

Empirical Evaluation of Removed Phosphorus Concentration Based on Its As-Beneficiated Content and Grain Size of Iron Ore Leached in H₂O₂

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ABSTRACT

Successful empirical evaluation of removed phosphorus concentration was carried out based on its as-beneficiated content and grain size of iron ore leached in hydrogen peroxide. A two-series natural logarithmic model was derived, validated and then used as a tool for the analysis. The model is expressed as;

$$P_R = -0.0038 \ln x + \ln \theta + 1.0882$$

The validity of the model was found to be rooted on the expression $P_R - 1.0882 = -0.0038 \ln x + \ln \theta$ 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 ore grain size considered shows standard errors of 4.6×10^{-4} and 4.53×10^{-4} % respectively. Furthermore, removed phosphorus concentration per unit ore grain size input as obtained from model-predicted and experimental results were 2.83×10^{-5} and 2.67×10^{-5} %/ μm respectively. Deviation analysis indicates that the maximum deviation of the model-predicted removed phosphorus concentration (from experimental results) is less than 1.5%. This translates into a confidence level of above 98%.

Keywords: Analysis, Phosphorus Removal, Initial Phosphorus content, Iron Ore Grain Size, Hydrogen Peroxide Solution.

INTRODUCTION

Structural failures of steel in service have been widely attributed to embrittlement resulting from presence of phosphorus above the admissible quantity. This has necessitated intensive research and development aimed at reducing the phosphorus content of produced molten pig iron to or below the admissible level.

Researches [1-6] have been carried out to remove phosphorus from steel during steel making. In all these works, low treatment temperature and high oxygen activity were revealed as the only essential and unavoidable process conditions which can enhance the rate of dephosphorization. Decomposition of CaCO₃ and high activity of produced CaO; a slag forming material is required for enhancement of the dephosphorization process with the phosphorus forming part of the slag.

It has been reported [7] that the removal of phosphorus from iron can be achieved only by oxidation during steel making, under a basic slag.

Past studies [8] have shown that phosphorus can be removed through leaching of the iron ore in oxalic acid solution. The work culminated in a model formulation for predicting the concentration of phosphorus removed during the leaching process. The model is expressed as;

$$P = 150.5/\mu\alpha \quad (1)$$

It was found to predict the removed phosphorus concentration, with utmost dependence on the final pH of the leaching solution and weight input of the iron oxide ore. The model indicates that the concentration of phosphorus removed is inversely proportional to the product of the weight input of the iron oxide ore and the final pH of the leaching solution. Process conditions considered during the formulation of the model [8] include: leaching temperature of 25°C, initial solution pH 5.5 and average ore grain size; 150µm.

Furthermore, a model was derived [9] for the evaluation of the concentration of dissolved phosphorus (relative to the final pH of the leaching solution) during leaching of iron oxide ore in oxalic acid solution. It was observed that the validity of the model is rooted in the relationship $\ln P = N/\alpha$ where both sides of the expression are approximately equal to 4. The model expressed as;

$$P = e^{(12.25/\alpha)} \quad (2)$$

depends on the value of the final pH of the leaching solution which varies with leaching time. In all, the positive or negative deviation of the model-predicted phosphorus concentration from its corresponding value obtained from the experiment was found to be less than 22%.

Phosphorus removal from iron ore is widely believed to be dependent on the leaching temperature. A model was formulated [10] to ascertain the possibility of predicting the concentration of phosphorus removed based on leaching temperature during leaching of iron oxide ore in oxalic acid solution. The phosphorus removed concentration predicted from the model;

$$P = [(1.8(T)^\tau)]^4 \quad (3)$$

was found to be dependent on leaching temperature ranging from 45-70°C and specified leaching time of 0.1381hr (497secs.) recorded during experiment, for its validity. It was found that the validity of the model is rooted in the expression $(P^{1/4})/N = (T)^\tau$ where both sides of the expression are correspondingly almost equal. The maximum deviation of the model-predicted values of P from the corresponding experimental values was found to be less than 29% which is quite within the range of acceptable deviation limit of experimental results.

The aim of this work is to carry out an empirical evaluation of removed phosphorus concentration based on its as-beneficiated content and grain size of iron ore leached in hydrogen peroxide.

