Predictability of Lead Extraction Response to the Operational Influence of Processing pH-Time Ratio (PPTR) in Bacteria Culture

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Abstract: Lead bioextraction rate in a mixed culture of Acidithiobacillus Ferrooxidans (ATF) and Acidithiobacillus Thiooxidans (ATT) containing galena concentrate was investigated based on a range of Processing pH – Time Ratios (PPTR); 0.0166 – 0.0058 hr^{-1}. Results of the investigation amply show that lead bioextraction rate decreases with increase in the leaching time which ranged from 210 - 490 hrs. An empirical model was derived, validated and used for the predictive analysis. The validity of the derived model expressed as; $\xi = 0.0104 \ln(\gamma/\vartheta) + 0.0001\delta - 0.00002\varepsilon + 0.063$ was rooted on the core model expression $\xi - 0.063 = 0.0104 \ln(\gamma/\vartheta) + 0.0001\delta - 0.00002\varepsilon$ where both sides of the expression are correspondingly approximately equal. Lead extracted per unit pH-time ratio & standard errors incurred in predicting the lead bioextraction rate for each value of the leaching pH-Time ratio were ≈ 0.92, 0.95 and 0.98 g/ dm^3 & 0.0008, 0.0005 and 0.0009 % as obtained from experiments, derived model and regression model-predicted results respectively. Furthermore the correlation between lead bioextraction rate and pH-Time ratio as obtained from experiment, derived model and regression model were all > 0.99. The maximum deviation of the model-predicted lead bioextraction rate (from experimental results) was less than 6%. This translated into over 94% operational confidence for the derived model as well as over 0.94 response coefficients to the operational influence of the processing pH-Time ratio during the hydrometallurgical process.

Key words: Lead Bioextraction Rate · Response · Mixed culture of ATT and ATF · pH-Time Ratio

INTRODUCTION

The unavoidable need for intensive and extensive research and development aimed at enhancing methods of extracting lead from its natural ores has been significantly prompted by the wide spectrum of lead applicability. The conventional step-wise roasting or hydrometallurgical process has been the basic method of lead extraction from galena. Conventional method of lead extraction has been environmental unfriendly due to series of liberated gases in the course of the process. Air pollution resulting from the roasting of lead ore has drawn lots of severe legislation, co-opted with stiff penalties by the government. Based on the foregoing, development of viable and sustainable alternative methods including hydrometallurgical routes which does not only eliminates atmospheric pollution due to production of SO_2, but remains environment friendly has been in progress.

Acid and alkaline leaching has gained very wide recognition as a viable and sustainable metal extraction route. This route gained a significantly high level of popularity due to its environment friendliness and ease of operation.

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Bioleaching has since been used in the past in mineral pretreatment of refractory sulfides, mainly in the gold, copper and uranium benefit. This technology has been proved to be cheaper, more efficient and environmentally friendly than roasting and high pressure moisture heating processes [1]. Microorganisms considered important in commercial mineral biooxidation processes are: Acidithiobacillus Thiooxidans, Acidithiobacillus Ferrooxidans and Acidithiobacillus Caldus, Leptospirillum Ferrooxidans and Acidiphilium Acidophilum [2]. The microorganisms, acidithiobacillus Ferrooxidans are able to oxidize ferrous ions and the reduced sulphur compounds, while acidithiobacillus Thiooxidans are able to oxide only reduced sulphur compound summarized by the global reaction [2, 3]. ATT an extremely acidophidic but not ferrous iron oxidizing of the Thiobacillus, is not able to solubilise heavy metal minerals in culture. Nevertheless ATT plays a role in metal leaching. The solubilising of sulphidic minerals by ATF is increased by cooperation with ATT as compared with the effect of ATF alone. It is assumed [4] that the cause of this enhancement is the oxidation of elemental sulphur, by ATT culminating in the formation of hydrogen sulphide as a result of the oxidation by ferric ion according the equation:

ATF in co-operation with ATT, disintegrate sulphidic ferrous iron containing minerals by oxidation and bring them to solution. Also when ATT is used together with ATF, the concentration of leached metal is far greater than that obtained when only ATF is used.

