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INVESTIGATION OF USABILITY OF FATTY ACIDS AS COPPER EXTRACTANT FROM LEACHED COPPER ORE

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ABSTRACT

This paper presents an experimental study on leaching and solvent extraction of copper from low-grade copper ore mined from Nasarawa (Nigeria) by fatty acids in petroleum-based diluents - methyl isobutyl ketone (MIBK), styrene, and kerosene. The leaching investigation showed that the optimum temperature, contact time, and H_2SO_4 concentration are 91.5°C, 39 minutes, and 2.9 M, respectively. Response Surface Methodology (RSM) was adopted for the optimization of the leaching conditions. The aqueous solution obtained from leaching of copper ore in sulfuric acid was used for the solvent extraction. The extraction studies showed that fatty acids in a petroleum-based organic solvent is an effective extractant for solvent extraction of copper. The fatty acids used in the studies were obtained by acidifying the soap that was produced when vegetable oil was treated with sodium hydroxide. It was also observed that diluents affect the percentage extraction of copper. Styrene achieved the highest percentage extraction, followed by kerosene and MIBK at 80 % and 90 % v/v diluents in fatty acids.

Contribution/Originality: This study is one of the very few studies which have investigated and ascertained the fact that fatty acids obtained from vegetable oil can be effectively used as a copper extractant in place of di-2-ethylhexyl phosphoric acid which is commonly used during solvent extraction.

1. INTRODUCTION

Copper is a malleable non-ferrous metal that is used extensively in many industries which include the construction industry, machinery manufacturing industry, electrical industry, defense industry, and other fields [1]. Due to the ubiquitous nature of copper, its ions are commonly found in industrial wastewater [2]. It is known that undue accumulation of copper ions in the body causes severe and chronic copper poisoning, which primarily affects the liver in the body. Therefore, it is essential to treat copper ions-laden wastewater before discharge.

Some of the various methods that can be used to get rid of copper ions from aqueous solution include solvent extraction, chemical precipitation [3, 4] coagulation-flocculation [3, 4] flotation [3, 4] ion exchange [3, 4] electro-oxidation [3, 4] membrane filtration [3, 4] and biosorption [4-6]. However, solvent extraction is commonly recognized as one of the most effective and promising methods of extracting copper ions from the aqueous solution [5]. For solvent extraction of metals, the solvent is made up of an extractant dissolved in a diluent [6]. In some cases, a third component, a phase modifier, can be added. The extractant is the active reagent that removes copper ions from the aqueous solution. Typical examples of solvents commonly used as an extractant in solvent extraction are di-2-ethylhexyl phosphoric acid, 5-nonylsalixylaldoxime [6] Cextrant 230 [1] and 2-hydroxy-5-nonbenzenphenone [7]. Diluents control the solvent condition for extraction. The typical petroleum-based organic diluents are kerosene, chloroform, dichloromethane, n-dodecane, isododecane, n-decanol, n-heptane, n-hexane, and cumene [5]. Phase modifier alleviates the emulsion and third layer formation.

The most commonly used extractant for the extraction of copper ions from aqueous solution by solvent extraction method is di-2-ethylhexyl phosphoric acid (D2EHPA). D2EHPA is a polar solvent with P=O, C–O–P and P–OH groups, which make it suitable to extract metallic ions such as copper ions from aqueous solution [8]. However, D2EHPA has a toxic effect that can cause severe skin burns and eye damage if haphazardly handled.

In this work, the usability of fatty acids, in place of D2EHPA, as the extractant in three petroleum-based organic diluents, was investigated. The fatty acids were obtained from vegetable oil, which is relatively cheaper and less toxic than D2EHPA. The three diluents used are methyl isobutyl ketone (MIBK), styrene, and kerosene. Also, the aqueous solution was gotten by leaching copper ore in sulfuric acid, and optimal conditions for the leaching process were examined. The effects of the different diluents loaded with the fatty acids on the extraction of copper ions were studied.

