Journal of Innovative Research in Engineering and Sciences 4(4), March, 2014.
ISSN: 2141-8225 (Print); ISSN: 2251-0524 (Online)
http://www.grpjournal.org/Journal/Category/JOIRES.aspx.
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# Factors Affecting Dephosphorization of Agbaja Iron Ore (Kogi State), Nigeria

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**Abstract:** The purpose of this research work is to determine the optimal factor combinations for dephosphorization of a Nigerian Agbaja iron deposit –the largest inferred deposit of about 1.250 billion tones. The process parameters used in dephosphorization include concentration, particle size and time dwell. Because of sequential experimentation, RSM [Response Surface Methodology] of central composite design (CCD) as used in estimating response surface of second order regression equation. The RSM is widely used as an optimization, development, and improvement technique for processes based on the use of factorial designs—that is, those in which the response variable is measured for all the possible combinations of the levels chosen of the factors. The main effect of a factor is defined as the variation in response caused by a change in the level of the factor considered, when the other ones are kept constant. The results generated from the experiment indicated that optimum conditions of dephosphorization of about ≤0.05 were obtainable at concentrations of 0.6M, dwell time of 35mins and particle size of 0.27mm respectively.

**Key Words:** Dephosphorization, Agbaja Iron Ore, Central Composite Design (CCD) Response Surface Methodology (RSM), Concentration and Particle Size.

## INTRODUCTION

Nigerian's proven Agbaja iron ore reserve estimated at about 1.25 billion tonnes is largest in the country. Although its iron content is about 47.50% (Obot and Anyakwo, 2011) but its phosphorus content is variously estimated at about 1.4 to 2.0%(Obiorah et al,2011).Since phosphorus beyond the threshold of 0.08% is untradeable (Cheng et al,1999 and Dukino et al, 2000), it follows that the Nigerian Agbaja iron ore is currently untradeable until a means of reducing it to an acceptable level (0.03-0.045%) is achievable. Agbaja iron ore is also of low silicon modulus ($Si0_2$ /$Al_20_3$= 0.89) and has fine texture.

The removal of phosphorus from iron and steel presents problems because of similarity of the standard free energies of formation of iron oxide and phosphorus pentoxide (Alafara et al 2005).Consequently, in the reducing conditions of the blast furnace to recover some 99.5% of the iron charged near complete reduction of phosphorus pentoxide from the acid blast furnace occurs. As the phosphorus in the ore impregnates the pig iron, there occur two distinct processes of tackling the problem: pyrometallurgical route and hydrometallurgical route. The first route employs basic slag during the conversion to steel. This technique covers the activity coefficient of phosphorous pentoxide in the slag (Li and Wen, 2004;Whitley 1923). The second route delves into ways of reducing phosphorous in the iron at a relatively low temperature.

Leaching of lean ores or complex ores in different acids has proved successful for several years. However, the leaching of phosphorous contaminated iron ore has made a very limited progress. This underscores the ongoing intense research in the area for several decades. Depending upon the degree of association of phosphorous with the minerals in the iron body, iron ore can be beneficiated in any of the three ways: smelting process, physical separation and chemical leaching (Kobal1990).As is well known, smelting process is effective for dispersion but with very high cost, and it is still under fundamental research. For physical separation, communition followed by wet magnetic separation or froth flotation is generally employed when the phosphatic gangue mineral appears as discrete inclusion in the iron body matrix (primary mineralization)(Kokal 1990, Kokal et al 2003, Fonesca et al 1994). Low phosphorous extraction, high grinding cost and iron loss are the major disadvantages of the method. However, when phosphorous is disseminated in the iron structure, possibly forming cryptocrystalline phosphates or solids solution with the iron oxide phases (secondary mineralization), the beneficiation can only proceed by chemical routes (Kokal 1990, Kokal et al 2003, Forserg and Asolfession, 1981).

