Print ISSN 2710-0200 *Full text available online at* *Ethiop J Nat Comp Sci.*
Electronic ISSN 2710-0219 *http://journal.uog.edu.et/index.php/EJNCS* *Vol. 5 (1) 703-712*
***https://doi.org/**10.20372/ejncs/Ch.2025.05*

ORIGINAL RESEARCH

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

Mustapha Mukhtar[1&2*], K. I. Omoniyi[2] & Faizuan Abdullah[3]

[1]Department of Chemistry, Federal College of Education, Zaria, Nigeria.
[2]Department of Chemistry, Faculty of Physical Sciences, Ahmadu Bello University, Zaria, Nigeria.
[3]Department of Chemistry, Faculty of Sciences, University Teknologi Malaysia, Johor, Malaysia.
* Correspondence Author: almukh33@gmail.com ; ORCID ID: 0000-0001-7315 -9512

Received: 21 August 2024; Accepted: 28 December 2024; Published: 08 January 2025

Abstract

This study is mainly concerned with applying an effective statistical tool to optimize the recovery of metal namely Fe, Cu, Pb, and Zn present in polymetallic sulphide ore of Zarara Hill using different concentrations of Hydrochloric acid. Another target was to optimize a multi-response recovery process by minimizing time, energy, and acid consumption during the leaching. Effective parameters and their levels, including acid molarity (0.5 – 9M) leaching time (5 – 120 min), temperature (28 – 80°C), and stirring speed (100 - 720 rpm) were optimized. A well-established statistical approach response surface methodology (RSM)) was applied to precisely quantify and interpret the effects. The smaller 'P' value for both Fe (0.0001), Cu (0.0003) Pb (0.0004) and Zn (0.0002) shows more significant coefficients. The R-squared values are 0.7434 (Fe), 0.9841 (Cu), 0.9945 (Pb) and 0.9858 (Zn) and the adjusted R-squared values are 0.6792 (Fe), 0.9471 (Cu), 0.9817 (Pb) and 0.9527 (Zn). It can be observed that all the R-squared values are close to one and each of the adjusted R-squared values is close to its corresponding R-squared value. These confirm the adequacy of the developed model. Finally an Atomic Absorption Spectrophotometry (AAS) for the quantification of Fe, Cu, Pb and Zn was developed and validated.

Key words: Polymetallic sulphide ore, Leaching, Optimization and Response surface Methodology

Introduction

Sulphide ores, despite appearing simple with respect to chemical formulae, are the most complex of all mineral ores. This is because, for example, chalcopyrite ($CuFeS_2$), a sulphide of Cu and Fe, may contain almost all the elements in the periodic table that form sulphides (for example, Pb, Hg, As, Te, Se, Zn, Cd, Ni, Co, etc.) with many of them in trace amount. This makes the utilization of sulphide ores rather problematic, for example, the chalcopyrite, $CuFeS_2$, which can readily be enriched by floatation processes to yield a concentrate which contains 30% Cu, 30% Fe and 30% S, the balance being Ni, Co, Ag, Zn and gangue minerals. Hydrometallurgical processes have been useful in the treatment of such ores, and seem exclusive reserve of complex oxides and sulphidic ores (Gerald *et* *al*., 2012). 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. This paper investigates the combined effects of concentration, time, temperature and stirring speed on the leaching process, and the process parameters were optimized using central composite design (CCD) in conjunction with Response surface methodology (RSM) method. A model was developed by using the design of experiment to determine the optimum leaching condition where the maximum metals of interest were obtained from the ore.

RSM uses quantitative data from the related experiment to determine regression model and to optimize a response (output variable) that is influenced by several independent variables (input variables) (Behera *et al.*, 2018). The aim of the experimental design is to optimize the response variables (Y) needed to find a suitable approximation for the true correlation between the independent variables and response surfaces. The experimental run is randomized in order to diminish the error and effect of the uncontrolled factors.

Rasoul *et al.* (2019) applied an effective statistical tool to optimize the recovery of metal content (i.e., Cu, Fe, Zn, Pb, Ni, Sn, and Al) embedded in waste printed circuit boards (WPCBs) using a leaching agent without any additive or oxidative agent. Another target was to optimize a multi-response recovery process by minimizing time, energy and acid consumption during the leaching. Effective parameters and their levels, including leaching time (20–60 min), temperature (25– 45°C), solid to liquid (S/L) ratio (1/8–1/20 g/ml), and acid molarity (1–2.7 M), were optimized. A well-established statistical approach (RSM) was applied to precisely quantify and interpret the effects. General optimum conditions for nine responses were introduced with the desirability of ≈ 85%.

