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# Recovery of Cu (II) and Cr (VI) Metals from Electroplating Liquid Waste Using Polymer Inclusion Membrane (PIM)

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# Abstract

Research on recovery of Cu (II) and Cr (VI) from electroplating liquid waste has been carried out using a Polymer Inclusion Membrane (PIM). PIM has a high stability to overcome the weakness of liquid membrane instability. The PIM membrane was placed between two phases namely the feed phase as a metal source of Cu (II) from electroplating waste with pH 3 and the receiving phase which is HNO<sub>3</sub> solution with pH 1 and pH 4.4 in the feed phase and pH 6.3 in the receiving phase with NaCl 2 N for metal Cr (VI). Recovery efficiency is known by determining the concentration of Cu (II) and Cr (VI) in the feed and receiving phases using AAS, while the membrane characterization were carried out using FTIR, SEM and UV-vis spectroscopy. The resulting PIM membrane has properties of thin, clear and flexible. AAS data showed that the percentage of PIM transport with stirring for 24 hours performed the highest percentage of Cu (II) metal transport from feed phase of 83.41% and transport in the receiving phase of 72.56%. While the percentage of optimum Cr (VI) transport was 97.8% in the feed phase and 76.5% in the receiving phase. The results of membrane characterization using FTIR and UV spectroscopy showed that the PIM membrane was quite stable. While the results of SEM show that there were no pores in the membrane so that the transport occurs by diffusion through the intermediate of the carrier compound.

Keywords: electroplating waste; liquid membrane; PIM

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# INTRODUCTION

The dominant factor causing environmental pollution is the presence of residual production waste from an industry in the form of heavy metal waste, including copper (Cu) and chrome (VI) metals. These metal wastes are from metal coating, electrolysis and pharmaceutical industries (Bandela *et al.*, 2016; Hidayati *et al.*, 2014; Djunaidi, 2017a). Cu (II) and Cr

(VI) Metals which are left in the water will accumulate and cause its concentration to exceed the threshold so that it has a negative impact on the environment (Winter, 2003; James *et al.*, 2013). To overcome this problem, recovery of Cu (II) and Cr (VI) heavy metals of electroplating waste is carried out using liquid membrane method which is one of the development of solvent extraction methods. However, its stability limits the liquid membrane for further application in the process of metal recovery and purification (Ulewicz and Walkowiak, 2006). Therefore, to overcome the instability of the membrane, a Polymer Inclusion Membrane (PIM) technique is developed.

The PIM method has advantages over other liquid membranes such as requiring a little carrier compound, has a high stability, the carrier which is lost during the process can be ignored, higher fluxes, simpler and more versatile operation (Kusumacahyu et al., 2006; Gadja et al., 2012; Kebiche-Senhadji et al., 2015). Recovery with PIM is largely determined by the selectivity and effectiveness of carrier compounds (Ulewicz and Walkowiak, 2006; Nghiem et al., 2006; Djunaidi, 2017b). Due to these facts, the PIM method is used in this research for the recovery of Cu (II) and Cr (VI) metals from electroplating waste. The PIM in this study was made from PVC base polymer, HTTA-TBP carrier compounds and DBE plasticizer which was dissolved into tetrahydrofuran (THF) for recovery of Cu (II). Whereas for recovery of Cr (VI) used a mixture of aliquat 336-TBP and aliquat 336-TOPO. The use of a mixture of HTTA-TBP as a carrier is proven to increase the effectiveness of Cu (II) metal recovery (synergy) (Widianingrum, 2005; Djunaidi et al., 2003). Recovery efficiency is known by determining the concentration of Cu (II) and Cr (VI) in the feed and recepient phases using AAS, the functional group changes are analyzed using FTIR, while the characterization of membrane stability using SEM and UV-vis spectroscopy.

#### **METHODS**

#### Apparatus

A set of PIM recovery cells, a set of glasswares, glass molds (petridish with diameters of 9.5, 11.5 and 13.5 cm), analytical balance, HACH EC20 pH meter, Atomic Absorption Spectrophotometer (AAS), FTIR and UV-Vis spectrophotometers, Scanning Electron Microscope (SEM).

