Synthesis of Poly(ethyl eugenyl oxyacetate) as Carrier For Separation of Heavy Metal Ions Fe(III), Cr(III), Cu(II), Ni(II), Co(II), and Pb(II) Using Liquid-Liquid Extraction Method

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Abstract. Synthesis of poly(ethyl eugenyl oxyacetate), PEEOA, has been conducted. The compound was applied to separate Fe(III), Cr(III), Cu(II), Co(II), and Pb(II) using a liquid-liquid extraction method. The effect of pH, polyeugenyl ethyl oxyacetic ion carrier concentration, extraction time, and metal concentration was optimized to obtain optimum condition. The result showed that the synthesized polyeugenyl ethyl oxyacetic has a yellow color with a melting point 127-130 °C and yield efficiency of 87%. The formation of polyeugenyl ethyl oxyacetic acid was confirmed with IR spectroscopy and 1H-NMR spectra. The appearance of the absorption band at 1759 cm⁻¹ as stretching vibration of carbonyl (C=O) ester and 1280 and 1373 cm⁻¹ as stretching vibration of carbonyl (C-O-C), chemical shift at 4.74 ppm for proton methylene (CH₂-C=O) and chemical shift at 1.27 ppm for proton methyl (O-CH₂-CH₃). The optimum condition for ion separation has occurred at pH 3-6 for ion Fe(III), pH 5 for ion Cr(III), Ni(II), Co(II), Cu(II), and Pb(II). The carrier volume was optimum at 5 mL (1 × 10⁻³ M) for Fe (III), 10 mL for Cr(III), Ni(II), and Co(II), and 15 mL for Cu(II), and Pb(II). The optimum extraction time was 2.5 and 20 hours for ion Fe(III) and Cr(III), respectively, and 36 hours for ion Cu(II), Ni(II), Co(II) and Pb(II). The concentration range of metals ion accurately extracted was 0.75 - 5 x 10⁻⁴ M for ion Fe(III); 0.75- 2.50 x 10⁻⁴ M for Cr(III), Ni(II), and Co(II) and 0.75-1 x 10⁻⁴ M for Cu(II) and Pb(II). Compared to other metal ions the respond polyeugenyl oxyacetic acid was best Fe(III) with selectivity order Fe(III) > Cr(III) > Cu(II) > Pb(II) > Ni(II) > Co(II).

1. Introduction

Mineral mining and metal industry activities have increased rapidly to fill the requirement of the metals, pure metals or alloys requirement. In general, the results of mining minerals still in an alloy. These conditions make the economic value of metal minerals is low. To obtain more pure metals from alloys, there is a need to conduct the separation process. The main obstacle obtaining pure metal is a sensitive and selective method for separating one metal from others [1–4].
A solvent extraction or liquid-liquid extraction technique is one of the methods that can be used to separate and purification process of metal. A liquid-liquid extraction technique was continuously studied and developed to increase the efficiency and selectivity of the metal separation and concentration in a small or industrial scale [5,6]. One of the efforts to increase the selectivity of certain metals or alloys can be made by obtaining new extractants from pure molecular compounds or broad molecular weight polymers. Generally, polymer extractants have advantages because they have a large separation capacity. The extractant is an essential component in the separation process has a role in increasing selectivity and efficiency in liquid-liquid extraction. Therefore it is essential to develop new extractant materials through synthesis for metal ions to be a target. One of the extractant material is ligands. The ligand requirements for proper extraction have several criteria, such as selective production, easy and simple, high extraction capacity, and safe for the environment [7,8].

