Variation of Membrane's Thickness : The Effect of Membrane's Performance on Copper (II) Ion

Soraya Nanis Hamdan, Dr Norin Zamiah Kassim Shaari, and Nurul Aida Sulaiman,

Faculty of Chemical Engineering, Universiti Teknologi Mara

Abstract— The purposes of this study are to characterize the industrial wastewater containing Copper (II) ion and to evaluate the performance of Composite membranes on the removal of Copper (II) ion. The integrated complexation method is used as its benefit is to overcome the restrictions of the existing methods in removing the heavy metal ions. For the characterization of wastewater, the result has shown that the water samples need to undergo further treatment before being discharged to the groundwater as the analysis results are out of the acceptable range of Environmental Quality (Industrial Effluent) Regulations 2009. Before performing the performance testing, the pH of the water sample was altered to 7 as the pre-treatment. Two types of composite membrane with i) A polymer blend of PVA and Chitosan as thin layer and ii) Hybrid membrane as thin layer, of thickness 60µm and 90µm were used. The final result shows that Composite membrane with Hybrid membrane as thin layer of 90µm was the best membrane to be used to filter the water sample with the removal percentage of 99.67%. Besides that, it has fulfilled the Environmental Act's requirement which the copper ion concentration need to be less than 1ppm.

Keywords— Chitosan, Copper ion, composite membrane, hybrid membrane, industrial wastewater

I. INTRODUCTION

Heavy metals pollution has become one of the most critical environmental problems today. It can give a very harmful risk to the public health and environment because of its hazardousness. The hazardousness depends on its ignitability, corrosivity, toxicity and reactivity. Some of the hazardous heavy metals are Lead, Cadmium, Zinc, Nickel, Manganese and Copper [1].

Copper is one of the most electrically conductive of all the metal elements. It has a physically bright reddish-brown in $^{\text{color}}$ which can take on green-hued patina when it is exposed to corrosive environments. Pure Copper has a very high melting point of 1083℃ and it is associated with complex formation in biological systems. Copper is an important engineering metal which is widely used for various engineering purposes. For instance, it is used for manufacturing of several alloys, ceramics and pesticide. Besides that, it is also used in manufacturing of electrical appliances, wires, electronics, automotive and etc [3].

Copper is a toxic metal that causes a disease named "Wilson's Diseases" [2]. It causes harmful biochemical effects, toxicity and hazards in living organisms including human and other living things. Its toxicity leads to severe mucosal irritation, corrosion, white spread capillary damage, hepatic and ranal damage, and central nervous system irritation followed by depression. Therefore, it is important to control the content of Copper concentration especially in industrial wastewater [2].

Industrial wastewater which contains high proportions of dissolve organic and inorganics solid, suspended solids, alkalinity or acidity and their different constituents may not be in same proportion as they exist in a normal domestic sewage. Every effluent has its standard before being discharged. In Malaysia, under an Environmental Act 1974, there is a regulation named as Environmental Quality (Industrial Effluent) Regulations 2009. One of the objectives of this regulation including to monitor a standard acceptable conditions for the discharge of the industrial and mixed effluent. Therefore, it is important to characterize the industrial wastewater so that the safeness to reuse it back for varied purposes can be ensured [16].

There are five types of characteristics of wastewater which are physical, chemical, biological, solids and chemical composition characteristics. Under those characteristics, the turbidity, Chemical Oxygen Demand (COD), pH, Biochemical Oxygen Demand (BOD), Total Suspended Solid (TSS) and the concentration of the metal ion (Cu^{2+}) are the parameters selected to be analysed.

The wastewater containing heavy metals should be pre-treated before being discharged to the environment. There are many methods to be used for pre-treatment and treatment of the wastewater, for instance physical separation, chemical and biochemical pre-treatment, ion-exchange processes, adsorption, simple reverse osmosis, physical-chemical treatment, solvent extraction, cementation, electrodialysis, photocatalysis, precipitation floatation and membrane filtration. From these methods, the most recommended as an effective and economical method is adsorption due to its capability in removing the suspended solid, organic compound, and inorganic contaminant particularly heavy metals.

