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Original Research Article

Optimization and Validation of a spectrophotometric Method for Trace Metal Quantification in Zarara Hill Ore, Kaduna State, Nigeria

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ABSTRACT

This study focused on optimizing the recovery of Fe, Cu, Pb, and Zn from polymetallic sulphide ore, collected from Zarara Hill, using hydrochloric acid leaching. The aim was to maximize metal recovery while minimizing leaching time, energy, and acid consumption. Parameters, acid concentration (0.5–9 M), leaching time (5–120 min), temperature (28–80 °C), and stirring speed (100–720 rpm), were optimized using Response Surface Methodology (RSM). The low p-values for Fe (0.0001), Cu (0.0003), Pb (0.0004), and Zn (0.0002) indicated statistically significant model terms. The R^2 values of 0.7434 (Fe), 0.9841 (Cu), 0.9945 (Pb), and 0.9858 (Zn), along with their corresponding adjusted R^2 values of 0.6792, 0.9471, 0.9817, and 0.9527, demonstrate strong model fit and reliability. Finally, a sensitive and validated analytical method based on Atomic Absorption Spectrophotometry (AAS) was established for accurate quantification of Fe, Cu, Pb, and Zn.

Keywords: Polymetallic sulphide ore, Leaching, Optimization and Response surface Methodology

INTRODUCTION

Sulphide ores are among the most complex mineral ores due to their diverse elemental composition. For instance, chalcopyrite ($CuFeS_2$) can contain various sulphide forming elements, such as Pb, Hg, As, Te, Se, Zn, Cd, Ni, and Co, in trace amounts. This compositional complexity makes their processing challenging. Even after enrichment through flotation, chalcopyrite concentrates typically contain about 30% Cu, 30% Fe, and 30% S, with additional minor elements and gangue minerals.

Hydrometallurgy has proven effective for treating such complex ores. The method involves leaching valuable metals into a suitable solution, followed by recovery through techniques such as solvent extraction, ion exchange, precipitation, or electro-winning.

In this study, the combined influence of acid concentration, leaching time, temperature, and stirring speed on the leaching process was investigated. Process optimization was carried out using Central Composite Design (CCD) coupled with Response Surface Methodology (RSM). A predictive model was developed to identify the optimal leaching conditions for maximizing the recovery of target metals from the ore.

The RSM employs quantitative experimental data to develop regression models and optimize response variables influenced by multiple independent factors (Behera et al., 2018). The goal of this experimental design is to identify the best-fit approximation for the true relationship between independent variables and the response surface. Randomizing experimental runs helps reduce error and minimize the impact of uncontrolled variables, thereby improving the model's reliability.

In a previous study, Rasoul et al. (2019) have successfully applied RSM as an effective tool to optimize the recovery of metals such as Cu, Fe, Zn, Pb, Ni, Sn, and Al from waste printed circuit boards through leaching without the use of any additives or oxidizing agents. Operational parameters, including leaching time (20–60 min), temperature (25–45 °C), solid-to-liquid ratio (1/8–1/20 g/ml), and acid molarity (1–2.7 M), were optimized. The statistical analysis provided a clear understanding of the effects of each factor, and optimal leaching conditions for nine response variables were achieved, with an overall desirability of approximately 85%.

Atomic Absorption Spectroscopy (AAS) is a sensitive analytical technique used to quantify metallic elements in a sample by measuring the amount of light absorbed by free atoms in the gaseous state. The amount of absorbed light is then correlated with the concentration of the element in the sample (Usman et al., 2017).

As part of the efforts to explore and utilize the abundant mineral resources of Nigeria, this study focused on applying Response Surface Methodology (RSM) to optimize leaching parameters for the extraction of Fe, Cu, Pb, and Zn from polymetallic sulphide ore sourced from Zarara Hill in Kaduna State, using HCl as the leaching agent. Furthermore, AAS was validated for the accurate determination of these metals in the resulting leachate.

