Extraction And Pre-Concentration of Zinc(Ii) Ion by Fatty Hydroxamic Acids Immobilized Onto Zeolit

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Abstract. Mining in Indonesia contributes significantly to mineral supplies nationally, but illegal mining activities can cause natural destruction, habitat loss and loss of biodiversity. This is because only the main metal, which is the gold taken while the other metal is discharged into the drain as waste. One of the metal ions to be waste is the zinc(II) ion. A method of zinc (II) ion extraction from other ions by using a column containing fatty hydroxamic acids – loaded zeolit (FHA-Zeo) is described. Several factors, which affect the extraction efficiency such as pH, sample volume, and concentration of eluent and flow rate, have been investigated. The maximum sorption capacity of FHA-zeo obtained was 88.38 mg/g. A quantitative recovery of zinc(II) ion from FHA-zeo column was obtained using 10% HNO₃ solutions as eluent with a pre-concentration factor up to 60. A method for separation of zinc(II) from lead(II) is proposed. A rapid sample throughput, a clean separation, a high pre-concentration factor and simplicity are the main advantages in these analytical procedures.

Key words: Fatty Hydroxamic Acids, Zeolit, FHA-Zeo, Pre-concentration

1. Introduction

Zinc, one of heavy metals waste in unauthorized mining processing, is an essential trace element of great importance for humans, animals and plants. Zinc(II) ions have various biochemical functions in cell metabolism, including cell replication, protein synthesis, gene expression and cell division. However, as a heavy metal, zinc has hazard and harmful impacts on human health and the environment because they are toxic even at very low concentrations. Thus, accurate detection of zinc ions at trace concentration levels in environmental or water samples is very important in analytical chemistry and environmental pollution monitoring [1, 2].

Flame atomic absorption spectrometry (FAAS) has been a useful technique to detect trace heavy-metal ions in various environmental [3, 4, 5, 6], food and beverages [7, 8, 9, 10], and water samples [11, 12, 13] because of its high selectivity, speed, easy instrument usage and low costs. However, there are many difficulties to determine low concentration of heavy-metal ions due to in sufficient sensitivity of the instrument and high interfering influences of matrix ions on the signal of the analytes [14, 15]. Thus, a pre-concentration and/or separation step is necessary. Pre-concentration is necessary to bring the concentration of the analytes into the dynamic range of the flame atomic absorption detector used, while separation is employed to eliminate potential interfering matrix constituents.
Separation and pre-concentration techniques are of great importance owing to the limited sensitivity of an analytical instrument for trace analysis. Several technologies have been widely used to pre-concentrate and separate trace metals, among them are liquid–liquid extraction by using complexing agents [16, 17, 18], and solid phase extraction [19, 20, 21, 22]. Liquid-liquid solvent extraction of metal chelating complexes has been used as a separation method for a long time. However, this method leads to many disadvantages. Among them are, usually, time consuming and labor intensive, use of large amounts of organic solvents for extraction and subsequent disposal of the solvent, which creates another environmental problem, and cannot be combines with FAAS or inductive couple plasma–atomic emission spectrometry (ICP-AES) due to the difficulties of introducing organic solvents into nebulizer of AAS or plasma of ICP-AES. Meanwhile, the solid phase extraction has low selectivity for metal ion adsorption [23].

A very efficient system for separation and pre-concentration of trace metal ions is immobilization of chelating agent on various supports. This method has several advantages over liquid-liquid extraction and solid phase extraction. The advantage includes pre-concentration from a larger sample volume and establishing higher concentration factors. In this paper, we report the results of our investigations on fatty hydroxamic acids (FHA), synthesized from ketapang (Terminalia cattapa L.) kernel oil, that immobilized onto zeolit to be used as an extractant for zinc(II) ions.

