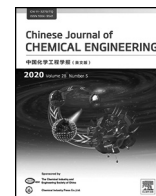




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Article

Optimization of a continuous ultrasound assisted oxidative desulfurization (UAOD) process of diesel using response surface methodology (RSM) considering operating cost

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ABSTRACT

A continuous-flow ultrasound-assisted oxidative desulfurization (UAOD) of partially hydro-treated diesel has been investigated using hydrogen peroxide-formic acid as simple and easy to apply oxidation system. The effects of different operating parameters of oxidation stage including residence time (2–24 min), formic acid to sulfur molar ratio (10–150), and oxidant to sulfur molar ratio (5–35) on the sulfur removal have been studied using response surface methodology (RSM) based on Box–Behnken design. Considering the operating costs of the continuous-flow oxidation stage including chemical and electrical energy consumption, the appropriate values of operating parameters were selected as follows: residence time of 16 min, the formic acid to sulfur molar ratio of 54.47, and the oxidant to sulfur molar ratio of 8.24. In these conditions, the sulfur removal and the volume ratio of the hydrocarbon phase to the aqueous phase were 86.90% and 4.34, respectively. By drastic reduction in the chemical consumption in the oxidation stage, the volume ratio of the hydrocarbon phase to the aqueous phase was increased up to 10. Therefore, the formic acid to sulfur molar ratio and the oxidant to sulfur molar ratio were obtained 23.64 and 3.58, respectively, which lead to sulfur removal of 84.38% with considerable improvements on the operating cost of oxidation stage in comparison with the previous works.

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1. Introduction

Sulfur-containing compounds in the middle distillate fuels have a major contribution to the environmental pollutants, causing acid rain due to SO_x and the bad smell of petroleum products due to the mercaptans [1,2]. The presence of organic sulfur-containing compounds in the fuels can cause corrosion in the combustion engines and other equipment [3]. Nowadays, very strict regulations have been legislated to minimize the amount of sulfur-containing compounds in the oil derivatives [4].

Hydrodesulfurization (HDS) is the conventional desulfurization technique in the industries to remove the sulfur-containing compounds from middle distillate fuels. For deep desulfurization, this method requires high temperature (up to 400 °C) and high pressure (up to 10 MPa) [2,5]. Furthermore, in this process, expensive catalysts and hydrogen as a reactant are required [6]. Thus, HDS is a costly technique for deep desulfurization [7]. In addition, the aliphatic sulfur-containing compounds can be eliminated easily using the HDS process [8,9], although this method is not efficient to remove the heterocyclic

sulfur-containing compounds such as dibenzothiophene and its derivatives, especially 4,6-dimethyldibenzothiophene [8,10]. This is due to the fact that in the complex sulfur-containing compounds such as dibenzothiophene, the availability of sulfur atom to the active sites of the catalyst is reduced due to the steric hindrance effect [11].

Several alternative methods have been proposed for the desulfurization of the middle distillate fuels. The most important methods are oxidative desulfurization [12,13], extractive desulfurization [14,15], adsorptive desulfurization [16,17], bio-desulfurization [18,19], chlorinolysis-based desulfurization [20], supercritical water-based desulfurization [20,21], and alkylation-based desulfurization [16].

A comparison of the proposed methods shows that a combination of oxidative and extractive desulfurization methods can be considered as an appropriate complementary and alternative method due to mild operating conditions. The advantages of this method are no need to hydrogen and its capability to remove the refractory sulfur-containing compounds, such as benzothiophene, dibenzothiophene in a mild operating condition [22–25].

In the oxidation/extraction process, the sulfur-containing compounds are converted into the corresponding sulfoxides and sulfones in the oxidation reaction at first. Then, the oxidized sulfur-containing compounds can be extracted using a polar solvent or separated through an adsorption process [26–28]. In the oxidation stage, a chemical system

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including oxidant and catalyst is required. The oxidant should have high selectivity for the sulfur-containing compounds, so that it should not oxidize other accompanying hydrocarbon compounds in the fuel [29,30]. The oxidants can be categorized into three groups: (1) Gaseous oxidants such as ozone, oxygen, and nitrogen oxide [31]. (2) Aqueous oxidants such as hydrogen peroxide, nitric acid, and HClO_3 [32]. (3) Solid oxidants such as oxone, sodium persulfate, and potassium superoxide [33]. In addition, the oil soluble oxidants are also used in the ODS [34]. According to the literature, hydrogen peroxide is the most widely applied oxidant due to its affordable price, high active oxygen content, environmental friendliness, and commercial availability [35,36]. The catalysts are usually classified as homogeneous and heterogeneous. The most common homogeneous catalysts are formic acid [35] and acetic acid [37]. The salts of transition metals, such as vanadium [38], molybdenum [39], and tungsten [40], and polyoxometalate [41] are the most widely applied heterogeneous catalysts.

