Central Composite Design In Optimization Of The Factors Of Dephosphorization Of Agbaja Iron Ore

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ABSTRACT: The purpose of this research effort is to determine the optimal factors for dephosphorization of a Nigerian Agbaja iron ore. The process parameters used in the study of optimization of dephosphorization includes pH, particle size, dwell time. Response Surface Methodology was used in fitting response surface of a second order regression equation $Y=\beta_0+\beta_1A+\beta_2B+\beta_3C+\beta_{12}AB+\beta_{13}AC+\beta_{23}BC+\beta_{11}A^2+\beta_{22}B^2+\beta_{33}C^2+e$. The result indicated that optimum conditions occurred at: pH 1.5, particle size 0.3mm and dwell time 60 minutes.

Keywords: Central Composite Design, Response Surface Methodology, Dephosphorization, Iron Ore, Concentration And Particle Size.

1. INTRODUCTION

The Nigerian proven iron ore deposit estimated at about 1.25 billon metric tons [Amadi, et al,1982,Uwadiale, 1991]with about 47.5%Fe is of high phosphorus content estimated variously as 0.76 0.86%[Anyakwo,Obot,2010] or 1.4 2.0%[Obiorah et al,2011]. Gainfull exploitation of this largest deposit anxiously awaits the dawn of a demonstrable means of economical removal of phosphorus to an acceptable level. Since phosphorus beyond the threshold of 0.08% is untradeable (Cheng et al,199, Dukino et al 2000), it follows that the Nigerian Agbaja iron ore is currently unmarketable until a means of reducing it to acceptable level (0.03-0.045%) is achievable. Agbaja iron ore is also of low silicon modulus $(SiO_2 /Al_2O_3 =0.89)$ 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 occurs 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 temperatures. 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 (kokal, 1990). 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),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 phosphorus removal of 96% at 0.3M leachant concentration, 30 minutes contact time and 1.2 dilution ratio. In the present study, the feasibility of further improving dephosphorization of Agbaja iron ore by leaching with two acid mixtures (H_2SO_4 and HCl) at different predetermined P^H levels, various ranges of particle size and contact time on one hand and optimization of process parameters and response variable on the other were investigated. Response surface designs are used to obtain precise information about factor effects including magnitude and direction. The number of factors is typically between two and six. It helps us to estimate linear, two factor interaction and nonlinear effects of all factors under study. They are used when there is prior indication of nonlinear behavior. Response Surface designs provide precise prediction of response within the experimental region and are useful in identifying optimum conditions (Oehlert and Gary, 2000; Montgomery and Douglas, 2005)

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 presentwithinthe iron ore were determined by atomic absorption spectrophotometry and titrimetric analysis.

2.3 Experimental Design
Design of experiment employing Response Surface Methodology, RSM of central composite design 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 ramdomly experimental runs and responses are shown in tables 2.1and 2.2

Table 2.1: Factor level of independent for dephosphorization using HCl and H_2SO_4 mixtures at predetermined pH

Variables	Lower Limit(-1)	Base level(0)	Upper limit(1)
Molar concentration M	0.8	2	3.2
Dwell time,mins	60	90	120
Particle Size,mm	0.2	0.3	0.4

Table 2.2: Full factorial experimental design of HCl and H_2SO_4 mixtures at predetermined pH

Independent variables				Responses P in filtrate (%)		
S/N	X1	X2	X3	Y1	Y2	Y
1	-1	-1	-1	0.02	0.04	0.03
2	1	-1	-1	0.03	0.05	0.04
3	-1	1	-1	0.04	0.06	0.05
4	1	1	-1	0.07	0.09	0.08
5	-1	-1	1	0.08	0.1	0.09
6	1	-1	1	0.09	0.11	0.1
7	-1	1	1	0.1	0.12	0.11
8	1	1	1	0.11	0.13	0.12
9	-1	0	0	0.05	0.07	0.06
10	1	0	0	0.08	0.1	0.09
11	0	-1	0	0.62	0.64	0.63
12	0	1	0	0.08	0.1	0.09
13	0	0	-1	0.65	0.07	0.06
14	0	0	1	0.08	0.1	0.09

2.4 Chemical preparation of leaching solutions

All leaching chemicals used were of laboratory grade, procured from Bridge Head Chemical market, Onitsha, Nigeria. Predetermined pHlevels of 0.8, 2.0 and 3.2 leaching solutions of mixtures of H_2SO_4 and HCl were prepared using buffer solution. Also, particle size ranges of 0.2mm, 0.3mm and 0.4mm were prepared in a standard shaker sieve at CVE laboratory, NnamdiAzikiwe University, Awka

2.5 Chemical Leaching Procedure

All leaching experiments were conducted in 250ml Erlenmeyer flasks. Briefly, for the first sample, a mixture of 20ml H_2SO_4 and HCL of predetermined pH was poured into a flaskcontaining 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 as in the design matrix at a temperature of about 60^oC. At the end of each leaching operations, 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 ^{o} C for 24 hours and stored in a dry environment for analysis. The respective leached liquors too were stored in flasks for analysis.

3.0 RESULTS AND DISCUSSION

The results of the experiments are presented in table (3.1) and figures (3.1) to 3.8. The chemical composition of Agbaja Iron ore is presented in Table 3.1.

Table 3.1: Chemical composition of Agbaja iron ore

Fe (Total)	47.37
Fe_2O_3	64.87
SiO_2	7.66
CaO	0.17
Al_2O_3	8.20
MgO	0.97
P_2O_5	1.70
S	0.05
LO_1	14.20

The chemical analysis of the ore sample (Table 4.1) shows that it is mainly hematite. Low silicon modulus (SiO_2/ Al_2O_3) of 0.93 and high phosphorus content of 1.70% which is untreatable (Jian and Sharma, 2004). Since the phosphorus contained in the iron ore concentrate is in non-sulphidic phase, the contaminant may be solubilized by a process of complexation, using a range of inorganic or organic acids. This is in agreement with the findings of Rawlings (2005). Effects of P^H, contact 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 factional experimental design with 6axial point's (a) and one centre point (n) was used in the study. The factor level of independent variables is shown in table 2.1 while the design matrix is shown in table 2.2 the parameters: P^H, Contact time (B) and particle size (C) was chosen as independent variables at two levels while phosphorus extraction is the output variable. The analysis is focused on how the phosphorus removal is influenced by the independent variables A, B and C. The range of independent variables is shown in table 2.1. In order to study the combined effects (interactions) of thesefactors, experiments were performed at different combination of the physical parameters using statistically designed experiment, (DOE++). Upon the determination of polynomial coefficients, statistical analysis (T-Test, P-Test etc) was performed to develop model that is adequate, significant and homogenous. Main effects, interaction effects and quadratic effects and response behaviors are explainedby Regression information, analysis summary and equation (3.1)