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 iron Agbaja iron ore was then sent for chemical analysis using X-ray fluorescence diffraction spectrometer and atomic absorption spectrophotometer.

Scrubbing process

Scrubbing was carried 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. 20litres 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 24hours. 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 stirred 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;

$$P_R - K = -S_e \ln x + \ln \theta \quad (4)$$

Introducing the values of K and S_e into equation (4)

$$P_R - 1.0882 = -0.0038 \ln x + \ln \theta \quad (5)$$

$$P_R = -0.0038 \ln x + \ln \theta + 1.0882 \quad (6)$$

Where

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

(x) = Iron ore grain size (μm)

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

$K = 1.0882$ and $S_e = 0.0038$. K and S_e are equalizing constant (determined using C-NIKBRAN [11])

Table 1: Variation of removed phosphorus concentration with iron ore grain size

P_R (%)	(x) (μm)	θ (%)
0.355	63	0.49
0.354	90	0.49
0.352	150	0.49
0.351	180	0.49
0.350	250	0.49

Boundary and Initial Conditions

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 H_2O_2 (due to air in the reactor). **Mass of iron oxide ore: (50 g)**, leaching time considered: 20 mins., input concentration of H_2O_2 : 2M, constant treatment temperature: 70°C, range of ore grain size; 63-250 μm , were also used.

The boundary conditions are: reactor oxygen atmosphere due to decomposition of H_2O_2 at the top 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.

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_2O_3
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Unit (%)	52.67	0.49	8.983	6.986
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Model Validation

The validity of the model is strongly rooted in equation (5) (core model equation) where both sides of the equation are correspondingly approximately equal. Table 3 also agrees with equation (5) following the values of $P_R - 1.0882 = -0.0038 \ln x + \ln \theta$ evaluated from the experimental results in Table 2.

Table 3: Variation of $P_R - 1.0882$ with $-0.0038 \ln x + \ln \theta$

$P_R - 1.0882$	$-0.0038 \ln x + \ln \theta$
-0.7290	-0.7290
-0.7304	-0.7304
-0.7323	-0.7323
-0.7330	-0.7330
-0.7343	-0.7343

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 ore grain size P_R^x (%/ (μm)) was calculated from the equation;

$$P_R^x = P_R / x \quad (7)$$

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 (63, 0.355) and (250, 0.350) following their substitution into the mathematical expression;

$$P_R^x = \Delta P_R / \Delta x \quad (8)$$

which is detailed as

$$P_R^x = P_{R2} - P_{R1} / x_2 - x_1 \quad (9)$$

Where

ΔP_R = Change in removed phosphorus concentrations of P_{R2} , P_{R1} at two input ore grain size values, x_2 , x_1 . Considering the points (63, 0.355) and (250, 0.35) for (x_1, P_{R1}) and (x_2, P_{R2}) respectively, and substituting them into equation (9), gives the slope as -2.67×10^{-5} % / (μm) which is the removed phosphorus concentration per unit input ore grain size during the actual leaching process.

A plot of the concentration of removed phosphorus against input ore grain size (as in Fig. 2) using derived model-predicted results gives a slope: -2.83×10^{-5} % / (μm) on substituting the points (63, 0.3592) and (250, 0.3539) for (x_1, P_{R1}) and (x_2, P_{R2}) respectively into equation (9). This is the model-predicted removed phosphorus concentration per unit input ore grain size.

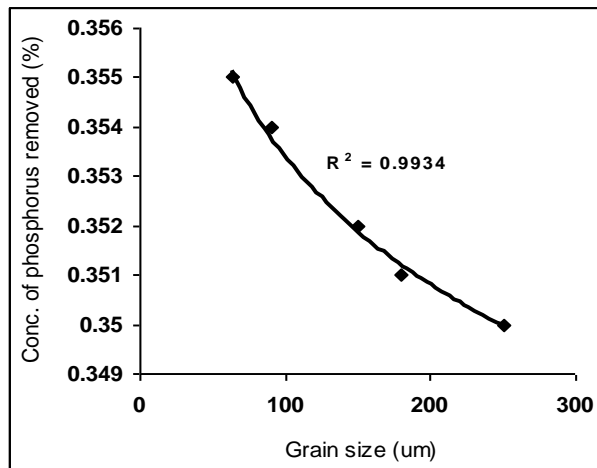


Fig. 1: Coefficient of determination between concentration of removed phosphorus and input ore grain size as obtained from the experiment

