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Recovery of Copper from Low Grade Ores by HNO_3 Leaching: Process Optimization and Solvent Extraction Studies using Soybean Fatty Acid

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Abstract: This paper presents the recovery of copper from a Nigerian low-grade copper ore containing 4.08 wt. % Cu via nitric acid leaching, followed by solvent extraction using soybeans oil fatty acid extractant. The leaching tests on the milled ore were done according to a 3-factor Central Composite Design with time, acid concentration and temperature as the selected process variables. Regression models were developed from the experimental data for the ore dissolution and the quantity of copper extracted, and the effects of the individual process variables and their interactions were determined from the leaching studies using analysis of variance (ANOVA). Results from the leaching tests indicate that the ore dissolution depends mainly on the leaching time. About 92 percent of the copper contents were recovered at optimum leaching time, temperature and nitric acid concentration of 29.5 min, 81.25 °C and 2.18 M, respectively. The solvent extraction studies show that copper can be extracted from aqueous media using soybeans fatty acid, with the performance of the diluents in terms of the quantity of Cu extracted being MIBK > kerosene > xylene.

Keywords: Copper Ore, Dissolution, Response Surface Methodology, Solvent Extraction, Soybeans Fatty Acid

I. Introduction

The depletion of the global deposits of economic grade metal ores has drawn the attention of researchers to the feasibility of recovering such metal values from secondary sources such as low-grade ores and electronic waste. These secondary sources are however, mostly difficult to process effectively using the conventional mineral processing routes since the processing routes for high grade ores have not proved to be cost effective when applied to the secondary sources such as low-grade ores [1 – 4] and electronic waste [5 – 8].

In recent times, attention has been drawn to the recovery of the desired metal values from secondary sources via hydrometallurgical methods, with the recovery of metal values from these sources via acid leaching and solvent extraction being studied by various researchers. The recovery of metal values from various secondary sources has been reported using media such as citric acid [9 - 11], oxalic acid [12, 13], hydrochloric acid [14 – 17], nitric acid [18 – 20] and sulphuric acid [7, 18, 21]. The choice of nitric acid in this study is due to its oxidizing attributes and the fact that many minerals dissolve readily in nitric acid media [22 – 24].

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Of the many methods used in extracting copper and other transition metals from aqueous media resulting from the acid-leaching of such metals, solvent extraction is one of the well-established methods that show a good promising result [25 – 27]. Solvent extraction as a separation technique for the selective recovery of metals from aqueous media usually employs an organic solvent which usually consists of components like the extractant, phase modifier and diluent. The diluents normally used in solvent extraction processes are mainly petroleum-based organic solvents such as chloroform [25, 28], kerosene [29, 30], n-dodecane [31], n-heptane [32], ketones such as methyl isobutyl ketone [29] or higher alcohols such as octanol [33]. So far, most of the metal recovery works via solvent extraction are based on petrochemicals – based extractants which are harmful to the environment, in addition to being expensive. There is need therefore, to explore the possibility of using vegetable oil based extractant systems in the recovery of metal values from aqueous media as these are largely inexpensive, non-toxic alternatives.

In this work, the quantitative leaching of a low-grade Nigerian copper ore using nitric acid was investigated, with respect to process parameters such as leaching time, nitric acid concentration and temperature. Preliminary studies were done on the recovery of the leached copper by solvent extraction using soybean fatty acid (SFA) as the organic extractant, and kerosene, xylene and methyl isobutyl ketone (MIBK) as diluents, with a view to studying the effect of diluents on the extent of recovery of the leached copper values using organic acid-based extraction systems.

II. Materials and Methods

A. Materials

The copper ore used were obtained from Ishiagu in Ebonyi State of Nigeria. Analar grade nitric acid was used for the dissolution studies and all solutions used in the study were prepared using deionized water. Other reagents used in this study were methyl isolbutyl ketone (MIBK), xylene, kerosene and soybean oil fatty acid. The analytical reagents such as nitric acid (70 %, Loba Chemie), MIBK (Merck millipore), sodium hydroxide (Loba Chemie) and xylene (BDH) were purchased from a chemical supplies shop in Ibadan, Nigeria. Kerosene was obtained from the central fuel station in Obafemi Awolowo University, Ile-Ife, Nigeria and was distilled before use. Soybeans oil fatty acid was prepared from refined soybeans oil obtained from the Central Market, Obafemi Awolowo University, Nigeria.

B. Sample Preparation and Analysis

The ore was crushed using a ring mill pulverizer and sieved to obtain particles sizes of at most 100 μm. The elemental composition of the milled ore was determined by Particle Induced X-Ray Emission (PIXE) spectroscopy run on a 1.7 MV Pelletron accelerator with 2.5 MeV protons. The current and charge values were 2.235 nA and 4.00 nC, respectively, and spectral analysis was done using the Gupixwin 2.2.0 software.

For each run of leaching experiment, 10 g of milled ore was mixed with 100 cm^3 of nitric acid in a 250 ml flask fitted with a reflux condenser, stirrer and a thermometer. The leaching duration was between 10 and 60 min, and the temperatures between 30 and 90 ºC. At the end of each run, the mixture was filtered and the residue washed using distilled water to remove the residual acid. The washed residue was dried to constant mass in an oven at 105 ^oC and weighed. The extent of dissolution of the ore was determined using the formula:

$$X = \frac{W_o - W_f}{W_o} \quad (1)$$

Where: W_o and W_f represent the initial and final masses of the sample, respectively and X is the mass fraction of ore dissolved. The amount of copper in the filtrates was determined using a Perkin Elmer AAnalyst100 atomic absorption spectrometer.