Forsberg and Asolfession (1981),Hang et al, (1994) and He and Zhou(2000),investigated dephosphorization with acid leaching, In their studies, the acid concentrations were very high and low phosphorous extractions were obtained. Obiorah et al (2011) investigated dephosphorization of Agbaja iron ore using leaching technique and got maximum degree of phosphorus removal of 96% at 0.3Mleachant concentration, 30 minutes dwell time and 1.2 dilution ratio.

The Agbaja sample consisted mainly of aggregates of brown, compact, fine-grained material with some larger, extremely friable particles. This ore was strongly magnetic. The sample of Corby ore consisted mainly of reddish-yellow fine-grained material with some dispersed solid lumps. The ore was not significantly magnetic. In the present study, the feasibility of further improving dephosphorization of Agbaja iron ore by leaching with two acid mixtures ($H_2S0_4$and HCl) at various ranges of particle size, concentration, dwelltimeon one hand and optimization of process parameters and response variable on the other were investigated.

## 2.0 MATERIALS AND METHODS

### 2.1 Sample Collection.

Iron ore samples of Agbaja iron ore collected from National Metallurgical Development Centre (N.M.D.C),Jos Plateau State, Nigeria were used for the experiment.

### 2.2 Determination of iron and phosphorus phase content of untreated ore

The phases in which iron and phosphorous were present within the iron ore were determined by atomic absorption spectrophotometry and titrimetric analysis.

### 2.3 Chemical preparation of leaching solutions

All leaching chemicals used were of laboratory grade, procured from Bridge Head Chemical market, Onitsha, Nigeria.1M, 0.6M and 0.2M leaching solutions of mixtures of $H_2S0_4$and HClwere prepared by diluting the concentrated form of the acid in distilled water. Also, particle size ranges of 0.2mm, 0.3mm and 0.4mm were prepared in a standard shaker sieve at Civil Engineering Laboratory, Nnamdi Azikiwe University, Awka.

### 2.4 Leaching Procedure

All leaching experiments were conducted in 250ml Erlenmeyer flasks. For the first sample, a mixture of 20ml $H_2S0_4$and HCl was poured into a flask containing 20g of Agbaja iron ore, stirred and left to leach in accordance with the design matrix. Similar operations were carried out upon the rest of the samples as shown in the design matrix (Table 2.1) and hand stirred and left to leach at different time durations at a temperature of about $60^oC$. At the end of each leaching operation, filtration followed and the residue/filtrate was removed and washed 3 times with distilled water. The treated ore samples were dried in an oven at $105^oC$ for 24 hours and stored in a dry environment for analysis. The respective leached liquors too were stored in flasks for analysis.

Design of experiment employing Response Surface Methodology, RSM of central composite design (CCD) was conducted for the leaching treatment based on $2^3$ full factorial design of experiment. The design matrix for the three variables, at two levels and fourteen randomly experimental runs and responses are shown Table 2.2.A second-order polynomial equation

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 + e \qquad (1)$$

was used to express dephosphorization as a function of independent variables (concentration, time dwell, and particle size).

Where:
Y represents dephosphorization,
A represents concentration,
B represents time dwell and
C represents particle size.

The coefficients of the response surface equation were determined using DOE++ 2011 software release.

**Table 2.1: Factor levels of independent variables for dephosphorization using two mixtures of HCl and $H_2SO_4$**

| Actual Values | | | | Coded Values | | |
|---|---|---|---|---|---|---|
| **Variables** | **Upper limit (1)** | | | | | |
| | **Lower limit (-1)** | **Base level (0)** | | **Low level** | **Midpoint** | **High level** |
| concentration M | 0.2 | 0.6 | 1 | -1 | 0 | 1 |
| Dwell time, mins | 30 | 45 | 60 | -1 | 0 | 1 |
| Particle size, mm | 0.2 | 0.3 | 0.4 | -1 | 0 | 1 |

