Maejo Int. J. Sci. Technol. **2020**, *14*(03), 283-292

Maejo International Journal of Science and Technology

ISSN 1905-7873
Available online at www.mijst.mju.ac.th

Full Paper

Modelling and optimisation of zinc recovery from sphalerite using response surface methodology

Ikechukwu Nnanwube [1,*], Judith Udeaja [2], Okechukwu Onukwuli [2], Victor Ugonabo [2] and Chidebe Uwaleke [3]

[1] Department of Chemical Engineering, Madonna University, Akpugo, Nigeria
[2] Department of Chemical Engineering, Nnamdi Azikiwe University, Awka, Nigeria
[3] Department of Science Education, Federal University, Ndufu-Alike, Nigeria
* Corresponding author, e-mail: ik.nnanwube@gmail.com

Received: 28 December 2019 / Accepted: 21 October 2020 / Published: 23 December 2020

Abstract: The effectiveness of a binary solution of acetic acid and sodium nitrate as a lixiviant for zinc recovery from sphalerite has been investigated in this study. Response surface methodology (RSM) was used to model the leaching process. RSM optimisation was carried out using a 5-level-5-factor central composite design to achieve a maximum zinc yield of 89.61% at a leaching temperature of 90º C, acid concentration of 6 M, stirring rate of 550 rpm, leaching time of 120 min., and sodium nitrate concentration of 0.6 M. A binary solution of acetic acid and sodium nitrate thus proves to be a good lixiviant for zinc recovery.

Keywords: sphalerite, Enyigba, zinc recovery, response surface methodology

---

INTRODUCTION

Sulphide minerals are one of the most important sources of valuable metals such as gold, silver, copper and zinc. Due to the strong sulphur binding to these minerals, metals are usually extracted by pyrometallurgical route [1]. However, a variety of problems such as high energy cost, shortage of high grade ores, environmental pollution and exploitation of smaller deposits have prompted the use of low temperature hydrometallurgical processes for the exploitation of base metals from their ores and concentrates [2]. Sphalerite is a common and widely distributed sulphide mineral. Many valuable deposits of sphalerite are found where hydrothermal activity or contact metamorphism has brought hot, acidic, zinc-bearing fluids in contact with carbonate rocks. There, sphalerite can be deposited in veins, fractures and cavities, or it can form as mineralizations or replacements of its host rocks. In these deposits, sphalerite is frequently associated with galena, dolomite, calcite, chalcopyrite, pyrite, marcasite and pyrrhotite. When weathered, the zinc often

Maejo Int. J. Sci. Technol. **2020**, *14*(03), 283-292

forms nearby occurrences of smithsonite or hemimorphite [3]. Zinc compounds are used in most industrial and commercial sectors. Zinc chloride is often added to lumber as a fire retardant and can be used as a wood preservative. Dimethylzinc ($Zn(CH_3)_2$) is used in a number of organic syntheses. Zinc sulphide (ZnS) is used in luminescent pigments (such as those on the hands of clocks), X-ray and television screens, and luminous paints [4].

Zinc has been recovered from sphalerite for decades using the conventional roast-leach-electrolysis process as well as pyrometallurgical processes which involve the reduction of zinc from roasted concentrate using carbon in horizontal retorts, vertical retorts, and imperial smelting furnace [1]. However, environmental pollution caused by the generation of SO_2 from the roasting stage of both processes and consequent environmental restrictions imposed on sulphide smelters motivated the development of alternative routes [5]. Consequently, two alternative processes were proposed in the 1970's and several leaching studies have been carried out through them. The first process involved direct leaching using oxidising agents such as acids [6, 7], ferric salts [8], alkalis [9], hydrogen peroxide [10], persulphate salts [11], among others. The second process involved pressure leaching using oxygen under pressure with some oxidising agents in autoclaves [12]. The leaching of sphalerite with a binary solution of acetic acid and sodium nitrate, proposed by us [13] and illustrated in Equation (1), has proved to be a viable means of recovering zinc from its ore owing to a synergistic action of acetic acid and sodium nitrate.

