

# Removal of Fe(II) From Wastewater by Using Integrated Complexation Method

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**Abstract—** Wastewater produced from electroplating industry contain metals that can be harmful when released to environment. Thus, by treating the wastewater using a proper treatment can help the metals in wastewater to be removed before being disposed to environment. In order to treat the wastewater, characterization of wastewater must be done. This purpose will determine which metals or contaminants present in the wastewater and shows the condition of wastewater before being disposed into environment. By doing the wastewater characterization, it also can determine which method is suitable to remove the contaminants contain in the wastewater. In this study, the composite membrane with hybrid membrane was fabricated to remove Fe(II) from wastewater. The composite membrane with thin film composite made up from polysulfone membrane as the support membrane and hybrid membrane as the barrier layer. Sol gel method was used to formulate the hybrid membrane where the hybrid membrane was made up from polymer blended consists of poly(vinyl) alcohol PVA and chitosan. Then the hybrid membrane will be cross linked with tetraethyl orthosilicate (TEOS). The polysulfone membrane was made up by using phase inversion method. Next, the atomic absorption spectroscopy (AAS) was used to determine the percentage removal of Fe(II) from wastewater after undergoes membrane treatment by using thin film composite membrane. Wastewater of company A needed to be treated using membrane filtration due to its value after characterization tests as it violates standard effluent discharge to environment. Removal of Fe(II) from wastewater using hybrid membrane is 99.89% at pH 10 compared than using composite membrane with polymer blended.

**Keywords—** wastewater, hybrid membrane, integrated complexation method

## I. INTRODUCTION

Globalization and industrialization become one of the factors that cause the environmental issues rises rapidly. All the environmental issues caused by chemical industries such as air pollution, water pollution, greenhouse effect, and soil sediment. Thus, variety methods are needed to treat all the problems that causes by the electroplating industries. The methods are important to reduce the emissions of uncontrolled chemicals produced from industries and cause the environment to be polluted. One of the major concerns of the environmental issues caused by chemical industries is the presence of heavy metal in wastewater and in industrial effluent. Over the last few years, the increases of contamination of heavy metals in water had become a major concern.

Heavy metals are the elements that have relatively high density and can become toxic at low concentrations. They also give bad effect to environment and human if produced uncontrollable. Thus,

to reduce the emission of heavy metals in wastewater, there are various methods can be effectively used. Reducing heavy metal contain in wastewater is not only cause to minimize the pollution that may occur but also to follow the guidelines of Environmental Quality Act 1974, an act that relates to control environment from being polluted.[1]

The wastewater produced by industries normally contain with heavy metals were responsible to control the concentration of heavy metals when doing waste disposal. Examples of heavy metals produced are mercury, iron, copper, zinc, cadmium, lead and aluminum. Some heavy metals are important for human's body to maintain body's metabolism but if consumed in excess, it can cause serious health effects and may lead to death.[2]

As the effluent produced different from one to other industries, different treatments were needed to treat waste produced such as ion exchange, chemical precipitation, membrane filtration, adsorption on new adsorbents, electrodialysis, photocatalysis, and biological methods. By comparing various methods to remove heavy metals from wastewater, membrane filtration possessed a lot of advantages such as requires low energy, high separation efficiency, no phase changing required, simple, heavy metal ions can be recycled and environmental friendly[3].

Furthermore, nowadays the most popular method to treat heavy metals from wastewater is membrane filtration as polymer can enhanced the ultrafiltration on membrane to remove the contaminants from wastewater. Polymer may enhanced the ultrafiltration as the blended polymer will form the interaction between hydrophobic side chain combination with intramolecular and intermolecular hydrogen bonds and this interaction improved the membrane's filtration. Thus, it also will improve the ultrafiltration process on the membrane.[4]

This study focuses on removing heavy metals using thin film composite membrane. Generally, the hybrid membrane may improve the thin film composite membrane's efficiency to remove heavy metals from wastewater. Furthermore, adjusting pH of solutions could increase the percentage of removal of heavy metal using the hybrid membrane.

