Full Paper

DISSOLUTION OF A NIGERIAN COPPER ORE IN SULPHURIC ACID: KINETICS AND OPTIMIZATION STUDIES

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ABSTRACT

The leaching of copper from a Nigerian copper ore using sulphuric acid was investigated. Elemental analysis of the ore was done using Particle-induced X-ray Emission (PIXE) spectroscopy with 2.5 MeV protons and this showed the major elements in the ore to be S (12.81 %), Fe (15.46 %), Cu (9.05 %) and Zn (1.15 %). The ore was milled to about 100 microns size using a Rocklabs ring mill and leaching tests were done according to a 3-factor Central Composite Design with leaching time, temperature and acid concentration as the design variables. Simple regression equations for the degree of dissolution and the quantity of Cu extracted were determined from the experimental data, and the main effects and interactions from the leaching studies were determined by the analysis of variance (ANOVA). Experimental results indicate that the dissolution rate is chemical reaction controlled, and the optimum percentage dissolution and concentration of copper in the leachate were found to be 14.89 % and 1.78 g/l, respectively while the optimum dissolution time, temperature, and acid concentration were found to be 65.7 min, 65.5 °C and 4.34 M, respectively. In conclusion, the dissolution kinetics of copper ore in sulphuric acid was found to be governed by the shrinking core model with chemical reaction as the rate-controlling mechanism. The activation energy for the dissolution process was found to be 16.04 $kJ.mol^{-1}$.

Keywords: Copper ore, Leaching, Response Surface Methodology, Optimization

1. INTRODUCTION

Copper was one of the first metals ever extracted and used by man, and it has made vital contributions to sustaining and improving society since the dawn of civilization (Doebrich, 2009). In pure form, copper is a brownish-red, fairly soft, malleable and very ductile metal. Copper ranks as the 25th most abundant among the elements in the earth's crust with an average concentration of 50–70 mg per kg (Kundig and Dresher, 2000; Engström, 2013) with the highest concentrations found in volcanic and basic rock.

Copper is a useful material with a wide range of applications due to its various desirable properties such as its excellent electrical and thermal conductivity (Doebrich, 2009), high resistance to corrosion (Ross, 2013) and ease of workability. Copper has found uses in various areas of application such as electrical appliances, process vessels, household articles (Kundig and Dresher, 2000), art objects (Scott, 2002), coins and medals (Hajivaliei *et al.*, 1999), and in military hardware (Winterhalter *et al.*, 2005). There is a smaller demand for copper for other purposes such as powder-metallurgical copper (Jayabharath *et al.*, 2007), materials for brakes and self-lubricating bearings (Chen *et al.*, 2014), graphite brushes (Klement *et al.*, 2015), and alloying additives for aluminum, iron, and steel (Davis, 2001).

The decline in the world deposits of high grade copper ores in recent times has drawn attention to complex low-grade sulphide ores. However, these ores are mostly difficult to treat effectively with conventional mineral processing methods (Rubio and Frutos, 2002; Adebayo *et al.*, 2003). Processes such as roasting, pressure oxidation, chemical oxidation or bioleaching that are available for the treatment of complex sulphide ores have proved to be rather complex and expensive (Gomez *et al.*, 1997; Han and Meng, 2003). Hence, attention has been drawn to the use of readily available and inexpensive reagents like sulphuric acid for recovery of the copper values. Although sulphuric acid may not be as effective as stronger oxidizing acids like nitric acid (Olubami *et al.*, 2006; Baba *et al.*, 2012), it is still preferred in terms of cost, corrosion wear and the ease of regeneration during electrowinning (Biswas and Davenport, 2013).

Nevertheless, studies have been centered on the processing of high grade ores, with little done on low-grade, complex sulphide ores of Nigerian origin. This study therefore investigates the leaching of copper from a Nigerian sulphide ore using sulphuric acid, considering the effect of process parameters such as acid concentration, leaching time and temperature.