The experimental design used in this study is a 3 – factor Central Composite Design (CCD) with α = 1.618 generated using Minitab v. 19 statistical software, which generated 20 experimental runs. The number of recommended design points was based on a full 2^k factorial design with the total numbers of experiments given by Montgomery [34]:

$$N = 2^k + 2k + m \quad (2)$$

Where:

N = total number of experiments,

k = number of factors, and

m = number of replicates.

For this study, the process variables selected are the acid concentration (x_1), leaching time (x_2) and temperature (x_3). The regression model is a second-order equation of the form:

$$Y = \delta_o + \delta_1 X_1 + \delta_2 X_2 + \delta_3 X_3 + \delta_{12} X_1 X_2 + \delta_{13} X_1 X_3 + \delta_{23} X_2 X_3 + \delta_{11} X_1^2 + \delta_{22} X_2^2 \cdot \quad (3)$$

Where: δ_o is the intercept term, δ_1, δ_2, δ_3 are the linear coefficients, δ_{12}, δ_{13}, δ_{23} are the interactive coefficients and δ_{11}, δ_{22}, δ_{33} are the quadratic coefficients. Y is the predicted response (% dissolution of the ore or quantity of copper leached), while X_1, X_2 and X_3 are the coded factors, which are related to the actual factors x_1, x_2 and x_3 in Table 1 by equation (4):

$$\boldsymbol{X_i} = \frac{x_i - x_o}{\Delta x} \quad (4)$$

Where: X_i is the coded value corresponding to x_i (the *i*th input), x_o is the mid value for the experimental design, and Δx is the step change. The coded and uncoded levels of the independent factors are shown in Table 1.

Table 1: Coded and uncoded levels of variables for the experimental design.

Variable	Symbol	Coded factor levels				
		-α	-1	0	+1	+α
Time (min)	x_1	6.36	20	40	60	73.64
$[HNO_3]$ (mol.dm^{-3})	x_2	1.32	2.0	3.0	4.0	4.68
Leaching Temperature (^{o}C)	x_3	26.36	40	60	80	93.64

C. Preparation of the Organic Phase

The organic phase used consists of soybeans fatty acid (SFA) as the extractant, with methyl isobutyl ketone (MIBK), xylene and kerosene serving as the diluents. The preparation of the soybeans fatty acid (SFA) starts with the production of soap from the soybean oil, following the cold process described by Warra et al. [35]. The soap stock obtained was heated in a water bath at 70^{o}C, while 4.68 M nitric acid was added gradually until soap dissolves, forming two layers. The fatty acid layer (the top layer) was separated from the mix using a separating funnel, and washed with distilled water to remove traces of nitric acid and other water-soluble matter present. The acid content of the fatty acid obtained was determined to be 83.1 wt. %.

D. Extraction Procedure

Experiments were carried out by shaking equal volumes (20 ml) of the organic phase (a mixture of organic solvents and fatty acid) and the aqueous phase in a separating funnel. The mixture was shaken vigorously in the separating funnel for ten minutes and left to stand for another 15 minutes, the mixture was allowed to stand in a separating funnel for phase disengagement. This step was carried out using all the three organic phases – kerosene, MIBK, and xylene. Finally, the aqueous sample was taken from the funnel for chemical analysis with an atomic absorption spectrophotometer (AAS). The per cent extraction (%E) of copper (II) ions was calculated according to:

$$\%E = \frac{[Cu]_i - [Cu]_f}{[Cu]_i} \times 100\% \quad (5)$$

Where: $[Cu]_i$ and $[Cu]_f$ are the initial and final concentrations of copper in the aqueous phase, respectively. All experiments were done at room temperature.

III. Results and Discussion

A. Elemental analysis of the copper ore

The PIXE spectrum of the copper containing ore (showing the major elements) is shown in Figure 1, while Table 2 shows the elemental composition in mass percentage. It is evident that the major elements of the ore are Si (32.29 %), Cu (4.08 %), Al (1.96%), and Fe (3.18%). The minor elements (<1.0 wt. %) are Mg, S, K, Cr and Ni. Other elements present in the ore at trace levels (< 0.1 wt. %) are P, Mn, and Zn. However, the constituents shown in Table 2 do not add up to 100% because the analytical technique used does not normally report compositions for elements with atomic numbers below 11.

