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Separation of Cu^{2+} , Cd^{2+} and Cr^{3+} in a Mixture Solution Using a Novel Carrier Poly(Methyl Thiazoleethyl Eugenoxy Acetate) with BLM (Bulk Liquid Membrane)

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Abstract. The separation process using a novel carrier polyeugenol has active groups N and S has been done with the technique BLM. Polyeugenol has groups active N and S was synthesized from eugenol which is then polymerized into polyeugenol. This polymeric compounds was then acidified become acidic poly (eugenoksi acetate). After the acid formed, then the synthesis was continued by add 4-methyl-5-tiazoleetanol to form esters poly (methyl thiazole eugenoxo ethyl acetate) (PMTEEA). The result of the synthesis was analyzed by FTIR and ^1H NMR. This polyester product synthesis was applied as a carrier for separating metal ions Cu^{2+} , Cd^{2+} and Cr^{3+} with variations in feed phase pH = 5 and pH = 7 in the membrane of chloroform using techniques BLM. Receiving phase after 24 hours was analyzed by AAS. In variations of feed pH = 5 ions was obtained 66.21% Cd^{2+} , 28.83% Cu^{2+} and 10.92% of Cr^{3+} , at pH = 7 was obtained 70.77% Cd^{2+} , 30.14% Cu^{2+} , and 3.72% of Cr^{3+} .

1. Introduction

Due to the discharge of large amounts of metal-contaminated wastewater, industries bearing heavy metals, such as Cd, Cr, Cu, Ni, As, Pb, and Zn, are the most hazardous among the chemical-intensive industries. Because of their high solubility in the aquatic environments, heavy metals can be absorbed by living organisms. Once they enter the food chain, large concentrations of heavy metals may accumulate in the human body. If the metals are ingested beyond the permitted concentration, they can cause serious health disorders [1].

One method for separating metal ions are liquid separation membrane [2]. In the liquid membrane technique, carrier compounds play an important function. Compounds carrier as a facilitator is determinant in the separation performance from the feed phase. A carrier compounds should has high ability to extraction via stable complex formation within the membrane, having high selective separation towards certain species, has good solubility as well as diffusion coefficient in the suitable organic solvent (membrane) and can be used in relatively a small amounts [3]. Besides that, a selectivity compounds carrier towards certain metal ions determined by the active groups on the carrier compound.

Carrier compounds will form complexes with metal ions through chemical bonds between the active group with a metal ion, this establishment is based on the theory HSAB (Hard and Soft Acids Bases), this theory states that in general the metal acid hard ions (such as alkali, alkali earth, and Cr^{3+})



will form stronger complex with the bases hard (such as RO⁻), ion acid soft metal (such as Cd²⁺) will form a stronger complex with a soft metal (such as RS), and metal acid borderline ions such as Cu²⁺ will form strongwe complex with a bases borderline (such as pyridine) [4].

Carrier compounds used in this study was poly (methyl thiazole eugenoksi ethyl acetate) (PMTEEA). PMTEEA has thiazole groups containing atoms of N and S was selective towards certain metal ions. PMTEEA was a derived compounds of polyeugenol. Polyeugenol is polymerised of eugenol. Eugenol contained in clove oil, has three active groups: allyl, methoxy and hydroxyl. From the hydroxyl groups can be substituted by more selective groups. make eugenol has potential as a selective compound carrier. Eugenol has been widely used for the separation of heavy metals, including eugenol polymer (polyeugenol) used to adsorb ion Fe (III) [5,6], as a functional polymer in membrane in situ [7] and in particles membrane [8,9]. Polyeugenol that has many OH groups (bases hard) has been researched the possibility of using as the carrier for separating metal ions Cr³⁺ [10] and the carrier compound that has active group N derived from polyeugenol has selective towards metal ion Cu²⁺ with percent transport 87, 54% [11]. In this study, we expected that the active group N which is borderline base ligand will selective binds towards Cu²⁺(bordrline acid metal), while the active ion/group S which is a soft base ligand will selective binds towards Cd²⁺ (soft acidic metal ion).