$$ZnS_{(s)} + 2NO_3^-{}_{(aq)} + 4H^+{}_{(aq)} \longrightarrow Zn^{2+}{}_{(aq)} + S^o{}_{(s)} + 2NO_{2\,(g)} + 2H_2O_{(l)} \qquad (1)$$

To the best of our knowledge, there are very few studies on the application of response surface methodology (RSM) in the modelling of zinc recovery from sphalerite. Hence the modelling and optimisation of zinc recovery from sphalerite in a binary solution of acetic acid and sodium nitrate is carried out in this study. A five-level-five-factor central composite rotatable design is deployed in the design of experiment. The process variables employed are leaching temperature, acid concentration, stirring rate, leaching time and sodium nitrate concentration.

MATERIALS AND METHODS

Materials

Sphalerite sample used for this study was obtained from Enyigba mining site, Abakaliki in Ebonyi state of Nigeria. The ore sample was pulverised and sieved using a 75-µm sieve. Analytical grade reagents and deionised water were used to prepare all solutions. From the result of X-ray fluorescence analysis, the major oxides in the ore are ZnO (31.671%) and SO_3 (29.806%) while the minor oxides are Na_2O (16.318%), Fe_2O_3 (11.973%), SiO_2 (4.656%), MgO (0.613%), Al_2O_3 (1.658%), CaO (2.008%) and Mn_2O_3 (1.029%). Oxides such as Cr_2O_3 (0.010%), TiO_2 (0.045%) and P_2O_5 (0.075%) occur as traces. The result also revealed a minor amount of chlorine (0.136%) while the ore exists mainly as ZnS (61.677%) [13].

Leaching Procedure

For the leaching experiments, a 500-mL flat-bottomed flask was used. The glass was fitted with a condenser to prevent loss through evaporation. Heating was provided with the aid of a magnetically-stirred hot plate. The calculated volumes of acetic acid and sodium nitrate solutions were added to the flask, which was then heated to the desired temperature at a stirring rate

Maejo Int. J. Sci. Technol. **2020**, *14*(03), 283-292

determined from the experimental design. Subsequently, a sample of the ore with a pre-determined weight was added. At the end of each reaction time, the undissolved material in the suspension was allowed to settle and separated by filtration. The resulting solution was diluted and analysed for zinc using an atomic absorption spectrophotometer (Varian AA240 model by Varian Spectroscopy, USA) [10].

Design of Experiment

The process variables that influence the removal of zinc from sphalerite were investigated using RSM combined with five-level, five-factor factorial design as established by Design Expert software 10.0 trial version (Stat-Ease Inc., Minneapolis, USA). The process variables studied were leaching temperature, acid concentration, stirring rate, leaching time and sodium nitrate concentration. The response variable was chosen as percentage yield of zinc and the factor levels were coded as –2, -1, 0, +1 and +2. The range and levels are shown in Table 1. A total of 32 runs were carried out to optimise the process variables and experiments were performed according to the actual experimental design matrix shown in Table 2. The experiments were performed randomly to avoid systemic error and the results were analysed using the analysis of variance (ANOVA), model summary statistics and response surface plots. In RSM the most widely used second-order polynomial equation developed to fit the experimental data and identify the relevant model terms is shown in Equation 2:

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{\substack{i=1 \\ j>1}}^{n-1} \sum_{j=2}^{n} \beta_{ij} x_i x_j + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \varepsilon \qquad (2)$$

where Y is the predicted response variable which is the percentage yield of zinc in this study, β_0 is the constant coefficient, β_i is the ith linear coefficient of the input variable x_i, β_{ii} is the ith quadratic coefficient of the input variable x_i, β_{ij} is the different interaction coefficients between the input variables x_i and x_j , and ε is the error of the model.