Fig.3.1: Normal probability plot lot of effect for dephosphorization using two acid mixtures (H_2SO_4 and HCl) at predetermined pH for p in filtrate.
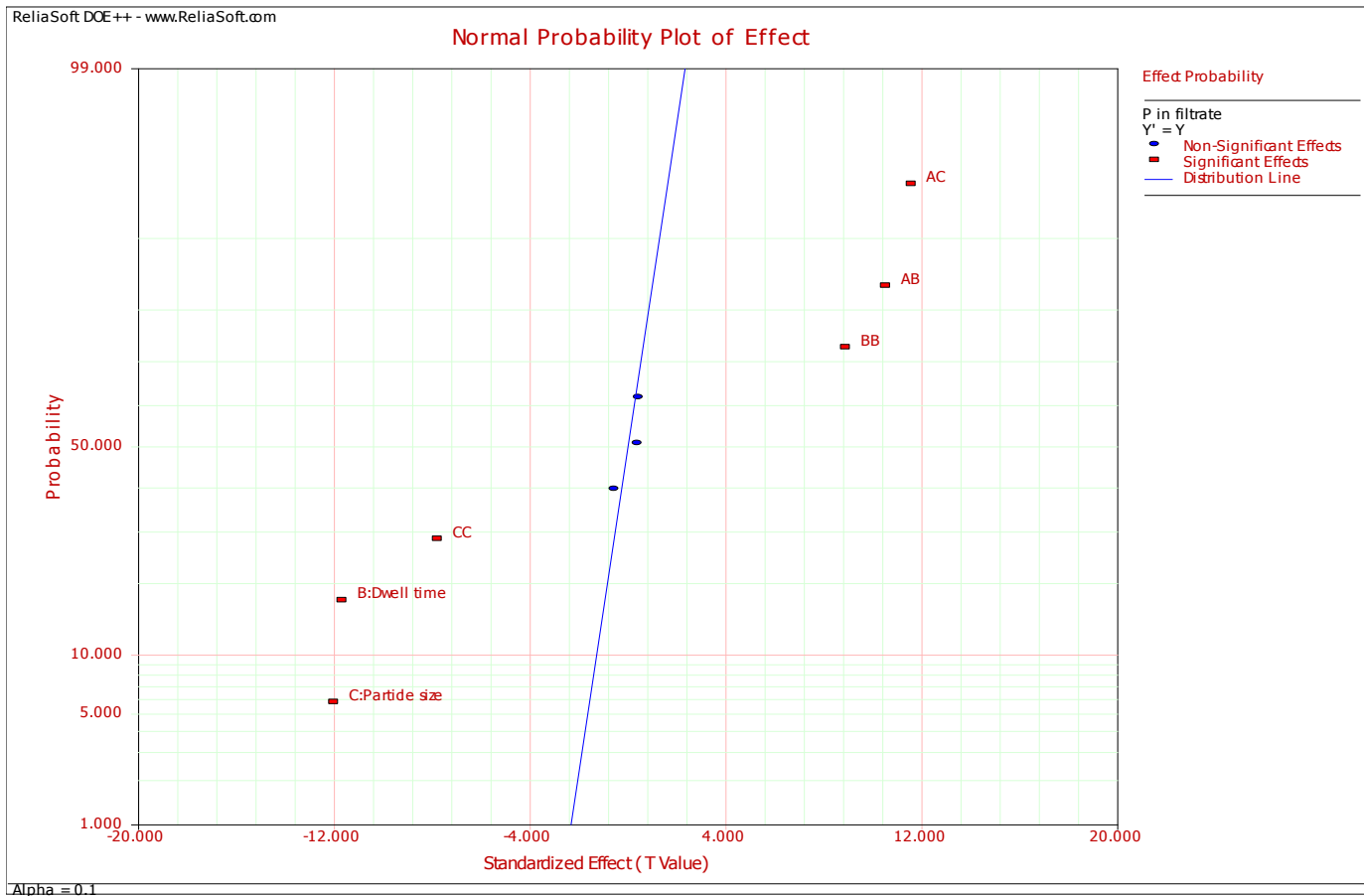
In figure 3.1, in which normality estimate of effects are shown, the statistical significance of both the main and interaction effects are easily seen. Here the interaction AC and main effects C have the largest effect because the lie farthest from the line that marks the non-significant effects.

Transform: Y' = Y

3.1 Factor Properties

Factor	Units	Type	LL	HL	LA	HA
A: pH	0.8	Quant	3.2	-0.0182		4.0182
B: Dwell time	mins	Quant	60	120	39.5462	140.4538
C: Particle size	mm	Quant	0.2	0.4	0.1318	0.4682

Significant Effects at Alpha = 0.1:
Name   P Value

3.2 Equation in terms of coded values:

0.0677
-0.0305 * A:pH
+0.0149 * B:Dwell time
-0.0284 * C:Particle size
-0.0604 * AB
+0.0280 * AC
-0.0205 * BC
-0.0100 * AA

+0.1648 * BB
-0.0518 * CC

Table 3.2: Regression information

Term	Coefficient	Standard Error	Low CI	High CI	T Value	P Value
Intercept	0.0677	0.0684	-0.0781	0.2135	0.99	0.3782
A:pH	-0.0305	0.0562	-0.1503	0.0893	-0.5429	0.616
B:Dwell time	0.0149	0.089	-0.1749	0.2047	0.1673	0.8752
C:Particle size	-0.0284	0.0634	-0.1635	0.1067	-0.4486	0.6769
AB	-0.0604	0.0868	-0.2455	0.1248	-0.695	0.5253
AC	0.028	0.0672	-0.1153	0.1712	0.4161	0.6987
BC	-0.0205	0.0672	-0.1637	0.1228	-0.3045	0.7759
AA	-0.01	0.0402	-0.0957	0.0757	-0.2485	0.816
BB	0.1648	0.0738	0.0076	0.3221	2.2348	0.0891
CC	-0.0518	0.056	-0.1713	0.0676	-0.9255	0.4071

BB   0.0891

3.3 Equation in terms of actual values:

0.8021
+0.0833 * A : pH
-0.0271 * B: Dwell time
+2.9744 * C: Particle size
-0.0017 * AB
-0.0017 * AC
-0.0017 * BC
-0.0017 * AA
+0.0002 * BB
-5.1847 * CC

