Optimization of Oxidative Desulfurization Reaction with \( \text{Fe}_2\text{O}_3 \) Catalyst Supported on Graphene Using Box-Behnken Experimental Method

Hameed Hussein Alwan\(^1\)*, Ammar Ali Ali\(^2\), Hasan F. Makki\(^3\)

\(^1\)Chemical Engineering Department, College of engineering, University of Babylon, Babylon, Iraq.
\(^2\)Water Resources Engineering Department, Al-Qasim Green University, Babylon, Iraq.
\(^3\)Chemical Engineering Department, College of engineering, University of Baghdad, Baghdad, Iraq.

Abstract

In this study, the catalyst activity of \( \text{Fe}_2\text{O}_3 \) supported on Graphene for Iraqi gas oil oxidation desulfurization (ODS) by hydrogen peroxide (\( \text{H}_2\text{O}_2 \)) was investigated. The prepared catalyst was synthesized by wet impregnation for ferric nitrate as a \( \text{Fe}_2\text{O}_3 \) precursor while Graphene represented as catalyst support. The synthesized catalyst was characterized by XRD, FTIR, and EDS analysis. The experiments were designed according to three-level for three variables by Box-Behnken experimental design: Stirring time, catalyst dosage and temperature while the sulfur removal efficiency acts as experiment response. Catalyst activity was studied by ODS reaction for Iraqi gas oil (sulfur content 9400 ppm) at temperature range (40-60 °C), stirring time (160-240 minutes) and catalyst dosage (0.5-2.5 g), the results show maximum sulfur removal efficiency 90% at stirring time, catalyst dosage and temperature 240 min, 1.5 g, and 60 °C, respectively. ANOVA analysis shows the important effect of each independent variable on sulfur removal efficiency (response) as following influential order; stirring time, reaction temperature and catalyst dosage. Kinetics calculation showed that the ODS reaction obeys pseudo first-order reaction with reaction rate constant equal 1.0837, 1.5893, and 2.5053 at temperature 40, 50, and 60 °C, respectively, while activation energy equal 36.26 kJ/mol.

Keywords: Oxidative desulfurization; ODS; Graphene; Design experiment; Box-Behnken; ANOVA

How to Cite: Alwan, H.H., Ali, A.A., Makki, H.F. (2020). Optimization of Oxidative Desulfurization Reaction with \( \text{Fe}_2\text{O}_3 \) Catalyst Supported on Graphene Using Box-Behnken Experimental Method. Bulletin of Chemical Reaction Engineering & Catalysis, 15(1), 175-185 (doi:10.9767/bcrec.15.1.6670.175-185)

Permalink/DOI: https://doi.org/10.9767/bcrec.15.1.6670.175-185

1. Introduction

Generally, raw gas and oil contain an amount of sulfur as impurities. Owing to environmental concerns, human health issues, and corrosion problems, many restrictions introduce to remove or reduce the sulfur content. Sulfur considers the precursor elements in the process of acid rain formation by consisting of sulfur oxide [1]. Besides, the presence of sulfur causes corrosion in the refineries facilities, reforming catalysts poisoning and undesirable odors [2]. The conventional method for sulfur removing from petroleum fractions is catalytic hydrodesulfurization. Hydrodesulfurization process (HDS) suggests using a suitable catalyst, usually, the sulfide of (Molybdenum, Mo; Tung-
The oxidative desulfurization (ODS) is a promising process for deep desulfurizing from petroleum fractions which can be carried out with mild operation conditions like room temperature and atmospheric pressure [5-6]. In comparison to the hydrodesulfurization process, the oxidative desulfurization process can be presented with temperature below 80 °C, high selectivity, and no expensive hydrogen. In terms of cost, HDS is more expensive than ODS due to high hydrogen pressure requirements for kinetic and catalyst stability purposes [7,8]. Several oxidation agents applied in ODS processes such as ozone, hydrogen peroxide, peracids and tertbutylhydroperoxide [9]. Among these agents, peroxides are very attractive due to their high reactivity and selectivity under mild operation conditions. The oxidation reaction can be done in non-acidic media, in existence of catalysts such as tungsten, vanadium or molybdenum supported on zeolite, silicates, molecular sieves, etc. [10]. The oxidative desulfurization process consists of two stages; first stage oxidation of sulfur compounds to forms have high polarity and the following stage is removing of oxidized sulfur compounds to present clean fuels [8,9]. Many researchers investigated applying various catalysis, like Cu, Ti, Cr, Mn, Fe, Co, W, and V, which are known as transition metal oxides [9]. Besides, the oxidation desulfurization process has been studied using various reactions like hydrogen peroxide formic acid, hydrogen peroxide-acetic acid, hydrogen peroxide-polyoxometalates, ozone, and photooxidation with molecular oxygen in the presence of sensitizers, such as: cyanoarenes [9]. Among all these reactions, the oxidation of DBT and its derivatives with hydrogen peroxide in acidic media considers as an attractive reaction due to that reaction carried out under ambient conditions and its high selectivity. Correspondingly, the use and the store of these peroxides on large scale considers dangerous. Figure 1 shows the common reaction of DBT oxidation by hydrogen peroxide in acidic media, in which sulfoxides and sulfones can be removed easily with an appropriate solvent as extract [10].