Table 1. Experimental range of independent variables with different levels

Independent variable	Unit	Symbol	Coded variable level				
			-2	-1	0	+1	+2
Leaching temp.	°C	A	45	60	75	90	105
Acid conc.	M	B	0.75	2.5	4.25	6.0	7.75
Stirring rate	rpm	C	100	250	400	550	700
Leaching time	min.	D	30	60	90	120	150
Sodium nitrate conc.	M	E	0.15	0.3	0.45	0.6	0.75

Maejo Int. J. Sci. Technol. **2020**, *14*(03), 283-292

Table 2. Experimental design for sphalerite dissolution in acetic acid and sodium nitrate solution with experimental and predicted values

Run	Leaching temp.(^{o}C)		Acid conc. (M)		Stirring rate(rpm)		Leaching time(min.)		Sodium nitrate conc.(M)		Zinc yield (%)	
	Coded	Real	Coded	Real	Coded	Real	Coded	Real	Coded	Real	Exp.	Pred.
1	+1	90	+1	6	-1	250	-1	60	+1	0.6	80.8	81.39
2	0	75	0	4.25	0	400	-2	30	0	0.45	70.7	71.49
3	+1	90	-1	2.5	-1	250	+1	120	+1	0.6	70.8	71.72
4	-1	60	+1	6	-1	250	+1	120	+1	0.6	70.9	72.14
5	0	75	0	4.25	0	400	0	90	0	0.45	87.7	87.17
6	0	75	0	4.25	0	400	0	90	-2	0.15	70.9	71.99
7	+1	90	+1	6	-1	250	+1	120	-1	0.3	80.8	81.24
8	+1	90	+1	6	+1	550	-1	60	-1	0.3	80.3	79.87
9	-1	60	+1	6	-1	250	-1	60	-1	0.3	63.1	62.90
10	0	75	-2	0.75	0	400	0	90	0	0.45	68.5	68.62
11	+1	90	+1	6	+1	550	+1	120	+1	0.6	88.6	89.61
12	-1	60	-1	2.5	-1	250	+1	120	-1	0.3	64.2	64.34
13	0	75	0	4.25	0	400	0	90	0	0.45	87.6	87.17
14	+1	90	-1	2.5	+1	550	+1	120	-1	0.3	80.8	80.70
15	0	75	0	4.25	0	400	0	90	0	0.45	87.8	87.17
16	-2	45	0	4.25	0	400	0	90	0	0.45	70.9	70.37
17	0	75	+2	7.75	0	400	0	90	0	0.45	85.1	83.97
18	0	75	0	4.25	0	400	0	90	+2	0.75	85.2	83.11
19	0	75	0	4.25	+2	700	0	90	0	0.45	85.3	85.24
20	+1	90	-1	2.5	+1	550	-1	60	+1	0.6	78.3	78.35
21	0	75	0	4.25	0	400	0	90	0	0.45	87.7	87.17
22	0	75	0	4.25	0	400	+2	150	0	0.45	85.6	83.81
23	-1	60	-1	2.5	+1	550	+1	120	+1	0.6	80.8	81.51
24	0	75	0	4.25	-2	100	0	90	0	0.45	68.2	67.26
25	0	75	0	4.25	0	400	0	90	0	0.45	85.4	87.17
26	-1	60	-1	2.5	-1	250	-1	60	+1	0.6	63.6	63.89
27	+2	105	0	4.25	0	400	0	90	0	0.45	85.5	85.02
28	0	75	0	4.25	0	400	0	90	0	0.45	85.8	87.17
29	+1	90	-1	2.5	-1	250	-1	60	-1	0.3	63.5	62.98
30	-1	60	-1	2.5	+1	550	-1	60	-1	0.3	63.1	62.37
31	-1	60	+1	6	+1	550	+1	120	-1	0.3	79.7	79.93
32	-1	60	+1	6	+1	550	-1	60	+1	0.6	79.8	80.18

RESULTS AND DISCUSSION

Statistical Analysis

The interactive effects of five process variables on the yield of zinc were studied using central composite design. A total of 32 experimental runs were performed for the process optimisation for 5 independent variables, i.e. leaching temperature (A), acid concentration (B), stirring rate (C), leaching time (D) and sodium nitrate concentration (E), while the yield of zinc was considered as the output variable. The model summary (Table 3) provides information on the ability of the model to account for the total variation in the dependent variable with respect to the independent variables. The model summary table presents the models considered by the Design Expert in analysis of the experimental design response and their statistical parameters.

