



Research Article

Optimization of Oxidative Desulfurization Reaction with Fe_2O_3 Catalyst Supported on Graphene Using Box-Behnken Experimental Method

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Received: 7th December 2019; Revised: 23rd December 2019; Accepted: 27th December 2019;
Available online: 28th February 2020; Published regularly: April 2020

Abstract

In this study, the catalyst activity of Fe_2O_3 supported on Graphene for Iraqi gas oil oxidation desulfurization (ODS) by hydrogen peroxide (H_2O_2) was investigated. The prepared catalyst was synthesized by wet impregnation for ferric nitrate as a Fe_2O_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. Copyright © 2020 BCREC Group. All rights reserved

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 Fe_2O_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-

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sten, W) promoted by (Nickel, Ni; Cobalt, Co) at high temperature and high hydrogen partial pressure supported on proper carrier comes with an active surface area like Alumina [3]. However, hydrodesulfurization is inefficient for removing some of the sulfur compounds in oil like heterocyclic sulfur compounds, benzothiophene and dibenzothiophene [4,5]. In 2005, the European community and USA limits sulfur contents in motor fuels to 40-50 ppm, while Germany limits the sulfur level to around 10 ppm since 2001 [4]. Hao *et al.* mentioned that many countries have released very strict regulations in regard to sulfur contents to be around 10 ppm [6]. This ultra-low sulfur considers as a real challenge for the traditional hydrodesulfurization process. Where the HDS process needs harsh operating conditions to remove a large amount of sulfur which resulting in reducing the quality of fuels. Therefore, alternative technology is required for high capacity sulfur removal that can be effective to reach these new regulations.

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 Fe₂O₃ supported on Graphene for Iraqi gas oil oxidation desulfurization (ODS) by hydrogen peroxide (H₂O₂) was investigated. This piece of work examines the sulfur loading on the Fe₂O₃ 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 H₂O₂, ferric nitrate (Fe(NO₃)₃·9H₂O), glacial acetic acid (CH₃COOH), sodium bicarbonate (NaHCO₃), sodium carbonate (Na₂CO₃), nitric acid (HNO₃), sulfuric acid (H₂SO₄), Acetonitrile (CH₃CN).

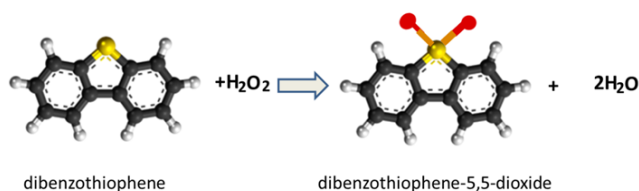


Figure 1. Oxidation desulfurization process of DBT [10]

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 poured 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		Levels		
	Coded	Actual	-1	0	1
Stirring time, min	x_1	X_1	160	200	240
Catalyst dosage, g	x_2	X_2	0.5	1.5	2.5
Temperature, °C	x_3	X_3	40	50	60

Table 2. Box-Behnken design matrixes.

Run	Design Parameters			Run	Design Parameters			Run	Design Parameters		
	x_1	x_2	x_3		x_1	x_2	x_3		x_1	x_2	x_3
1	-1	0	1	6	0	-1	1	11	0	1	1
2	0	0	0	7	1	-1	0	12	0	-1	-1
3	0	0	0	8	1	1	0	13	-1	-1	0
4	0	0	0	9	1	0	1	14	-1	1	0
5	0	1	-1	10	1	0	-1	15	-1	0	-1

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).

$$SR\% = \frac{S_0 - S_f}{S_0} \times 100 \quad (1)$$

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

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].

$$N = 2k(k-1) + r \quad (2)$$

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).

$$x_i = \frac{X_i - X_0}{\Delta X_i}; \quad i = 1, 2, 3 \quad (3)$$

Where X_0 is real value for the independent variable at the center level, and ΔX is the interval value. Table 2 shows the matrixes 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].

$$y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j + \varepsilon \quad (4)$$

Where y is predicated response, β_0 is the intercept coefficient, β_i is the linear effect (slope) of input variable x_i , β_{ij} is interaction effect of linear by linear between two input variables x_i , and β_{ii} 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° , and 62.09°

