R. O. Ajemba and O. D. Onukwuli / International Journal of Engineering Research and Applications (IJERA) ISSN: 2248-9622 www.ijera.com
Vol. 2, Issue 5, September- October 2012, pp.732-742

Determination Of The Optimum Dissolution Conditions Of Ukpor Clay In Hydrochloric Acid Using Response Surface Methodology

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ABSTRACT

Ukpor clay was dissolved in solutions of hydrochloric acid to investigate its dissolution rate. Response surface methodology was employed to determine the optimum conditions for the dissolution. The experiments were performed within the ranges of the process variables as mentioned herein: 400 – 800^{0}C for calcination temperature; 0.5 – 4 mol/L for acid concentration; 0.02 – 0.10 g/ml for clay to acid ratio; 60 – 120^{0}C for reaction temperature; and 90 to 720 rpm for stirring speed. The analysis of variance indicated that a second order polynomial regression equation was appropriate for fitting the experimental data. The experimental confirmation tests showed a correlation between the predicted and experimental response values (R^2 = 0.9400). The optimum conditions for the process variables were obtained as: 668^{0}C for calcination temperature; 2.93mol/l for acid concentration; 0.027g/ml for clay to acid ratio; 107^{0}C for reaction temperature; and 368rpm for stirring speed. Under these conditions the dissolution rate was 97.85%.

Keywords: Optimization; calcination; dissolution; hydrochloric acid; ANOVA; clay

1. INTRODUCTION

Clay dissolution in acid medium is gaining serious academic attention in the recent time. This is as a result of the need of a low cost source of metallic ores. Clay is a well known aluminous and siliceous material from which the metallic ions can be replaced by the hydrogen ions from inorganic acids. Metallic ions such as Al^{3+}, Fe^{3+}, Mg^{2+}, and sometimes Mn^{2+} can be extracted from the clay mineral by dissolution in acid mediums. Dissolution of various metal ores in different acidic media has been investigated by a great number of authors [1 – 7]. Depending on the extent of acid dissolution, the resulting solid product contains unaltered layers and amorphous three-dimensional cross-linked silica, while the ambient acid solution contains ions according to the chemical composition of the clay and acid used. The extent of the dissolution reaction depends on both clay mineral type and reaction conditions, such as the acid/clay ratio, acid concentration, time and temperature of the reaction [8 – 10].

Most of the reports in the literature on dissolution of ores in acidic media were conducted using the conventional method of investigation, by varying one factor whilst maintaining all other factors constant. This conventional method is cumbersome and time consuming and has low efficiency when it comes to optimizing the process [11, 12]. Process factors do interact with each other, but this interaction cannot be investigated using the conventional method. Response surface methodology (RSM) technique helps in overcoming the limitations of the conventional method of analysis. The main objective of RSM is to check the optimum operational conditions for a given system and determine a region that satisfies the operational specifications [13]. It helps in obtaining a second-order polynomial prediction equation or some other mathematical equations to describe the experimental data obtained at some particular combinations of the input variables.

In this work, the determination of the optimum extraction of Al^{3+} ion which is one of the most important metal ores present in clay minerals and can be extracted by dissolution is the target. The clay mineral from Ukpor will be calcined before dissolution in hydrochloric acid and RSM will be used to optimize the dissolution parameters, thereby ensuring high dissolution efficiency and determining the interactive effects of the calcination temperature, reaction temperature, acid concentration, particle size, clay/acid ratio, and stirring speed on the dissolution process.

2. MATERIALS AND METHODS

The clay samples from Ukpor was mined from the region and separated from dirt that contaminated them. The mined clay was wet and was sun-dried for three days after which the dried sample was grinded with mortar and sieved with 75µm sieve size. The sieved samples were then calcined in a furnace with a temperature range of 100^{0}C to 1200^{0}C. The calcination temperature was chosen in the range of 500^{0}C to 800^{0}C for all the samples. The calcination time was also varied between 0.3 to 8 hours. The clay was characterized

with X-ray fluorescence to ascertain the chemical composition.

2.1. Dissolution experiment

The calcined samples were then ground and sieved into various particle sizes and labeled accordingly. For each experiment, 10 g of the sized fractions was weighed out and reacted with already determined volume of the acids in a 250 ml bottomed flask. The flask and its contents were heated to a fixed temperature of 70^0C while on a magnetic stirring plate and stirring was continued throughout the reaction duration. Also the reactor was fitted with a condenser to prevent losses by evaporation. After the reaction time was completed, the suspension was immediately filtered to separate un-dissolved materials, washed three times with distilled water. The resulting solutions were diluted and analyzed for aluminum ion using MS Atomic Absorption Spectrophotometer. The residue was also collected, washed to neutrality with distilled water, air dried and oven dried at 60^0C and then reweighed. The difference in weight was noted for determining the fraction of the alumina ore that dissolved.

2.2. Design of Experiment

The process variables affecting the dissolution of Ukpor clay in sulphuric acid were investigated using RSM combined with five-level, five-factor fractional factorial design as established by Design Expert software (8.0.1 trial version). The process variables were calcination temperature of 500 – 800^0C, reaction temperature of 60 – 120^0C, acid concentration of 0.5 – 4mol/l, solid/liquid ratio of 0.02 – 0.10g/ml, and stirring speed of 90 – 720rpm. The response variable was chosen as % yield of alumina. The factor levels were coded as –α, - 1, 0, +1 and +α. The range and levels are shown in Table 1.

A total of 31 runs were carried out to optimize the process variables and experiments were performed according to the actual experimental design matrix shown in Table 2. The experiments were performed randomly to avoid systemic error. The results were analyzed using the coefficient of determination, analysis of variance (ANOVA), and response plots. In RSM, the most widely used second-order polynomial equation developed to fit the experimental data and identify the relevant model terms may be written as:

$$Y = \beta_0 + \sum\beta_i x_i + \sum\beta_{ii} x_{ii}^2 + \sum\beta_{ij} x_i x_j + \varepsilon \quad (1)$$

Where Y is the predicted response variable, in this study the % yield of alumina, β_0 is the constant coefficient, β_i is the ith linear coefficient of the input variable x_i, β_{ii} is the ith quadratic coefficient of the input variable x_i, β_{ij} is the different interaction coefficients between the input variables x_i and x_j, and ε is the error of the model.