Atomic Absorption Spectroscopy (AAS) is an analytical technique used to determine the concentration of metallic elements in a sample by measuring the amount of light absorbed by the atoms of those elements in a gaseous state. It uses the principle that atoms and ions can absorb light at specific and unique wavelengths. When this specific wavelength of light is provided, the energy (light) is absorbed by the atom. Electrons in the atom move from the ground state to an excited state. The amount of light absorbed is measured and the concentration of the element in the sample can be calculated (Usman *et al.,* 2017).

As part of a research work necessary for developing some of the largely available mineral resources in Nigeria, study reported in this article will be carried out to establish the application of RSM for optimization of leaching parameters to be used in winning iron, copper, lead and zinc from other numerous minerals existing in sulphide ore, located in Zarara Hill of Kaduna State, Nigeria, using HCl as the leachant and to validate AAS for the determination of these metals in the leached liquor. Method validation is an important aspect in quantitative analysis. According to ISO/IEC 17025 (2005), method validation intends to guarantee that the method meets the acceptable criteria. Therefore this study deals with optimization using RSM and Validation of Atomic Absorption Spectrophotometry for Determination of Fe, Cu, Pb, and Zn in Polymetallic Sulphide Ore Obtained from Zarara Hill, Kaduna State, Nigeria.

Materials and Methods

Materials

The polymetallic sulphide ore used for this research was mined from Zarara Hill in Kaduna State, Nigeria (Fig.1) by the geology department, Ahmadu Bello University, Zaria, Nigeria. All reagents were of analytical grade. Distilled deionized water was used to prepare HCl of different concentrations. All glassware used were cleaned by soaking in detergent solution, then rinsing with distilled water.