The equation therefore is $Y = 0.8021+0.0833A-0.0271B+2.9744C-0.0017AB-0.0017AC-0.0017BC-0.0017A^2+0.0002B^2-5.1847C^2$

Note: LL – low level
         HL -   high level
         LA-   low Alpha
         HA-   high Alpha

In figure 3.2, is instantly seen the significant and non-significant effects both of main factor effects and interaction effects and quadratic effects simultaneously of the main effects. It can be seen that particle size and contact time play dominant roles while the pH is least. The interaction factors AC, AB are significant with AC more significant. The quadratic effects of B^2 and C^2 are significant with B^2 being greater while the interaction effect of BC and quadratic effect of A^2 and main effect A are non-significant. These non-significant effects are included in the model to preserve model hierarchy. In figure 3.3, is seen the contribution of the three independent variables of pH, contact time and particle size to dephosphorization process. Here particle size contributes most significantly comparatively, and dephosphorization reaches about 0.08 at pH 0.8 and contact time of 60mins. Fig. 3.4: The interaction plot for dephosphorization using two acid mixtures (H_2SO_4 and HCl) at predetermined pH for p in filtrate. It could be seen in figure 4.23 that dephosphorization optimizes from pH 0.8 to 1.5,and particle size of 0.3mm and reaches a value of about 0.04%. In figure 3.5, the interactions between factors are shown. In the right of the uppermost plot, the interaction AC and AB are seen. in the case of AB, dephosphorization increases initially when the curves move from low level (-1) to high level (1) up to Centre point mean and then increases when the curves move from high (1) to low level (-1) i.e. at pH of about 0.8 and contact time of 60 min and particle size of 0.3,dephosphorization reaches about o.04%,while in the case of AC, beyond the Centre point mean dephosphorization process increases when the curves move from high level (1) to low level(-1)i.e. optimizes at about pH of range 0.8 to 1.5 and particle size of 0.2 to 0.3 at dwell time of about 60minutes and reaches a value of about 0.03%. In the Centre and lower plots, the dephosphorization process records no marked improvements as the interaction are relatively non-significant. In figure 3.6 is seen the ideal optimal solution for dephosphorization (model based only on significant effects) and how the independent variables affect it. Here relatively low pH, high contact time and particle size favor ideal dephosphorization phenomenon. In figure 3.7b as in preceding surface plot dephosphorization is favorable at about pH of 1.7 and particle size of 0.3mm and contact time of 90mins i.e. Dephosphorization is <0.05% at (these ranges) this points In figure 3.8(a) is seen the characteristics of the response surface as relates to two factors at a time. i.e. how dephosphorization process occurs under the influence of pH and dwell time at constant particle size of 0.3mm and under the influence of pH and dwell time at constant particle size of 0.3mm and under the influence of pH and particle size at constant time of 90mins and under the influence of contact time and dwell time at constant pH of 2.Since the morphology of the contour plots are similar only one is hereby presented. Here pH of up to 1.5 and contact time of 65 to 140mins favor dephosphorization.

Fig. 3.2: Pareto chart for dephosphorization using two acid mixtures (H_2SO_4 and HCl) at predetermined pH for p in filtrate
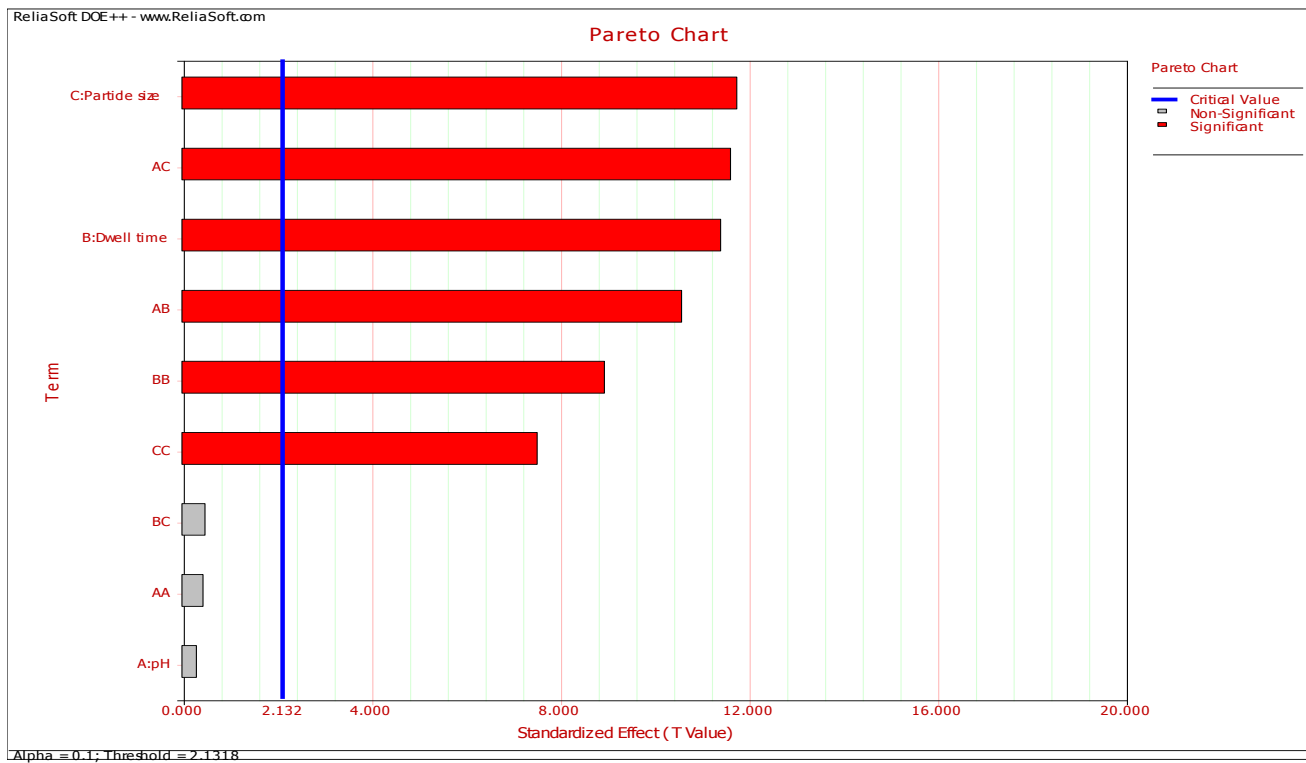

