

An Investigation of Performance of Ni/Clinoptilolite Nanoadsorbents in Desulfurization of Gas Oil: Experimental Design and Modeling

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Abstract

The removal of sulfur compounds from petroleum is extremely necessary for industrial and environmental reasons. Sulfur in transportation fuels is a major air pollution source. In this work, the efficiency of nanostructured Ni-clinoptilolite adsorbent was investigated in the removal of sulfur from gas oil. For this purpose, the design of experiments was performed by selecting effective factors in desulfurization process. Response surface methodology was selected to model the desulfurization process. Ni-containing nanoadsorbents were prepared by a wet-impregnation method. Gas oil model containing 300 ppmW sulfur was prepared by dissolving a calculated amount of dibenzothiophene (DBT) in n-decane. The concentration of DBT in n-decane was determined by UV-Visible spectrophotometer. The results revealed that sulfur removal extremely depended on the amount of metal and the nature of both metal and support. 5% Ni/support adsorbent resulted in higher sulfur removal efficiency. The optimum ratio of H₂O₂ to gas oil in the studied conditions was in the range of 5% (v/v) and 240 minutes for the best desulfurization performance during the process.

Keywords: Desulfurization, Clinoptilolite, Nickel Supported Nanoadsorbent, Response Surface Methodology, Optimization

1. Introduction

A new method for the removal of the sulfur content in fuel oil is needed today to meet the future legislation on sulfur content, e.g. lower than 50 ppm. The conventional method for reducing sulfur is catalytic hydrodesulfurization (HDS) under severe conditions (Brown et al., 1989). It has been reported that methyl substitution at 4 and 6-positions of dibenzothiophene (DBT) remarkably retards the rate of HDS, and 4-methyldibenzothiophene (4-MDBT) or 4,6-dimethyldibenzothiophene (4, 6-DMDBT) are thus very difficult to convert due to their steric-hindrance even under deep desulfurization conditions. In fact, the reactivities of DBT's decrease in the order of DBT > 4-MDBT > 4,6-DMDBT (Babich and Moulijn, 2003; Nimwattanakul et al., 2006).

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Sulfur-bearing compounds available in most of oil fractions are so undesirable because of the adverse effects on process prosperity, catalyst performance, and environmental problems. They also reduce the performance of the engines during the combustion process. The high temperature and pressure for conventional hydrodesulfurization are the most restrictions upon this method. Beside these disadvantages of the hydrodesulfurization, using expensive cobalt molybdenum catalyst and high consumption of hydrogen are the other disadvantages of this method. According to the limitation imposed by the International Fuel Quality Centre (IFQC), the sulfur content of gas oil and gasoline must be reduced to 10 ppm before 2010 (Choi et al., 2004). The newest methods for the removal of sulfur-bearing compounds are selective adsorption from transportation fuels. The major advances in petroleum refining as well as for fuel cell application will be acquired because of the ambient temperature and pressure accomplished by this method. However, all of the adsorptive materials used for the desulfurization process from the fuel derivatives were ineffective until now, and all of the studies on nonconventional adsorption have not yielded enough efficiency to scale up to industrial production (Breysse et al., 2003). Some of the selective and high capacity sulfur adsorbents that have been discovered are listed below. Zeolites containing cuprous or silver cations prepared by the ion exchange of zeolites using known ion-exchange procedures are the class of adsorbents that bind thiophenic compounds selectively by π -complexation (Rashidi et al., 2015; Zhi-zhong, 2008).

Various studies on oxidative desulfurization (ODS) have been reported. The reactivity of sulfur compounds for oxidation is increased with the increase of electron density on sulfur atom. The reactivities of DBT derivatives are influenced by the electron donation of substituted methyl groups, so the reactivity decreases in the order of 4,6-DMDBT > 4-MDBT > DBT, reversing the order of reactivities for HDS. After oxidation, the sulfur compounds are transformed to sulfones. The extraction of sulfones is considered to be a useful method for removal (Song, 2003; Teymouri et al., 2013).