However, treatment by membrane filtration that using a thin film composite membrane will be discussed further in this chapter because of its benefit to overcome the restrictions of the existing method in removing the heavy metal ions. Thin film composite membrane is one of the types of membrane filtration that composed of two layers bonded together so that it can withstand the mechanical stresses generated by the operating conditions [7]. Hybrid membrane is a combination of polymer materials that composed at least two different polymers of organic and inorganic materials. In this research, a dense ultrathin rejection layer were developed which is made up of polymer blend of polyvinyl alcohol (PVA) with chitosan and cross linked with inorganic polymer as barrier layer of TFC membrane. The porous support layer is made up of polysulfone membrane. The chitosan has been claimed as unique because of its properties as chelating agent and its ability to absorb various organic compound including heavy metals effectively [1].

The objectives of this study are to characterize the industrial wastewater containing Copper (II) ions and to evaluate the performance of composite membrane on the removal of Copper (II) ions. There are two types of composite membrane used which the first is composite membrane with a polymer blend of PVA and chitosan as the thin layer, the other one is composite membrane with Hybrid membrane as a thin layer. The performances of the composite membranes were evaluated by using two different thicknesses, which are 60 and $90\mu m$. The samples of wastewater containing copper ion was obtained from Electroplating industry of Company A in Seksyen 27, Shah Alam. The first sample was named as Copper I solution, which was collected from the chroming line of the industry and the concentration of the copper ion is very high since it has not been treated yet. Second sample was named as Copper II solution, which was collected at the settling tank of the industry. Both samples were used for the characterization of wastewater, meanwhile only Copper II solution was used for the composite membrane performance's testing.

II. METHODOLOGY

A. *Materials*

1. *Preparation of Composite membrane with a polymer blend of PVA and Chitosan as thin layer*

The materials required for the preparation of composite membrane that were obtained from Sigma Aldrich, Malaysia are :

Polyvinyl Alcohol (PVA) with hydrolysis degree of 87-89% with a molecular weight between 85,000-124,000. Polysulfone resin pellet with a molecular weight between 44,000-53,000. Hydrochloric acid with 37% purity as catalyst. Commercial chitosan with deacetylation degree between 84.8 $\pm$ 1.2%

The material obtained from Merck, Malaysia is 1-methyl-2-pyrrolidone (NMP) with a purity of 99%. The deionized water was also used as a solvent. All of these materials were employed without further purification.

2. *Preparation of Composite membrane with Hybrid membrane as thin layer*

The materials required for the preparation of thin film composite membrane that were obtained from Sigma Aldrich, Malaysia are :

Polyvinyl Alcohol (PVA) with hydrolysis degree of 87-89% with a molecular weight between 85,000-124,000. Polysulfone resin pellet with a molecular weight between 44,000-53,000. Tetraethylorthosilicate (TEOS) with 99% purity. Hydrochloric acid with 37% purity as catalyst. Commercial chitosan with deacetylation degree between 84.8 $\pm$ 1.2%

The material obtained from Merck, Malaysia is 1-methyl-2-pyrrolidone (NMP) with a purity of 99%. The deionized water was also used as a solvent. All of these materials were employed without further purification.

Hybrid membrane solution and polymer blend of PVA and Chitosan solution.The material obtained from Merck, Malaysia is 1-methyl-2-pyrrolidone (NMP) with a purity of 99%. The deionized water was also used as a solvent. All of these materials were employed without further purification.

B. *Methods*

1. *Preparation of Polysulfone Support Membrane*

The phase inversion technique was used for this preparation. 13g of polysulfone beads was dissolved in 87g of N-methyl-2-pyrollidone (NMP) to produce polysulfone polymer solution of 13wt% polymer concentration. The solution was stirred continuously for approximately 4 to 6 hours at 60℃ until it became homogenous. The solution was left for several hours at room temperature to remove air bubbles. The applicator was used to cast the polysulfone solution onto the glass plate with adjusted thickness. The film was immersed in the water as a coagulation medium for one hour. The film was left in a large amount of water for 24 hours. The film was cured in an oven for one hour.