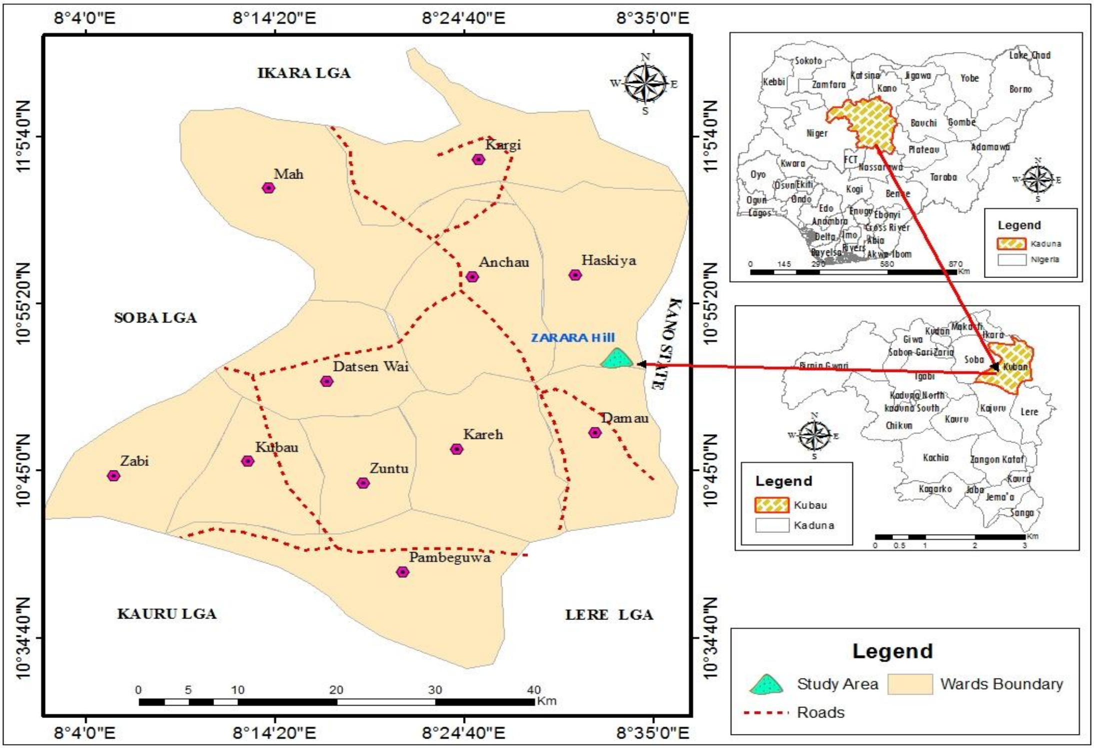


Figure 1: Map of Kubau LGA Showing Zarara Hill

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

Sample Preparation

Samples of the ore were crushed, ground and sieved to a size sufficiently fine to liberate the valuable minerals from one another using a crusher, ball mill and automatic sieve shaker respectively. The elemental analysis of the ore sample was carried out using ICP-OES (Perkin Elmer Avio 200, USA). The sieved ore was then roasted at 1000°C for 2 hours. This process turns metal sulphides into metal oxides, which are more soluble in leaching agents.

Design of Leaching Experiments

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 (0.5–9M), leaching time (5–120 min), temperature (28–80°C), and stirring speed (100–720 rpm) on the leaching recovery of the metals from the ore were investigated based on Central Composite Design (CCD) RSM (Rasoul *et al.,* 2019). Four responses, namely, for Fe, Cu, Pb and Zn recoveries were chosen. 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)	28	80
Stirring Speed (rpm)	100	720

A 250 mL glass reactor with a mechanical stirrer was used for the leaching experiment. The reactor was filled with 100 mL of HCl (0.5 M – 9M) which was heated to the desired temperature (Baba and Adekola, 2010). For every leaching experiment, the solution mixture was freshly prepared by dissolving 10 g/L of the sulphide ore in HCl at 28℃ to 80℃ by Aydogan *et al.* (2007a).

The filtered solutions after leaching were analyzed by AAS to quantitatively measure the content of Fe, Cu, Pb and Zn in mg/L which was then converted to mg/kg (ppm) (equation 1).

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

The fraction of each metal leached, was calculated (equation 2) and used as the response variable. The amount of metals leached were determined using AAS while the total amount of the metals in the ore was determined using ICP-OES.

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

The design matrix and all responses for the leaching using HCl are presented on Table 2.

From the output proposed by the Design-Expert software, the quadratic model was not aliased. Analysis of variance (ANOVA) was used to determine the statistical significance. The coefficient of R^2 was used to determine the precision of the fitted polynomial model. The probability value (P-value) at the 95% confidence level (α = 0.05) was used to evaluate the significant model terms.

Design of experiments and all responses for the leaching using HCl, are presented in Table 2.

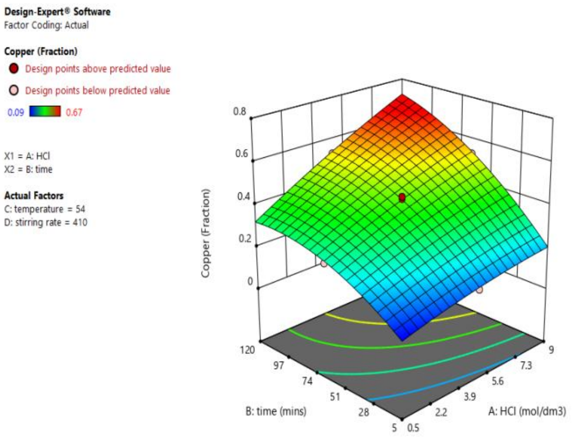
Table 2: Design of experiments and all responses for the leaching using HCl

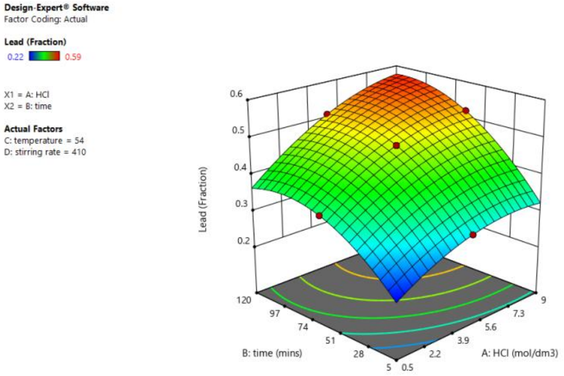
Std	Run	Factor 1: HCl (M)	Factor 2: Time (mins)	Factor 3: Temp. (°C)	Factor 4: Stirring speed (rpm)	Response (1) Fe	Response (2) Cu	Response (3) Pb	Response (4) Zn
20	1	4.75	62.5	54	410	0.09	0.44	0.48	0.51
14	2	4.75	62.5	80	410	0.38	0.51	0.53	0.58
18	3	4.75	62.5	54	410	0.1	0.43	0.48	0.51
3	4	9	5	80	720	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