Table 3. Model summary

Source	Standard deviation	R^2	Adjusted R^2	Predicted R^2	PRESS*	Remark
Linear	5.67	0.6531	0.5864	0.5453	1095.46	
2FI	6.74	0.6983	0.4155	-3.5358	10926.62	
Quadratic	1.48	0.9900	0.9719	0.8016	477.94	Suggested
Cubic	1.27	0.9960	0.9793	-0.6631	4006.36	Aliased

* Predicted residual error sum of squares

The statistical parameters computed for the selection of the best fitted model comprise the P-value, degrees of freedom, lack of fit, coefficient of determination (R^2), coefficient of variation (C.V.), standard deviation and signal to noise ratio. By convention, the model with non-significant lack-of-fit p-value (and also not aliased) and highest R^2 values is normally selected. From the model summary table (Table 3), the quadratic model gives the best fitting with the highest adjusted and predicted R^2 values of 0.9719 and 0.8016 respectively. The high adjusted model R^2 value (0.9719) indicates that the 5 independent variables of the quadratic model define the design response better than other models. The high predicted R^2 value (0.8016) suggests that further predictions can be done using the model equation that will be generated. The difference between the predicted and adjusted R^2 values of 0.1703 shows that the model is not over fitted (the model is over fitted when the predicted R^2 is distinctly smaller than the adjusted R^2 [14]. Hence it can be inferred based on the comparison of the model parameter (R^2 value) that the combined interaction of the five independent variables with the predicted yield of zinc can be described using the quadratic model. The predicted residual error sum of squares (PRESS) shown in the table is a measure of how the model fits each point in the design. The lowest PRESS value of 477.94 for the quadratic model shows that it describes the experimental design responses better than other models and also shows its reliability for predicting responses [10].

In support of the test of fitness in Table 3, ANOVA test confirms the overall adequacy (significance) and evaluates the significance of the respective model terms. Table 4 shows the ANOVA test result with model F-value of 54.59. The significance of the model terms was evaluated based on the P-value of the model terms. A model term with P-value less than the alpha level (0.05) is significant, while if it is above the alpha level, the model variable has insignificant effect on the model. From Table 4, 12 model terms (A, B, C, D, E, AB, DE, A^2, B^2, C^2, D^2, E^2) are statistically significant while the remaining eight are insignificant. The Cor total shown in Table 4 shows the amount of variation around the mean of the observations. The model explains part of it, the residual explains the rest.

Maejo Int. J. Sci. Technol. **2020**, *14*(03), 283-292

Table 4. ANOVA for response surface quadratic model

Source	Coefficient estimate	Sum of squares	Degree of freedom	F-value	P-value (Prob > F)
Model	87.17	2384.92	20	54.59	< 0.0001
A	3.66	321.93	1	147.38	< 0.0001
B	3.84	353.43	1	161.80	< 0.0001
C	4.50	485.10	1	222.08	< 0.0001
D	3.08	227.55	1	104.17	< 0.0001
E	2.78	185.37	1	84.86	< 0.0001
AB	0.96	14.63	1	6.70	0.0252
AC	-0.59	5.64	1	2.58	0.1364
AD	-0.49	3.90	1	1.79	0.2084
AE	-0.74	8.85	1	4.05	0.0693
BC	-0.51	4.10	1	1.88	0.1980
BD	-0.76	9.15	1	4.19	0.0653
BE	-0.36	2.03	1	0.93	0.3557
CD	0.79	10.08	1	4.61	0.0548
CE	0.57	5.18	1	2.37	0.1520
DE	-1.68	45.23	1	20.70	0.0008
A^2	-2.37	164.35	1	75.24	< 0.0001
B^2	-2.72	216.55	1	99.14	< 0.0001
C^2	-2.73	218.55	1	100.05	< 0.0001
D^2	-2.38	166.09	1	76.04	< 0.0001
E^2	-2.40	169.60	1	77.64	< 0.0001
Residual		24.03	11		
Lack of fit		18.05	6	2.52	0.1652
Pure error		5.98	5		
Cor total		2408.95	31		