2.Preparation of Composite membrane with a polymer blend of PVA and Chitosan as thin layer

The thin film composite membrane consists of hybrid membrane as the barrier layer and polysulfone membrane as the support layer. A thin layer was formed by coating the 2 wt% chitosan concentration in 10 wt% PVA solution onto polysulfone support membrane by using a glass rod. The membrane produced was left for 24 hours at room temperature and was cured in an oven for one hour at 45℃.

3. Preparation of Composite membrane with Hybrid membrane as thin layer

The thin film composite membrane consists of hybrid membrane as the barrier layer and polysulfone membrane as the support layer. A thin layer was formed by coating the hybrid membrane with 2 wt% chitosan concentration in 10 wt% PVA solution onto polysulfone support membrane by using a glass rod. The membrane produced was left for 24 hours at room temperature and was cured in an oven for one hour at 45℃.

4.Characterization of Industrial Wastewater

The characterization of the industrial wastewater including Turbidity, COD, TSS, BOD, pH, and Copper ion concentration was determined by using turbidity meter, spectrometer, BOD test meter, pH meter and AAS respectively.

5.Performance Testing of Composite Membrane

i) Membrane Filtration Rig

The pH of 100 mL of wastewater sample was altered to 7. Then, it was filled into the membrane rig filtration which installed with the desired membrane for filtration process. The pressure was constant for each type of membrane.

ii) Atomic Adsorption Spectrometer (AAS)

Atomic Absorption measurement for Copper was made by using a polarised Zemen Z-2000 Hitachi. Flame atomic absorption spectrometer was equipped with hollow cathode lamps of photon at condition 324.8 nm of wavelength, 7.5 mA of current, 2.0 L/min air-acetylene, 1.3 nm of bandpass, 0.75 cm of burner height and 0 to 30 mg/L of standard interval

iii) Flux Performance

Flux performance is the rate of solute or particle transport in the feed side from the bulk solution toward the membrane. The pressure-driven flow across the membrane convectively transports solutes toward the upstream surface of the membrane. If the membrane is partially, or completely, retentive to a given solute, the initial rate of the solute transport toward the membrane, J.C, will be greater than the solute flux through the membrane, J.C_p. This causes the retained solute to accumulate at the upstream surface of the membrane. This phenomenon is generally referred to as concentration polarization (*Aimar,1993).* Flux can be calculated by using the formula as follows :

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

where J is the flux rate (mL/cm².min) , V is the volume of the filtered sample (mL), A is the membrane surface area (cm²) and t is the time taken to collect each sample (min).

iv) Percentage Removal

The percentage removal performance is referred to the amount of Copper (II) ion, Cu^{2+} being removed from the initial solution. This removal indicates the capability of the membrane to filter the Copper (II) ion, Cu^{2+} contained in the water sample. The removal percentage performance can be calculated as follows :

$$\% \text{ Removal} = \frac{Initial\ copper\ (II) conc. - Final\ copper\ (II) conc.}{Initial\ copper\ (II) concentration} \times 100 \quad (2)$$

III. RESULTS AND DISCUSSION

A. *Characterization of Industrial Wastewater*

By comparing the results from Table 1 with the allowable conditions in Table 2, turbidity and BOD for Copper I and Copper II solution are under acceptable conditions. On the other hands, for the COD, pH, TSS and Copper ion concentration for the three solutions, it was found out that they are out of the acceptable range except for COD for Copper II solution. Therefore, it was confirmed that the three solutions need a further treatment before they can be discharged to the groundwater.