Open-system predictive assessment of lead extraction rate during biooxidation of galena by *Acidithiobacillus ferrooxidans* (ATF) has been carried out [5] based on the leaching time and final pH of leaching solution using a derived model. The model;

$$\gamma = -0.0176\,(\ln t + \ln \alpha) + 0.135 \qquad (1)$$

Indicates an logarithmic relationship between lead extraction rate and combined input of time and pH. Results were predicted using regression model (standard model) and then plotted along side with results from the experiment and derived model to compare their respective spread and trend so as to establish the degree of validity of the derived model.

The standard errors incurred in predicting lead extraction rate for each value of the leaching time and final leaching solution pH considered, as obtained from derived model and experiments are 5.15×10^{-4} and 4.66×10^{-4} % as well as 1.26×10^{-3} and 1.54×10^{-3} % respectively.

The correlations between lead extraction rate and leaching time as obtained from derived model and experimental results were evaluated to be same (0.9959) and between lead extraction rate and final pH of leaching solution 0.9596 and 0.9749 respectively. The concentration of lead extracted within a leaching time interval 210-490 hrs as obtained from derived model and experiment are 3.136 and 3.108 g/dm^3 respectively.

Deviational analysis indicates that the maximum deviation of the model-predicted lead extraction rate from the corresponding experimental value is less than 10%. It was also found that the validity of the model is rooted on the core expression $7.4074\,\gamma = -0.1304\,(\ln t + \ln \alpha) + 1$ where both sides of the expression are correspondingly approximately equal.

Studies [6] were carried out to ascertain the predictability of maximum lead extraction based on optimized leaching time during biooxidation of galena by Acidithiobacillus Thiooxidans. Series of experiments were carried out and a model was derived from the results to predict lead extraction rates and optimize the leaching time. Results generated from the research indicate that the concentration of extracted lead increases with increase in the leaching time. Evaluation of the derived model:

$$\beta = -0.00002\,\alpha^2 + 0.0148\alpha + 1.641 \qquad (2)$$

To determine maximum lead extraction and the associated optimum leaching time gave 4.379 g/dm^3 at 370 hrs respectively even though the model also predicted lead extraction: 4.371 g/dm^3 at a leaching time of 350 hrs. This strongly implies that maximum lead extraction of ≈ 4.4 g/dm^3 is achievable during the biooxidation process at a leaching time range 350-370 hrs.

Extracted lead concentrations per unit leaching time as obtained from experiment and derived model are 3.85×10^{-3} and 3.6×10^{-3} g/dm^3 respectively. The validity of the model was rooted on the expression $0.6094\,\beta = -1.2188 \times 10^{-5}\,\alpha^2 + 9.0189 \times 10^{-3}\alpha + 1$ where both sides of the expression are correspondingly approximately equal.

The maximum deviation of the derived model predicted extracted lead concentration from the corresponding experimental value was less than 8%.

The present work presents a factorial analysis of lead bioextraction (from galena) using mixed cultures of Acidithiobacillus Ferrooxidans and Acidithiobacillus Thiooxidans. An empirical model is expected to be formulated for this analysis.

MATERIALS AND METHODS

Galena from Ishiagu (Ebonyi state, Nigeria) was homogenized, crushed and sieved to a grain size of 100 μm using sieve analysis technique.

100 cm³ leaching medium (2.0 g/dm³ Fe (ii) sulphate liquid medium) supplemented with 6.0 g of 100 μm grain sized galena concentrate (loose particles) was put in 7 flasks. Bacteria: ATF and ATT were obtained from red soil shown in Figure 2(b). The volume of the bacteria (ATF + ATT) culture inoculum used was 12 cm³ for all the flasks. The 7th flask was without bacteria and is identified as control.

The initial pH of each leaching medium used was 4.0. The experiments were started under exactly the same solution conditions of pH and redox potential (0.9926V) of leaching medium in bacteria and uninoculated control leaching and spanned through 210 hrs. The leaching temperature was maintained at room temperature; 28°C. The experiments were repeated for leaching times 280, 350, 380 and 420 hrs and the corresponding leached out lead chemically analyzed. Detailed experimental procedures are stated in the report [7].
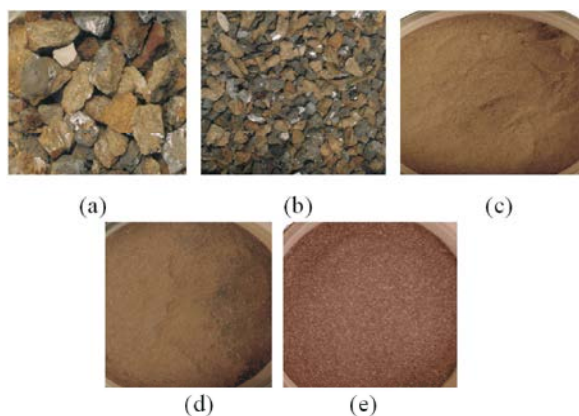

