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Extraction Behaviour of Cu^{2+} Ions with Used Cooking Oil-Based Organic Solvent

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Abstract. The aim of this work was to study the extraction behaviour of Cu^{2+} ions from aqueous solution with used cooking oil-based organic solvent. The used cooking oil-based organic solvent was composed of di-2-ethylhexylphosphoric acid (extractant), tributylphosphate (phase modifier) and used cooking oil (diluent). Effects of equilibrium pH (2-6), extractant concentration (10-100 mM) and operating temperature (25-47 ^{o}C) on Cu^{2+} ion extraction from aqueous solution were investigated. It was found that used cooking oil-based organic solvent is a potential green and low-cost organic solvent for Cu^{2+} ion extraction from aqueous solution.

Keywords: extraction, Cu^{2+} ions, used cooking oil, di-2-ethylhexylphosphoric acid

1. Introduction

Cu^{2+} ion is one of the common metal ions found in the industrial wastewater and excessive accumulation of Cu^{2+} ions in the human body will cause acute and chronic copper poisoning. Hence, it is essential to treat the Cu^{2+}-laden industrial wastewater prior to charge.

There are several methods that have been used to remove Cu^{2+} ions from aqueous solutions such as membrane filtration, ion-exchange, absorption, chemical precipitation and coagulation-flocculation [1]. Among these methods, solvent extraction is one of the well-established methods that show a good promising result in removing Cu^{2+} ions from aqueous solutions [2]. This method employs an organic solvent consisting of three components in extracting Cu^{2+} ions which include extractant, phase modifier and diluent. Extractant is the active component in extraction, phase modifier reduces the emulsion and third layer formation and diluent controls the solvent condition for extraction. In most cases, diluent is the bulk component which accounts for more than 85 vol% in the organic solvent [3]. The classical diluents used in solvent extraction processes are mainly petroleum-based organic solvents such as hexane, heptane, chloroform and toluene which are toxic and non-renewable [4]. This would cause severe environmental hazards when the toxic solvents are lost to the environment. To overcome this problem, replacement of the toxic petroleum-based organic solvents with green solvents in solvent extraction is indispensable.

In this work, a used cooking oil-based organic solvent was used as a green solvent in Cu^{2+} ion extraction. It consists of used cooking oil as a diluent, di-2-ethylhexylphosphoric acid (D2EHPA) as an extractant and tributylphosphate (TBP) as a phase modifier. In fact, unused cooking oil has been used in solvent extraction processes [5]-[7] but it is less attractive due to its higher cost and competition as a food commodity. The aim of this work was to study the extraction behaviour of Cu^{2+} ions from aqueous solutions by a used cooking oil-based organic solvent. Effects of operating parameters like equilibrium pH (pH_{eq}), D2EHPA concentration and temperature on the efficiency of Cu^{2+} ion extraction were investigated.

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2. Materials and Methods

2.1. Materials

The used cooking oil was collected from a local restaurant and was pre-treated to remove solid particles and excessive water. Copper sulphate pentahydrate ($CuSO_4.5H_2O$) (R&M Chemicals ≥ 99.6% purity), di-2-ethylhexylphosphoric acid (D2EHPA) (Acros Organics, ≥ 99% purity), tributylphosphate (TBP), sodium hydroxide (NaOH), sodium sulphate (Na_2SO_4) and sulphuric acid (H_2SO_4) (Merck, ≥ 99% purity) were used as received.

2.2. Extraction Procedure

A volume of the prepared organic phase (a mixture of D2EHPA (extractant), TBP (phase modifier) and used cooking oil (diluent)) was mixed with the prepared Cu^{2+}-containing aqueous phase (a mixture of 100 mg/L $CuSO_4.5H_2O$, 250 mg/L Na_2SO_4 and distilled water) at 1:1 organic to aqueous phase ratio in a glass-stoppered bottle. The bottle was shaken by an orbital shaker at 100 rpm for 5 minutes. After mixing for another 5 minutes, the mixture was allowed to stand to separate. A syringe with a small tube at the tip was used to take some sample from the aqueous phase and its pH was measured with a pH meter. If the pH measured was different from the desired pH_{eq}, the sample was returned to the bottle and its pH was adjusted with 1 M H_2SO_4 or 1 M NaOH. After another round of mixing, the mixture was allowed to separate and the pH was measured and adjusted again. This test was continued until the desired pH_{eq} was obtained. Next, the mixture was transferred into a separating funnel for phase disengagement and, finally, some aqueous sample was taken from the funnel for chemical analysis with an atomic absorption spectrophotometer (AAS) after appropriate filtration and dilution. The percent extraction (%E) of Cu^{2+} ion was calculated according to:

$$\%E = \frac{[Cu]_{o,aq} - [Cu]_{f,aq}}{[Cu]_{0,aq}} \times 100\% \quad (1)$$

Where $[Cu]_{o,\ aq}$ is the initial Cu^{2+} ion concentration in the aqueous phase and $[Cu]_{f,aq}$ is the final Cu^{2+} ion concentration in the aqueous phase. All experiments were carried out in duplicate or triplicate at room temperature (25^{o}C) and the relative standard deviation between replicate samples within an experiment range was less than 1%.