Table 1 : The result of the characterization of Industrial Wastewater

Parameter	Value	
	Copper I solution	**Copper II solution**
Turbidity	45 NTU	1.66 NTU
COD	6300 mg/L	21.3 mg/L
pH	0.31	2.21
BOD	1.65 mg/L	0.67 mg/L
TSS	10433.33 mg/L	51.33 mg/L
Copper ion concentration	55,318 mg/L	277.20 mg/L

Table 2 : Standard B for industrial mixed effluent

Parameter	Value
Turbidity	50 NTU
COD	200 mg/L
pH	5.5 – 9.0
BOD	40 mg/L
TSS	100 mg/L
Copper ion concentration	1.0 mg/L

B. *Performance Testing of the Composite Membrane*

In this experiment, the two types of composite membranes with, i) A polymer blend of PVA and chitosan as thin layer and ii) Hybrid membrane as thin layer of thickness 60μm and 90 μm were used. The experiments were conducted for three hours and the filtered samples were collected every one hour. Then, the performances of the composite membrane in term of flux and percentage removal of Copper (II) ions were evaluated. Before the filtration was made, the pH of Copper II solution was altered to 7 as the pre-treatment of this experiment.

1) Flux Performance

From Figure 1 and Figure 2, the flux performance of Membrane A and Membrane B of 90 μm is lower than Membrane A and Membrane B of 60 μm across the time. By referring to the relation between volume and flux in Formula A, it shows that the lower the volume of the filtered water sample collected, the lower the flux performance. This is due to the concentration polarization where the retained solute accumulated at the upstream surface of the membrane which causes only certain amount of liquid to pass through it. Not only that, there are various resistances that hindering mass transfer through the membrane including the boundary layer, gel layer, pore blocking and adsorbed layer resistance [21].

By giving a closer look to the flux rate of Membrane A of 60 μm at the 3rd hour, it shows that the flux is slightly increased than the 2nd hour. This indicates that the membrane was reducing in strength during the third hour causes the volume to slightly increase from before. On the other hand, this problem did not occur towards Membrane B as it has a good mechanical property. From Figure 3 it shows that the flux performance of Membrane A of 60 μm is the highest, followed by Membrane A of 90 μm and Membrane B of 60 μm and lastly Membrane B of 90 μm. What differ these four membranes is not only the thickness of the polysulfone membrane, but also the coating of the membrane itself.

Since Membrane B is coated with PVA, chitosan and TEOS, it causes the membrane becomes compact and less porous compared to Membrane A which is only coated with PVA and chitosan. Therefore the permeability of the Membrane B become lower compared to Membrane A. Apart from that, these results indicate that the concentration polarization of Membrane B is higher where the retained solute of Membrane B were accumulated more on the membrane surface compared to Membrane A.

Table 3 and Table 4 showing the volume of permeate and the calculated flux for three hours.

Table 3 : Volume of the filtered sample in three hours

Composite Membrane	Thickness	Volume (mL)		
		1st hour	**2nd hour**	**3rd hour**
Membrane A	**60μm**	19.60	17.90	18.10
	90μm	13.10	12.90	12.70
Membrane B	**60μm**	17.10	12.50	12.40
	90μm	13.70	11.10	10.90

Table 4 : Flux Performance of the composite membranes in three hours

Composite Membrane	Thickness	Flux, J (mL/cm^2.min)		
		1st hour	**2nd hour**	**3rd hour**
Membrane A	**60μm**	0.01883	0.01720	0.01739
	90μm	0.01258	0.01239	0.01220
Membrane B	**60μm**	0.01643	0.01201	0.01191
	90μm	0.01316	0.01066	0.01047