Fig. 1: (a) galena (as mined) (b) crushed and ground galena (c) galena concentrate (d) galena concentrate sieved to 100μm for the bioextraction process
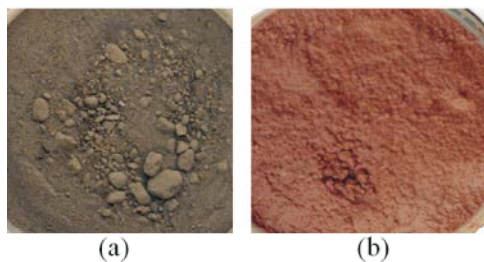

Fig. 2: (a) residue from the bioleaching process (b) source of ATF and ATT

RESULTS AND DISCUSSIONS

Variation of Extracted Lead with Leaching pH-Time Ratio: The effect of leaching pH –Time ratio at constant leaching temperature and ore mass-input indicates that the concentrations of extracted lead increases with increase in the leaching time which ranged from 210-490 hrs. Table 1 shows that for each experimental set up, the final pH-time ratio drops with decrease in concentrations of extracted lead. Also, the final solution pH drops compared to the initial solution pH. This was attributed to dissolution of hydrogen sulphide (H_2S) in the leaching solution thereby enhancing the inherent acidity level.

Formation of H_2S was due to elemental sulphur oxidation by ATT as a result of oxidation by ferric ion. The action of ATT in the mixed culture of ATF + ATT was strongly believed to have significantly enhanced solubilising of PbS as a result of elemental sulphur oxidation. This is in line with previous research [4]. Equations of these reactions are shown:

$$Pb^{2+}S^{2-} + 2Fe^{3+} \rightarrow Pb^{2+} + 2Fe^{2+}S° \qquad (3)$$
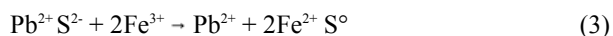
This oxidation produces hydrogen ions which in turn attack the minerals according to the following equations:

$$PbS + 2H^+ \rightarrow Pb^{2+} + H_2S \qquad (4)$$

The microstructure of the control sample (a) (leached in same solution without bacteria) is very whitish in colour. The SEM analysis of the process residues at leaching times: between 210 and 490 hrs & pH – Time ratios: 0.0166 and 0.0058 hr^{-1} shows whitish substance sparsely distributed on the lead structures (Figs. 3 (b) - (f)). This was suspected to be secretions from the microbes used in the leaching process.

The galena residue structures at 350hrs process time (Figure 3(d)) show sleek-like and jelly-like appearance. This was attributed to the wriggling movement of the microbes in the course of their activities. In contrast, the residue structures at 420 and 490 hrs process time (Figures 3(e) and (f) were larger than those at 280 and 350 hrs process time. This was perceived as lead particles clogged together by large quantity of periodic sticky-secretions by the bacteria during the leaching process.

Model Formulation: Computational analysis of experimental results in Table 1; generated during the leaching process indicates that;

Table 1: Variation of lead bioextracted rate (ξ) with final pH (γ), leaching time (ϑ) and pH-time ratio (γ/ϑ)