**Table 2.2:Design Matrix of DOE and responses of full Factorial experimental design for dephosphorization using 2 acid mixtures of HCl and $H_2SO_4$**

| Independent variables | | | | Responses P in filtrate(%) | | |
|---|---|---|---|---|---|---|
| **S/N** | **A** | **B** | **C** | **Y1** | **Y2** | **Y** |
| 1 | -1 | -1 | -1 | 0.65 | 0.67 | 0.66 |
| 2 | 1 | -1 | -1 | 0.54 | 0.56 | 0.55 |
| 3 | -1 | 1 | -1 | 0.43 | 0.45 | 0.44 |
| 4 | 1 | 1 | -1 | 0.32 | 0.34 | 0.33 |
| 5 | -1 | -1 | 1 | 0.21 | 0.23 | 0.22 |
| 6 | 1 | -1 | 1 | 0.1 | 0.12 | 0.11 |
| 7 | -1 | 1 | 1 | 0.05 | 0.07 | 0.06 |
| 8 | 1 | 1 | 1 | 0.03 | 0.05 | 0.04 |
| 9 | -1 | 0 | 0 | 0.54 | 0.56 | 0.55 |
| 10 | 1 | 0 | 0 | 0.23 | 0.25 | 0.24 |
| 11 | 0 | -1 | 0 | 0.34 | 0.36 | 0.35 |
| 12 | 0 | 1 | 0 | 0.61 | 0.63 | 0.62 |
| 13 | 0 | 0 | -1 | 0.61 | 0.63 | 0.62 |
| 14 | 0 | 0 | 1 | 0.34 | 0.36 | 0.35 |

## 3.0 RESULTS AND DISCUSSION

Atomic Absorption Spectroscopy,AAS and titrimetricanalysisreveal the chemical composition as in shown Table 3.1. As phosphorus contained in the ore, is in non-sulphidic phase, acid leaching presents the option for its extraction.

Effects of concentration, dwell time and particle size were investigated by using response surface methodology. The levels of independent parameters (Table 2.1) were determined based on preliminary experiments.

A $2^3$ full factorial experimental design with 6axialpoints(a)and one centre point (n) was used in the study. The factor level of independent variables is showninTable2.1 while the design matrix is shown in Table 2.2.The parameters: concentration (A), dwelltime(B)and particle size (C) were chosen as independent variable at two levels while phosphorus extraction is the output variable. The analysis is focused on how dephosphorizationis influenced by the independent variables A, B and C.The range of independent parametersis shown in Table 2.1.The experimental values of dephosphorization under different treatment conditions are presented in Table 2.2.The regression coefficients for the second-order polynomial equations and results for the linear, interaction terms, quadratic termsare presented in Table 3.2.In order to study the combined effects (interactions) of these factors, experiments were performed at different combinations of the physical parameters using statistically designed experiment. Upon the determination of polynomial coefficients, statistical analysis (T-Test, P-Testetc] was performed to develop model that is adequate, significant and homogenous. Main effects, interaction effects and quadratic effects and response behaviors are explained by Regression information, analysis summary, Table 3.3 and model equation 2.

**Table 3.2 Experimental Values of Dephosphorization Under Different Treatment Conditions**

| Regression information | | | | | | |
|---|---|---|---|---|---|---|
| Term | Coefficient | Standard Error | Low CI | High CI | T Value | P Value |
| Intercept | 4.53 | 1.1 | 2.08 | 7 | 3.9 | 0 |
| A:concentration | 0.07 | 0 | -0 | 0.1 | 2 | 0.1 |
| B:dwell time | -0.1 | 0 | -0.1 | 0 | -2 | 0.1 |
| C:particle size | -0 | 0 | -0.1 | 0 | -1 | 0.2 |
| AB | -0.1 | 0 | -0.2 | 0 | -1 | 0.2 |
| AC | 0.12 | 0 | 0.03 | 0.2 | 2.8 | 0 |
| BC | 0.01 | 0 | -0.1 | 0.1 | 0.1 | 0.9 |
| | -1.4 | 0.4 | -2.3 | -1 | -4 | 0 |
| BB | -1.4 | 0.4 | -2.2 | -1 | -4 | 0 |
| CC | -1.4 | 0.4 | -2.3 | -1 | -4 | 0 |

