

Waste Cooking Oil-Based Organic Solvent as A Potential Green and Low-Cost Solvent for Metal Extraction

Siu Hua Chang

Abstract—A waste cooking oil-based organic solvent was used to extract Cu(II) ions from aqueous solution in place of the conventional petroleum-based organic solvents in this work. The waste cooking oil-based organic solvent was composed of di-2-ethylhexylphosphoric acid (extractant) and tributylphosphate (phase modifier) dissolved in waste cooking oil (diluent). Effects of equilibrium pH (2-5) and extractant concentration (55-95 mM) on Cu(II) ion extraction from aqueous solution were investigated. A comparison of Cu(II) ion extraction with fresh cooking oil and hexane was also conducted. It was found that waste cooking oil-based organic solvent is a potential green and low-cost organic solvent for metal extraction.

Keywords— waste cooking oil, extraction, Cu(II).

I. INTRODUCTION

OVER the past few decades, the increasing global concern about environmental issues has prompted the revolutionary technological advances of a wide range of separation techniques including solvent extraction. Being one of the oldest techniques that has been used in hydrometallurgical processes, solvent extraction is well-established, easy to operate and efficient. However, one of the major drawbacks of this technique is the use of petroleum-based organic solvents like hexane, heptane, toluene and chloroform which are toxic and non-renewable [1]. This poses a severe threat to human health when these toxic solvents are exposed to the environment. Moreover, these solvents can be very costly due to the limited resources. Therefore, replacement of these toxic solvents with green, low-cost and renewable solvents like waste cooking oil is indispensable.

Cooking oil is a lipid material derived primarily from fruits and seeds of plants such as oil palm fruit, soybean, sunflower seeds, peanuts and corns which is used in frying, baking and other types of cooking. It consists mostly (>90%) of triglycerides which are glycerol molecules with three long-chain fatty acids attached at the hydroxyl groups via ester linkage [1], and thus it is a carbon-based solvent. Cooking oil possesses several favourable physical properties for solvent extraction like low melting point, low dielectric constant, low density and low Hildebrand solubility parameter which are comparable to those of petroleum-based organic solvents [1].

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Nevertheless, it usually portrays a relatively higher viscosity than petroleum-based organic solvents which is an unfavourable feature for solvent extraction. Fortunately, this could be overcome by heating it to high temperature, mixing it with suitable viscosity reducers or stirring it to minimize the boundary layer resistance [1]. The higher flash point and lower vapour pressure of cooking oil than those of petroleum-based organic solvents [1], however, are the upsides of cooking oil that contribute to its green attributes. As a matter of fact, fresh cooking oil has been used successfully as a solvent in recovery solutes like metal ions [2], dye stuff [3], [4] and phenol [5] from aqueous solutions. However, fresh cooking oil is a food commodity and its application in solvent extraction would only aggravate the food crisis, and thus this should be avoided for future global food security. On the other hand, waste cooking oil, which is a waste product produced abundantly by household kitchens, restaurants and other food processing facilities, is not threatening the food security and much cheaper in cost. Therefore, this work aimed to investigate the feasibility of using waste cooking oil-based organic solvent in metal extraction from aqueous solution. Effects of equilibrium pH (pH_{eq}) and extractant concentration on Cu(II) ion extraction by using a waste cooking oil-based organic solvent were explored. A comparison of extraction efficiency with fresh cooking oil- and petroleum-based organic solvents was also conducted.

II. MATERIALS AND METHODS

A. Materials

The waste cooking oil was collected from a local restaurant and was pre-treated to remove solid particles and excessive water, whereas the fresh cooking oil was bought from a local department store and was used as received. Hexane (Merck, $\geq 95\%$ purity), copper sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) (R&M Chemicals $\geq 99.6\%$ purity), di-2-ethylhexylphosphoric acid (D2EHPA) (Acros Organics, $\geq 99\%$ purity), tributylphosphate (TBP), sodium hydroxide (NaOH), sodium sulphate (Na_2SO_4) and sulphuric acid (H_2SO_4) (Merck, $\geq 99\%$ purity) were used as received.

