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Central composite design for optimization and formulation of desulphurization of iron ore concentrate using atmospheric leaching process

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Abstract

Owing to the negative effects of sulphur in iron ore on steelmaking process and environment, a tank leaching process was performed in atmospheric conditions to remove the sulphur from the iron ore concentrate and simultaneously to transform sulphide minerals into useful by-products. To achieve desirable sulphur removal rate and efficiency, central composite design was adopted as a response surface methodology for the optimization and evaluation of the process. A full-quadratic polynomial equation between the sulphur removal and the studied parameters was established to assess the behaviour of sulphur removal as a function of the factors and to predict the results in various conditions. The optimum conditions were obtained based on the variance tests and response surface plots, from which the optimized ranges for each factor resulting in the best response (corresponding to the highest percentage of desulphurization) could be then achieved. The results show that most desirable conditions are atmospheric leaching in 1.39 mol/dm^3 nitric acid and 0.88 mol/dm^3 sulphuric acid for 47 h. The designed process under the optimized desulphurization conditions was applied to a real iron ore concentrate. More than 75% of the total sulphur was removed via the leaching process. In addition to the desulphurization, the conversion of sulphide-bearing minerals into useful by-products, extraction of valuable metals, and executing the process under atmospheric conditions are the other advantages of the proposed method.

Keywords Desulphurization · Iron ore concentrate · Sulphide mineral leaching · Central composite design · Atmospheric leaching process

1 Introduction

The mechanical properties of the iron and steel products are deleteriously affected by their sulphur element, which is mostly from the high sulphur raw materials [1]. Decreasing the sulphur content of iron ore concentrate will improve the quality and cleanliness of the produced steel designated for the manufacturing of a broad range of materials from construction materials to medical devices. It has been demonstrated that the reason behind the failure of steel used in the very hot environment is the presence of high concentration of iron sulphide in steel crystals [2, 3]. The rate of intergranular corrosion of stainless steel increases with increasing sulphur concentration at grain boundaries in highly oxidizing solutions [4]. In addition, the presence of sulphur in iron ore concentrates causes environmental issues by emitting sulphur dioxide during the preheating and roasting process of iron ore pellets [2, 5].

For these reasons, many attempts have been made to remove or decrease the sulphur content from the iron ore concentrates prior to the subsequent pelletizing process [6–13]. However, in order to reduce the overall cost, it is advised to limit the use of hazardous substances, decrease waste streams, produce high value by-products, and remove the limitations from particle size.

Desulphurization of iron ore concentrates may be achieved by using both physical and chemical methods.

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Physical processes are cost-effective methods but are not effective in separating the finely dispersed sulphide minerals and those bound to the mineral structure. The common iron ore desulphurization method is flotation. However, the dependence of flotation efficiency on the particle size responsible for its need for grinding to a certain particle size, as well as no transformation of sulphide minerals to useful by-products in the flotation process, has led researchers to make efforts to replacing the flotation process in the desulphurization of iron ore. Also, it is important to note that the energy consumption of ore combination, especially during the grinding process, is about to rise in the coming years [14].

Leaching is a typical chemical method that is capable of extracting the sulphide minerals from the iron ore concentrates. In the leaching process, the iron ore is mixed with the leaching agent when its sulphur is extracted as a result of the reactions between chemicals and sulphur-bearing minerals. Meanwhile, these minerals are converted into a soluble fraction or removable matter, resulting in an easy separation from the iron ore concentrate. Significant steps were also taken to enhance the reaction of sulphur minerals with the leaching agents. These may include the optimization of some parameters, for example the concentration of the leaching agents and the leaching time, which were found to largely affect the processing rate and efficiency. Removal of the impurities and dissolution of sulphur minerals for coal cleaning [15–17] and recent cases of the removal of sulphur and other impurities from iron ore concentrate using the leaching and bioleaching processes have been reported [5, 18–20]. Unlike the flotation process, it is usually not critical to have a certain particle size for the leaching process. Another major advantage of the leaching method is its potential to transform the mineral pyrite into useful by-products such as elemental sulphur [5]. However, despite these advantages of leaching process, using high operational temperatures during the process is an important issue that may hinder its further development.

