Desulfurization of coal by HNO_3 leaching: Optimization of influential factors using Box-Behnken design

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Abstract

Sulfur is one of the most significant impurities in coal, which reduces the quality of coal and also results in environmental pollution. This work was aimed to investigate the removal of sulfur from coal by the leaching method employing parameters expected to affect the removal rate such as acid concentration (10-30%), temperature (40-80 °C), and reaction time (40-100 min). A response surface methodology using Box-Behnken design was employed to maximize, model, and evaluate the factors affecting the desulfurization process. The results obtained indicated that the desulfurization value increased with increase in the acid concentration, temperature, and reaction time. A quadratic model with a high correlation coefficient (R^2=0.98) is proposed and developed for the relationship between the removal value and the influential factors. The modeling results demonstrated that the significance degree of factors was in the order of acid concentration>temperature>reaction time. It was also found that the maximum desulfurization (about 87%) could be obtained under the optimal conditions of acid concentration=25%, temperature=80 °C, and leaching time=84 minutes.

Keywords: *Coal, Desulfurization, Optimization, Sulfur, Leaching, Nitric Acid.*

1. Introduction

Coal is one of the world's most abundant fossil fuel resources. It is an important source of energy to industry despite its hazards to the communities. It is not a clean fuel as it contains ash and sulfur [1, 2]. Sulfur compounds are converted to sulfur oxides during combustion, and they ultimately lead to acid rain. Sulfur dioxide and other combustion-related pollutants from sulfur-containing fuels also lead to environmental concerns. In fact, sulfur oxide (SO_x) emission as a pollutant is a real threat to both the ecosystem and the human health [1, 3]. Hence, a clean energy production has attracted numerous research efforts to develop new and innovative techniques to use coal with less environmental effects.

Sulfur in coal is found in both the organic and inorganic forms. The inorganic sulfur is mainly in two forms, as ferrous disulfides (mainly pyrite) and as sulfate. The organic and pyritic sulfur contents are almost equally partitioned in many coals, and the sulfate form is usually very small [4-6]. Pyritic sulfur refers to ferrous disulfide, and is usually removed by the physical separation methods such as froth flotation and gravity separation. Up to 50% of inorganic sulfur can be removed by the froth flotation process. Organic sulfur is fixed in the chemical structure of coal, and it is often much more difficult to remove than the inorganic sulfur. Organic sulfur is partially removed by breaking its chemical bonds using chemical methods (such as leaching) [4-6].

Demirbaş and Balat [7] have investigated coal desulfurization using the physical, chemical, and biological methods. They have expressed that physical and biological methods are ineffective and time-consuming, and they can be applied only on the bench scale, while the chemical techniques (aqueous solutions of strong inorganic acids such as hydrochloric acid and phosphoric acid) are effective in coal desulfurization. They have also

reported that chemical desulfurization of coal with various oxidizing agents, ferric sulfate, hydrogen peroxide, and performic acids are effective for the removal of ash and pyretic and sulfate sulfur but yield only a small reduction of organic sulfur [7].

The effect of chemical cleaning of coal with KOH and HCl for desulfurization has been investigated at 95 °C and 150 °C by Mukherjee and Borthakur [8]. Increasing the KOH concentration and temperature were important factors in desulfurization. A two-step process was required for an almost complete removal of the inorganic sulfur, 11–15% organic sulfur from the coal samples at 95 °C, and the later increases to about 35–37% at 150 °C.

Jorjani et al. [9] have used microwave irradiation and peroxyacetic acid washing combination as an effective process for the removal sulfur from coal. They reported that particle size reduction and microwave irradiation had positive effects on the desulfurization process, and under the optimized conditions, the pyritic, organic, and total sulfur decreased from the initial percentage values of 0.77%, 0.67%, and 1.44% to 0.06%, 0.42%, and 0.48%, respectively.