**Table 3.3: Analysis summary for dephosphorization using two acid mixtures (HCl and $H_2SO_4$) for p in filtrate**

phosphorus in filtrate results

Transform: Y' = Y

Factor properties

| Factor | Name | Units | Type | Low Level | High Level | Low Alpha | High Alpha |
|---|---|---|---|---|---|---|---|
| A | concentration | M | Quant | 0.2 | 1 | -0.0727 | 1.2727 |
| B | Dwell time | Mins | Quant | 30 | 60 | 19.7731 | 70.2269 |
| C | particle size | Mm | Quant | 0.2 | 0.4 | 0.1318 | 0.4682 |

**Significant effects at alpha = 0.1:**

| **Name** | **P Value** |
|---|---|
| AC | 0.0499 |
| AA | 0.0214 |
| BB | 0.0239 |
| CC | 0.022 |

Equation in terms of coded values:

| | |
|---|---|
| 4.5318 | |
| +0.0678 | * A:concentration |
| -0.0672 | * B:time dwell |
| -0.0494 | * C:particle size |
| -0.0600 | * AB |
| +0.1225 | * AC |
| +0.0050 | * BC |
| -1.4431 | * AA |
| -1.3954 | * BB |
| -1.4308 | * CC |

Equation in terms of actual values:

| | |
|---|---|
| -23.5767 | |
| +10.5244 | * A:concentration |
| +0.5587 | * B:dwell time |
| +83.3650 | * C:particle size |
| -0.0100 | * AB |
| +3.0625 | * AC |
| +0.0033 | * BC |
| -9.0196 | * AA |
| -0.0062 | * BB |
| -143.0768 | * CC |