The model equations generated both in terms of coded factors and actual factors for the significant model terms are presented in Equations 3 and 4 respectively. The C.V. value of 1.90% and the adequate precision value of 22.753 (Table 5) indicate that the model can be considered reasonably reproducible and can be used to navigate the design space.

$$\text{Yield} = 87.17 + 3.66\,A + 3.84\,B + 4.50\,C + 3.08\,D + 2.78\,E + 0.96\,AB - 1.68\,DE - 2.37\,A^2 - 2.72\,B^2 - 2.73\,C^2 - 2.38\,D^2 - 2.40\,E^2 \quad (3)$$

$$\text{Yield} = -138.18 + 2.02 * \text{Leaching temp.} + 9.68 * \text{Acid conc.} + 0.13 * \text{Stirring rate} + 0.82 * \text{Leaching time} + 168.78 * \text{Sodium nitrate conc.} + 0.04 * \text{Leaching temp.} * \text{Acid conc.} - 0.37 * \text{Leaching time} * \text{Sodium nitrate conc.} - 0.01 * \text{Leaching temp.}^2 - 0.89 * \text{Acid conc.}^2 - 1.21\text{E-004} * \text{Stirring rate}^2 - 2.64\text{E-003} * \text{Leaching time}^2 - 106.87 * \text{Sodium nitrate conc.}^2 \quad (4)$$

Maejo Int. J. Sci. Technol. **2020**, *14*(03), 283-292

Table 5. Summary of regression values

Std. Dev.	Mean	C.V. %	PRESS	Adeq. precision
1.48	77.72	1.90	477.94	22.753

Figure 1 shows the plot of actual (experimental) versus predicted zinc yields shown in Table 2. From the plot, it can be observed that the points are evenly distributed within the line of reference. This is an indication of good correlation between the model predicted values and the experimental values.

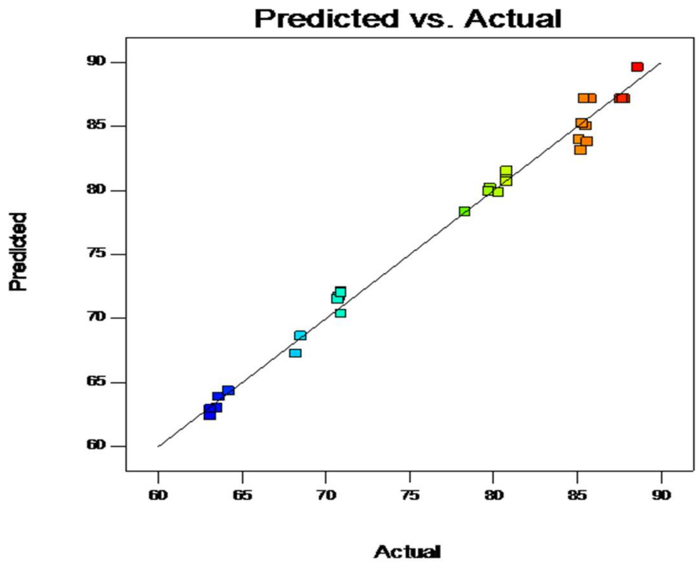

Figure 1. Plot of predicted values versus experimental values of zinc yields (Different colours represent different yield ranges of Zn.)

