Extraction of copper ions from aqueous solutions with oleic acid as green solvent

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Abstract. This research aimed to extract copper ions from aqueous solutions with oleic acid as a green solvent. The effects of pH equilibrium, temperature, and sodium sulphate (Na₂SO₄) concentration were investigated and the optimum conditions for maximum extraction of copper ions were determined. The findings revealed that the extraction of copper ions increased with equilibrium pH and temperature before it reached a plateau, while it increased and achieved a peak before it decreased with sodium salt concentration. The highest extraction of copper ions was achieved at 94% under the following optimum conditions: equilibrium pH of 4, temperature 55°C and 400 mM of Na₂SO₄. Therefore, it can be concluded that oleic acid is a potential green solvent for extracting copper ions from aqueous solutions.

1. Introduction
Worldwide growth in industrialization is one of the main causes of heavy metal pollution in water. Heavy metal ions such as copper, cadmium, lead, nickel, and chromium which are discharged into waterways by unscrupulous industries pose a severe threat to the environment and human health [1]. Copper ions are one of the toxic metal ions discharged abundantly by industries such as printed board manufacturing, metal finishing, and plating, semiconductor manufacturing, petrochemicals and refineries [2]. Various detrimental impacts of copper ions on human health and other living organisms in the environment are well-documented in the literature [3]. Various methods such as ion exchange [4], adsorption [5], membrane filtration [6] and chemical precipitation [7] have been used to remove copper and other heavy metal ions from aqueous solutions. However, these methods have their own inherent limitation such as the production of high sludge, less efficiency, sensitive operation condition, high capital and operation cost [8-9]. Solvent extraction is an attractive method to remove copper ions from aqueous solutions due to its relatively simple process and low cost [10].

In solvent extraction, the conventional organic solvents used such as kerosene, chloroform, dichloromethane, toluene benzene, n-heptane and cyclohexane [11] are mostly derived from petroleum resources. These petroleum-based solvents are toxic, highly flammable, non-biodegradable and detrimental to the environment. Moreover, the huge amount of solvent used in solvent extraction tends to increase the cost of production, cost of storage and also create a problem of hazardous-solvent disposal [11]. Considering these limitations, the search for green solvents to replace the toxic petroleum-based solvent is urgently needed for the sustainable development of the solvent extraction process.
Carboxylic acid such as lauric acid, palmitic acid, capric acid, and oleic acid are derived from vegetable oil and are considered less toxic compared to other extractants from petroleum-based solvents. Carboxylic acids have been studied as extractants for copper ions and have been shown to exhibit good extraction and separation efficiency. Guerdouh & Barkat [12] have successfully investigated the effect of several organic solvents (cyclohexane, dichloromethane, toluene, chloroform, 1-octanol and methyl isobutyl ketone) on the extraction of copper ions using lauric acid as extractants, while Ghanadzadeh & Abbasnejad [13] studied the removal of copper ions using lauric acid diluted in benzene. Synergistic extraction of copper ions from sulphate medium with capric acid and tri-n-octylphosphine oxide in chloroform were reported by Adjel et al. [14]. However, all these carboxylic extractants still utilize petroleum-based solvent as the diluent in the organic phase.

Oleic acid is an example of carboxyl acid derived from vegetable oil such as palm, sesame seeds, sunflower, olive and rapeseed [15-16]. It is an eco-friendly, biodegradable and renewable solvent. However, it has not been used to extract metal ions such as copper ions from aqueous solution. Hence, this research aimed to extract copper ions from aqueous solutions with oleic acid as a green solvent. The effects of pH equilibrium, temperature, and sodium sulphate (Na₂SO₄) concentration were investigated and the optimum conditions for maximum extraction of copper ions were determined. Oleic acid was used as a sole solvent throughout the experiments and the role of oleic acid in copper ion extraction was also discussed.

2. Methodology
2.1 Materials and equipment’s
Oleic acid (QReC, ≥99% purity), copper (II) sulphate pentahydrate (CuSO₄·5H₂O) (Merck, ≥99% purity), sulphuric acid (H₂SO₄) (QReC, 95-97% purity), sodium hydroxide (NaOH) (Merck, ≥99% purity) and sodium sulphate (Na₂SO₄) (QReC, ≥99% purity) were used as received without further purification. A pH meter (HANNA, HI-202) was used to determine the pH of the aqueous phase before and after extraction. The concentration of copper ions in the aqueous phase was analyzed by Inductively Coupled Plasma (ICP) (Perkin Elmer, Optima 7000 DV).

2.2 Preparation of aqueous phase
The aqueous phase was prepared by dissolving an appropriate amount of CuSO₄·5H₂O in distillate water loaded with an appropriate amount of Na₂SO₄.