Fig. 3.3: The main effect plot for dephosphorization using two acid mixtures (H_2SO_4 and HCl) at predetermined pH for p in filtrate
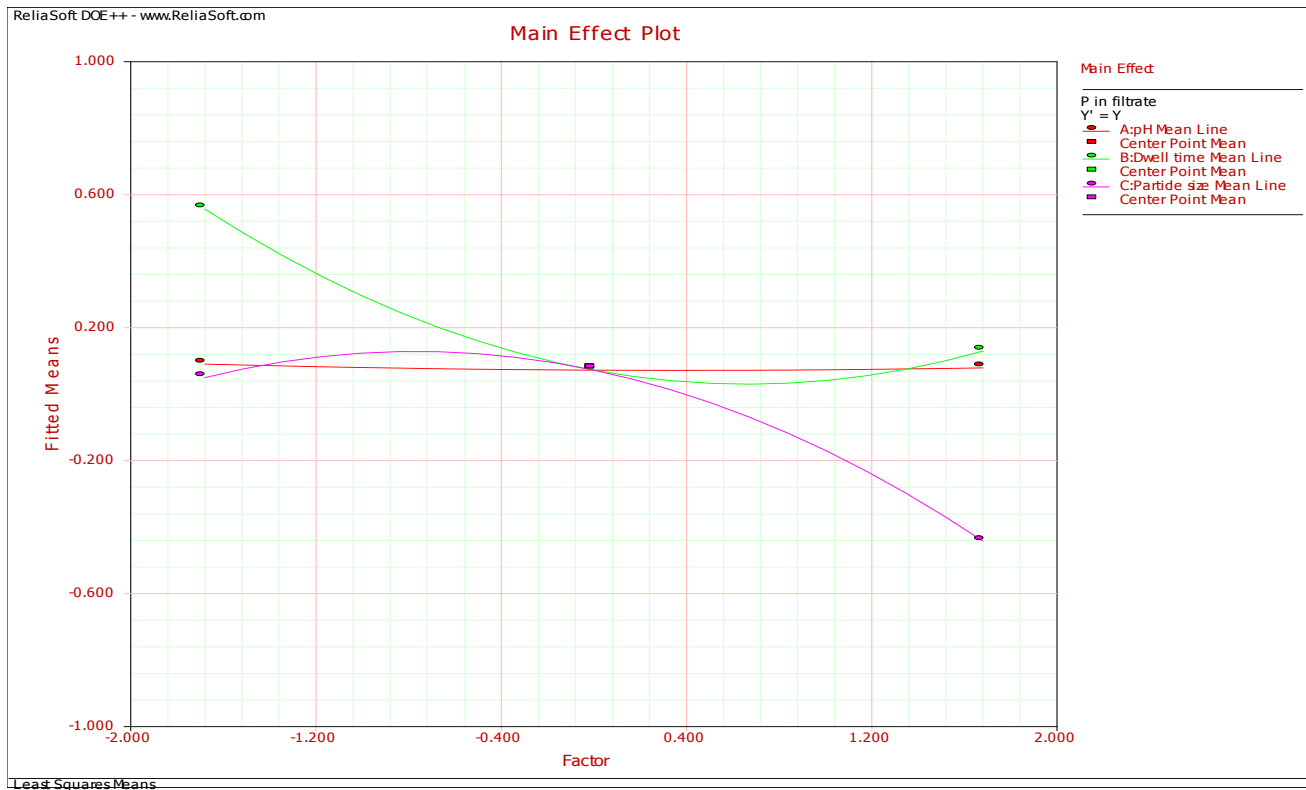