#### Materials

Electroplating liquid waste from waste water treatment Kejambon Tegal, polyvinyl chloride (PVC) as basic polymer, HTTA and TBP as carrier compounds, dibutyleter (DBE), THF, HNO<sub>3</sub> 0.1 N, aquadest, HCl, NaOH, Aliquat 336 S, TOPO and TBP. The research was carried out in two stages: separation of Cu (II) and Cr (VI). Separation of Cu (II) was carried out using HTTA:TBP as carrier, while Cr (VI) was carried out using Aliquat:TOPO and Aliquat: TBP.

# Separation of Cu (II) from Electroplating Waste Membranes-fabrication

Preparation of HTTA-TBP (4:1) Carrier Compounds. One mL of TBP p.a was put into a 10 mL measuring flask then THF solvent was added to the boundary mark and shaken until homogeneous. Then 0.0888 g HTTA 0.08 M plus 0.277 mL 0.02 M TBP was put in a 5 mL measuring flask then THF is added to the boundary mark and shaken to be homogeneous.

## Polymer Inclusion Membrane (PIM) preparation

Twenty five mL of PVC solution and 5 mL of a carrier compound solution were mixed with 1.5 mL plasticizer (DBE). The mixture was then put into the petridish and the mixture was left at room temperature for 48 hours until the THF solvent evaporates. The dried membrane is cut to the size of the PIM cell needed (Gardner *et al.*, 2005).

# Cu<sup>2+</sup> Metal Recovery using PIM Feed solution preparation

The feed solution used was 20 mL of electroplating liquid waste with dilutions of 100, 50 and 0 times. The feed solution used was a waste solution with a fixed pH 3.

#### **Preparation of receiving solution**

The receiving solution used in the stirring process was 0.1 M HNO<sub>3</sub> solution

### Separation of Cr (VI) from Electroplating Waste Preparation of feed phase and receiving phase solution

The sample used as the feed phase was electroplating waste containing chromium (VI) with dilution variations of 25, 10 and 0 times (0 times means without dilution). The concentration of chromium (VI) solution was initially 1055 ppm, while for the receiving phase NaCl 2 N was used. Then the pH conditioning was carried out for both solutions, pH 4.4 in the feed phase and pH 6.3 in the receiving phase (Choi and Moon, 2004).

#### **PIM preparation**

Polymer Inclusion Membrane (PIM) was carried out based on Gardner (2005). A total of 0.3125 g of basic polymer (PVC) was dissolved in 25 ml of THF. Stirring with a magnetic stirrer was carried out for 30-60 minutes or when it dissolved completely. Then proceed with making of 0.1 M carrier solution with a ratio variation of carrier compound of Aliquat:TOPO = 4:1 using 5 ml volumetric flask using THF solvent. For the single carier compound, Aliquat 336 was used as much as 0.1 M and for the mixed carrier compound Aliquat 336-TOPO used was 0.1 M. 25 ml of PVC solution and 5 ml of carier solution was carefully mixed with 1.5 ml of plasticizer (DBE). After everything was mixed, the mixture was put in a glass mold (diameter 13.5 cm). The mixture was left at room temperature for 48 hours until the THF solvent evaporated. The dried membrane was taken and cut into the size of the PIM cell needed.

## **Separation Process (Metal Ion Transport)**

The PIM membrane was placed between the feed phase as a source of analytes and the receiving phase as a result of separation. The feed phase was electroplating waste containing chrome metal with a pH of 4.4. Whereas the receiving phase was 2 N NaCl solution with pH 6.3. Then it was stirred in each chamber for 1x24 hours and 3x24 hours with constant

(Djunaidi et al.)

speed. The separation process occurred when the color of the solution in each chamber changes.

#### **Membrane Stability**

To determine the stability of the PIM membrane, UV-vis analysis was carried out on the membrane sample, the feed phase and the receiver before and after stirring in the recovery process of Cu (II) metal.

#### **RESULTS AND DISCUSSION** Polymer Inclusion Membrane (PIM) Fabrication

The Polymer Inclusion Membrane (PIM) was carried out by mixing PIM components, namely PVC (polyvinil chloride) as polymer base, HTTA:TBP (4:1) as carrier compounds, Aliquat, TBP and TOPO and DBE (dibutylether) as plasticizer dissolved in THF solvent to produce PIM membranes. The membranes are thin, clear, not brittle and able to effectively separate Cu (II) and Cr (VI) metals (Figure 1)





a b Figure 1. (a) Polymer Inclusion Membran (PIM) for the separation of Cu (II), (b) Polymer Inclusion Membrane (PIM) for the separation of Cr (VI)



Figure 2. Morphology of PIM membrane with a diameter of 11.5 cm, (a) membrane surface of 5000× magnification, (b) cross section of 1000× magnification

Scanning Electron Microscopy (SEM) analysis with 5000x magnification (Figure 2a) shows that the surface morphology of the PIM membrane is not porous. Whereas from the results of the cross section photos with 1000x magnification (Figure 2b) obtained the cross-sectional thickness of the membrane is 85.71  $\mu$ m. Non-porous PIM membranes can be used for transport of Cu (II) metals that occur diffusely through intermediaries of HTTA-TBP (4: 1) carrier compounds.