2.3 Extraction procedure
An equal volume of the organic and aqueous phase was mixed in a glass-stoppered. A hot plate with a magnetic stirrer bar was used to mix organic and aqueous phase solution at 300 rpm for 8 minutes. After mixing, the mixture was allowed to stand for 5 minutes to separate. A syringe with a small needle was used to take 6 mL of the sample from the aqueous phase and it was measured with a pH meter. The pH value was adjusted with a few drops of 1 M NaOH or 1 M H₂SO₄ in order to obtain the desired pH equilibrium. After that, the mixture was stirred again for 8 minutes and the process was continued until the desired pH equilibrium was achieved. Then, the mixture was transferred into a separating funnel for phase disengagement. Lastly, 6 mL of the sample was taken out from the aqueous phase for analysis by using ICP after filtration and dilution. The percentage extraction (%E) of copper was calculated according to equation (1) [17]:

\[ %E = \frac{[Cu]_{aq,f} - [Cu]_{aq,i}}{[Cu]_{aq,i}} \times 100 \]  

where \([Cu]_{aq,i}\) is the initial copper concentration in the aqueous phase and \([Cu]_{aq,f}\) is the final copper concentration in the aqueous solutions.
3. Results and Discussion

3.1 Effect of equilibrium pH

Figure 1 shows the effect of equilibrium pH on the extraction of copper ions from aqueous solution by using oleic acid. Other parameters were fixed at a temperature of 45 °C and 300 mM of Na$_2$SO$_4$. The results reveal that $\%E$ increased from 68 to 80% when the equilibrium pH increased from 3.0 to 4.5. The high pH dependence of the extraction of copper ions could be explained from the general extraction equation (2) [12]:

\[
(Cu^{2+})_{aq} + \frac{2+m}{2} (HR)_{org} \rightleftharpoons (CuR_2(HR)_m)_{org} + (2H^+)_{aq}
\]  

(2)

where the subscripts $aq$ and $org$ correspond to the aqueous and organic phases, respectively, (HR)$_2$ represents the dimeric form of lauric acid, and $m$ is the number of monomeric lauric acid engaged in the Cu(II)-organic complex. According to equation (2), as the equilibrium pH increases (decreasing H$^+$), the equilibrium position moves to the right side and, thus, gives rise to the increase $\%E$. In contrast, as the equilibrium pH decreases (increasing H$^+$), the equilibrium position shifts to the left side and $\%E$ decreases. Accordingly, increasing the equilibrium pH increased the $\%E$ of copper ions. A similar finding was reported by Guerdouh & Barkat [12] who extracted copper ions with lauric acid diluted in various aromatic and aliphatic solvents. Adjel et al. [14] studied the extraction of cobalt ions with mixtures of capric acid and tri-n-octylphosphine oxide and discovered that the extraction of cobalt ions increased significantly with equilibrium pH. Since the further increase in the equilibrium pH beyond 4.0 did not give significant increment in $\%E$, it was selected as the optimum equilibrium pH for future study.

![Figure 1. Effect of equilibrium pH on $\%E$ of copper ions.](image)

3.2 Effect of temperature

The effect of temperature on the extraction of copper ions was examined in the range of 35°C to 65°C with other parameters fixed at an equilibrium pH of 4 and Na$_2$SO$_4$ concentration of 300 mM. The results presented in Figure 2 shows that the $\%E$ of copper ions from aqueous solution increased with temperature. At 35°C, the removal percentage of copper was 39% and increased to 75% at 45°C. After that, it reached the highest point at 55°C where 86% of copper was extracted. This finding agrees well with Adhikari et al. [18] who used 2-ethylhexylphosphonic acid mono-2-ethylhexy ester (EHPNA) to
extract zinc ions and found that the extraction of zinc ions increased with temperature. Aidi et al. [19] also found similar results for the extraction of copper ions using capric acid and cyclohexane. These findings could be explained from the reduction of viscosity of oleic acid at a high temperature which increased the mass transfer rate and improved the contact between aqueous and organic phases [20-21]. Since the further increase in the temperature beyond 55 did not give significant increment in %E, it was selected as the optimum temperature for future study.

Figure 2. Effect of temperature on %E of copper ions.

3.3 Effect of Na₂SO₄ concentration
Figure 3 shows the effect of salt concentration on the extraction of copper ions using oleic acid was examined by varying the concentration of Na₂SO₄ from 300 to 500 mM under the optimum equilibrium pH of 4 and temperature of 55°C. It shows that the %E of copper ions increased gradually with the concentration of Na₂SO₄ from 85% at 300 mM of Na₂SO₄ to 86% at 350 mM of Na₂SO₄. The %E then increased dramatically and reached the highest point at 400 mM of Na₂SO₄ with 94% extraction. The increase %E with Na₂SO₄ could be explained from the ‘salting-out’ effect resulting from the decrease in the solubility of copper ions as extractable species from the aqueous phase [22] and, thus, increasing the tendency of copper ions to move from aqueous to the organic phase. This result agrees well with Devi & Nayak [23] who used LIX984N to extract copper ions and found that the %E of copper ions increased with Na₂SO₄ concentration. Jafaria et al. [24] also reported a similar trend in the extraction of zinc ions from chloride solution using D2EHPA. However, the %E of copper ions was found to decrease from 84% at 450 mM of Na₂SO₄ to 80% at 500 mM of Na₂SO₄. This could be explained by the rise in the viscosity of the solution when the concentration of Na₂SO₄ exceeded 400 mM, which in turn increased the mass transfer resistance and thus reduced the %E of copper ions [20].
4. Conclusion
Copper ions were successfully extracted by oleic acid as a green solvent from aqueous solutions. It was found that the extraction of copper ions increased with equilibrium pH and temperature before it reached a plateau, while it increased and achieved a peak before it decreased with sodium salt concentration. Under the optimum conditions, namely, equilibrium pH of 4, temperature 55°C and Na$_2$SO$_4$ concentration of 400 mM, the highest extraction of copper ions was achieved at 94%.

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