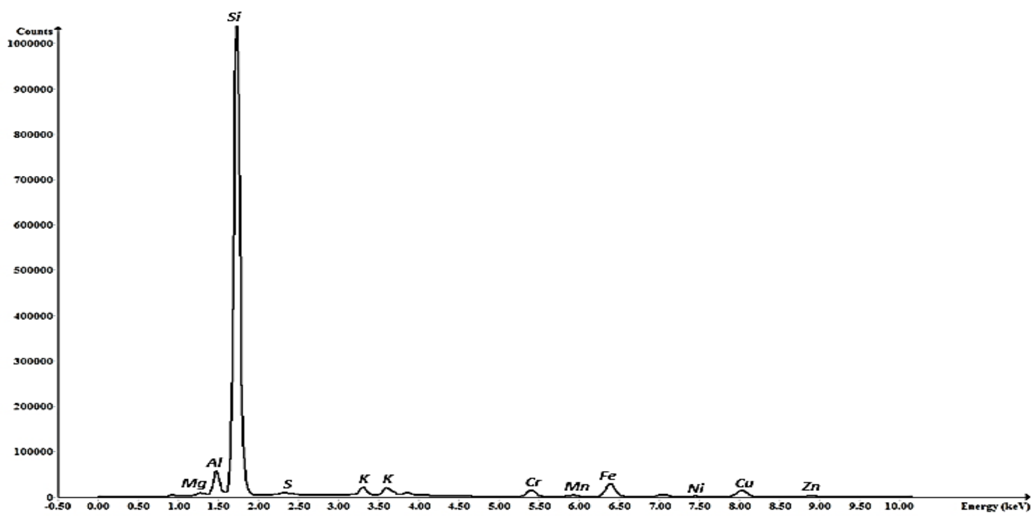

Figure 1: PIXE spectrum of the ore sample

Table 2: Elemental analysis of the copper ore used

Element	Composition (wt. %)
Mg	0.18
Al	1.96
Si	32.29
P	0.06
S	0.21
K	1.15
Cr	1.12
Mn	0.09
Fe	3.18
Ni	0.20
Cu	4.08
Zn	0.07

B. Leaching studies

The relationship between the responses (fraction of ore dissolved, and % Cu leached) and the independent variables (leaching time, leaching temperature and nitric acid concentration) were studied with a view to optimizing the leaching process. The design table in terms of the actual variables and the responses (% dissolution and quantity of copper leached) are presented in Table 3, while Table 4 shows the regression models relating the inputs (in terms of coded variables) and the responses. The ANOVA showing the significance of fit for the quadratic models obtained for the experimental data are presented in Tables 5 and 6. As indicated in Tables 4 and 5, entries with P-values lower than 0.05 are significant model terms. The quadratic models are significant ($P < 0.05$), accounting for over 98% of the observations. The leaching time was found to be the most important factor, followed by the acid concentration as shown on the Pareto charts in Figures 2 and 3.

The response surface contour plots for the fraction of ore dissolved and the quantity of copper leached, in relation to leaching time, acid concentration and leaching temperature are illustrated in Figures 4 and 5, with the input factors kept at their mid-point levels in (a), (b) and (c), respectively. The contour plots also support the information presented on the Pareto charts that the dissolution as well as the leaching of copper depends mainly on the dissolution time. The optimal fractional dissolution and amount of copper leached for the conditions under study such that the optimal leaching of copper does not necessarily require high fractional dissolution values for the ore were found to be 0.097 and 91.18 %, respectively for an optimum temperature, acid concentration and leaching time of 81.25^{o}C, 2.18 M and 29.5 min, respectively.

Table 3: Actual and predicted responses for the leaching process

Run	Time (min)	$[HNO_3]$ (Mol/dm^3)	Temperature (^oC)	Fraction of ore dissolved		% Cu leached	
				Actual	Predicted	Actual	Predicted
1	40	4.68	60	0.103	0.105	91.42	91.60
2	40	3	60	0.122	0.122	91.66	91.71
3	60	2	40	0.118	0.120	92.07	92.17
4	73.64	3	60	0.133	0.134	93.02	92.96
5	6.36	3	60	0.053	0.053	90.44	90.49
6	20	4	40	0.067	0.068	90.82	90.71
7	60	2	80	0.135	0.133	92.63	92.75
8	40	3	60	0.124	0.122	91.68	91.71
9	20	4	80	0.066	0.063	90.65	90.56
10	40	3	60	0.121	0.122	91.70	91.71
11	20	2	80	0.078	0.078	90.83	90.78
12	40	3	26.36	0.107	0.105	91.42	91.30
13	60	4	80	0.155	0.154	93.29	93.13
14	40	1.32	60	0.129	0.128	92.40	92.20
15	40	3	60	0.124	0.122	91.72	91.71
16	40	3	60	0.121	0.122	91.74	91.71
17	40	3	60	0.123	0.122	91.73	91.71
18	60	4	40	0.11	0.109	91.63	91.68
19	40	3	93.64	0.109	0.112	91.54	91.65
20	20	2	40	0.116	0.116	91.65	91.82

Table 4: Regression Coefficients of fitted equations for the ore dissolution process

$$(Y = \delta_o + \delta_1 X_1 + \delta_2 X_2 + \delta_3 X_3 + \delta_{12} X_1 X_2 + \delta_{13} X_1 X_3 + \delta_{23} X_2 X_3 + \delta_{11} X_1^2 + \delta_{22} X_2^2 + \delta_{33} X_3^2)$$

Regression equation coefficients	Response (Y)	
	fraction dissolved	% copper leached
δ_o	0.122	91.706
δ_1	0.024	0.732
δ_2	-0.007	-0.179
δ_3	0.002	0.105
δ_{11}	-0.010	0.007
δ_{22}	-0.002	0.071
δ_{33}	-0.005	-0.081
δ_{12}	0.009	0.155
δ_{13}	0.013	0.400
δ_{23}	0.008	0.219
R^2	0.9962	0.9793
Adjusted R^2	0.9927	0.9606