2. EXPERIMENT

2.1. Material Collection and Preparation

The copper ore used for this research work was obtained from Nasarawa State, the north-central zone of Nigeria. This copper ore was pulverized and sieved to produce particle size in range 0.1mm-0.4mm.

2.2. Analytical Instrument and Apparatus

The elemental analysis of the copper ore was determined by Particle Induced X-ray Emission analysis (PIXE) using 2.5 MeV protons from a 1.7 MV Tandem Accelerator. The current and the charge used in the analysis were 0.26 nA and 0.5 μC respectively, and the spectrum obtained was inspected using the Gupixwin software, v 2.1. An atomic Absorption Spectrophotometer (AAS) was used to measure the concentration of Cu (II) ions in the aqueous phase after leaching and after extraction of copper ions. A hot plate with a magnetic stirrer (Model AM-3250B) was used for stirring at different temperatures.

2.3. Reagent

The reagents used were analytical grades, and distilled water was used for the preparation of all aqueous solutions. The reagents used are as follows: sulphuric acid, methyl isobutyl ketone, styrene, and distilled kerosene.

2.4. Leaching Procedure

The leaching procedure adopted in this work followed the procedure implemented by Baba, et al. [9]. Sieved sample of the pulverized copper ore was used for this study in different concentrations of H_2SO_4, stirred at different contact time, and at fixed temperature of 26.36°C. 1.0g of a sieved sample was weighed and then transferred into 500ml conical flask containing 100ml of 3.00 M H_2SO_4. The reaction mixture was agitated with the aid of magnetic stirrer. The mixture was stirred and heated at 26.36°C for various contact time 6.36, 20.00, 40.00, 60.00, and 73.64 minutes. The solution was cooled and filtered into a standard flask at the end of each period. The residue was collected, washed to neutrality with distilled water, air-dried and oven-dried, and then reweighed. This same procedure described above was re-run in the order shown in Table 1 for H_2SO_4 concentrations of 1.32, 2.00, 3.00, 4.00, and 4.68 M and temperature of 93.64, 40.00, 80.00, 60.00, and 26.36°C. The optimum contact time, H_2SO_4 concentration, and temperatures for the leaching process were determined using Response Surface Methodology (RSM). The design matrix for the central composite design is shown in Table 1. The aqueous solution gotten from leaching of copper ore at the optimum conditions was used for solvent extraction studies.

2.5. Preparation of Fatty Acids

Soap solution was prepared by treating vegetable oil with sodium hydroxide solution. The process of making soaps by treating vegetable oils with basic substances is called saponification. In this experiment, 100 g of NaOH pellet was dissolved in 200 ml of distilled water to give NaOH solution. This NaOH solution was added to 500 ml of vegetable oil. The mixture was stirred for about 5 minutes with the aid of mechanical stirrer until the mixture formed a thick solution. The soap obtained was then acidified to produce fatty acids. For the acidification, the soap was heated on a hot plate while 4.68 M sulphuric acid was added gradually until soap solution formed three different layers. The fatty acid layer was separated from the three layers with the aid of separating funnel, and it is used for extraction study.

2.6. Extraction Procedure

These experiments were carried out batch-wise at room temperature by mixing equal volume of fatty acid in kerosene and the aqueous solution of the leached copper ore in a glass stoppered bottle. The glass stoppered bottle was shaken vigorously for 5 minutes and was allowed to stand in a separating funnel for another 15 minutes to ensure phase disengagement. After that, the aqueous phase was separated from the organic phase and then analyzed with an Atomic Absorption Spectrophotometer (AAS) after appropriate filtration and dilution.

Table-1. Design matrix for the central composite design.