Table 1: Experimental range of the independent variables, with different levels, to study alumina production during the dissolution of local clays in sulphuric, hydrochloric, and nitric acids

Independent variable	Symbol	Range and levels				
		-α	-1	0	+1	+α
Calcination temp (^{0}C)	X_1	350	500	650	800	950
Leaching temp. (^{0}C)	X_2	30	60	90	120	150
Acid Conc. (mol/l)	X_3	-1.25	0.5	2.25	4.0	5.75
S/L Ratio (g/l)	X_4	0.01	0.02	0.03	0.04	0.05
Stirring Rate (rpm)	X_5	-225	90	315	720	1035

Table 2: Experimental design/plan for alumina leaching from local clays

Run order	Calcin Temp (^{0}C), X_1		Leach Temp (^{0}C), X_2		Acid Conc. (mol/l), X_3		Solid/Liquid Ratio (g/l), X_4		Stirring Speed (rpm), X_5		% Yield	
	Coded	Real	Coded	Real	Coded	Real	Coded	Real	Coded	Real	Exp.	Pred.
1	-1	500	-1	60	-1	0.5	-1	0.02	+1	720	34.8	36.3
2	+1	800	-1	60	-1	0.5	-1	0.02	-1	90	57.8	54.4
3	-1	500	+1	120	-1	0.5	-1	0.02	-1	90	42.6	41.0
4	+1	800	+1	120	-1	0.5	-1	0.02	+1	720	65.0	63.7
5	-1	500	-1	60	+1	4.0	-1	0.02	-1	90	39.6	40.5
6	+1	800	-1	60	+1	4.0	-1	0.02	+1	720	55.4	56.5
7	-1	500	+1	120	+1	4.0	-1	0.02	+1	720	50.7	53.6
8	+1	800	+1	120	+1	4.0	-1	0.02	-1	90	67.0	65.0
9	-1	500	-1	60	-1	0.5	+1	0.04	-1	90	33.7	31.0
10	+1	800	-1	60	-1	0.5	+1	0.04	+1	720	37.5	35.1
11	-1	500	+1	120	-1	0.5	+1	0.04	+1	720	40.2	39.6
12	+1	800	+1	120	-1	0.5	+1	0.04	-1	90	59.0	53.5
13	-1	500	-1	60	+1	4.0	+1	0.04	+1	720	44.9	46.7

14	+1	800	-1	60	+1	4.0	+1	0.04	-1	90	47.6	44.5
15	-1	500	+1	120	+1	4.0	+1	0.04	-1	90	45.3	44.0
16	+1	800	+1	120	+1	4.0	+1	0.04	+1	720	66.0	65.0
17	-2	350	0	90	0	2.25	0	0.03	0	405	43.0	40.4
18	+2	950	0	90	0	2.25	0	0.03	0	405	60.0	66.7
19	0	650	-2	30	0	2.25	0	0.03	0	405	46.0	47.0
20	0	650	+2	150	0	2.25	0	0.03	0	405	64.0	67.1
21	0	650	0	90	-2	-1.25	0	0.03	0	405	44.0	49.9
22	0	650	0	90	+2	5.75	0	0.03	0	405	67.0	65.2
23	0	650	0	90	0	2.25	-2	0.01	0	405	57.4	56.2
24	0	650	0	90	0	2.25	+2	0.05	0	405	38.0	43.3
25	0	650	0	90	0	2.25	0	0.03	-2	-225	34.0	41.2
26	0	650	0	90	0	2.25	0	0.03	+2	1035	50.0	46.9
27	0	650	0	90	0	2.25	0	0.03	0	405	71.0	69.4
28	0	650	0	90	0	2.25	0	0.03	0	405	69.0	69.4
29	0	650	0	90	0	2.25	0	0.03	0	405	70.0	69.4
30	0	650	0	90	0	2.25	0	0.03	0	405	70.0	69.4
31	0	650	0	90	0	2.25	0	0.03	0	405	71.0	69.4

3. RESULTS AND DISCUSSIONS

3.1. Characterization

The results of the X-ray fluorescence analysis are shown in Table 3. The results show that Ukpor clay is composed of mainly silica, alumina and iron oxides, and other trace oxides like calcium oxide, magnesium oxide, titanium oxide, potassium oxide and others.

Table 3: Chemical composition of Ukpor clay determined by XRF

Chemical constituent	Composition (%)
Al_2O_3	26.9
SiO_2	48.6
Fe_2O_3	17.13
CaO	0.08
MnO	0.003
MgO	0.329
P_2O_5	0.2
TiO_2	2.06
V_2O_5	0.14
CuO	0.064
ZnO	0.008
Rb_2O	1.15
Loss on ignition (LOI)	3.05

3.2. Statistical Analysis

The second-order model tested at the 95% confidence level obtained for extraction of Al_2O_3 from Ukpor clay is as follows:

$$Y_{Al2O3} = 69.37 + 6.56X_1 + 5.02X_2 + 3.83X_3 - 3.23X_4 + 1.41X_5 + 2.06X_1X_2 - 0.78X_1X_3 - 1.97X_1X_4 - 1.05X_1X_5 - 0.09X_2X_3 + 0.57X_2X_4 + 0.88X_2X_5 + 1.31X_3X_4 + 2.07X_3X_5 + 0.26X_4X_5 - 3.95X_1^2 - 3.08X_2^2 - 2.95X_3^2 - 4.90X_4^2 - 6.33X_5^2 \quad (3)$$

The results were analyzed by using ANOVA i.e. analysis of variance suitable for experimental design used and shown in Table 4. The ANOVA of the quadratic regression model indicates that the model is significant. The model F-value of 7.83 implied the model to be significant. Model F-value was calculated as ratio of Adj. mean square of the regression and Adj. mean square of the residual. The model P-value (Prob. > F) is very low which reiterates the model significant. The P-values were used as a tool to check the significance of each of the model coefficients. These values are all given in Table 3. The smaller the P-value the more significant is the corresponding coefficient. Values of $P < 0.05$ indicate the model terms to be significant. In Table 3, the values of P for the coefficients estimated indicate that among the tested variables used in the design, X_1, X_2, X_3, X_4, X_1^2, X_2^2, X_3^2, X_4^2 and X_5^2 (where X_1 = Calcination temperature, X_2 = leaching temperature, X_3 = acid concentration, X_4 = stirring rate, and X_5 = liquid/solid ratio,) are significant model terms. The model equation with the significant coefficients is shown in Equation (4).