Response Surface Plots

The model equations were solved for the various interaction effects on zinc yield considering at any instance of the interaction between two factors only, assuming the other variables were set at their mean coded value of zero. The combined effects of adjusting the process variables within the design space were described using the 3D surface plots. The interactive effect of leaching temperature and acid concentration is shown in Figure 2a. As the leaching temperature is increased from 60° C to 84° C and the acid concentration from 2.5 M to 5.3 M, the percentage recovery of zinc increases from 80% to 90%. As the acid concentration increases beyond 5.3 M, no further increase in zinc recovery is recorded. As the acid concentration increases beyond a peak value, the number of hydrogen ions in the solution might decrease as a result of the decrease in the amount of water. In addition, as the acid concentration increases and the rate of formation of the product increases, the amount of product gets to a saturation value near the solid particle and forms a sparingly soluble product film layer around the particle, leading to a decrease in dissolution rate [15].

The interactive effect of leaching temperature and stirring rate is shown in Figure 2b. As the leaching temperature is increased from 66° C to 84° C, the recovery of zinc increases from 85% to 89.5%, while as the stirring rate is increased from 310 rpm to 490 rpm, the recovery of zinc increases from 84% to 89%. The interactive effect of leaching temperature and leaching time is shown in Figure 2c. As the leaching temperature is increased from 60° C to 84° C, Zn recovery increases from 82.5% to 88%, while as the leaching time increases from 60 min. to 110 min., zinc recovery increases from 83.5% to 88%. The interactive effect of leaching temperature and sodium nitrate concentration is shown in Figure 2d. As the nitrate concentration increases from 0.3 M to 0.54 M, zinc recovery increases from 84% to 88%, while as the leaching temperature increases from 60° C to 84° C, zinc recovery increases from 82.5% to 87.5%. Increasing the leaching temperature of a leachant increases the number of molecules whose kinetic energy is equal to or greater than the activation energy, thus increasing the rate of solute recovery. Increasing the leaching temperature also makes enough energy available for atomic and molecular collisions and the interaction between the solute particles and the lixiviant increases the dissolution rate. In addition, the reaction constant, mass transfer coefficient and diffusivity are promoted by increasing temperature [15, 16].