Std. order	Run order	Time (Min)	Conc. (M)	Temp (°C)
12	1	40.00	4.68	60.00
18	2	40.00	3.00	60.00
2	3	60.00	2.00	40.00
10	4	73.64	3.00	60.00
9	5	6.36	3.00	60.00
3	6	20.00	4.00	40.00
6	7	60.00	2.00	80.00
17	8	40.00	3.00	60.00
7	9	20.00	4.00	80.00
20	10	40.00	3.00	60.00
5	11	20.00	2.00	80.00
13	12	40.00	3.00	26.36
8	13	60.00	4.00	80.00
11	14	40.00	1.32	60.00
15	15	40.00	3.00	60.00
16	16	40.00	3.00	60.00
19	17	40.00	3.00	60.00
4	18	60.00	4.00	40.00
14	19	40.00	3.00	93.64
1	20	20.00	2.00	40.00

Source: Authors' computation with MiniTab.

The above procedure was repeated using organic phase comprising fatty acid (extractant) and three different diluents (MIBK, styrene, and kerosene) in ratio 1:4, 1:5, and 1:10 respectively. The percent extraction of copper ions was determined by using Equation 1.

$$\% = \frac{[Cu]_1 - [Cu]_2}{[Cu]_1} x100\% \qquad (1)$$

Where $[Cu]_1$is the initial Cu^{2+} ion concentration in the aqueous phase and $[Cu]_2$ is the final Cu^{2+} ion concentration in the aqueous phase.

3. RESULTS AND DISCUSSION

3.1. Elemental Analysis

The PIXE spectrum presented in Figure 1 shows the major constituents of the copper ore to be aluminum (1.72 %), silicon (27.45 %), iron (2.87 %,), copper (3.47 %), and lead (3.43 %) with magnesium, phosphorus, sulphur, potassium, chromium, nickel, zinc, arsenic and manganese occurring in traces. The result of the elemental analysis of the copper ore by PIXE spectroscopy is summarized in Table 2.

Table-2. Elemental composition of the low-grade copper ore.

Element	Mg	Al	Si	P	S	K	Cr	Mn	Fe	Ni	Cu	Zn	As	Pb
Conc.(% wt)	0.15	1.72	27.45	0.05	0.18	0.98	0.95	0.08	2.87	0.17	3.47	0.06	0.72	3.43