In this work, the efficiency of nanostructured Ni-clinoptilolite adsorbent was investigated in the removal of sulfur from gas oil. Ni-adsorbents were prepared by a wet-impregnation method. Gas oil model containing 300 ppmW sulfur was prepared by dissolving a calculated amount of DBT in n-decane. The concentration of DBT in n-decane was determined by UV-Visible spectrophotometer. To improve the adsorbent efficiency for sulfur compounds removal, a minimum amount of hydrogen peroxide was used as an oxidizing agent. Eventually, the effects of metal loading, type of support, and H₂O₂ dosage on the efficiency of sulfur removal were studied.

Response surface methodology was employed to study the influence of experimental parameters on the desulfurization efficiency of gas oil by oxidative process using Ni-clinoptilolite. The sulfur removal efficiency was selected as the response for the optimization, and the functional relationship between the response and the most significant independent variables (factors) was established by means of the experimental design. Three main factors were chosen as independent variables: dosage of H₂O₂, treatment time, and the percentage of Ni-supported on the clinoptilolite (Arcoya et al., 1997; Kyan and Oswald, 1997; Yetilmezsoy et al., 2009). The optimization of experimental parameters is usually assessed by the systematic variation of one parameter while the others are maintained constant. This approach is unable to predict the optimized conditions of the process. In this respect, experimental designs are appropriate tools for process optimization (Annadurai and Sheeja, 1998; Bezerra et al., 2008). In fact, the experimental design allows a considerable reduction in the number of experiments and a rapid interpretation. In the experimental design, it is possible to study a large number of factors and to detect the possible interactions between them. All the parameters are

simultaneously applied in order to calculate their relative effect (Choi et al., 2004; Mansouri et al., 2014).

2. Experimental

2.1. Materials and reagents

Clinoptilolite was obtained from Semnan deposits in north-east of Iran. Hydrogen peroxide, n-decane, dibenzothiophene, and Ni (NO₃)₂·6H₂O were purchased from Merck (Germany).

In order to reduce the size of particles to 250-420 μm using an up-to-down method, the sample was ground and screened. The impurities of the ground materials were removed by using a magnet bar, by using ultrasonic cleaning, by refluxing, and by washing several times by deionized water. For the removal of the carbonate impurities, the ground material was dissolved in 1 N sodium acetate solution. The chemicals used were reagent grade and the solutions were prepared with deionized water. A series of Ni/clinoptilolite adsorbents was prepared using the incipient wetness impregnation technique. Supported Ni-adsorbents with different Ni loadings were prepared by impregnating an appropriate amount of Ni (NO₃)₂·6H₂O onto supports followed by drying at 110 °C and calcining at 550 °C for 4 hrs in air.

2.2. Catalyst characterization

Scanning electron microscopy images were captured by (TESCAN) microscope of Ardabil University. The structural characterization of catalysts was investigated by X-ray diffraction (XRD) technique to analyze the fresh and used catalysts qualitatively and quantitatively. The XRD patterns of the samples were obtained by using the Razi Metallurgical Research Center X-ray diffractometer system.

2.3. Catalytic activity

The oxidation of the model sulfur compounds was conducted in a flask with a magnetic stirrer. A 100 mL portion of n-decane solution containing dibenzothiophene as sulfur compounds (300 ppm) and 1 gr. of the adsorbent were added to the flask. The mixture was stirred, and an amount of 5 wt.% H₂O₂ was added. The reaction was continued for 60, 150, and 240 min. The evolution of oxidative desulfurization as was monitored using a UV-Vis spectrophotometer (TG+80, Urmia university). The performance of the process was evaluated by analyzing the response of dibenzothiophene oxidation percentage (yield) after a fixed stirring time:

$$Y(\%) = \left[\frac{C_0 - C_t}{C_0} \right] \times 100 \quad (1)$$

where, C₀ is the initial DBT concentration, and C_t stands for the DBT concentration after treatment by Ni-clinoptilolite.

2.4. Design of experiments

Response surface methodology (RSM) was developed by Box and collaborators in the 50's. This term was originated from the graphical perspective generated after fitting the mathematical model, and its use has been widely adopted in texts on chemo metrics. RSM consists of a group of mathematical and statistical techniques that are based on the fit of empirical models to the experimental data obtained in

relation to experimental design (Ghaffari-Moghaddam et al., 2014). Toward this objective, linear or square polynomial functions are employed to describe the system studied and to consequently explore (modeling and displacing) experimental conditions until its optimization. In this technique, the main objective is to optimize the response surface that is influenced by process parameters. RSM also quantifies the relationship between the controllable input parameters and the obtained response surfaces. Process optimization by RSM is faster for gathering experimental research results than the rather conventional, time consuming one factor at a time approach (Annadurai and Sheeja, 1998; Aslan, 2008; Bas and Boyaci, 2007; Baş and Boyaci, 2007; Bezerra et al., 2008; Khataee et al., 2010; Yetilmezsoy et al., 2009).