The response surface methodology (RSM) is a collection of statistical and mathematical methods that are useful for modelling and analysing engineering problems, which is widely used in designing experiments and evaluating the effects of different experimental factors [21, 22]. It is performed based on the central composite rotatable design (CCRD), the Box–Behnken design, the one-factor design, the D-optimal design, the user-defined design, and the historical data design. The CCRD is an effective alternative to the factorial design, originally developed by Box and Wilson [23]. This method allows estimating the second-degree polynomial of the relationships between the independent and dependent variables and consequently formulating the sulphur removal from the iron ore concentrate.

In this study, the researchers have concentrated on improving the existing methods and developing new ways for iron ore desulphurization. The desulphurization of iron ore was performed by an atmospheric leaching process in an oxidizing environment aiming at optimizing the leaching parameters that affect the desulphurization of iron ore concentrate. In order to achieve the highest leaching rate and efficiency, the response surface methodology was used to design a model to find out how the variables are related to each other and how they influence the response. Moreover, the optimal conditions for effective desulphurization of the iron ore concentrate were determined by CCRD.

2 Material and methods

2.1 Sample collection and grinding

The iron ore concentrate was obtained from a ball milling-wet magnetic separation process in the Gol-e-Gohar complex. In order to ensure the homogeneity and representativeness of the sample, 300 g of samples were collected every 8 h for 10 d. The chemical content and mineralogy of the concentrate are shown in Table 1 and Fig. 1, respectively. It was a typical magnetite concentrate consisting of minor amounts of quartz and pyrite. It contains 21.1% FeO and a high sulphur content of 1.4%. The concentrate was then dried and homogenized for subsequent desulphurization tests. The particle size of the concentrate was < 10 μm. In this study, the ball mill was used to prepare a smaller particle size for the experiments.

2.2 Solutions, chemicals, and experimental procedure

All the experiments were carried out in solutions containing diluted nitric acid and sulphuric acid. Deionized water (electrical conductivity: 1–3 μS cm^{-1}) was used in the preparation of all aqueous solutions.

The leaching process was performed in a 250 cm^3 Erlenmeyer flask on an electric heater. For each leaching treatment, a 20 g sample of the concentrate, along with 100 cm^3 of the leaching agent solution, was added to the flask and heated for a given time. After the completion of the leaching process, the solid residues were separated

Table 1 Chemical composition of iron ore concentrate (%)

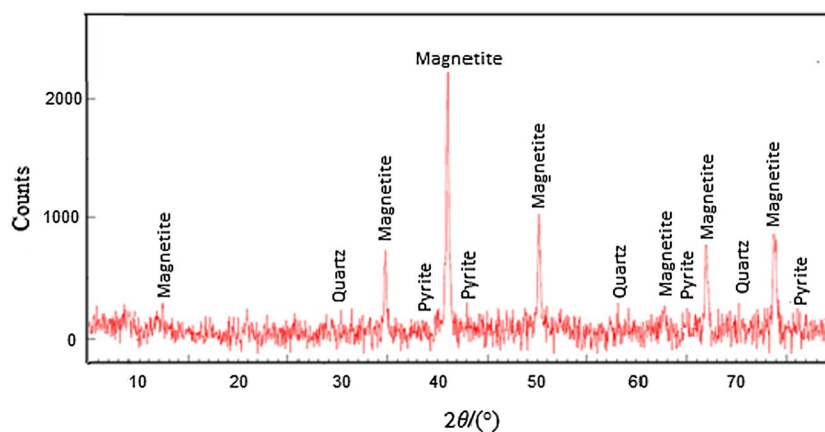| Fe	FeO	S	SiO$_2$	Al$_2$O$_3$	CaO	MgO
66.5	21.1	1.4	2.35	0.24	0.52	1.74

Fig. 1 XRD pattern of iron ore concentrate

on a 0.45-µm filter and stored in a desiccator for further experiments. The filtered sample was extracted with toluene to remove the elemental sulphur produced during the process. Then, the efficiency of the leaching process was determined by measuring the amount of sulphur before and after the leaching tests.