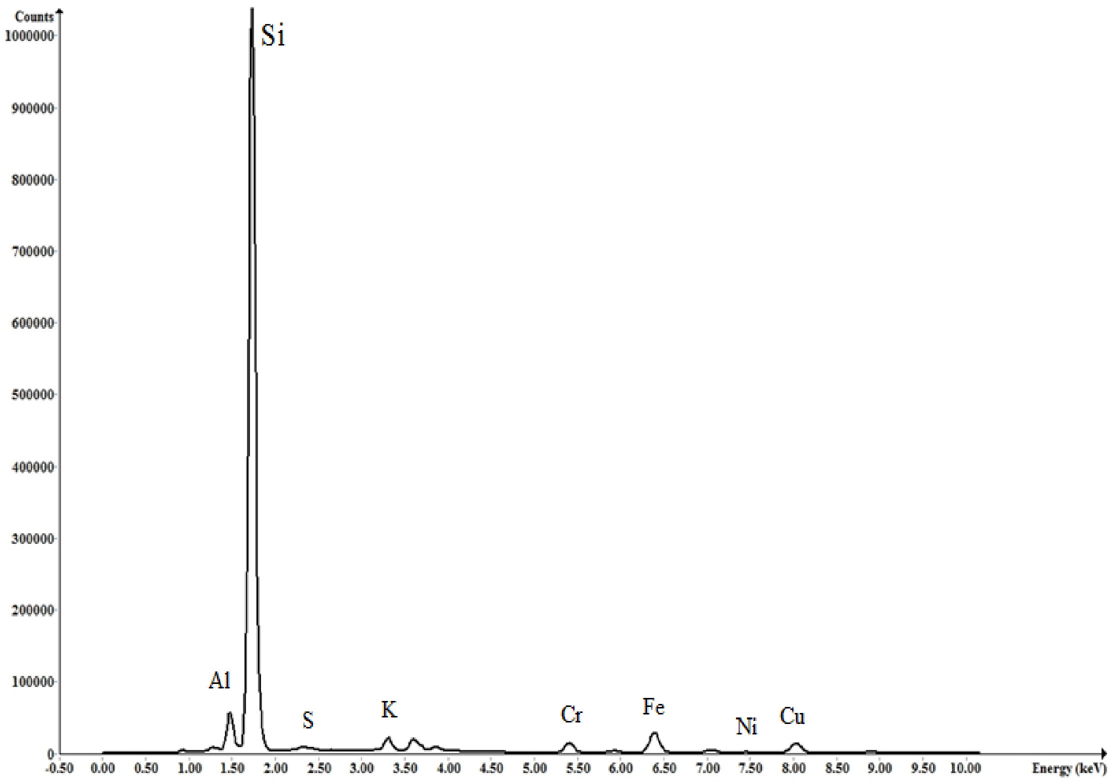

Figure-1. PIXE spectrum of the copper ore.

The copper ore used for this study is a silicate-containing low-grade copper. It has 3.47 % wt. of copper. As shown in Table 2, silicon is the dominant element in the ore with the highest percentage weight of 27.45%. Flotation followed by high-pressure oxidative leaching is one of the efficient methods that can be used to recover copper from silicate-containing low-grade copper [10].

3.2. Leaching Studies: Determination of Optimum Leaching Condition

Contact time, sulphuric acid concentration, and temperature greatly influenced the leaching of copper ore. The optimum conditions of the involved parameters which generated the maximum values of response with desirability close to 1 are shown in Table 3. The reduced regression models for the concentration of copper in the acid solution is given as follows:

$$[Cu] = 1.6901 + 1.3422x - 0.5680y + 1.3184x - 1.6902xy - 2.0681yz + 1.8281x^2 \quad (2)$$

Where [Cu] = concentration of copper in the acid solution, x = contact time, y = acid concentration, and z = temperature.

In Equation 2, the synergistic effects on the responses are shown by the positive coefficients while their antagonistic effects are shown by the negative coefficients. Having assessed the model, it was found to be statistically adequate from the analysis of variance.

Table-3. Optimum leaching conditions of copper ore.

Contact time (mins)	Temperature (°C)	Acid concentration (M)	Desirability
39	91.5	2.9	0.98196

For the model in Equation 2, the following values are obtained: S = 0.387990, R-Sq = 95.62%, R-Sq(pred) = 65.44%, and R-Sq(adj) = 91.67%. The 3-D surface plots of concentration of copper leached at constant time, acid concentration and temperature are shown in Figure 2, Figure 3 and Figure 4, respectively.

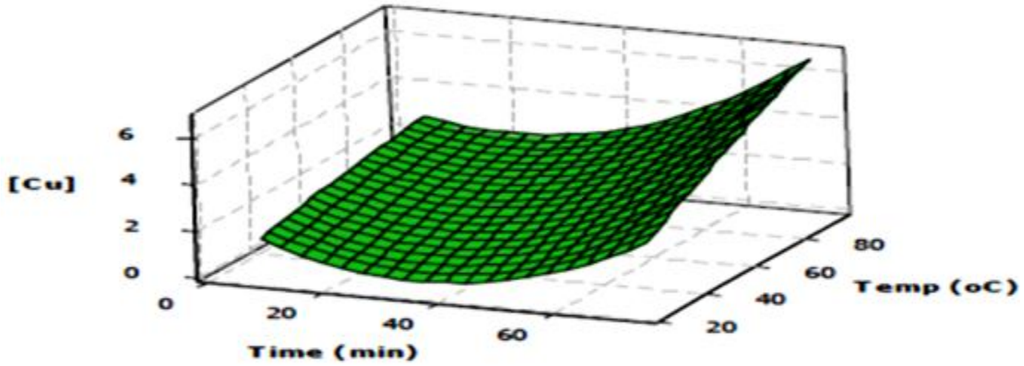

Figure-2. Surface plot of [Cu] vs. temp (°C) and time (min) at a constant acid concentration of 3 M.