#### **FTIR Analysis**

Determination of the active functional group of PIM membrane was carried out using FTIR spectrophotometer. The results of membrane analysis before stirring are shown in the Figure 3.



Figure 3. FTIR spectra of PIM membrane before stirring

FTIR spectra (Figure 3) before stirring membrane showed a sharp absorption band in the region of 3032.1 cm<sup>-1</sup> which shows the presence of unsaturated CH groups (=CH-) (from HTTA), medium absorption bands in regions of 2924.09 and 2854.65 cm<sup>-1</sup> indicates the presence of an alkyl group (-CH<sub>3</sub>) (from TBP), absorption in the area of 1720.5 cm<sup>-1</sup> with an overtone in the area of 3441.01 cm<sup>-1</sup> indicates the carbonyl group (C=O) (from HTTA), absorption band in the region of 1604.77 cm<sup>-1</sup> indicated the presence of  $\beta$ -diketone, 1357.87 cm<sup>-1</sup> indicates CF group (from HTTA), 1257.59 cm<sup>-1</sup> shows PO group (from TBP), 1064.71-1203.58 cm<sup>-1</sup> shows the presence of an ether group (-O-) (from DBE), 740.67 cm<sup>-1</sup> shows a methylene series, 609.51 cm<sup>-1</sup> showed a C-group Cl (from PVC) (Sastrohamidjoyo, 2001). This shows that there are compounds of the PIM membrane constituent components.

#### **Effect of Feed Phase Concentration**

Membrane B was used in feed phase samples with variations in dilution concentrations of 0x, 50x and 100x with stirring for 24 hours. The results obtained are shown in Table 1.

Table 1. Effect of variations in sample concentration
on Cu (II) metal transport

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Table 1 data shows that the transport of Cu (II) metal at 100x dilution using HTTA-TBP membrane perfroms a large percentage of transport, whereas with increasing waste sample concentrations at 50x dilution and without dilution (0x) indicates a decrease in the percentage of transport in the receiving phase. This is due to the greater concentration (concentrated) of the feed phase causing fewer cations to be transported from the feed phase to the receiving phase. Membrane performance capability decreases due to the number of waste sample matrices and the more concentrated the

sample can cause difficulty in transporting  $Cu^{2+}$  metal through the membrane to the receiving phase.

#### **Effect of Membrane Thickness**

Membrane thickness variations were obtained using a variation of the diameter of the petridish membrane A, B and C mold with the feed phase concentration used was 50x dilution. This concentration was chosen because it was a medium concentration, so it was not too thick and not too thin. Stirring was carried out for 24 hours. The results obtained are shown in Table 2.

 Table 2. Effect of membrane thickness variations on

 Cu (II) metal transport

Cu (II) inclui transport			
	Transport	Transport	
Variation of membrane	percentage	percentage in	
thickness	in the feed	the receiving	
(Petridish diameter)	phase	phase	
	(%)	(%)	
Membrane A (9.5 cm)	6.76	6.56	
Membrane B (11.5 cm)	78.87	68.41	
Membrane C (13.5 cm)	83.41	72.56	

The data in Table 2 shows that the thinner the membrane or the larger the diameter of the membrane, the more percentage of transport in the feed phase and the better the transport to the receiving phase. Conversely, the thicker the membrane, the less cations are transported to the receiving phase because the diffusion rate is slower. This can be explained by Fick's law (Wijmans and Baker 1995) J = -D dc/dx which states that the diffusion rate is inversely proportional to the thickness of the interphase layer/flux distance. From this equation it can be seen that the thicker the membrane, the longer the flux distance taken by the HTTA-TBP complex with Cu<sup>2+</sup> metal to get to the receiving phase which causes the diffusion rate to be low so that the percentage of transport to the receiving phase decreases.