To date, polymer ligands have been developed to meet the criteria for ligands with excellent extraction capabilities. Polymers such as polyeugenol and its derivatives have developed as one of the new ligands for the separation of Fe (III), Cu (II), Ni (II), Co (II), and Pb (II) metal ions by solvent extraction method with the selectivity sequence Fe (III)> Cr (III)> Cu (II)> Pb (II)> Ni (II)> Co (II) [9–12]. In addition, polyeugenyl oxyacetate as a derivative of polyeugenol can be synthesized by adding a functional group of acetate from polyeugenol with chloroacetic acid to function as a suitable ligand. The ability of a carrier to bind metals depends on the number of active groups bound to the polymer, while its selectivity for metal targets depends on the size of the cavity and the rigid molecular structure [13–15]. The carrier capability for separation influenced by several factors there i.e metal acidity, carrier alkalinity, and metal or carrier size. However, based on the literature study until now studies of the behavior of polyeugenyl oxyacetate ligands as extractants to extract Fe (III), Cu (II), Ni (II), Co (II), and Pb (II) metals have never been done. In this research, a study has been conducted to determine the extraction behavior of Fe (III), Cu (II), Ni (II), Co (II), and Pb (II) metal ions using poly (ethyl eugenol oxyacetate) extractant.

2. Experimental

2.1 Materials

The materials used in this experiment were polyeugenol, ethyl chloroacetate, ethanol, chloroform, diethyl ether, NaOH, Na2SO4 anhydrous, NaCl, HCl, Fe(NO3)3·9H2O, Cr(NO3)3·6H2O, Ni(NO3)2·6H2O, Cu(NO3)2·3H2O, and Pb(NO3)2.

2.2. Synthesis of Poly(ethyl eugenol oxyacetate) (PEEOA)

3,9 gram of polyeugenol, 2,9 gram (0.02398 mol) of ethyl-2-chloroacetate, 3,6 gram (0.02398 mol) of sodium iodide, and 4,1 gram (0.0312 mol) of potassium carbonate were added into 250 mL three-neck flask equipped by a condenser. 150 ml of dry acetone was added into the three-neck flask then the mixtures was heated at 60 °C under flowing nitrogen gas. The mixtures was refluxed for 24 hours. After being refluxed, the solution was cooled. The excess of potassium carbonate was filtered the then filtrate was evaporated. The obtained residue was dissolved in chloroform and washed three times with 1 M HCl and once with saturated NaCl solution; It was then dried with anhydrous sodium sulfate (Na2SO4). The filtrate was evaporated to dryness and re-crystallized using absolute ethanol.

2.3. Separation of Fe(III), Cu(II), Ni(II), Co(II), and Pb(II) by liquid-liquid extraction using PEEOA

The solutions of Fe(III) pH was adjusted (3, 4, 5, and 6) then added into the extraction tube; then 10 ml of 10–3 M PEEOA solution was added into each extraction tube. The extraction tubes were closed; then shaken by a shaker for 20 hours at room temperature. After the extraction completed, the solution separated between water and an organic phase in the separating funnel. The concentration of the metal ion, Fe(III), in the water phase was analyzed by atomic absorption spectrometry (AAS). The same treatment was done for Cr(III), Cu(II), Ni(II), Co(II), and Pb(II); the optimum pH for each metal was obtained. The result of pH optimization was used to optimize the concentration of the carrier (5, 10,
15, and 20 mL), the extraction time (5, 10, 15, 20, and 36 hours), and the metal concentration (0.75x10^{-4}, 10^{-4}, 2.5x10^{-4}, 5x10^{-4}, and 7.5x10^{-4} M), to get the optimum condition.

3. RESULTS AND DISCUSSION

3.1 Synthesis and characterization PEEOA

PEEOA compound obtained by synthesis was yellow crystalline solid with melting point 127-130 °C and 87% yield. The FT-IR spectra of PEEOA shown in Figure 1.