$$Y = 69.37 + 6.56X_1 + 5.02X_2 + 3.83X_3 - 3.23X_4 - 3.95X_1^2 - 3.08X_2^2 - 2.95X_3^2 - 4.90X_4^2 - 6.33X_5^2 \quad (4)$$

In terms of the actual factors the model equation is as follows:

$$\%\ Yield_{Al2O3} = -30.96 + 0.09 * \text{Calcination temperature} + 0.60 * \text{leaching temperature} + 6.53 * \text{acid concentration} + 0.05 * \text{Stirring rate} - 5.08 * \text{Calcination temperature}^2 - 3.07 * \text{Leaching Temperature}^2 - 1.16 * \text{Acid Concentration}^2 - 4.04 * \text{stirring rate}^2 - 35355.45 * \text{Solid/Liquid ratio}^2 \quad (5)$$

The coefficient of regression (R^2), calculated as the ratio of the regression sum of squares to the total sum of squares, was found to be 0.9400, this indicates that 94.00% of the variability in the yield data is explained by the regression model, showing a very good fit of the model. The S-value of 0.2471 and R-Sq (adj.) value of 0.8200 indicates a better fitting model. S is the square root of the error mean

square, MS_E, and represents the "standard error of the model" and a lower value of S indicates a fitting model. R-Sq (adj.) indicates how well the model fits the observed data.

Table 4: ANOVA for response surface quadratic model

Source	Coefficient Estimate	Sum of Squares	Degree of Freedom	F-value	P-value (Prob. > F)
Model	69.37	4531.55	20	7.83	< 0.000
X_1	6.56	326.30	1	59.19	< 0.000
X_2	5.02	225.38	1	40.89	< 0.000
X_3	3.83	308.92	1	56.04	< 0.006
X_4	-3.23	46.42	1	8.42	0.015
X_5	1.41	118.71	1	21.53	0.227
X_1X_2	2.06	0.48	1	0.086	0.157
X_1X_3	-0.78	4.58	1	0.83	0.574
X_1X_4	-1.97	12.63	1	2.29	0.174
X_1X_5	-1.06	8.72	1	1.58	0.450
X_2X_3	-0.09	13.13	1	2.38	0.946
X_2X_4	0.57	0.26	1	0.048	0.681
X_2X_5	0.88	0.11	1	0.020	0.527
X_3X_4	1.31	0.0028	1	0.0005	0.354
X_3X_5	2.07	0.69	1	0.13	0.155
X_4X_5	0.26	6.39	1	1.16	0.853
X_1^2	-3.95	211.95	1	38.45	< 0.003
X_2^2	-3.08	392.53	1	71.21	< 0.013
X_3^2	-2.95	644.27	1	116.88	< 0.015
X_4^2	-4.90	825.83	1	149.81	< 0.000
X_5^2	-6.33	641.06	1	116.29	< 0.000
Residual		289.43	10		
Lack of fit		286.63	6	68.25	< 0.001
Pure Error		2.80	4		
Cor. Total		4820.98	30		

Std Dev. = 2.34; Mean = 52.95; C.V.% = 3.57; PRESS = 590.63; R^2 = 0.9400; Adj. R^2 = 0.8200; Predicted R^2 = 0.8006; Adeq. Precision = 17.001; S = 0.2471.

To determine the adequacy of the models depicting the removal of alumina by the dissolution of Ukpor clay in hydrochloric acid, two different tests, i.e. the sequential model sum of squares and the model summary statistics, were conducted. The corresponding results are tabulated in Table 5. The results from the sequential model indicated that the 2FI model did not provide a good description of the experimental data. From the model summary statistics, it can be seen that the "Predicted R^{2}" of 0.8006 was in reasonable agreement with the "Adjusted R^{2}" of 0.8200 for the quadratic model. Furthermore, the quadratic model had maximum "Predicted R^{2}" and "Adjusted R^{2}" values. The afore-mentioned results indicate that the quadratic model provided an excellent explanation for the relationship between the independent variables and the corresponding response.

Table 5: Adequacy of the Model Tested

Source	Sum of squares	Degree of freedom	Mean squares	F-value	P-value	Remarks
Sequential model sum of squares						
Linear	2288.65	5	457.73	15.81	0.000	Significant
2FI	271.85	10	27.19	0.94	0.538	Not significant
Quadratic	1971.05	5	394.21	13.62	< 0.000	Significant
Cubic	119.05	15	7.94	3.20	0.0244	Significant
Source	**Standard Deviation**	**R^2**	**Adjusted R^2**	**Predicted R^2**	**PRESS**	**Remarks**
Model summary statistics						
Linear	6.54	0.3436	0.2578	0.2919	2054.01	Inadequate

						signal
2FI	7.39	0.3802	0.0897	0.1720	2336.00	Inadequate signal
Quadratic	2.35	0.9400	0.8200	0.8006	590.63	Adequate signal
Cubic	1.58	0.9694	0.9086	0.6205	788.48	Inadequate signal

The data were also analyzed to check the correlation between the experimental and predicted dissolution yield (Y %), as shown in Fig. 1. The experimental values were the measured response data for the runs designed by the CCRD model, while the predicted values were obtained by calculation from the quadratic equation. It can be seen from Figure 1 that the data points on the plot were reasonably distributed near to the straight line (R^2 = 0.9400), indicating a good relationship between the experimental and predicted values of the response, and that the underlying assumptions of the above analysis were appropriate.