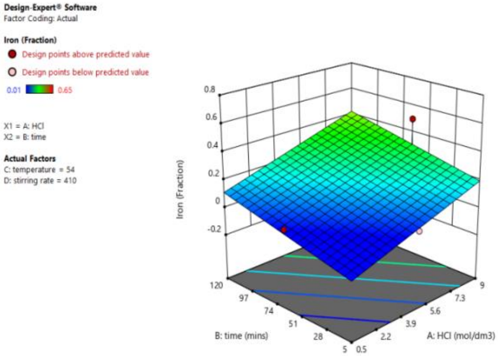
Optimization by response surface modelling

The vital part of the experimental study was to determine the optimum leaching process condition where maximum leaching of Fe, Cu, Pb and Zn can be obtained from aforesaid site. Optimization of the leaching variable parameter was carried out in a numerical optimization method. The optimum operating conditions for the Fe, Cu, Pb and Zn recovery from the sulphide ore by leaching process were 8.99 ≈ 9M HCl acid concentration by molarity, reaction temperature 79.999 ≈ 80°C, leaching time 47.7 ≈ 48 min and stirring speed of 100 rpm. The predicted responses are 0.43 fraction of iron, 0.446 fraction of copper, 0.4888 fraction of lead and 0.561 fraction of zinc.

Fig. 1 shows the 3D surface plots of responses (in z-axis) as a function of HCl concentration (A) and time (B) which are the most influential interactions. It can be seen that optimum conditions for each response are different and it needs a compromise among all responses which is solved by multi-response optimization. Accordingly, finding unique conditions that all the responses are in 100% satisfaction seems to be impossible. Thus, using statistical approaches to calculate general conditions for all the responses seemed mandatory.







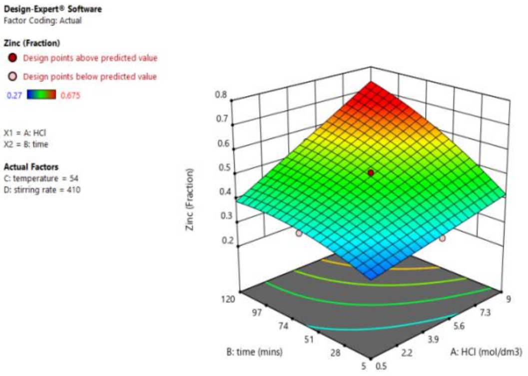


Figure 1. The 3D surface plot of responses as a function of time and HCl concentration.

Method validation

Method validation was performed by assessing several analytical figures of merit, according to International Conference on Harmonization (ICH) 1994, namely linearity and range, Limit of Detection (LoD) and Limit of Quantification (LoQ). The LOD is the lowest concentration of analyte that can be detected and reliably distinguished from zero, but not necessarily quantified (EllsyaAngeline and Abdul, 2016).

The LOQ can be defined as the lowest concentration of analyte that can be determined quantitatively with an acceptable level of precision (EllsyaAngeline and Abdul, 2016).

Linearity was demonstrated by analyzing six different concentrations of Zn, Cu and Pb. These values were used for the evaluation of linearity and range. The Coefficient Correlation, slope and intercept were calculated from their various calibration curve and regression statistics.

Sensitivity of an analytical method can be described by values of Limit of Detection (LOD) and Limit of Quantification (LOQ). In order to get LOD and LOQ values, five blank samples were measured. The values of LOD and LOQ were calculated using equations 3 and 4 respectively.

$$LOD = \frac{3.3SE}{b} \qquad \text{............(3)}$$

$$LOQ = \frac{10SE}{b} \qquad \text{...............(4)}$$

Where; SE is the Standard Error and b is the slope of the regression equation at a low concentration level (from the Calibration curve and the Regression Statistic table)

Results and Discussion

RSM results for leaching using HCl are provided in Table 3. From the output proposed by the Design-Expert software for HCl, the quadratic model was not aliased. In order to fit a good model, a test for the significance of the regression model and individual model coefficients with lack of fit test was performed. Usually, the significant factors were ranked based on P-value (probability value) with a 95% confidence level. Table 4 shows the ANOVA for the data generated.