Applying a combination of flotation and leaching processes with a mixture of potassium hydroxide and ethanol as the solvent were used in the leaching method for desulfurization of coal [10]. The increase in the potassium hydroxide concentration had a positive effect on the sulfur reduction. Increasing the methanol concentration (alone) as an organic solvent was not able to dissolve the inorganic sulfur and remove it. According to froth flotation and leaching, 66.41% and 32.89% of the total sulfur were removed, respectively. In the leaching method, the maximum sulfur reduction happened at a methanol concentration of 10%, potassium hydroxide concentration of 0.2 g g^{-1}, a time period of 30 min, and a temperature of 120 °C. Consequently, in both processes, the maximum amount of total percentage sulfur reduction was obtained to be 82.5%.

A mixture of sulfuric acid and hydrogen peroxide, as the oxidant, was used for coal desulfurization [11]. The best condition for pyrite dissolution in carbon was observed with 1 M hydrogen peroxide and 0.5 M sulfuric acid at a temperature range of 40- 60 °C. In this condition, dissolution of pyrite was obtained to be around 50% in the first 30 min. In another work, pyrite sulfur was removed using the flotation and leaching methods by sulfuric acid [12]. The sulfur reduction rate was improved by increasing the amount of collectors and particle size, and also by decreasing the amount of frother and solid weight percentage. About 52.9% of pyrite sulfur was removed by the flotation process under the optimum conditions of 1 kg/t collector, 50 g/t frother, particle size of 100 mesh, solid percentage of 5%, and 3 min flotation time, whilst using the leaching method, the removal amount of pyrite sulfur was 13%.

Application of chemical desulfurization was studied by the molten caustic leaching (MCL) method by Wahab et al. [13]. They have reported that the removal value of sulfur could reach about 40% by increasing coal to caustic ratio and decreasing the particle size at 250 °C within 1 h.

As it can be viewed in the literature, the chemical methods are effective in the removal of coal, and hence, the objective of this work was to focus to reduce the sulfur content in coal using nitric acid leaching. In this work, response surface modeling based on the Box-Behnken design was employed to determine the effects of important parameters and to optimize the desulfurization process.

2. Materials and analysis of coal sample
2.1. Materials
The coal samples required were obtained from Eastern Alborz coal washing plant, located in the Semnan Province in NE Iran. The samples collected from flotation of concentration.

HCl (37%) and HNO$_3$ (65%) (supplied from Merck, Germany) were used as lixiviant for coal desulfurization in the leaching process.

The samples were prepared and ground by Jaw crusher and ball mill so that 85% of particles were less than 250 μm in diameter. Then analysis of coal was carried out to measure the amount of ash, volatile matter, sulfate, and pyrite sulfur.

2.2. Analysis of coal ash and volatile matter content by standard tests
The ash content of the coal sample was determined using an electric furnace by weighting the residue remaining after burning the sample between 700 °C to 750 °C within 2 h using the weight of the crucible containing 1 g of the sample (see Eq. 1).

$$Ash = \frac{W_{CR} - W_C}{W} \times 100 \qquad (1)$$

where:
W$_R$: weight of the crucible and ash residue (g);
W$_{CR}$: weight of the empty crucible (g);
W: weight of the original coal sample (g).

In order to determine the amount of volatile matter, 3 g of the coal sample was loaded into crucibles with self-sealing covers and heated to the desired final temperature of 950 °C and held at this temperature for 7 minutes. Then the percentage of the volatile matter was calculated using Eq. 2.

$$VM = \frac{W - (W_{CCR} - W_{CC} - ash)}{W} \times 100 \qquad (2)$$

where:
VM: percentage of the volatile matter;
W_{CCR}: weight of the crucible, cover, and material residue (g);
W_{CC}: weight of the empty crucible and cover (g);
W: weight of the original coal sample (g).

2.3. Sulfate, pyrite, and organic quantity determination

A 2 g coal concentrate sample was poured into a prepared 50-mL HCl solution (including 20 mL HCl and 30 mL distilled water). In order to reduce the total volume to 20 mL, the mixture was heated and the remaining sediment was washed with distilled water. Then the percentage of the sulfate sulfur extracted was measured by the emission spectrometry method using the following equation:

$$S_s = \frac{C_{SO_4} \times M_S \times V}{M_{SO_4} \times W} \times 100 \qquad (3)$$

where:
S_S: percentage of sulfate sulfur;
C_{SO4}: sulfate ion concentration (mg/L);
M_S: sulfur atomic mass;
V: solution volume (L);
M_{SO4}: sulfate molecular mass;
W: weight of sample used (mg).