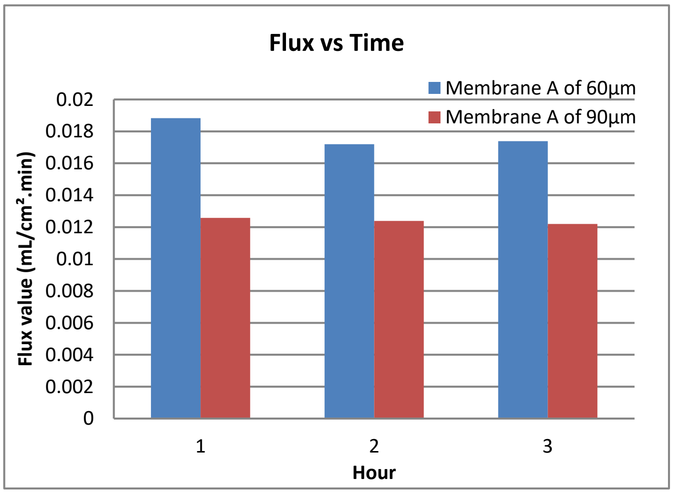

Figure 1 : Flux Performance of membrane A in three hours

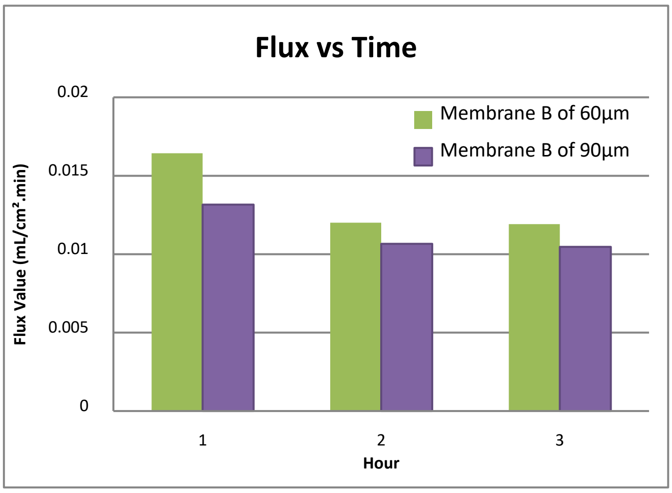

Figure 2 : Flux of Membrane B in three hours

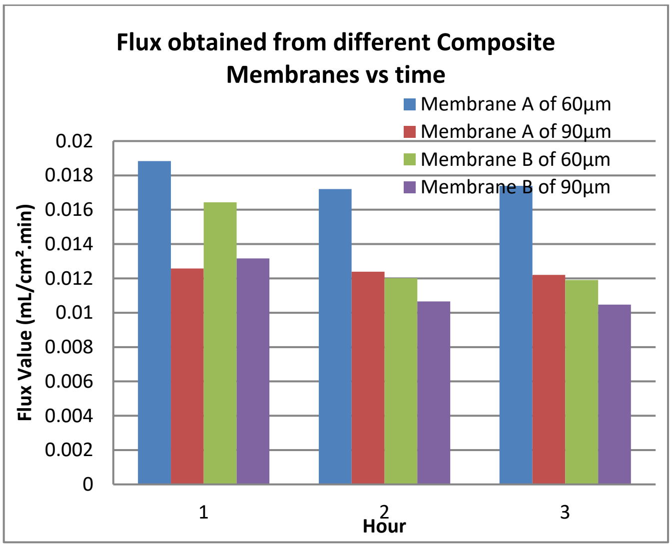

Figure 3 : Flux of Membrane A and B in three hours

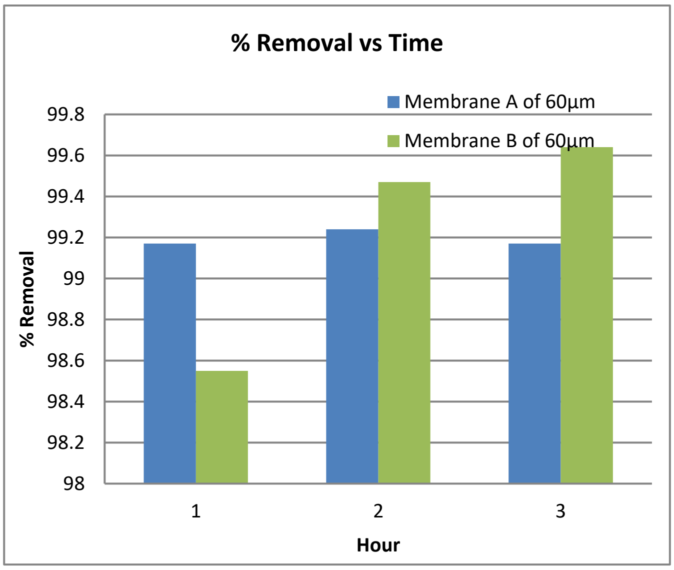

Figure 4 : The percentage removal of Membrane A and Membrane B of 60 µm in three hours

2) *Percentage Removal Performance*

From Figure 4, it shows that the removal percentage of Membrane B of 60 µm is higher than Membrane A of 60 µm, same goes to Figure 5 that shows the removal of Membrane B of 90 µm is higher than Membrane A of 90 µm. Besides that, the performance of membrane of thickness 90 µm was higher compared to 60 µm. This is because membrane of thickness 90 µm is compact causing it to have a higher permeation resistance compared to membrane of thickness 60 µm [22].

Figure 6 shows that the removal percentage of Membrane B is higher than Membrane A. The results indicate that the performance of both membranes from Membrane B is better than Membrane A. This is because, membrane B