## II. METHODOLOGY

### A. Materials characterization of wastewater

In the preparation to determine the characteristics of wastewater, materials that were used were wastewater from Company A with labelled Fe(1): wastewater from equalization tank and Fe(2): wastewater from settling tank, distilled water, deionized water, digestion solution for COD, ferric chloride, magnesium sulphate, calcium chloride, and phosphate buffer solution.

### B. Materials for preparation of thin film composite membrane

In the preparation of thin film composite membrane, hybrid membrane solution, polysulfone resin pellet (MW: 44000-53000), 99% purity of 1-methyl-2-pyrrolidone (NMP), and deionized water were used.

### C. Methods of dilution solution

1mL of Fe(1) was poured into 250 mL volumetric flask. Then, distilled water was filled in the volumetric flask to mark up the solution until 250 mL. The dilution solution of Fe(1) was shake until the solution was completely dissolved. The steps were repeated to dilute Fe(2).

### D. Determination concentration of Fe(II) in wastewater

1mL of Fe(1) was poured into 100mL volumetric flask. Then, distilled water was filled in the volumetric flask until it reached its mark on its neck. The dilution solution of Fe(1) was shake until the solution was completely dissolved. Next, the concentration of iron(Fe) in the dilution solution was analyzed by Atomic Absorption Spectroscopy (AAS). The reading of concentration of Fe and colour obtained were recorded.

### E. pH test

50 mL of Fe(1) was poured into a beaker. Then, the electrode of pH meter was put into the beaker and it must be completely immersed with the wastewater. The electrode of pH meter was immersed in about 30 seconds or longer to obtain a stable pH reading. The pH reading was recorded when the pH meter had the stable reading of Fe(1)'s pH. The electrode was rinsed properly with distilled water and slightly dabbed with a tissue. The steps were repeated to get the pH reading of Fe(2).

### F. Turbidity test

Fe(2) was filled in the sample cell. Then, the sample cell was put into the turbidimeter and the reading of turbidimeter was recorded. If the range of the reading was higher than 1500 NTU, the solution in the sample cell must be diluted due to the turbidimeter couldn't read the turbidity value.

### G. Chemical oxygen demand (COD) test

COD reactor was set to be heated by 150°C. Four vials were labelled according the sample tested while one vial was labelled as the blank sample. The vials were labelled according the sample tested as, Vial A : Fe(1), Vial B : Fe(1) diluted in 250 mL, Vial C : Fe(2) and Vial D : Fe(2) diluted in 100 mL. All vials were filled in with digestion solution and the blank sample was filled with 2mL of deionized water. The vials were mixed well. Next, all the vials were put into the COD reactor for two hours. After two hours, the samples were let to cool in the COD reactor until the temperature reached 120 °C. Took out all the samples vials and shake it. The samples were placed at a cooling rack and let the vials cooled down to room temperature. The spectrometer was set with program code 435. After the samples cooled, put the vial into the spectrometer to take the reading of COD. The COD readings were recorded for all vials. As in vial B and D , the recorded reading must be multiplied by each dilution factor.

### H. Biochemical oxygen demand (BOD) test

Firstly, dilution water was prepared. 2000mL of distilled water was filled in a beaker. Then, 2mL for each ferric chloride, magnesium sulphate, calcium chloride and phosphate buffer solution were dropped into the beaker using pipette.

50mL of Fe(1) was filled in two BOD bottles another 50mL of Fe(II) in another two BOD bottles. The BOD bottles were

labeled as A : Fe(1), B : Fe(1), C : Fe(2) and D : Fe(2). After that, the bottles were filled in with the prepared dilution water from (a) until no air space and airtight seal were used. Bottle A and C were stored into a thermostatic cabinet for five days. Then, the DO meter was used to measure the initial dissolved oxygen (DO) concentration in bottle B and D. The reading of initial DO for both bottles was recorded. After five days, the reading for final DO was taken using the DO meter with bottle A and C as the sample. The DO reading was recorded and BOD<sub>5</sub> can be calculated using the formula.

### I. Total Suspended Solid (TSS) test

Spectrometer was set with program code 630. 10mL of distilled water was filled into the sample cell as the blank cell while 10mL for each Fe(1) and Fe(2) was filled into each sample cells. The blank cell was put into the spectrometer and Zero button was pushed to get zero value. Next, sample cell with Fe(1) was put into the spectrometer and Read button was pushed to obtain the value of TSS for the sample test. The value obtained was recorded. The steps were repeated with sample cell of Fe(2).