![Figure 1 IR spectra of (A) polueugenol; (B) Poly(ethyl eugenyl oxyacetate)](image)

In Figure 1, a strong absorption at 1735.8 cm\(^{-1}\) region shows the carbonyl stretching vibration (C=O) acid. The absorption at 3425.3 cm\(^{-1}\) region is from -OH absorption and strong absorption at 2931.6 cm\(^{-1}\) region show the existence of alkyl. Strong absorption at 1512.1 cm\(^{-1}\) and 1596.9 cm\(^{-1}\) regions show the existence of aromatic compounds whereas the absorption at 1458.1 cm\(^{-1}\) contains the methylene group (-CH\(_2\)) and the absorption between 1300 cm\(^{-1}\) - 1050 cm\(^{-1}\) from stretching vibration O-C aromatic. A fundamental difference of polyeugenyl oxyacetate and polyeugenol is absorption at 1735.8 regions as a vibration absorption of carbonyl stretching (C=O) acid.

The analysis of \(^1\)H-NMR spectra shows absorption in some areas shown in Figure 2. In Figure 2 the \(\delta\) value at 6.8 ppm is a stretching vibration of aromatic proton, the \(\delta\) value at 4.6 ppm is a stretching vibration of carboxyl proton (CH\(_2\)-C=O), the \(\delta\) value at 3.8 ppm is stretching vibration attached to a methoxy group (\(-\text{OCH}_3\)) and the \(\delta\) value at 0.8–1.2 ppm is the stretching vibration of methylene CH\(_2\)-CH\(_3\).
Based on the IR and $^1$H-NMR data polyeugenol and poly (ethyl eugenyl oxyacetate) compounds as synthesis target can be formed with the prediction structure shown in Figure 3.

![Figure 2 $^1$H-NMR spectra of (A) polyeugenol; (B) Poly(ethyl eugenyl oxyacetate)](image)

**Figure 2** $^1$H-NMR spectra of (A) polyeugenol; (B) Poly(ethyl eugenyl oxyacetate)

3.2 **Determination of extraction parameters with a carrier of poly eugenol acetate**

To analysis, a carrier’s ability of synthesized polyeugenyl acetate in separating Fe(III), Cu(II), Ni(II), Co(II), and Pb(II) metal ions in a solution through an experiment of the liquid-liquid extraction, the affected factors need to be optimized.
3.3 Effect of pH

The ability of polyeugenol acetate to separate Fe(III), Cu(II), Ni(II), Co(II), and Pb(II) metal ions using extraction method is related to the capacity of polyeugenol acetate to accommodate metal ion through a proton exchange at the active group of acetate. Six tested metal ions show that the maximum number of extracted ions are at pH 3–6 for Fe(III), pH 5 for Cr(III), Ni(II), Co(II), and pH 6 for Cu(II), Pb(II) as shown in Figure 4.

![Graph of pH of the solution versus percentage extraction](image_url)

**Figure 4** Graph of pH of the solution versus percentage extraction

Figure 4 shows that the rising of pH causes the decreasing of the metal concentration in the water phase or the increasing of the percentage extraction particularly for Fe(III), Cr(III), Cu(II), and Pb(II) ions although Ni(II) and Co(II) also extracted. At pH, more than 5 or above optimum pH, the extraction percentage result for Cr(III), Ni(II), and Co(II) ions is decreases because the possibility of the metal ions undergoes hydrolysis or precipitation. It makes the amount of metal ions that form a complex is small. This result according to the nature of the acid carrier—the ability to form a complex with metal ion was greatly influenced by pH, the metal ion speciation in the solution and the acidity of metal which will be separated. In addition, this result is another possibility caused by differences in size, hydration level, and complex bond constants formed from each metal ion by the functionalization of oxyacetate polyeugenyl [1,2,16].