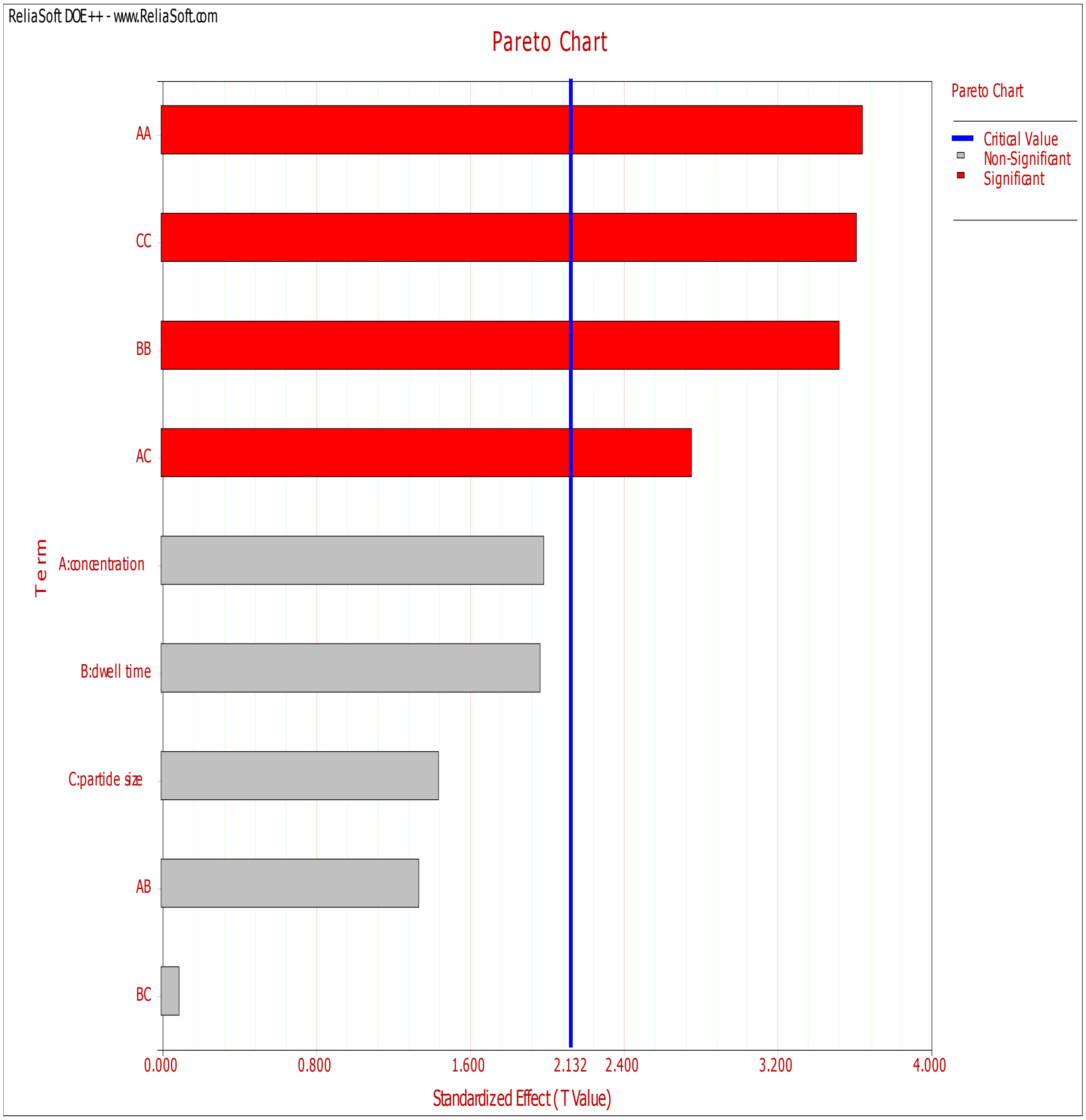

**Fig. 3.1: Pareto chart for dephosphorization using two acid mixtures (HCl and $H_2SO_4$) for P in filtrate.**

From the foregoing, the model equation becomes

$$Y = -23.5767 + 10.5244A + 0.5587B + 83.3650C - 0.0100AB + 3.0625AC + 0.0033BC - 9.0196A^2 - 0.0062B^2 - 143.0768C^2 \quad (2)$$

The corresponding pareto charts, surface plot, contour plot and fitted vs. actual plot are shown in figures 3.1.

In Fig. 3.1: is seen instantly both main effects, interaction effects, and quadratic effects in second order polynomial. Here, the quadratic effects of concentration, $A^2$, particle size $C^2$and time dwell $B^2$,and the interaction effect of AC contribute significantly to the model at 5% with the $A^2$ and $C^2$ being the greatest, while the main effects A,B and C are relatively not significant with C being the least. Also, the interactionAB is not significant comparatively while the least of all is BC.

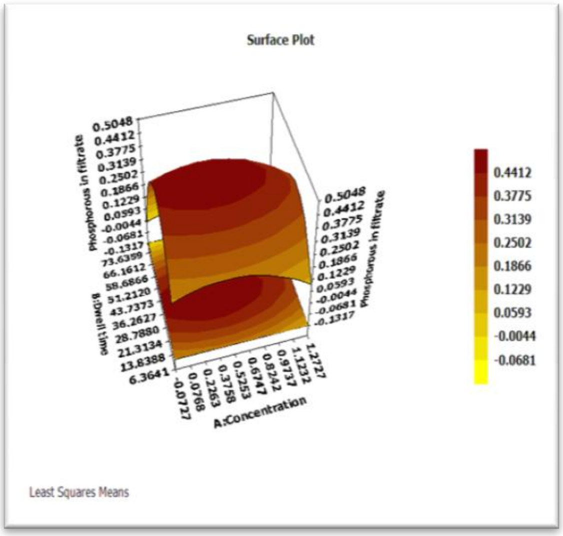

**Fig. 3.2(a)**Surface plot for dephosphorization as a function of concentration and dwell time at constant particle size of 0.3mm

