

Empirical Analysis of Phosphorus Removal Based on Its As-Beneficiated Concentration and Mass-Input of KClO_3

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ABSTRACT

Empirical analysis of phosphorus removal was carried out based on its as-beneficiated concentration and mass-input of KClO_3 . A model was derived and used as a tool for the analysis. The model is expressed as:

$$P_R = -0.0005 \alpha^2 + 0.01\alpha + 0.0024 \gamma^2 + 0.0181$$

The validity of the two-factorial model was found to be rooted on the expression $100 P_R + 1.81 = -0.05 \alpha^2 + \alpha + 0.24 \gamma^2$ where both sides of the expression are correspondingly approximately equal. Statistical analysis of the derived model-predicted, regression model-predicted and experimental removed phosphorus concentrations for each value of the mass-inputs of KClO_3 considered shows standard errors of 0.0015, 3.45×10^{-5} and 0.0025% respectively. Furthermore, removed phosphorus concentration per unit mass-input of KClO_3 as obtained from derived model-predicted, regression model-predicted and experimental results were 3.0×10^{-3} , 2.975×10^{-3} and $2.475 \times 10^{-3} \% \text{ g}^{-1}$ respectively. Deviation analysis indicates that the derived model gives best-fit process analysis with a deviation range of just 1.35 – 12.29%, from experimental results and invariably an operational confidence level range 87.71-98.65%. The deviation range corresponded to the removed phosphorus concentration range: 0.0213-0.0333 % and KClO_3 mass-input range: 11-15g. This implies that the derived model can exclusively be significantly useful and viably operational within these process conditions.

Keywords: Empirical Analysis, Phosphorus Removal, KClO_3 , Agbaja Iron Ore.

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INTRODUCTION

Several steel structures fail in service due to embrittlement caused by presence of phosphorus above the admissible quantity. This therefore necessitates full scale researches geared on reducing the phosphorus content of pig iron (which eventually transforms into steel) to or below the admissible level.

Past research [1] has shown the possibility of dephosphorizing iron ore by breaking the phosphorus-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 aphosphorus 9K culture and pH of original ore slurry kept at a range of 1.5 to 3.5. The research was found suitable for direct-extracting and dephosphorizing phosphor-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 for phosphorus removal have been evaluated based on the use of several types of fungi and bacteria, some being acid producing. Recently, *Aspergillus niger* and their cultural filtrates were used for removing phosphorus from Agbaja (Nigeria) iron oxide ore. The results of this work [2] show that phosphorus removal efficiencies at the end of the 49 days of the leaching process are 81, 63 and 68% for 5, 100 and 250 mesh grain sizes respectively.

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

A model has been derived for predictive 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.

Phosphorus removal has been observed [7] to also be dependent on leaching temperature. The model derived using experimental results generated previously [7] indicated that at a leaching temperature range 45-70⁰C, the maximum deviation of the model-predicted removed phosphorus concentration (from the corresponding experimental values) was less than 29%.

The aim of this work is to empirically analyze phosphorus removal based on its as-beneficiated concentration and mass-input of KClO₃. The essence of this work is to ascertain the level of dephosphorization achievable at different mass-input of KClO₃ where all other input process parameters are kept constant.

MATERIALS AND METHODS

Agbaja (Nigeria) iron ore concentrate used for this work was obtained from Nigeria Metallurgical Development Centre (NMDC) Jos. This concentrate was dried in air (under atmospheric condition) and used in the as-received condition with particle size; 150 μ m. A weighed quantity of the dried iron ore concentrate was mixed with different proportions of powdered KClO₃ (obtained from Fisher Scientific Company Fair Lawn, New Jersey, USA) as weighed with a triple beam balance at NMDC laboratory. Iron crucibles were filled with the sample mixtures of 11g of KClO₃ and 50g of ore concentrate. These samples in the crucibles were then heated to a temperature of 500⁰C in a Gallenkamp Hot pot electric furnace at NMDC Laboratory for 600 secs. and thereafter were emptied on white steel pans for observation. The experiment was repeated using varied combination of mass-input of KClO₃ i.e 12, 13, 14, 15, 16g and constant treatment temperature of 400⁰C, while the mass-input of the ore is kept constant. Weighed quantities of the sample mixtures for each experiment set were taken (after being heated) for chemical analysis (to determine percentage phosphorus removal) using wet analysis method. The average of the removed phosphorus concentration determined in each experiment set was taken as the precise result.