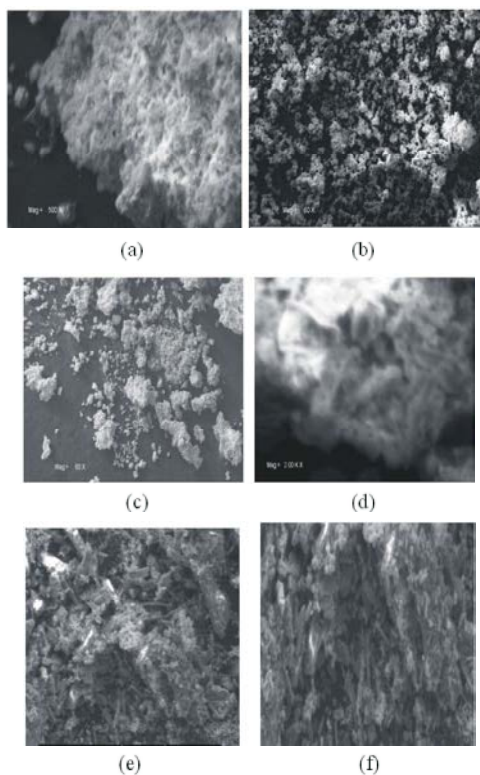| (ε)	(δ)	(γ/ϑ)	(ϑ)	(γ)	(ξ)
28	2	0.0166	210	3.48	0.0195
28	2	0.0111	280	3.12	0.0157
28	2	0.0086	350	3.02	0.0137
28	2	0.0068	420	2.87	0.0105
28	2	0.0058	490	2.83	0.0084

Fig. 3: SEM of bioleaching residues (b), (c) (d), (e) and (f) after 210, 280, 350, 420 and 490 hrs process time respectively

$$\xi - S_e \approx S \ln(\gamma / \vartheta) + N\delta - K\varepsilon \qquad (5)$$

Introducing the values of S_e, S, N and K into equation (5) reduces it to;

$$\xi - 0.063 = 0.0104 \ln(\gamma / \vartheta) + 0.0001\delta - 0.00002\varepsilon \qquad (6)$$

$$\xi = 0.0104 \ln(\gamma / \vartheta) + 0.0001\delta - 0.00002\varepsilon + 0.063 \qquad (7)$$

where,

(ξ) = Lead bioextraction rate (g/dm³ hr⁻¹)

(γ) = Final pH of leaching solution

(ϑ) = Leaching time (hr)

(ε) = Leaching temperature (°C)

δ = Mass-input of galena (g)

(γ/ϑ) = pH – Time ratio (hr⁻¹)

$S_e = 0.063$, $S = 0.0104$, $N = 0.0001$ and $K = 0.00002$ empirical constants determined using C- NIKBRAN [8]

Boundary and Initial Condition: Consider galena placed in a flask containing leaching solution (2.0 g/dm³ Fe (II) liquid medium) and supplemented with 6.0g of 100µm grain sized galena concentrate. The flask atmosphere is not contaminated i.e (free of unwanted bacteria, gases and dusts). Initially, atmospheric levels of oxygen are assumed just before the commencement of the process (due to air in the flask).

Range of leaching time and pH – Time ratio used were 210-490 hrs and 0.0166 – 0.0058 hr⁻¹ respectively. Treatment temperature: 28°C, initial pH: 4.0, redox potential: 0.9926, volume of leaching solution: 100cm³ and ore grain size: 100 µm were also used. The boundary conditions are: flask oxygen atmosphere for enhancement of Fe (II) oxidation. At the bottom of the particles, a zero gradient for the gas scalar are assumed and also for the gas phase at the top of the particles. The sides of the particles are taken to be symmetries.

Model Validation: The validity of the model was strongly rooted in the core model equation (equation (6)) where both sides of the equation are correspondingly approximately equal.

Table 2 also agrees with equation (6) following the values of ξ - 0.063 and 0.0104 ln (γ / ϑ) + 0.00001δ - 0.00002ε evaluated from the experimental results in Table1.

The derived model was also validated by comparing the extracted lead concentrations as predicted by the model and obtained directly from the experiment. This was done using various evaluative techniques such as statistical, graphical, computational and deviational analysis.

Table 2: Variation of ξ - 0.063 with 0.0104 ln(γ/ϑ) + 0.0001δ - 0.00002ε

ξ - 0.063	0.0104 ln(γ/ϑ) + 0.0001 δ - 0.00002ε
-0.0435	-0.0430
-0.0473	-0.0472
-0.0493	-0.0498
-0.0507	-0.0523
-0.0525	-0.0539