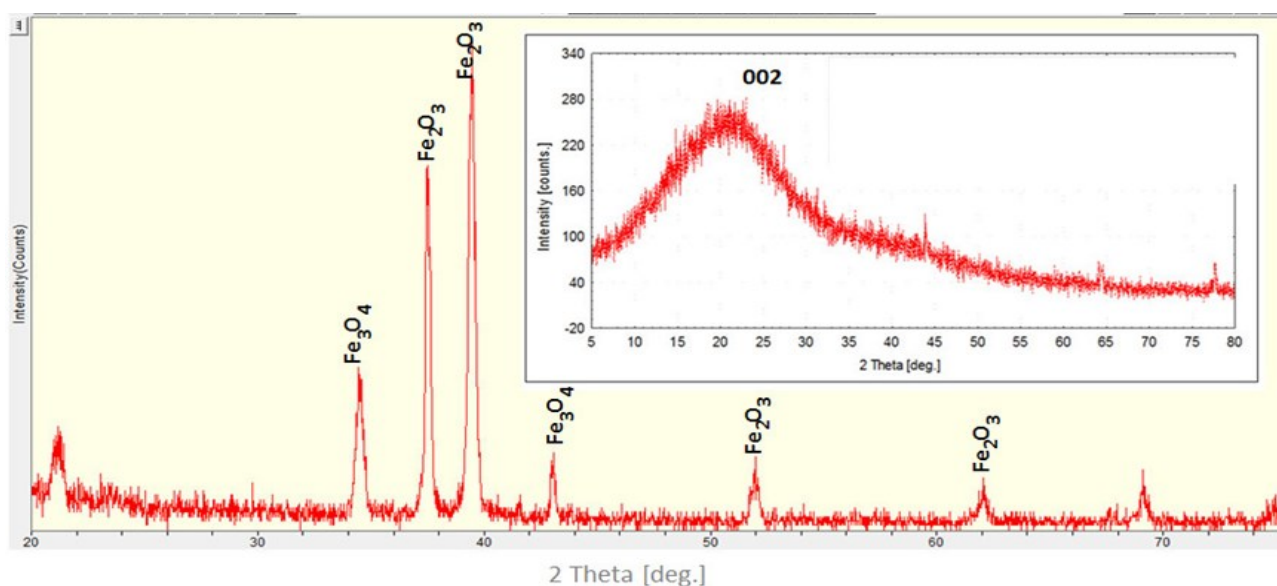


Figure 2. XRD pattern for Fe₂O₃/Graphene catalyst. Inset pattern shows XRD pattern for Graphene prepared from Iraqi date syrup [11].

which referred to Fe_2O_3 (hematite) and Fe_3O_4 (magnetite) while the peaks at $2\theta = 33.89^\circ$, 39.47° , and 43.07° , 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 \AA . 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 $d_{002} = 3.742 \text{ \AA}$ (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-

