

Model for evaluation of Phosphorus Removal Based on Its As-Beneficiated Content and Input Concentration of H₂O₂

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ABSTRACT

Predictive analysis of phosphorus removal was carried out based on its as-beneficiated content and input concentration of hydrogen peroxide. A two factorial model was derived, validated and then used as a tool for the analysis. The model is expressed as;

$$P_R = 0.00002\beta^2 + 0.0001\beta + 2\theta^2 + 0.1\theta - 0.161$$

The validity of the model was found to be rooted on the expression $P_R - 2\theta^2 - 0.1\theta = 0.00002\beta^2 + 0.0001\beta - 0.161$ where both sides of the expression are correspondingly approximately equal. Statistical analysis of the model-predicted and experimentally removed phosphorus concentrations for each value of the input concentration of hydrogen peroxide considered shows standard errors of 1.86×10^{-4} and 3.16×10^{-4} % respectively. Furthermore, removed phosphorus concentration per unit input concentration of hydrogen peroxide as obtained from model-predicted and experimental results were 3.38×10^{-4} and 3.75×10^{-4} %/M respectively. Deviation analysis indicates that the maximum deviation of the model-predicted removed phosphorus concentration (from experimental results) is less than 2%. This implies that the derived model operates with a confidence level of above 98%.

Keywords: *Analysis, Phosphorus Removal, Initial Phosphorus content, Hydrogen Peroxide Solution, Agbaja Iron Ore.*

I. INTRODUCTION

Series of steel structures failure in service due to embrittlement caused by presence of phosphorus above the admissible quantity. There is therefore unavoidable need for a full scale research and development targeting the reduction of the phosphorus content of produced molten pig iron to or below the admissible level.

It has been reported [1] that iron ore can possibly be dephosphorized by breaking the phosphor-containing iron ore into granules of less than 0.074mm and then mixing it with iron pyrite pre-broken to the granules of less than 0.074mm based on mass percent of 5%-20%. In this process, the mass concentration of ore slurry was adjusted to 10%-20% by the aphosphorosis 9K culture and pH of original ore slurry kept at a range of 1.5 to 3.5. The research was found very viable for direct-extracting and dephosphorizing phosphorus-containing iron ore using bacteria, giving a yield of above 80% within 30-45 days. In countries having high phosphorus-iron ore, the highlighted dephosphorization process is capable of providing a reliable technical support; giving good dephosphorization at low cost.

Some biological processes have been evaluated for phosphorus removal using several types of fungi and bacteria, some being acid producing [2]. *Aspergillus niger* and their cultural filtrates were used for removing phosphorus from Agbaja (Nigeria) iron oxide ore, recording efficiencies of 81, 63 and 68% for 5, 100 and 250 mesh grain sizes respectively at the end of the 49 days of the leaching process.

Studies [3-5] on iron ore dephosphorization using hydrometallurgy has shown that phosphorus removal during leaching using oxalic acid solution, is highly dependent on the final pH of the leaching solution (which varies with time), and other factor such as initial solution pH, initial leaching temperature, mass-input of the iron oxide ore and ore mineralogy etc.

A predictive model has been derived for empirical analysis of the concentration of phosphorus removed during leaching of iron oxide ore in sulphuric acid solution [6]. The work indicated that phosphorus removal from the iron oxide ore as obtained from experiment and derived model is dependent on the initial and final pH of the leaching solution. This is because the final pH of the leaching solution is greatly determined by the initial pH which is function of hydrogen ion concentration.

Research [7] has shown that phosphorus removal also depends on leaching temperature. The model derived using experimental results generated previously [7] indicated that at a leaching temperature range 45-70°C, the maximum deviation of the model-predicted removed phosphorus concentration (from the corresponding experimental values) was less than 29%.

The recent work [8] has shown that phosphorus removal depends on the rate of iron extracted and input concentration of hydrogen peroxide. The model derived using experimental result from this work [8] showed that the maximum deviation of the model-predicted for removal of phosphorus from experimental result

was less than 6%. The aim of this work is to carry out a model evaluation of removed phosphorus concentration based on its as-beneficiated content and input concentration of H₂O₂.

