Wastewater

The industrial wastewater obtained from Company Y was added with a few drop of nitric acid to maintain the concentration of Cu (II) ions in wastewater. After that, the wastewater are properly stored in the dark room and at a low temperature. Then, the wastewater was characterized by using the tests below:

i. Biochemical Oxygen Demand (BOD)

Firstly, to ensure the proper biological activity during BOD test, the wastewater sample must be free of chlorine and between pH 6.5-7.5. 2 L of deionized water is filled inside 2 L of beaker. After that, the deionized water was aerated around 1 hour. 2 mL of each solvent was added into 2L of beaker that containing dilution water by using micro pipette. Specialized 300 mL BOD bottle was used which should allow full filling and no air space. Two BOD bottle was filled with 50mL of wastewater respectively, then top up with dilution water until reached neck of bottles. One BOD bottles containing the wastewater with cap was properly stored inside dark incubator at 20˚C for 5 days. While, another one bottle without cap was tested on that day by using BOD Test System to measure initial dissolved oxygen concentration. After 5 days, the stored wastewater was tested by BOD Test System to measure a final dissolved oxygen (DO) concentration. The DO reading was recorded and BOD_5 can be determined.

ii. Chemical Oxygen Demand (COD)

For COD Test, one vial was marked as a "blank" and another vials was labelled as "wastewater" that contain Cu (II) ions by using COD vials with range 20-1500 mg/L. Each vial was contained of 2 mL of COD reagent with orange color appearance. In the case of the "blank," 2 mL of deionised water was added to the corresponding vial. While, 2mL of wastewater was added to another vials. Then, mixed well and then the color of wastewater was observed. Then, no change in color for wastewater sample where the sample remain in orange color. The samples are placed into COD reactor for two hours at 150˚C. After 2 hours, waited until temperature drop to 120˚C and take out all vials from COD reactor to cooling rack for about 15 minutes to allow the vials cooled down to room temperature. Then, COD reading was read by put cooled vials inside the spectrometer where it was set with program code 435.

iii. Total Suspended Solid (TSS)

10mL of insulin water was filled into sample cell and marked as blank sample. Another 10mL of wastewater is marked as copper samples. The blank cell was placed into spectrometer and zero button was pressed to obtain zero value. Then, continued with copper sample and read button was pressed to obtain the value of TSS.

iv. Turbidity

The wastewater sample that containing Cu (II) ions was filled fully inside the corresponding bottle sample. Then, the sample was placed inside turbidimeter. The reading of turbidimeter in NTU was recorded.

v. pH test

Firstly, electrode of pH meter was placed inside the wastewater sample and the measure button was pressed. Then, the electrode will leave in the sample around 1-2 minutes. Once the reading has stabilized, the measure button was pressed again. Therefore, the pH value was showed. Lastly, the electrode is rinse using distilled water and dried it with lint-free tissue.

vi. Concentration

Atomic absorption spectroscopy (AAS) was used to determine the concentration of a wastewater sample from that containing copper ions. 1 mL of sample was poured into 100 mL volumetric flask. Then, distilled water was filled until reached line on its neck. Then, the solution was shaken well and the dilution solution was analysed using AAS. The calibration curve and absorbance of the sample is used to obtain the concentration of the sample.

E. Performance Testing

To carry out performance testing of both types of fabricated thin film composite (TFC) by using dead end filtration, pH adjustment of feed Cu (II) ions solution was conducted in order to evaluate the effect of pH on percentage removal of Cu (II) ions and flux rate. Therefore, pH was varied at 2.35 (without pH adjustment), 7 and 9 by adding caustic (sodium hydroxide) into the solution and then as resulted a metal hydroxide solid or precipitate is formed (Ayres, Davis, & Gietka, 1994). According to Ayres, Davis, & Gietka (1994), the high pH of feed solution corresponds to high hydroxide concentration. To investigate the percent Cu(II) ion removal and flux rate, the adjusted pH of feed solution was carried out by using membrane filtration RIG at pressure 14 bars and then the sample volume was collected every 1 hours. Thus, the permeate flux (J), $mL/cm^2.min^{-1}$ was determined by using the Eq. (1).

$$Flux,\ J = \Delta V / A.\Delta t \qquad (1)$$

Where, ΔV (mL) is the volume of permeate sample, A is an effective membrane area in cm^2, and Δt is permeate time.

Then, the permeate sample was collected for metal analysis by using Atomic Absorption Spectroscopy (AAS) (Rahman et al., 2016). AAS is an instrument to measure the concentration of copper ions inside permeate solution. Then, the rate of percentage copper ions removal was determined by using the Eq. (2).

$$R\% = (C - C_{permeate} / C) \times 100 \qquad (2)$$

Where, $C_{permeate}$ is the permeate concentration and C is the concentration inside the test cell.