In order to design experiments to predict the optimum condition, Box-Behnken design (BBD) was used. The method suggests a point selection from the three-level factorial arrangement, allowing the efficient estimation of the first- and second-order coefficients of the mathematical model. In Box–Behnken designs, the experimental points are located on a hyper sphere equidistant from the central point. Its principal characteristics are as follows:

- 1) It requires an experiment number according to $N= 2k(k-1) + cp$, where k is the number of factors, and (cp) represents the number of the central points;
- 2) All factor levels have to be adjusted only at three levels $(-1, 0, +1)$ with equally spaced intervals between these levels.

To find the optimum conditions for the degradation of desulfurization, a Box Behnken design (BBD) was adopted to evaluate the combined effect of 3 factors (variables), i.e. dosage of H_2O_2 as an oxidizing agent (0-0.25 mL), treatment time (60-240 min), and the weight percentage of Ni (5-10). For three variables ($n = 3$) and two levels (high (+) and low (-)), the total number of experiments was 17 (listed in Table 1). The data set obtained from BBD was used for the optimization of the response of desulfurization percentage.

The response surface methodology was used to fit the experimental data. In the RSM, the responses can be simply related to chosen factors by first-order or second-order polynomial models. The first-order model uses a low-order polynomial model, which is appropriate for describing a flat surface, according to the equation:

$$y = \beta_0 \sum_{i=1}^k \beta_i x_i + \varepsilon \quad (2)$$

where, y is the predicted response; β_0 and β_i represent the constant term and coefficients of the linear parameters respectively; x_i stands for the variables, and ε is the random error.

If interaction terms are included, the first-order model can then be represented as follows:

$$y = \beta_0 \sum_{i=1}^k \beta_i x_i + \sum_{1 \leq i < j \leq k} \beta_{ij} x_i x_j + \varepsilon \quad (3)$$

where β_{ij} represents the coefficients of the interaction parameters x_i and x_j . A second-order model may be studied in order to locate the optimum point. A second-order model is given by:

$$y = \beta_0 \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i x_j + \sum_{1 \leq i \leq j}^k \beta_{ij} x_i x_j + \varepsilon \quad (4)$$

where, β_{ii} represents the coefficients of the quadratic parameter.

Statistical analysis was performed using the software package Minitab v.17 and a regression model was proposed. The analysis of variance (ANOVA) was performed based on the proposed model to find the interaction between the process variables and the response. The quality of the fit for the polynomial model was expressed by the coefficient of determination (R^2 , R^2_{adj}), and statistical significance was checked by the F -value, P -value, and adequate precision in the same program. Model terms were selected or rejected based on the probability value with 95% confidence level ($P > 0.05$). Finally, three-dimensional response surface plots and contour plots were drawn in order to visualize the individual and the interaction effects of the independent variables on desulfurization (Aslan, 2008).

According to the three factors selected for DOE, 17 experiments suggested by Minitab v.17 software.

Table 1

The 3-factor Box Behnken design matrix (independent variables and their coded and actual levels: amount of H_2O_2 as an oxidizing agent (mL), time of reaction (min), weight percentage of Ni (%)) and the experimental results (desulfurization (%)) from gas oil.