Table 5: ANOVA for the response model for the fractional dissolution of the ore

Source	Df [a]	SS [b]	MS [c]	F	P
Model	9	0.012646	0.001405	289.29	<0.001
Time (min), X_1	1	0.007760	0.007760	1597.72	<0.001
Concentration(M), X_2	1	0.000630	0.000630	129.61	<0.001
Temperature (°C), X_3	1	0.000051	0.000051	10.48	0.009
X_1^2	1	0.001506	0.001506	310.09	<0.001
X_2^2	1	0.000063	0.000063	12.98	0.005
X_3^2	1	0.000349	0.000349	71.81	<0.001
X_1X_2	1	0.000666	0.000666	137.15	<0.001
X_1X_3	1	0.001275	0.001275	262.53	<0.001
X_2X_3	1	0.000528	0.000528	108.74	<0.001
Lack of Fit	5	0.000039	0.000008	4.11	0.073
Pure Error	5	0.000010	0.000002		
Total	19	0.012694			

a: Degrees of freedom, b: Sum of squares, c: Mean squares

Table 6: ANOVA for the response model for copper concentration in the leachate

Source	Df [a]	SS [b]	MS [c]	F	P
Model	9	9.9482	1.10536	53.03	<0.001
Time (min), X_1	1	7.3198	7.31979	351.18	<0.001
Concentration(M), X_2	1	0.4350	0.43498	20.87	0.001
Temperature (°C), X_3	1	0.1508	0.15083	7.24	0.023
X_1^2	1	0.0006	0.00062	0.03	0.867
X_2^2	1	0.0721	0.07209	3.46	0.093
X_3^2	1	0.0944	0.09439	4.53	0.059
X_1X_2	1	0.1930	0.19298	9.26	0.012
X_1X_3	1	1.2802	1.28025	61.42	<0.001
X_2X_3	1	0.3840	0.38396	18.42	0.002
Lack of Fit	5	0.2040	0.04080	45.83	<0.001
Pure Error	5	0.0045	0.00089		
Total	19	10.1567			

a: Degrees of freedom, b: Sum of squares, c: Mean squares

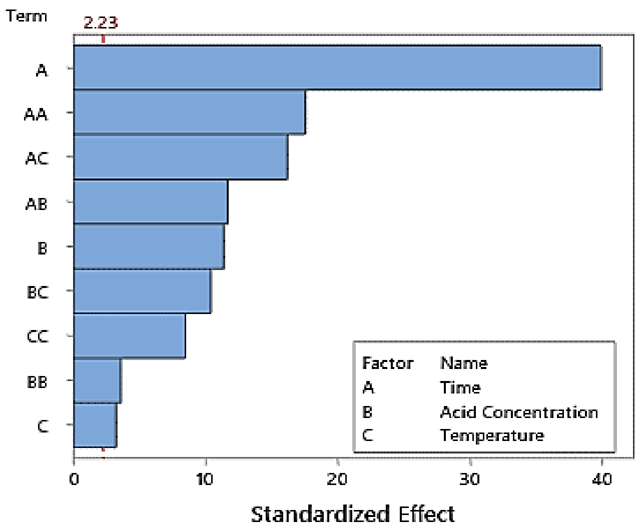

Figure 2: Pareto chart of the standardized effects for mass fraction of ore dissolved

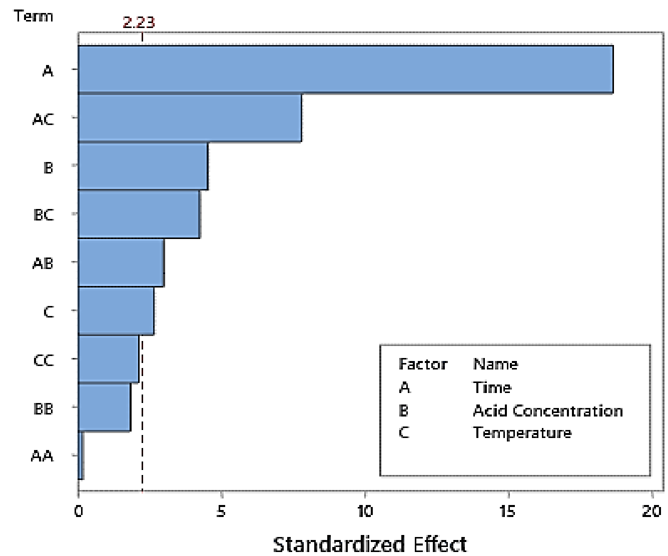

Figure 3: Pareto chart of the standardized effects for % Cu leached

Preliminary Solvent Extraction Studies

From Table 1, it was observed that copper (Cu) and iron (Fe) are the major elements in the ore. Since both metals are soluble in nitric acid, it is desirable to have an extraction system that will preferentially extract Cu, while suppressing Fe. Figures 5 - 7 show the relative extraction of copper and iron using the SFA prepared earlier, with MIBK xylene and kerosene, respectively as diluents.

The extraction of copper was observed to increase with increasing SFA concentration. However, the percentage extraction of iron also increased, as shown in Figures 6 – 8. For the MIBK media, the degree of separation for Cu and Fe was observed to be higher, compared to the xylene and kerosene media. Figure 6 however shows that using pure MIBK, 50% of the Cu and 8% of the iron was extracted. On the other hand, the extraction of Cu and Fe in kerosene was observed to be better than in xylene and these results may be attributed to nature of the solvents. Although kerosene and xylene are both non-polar solvents, kerosene is a mixture of aliphatic hydrocarbons while xylene is aromatic. The results agree with the findings of Halim et al. [36] in their study of the extraction of copper from aqueous media using oleic acid as the extractant.

