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Effect of thickness of porous polysulfone membranes on removal of ferum ions

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Abstract

Membrane separation has been widely used in the removal of heavy metal from wastewater. Chemical precipitation, ion exchange, and adsorption are the examples of conventional treatment that have significance disadvantages which are incomplete removal and high energy consumption, thus lead to disposal of toxic sludge. In this research, the wastewater from electroplating industry containing high concentration of ferum ion was treated by using an integrated complexation method through a thin film composite membrane. The composite comprises of polysulfone as support layer with either polymer blend of PVA/chitosan and hybrid membrane respectively as the top layer. Treatment process was conducted at pH 7, room temperature, and pressure of 12 bar. The thickness of polysulfone was varied at 60 μm and 90 μm. Results showed that the treated wastewater contained ferum concentration below than the acceptable range and the composite membrane with hybrid membrane as thin layer with polysulfone at 90 μm thickness yield the best performance.

Article Info

1.0 Introduction

Hybrid membrane has good mechanical and thermal properties as compared to membrane from pure polymer (Ye et al., 2007) and it normally formulated from a combination of at least two different polymer materials (Wegst & Ashbyk, 2007). Polysulfone is prepared through phase inversion method where the process involves the transformation of the liquid or soluble state into a solid state (Mulder, 2000). The polysulfone in crystal form is subjected under high temperature until it melted. The high viscosity of polysulfone will eventually turn into solid after being soaked in water.

Chitosan is a biopolymer, which composed of abundant natural polymer called chitin (Muzzarelli, 1973). Chitosan has been claimed as unique material because the ability to act as chelating agent to form metal complexes (Majeti & Kumar, 2000; Wendy et al., 1999). It also consists of hydroxyl and amino groups which help to absorb various organic compounds effectively (Luo et al., 2005). However, it has poor mechanical stability and biodegradability (Zheng et al., 2000).

Ferum is one of the most abundant elements of the earth's crust. Its presence in groundwater above the allowable concentration will result in problems such as reddish water, metallic taste, odour, turbidity, staining of laundry, and plumbing fixtures (Das et al., 2007). For humans, the excessive consumption of ferum may lead to impairment of haematopoiesis by destroying the progenitor cells as well as the microenvironment for haematopoiesis. If ferum overload is left untreated, it may lead to hemochromatosis, which damages different organs of the body. As described by Khatri et al. (2017), there are few methods to remove ferum ions which comprises of conventional strategies, biological strategy, membrane technology-based strategy and nanotechnology-based strategy.

Membrane technology-based strategy includes polymer-enhanced ultrafiltration, which is widely used nowadays. This technology is considered as suitable alternative to replace the conventional techniques for ferum removal from aqueous systems due to high percentage of ferum could be removed (90%). However, it has limitations such as fouling membrane and cake formation which decrease the removal efficiency of the process after few cycles of operation (Khatri et al., 2017). Therefore, some improvements need to be done on this process. In this current study, the method to remove ferum ions is using thin film composite membrane which represents an integrated complexation method. This method is anticipated to overcome the limitation portrayed by polymer-enhanced ultrafiltration process because the adsorption

and filtration of the heavy metal ions occur simultaneously on the membrane's surface.

The thin film composite consists of hybrid membrane from polymer blend of PVA/Chitosan which is cross-linked with tetraethylorthosilicate (TEOS) as the barrier layer and polysulfone as the porous support. The purpose of coating the porous support with the barrier layer, is to improve the selective permeability of water, increase the performance on ferum ions removal as well as to improve the mechanical strength of the membrane. As for a control, the barrier layer from polymer blend of PVA/chitosan are formulated. The thickness of polysulfone was varied at 60 µm and 90 µm. Therefore, the purpose of this study is to investigate the effect of different thickness of polysulfone membrane as the support on the efficiency of thin film composite membrane to remove ferum ions from a wastewater solution.

2.0 Methodology

2.1 Characterisation of wastewater

All the reagents for wastewater characterisation (such as digestion solution for COD, ferric chloride, magnesium sulphate, calcium chloride, and phosphate buffer solution) were purchased from Merck, Malaysia. The characterisation of waste water such as biological oxygen demand (BOD), chemical oxygen demand (COD) and total suspended solid (TSS) analyses were conducted according to standard method ASTM D888, D1252-9, and ASTM D5907-13, respectively. As for pH test, approximately 50 ml of the wastewater was poured into a beaker. Then, the electrode of pH meter was immersed into the wastewater. The pH reading was recorded once the stable reading was achieved. The concentration of ferum ion in the wastewater was determined by using an atomic absorption spectroscopy (AAS) instrument, Model AAS Z2000, Hitachi.

2.2 Preparation of polysulfone support membrane.

Phase inversion method was used to prepare polysulfone membrane. Thirteen grams of polysulfone bead was dissolved in 87 g of N-methyl-2-pyrollidone (NMP) to produce polysulfone polymer solution (13 wt.%). The mixture was stirred continuously for approximately 4–6 hours at 60 °C to obtain homogenous solution. The solution was left for several hours at room temperature to remove any air bubbles. Then the solution was cast into a membrane film by using an applicator, which was purchased from H.J. Unkel, where the film's thickness was adjusted to 60 µm and 90 µm, respectively. The film was immediately immersed in water as coagulation medium for one hour. Then, the resultant membrane was soaked in a large amount of water for 24 hours. It was then left to dry under the sun before being heat cured in an oven for another one hour at 45 °C.