The residue from the sulfate determination was used for the determination of the pyritic sulfur content. 1 g sample was added to a mixture of 15 mL nitric acid (65%) and 100 mL water, and then the mixture was boiled gently for about 50 minutes. Thereafter, the mixture was filtered, and the filtrate was analyzed by an atomic absorption spectrometer for its iron content, and finally, the pyritic sulfur was determined according to the following equations:

$$Fe_{Py} = \frac{C_{Fe} \times V}{W} \times 100 \qquad (4)$$

$$S_{Py} = Fe_{Py} \times \frac{2 \times M_S}{M_{Fe}} \qquad (5)$$

where:
Fe_{Py}: percentage of pyritic iron;
C_{Fe}: iron ion concentration (mg/L);
V: solution volume (L);
W: weight of the sample (mg);
S_{py}: percentage of pyritic sulfur;
M_S: sulfuratomic mass;
M_{Fe}: iron atomic mass;
$(2 \times M_S)/M_{Fe}$: sulfur to iron ratio in pyrite.

The organic sulfur content was obtained by calculating the difference between the total sulfur content and the sum of pyritic and sulfatic sulfur contents. The results obtained and the elemental analysis results for the coal sample are presented in Table 1.

Table 1. Analysis of Eastern Alborz coal concentrate sample (dry basis).

	(wt.%)
Proximate analysis	
Ash	15.37
Volatile matter	24.05
Fixed carbon	60.54
Ultimate analysis	
Carbon	73.59
Hydrogen	3.83
Nitrogen	1.54
Sulfur	1.35
Oxygen (by difference)	19.69
Different forms of sulfur	
Sulfate S	0.07
Pyritic S	1.06
Organic S	0.22

3. Methods
3.1. Experimental design
The experiments were designed using the response surface methodology (RSM) approach. RSM is a modeling technique based on the relationship between a set of experimental parameters and the estimated results according to the mathematical and statistical methods [14]. RSM can improve the experimental conditions with a minimum number of experiments, which includes selecting a number of operating parameters, evaluating the main factors and the interaction between variables, model fitting, observing the influence of the parameters based on the response curves, and estimating the condition optimization [15, 16]. A Box-Behnken design was chosen, which included 15 experiments of three variables at three levels (-1, 0, 1) (Table 2) as it needs a fewer number of runs than the central composite design (CCD).

Factor	Symbol	Low (-1)	Medium (0)	High (+1)
Temperature (°C)	A	40	60	80
Acid concentration (%)	B	10	20	30
Time (min)	C	40	70	100

In order to predict the responses and determine a critical point (maximum or minimum), the results obtained were fitted to consider the behavior of each variable and their interactions that explained the quadratic polynomial as given in Eq. 6 [17]:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{1 \langle i \langle j}^{k} \beta_{ij} x_i x_j + \sum_{1 \langle i \langle j}^{k} \beta_{ii} x_i^2 + \varepsilon \qquad (6)$$

where Y is the predicted response value; x_i and x_j are the experimental factor codes; β_0 is the constant term; k is the number of factors being studied; β_i, β_{ij}, and β_{ii} are the linear, interaction, and squared coefficients, respectively; and ε is the residual corresponding to the experiments.

3.2. Leaching experiments

The experiments were conducted based on the Box-Behnken design; the experimental design matrix is presented in Table 3. The leaching experiments were carried out in a glass reactor of 250 mL, which was heated on a hot plate equipped with a digital controlled magnetic stirrer. A 7 g representative sample was selected

for each leaching test and desulfurized using a 50 mL aqueous solution, and the desired temperature and leaching time with a stirring rate of 700 rpm. It should be pointed out that the leaching liquor was prepared using distilled water and the analytical grade HNO_3 reagent at predetermined concentrations. After each experiment, the sample was filtered and analyzed to determine the total sulfur content by ICP:

$$SR\% = \frac{C_S \times V}{W \times S_T} \times 100 \qquad (7)$$

where:
SR: percentage of sulfur removal;
C_S: sulfur concentration (mg/L);
V: solution volume (L),
W: weight of the coal samples (mg);
S_T: percentage of the total sulfur content in the coal sample.
The actual and predicted response values (sulfur reduction %) obtained from the leaching process is demonstrated in Table 3.