2. MATERIALS AND METHODS

The ore used for this investigation was sourced from Ishiagu in Ebonyi State of Nigeria. Analar grade sulphuric acid (98 %, Lobachemie) was used in this work and distilled water was used in the preparation of all solutions.

2.1. Sample Preparation and Analysis

The elemental composition of the ore was determined by Particle Induced X-Ray Emission (PIXE) spectroscopy using the sample preparation and analysis method described by Obiajunwa and Nwachukwu (2000). PIXE spectroscopy was chosen because it is a fast non-destructive analytical technique capable of simultaneous determination of light and heavy elements in solid samples, has a detection limit of less than 1 ppm for many elements and precision of ±10% or better for the trace elements (Benyaich *et al.*, 1997; Sanda and Taiwo, 2012; Pérez *et al.*, 2016). PIXE analysis was done on the ore using 2.5 MeV Protons from a 1.7 MV Tandem Accelerator using charge and current values of 4.0 μC and 3.23 nA, respectively. The spectrum obtained were analysed using the Gupixwin software (version 2.2.0).

2.2. Acid Leaching

The ore was milled to 100 μm using a Rocklabs ring mill. For the leaching experiment, 5 g of milled ore was mixed with 100 ml of sulphuric acid in a 250 ml glass reactor fitted with a reflux condenser and a thermometer. The leaching was performed under magnetic stirring (200 rpm) at leaching temperatures between 30 and 90 ºC, and leaching durations between 10 and 60 min. At the end of each run, the mixture was filtered and the residue washed using distilled water to get rid of residual acid, dried in an oven at 105 ºC for 1 h and weighed. The amount of copper in the filtrates was determined using a ***Perkin Elmer AAnalyst100*** atomic absorption spectrometer (AAS). The extent of dissolution of the ore was determined by 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 (g), respectively and X is the mass fraction of ore dissolved.

2.3. Acid leaching optimization studies

A 3 – factor Central Composite Design (with α = 1.618) was employed in this work and the experimental design was done using Minitab statistical software (version 16.1.1), which generated 20 experimental runs. Three independent formulation variables were selected for this study and these are the concentration of the acid, leaching time and temperature. The numbers of design points in the CCD are based upon a full 2^k factorial and the total numbers of experiments is given by (Montgomery *et al.*, 2009):

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

where N is the total number of experiments, k is the number of factors, and m is the number of replicates. Multiple linear regression analysis was used, and the data was fitted as a second-order equation of the form:

$$Y = \delta_o + \delta_1 X_1 + \delta_2 X_2 + \delta_3 X_3 + \delta_{12} X_1 X_2 + \delta_{13} X_1 X_3 + \delta_{23} X_2 X_3 + \delta_{11} X_1^2 + \delta_{22} X_2^2 + \delta_{33} X_3^2 \quad (3)$$

Where Y is the predicted response (% dissolution of the ore or copper concentration in the filtrate), 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. In addition, the terms 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):

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

where X_i is the coded value for the ith input (that is, X_i), x_o is the mid value for the experimental design, and Δx is the step change (i.e. the difference between the upper design value of x and the mid value). 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
Leaching Temperature (ºC)	x_1	26.36	40	60	80	93.64
Time (min)	x_2	6.36	20	40	60	73.64
[H_2SO_4] ($mol.dm^{-3}$)	x_3	1.32	2.0	3.0	4.0	4.68

3. RESULTS AND DISCUSSION

The results obtained from the study are presented and discussed as follows:

3.1. Elemental Analysis:

The PIXE spectrum shown in Figure 1 shows the major constituents of the ore to be aluminium (1.21 %), silicon (4.07 %), sulphur (12.81 %), calcium (1.33 %), iron (15.46 %), copper (9.05 %), zinc (1.15 %), and arsenic (1.19 %), with magnesium, potassium, titanium, chromium, manganese, nickel, and tin occurring in traces. The result of the elemental analysis is presented in Table 2.