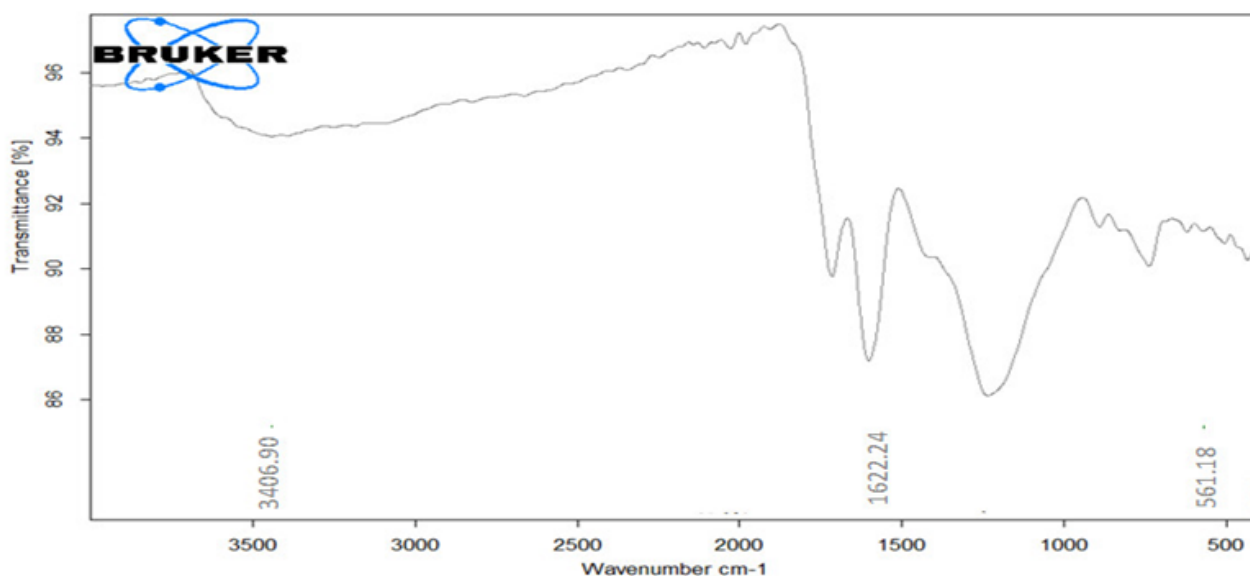


Figure 3. FTIR spectra for Fe_2O_3 /Graphene catalyst

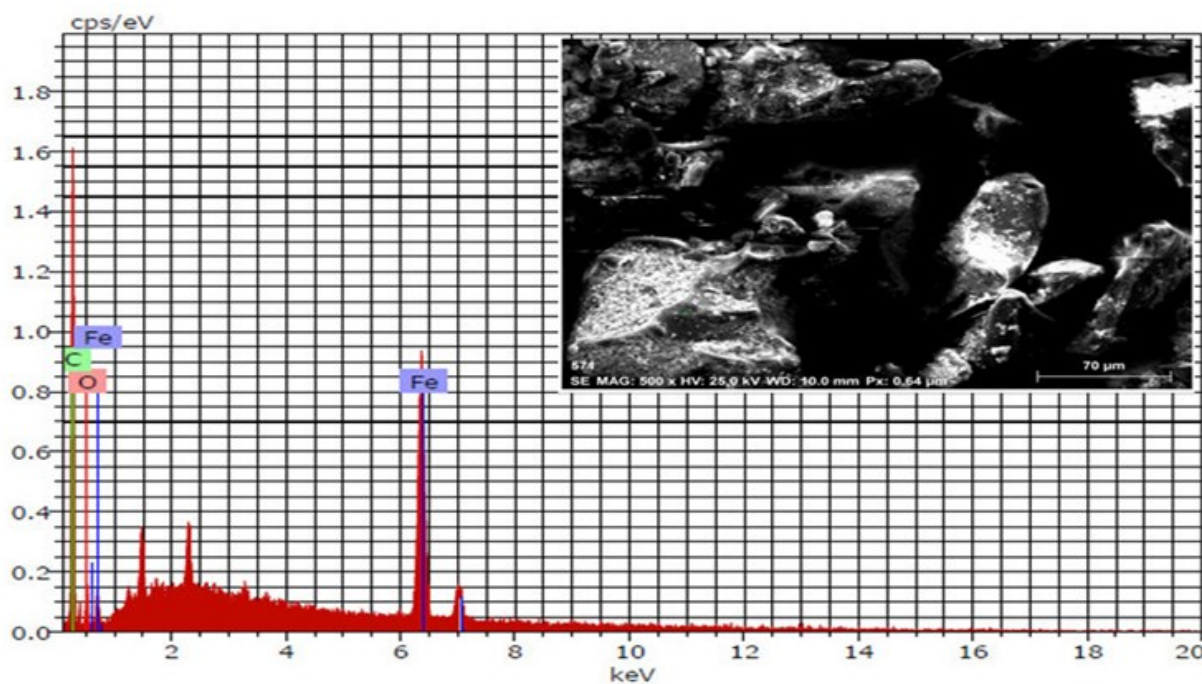


Figure 4. EDS analysis (elements mapping) for prepared catalyst. Inset shows the SEM image for catalyst.