The ultrasound-assisted oxidative desulfurization (UAOD) has been presented as an appropriate technology for the deep desulfurization of the middle distillate fuels such as diesel. Ultrasonic irradiation enhances the oxidation rate of sulfur-containing compounds by effective mixing between the hydrocarbon and aqueous phases and creating a fine emulsion. The interphase mass transfer rate in the UAOD system can be increased due to the creation of the cavities in the liquid fuels and increasing the liquid–liquid interfacial area for the viscous films containing gas-filled bubbles [27,42–45]. Ultrasonic cavitation involves physical effects (*i.e.*, formation of the fine emulsion between the hydrocarbon and aqueous phases) and chemical effects (*i.e.*, production of radicals through transient collapse of the cavitation bubbles). The transient collapse of the cavitation bubbles results in high local pressures (up to 100 MPa) and high local temperatures (up to 5000 K) that increase the interphase mass transfer and the overall reaction rate in the UAOD system [11,46].

Several studies on the desulfurization of different fuels using UAOD have been reported in the batch and continuous modes. Jalali and Sobati [3] studied the desulfurization of gas oil using UAOD in a batch-mode reactor. Wan *et al.* [47] applied a probe-type ultrasound reactor in the recirculation loop continuous flow and a continuous flow sonoreactor to study the desulfurization of marine gas oil using oxidative technique. Najafi *et al.* [48] employed a bench scale ultrasonic reactor to investigate the effective parameters on the oxidative desulfurization method. Chen *et al.* [49] tested a continuous-flow probe-type ultrasound reactor to evaluate the desulfurization of the diesel fuel and pyrolysis oil.

According to our literature survey, there are only two reports available on the sulfur removal from diesel in a continuous-flow UAOD process using formic acid and hydrogen peroxide as simple and easy to apply oxidation system. In the first report, Rahimi *et al.* [1] optimized the operating conditions of UAOD in a batch-mode reactor. Then, they conducted some experiments in the continuous mode corresponding to the best batch conditions to minimize the residence time and the volume ratio of the aqueous to hydrocarbon phases in a double-compartment reactor. The main concern of this study was to investigate the impact of different strategies of aqueous phase injection on the sulfur removal. In another work, Rahimi *et al.* [50] investigated the application of a novel cylindrical multi-probe continuous-flow UAOD system. In this study, computational fluid dynamics (CFD) was also applied to provide some insights regarding the UAOD reactor scale up. The majority of the studies on the desulfurization of the fuels using ultrasonic irradiation were performed in the batch-mode reactors. The comparison of ultrasonic-assisted processes in the batch-mode and the continuous-mode reveals that the continuous-flow system is more beneficial due to its higher controllability, larger productivities, greater economic value and less environmental effects. According to the literature survey, although few works have investigated the effects of different parameters on the sulfur removal in a continuous-flow UAOD system, no study was conducted with the aim of selection of appropriate operating variables to reduce the operating cost in the desulfurization

processes from middle distillate fuels using simple hydrogen peroxide and formic acid system. In addition, there is no study targeting the operating cost reduction through decreasing the chemical consumption in a continuous-flow UAOD process.

One of the main limitations in the ODS and UAOD studies is the high oxidation time. In addition, in the continuous-flow UAOD studies, a proper statistical analysis, reflecting the interaction between independent parameters and the effect of each parameter on the response variable has not been reported. Moreover, UAOD demands high amount of chemicals that would mean high operating costs. Therefore, in this study, response surface methodology based on Box–Behnken design was applied to investigate the interactions between different operating parameters and the effects of them on the sulfur removal using UAOD process in a continuous-flow reactor. In addition, the best operating parameters of the oxidation process including the residence time, formic acid to sulfur molar ratio, and oxidant to sulfur molar ratio was selected by considering the operating cost. Finally, the chemical consumption and operating cost of the continuous-flow oxidation process were decreased considerably in comparison with the others studies.