As shown in Table 2, the constituents do not add up to 100%. The reason for this is that the analytical technique used (that is, PIXE) is best suited for elements with atomic numbers greater than 18.

Components such as oxygen (from oxides) and carbon (from carbonates) which are common to many mineral ores are not reported by this technique, and should account for the deficit observed here. In addition, the detector commonly used for PIXE is silicon based and might not detect silica (Rodríguez-Fernández *et al.*, 1994; Sanda and Taiwo, 2016).

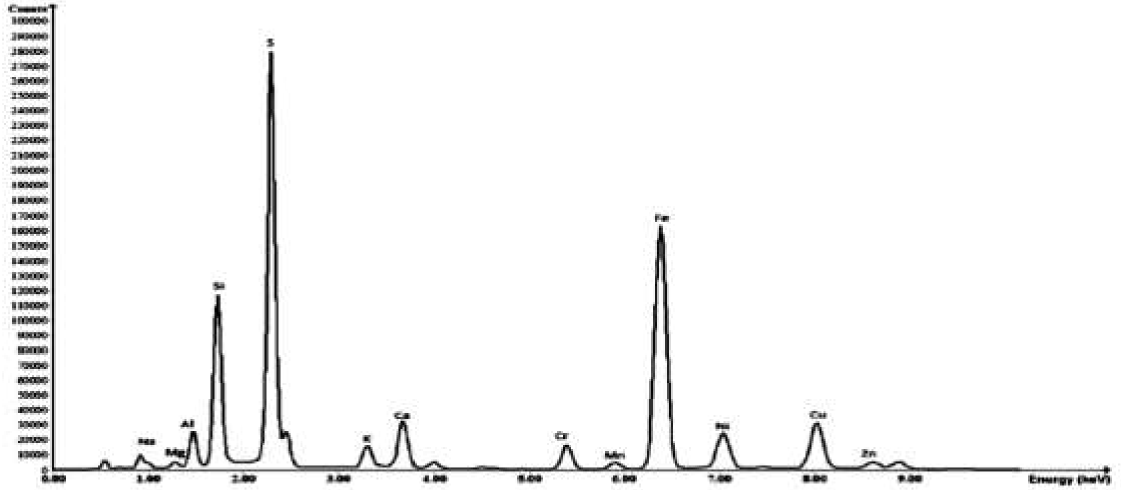

Figure 1: PIXE spectrum of the copper ore showing the major elements present

Table 2: Elemental composition of the copper ore used

Element	Composition (% w/w)
Mg	0.1
Al	1.21
Si	4.07
S	12.81
K	0.66
Ca	1.33
Ti	0.04
Cr	0.9
Mn	0.17
Fe	15.46
Ni	0.24
Cu	9.05
Zn	1.15
As	1.19
Sn	0.24

3.2. Ore Dissolution Study Using Response Surface Methodology:

The relationship between the responses (fraction of ore dissolved, and concentration of copper in the leachate) and three independent variables (temperature, dissolution time and acid concentration) were studied in order to optimize the process. The design matrix in actual terms and the experimental results of RSM are presented in Table 3. The experimental data were fitted to Equation (3) to obtain mathematical regression quadratic models for the relationship between the responses (fraction dissolved and copper concentration) and the experimental factors (Table 4).