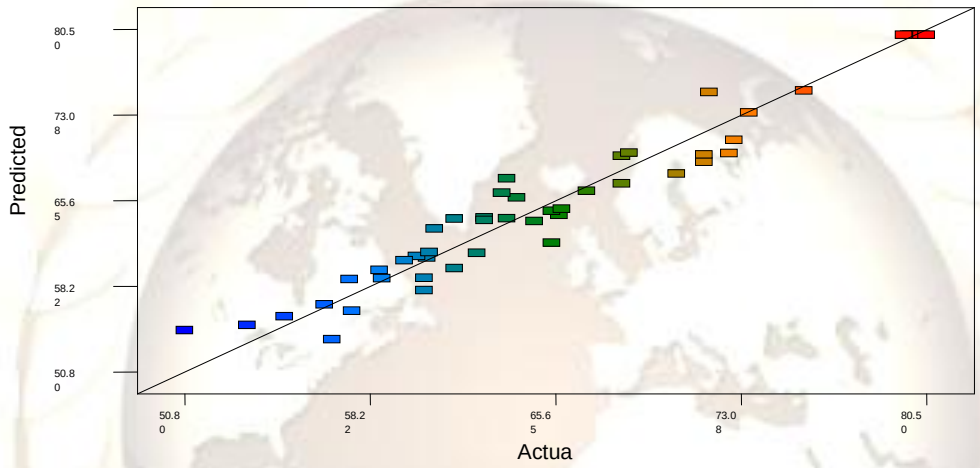

Figure 1: Predicted values versus the experimental values.

The main effects of the process variables on the response variable are plotted in Fig. 2. The figure shows that increasing the calcination temperature, leaching temperature, and acid concentration increases the % yield, while solid/liquid ratio and stirring speed has no statistical significant effect on the response and should be held constant at the center values.

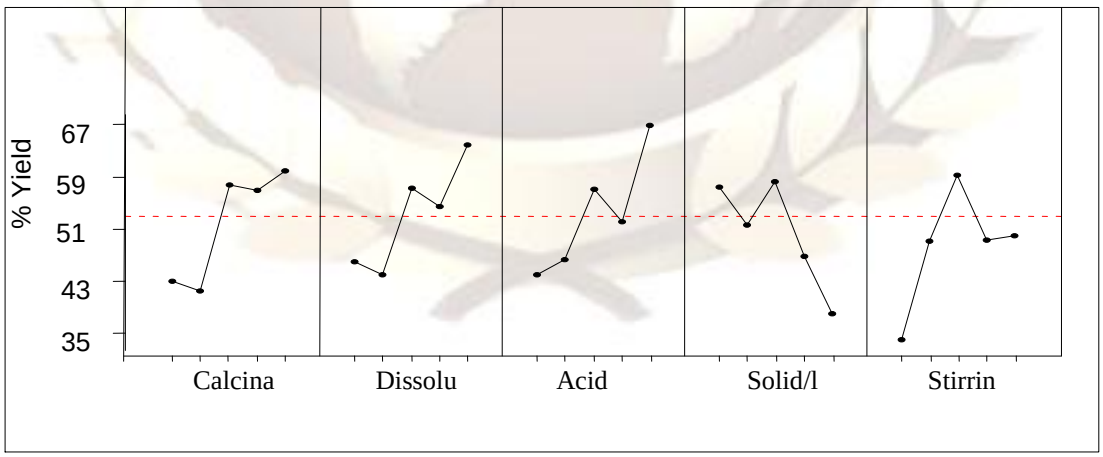

Figure 2: Main effects plot of the process variables.

3.3. Response surface plots

The three-dimensional response surface plots, obtained as a function of two factors maintaining all other factors constant at the mid-values, are helpful in understanding both the main effects and the interaction effects of these

five factors. The corresponding contour plots, represented by the projection of the response surfaces in the x-y plane, provide a straightforward determination of the effects of the independent variables on the dependent variable. The three-dimensional response surface plots and related contour plots obtained are depicted in Figs. 3 to 14. Fig. 3 shows the dependency of alumina yield on calcination temperature and leaching temperature. Alumina yield increased with increase in calcination temperature to about 730^0C and thereafter yield remained constant with further increase in Calcination temperature, this is in agreement with the findings of Ata et al, [14]. The same trend was observed in Figs. 4 to 6. Increase in leaching temperature resulted in increase in alumina yield up to 107^0C and thereafter decreased gradually. This is evident from Figs. 4, 7, 8 and 9. Low levels of solid/liquid ratios resulted in higher % yield as shown in Figs. 6, 9, 11, and 12.

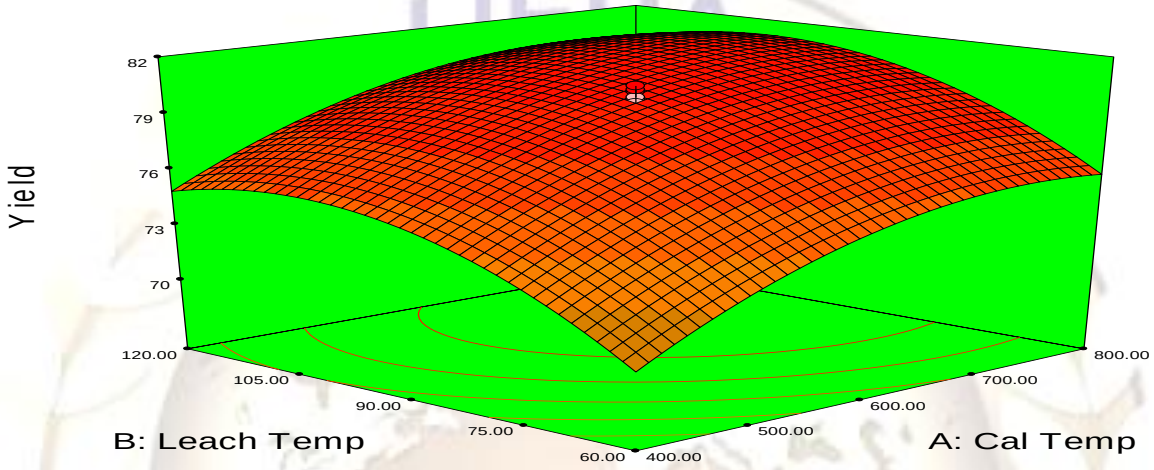

Figure 3: 3D plot showing the effect of calcination temp and leaching temp. on % yield.