Table 3. Observed responses in Box-Behnken design for desulfurization.

Exp. No	Std. No	A: Temperature (°C)		B: Acid concentration (%)		C: Time (min)		Sulfur reduction (%)	
		coded	uncoded	coded	uncoded	coded	uncoded	Experimental	predicted
3	1	-1	40	1	30	0	70	39.38	40.25
1	2	-1	40	-1	10	0	70	2.24	3.49
5	3	-1	40	0	20	-1	40	19.79	21.16
15	4	0	60	0	20	0	70	53.09	46.54
9	5	0	60	-1	10	-1	40	4.49	1.87
2	6	1	80	-1	10	0	70	27.90	27.03
10	7	0	60	1	30	-1	40	44.23	41.98
14	8	0	60	0	20	0	70	41.56	46.54
13	9	0	60	0	20	0	70	44.98	46.54
12	10	0	60	1	30	1	100	61.64	64.26
4	11	1	80	1	30	0	70	86.15	84.90
7	12	-1	40	0	20	1	100	36.23	32.73
6	13	1	80	0	20	-1	40	48.26	51.75
8	14	1	80	0	20	1	100	71.70	70.33
11	15	0	60	-1	10	1	100	7.49	9.73

4. Results and discussion
4.1. Statistical analysis

The Design Expert software was used for the regression and graphical analysis of the experimental data using the Analysis of Variance (ANOVA) to check the adequacy of the proposed model [18]. The quality of the polynomial modal was estimated by the R^2, adjusted R^2, predicted R^2

(coefficients of determination), adequacy precision, and lack-of-fit values. The significance of each variable term in the fitted equations was determined by the high F and low P (less than 0.05) values of the regression model [19]. The ANOVA results for desulfurization of coal are summarized in Table 4, which denotes the quadratic model at 95% confidence level

(P < 0.05) that was fitted on the experimental data, which revealed that it was statistically significant. The influence of all variables and the quadratic term of acid concentration (A^2) are significant in coal desulfurization, while the nitric acid concentration has the most effect on the sulfur recovery. However, the interaction between the selective parameters did not have a main effect on sulfur reduction.

Moreover, the perturbation plot applied to identify the combined effects of factors on desulfurization (shown in Figure 1) can confirm the results obtained from Table 4.

Table 4. ANOVA for response surface quadratic model for sulfur removal.

Source	Sum of squares	Degree of freedom	Mean square	F-value	p-value	Importance
Model	8066.69	9	896.30	35.34	0.0005	significant
A	2324.89	1	2324.89	91.66	0.0002	
B	4478.76	1	4478.76	176.57	<0.0001	
C	454.36	1	454.36	17.91	0.0082	
AB	111.38	1	111.38	4.39	0.0903	
AC	12.27	1	12.27	0.48	0.5177	
BC	51.93	1	51.93	2.05	0.2119	
A^2	44.06	1	44.06	1.74	0.2447	
B^2	453.11	1	453.11	17.86	0.0083	
C^2	132.93	1	132.93	5.24	0.0707	
Residual	126.82	5	25.36	-	-	
Lack-of-fit	56.64	3	18.88	0.54	0.7016	Not significant
Pure error	70.19	2	35.09	-	-	
Total	8193.51	14	-	-	-	
$R^2 = 0.98$, $R^2_{adj} = 0.96$, $R^2_{pred} = 0.87$, Adeq. precision = 20.19						
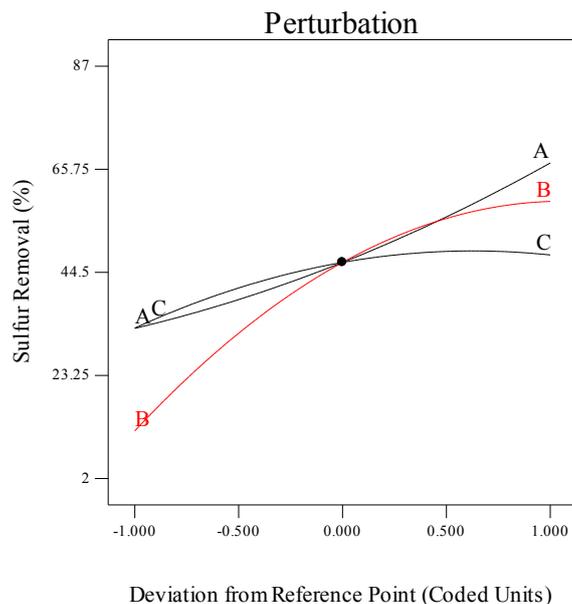
Figure 1. Perturbation plot for desulfurization of coal.