II. MATERIALS AND METHODS

Agbaja (Nigeria) iron ore was mined and collected from the deposit, beneficiated and the resultant concentrate used for this research work. The iron ore was crushed for the purpose of liberation size. Tyler standard was employed to produce particle size of 250µm. The raw Agbaja iron ore was then sent for chemical analysis using X-ray fluorescence diffraction spectrometer and atomic absorption spectrophotometer

Scrubbing process

Scrubbing was carried out to remove argillaceous materials from the raw iron ore. The iron ore was poured into a head pan and water was poured to a reasonable level. The ore was washed and the water decanted. This was repeated for five times until clear water was observed. At this point 5g of sodium silicate and 25drops of oleic acid were sprinkled and distributed uniformly throughout the ore. 20liters of distilled water was also introduced into the pan and the content mixed thoroughly. After mixing, the argillaceous materials were removed leaving behind the iron ore. The residue was washed thoroughly and was sun dried for 24 hours. Some quantities were sent for chemical analysis.

Chemical leaching process

The dried scrubbed iron was further pulverized and sieved to obtain particle sizes of 63, 90, 150, 180 and 250µm. Analar grade of hydrogen peroxide solutions of different moles of 2, 4, 6, 8 and 10 were prepared. 50g of particle size of 63µm of scrubbed iron ore was poured into a beaker(reactor). 10ml of 2M of hydrogen peroxide was poured into the beaker containing the iron ore. The mixture was thoroughly mixed to ensure homogeneity. The content was allowed to leach for 20, 40, 60, 80, and 100 minutes at 70°C. At the end of each period, the solution was cooled and filtered. The residue was collected, washed to neutrality with distilled water, air dried and sun dried at 150°C for 24 hours. The experiment was repeated for different concentrations and particle sizes. The samples were analyzed using atomic absorption spectrophotometer and X- ray fluorescence diffraction spectrometer.

Model Formulation

Experimental data obtained from the highlighted research work were used for the model derivation. Computational analysis of these data shown in Table 1, gave rise to Table 3 which indicate that;

$$P_R - K\theta^2 - S\theta = S_e\beta^2 + N_e\beta - N \tag{1}$$

$$\text{Introducing the values of } K, S, S_e, N_e \text{ and } N \text{ into equation (1)} \tag{2}$$

$$P_R - 2\theta^2 - 0.1\theta = 0.00002\beta^2 + 0.0001\beta - 0.161 \tag{2}$$

$$P_R = 0.00002\beta^2 + 0.0001\beta + 2\theta^2 + 0.1\theta - 0.161 \tag{3}$$

Where

(P_R) = Conc. of removed phosphorus (%)

(β) = Input conc. of hydrogen peroxide (%)

(θ) = Initial conc. of phosphorus in iron ore (before leaching) (%)

$$K = 2, S = 0.1, N = 0.16, S_e = 0.00002, N_e = 0.0001$$

K, S, N, S_e, and N_e are equalizing constant (determined using C-NIKBRAN [9])

Table 1: Variation of removed phosphorus concentration with input concentration of H₂O₂

P _R (%)	(β) (M)	θ (%)
0.364	2	0.49
0.365	4	0.49
0.365	6	0.49
0.366	8	0.49
0.367	10	0.49

Boundary and Initial Condition

Consider iron ore (in a reactor) placed with in hydrogen peroxide solution (oxidant).The reactor atmosphere is not contaminated i.e (free of unwanted gases and dusts). Initially, atmospheric levels of oxygen are assumed just before the decomposition of H₂O₂ (due to air in the reactor). **Mass of iron oxide ore: (50 g)**, leaching time considered: 60 mins., range of input concentration of H₂O₂: 2-10M, constant treatment temperature: 70°C, ore grain size; 150µm, were also used.

The boundary conditions are: reactor oxygen atmosphere due to decomposition of H₂O₂ at the top and bottom of the ore particles interacting with the gas phase. 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 reduced iron is stationary. The sides of the particles are taken to be symmetries.