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 Presented in Table 4.3 for HCl

Response	Std. dev.	Mean	C. V. %	R-squared	Adj. R-quared	Adeq. 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

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

After modeling and proposing a forth-degree polynomial model for each response, the adequacy of the proposed models was confirmed using ANOVA as presented in Table 4. From the output proposed by the Design-Expert software, the quadratic model was not aliased. In order to fit a good model, a test for the significance of the regression model and individual model coefficients with a lack of fit test was performed. Usually, the significant factors were ranked based on P-value with a 95% confidence level. Table 4 shows the ANOVA (p-value) for the data generated. The smaller 'P' value for both Fe (0.0001), Cu (0.0003) Pb (0.0004) and Zn (0.0002) show more significant of the corresponding coefficients The R-square values for HCl (Table 4) are 0.7434 (Fe), 0.9841 (Cu), 0.9945 (Pb) and 0.9858 (Zn) and the adjusted R-squared values are 0.6792 (Fe), 0.9471 (Cu), 0.9817 (Pb) and 0.9527 (Zn). It can be observed that all the R-squared values are close to one and each of the adjusted R-squared values is close to its corresponding R-squared value. These confirm the adequacy of the developed model. In this statistical design, the more the R-square and adjusted R-square values are close to 1 and each other, the more accurate the model is (Rasoul *et al.,* 2019).

The next criterion is "adequate precision" which measures the signal-to-noise ratio. It is found that values higher than 4 indicate an adequate signal (Rasoul *et. al.*, 2019). Table 4, indicates that the adequate precision for HCl as leachant is 12.5971 (Fe), 19.5896 (Cu), 33.7371 (Pb) and 20.9878 (Zn). These values are much higher than four (4), which proves the accuracy of the model.

RSM was used to investigate the individual and interaction effects of the four factors on Fe, Cu, Pb and Zn leaching from the roasted sulphide ore. Based on ANOVA and the effects of experimental factors on the metal leaching, the corresponding three-dimensional response surface plots, the acid concentrations, temperature, time and stirring speed have significant effects on the leaching of these metals from the roasted ore. By the use of response surface analysis method, it was observed that the leaching parameters influence dissolution. Acid concentration, time and temperature were found to have the major effect on the Fe, Cu, Pb and Zn dissolution in comparison to stirring speed.

Validation of Atomic Absorption Spectrophotometry

The purpose of this study is to validate the use of AAS for the determination of Fe, Zn, Cu and Pb in a roasted polymetallic sulphide ore after leaching using HCl solution. According to ICH (1994) for the determination of the recovery, the spiking technique was used, i.e. the known concentration of Fe, Cu, Pb and Zn solution were added to a blank solution, and the resulting spiked samples were measured, calculated, and compared to the known value of Fe, Cu, Pb and Zn solution added. Table 5 and 6 presents Validation Measurements for iron, copper, lead and zinc. These gives the concentration of the elements used in the experiment and the corresponding absorption determined from the AAS. The absorbance was plotted against the concentration of each trace elements and the R-square value for each element was determined.

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

Linearity was demonstrated by analyzing six different concentrations of Fe, Zn, Cu and Pb. The accurately measured standard working solutions of Fe are 1.0, 1.5, 2.0, 2.5 and 3.0 ppm, 0.15, 0.3, 0.45, 0.6 and 0.75 ppm (Zn); 0.4, 0.7, 1.0, 1.3, 0.8 and 1.6 ppm (Cu) and 0.8, 1.6, 2.4, 3.2 and 4.0 ppm (Pb) as presented in Table 5 and 6. These values were used for evaluation of linearity and range (Table 7). The Coefficient Correlation, slope and intercept were calculated from their various calibration curve and regression statistics. The coefficient correlation (r) values obtained corresponding to the linear regression equation were 0.998736 (Fe), 0.998982 (Zn), 0.999996 (Cu) and 0.999904 (Pb). According to EllsyaAngeline and Abdul (2016), the analytical method was linear over certain concentration ranges if the r-values obtained are higher than 0.995. Table 7 compiled the linearity and range parameters for analysis of Fe, Zn, Cu and Pb.