### J. Preparation of porous support membrane

13g of polysulfone pellet was dissolved into the solvent, 1-methyl-2-pyrrolidone to prepare 13 wt. % polysulfone. The mixture was stirred continuously at 60°C condition for five hours until it forms homogenous mixture. The homogenous mixture then was left at room temperature to remove the forming air bubbles. Polysulfone solution was casted onto a glass plate using casting membrane applicator by adjusting the thickness to 90μ. The polysulfone membrane was left overnight in the coagulation bath at room temperature.[1]

### K. Preparation of thin film composite membrane

The polysulfone membrane was placed on a glass plate. Next, the hybrid membrane solution was casted on the polysulfone as a thin layer to form a thin film composite membrane. Glass rod was used for the casting process. The composite membrane was left at room temperature for 24 hours. Then, the composite membrane was heated at 45°C in an oven for one hour.[1]

### L. Performance testing

pH of the wastewater [Fe(1)] was adjusted to 7 and 10. Then, the thin film composite membrane was installed in the membrane filtration rig with nitrogen gas was set at 12 bars. The Fe(1) solution then poured into the stirred cell. After being permeated, the concentration of Fe(2) was determined by Atomic Absorption Spectroscopy.[5]

## III. RESULTS AND DISCUSSION

### A. Characterization of wastewater

As the company A is an electroplating company, thus the wastewater produced must be complied with Standard B of effluent standard by Environmental Quality Act 1974 (EQA). Based on characterization test on wastewater Fe(1) and Fe(2), it shows that wastewater from requires more treatment as the value the tests were not compatible with given effluent standard by EQA. [6]

Table 1: Characterization test on wastewater

| Test | Wastewater | Value |
|------|------------|-------|
|------|------------|-------|

|           |          |                 |
|-----------|----------|-----------------|
| pH        | a) Fe(1) | a) 1.95         |
|           | b) Fe(2) | b) 2.2          |
| Turbidity | a) Fe(1) | a) 160 NTU      |
|           | b) Fe(2) | b) 74 NTU       |
| COD       | a) Fe(1) | a) 666.7 mg/L   |
|           | b) Fe(2) | b) 28933.3 mg/L |
| BOD       | a) Fe(1) | a) 50.94 mg/L   |
|           | b) Fe(2) | b) 5.04 mg/L    |
| TSS       | a) Fe(1) | a) 11.7 mg/L    |
|           | b) Fe(2) | b) 1.7 mg/L     |

### B. Percentage removal of Fe(II) from wastewater

Based on Fig. 1, the percentage removal of Fe(II) at pH 1.95 for both composite membrane with polymer blended and hybrid membrane only occurred in the first sixty minutes. As the time taken became longer, there were no removal of Fe(II) from wastewater using both composite membranes.

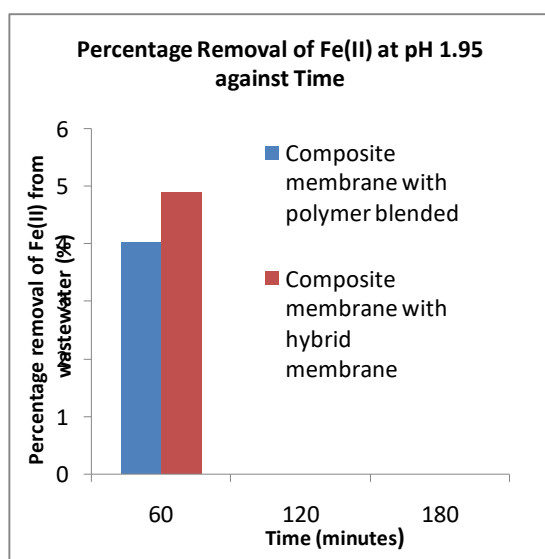


Fig. 1 : Percentage removal of Fe(II) at pH 1.95 against time

Based on Fig. 2, removal of Fe(II) from wastewater at pH 7 increases along the time for both composite membranes. From the results obtained for removal of Fe(II) from wastewater at pH 7, both composite membranes in Fig. 2 show a better performance than Fig. 1. However, the percentage removal of Fe(II) from wastewater using composite membrane with hybrid membrane was more efficient than using the composite membrane with polymer blended. It can be shown from the third hour of removal process, the highest removal of Fe(II) using composite membrane with hybrid membrane is 99.22% compared to the highest removal of Fe(II) from wastewater using composite membrane with polymer blended at 95.77%.