3.4 Effect of polyeugenyl oxyacetate concentration

The concentration of polyeugenyl oxyacetate or the number of polyeugenol oxyacetate moles in organic solution will influence the number of moles of metal ion extracted from the water phase shown in Figure 5 and 6.
Figure 5 shows that the increasing of polyeugenyl oxyacetate concentration in the organic phase will increase the number of extracted ions Fe(III), Cr(III), Ni(II), Pb(II), Co(II), and Cu(II), an indication of the smaller concentration of metal ions in water phase. In the case of Fe(III) ions, all the metals in the solution have extracted 100%. This result occurs because the number of active cluster carrier increased the lead to more capacity to bind metal ions in the aqueous phase and then diffuse into the organic phase [1,2]. While at the higher concentration, the number of extracted metal ions decreased because the existence of metal ions in the solution is not found. The metal ions Cr(III), Ni(II), Pb(II), Co(II), and Cu(II) have the same tendency, but the ability of extracted metal is smaller than that of Fe(III) ion.
3.5 Effect of extraction time
The extraction time will affect the number of metal ions extracted from the water phase to the organic phase because the longer the contact time between the ion carrier solution and metal solution more the complex formed. Afterward, ion metals diffuse into the organic phase as in Figure 7.

![Figure 7 Graph of extraction time versus percent extraction](image)

Figure 7 Graph of extraction time versus percent extraction

Figure 7 shows that increasing the length of extraction time has an impact on the number of extracted metal ions. The longer the contact time between ligand and metal solution make more the metal ions change into a complex in the water phase than extracted into the organic phase. In a short time (10 hours), the extraction rates slow because the contact time between the organic phase and the water phase is relatively short. The extraction rate will rise according to the extraction time. It showed by increasing the percentage of metal ions. The maximum extraction percentage of metal ions achieved at 36 hours except for Fe(III) ions. Fe(III) ions metal requires a shorter time than Cr(III), Ni(II), Pb(II), Co(II), and Cu(II) ions. All of Fe(III) metal ions have been extracted in the water phase to the organic phase in extraction time 2.5 hours [17,18].

3.6 Effect of metal concentration
The number of metal concentrations in solution will affect the ability of the carrier with the fixed concentration to be extracted from the water phase to the organic phase as in Figure 8. Effect of metal concentration on the percent extraction at pH 4 with 5 mL carrier (Fe(III) ion), pH 5 with 10 mL carrier (Cr(III), Ni(II), and Co(II)), and pH 6 with 15 mL carrier (Cu(II) and Pb(II)), the concentration of each metal is $10^{-4}$ M and the carrier concentration of oxyacetate is $10^{-3}$ M.
Figure 8 Graph of metal concentration versus extraction

Figure 8 shows that the extraction of metal ions is affected by metal ions concentration of Fe(III), Cr(III), Ni(II), Pb(II), Co(II), and Cu(II) in the water phase. When the concentration of metal ions in water phase increases, the number of metal ions also extracted increases by an indicated of the smaller concentration of metal ions in the water phase. This result is likely due to higher metal ion concentrations at the interface of the organic phase compared to low concentrations. However, at the higher metal concentration, the extracted metal ions become smaller. The possibility caused by the carrier having the number of active groups (site) with the fixed concentration; consequently, the number of metal ion concentrations which can be exchanged becomes limited. At a particular concentration, all of the carrier active groups (situs) have bound the metal ions. In this condition, even though the concentration of metal ions increases, no impact on increasing the number of the extracted metal ions. However, it will only decrease because the metal activities in the solution become lower, so the metal ions that form the complex was reduced. Fe(III) has the best-extracted ability than other metals because Fe(III) has the more significant load and the suitability of the size of metal with the ligand, although Cr(III) also has the same load [7,17].

4. Conclusions
Polyeugenyl oxyacetate can be synthesized by polyeugenol and chloroacetic acid which refluxed for 30 hours and characterized by IR and 1H-NMR spectra. The synthesized Polieugenyl oxyacetate used for the separation of Fe(III), Cr(III), Ni(II), Pb(II), Co(II), and Cu(II) ions by solvent extraction method. The Fe (III) ion with a broader pH range (3–6), the smaller mole ratio of the carrier: metal (5:1), the shorter extraction time (2,5 hours), and the metal concentration still be extracted fully (0,75–5 x 10^-4 M) is the best respond of the carrier of polyeugenyl oxyacetate compared to the other ions analyzed with the selectivity sequence of Fe(III) > Cr(III) > Cu(II) > Pb(II) > Ni(II) > Co(II).

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