2. Materials and Methods

2.1. Materials

All of the chemicals used in this work were of analytical grade and were obtained from Merck (Darmstadt, Germany) or Fluka (Buchi., Switzerland) and bidistilled/deionized water was used in all experiments. Hydroxylamine hydrochloride, sodium phosphate, sodium hydroxide, phosphoric acid, vanadium pentoxide and nitrate salts of copper, zinc, cobalt and nickel were of the highest purity available and used without any further purification. The standard stock solutions of metal ions (1000 mg L⁻¹) were prepared by dissolving nitrate salts of the metals in 0.5 mol L⁻¹ HNO₃. The standard solutions used for calibration were prepared by diluting the metal stock solutions with 0.5 mol L⁻¹ HNO₃ before use. Non-edible and non-commercial oil, that is ketapang kernel oil was extracted from ketapang fruit kernel. The oil purified by drain off into chromatography column and eluted using a mixture of hexane-diethyl ether (87:13, v/v). Atomic absorption spectrophotometer (AAnalyst 400 Perkin Elmer) with an air-acetylene flame was used for the metal ion analysis.

2.2. Procedure

2.2.1. Synthesis and characterization of FHA. The FHA was prepared as described in our previous publication with a little modification. The reaction was carried out by reacting a required amount of ketapang kernel oil with hydroxylamine in the present of Lyposyme in a 100 mL stoppered flask. The mixture was incubated in water shaker batch at 100 rpm. The FHA formed in water-hexane interface was then separated from the water and the lipase by filtration. To obtain the solid FHA, the hexane fraction was cooled in a refrigerator (<-5°C) for 5 h and then filtered and washed by hexane for several times and dried in vacuum desiccator over phosphorous pentoxide for 24 h [24]

Qualitative analysis of hydroxamic acid groups on FHA was carried out by observes the colored complex formed after the methanolic solution of the FHA was reacted with iron (III), copper (II) and vanadium (V) in a dilute hydrochloric acid solution. The amount of the hydroxamic acid group
was estimated based on nitrogen content of the dry FHA by using Kjeldahl method. FTIR spectra of FHA were recorded with Fourier Transform Infrared Spectrophotometer (Perkin Elmer FTIR-Frontier, USA) using KBr disk.

2.2.2. Preparation of the FHA loaded zeolit (FHA-Zeo). The zeolite was activated by heating in a furnace at 450 for 2 h. The activated zeolite (0.5 g) was mixed and shaken with 2000 ppm of FHA solution in methanol at 35 rpm for 12 h. The mixture was filtered and then kept in refrigerator.

2.2.3. Effect of pH on metal ions uptake by FHA-Zeo. The effect of pH on metal ions uptake by FHA-Zeo was determined by batch equilibrium techniques. The metal ion (20 mL, 0.001 M) was shaken with 100 mg of FHA-Zeo for 12 h to ensure the equilibrium is attained in all cases. The pH of the metal solutions was adjusted to 1-6 with 0.01 M phosphate buffer solutions before shaken. After the equilibration, the concentration of ion in solution was determined by AAS for the calculation of sorption capacity.

2.2.4. General extraction and desorption procedures on zinc(II) ion uptake by column technique. FHA-Zeo (4g) was packed into a column with an internal diameter 1 cm to 10 cm height. A 1000 mL solution containing the desired concentration of zinc(II) ion at pH 5, adjusted with 0.01 M of phosphate buffer was passed through the column. The concentration of zinc(II) ion before and after passing the column was determined using FAAS for the calculation of percentage sorption of zinc(II) ion. The columnar stripping of copper (II) ion was performed using nitric acid solution as eluent. The acid was passed through the column containing FHA-Zeo-Ni. The successive fractions of effluent (3 mL) were collected. The concentration of copper after stripping was determined using FAAS for the calculation of percentage recovery.

3. Results and Discussion

3.1. Characterization of the FHA

Complexes of the FHA with vanadium (V), iron (III) and copper (II) are purple, dark red and green, respectively. These are the common color of the complexes observed when these metal ions are reacted with hydroxamic acids [24]. FTIR spectrum of the FHA (Figure 1b) shows the characteristic absorption bands of monosubstituent amides at 3050 - 3500 cm\(^{-1}\) (medium peak), 1650 - 1750 cm\(^{-1}\) (sharp peak) and 1450 – 1600 cm\(^{-1}\) (medium peak), which indicate the presence of O-H and N-H stretching and bending modes. Absorption bands that appear at 2800 – 3000 cm\(^{-1}\) (sharp and medium peaks) and 1024 cm\(^{-1}\) are due to C-H stretching and bending respectively. Both qualitative tests above support that the FHA is successfully produced from the ketapang kernel oil.
Figure 1. FTIR spectra of Ketapang kernel oil (a) and FHA (b)

The nitrogen content of the dry FHA analyzed by Kjeldahl method was found to be 4.19%. This indicates that there is 2.99 mmol/g of hydroxamic acid groups in one gram of the FHA. Meanwhile, the maximum sorption capacity obtained of the FHA immobilization onto zeolite was 4.31 mg/g.

