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# Leaching parameters Optimization and kinetic studies for leaching of copper from Zarara Hill Sulphide ore in HCl, $H_2SO_4$ and $HNO_3$ solutions

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## *Abstract*

This study used HCl, $H_2SO_4$ and $HNO_3$to optimize and study the kinetics of copper dissolution from Zarara Hill sulphide ore. Fe, Zn, Cu, Pb, and S are the main elements found in the ore, according to the ICP-OES technique, while Co, Ni, Mo, and Cd are the minor elements. Response Surface Methodology (RSM) was used to model, optimize and evaluate the effects and interactions of the influential specifications on the recovery of copper using the acid solutions. A regression model significant test and an individual model coefficients with lack of fit test were conducted in order to fit a good model. With a 95% confidence level, the significant components were sorted using the P-value (probability value). The smaller 'P' values from the ANOVA generated for both $HNO_3$, HCl and $H_2SO_4$ show more significant of the corresponding coefficients. Dissolution kinetics, studies shows that for zinc dissolution, the order of reaction with regard to $H^+$ ion concentration using HCl, $H_2SO_4$ and $HNO_3$ were 0.67, 0.53 and 0.46 respectively.

And the activation energy was calculated from Arrhenius plot and were found to be 19.7, 22.7 and 20.6 kJ/mol for HCl, $H_2SO_4$ and $HNO_3$ dissolutions respectively.

**Key words**: Sulphide ore, acids, leaching, copper, optimization, kinetic.

## Introduction

Complex sulphide ore is a common mineral and is found in almost all sulphide deposits and is often disseminated through igneous rock (Baba *et al.,* 2012). Sulfide oxidation is one method for treating complex sulphide ores that produces water-soluble sulphates or oxides. Roasting, pressure oxidation, chemical oxidation, and bioleaching are some methods of sulfur oxidation. Conventionally employed procedures are costly and intricate. Hydrometallurgical method has remained the most prominent method in winning many metals from their ores. The process typically entails extracting metals from their ores by leaching them into an appropriate solution, from which they can be readily recovered (won back) using methods like solvent extraction, ion exchange, precipitation, and electro-winning. Various work were done on copper and lead leaching using different leaching solutions and with various leaching conditions by Ajibola and Jimoh (2014). As a result, the use of readily accessible and reasonably priced reagents such as sulfuric acid, hydrochloric acid, and nitric acid for base metal recovery and methods of improving the dissolution kinetics has gained attention. Chalcopyrite is a mineral that contains about 70% of the world's copper reserves. Nowadays, a high-temperature smelting process with unfavorable environmental side effects is used to extract copper from high-grade chalcopyrite (Thomas, 2009). The past 25 years have seen a sharp rise in both the global supply and demand for chalcopyrite, or copper. However, the demand for mineral commodities has grown since major developing nations joined the global market. The Andean region of South America has become the world's most productive copper region in the past 20 years. About 45% of the copper produced worldwide in 2007 came from the Andes Mountains in the United States. Arizona, Utah, Mexico, Nevada, or Montana provide almost all of the copper produced in the United States, which accounts for 8% of total production. Therefore this research will focus on optimization and kinetics of copper dissolution from Zarara Hill sulphide ore using $HNO_3$, HCl and $H_2SO_4$

### Materials and Methods

This study made use of a polymetallic sulphide ore that was mined in March

2019 from Zarara Hill in Kaduna State, Nigeria (Figure 1). Using a crusher, ball mill, and automatic sieve shaker, samples of the ore were crushed, ground, and sieved to a size of 0.1 mm, which is fine enough to separate the valuable minerals from one another.

Following the ore's pretreatment and beneficiation, the concentrate was roasted in a muffle furnace at 1000 degrees Celsius for two hours in a favorable atmosphere. This process turns metal sulphides into metal oxides, which are more soluble in leaching agents.