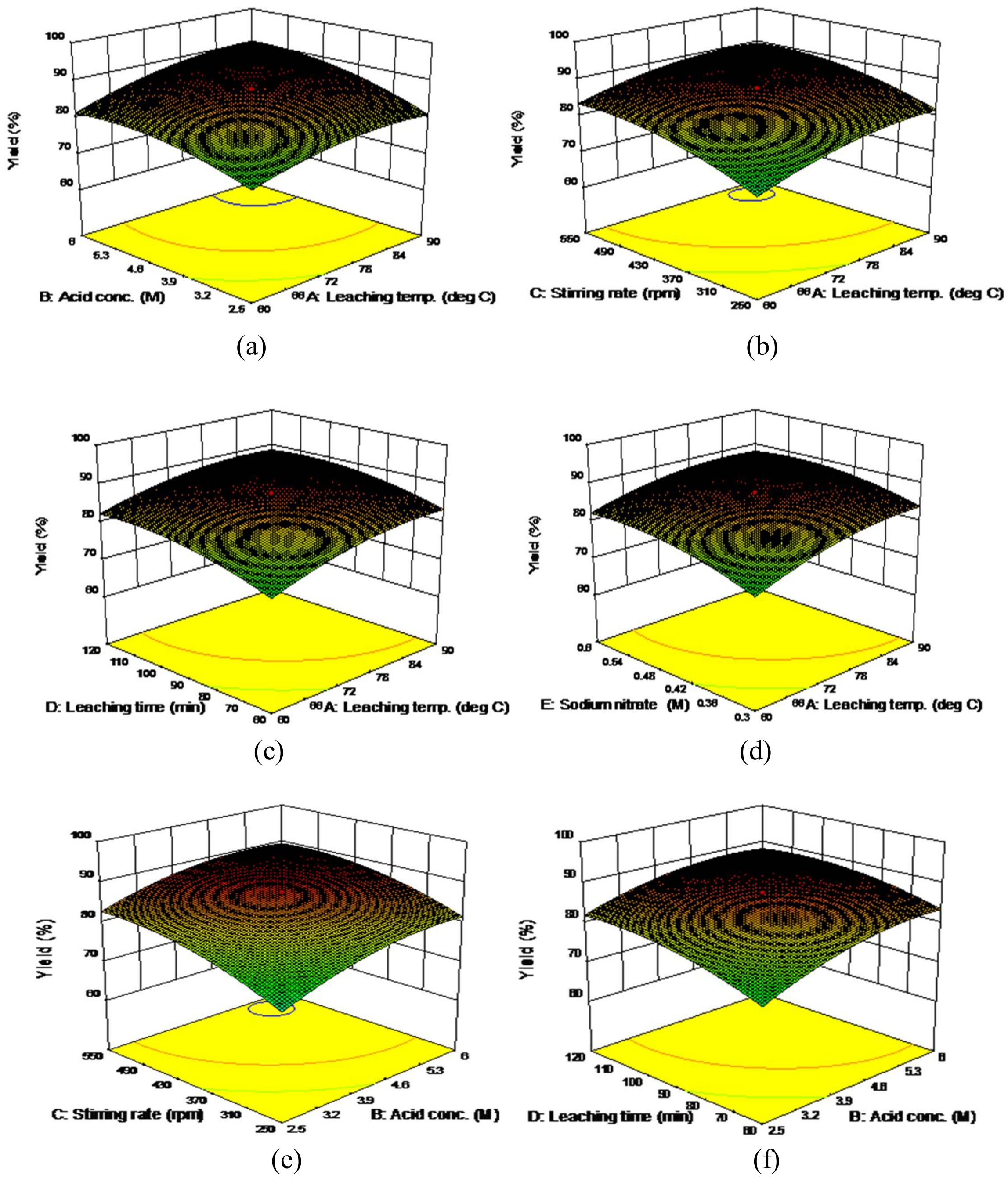

Figure 2. 3D plots of effects of process variables on zinc dissolution.

The interactive effect of acid concentration and stirring rate is presented in Figure 2e. As the stirring rate is increased from 250 to 550 rpm, zinc recovery increases from 81.8% to 89%, while as the acid concentration increases from 2.5 M to 5.3 M, zinc recovery increases from 83% to 90%. Figure 2f shows the interactive effect of acid concentration and leaching time. As the acid concentration increases from 2.5 M to 5.3 M, zinc recovery increases from 82.3% to 88%, while as the leaching time increases from 60 min. to 110 min., zinc recovery increases from 83.5% to 87.8%.

Process Optimisation Using RSM

This study was aimed at determining the optimum conditions for sphalerite dissolution in a binary solution of acetic acid and sodium nitrate. The optimisation tool of central composite design of Design Expert software was deployed for the optimisation study. A usual approach which involves choosing the best conditions based on economic considerations was adopted. In addition, the effect of each of the variables on the response was considered. On the basis of the conditions stated above, the central composite design predicted optimum conditions of 90^{o} C leaching temperature, 6 M acid concentration, 550 rpm stirring rate, 120 min. leaching time and 0.6 M sodium nitrate concentration. At these conditions, about 89.6% zinc was recovered. The result was validated by performing three independent experimental replicates, at which about 88.3% zinc recovery was recorded. The percentage of zinc recovered from this study is slightly lower than the value (92.4%) obtained from our previous study [13]. However, the result obtained from this study shows that the optimisation process used is a viable route for zinc recovery from its ore from economic considerations.

CONCLUSIONS

This study focuses on optimising zinc recovery from sphalerite using a binary solution of acetic acid and sodium nitrate as lixiviant. The central composite design of RSM was deployed for optimization study. Optimum conditions predicted include a leaching temperature of 90^{o} C, acetic acid concentration of 6 M, stirring rate of 550 rpm, leaching time of 120 min. and sodium nitrate concentration of 0.6 M, at which conditions about 89.6% recovery of zinc can be achieved.