2.3 Preparation of thin film composite membrane

In the preparation of thin film composite membrane, solution from polymer blend of chitosan with polyvinyl alcohol, hybrid membrane solution polymer blend cross linked with tetraethylorthosilicate, polysulfone resin pellet (Molecular weight: 44000–53000), 99% purity of 1-methyl-2-pyrrolidone (NMP), and deionised water were used. All the chemicals used for the preparation of hybrid membrane solution and polysulfone were obtained from Sigma Aldrich, Malaysia, whereas the 1-methyl-2-pyrrolidone (purity 99%) was obtained from Merck, Malaysia. Two types of membrane solutions, namely a solution from polymer blend PVA/chitosan and a hybrid membrane solution were prepared. Each solution was coated on the polysulfone membrane with thickness of 60 µm, by using a glass rod. The membrane was left for 24 hours at room temperature and subsequently place in oven for one hour at 45 °C (Shaari et al., 2012; Sulaiman et al., 2016). The above procedures were repeated for polysulfone membrane with a thickness of 90 µm. The resultant composites were labelled as;

  i. Composite A: polysulfone with polymer blend PVA/chitosan as the barrier layer.
 ii. Composite B: polysulfone with hybrid membrane as the barrier layer.

2.4 Performance testing on composite membranes

Performance testing on the removal of ferum ions was conducted by using a dead-end typed of membrane testing rig. Two types of thin film composite membranes had been used, where each type has two different thickness of polysulfone (support) membrane that is 60 µm and 90 µm, respectively. Flux performance is the rate of solute or particle transport in the feed side from the bulk solution towards the membrane. The flow was driven by pressure across the

membrane which it transports the solutes over the top of a membrane surface. If the membrane is partially, or completely, retentive to a given solute, it will eventually cause the retained solute to accumulate at the upstream surface of the membrane. This phenomenon is generally called as concentration polarization (Aimar et al., 1993). Flux can be calculated by using the formula as given in Eq. (1).

$$J = \frac{V}{A \cdot t} \tag{1}$$

where:

J is the flux rate (ml/cm²m·min)
V is the volume of the filtered sample (ml)
A is the membrane surface area (cm²)
t is the time taken to collect each sample (min).

In addition to that, the percentage removal was calculated which determine the performance of the membrane to filter the ferum ions that contained in the wastewater sample. The equation used is as shown in Eq. (2).

$$\% \text{ removal} = \frac{(C_{Fe})_{feed} - (C_{Fe})_{permeate}}{(C_{Fe})_{feed}} \times 100 \tag{2}$$

where, $(C_{Fe})_{feed}$ is the ferum concentration in feed solution and $(C_{Fe})_{permeate}$ is the ferum concentration in permeate.

3.0 Results and discussion

3.1 Characterisation of industrial wastewater

Table 1 shows the result from characterization of the wastewater and comparison with the Standard B of the effluent parameters (Environmental Quality Regulation, 2009). Based on Table 1, it is clearly seen that the concentration of ferum ion in the wastewater is too high as compared to the standard. Therefore, treatment by using the fabricated thin film composite membrane is vital.

Table 1: Characteristics of the wastewater.

Parameter	Wastewater	Standard B
pH	1.95	5.5–9.0
COD (mg/L)	666.7	200
BOD (mg/L)	50.94	50
TSS (mg/L)	11.70	100
Fe concentration (mg/L)	281.91	5.0

3.2 Performance of composites on the permeate flux

Based on Fig. 1 (a) and (b), it was observed that for both types of composites, polysulfone thickness at 60 µm yield better flux as compared to that of 90 µm. It was observed also for all types of composite membranes, the flux obtained showed a decreasing reading from first hour until third hours of filtration time. This situation is due to the concentration polarisation where the retained solute at the top surface was accumulated and the water can no longer pass through it. By comparing the permeate flux between composite A and B, comparable performance was portrayed by both composites for 90 µm support thickness. However, for 60 µm support thickness, the reduction of flux for composite B was lower throughout three hours of filtration time as compared to composite A. This situation could be related to the hydrophilic character of the composite with a hybrid membrane as the barrier layer.

3.3 Percentage removal of ferum (II) ions

From Table 2, it shows that the percentage removal of ferum ions increases with the increase in filtration time. Only 78% removal was achieved after an hour of filtration by using composite A with 60 µm support thickness, but for the same thickness, 94.5% removal of ferum ions was achieved by composite B. For both composites with 90 µm support thickness, composite B has higher removal in the first hour of filtration time and it gradually increases until three hours. However composite B shows approximately constant removal of ferum ions until three hours.

This situation is due to the cross-linking process of the polymer blend PVA/chitosan for composite B which has formed a compact and less porous structure that assists the composite to trap more heavy metal ions as compared to composite A.