In this study, the catalyst activity of Fe$_3$O$_4$ supported on Graphene for Iraqi gas oil oxidation desulfurization (ODS) by hydrogen peroxide (H$_2$O$_2$) was investigated. This piece of work examines the sulfur loading on the Fe$_3$O$_4$ catalyst supported on graphene synthesized for ODS reaction to remove sulfur compounds from Iraqi gas oil. Where the study carried out using Box-Behnken experimental design method with three-level variables. The maximum reachable of sulfur removal efficiency was 90%. Analysis variation study using ANOVA has been performed to investigate the impact of various parameters on the sulfur removal efficiency like stirring time, reaction temperature and catalyst dosage.

2. Materials and Methods

2.1 Materials

Iraqi gas oil with sulfur content (9400 ppm) provided from Najaf refinery, graphene prepared from dehydration of Iraqi date syrup described by Makki & Alwan [11]. Analytical grade chemicals reagents used in this study hydroxide peroxide H$_2$O$_2$, ferric nitrate (Fe(NO$_3$)$_3$.9H$_2$O), glacial acetic acid (CH$_3$COOH), sodium bicarbonate (NaHCO$_3$), sodium carbonate (Na$_2$CO$_3$), nitric acid (HNO$_3$), sulfuric acid (H$_2$SO$_4$), Acetonitrile (CH$_3$CN).

---

**Figure 1.** Oxidation desulfurization process of DBT [10]
2.2 Catalyst Preparation and Characterizations

The proposed catalyst is ferric oxide Fe₂O₃ supported on graphene and it was synthesized by wet impregnation method. Graphene surface functionalized by pouring into a mixture of concentrated sulfuric acid and nitric acid at 50 °C under the sonication condition for 2 hours. Next, washing graphene with distilled water to removed acidic trace and filtration. Finally, functionalized graphene dried at 110 °C for 4 hours’ duration under vacuum. Ten grams of functionalized graphene pored into three necks round bottom which immersed in an ultrasonic bath and connected to vacuum a pump for moisture removal. Specific amounts of ferric nitrate (Fe(NO₃)₃.9H₂O) dissolved in distilled water and added to functionalized graphene drop by drop to produce catalyst contains 10 wt.% of Fe₂O₃ on graphene. During the impregnation step adding sodium bicarbonate (1 M) solution at pH range 8-9 as a precipitation agent for getting good precipitation. The impregnated catalyst dried at 100 °C for a single night and calcined at 450 °C for 4 hours.

Fourier - Transform Infrared Spectroscopy (FTIR) spectra abstained on BRUKER Model PLATINUM-ATR Alpha series Germany over range 4000-400 cm⁻¹ at room temperature. X-ray diffraction (XRD) pattern was got on Shimadzu Model XRD- 6000 Japan, while Energy Dispersive X-ray Spectrometry (EDS) maps done on BRUKER Model X Flash 6110 Germany which attached with scanning electron microscope (SEM) FEI model QUANTA 450.