Method validation is a critical component of quantitative analysis. In line with International Organization for Standardization (ISO)/IEC 17025 (2005) guidelines, validation ensures that the analytical method consistently meets predefined performance criteria. Therefore, this research integrates process optimization using RSM with validation of AAS to establish a reliable analytical method for the efficient recovery and quantification of Fe, Cu, Pb, and Zn from Zarara Hill sulphide ore.

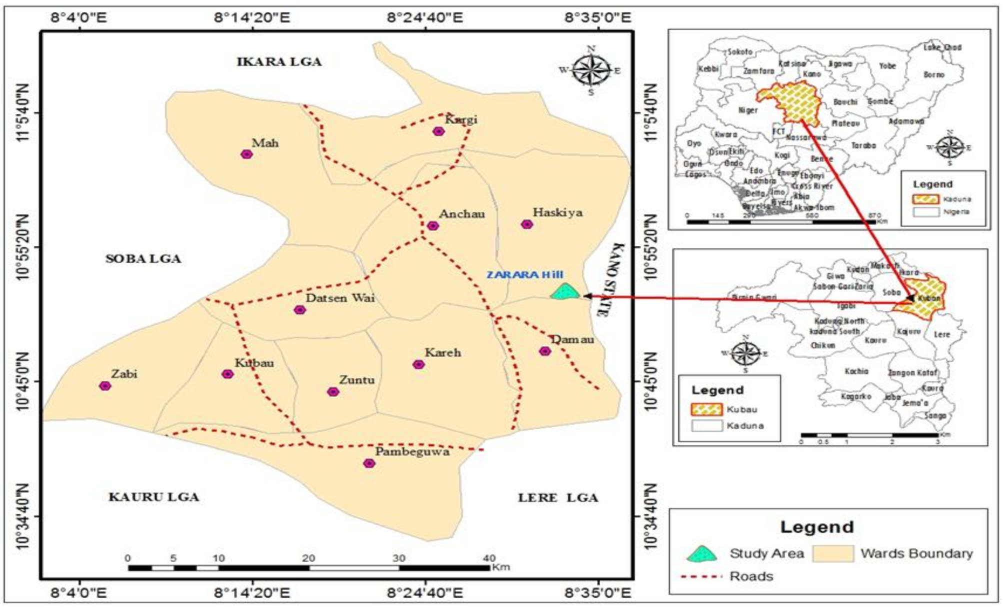
MATERIALS AND METHODS

Materials

The polymetallic sulphide ore utilized in this study was obtained from Zarara Hill, Kaduna State, Nigeria, through the support of the Geology Department of Ahmadu Bello University, Zaria (Figure 1). All reagents employed were of analytical grade. Distilled deionized water was used to prepare hydrochloric acid (HCl) solutions of varying concentrations. Prior to use, all glassware was cleaned by soaking in a detergent solution and subsequently rinsed with distilled water.

Figure 1: Map of Kubau LGA Showing Zarara Hill

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



The collected ore samples were crushed, ground, and sieved using a crusher, ball mill, and automatic sieve shaker, respectively. Subsequently, the sieved ore was subjected to roasting at 1000 °C for 2 h, to convert the metal sulphides into their corresponding metal oxides, thereby enhancing their solubility and reactivity during the subsequent leaching process. Elemental composition was determined using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (PerkinElmer Avio 200).

The leaching experiments were designed using Design Expert (Stat-Ease, Inc., Minneapolis, USA). Based on preliminary trials, four important variables were selected for investigation: acid concentration (0.5–9 M), leaching time (5–120 min), temperature (28–80 °C), and stirring speed (100–720 rpm). The design followed the Central Composite Design (CCD) under the framework of Response Surface Methodology (RSM) (Rasoul et al., 2019). The factors and their respective levels used in the experimental design are summarized in Table 1.