#### **Effect of Membrane Reuse**

The performance of HTTA-TBP membrane 0.08 M:0.02 M for 1 to 3 times usage is shown in Table 3.

Table 3. Effect of membrane reuse on Cu (II) metal transport

transport			
Variation of membrane reuse (times)	Transport percentage in the feed phase (%)	Transport percentage in the receiving phase (%)	
1 time	87.87	84.94	
2 times	83.40	84.81	
3 times	78.94	55.01	

From the results presented in Table 3. It was concluded that there was a decrease in membrane transport ability (seen from the percentage of transport in the feed phase) which was decreasing due to the use of n times the membrane as well as a decrease in the

percentage of transport in the receiving phase. This shows a decrease in the ability of the membrane to be used more than 1 time using the membrane. This is likely to occur due to the closure of the membrane surface after stirring by the waste matrix so that it blocks the transport of Cu (II) to the receiving phase.

#### The Use of Blank Membrane

The fabrication of blank membrane without carrier compound was carried out as a comparison of PIM membrane with HTTA-TBP carrier compound. Recovery using blank membrane under 24 hours stirring showed the percentage of Cu (II) transport was 0% (no metal transport occurred) from the feed phase to the receiving phase. This was due to the absence of a carrier compound in the blank membrane. Therefore, it can be concluded that the Cu (II) metal transport capability occurs due to the role of the carrier compound in the membrane.

# Characterization of Membrane after Stirring FTIR spectra analysis

FTIR analysis on the PIM membrane after the stirring process was used to determine the presence of a functional group that was likely to disappear from the membrane. The FTIR membrane PIM spectra after stirring (Figure 4) showed that in the PIM membrane the results of the stirring contained the same PIM membrane constituent compound with FTIR spectra before stirring. Peak shifts that occur maybe caused by the effect of complex formation that occurs between Cu (II) and HTTA-TBP carrier compounds in the membrane, for example in 1357 to 1327 cm<sup>-1</sup> (C-F); 1064 to 1072 cm<sup>-1</sup> (ether group) and so on.



Figure 4. FTIR spectra of the PIM membrane after stirring

## PIM membrane stability analysis

UV analysis was carried out to determine the stability of the PIM membrane in the membrane sample, feed phase and receiver before and after stirring in the recovery process of Cu (II) metal. Membrane stability is indicated by the absence of a spectrum of membrane-forming organic compounds in both the feed phase and the receiving phase. UV analysis data is shown in Figure 5.



Figure 5. (a) UV spectra of PIM membranes, (b) UV spectra of the feed phase after stirring

Based on the results of the analysis presented in Figure 5a, the maximum wavelength of the membrane was obtained at 382.5 nm. The PIM membrane is composed of organic compounds that have a chromophore group (-C=O; -P=O and thenoyl groups) so as to absorb at wavelengths of the UV region. From the UV spectrum of the electroplating waste feed phase (Figure 5b), the maximum wavelength ( $\lambda_{max}$ ) after stirring was obtained at 257.0 nm with an absorbance of 0.503. While the UV spectrum of the receiving phase after stirring is as shown in Figure 6.



Figure 6. (a) UV spectra of the receiving phase after stirring, (b) UV UV spectra of artificial Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O

The UV spectrum of Figure 6a shows the  $\lambda_{max}$  of the receiving phase after stirring was 303.0 nm with an absorbance of 0.586. The peak formed in the receiving phase is the overlapping between HNO<sub>3</sub> from the receiving phase and Cu2+ from the feed phase that forms Cu(NO<sub>3</sub>)<sub>2</sub> complex salt. As a comparison, UV analysis of artificial Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O was carried out as a proof of the formation of Cu(NO<sub>3</sub>)<sub>2</sub> complex salt (Figure 6b). The results of the analysis show that the maximum wavelength of the artificial Cu(NO<sub>3</sub>)<sub>2</sub> was 301.0 nm and the peak that appears was the same as the peak in the receiving phase after stirring. From the results of UV analysis of Figure 6b, the spectra that appeared showed no absorption of the constituent components of the membrane (at  $\lambda_{max}$  of 382.5 nm) that appeared in the feed phase and the receiving phase after stirring. This proves that no organic compounds that make up the PIM membrane are dissolved in the feed phase and the receiving phase. So it can be concluded that the PIM membrane used is quite stable.

