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Process Optimization of Sulphuric Acid Leaching of Alumina from Nteje Clay Using Central Composite Rotatable Design

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***Abstract–* Response surface methodology was employed to optimize the sulphuric acid leaching of alumina from Nteje clay. Such optimization was undertaken to ensure a high efficiency over the experimental ranges employed, and to evaluate the interactive effects of the calcination temperature, leaching temperature, acid concentration, solid-to-liquid ratio, and stirring speed on the leaching process in order to improve the conditions employed in the batch process. A total of 48 leaching experiments were carried out employing the detailed conditions designed by response surface methodology based on the central composite rotatable design. The analysis of variance (ANOVA) 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 responses ($R^2 = 0.9357$). The optimum conditions for the process parameters were obtained as: 675 ^{0}C calcination temperature; 97 ^{0}C leaching temperature; 2.97 mol/l acid concentration; 0.03 g/ml solid-to-liquid ratio; and 476 rpm stirring speed. Under these optimum leaching conditions, an 81.87% alumina was achieved.**

Keywords– Optimization, Response surface methodology, Alumina, Leaching and Clay

I. INTRODUCTION

Almost all the high purity alumina required for the production of aluminium metal is manufactured by the well-known Bayer process, utilizing high grade bauxite ores as raw materials. However, the reserves of bauxite are limited in comparison with aluminous raw materials such as clay, which occur in extensive deposits within Nigeria. Numerous efforts have been made to utilize low value aluminous raw materials and to recover alumina therefrom by extraction with mineral acids to dissolve the alumina present and to separate it from the siliceous components (Brown and Hrishikesan, 1966; Dong and Ubaldi, 2001; Bazin et al, 2005; Shyu and Hwang, 2011). Clay minerals are composed essentially of silica, alumina or magnesia or both, and water, but iron substitutes for aluminium and magnesium in varying degrees. The water is readily removed by calcination.

Treatment of clays with strong inorganic acids is frequently called “acid dissolution” or “acid activation” of clays. Depending on the extent of acid activation, the resulting solid product also 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 (Abali et al, 2006; Lui et al, 2010).

Al-Zahrani and Abdel-Majid, (2004), studied the production of liquid alum from local Saudi clay and their results revealed that the optimum conditions for 90.9% Al_2O_3 to be produced were: 700^{0}C calcination temperature; -65 mesh size; 40 wt % acid; two hours leaching period; and under boiling point of the acid. Lai-shi, et al, (2011) investigated the extraction of alumina from fly ash using sulphuric acid. Their results showed optimum conditions of 200 – 210 ^{0}C reaction temperature, 80 minutes leaching time, 5:1 solid/liquid ratio, and 300 r/min stirring speed, and under these conditions 87% Al_2O_3 was extracted. Al-Ajeel and Al-Sindy, (2006), examined alumina recovery from Iraqi kaolinitic clay and reported that the optimum conditions for the extraction of 99% alumina were: 720^{0}C calcination temperature; 45 minutes leaching time; 28% acid concentration; and 100^{0}C extraction temperature.

In this work, the optimum process conditions for the leaching of alumina from calcined Nteje clay in sulphuric acid is studied applying the central composite design of the response surface methodology.

II. MATERIALS AND METHODS

A. Calcination

The clay samples from Nteje were mined from the region and separated from the dirt that contaminated them. The mined clays were wet and they were sun-dried for three days after which the dried samples were ground 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 450^{0}C to 900^{0}C for all the samples. The calcination time was 2 hours.

B. Leaching 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 acid 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. 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.

C. Design of Experiment

In order to examine the combined effect of the five different factors (independent variables) calcinations temperature, leaching temperature, acid concentration, liquid to solid ratio, and stirring rate on alumina extraction and derive a model, a central composite rotatable design of $2^5 = 32$ plus 6 centre points and (2 x 5 = 10) star points leading to a total of 48 experiments were performed. The factors levels with the corresponding real values are shown in Table 1, while the design matrix, experimental values and predicted values are shown in Table 2. The matrix for the five variables was varied at five levels (-α, -1, 0, +1, and +α). As usual, the experiments were performed in random order to avoid systematic error.

To validate the chosen experimental design and proposed quadratic polynomial equation, six different experiments were performed at the predicted optimum process parameter values.