B. Extraction Procedure

A volume of the prepared organic phase (a mixture of 85 mM D2EHPA (extractant), 60 mM TBP (phase modifier) and

waste cooking oil (diluent)) was mixed with the prepared Cu(II)-containing aqueous phase (a mixture of 100 mg/L $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 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(II) ion was calculated according to:

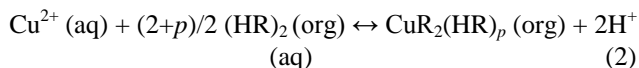
$$\%E = \frac{[Cu]_{i,aq} - [Cu]_{f,aq}}{[Cu]_{i,aq}} \times 100\% \quad (1)$$

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

III. RESULTS AND DISCUSSION

A. Effect of pH_{eq}

The effect of pH_{eq} (2-5) on %E of Cu(II) ions by using the waste cooking oil-based organic solvent is shown in Figure 1. During the experiments, the initial Cu(II) ion concentration in the aqueous phase was fixed at 100 mg/L and the concentration of D2EHPA in the oil phase was fixed at 85 mM. In Fig. 1, a sigmoid curve where %E was the minimum at pH_{eq} of 2.0, but increased dramatically from 3.3 to 4.1 and achieved its maximum from 4.5 to 5.0 was shown. This high pH-dependency behaviour was due to the use of D2EHPA as extractant in the organic phase. As a cationic extractant, it extracted Cu(II) ions by exchanging its hydrogen ions with Cu(II) ions to form neutral Cu-organic complexes [6]. The general extraction equation involved is given by [7]:



where $(\text{HR})_2$ is a dimeric form of D2EHPA and p is the number of molecules of D2EHPA engaged in the reaction which, in most cases, has a value of 2 for Cu(II) when aliphatic organic solvents are used. Based on Eq. (1), the equilibrium position shifts to the right when pH_{eq} increases and it shifts to the left when pH_{eq} decreases. This explains the high %E obtained at high pH_{eq} and the low %E attained at low pH_{eq} . The pH-extraction isotherm of Cu(II) ions by D2EHPA

dissolved in waste cooking oil obtained in this work (Fig. 1) agreed well with the other similar isotherms reported in the literature [8]. Since a plateau was achieved at pH_{eq} of 4.5 (Fig. 1), it was selected for further studies.

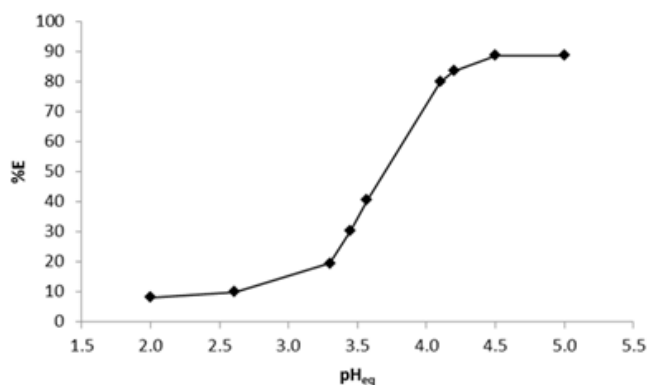


Fig. 1: Effect of pH_{eq} on Cu(II) ion extraction with waste cooking oil-based organic solvent

B. Effect of D2EHPA Concentration

Fig. 2 shows the effect of D2EHPA concentration (55-95 mM) on Cu(II) ion extraction with the waste cooking oil-based organic solvent. During the experiments, the initial Cu(II) ion concentration in the aqueous phase was fixed at 100 mg/L and the pH_{eq} was remained constant at 4.5. It was found that %E increased with D2EHPA concentration steadily until it reached a plateau at 85 mM. At D2EHPA concentrations below 85 mM, the increment of %E was due to the inadequate amount of D2EHPA for Cu(II) ion extraction. On other hand, at the D2EHPA concentrations above 85 mM, a saturation point was achieved where D2EHPA molecules were saturated with Cu(II) ions. Since a plateau was achieved at D2EHPA concentration of 85 mM (Fig. 2), it was chosen for further studies.