From the preliminary results obtained from the extraction studies, it can be deduced that vegetable oil fatty acids have the potentials of being used as readily available and inexpensive non-toxic alternatives for the rather expensive specialty solvents commonly used in the hydrometallurgical recovery of metal values from aqueous media.

IV. CONCLUSION

In this study, the dissolution of a low-grade Nigerian copper ore in nitric acid was examined. The results showed that the rate of dissolution and the amount of copper leached depend mainly on the dissolution time and that 91 % of the copper values was leached at the optimum leaching conditions. The results obtained from the solvent extraction studies have established the feasibility of using soybean fatty acid to extract metal ions such as Cu and Fe from aqueous solutions. The choice of solvent has a great effect on the extraction efficiency, with MIBK showing better performance in terms of the extraction of Cu, than xylene or kerosene.

REFERENCES

[1] Sajjad W, Zheng G, Din G, Ma X, Rafiq M, Xu W. "Metals extraction from sulfide ores with microorganisms: The bioleaching technology and recent developments". *Transactions of the Indian Institute of Metals*. Vol. 7, no. 72, 2019, pp. 559-579.

[2] Norgate, T., and Jahanshahi, S. "Low grade ores - Smelt, leach or concentrate?" *Minerals Engineering*, Vol. 23, no. 2, 2010. https://doi.org/10.1016/j.mineng.2009.10.002

[3] Olubambi, P. A., Ndlovu, S., Potgieter, J. H., and Borode, J. O. "Influence of applied mineralogy in developing an optimal hydrometallurgical processing route for complex sulphide ores". *Mineral Processing and Extractive Metallurgy Review*, Vol. 27, no 2, 2006. https://doi.org/10.1080/08827500600563350

[4] Olubambi, P. A., Ndlovu, S., Potgieter, J. H., and Borode, J. O. "Effects of ore mineralogy on the microbial leaching of low grade complex sulphide ores". *Hydrometallurgy*, vol. 86, nos. 1–2, 2007. https://doi.org/10.1016/j.hydromet.2006.10.008

[5] Kamberović, Ž., Ranitović, M., Korać, M., Andjić, Z., Gajić, N., Djokić, J., and Jevtić, S. "Hydrometallurgical process for selective metals recovery from waste-printed circuit boards". *Metals*, vol. 8, no. 6, 2018. https://doi.org/10.3390/met8060441

[6] Nithya R, Sivasankari C, and Thirunavukkarasu A. "Electronic waste generation, regulation and metal recovery: a review. *Environmental Chemistry Letters*. Vol. 19, 2021 pp. 1347-1368.

[7] Tian, X., Yin, X., gong, Y., Wu, Y., Tan, Z., and Xu, P. "Characterization, recovery potentiality, and evaluation on recycling major metals from waste cathode-ray tube phosphor powder by using nitric acid leaching". *Journal of Cleaner Production*. Vol. 135, 2016 https://doi.org/10.1016/j.jclepro.2016.07.044

[8] Tuncuk, A., Stazi, V., Akcil, A., Yazici, E. Y., and Deveci, H. "Aqueous metal recovery techniques from e-scrap: Hydrometallurgy in recycling". *Minerals Engineering*. Vol. 25, no 1, 2012. https://doi.org/10.1016/j.mineng.2011.09.019

[9] Astuti, W., Hirajima, T., Sasaki, K., and Okibe, N. "Comparison of effectiveness of citric acid and other acids in leaching of low-grade Indonesian saprolitic ores". *Minerals Engineering*, 85, 2016. https://doi.org/10.1016/j.mineng.2015.10.001

[10] Meng F, Liu Q, Kim R, Wang J., Liu G and Ghahreman A. "Selective recovery of valuable metals from industrial waste lithium-ion batteries using citric acid under reductive conditions: Leaching optimization and kinetic analysis". *Hydrometallurgy*. Vol. 191, 105160, 2020.

[11] Padh B, Das M. and Reddy B. R. "A roast-leach process for the recovery of vanadium from vanadium-bearing gasifier slag (VBGS) using citric acid as a green reagent: Leaching studies and statistical analysis for sustainable processing". *Hydrometallurgy*, 106020, 2023.

[12] Sahoo, R. N., Naik, P. K., and Das, S. C. "Leaching of manganese from low-grade manganese ore using oxalic acid as reductant in nitric acid solution". *Hydrometallurgy*, Vol. 62, No. 3, 2001. https://doi.org/10.1016/S0304-386X(01)00196-7

[13] Xu, L., Yang, H., Liu, Y., and Zhou, Y.

"Uranium leaching using citric acid and oxalic acid". *Journal of Radioanalytical and Nuclear Chemistry*. Vol. 321, No. 3, 2019, https://doi.org/10.1007/s10967-019-06673-9

[14] Baba, A Alafara, Adekola, F., and Folashade, A. "Quantitative leaching of a Nigerian iron ore in hydrochloric acid". *Journal of Applied Sciences and Environmental Management*. Vol. 9, No 3, 2006. https://doi.org/10.4314/jasem.v9i3.17346

[15] Baba, Alafara A., and Adekola, F. A. "Hydrometallurgical processing of a Nigerian sphalerite in hydrochloric acid: Characterization and dissolution kinetics". *Hydrometallurgy*. Vol. 101, Nos 1–2, 2010. https://doi.org/10.1016/j.hydromet.2009.12.001

[16] Mystrioti, C., Nymphodora P., and Anthimos X. "Selective Recovery of Iron by Solvent Extraction from Ni-Laterite Leach Solutions, as Precursor for the Synthesis of High Added-Value Nanomaterials." *Circular Economy and Sustainability,* 2021, pp. 1-13.