Run	V(H_2O_2 , mL)	Time (min)	Ni (wt.%)
1	0	150	10
2	0.125	150	7.5
3	0.125	240	5
4	0	240	7.5
5	0.125	60	10
6	0.25	150	10
7	0	60	7.5
8	0.125	240	10
9	0.125	150	7.5
10	0.125	60	5
11	0.25	240	7.5
12	0.25	60	7.5
13	0.25	150	5
14	0.125	150	7.5
15	0	150	5

3. Results and discussion

3.1. Catalyst determination

Figures 1 and 2 show the observed XRD patterns for the clinoptilolite catalysts with different amounts of Ni supported on clinoptilolite. It is found that the metallic Ni peaks ($2\theta=36^\circ$ and 44.5°) of lower

metal loading catalysts are weaker and broader than that of the catalysts with higher metal loading. This suggests that the Ni crystallite size is smaller on lower Ni loading catalysts than on the catalysts with a high Ni content. Figure 3 illustrates the scanning electron microscopy of the Ni-clinoptilolite proving the nanostructure of the synthesized catalyst and the agglomeration synthesis of the catalyst.

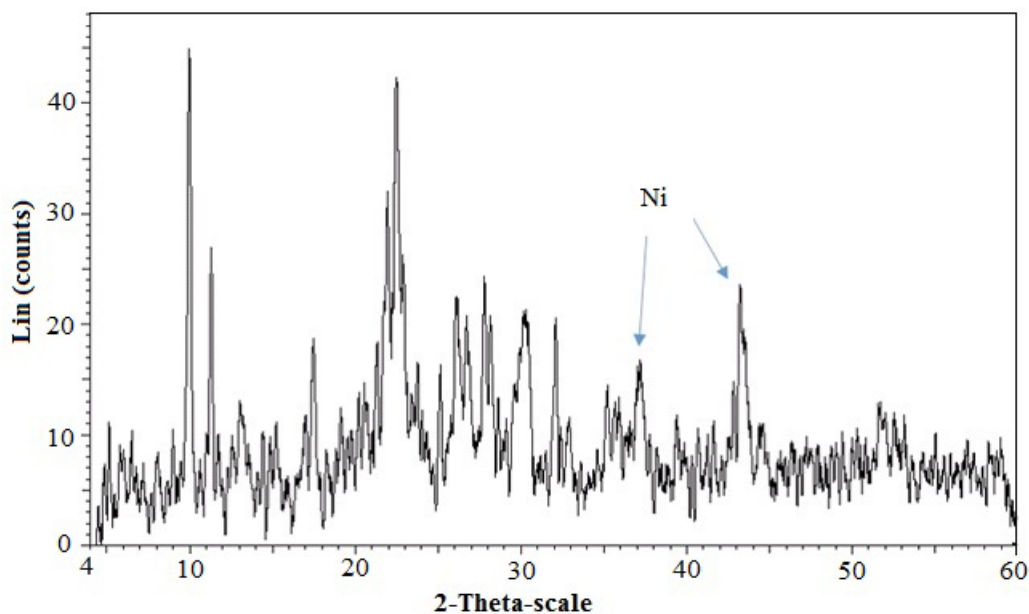


Figure 1

XRD pattern of clinoptilolite catalyst coated with 7.5% Ni.