# Separation of Cr (VI) from Electroplating Waste Effect of composition of carrier compounds

Carrier compounds are very influential in metal separation techniques using PIM. The carrier compound will form a complex with species in the receiving phase. In this study, the anion carrier compounds used were Aliquat 336 and TOPO. Aliquat 336 is an organic compound for anion exchange. This compound has a long chain organic base, a large molecular weight and is not soluble in water. This group has the ability to selectively bind with nitrate ions or other negatively charged ions. On the other hand, TOPO is a non ion (neutral) solvent that has the ability to extract metal ion complexes (De Anil, 1970). Data of chromium (VI) metal transport with variations of carrier compounds are shown in Table 4.

Table 4. Percentage of chromium metal (VI) ion transport with variations of carrier compounds after 24

hours			
Comion	Transport percentage (%)		
callel	Feed	Receiving	Membrane
compounds	phase	phase	phase
Aliquat 336	97.5	73.8	23.7
TOPO	0	0	0
Aliquat 336-	97.4	72.7	24.7
TOPO			

Table 4 illustrates the comparison of whether or not there was a synergy effect on the chrome (VI) metal ion transport process. Synergy effect is a mutually reinforcing effect which results in an increase in extraction results by utilizing extracting solvents. To determine the synergy effect of this chromium (VI) metal ion transport process, a single carrier aliquat 336 or TOPO was used. Table 4 also illustrates that the transport process using a single compound Aliquat 336 gives good results. Aliquat 336 (anion carrier) releases Cl<sup>-</sup> in the membrane-feed interface phase and binds HCrO<sub>4</sub><sup>-</sup> ion in the feed phase. The HCrO<sub>4</sub><sup>-</sup> ion which has been bound by Aliquat 336 diffuses towards the receiving membrane interface then the HCrO<sub>4</sub><sup>-</sup> ion is released into the receiving phase to be replaced by Cl<sup>-</sup>. The transport process takes place back and forth continuously (Figure 7). The single TOPO carrier compound did not provide good chrome metal ion transport results. TOPO cannot carry out the process of transporting chrome (VI) metal ions. This was because the experimental conditions were not optimal conditions for TOPO (alkaline conditions). The transport process using Aliquat 336-TOPO mixture compound and Aliquat 336 single compound gave almost the same results. Therefore, it can be concluded that the mixture of Aliquat 336-TOPO does not provide a synergy effect and is also not an antisinergy.

#### Effect of feed phase concentration

The effect of the feed phase concentration can be determined by conducting a sample dilution variation of 25, 10 and 0 times dilution. The results obtained can be seen in Table 5.



Figure 7. Transport mechanism of HCrO<sub>4</sub><sup>-</sup> ions via PIM with a single carrier compound of Aliquat 336

Table 5. Percentage of chromium (VI) metal ion
transport with variations in the concentration of the
feed phase

iced pliase				
Dilution	Transport percentage (%)			
(times)	Feed	Receiving	Membrane phase	
(times)	phase	phase		
0 time	47.6	46.3	1.3	
10 times	97.5	73.8	23.7	
25 times	97.8	76.5	21.3	

From Table 5, it can be seen that the chrome metal ion transport results in 25 times of dilution was greater than that of the 10 times and 0 times of dilution. In other words, the more concentrated the feed phase solution, the fewer metal ions transported from the feed phase to the receiving phase. This shows the ability of the membrane to decrease due to the number of matrices and concentrations of the sample so that it has a high viscosity.

One factor that influences PIM is viscosity. The smaller the viscosity, the easier the liquid flows, so that there is a dependence on intermolecular forces between the fluid molecules. The stronger the intermolecular force will usually increase viscosity. It can be said that the more concentrated the solution or the greater the viscosity of the solution, the stronger the intermolecular attractions, resulting in the difficulty of metal ions in the solution to diffuse due to the strong bonding of metal ions with the matrix. This causes the difficulty of the ability of the carrier compound to break the metal ion bond with the matrix. The best results were obtained at 25 times of dilution with levels of chromium metal (VI) ion transported to the feed phase by 97.8% and transported to the receiving phase by 76.5%.

## Effect of stirring time

To determine the effect of stirring time on the chromium (VI) ion transport process, stirring was

carried out for 72 hours with a sampling time interval every 24 hours. The results obtained can be seen in Table 6.