Statistical Analysis: The standard errors in predicting the lead bioextraction rate for each value of the leaching pH-time ratio as obtained from experiments, derived model and regression model-predicted results were 0.0008, 0.0005 and 0.0009% respectively.
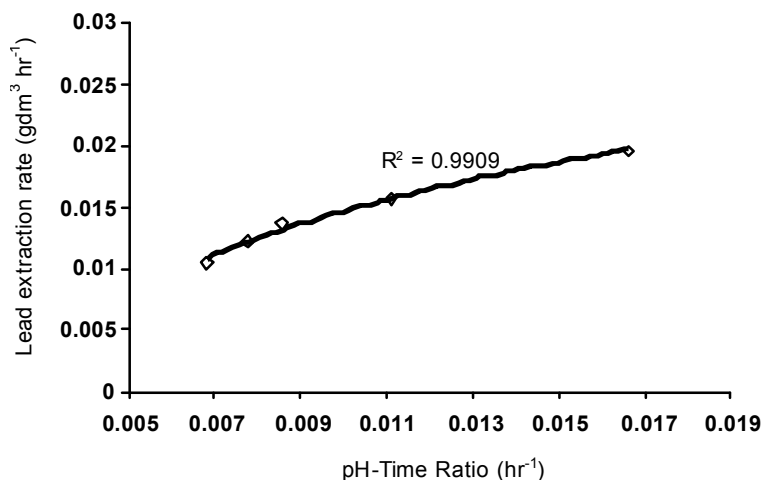
Fig. 4: Coefficient of determination between the lead extraction rate and leaching pH -Time ratio as obtained from experiment
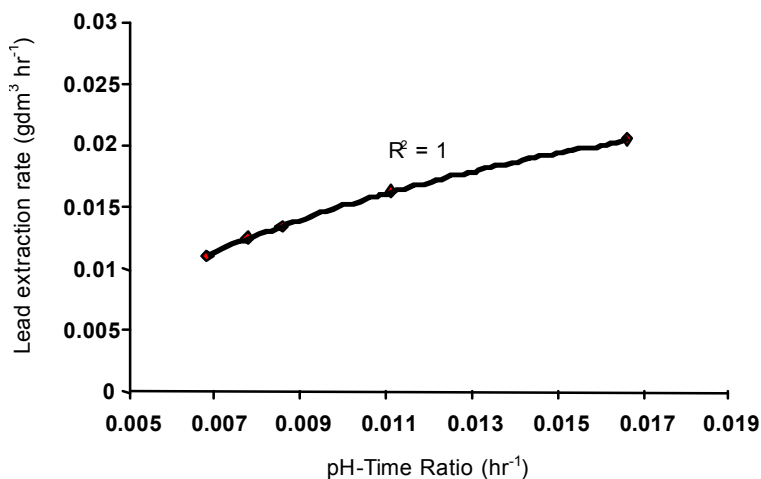

Fig. 5: Coefficient of determination between the lead extraction rate and leaching pH -Time ratio as predicted by model

The correlation coefficients between extracted lead concentration and pH-time ratio were calculated from the results of derived model and experiment. This was done by considering the coefficients of determination R^2 from Figures (4) and (5) after which they are evaluated using the expression:

$$R = \sqrt{R^2} \tag{8}$$

The evaluated correlations (using Microsoft Excel version 2003) are shown in Table 3. These evaluated results indicate that the derived model predictions are significantly reliable, considering the proximate agreement between actual experimental and model-predicted results.

Table 3: Comparison of the correlations evaluated from derived model predicted and ExD results based on pH- time ratio