[17] Wahab W, Deniyatno D, Saranga M and Supriyatna Y. I. "Kinetics study of leaching ore nickel laterite using hydrochloric acid in atmosphere pressure". *Riset Geologi dan Pertambangan*. Vol. 32, No.1, 2022, pp. 14-26.

[18] Kumar, M., Lee, J. C., Kim, M. S., Jeong, J., and Yoo, K.. "Leaching of metals from waste printed circuit boards (WPCBs) using sulfuric and nitric acids". *Environmental Engineering and Management Journal*. Vol. 13, No. 12, 2014 https://doi.org/10.30638/eemj.2014.290

[19] Ajiboye, E. A., Panda, P. K., Adebayo, A. O., Ajayi, O. O., Tripathy, B. C., Ghosh, M. K., and Basu, S. "Leaching kinetics of Cu, Ni and Zn from waste silica rich integrated circuits using mild nitric acid". *Hydrometallurgy*. Vol. *188*, 2019, pp. 161-168.

[20] Huynh, T. H., Ha, V. H., and Vu, M. T. "Leaching of yttrium and europium from fluorescent lamp phosphor powder using nitric acid: kinetics and optimization". *Geosystem Engineering*, 2022, pp. 1-15.

[21] Sun, Y., Fu, G., and Jiang, L. (2021). "Reductive leaching of low-grade manganese oxide ores using pretreated straw as reductant". *Mineral Processing and Extractive Metallurgy*: *Transactions of the Institute of Mining and Metallurgy*. Vol. 130, No. 1, 2021, https://doi.org/10.1080/25726641.2018.1505210

[22] Biswas, A. K., and Davenport, W. G. "Extractive Metallurgy of Copper — Third Edition". *Mineral Resources Engineering*. Vol. 04, No. 2, 1995. https://doi.org/10.1142/s0950609895000205

[23] Zhang, Y. L., Wang, C. Y., Yang, Y. Q., Yin, F., and Ma, B. Z. "Pressure nitric acid leaching of alkali-pretreated low-grade limonitic laterite". *Rare Metals*. Vol. 34, No. 1, 2015. https://doi.org/10.1007/s12598-014-0432-y

[24] Ajiboye, E. A., Panda, P. K., Adebayo, A. O., Ajayi, O. O., Tripathy, B. C., Ghosh, M. K., and Basu, S. "Leaching kinetics of Cu, Ni and Zn from waste silica rich integrated circuits using mild nitric acid". *Hydrometallurgy*. Vol.188, 2019, pp. 161-168.

[25] Ak, M., Taban, D., and Deligöz, H. "Transition metal cations extraction by ester and ketone derivatives of chromogenic azocalix[4]arenes". *Journal of Hazardous Materials*, Vol. 154, Nos. 1–3, 2008, https://doi.org/10.1016/j.jhazmat.2007.09.104

[26] Memon, S., Akceylan, E., Sap, B., Tabakci, M., Roundhill, D. M., and Yilmaz, M. (2003). "Polymer Supported Calix[4]Arene Derivatives for the Extraction of Metals and Dichromate Anions. Journal of Polymers and the Environment". Vol. 11, No. 2, 2003, https://doi.org/10.1023/A:1024223922541

[27] Li, X., Monnens, W., Li, Z., Fransaer, J.,

and Binnemans, K. “Solvometallurgical process for extraction of copper from chalcopyrite and other sulfidic ore minerals”. *Green Chemistry*. Vol. *22, No. 2*, 2020, pp. 417-426.

[28] Guerdouh, A., and Barkat, D. “Influence of the solvent on the extraction of copper(II) from nitrate medium using salicylideneaniline”. *Journal of Dispersion Science and Technology*. Vol. 38, No. 7, 2017. https://doi.org/10.1080/01932691.2016.1215926

[29] Sanda, O., and E. A. Taiwo. "Solvent extraction of tantalum (V) from aqueous sulphate/fluoride solution using trioctyl phosphine oxide in MIBK." *Hydrometallurgy* Vol. 127, 2012, pp. 168-171. https://doi.org/10.1016/j.hydromet.2012.08.006

[30] Takahashi, V. C. I., Botelho Junior, A. B., Espinosa, D. C. R., and Tenório, J. A. S. “Enhancing cobalt recovery from Li-ion batteries using grinding treatment prior to the leaching and solvent extraction process”. *Journal of Environmental Chemical Engineering*, Vol. 8, No. 3, 2020. https://doi.org/10.1016/j.jece.2020.103801

[31] Simonin, J. P., Hendrawan, H., Dardoize, F., and Clodic, G. "Study of salt effects on the kinetics of extraction of cobalt (II) and zinc (II) at trace level by D2EHPA in n-dodecane." *Hydrometallurgy* Vol. 69, Nos. 1-3, 2003, pp. 23-38. https://doi.org/10.1016/S0304-386X(02)00211-6

[32] Morais, B. S., and Marcelo B. M. "Characterisation of the reactive test system $ZnSO_4$/D2EHPA in n-heptane." *Hydrometallurgy* Vol. 74, Nos.1-2, 2004, pp. 11-18.

