Removal of Cu(II) Ions from Wastewater Through the Integrated Complexation Process

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Abstract: In this study, a wastewater from electroplating industry had been used as the source of copper ion. As the pH and concentration of copper were exceeded the allowable limit for effluent discharge for standard B, treatment on the wastewater was given through thin film composites to reflect the integrated complexation process where two types of barrier layers were used and they are membrane from polymer blend Chitosan/Polyvinyl Alcohol (PVA) and hybrid membrane, respectively. Results showed that composite with hybrid membrane displayed better performance and pH 7 of feed solution was found as the best parameter.

Key words: Copper, wastewater, thin film composite, characterization, pH, solution

INTRODUCTION

Globalization and industrialization have become one of the factors that caused the environmental issues rises rapidly. The environmental issues such as air pollution, water pollution, greenhouse effect and soil sediment are normally caused by the chemical industries. One of the major concerns is the discharge of high concentration heavy metals in receiving water.

Heavy metals are the elements with relatively high density and can become toxic at low concentrations. They also give bad effects to environment and human if it is produced uncontrollably. Thus, to reduce the emission of heavy metals in wastewater, there are various methods that can be effectively used in order to ensure the concentration of the contaminants conform to the guidelines of Environmental Quality Act 1974 Malaysia which an act that relates to control the environment from being polluted (Gunatilake, 2015).

Copper (Cu) is naturally discovered from the earth's crust which is remarked 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+}). At low concentration, it becomes vital trace element to all plants and animals and are mainly for human (Taskin *et al.*, 2016). Copper is essential for human for proper functioning and metabolic processes and also for plants and animals where copper plays a main role in various oxidation-reduction reaction. However, at high concentration, it becomes highly toxic for aquatic organism such as fish (Taskin *et al.*, 2016).

There are several established methods of heavy metal removal such as chemical precipitation, ion-exchange, adsorption, membrane filtration and electrochemical treatment (Fu and Wang, 2011; Yasim *et al.*, 2016; Maarof *et al.*, 2017). However these processes have significant disadvantages such as incomplete removal, high energy consumption and production of toxic sludge (Barakat and Schmidt, 2010; Aeisyah *et al.*, 2013). Polymer complexation-ultrafiltration on the other hand has been proven as a technology to separate heavy metals from wastewater (Barakat and Schmidt, 2010). Several types of water-soluble polymeric ligands that have shown powerful material to form complexes with heavy metal ions are chitosan and chitin as biopolymer and synthetic macroligands such as carboxylmethyl cellulose, poly (acrylic acid), polyvinyl alcohol and polyvinyl ethylenimine (Barakat and Schmidt, 2010). The complexing agents are added to the fed water to form high molecular weight with heavy metal ions which is then prevented to pass through the ultrafiltration/nanofiltration membranes. However, the drawback of polymer complexation-ultrafiltration process is a higher amount of polymer to be utilized (Bessbousse *et al.*, 2008). Besides that there is a risk of severe fouling on a membrane's surface due to lower diffusivity of the large-size complexed species and their lower hydrophilicity after charge coupling in the complexes (Mbareck *et al.*, 2009).

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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 (Bessbousse *et al.*, 2008).

In this process which is called as the integrated complexation process, the complexation process of heavy metals and its separation occur simultaneously on the membrane's surface. This method provides more efficient in separation owing to the lesser amount of polymer to be used and also lesser area to be occupied (11). Therefore, in this study, the separation process of copper ion was carried out through the thin Film Composite (TFC) membrane which reflects the integrated complexation process. The TFC membrane was fabricated from hybrid membrane as the barrier layer and polysulfone as the porous support. The hybrid membrane was formulated from polymer blend of Polyvinyl Alcohol (PVA) and chitosan which was then cross linked with Ttetraethyl Orthosilicate (TEOS).

As one of the raw materials in this study, chitosan is widely used in different industries such as medical industry, textile industry and pharmaceutical. It is also used in wastewater treatment, food processing, cosmetic and also agriculture due to its good coagulation properties, high permeability and tensile strength (He *et al.*, 2015). Chitosan is a nontoxic and environmental friendly material as well as low-cost (El-hefian *et al.*, 2010). Chitosan is a bio sorbent that is able to perform high sorption capacity for several metal ions such as copper and ferum ions from industrial wastewater because it contains reactive amino and hydroxyl functional groups (He *et al.*, 2015).