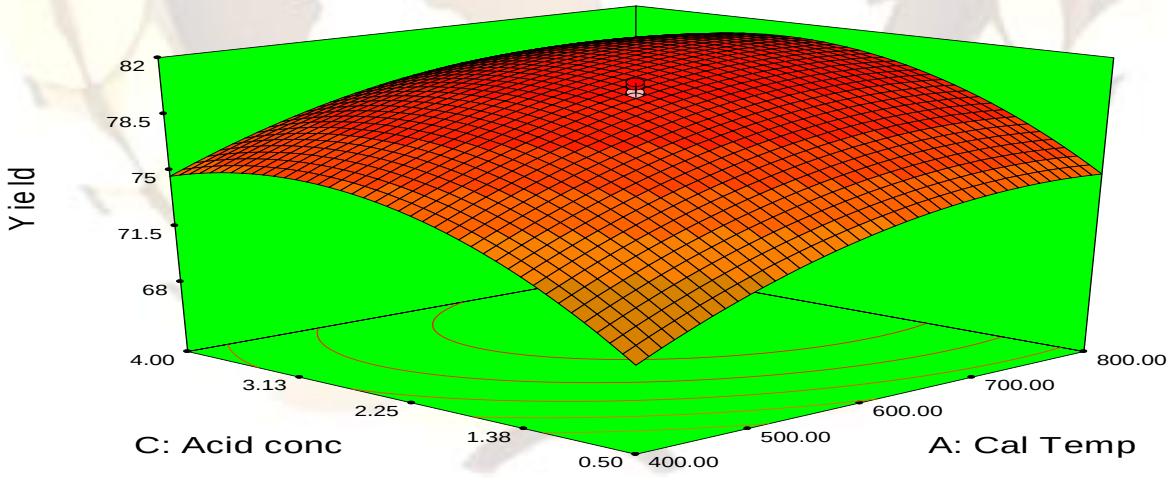

Figure 4: 3D plot of the effect of calcination temp and acid concentration on % yield.

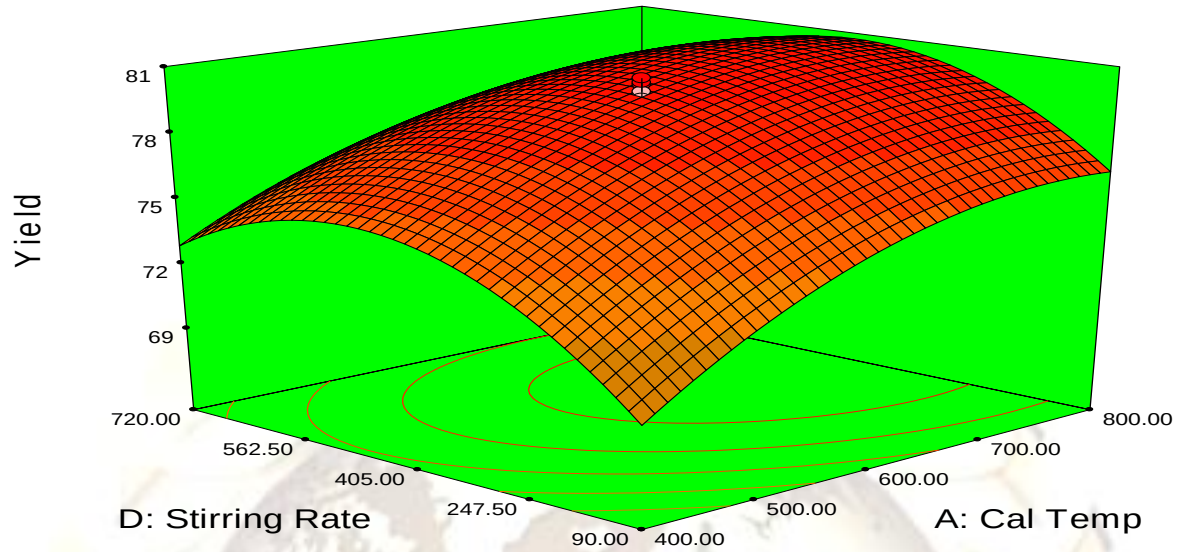

Figure 5: 3D plot of the effect of calcination temp and stirring rate on yield.

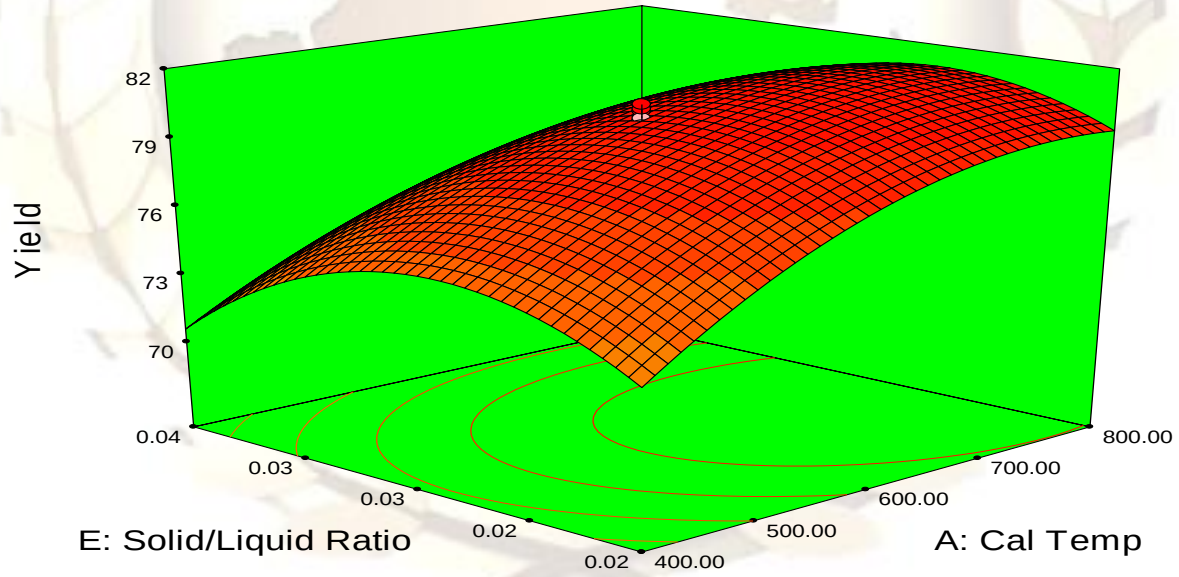

Figure 6: 3D plot of effect of calcination temp and solid/liquid ratio on % yield.