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

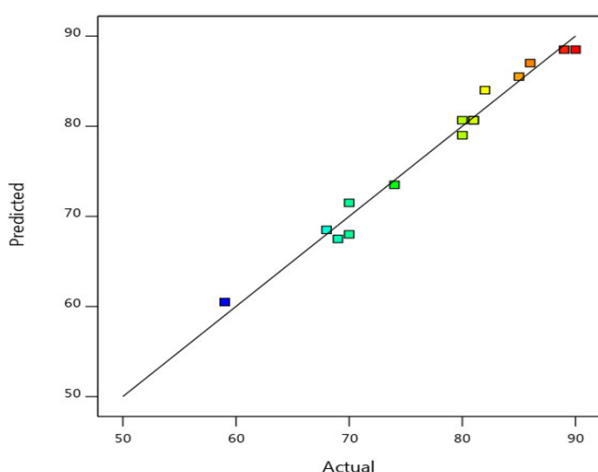


Figure 5. Experimental and predicted response plot.

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).

$$y = 80.67 + 8.0x_1 - 2.0x_2 + 6.0x_3 - 0.5x_1x_2 + 2.5x_1x_3 + 3.5x_2x_3 - 4.58x_1^2 + 2.58x_2^2 - 4.08x_3^2 \quad (5)$$

The analysis of variance results for the predicted 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 R² (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 predicted 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*₂*x*₃, *x*₁², *x*₂², and *x*₃² are significant parameters because of their values

Table 3. Experimental (observed) and predicted sulfur removal efficiencies at different conditions

Run	Coded Variables			Actual Variables			Response S%	
	<i>x</i> ₁	<i>x</i> ₂	<i>x</i> ₃	Reaction time	Catalyst dosage	Temperature	Experimental	Predicted
1	-1	0	1	160	1.5	60	69	67.51
2	0	0	0	200	1.5	50	81	80.67
3	0	0	0	200	1.5	50	80	80.67
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

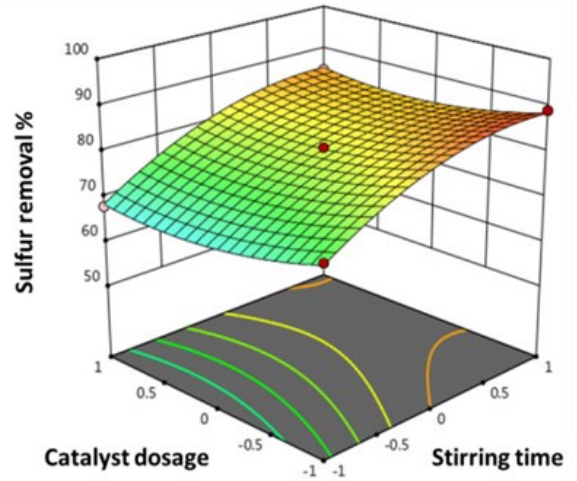
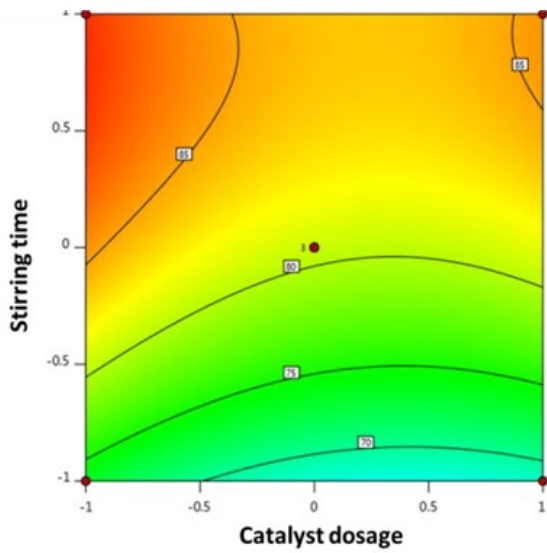


Figure 6. 2-D and 3-D plot of sulfur removal efficiency vs stirring time and catalyst dosage.