Although, chitosan is a strong adsorbent to remove heavy metals but it has low mechanical properties and poor chemical resistance. Therefore, in this study, a blend of chitosan/Polyvinyl Alcohol (PVA) is selected as the polymer matrix which is cross-linked with Tetraethyl Orthosilicate (TEOS) as inorganic material by sol-gel method. Besides ensuring strong binding affinities toward selected metal ions and high metal ion adsorption capacities, this cross-linking process is conducted to stabilize the chitosan from degradation and blending with PVA will improve its chemical resistance and mechanical properties (Kumar *et al.*, 2009). Generally, sol-gel method is applied for the formulation of organic-inorganic hybrid materials (Dhawade and Jagtap, 2012) due to its simplicity and ease of handling. Formulation of polysulfone membrane as the porous support layer is through phase inversion method. In this study, polysulfone with 13 wt. % had been chosen as the concentration for support membrane (Sulaiman *et al.*, 2016a, b). The main objective of this study is to characterize the wastewater that

contains Cu(II) ions and to evaluate the performance of the fabricated thin film composite membrane on the removal of these ions. In this study the pH of feed solution was varied and for the purpose of investigating on the significance improvement portrayed by TFC with hybrid membrane as the barrier layer, another TFC with membrane from polymer blend of chitosan/PVA was used as a control.

MATERIALS AND METHODS

Few liters of wastewater had been collected from electroplating industry (Company A) that contains copper ions. For preservation purpose, a few drops of nitric acid wereadded into the wastewater before the containers were stored in the cold room. Chemicals involved in the characterization of wastewater include deionized water and solvents for Biochemical Oxygen Demand (BOD) test such as ferric chloride, magnesium sulfate, calcium chloride and phosphate buffer. Other materials include Chemical Oxygen Demand (COD) reagent as a digestion solution for COD with a range of 20-1500 mg/L, nitric acid and distilled water. All the reagents for wastewater characterization were purchased from Merck, Malaysia.

In the preparation of thin film composite membrane, the material used were polyvinyl alcohol with a hydrolysis degree of 87-89% (MW: 85, 000-124, 000), polysulfone resin pellet (MW; 44,000-53,000), Tetraethylorth osilicate (TEOS) with 99% purity, hydrochloric acid with 37% purity as catalyst, acetic acid and commercial chitosan (deacetylation degree 84.81.2%). All of these chemicals were obtained from Sigma Aldrich, Malaysia. 1-methyl-2-pyrrolidone (purity 99%) was obtained from Merck, Malaysia.

Fabrication of thin film composite membrane: The preparation of the hybrid membrane solution was according to Sulaiman *et al.* (2016a, b). For the preparation of 13 wt.% polysulfone as the support membrane, 13 g of polysulfone resin pellet was dissolved in 87 g 1-methyl-2-pyrrolidone. The mixture was then stirred continuously for 5 h at 60°C. The homogenous solution was left to cool at room temperature in order to remove air bubbles. After that, the solution was cast onto a glass plate by using a casting knife with a thickness of 90 μm. Then, the polysulfone membrane was kept in the coagulation bath for about 24 h at room temperature. Lastly, the membrane was heat-cured in an oven at 45°C for 1 h (Sulaiman *et al.*, 2016a, b). In the preparation of the thin film composite, polysulfone that act as the base support membrane was placed on the glass plate. Next, the hybrid membrane solution was

poured onto the base support membrane. A thin layer of the solution was cast by using a glass rod. After that, the thin film composite membrane was left in a room temperature for 24 h for curing. Next, prior to the performance testing of the thin film composite membrane, the membrane was dried in an oven for 1 h at 45°C (Sulaiman *et al.*, 2016a, b).

Characterization of wastewater: The wastewater was characterized by using the tests.

Biochemical Oxygen Demand (BOD): The BOD test was conducted according to standard method ASTM D888. Firstly, 2 L of deionized water was filled inside 2 L of beaker. After that, the deionized water was aerated for 1 h. About 2 mL of each solvent was added into the beaker by using a micro pipette. Specialized 300 mL BOD bottle was used which should be filled until the brim with no air space. Two BOD bottles were used where 50 mL of the wastewater was filled inside each bottle. Then each bottle was topped up with dilution water until full volume. One bottle was capped and stored inside a dark incubator at 20°C for 5 days. Next, another bottle was being tested by using BOD Test System to measure initial dissolved oxygen concentration. After 5 days, a final Dissolved Oxygen (DO) concentration was tested on the stored bottle. The DO reading was recorded and BOD_5 was determined.