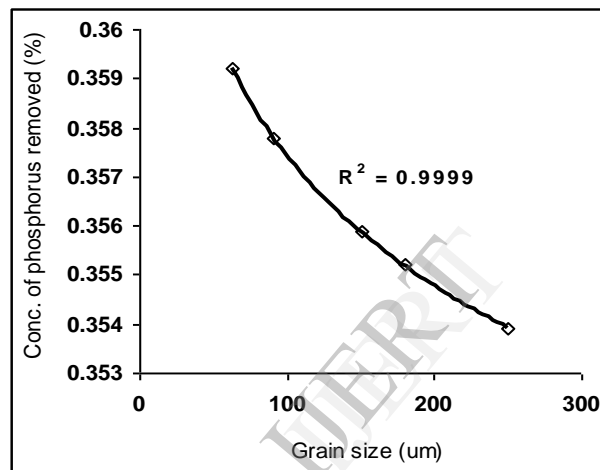


Fig. 2: Coefficient of determination between concentration of removed phosphorus and input ore grain size as obtained from derived model

The negative signs preceding $- 2.67 \times 10^{-5} \% / (\mu\text{m})$ and $- 2.83 \times 10^{-5} \% / (\mu\text{m})$ indicates that the slopes are negative. Therefore, the magnitudes of the removed phosphorus concentration per unit input ore grain size as obtained from experiment and derived model are $2.67 \times 10^{-5} \% / (\mu\text{m})$ and $2.83 \times 10^{-5} \% / (\mu\text{m})$ respectively. A comparison of this set of values for removed phosphorus concentration (per unit input ore grain size) also shows proximate agreement and a high degree of validity of the derived model.

Statistical Analysis

Standard errors (STEYX)

The standard errors in predicting the removed phosphorus concentration (using results from derived model and experiment) for each value of the input ore grain size are 4.6×10^{-4} and $4.53 \times 10^{-4} \%$ respectively. The standard error was evaluated using Microsoft Excel version 2003.

Correlation

Also the correlations between removed phosphorus concentration and input concentration of H_2O_2 as obtained from derived model and experiment considering the coefficient of determination R^2 from Figs. 1 and 2 was calculated using the equation;

$$R = \sqrt{R^2} \quad (10)$$

The evaluations show correlations 0.9999 and 0.9967 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.

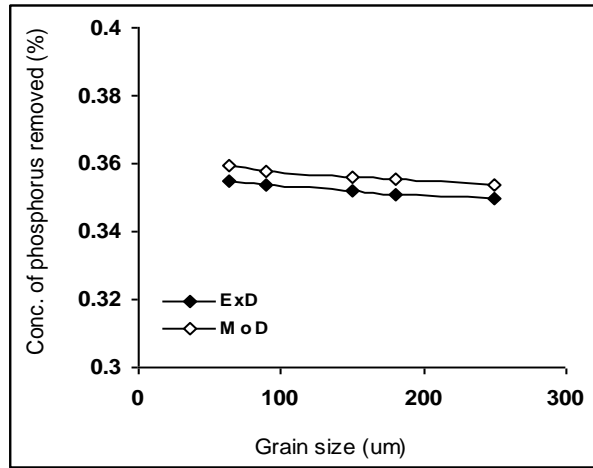


Fig. 3: Comparison of the concentrations of removed phosphorus (relative to input ore grain size) as obtained from experiment and derived model

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 (H_2O_2) 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

$$Dn = \left(\frac{P_v - E_v}{E_v} \right) \times 100 \quad (11)$$

Where

P_v = Removed phosphorus concentration as predicted by derived model

E_v = Removed phosphorus concentration as obtained from experiment [8]

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

$$Cr = -Dn \quad (12)$$

Therefore

$$Cr = - \left(\frac{P_v - E_v}{E_v} \right) \times 100 \quad (13)$$

Introduction of the corresponding values of Cr from equation (13) into the derived model gives exactly the removed phosphorus concentration as obtained from experiment.