[33] Guerdouh, A., and Barkat, D. “Experimental study of the extraction of chromium (III) from nitrate medium by lauric acid”. *Metallurgical and Materials Engineering*, Vol. 24, No. 3, 2018, pp. 189 – 197. https://doi.org/10.30544/385

[34] Montgomery, D. C. *Design and analysis of experiments*. John Wiley & sons, 2017.

[35] Warra, A., Hassan, L., Gunu, S., and Jega, S. “Cold- Process Synthesis and Properties of Soaps Prepared from Different Triacylglycerol Sources”. *Nigerian Journal of Basic and Applied Sciences*, Vol. 18, No. 2, 2010. https://doi.org/10.4314/njbas.v18i2.64350

[36] Halim, S. F. A., Chang, S. H., and Ahmad, S. K. N. “Extraction of copper ions from aqueous solutions with oleic acid as green solvent”. *Journal of Physics: Conference Series*, Vol. 1349, No. 1, 2019 https://doi.org/10.1088/1742-6596/1349/1/012128

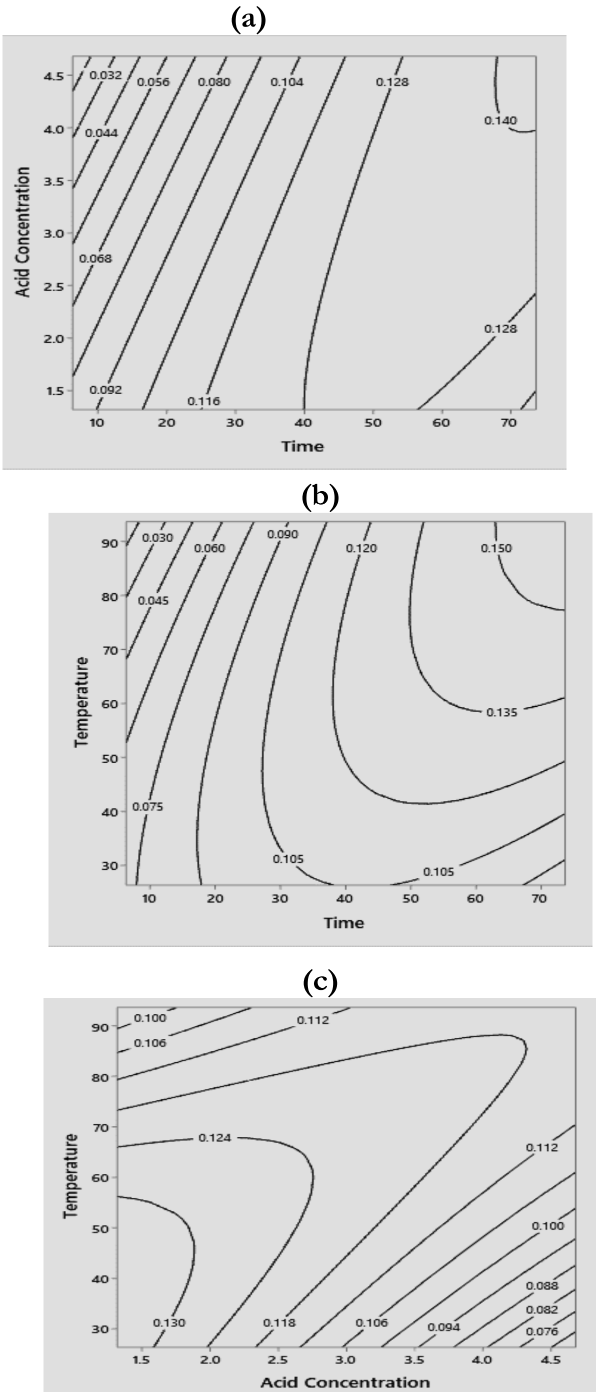

Figure 4: Response surface contour plots for fractional dissolution of the copper ore