Chemical Oxygen Demand (COD): The COD test was conducted according to standard method ASTM D1252-9. Two COD vials with range of 20-1500 mg/L were used where one vial was marked as 'blank' and another one as 'wastewater'. The 2 mL of COD reagent with orange color was added into each vial. Then, 2 mL of deionised water was added into the 'blank' vial and 2 mL of wastewater was added to 'wastewater' vial. The mixture was mixed well and then the color of wastewater was observed. The samples were placed in the COD reactor for two hours at 150°C. The vials were transferred to a cooling rack and left for 15 min to allow the vials to cool down to room temperature. Finally, COD of wastewater was recorded through a spectrometer where it was set with program code 435 (Fig. 1).

Total Suspended Solid (TSS): The TSS test was conducted according to standard method ASTM 208D. 10 mL of insulin water was filled into sample cell and marked as blank sample. About 10 mL of wastewater was filled into another sample cell. The blank cell was placed into spectrometer and zero button was pressed to obtain zero value. It was then replaced with the cell that contained the wastewater and the value of TSS was recorded.
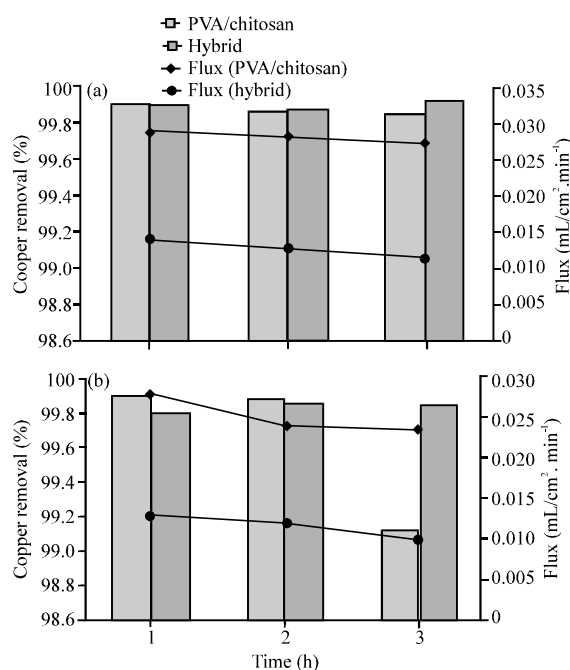

Fig. 1: Percentage removal of Cu(II) ions and the permeate fluxes at: a) pH 7 and b) pH 10 by using composite membrane with two types of barrier layers

pH test: About 50 mL of the wastewater was poured into a beaker. Next, the electrode of pH meter was immersed into the wastewater. The pH reading was recorded once the stable reading was achieved.

Concentration of copper ions: Atomic Absorption Spectroscopy (AAS) was used to determine the concentration of copper ions in the wastewater. The 1 mL of water sample was poured into 100 mL volumetric flask. The distilled water was then filled inside the flask until it was full. The solution was shaken well and the dilution solution was analysed by using AAS. Prior to the analysis, the sample dilution was carried out to generate a calibration curve for the metal. From the calibration curve, the concentration of copper ions in the waste water was identified.

Performance testing: Prior to the treatment process by using the fabricated Thin Film Composite (TFC), pH adjustment was carried out on the wastewater by adding caustic (sodium hydroxide) into the solution. pH was adjusted to pH 7 and 10. After that the filtration process was carried out by using membrane filtration rig at a pressure of 14 bars. The permeated sample was collected every 1 h. Then, the permeate flux (J), $mL/cm^2.min^{-1}$ was determined by using Eq. 1:

Table 1: Characteristics of wastewater in comparison with standard B effluent discharge

Parameter/unit	Standard B	Wastewater (Company A)
Biochemical Oxygen Demand (BOD$_5$) mg/L	50	8.49
Chemical Oxygen Demand (COD) mg/L	100	21.00
Total Suspended Solis (TSS) mg/L	100	51.00
pH	5.5-9	2.21
Copper (mg/L)	1.0	277.00

Table 2: Percentage of copper removal from wastewater by using different formulations of barrier layer

pH	Hours	Composite membrane with polymer blend of chitosan/PVA (%)	Composite membrane with hybrid membrane (%)
2.21	1	0.000	32.840
	2	0.000	0.000
	3	0.000	0.000
7	1	99.910	99.900
	2	99.870	99.890
	3	99.850	99.930
10	1	99.920	99.800
	2	99.910	99.870
	3	99.140	99.870

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

Where:

V (mL) = The Volume of permeate sample
A = An effective membrane area in cm^2
t = The filtration time

Then, the sample was also analyzed by using Atomic Absorption Spectroscopy (AAS) to measure the concentration of copper ions. The percentage of copper ions removal was determined by using the Eq. 2:

$$R = \frac{(C-C_{permeate})}{C} \times 100 \quad (2)$$

Where:

$C_{permeate}$ = The Copper ion concentration in the permeate solution
C = The Concentration of copper ion in the feed solution

RESULTS AND DISCUSSION

Characteristic of the wastewater: The characteristics of industrial wastewater must comply to the standard B of effluent standard by standard B of the environmental quality (Sewage and Industrial Effluents) Regulation 1979 and the Environmental Quality Acts 1974 before it could be discharged to the river or drainage system. Based on result from the characterization analysis as shown in Table 1, it was observed that all parameters are within the allowable range of the effluent standard except for pH and concentration of copper ion. The concentration of copper is too high compared to standard B and pH of wastewater is too acidic. Based on Table 1, a neutralization step was required as a pretreatment for the wastewater before discharging. This is done in order to save the aquatic life.