Table 1: Levels of the independent variables

Independent variable	Symbol	Range and levels				
		-α	-1	0	+1	+α
Calcination temp (^{0}C)	X_1	275	450	625	800	975
Leaching temp. (^{0}C)	X_2	45	70	95	120	145
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	405	720	1035

Table 2: Design matrix processed by Design Expert 7.1.6 Trial version

Std order	**Calcination Temp. (^{0}C), X_1**		**Leaching Temp (^{0}C), X_2**		**Acid Concentration (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. values	Predicted values
1	-1	450	-1	70	-1	0.5	-1	0.02	-1	90	43.7	46.3
2	+1	800	-1	70	-1	0.5	-1	0.02	-1	90	56.9	57.4
3	-1	450	+1	120	-1	0.5	-1	0.02	-1	90	58.9	57.7
4	+1	800	+1	120	-1	0.5	-1	0.02	-1	90	60.8	59.8
5	-1	450	-1	70	+1	4.0	-1	0.02	-1	90	57.6	58.9
6	+1	800	-1	70	+1	4.0	-1	0.02	-1	90	63.8	64.6
7	-1	450	+1	120	+1	4.0	-1	0.02	-1	90	66.8	66.5
8	+1	800	+1	120	+1	4.0	-1	0.02	-1	90	70.1	71.4
9	-1	450	-1	70	-1	0.5	+1	0.04	-1	90	58.9	59.0
10	+1	800	-1	70	-1	0.5	+1	0.04	-1	90	62.9	63.6
11	-1	450	+1	120	-1	0.5	+1	0.04	-1	90	59.9	60.3
12	+1	800	+1	120	-1	0.5	+1	0.04	-1	90	69.8	70.3
13	-1	450	-1	70	+1	4.0	+1	0.04	-1	90	67.4	66.8
14	+1	800	-1	70	+1	4.0	+1	0.04	-1	90	67.5	66.9
15	-1	450	+1	120	+1	4.0	+1	0.04	-1	90	70.5	70.9
16	+1	800	+1	120	+1	4.0	+1	0.04	-1	90	71.9	77.2
17	-1	450	-1	70	-1	0.5	-1	0.02	+1	720	46.7	47.5
18	+1	800	-1	70	-1	0.5	-1	0.02	+1	720	57.9	58.4
19	-1	450	+1	120	-1	0.5	-1	0.02	+1	720	58.9	59.1
20	+1	800	+1	120	-1	0.5	-1	0.02	+1	720	60.4	62.3
21	-1	450	-1	70	+1	4.0	-1	0.02	+1	720	59.8	59.6
22	+1	800	-1	70	+1	4.0	-1	0.02	+1	720	65.8	65.4
23	-1	450	+1	120	+1	4.0	-1	0.02	+1	720	58.4	58.3
24	+1	800	+1	120	+1	4.0	-1	0.02	+1	720	65.9	66.1
25	-1	450	-1	70	-1	0.5	+1	0.04	+1	720	50.5	51.8

26	+1	800	-1	70	-1	0.5	+1	0.04	+1	720	53.8	54.2
27	-1	450	+1	120	-1	0.5	+1	0.04	+1	720	51.6	52.0
28	+1	800	+1	120	-1	0.5	+1	0.04	+1	720	60.4	63.1
29	-1	450	-1	70	+1	4.0	+1	0.04	+1	720	54.9	55.3
30	+1	800	-1	70	+1	4.0	+1	0.04	+1	720	68.9	69.3
31	-1	450	+1	120	+1	4.0	+1	0.04	+1	720	60.4	60.3
32	+1	800	+1	120	+1	4.0	+1	0.04	+1	720	70.2	70.1
33	-2	275	0	95	0	2.25	0	0.03	0	405	58.7	59.2
34	+2	975	0	95	0	2.25	0	0.03	0	405	64.8	64.2
35	0	625	-2	45	0	2.25	0	0.03	0	405	54.8	56.0
36	0	625	+2	145	0	2.25	0	0.03	0	405	60.4	61.4
37	0	625	0	95	-2	-1.25	0	0.03	0	405	50.6	51.4
38	0	625	0	95	+2	5.75	0	0.03	0	405	61.8	64.9
39	0	625	0	95	0	2.25	-2	0.01	0	405	49.2	50.4
40	0	625	0	95	0	2.25	+2	0.05	0	405	58.8	59.6
41	0	625	0	95	0	2.25	0	0.03	-2	--225	62.8	60.5
42	0	625	0	95	0	2.25	0	0.03	+2	1035	53.7	56.3
43	0	625	0	95	0	2.25	0	0.03	0	405	79.6	80.5
44	0	625	0	95	0	2.25	0	0.03	0	405	79.3	78.8
45	0	625	0	95	0	2.25	0	0.03	0	405	79.9	79.8
46	0	625	0	95	0	2.25	0	0.03	0	405	80	80.2
47	0	625	0	95	0	2.25	0	0.03	0	405	80.1	80.2
48	0	625	0	95	0	2.25	0	0.03	0	405	79.7	80.3