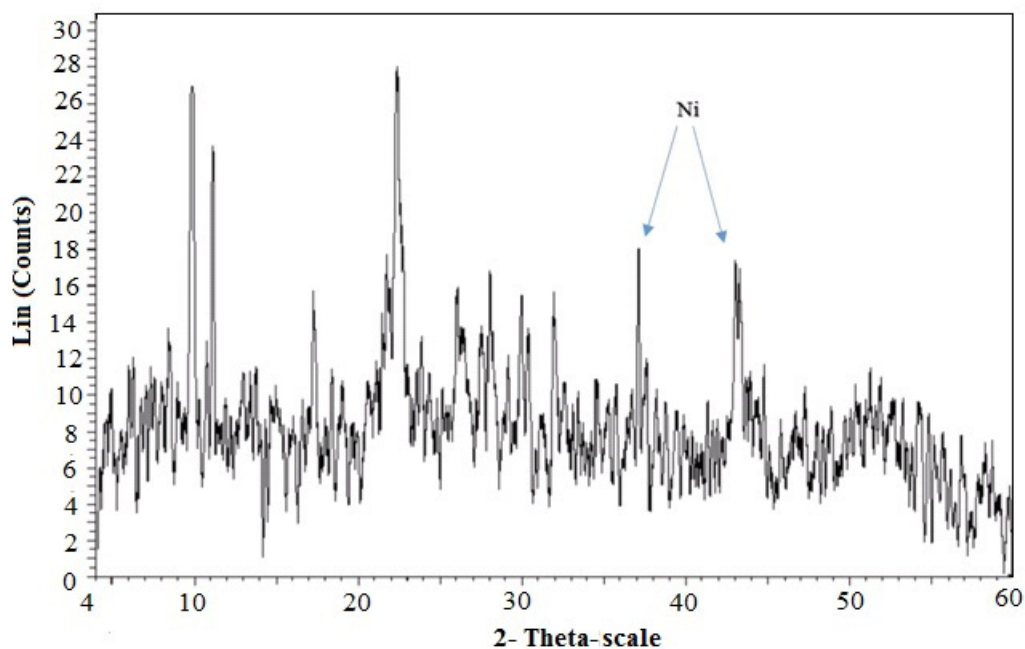


Figure 2

XRD pattern of clinoptilolite catalyst coated with 10% Ni.

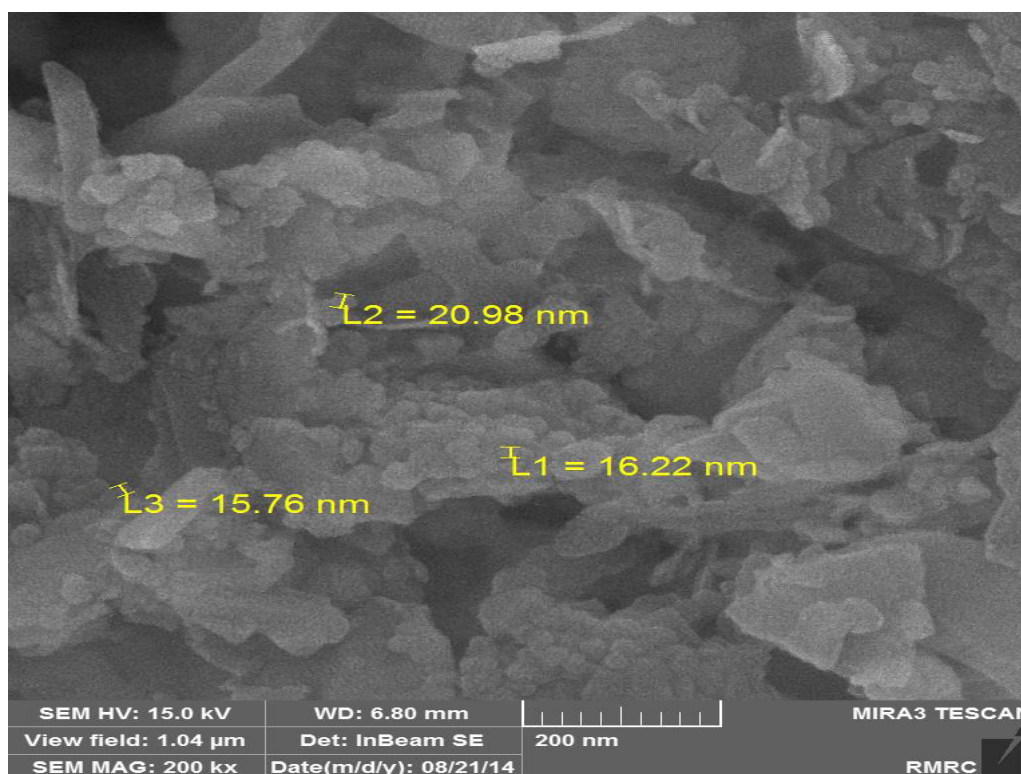


Figure 3
Scanning electron microscopy (SEM) of the Ni-clinoptilolite.

3.2. RSM modeling and optimization of desulfurization treatment

Response surface designs are useful for modeling a curved quadratic surface to continuous factors. A response surface model can pinpoint a minimum or maximum response if one exists inside the factor region. Three distinct values for each factor are necessary to fit a quadratic function, so the standard two-level designs cannot fit curved surfaces. Box Behnken design was used in this study for the optimization and modeling of the process. The Box-Behnken design is an alternative to central composite designs. One distinguishing feature of the Box-Behnken design is that there are only three levels per factor.