2.3 Statistical software

Design Expert is a software that helped us to design and interpret the multi-factor experiments [24]. Thus, this software was applied in this study to design the experiments and to model and analyse the obtained results.

2.4 Design of experiments

The experimental variables that can affect the desulphurization results were the initial concentrations of nitric and sulphuric acids and the leaching time. Although the stirring rate and temperature might be important, these factors were ignored and all the experiments were carried out under atmospheric conditions without stirring. A CCD with 20 runs and six replicates of the central points were selected to determine the optimum concentrations of nitric acid and sulphuric acid, as well as the ideal time for leaching to obtain maximum desulphurization rate and efficiency. For each factor, five levels were defined as the following codes: $-1.3, -1, 0, +1,$ and $+1.3$. The levels of the chosen independent variables used in the experiments are given in Table 2. High concentration of leaching agent was believed to complicate the regeneration of the stoichiometric amount of circulating acid [25]; therefore, a moderate concentration of sulphuric and nitric acid was selected to design experiments.

Table 2 Variables, their codes, and real experimental values used in central composite design

Variable	− 1.3	− 1	0	+ 1	+ 1.3
Concentration of nitric acid/ ($mol\ dm^{-3}$)	0.27	0.5	1.25	2	2.23
Concentration of sulphuric acid/ ($mol\ dm^{-3}$)	0.14	0.25	0.63	1	1.11
Time/h	6.6	12	30	48	53

3 Results and discussion

The simplified oxidation reaction for sulphide minerals in iron ore with nitric acid is as follows [26]:

$$2FeS_2 + 10HNO_3 = 2Fe^{3+} + 2H^+ + 4SO_4^{2-} + 10NO + 4H_2O \tag{1}$$
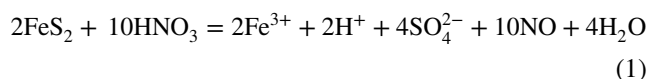
And because of the interaction of anions and cations in solution, the reaction could be written as:

$$2FeS_2 + 10HNO_3 = Fe_2(SO_4)_3 + H_2SO_4 + 10NO + 4H_2O \tag{2}$$
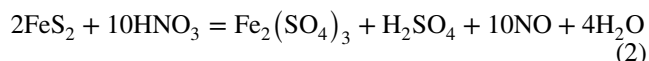
According to this reaction, 800 g iron (III) sulphate, 98 g sulphuric acid, 300 g NO gas and 72 g water will be produced per 240 g of pyrite dissolution along with 630 g nitric acid consumption.

In order to investigate the efficiency of leaching for sulphur removal, the sulphur content of the concentrate was measured before and after the leaching process, and the percentage of sulphur removal was obtained using the following equation:

$$\eta_S = \frac{S_i - S_f}{S_i} \times 100 \tag{3}$$

where η_S is the sulphur removal, %; and S_f and S_i refer to the final and the initial sulphur content of the iron ore concentrate, respectively.

The complete design matrix of the full factorial CCD, along with both the response values from the experimental works, is given in Table 3.

Among the 20 experiments shown in Table 3, six runs (run No. 8, 11, 13, 16, 18, and 20) were the repetition of the central point. In these experiments, all the factors are in the central point of their values. The inclusion of the central points allows to check whether the fitted model is adequate or needs to include some quadratic terms to allow curvature. The similarity among the responses of these five experiments can be a sign of the accuracy of the experiment process and pure error derived from the repetitions of the central point. The iron recovery in all experiments was above 93%, and also > 50% of lead and 60% of copper was extracted during the experiments.