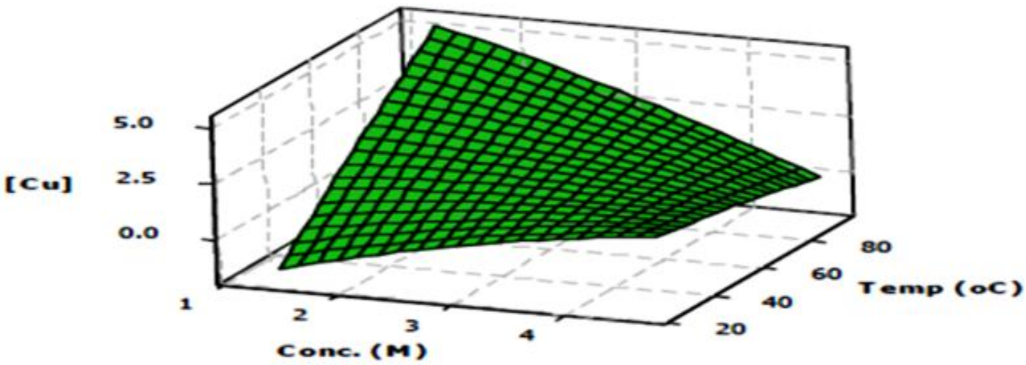

Figure-3. Surface plot of [Cu] vs. temp (°C) and Acid Conc. (M) at a constant time of 40 mins.

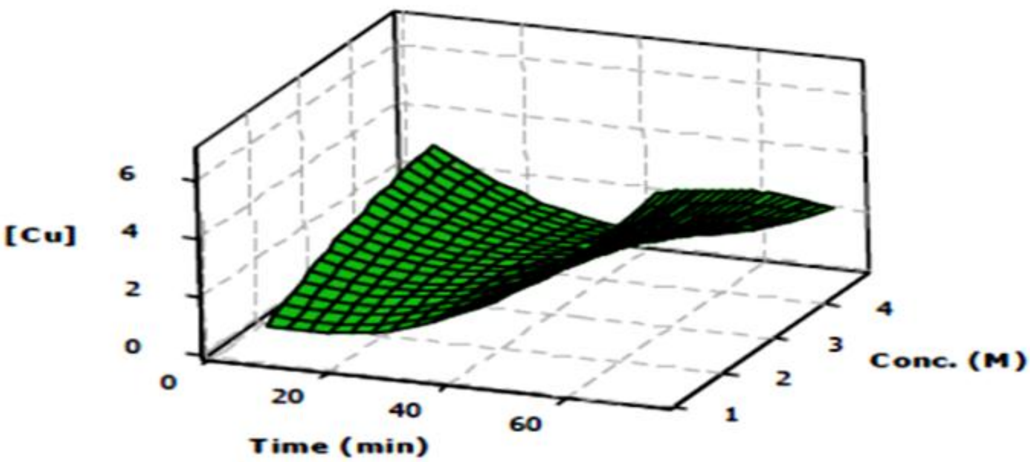

Figure-4. Surface plot of [Cu] vs. Acid Conc. (M) and time (min) at a constant temperature of 60°C.

3.3. Solvent Extraction Studies

Figure 5 shows the percentage extraction of copper ions from aqueous solution by fatty acid petroleum-based organic solvents. An aqueous phase comprising an initial concentration of 17.921 g/L of copper ions and room temperature were employed. As observed in Figure 5, fatty acid demonstrated significant potential to extract copper ions from the pregnant leach solution. Percentage extraction by the fatty acid and the diluents ranges from 83 % to 94 %. This range of percentage extraction is as high as the percentage extraction obtained if D2EHPA is used as an extractant. The percentage extraction of copper obtained in the work of Paulo and Leite [11] falls in the range of percentage extraction obtained in this work. Also, this result supports the reports by Kyuchoukov and Hadjiev [12] and Rice [13] that fatty acids have appropriate physical properties that make them useful as extractants in the recovery of heavy metals.