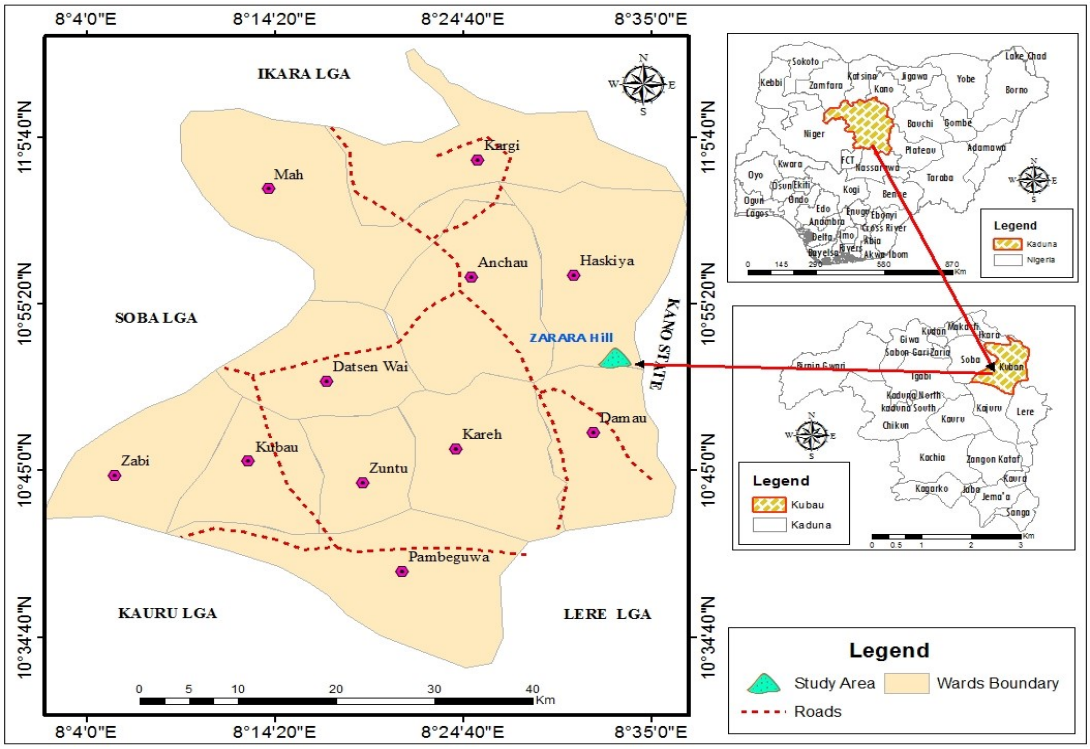



**Figure 1: Map of Kubau LGA Showing Zarara Hill.**

Source: GIS Lab Department of Geography ABU Zaria, Using Arc GIS 10.3 Software.

**Design of Experiment**

The experiments were design using Design Expert (Stat-Ease, Inc., Minneapolis, USA). Based on the literature and initial experiments, effects of four parameters including acid concentration (0.5–12M), leaching time (5–120 min), temperature (28–80°C), and strirring speed (100–720 rpm) on the leaching recovery of the metals from the ore were examined using the Response Surface Methodology of Central Composite Design (CCD) (Rasoul *et al.,* 2019). Table 1 shows the factors and their respective levels.

**Table 1: Factors and Their Respective Levels**

| Factors | Low Level | High Level |
|---|---|---|
| **Acid Concentrations (M)** | 0.5 | 9 |
| **Leaching Time (mins)** | 5 | 120 |
| **Temperature (°C)** | 38 | 80 |
| **Stirring Speed (rpm)** | 100 | 720 |

Cu fraction recovered was chosen as the response for both HCl, $HNO_3$ and $H_2SO_4$. Following each run, the mixture was diluted to 25 $cm^3$ and filtered before being subjected to an Atomic Absorption Spectrometry (AAS) analysis for Cu. Equation 1 was then used to convert the concentration from mg/L to mg/kg.

$$Recovery\ \left(\frac{mg}{kg} or\ ppm\right) = \frac{Conc.of\ metal\ \left(\frac{mg}{L}\right)\ X\ Vol.of\ sample\ (L)}{Sample\ weight\ (kg)} \quad \text{..... (1)}$$

The fraction of each metal leached, was calculated (equation 2) and used as the response variable.

$$Fraction\ of\ metal = \frac{metal\ extracted\ by\ leaching\ solution}{total\ amount\ of\ the\ metal\ in\ the\ ore} \quad \text{.....(2)}$$

The Design-Expert software's output showed that the quadratic model was not aliased. The statistical significance was assessed using analysis of variance (ANOVA). The precision of the fitted polynomial model was assessed using the coefficient of $R^2$. The significant model terms were assessed using the probability value (P-value) at the 95% confidence level ($\alpha = 0.05$).

