Removal of Cu(II) ions from aqueous solution by fatty hydroxamic acids immobilized onto bentonite

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Abstract. The mining business in Indonesia has a large contribution to economic growth and the supplies of domestic minerals. However, if the mining business is conducted illegally and does not use the good mining practice, it will not only harm the country but also risk endangering human safety due to environmental damage caused. In gold mining process, only the main metal, that is gold, is taken while the other metal is discharged into the sewer as waste. One of the metal ions to be waste is copper ion, Cu(II) ion. In this study, removal of Cu(II) ions from illegal gold mining waste was carried out using fatty hydroxamic acids (FHA) immobilized onto bentonite. The FHA used is enzymatically synthesized from Jatropha curcas L. kernel oil. The effects of Cu(II) ion pH and FHA concentration on copper removal have been investigated. The presented results indicated that the extraction of Cu(II) ion was very sensitive to the copper ion pH and extractant concentration. The optimum pH of Cu(II) ion adsorption by FHA-Bentonite (FHA-Bent) is pH 5. A quantitative recovery of Cu(II) ion from FHA-Bent was obtained using 10% HNO₃ solutions as eluent with a pre-concentration factor up to 60.

1. Introduction
In general, heavy metal is defined as an element having a density greater than 5 g/cm³ or an element having a relative molecular weight of 63 to 200. Heavy metals are toxic, carcinogenic and non-biodegradable [1]. Therefore, in accordance with the Government Regulation of the Republic of Indonesia Number 101 of 2014, heavy metal waste is classified as a hazardous and toxic material. Heavy metal ions tend to accumulate in the tissues of living organisms and, even in small amounts, can cause illness and health problems [2]. Industrial waste containing heavy metals is usually directly or indirectly discharged into the environment. Some heavy metals contained in industrial waste that must be processed before being disposed of into the environment are copper, zinc, nickel, cadmium, mercury, chromium and lead. In illegal gold mining, only gold is taken, while other metals are disposed of as waste. One metal ion that is discharged into the environment with a high concentration is Cu(II) ion [3]. Copper is classified as an essential heavy metal, which means that although copper is toxic, it is needed by the body even in small amounts. However, Cu(II) ion shows moderate toxicity to human and animals [4]. High levels of copper in the blood will cause various disorders including coma, gastrointestinal distress, hypotension and jaundice. Long-term copper accumulation in the body can also damage the kidneys and liver [5].
Due to the high level concentration of Cu(II) ion in illegal gold mining waste, which can cause harmful effects on humans and the environment, it is necessary to pre-treat properly before being discharged into the environment. Faced with these problems, there is a need to use treatment methods that reduce or eliminate Cu(II) ion from watercourses. A variety of Cu(II) ion removal techniques have been studied, such as chemical precipitation [6], flotation [7], ion exchange [8], electrochemical process [9], adsorption [10] and membrane process [11]. Other methods that are widely used to removal of Cu(II) ions are solvent extraction. Suhendra has been using this method to separate and pre-concentrate of Cu(II) ion by a chelating agent, fatty hydroxamic acids, which synthesized enzymatically from palm olein [12]. Solvent extraction is the most commonly used method for extraction of metal ions, but there are disadvantages, such as difficulty of metal ion recovering, high-energy requirements and production of sludge [1,13,14].

An efficient and selective method for extraction of metal ions in aqueous media is to use chelating agents which are immobilized onto the adsorbent [15]. One of the superior reagent for extraction of metal ions is hydroxamic acids (HA). HA, general formula R-CO-NHOH, is a derivative compound of hydroxylamine and carboxylic acid. However, HA has the chelating properties of metal ions which are selectively stronger than carboxylic acids [16]. In this work, we use fatty hydroxamic acid (FHA), which is synthesized enzymatically from Jatropha curcas oil, which is immobilized onto bentonite as an extractant for removal of Cu(II) ions from aqueous media. FHA is a long chain HA that has a hydrophobic and hydrophilic group. The hydrophobic group of FHA will be adsorbed by the bentonite surface, while the hydrophilic group is a chelating agent that is selective for Cu(II) ions. The use of bentonite as a supporting matrix of FHA is due to its abundant availability, low price, besides it has a large surface area [17].