Table 2: Percentage removal of ferum ions through composite A and B at various thickness of support membrane.

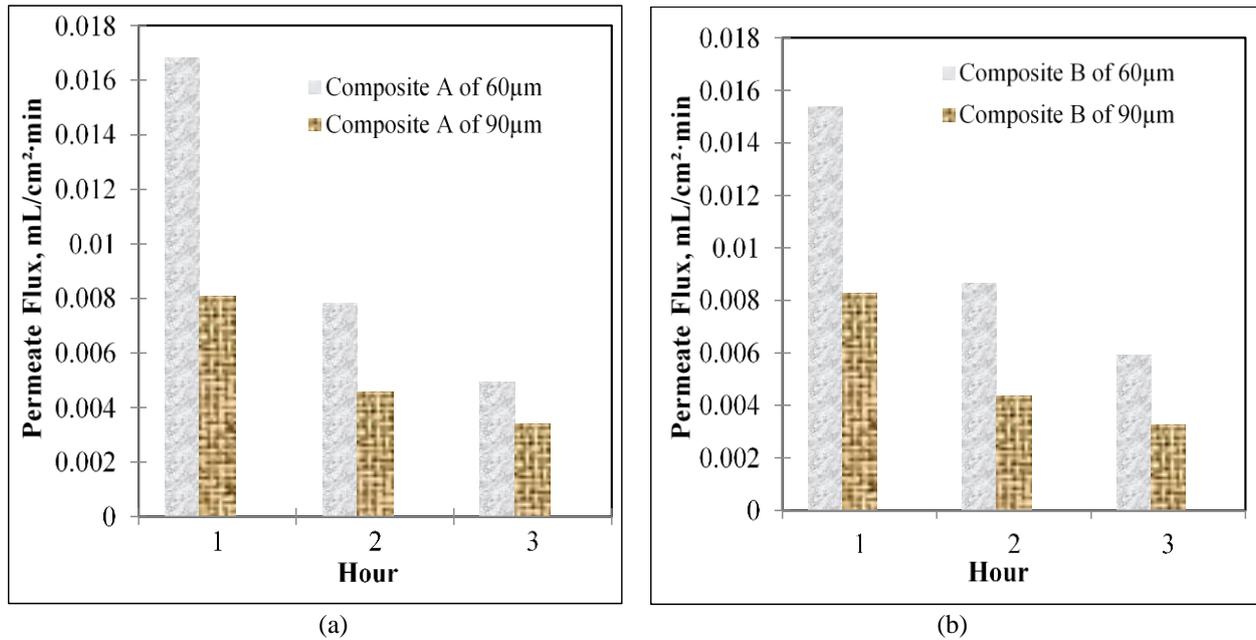| Composite Membrane	Thickness (µm)	Percentage removal (%)		
		1st hour	2nd hour	3rd hour
Composite A	60	77.94	83.77	93.68
	90	95.21	95.71	95.77
Composite B	60	94.50	95.50	95.60
	90	98.60	99.15	99.22

(a) (b)

Fig. 1: Permeate fluxes for three hours filtration process through (a) composite A, and (b) composite B.

The highest removal of ferum ions was achieved at 99.22% after three hours of filtration by using composite B with 90 µm support thickness. It shows that the compact structure of barrier layer together with thicker layer of support membrane has contributed towards high adsorption of ferum ions.

3.4 Concentration of ferum ions before and after filtration through thin film composite membranes

Table 3 and 4 shows the initial and final concentration of ferum ions in the wastewater. Based on the Environmental Act 1974, under Environmental Quality (Industrial Effluent) Regulations 2009, the maximum allowable concentration of ferum ions to be discharged to groundwater is 5.0 ppm.

Therefore, based on Table 4, only composite B with 90 µm support thickness has fulfilled the act's requirements, where even after one hour of filtration, the concentration of ferum ion is already 2.518 ppm. Therefore, it is concluded that composite B of 90 µm is the best membrane to be used to filter the industrial wastewater sample.

4.0 Conclusions

Based on the results obtained, the thin film composite with the hybrid membrane layer has a potential to be used for treating wastewater that contains high concentration of ferum ions. Other than the efficient adsorption of metal ions by the hybrid

Table 3: Concentration of ferum (II) ions before filtration through thin film composite membranes.

Composite Membrane	Thickness (µm)	Initial Ferum (II) ions Concentration (ppm)
Composite A	60	312.59
	90	250.85
Composite B	60	241.29
	90	242.32

Table 4: Concentration of ferum (II) ions after filtration through thin film composite membranes.

Composite Membrane	Thickness (µm)	Final Ferum (II) ions Concentration (ppm)		
		1st hour	2nd hour	3rd hour
Composite A	60	68.955	50.725	19.765
	90	12.000	10.750	10.610
Composite B	60	13.245	10.750	10.610
	90	2.518	2.065	1.884

membrane, thicker layer of porous support membrane also contributes to the higher removal of the metal ions. The ferum concentration in the treated wastewater is within the permissible limit to be discharged to the groundwater.

Acknowledgment

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