**Leaching of ore by agitation process**

A 250 $cm^3$ beaker was used as the reactor for the leaching experiments, and it was heated on a hot plate with a thermometer and a digitally controlled magnetic stirrer.

The beaker was placed on a hot plate after a specific volume of the acid solution (leachant) was added. The ground ore sample was added to the beaker once the solution had reached the appropriate temperature, and the contents were swirled at a predetermined pace. 10 g/L of the roasted ore was dissolved in varying molar concentrations of HCl (0.5M to 9M), $HNO_3$ (0.5M to 9M) and $H_2SO_4$ (0.5M to 12M) to create a fresh solution mixture for each leaching experiment at 28°C to 80°C (Mukhtar *et al.,* 2023, Baba *et al.,* 2009, 2012; Aydogan *et al.,* 2005).

In order to determine the best leachant, the amount of Cu dissolved was determined after 5, 10, 30, 60 and 120 minutes contact time and stirring speed of 100 to 720 revolution per minute (rpm) for the different molar concentrations of HCl, $HNO_3$ and

$H_2SO_4$ acids, using Atomic Absorption Spectroscopy (AAS). Using this process, the impact of temperature, stirring speed, leaching time, and acid concentration on Cu dissolution was examined.

The determination of the concentration of leached metal was done by accurately withdrawing 5 $cm^3$ of the liquor and then filttered using a Whattman No. 42 filter paper. The filtrate was diluted to 25 $cm^3$ and then analyzed.

The percentage of zinc leached in each experimental set up were calculated from equation 3

$$R = \frac{M_1}{M_o} \times 100 \quad \text{.....(3)}$$

Where R is the percentage recovery of each of the metal $M_0$ is the mass of copper in the ore sample from ICP-OES result and $M_1$ is the mass of the copper leached (Bayati *et al.,* 2017).

Other parameters like temperature, contact time, and stirring speed were optimized using the concentration of each leachant that produced the highest copper recovery. Using the Arrhenius plot (a plot of lnk versus 1/T (K-1)), the activation energy was estimated.

## RESULTS

**Table 2: Elemental Composition of the Sulphide Ore**

| | Fe | Cu | Pb | Zn | Co | Ni | Mo | Cd | S |
|---|---|---|---|---|---|---|---|---|---|
| **Metal Conc. (mg/kg) ±0.3** | 68440 | 26387 | 25130 | 27477 | 24.54 | 13.4 | 833.7 | 21.6 | 33017 |