Fig. 3.4: The interaction plot for dephosphorization using two acid mixtures (H_2SO_4 and HCl) at predetermined pH for p in filtrate.
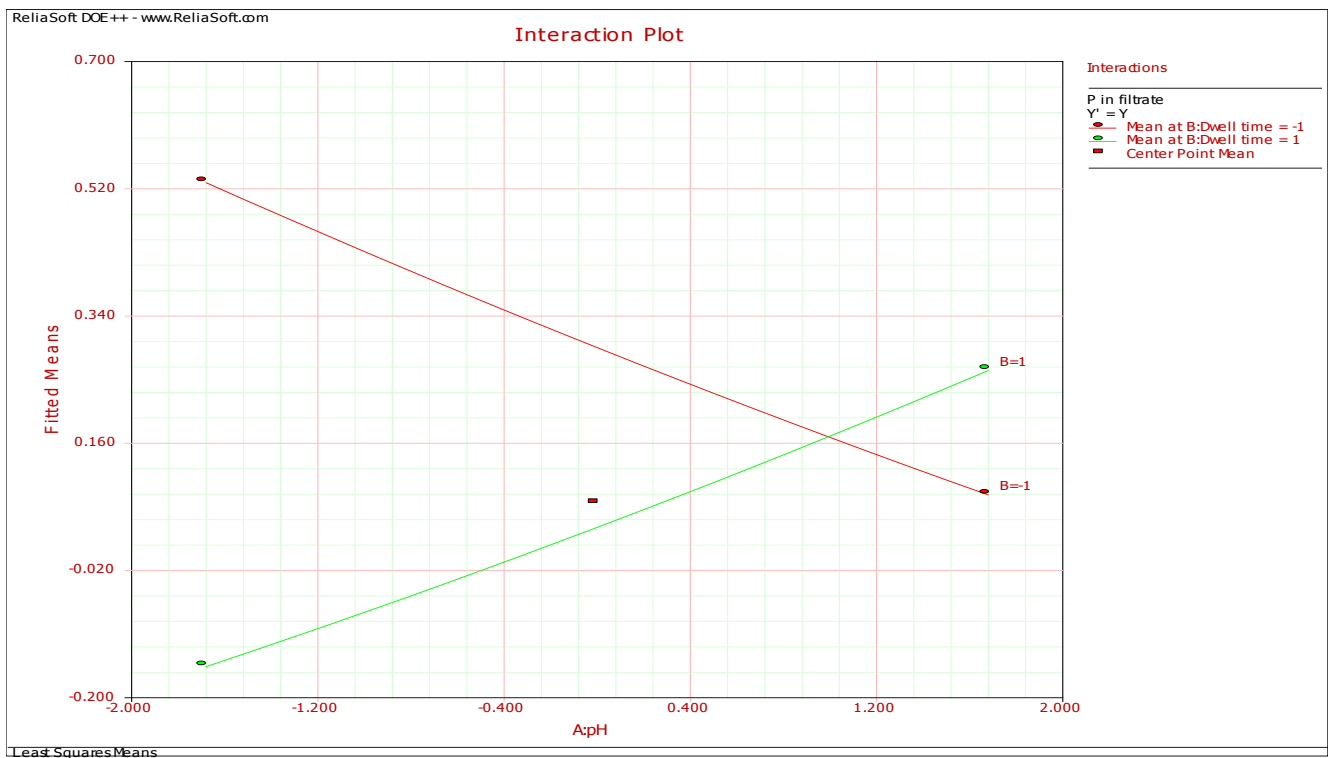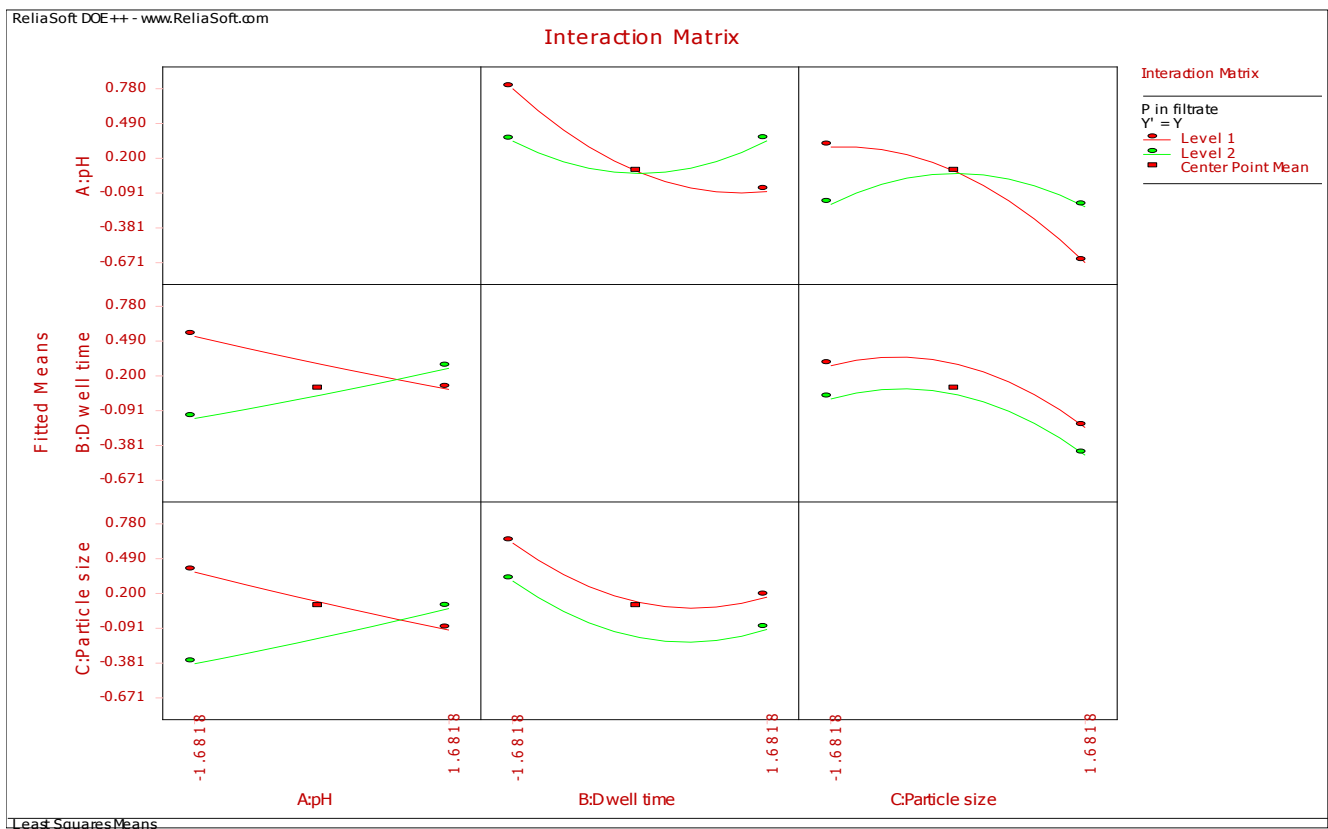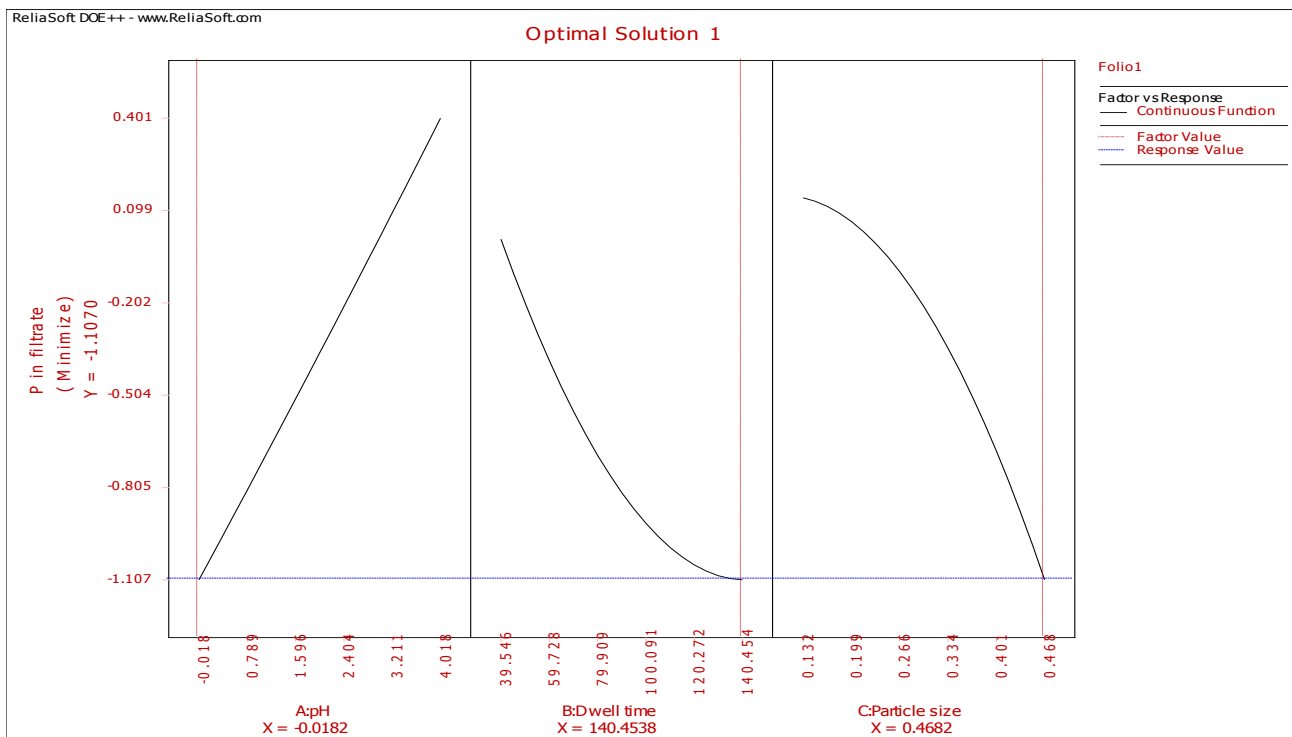
Fig. 3.5: The interaction matrix plot for dephosphorization using two acid mixtures (H_2SO_4 and HCl) at predetermined pH for p in filtrate.