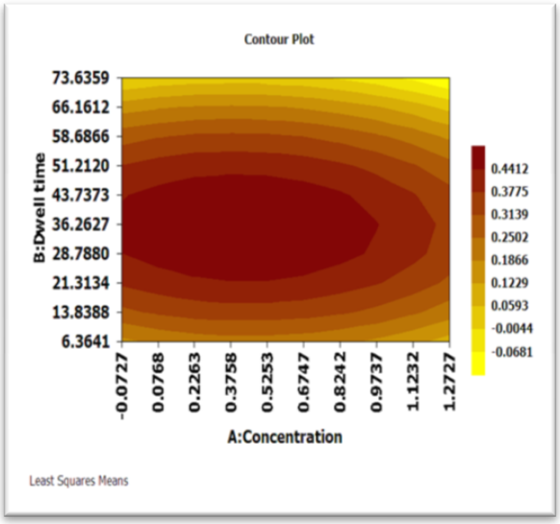

**Fig. 3.2(b)**Contourplot for dephosphorization as a function of concentration and dwell time at constant particle size of 0.3mm

In figures 3.2, it could be observed that dephosphorization of ≤ 0.05 is attained at concentration of about 0.65M and dwell time of about 20mins at particle size of 0.3mm.

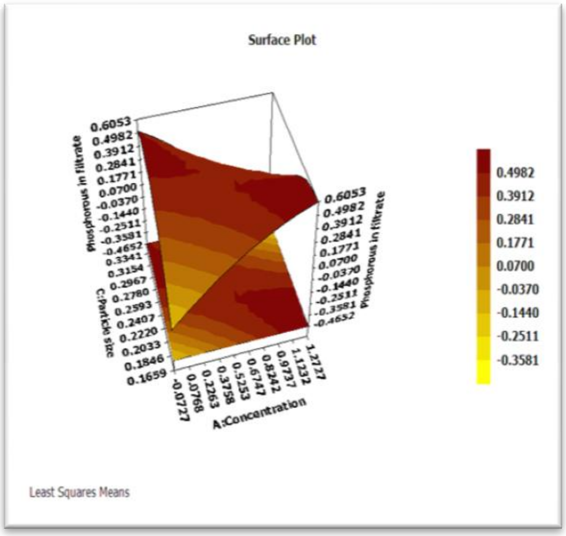

**Figure 3.3(a)**Surface plot of dephosphorization as a function of concentration and particle size at constant dwell time of 45mins.

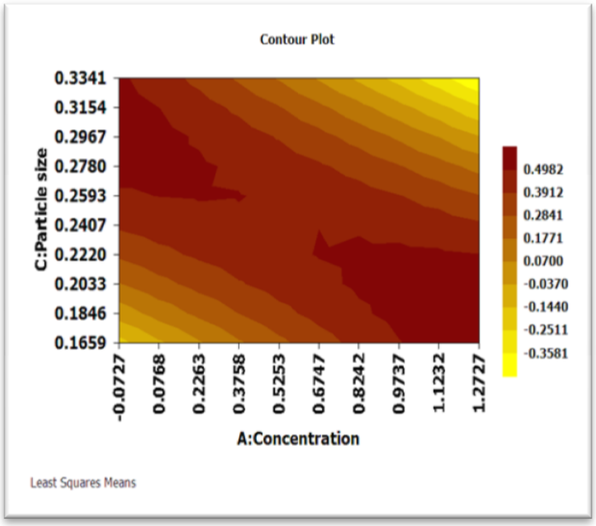

**Figure 3.4(b)**Contour plotof dephosphorization as a function of concentration and particle size at constant dwell time of 45mins.

It could be seen in figure 3.3 that dephosphorization of ≤ 0.5 isattained at concentration of about 0.62M and particle size of about 0.24mm and dwell time of 45minutes.