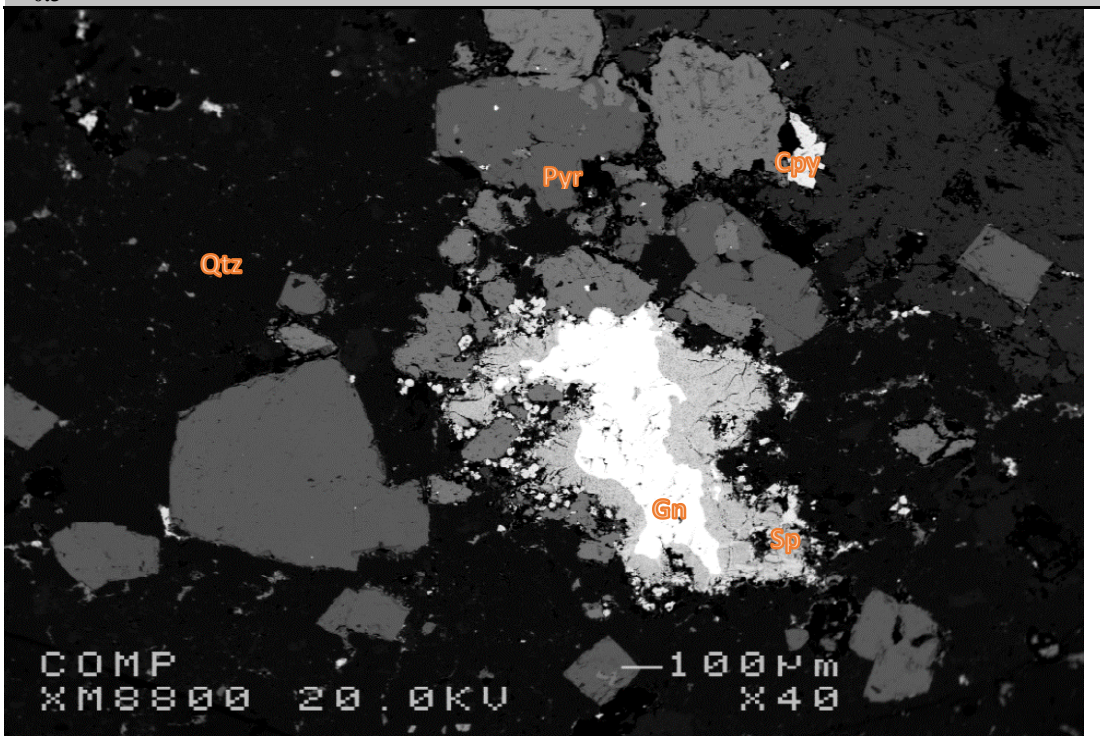



**Figure 2: Photomicrograph of the Raw Zarara Hill Sulphide Ore**

**Sp = Sphalerite, Pyr = Pyrite, Cpy = Chalcopyrite, Gn = Galena and Qtz = Quartz**

Table 1 summarizes the results of the elemental analysis of the powdered sulphide ore using the ICP-OES technique. It shows that Fe, Zn, Cu, Pb, and S were the major elements found, while Co, Ni, Mo, and Cd were the minor elements. The photomicrograph images of the ore (Figure 2) show further that the dominant minerals in the ore are quartz ($SiO_2$), Pyrite (FeS), Chalcopyrite (CuFeS), Sphalerite (ZnS), Galena (PbS) with Covellite and Iron oxides in low amount.

**Leaching of Zn from Zarara Hill Sulphide Ore Using Surface Response Method**

Surface Response Method results for leaching of copper using HCl, $H_2SO_4$ and $HNO_3$ are provided in Table 3, 4 and 5 respectively. Following each response's modeling and proposal of a fourth degree polynomial model, the models' suitability was verified using ANOVA, as shown in Table 6 for HCl, $H_2SO_4$ and $HNO_3$.

From the output proposed by the Design-Expert software for HCl, $H_2SO_4$ and $HNO_3$ the quadratic model was not aliased. The regression model and individual model coefficients were tested for significance using the lack of fit test in order to fit a good model. The P-value, or probability value, with a 95% confidence level was typically used to rank the significant factors. Table 6 shows the ANOVA (p-value) for the data generated. The smaller 'P' value for both HCl (0.0003), $H_2SO_4$ (0.0012) and $HNO_3$ (<0.0001) show more significant of the corresponding coefficients. It can also be observed that all the R-squared values are close to one and each of the adjusted R-squared values are close to its corresponding R-square value. These confirm the adequacy of the developed model. The more closely the R-squared and adjusted R-squared values resemble 1 and one another in this statistical design, the more accurate the model is (Rasoul et al., 2019).

**Table 3: Experimental Factors for HCl, Actual Units and Experimental Response**

| Name | Units | Type | Std. dev. | Low | High |
|---|---|---|---|---|---|
| **$H_2SO_4$ Conc.** | $mol/dm^3$ | Factor | 0 | 0.5 | 9 |
| **time** | mins | Factor | 0 | 5 | 120 |
| **temperature** | $^oC$ | Factor | 0 | 28 | 80 |
| **stirring rate** | rpm | Factor | 0 | 100 | 720 |
| **Copper** | Fraction | Response | 0.0365723 | 0.09 | 0.67 |