For a good fit of a model, R^2 should be at least 0.8. Meanwhile, the closer the R^2 value to 1 shows a stronger prediction of responses by the model [20, 21]. In this model, the "R-squared", "adj R-squared", and "pred R-squared" values were found to be 0.98, 0.96, and 0.87 for sulfur recovery, respectively. Besides, the lack-of-fit value is not significant for the response with a P-value of 0.7 fitted to all data (P-value > 0.05 is not significant) because a non-significant lack-of-fit is good. Also "Adeq Precision" measures the signal-to-noise ratio; indeed it compares the range of the predicted values at the design points to the average prediction error [22]; a ratio greater than 4 is desirable. The ratio was found to be 20.19, which indicates a sufficient signal. The results obtained were tabulated in Table 4.

Figure 2 represents the relationship between the experimental data and the predicted value with a satisfactory correlation coefficient (0.98). The

predicted points around the diagonal line were close to the actual values, which confirmed the validity of the model.

The empirical relationship between the variables in the terms of coded units (A, B, and C) and the responses of leaching process (SR) were explained as a quadratic polynomial model, which predicts the sulfur reduction rate through the Box-Behnken design, as given in Eq. 8:

$$\begin{aligned} SR = &+46.54 + 17.05 \times A + 23.66 \times B + \\ &7.54 \times C + 5.28 \times A \times B + \\ &1.75 \times A \times C + 3.60 \times B \times C + \\ &3.45 \times A^2 - 11.08 \times B^2 - 6.00 \times C^2 \end{aligned} \quad (8)$$
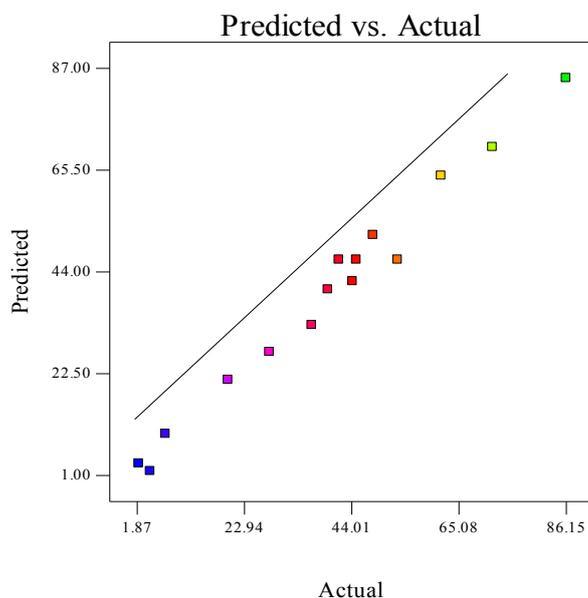
Figure 2. Scatter diagram of predicted results versus actual values for coal desulfurization.

4.2. Effects of interactive data by response surface modeling

In order to provide a better understanding of the effect of the variables on coal desulfurization, the 3D surface plots against any two variables were studied, while holding another variable constant at its center point. In addition, the corresponding contour plots represent the x-y plane by the plan of response surface to provide a determination of the effective parameters.

The effects of acid concentration and temperature at the 3D plot while the time factor is fixed in 70 min (center value of time) and its contour plot are represented in Figure 3. The acid concentration and temperature factors were found to be the most important variables in the S recovery. Meanwhile, by considering the high content of pyrite present in total sulfur (about 78% in this study) and applying nitric acid as a strong reagent for oxidizing of pyrite sulfur [23], the reaction rate raised. As a consequence, the maximum total sulfur reduction (around 86%) was obtained in high levels of temperature and concentration of nitric acid because the nitric acid dosage and temperature are the effective parameters for increasing the dissolution rate of pyrite sulfur [24].