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)	28	80
Stirring Speed (rpm)	100	720

The leaching experiments were conducted in a 250 mL glass reactor equipped with a mechanical stirrer to ensure uniform mixing. The reactor was filled with 100 mL of hydrochloric acid (0.5–9 M) and heated to the desired temperature as described by Baba and Adekola (2010). For each experimental run, the leaching solution was freshly prepared by dissolving 10 g/L of the sulphide ore in HCl at temperatures ranging from 28 °C to 80 °C, following the procedure of Aydogan et al. (2007a). After leaching, the filtrate was analyzed using AAS for the contents of Fe, Cu, Pb, and Zn in mg/L. The concentrations were calculates in mg/kg using Equation (1):

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

The fraction of each metal leached from the ore was calculated using Equation (2) and used as the response variable for optimization. The concentration of metals dissolved in the leachate was quantified using (AAS), while the total metal content in the original ore was determined by (ICP-OES).

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

Table 2: Design of experiments and all responses for the leaching using HCl

Std	Run	Factor 1: HCl (M)	Factor 2: Time (mins)	Factor 3: Temp. (°C)	Factor 4: Stirring speed (rpm)	Response (1) Fe	Response (2) Cu	Response (3) Pb	Response (4) Zn
20	1	4.75	62.5	54	410	0.09	0.44	0.48	0.51
14	2	4.75	62.5	80	410	0.38	0.51	0.53	0.58
18	3	4.75	62.5	54	410	0.1	0.43	0.48	0.51
3	4	9	5	80	720	0.09	0.28	0.39	0.37
1	5	9	120	80	100	0.65	0.67	0.59	0.675
12	6	4.75	120	54	410	0.13	0.53	0.51	0.55
19	7	4.75	62.5	54	410	0.1	0.44	0.48	0.51
15	8	4.75	62.5	54	100	0.08	0.4	0.46	0.39
13	9	4.75	62.5	28	410	0.06	0.28	0.42	0.43
7	10	0.5	120	80	720	0.07	0.31	0.42	0.46
16	11	4.75	62.5	54	720	0.08	0.41	0.47	0.42
8	12	0.5	5	28	100	0.08	0.09	0.22	0.27
4	13	0.5	120	28	720	0.03	0.21	0.38	0.34

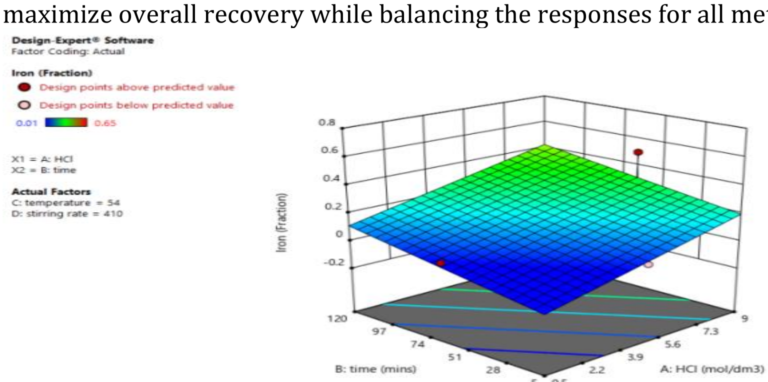
2	14	9	120	28	100	0.5	0.56	0.54	0.53
6	15	0.5	5	80	100	0.01	0.15	0.28	0.34
9	16	0.5	62.5	54	410	0.03	0.27	0.36	0.37
11	17	4.75	5	54	410	0.02	0.15	0.31	0.35
10	18	9	62.5	54	410	0.5	0.53	0.52	0.6
5	19	9	5	28	720	0.04	0.14	0.27	0.3
17	20	4.75	62.5	54	410	0.1	0.44	0.48	0.51
21	21	4.75	62.5	54	410	0.1	0.44	0.48	0.51

The design matrix, along with all response values obtained from the leaching experiments, is summarized in Table 2. The results indicated that the quadratic model was not aliased, confirming the suitability of the chosen experimental design. Analysis of variance (ANOVA) was performed to evaluate the statistical significance of the model and its terms. The coefficient of determination (R^2) was used to assess the accuracy and reliability of the fitted polynomial model. Model significance was determined based on the probability value (p value) at a 95% confidence level.