2. Method
2.1. Materials and instrumentation
Jatropha curcas oil is a non-edible and non-commercial vegetable oil. This oil is extracted from the seeds of Jatropha curcas using the Cunnif method [18]. Before being used, Jatropha curcas oil was purified using column chromatography with Silica Gel 60 (0.063 - 0.200 mm, Merck Germany) as an adsorbent and eluted using a mixture of hexane-diethyl ether (87:13, v/v) [19]. Analytical-grade of hydroxylamine hydrochloride, hydrochloric acid, sodium hydroxide, sodium phosphate, phosphoric acid, acetic acid, hexane, methanol, vanadium pentoxide, copper nitrate, nickel nitrate and lead nitrate (all from Merck, Germany) were used without any further purification. The lipase used was Lipzyme TL (Thermomyces lanuginose), an immobilized lipase (Novo Nordisk, Denmark). Metal ions preparation: the Cu(II), Ni(II) and Pb(II) ions stock solution (1000 mg L\(^{-1}\)) prepared by dissolving of the copper, nickel and lead nitrates with deionized water containing 0.5 mol L\(^{-1}\) HNO\(_3\). All standard solution were prepared by diluting the stock solutions with deionized water. All metal ions analysis were done using Atomic Absorption Spectrophotometer (AAS, AAnalyst 400 Perkin Elmer, USA) with an air-acetylene flame.

2.2. Methods
2.2.1. Preparation of FHA. The procedure of synthesis of FHA from Jatropha curcas oil was described in our previous publication with some modifications [20]. The synthesis was carried out by reacting Jatropha curcas oil (2 g) dissolved in 20 mL of hexane with hydroxylamine (6 mmol), and Lipzyme TL (30 mg) in stoppered flask and shaked the mixture in shaker bath at speed of 150 rpm and temperature of 40°C for 20 h. FHA formed in the hexane fraction, separated from the water fraction, and lipase. The hexane fraction was then cooled in a refrigerator at temperature of < 5°C and then collected by filtration.

2.2.2. FHA Characterization. Qualitative tests of HA groups are carried out by reacting the FHA methanolic solutions with 0.1 M of solution of iron (III), copper (II) and vanadium (v). Changes in brown
to red, blue to green and yellow to dark brown occur when the HA group forms a colored complexes with iron (III), copper (II) and vanadium (v) ions, respectively. Qualitative tests on the HA group were also carried out using the FTIR Spectrophotometer (Perkin Elmer FTIR-Frontier, USA). Meanwhile, the quantitative test of the HA group was carried out by determining the nitrogen content using the Kjeldahl method.

2.2.3. Immobilization of FHA on bentonite (FHA-Bent). Bentonite activation was carried out using the method developed by Salem and Karimi [21], with several modifications. Bentonite clay ± 100 mesh was washed, dried and then activated using sulfuric acid solution of concentration 2 M. The activation was done by heating a mixture of sulfuric acid and 5 g of clay for one hour at 90°C. The yield is filtered, then washed with hot water until the pH of washing water ≥ 3. Dried the bentonite in an oven at 105°C until the weight constant. About 0.5 g activated bentonite was mixed with 100 mL of 2000 ppm FHA methanolic solution, shaken at 40 rpm for 10 h. FHA-Bent formed was filtered and then kept in the refrigerator at 4°C.

2.2.4. Effect of pH on Metal Ions Adsorption. This procedure refers to the method developed by Zhao et al. (2010) [22], which is modified. The adsorption procedure as follow: A mixture of 2 mmol solution of metal ions (copper, lead or nickel) and 100 mg of FHA-Bent in a 200 mL of Erlenmeyer flasks was shaking at 35 rpm for 6 h. Before mixing, the pH of the metal ion solution is adjusting at pH 1 to 6 using 0.01 M phosphate buffer solution. After the equilibrium is reached, the concentration of metal ions in the solution is determined using the flame atomic adsorption spectrophotometer.