2. Methodology

Polymers synthesized used as a carrier substance in heavy metal recovery used Bulk Liquid Membrane (BLM) techniques. Metal solution containing each 30 ppm Cr³⁺, Cu²⁺ and Cd²⁺ with variations in pH = 5 and pH = 7 as feed phase and HCl as the receiving phase (stripping phase). pH was kept constant, pH = 1. The remaining heavy metals in feed phase and transported in receiving phase were determined by AAS.

2.1. Materials.

The materials were purchased from SIGMA-Aldrich, Eugenol, BF₃-diethylether while other reagents were purchased from E Merck, Germany: SOCl₂, 4-methyl-5-thiazoleethanol, NaOH, chloroacetic acid, CrCl₃·6H₂O, CuCl₂·2H₂O, CdCl₂·H₂O. Chloroform, Methanol, Diethylether and demineralized water were purchased from Bratachem.

2.2. Instrumentation

The instruments used to characterization of PMTEEA in this study were FTIR Spectrophotometer (Shimadzu 8201PC), and GC MS (Shimadzu QP2010S), NMR ¹H JEOL-MY60, analytical balance (Mettler Toledo AB54-S), Atomic Absorption Spectrophotometer (Perkin Elmer), pH meter (HACH E C20).

2.2.3. Equipments. Laboratory Glassware and a set of tools BLM (U tube, Fig 1).

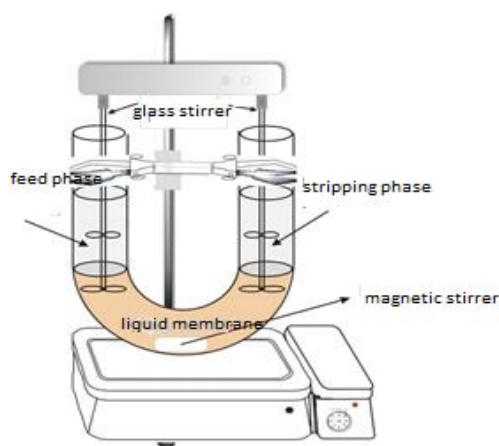


Figure 1. U Tube BLM

3. Procedure

3.1. Liquid Membrane Preparation

0.7 g PMTEEA was dissolved in 30 mL of chloroform.

3.2. Recovery process

A solution of 30 mL PMTEEA was poured in the U tube was placed between the feed phase and phase receiver each 13 mL, then stirred for 24 hours.

3.3. Measurement of pH

After the feed phase and stripping phase through the mixing process for 24 hours, the pH was measured by pH meter on both side.

3.4. Analysis by AAS

Analysis of the metal ion content in the feed phase and phase receiver after the separation process was done by atomic absorption spectrometer.

3.5. Synthesis of Compounds Carrier PMTEEA

3.5.1. Synthesis Polyeugenol. Eugenol (5.8 g) was put in a 3-necked flask, then 0.25 mL of boron trifluoride diethyl ether, $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ was added as catalyst. The addition was done 4 times every hour while stirring with magnetic stirrer at room temperature. The occurrence of a reaction can be characterized by the color change of the solution into red. After the last addition of the catalyst, the polymerization was allowed to continue up to 12-16 hours, after which 1 mL of methanol was added to stop the reaction. The gel produced was dissolved in chloroform and put into a separating funnel and then washed repeatedly with distilled water until neutral. The organic layer was transferred into a 50 mL erlenmeyer flask and added with anhydrous Na_2SO_4 . The liquid was separated by decantation. Afterwards, the solvent was evaporated in rotary evaporator at 40 °C. The residue obtained was further dried in the desiccator, and was subsequently weighed and characterized using FT-IR.

3.5.2. Synthesis Poly Eugenoxi Acetic Acid . A total of 5 g of polyeugenol was added to the boiling flask size of 100 ml, and then added a solution of 17.5 mL NaOH 33% (33 g NaOH in 100 mL) of. Subsequently the mixture was stirred for approximately for 30 minutes, and added 12.5 mL of a 50% solution of chloroacetic acid (50 g in 100 mL water) slowly with a pipette and stirred constantly. The mixture was heated in a water bath with a temperature of 80-90° C. Heating was carried out for 2 hours, then cooled and acidified with 6 M HCl until pH reached 1. Step further was extracted with diethylether for 3 times, each 50 mL. Ether extracts were combined and extracted with sodium bicarbonate 5% w / v for 3 times each 30 mL, and then the water layer was acidified with 6 M HCl to pH = 1. The subsequent steps were filtered, dried and weighted. The results were analyzed by FTIR and ^1H NMR.