3. Results and Discussion

3.1. Effect of pH_{eq} on Cu^{2+} ion Extraction

Fig. 1 shows the effect of pH_{eq} on Cu^{2+} ion extraction from aqueous solution with used cooking oil-based organic solvent at room temperature (25^{o}C). An aqueous phase containing an initial concentration of 100 mg/L of Cu^{2+} ions and an organic phase loaded with 85mM D2EHPA and 60mM TBP were applied. A sigmoid curve was obtained where %E was the lowest at pH_{eq} 2.5 and it increased sharply from 3.0 to 4.0 before it achieved its maximum at 4.5 to 5.4. It was discovered that this finding was similar to those reported by Oshima et al.[8] for Cu^{2+} extraction with D2EHPA. By considering a dimeric form of D2EHPA in used cooking oil, the general equation for the Cu^{2+} extraction can be expressed as [9]:

$$Cu^{2+}_{aq} + ([2+n]/2)\, H_2R_{2(org)} \overset{K_{ex}}{\leftrightarrow} Cu(R_2)(HR)_{n(org)} + 2H^+_{aq} \quad (2)$$

Where H_2R_2 is D2EHPA in the dimeric form and n is the number of D2EHPA molecules that take part in the reaction. Usually the value of n equals to 2 when the reaction involves aliphatic organic solvent [9]. Based on Eq. (2), the decrease in H^+ ions shifts the equilibrium of reaction to the right and increases the Cu^{2+} ions extraction. The decrease in H^+ ions means increasing in pH_{eq}, and thus this explains the high %E at high $pH_{eq.}$ However, to avoid the formation of $Cu(OH)_2$ at pH_{eq} more than 5, pH_{eq} of 4.5 was selected for further study.

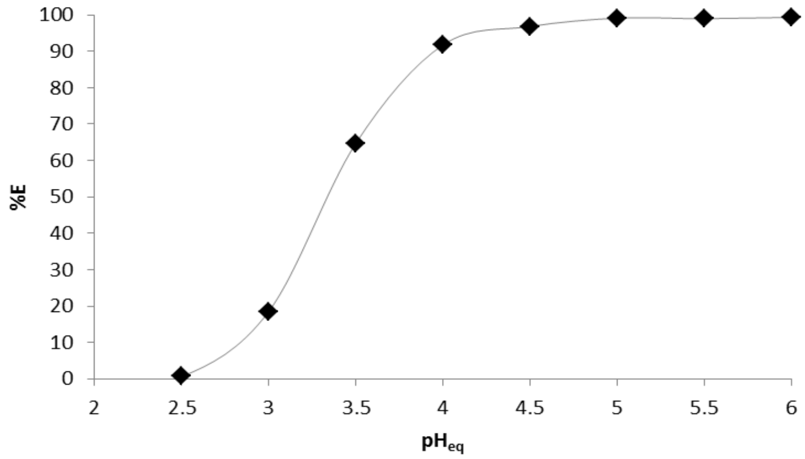

Fig. 1: Effect of pH_{eq} on Cu^{2+} ion extraction by used cooking oil-based organic solvent

3.2. Effect of D2EHPA Concentration on Cu^{2+} Ion Extraction

The effect of D2EHPA concentration loaded in used cooking oil on the Cu^{2+} ion extraction from aqueous solution is shown in Fig. 2. An aqueous phase containing an initial concentration of 100 mg/L of Cu^{2+} ions, pH_{eq} of 4.5 and operating temperature at 25°C were employed. It was found that %E increased dramatically from 62% at 10 mM of D2EHPA to 89% at 20 mM of D2EHPA. It then increased gradually from 20 to 60 mM of D2EHPA, reached a plateau from 60 to 90 mM of D2EHPA and decreased slightly from 90 to 100 mM. This implies that the extraction of Cu^{2+} ions was influenced by the concentration of D2EHPA and that D2EHPA was an effective extractant for Cu^{2+} ions. This finding was consistent with those reported by Zhang et al. [10] and Venkateswaran et al. [11]. Nevertheless, the slight reduction in %E at D2EHPA concentration of more than 90mM was possibly caused by high viscosity of the organic phase due to the large amount of D2EHPA added in the organic phase and consequently hindered the mass transfer process. Since there was no significant rise in the %E at D2EHPA concentration above 20 mM, D2EHPA concentration of 20 mM was selected for further study.