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;

$$K P_R + S_e \approx - N\alpha^2 + \alpha + S \gamma^2 \quad (1)$$

Introducing the values of K, N, and S, into equation (1)

$$100 P_R + 1.81 = - 0.05 \alpha^2 + \alpha + 0.24 \gamma^2 \quad (2)$$

$$100 P_R = - 0.05 \alpha^2 + \alpha + 0.24 \gamma^2 + 1.81 \quad (3)$$

$$P_R = \left(\frac{- 0.05 \alpha^2 + \alpha + 0.24 \gamma^2 + 1.81}{100} \right) \quad (4)$$

$$P_R = - 0.0005 \alpha^2 + 0.01\alpha + 0.0024 \gamma^2 + 0.0181 \quad (5)$$

Where

P_R = Conc. of removed phosphorus (%)

(γ) = As- beneficiated phosphorus content of the ore (%)

$K = 100$; Equalizing constant (determined using C-NIKBRAN (Nwoye, 2008))

$S_e = 1.81$; Equalizing constant (determined using C-NIKBRAN (Nwoye, 2008))

(α) = Mass-input of $KClO_3$ (g)

$N = 0.05$; Equalizing constant (determined using C-NIKBRAN(Nwoye, 2008))

$S = 0.24$; Equalizing constant (determined using C-NIKBRAN (Nwoye, 2008))

Table 1: variation of removed phosphorus concentration with mass-input of $KClO_3$ [3]

P_{AB}	Mass of $KClO_3$ (g)	P_R (%)
0.9	11	0.022
0.9	12	0.031
0.9	13	0.040
0.9	14	0.053
0.9	15	0.064
0.9	16	0.083

P_{AB} = As-beneficiated concentration of phosphorus in iron ore

Boundary and Initial Condition

Consider iron ore (in a furnace) mixed with potassium chlorate (oxidant).The furnace atmosphere is not contaminated i.e (free of unwanted gases and dusts). Initially, atmospheric levels of oxygen are assumed just before the decomposition of $KClO_3$ (due to air in the furnace). Mass of iron oxide ore: (50g), treatment time: 600 secs., constant treatment temperature: 400°C, ore grain size; 150 μ m, and mass of $KClO_3$; (11-16g) were also used.

The boundary conditions are: furnace oxygen atmosphere due to decomposition of $KClO_3$ (since the furnace was air-tight closed) 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.

RESULTS AND DISCUSSIONS

The result of the chemical analysis carried out on the beneficiated iron ore concentrate is presented in Table 2. The table shows that the percentage of phosphorus present in the as-beneficiated ore is 0.9%.

Table 2: Result of chemical analysis of iron ore used [3]

Element/Compound	Fe	P	SiO ₂	Al ₂ O ₃
Unit (%)	78.6	0.90	5.30	11.0

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 $100P_R + 1.81$ and $-0.05\alpha^2 + \alpha + 0.24\gamma^2$ evaluated from the experimental results in Table 1.

Table 3: Variation of $100P_R + 1.81$ with $-0.05\alpha^2 + \alpha + 0.24\gamma^2$

$100P_R + 1.81$	$-0.05\alpha^2 + \alpha + 0.24\gamma^2$
5.01	5.1444
5.39	4.9944
4.78	4.7444
4.54	4.3944
4.02	3.9444
3.79	3.3944

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 mass-input of KClO₃ evaluated from model-predicted results with those from actual experimental results

Removed phosphorus concentration per unit mass-input of KClO₃ P_R^M (%/g) was calculated from the equation;

$$P_R^M = P_R / M \quad (6)$$

Therefore, a plot of the concentration of phosphorus removed against mass-input of KClO₃ as in Fig. 1 using experimental results in Table 1, gives a slope, S at points (11, 0.032) and (15, 0.0221) following their substitution into the mathematical expression;

$$P_R^M = \Delta P_R / \Delta M \quad (7)$$

Equation (7) is detailed as

$$P_R^M = P_{R2} - P_{R1} / M_2 - M_1 \quad (8)$$

Where

ΔP_R = Change in removed phosphorus concentrations of P_{R2}, P_{R1} at two mass-input values of KClO₃ M_2, M_1 . Considering the points (11, 0.032) and (15, 0.0221) for (M_1, P_{R1}) and (M_2, P_{R2}) respectively, and substituting them into equation (8), gives the slope as -2.475×10^{-3} %/g which is the removed phosphorus concentration per mass-input of KClO₃ during the actual desulphurization process.