OPTIMIZATION BY RESPONSE SURFACE MODELLING

The optimal conditions predicted for metal recovery were approximately 9 M HCl, a reaction temperature of 80 °C, a leaching time of 48 minutes, and a stirring speed of 100 rpm. Under these conditions, the predicted fractions of metals leached were 0.43 for Fe, 0.446 for Cu, 0.4888 for Pb, and 0.561 for Zn.

Figure 1 presents 3D surface plots illustrating the responses (z-axis) as functions of HCl concentration (A) and leaching time (B), highlighting the most significant interactions. It is evident that the optimum conditions vary for each metal, making it challenging to achieve 100% recovery for all simultaneously. Consequently, a compromise must be made through multi-response optimization. Statistical approaches provide a rational means to determine general conditions that maximize overall recovery while balancing the responses for all metals.



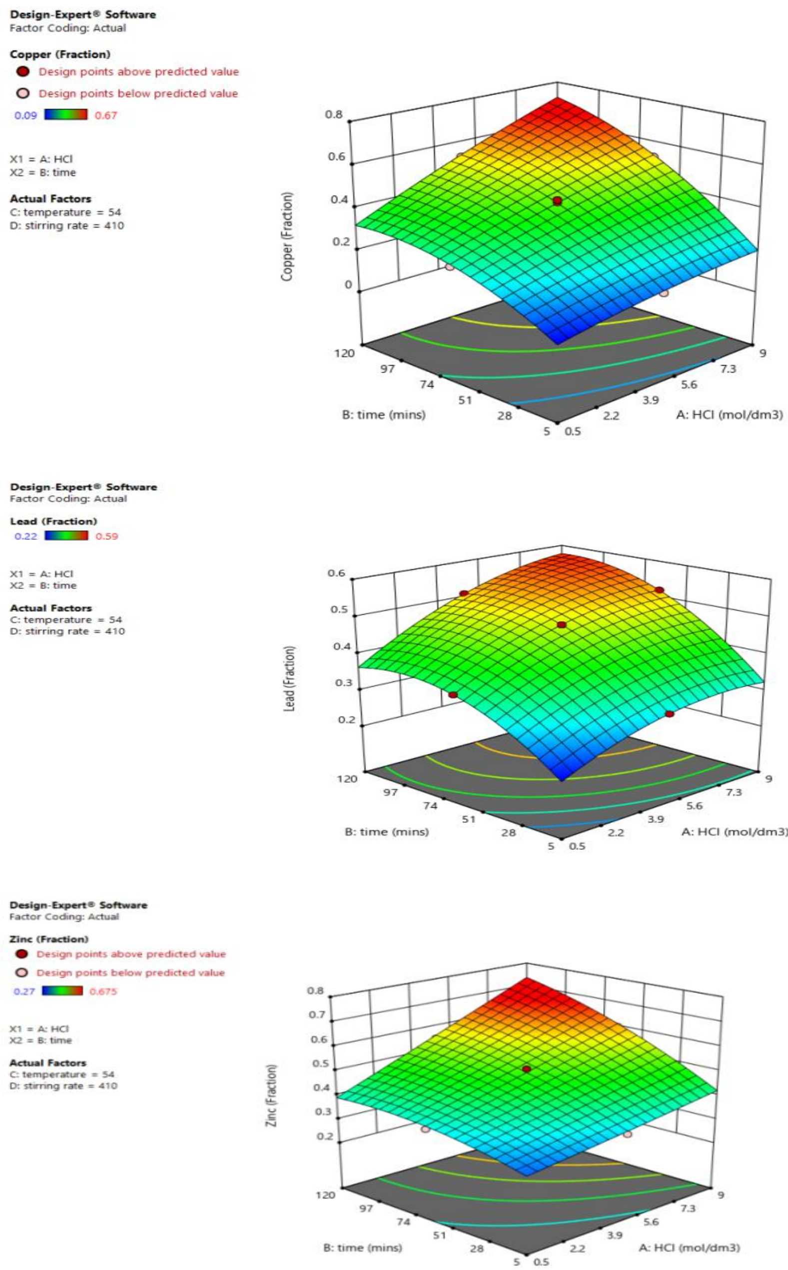


Figure 1. The 3D surface plot of responses as a function of time and HCl concentration.

Method Validation

Method validation was performed by assessing several analytical figures of merit, including linearity and range, limit of detection (LOD) and limit of quantification (LOQ). Linearity was assessed by analyzing six different concentrations of Zn, Cu and Pb and correlation coefficients were calculated by regression. In order to get LOD and LOQ values, five blank samples were measured. The values of LOD and LOQ were calculated as three and ten times the standard deviation of the blank signal divided by the slope.

RESULTS AND DISCUSSION

The results of the HCl leaching experiments are summarized in Table 3. The output confirmed that the quadratic model was not aliased, indicating the appropriateness of the selected model. To ensure a reliable fit, the significance of the regression model and individual model coefficients was evaluated using ANOVA, along with a lack-of-fit test. Significant factors were identified and ranked based on their p values at a 95% confidence level. The detailed ANOVA results for the leaching data are presented in Table 4.