III. RESULTS AND DISCUSSIONS

Table 2 shows the combined effects of the process parameters on the experimental leaching efficiency of alumina. Generally, it was observed that alumina extraction increases with the increase in calcination temperature, leaching temperature, acid concentration, and stirring speed, and decreased with increasing solid/liquid ratio.

The data generated from the leaching experiments were statistically analyzed to identify the significant main, interaction, and quadratic effects. Multi-regression analysis was performed on the data to obtain quadratic response surface model for alumina leaching.

The final second-order (quadratic model) polynomial predictive equation obtained for the analysis of Al_2O_3 leaching from Nteje clay is presented in Equation 1 as follows:

$$Y_{Al2O3} = 79.92 + 2.69X_1 + 2.11X_2 + 3.57X_3 + 1.61X_4 - 1.95X_5 - 0.43X_1X_2 - 0.17X_1X_3 + 0.016X_1X_4 + 0.69X_1X_5 - 0.65X_2X_3 - 0.57X_2X_4 - 0.69X_2X_5 - 0.0003X_3X_4 + 0.009X_3X_5 - 1.67X_4X_5 - 3.09X_1^2 - 3.82X_2^2 - 4.07X_3^2 - 4.46X_4^2 - 3.71X_4X^5 \quad (1)$$

The adequacy of the model was tested using the sequential model sum of squares and the model summary statistics as shown in Table 3. From the table it can be seen that the regression coefficient of the quadratic model is 0.9357 which shows that the model adequately explains 93.57% of the variation and also the R^2 adj. of 0.8880 is in reasonable agreement with the R^2 predicted of 0.7607 for the quadratic model. The model F-value of 46.55 is higher than the F_{Table} of 2.52 (at 0.05 significance level). This further indicates that the model adequately fits the experimental data.

Table 3: Adequacy of the Model

Source	**Sum of squares**	**Degree of freedom**	**Mean squares**	**F-value**	**P-value**	**Remarks**
Sequential model sum of squares						
Linear	1335.34	5	267.07	4.37	0.0027	Significant
2FI	150.19	10	15.02	0.20	0.9949	Not significant
Quadratic	2162.90	5	432.58	46.55	< 0.0001	Significant
Cubic	63.70	15	12.48	2.35	0.0712	Not Significant
Source	**Std Dev**	**R^2**	**Adjusted R^2**	**Predicted R^2**	**PRESS**	**Remarks**
Model summary statistics						
Linear	7.81	0.3425	0.2642	0.2485	2930.47	Inadequate signal
2FI	8.69	0.3810	0.0908	0.1610	3271.68	Inadequate signal
Quadratic	3.05	0.9357	0.8880	0.7607	933.11	Adequate signal
Cubic	2.30	0.9837	0.9360	0.3683	2463.18	Inadequate signal

The coefficients of the response surface model as given in Eq. (1) were evaluated using the Design Expert Software. Fischer's F test indicated that all of the linear terms, interaction between stirring rate and solid/liquid ratio, and all the quadratic terms were highly significant ($p < 0.05$). The analysis of variance (ANOVA) and the values of coefficients are presented in Table 4 which indicate that the model is highly significant as the F_{model} value (46.55) is very high compared to the tabular F-value (2.52 at $p = 0.05$). Equation (1) reduces to the following equation after removing the insignificant model terms:

$$Y = 79.92 + 2.69\,X_1 + 2.11\,X_2 + 3.57\,X_3 + 1.61\,X_4 - 1.95\,X_5 - 1.67\,X_4X_5 - 3.09\,X_1^2 - 3.82\,X_2^2 - 4.07\,X_3^2 - 4.46\,X_4^2 - 3.71\,X_5^2 \qquad (2)$$