Table 1. Independent (controllable) variables and their levels.

| Variables, unit | Symbol | Coded | Actual |
|-----------------|--------|-------|--------|
| Stirring time, min | x₁ | -1 | 0 1 |
| Catalyst dosage, g | x₂ | 0.5 | 1.5 2.5 |
| Temperature, °C | x₃ | 40 50 60 |

2.3 Oxidative Desulfurization Procedure

The oxidative desulfurization ODS process investigated under the effect of following independent variables; reaction temperature, stirring time (period of batch), and weight of catalyst dosage arranged according to Box–Behnken experimental design. The oxidation process starts by heating 100 ml of gas oil using the magnetic stirrer heater to reach the required temperature, 10 mL of hydrogen peroxide, 5 mL of glacial acetic acid with the required weight of catalyst added to gas oil. The stirring continues for the designed time following the Box-Behnken matrix, in which the reaction stopped by adding sodium carbonate solution (2 g dissolved in 20 mL distilled water) after the required time [12]. After the oxidation reaction, oxidized sulfur extracted using acetonitrile at the ambient temperature where the oil phase separated. The loading capacity of sulfur measured by X-ray fluorescence (Sulfur Meter model RX-620SA/Tanka Scientific) and total sulfur removal efficiency calculated according to Equation (1).

\[
SR\% = \frac{S_0 - S_f}{S_0} \times 100
\]

where, SR% is sulfur removal efficiency, S₀ denotes sulfur in raw oil, and S_f is sulfur after oxidation.

2.4 Design of Experiment

Response Surface Methodology (RSM) is a mathematical and statistical method collection that is useful to model and analyze engineering problems as well as it can be used as an optimization technique to evaluate the correlation between observed experimental responses with controllable variables [13]. The Box-Behnken method is one of the most RSM methods used for the design of experimental and it can be described as a central–composite design CCD. Box-Behnken design method has the ability to study experiments with a possible minimum

Table 2. Box-Behnken design matrixes.

| Run | Design Parameters | Run | Design Parameters | Run | Design Parameters |
|-----|------------------|-----|------------------|-----|------------------|
|     | x₁  | x₂  | x₃  |     | x₁    | x₂    | x₃    |     | x₁     | x₂    | x₃     |
| 1   | -1  | 0   | 1   | 6   | 0     | -1    | 1     | 10  | 0      | 1     | -1     |
| 2   | 0   | 0   | 0   | 7   | 1     | -1    | 0     | 11  | 0      | 1     | -1     |
| 3   | 0   | 0   | 0   | 8   | 1     | 1     | 0     | 12  | 0      | -1    | -1     |
| 4   | 0   | 0   | 0   | 9   | 1     | 0     | 1     | 13  | -1     | -1    | 0      |
| 5   | 0   | 1   | -1  | 10  | 1     | 0     | -1    | 14  | -1     | 1     | 0      |
number of experiments with a high degree of accuracy compared with classical methods. The number of experiments required to cover the variables range was established according to the Box-Behnken matrix which is determined by Equation (2) [14].

\[ N = 2k(k - 1) + r \]  

(2)

Where \( N \) is the number of experiments, \( k \) is the number of variables, and \( r \) is the replicate number of central points (3-6).

The method stated that variables levels adjusted at only three levels (-1, 0, +1) and intervals between these levels are equal. For three variables Box-Behnken design the total number of experiments that determined by Equation (2) are 12 plus three replicate numbers of central points and the total will be 15 experiments to estimate the effects of independent variables on the oxidation process. Compared to Box-Wilson experimental design method needs 27 runs to cover three independent variables system.

Table 1 shows \( X_1, X_2, \) and \( X_3 \) the actual variables (factor) chosen for this design with three levels low (-1), intermediate (0), and high (+1) values. The coded variables \( (x_1, x_2, \) and \( x_3) \) were related to actual variables by Equation (3).

\[ x_i = \frac{X_i - X_0}{\Delta X_i}, \quad i = 1, 2, 3 \]  

(3)

Where \( X_0 \) is real value for the independent variable at the center level, and \( \Delta X \) is the interval value. Table 2 shows the matrices for Box-Behnken was for optimization of the oxidation desulfurization process in terms of estimation of the effects of stirring time, catalyst dosage, and reaction temperature on the sulfur removal efficiency, the experimental observation arranged at random orders [13].

The observed results for the effects of Stirring time, catalyst dosage, and reaction temperature on oxidative desulfurization can be fitted as second-order polynomial by the aim of Design-Expert software, and it can be used to predict optimum point, for three variables where the second-order polynomial represents by Equation (4) [15].

\[ y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ij} x_i^2 + \sum \beta_{iii} x_i^3 + \varepsilon \]  

(4)

Where \( y \) is predicated response, \( \beta_0 \) is the intercept coefficient, \( \beta_i \) is the linear effect (slope) of input variable \( x_i \), \( \beta_{ij} \) is interaction effect of linear by linear between two input variables \( x_i \), and \( \beta_{iii} \) is squared effect.