3.1 Selection of model and formulation of desulphurization

Analyses of variance (ANOVA) and least squares techniques were used to evaluate the statistical significance of the constructed models. The ANOVA includes determination of the factor(s) that significantly affect(s) the response by using the Fisher statistical test (F test). The significance and the magnitude of the estimated coefficients of each variable and all

their possible interactions with the response variable(s) were determined. Such coefficients represented the improvement expected in the response when the variable was set from low to high values. Effects with a confidence level < 95% (effects with a P value higher than 0.05) were discarded and pooled into the error term, and a new analysis of the variance was performed for the reduced model. Six replicates of the central point were performed to estimate the experimental error.

The ANOVA, made for response surface model, is shown in Table 4. As can be observed, the P value for this model is < 0.0001, which indicates that the model is considered to be highly significant from the statistical point of view.

The experimental results given in Table 4 were fitted in a model equation by applying multiple regression analysis for sulphur reduction (using the abovementioned software). The cumulative effects of the variables, and their mutual interactions and the polynomial equations for the responses were validated using the statistical analysis of the variance.

The model equation regarding the desulphurization process was expressed as a function of nitric acid concentration, sulphuric acid concentration and leaching time. Each term with a P value > 0.05 was removed from the main equation. None of the factors was found to be significant enough to be eliminated. The reduced model using significant linear, quadratic and interaction parameters was defined in the form of a polynomial equation. As shown in Table 4, the highest order of the polynomial models was 2FI, quadratic and cubic, in which the additional terms were significant.

Table 3 Design matrix of full factorial CCD

Run number	Nitric acid concentration/ (mol dm^{-3})	Sulphuric acid concentration/ (mol dm^{-3})	Time/h	Sulphur content of concentrate/%	Sulphur removal/%
1	0	0	1.3	0.27	80.9
2	1	− 1	1	0.38	72.8
3	− 1.3	0	0	1.31	6.4
4	− 1	1	− 1	0.96	31.1
5	0	1.3	0	0.40	71.7
6	− 1	1	1	0.25	82.1
7	1.3	0	0	0.22	84.1
8	0	0	0	0.64	54.3
9	− 1	− 1	1	0.85	39.4
10	0	− 1.3	0	0.82	41.5
11	0	0	0	0.44	68.6
12	− 1	− 1	− 1	1.34	4.3
13	0	0	0	0.42	70.0
14	1	− 1	− 1	0.33	76.1
15	1	1	1	0.23	83.9
16	0	0	0	0.59	58.2
17	1	1	− 1	0.24	82.8
18	0	0	0	0.55	60.8
19	0	0	− 1.3	0.61	56.5
20	0	0	0	0.56	60.0

Table 4 Sequential model sum of squares

Source	Sum of squares (SS)	Degrees of freedom (d.f.)	Mean square (MS)	F value	P value Prob > F	Remark
Mean versus total	6.50	1	6.50			
Linear versus mean	1.67	3	0.56	18.6	< 0.0001	
2FI versus linear	0.27	3	0.09	5.5	0.0116	Suggested
Quadratic versus 2FI	0.11	3	0.04	3.9	0.0454	Suggested
Cubic versus quadratic	0.05	4	0.01	1.6	0.2787	Aliased
Residual	0.05	6	0.01			
Total	8.65	20	0.43			

Table 5 Model summary statistics

Source	SD	R^2	Adj. R^2	Pred. R^2	PRESS
2FI	0.13	0.90	0.86	0.79	0.46
Quadratic	0.10	0.95	0.91	0.75	0.53

However, since the cubic model was aliased, the quadratic and 2FI models were selected. The final empirical models are shown in Eqs. (4) and (5), respectively.