More so, Figure 5 shows the effects of diluents (MIBK, kerosene, and styrene) on the extraction efficiency. It was observed that styrene achieved the highest percentage extraction, followed by kerosene and MIBK at 10 % and 20% v/v fatty acid in diluents. This can be deduced from the fact that an increase in the dielectric constant of diluents leads to a reduction in the effectiveness of extraction [6]. It was found that the percentage extraction of copper ions decreases as the dielectric constant of the diluents increases (2.4 for styrene > 2.8 for kerosene > 13.1 for MIBK). Diluents that have higher dielectric constant interacts more with water. This interaction with water leads to the likely co-extraction of water together with the metal complex from the interfacial aqueous region. This reduces the capacity of the solvent and results in less extractant being accessible for a reaction at the aqueous boundary layer that is adjacent to the liquid-liquid interface [6]. However, the trend of percentage extraction at 25% v/v fatty acid in diluents when compared with those at 10 % and 20 % v/v was found to be an anomaly.

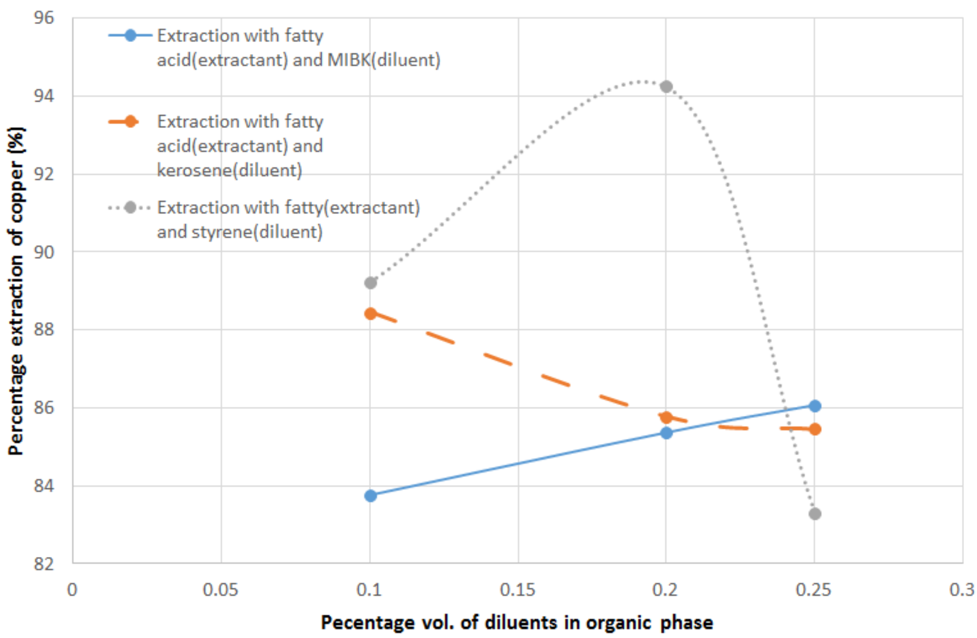

Figure-5. Effect of diluents on copper extraction.

4. CONCLUSION

For the leaching studies, the optimum experimental conditions for the leaching of the pulverized low-grade copper ore in H_2SO_4 were found to be temperature of 91.5°C, contact time of 39 minutes and H_2SO_4 concentration of 2.9 M. The Response Surface Methodology (RSM) used for the leaching optimization gave the values: S = 0.387990, R-Sq = 95.62%, R-Sq(pred) = 65.44%, and R-Sq(adj) = 91.67 %. Finally, this study has shown that fatty acids obtained from vegetable oil can be used as effective extractant to extract copper from low-grade copper ore by solvent extraction method. The highest percentage extraction of 94% was obtained when styrene is used as the petroleum-based diluent at 80 % v/v in fatty acid (extractant).

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