was coated with a cross linker TEOS which able to form a compact and less porous structure to the membrane which assists the membrane to trap more heavy metal ions compared to Membrane A which was not coated with TEOS.

For Membrane A of 60 µm, it shows decreasing performance at the 3rd hour. This resulted from the reducing in strength of the membrane at the third hour. The weakness in strength of the membrane was also proven as the volume and permeates flux of the membrane increases. It is therefore concluded that Membrane B of 90 µm is the best membrane showing the highest removal percentage of Copper (II) ions followed by Membrane B of 60 µm, Membrane A of 90 µm and Membrane A of 60 µm.

Table 5 : Removal percentage of the composite membranes in three hours

Composite Membrane	**Thickness**	**Removal percentage (%)**		
		1st hour	**2nd hour**	**3rd hour**
Membrane A	**60µm**	99.17	99.24	99.17
	90µm	98.87	99.02	99.20
Membrane B	**60µm**	98.55	99.47	99.64
	90µm	99.39	99.67	99.67

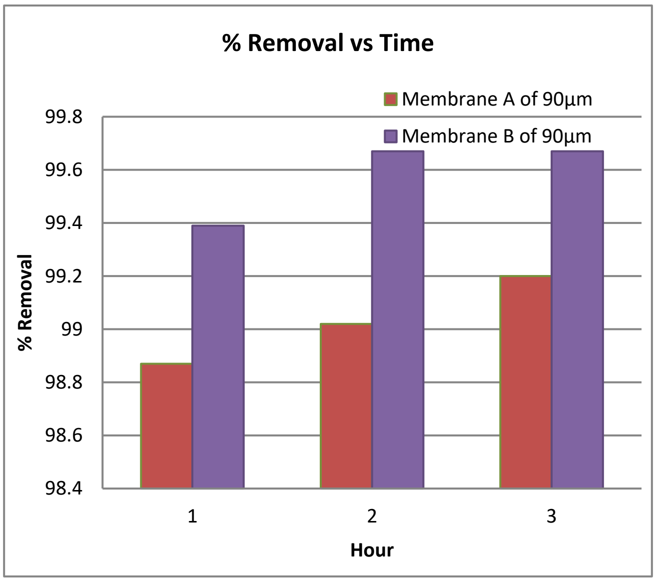

Figure 5 : The percentage removal of Membrane A and Membrane B of 90 µm in three hours