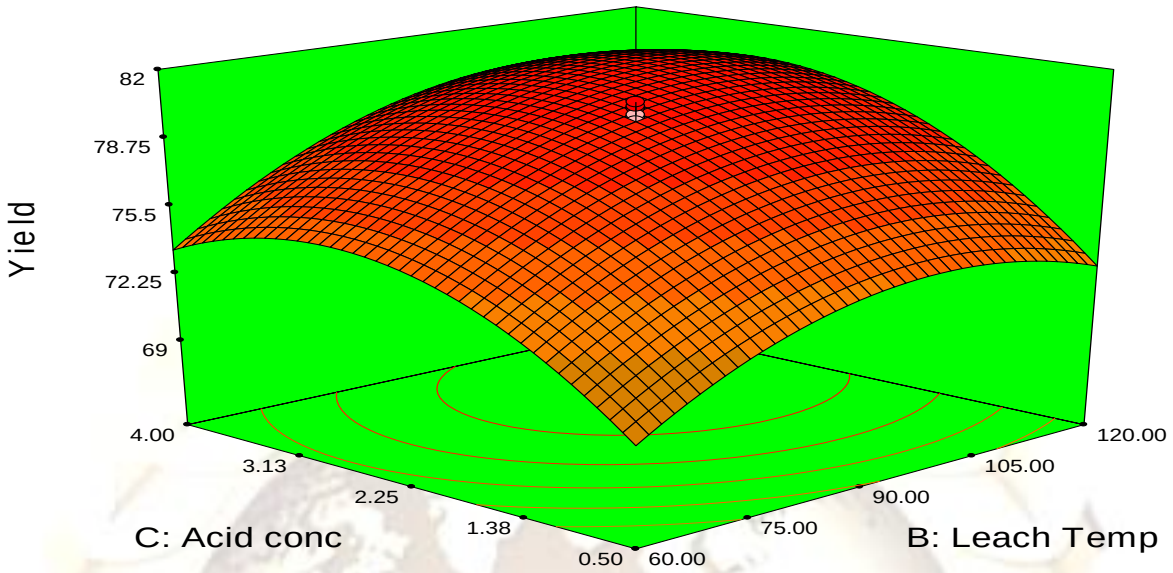

Figure 7: 3D plot of leaching temp and acid concentration on % yield.

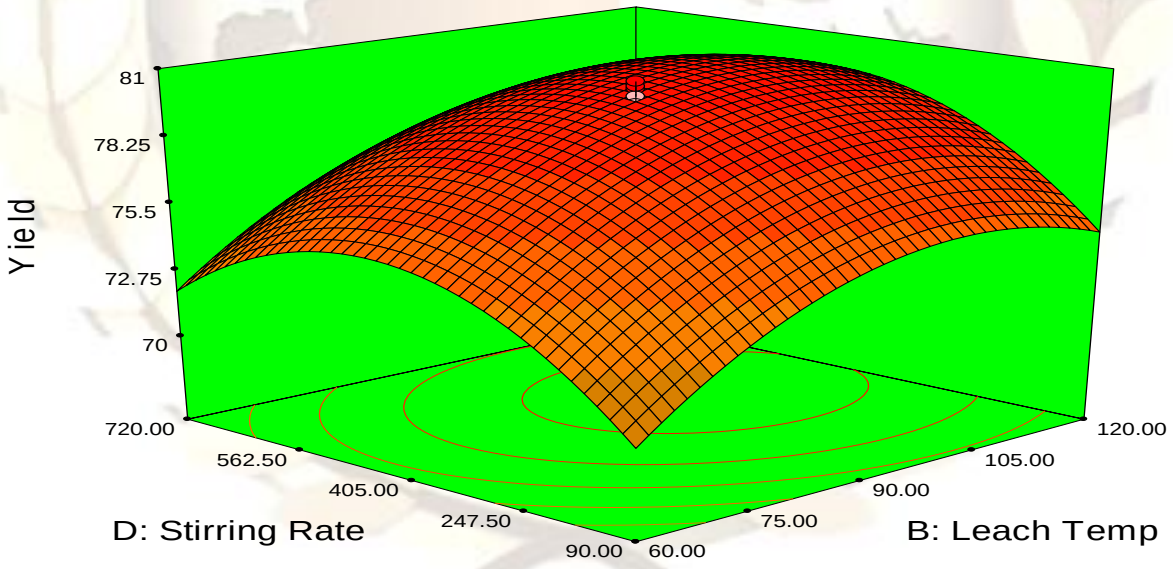

Figure 8: 3D plot of the effect of leaching temp and stirring rate on % yield.