Table 3: Actual and predicted responses for the copper ore leaching process

Run	Temperature (^{o}C)	Time (min)	[H_2SO_4] (g/L)	Fraction dissolved		[Cu] (g/dm^3)	
				Actual	Predicted	Actual	Predicted
1	60.00	40.00	4.68	0.100	0.106	1.738	1.759
2	60.00	40.00	3.00	0.122	0.122	1.516	1.511
3	40.00	60.00	2.00	0.117	0.123	1.382	1.383
4	60.00	73.64	3.00	0.130	0.136	1.410	1.417
5	60.00	6.36	3.00	0.059	0.054	1.220	1.220
6	40.00	20.00	4.00	0.061	0.067	1.560	1.549
7	80.00	60.00	2.00	0.137	0.131	1.538	1.543
8	60.00	40.00	3.00	0.118	0.122	1.518	1.511
9	80.00	20.00	4.00	0.070	0.063	1.270	1.264
10	60.00	40.00	3.00	0.124	0.122	1.513	1.511
11	80.00	20.00	2.00	0.074	0.079	1.416	1.418
12	26.36	40.00	3.00	0.110	0.105	1.550	1.552
13	80.00	60.00	4.00	0.157	0.153	1.700	1.685
14	60.00	40.00	1.32	0.133	0.128	1.670	1.657
15	60.00	40.00	3.00	0.120	0.122	1.506	1.511
16	60.00	40.00	3.00	0.126	0.122	1.502	1.511
17	60.00	40.00	3.00	0.122	0.122	1.510	1.511
18	40.00	60.00	4.00	0.118	0.112	1.667	1.659
19	93.64	40.00	3.00	0.102	0.109	1.442	1.447
20	40.00	20.00	2.00	0.112	0.115	1.560	1.569

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

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

	Response (Y)	
Regression equation coefficients	fraction dissolved	copper concentration
δ_o	0.122	1.511
δ_1	0.041	0.099
δ_2	-0.011	0.051
δ_3	0.002	-0.053
δ_{11}	-0.027	-0.192
δ_{22}	-0.005	0.197
δ_{33}	-0.015	-0.011
δ_{12}	0.027	0.209
δ_{13}	0.031	0.220
δ_{23}	0.023	-0.095
R^2	0.9640	0.9956
Adjusted R^2	0.9317	0.9916

ANOVA for studying the significance of fit from the quadratic equations for the experimental data is shown in Tables 5 and 6, with P-values lower than 0.05 indicating significant model terms. The quadratic models are significant ($P < 0.001$), accounting for over 96 % of the observations. The extent of the dissolution of the ore in sulphuric acid depends on the leaching time and the concentration of acid used.

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	0.012477	0.001386	29.79	< 0.001
Time (min), X_1	1	0.008042	0.008042	172.83	< 0.001
Concentration(M),X_2	1	0.000586	0.000586	12.60	0.005
Temperature (°C), X_3	1	0.000020	0.000020	0.43	0.526
X_1^2	1	0.001149	0.001300	27.93	< 0.001
X_2^2	1	0.000020	0.000043	0.91	0.362
X_3^2	1	0.000425	0.000425	9.13	0.013
X_1X_2	1	0.000722	0.000722	15.52	0.003
X_1X_3	1	0.000968	0.000968	20.80	0.001
X_2X_3	1	0.000545	0.000545	11.70	0.007
Lack of Fit	5	0.000425	0.000085	10.63	0.011
Pure Error	5	0.000040	0.000008		
Total	19	0.012943			

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	0.325993	0.036221	251.09	<0.001
Time (min), X_1	1	0.046926	0.046926	325.30	<0.001
Concentration(M),X_2	1	0.012637	0.012637	87.60	<0.001
Temperature (°C), X_3	1	0.013328	0.013328	92.39	<0.001
X_1^2	1	0.079821	0.066300	459.61	<0.001
X_2^2	1	0.071552	0.070087	485.86	<0.001
X_3^2	1	0.000212	0.000212	1.47	0.253
X_1X_2	1	0.043956	0.043956	304.71	<0.001
X_1X_3	1	0.048516	0.048516	336.32	<0.001
X_2X_3	1	0.009045	0.009045	62.70	<0.001
Lack of Fit	5	0.001266	0.000253	7.19	0.025
Pure Error	5	0.000176	0.000035		
Total	19	0.327436			

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

The response surface three dimensional (3D) plots for process in relation to temperature, acid concentration and time are illustrated in Figures 2 and 3, with the process variables kept at their mid-point levels in (a), (b) and (c), respectively. From the studies, it was found that temperature and acid concentration play an important role in the process.