III. RESULTS AND DISCUSSION

A. Characteristic and Sampling of Wastewater

Based on analyses, conducted on the wastewater is below the effluent limit. Thus, the wastewater obey the Standard (B) of Environmental Quality (Sewage and Industrial Effluents) Regulation 1979 and Environmental Quality Acts 1974. However, only two parameter not obey the Standard B which is pH value and concentration of wastewater, supposedly the pH effluent limit is 5.5-9 but the wastewater is too acidic. Therefore, neutralization step was required to save aquatic life While, Standard B state that the concentration of copper metal is 1.0 mg/L. Thus, the wastewater do not comply the industrial effluent due to concentration too high. Therefore, the copper metal must be removed from wastewater to reduce the effect to the environment. The typical characteristic of industrial wastewater is illustrated in Table 1.1.

Table1.1: Typical Characteristic of Industrial Wastewater

Parameter	Reading
Biochemical Oxygen Demand (BOD_5)	8.49 mg/L
Chemical Oxygen Demand (COD)	21 mg/L
Total Suspended Solis (TSS)	51 mg/L
Turbidity	1.66 NTU
pH test	2.21
Concentration	2.77×10^2 mg/L

B. Effect of pH of feed solution on copper (II) ions removal

The effect of pH is an important parameter on the adsorption of copper ions due to its effect the solubility of the metal ions, degree of ionization of the adsorbate during reaction and also effect the concentration of opposite ions on the functional groups of adsorbent (Abdelwahab, Hassan, Mostafa, & Sadek, 2016). The impact on copper ion removal with various pH (acidic, neutral, and alkaline) of feed solution were carried out by different membrane which is composite membrane with hybrid membrane of thin layer and composite membrane with polymer blended of PVA/chitosan. For the membrane from polymer blend layer, no removal of copper (II) ions was observed. In contrast for hybrid membrane, in acidic of feed solution without pH adjustment, the percentage removal is about 32.84% only for first hour. While, another two hours the hybrid membrane can't withstand with high pressure resulting of no removal observed. However, the percentage of copper removal is too high where it has achieved more than 90% when in neutral (pH=7) and alkaline (pH=10) condition for both membranes respectively. Based on research, the highest percentage of copper removal occurred at pH 7 and 10 due to copper ions inside feed solution formed insoluble precipitate and then adsorption is increased (Ayres et al., 1994). But, with the increase time of adsorption, composite membrane with hybrid membrane shows a consistent value unlike that with polymer blend where the value decreased. This is illustrated in Table 1.2 and Figure 1.3 (a) to (c).

Table 1.2: Percentage of Copper Removal from feed solutions.

pH	Hours	Composite membrane with polymer blended PVA/chitosan (%)	Composite membrane with hybrid membrane (%)
Without pH adjustment (2.35)	1	0	32.84
	2	0	0
	3	0	0
7	1	99.91	99.90
	2	99.87	99.89
	3	99.85	99.93
10	1	99.92	99.80
	2	99.91	99.87
	3	99.14	99.87

Further research found that the combination of chitosan/PVA result the amine group that present in PVA is protonated especially in acidic media and by addition of TEOS will assists to the agglomeration ability that promotes surface of adsorption (Rahman et al., 2016).

Therefore, the optimum pH for copper ion removal for both membranes is pH 7 and pH10 of the feed solution. Kassim Shaari et al. (2016), also discovered similar performance in their research studies. While hybrid membrane is much better in removal of copper ion especially at pH 7 compare to composite membrane with polymer blended with PVA/chitosan layer. In order to avoid the effect of hydroxide precipitation, pH 7 was selected (Rahman et al., 2016).