Analysis	Based on pH –Time Ratio	
	ExD	D-Model
CORREL	0.9954	1.0000

Graphical Analysis: Comparative graphical analysis of Figure 6 shows extremely close alignment of the curves from the experimental (ExD) and model-predicted (MoD) extracted lead concentration relative to the leaching pH-time ratio. Furthermore, the degree of alignment of these curves is indicative of the proximate agreement between both experimental and model-predicted extracted lead concentration.
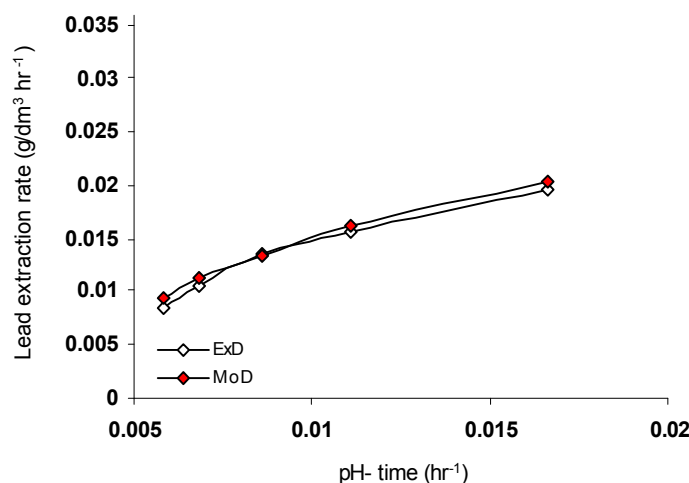
Fig. 6: Comparison of lead extraction rates (relative to pH -time ratio) as obtained from experiment, and derived model
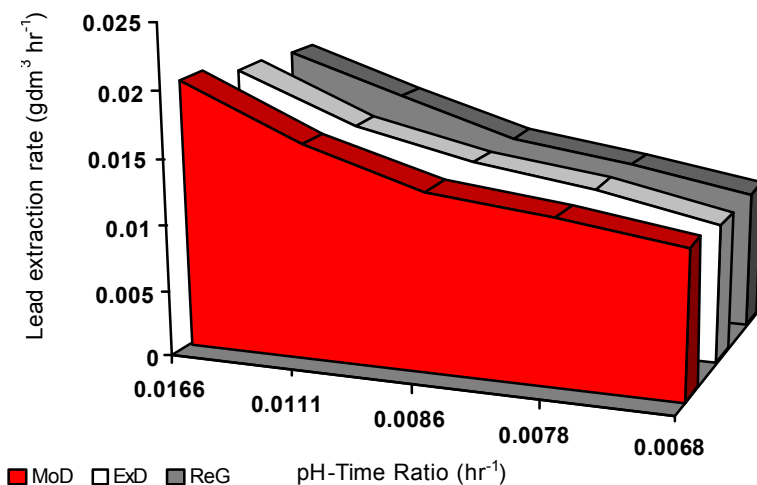

Fig. 7: Comparison of lead extraction rates (relative to pH-Time ratio) as obtained from experiment, derived model and regression model

Comparison of Derived Model with Standard Model: The validity of the derived model was further verified through application of the regression model (Reg) (Least Square Method using Excel version 2003) in predicting the trend of the experimental results. Analysis of Figure 7 shows very close alignment of curves which depicted significantly similar trend of data point's distribution for experimental (ExD), derived model (MoD) and regression model-predicted (ReG) results of extracted lead concentration.

Computational Analysis: Comparative analyses of the extracted lead concentrations evaluated from experimental, derived model-predicted and regression model predicted results were carried out to ascertain the degree of validity of the derived model. This was done by comparing evaluated results of extracted lead concentrations per unit pH-Time ratio Ꮂ during the leaching process.

Extracted lead concentration per unit pH-Time ratio Pb / Ꮂ (g/dm³) was calculated from the equation;

$$Pb_Ꮂ = Pb/Ꮂ \qquad (9)$$

Re-written as

$$Pb_Ꮂ = \Delta Pb /\Delta Ꮂ \qquad (10)$$

Equation (10) is detailed as;

6

$$Pb_b = Pb_2 - Pb_1/\text{Ђ}_2 - \text{Ђ}_1 \qquad (11)$$

where,

ΔPb = Change in the extracted lead concentration Pb_2, Pb_1 at leaching times Ђ_2, Ђ_1.

Considering the points (0.0166, 0.0195) & (0.0068, 0.0105), (0.0166, 0.0204) & (0.0068, 0.0111) and (0.0166, 0.0202) & (0.0068, 0.0106) as shown in Figure 7 and designating them as $(Pb_1, \text{Ђ}_1)$ & $(Pb_2, \text{Ђ}_2)$ for experimental, derived model and regression model predicted results respectively and then substituting them into equation (11), gives the slopes: ≈ 0.92, 0.95 and 0.97 g/dm³ respectively as their corresponding extracted lead rate per unit pH-Time ratio. The proximity between these values indicates significantly high validity level for the derived model.

Deviational Analysis: Critical Comparative analysis of extracted lead concentrations obtained from experiment and derived model show insignificant deviation on the part of the model-predicted values relative to values obtained from the experiment. This is attributed to the fact that the surface properties of the ore and the physiochemical interactions between the ore and bioleaching solution, which played vital roles during the extraction process, were not considered during the model formulation.