Analysis of Variance ANOVA is a statistical method to decision-making for the purpose of detecting the differences in the rate of performance of the variables examined, where the sum of squares and F-statistics are used to know the relative importance of processing data analyzed and measurement of errors and uncontrolled parameters.

3. Result and Discussion

3.1 Characterization of Prepared Catalyst

X-ray diffraction (XRD) patterns show significant peaks at \( 2\theta = 35.52^\circ, 52.98^\circ, \) and \( 62.09^\circ \)

![Figure 2. XRD pattern for Fe3O4/Graphene catalyst. Inset pattern shows XRD pattern for Graphene prepared from Iraqi date syrup [11].](image-url)
which referred to Fe$_2$O$_3$ (hematite) and Fe$_3$O$_4$ (magnetite) while the peaks at $2\theta = 33.89^\circ$, $39.47^\circ$, and $43.07^\circ$, this agrees with Ugal et al. work [12]. In addition, the XRD pattern shows a small peak around $2\theta = 28.9^\circ$ which refers to disordered amorphous sheets of Graphene for iron/Graphene nano-composites and this shows good agreements with Lima et al. findings [16]. The average crystal size calculated by Scherrer formula using full-width at half maximum (FWHM) at a stronger diffraction peak, where the average crystal size found to be 7.14 Å. The inset figure in Figure 2 is for prepared Graphene, it shows wide peak centered at $2\theta = 23.758^\circ$ for plane (002) with d-spacing d002 = 3.742 Å (0.374 nm) and this is agree with [17,18].

FTIR spectrum used to identify functional groups within the sample in sample; the broad peak at about 3406 cm$^{-1}$ is ascribed as vibration for bonded OH group. The bond at 1200 cm$^{-1}$ and 1620 cm$^{-1}$ due to C-H and C=C aro-

![FTIR spectra for Fe$_2$O$_3$/Graphene catalyst](image1.png)

**Figure 3.** FTIR spectra for Fe$_2$O$_3$/Graphene catalyst

![EDS analysis (elements mapping) for prepared catalyst. Inset shows the SEM image for catalyst.](image2.png)

**Figure 4.** EDS analysis (elements mapping) for prepared catalyst. Inset shows the SEM image for catalyst.
matic, while the peak at about 560 cm\(^{-1}\) represents Fe-O vibration. In addition, the possible reason behind the vibration between about 1600-1200 cm\(^{-1}\) is that as a complexes formation either for bidentate or monodentate which comes from the carboxyl group with iron as shown in Figure 3. EDS analysis refers to the presence of iron and oxygen as well as the support (carbon) Figure 4.

3.2 Results of the Oxidation Desulfurization Reaction

Table 3 shows the sulfur content in final product measured for all the 15 experiments and the sulfur removal efficiency, as well as, the sulfur removal efficiency using Equation (5). Experiments results fitted as a second-order polynomial (quadratic model) with Box-Behnken design and by the aim of Design-Expert software version 11. The relationship between sulfur removal efficiency and independent variables based on the fitting results shown in Equation (5).

\[
y = 80.67 + 8.0x_1 - 2.0x_2 + 6.0x_1^2 - 0.5x_1x_2 + 2.5x_3x_1 + 3.5x_2x_1 - 4.58x_1^2 + 2.58x_1^2 - 4.08x_1^2
\]  

The analysis of variance results for the predicated model shown in Table 4, by the aim of Design-Expert software, which shows a good fitting data for the second-order (quadratic) model. ANOVA analysis shows that \(F\)-value is 29.11 for regression which is greater than the tabulated value from the standard distribution table Fisher’s \(F\)-test value obtained, \((F_{9,5,0.05} = 4.77)\). The high \(R^2\) (0.9813) indicates that the assumed model is reasonably well-fitting with actual data. The experimental points are very little diverging from the points that predicated by the quadratic model (Equation (5)) which illustrated graphically with 45° line as shown in Figure 5 which indicate again a good fitting for the suggested model. Low \(P\)-value (\(P < 0.05\)) referred the parameter in the suggested model is statistically highly significant. In this work, the terms of \(x_1, x_2, x_3, x_1x_2, x_1^2, x_2^2, x_3^2\) are significant parameters because of their values.