III. RESULTS AND DISCUSSIONS

The result of the chemical analysis carried out on the beneficiated iron ore concentrate is presented in Table 1. The table shows that the percentage of phosphorus present in the as-beneficiated ore is 0.49%.

Table 2: Result of chemical analysis of iron ore used

Element/Compound	Fe	P	SiO ₂	Al ₂ O ₃
Unit (%)	52.67	0.49	8.983	6.986

Model Validation

The validity of the model is strongly rooted in equation (2) (core model equation) where both sides of the equation are correspondingly approximately equal. Table 3 also agrees with equation (2) following the values of P_R - 2θ² - 0.1θ and 0.00002β² + 0.0001β - 0.161 evaluated from the experimental results in Table 2.

$P_R - 2\theta^2 - 0.1\theta$	$0.00002\beta^2 + 0.0001\beta$
-0.1652	-0.1606
-0.1642	-0.1603
-0.1642	-0.1597
-0.1632	-0.1589
-0.1622	-0.1580

Table 3: Variation of $P_R - 2\theta^2 - 0.1\theta$ with $0.00002\beta^2 + 0.0001\beta - 0.161$

Furthermore, the derived model was validated by comparing the removed phosphorus concentration predicted by the model and that obtained from the experiment. This was done using various evaluative techniques such as computational, statistical, graphical and deviational analysis.

Computational Analysis

Computational analysis of the experimental and model-predicted removed phosphorus concentration was carried out to ascertain the degree of validity of the derived model. This was done by comparing phosphorus removal per unit input concentration of H_2O_2 .

Removed phosphorus concentration per unit input concentration of H_2O_2 , P_R^β (%/M) was calculated from the equation;

$$P_R^\beta = P_R / \beta \tag{4}$$

Therefore, a plot of the concentration of phosphorus removed against input concentration of H_2O_2 as in Fig. 1 using experimental results in Table 2, gives a slope, S at points (2, 0.364) and (10, 0.367) following their substitution into the mathematical expression;

$$P_R^\beta = \Delta P_R / \Delta \beta \tag{5}$$

which is detailed as

$$P_R^\beta = P_{R2} - P_{R1} / \beta_2 - \beta_1 \tag{6}$$

Where

ΔP_R = Change in removed phosphorus concentrations of P_{R2} , P_{R1} at two input concentration values of H_2O_2 , β_2, β_1 . Considering the points (2, 0.364) and (10, 0.367) for (β_1, P_{R1}) and (β_2, P_{R2}) respectively, and substituting them into equation (6), gives the slope as 3.75×10^{-4} %/M which is the removed phosphorus concentration per unit input concentration of H_2O_2 during the actual leaching process.

A plot of the concentration of removed phosphorus against input concentration of H_2O_2 (as in Fig. 2) using derived model-predicted results gives a slope: 3.38×10^{-4} %/M on substituting the points (2, 0.3685) and (10, 0.3712) for (β_1, P_{R1}) and (β_2, P_{R2}) respectively into equation (6). This is the model-predicted removed phosphorus concentration per unit input concentration of H_2O_2 .

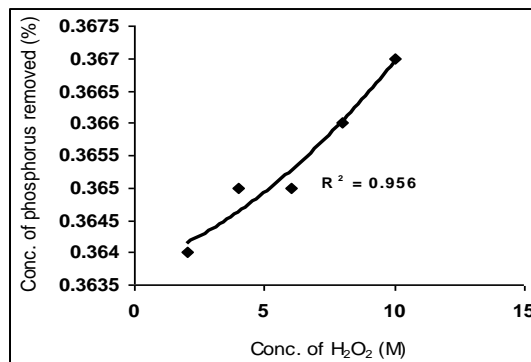


Fig. 1: Coefficient of determination between concentration of removed phosphorus and input concentration of H_2O_2 as obtained from the experiment

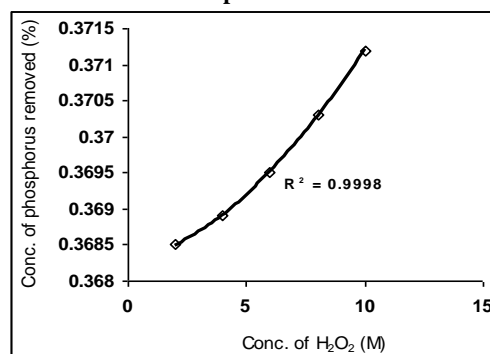


Fig. 2: Coefficient of determination between concentration of removed phosphorus and input concentration of H_2O_2 as obtained from derived model

A comparison of this set of values for removed phosphorus concentration (per unit input concentration of H₂O₂) also shows proximate agreement and a high degree of validity of the derived model.