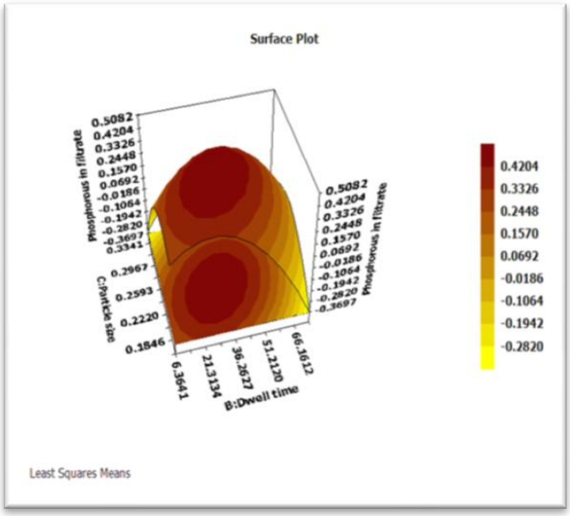

**Figure 3.4(a)** Surface plot of dephosphorization as a function of dwell time and particle size at constant concentration of 0.6M

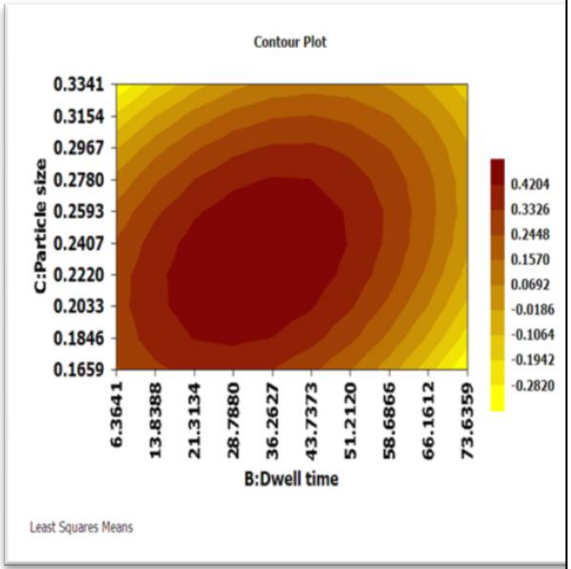

**Fig. 3.4(b)** Contour plot for dephosphorization as a function of dwell time and Particle size at constant concentration of 0.6M

In figure 3.4 is observed that dephosphorization of ≤0.05% is attained at dwell time of about 50minutes and particle size of about 0.27mm and concentration of 0.6M. Therefore, the most appropriate value of the independent parameters from the model to reach dephosphorization of ≤0.05% is concentration of about 0.62M,dwell time of about35minutes and particle size of about 0.27mm. It is pertinent to note that the value of output responses are tied to the intensity of the color of surface plots. The plots provide avenue to observe the surface area of the curve within which the process can perform at optimal level based on the effects of interaction of the variables under consideration. Suffice it to say that without DOE++, the significance of these interactions would have been lost if the experiments were conducted by traditional technique. RSM is necessary in providing precise prediction of responses within the experimental region and identifying optimum conditions.

## 4. CONCLUSION

The optimum value of dephosphorization of about ≤ 0.05% from the model developed within the experimental region of interest is attained at concentration of about 0.6M, dwell time of about 35mins and particle size of about 0.27mm. Consequently, the dephosphorization optimization process has been greatly enhanced by the use of statistically designed experiments. Traditional methods frequently will not find an optimum solution as efficiently as a designed experiment and most notably, without being able to uncover important interaction effects.

## ACKNOWLEDGEMENT

We sincerely thank Prof. Ajiwe V.I of the Department of Industrial Chemistry, NAU who with his laboratory assistants made the experiment possible. My unalloyed thanks goes to Prof. Ofoedu Eric of the Department of Mathematics who assisted me immensely in the statistical analysis. I thank immensely Mr. Stanley Nwakpa who made arduous mathematical calculations easy with this DOE++ software. To countless souls whose names could not be specifically mentioned, I say a huge thanks to you all.

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