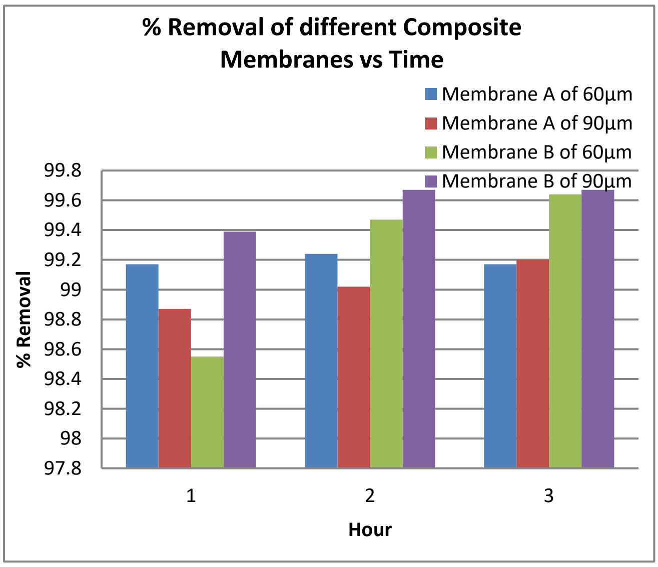

Figure 7 : The percentage removal of different Composite Membranes in three hours

3) Concentration of Copper (II) ions before and after filtration in three hours

From Table 6, it shows the initial and final concentration Copper (II) ions in the industrial wastewater before and after the membrane filtration. Therefore, based on Table 6, after the three hours of filtration, only Membrane B of 90 µm has fulfilled the act's requirements. The final concentration of copper (II) ions after three hours filtration for Membrane B of 90 µm is 0.92 ppm which is below the allowable condition. Therefore, it is concluded that Membrane B of 90 µm is the best membrane to be used to filter the industrial wastewater sample and the wastewater filtered by this membrane can be discharged directly to the groundwater.

Table 6 : Concentration of Copper ion before and after membrane filtration

Composite Membrane	**Thickness**	**Initial Copper (II) ions Concentration (ppm)**	**Final Copper (II) ions Concentration (ppm)**		
			1st hour	**2nd hour**	**3rd hour**
Membrane A	**60µm**	283.05	2.340	2.140	2.340
	90µm	277.70	3.130	2.735	2.222
Membrane B	**60µm**	282.58	4.105	1.490	1.010
	90µm	282.58	1.725	0.920	0.920

IV. CONCLUSION

From the experiment, Membrane A of 60 µm is not suitable to be used to filter industrial wastewater sample because it encounters a reducing in membrane strength at the third hour onwards. This was proven when the volume and permeate flux increases and the removal percentage decrease during the third hour. Meanwhile for Membrane A of 90 µm and Membrane B of 60 µm, even though both of these membranes do not encounter reducing in membrane strength problem, still they cannot be used to filter industrial wastewater because the final copper (II) ions concentration of the filtered sample was above the acceptable conditions and thus it does not fulfill the act's requirement. However, for Membrane B of 90 µm, it shows the best result of removal percentage of copper (II) ions. Besides that, the final concentration of the Copper (II) ions contained in the industrial wastewater sample is below the acceptable range for it to be discharged to the groundwater. In a conclusion, Membrane B of 90 µm is a favorable membrane to be used to filter Copper (II) ions in the industrial wastewater sample as it is high in removal performance and has fulfilled the Environmental Act's requirement for effluent discharge.

ACKNOWLEDGMENT

Thank you to my supervisor and co-supervisor, Dr Norin Zamiah Kassim Shaari and Nurul Aida Sulaiman and Universiti Teknologi Mara.

References

[1] Barakat, M.A ; (2011). New trends in removing heavy metals from industrial wastewater. *Arabian Journal of Chemistry,4, 361-377.*

[2] Shrivastava, A. K. (2009). A review on copper pollution and its removal from water bodies by pollution control technologies. *Indian Journal of Environmental Protection*, *29*(6), 552-560.

