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Iron leaching from bauxite ore in hydrochloric acid using response surface methodology

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Abstract

In this work, hydrochloric acid is used to remove iron impurities in the bauxite ore contained in the diasporite mineral located in the Sari region. The bauxite ore was calcined at different temperatures and times, and then dissolved in a hydrochloric acid solution. After determining the optimum calcination conditions in 1 h at 900 °C, the response surface methodology (RSM) with four factors in five levels was employed in order to evaluate the effects of calcination temperature, calcination time, acid concentration, and leaching time on the iron leaching efficiency. A quadratic model is proposed using this methodology to correlate the leaching variables. The test results indicate that the model is consistent with the experimental data, and that the most important varriables involved are the acid concentration, leaching time, and squared term of calcination temperature (A^2). The maximum iron recovery was 94.97%, and the Fe grade in the solids remained was 2.35% at the calcination temperature of 900 °C, a calcination time of 1 hour, and a leaching time of 2 h in hydrochloric acid (6 mM).

Keywords: *Optimization, Bauxite, Leaching, Iron Removal, Response Surface Methodology (RSM).*

1. Introduction

Clay-like sediments, composed mainly of alumina and iron oxide, and being practically devoid of silica, have been first described by Bethier in 1821 [1]. From an industrial perspective, bauxite is a natural material that can be economically processed to high-purity alumina in the Bayer Process, thus making bauxite the main aluminum ore. Bauxite consists primarily of a mixture of aluminum hydroxides, gibbsite (γ-$Al_2O_3.3H_2O$), boehmite (γ-$Al_2O_3.H_2O$), and, to a lesser extent, diasporite (α-$Al_2O_3.H_2O$), clay (mainly kaolinite), iron oxides, quartz, titanium oxide, water, and a variety of other minerals. Bauxite can be structure-less, granular or earthy, pisolitic and concretionary, massive or stratified, or largely pseudomorphic after the parent rocks. Older bauxites that may have been subjected to burial are hard and compact, with boehmite and diaspora commonly being the dominant aluminous minerals. More recent bauxites are generally softer, with gibbsite commonly being the dominant aluminous mineral [1-7].

The presence of impurities, particularly iron-bearing materials, impairs the characteristics of clay, and affects its utility for various applications [8]. Removal of iron from bauxite has recently become the objective of many research works, for two reasons: low-iron bauxite having less than about 2% Fe_2O_3 finds applications in the production of refractory, and removal of iron from bauxite prior to the Bayer process reduces the disposal amount of red mud and provides high alumina content. Traditionally, iron present in clays is removed by the physical separation techniques, although acid washing has proved to be more effective, and is thus gaining wide acceptance [9-11]. Recent studies have shown that even traces of iron can be removed by acid washing [11]. Researchers have found that iron could be removed by hydrochloric acid leaching, almost completely [4, 12-16]. Both inorganic and organic acids have been used for leaching iron oxides. The results obtained from the investigations carried out on leaching of the iron oxides present in oxalic acid solutions dominate the published literatures. Chiarizia and Horwitz [17] have studied dissolution of goethite in several organic acids in the presence of reducing agents. Panias et al. [18] have examined the dissolution mechanisms of the iron oxides present in aqueous oxalic acid solutions. Lee et al. [19] have worked on the optimization of pH levels, and pH control of the leaching solution of oxalic acid. Ambikadevi and Lalithambika [20] have tested several organic acids, and concluded that oxalic acid is the most efficient compound that can be used to dissolve iron oxides from ceramic minerals. Some researchers have determined the reaction rates, rate controlling steps, and reaction mechanisms for leaching of iron using both organic (i.e. oxalic acid) and inorganic (i.e. HCl) acids [4, 17, 21-23]. However, scopes for further investigations on the leaching kinetics of iron oxides in clays still exist.

Optimization can be defined as a process of improving an existing condition, apparatus or system such as a metallurgical process. Therefore, studies on modeling and optimization to discover the best qualification of these processes is very important. In order to overcome this problem, optimization studies have been carried out using the response surface methodology (RSM). This methodology consists of a group of mathematical and statistical techniques used in the development of an adequate functional relationship between a response of interest, y, and a number of associated control (or input) variables denoted by (x_1, x_2,..., x_k) [24].