Fig. 3.6: Optimal solution plot for dephosphorization using two acid mixtures (H_2SO_4 and HCl) at predetermined pH for P in filtrate

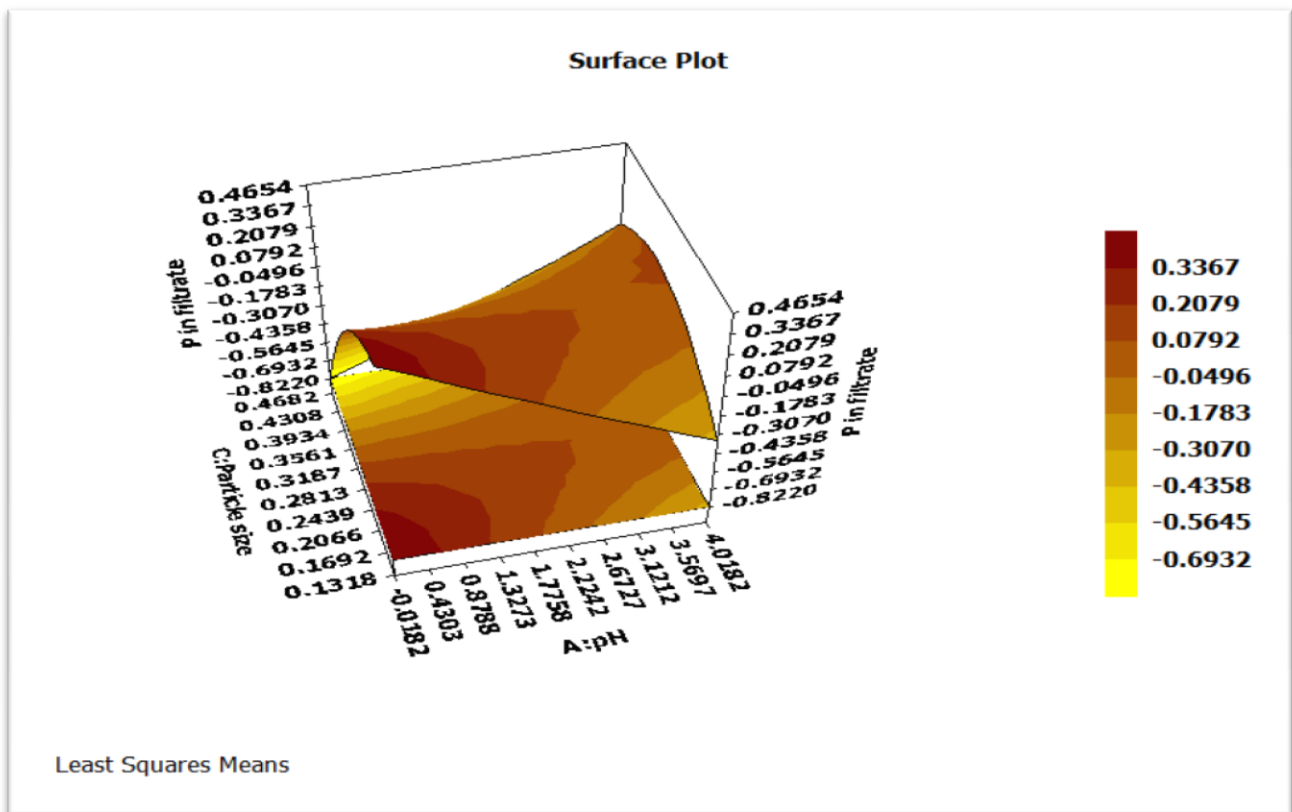**Fig.3.7a:** Surface plot dephosphorization using two acid mixtures (H_2SO_4 and HCl) at predetermined pH for P in filtrate