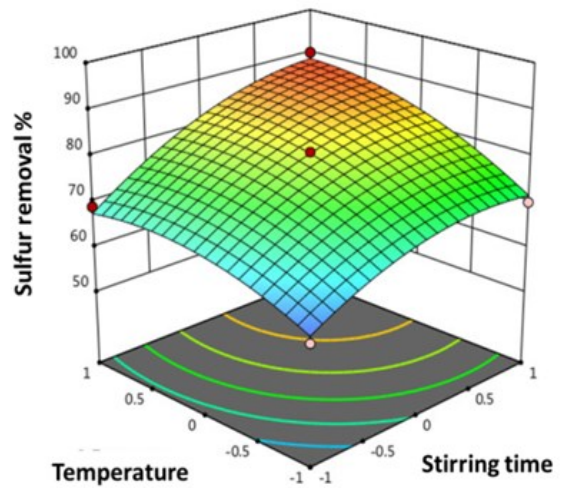
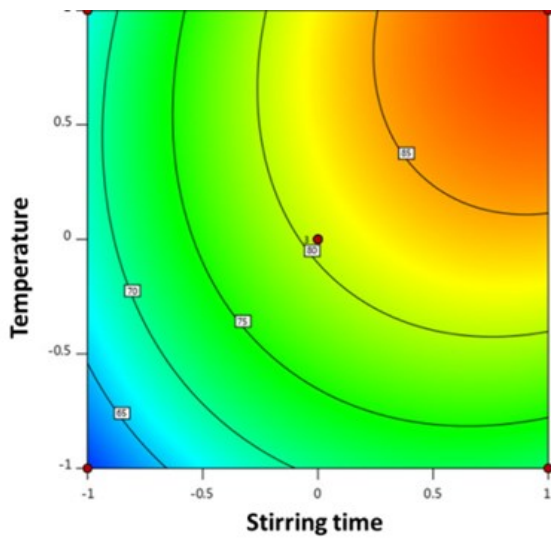


Figure 7. 2-D and 3-D plot of sulfur removal efficiency vs stirring time and temperature.

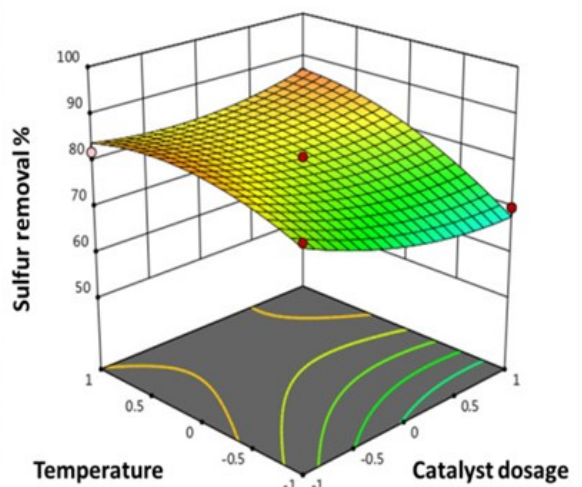
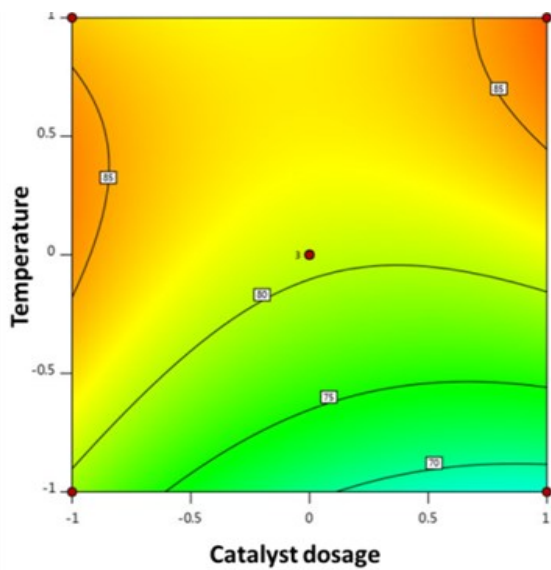


Figure 8. 2-D and 3-D plot of sulfur removal efficiency vs temperature and catalyst dosage.