In terms of the actual process variables values, the model becomes,

$$\%\ \text{Yield} = -60.63 + 0.103 * \text{Calcination temperature} + 0.9999 * \text{Leaching temperature} + 9.42 * \text{Acid concentration} + 0.063 * \text{Stirring rate} + 2243.64 * \text{Solid/liquid ratio} - 0.0077 * \text{Calcination temperature}^2 - 0.004 * \text{Leaching temperature}^2 - 1.329 * \text{Acid concentration}^2 - 0.0045 * \text{Stirring rate}^2 - 37098.04 * \text{Solid/liquid ratio}^2 \qquad (3)$$

Table 4: ANOVA for response surface quadratic model

Source	Coefficient Estimate	Sum of Squares	Degree of Freedom	F-value	P-value (Prob. > F)
Model	79.92	3648.43	20	19.63	< 0.0001
X_1	2.69	313.93	1	33.79	< 0.0001
X_2	2.11	192.11	1	20.67	0.0001
X_3	3.57	551.37	1	59.34	< 0.0001
X_4	1.61	112.91	1	12.15	0.0017
X_5	-1.95	165.02	1	17.76	0.0003
X_1X_2	-0.43	6.04	1	0.65	0.4272
X_1X_3	-0.17	0.95	1	0.10	0.7522
X_1X_4	0.016	0.0078	1	0.00084	0.9771
X_1X_5	0.69	15.26	1	1.64	0.2109
X_2X_3	-0.65	13.65	1	1.47	0.2360
X_2X_4	-0.57	10.24	1	1.10	0.3032
X_2X_5	-0.69	15.26	1	1.64	0.2109
X_3X_4	-0.0003	0.0003	1	0.00003	0.9954
X_3X_5	0.0094	0.0028	1	0.0003	0.9862
X_4X_5	-1.67	88.78	1	9.55	0.0046
X_1^2	-3.09	490.01	1	52.74	< 0.0001
X_2^2	-3.82	750.21	1	80.74	< 0.0001
X_3^2	-4.07	850.44	1	91.52	< 0.0001
X_4^2	-4.46	1020.64	1	109.84	< 0.0001
X_5^2	-3.71	705.81	1	75.96	< 0.0001
Residual		250.88	27		
Lack of fit		250.45	22	131.35	< 0.0001
Pure Error		0.43	5		
Cor. Total		3899.31	47		

Std Dev. = 3.05; Mean = 62.63; C.V.% = 4.87; PRESS = 933.11; $R^2 = 0.9357$; Adj. R^2 0.8880; Predicted $R^2 = 0.7607$; Adeq. Precision = 15.634; S = 0.3412.

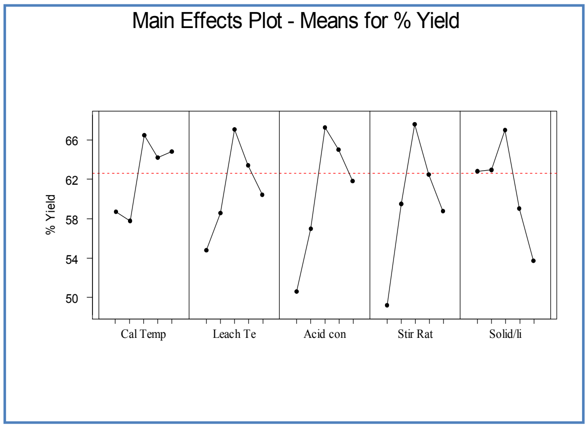


Fig. 1: The effect of each parameter on the % yield of alumina

The order of graphs in Fig. 1 is according to the degrees of the influences of factors on the leaching process. The optimal level of a process quantity is the level with the highest % yield value calculated by Eq. (2).

Plot of the residuals in Fig. 2 shows high correlation and the linear correlation plot (Fig. 3) drawn between the predicted and actual response demonstrated high value of R^2 (0.9357), indicating excellent goodness of fit ($p < 0.05$).