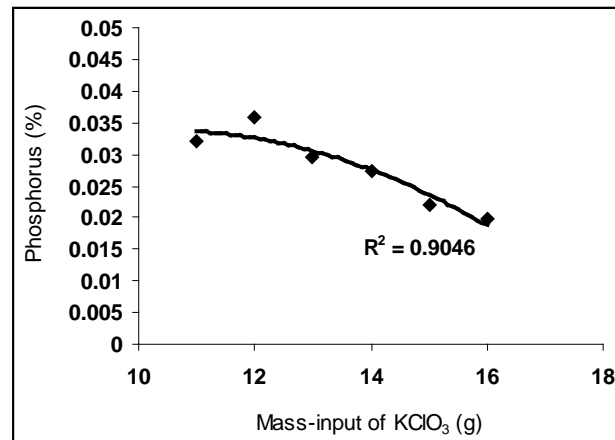


Fig. 1: Coefficient of determination between concentration of removed phosphorus and mass-input of KClO₃ as obtained from the experiment.

A plot of the concentration of removed phosphorus against mass-input of KClO₃ (as in Fig. 2) using derived model-predicted results gives a slope: $-3.0 \times 10^{-3} \text{ %/g}$ on substituting the points (11, 0.0333) and (15, 0.0213) for (M_1, P_{R1}) and (M_2, P_{R2}) respectively into equation (8). This is the model-predicted removed phosphorus concentration per mass-input of KClO₃.

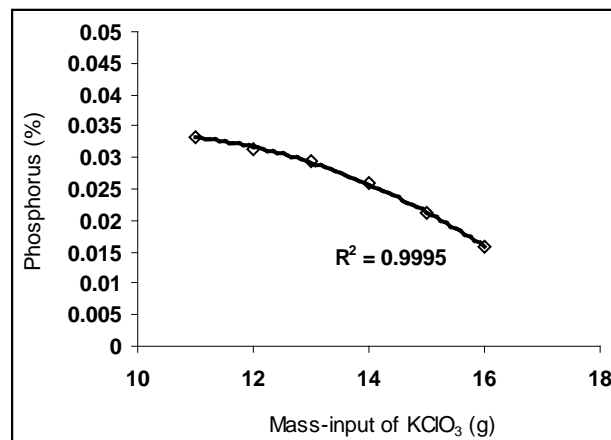


Fig. 2: Coefficient of determination between concentration of removed phosphorus and mass-input of KClO₃ as obtained from derived model.

Similarly, a plot of the concentration of phosphorus removed against mass-input of KClO_3 (as in Fig. 3) using regression model-predicted results gives a slope: $2.975 \times 10^{-3} \text{ %/g}$ on substituting the points (11, 0.0352) and (15, 0.0233) for (M_1, P_{R1}) and (M_2, P_{R2}) respectively into equation (8). This is the regression model-predicted removed phosphorus concentration per mass-input of KClO_3 .

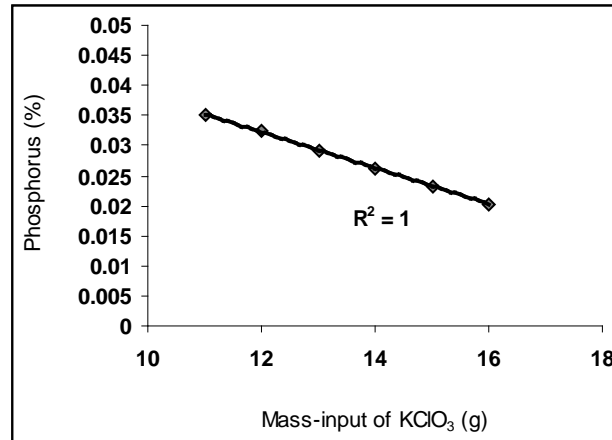


Fig. 3: Coefficient of determination between concentration of removed phosphorus and mass-input of KClO_3 as obtained from regression model.

A comparison of this set of values for removed phosphorus concentration (per unit mass-input of KClO_3) also shows proximate agreement and a high degree of validity of the derived model.

It is important to state that the evaluated removed phosphorus concentrations per unit mass-input of KClO_3 as obtained from derived model, regression model and experiment are just the magnitude of the value. The associated negative signs preceding the evaluated values signify that the associated slopes from which the evaluations were done were all negative.