2.2.5. General procedures of adsorption and desorption of metal ions. This general procedure for adsorption and desorption refers to our previous publication with a slight modification [23]. Extraction procedure in the column as follows: 4 g of FHA-Bent was packed into a column that has an internal diameter of 1 cm and a height of 15 cm. 1 L of a solution containing metal ion (copper, lead or nickel) with a certain concentration at pH 5 is passed through in the column. The percentage of adsorbed metal ions was carried out by measuring the metal ion concentration before and after passing through the column using AAS. The desorption procedure as follow: desorption of metal ions from the column was carried out using nitric acid as an eluent. Nitric acid (1-15%) is passed through into the column containing the FHA-Bent-Metal ion. Every 3 mL of effluent fractions are collected successively. The percentage of metal ion recovery was carried out by determining the desorption concentration of metal ions using AAS.

3. Result and Discussion
3.1. Synthesis of FHA
Characterization of the FHA synthesized from *Jatropha curcas* oil shows that the HA group has actually been formed. This is characterized by the formation of a colored complexes between FHA with copper (II), iron (III) and vanadium (v). The colors formed are green, dark red and purple, each for the complexes of FHA-copper, FHA-iron and FHA-vanadium. This characteristic is in accordance with the research conducted by Suhendra et al., 2005 [18]. The formation of the HA group is also indicated by the FTIR spectrum (Figure 1a). The HA group in Figure 1a is shown by absorption bands at wave numbers of 3050-3500 cm\(^{-1}\), 1650-1750 cm\(^{-1}\) and 1450-1600 cm\(^{-1}\) which are typical absorption bands for monosubstituted amides. Meanwhile, the absorption bands that seen at wave numbers 2800-3000 cm\(^{-1}\) and 1020-1025 cm\(^{-1}\) are absorption bands of the C-H group stretching and bending respectively. Analysis of the nitrogen content of the FHA using the Kjeldahl method was obtained 2.02%. This shows that there are 1.44 mmol HA groups in 1 g of FHA.
3.2. Adsorption of metal ions at Various pH

Adsorption capacity (mg / g adsorbent) is one of the important factors that must be determined in the process of adsorption of metal ions with adsorbents. Adsorption capacity is used to determine the amount of adsorbent needed to quantitatively remove certain metal ions from aqueous media. The effect of pH on the adsorption of metal ions on FHA-Bent system was carried out using a batch method. The metal ions used were Cu(II), Pb(II) and Ni(II) ions. The results (Table 1) show that all metal ions used were adsorbed on the FHA-Bent system. However, at pH 5 it appears that the copper ion adsorbed better than lead and nickel ions. This is probably due to the stability of the FHA-Cu complex occurred at pH 5. Therefore, pH 5 is used for the study of adsorption and desorption of copper ions in the presence of other metal ions in one system.

| Metal Ion | pH1 | pH2 | pH3 | pH4 | pH5 | pH6 |
|-----------|-----|-----|-----|-----|-----|-----|
| Cu(II)    | 0.00| 0.12| 0.21| 2.06| 3.06| 2.08|
| Pb(II)    | 0.00| 0.00| 0.16| 0.74| 1.76| 2.01|
| Ni(II)    | 0.00| 0.03| 0.33| 0.47| 1.54| 1.97|

3.3. Effect of sample flow rate on sorption of Cu(II) ion using column method

This study was conducted by varying the flow rate from 0.3 to 2 mL min⁻¹ below the optimum pH (pH 5) (as determined using the batch method). The purpose of this study was to determine the optimal flow rate of adsorption of Cu(II) by the FHA-Bent system in a chromatography column. The result (Figure 2) shows that the sorption of Cu(II) ion on the FHA-Bent was higher than 98% at the flow rate of 0.3 mL min⁻¹. The sorption decreases with the increase of the flow rate. The high adsorption capacity at the flow rate of 0.3 mL min⁻¹ is caused by the longer contact time between metal ions and the FHA-Bent.
Effect of nitric acid concentration on desorption of FHA-Bent-Cu