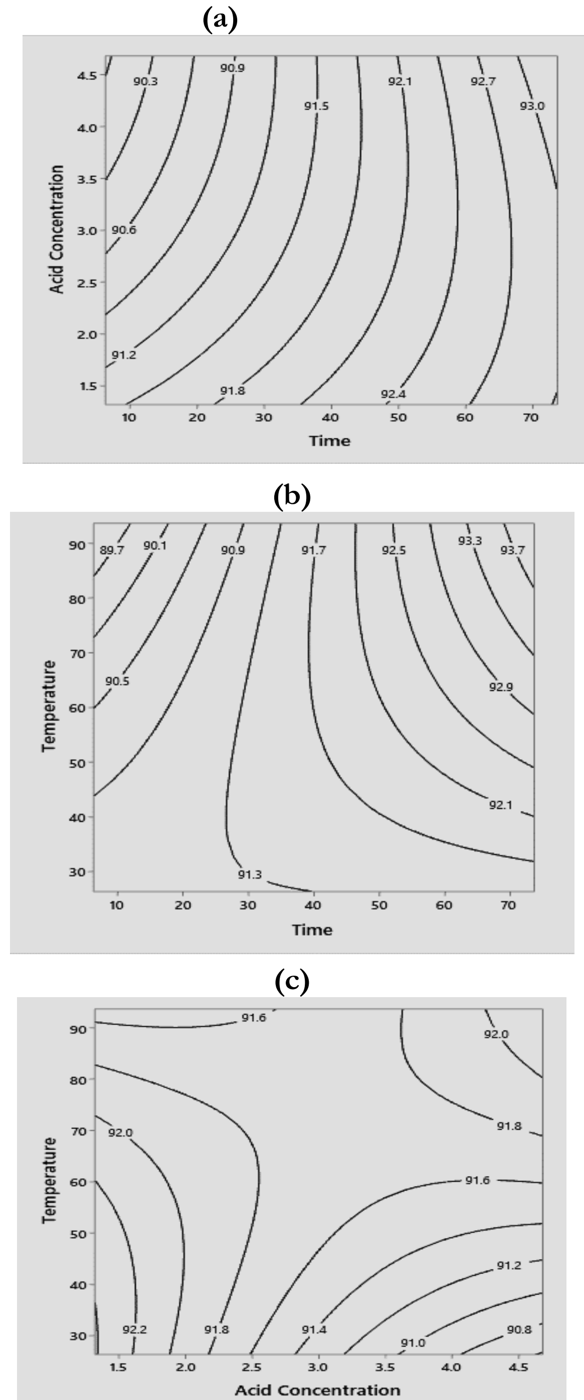

Figure 5: Response surface contour plots for the amount of copper leached

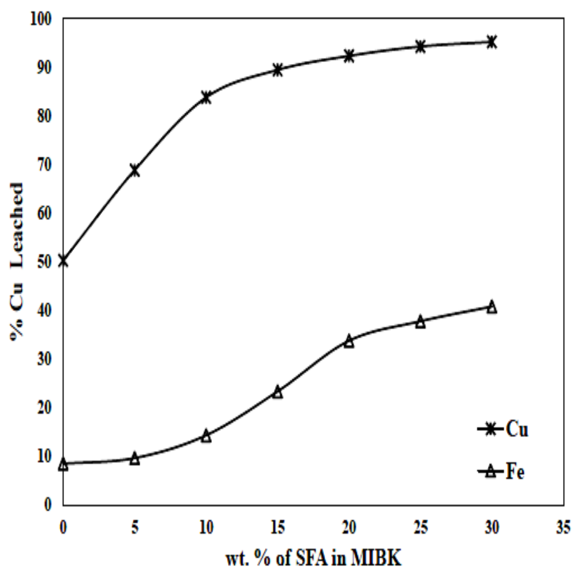

Figure 6: Effect of SFA concentration in MIBK media on the extraction of Cu and Fe

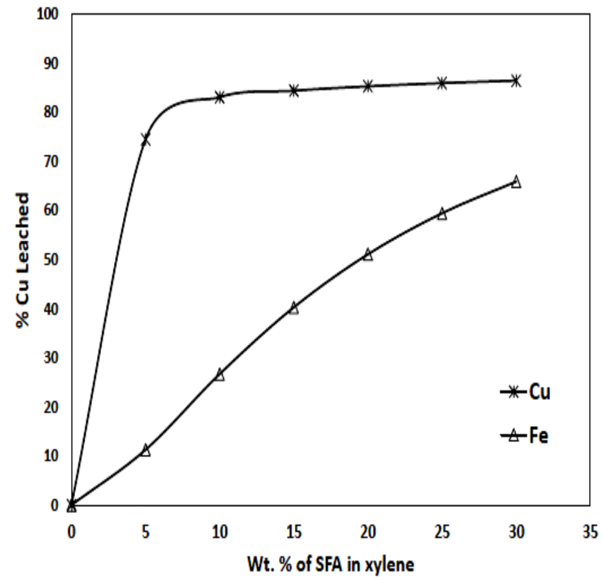

Figure 7: Effect of SFA concentration in xylene media on the extraction of Cu and Fe

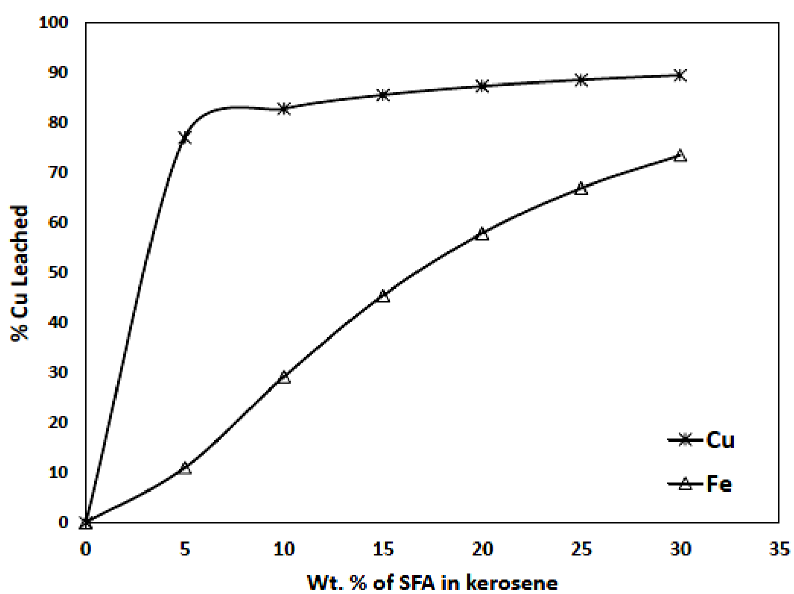

Figure 8: Effect of SFA concentration in kerosene media on the extraction of Cu and Fe