[3] Singh, R. (2005). Hybrid membrane systems—applications and case studies. *Hybrid Membrane Systems for Water Purification, Elsevier Science, Amsterdam*, 131.

[4] Negrea, A., Ciopec, M., Lupa, L., Muntean, C., & Negrea, P. (2008). Studies regarding the copper ions removal from waste waters. *Chem. Bull. POLITEHNICA Univ*, *53*, 93-97.

[5] Salam, O. E. A., Reiad, N. A., & ElShafei, M. M. (2011). A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents. *Journal of Advanced Research*, *2*(4), 297-303.

[6] Borbély, G., & Nagy, E. (2009). Removal of zinc and nickel ions by complexation–membrane filtration process from industrial wastewater. *Desalination*, *240*(1), 218-226.

[7] Arbabi, M., & Golshani, N. (2016). Removal of copper ions Cu (II) from industrial wastewater. *International Journal of Epidemiologic Research*, *3*(3), 283-293.

[8] Horsfall, M. J., Arbia, A. A., & Spiff, A. I. (2003). Removal of Cu (II) and Zn (II) ions from wastewater by cassava (Manihot esculenta Cranz) waste biomass. *African Journal of Biotechnology*, *2*(10), 360-364.

[9] Saniedanesh, M., Wan Alwi, S. R., & Abdul Manan, Z. (2013). Potential of heavy metal recovery from wastewater and sewage sludge.

[10] Sulaiman, N. A., Shaari, N. Z. K., & Rahman, N. A. (2016). Removal of Cu (II) and Fe (ii) Ions Through Thin Film Composite (TFC) With Hybrid Membrane. *JOURNAL OF ENGINEERING SCIENCE AND TECHNOLOGY*, 36-49.

[11] Sawyer, C. N., & McCarty, P. L. (1978). Chemistry for environmental engineers. *New York. Mc Graw-Hill Book Company*.

[12] Kiepper, B. (2010). Understanding Laboratory Wastewater Tests. *Organics (BOD, COD, TOC, O &G). The University of Georgia and Ft. Valley State University, Georgia, USA.*

[13] O'Dell, J. W. (1993). Determination of turbidity by nephelometry.

[14] Dogar, N. A., Nawaz, M., Majeed, M., & Saeed, A. B. Characterization and Treatment of Wastewater from Sapphire Textile Industry, Pakistan.

[15] Lewis, J. (1985). Pretreatment of Industrial Waste. *EPA J.*, *11*, 5.

[16] Environmental Requirements Department of Environment, Ministry of Natural Resources and Environment (2010).

[17] Tchobanoglous, G., & Burton, F. L. (1991). Wastewater engineering. *Management*, *7*, 1-4.

[18] Operation of municipal wastewater treatment plants: Study guide. (2007). Alexandria, VA.: Water Environment Federation.

[19] R. C. (Ed.). (n.d.). Thin Film Composite (TFC) - Reverse Osmosis Systems. Retrieved from http://reverseosmosischemicals.com/reverse-osmosis-guides/reverse-osmosis-glossary-terms/thin-film-composite-tfc-reverse-osmosis-systems

[20] W.S.W. Ngah, L.C Teong and M.A.K.M Hanafiah (2011). Adsorption of dyes and heavy metal ins by chitosan composites : A review, Carbohyd. Polym. *Vol 83, 4, 1446-1456.*

[21] Wenten, I. G., & Ganesha, J. (1996). Ultrafiltration in water treatment and its evaluation as pre-treatment for reverse osmosis system. *Institut Teknologi Bandung*.

[22] C. K. Yeom and K.-H. Lee, (1997) "A study on desorption resistance in pervaporation of single component through dense membranes," *Journal of Applied Polymer Science, vol. 63, no. 2, pp. 221–232.*

[23] A. Raisi and A. Aroujalian (2011). "Aroma compound recovery by hydrophobic pervaporation: the effect of membrane thickness and coupling phenomena," *Separation and Purification Technology, vol. 82, no. 1, pp. 53–62.*