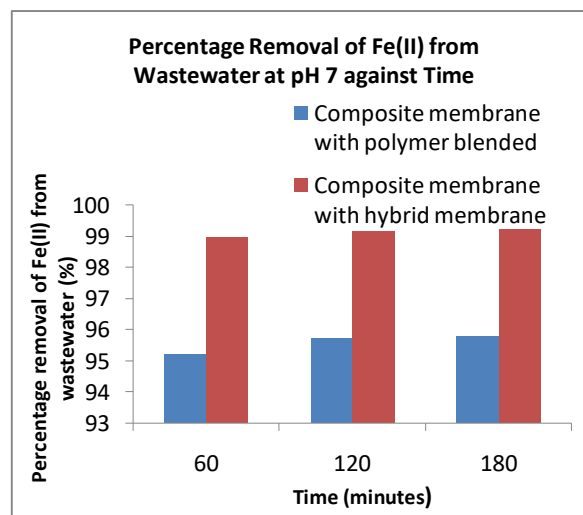


Fig. 2 : Percentage removal of Fe(II) from wastewater at pH 7 against time

Based on Fig. 3, the percentage removal of Fe(II) from wastewater using composite membrane with hybrid membrane has the highest removal at the first hour with 99.89% compared to the percentage removal of Fe(II) using composite membrane with polymer blended. As the time taken for removal of Fe(II) from wastewater become longer, the efficiency of composite membrane with polymer blended increases but the efficiency of composite membrane with hybrid membrane slightly decreases.

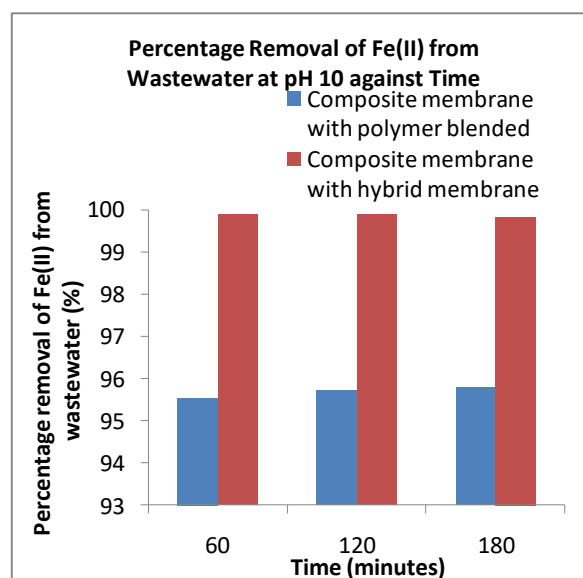


Fig. 3: Percentage removal of Fe(II) from wastewater at pH 10 against time

### C. Effect of pH on percentage removal of Fe(II)

Basically, as the wastewater contains metal entered the treatment process, the metals were stable, dissolved in aqueous form and unable to form solids. As no adjusting pH process before using membrane filtration process to treat the wastewater, the metals in wastewater will not form the insoluble precipitates.

These precipitation formed by adjusting the pH with injecting sodium hydroxide, NaOH into the wastewater. The treatment by hydroxide precipitation will cause the concentration of metal in wastewater becomes lower and easy to be removed.

However, based on Fig. 1, there were no removal of Fe(II) in the second and third hour as the pH of wastewater was not adjusted. Thus, it makes the membrane's performance rejecting the

wastewater to be treated as the membrane finds it is difficult to be filtered by the wastewater that has lower pH due to the concentration of Fe(II) was so higher and cannot be filtered.

Based on both Fig. 2 and Fig. 3, the percentage removal of Fe(II) along the time with adjusting pH become increases. Thus, it shows that before treating the wastewater using membrane filtration, treatment of hydroxide precipitation need to be done first. The results show the efficiency for removal of Fe(II) at pH 7 and 10 were higher as by adjusting the pH, the concentration of Fe(II) in wastewater decreases and forming precipitates. These precipitates will settle down and causes the removal of Fe(II) become easier. It also helps the membrane's performance became efficiently.