2. Experimental

2.1. Materials

Partially hydro-treated diesel fuel as a feedstock with total sulfur content of $2760 \text{ mg} \cdot \text{kg}^{-1}$ was supplied by Bandar Abbas refinery in Iran. The specifications of the fuel are given in Table 1. Formic acid (85 wt%), hydrogen peroxide (35 wt%), and dimethylformamide ($\geq 99.8\%$) were purchased from the Merck Co (Germany).

2.2. Method of analysis

The Rigaku sulfur analyzer (Rigaku NEXQC +, Japan) was used to measure the total sulfur content of the samples in the detection range of 0–5 wt% of sulfur with a lowest detection limit of $25 \text{ mg} \cdot \text{kg}^{-1}$. The test method was based on the energy dispersive X-ray fluorescence technique according to the ASTM D4294.

The gas chromatograph equipped with sulfur chemiluminescence detector (GC-SCD Agilent-8355) was applied to compare the chromatograms of the sulfur-containing compounds in the untreated and treated diesels. The chromatography column was fused-silica capillary (CP-Sil 8 CB, 0.32 mm ID, from Supelco Company). The injector and detector were adjusted at 220°C and 270°C , respectively. In addition, helium was used as the carrier gas with a constant rate of $2.5 \text{ ml} \cdot \text{min}^{-1}$.

Table 1
Properties of diesel feedstock

Characteristic	Content	Test method
Density at $15^\circ\text{C} / \text{kg} \cdot \text{m}^{-3}$	842	ASTM D4052
Sulfur content $/ \text{mg} \cdot \text{kg}^{-1}$	2760	ASTM D4294
Kinematic viscosity at $40^\circ\text{C} \times 10^6 / \text{m}^2 \cdot \text{s}^{-1}$	4.12	ASTM D445
Flash point $/^\circ\text{C}$	80	ASTM D93
Water content $/ \text{mg} \cdot \text{kg}^{-1}$	37	ASTM D6304
Cetane index	55.20	ASTM D4737
Distillation range $/^\circ\text{C}$		ASTM D86
Initial boiling point (I.B.P)	213	
5%	244	
10%	253	
20%	272.5	
30%	284.5	
40%	295	
50%	302	
60%	312	
70%	322	
80%	336	
90%	358.5	
95%	372.5	
Final boiling point (F.B.P)	388	

Other characteristics of the diesel feedstock and treated diesel such as viscosity, density, flash point, water content, cetane index, and distillation curve were measured by applying the test methods of ASTM D445, ASTM D4052, ASTM D93, ASTM D6304, ASTM D4737 and ASTM D86, respectively.

2.3. Experimental setup and procedures

2.3.1. Continuous-flow UAOD setup

The continuous-flow oxidation experiments of the diesel fuel under ultrasonic irradiation were carried out in a jacket type glass reactor with a working volume of 125 ml (Fig. 1). The reactor was equipped with a thermometer to detect the reaction temperature and a condenser to condense the generated vapors inside the reactor. Since, the oxidation reaction is exothermic, a circular constant-temperature water bath was used to adjust the temperature by passing water through the reactor jacket.

In each UAOD run, the reactants were directly irradiated by a titanium ultrasonic horn (12 mm diameter) with a frequency of 20 kHz (UTD 400, Ultrasound Technology Development Company, Iran) which was placed inside the reactor vertically.

At the beginning of each run, 125 ml of diesel was introduced into the reactor in such a way that 1 cm of the ultrasound probe was immersed into the fuel. Then, the fuel was heated to 50 °C (*i.e.*, temperature of the oxidation reaction). A flow of the diesel (*i.e.*, hydrocarbon phase) and a mixture of formic acid 85 wt% and hydrogen peroxide 35 wt% (*i.e.*, aqueous phase) were continually introduced into the reactor using a peristaltic pump and a syringe pump, respectively, to control the input flow rates. Output flow rate was also controlled using a peristaltic pump. To enhance the contact area and the mass transfer rates between the aqueous and hydrocarbon phases, the aqueous phase was injected into the reaction medium through a glass nozzle at a distance of 3 cm from the horn tip. The ultrasonic power was regulated at 360 W in all of the experiments. In addition, the residence time of the reactants inside the reactor was selected according to the

experimental design. Continuous-flow oxidation reaction was carried out for 1 h to reach a steady state in the oxidation reaction, and then the output product of the reactor was poured into a separatory funnel to separate the hydrocarbon and aqueous phases. After the phases were separated, the hydrocarbon phase was washed with distilled water to remove any entrained aqueous phase. The hydrocarbon phase was later sent to an extraction stage to remove its sulfur-containing compounds.