Statistical Analysis

Standard errors (STEYX)

The standard errors (STEYX) in predicting the removed phosphorus concentration (using results from derived model and experiment) for each value of the input concentration of H₂O₂ are 1.86 x 10⁻⁴ and 3.16 x 10⁻⁴ % respectively. The standard error was evaluated using Microsoft Excel version 2003.

Correlation

Also the correlations between removed phosphorus concentration and input concentration of H₂O₂ as obtained from derived model and experiment considering the coefficient of determination R² from Figs. 1 and 2 was calculated using the equation;

$$R = \sqrt{R^2} \tag{7}$$

The evaluations show correlations 0.9999 and 0.9778 respectively. These evaluated results indicate that the derived model predictions are significantly reliable and hence valid considering its proximate agreement with results from actual experiment.

Graphical Analysis

Comparative graphical analysis of Fig. 3 shows very close alignment of the curves from model-predicted removed phosphorus concentration (MoD) and that of the experiment (ExD). The degree of alignment of these curves is indicative of the proximate agreement between both experimental and model-predicted phosphorus removed concentration

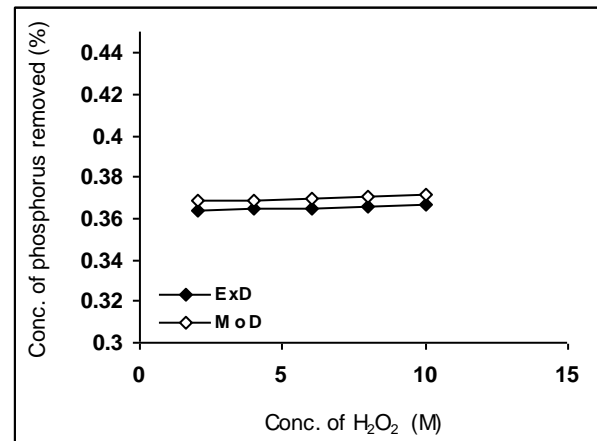


Fig. 3: Comparison of the concentrations of removed phosphorus (relative to input concentration of H₂O₂) as obtained from experiment and derived model

Deviational Analysis

Analysis of removed phosphorus concentrations from the experiment and derived model revealed deviations 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 iron ore and the physiochemical interactions between the ore and the oxidant (H₂O₂) which were found to have played vital roles during the process were not considered during the model formulation. This necessitated the introduction of correction factor, to bring the model-predicted removed phosphorus concentration to those of the corresponding experimental values.

Deviation (Dn) of model-predicted removed phosphorus concentration from that of the experiment is given by

$$Dn = \left(\frac{Pv - Ev}{Ev} \right) \times 100 \tag{8}$$

Where

Pv = Removed phosphorus concentration as predicted by derived model

Ev = Removed phosphorus concentration as obtained from experiment

Correction factor (Cr) is the negative of the deviation i.e

$$Cr = -Dn \tag{9}$$

Therefore

$$Cr = - \left(\frac{Pv - Ev}{Ev} \right) \times 100 \tag{10}$$

Introduction of the corresponding values of Cr from equation (10) into the derived model gives exactly the removed phosphorus concentration as obtained from experiment.