#### D. Membrane Flux

Based on Table 2, the results of calculating membrane flux for both composite membranes show that less membrane fouling occur during the experiment. As the hybrid membrane was membrane that had been modified by adding TEOS into the composite membrane, it exhibited lower transmembrane pressure and improved the membrane from being fouled. By modifying the surface of the membrane, it will decrease the pore size of the membrane effectively.[7]

However, as the calculated membrane flux for both membranes resulting increases in value, no membrane fouling happen during the experiment. Membrane fouling is easy to occur when the membrane was made up using the phase inversion method. This is due to the phase inversion method where water was used as the non-solvent with hydrophobic polymer as the solvent to fabricate the membrane. As the hydrophobic membrane solutes in the water, the water caused the membranes to foul through strong hydrophobic interactions that occur in the membrane. [7]

As both membranes contain surface modification, it can help in controlling the membrane fouling from occurs during the experiment. The surface modifications help to control membrane fouling as the polymer membrane was hydrophobic and the modification on membrane's surface usually directed the surface of membrane to hydrophilic.[7]

If the membrane contains hydrophilic surfaces, the membrane will attract a strongly bound layer of water molecules. This layer of water molecules will acts as the buffer on the adhesion of hydrophobic foulants. Thus, as the membrane having hydrophilic surface modifications, it will form a thin and highly permeable dense film. This film will helps in reducing membrane's permeance as it will contributes to overall mass transfer resistance of the membrane.[7]

Based on Table 2, as both composite membranes have increases value in membrane flux, thus it shows that the membrane mass transfer resistance for both composite membranes was lower. This resulting to the experiment of filtration Fe(II) from wastewater, only membrane itself was acted as the resistance as there is no foulants accumulate at the membrane.[8]

| Membrane                                | pH   | Flux (mL/cm <sup>2</sup> .min) |                          |                          |
|-----------------------------------------|------|--------------------------------|--------------------------|--------------------------|
|                                         |      | J <sub>1</sub>                 | J <sub>2</sub>           | J <sub>3</sub>           |
| Composite membrane with polymer blended | 1.95 | 8.165 × 10 <sup>-3</sup>       | 0.0131                   | 0.0161                   |
|                                         | 7    | 8.069 × 10 <sup>-3</sup>       | 9.126 × 10 <sup>-3</sup> | 0.0102                   |
|                                         | 10   | 9.126 × 10 <sup>-3</sup>       | 0.0136                   | 0.0152                   |
| Composite membrane with hybrid membrane | 1.95 | 8.454 × 10 <sup>-3</sup>       | 0.0128                   | 0.0158                   |
|                                         | 7    | 8.262 × 10 <sup>-3</sup>       | 8.742 × 10 <sup>-3</sup> | 9.799 × 10 <sup>-3</sup> |
|                                         | 10   | 8.742 × 10 <sup>-3</sup>       | 0.0121                   | 0.0130                   |

#### IV. CONCLUSION

From the experiment, wastewater Fe(1) was chosen as the sample test for performance testing of membrane due to its contamination present in the wastewater was higher than wastewater Fe(2). This was proven by the results of BOD for both type wastewaters and it can be concluded that wastewater Fe(1) need the highest oxygen than wastewater Fe(2) to degrade organic matter. Thus, it requires membrane filtration to remove the contaminations from it efficiently. Based on the results obtained, by using the thin film composite to remove Fe(II) from wastewater, using composite membrane with hybrid membrane was highly efficiently compared by using composite membrane with polymer blended. This was proven as the time taken increases, the volume of wastewater being filtered increases, membrane flux become decreases and percentage removal of Fe(II) also increase. However, percentage removal of Fe(II) using composite membrane with hybrid membrane also increases as the pH had been adjusted. Thus, in conclusion, composite membrane with hybrid membrane with wastewater pH 10 provides the best removal of Fe(II) due to percentage removal of Fe(II) from wastewater was the highest and can be discharged as it's qualify the acceptable range of Standard B of the effluent discharge of EQA (1974).

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Table 2: Membrane Flux

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