The interaction between temperature and time on desulfurization at constant acid concentration (20%) and its contour plot can be seen in Figure 4, as the reaction time had the smallest effect in comparison to the other parameters. Since the desulfurization reaction is exothermic [5] and a higher temperature has a positive effect on the reaction rate, the sulfur removal performance was better during the first selective minutes.

The 3D response of coal leaching efficiency and contour plot corresponding to acid concentration and time by keeping the temperature at the middle value 60 °C is given in Figure 5. Since the pyrite sulfur content can be dissolved in nitric acid solution and the interaction between FeS_2 and HNO_3 is very sensitive to concentration [23], desulfurization of coal was enhanced by increasing the nitric acid concentration. However, removal of sulfur was insignificant in a high level of time because the decrease in the organic sulfur in high rank coals was very low because most part of their sulfur was thiophenic [25]. Therefore, desulfurization of this type of sulfur is possible only by cleaving the C-S bonds [26]. For this reason, a complete removal of the organic portion is difficult.
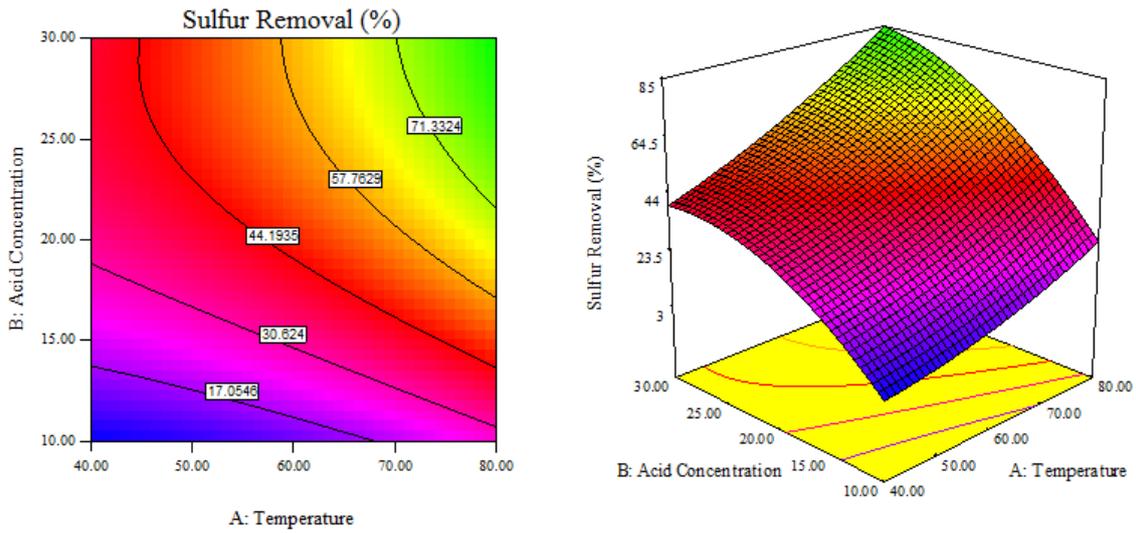
Figure 3. Contour and surface plots of sulfur removal versus acid concentration and temperature in 70 min.
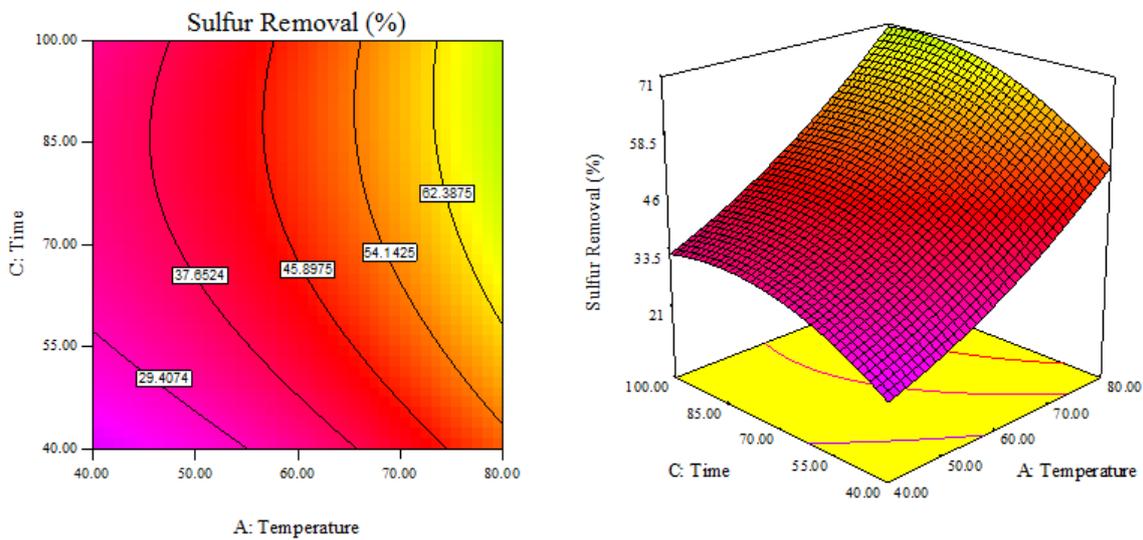
Figure 4. Contour and surface plots of sulfur removal versus time and temperature at an acid concentration of 20%.
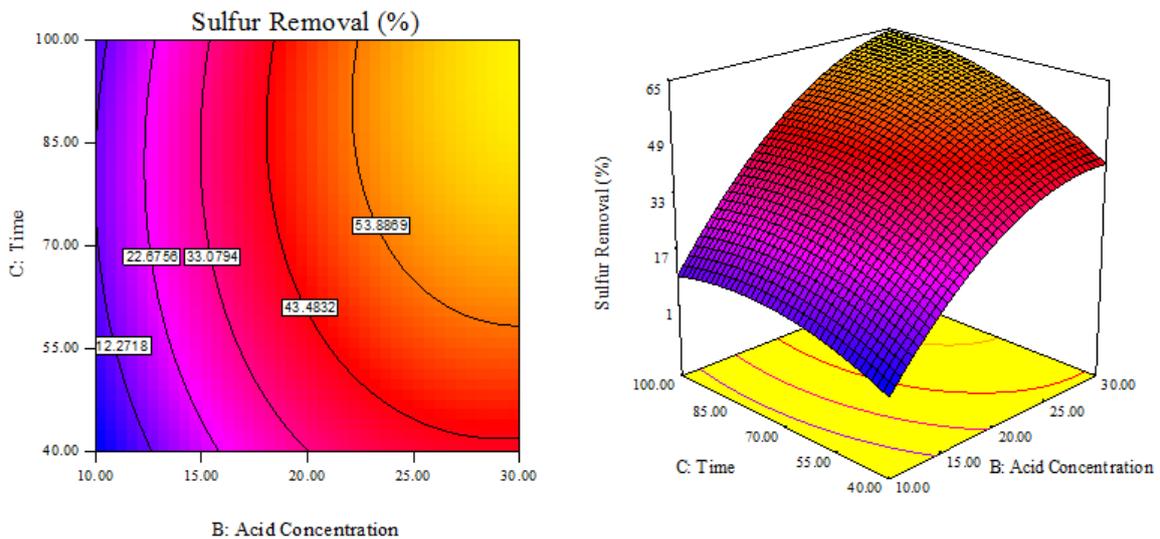
Figure 5. Contour and surface plots of sulfur removal versus time and acid concentration at 60 °C.