Fig. 3.7b: Surface plot for dephosphorization using two acid mixtures (H_2SO_4 and HCl) at predetermined pH for P in filtrate
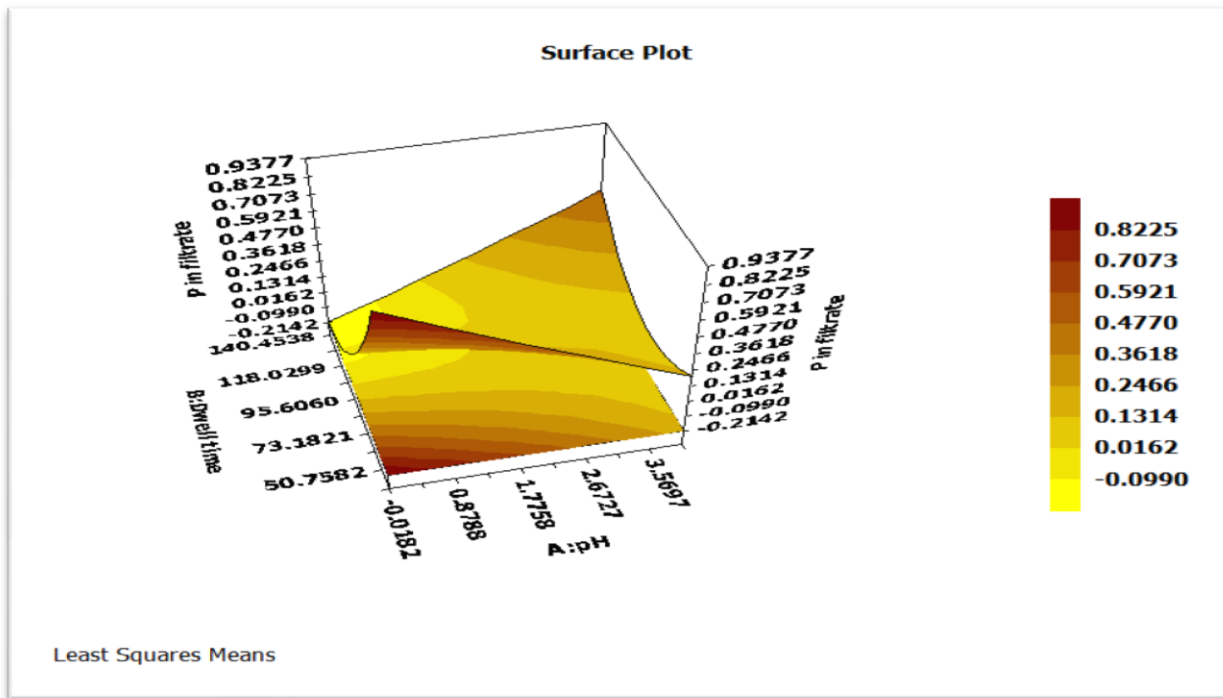
Fig. 3.8a: The contour plot for dephosphorization using two acid mixtures (H_2SO_4 and HCl) at predetermined pH for P in filtrate
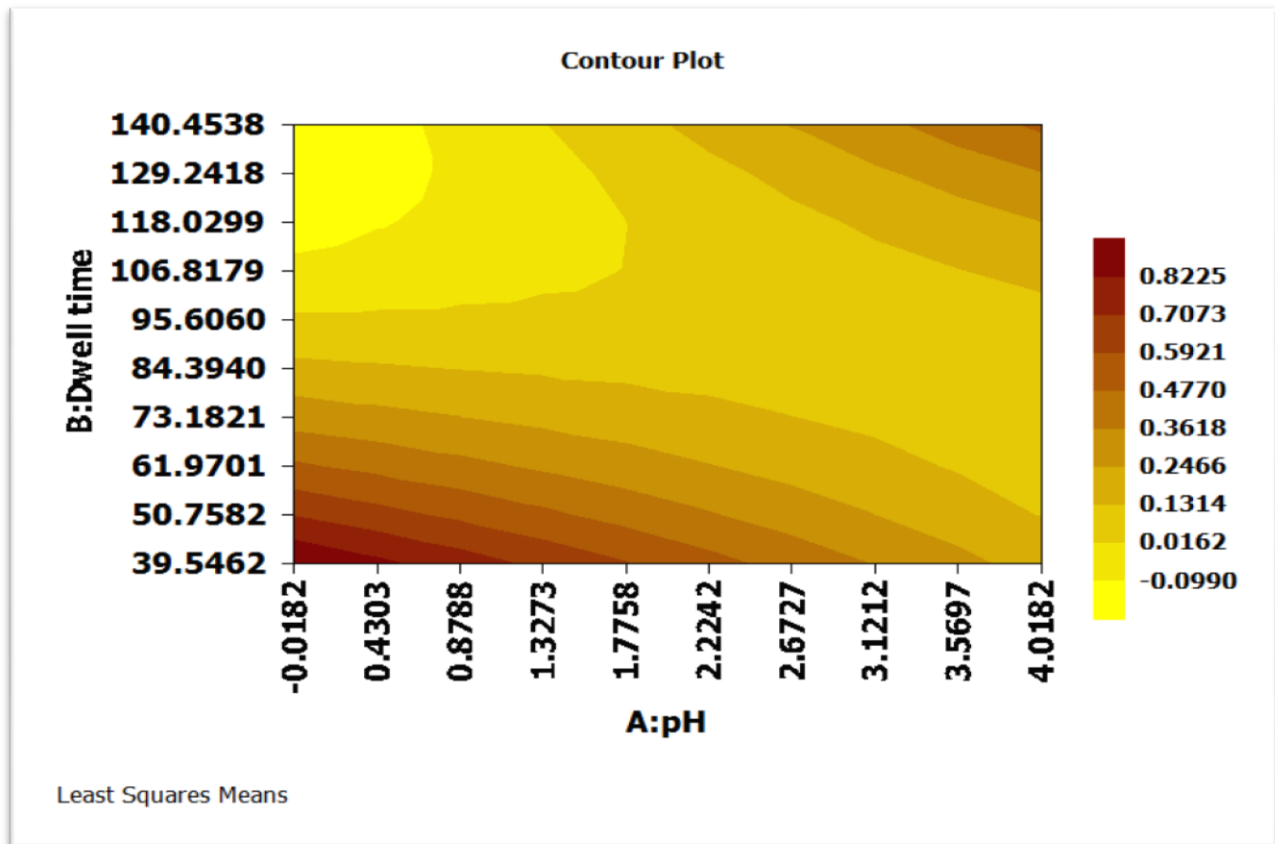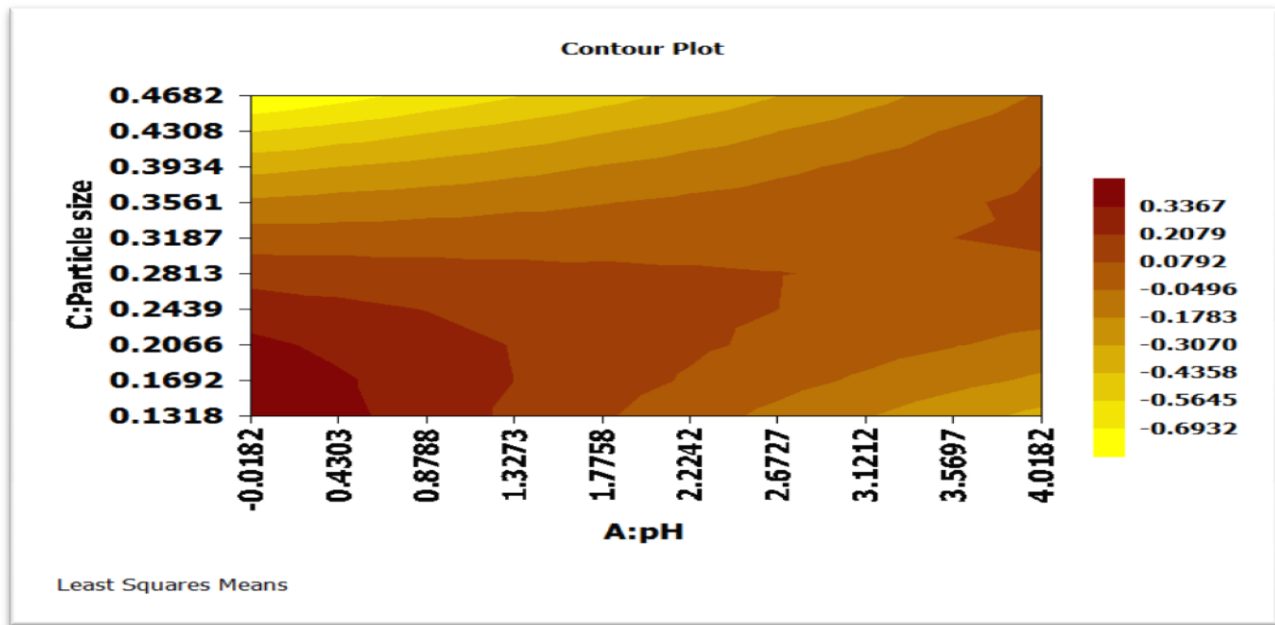

Fig. 3.8b: The contour plot for dephosphorization using two acid mixtures (H_2SO_4 and HCl) at predetermined pH for P in filtrate

Contour Plot

In figure3.8b pH of about 1.5 and particle size of about 0.3mm and dwell time of 90min favor dephosphorization process.