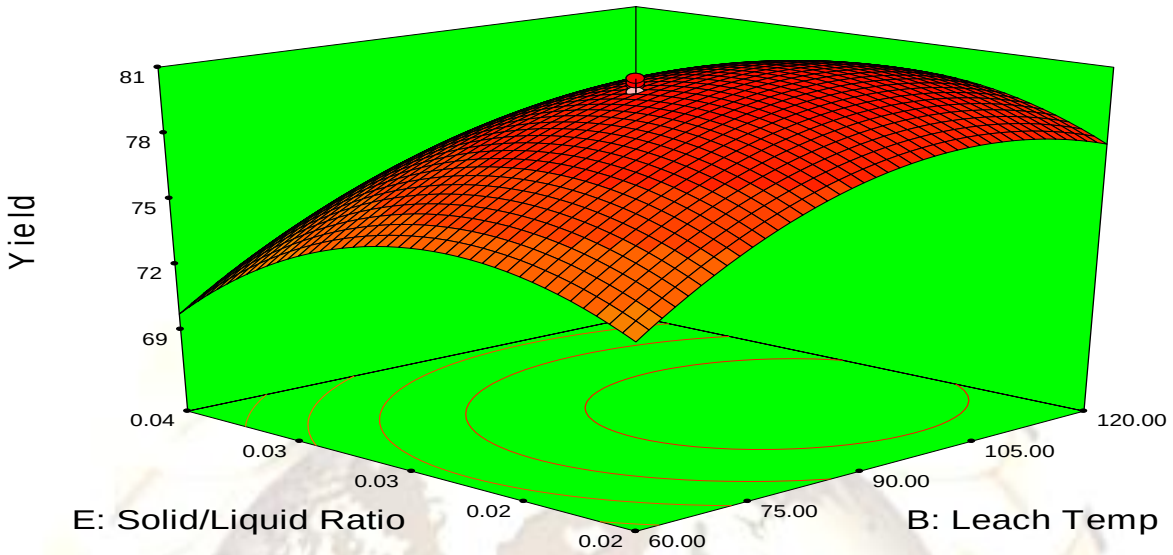

Figure 9: 3D plot of the effect of leaching temp and solid/liquid ratio on % yield.

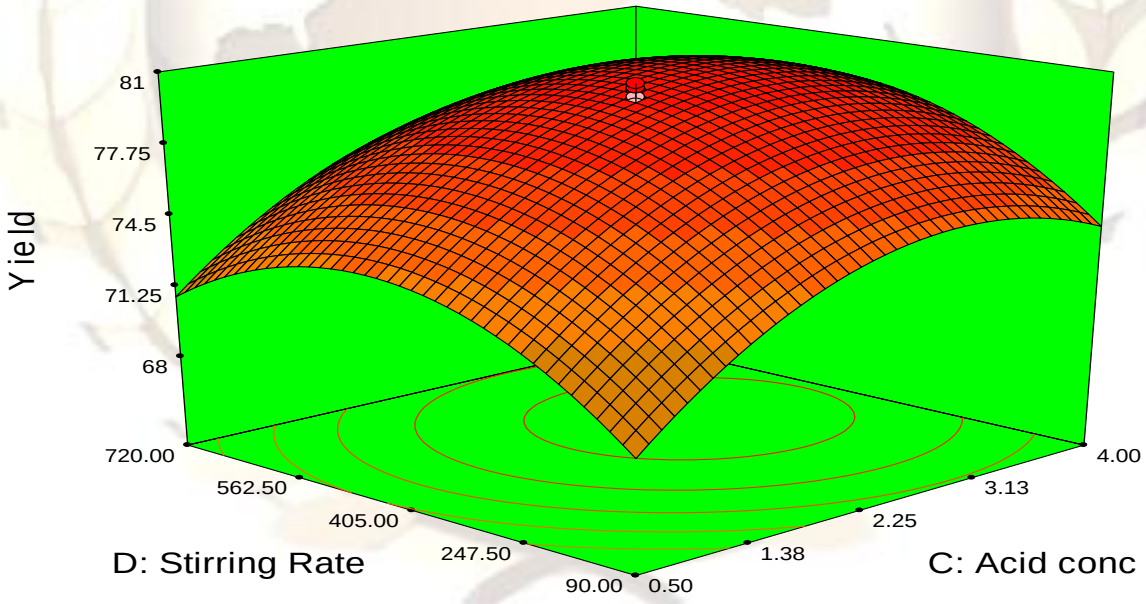

Figure 10: 3D plot of the effect of acid concentration and stirring rate on % yield.

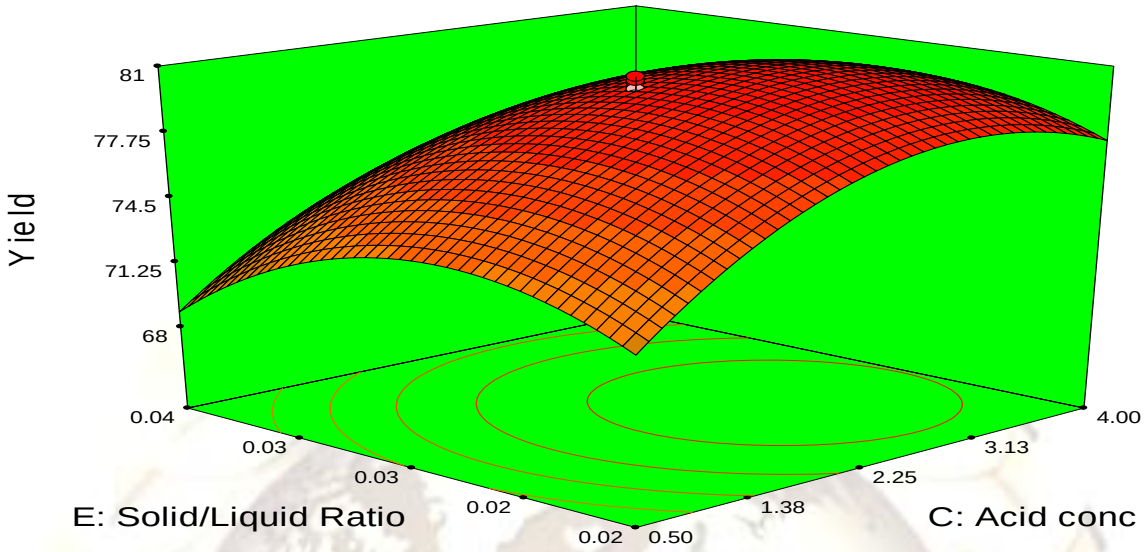

Figure 11: 3D plot of the effect of acid concentration and solid/liquid ratio on % yield.