This invariably necessitated the introduction of correction factor, to bring the model-predicted extracted lead concentration to those of the corresponding experimental values.

The deviation Dv, of model-predicted extracted lead concentration from the corresponding experimental result was given by;

$$Dv = \left(\frac{P_{MoD} - P_{ExD}}{P_{ExD}} \right) \times 100 \qquad (12)$$

Figure 8 shows that the maximum deviation of the model-predicted concentrations of lead extraction rate from the corresponding experimental values was less than 6% and quite within the acceptable deviation limit of experimental results.

This invariably translated into over 94% operational confidence for the derived model as well as over 0.94 response coefficients to the operational influence of the processing pH-Time ratio during the hydrometallurgical process.
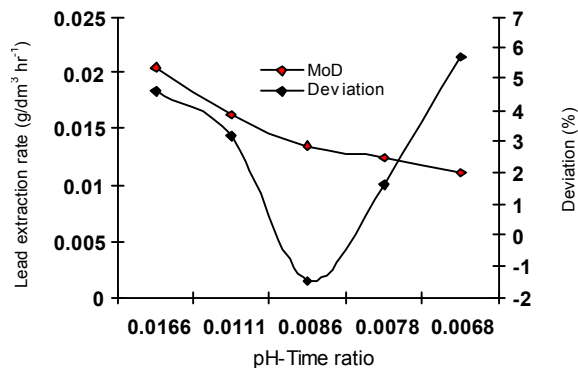

Fig. 8: Variation of deviation of model-predicted lead extraction rate (from experimental values) with the pH - Time ratio

Table 4: Variation of correction factor (to model-predicted extracted lead extraction rate) with pH -Time ratio

pH/Time (hr^{-1})	Cf (%)
0.0166	- 4.62
0.0111	- 3.18
0.0086	+1.46
0.0068	- 1.63
0.0058	- 5.71

Correction factor, Cf to the model-predicted results is given by;

$$Cf = -\left(\frac{P_{MoD} - P_{ExD}}{P_{ExD}} \right) \times 100 \qquad (13)$$

Comparative analysis of Figure 8 and Table 4 indicates that the evaluated correction factors are negative of the deviation as shown in equations (12) and (13).

Table 4 shows that the maximum correction factor to the model-predicted lead extracted rate in order to obtain the experimental results is less than 6%.

The correction factor took care of the negligence of operational contributions of surface properties of the ore and the physiochemical interactions between the ore and bioleaching solution, which played vital roles during the extraction process.

It is very pertinent to state that the deviation of model predicted results from that of the experiment is just the magnitude of the value. The associated sign preceding the value signifies that the deviation is a deficit (negative sign) or surplus (positive sign).

CONCLUSIONS

Lead bioextraction rate in a mixed culture of Acidithiobacillus Ferrooxidans (ATF) and

Acidithiobacillus Thiooxidans (ATT) containing galena concentrate was investigated based on the operational influence of the processing pH-Time ratio (PPTR). Lead bioextraction rate decreases with increase in the leaching time which ranged from 210 - 490 hrs. An empirical model derived and validated for the predictive analysis of lead extraction rate indicated that the pH-Time ratio played vital role in determining the extent of lead extraction. The validity of the derived model was rooted on the core model expression $\xi - 0.063 = 0.0104 \ln(\gamma/\vartheta) + 0.0001 - 0.00002\varepsilon$ where both sides of the expression are correspondingly approximately equal. Lead extraction rate per unit pH-time ratio & standard errors incurred in predicting the lead bioextraction rate for each value of the leaching pH-Time ratio were ≈ 0.92, 0.95 and 0.98 g/ dm^3 & 0.0008, 0.0005 and 0.0009 % as obtained from experiments, derived model and regression model-predicted results respectively. Furthermore the correlation between lead bioextraction rate and pH-Time ratio as obtained from experiment, derived model and regression model were all > 0.99. The maximum deviation of the model-predicted lead bioextraction rate (from experimental results) was less than 6%. This translated into over 94% operational confidence for the derived model as well as over 0.94 response coefficients to the operational influence of the processing pH-Time ratio during the hydrometallurgical process.

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