Sample explanation of RSM of central composite design of 2^3 full factorial experiments for dephosphorization of Abgaja iron ore using two acid mixtures (H_2SO_4 and HCl) at predetermined pH values were illustrated. The anova table and regression information from the analysis was first shown. From theses both the significant effects, equations in terms of coded and actual values are seen. The detailed information is as follows:P in filtrate (effect points).

3.4 Main effects:
Main effects (an outcome that is a consistent difference between levels of a factor). The main effect of pH is -1 and when pH is +1 i.e. low and high value and determine the total percentage of phosphorus retained in residue variation in due to pH. In the first case the percentage phosphorus retained in residue at low and high pH value are 0.09 and 0.07 respectively. In the case of dwell time the value is 0.56% and 0.13% respectively. In case of particle size the value obtained is 0.05 and -0.44% respectively. This proves best result comparatively. Next we do the same for dwell time and particle size and compare the phosphorus retained in residue for the three factors. The highest value showed the trouble component or factor that causes higher variation in the percentage phosphorus retained in residue. The main effects are plotted for easier view of the components or factors or elements sensitivities to percentage phosphorus retained in filtrate.

3.4.1 S actual value

P in filtrate (data points)

Points	X	Y
1	0.110	0.130
2	0.100	0.106
3	0.100	0.080
4	0.090	0.091
5	0.060	0.079
6	0.090	0.074
7	0.080	0.072
8	0.050	0.072
9	0.060	0.060
10	0.030	0.050
11	0.040	0.042

Effect probability

Effect	X	Y
AC	11.732	94.444
AB	10.688	83.333
BB	9.053	72.222
CC	-7.626	27.778
B: dwell time	-11.521	16.667
BC	0.582	61.111
AA	0.537	50.000

4.0 CONCLUSION
Main effects, interaction effects and quadratic effects of the parameters and response behavior are explained by equation 3.1 which is adequate, significant and homogeneous within the experimental region. Consequently, optimal dephosphorization of about 0.04% within the experimental space occurred at predetermined P^H of 1.5, dwell time of about 60 minutes and particle size of 0.3 mm.

5.0 ACKNOWLEDGEMENT

6.0 REFERENCES

[1]. Alafara, A. B; Adekola, F.A.O.[2005] Bioline. Journal of Applied Sciences and Environmental Management,vol 9(3),15-20

[2]. Amadi N.J Odunaike, AA and Marthur, G.P (1982) Preliminary Bench Scale Beneficiation stududies with three lumps of iron ore sample from Agbaja. Central Metallurgical Reseach and Development institute Jos, Nigeria.

[3]. AnyakwoC.N, and Obot O.W (2010) Phosphorus Removal Capability of aspergillusTerreus and Bacillus Subtilis from Nigeria's Agbaja iron Ore.US Journal of Minerals and Materials Characterization and Engineering Vol 9 No 12 P1131-1138.

[4]. Dukino,R.D,England, B.M,Kneshaw,M[2000] Phosphorus Distribution in BIF~ derived iron ores of Hamersley Province,WesternAustralia.TransInstn Mineral Metal[sect B,EarthSci]109,B168-B176.

[5]. Fonesca D., Souza C. and Arajuo A.[1994] Hydrometallurgical routes for the reduction of phosphorous in iron ores. In Wilkomirsky I. Sanchez M., Hecker, C. and Sutulov A. Eds. Chemical metallurgical, IV meeting of the Hemisphere on mineral Technology. Universidad de concepcion. Conception-Chile, Vol.III.:83-92.

[6]. Forsberg R. and Asolfesson G.[1981] Dephosphoration of high-phosphorous iron resources by means of acid bleaching, Erzm et al , 34:316-322.

[7]. Hang J., Yang V. and Xie H. A study on the dephosphoration of iron ore by phosphorus dissolving agent accompanied with thiobacillus. Journal of Nanjing Forestry University, 1994: 18(2):25-29.

[8]. He L. and Zhou J. Characteristics of Meishan iron ore with high phosphorous-bearing and feasibility of biodephosphorization. Gold Journal, 2000: 2(1):26-29.

[9]. Kokal H.R. The origin of phosphorous in iron making raw materials and methods of removal. AIME Proceeding, 51st Annual Mining symposium Duluth-Minnesota, January 17-18, 1990:225-258.

[10]. Kokal R., Singh M.T. and Naygyonov V.A. Removal of phosphorous from Lisakogsky Iron Ore by roast-leach process. In Young C.A. *et al.*, Hydrometurlogy, Proceedings of fifth international symposium, 2003.

[11]. Li X. and Wen S. an overview of the present statues of dephosphorization of iron. Metallic ore dressing abroad, 2004:41:4-7.

[12]. Whiteley J. H. The Dephosphorization of iron in the basic furnace.Proc.CleavelandInstn. Engr., 1923:59: 36-55.

[13]. Uwadiale, G.G.O.O Bennficiation Studies of Agbaja Iron Ore, Ph. D thesis University of Strathclyde, June 1984, 341 PP.

[14]. Uwadiale, G.G.O.O and Nwoke, M.A.U, beneficiation of Agbaja Iron Ore by Reduction Rostiny- Magnetic Setaration Semi Pilot plant Scale-up and Establisment of Residence Point of Phosphorus national Steel Council, MetLLURGICAL Research and Tests Division, Jos, Nigeria,June 1983.

[15]. Montgomery, Douglas C. (2005). Design and Analysis of Experiments Response surface method and designs. New Jersey, John Wiley and Sons, Inc.

[16]. Oehlert, Gary W. 2000. Design and analysis of experiments, Reponse surface design. New York, W.H. Freeman and Company.

[17]. Obiorah, S. M. O., Menkiti, M.C. and Nnuka, E.E (2011) Benefication Processing of Agbaja Iron Ore by Chemical Leaching Technique New York Science Journal Vol4 (5) P22-27.