2.3.2. Extraction procedure

Extraction experiments were performed in a 100-ml flask at the ambient temperature and pressure. In each experiment, 30 ml of the hydrocarbon phase was poured into the flask. Then, 30 ml of dimethylformamide as an extractant was added to the fuel to remove the sulfur-containing compounds. Extraction process was performed on a stirrer with 875 r·min⁻¹ stirring rate for 30 min. After the extraction process, the mixture was poured into a separatory funnel to separate the hydrocarbon and aqueous phases. After separating the hydrocarbon and aqueous phases, the obtained hydrocarbon phase was washed with distilled water to remove any entrained aqueous phase. Finally, the hydrocarbon phase was used to determine its total sulfur content.

2.4. Experimental design

In this study, the response surface methodology based on Box–Behnken design was used to analyze the results and to find the optimal value for the independent variables affecting the response. In the Box–Behnken method, three levels are required which are coded as -1 (low level), 0 (middle level), and $+1$ (high level). According to our preliminary evaluation, the residence time (R_t), the formic acid to sulfur molar ratio (n_a/n_s), and the oxidant to sulfur molar ratio (n_o/n_s) were selected as independent variables affecting the sulfur removal (response) in the continuous-flow UAOD system in the ranges of 2–24 min, 10–150, and 5–35, respectively. Table 2 shows the experimental ranges

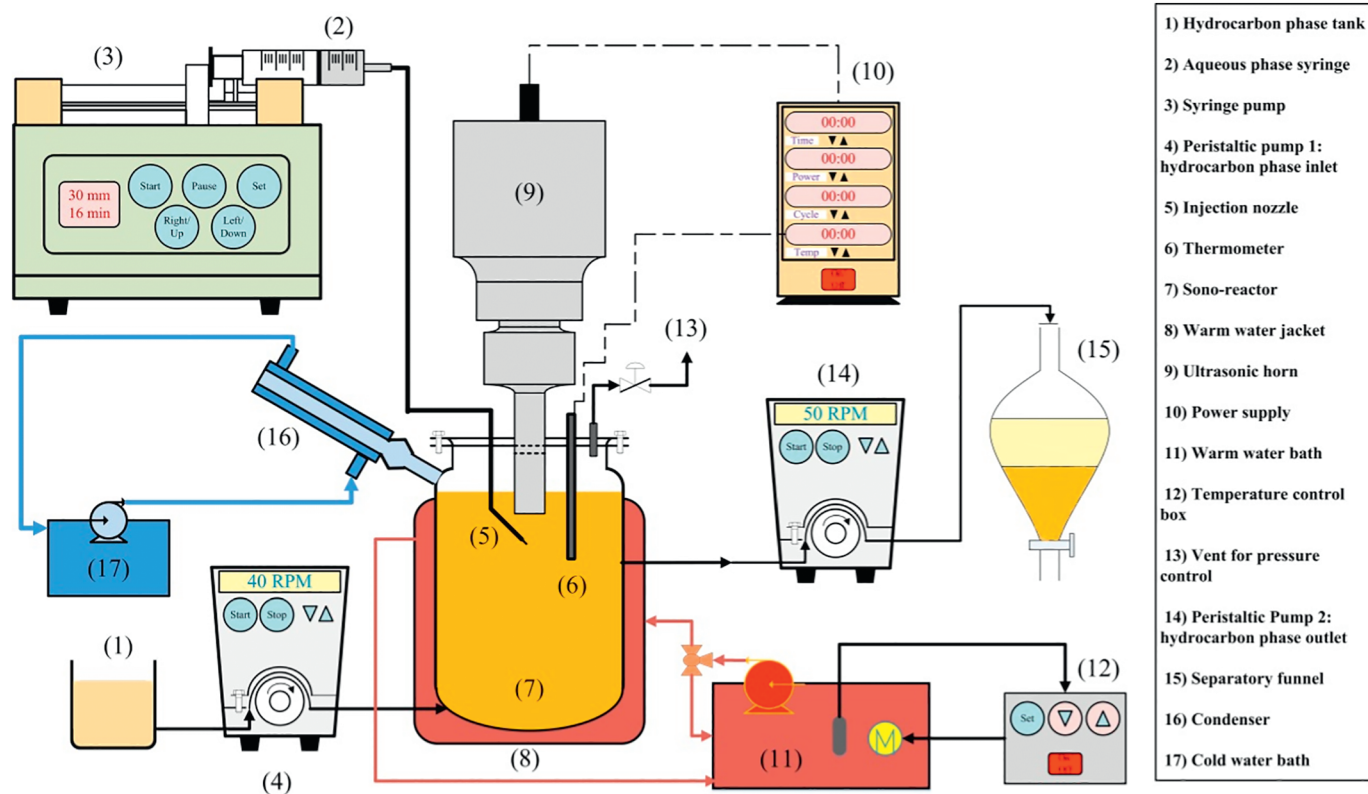


Fig. 1. Schematic diagram of the probe-type reactor in the continuous-flow UAOD process.