Statistical Analysis

The standard errors (STEYX) in predicting the removed phosphorus concentration (using results from derived model, regression model and experiment) for each value of the mass-input of KClO_3 are 0.0015, 3.45×10^{-5} and 0.0025 % respectively. The standard error was evaluated using Microsoft Excel version 2003.

Also the correlations between removed phosphorus concentration and mass-input of KClO_3 as obtained from derived model, regression model and experiment considering the coefficient of determination R^2 from Figs. 1-3 was calculated using the equation;

$$R = \sqrt{R^2} \quad (9)$$

The evaluations show correlations 0.9997, 1.0000 and 0.9511 respectively. These evaluated results indicate that the derived model predictions are significantly reliable and hence valid considering its proximate agreement with results from regression model and actual experiment.

Graphical Analysis

Comparative graphical analysis of Fig. 4 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.

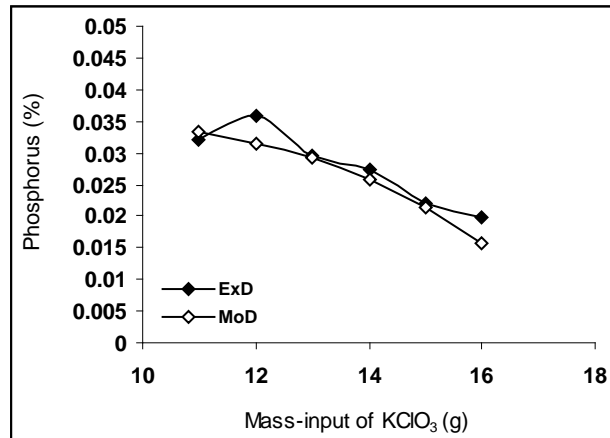


Fig. 4: Comparison of the concentrations of removed phosphorus (relative to mass-input of KClO₃) as obtained from experiment and derived model.

Comparison of derived model with standard model

The validity of the derived model was further verified through application of the linear regression model (ReG) in predicting the trend of the experimental results. Comparative analysis of Fig. 5 shows very close alignment of curves and significantly similar trend of data point's distribution for experimental (ExD), derived model-predicted (MoD) and regression model predicted (ReG) results of removed phosphorus concentration.

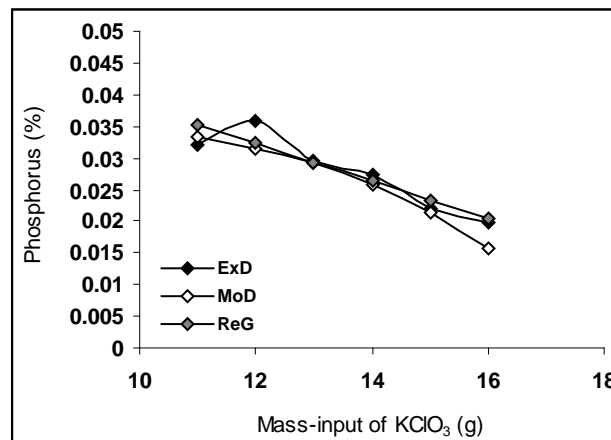


Fig. 5: Comparison of the concentrations of removed phosphorus (relative to mass-input of KClO₃) as obtained from derived model, regression model and experiment.

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 (KClO_3) 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 (D_n) of model-predicted removed phosphorus concentration from that of the experiment is given by

$$D_n = \left(\frac{P_v - E_v}{E_v} \right) \times 100 \quad (10)$$

Where

P_v = Removed phosphorus concentration as predicted by derived model

E_v = Removed phosphorus concentration as obtained from experiment

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

$$C_r = -D_n \quad (11)$$

Therefore

$$C_r = - \left(\frac{P_v - E_v}{E_v} \right) \times 100 \quad (12)$$

Introduction of the corresponding values of C_r from equation (12) into the derived model gives exactly the removed phosphorus concentration as obtained from experiment.