3.2. Effect of pH on sorption of Zn(II), Cu(II) and Pb(II) at FHA-Zeo

The sorption behavior of Zn(II), Cu(II) and Pb(II) on FHA-Zeo at different pH values was examined by using batch method. The results show that all metal ions are absorbed into FHA-Zeo at the various pH used (Table 1). However, the highest capacity shows by FHA-Zeo-Zn(II) complex. The capacity sorption of the FHA-Zeo is an important factor to determine the amount of FHA-Zeo that required to quantitatively remove a specific metal ion from a solution.

Table 1. Metal ions sorption of FHA-Zeo at various pH

| Metal Ion | Sorption Capacity (mg/g) |
|-----------|--------------------------|
|           | pH 1 | 2 | 3 | 4 | 5 | 6 |
| Zn (II)   | 0.00 | 0.00 | 1.1 | 5.4 | 17.2 | 9.5 |
| Cu (II)   | 0.00 | 0.00 | 0.01 | 2.14 | 3.74 | 5.08 |
| Pb (II)   | 0.00 | 0.03 | 0.53 | 3.24 | 6.53 | 8.25 |

3.3 Pre-concentration and separation of Zn(II) from Cu(II) and Pb(II)

The pre-concentration and separation studies of zinc(II) ion was carried out by extracting 1000 mL solution containing 100 ppm zinc(II) ion at pH 5. In addition to zinc(II) ion, the solution also containing 100 ppm of copper(II) and lead(II) ion, respectively. The sorption of metal ions was performed at eluent flow rate of 0.3 mL min⁻¹. The results (Table 2) show that almost 100% of the zinc
is absorbed into the FHA-Zeo. Meanwhile copper and lead are absorbed 38 and 57%, respectively. This indicates that complex of zinc(II)-FHA-Zeo on the resin is more stable than complexes of copper(II)- and lead(II)-FHA-Zeo. The difference of sorption capacity will affect to the retention of metal ions during desorption from the FHA-Zeo.

**Table 2.** Metal ions sorption on FHA-Zeo at pH 5

| Metal Ion | Concentration (ppm) | Sorption (%) |
|-----------|---------------------|--------------|
| Zn        | 100                 | 96.3         |
| Cu        | 100                 | 38.9         |
| Pb        | 100                 | 56.7         |

Desorption of the metal ions from FHA-Zeo was performed using 10% of nitric acid as eluent, at flow rate of 0.5 mL min\(^{-1}\). The results show that the percentage recoveries for all pre-concentration factors are more than 99%. This is indicating that the FHA-Zeo can be applied for the pre-concentration of zinc(II) ion in aqueous media. Figure 1 shows the results of desorption of metal ions from the FHA-Zeo at the column. It can be seen that zinc is separated well from both copper and lead, while copper and lead we’re not separated. This is probably because the stability of these two complexes is very similar.

**Figure 2.** Separation of zinc(II) from copper(II) and lead(II). zinc extracted 96.3 ppm, total desorption 99.87%. copper extracted 3.89 ppm, total desorption 98.94%. lead extracted 56.7 ppm, total desorption 99.93%

4. **Conclusion**

The present studies highlight that immobilization of FHA onto zeolite is an effective method for extraction and pre-concentration of zinc(II) ion in water sample. A pre-concentration process has been proposed for the determination of zinc(II) ion in water samples, which contain trace
concentrations of zinc that they cannot be measured directly by FAAS. A quantitative recovery of zinc(II) ion from FHA-zeo column was obtained using 10% HNO₃ solutions as eluent with a pre-concentration factor up to 60. Extraction data obtained indicate clean separations of zinc(II) from copper(II) and lead(II) ions with reasonably good separation factors.

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