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).

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

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

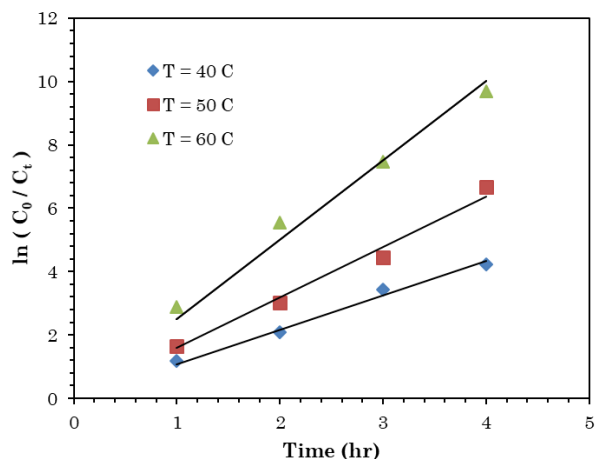


Figure 10. The plot of $\ln(C_0/C_t)$ vs time at studied temperature.

a specific time, then marginally decreased. The possible reason behind this is the interaction between H_2O_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

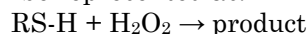
Table 4. ANOVA analysis results for RSM for quadratic model.

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					

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:



$$-\frac{d[C_S]}{dt} = k[C_{\text{H}_2\text{O}_2}]^m [C_S]^n \quad (7)$$

By assume that hydrogen peroxide in excess amount, thus the H_2O_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:

$$-\frac{d[C_S]}{dt} = k'[C_S] \quad (8)$$

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

At $t = 0 \rightarrow C_s = C_0$ and at $t = t \rightarrow C_s = C_t$

$$\ln\left(\frac{C_0}{C_t}\right) = k't \quad (9)$$

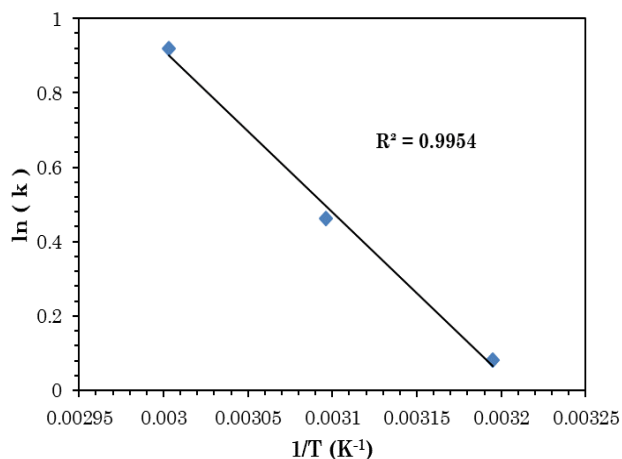


Figure 11. Effect of temperature on reaction rate constant.

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 $\ln(C_0/C_t)$ 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_2O_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_2O_2

Catalyst	Activation energy, kJ/mol	Reference
$\text{H}_3\text{PW}_{12}\text{O}_{40}$	45.9	[21]
$\text{H}_3\text{PMO}_{12}\text{O}_{40}$	29.0	[21]
$\text{H}_3\text{SiW}_{12}\text{O}_{40}$	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., Rodríguez-Castellón, E., Jiménez-López, A. (1999). Characterization of Ni, Mo, and Ni–Mo catalysts supported on alumina-pillared α -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). Hydrodesulphurization 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 H_2O_2 /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., Murrrieta, 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., Fraustro-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., Kidena, 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 Fe_2O_3 and Pd Loaded over Activated Carbon as Catalysts. *Oriental Journal of Chemistry*, 34(2), 1091–1097. doi:10.13005/ojc/340261.
- [13] Mourabet, M., El Rhilassi, A., El Boujaady, H., Bennani-Ziatni, 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, S3292–S3302. 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. (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 pyoxometalate/H₂O₂ 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.