3.5.3. Synthesis PMTEEA . Amount of 3 g of polyeugenoxi acetic acid was added to three neck flask of 100 mL size with additional equipment (an addition funnel, reflux) and .added by 3 ml of thionyl chloride dropwise. Then the mixture was refluxed for 150 minutes in a warm water bath (40 ° C), and then allowed to cool. Subsequently added to the mixture was added 2.5 mL tiazoletanol dropwise and refluxed again in the warm water bath (40° C) for 6 hours. After cooled, the results obtained were dissolved in chloroform and washed with water. The extraction was dried with anhydrous sodium sulphate, filtered and then evaporated to remove the remaining solvent. The results obtained were analyzed by FTIR and ^1H NMR and also GC MS.

4. Results and Discussion

4.1. Synthesis Polyeugenol

The result of polyeugenol synthesis was reported [9,by Djunaidi, et al, 2010 and 2015. Polyeugenol synthesis then was used for synthesised polyeugenoxi acetic acid.

4.2. Synthesis Poly (Eugenoksi Acetic) Acid

Polyeugenol synthesised has a phenol group, allyl and methoxy. It makes polyeugenol can be synthesized into other compounds such as in the form of poly eugenoxi acetic acid. Polyeugenol has hydroxy groups which can react with bases to form polyeugenolat salts. Proton in OH is easily separated because the shape of the anion stabilized by the resonance of the benzene ring. The addition of NaOH excess were intended to obtain salts as much as possible. This polyeugenolat sodium salt was reacted with chloroacetic acid to form polyeugenoxi acetic acids and then purified with diethyl ether to remove nonpolar impurities and extracted with sodium carbonate to remove impurities- which is polar (figure 2). The results obtained acid synthesis of poly (eugenoxi acetate) with a yield of 4.53 g of 90.6%.

The following reaction mechanisms that occur:

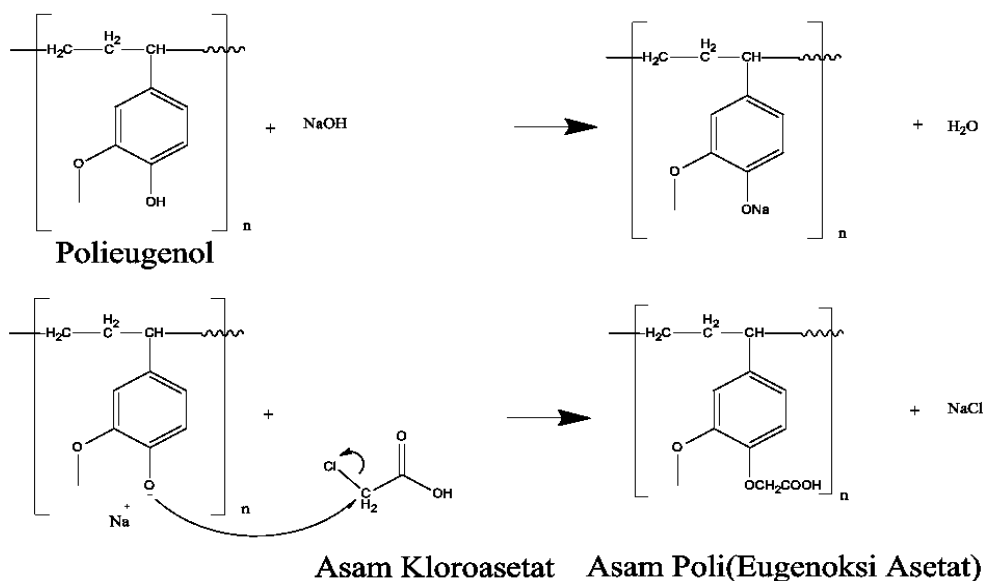


Figure 2: Mechanism acid synthesis reaction of poly (eugenoxi acetate)

Whereas the FTIR spectra was obtained as follows:

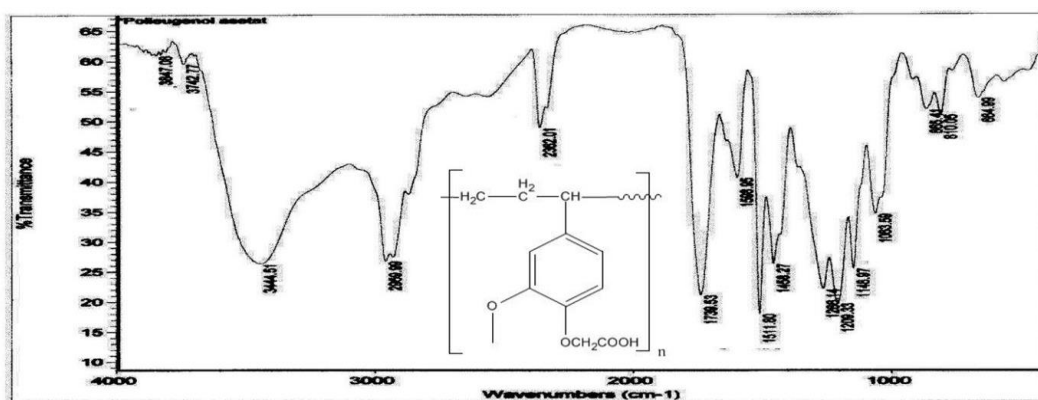


Figure 3. FTIR spectra of compounds polyeugenoxi acetic acid

FTIR spectra appear (figure 3) on acid carbonyl group shown in the bands 1739 cm⁻¹. This indicates there has been a carboxylation reaction in the presence of acetate groups on polyeugenol. While the ¹H NMR spectra was as follows:

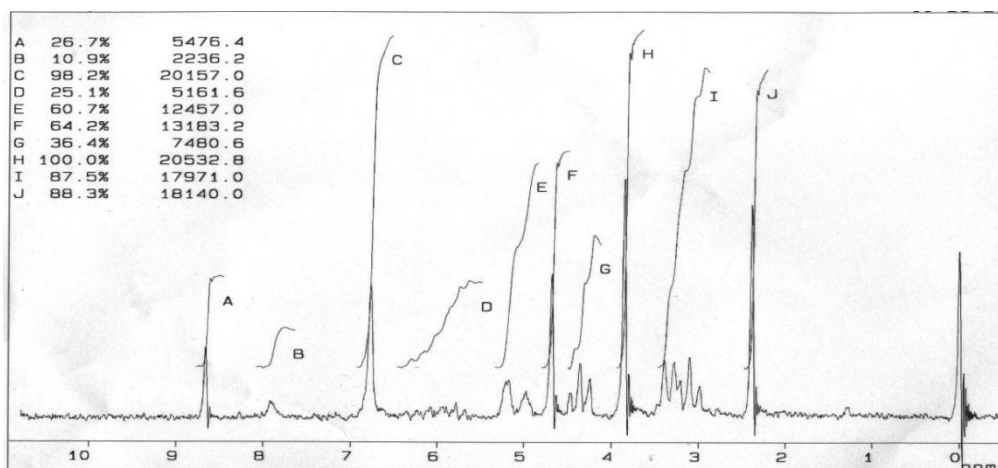


Figure 4. ¹H NMR acid compound polyeugenoksi acetic acid

Table 1. Correlation of ¹H NMR signals (figure 4) to the type of proton polyeugenoxi acetic acid

Chemistry Shift δ (ppm)	Integration	Information
6.7-7	3 H	-C ₆ H ₃ , s
4.6	2 H	-OCH ₂ -, s
3.8	3 H	-OCH ₂ -, s
0.5-1.5	3 H	-CH ₂ -CH ₂ -, m

Spectrum -IR of poly eugenoxi acetic acid (figure 4) was similar to the spectra poly eugenoxi acetic acid through the monomer way synthesis [12].