Table 2
Experimental ranges and levels of independent variables in the continuous condition

Factor	Symbol coded	Range and levels		
		−1	0	1
Residence time, R_t /min	X_1	2	13	24
Acid formic to sulfur molar ratio, $(n_a/n_s)/\text{mol} \cdot \text{mol}^{-1}$	X_2	10	80	150
Oxidant to sulfur molar ratio, $(n_o/n_s)/\text{mol} \cdot \text{mol}^{-1}$	X_3	5	20	35

and the levels for three independent variables for the continuous-flow UAOD system.

According to the Box–Behnken, 17 experimental runs were required, which included 5 replicates of the central run.

In order to correlate the desulfurization of the continuous UAOD process, a quadratic polynomial equation was developed as a function of independent variables and their interactions. The mathematical model for the response can be expressed as follows:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \sum_{j=i+1}^k \beta_{ij} X_i X_j + \sum_{i=1}^k \beta_{ii} X_i^2 + \varepsilon \quad (1)$$

where Y is response variable, X_i and X_j are factors (i.e., coded independent variables). In addition, k is the number of the variables; ε is error; β_0 , β_i , β_{ij} , and β_{ii} are the intercept coefficient (offset), the linear regression coefficients, the interaction coefficients, and the quadratic regression coefficients, respectively. In all experiments, the sulfur removal (S_r), as the response variable, was calculated as follows [1,3]:

$$\text{Sulfur removal} = \frac{S_i - S_f}{S_i} \times 100\% \quad (2)$$

where S_i and S_f are the total sulfur content of the feedstock and the treated fuel, respectively.

It should be noted that the experiments were repeated twice and the relative standard deviation for the sulfur removal was less than 1%.

3. Results and Discussion

3.1. Statistical analysis

The values of the independent variables, including R_t , n_a/n_s , and n_o/n_s , the predicted and actual response, and the error between the actual and predicted response are given in Table 3.

Using the conditions given in Table 3, the volume of the reactants and the volume flow rate of each component involved in the oxidation system are calculated as shown in Table 4.

The quadratic correlations proposed by RSM for the sulfur removal of diesel in terms of the actual and the coded factors are as follows:

$$\begin{aligned} S_r (\text{Actual}) = & +65.75528 + 1.51224 \times (R_t) + 0.17054 \times (n_a/n_s) \\ & + 0.10367 \times (n_o/n_s) - 1.76623 \times 10^{-3} \times (R_t) \times (n_a/n_s) \\ & + 1.04545 \times 10^{-3} \times (R_t) \times (n_o/n_s) + 2.55476 \times 10^{-3} \\ & \times (n_a/n_s) \times (n_o/n_s) - 0.038310 \times (R_t)^2 - 8.55204 \times 10^{-4} \\ & \times (n_a/n_s)^2 - 8.92444 \times 10^{-3} \times (n_o/n_s)^2 \end{aligned} \quad (3)$$

$$\begin{aligned} S_r (\text{Coded}) = & +88.14 + 4.35 \times X_1 + 4.33 \times X_2 - 0.53 \times X_3 \\ & - 1.36 \times X_1 \times X_2 + 0.17 \times X_1 \times X_3 + 2.68 \times X_2 \\ & \times X_3 - 4.64 \times X_1^2 - 4.19 \times X_2^2 - 2.01 \times X_3^2 \end{aligned} \quad (4)$$

where X_1 , X_2 , and X_3 are the coded parameters for the R_t , n_a/n_s , and n_o/n_s , respectively.

In order to ensure the proposed model is consistent with the experimental data, it is necessary to investigate the statistical parameters including squared correlation coefficient (R^2), adjusted squared correlation coefficient (R_{adj}^2), F -value, P -value, and the coefficient of variation (C.V.). Table 5 shows the effects of the independent variables and their interactions on the response.