![Figure 5. Experimental and predicated response plot.](image)

| Run | Coded Variables | Actual Variables | Response S% | Experimental | Predicted |
|-----|----------------|------------------|-------------|--------------|-----------|
| 1   | -1 0 1         | 160 1.5 60       | 69          | 67.51        |
| 2   | 0 1 0         | 200 1.5 50       | 81          | 80.67        |
| 3   | 0 0 0         | 200 1.5 50       | 60          | 58.01        |
| 4   | 0 0 0         | 200 1.5 50       | 81          | 80.67        |
| 5   | 0 1 -1        | 200 2.5 40       | 70          | 68.01        |
| 6   | 0 1 1         | 200 0.5 60       | 82          | 84.01        |
| 7   | 1 -1 0        | 240 0.5 50       | 89          | 88.51        |
| 8   | 1 1 0         | 240 2.5 50       | 85          | 85.51        |
| 9   | 1 0 1         | 240 1.5 60       | 90          | 88.51        |
| 10  | 1 0 -1        | 240 1.5 40       | 70          | 71.51        |
| 11  | 0 1 1         | 200 2.5 60       | 86          | 87.01        |
| 12  | 0 -1 -1       | 200 0.5 40       | 80          | 79.01        |
| 13  | -1 -1 0       | 160 0.5 50       | 74          | 73.51        |
| 14  | -1 1 0        | 160 2.5 50       | 68          | 68.51        |
| 15  | -1 0 -1       | 160 1.5 40       | 59          | 60.51        |

Copyright © 2020, BCREC, ISSN 1978-2993
Figure 6. 2-D and 3-D plot of sulfur removal efficiency vs stirring time and catalyst dosage.

Figure 7. 2-D and 3-D plot of sulfur removal efficiency vs stirring time and temperature.

Figure 8. 2-D and 3-D plot of sulfur removal efficiency vs temperature and catalyst dosage.
are less than 0.05. Meanwhile, $P$-value for the term of $x_1x_2$ is not significant via its value larger than 0.05 and $x_1x_3$ is slightly significant because its $P$-value is slightly larger than 0.05, that lead rewrite Equation (5) as below in Equation (6).

$$y = 80.67 + 8.0x_1 - 2.0x_2 + 6.0x_3 + 2.5x_1x_3 + 3.5x_2x_3 - 4.58x_1^2 + 2.58x_2^2 - 4.08x_3^2$$ (6)

Based on the results, stirring time shows the highest effect on the sulfur removal efficiency followed by the temperature of reaction and catalyst dosage as predicated according to their F-value 123.87, 69.68, and 7.74, respectively listed in ANOVA results in Table 4. Generally, reactions require time for completion, and it is clearly visible that sulfur removal efficiency initially increasing with reaction time to a specific time, then marginally decreased. The possible reason behind this is the interaction between $\text{H}_2\text{O}_2$ (oxidizing agent) with sulfur components due to the losses in the oxidation agent with time.

The interactive effect of each two independent variables on sulfur removal efficiency was determined by illustrating response (sulfur removal efficiency) as two dimensional (2D) and three dimensional (3D) plots. As shown in Figure 6, temperature was kept at 50 °C while catalyst dosage and stirring time were kept constant at 1.5 g and 200 minutes, respectively. Noticeably, sulfur removal efficiency varies with stirrer time to a great extent compared to catalyst dosage.

Figure 7 shows the effects of the temperature of reactions and stirring time on the sulfur efficiency. The results illustrate that increases both variables result in increasing sulfur removal efficiency. On the other hand, Figure 8 represents the effect of temperature of reaction and catalyst dosage on the response, where the temperature of reaction shows high effects compared to catalyst dosage.