For the quadratic model,

$$R_1 = +0.55 - 0.3A - 0.16B - 0.14C + 0.092AB + 0.16AC - 0.035BC + 0.11A^2 + 0.016B^2 - 0.085C^2 \qquad (4)$$

and for the 2FI model,

$$R_2 = +0.57 - 0.32A - 0.16B - 0.14C + 0.092AB + 0.16AC - 0.035BC \qquad (5)$$

where A is the nitric acid concentration, (mol dm^{-3}); B is the sulphuric acid concentration, (mol dm^{-3}); C is the leaching time, h; and R_1 and R_2 are the model response, i.e. sulphur removal percentage.

The statistical significance of these equations was checked using the F test. The values of R^2, SD, and the predicted R^2, corresponding to the sulphur removal process obtained from Eqs. (4) and (5), are given in Table 5. R^2 was found to be 0.90 and 0.95 for the 2FI and quadratic models, respectively. The closer to 1 or − 1 the value of R^2 is, the better the model predictions are. In other words, high values of R^2 indicate that the equation is capable of representing the system under a given experimental domain. Therefore, a quadratic model was chosen because this model could explain about 95% of the total variations in the system while the 2FI model described 90% of the variations (Table 5). In order to show the quality of fitness of the polynomial model, R^2 can be used. However, the adjusted regression coefficient (Adj. R^2) and the prediction regression coefficient (Pred. R^2) are better criteria compared to the absolute regression coefficient, as

R always decreases when a regression variable is eliminated from the model. In statistical modelling, Adj. R^2, which takes the number of regression variables into account, is usually selected because of its high predictive capacity. These parameters are approximated using the predicted residual error sum of squares (PRESS). Hence, R^2, Adj. R^2, and Pred. R^2 are very convenient in obtaining a quick impression of the overall fit and the predictive capacity of a constructed model.

Each studentized residual in Fig. 2 is the residual divided by the estimated standard deviation of that residual. It measures the number of standard deviations separating the actual and predicted values. The normal probability plot (Fig. 2) indicates whether the residuals follow a normal distribution, in which the points will follow a straight line. Since an S-shaped curve is not formed, neither a response transformation is needed nor is any apparent problem with normality present.

Figure 3 shows a plot of the residuals against the experimental run order, which is used to check for lurking variables that may have influenced the response during the experiments. The plot should show a random scatter while the trend indicates a time-dependent lurking variable in the background. Blocking and randomization provide insurance against trends running the analysis.

3.2 Model validation and fitness of the model

The performance of the model was checked by the lack of fit test and the determination coefficient (percentage of variability in the response that can be explained by the model), as mentioned in Sect. 3.1. Table 6 shows the degrees of freedom and F values for the evaluation of the quadratic model.