RSM reduces the number of experimental trials needed to evaluate multiple parameters and their interactions. Therefore, it is less laborious and time-consuming than the other approaches used [25].

Box et al. have suggested to use a first-degree polynomial model to approximate the response variable. They have acknowledged that this model is only an approximation, not accurate, although such a model is easy to estimate and apply, even when little is known about the process [26, 27]. Moreover, it is easy to estimate the parameters in a second-order model using the method of least squares. The D-optimality criterion enables a more efficient construction of a quadratic model [28]. The objective is to select the P-design points from a larger set of candidate points. Equation (1) can be expressed in matrix notation, as:

$$Y = X \times B + \varepsilon \tag{1}$$

where Y is a vector of observations, ε is a vector of errors, X is the matrix of the values of the design variables at plan points, and B is the vector of tuning parameters. B can be estimated using the least-squares method, as:

$$B = \left(X^T \times X\right)^{-1} X^T Y \tag{2}$$

The D-optimality criterion states that the best set of points in the experiment maximizes the determinant $|X^T X|$. "D" stands for the determinant of the X^TX matrix connected to the model. From a statistical point of view, a D-optimal design arrives to the response surface models, for which the maximum variance of the prophesied responses is minimized. This means that indication of the experiments minimizes the errors in the estimated coefficients of the response model [27]. Until now, there has been little information reported on the optimization of the leaching process of a copper ore using RSM.

In the present work, leaching of iron contained in the bauxite ore located in the Sari region was investigated. The objective of this work was to optimize the leaching conditions of iron concentrates by HCl solution using RSM, and to evaluate the main effects of some physic-chemical and operational parameters involved, as well as their interactions.

2. Materials and method

2.1. Sample preparation and characterization

The bauxite sample under investigation was collected from an exploration zone in Sari bauxite. X-ray fluorescence (XRF) analysis of the sample demonstrated the presence of 35.06% alumina, 45.22% silica, and 19.72% iron in it.

2.2. Leaching experiments

Leaching experiments were carried out in a glass tank reactor containing 200 mL of suspension and 40 g of samples. The leaching temperature was constant, equal to 95 °C. The optimum concentration of hydrochloric acid was determined by leaching in 4, 6, 8, 10, and 12 mM of aqueous hydrochloric acid solutions. Subsequent leaching experiments were performed in the optimized acid concentration at 700, 800, 900, 1000, and 1100 °C, and for 1, 1.5, 2, 2.5 and 3 h at each temperature. A constant stirring speed of 1000 rpm was maintained during all leaching experiments. At the end of leaching for a specified period of time and temperature, 5 mL of the pulp samples were taken for analysis from the reactor, cooled, centrifuged for 3 minutes at 5000 rpm in order to remove the solids, and used for the estimation of iron. Distilled water was used in all experiments.

2.3. Experimental design

RSM is a useful approach for modeling and analysis of the problems in which a response of interest is influenced by several variables, and the objective is to optimize the response [27]. These types of designs are always optional, regardless of the type of model the experimenter wishes to fit (for example, first order, first order plus some interactions, full quadratic, cubic, etc.) or the objective specified for the experiment (for example, screening, response surface, etc.). Response surfaces were drawn for the experimental results procured from the effects of four variables on the particle size, redox potential, temperature, and chalcopyrite to coated pyrite by silver ratio, in order to determine the single and cumulative effects of these variables, and also their reciprocal interactions.

In this work, the experimental data were analyzed using the Design-Expert software (Demo version 7.0.0) from Stat-Ease Inc. The four parameters at three levels were considered to be independent variables in the examination. To simplify the calculations, the factors were given with codes: calcination temperature (A), calcination time (B), acid concentration (C), and leaching time (D).

3. Results and discussion

3.1. Compositional analysis of bauxite

Composition of the bauxite, as determined by X-ray fluorescence, is shown in Table 1. The results obtained from the 27 experiments carried out were used to appraise the response variable, i.e. leaching efficiency, and also the experiments designed using RSM. The experimental results obtained for iron recovery in each case are presented in Table 2, and using the results listed in this table, data analysis was performed for the response variable.