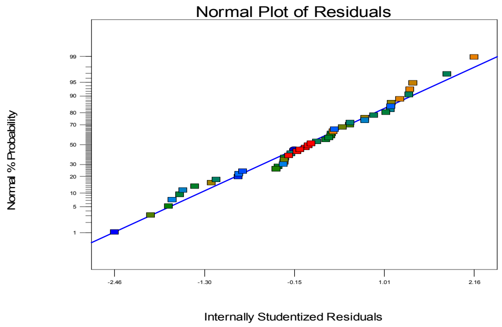


Fig. 2: Plot of residuals

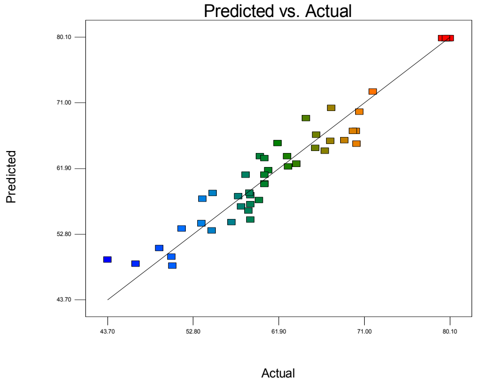
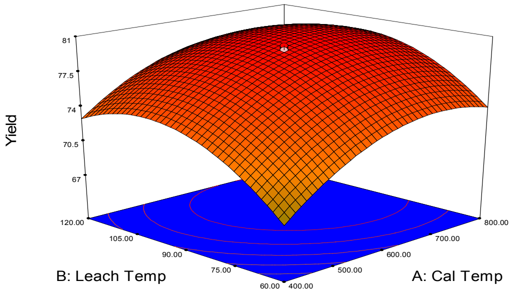


Fig. 3: Plot of actual and predicted values of % yield

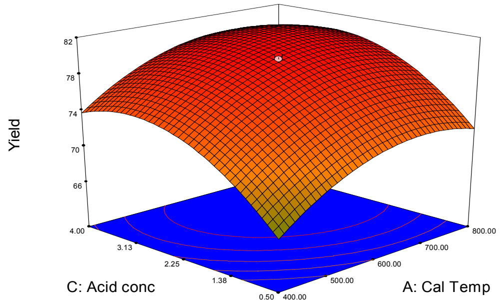
IV. RESPONSE SURFACE PLOTS

The interaction effects of variables on the alumina production by the dissolution of clay in acid medium were studied by plotting 3D surface curves against any two independent variables, while keeping another variable at its central level. The 3D curves of the calculated response (alumina production) plots from the interactions between the variables are shown in Fig. 4(a) – Fig. 4(j), using the Design Expert statistical software, 7.1.6 trial version. 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.

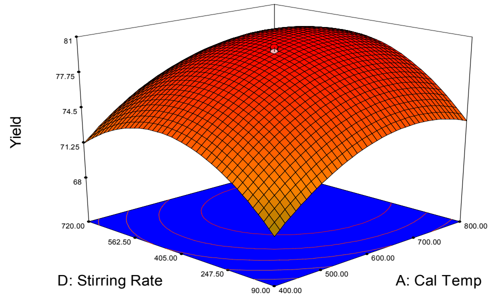
Fig. 4(a) shows the dependency of alumina/dissolution on calcination temperature and leaching temperature. The alumina production increased with increase in calcination temperature to about 700 – 720^{0}C and thereafter alumina production decreased slightly with further increase in calcination temperature. The same trend was observed in Fig. 4(b), Fig. 4(c), and Fig. 4(d). Increase in leaching temperature increased alumina production slightly up to 100 – 110^{0}C, thereafter the production decreased slightly. This was evident from Fig. 4(a), Fig. 4(e), Fig. 4(f), and Fig. 4(g). Fig. 4(a), Fig. 4(e), Fig. 4(i), and Fig. 4(h), show that the yield of alumina increased with acid concentration up to 3.0mol/l and thereafter remained constant. Fig. 4(d), Fig. 4(g), Fig. 4(i), and Fig. 4(j) show that the percent yield decreases with increase in solid/liquid ratio.



(a)



(b)