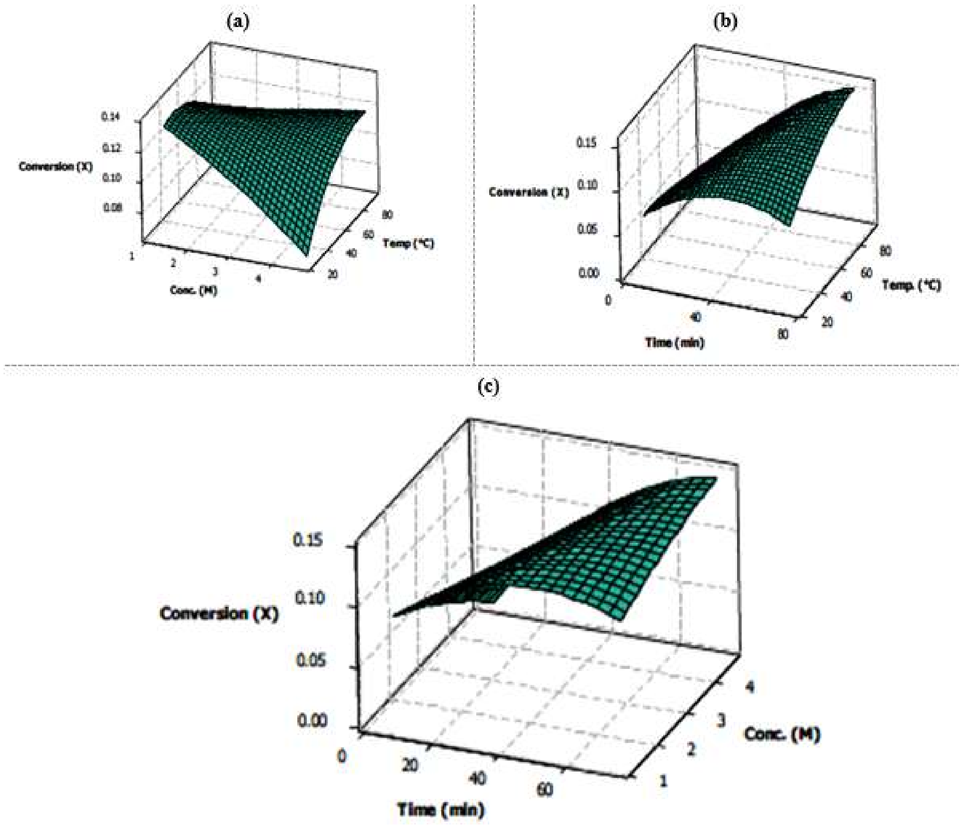

Figure 2: Response surface 3D plots for the fractional dissolution of the ore

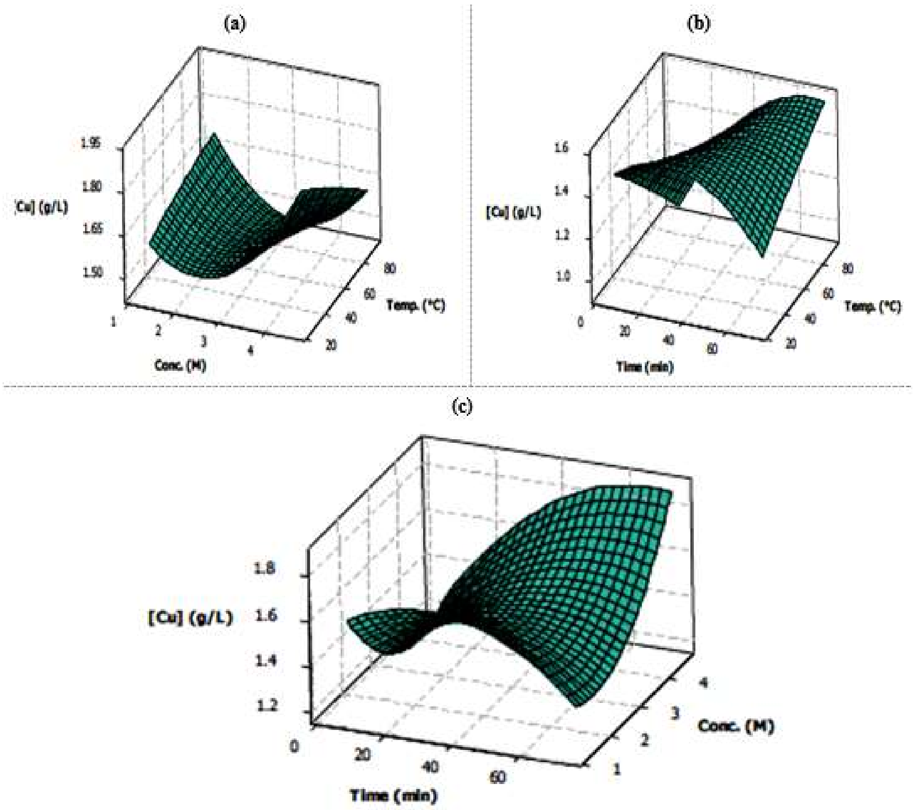

Figure 3: Response surface 3D plot for the amount of copper leached

The optimum fractional dissolution and amount of copper leached for the conditions under study were found to be 0.1489 and 1.776 g/dm^3, respectively for an optimum temperature, acid concentration and leaching time of 65.51 °C, 4.35 M and 65.74 min, respectively as shown by the Minitab 16 Optimization plots in Figure 4.

3.3. Dissolution kinetics:

The effect of temperature on the rate of the copper ore dissolution was investigated using temperature range 30 – 90 °C (303 – 363 K), keeping the concentration of the acid constant at 4.34 M (that is, the optimal leaching concentration obtained from the RSM). The result of this investigation is presented in Figure 5.

From the result in Figure 5, it is observed that increasing the temperature is accompanied by increase in the dissolution rate. Similar studies have also shown that the dissolution rate of ores in acid media tends to increase with increase in leaching temperature (Bingöl and Canbazoğlu, 2004; Noaparast *et al.*, 2015; Sanda and Taiwo, 2016; Baba *et al.*, 2017).

Due to reduction in both the mass of solid and the particle size during leaching, the shrinking particle model is always applied to describe the leaching kinetics (Liddell, 2005; Safari *et al.*, 2009; Sanda and Taiwo, 2016; Baba *et al.*, 2017). Consequently, the dissolution mechanism of the ore is based on two main kinetic models, which are the diffusion controlled model (equation 5) and the surface chemical reaction model (equation 6):

$$1 - 3(1 - \mathrm{X})^{\frac{2}{3}} + 2(1 - \mathrm{X}) = \mathrm{k_r t} \qquad (5)$$

$$k_r t = 1 - (1 - X)^{\frac{1}{3}} \qquad (6)$$

where k_r is the apparent rate constant and X is the fractional dissolution.

It was observed that of the two kinetic models, the dissolution data fitted well to the surface chemical reaction model (that is, Equation 6) as shown in Table 7 and Figure 6.