4.3. Synthesis of PMTEEA

This compound was esterified use thionyl chloride to converse the polyeugenoxi acetic acid into hydrochloric acid. The hydrochloric acid formed then was reacted with an alcohol (4-Methyl-5-Thiazoletanol). The result was 2.9361 g blackish brown solid. The yield results was 97.9%. The following reaction mechanisms that occur:

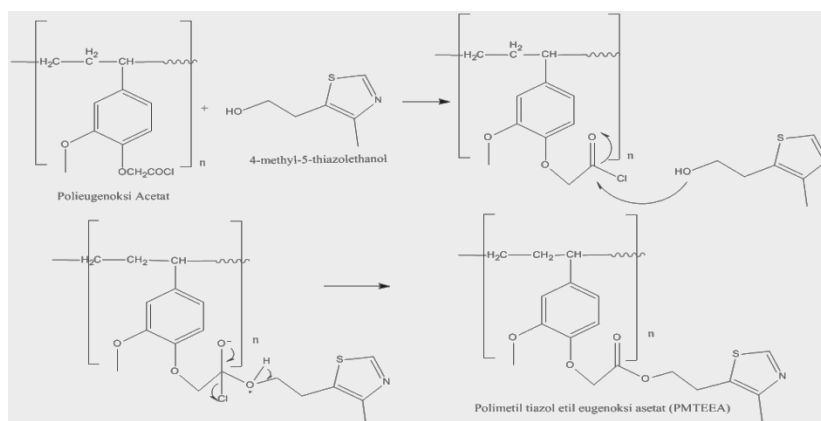


Figure 5. The mechanism of the synthesis reaction PMTEEA

FTIR analysis of the product was presented in the figure 6 :

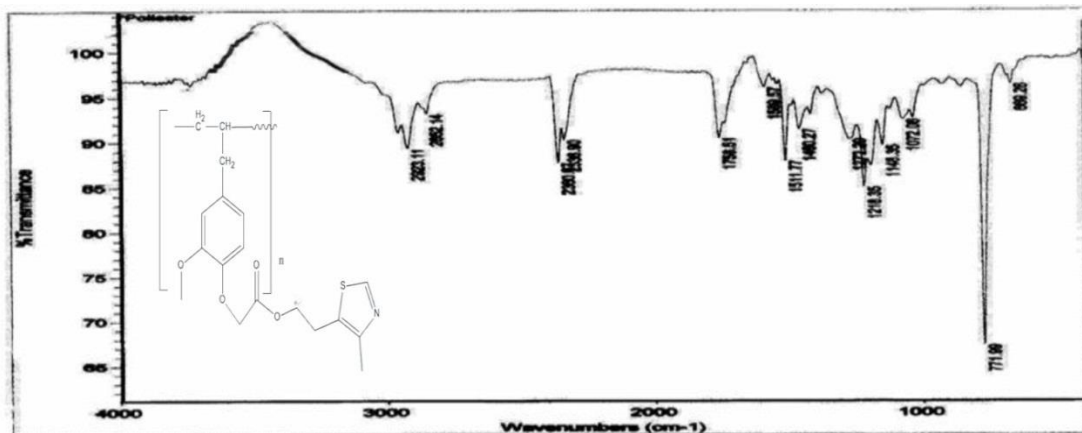


Figure 6. FTIR spectra PMTEEA (with solvents)

The FTIR spectra (figure 6) showed loss of the OH group ($3400\text{-}3500\text{ cm}^{-1}$) which was replaced with a methyl group thiazole ethanol and the appearance of an absorption band in the region ester carbonyl group (1758 cm^{-1}) which showed an esterification reaction. (Table 3.2 distinguishes acid FTIR results poly (eugenoksi acetate) with PMTEEA).

Table 2. Results of the analysis of the infrared spectra PMTEEA.

Group	Absorption (cm^{-1})	
	Polyeugenoxy acetic acid	PMTEEA
Hydroxyl	3400-3500	-
Carbon saturated	2960	2923
Carbonyl ester	-	1758
Carbonyl acid	1739	-
Metylen	1458	1460
Eter (C-O)	1300-1000	1300-1000

PMTEEA compounds was tested by ^1H NMR instrument for strengthening that the esterification reaction occurred. ^1H NMR spectra following (figure 7):