3.2. Statistical analysis

Statistical significance of the model was evaluated by the values for F, P, correlation coefficient, and the analysis of variance (ANOVA). The effects of the entire model terms were calculated, and the statistics for F-values (Fisher variation ratio), lack of fit, and R^2-values were used to compare the models. The statistical analysis performed showed that quadratic model was the most fitted model for the experimental results. This statistical tool was required to test the significance and adequacy of the model. The mean squares (MS) were obtained as: MS = SS/DF, where SS is the sum of squares of each variation source, and DF is the respective degree of freedom.

Table 1. Mineralogical composition of sample (XRF analysis).

Chemical syntax	Weight of mineral (%)
SiO_2	20.49
Al_2O_3	35.06
Fe_2O_3	19.72
CaO	6.52
MgO	0.33
So_3	0.14
P_2O_5	0.25
Cr_2O_3	0.14
Na_2O	0.16
K_2O	0.18
TiO_2	3.15
SrO	0.29
L.O.I	13.44
Total	100

The Fisher variation ratio (F-value) is a statistically valid measure of how well the factors describe the variation in the data around its mean. It can be calculated from ANOVA, as follows: F-value = MS (due to the model variation)/MS (due to the error variance) [21]. F-value and a very low p-value infer the significance of the model. The Model F-value of 22.89 implies that the model is significant. For fitting the model, the F-value greater than unity explains adequately the variation in the data around its mean value; in addition, the estimated factor effects are real [29].

The model fittness was examined by the definition of the correlation coefficient (R^2). The correlation coefficient values provide a measure of how much variability in the observed response values can be explained by the experimental factors and their interactions. In this case, the value of the determination coefficient (R^2 = 0.96) was indicated.

The closer the correlation coefficient is to 1, the more fitted is the model, and the better it predicts the response. The value for the adjusted determination coefficient (adjusted R^2 = 0.91) was also high, indicating a high significance of the model. The value of the predicted correlation coefficient was also high, which supports a high significance of the model and the coefficient R^2.

The regression equation after ANOVA represented the level of iron recovery as a function of the calcination temperature, calcination time, acid concentration, and leaching time.

Table 2. RSM design matrix and results of experiments.

Std. no	Leaching time (h)	Acid concentration (mM)	Calcination time (h)	Calcination temperature (°C)	Response (Fe recovery %)
	D	C	B	A	
1	1.5	6	0.65	800	41.15
2	1.5	6	0.65	1000	43.97
3	1.5	6	1.35	800	44.2
4	1.5	6	1.35	1000	46.98
5	1.5	10	0.65	800	51.78
6	1.5	10	0.65	1000	51.07
7	1.5	10	1.35	800	52.4
8	1.5	10	1.35	1000	54.18
9	2.5	6	0.65	800	57.58
10	2.5	6	0.65	1000	61.47
11	2.5	6	1.35	800	60.45
12	2.5	6	1.35	1000	65.18
13	2.5	10	0.65	800	67.88
14	2.5	10	0.65	1000	88.24
15	2.5	10	1.35	800	80.46
16	2.5	10	1.35	1000	93.11
17	2	8	1	700	49.47
18	2	8	1	1100	43.29
19	2	8	0.35	900	44.4
20	2	8	1.65	900	66.92
21	2	4	1	900	43.45
22	2	12	1	900	94.97
23	1	8	1	900	52.64
24	3	8	1	900	88.52
25	2	8	1	900	77.51
26	2	8	1	900	79.01
27	2	8	1	900	81.65

By implementing the multiple regression analysis on the experimental data, the experimental results of design were fitted with a quadratic polynomial equation. The final equation in terms of the coded factors was developed based on the experimental design, as:

$$Y = 79.93 + 1.5\,A + 3.29\,B + 9.22\,C + 10.85\,D + 3.24\,CD - 8.33\,A^2 - 6.01\,B^2 - 2.62\,C^2 - 2.28\,D^2 \quad (3)$$

where Y is the iron recovery (response) in percentage; and A, B, C, and D are the coded values of the design variables. Values greater than 0.10 indicate that the model terms are not significant with a confidence level of 90%. Referring to ANOVA, it can be deduced that the C and D variables and the quadratic term A^2 are obviously significant. In addition, due to the greater F-value of the leaching time, it is the most important variable in the response.