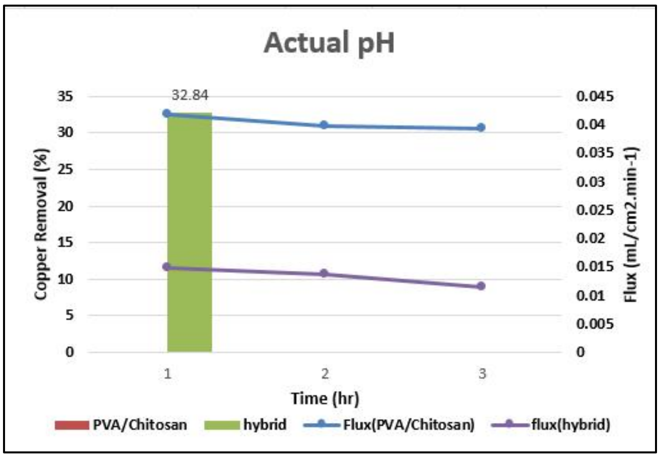
C. *Effect of pH on permeate flux rate*

From Figure 1.3(a) to (c) it can be seen the trend of permeate flux rate by varying the pH values. The graph illustrate at the higher in permeate flux for both hybrid membrane and polymer blended with PVA/ chitosan layer at acidic condition. Mayur Ramesh Dalwani (2011), also found the similar behaviour in their research. Hence, permeate flux decreases with time and increasing with pH of feed solution owing to decreasing of driving force (A.Mohammed, Al-Alawy, & Hussein, 2015). This is illustrated in Table 1.3.

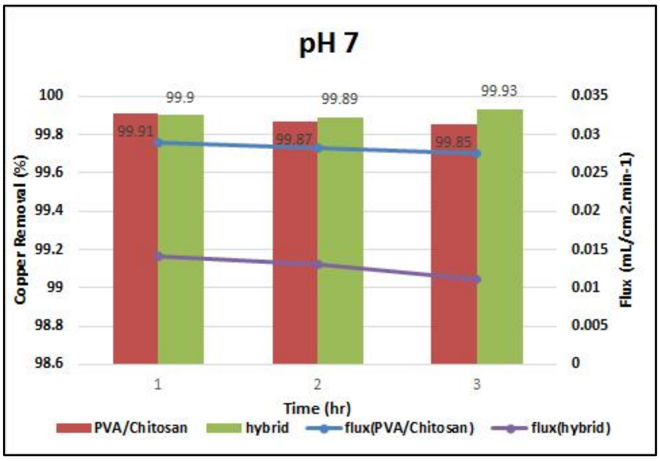
Table 1.3: Permeate flux of sample from wastewater solution

Membrane	pH	Flux (mL/cm^2.min)		
		J_1	J_2	J_3
Composite membrane with polymer blended with PVA and chitosan layer	Without pH adjustment (2.35)	0.0418	0.0399	0.0393
	7	0.0289	0.0283	0.0276
	10	0.0283	0.0246	0.0238
Composite membrane with hybrid membrane at thin layer	Without pH adjustment (2.35)	0.0148	0.0137	0.0114
	7	0.0141	0.0130	0.0111
	10	0.0134	0.0125	0.0106

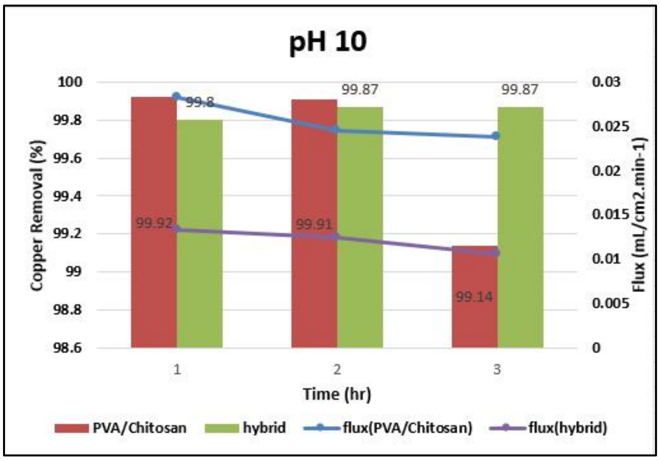
*operate at pressure 14 bar with 1 hour time interval by using 17.3495cm^2, area of porous support.



(a)



(b)



(c)

Figure 1.3 (a) to (c): Percent removal of Cu (II) ions and permeate flux of composite membrane with hybrid membrane of thin layer and composite membrane with polymer blended with PVA/chitosan layer.

IV. Conclusion

Based on Standard B, all parameter used for characterize wastewater was comply the effluent limit. However, both concentration and pH parameter was not obey the Standard B. Thus, the application of membrane technology in industrial wastewater treatment has become one of key solution in order to remove copper ions in wastewater. Based on the performance testing, it show that composite membrane with hybrid membrane of thin layer was selected as the best membrane for removal of copper (II) ions at optimum pH 7 as compare to composite membrane with polymer blend. Based on the result, the adsorption of heavy metal that containing in industrial wastewater such as copper (II) ions is more effective at high pH compare to low pH. Thus, the process in removing heavy metal by using integrated complexation method is successful.

RECOMMENDATIONS

For further improvement on this research, the calcium carbonate can be used to adjust the pH of feed solution in order to reduce the precipitation. Furthermore, the characterization of wastewater must be repeat again after the filtration process in order to make sure wastewater comply the effluent limit (Standard B).

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