The 3-factor BBD matrix and experimental results obtained for the desulfurization from gas oil are presented in Table 1. Based on the experimental design (Table 1), a response surface model relating the desulfurization efficiency to independent variables was constructed to fit the experimental data. The linear model in terms of coded variables that approximated the efficiency of desulfurization process may be written as follows:

$$Y = b_0 + b_1 \times A + b_2 \times B + b_3 \times C + b_{11} \times A \times A + b_{12} \times A \times B + b_{13} \times A \times C + b_{22} \times B \times B + b_{33} \times C \times C + b_{32} \times C \times B \tag{5}$$

where, Y is a response variable of sulfur removal efficiency. The b_i are regression coefficients for linear effects; b_{ii} represents the regression coefficients for squared effects; b_{ik} is the regression coefficients for interaction effects, and x_i stands for coded experimental levels of the variables.

$$Y = 42.25 - 12.645A - 9.34B + 4.02C + 2.97625A \times A + 0.9425A \times C + 4.62125B \times B + 10.006C \times C - 1.4075C \times B \quad (6)$$

The models explained perfectly the experimental range studied as can be seen from the comparison of the graphical representation of actual values with the predicted ones (Figure 4).

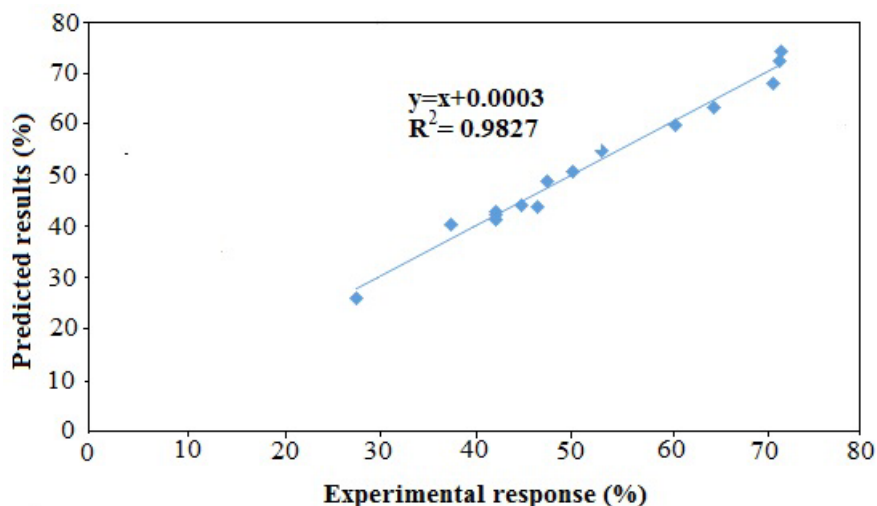


Figure 4

Comparison of the experimental results of desulfurization efficiency (CR%) with those calculated via Box-Behnken design resulted equation.

Table 2 shows the results of ANOVA analysis of the linear model for the desulfurization process of gas oil. Larger F -values and smaller P -values are an indication of the significance of the model.

Table 2
Analysis of variance (ANOVA) for the fit of MO removal efficiency from Box-Behnken design.

Source	Degree of freedom (DF)	Sequential sum of squares	Adjusted sum of squares	Adjusted mean of squares	F -value	P -value
Regression	7	2708.06	2708.055	386.865	13.98	0.001
Linear	3	2088.64	584.958	194.986	7.04	0.016
Square	2	554.50	554.502	277.251	10.02	0.009
Interaction	2	64.92	64.915	32.458	1.17	0.364
Residual Error	7	193.78	193.77	27.682	-	-
Lack-of-Fit	5	185.14	185.141	37.028	8.57	0.018
Pure Error	2	8.64	8.637	4.318	-	-
Total	14	2901.83	-	-	-	-

The model F -value of 13.98 and P -value smaller than 0.001 implied the high significance of the model. There was only a 0.01% chance that the “Model F -value” could occur due to noise. P -values less than 0.05 indicated which model terms are significant. In this case, all the factors were highly significant because P -value is smaller than 0.05. The “Lack of Fit F -value” of 8.57 and P -value of 0.018 implied that the lack of fit was not significant relative to the pure error. The non-significant

lack-of-fit indicated the good predictability of the model. The coefficient of determination (R^2) is defined as the ratio of the explained variable to the total variation and is a measure of the degree of fit. It was found that the predicted values matched the experimental values reasonably well with $R^2 = 0.9827$. This implied that 98.27% of the variations for sulfur compounds removal were explained by the independent variables, and this also meant that the model did not explain only 1.73% of variation. The R^2 of 0.9827 was in reasonable agreement with Adj. R^2 of 0.9827, also indicating good predictability of the model (Table 3).