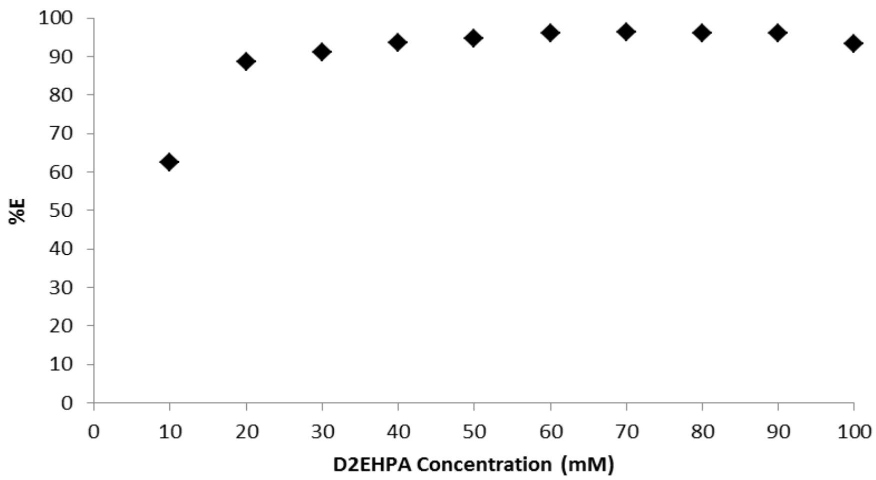

Fig. 2: Effect of D2EHPA concentration on Cu^{2+} ion extraction by used cooking oil-based organic solvent

3.3. Effect of Temperature on Cu^{2+} Ions Extraction

Fig. 3 shows the effect of operating temperature on the extraction of Cu^{2+} ions from aqueous solution with used cooking oil-based organic solvent. An aqueous phase containing an initial concentration of 100 mg/L of Cu^{2+} ions, pH_{eq} of 4.5 and D2EHPA concentration of 20 mM were employed. During the experiments, a water bath was used to provide a constant operating temperature in the aqueous-organic system. It was found that the %E did not vary much when the temperature was increased from 25 to 47°C. Theoretically, high temperature tends to reduce the viscosity of organic phase which would increase the diffusion rate of solutes in the organic phase. This hypothesis is supported by findings from previous researchers like Mortaheb et al. [12] and Muthuraman et al. [13]. However, in this study, no significant effect was observed on the Cu^{2+} ion extraction between room temperature and other higher temperatures. Since operation at room temperature is more economical, room temperature of 25°C was selected as the optimum operating temperature.

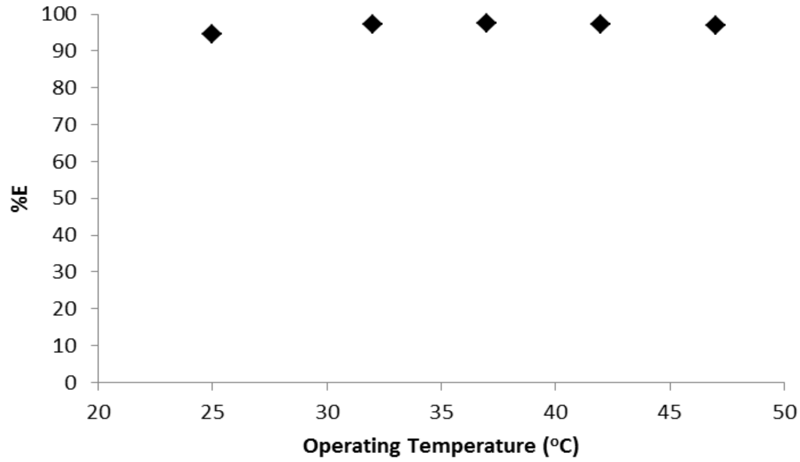

Fig. 3: Effect of operating temperature on Cu^{2+} ions extraction by used cooking oil-based organic solvent

4. Conclusion

A used cooking oil-based organic solvent composing of di-2-ethylhexylphosphoric acid (extractant) and tributylphosphate (phase modifier) dissolving in used cooking oil was used to extract Cu(II) ions from aqueous solution. It was found that Cu^{2+} ion extraction increased with equilibrium pH and di-2-ethylhexylphosphoric acid concentration, but it did not vary much with increasing operating temperature. The optimum equilibrium pH, di-2-ethylhexylphosphoric acid concentration and operating temperature for Cu^{2+} ion extraction from aqueous solution with used cooking oil-based organic solvent were determined as follows: 4.5, 20 mM and 25°C.

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