It was anticipated that the treatment by using the fabricated thin film composite membrane could reduce concentration of copper in the wastewater.

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 the effecton the solubility of the metal ions, degree of ionization of the adsorbed material during reaction and also on the concentration of opposite ions on the functional groups of adsorbent (Abdelwahab *et al.*, 2016). Based on Table 2, at pH 2.21, no removal of copper (II) ions was observed for membrane from polymer blend layer throughout 3 h of filtration time. In contrast to hybrid membrane, 32.84% removal was achieved for first hour of filtration but no removal was observed for the next 2 h. However, at pH 7 and 10 both types of membrane portrayed a good performance where more than 99% of copper ion could be removed. Based on the previous research by Ayres *et al.* (1994) the highest percentage of copper removal occurred at pH 7 and 10 because copper ions inside the feed solution formed insoluble precipitate and therefore the adsorption is increased. However, with the increase in the filtration time until three hours, the composite membrane with hybrid membrane layer shows a slight increase in percentage copper removal unlike that with polymer blend where the value decreased. This situation could be related to a better mechanical properties with the presence of TEOS in the hybrid membrane as compared to membrane from the polymer blend of Chitosan/PVA (Sulaiman *et al.*, 2016a, b).

Furthermore, the increase in the adsorption ability of the hybrid membrane towards the copper ion as compared to that without TEOS could be related to the situation as described by Sulaiman *et al.* (2016a, b) that the combination of chitosan/PVA resulted to a protonation of the amine group in PVA, especially in acidic media that

Table 3: Permeate fluxes from filtration at different pH of feed solution with two formulations of barrier layer

Membrane/pH	Flux (mL/cm².min)		
	J_1	J_2	J_3
Composite membrane with polymer blend of chitosan/PVA layer			
2.21	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			
2.21	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 of sampling by using 17.3495 cm² of effective membrane area

happens during sol gel reaction. Furthermore, by addition of TEOS, it will enhance the agglomeration ability to promote more surface of adsorption. Based on Table 2, pH 7 was found to be an optimum parameter for feed solution on copper ion removal with the advantage to avoid the effect of hydroxide precipitation and also due to comparable performance with pH 10 of feed solution (Sulaiman *et al.*, 2016a, b).

Effect of pH on permeate flux rate: Table 3 shows the values of permeate flux by varying the pH of feed solution with two formulations of the barrier layer. Based on Table 3, fluxes were higher at the acidic condition of the feed solution which could be correlated with zero removal of copper ion by the barrier layer from polymer blend as depicted in Table 2. Based on Table 3, it was illustrated that the fluxes decreased with the increase in the filtration time. This situation was due to the concentration polarization where more copper ions were retained on the membrane and caused a resistance to the flow (Gohil and Ray, 2009). Another trend was observed where with the same type of barrier layer, the fluxes decreased with the increase in pH. A similar behavior was also observed by other research where the decrease in permeate flux with time and the increase in the flux with pH of feed solution were owing to decreasing of driving force (Mohammed *et al.*, 2015). However, as compared to composite membrane with polymer blend, composite membrane with hybrid membrane showed a lower flux for each pH of feed solution. This phenomenon was arisen from the denser structure of hybrid membrane resulting from the incorporation of TEOS (Shaari and Rahman, 2013). But this slight weakness could be compensated with better removal of copper ions as depicted in Table 2 and good mechanical and thermal properties of the hybrid membrane as reported by Shaari and Rahman (2013).

CONCLUSION

Based on the results obtained, treatment of the wastewater by using thin film composite with hybrid

membrane was able to reduce the concentration of copper ion in the solution until 0.27-0.36 mg/L which comply to the Standard B of effluent. Hybrid membrane was preferred than polymer blend due to it portrayed an increment in percentage removal of copper throughout the filtration time unlike the polymer blend that showed a decrement. pH 7 was selected as the optimum pH as compared to pH 10 for feed solution due to a comparable percentage copper removal at both pH.

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