4.3. Optimization of desulfurization process

The desulfurization process of coal was optimized using the Design Experts software and quadratic programming (Eq. 8) to maximize the removal rate within the experimental range (Figure 6). As observed, the reduction rate of sulfur was achieved to be 86.96% under the optimal conditions. Also in order to confirm the accuracy

of the predicted model, three extra desulfurization experiments were conducted at the predicted optimum conditions including the temperature 80 °C, acid concentration of 25%, and leaching time of 84 min. Under these conditions, the average of three extra tests was about 86.54%, which proved the suitability and accuracy of the model.

Temperature = 79.97   Acid Concentration = 27.70

Time = 83.66   Sulfur Removal (%) = 86.9593

Desirability = 1.000
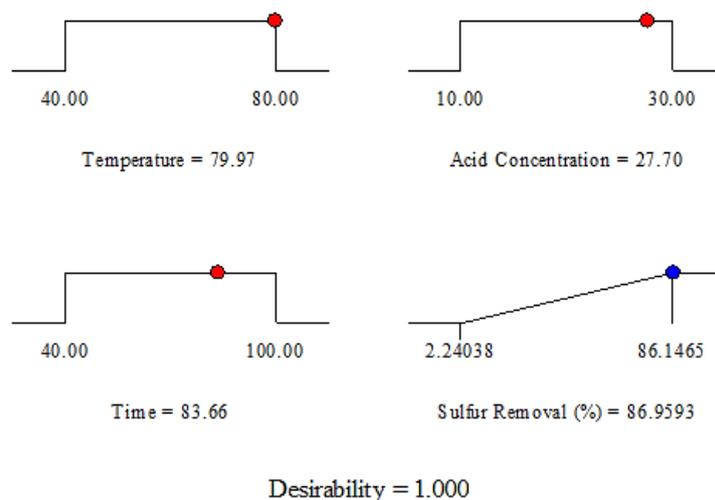
Figure 6. Optimum conditions for sulfur removal.

5. Conclusions

The removal process of sulfur from Eastern Alborz coal washing plant was carried out using nitric acid leaching. Response surface modeling combined with the Box-Behnken design was used to optimize the desulfurization process. A second-order model (with $R^2 = 0.98$) was proposed to gain a better understanding of the behavior of the effects of factors and process. The findings indicated that the nitric acid concentration was the most influential parameter in the desulfurization process. The removal rate enhanced with an increase in the acid concentration, temperature, and reaction time. The optimal conditions were found to be 80 °C, 84 min for the leaching time, and 25% for the acid concentration. Under these conditions, the highest reduction rate of sulfur was achieved to be about 87%.

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گوگردزدایی از زغال‌سنگ به‌وسیله لیچینگ با اسید نیتریک: بهینه‌سازی عوامل مؤثر با استفاده از طرح باکس- بنکن

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چکیده:

گوگرد یکی از مهم‌ترین ناخالصی‌های موجود در زغال‌سنگ است که کیفیت زغال‌سنگ را تحت تأثیر قرار داده و آلودگی‌های زیست‌محیطی را منجر می‌شود. این تحقیق با هدف بررسی حذف گوگرد از زغال‌سنگ با به‌کارگیری روش فروشویی و با استفاده از تأثیر پارامترهای مورد نظر بر روی میزان حذف، مانند غلظت اسید (۱۰-۳۰٪)، دما (۸۰-۴۰ درجه سانتی‌گراد) و زمان واکنش (۴۰-۱۰۰ دقیقه) انجام گرفت. روش سطح- پاسخ با به کارگیری طرح باکس- بنکن به منظور بهینه‌سازی، مدل‌سازی و ارزیابی فاکتورهای مؤثر بر فرآیند گوگردزدایی به کار گرفته شد. نتایج به دست آمده نشان داد که میزان گوگردزدایی با افزایش غلظت اسید، دما و زمان واکنش، افزایش می‌یابد. یک مدل درجه دوم با ضریب همبستگی بالا (R^2 =۰/۹۸) پیشنهاد و به منظور بررسی ارتباط بین میزان حذف و عوامل مؤثر، بسط داده شد. نتایج مدل‌سازی نشان داد که غلظت اسید، دما و زمان واکنش به ترتیب مهم‌ترین عوامل در حذف گوگرد بودند. همچنین مشخص شد که بیشترین میزان گوگردزدایی (حدود ۸۷٪) می‌تواند تحت شرایط بهینه غلظت اسید ۲۵٪، دمای ۸۰ درجه سانتی‌گراد و زمان واکنش ۸۴ دقیقه حاصل شود.

کلمات کلیدی: زغال‌سنگ، گوگردزدایی، بهینه‌سازی، گوگرد، لیچینگ، نیتریک اسید.