3.3 Desirability Function

The desirability function is a technique used for the determination of optimum settings for independent variables effect on response. The process depends on nominate best levels of independent variables that lead to the most desirable response (optimum) [19]. For this system, the optimum conditions to maximize the sulfur removal efficiency are that $X_1 = 0.646$, $X_2 = 1$, and $X_3 = 1$, these are corresponding to stirring time = 225 minutes, catalyst dosage = 2.5 grams, and temperature = 60 °C which lead to

![Figure 10. The plot of ln ($C_0/C_t$) vs time at studied temperature.](image)

| Source | Sum of Squares | df | Mean Square | $F$-value | $P$-value | Notes |
|--------|----------------|----|-------------|-----------|-----------|-------|
| Model  | 1082.9         | 9  | 120.33      | 29.11     | 0.0009    | significant |
| $X_1$-Time | 512           | 1  | 512         | 123.87    | 0.0001    | significant |
| $X_2$-Dosage | 32            | 1  | 32          | 7.74      | 0.0388    | significant |
| $X_3$-Temp. | 288           | 1  | 288         | 69.68     | 0.0004    | significant |
| $X_1X_2$ | 1             | 1  | 1           | 0.242     | 0.6436    | non-significant |
| $X_1X_3$ | 25            | 1  | 25          | 6.05      | 0.0573    | slightly significant |
| $X_2X_3$ | 49            | 1  | 49          | 11.85     | 0.0184    | significant |
| $X_1^2$ | 77.56         | 1  | 77.56       | 18.77     | 0.0075    | significant |
| $X_2^2$ | 31.41         | 1  | 31.41       | 7.6       | 0.04      | significant |
| $X_3^2$ | 61.56         | 1  | 61.56       | 14.89     | 0.0119    | significant |

| $R^2$   | 0.9813 |
| Adjusted $R^2$ | 0.9476 |
| Predicted $R^2$ | 0.7087 |

Copyright © 2020, BCREC, ISSN 1978-2993
maximum sulfur removal efficiency equal to 0.922.

3.4 Oxidation Desulfurization Reaction Kinetics

Kinetics for ODS reaction studies under various temperatures against time using optimum catalyst dosage at 2.5 g. The total sulfur content measured with time (1, 2, 3, 4) hours and temperatures (40, 50, 60) °C. Assume oxidation reaction can be represented as:

\[ \text{RS-H + H}_2\text{O}_2 \rightarrow \text{product} \]

By assume that hydrogen peroxide in excess amount, thus the H\(_2\)O\(_2\) term dependent can be neglected. Many researchers had been reported that oxidation reaction obeys pseudo first order reaction therefore Equation (7) can be written by assuming n = 1 as:

\[ -\frac{d[C_s]}{dt} = k'[C_{H_2O_2}]^n[C_s]^m \]  

Where \( k' \) is apparent rate constant, integration Equation (8) between below limit:

At \( t = 0 \rightarrow C_s = C_0 \) and at \( t = t \rightarrow C_s = C_t \)

\[ \ln \left( \frac{C_0}{C_t} \right) = k't \]  

Figure 11. Effect of temperature on reaction rate constant.

Table 5. Rate constant values with temperature with correlation factor \( R^2 \).

| Temperature (°C) | Rate Constant | \( R^2 \) |
|-----------------|---------------|-----------|
| 40              | 1.0837        | 0.9892    |
| 50              | 1.5893        | 0.9835    |
| 60              | 2.5053        | 0.9786    |

Where \( C_s \), \( C_0 \) and \( C_t \) are sulfur concentration, initial sulfur concentration and final sulfur concentration [mol/L], \( t \) is time in hour and \( k \) is the reaction rate constant [h\(^{-1}\)].

Plotting ln \( (C_s/C_t) \) against time for various temperatures give straight line represent the rate constant, the straight line with high \( R^2 \) which confirms the assumption of kinetics of pseudo first order reaction as shown in Figure 10 and Table 5, as seen in table reaction rate constant is increasing with increased temperature because its strongly temperature dependent [20].

The activation energies (\( E_a \)) for ODS reaction estimated according to Arrhenius equation \([k = k_0 \exp(-E_a/RT)]\) from plot (ln \( k \)) vs (1/T) as shown in Figure 11, the apparent activation energy value is 36.26 kJ/mol. The estimated activation energy value was close to many estimated values in previous work as shown in Table 6.