The larger F -value and the smaller P -value means the more importance of the corresponding term in the proposed correlation for S_r , so that a P -value smaller than 0.05 is considered to be important. Therefore, the relative importance of the independent factors is as follows: R_t with a F -value of 62.93, n_a/n_s with a F -value of 62.21, and n_o/n_s with F -value of 0.93. According to Table 5, P -value and F -value for the proposed correlation are 0.0002 and 24.90, respectively, which indicate that the terms of the developed model are significant. Furthermore, P -values and F -values for the terms of the proposed correlation indicate that X_1 , X_2 , $X_2 X_3$, X_1^2 , X_2^2 , and X_3^2 are the most significant variables. The statistical parameters of the developed quadratic correlation are summarized in Table 6.

According to Table 6, the squared correlation coefficient (R^2) for the proposed model is 0.9697, which confirm that the correlation fits the experimental data with a high level of confidence. In other words, 96.97% of the total variation in the response is justified by the proposed quadratic correlation. The coefficient of variation (C.V.) describes the

Table 3
Corresponding predicted and actual response for the sulfur removal of the diesel

Run	R_t /min	$(n_a/n_s)/\text{mol} \cdot \text{mol}^{-1}$	$(n_o/n_s)/\text{mol} \cdot \text{mol}^{-1}$	Final sulfur concentration / $\text{mg} \cdot \text{kg}^{-1}$	S_r /%	Predicted S_r /%	Error /%
1	2	10	20	882	68.04	69.27	1.81
2	24	10	20	571	79.31	80.70	1.75
3	2	150	20	496	82.03	80.64	1.69
4	24	150	20	335	87.86	86.63	1.40
5	2	80	5	625	77.35	77.84	0.63
6	24	80	5	390	85.87	86.20	0.34
7	2	80	35	641	76.77	76.44	0.43
8	24	80	35	387	85.98	85.49	0.57
9	13	10	5	482	82.54	80.82	2.08
10	13	150	5	463	83.22	84.11	1.07
11	13	10	35	682	75.29	74.40	1.18
12	13	150	35	367	86.70	88.42	1.98
13	13	80	20	328	88.12	88.14	0.02
14	13	80	20	340	88.68	88.14	0.61
15	13	80	20	348	88.39	88.14	0.28
16	13	80	20	345	88.50	88.14	0.41
17	13	80	20	359	86.99	88.14	1.32

Table 4

The volume of the reactants and the associated volume flow rate in the experimental design

Run	Volume of gas oil /ml	Volume of formic acid /ml	Volume of oxidant /ml	Total volume/ml	Volume flow rate of gas oil/ ml·min ⁻¹	Volume flow rate of formic acid /ml·min ⁻¹	Volume flow rate of oxidant /ml·min ⁻¹	Volume ratio of the hydrocarbon to aqueous phases /ml·ml ⁻¹
1	107.20	3.50	14.40	125	53.58	1.72	7.20	6
2	107.20	3.50	14.40	125	4.46	0.14	0.60	6
3	77.30	37.30	10.40	125	38.67	18.64	5.20	1.62
4	77.30	37.30	10.40	125	3.22	1.55	0.43	1.62
5	96.80	24.90	3.30	125	48.42	12.45	1.63	3.44
6	96.80	24.90	3.30	125	4.04	1.04	0.14	3.44
7	83.80	21.50	19.70	125	41.88	10.77	9.85	2.03
8	83.80	21.50	19.70	125	3.49	0.90	0.82	2.03
9	117.30	3.80	3.90	125	9.02	0.29	0.30	15.21
10	82.50	39.80	2.80	125	6.34	3.06	0.21	1.94
11	98.60	3.20	23.20	125	7.59	0.24	1.78	3.74
12	72.80	35.10	17.10	125	5.60	2.70	1.32	1.39
13	89.80	23.10	12.10	125	6.91	1.78	0.93	2.55
14	89.80	23.10	12.10	125	6.91	1.78	0.93	2.55
15	89.80	23.10	12.10	125	6.91	1.78	0.93	2.55
16	89.80	23.10	12.10	125	6.91	1.78	0.93	2.55
17	89.80	23.10	12.10	125	6.91	1.78	0.93	2.55

Table 5

ANOVA results for the coefficients of the variables in the presented quadratic correlation