3.3. Studying effects of parameters and their interactions on iron recovery

The 3D plots presented in Figure 1 show the effects of the interactions between the concentration of hydrochloric acid and leaching time on the sample iron recovery at the calcination temperature of 900 °C and the calcination time of 1 h. It indicates that the recovery of iron increases with increase in the concentration of hydrochloric acid and the leaching time. It is evident that the rate of iron dissolution is directly affected by the hydrogen ion concentration in the leach liquor. The higher is the concentration of hydrochloric acid, the higher the extent of dissolution of iron oxide is. The maximum iron recovery was obtained with rises in the acid concentration and leaching time.

Figure 2 shows the effects of acid concentration and calcination temperature on the leaching rate of iron oxide in the bauxite sample at the calcination and leaching times of 1 h and 2 h, respectively. It can be seen that during the leaching, at all the acid concentrations under investigation, the leaching rate was rather fast. In fact, with increase in the acid concentration, the Fe recovery increases but with increase in temperature to 900 °C, outset increases the recovery and then decreases it.

The results obtained for the acid concentration show that increase in the acid concentration increases the recovery of Fe to the solution, and this result is similar to all the results obtained from the previous studies.

The interaction effects of the calcination time and temperature at the acid concentration of 8 mM and leaching time of 2 h are shown in Figure 3. It can be indicated that with increase in both parameters, the Fe recovery increases. With temperature reaching 900 °C and leaching time of 1.5 h, the recovery began to decline. The calcination time was 1 h in the maximum recovery. Table 2, indicates that the recovery at different times is almost constant, and after 1 h, it increased, and then it did not have a significant effect (about a few percent) on the dissolution rate as well.

Effects of the calcination temperature and leaching time at the calcination time of 1 h and acid concentration of 8 mM have been shown in Figure 4. This figure indicates that the recovery increased with increase in the leaching time. However, increase in the calcination temperature first increased the recovery, and then decreased it. The reason for this can be seen with the start of a new phase of Fe^{3+}: the dissolution of iron increases with the release of Fe to form this phase.

Interactions of the leaching time and calcination time at the calcination temperature of 900 °C and acid concentration of 8 mM are shown in Figure 5. The recovery increases with increase in the leaching time, and by increasing the calcination time, the recovery of iron decreases at first.

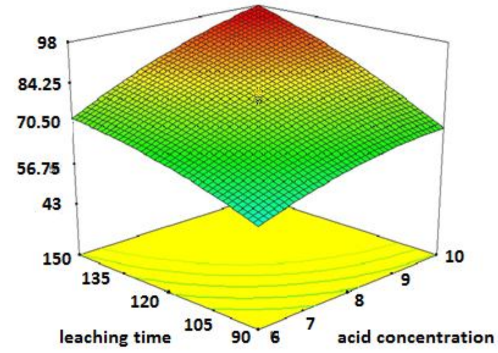

Figure 1. Response surface plots for effects of leaching time and acid concentration at calcination temperature of 900 °C and calcination time of 1 h.

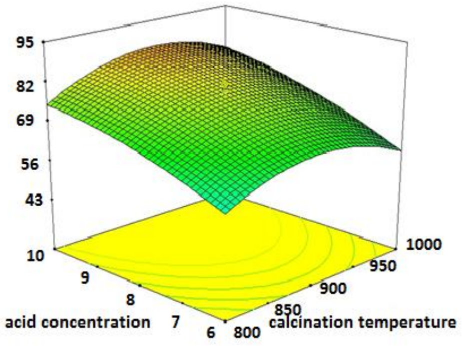

Figure 2. Response surface plots for effects of calcination temperature and acid concentration at leaching time of 2 h and calcination time of 1 h.