4. Conclusion

The catalyst characterizations indicate that Fe\(_2\)O\(_3\) was successfully dispersed on the Graphene surface. The sulfur removal efficiency reached 90% at following operating conditions; 240 min stirring time, 1.5 g catalyst dosage, and 60 °C temperature. The results analyzed with Box–Behnken experimental design by the aim of Design-Expert software shows that among three studied variables (stirring time, catalyst dosage and temperature), stirring time has the highest impact on sulfur removal efficiency via its F-value from ANOVA analysis. The suggested model (second-order polynomial) for experimental results show good convergence with predicated data due to its high \( R^2 \) coefficient value (0.9813). The optimization analysis for the statistical model predicted that maximum removal efficiency (0.922) could be estimated by values of three studied process variables; stirring time at 225 min, catalyst dosage at 2.5 grams and temperature at 60 °C. The ODS reaction was obeyed pseud first-order reaction with apparent activation energy value

Table 6. Activation energy for dibenzothiophene for various catalyst /H\(_2\)O\(_2\)

| Catalyst          | Activation energy, kJ/mol | Reference |
|-------------------|----------------------------|-----------|
| H\(_3\)PW\(_{12}\)O\(_{40}\) | 45.9                       | [21]      |
| H\(_3\)PMO\(_{12}\)O\(_{40}\) | 29.0                       | [21]      |
| H\(_3\)SiW\(_{12}\)O\(_{40}\) | 28.3                       | [21]      |
| HPW/aEVM          | 30.3                       | [22]      |
equal to 36.26 kJ/mol. The sulfur removal efficiency increased with increasing stirring time, catalyst dosage and temperature. The study graded the impact of parameters on the sulfur removal efficiency to be in the order; stirring time, reaction temperature and catalyst dosage. The ODS reaction show activation energy equal to 36.26 kJ/mol. The reaction kinetics has been studied under various range of temperatures and time, while the hydrogen peroxide assumed to be excess and the reaction is first order reaction.

Acknowledgements

The authors would like to acknowledge to Mr. Riyadh Noaman manager of Chemical and Petrochemical Research Center / Corporation of Research and Industry Development /Ministry of Industry & Minerals and Mr. Quraish , Mr. Zuhair for their help in measuring sulfur content to support in this research.

References

[1] Liu, S., Wang, B., Cui, B., Sun, L. (2008). Deep desulfurization of diesel oil oxidized by Fe(VI) systems. *Fuel*, 87(3), 422–428. doi: 10.1016/j.fuel.2007.05.029.

[2] Mérida-Robles, J., Rodriguez-Castellón, E., Jiménez-López, A. (1999). Characterization of Ni, Mo, and Ni-Mo catalysts supported on alumina-pillared a-zirconium phosphate and reactivity for the thiophene HDS reaction. *Journal of Molecular Catalysis A: Chemical*, 145(1-2), 169–181. doi: 10.1016/s1381-1169(99)00048-5.

[3] Prabhu, N., Dalai, A.K., Adjaye, J. (2011). Hydrodesulfurization and hydrodenitrogenation of light gas oil using NiMo catalyst supported on functionalized mesoporous carbon. *Applied Catalysis A: General*, 401 (1-2), 1–11. doi: 10.1016/j.apcata.2011.04.019.

[4] Babich, I. (2003). Science and technology of novel processes for deep desulfurization of oil refinery streams: a review. *Fuel*, 82(6), 607–631. doi: 10.1016/s0016-2361(02)00324-1.

[5] Ding, Y., Zhu, W., Li, H., Jiang, W., Zhang, M., Duan, Y., Chang, Y. (2011). Catalytic oxidative desulfurization with a hexatungstate/aqueous H2O2/ionic liquid emulsion system. *Green Chemistry*, 13(5), 1210-1216. doi: 10.1039/c0gc00787k.

[6] Hao, L., Hurlock, M.J., Li, X., Ding, G., Kriegsman, K.W., Guo, X., Zhang, Q. (2019). Efficient Oxidative Desulfurization Using a Mesoporous Zr-based MOF. *Catalysis Today*, (Article In Press). doi: 10.1016/j.cattod.2019.04.012.

[7] Caero, L.C., Hernández, E., Pedraza, F., Murrieta, F. (2005). Oxidative desulfurization of synthetic diesel using supported catalysts. *Catalysis Today*, 107-108, 564–569. doi: 10.1016/j.cattod.2005.07.017.

[8] Bagiyan, G.A., Koroleva, I.K., Soroka, N.V., Ufimtsev, A.V. (2004). Kinetics of the Catalytic Oxidation Reactions of Thiol Compounds in Aqueous Solutions in the Presence of Copper Ions. *Kinetics and Catalysis*, 45(3), 372-380. doi:10.1023/b:kica.0000032171.81652.91.