Coded parameters of correlation	Coefficient Estimate	Sum of squares	Degree of freedom	Mean square	F-value ^①	P-value ^② Prob > F	
Model		540.03	9	60.00	24.90	0.0002	Significant
X ₁	4.35	151.64	1	151.64	62.93	<0.0001	
X ₂	4.33	149.90	1	149.90	62.21	<0.0001	
X ₃	-0.53	2.25	1	2.25	0.93	0.3664	
X ₁ X ₂	-1.36	7.40	1	7.40	3.07	0.1232	
X ₁ X ₃	0.17	0.12	1	0.12	0.05	0.8305	
X ₂ X ₃	2.68	28.78	1	28.78	11.94	0.0106	
X ₁ ²	-4.64	90.48	1	90.48	37.55	0.0005	
X ₂ ²	-4.19	73.94	1	73.94	30.68	0.0009	
X ₃ ²	-2.01	16.98	1	16.98	7.05	0.0327	
Residual		16.87	7	2.41			
Lack of Fit		15.06	3	5.02	11.12	0.0507	Not significant

^① The mean square of the factor divided by the mean square of the residual.^② Significance probability.

standard deviation relative to the mean. The model accuracy is high if C.V. is lower than 1.87. Adequate precision of the proposed model is equal to 31.09, which indicates that the noise ratio of the model is placed in the acceptable range.

The residual is defined as the difference between the predicted and actual values. Fig. 2a represents the normal probability diagram of the residuals. As can be seen, the points are located almost on a straight line, which signifies that the residuals follow a normal distribution.

Fig. 2b shows the residuals versus the predicted response values. The points are randomly distributed between -4.82 and 4.82, and the number of the points above the horizontal line is equal to the number of the points under the line. This trend confirms the accuracy of the developed correlation.

Table 6

Statistical parameters of the response surface quadratic correlation

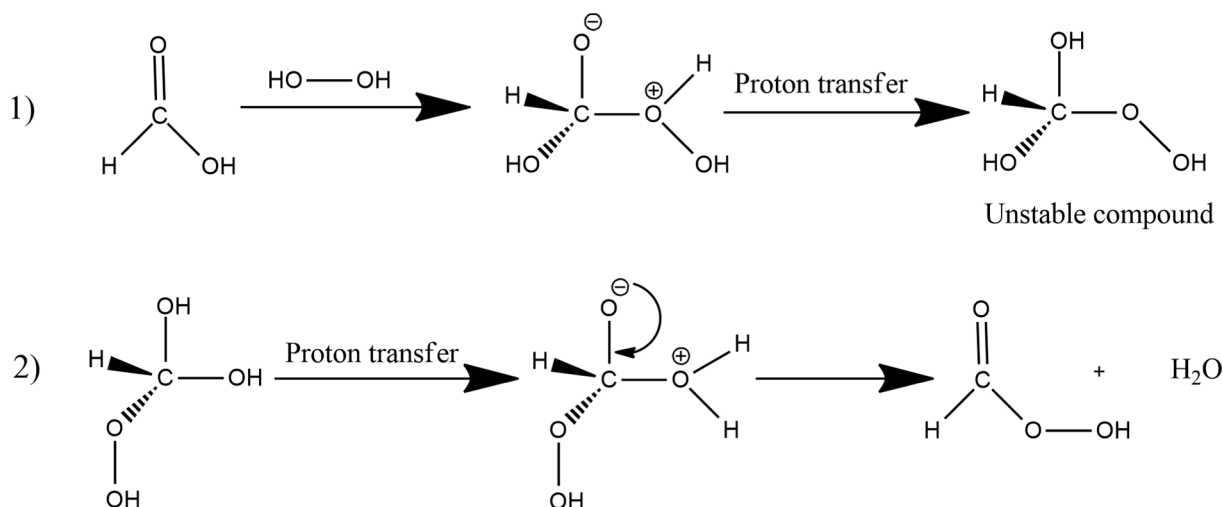
Std.Dev.	1.55	R-squared	0.9697
Coefficient of variation	1.87%	Adjusted R-squared	0.9408
Adequate precision	31.09	Predicted R-squared	0.9122

Fig. 2c displays the predicted versus experimental values of the sulfur removal. As can be observed, the predicted values are in good agreement with the experimental data.