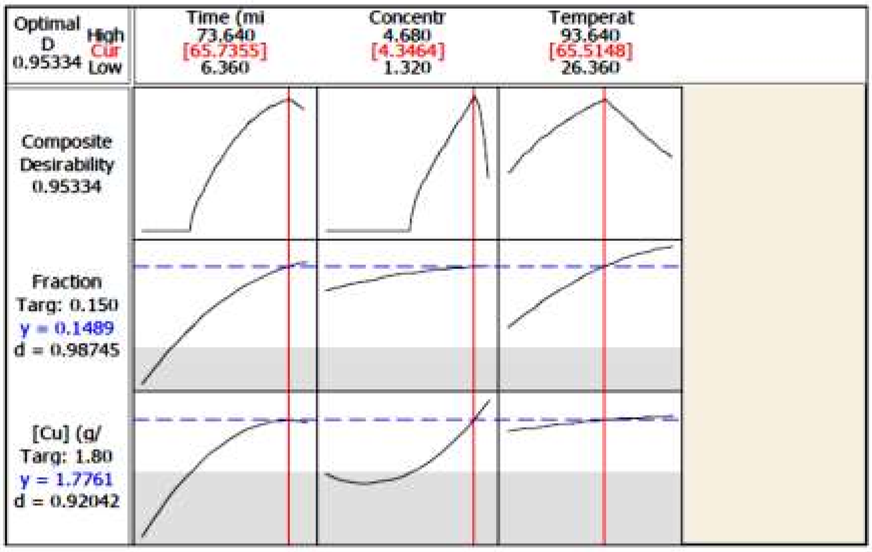

Figure 4: Optimization plots for the dissolution of the copper ore for the conditions under study

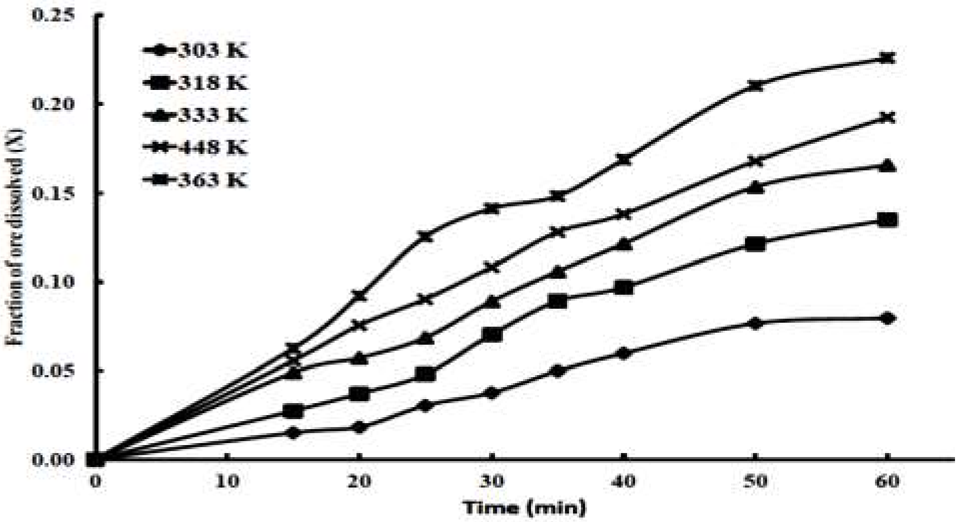

Figure 5: Extent of dissolution of the ore at various temperatures and times, with [H_2SO_4] = 4.35 M

Table 7: Comparison of the rate constants and correlation fit for both models considered

Temperature, T (K)	Apparent rate constants (k_r, min^{-1}) ×10^4		Correlation coefficients (R^2)	
	Chemical reaction controlled	Diffusion Controlled	Chemical reaction controlled	Diffusion Controlled
303	4.68	0.50	0.959	0.782
318	8.01	0.87	0.976	0.814
333	10.32	1.37	0.991	0.840
348	12.01	1.85	0.993	0.881
363	14.86	2.78	0.977	0.899

From Figure 6, it can be deduced that the dissolution of the ore in sulphuric acid is predominantly chemical reactions controlled, with the dissolution model in mathematical form written as shown below:

$$1-(1-X)^{\frac{1}{3}} = k_o \exp\left(-\frac{E_a}{RT}\right).t \quad (7)$$

Where $k_r = k_o \exp\left(-\frac{E_a}{RT}\right)$ (8)