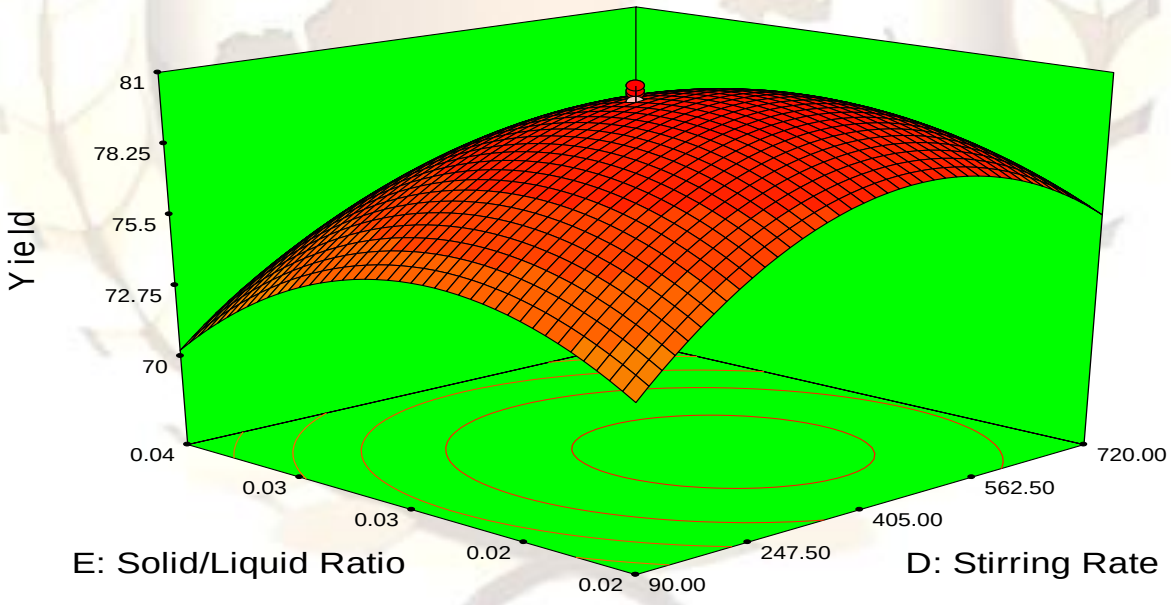

Figure 12: 3D plot of the effect of stirring rate and solid/liquid ratio on % yield.

3.4. Numerical Optimization

One of the primary objectives of the present study was to find the optimum process parameters for maximizing the dissolution of Ukpor clay in hydrochloric acid solution. The model capable of predicting the maximum dissolution capacity showed that the optimum values of the process variables were a calcination temperature of 668.54^0C, a leaching temperature of 107.22^0C, an acid concentration of 2.93 mol/l, a stirring rate of 368.24 rpm, and a solid/liquid ratio of 0.027g/ml. Under these conditions, the predicted dissolution % yield was 97.85, which was in good agreement with the experimental value of 97.67%.

4. CONCLUSION

The optimum levels of the process parameters for the dissolution of Ukpor clay in hydrochloric acid solution were investigated in this work using response surface methodology. Highly accurate model developed showed that the percentage yield of alumina from Ukpor clay was influenced by calcination temperature, leaching temperature, acid concentration, stirring speed and solid/liquid ratio. The optimum leaching conditions of alumina recovery from Ukpor clay are 668.54 ^{0}C calcination temperature, 107.22 ^{0}C leaching temperature, 2.93 mol/L acid concentration, 368.24 rpm stirring speed, and 0.027 g/ml solid/liquid ratio and under these conditions about 97.85% of the alumina content of the clay sample would have been removed. The above results show that Ukpor clay is a good source for alumina and the method employed is efficient for maximum production.

REFERENCES

[1] Abali Y., Colak S., Yapici S., "The optimization of the dissolution of phosphate rock with Cl_2-SO_2 gas mixture in aqueous medium," *Hydrometallurgy, 46*, 1997, 27 – 35.

[2] Abali Y., Salih B., Kadir A., Ali V., Optimization of dolomite ore leaching in hydrochloric acid solutions, *Physicochemical Problems of Mineral Processing, 46*, 2011, 253 – 262.

[3] Veglio F., Ubaldin S., Optimization of pure stibnite leaching conditions by response surface methodology, *European Journal of Mineral Processing & Environmental Protection, 1 (2)*, 2001, 103 – 112.

[4] Uzun D., Gulfen M., Dissolution of iron and aluminium from red mud in sulphuric acid solution, *Indian Journal of Chemical Technology, 14*, 2007, 263 – 268.

[5] Numluk P., Chaisena A., Sulphuric acid and ammonium sulphate leaching of alumina from Lampang clay, *E-Journal of Chemistry, 9(3)*, 2012, 1364 – 1372.

[6] Abdulwahab A., Suad A., Alumina recovery from Iraqi kaolinitic clay by hydrochloric acid route, *Iraqi Bulletin of Geology & Mining, 2 (1)*, 2006, 67 – 76.

[7] Zafar I. Z., Ashraf M., Reaction kinetic model for dissolution of low grade bauxite rock in sulphuric acid, *Journal of Chemical Society of Pakistan, 30 (1)*, 2008, 49 – 54.

[8] Lai-shi L., Yu-sheng W., Ying-ying L., Yu-chun Z., Extraction of alumina from coal fly ash with sulphuric acid leaching method, *The Chinese Journal of Process Engineering, 11 (2)*, 2011, 254 – 258.

[9] Li D., Park K., Wu Z., Guo X., Response surface design for nickel recovery from laterite by sulfation-roasting-leaching process, *Transactions of Nonferrous Metallurgy Society of China, 20*, 2010, s92 – s96.

[10] Narayana S. K., King P., Gopinadh R., Sreelakshmi V., Response surface optimization of dye removal by using waste prawn shells," *International Journal of Chemical Sciences & Applications, 2 (3)*, 2011, 186 – 193.

[11] Yartasi A., Copur M., Ozmetin C., Kocakerim M., Temur H., An optimization study of dissolution of oxidized copper ore in NH3 solutions, *Energy Education, Science and Technology, 3*, 1999, 77.

[12] Shyi-Liang S., Hwang L., Process optimization of vacuum fried carrot chips using central composite rotatable design, *Journal of Food & Drug Analysis, 19 (3)*, 2011, 324 – 330.

[13] Box G. E. P., Hunter W. G., and Hunter J. S., *Statistics for experimenters: an introduction to design, data analysis and model building*, (Wiley and Sons, New York, 1978).

[14] Ata O. N., Colak S., Ekinci Z., Copur M., Determination of the optimum conditions for the dissolution of stibnite in HCl solution, *Chemical and Biochemical Engineering Quarterly, 24*, 2001, 409.