Table 3: Experimental Factors for HCl, Actual Units and Experimental Responses

Name	Units	Type	Std. dev.	Low	High
HCl	mol/dm^3	Factor	0	0.5	9
time	mins	Factor	0	5	120
temperature	°C	Factor	0	28	80
stirring rate	rpm	Factor	0	100	720
Iron	Fraction	Response	0.103795	0.01	0.65
Copper	Fraction	Response	0.0365723	0.09	0.67
Lead	Fraction	Response	0.0132746	0.22	0.59
Zinc	Fraction	Response	0.0233821	0.27	0.675

Table 4: The R-squared and adequate precision values of the experimental responses.

Response	SD	Mean	CV (%)	R-squared	Adjusted R-squared	Adequate precision	p value
Iron	0.1038	0.1543	67.27	0.7434	0.6792	12.5971	0.0001
Copper	0.0366	0.3657	10.00	0.9841	0.9471	19.5896	0.0003
Lead	0.0133	0.4319	3.07	0.9945	0.9817	33.7371	0.0004
Zinc	0.0234	0.4536	5.16	0.9858	0.9527	20.9878	0.0002

*SD = Standard deviation, CV = Coefficient of variance

The small P-values obtained for Fe (0.0001), Cu (0.0003), Pb (0.0004), and Zn (0.0002) indicate that the corresponding coefficients are highly significant. The R^2 values for HCl leaching were 0.7434 (Fe), 0.9841 (Cu), 0.9945 (Pb), and 0.9858 (Zn), with adjusted R^2 values of 0.6792, 0.9471, 0.9817, and 0.9527, respectively. The proximity of all R^2 values to one, and the closeness of adjusted R^2 values to their corresponding R^2, confirms the reliability and adequacy of the developed models. In statistical modeling, higher R^2 and adjusted R^2 values that are near unity and close to each other indicate greater accuracy and predictive capability of the model (Rasoul et al., 2019).

Another important criterion in model evaluation is adequate precision, which measures the signal-to-noise ratio. Values greater than 4 are considered indicative of an adequate signal (Rasoul et al., 2019). As shown in Table 4, the adequate precision values were 12.5971 (Fe), 19.5896 (Cu), 33.7371 (Pb), and 20.9878 (Zn), all well above the threshold of 4, confirming the reliability and accuracy of the models.