R is the universal gas constant, E_a is the activation energy and T is the temperature in Kelvin. Equation (8) can be written in logarithmic form:

$$\ln k_r = \ln k_o - \left(\frac{E_a}{R}\right).\frac{1}{T} \quad (9)$$

From the plot of $\ln k_r$ against $\frac{1}{T}$ (Figure 7), the activation energy E_a and the Arrhenius constant were found to be 16.04 kJ.mol^{-1} and 0.316 min^{-1}, respectively so that the kinetic model for the dissolution becomes:

$$1-(1-X)^{\frac{1}{3}} = 0.316 \exp\left(-\frac{16.04}{RT}\right).t \quad (10)$$

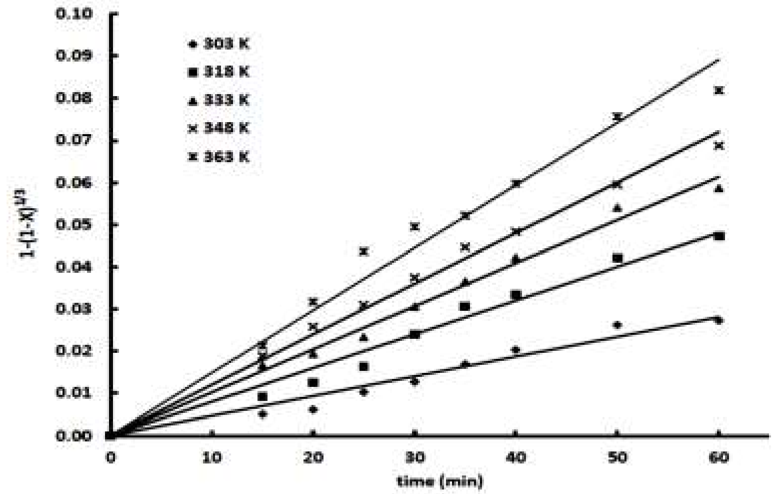

Figure 6: Plot of $1-(1-X)^{\frac{1}{3}}$ against contact time

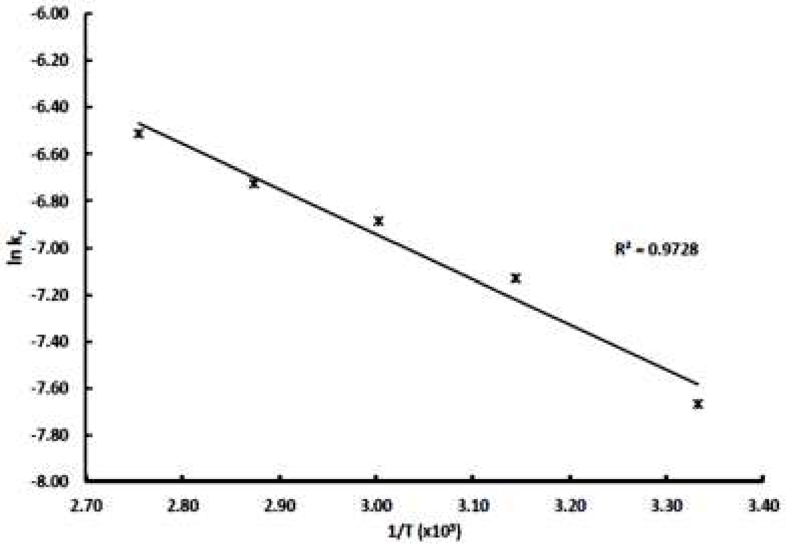

Figure 7: Arrhenius plot for the copper ore dissolution in 4.34 M H_2SO_4

4. CONCLUSIONS

In this study, the dissolution of a Nigerian sulphidic copper ore in sulphuric acid was examined. The results showed that the reaction rate increases with acid concentration and reaction temperature and that at the optimum leaching conditions, the extent of dissolution was 14.89 % . The dissolution kinetics was found to be governed by the shrinking core model with chemical reaction as the rate-controlling mechanism and a value of 16.04 kJ.mol^{-1} was obtained as activation energy (E_a), for the dissolution process.

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