**Table 4: Experimental Factors for $H_2SO_4$, Actual Units and Experimental Response**

| Name | Units | Type | Std. dev. | Low | High |
|---|---|---|---|---|---|
| **$H_2SO_4$** | mol/dm$^3$ | Factor | 0 | 0.5 | 12 |
| **time** | mins | Factor | 0 | 5 | 120 |
| **temperature** | $^oC$ | Factor | 0 | 28 | 80 |
| **stirring rate** | rpm | Factor | 0 | 100 | 720 |
| **Copper** | Fraction | Response | 0.0260184 | 0.077 | 0.364 |

**Table 5: Experimental Factors for $HNO_3$, Actual Units and Experimental Response**

| Name | Units | Type | Std. dev. | Low | High |
|---|---|---|---|---|---|
| **$HNO_3$** | mol/dm$^3$ | Factor | 0 | 0.5 | 9 |
| **time** | mins | Factor | 0 | 5 | 120 |
| **temperature** | $^oC$ | Factor | 0 | 28 | 80 |
| **stirring rate** | rpm | Factor | 0 | 100 | 720 |
| **Copper** | Fraction | Response | 0.0236778 | 0.078 | 0.54 |

**Table 6: The Experimental Responses, R-squares and Adequate Precision Values for HCl, $H_2SO_4$ and $HNO_3$**

| Response | Std. dev. | Mean | C. V. % | R-squared | Adj. R-squared | Adeq. precision | P-value |
|---|---|---|---|---|---|---|---|
| **HCl** | 0.0366 | 0.3657 | 10.00 | 0.9841 | 0.9471 | 19.5896 | 0.0003 |
| **$H_2SO_4$** | 0.0260 | 0.2285 | 11.39 | 0.9747 | 0.9155 | 14.0638 | 0.0012 |
| **$HNO_3$** | 0.0237 | 0.3190 | 7.42 | 0.9893 | 0.9644 | 23.5316 | <0.0001 |

Std. dev. = Standard deviation, C.V = Coefficient of variance, Adj R-squared = Adjusted R-squared

"Adequate precision," which gauges the signal to noise ratio, is the next criterion. An adequate signal is indicated by values greater than 4 (Rasoul et al., 2019). Table 6, indicates that the adequate precision for HCl as leachant is 19.5896. These values are much higher than four (4), which demonstrate the model's sufficiency. Also, from Table 6, the adequate precision values when $H_2SO_4$ was used as leachant is 14.0638 which are also far higher than four, confirming the accuracy of the model. Further, the adequate precision values for the $HNO_3$ experimental responses is 23.5316.

**Response Surface Modelling Optimization**

The most crucial part of this work is estimating the ideal leaching conditions that will yield the highest zinc recovery from the sulphide ore using HCl, $H_2SO_4$, and $HNO_3$. A numerical optimization technique was used to study the optimization of the leaching parameters. Table 7 provides information on optimization conditions.

**Table 7: Model validation and ideal processing parameters for the copper fraction derived from numerical optimization**

| Acid used | Acid concentration | Time | Temperature | Stirring speed | Copper fraction | |
|---|---|---|---|---|---|---|
| | | | | | Predicted | Experimental |
| **HCl** | 8.98 | 112.4 | 79.2 | 471.25 | 0.684 | 0.670 |
| **$H_2SO_4$** | 8.00 | 111.1 | 52.9 | 386.26 | 0.366 | 0.364 |
| **$HNO_3$** | 8.99 | 108.4 | 79.9 | 100.05 | 0.549 | 0.540 |

The predicted and experimental values obtained for the fraction of copper leached from the sulphide ore using HCl were 0.684 and 0.670 respectively, 0.366 and 0.364 respectively for $H_2SO_4$ while the predicted and experimental values obtained for the fraction of copper leached from the sulphide ore using $HNO_3$ was 0.549 and 0.540 at their various optimum leaching conditions (Table 7). For HCl, $H_2SO_4$ and $HNO_3$, the difference between the experimental and predicted results is less than 1%. Consequently, the findings demonstrate that the developed model is capable of accurately forecasting the recovery of copper.