The study of Cu(II) ion desorption from the column (FHA-Bent-Cu) was carried out using various concentrations of nitric acid (5 - 12.5%) as eluent. This study aims to determine the optimal flow rate of eluents in the desorption of Cu(II) ions from the FHA-Bent-Cu system. The volume of nitric acid used was 20 mL at a eluent flow rate of 0.5 mL min$^{-1}$. Figure 5 showsthat the optimum desorption of Cu(II) ions from FHA-Bent-Cu occurs at the concentration of HNO$_3$ equal or greater than 10%. This is due to the stability of the FHA-Cu complex at the lowest point. Therefore, the concentration of 10% HNO$_3$ was chosen as eluent for subsequent experiment.

3.4. Effect of nitric acid concentration on desorption of FHA-Bent-Cu

Figure 3. Effect of HNO$_3$ concentrations on the desorption of copper (II) ion from FHA-Bent-Cu. Cu(II) ion 20 ppm. pH: 5. Acid volume: 20 mL. Eluent flow rate of 0.5 mL min$^{-1}$

3.5. Separation study

The separation study of copper (II) ions from lead (II) and Nickel (II) ions was carried out by extracting 1 L of solution containing 100 ppm copper (II), lead (II) and Nickel (II) ions. The adsorption of copper, lead and nickel ions were performed at 0.3 mL min$^{-1}$ of flow rate. Table 2 shows that more than
95% of Cu(II) ions were absorbed on the FHA-Bent system in the column. This result indicating that at pH 5, the FHA-Bent-Cu complexes is more stable compared to FHA-Bent-Pb and FHA-Bent-Ni.

**Table 2.** Metal ions adsorption on FHA-Bent at pH 5

| Metal Ions | Concentration (ppm) | Adsorption (%) |
|------------|---------------------|----------------|
| Cu         | 100                 | 95.9           |
| Pb         | 100                 | 41.5           |
| Ni         | 100                 | 54.7           |

Meanwhile, the study of pre-concentration factor shows that the percentage recovery of copper ions are more than 99% (Table 3). This results shows that FHA-Bent can be used as an agent for pre-concentration of copper ion in aqueous media.

**Table 3.** Pre-concentration factor for Cu(II) ion on FHA-Bent

| Vol. of Solution Passed (mL) | Concentration (ppm) | Final Elution Vol. (mL) | Recovery (%) | Pre-concentration Factor |
|------------------------------|---------------------|-------------------------|--------------|-------------------------|
| 1000                         | 100                 | 15                      | 99.01        | 66.67                   |
| 1000                         | 100                 | 20                      | 99.32        | 50                      |
| 1000                         | 100                 | 25                      | 99.67        | 40                      |

The separation of copper ion from lead and nickel ions was carried out using nitric acid (10%) as eluent and 0.5 mL min⁻¹ of flow rate. The result (Figure 4) shows that copper(II) ion is separated well from lead(II) and nickel(II) ions. Meanwhile, the lead(II) and nickel(II) are not separated. It indicating that the complexes stability constants of the lead-FHA and nickel-FHA are very close.

![Figure 4. Separation of copper ion from lead and nickel ions](image)

4. Conclusion

Fatty hydroxamic acids that enzymatically synthesized from *Jatropha curcas* L. kernel oil was successfully immobilized onto bentonite and efficiently removes copper from aqueous media. The experiments produced several optimum conditions for the removal of copper ions from aqueous media. The optimum conditions are adsorption of copper ion by FHA-Bent at pH of 5, adsorption flow rate
of 3 mL/min, eluent used for desorption is nitric acid (10%), and highest pre-concentration factor for the adsorption of copper ion is 66.67.

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