Table 6. Percentage of chrome (VI) metal ion
transport with variations in stirring time

Stirring time	Transport percentage (%)		
(hours)	Feed	Receiving	Membrane
(nours)	phase	phase	phase
24	47.6	46.3	1.3
48	69.2	57.07	12.13
72	86	59	27

The process of mixing chrome metal ion transport (VI) was carried out for 72 hours with sampling variation every 24 hours. The best percentage of transport produced by the PIM membrane was the sampling time of 72 hours. The transport percentage obtained in the feed phase and receiving phase were 86% and 59%, respectively. It can be concluded that the longer the stirring time in the transport process will result in a higher percentage of metal ion transport.

#### Effect of membrane reuse

Variation of reuse aims to determine the ability of membrane extraction in transporting metal ions. The results obtained can be seen in Table 7.

Table 7. Percentage of chrome (VI) metal ion transport with variations in usage of n times

d'unsport with variations in asage of withes			
	Transport percentage (%)		
Reusage	Feed	Receiv	Membrane phase
(times)	phase	ing	
	_	phase	
1	97.4	72.7	24.7
2	97.1	65.9	31.2
3	96.9	59	37.9

Table 7 shows that after the third use, the percentage of transport from the feed phase decreased as well as the percentage (%) of transport to the receiving phase. This is due to the deposition of waste matrix on the surface of the membrane, causing slow transport in the metal ion transport process. The best results were obtained in the first application (1 time) with the concentration of chromium metal (VI) ion transported to the feed and the receiving phase of 97.4% and 72.7%, respectively.

# PIM Characterization Using SEM (Scanning Electron Microscopy)

Membrane characterization using the SEM method was intended to determine the morphology of the membrane surface. The results of the analysis showed that the membrane produced was homogeneous (as seen as one phase), has no pore (as seen in Fig. 8). Therefore it can be concluded that the membrane is ready to be used for the transport of chromium (VI) metal ions because the PIM works by the diffusion process by the carrier compound.



Figure 8. SEM of Polymer Inclusion Membrane (PIM)

#### **PIM Characterization Using FTIR Spectrometer**

The membrane formed was characterized by FTIR before and after the metal ion transport process. This was intended to determine the functional groups of the constituent components of the membrane before and after the metal ion transport process. According to Nghiem *et al.* (2006), although some FTIR studies state that there is no sign of covalent bond formation between plasticizer carrier compounds and basic polymers, it seems that they are bonded to one another by forming secondary bonds such as hydrophobic, Van der Waals or hydrogen bonds. So that the PIM is more stable than SLM or other liquid membranes. The results of PIM analysis using FTIR spectrometers was shown in Figure 9.



Figure 9. FTIR spectra of PIM before being used for the transport process

Figure 9 shows functional groups contained in membranes before being used for metal transport processes. The bands at 2862.36 cm<sup>-1</sup> are C-H alkane stretch bands, 1373.72 cm<sup>-1</sup> and 1535.34 cm<sup>-1</sup> are alkyl CH<sub>3</sub> bands, 1172.72 cm<sup>-1</sup> is P=O and 1103.28 cm<sup>-1</sup> bands is a C-O ether band. The N group of Aliquat 336 compound is a quaternary ammonium so it does not have a hydrogen bond because all of its hydrogen atoms are substituted. Hence there is no peak on FTIR spectra.

Figure 10 shows functional groups contained in the membrane after being used for metal transport processes. The band in the area of 2854.65-2924.09 cm<sup>-1</sup> is the C-H alkane stretch band, 1427.32 cm<sup>-1</sup> is the alkyl CH<sub>3</sub> band, 1265.30 cm<sup>-1</sup> is the P=O and 1103.28 band is the C-O ether band. The functional groups contained in the membrane after use were not significantly different from that of in the membrane before use. This showed that the membrane was stable, because there were no new peaks which indicate the emergence of another group. In addition, there was no functional constituent of the membrane that was lost before and after the metal ion transport process.



Figure 10. FTIR spectra of PIM after being used for the transport process

#### CONCLUSIONS

It can be concluded that the PIM membrane produced has properties of thin, clear and flexible so that the PIM method can be used for recovery of Cu (II) and Cr (VI) metals in electroplating waste. The results of AAS showed that the PIM transport with stirring for 24 hours resulted in the highest percentage of Cu (II) metal transport from the feed phase of 83.41% and transport in the receiving phase of 72.56%. The transport of chromium (VI) metal ions was affected by the aliquat 336 carrier compound and a mixture of aliquat 336-TOPO. Both affect transport more than TOPO alone. The feed phase with an initial concentration of 8.5 ppm, stirring time for 72 hours showed that the use of the first use of the membrane resulted in the highest percentage of metal ion transport. The highest percentage of transport in the feed dan the receiving phases were 97.8% and 76.5%, respectively. Membrane characterization using FTIR and UV spectroscopy showed that the PIM membrane was quite stable, while the SEM showed that there were no pores in the membrane so that the transport occurred through diffusion using the carrier compound.