Table 3
Statistical measures and performance of the RSM using the analysis of variance (ANOVA).

S	R^2	$R^2(\text{adj.})$
5.261	98.27%	86.6%

Three-dimensional response surface plots computed by means of the response surface model for desulfurization are shown in Figures 5-8, revealing the predicted effects of factors upon response.

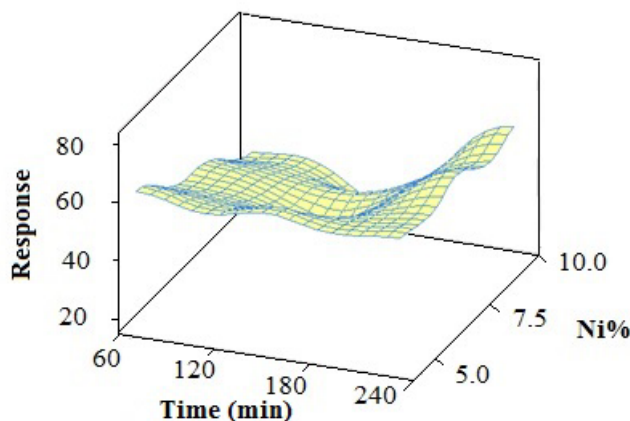


Figure 5
The response surface plot for desulfurization efficiency (CR%) as the function of Ni (wt.%) and treatment time (min).

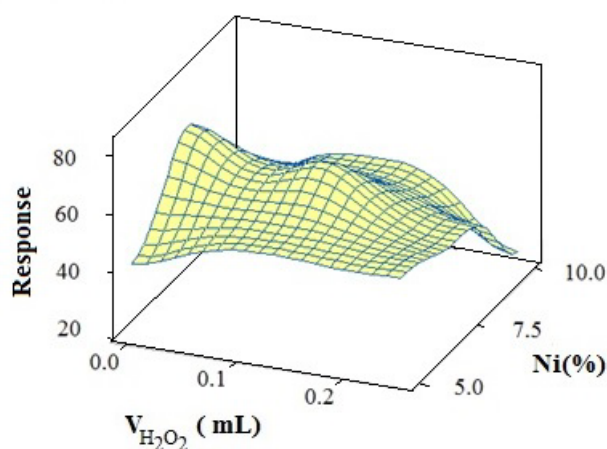


Figure 6
The response surface plot for desulfurization efficiency (CR%) as the function of H₂O₂ (mL) and Ni (wt.%).

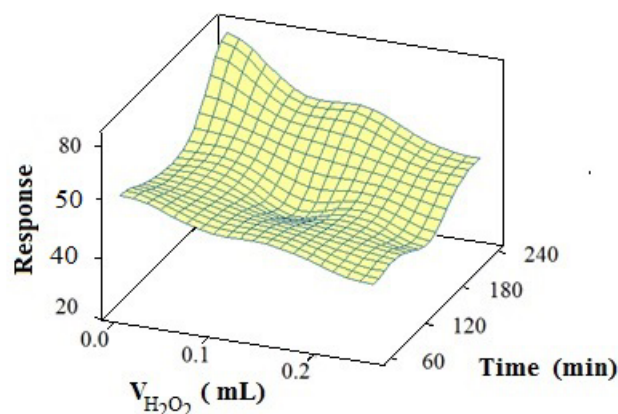


Figure 7

The response surface plot for desulfurization efficiency (CR%) as the function H_2O_2 (mL) and treatment time (minute).