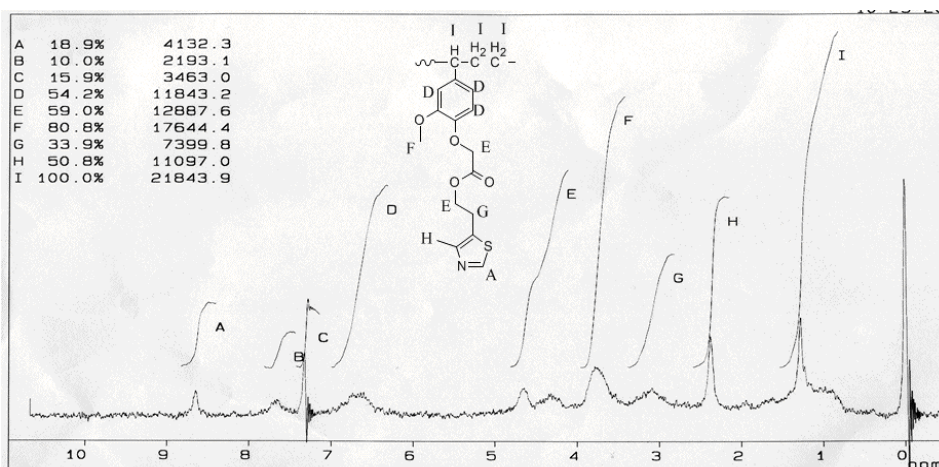


Figure 7. ^1H NMR PMTEEA

Peak at $8.5\ \delta$ (figure 7) indicates that the hydrogen atoms of the thiazole group has been entered in the acid poly eugenoxi acetic acid. The loss of OH peak at $5.5\ \delta$ on the compound 4-methyl-5-

tiazoletanol showed that the formation of esters. While the peak at 7.3 δ showed that the H atom of chloroform which has not evaporated.

4.4. Transport Mixed Metal Ion BLM Technique Using Active Compounds Carrier PMTEEA.

In this application, 0.7 g PMTEEA as compound carrier was dissolved in 30 mL of chloroform, with the feed phase was a mixture of metal ions Cu^{2+} , Cd^{2+} and Cr^{3+} in buffers pH = 5 and pH = 7, while stripping phase was a solution HCl pH = 1. The recovery process using BLM method was based on the formation of a stable complex between the ligand to the central atom. BLM process was carried out for 24 hours with continuous stirring.

Table 3 indicated that after stirring for 24 hours there was decreased pH in the feed phase and the increase in the pH in the receiving phase. This was because at the time of contact between the feed and the membrane phase, carrier compounds would form complexe with metal ions, will then be taken to the interface layer membrane-phase stripping. In this layer carrier compound released metal ions bounded and replaced with H^+ and then migrate to the interface layer membrane- feed phase to be released and replaced with a metal ion. This process occurs repeatedly until no metal ions can be exchanged. The mechanism of transport of metal ions from the feed phase to receiving phase through the chloroform membrane as shown in the picture below (figure 8).

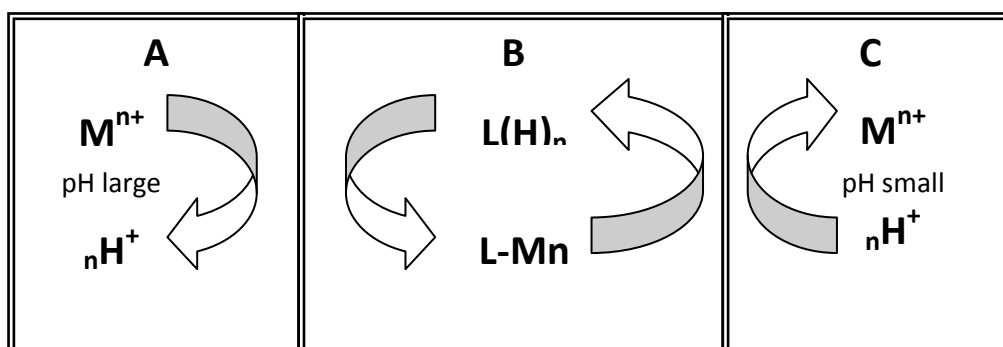


Figure 8. The mechanism of transport of metal ions from the receiving phase to phase feed through the membrane chloroform

A: feed phase B: organic phases C: phase receiver

L: carrier M: metal ion

Table 3. Changes in pH before and after stirring at BLM

pH buffer	pH Feed phase		pH stripping phase	
	pH _{t=0}	pH _{t=24}	pH _{t=0}	pH _{t=24}
5 ^a	5.01	4.2	1.0	3.06
7 ^b	7.4	4.3	1.0	2.91