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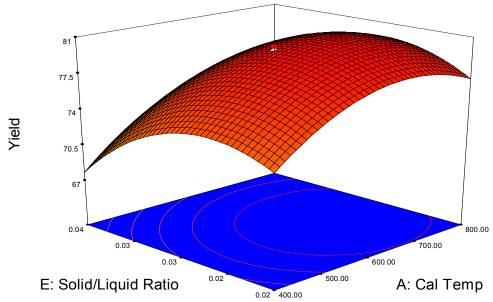
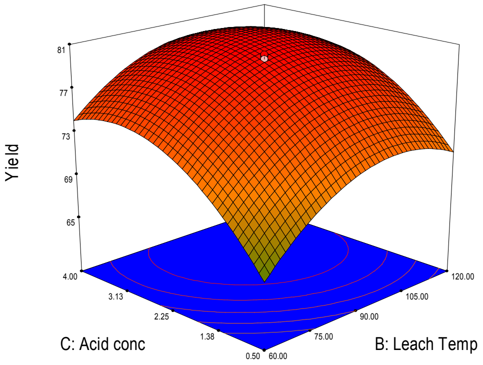
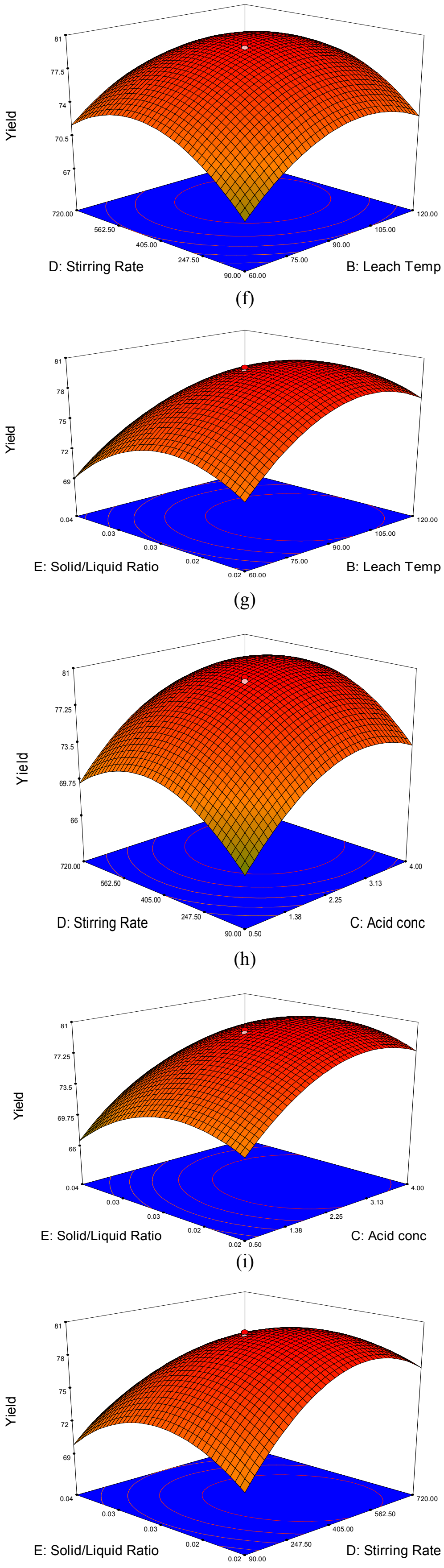


(d)



(e)



(f)

(g)

(h)

(i)

(j)

Fig. 4: 3D plots for % yield versus (a)leaching temperature and calcination temperature (b) calcination temperature and acid concentration (c) calcination temperature and solid-to-liquid ratio (d) calcination temperature and stirring speed (e) leaching temperature and acid concentration (f) leaching temperature and solid-to-liquid ratio (g) leaching temperature and stirring speed (h) acid concentration and solid-to-liquid ratio (i) acid concentration and stirring speed (j) solid-to-liquid ratio and stirring speed

V. NUMERICAL OPTIMIZATION

The optimum conditions predicted for synthesizing 81.87% yield in the dissolution/production of alumina from Nteje clay were as follows: Calcination temperature, 675.15 ^{0}C; leaching temperature, 96.88 ^{0}C; acid concentration, 2.97 mol/l; solid/liquid ratio, 0.03 g/ml; and stirring rate, 475.54 rpm. The optimization was performed using the numerical method of the Design Expert version 7.1.6 by State Ease U. S. A. This value is in close agreement with the experimental value of 82.04%, performed at the same optimum values of the process variables.

VI. CONCLUSION

The results of response surface methodology (RSM) showed that the dependent variable, % yield of alumina, is significantly affected by the leaching conditions such as calcination temperature, leaching temperature, acid concentration, solid/liquid ratio, and stirring speed. Among these independent variables, acid concentration and calcination temperature were the most important factors. The percent alumina yield was positively correlated with calcination temperature, leaching temperature, acid concentration, and stirring speed, but, negatively correlated with solid/liquid ratio. Based on the central composite rotatable design (CCRD), three-dimensional plots and the contour plots, the optimal leaching conditions of alumina from Nteje clay are: calcination temperature of 675.15^{0}C; leaching temperature of 96.88^{0}C; acid concentration of 2.97mol/l; solid/liquid ratio of 0.03 g/ml; and stirring speed of 475.54 rpm.

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