REFERENCES

1. M. Al-Harahsheh and S. Kingman,“The influence of microwaves on the leaching of sphalerite in ferric chloride”, *Chem. Eng. Process.*, **2007**, *46*, 883-888.
2. C. I. Nwoye, J. T. Nwabanne and J. U. Odo, “ Open system leaching of sphalerite in butanoic acid solution and empirical analysis of zinc extraction based on initial solution pH, leaching time and ore mass-input”, *Res. J. Chem. Sci.*, **2013**, *3*, 25-31.
3. I. A. Nnanwube, “Kinetics and optimization studies on the hydrometallurgical recovery of zinc, lead and alumina from their parent matrices”, *PhD Thesis*, **2019**, Nnamdi Azikiwe University, Nigeria.
4. O. D. Onukwuli and I. A. Nnanwube, “Hydrometallurgical processing of a Nigerian sphalerite ore in nitric acid: Characterization and dissolution kinetics, *Int. J. Sci. Technoledge,* **2018**, *6*, 40-54.
5. A. A. Baba and F. A. Adekola, “Hydrometallurgical processing of a Nigerian sphalerite in hydrochloric acid: Characterization and dissolution kinetics”, *Hydrometall.*, **2010**, *101*, 69-75.

Maejo Int. J. Sci. Technol. **2020**, *14*(03), 283-292

6. M. Copur, "An optimisation study of dissolution of Zn and Cu in ZnS concentrate with HNO_3 solutions", *Chem. Biochem. Eng. Quart.*, **2002**, *16*, 191-197.
7. E. Guler, "Pressure acid leaching of sphalerite concentrate: Modeling and optimization by response surface methodology", *Physicochem. Probl. Miner. Process.*, **2016**, *52*, 479-496.
8. S. M. C. Santos, R. M. Machado, M. J. N. Correia, M. T. A. Reis, M. R. C. Ismael and J. M. R. Carvalho, "Ferric sulphate/chloride leaching of zinc and minor elements from a sphalerite concentrate", *Miner. Eng.* **2010**, *23*, 606-615.
9. C. Zhang, Y. Zhao, C. Guo, X. Huang and H. Li, "Leaching of zinc sulphide in alkaline solution via chemical conversion with lead carbonate", *Hydrometall.*, **2008**, *90*, 19-25.
10. I. A. Nnanwube, J. N. Udeaja and O. D. Onukwuli, "Modeling and optimization of zinc recovery from Enyigba sphalerite in a binary solution of acetic acid and hydrogen peroxide", *Sigma J. Eng. Nat. Sci.*, **2020**, *38*, 589-601.
11. M. N. Babu, K. K. Sahu and B. D. Pandey, "Zinc recovery from sphalerite concentrate by direct oxidative leaching with ammonium, sodium and potassium persulphates", *Hydrometall.*, **2002**, *64*, 119-129.
12. Y. Gu, T. Zhang, Y. Liu, W. Mu, W. Zhang, Z. Dou and X. Jiang, "Pressure acid leaching of zinc sulphide concentrate", *Trans. Nonferrous Metals Soc. China*, **2010**, *20(Suppl.)*, s136-s140.
13. I. A. Nnanwube, J. N. Udeaja and O. D. Onukwuli, "Kinetics of zinc recovery from Enyigba sphalerite in a binary solution of acetic acid and sodium nitrate", *Aust. J. Basic Appl. Sci.*, **2020**, *14*, 1-11.
14. M. C. Menkiti, G. Sekeran, V. I. Ugonabo, N. U. Menkiti and O. D. Onukwuli, "Factorial optimization and kinetic studies of coagulation–flocculation of brewery effluent by crab shell coagulant", *J. Chinese Adv. Mater. Soc.*, **2016**, *4*, 36-61.
15. A. Sobouti, B. Rezai, F. S. Hoseinian and D. Moradkhani, "Optimization and kinetics studies of lead concentrate leaching using fluoroboric acid", *Physicochem. Probl. Miner. Process.*, **2019**, *55*, 1014-1027.
16. F. Kocan and U. Hicsonmez, "Leaching of celestite in sodium hydroxide solutions and kinetic modeling", *J. Dispers. Sci. Technol.*, **2019**, *40*, 43-54.