^a pH buffer 5: mixture of metal ion (Cr^{3+} , Cd^{2+} and Cu^{2+}) in a buffer solution with pH = 5

^b pH 7 buffer: : mixture of metal ion (Cr^{3+} , Cd^{2+} and Cu^{2+}) in a buffer solution with pH = 7

4.5 Metal Ion Transport In the feed phase pH = 5 and pH = 7

In this experiment, 0.7 g PMTEEA was dissolved in chloroform as membrane phase and feed phase adjusted at various pH = 5 and pH = 7 to test the selectivity and effectiveness of the transport of metal ions on the effect of feed concentration. pH = 5 and pH = 7 was used because all of metal ions can be extracted at a pH near neutral (Hiratani, et al, 1992). In addition, according to a study [13] most of the reaction complex formation required a very low level of acidity or slightly alkaline as a condition to get a perfect extraction. Results transport mix metal ion was shown in Figure 9 and Table 4.

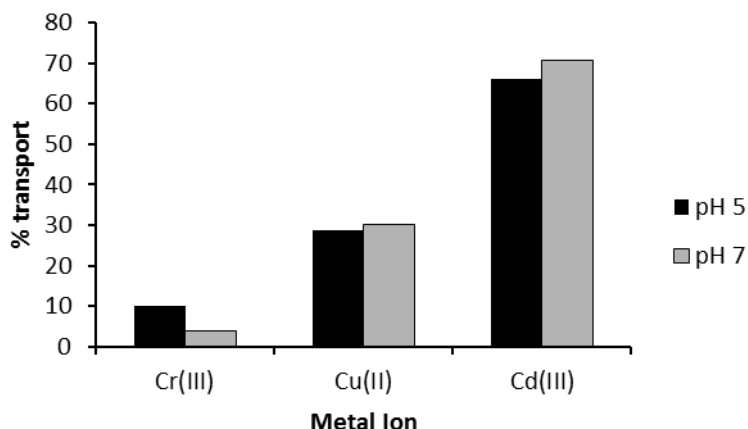


Figure 9. Diagram of metal ion transport in feed phase in feed pH = 5 and pH = 7

Table 4. Percent transport of metal ions in the receiving phase

Metal Ion	% Transport at receiving phase	
	pH (Feed phase) = 5	pH (receiving phase) = 7
Cr ³⁺	10.92	3.72
Cu ²⁺	28.83	30.14
Cd ²⁺	66.21	70.77

Ligands PMTEEA has active group S and N, based on the theory HSAB Pearson (1963) [4], which states that in general ions hard metals (such as alkali metals, alkaline earth, and Cr³⁺) form stronger complex with donor atoms hard (such as RO⁻), ion soft metals (such as Cd²⁺) form a stronger complex with donor atoms of soft (such as S), and the metal ions borderline as Cu²⁺ with donor atoms borderline such as pyridine (N), then the active group S binds to complex strongly with Cd²⁺ whereas the active group N complex binds strongly with Cu²⁺. Cahyono [11] has been conducting research using eugenol has N as a carrier, his study indicated that the carrier more selective towards Cu²⁺ followed next by Cd²⁺ and Cr³⁺. Similarly, HSAB theory was worked in the selective transport OH group of polyeugenol toward metal ions Cr³⁺ [10].

Cd²⁺ was transported greatest at pH = 5 and pH = 7 because the S atom in the thiazole group has a great affinity towards Cd²⁺ compared with the N atom to Cu²⁺. In addition, the percent metal ion transport at pH = 7 was slightly larger than at pH = 5. This was because most of the reactions of complex formation, required a very low level of acidity or slightly alkaline as a condition to get a perfect extraction [13].

5. Conclusion

Poly methyl thiazole eugenoksi ethyl acetate) (PMTEEA) could be synthesized from eugenol (especially from polyeugenol). PMTEEA could be used as a carrier for the recovery Cd²⁺, Cu²⁺ and Cr³⁺ with Bulk Liquid Membrane (BLM) Technique. At pH 5 and 7 feed phase the sequences of transport in BLM were Cd²⁺, Cu²⁺, and Cr³⁺ that proved HSAB theory works.

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