Minimum 3 lacks of fit d.f. and 4 d.f. for pure error are recommended to ensure a valid lack of fit test. Fewer d.f. will lead to a test that may not detect the lack of fit. Hence, the cubic model is rejected. Also, the results in Table 4 show that the F value is not significant and there is no lack of fit for the quadratic model.
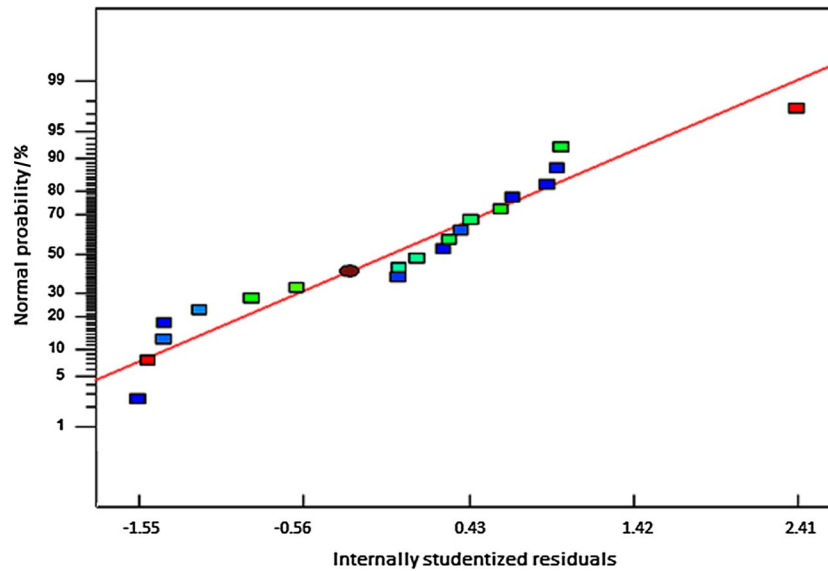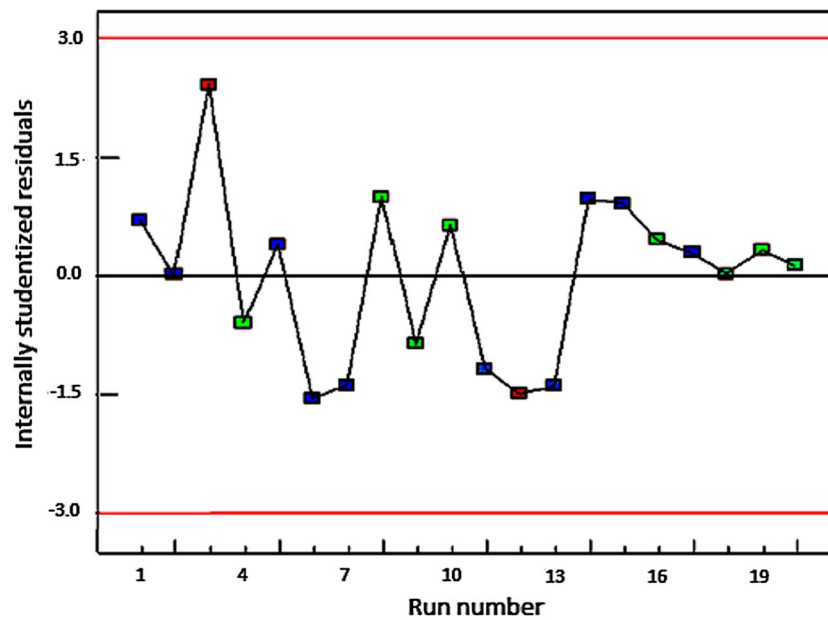
Fig. 2 Normal plot of residuals

Fig. 3 Residuals versus run number

Table 6 Degrees of freedom for the quadratic model

Name	Sum of squares	Degrees of freedom	F value
Model	2.04	9	22.9
Residuals	0.099	10	
Lack of fit	0.062	5	1.67
Pure error	0.037	5	
Corrected total		19	

In order to validate the model, a new series of experiments were carried out. Each treatment was a combination of all studied variables. Variable levels were chosen randomly within the range of the values used in the design. Validation treatments are listed in Table 7. These results indicate that the model and the polynomial formula, calculated for the desulphurization process, are appropriate.

Table 7 Validation treatments, responses, and predicted responses of the model

Treatment			Response	Predicted response
N level	S level	Time level		
0.6	0.6	48	0.6	0.55
1.0	0.7	24	0.71	0.68
1.8	0.4	12	0.29	0.35
1.5	0.9	40	0.31	0.28
0.6	0.4	16	1.12	1.2

3.3 Interaction of factors and optimization

The range checked for the three variables (nitric acid concentration, sulphuric acid concentration, and leaching time) was selected in such a way that the recycling of nitric acid to the leaching cycle as well as maximum performance and sulphur removal rate, is achieved. The concentration of nitric acid directly influences desulphurization, as mentioned in Eq. (1). Additionally, as the catalyst intensifier, sulphuric acid strengthens the dissolution of sulphur-bearing minerals. Higher concentrations of nitric acid and sulphuric acid result in the increase of desulphurization rate while nitric acid recycling decreases with the increase in the acid concentration.