Sensitivity assay

Sensitivity of an analytical method can be described by values of LOD and LOQ.

The respective values of LOD and LOQ were calculated using equation 3 and 4 and were found to be 0.047 and 0.142 µg/mL (Zn), 0.005 and 0.016 µg/mL (Cu), 0.0076 and 0.023 µg/mL (Pb), as well as 1.814 and 5.498 µg/mL (Fe).

Conclusion

After modeling and proposing a forth-degree polynomial model for each response, the adequacy of the proposed models was confirmed using ANOVA. From the output proposed by the Design-Expert software, the quadratic model was not aliased. In order to fit a good model, a test for the significance of the regression model and individual model coefficients with a lack of fit test was performed. The significant factors were ranked based on P-value (probability value) with 95% confidence level. The smaller 'P' values from the ANOVA generated for both Fe, Cu, Pb and Zn show more significant coefficients. The R-squared values and the adjusted R-squared values were evaluated. It can be observed that all the R-squared values are close to one and each of the adjusted R-squared values is close to its corresponding R-Squared value, these confirm adequacy of the model. In this statistical design, the more the R-square and adjusted R-square values are close to 1 and each other, the more accurate the model is.

The validation parameters of both methods fit the criteria required by the International Conference on Harmonization (ICH). The validated methods were successfully used for quantitative analysis of Fe, Cu, Pb and Zn in Zarara Hill leached liquor.

Acknowledgement

The authors thank Dr. S. S. Magaji of the Department of Geology Ahmadu Bello University, Zaria for assisting with the ore sample. We would also like to acknowledge Dr. Faizuan Abdullah of the chemistry department, Universiti Teknologi Malaysia whose laboratory was used for the research work.

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

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

Funding

The authors declare that no funds, grants or other support were received during the preparation of this manuscript.

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.

REFERENCES

Aydogan, S., Erdemoglu, M., Ucar, G., Aras, A. (2007a). Kinetics of galena dissolution in nitric acid solutions with hydrogen peroxide. *Hydrometallurgy,* 88 (1–4), 52–57. 10.1016/j.hydromet.2007.03.005

Baba, A. A. and Adekola, F. A. (2010). Hydrometallurgical processing of a Nigerian sphalerite in hydrochloric acid: Characterization and dissolution kinetics. *Hydrometallurgy,* 101: 69–75. doi:10.1016/j.hydromet.2009.12.001

Behera, S. K., Himanshu, M., Sudipto C. and B.C. Meikap, B. C. (2018). Application of response surface methodology (RSM) for optimization of leaching parameters for ash reduction from low-grade coal. *International Journal of Mining Science and Technology*, https://doi.org/10.1016/j.ijmst.2018.04.014.

Gerald O. O., Achusim-Udenko, A. C., Nwoko, C.I.A., and Ogwuegbu M. O. C. (2012). Chemistry, Processes and Problems of Complex Ores Utilization: Hydrometallurgical Options. *International Journal of Chemical Scence, 10(1), 112-130*

International Conference on Harmonisation (ICH), (1994). Validation of Analytical Procedures: Text and Methodology, accessed from:*http://www.ich.org/fileadmin/Public_ Web_Site/ ICH_Products/Guidelines/Quality/Q2_R1/Step4/Q2_ R1_Guideline.pdf., 19/04/2011.*

ISO/IEC 17025. (2005). General requirements for the competence of testing and calibration laboratories.

Montgomery, D. C. (2014). Design and analysis of experiments. *8th ed. New York: John Wiley and Sons*.

Rasoul, K. N., Farshid P., Rabeeh G., Mohammad A., Ravindra R., Yen-Hao, C. and Veena, S. (2019). Recovery of heavy metals from waste printed circuit boards: statistical optimization of leaching and residue characterization. *Environmental Science and Pollution Research*, 26, 24417–24429. https://doi.org/10.1007/s11356-019-05596-y

Usman A. I, Seydou H, Abubakar A, Bala MS. (2017). Validation of Atomic Absorption Spectroscopy (AAS) for Trace Elements Analysis of Environmental Samples. *Research & Reviews: Journal of Physics*, 6(2), 8–13. https:doi.org/10.37591/rrjophy.v6i2.139.