### REFERENCES

Bandela, N.N., Gmais, S.A., Mehta, T., and Kasuhik, G., (2016). Heavy Metal Removal by Isolates from Domestic and Industrial Waste Water, *Journal of Materials and Environmental Science*, 7(12), pp. 4589-4595.

Djunaidi, M.C., Triatmo M.A., and Gunawan, G., (2003), Pemulihan (Recovery) dan Pemisahan Selektif Logam Berat (Zn, Cu Dan Ni) dengan Pengemban Sinergi Menggunakan Teknik SLM, *Jurnal Sains dan Aplikasi*, 6, pp. 17-19

Djunaidi, M.C., Lusiana, R.A, and Maya D.R, (2017a), Recovery of Chromium Metal (VI) Using Supported Liquid Membrane (SLM) Method, A Study of Influence of NaCl and pH in Receiving Phase on Transport, *IOP Conference Series: Material Science Engineering*, 205 012010.

Djunaidi, M.C., Khabibi, and Nurfitriana, R., (2017b), Pemisahan Krom(VI) dari Limbah Elektroplating Menggunakan Metode *Polymer Inclusion Membrane* (PIM), *Alchemy Jurnal Penelitian Kimia*, 13(1), pp. 119-132

Gadja, B. and Bogacki, M.B., (2012), The Application of Polymer Inclusive Membranes for Removal of Heavy Metal Ions from Waste Solutions, *Journal of Achievements in Materials and Manufacturing Engineering*, 55(2), pp. 673-678.

Gardner, J.S., Peterson, Q.P., Walker, J.O., Jensen B. D., Adhikary, B., Harrison, R.G., and Lamb, J.D., (2005), Anion Transport through Polymer Inclusion Membrane Facilitated by Transition Metal Containing Carriers, *Journal of Membrane Sciences*, 277(1-2), pp. 165-176

Hidayati, N., Surtiningsih, T., and Ni'matuzahroh, (2014), Removal of Heavy Metals Pb, Zn and Cu from Sludge Waste of Paper Industries Using Biosurfactant, *Journal Bioremediation and Biodegradation*, 5(7), pp. 1-3.

James, O.O., Nwaeze, K., Mesagan, E., Agbojop, M., Saka, K.L., and John, D., (2013), Concentration of Heavy Metals in Five Pharmaceutical Effluents in Ogun State, Nigeria, *Bulletin of Environmental Pharmacology and Life Science*, 2(8), pp. 84-90.

Kebiche-Senhadji, O., Mansouri, L., and Benamor, M., (2015), Consideration of Polymer Inclusion Membranes Containing D2EHPA for Toxic Metallic Ion (Pb<sup>2-</sup>) Extraction Recovery, 5<sup>th</sup> International Conference on Environment Science and Engineering Volume 83 of IPCBEE, pp. 169-176.

Nghiem, L.D., Mornane, P., Potter, I.D., Perera, J.M., Cattrall, R.W., and Kolev. S. D., (2006), Extraction and Transport of Metal Ions and Small Organic Compounds Using Polymer Inclusion Membranes (PIMs), *Journal* of Membrane Science, 281, pp. 7–41.

Ulewicz, M. and Walkowiak, W., (2006), Removal of Zn(II), Cd(II) and Pb(II) Using Polymer Inclusion Membrane Transport with Proton Ionizable Db-16-C-5 Crown Ethers, *Physicochemical Problems of Mineral Processing*, 40, pp. 185-194.

Widianingrum, K.F., (2005), Ekstraksi Cu (II) dan Zn (II) Menggunakan Ekstraktan HTTA-TBP dan D2EHPA-TBP, *Skripsi*, Undip, Semarang

Wijmans, J.G. and Barker, R.W., (1995), The Solution Diffusion Model-A Review, *Journal Membrane of Science*, 107, pp. 1-21.

Winter, M., (2003), *Copper*, The University of Sheffield and Web Elements Ltd, UK