Based on ANOVA results and the generated three-dimensional response surface plots, it was evident that acid concentration, temperature, leaching time, and stirring speed significantly influence metal extraction. Among these factors, acid concentration, leaching time, and temperature were identified as having the most pronounced effects on the dissolution of Fe, Cu, Pb, and Zn, whereas stirring speed exhibited a comparatively smaller impact. This analysis highlights the critical role of the parameters in controlling metal leaching efficiency.

Validation of Atomic Absorption Spectrophotometry

This study also aimed to validate the use of AAS for the determination of Fe, Cu, Pb, and Zn in roasted polymetallic sulphide ore following HCl leaching. In accordance with ICH guidelines (1994), the spiking experiment was employed for recovery assessment. Tables 5 and 6 summarize the validation parameter values for Fe, Cu, Pb, and Zn.

Table 5: Validation Measurements

Sample	Iron			Copper		
	Abs.	Entered Conc. (ppm)	Calculated Conc. (ppm)	Abs.	Entered Conc. (ppm)	Calculated Conc. (ppm)
Blank	0.0000	0	-0.060	0.0000	0	0.002
S1	0.1201	1.0	1.028	0.0380	0.4	0.398
S2	0.1770	1.5	1.544	0.0670	0.7	0.699
S3	0.2332	2.0	2.053	0.0959	1.0	1.001
S4	0.2837	2.5	2.510	0.1246	1.3	1.299
S5	0.3295	3.0	2.925	0.1535	1.6	1.601

Table 6: Validation Measurements

Sample	Lead			Zinc		
	Abs.	Entered Conc. (ppm)	Calculated Conc. (ppm)	Abs.	Entered Conc. (ppm)	Calculated Conc. (ppm)
Blank	0.0000	0	0.018	0.0000	0	-0.015
S1	0.0120	0.8	0.773	0.0794	0.15	0.154
S2	0.0251	1.6	1.598	0.1527	0.3	0.310
S3	0.0378	2.4	2.399	0.2242	0.45	0.463

S4	0.0510	3.2	3.229	0.2903	0.6	0.604
S5	0.0630	4.0	3.984	0.3512	0.75	0.734

Table 7: Linear regression data for the calibration curve of Fe, Zn, Cu and Pb

Parameters	Fe	Cu	Pb	Zn
Linearity Range	1.0 – 3.0	0.4 – 1.6 mg/L	0.8 – 4.0 mg/L	0.15 – 0.75 mg/L
R^2	0.998736	0.999996	0.999904	0.998982
Slope	0.11037	0.09602	0.01589	0.46857
Intercept	0.00661	-0.00019	-0.00028	0.00724

CONCLUSION

Fourth degree polynomial models were developed for each response, and their adequacy was confirmed using ANOVA. The Design-Expert software output indicated that the quadratic models were not aliased, confirming the suitability of the chosen model structure. Significance tests for both the overall regression models and individual model coefficients, along with lack-of-fit assessments, were performed. Significant factors were ranked based on their P-values at a 95% confidence level, with smaller p values for Fe, Cu, Pb, and Zn indicating highly significant coefficients. The R^2 and adjusted R^2 values for all models were close to one, and each adjusted R^2 was close to its corresponding R^2, confirming the reliability and accuracy of the models. The validated methods were successfully applied for the quantitative determination of Fe, Cu, Pb, and Zn in the leachates obtained from Zarara Hill sulphide ore, demonstrating their suitability for accurate and reliable metal analysis.

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Declaration

Statement of Ethical Clearance

Approval was obtained from the local ethics committee. It is also ensured that the research leads to beneficial outcomes.

Availability of Data

The authors declare that the data supporting the findings of this study are available within the paper. Should any raw data files be needed in another format they are available from the corresponding author upon reasonable request.

Conflict of Interest

The authors states that there is no conflict of interest.

Funding

The authors declare that no funds were received for this research.

Authors' 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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