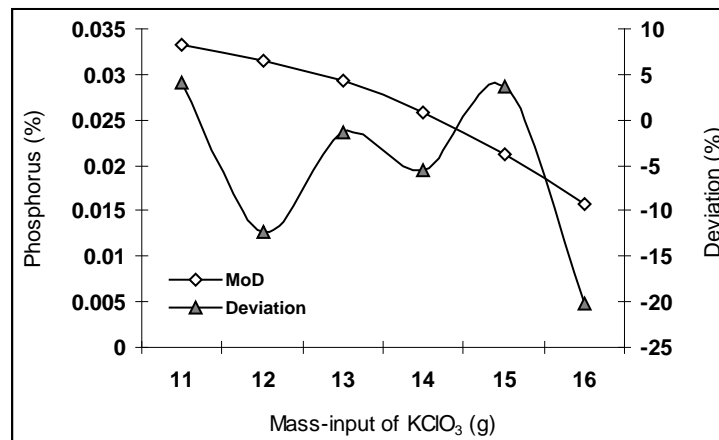


Fig. 6: Variation of model-predicted removed phosphorus concentration with associated deviation from experimental results (relative to mass-input of KClO_3).

Fig. 6 shows that the maximum deviation of the model-predicted removed phosphorus concentration from the corresponding experimental values is less than 21% and quite within the acceptable deviation limit of

experimental results. The figure show that the least and highest magnitudes of deviation of the model-predicted removed phosphorus concentration (from the corresponding experimental values) are -1.35 and -20.2 % which corresponds to removed phosphorus concentrations: 0.0293 and 0.0158 %, as well as KClO_3 mass-inputs: 13 and 16g respectively.

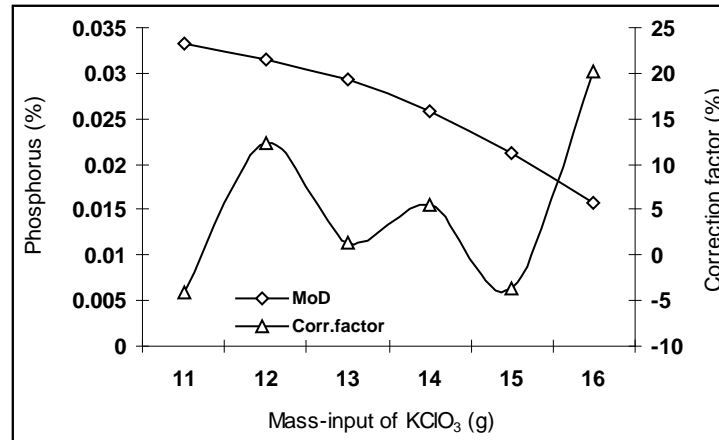


Fig. 7: Variation of model-predicted removed phosphorus concentration with associated correction factor (relative to mass-input of KClO_3)

Comparative analysis of Figs. 6 and 7 indicates that the orientation of the curve in Fig. 7 is opposite that of the deviation of model-predicted removed phosphorus concentration (Fig. 6). This is because correction factor is the negative of the deviation as shown in equations (11) and (12).

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 (KClO_3) which have played vital roles during the process, but were not considered during the model formulation. Fig. 7 indicates that the least and highest magnitudes of correction factor to the model-predicted removed sulphur concentration are + 1.35 and + 20.2 % which corresponds to removed phosphorus concentrations: 0.0293 and 0.0158 %, as well as KClO_3 mass-inputs: 13 and 16g 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

The derived model empirically analyzed phosphorus removal based on its as-beneficiated concentration and mass-input of KClO_3 . The validity of the two-factorial model was rooted on the expression $100 P_R + 1.81 = -0.05 \alpha^2 + \alpha + 0.24 \gamma^2$ where both sides of the expression are correspondingly approximately equal. Statistical analysis of the derived model-predicted, regression model-predicted and experimental removed phosphorus concentrations for each value of the mass-inputs of KClO_3 considered shows standard errors of 0.0015, 3.45×10^{-5} and 0.0025% respectively. Furthermore, removed phosphorus concentration per unit mass-input of KClO_3 as obtained from derived model-predicted, regression model-predicted and experimental results were 3.0×10^{-3} , 2.975×10^{-3} and $2.475 \times 10^{-3} \% \text{ g}^{-1}$ respectively. Deviation analysis indicates that the derived model gives best-fit process analysis with a deviation range of just 1.35 –

12.29%, from experimental results and invariably an operational confidence level range 87.71-98.65%. The deviation range corresponded to the removed phosphorus concentration range: 0.0213-0.0333 % and KClO_3 mass-input range: 11-15g. This implies that the derived model can exclusively be significantly useful and viably operational within these process conditions.

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