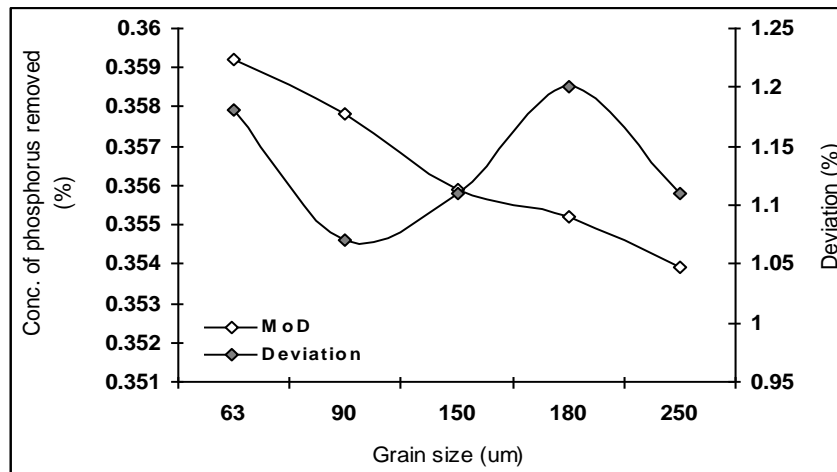


Fig. 4: Variation of model-predicted removed phosphorus concentration with associated deviation from experimental results (relative to input ore grain size)

Fig. 4 shows that the maximum deviation of the model-predicted removed phosphorus concentration from the corresponding experimental values is less than 1.5% 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 + 1.07 and + 1.2 % which corresponds to removed phosphorus concentrations: 0.3578 and 0.3552 % and input ore grain size: 90 and 180 μm respectively.

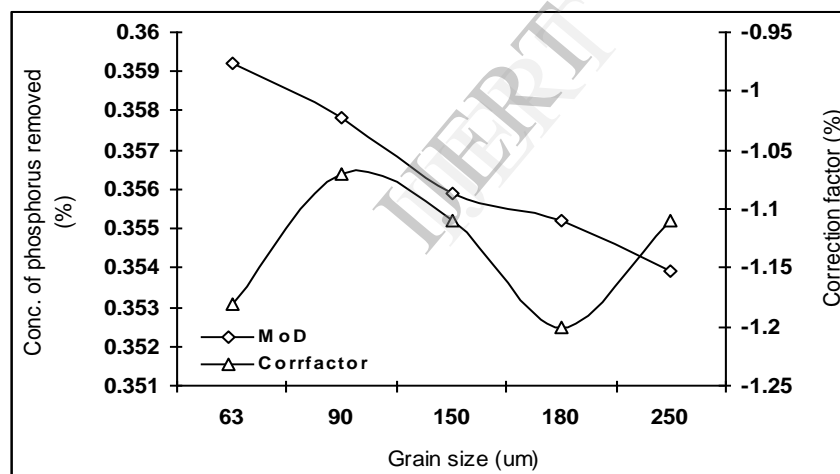


Fig. 5: Variation of model-predicted removed phosphorus concentration with associated correction factor (relative to input ore grain size)

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 (12) and (13).

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 (H_2O_2) which have played vital roles during the process, but were not considered during the model formulation. Figs. 9 and 10 indicate that the least and highest magnitudes of deviation of the model-predicted removed phosphorus concentration (from the corresponding experimental values) are - 1.07 and - 1.2 % which corresponds to removed phosphorus concentrations: 0.3578 and 0.3552 % and input ore grain size: 90 and 180 μm 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).

CONCLUSIONS

Successful empirical evaluation of removed phosphorus concentration was carried out based on its as-beneficiated content and grain size of iron ore leached in hydrogen peroxide. A two-series natural logarithmic model was derived, validated and then used as a tool for the analysis. Statistical analysis of the model-predicted and experimentally removed phosphorus concentrations for each value of the input ore grain size considered shows standard errors of 4.6×10^{-4} and 4.53×10^{-4} % respectively. Furthermore, removed phosphorus concentration per unit ore grain size input as obtained from model-predicted and experimental results were 2.83×10^{-5} and 2.67×10^{-5} %/ (μm) respectively. Deviation analysis indicates that the maximum deviation of the model-predicted removed phosphorus concentration (from experimental results) is less than 1.5%. This translates into a confidence level of above 98%.

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