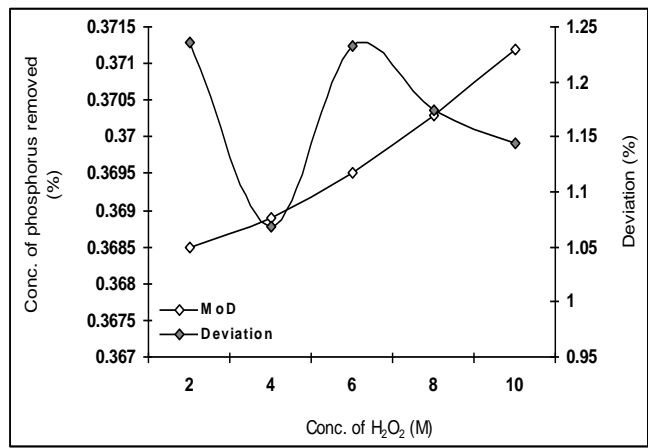


Fig. 4: Variation of model-predicted removed phosphorus concentration with associated deviation from experimental results (relative to input concentration of H₂O₂)

Fig. 4 shows that the maximum deviation of the model-predicted removed phosphorus concentration from the corresponding experimental values is less than 2% and quite within the acceptable deviation limit of experimental results. The figure shows that the least and highest magnitudes of deviation of the model-predicted removed phosphorus concentration (from the corresponding experimental values) are +1.0685 and +1.2363 % which corresponds to removed phosphorus concentrations: 0.3689 and 0.3685 % and input concentrations of H₂O₂: 4 and 2Moles respectively.

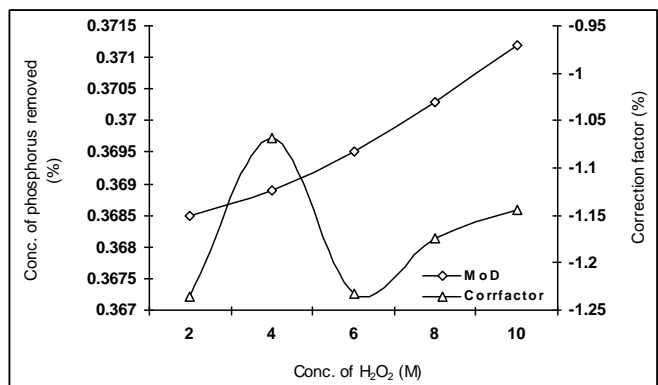


Fig. 5: Variation of model-predicted removed phosphorus concentration with associated correction factor (relative to input concentration of H₂O₂)

Comparative analysis of Figs. 4 and 5 indicates that the orientation of the curve in Fig. 5 is opposite that of the deviation of model-predicted removed phosphorus concentration (Fig. 4). This is because correction factor is the negative of the deviation as shown in equations (9) and (10). It is believed that the correction factor takes care of the effects of surface properties of the iron ore and the physiochemical interactions between the ore and the oxidant (H₂O₂) which have played vital roles during the process, but were not considered during the model formulation. Figs. 9 and 10 indicates that the least and highest magnitudes of correction factor to the model-predicted removed phosphorus concentration (from the corresponding experimental values) are -1.0685 and -1.2363 % which corresponds to removed phosphorus concentrations: 0.3689 and 0.3685 % and input concentrations of H₂O₂: 4 and 2Moles respectively. It is important 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).

IV. CONCLUSIONS

Predictive analysis of phosphorus removal was carried out based on its as-beneficiated content and input concentration of hydrogen peroxide. A two factorial model was derived, validated and then used as a tool for the analysis. The validity of the derived model was rooted on the expression $P_R - 2\theta^2 - 0.1\theta = 0.00002\beta^2 + 0.0001\beta - 0.161$ where both sides of the expression are correspondingly approximately equal. Statistical analysis of the model-predicted and experimentally removed phosphorus concentrations for each value of the input concentration of hydrogen peroxide considered shows standard errors of 1.86×10^{-4} and 3.16×10^{-4} % respectively. Furthermore, removed phosphorus concentration per unit input concentration of hydrogen peroxide as obtained from model-predicted and experimental results were 3.38×10^{-4} and 3.75×10^{-4} %/M respectively. Deviation analysis indicates that the maximum deviation of the model-predicted removed phosphorus concentration (from experimental results) is less than 2%. This implies that the derived model operates with a confidence level of above 98%.

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