**Dissolution Kinetics of the Metals from the Ore**

Two shrinking core models (equation 4 and 5) were examined for this analysis in order to gain a better understanding of how copper dissolves in HCl, $H_2SO_4$ and $HNO_3$ media. Aydogan et al. (2007a,b), Mukhtar et al. (2023) Baba and Adekola (2010) Baba and Adekola (2012) are among the authors who have previously used the kinetic models.

$$1 - (1 - X)^{1/3} = K_2 t \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

$$\left(1 - \frac{2}{3}X\right) - (1 - X)^{2/3} = K_3 t \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

All the studied data were found to best fit equation 5 for diffusion control model with correlation coefficient ($R^2$) for both HCl, $H_2SO_4$ and $HNO_3$ dissolution being above 0.97. Therefore the relation: $1 - (2/3)X - (1 - X)^{2/3} = K_3t$, gave a correlation coefficient ranges of 0.9974 – 0.9998, 0.9982 – 0.9999 and 0.9979 – 0.9998 with straight line passing through the origin for copper dissolutions in HCl, $H_2SO_4$ and $HNO_3$ respectively. The order of reaction with respect to $H^+$ ion concentration for copper

dissolution in HCl, $H_2SO_4$ and $HNO_3$ is therefore 0.67, 0.53 and 0.46, respectively, according to the dissolution kinetics studies. Additionally, the activation energy for the dissolution of HCl, $H_2SO_4$ and $HNO_3$ was determined to be 19.7, 22.7, and 20.6 kJ/mol based on the Arrhenius plot.

The activation energy of copper leaching using HCl (19.7 kJ/mol), $H_2SO_4$ (22.7 kJ/mol) and $HNO_3$ (20.6 kJ/mol) from the polymetallic sulphide ore containing Chalcopyrite (CuFeS) are all below 40 kJ/mol. According to the literature, chemical reaction-controlled processes are highly reliant on the reaction temperature, whereas diffusion-controlled processes are only marginally reliant. Diffusion-controlled processes typically have activation energies below 40 kJ/mol, whereas chemically controlled processes typically have activation energies above 40 kJ/mol (Ekmekyapar et al., 2015).

## Conclusion

The sulphide ore's elemental composition revealed that its major elements are Fe (68440 mg/kg), Zn (27477 mg/kg), Cu (26387 mg/kg), Pb (25130 mg/kg), and S (33017 mg/kg). Low to trace amounts of Co, Ni, Mo, and Cd are also present. According to photomicrography which was used to ascertain its mineralogical composition, the polished sections' predominant minerals are quartz (SiO2), pyrite (FeS), chalcopyrite (CuFeS), sphalerite (ZnS), and galena (PbS), with trace amounts of covellite and iron oxides.

To model, optimize, and assess the impacts and interactions of the key parameters on copper recovery, Response Surface Methodology (RSM) was used. Following the creation of a fourth degree polynomial model for every response, an ANOVA was used to verify the models' suitability. From the output proposed by the Design-Expert software, the quadratic model was not aliased. The regression model and individual model coefficients were tested for significance using the lack of fit test in order to fit a good model. With a 95% confidence level, the P-value (probability value) was used to rank the significant factors. The ANOVA's smaller "P" values for HCl, $H_2SO_4$ and $HNO_3$ indicate that the corresponding coefficients are more significant. The R-square values for HCl, $H_2SO_4$ and $HNO_3$ and the adjusted R-squared values were evaluated. The model's adequacy is confirmed by the fact that all of the R-squared values are near to one and that each adjusted R-squared value is near to its corresponding R-squared value. The more closely the R-squared and adjusted R-squared values in this statistical design resemble 1 and one another, the more accurate the model is.

For copper dissolution using HCl, $H_2SO_4$ and $HNO_3$, the order of reaction with respect to $H^+$ ion concentration was 0.67, 0.53, and 0.46, respectively, according to dissolution kinetics studies. Additionally, the activation energy for HCl, $H_2SO_4$ and $HNO_3$ dissolutions was determined to be 19.7, 22.7, and 20.6 kJ/mol respectively based on the Arrhenius plot.

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## Conflict of Interest Statement

On behalf of all authors, the corresponding author states that there is no conflict of interest.

## Author Contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Mukhtar Mustapha under the supervision of Omoniyi K. I. and Faizuan Abdullah. The draft of the manuscript was written by Mukhtar Mustapha and all authors approved the final manuscript,

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