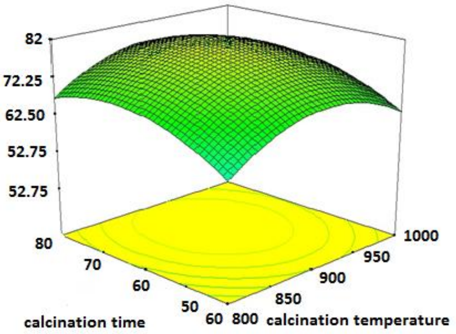

Figure 3. Response surface plots for effects of calcination temperature and calcination time at acid concentration of 8 mM and leaching time of 2 h.

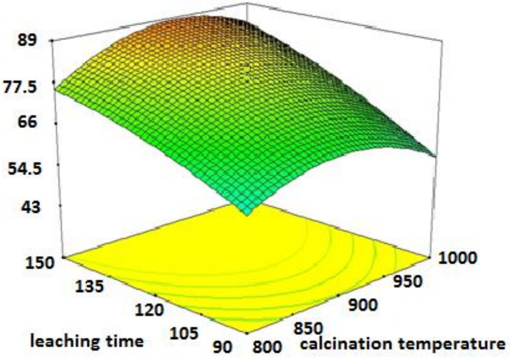

Figure 4. Response surface plots for effects of calcination temperature and leaching time at acid concentration of 8mM and calcination time of 1 h.

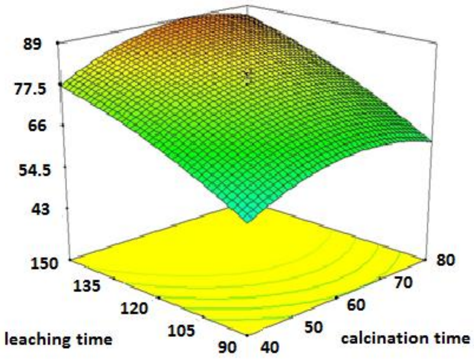

Figure 5. Response surface plots for effects of calcination time and leaching time at calcination temperature of 900 °C and acid concentration of 8 mM.

4. Conclusions

The results obtained from this study are summarized as follow:

- Response surface methodology (RSM) was effective for the optimization of the leaching process, and a quadratic model suggested by the methodology was in good agreement with the experimental data, at a correlation coefficient (R^2) of 0.96.
- Acid concentration and leaching time had a positive effect on the response. Increasing both parameters caused significant increase in the iron recovery.
- The quadratic term of calcination temperature was obviously significant.
- Maximum recovery of Fe was, in best, 94.97%, using the hydrochloric acid concentration of 1.2 M, 900 °C calcination temperature, calcination time of 1 h, and leaching time of 2 h, and the Fe grade in the remaining solids was 2.35%.

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لیچینگ آهن از کانی بوکسیت در اسیدکلریدریک با استفاده از روش طراحی سطح- پاسخ

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چکیده:

در این تحقیق، امکان حذف آهن از نمونه بوکسیت منطقه ساری با استفاده از اسیدکلریدریک مورد بررسی قرار گرفت. کانی بوکسیت پس از کلسیناسیون در دما و زمان‌های مختلف، در محلول اسیدکلریدریک شستشو شد. طراحی آزمایش به روش سطح- پاسخ با داشتن چهار پارامتر در پنج سطح مختلف انجام شد. تأثیر پارامترهای دمای کلسیناسیون، زمان کلسیناسیون، غلظت اسید و زمان انحلال مورد بررسی قرار گرفت. با توجه به نتایج به‌دست‌آمده، مدل درجه دوم انتخاب و با ضریب همبستگی قابل‌قبول برازش شد. نتایج نشان داد غلظت اسید، زمان انحلال و مجذور دما مؤثرترین پارامترها در آزمایش‌های انحلال آهن از کانی بوکسیت است. بیشترین مقدار بازیابی ۹۴/۹۷ ٪ و مقدار آهن در جامد باقیمانده برابر ۲/۳۵٪ در شرایط دمای کلسیناسیون ۹۰۰ درجه سانتی‌گراد، زمان کلسیناسیون یک ساعت، غلظت ۶ مولار اسیدکلریدریک در زمان انحلال ۲ ساعت به دست آمد.

کلمات کلیدی: بهینه‌سازی، بوکسیت، انحلال آهن، روش سطح- پاسخ.