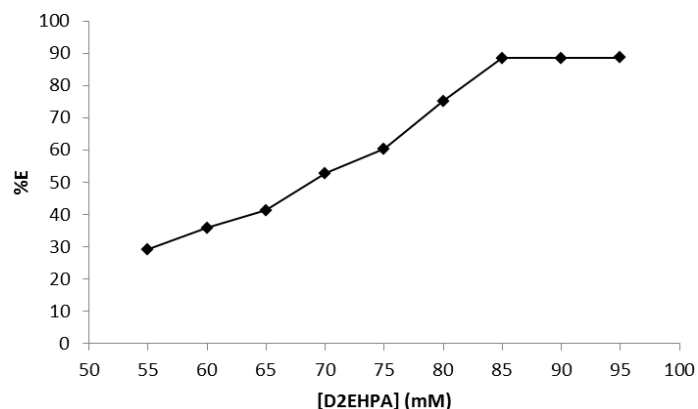


Fig. 2: Effect of D2EHPA concentration on Cu(II) ion extraction with waste cooking oil-based organic solvent.

C. Effect of Diluent

Fig. 3 shows the effect of different types of diluent (waste cooking oil, fresh cooking oil and hexane) on Cu(II) ion extraction from aqueous solution. During the experiments, the initial Cu(II) ion concentration in the aqueous phase was varied from 25-500 mg/L, whereas pH_{eq} and D2EHPA concentration were fixed at 4.5 and 85 mM, respectively. It

was found that hexane achieved the highest %E throughout all initial Cu(II) ion concentrations studied, followed by fresh cooking oil and waste cooking oil. This may be deduced from the fact that hexane is much less viscous (0.297 mPa.s @ 25°C [1]) than cooking oil (>40 mPa.s @ 25°C [1]) which is attributed to its simpler straight-chain aliphatic structure [1]. The high viscosity of cooking oil caused by its intermolecular attractions of long-chain fatty acids is an undesirable feature in solvent extraction as it may hinder the solute transport in the organic phase. Nevertheless, this problem could be alleviated by mixing the cooking oil with appropriate viscosity reducers, heating the oil to elevated temperature or stirring the oil to minimize the boundary layer resistance. The higher %E attained by fresh cooking oil compared with waste cooking oil could be explained by the formation of a thinner unstable emulsion layer between the organic and aqueous phases. This emulsion layer could, however, be diminished by increasing the amount of phase modifier [2] in the cooking oil.

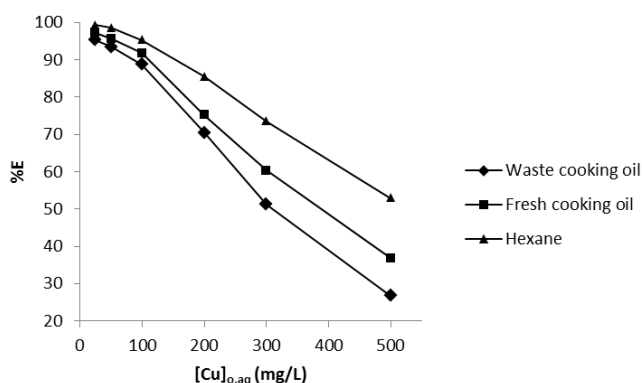


Fig. 3: Effect of diluent on Cu(II) ion extraction from aqueous solution.

IV. CONCLUSION

A waste cooking oil-based organic solvent composing of di-2-ethylhexylphosphoric acid (extractant) and tributylphosphate (phase modifier) dissolving in waste cooking oil was used to extract Cu(II) ions from aqueous solution. It was found that equilibrium pH of 4.5 and di-2-ethylhexylphosphoric acid concentration of 85 mM were required to extract Cu(II) ions up to 90%. The high pH-dependency behaviour of this extraction process was because of the use of D2EHPA as extractant in the organic phase which extracted Cu(II) ions by exchanging its hydrogen ions with Cu(II) ions to form neutral Cu-organic complexes. A comparison of Cu(II) ion extraction among different types of diluent revealed that hexane, which was the least viscous, achieved the highest extraction, followed by fresh cooking oil and waste cooking oil. The higher extraction attained by fresh cooking oil compared with waste cooking oil could be explained by the formation of a thinner unstable emulsion layer between the organic and aqueous phases which could be diminished by increasing the amount of phase modifier in the cooking oil.

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