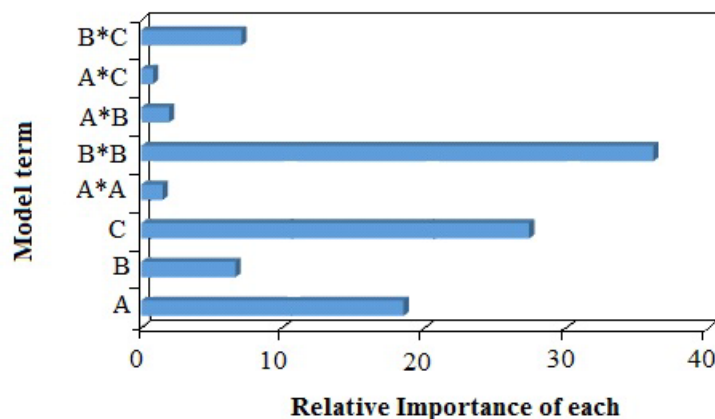


Figure 8

The results of Pareto analysis

Figure 5 illustrates the effect of treatment time and the weight percentage of Ni-supported on clinoptilolite on desulfurization efficiency (CR%) for an initial DBT concentration. It is observed that the removal efficiency was enhanced with increasing treatment time (min) and decreasing the weight percentage of Ni, and at least more than 74% sulfur removal was obtained after 150 minutes at a 5 wt.% of Ni-supported on clinoptilolite. It is also obvious that both of these two independent variables are so important in sulfur removal. Since adding Ni on the surface of clinoptilolite occupies the active desulfurization sites on the catalyst, increasing the amount of Ni causes less efficiency of the Ni-clinoptilolite in the treatment process.

Figure 6 depicts the effectiveness of hydrogen peroxide and Ni in the desulfurization of the gas oil. As it can be seen, the addition of hydrogen peroxide as an oxidizing agent decreases desulfurization efficiency because of the conjuncture of nanoadsorbent and thus the reduction of the surface/volume ratio.

Figure 7 shows the effect of treatment time and the amount of H_2O_2 (mL) on desulfurization process efficiency. As it is inferred from Figure 7, an increase in treatment time causes the maximum adsorption of sulfur compound on the adsorbent, so more sulfur compounds are transformed into

sulfone in desulfurization process. The contour plots of all the factors involved in desulfurization process efficiency are shown in Figure 8 with so near proximity of the proposed information about the factors sensitivity in the process.

3.3. Determination of optimal conditions for methyl orange removal

The desired goal in terms of sulfur compound removal efficiency was defined as “maximize” to achieve the highest treatment performance. The optimum values of the process variables in the optimum conditions are 5 wt.%, 0 (mL), and 240 (min) for the amount of Ni-supported on clinoptilolite, dosage of hydrogen peroxide (H_2O_2) as an oxidizing agent reagent, and treatment time respectively. After verification through a further experimental test with the predicted values, the result indicates that the maximum sulfur compounds removal efficiency was obtained when the values of each parameter were set as the optimum values. It implies that response surface methodology gives the optimized conditions to obtain the maximum desulfurization efficiency in the adsorptive process using Ni-clinoptilolite..

4. Conclusions

The RSM model constructed out of the experimental data correlated fairly well ($R^2=0.9827$ for response surface methodology). Furthermore, two validation experiments were performed and the response of the model was found in agreement with the experimental results. The nobility of the work was to use the best amount of materials and methods in order to modify the synthesized catalyst for effective proficiency in desulfurization process. The model indicated that treatment time had the highest positive effect on sulfur compound removal efficiency as observed through beta regression coefficients, whereas the dosage of hydrogen peroxide had less positive effects on desulfurization efficiency. Thus, both the oxidizing agent and the metal (Ni) loaded on clinoptilolite cause less efficiency in desulfurization process because of adverse interactions with the sulfur adsorption. Although an increase in treatment time enhances the efficiency of the process, it did not change after 240 minutes. Therefore, time is effective until all the active sites of Ni are occupied by sulfur compounds. Energy conservation in the process can be better achieved by increasing the treatment time and by reducing the amount of Ni-supported catalyst; however, this will ultimately increase the reactor size. The methods used to optimize the proficiency of the process could be performed in each part of industrial desulfurization plants in order to purify the gas oil product from any unwanted sulfur compounds.

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Nomenclature

ANOVA	: Analyze of variance
BBD	: Box-Behnken design
DBT	: Dibenzothiophene
IFQC	: International Fuel Quality Centre
Ni	: Nickel
RSM	: Response surface methodology

SEM	: Scanning electron microscopy
UV	: Ultra violet
XRD	: X-ray diffraction

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