[9] Cedeño-Caero, L., Gomez-Bernal, H., Frausto-Cuevas, A., Guerra-Gomez, H.D., Cuevas-Garcia, R. (2008). Oxidative desulfurization of synthetic diesel using supported catalysts. *Catalysis Today*, 133-135, 244–254. doi: 10.1016/j.cattod.2007.12.017.

[10] Murata, S., Murata, K., Kidenka, K., Nomura, M. (2004). A Novel Oxidative Desulfurization System for Diesel Fuels with Molecular Oxygen in the Presence of Cobalt Catalysts and Aldehydes. *Energy & Fuels*, 18(1), 116–121. doi: 10.1021/ef034001z.

[11] Makki, H.H., Alwan, H.H. (2019). Synthesis and characterization of Graphene produced from Iraqi date syrup. *Association of Arab Universities Journal of Engineering Sciences*, 26(1), 49–54.

[12] Ugal, J.R., Jima’a, R.B., Al-Jubori, W.M.K., Abbas, B.F., Al-Jubori, N.M. (2018). Oxidative Desulfurization of Hydrotreated Gas Oil using Fe3O4 and Pd Loaded over Activated Carbon as Catalysts. *Oriental Journal of Chemistry*, 34(2), 1091–1097. doi:10.13005/ojc/340261.

[13] Mourabot, M., El Rhilassi, A., El Boujaudy, H., Bennani-Ziatmi, M., Taitai, A. (2017). Use of response surface methodology for optimization of fluoride adsorption in an aqueous solution by Brushite. *Arabian Journal of Chemistry*, 10, S329-S332. doi: 10.1016/j.arabjc.2013.12.028.

[14] Ferreira, S.L.C., Bruns, R.E., Ferreira, H.S., Matos, G.D., David, J.M., Brandão, G.C., da Silva, E.G.P., Portugal, L.A., dos Reis, P.S., Souza, A.S., dos Santos, W.N.L., Bruns, R.E., Ferreira, H.S. (2007). Box-Behnken design: An alternative for the optimization of analytical methods. *Analytica Chimica Acta*, 597(2), 179–186. doi: 10.1016/j.aca.2007.07.011.

[15] Mazaheri, H., Lee, K.T., Bhatia, S., Mohamed, A.R. (2010). Subcritical water liquefaction of oil palm fruit press fiber in the presence of sodium hydroxide: An optimisation study using response surface methodology. *Bioresource Technology*, 101(23), 9335–9341. doi: 10.1016/j.biortech.2010.07.004.
[16] Lima, S.B., Borges, S.M.S., Rangel, M.d.C., Marchetti, S.G. (2013). Effect of Iron Content on the Catalytic Properties of Activated Carbon-Supported Magnetite Derived from Biomass. *Journal of the Brazilian Chemical Society*, 24(2), 344–354. doi: 10.5935/0103-5053.20130044.

[17] Al-Saadi, T.M., Jihad, M.A.K. (2015). Preparation and characterization of Graphene / PMMA composite. *International Journal of Advanced Research in Science, Engineering and Technology*, 2(10), 902-909.

[18] Choi, W., Lahiri, I., Seelaboyina, R., Kang, Y.S. (2010). Synthesis of Graphene and its applications: A review. *Critical Reviews in Solid State and Materials Sciences*, 35, 52-71.

[19] Mamaghani, A.H., Fatemi, S., Asgari, M. (2013). Investigation of Influential Parameters in Deep Oxidative Desulfurization of Dibenzothiophene with Hydrogen Peroxide and Formic Acid. *International Journal of Chemical Engineering*, 2013, 1–10. doi: 10.1155/2013/951045.

[20] Fogler, H.S. (2005). *Elements of chemical reaction engineering*, 4th edition, Prentice Hall, New York, pp. 91.

[21] Choi, A.E., Roces, S., Dugos, N., Wan, M.-W. (2016). Mixing-assisted oxidative desulfurization of model sulfur compounds using polyoxometalate/H\text{2}O\text{2} catalytic system. *Sustainable Environment Research*, 26(4), 184-190. doi: 10.1016/j.serj.2015.11.005.

[22] Huang, P., Luo, G., Kang, L., Zhu, M., Dai, B. (2017). Preparation characterization and catalytic performance of HPW/aEVM catalyst on oxidative desulfurization. *RSC Advances*, 7, 4681-4687.