In the CCD, the response of desulphurization can be assessed and compared with respect to its optimum conditions. A comparison can be made based on the obtained profiles for the sulphur content of the concentrate after leaching, using their respective polynomial equations and the response surface graphs of the sulphur content as shown in Fig. 4. The optimal value for each parameter, extracted from these

surface graphs, was found to be 1.39 mol/dm^3 (8.8% V/V) for the concentration of nitric acid and 0.88 mol/dm^3 (4.9% V/V) for the concentration of sulphuric acid, and the leaching time was 47 h. The best response or the highest percentage of desulphurization was observed under optimized condition.

Confirmatory tests were also performed using the optimum setting to test the validity of the results suggested by the models. The percentage of sulphur removal was obtained to represent the accuracy and capability of the used theoretical models.

4 Conclusions

1. The iron ore sample contains high levels of sulphur impurity, and pyrite is as the main sulphur mineral phase.

2. The response surface methodology was a valuable approach for modelling and optimizing the desulphurization of iron ore concentrate using the leaching process. In order to obtain the optimized conditions for the sulphur removal, the experiments were designed using CCD method. Response surface plots and contour maps were drawn to show how the responses varied with changes in different levels for various operating factors. The desulphurization of the iron ore concentrate using chemical leaching method was successfully modelled with a high correlation coefficient. Optimized conditions were applied experimentally on a real sample and an acceptable response was achieved.

3. Three main parameters including sulphuric and nitric acid concentrations and the leaching time were con-
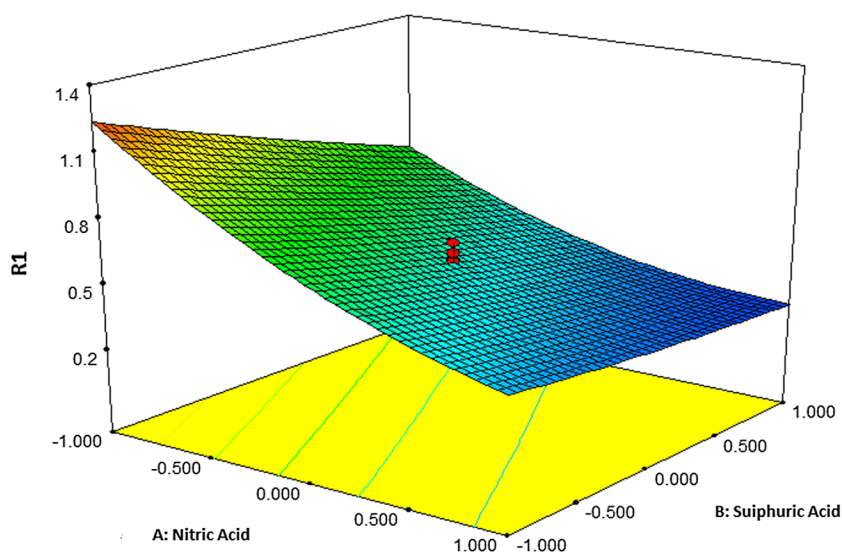
Fig. 4 3D surface graph for sulphur removal

sidered in a central composite response surface design. The concentration of nitric acid had the most significant effect on the desulphurization rate. A better desulphurization rate could be achieved at higher concentrations of acid. Also, longer leaching time in low acid concentrations had the same efficiency. Therefore, there are two ways to effectively remove sulphur from the iron concentrate: high leaching time in low acid concentration and low leaching time in high acid concentration. Since time is a more important parameter in the industry, the second way is preferred.

4. Finally in this research, in addition to the removal of sulphur and formulation of desulphurization, the sulphur-bearing minerals were converted into useful by-products, and this could be an incentive for alternative flotation.

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