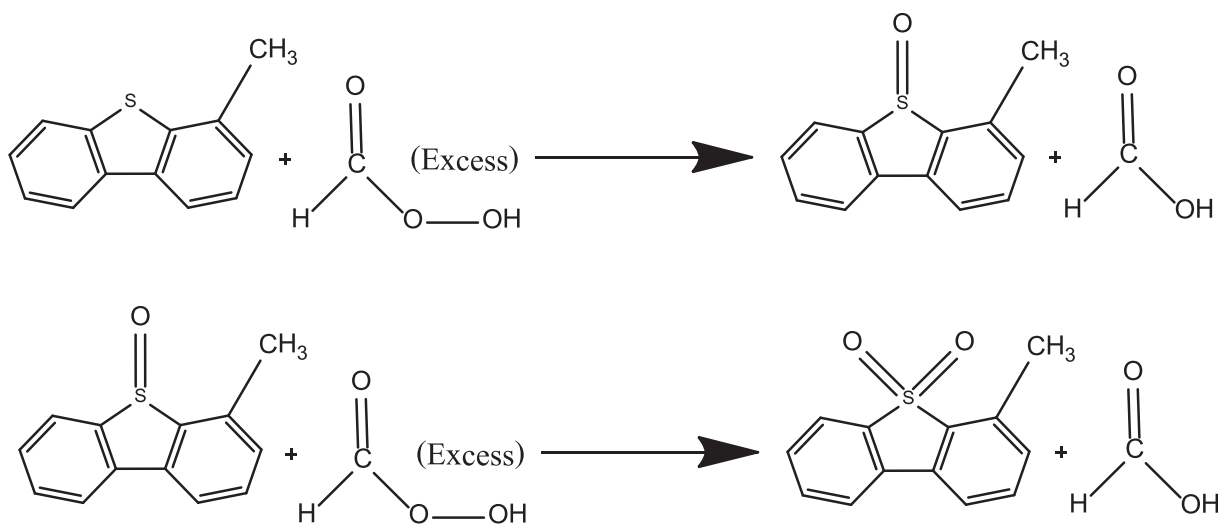
3.2. Oxidation mechanism

Using oxidation reaction, the sulfur-containing compounds are converted to the corresponding sulfoxides and sulfones with high polarity, which can be removed using an extraction or adsorption process. In the UAOD system, the ultrasound irradiation increases the interphase mass transfer rate and cavitation, which results in a better emulsification of the hydrocarbon and aqueous medium and higher overall oxidation rate [51]. In the UAOD process, formic acid and hydrogen peroxide react and produce peroxyformic acid, which is an important oxidation agent. The reaction mechanism for the formation of peroxyformic acid, oxidation of sulfur-containing compounds into corresponding sulfoxides and sulfones are expressed as follows [25,52]:

- 1- An unstable intermediate compound is produced by the reaction of the formic acid with the hydrogen peroxide, which is quickly decomposed into peroxyformic acid and water.



2-In the second step, the peroxyformic acid oxidizes the sulfur-containing compounds, such as 4-methyldibenzothiophene, into the corresponding sulfoxides and sulfones.



3.3. Interaction between different operating parameters

Fig. 3 shows the interaction between different operating parameters (R_t , n_a/n_s , and n_o/n_s) and S_r as the response variable. It should be noted that the interaction between two variables is studied by keeping the other variable constant at its optimal value.

Fig. 3a displays the interaction between n_a/n_s and n_o/n_s with S_r when R_t is fixed at 16 min. As it can be observed, for the low values of n_a/n_s , S_r increases slowly by increasing n_o/n_s from 5 to around 13. To explain this trend, it can be said that in the oxidation reaction, the required moles of the formic acid and oxidant to generate 1 mol of peroxyformic acid are equal to 1. Therefore, at the low values of n_a/n_s , the possibility of the peroxyformic acid formation and thus the S_r increases by increasing n_o/n_s until n_a/n_s is approximately equal to n_o/n_s . However, increasing n_o/n_s from 13 to 35 decreases S_r slightly. Since the hydrogen peroxide contains abundant amount of water, surplus amount of aqueous hydrogen peroxide solution dilutes the oxidation reaction media resulting in

lower peroxyformic acid concentration and lower S_r . Furthermore, this trend can be attributed to the production of hydroxyl radical scavenger, which prevents the generation of the desired reactive perhydroxyl radicals and leads to the activation of side reactions [1,3]. In the higher values of n_a/n_s , increasing n_o/n_s increases the formation of peroxyformic acid, which leads to higher S_r . It can be said that in the higher values of n_a/n_s , the surplus formic acid could extract the oxidized sulfur-containing compounds (sulfoxides and the sulfones). In addition, the high values of n_a/n_s increase the acidity of the medium, which could enhance the oxidation reaction efficiency [53].

At the lower values of n_o/n_s , S_r increases by increasing n_a/n_s from 10 to 110 due to increasing the generation of the peroxyformic acid. However, increasing n_a/n_s from 110 to 130 reduces S_r slightly. This behavior can be attributed to increasing the stability of the peroxyformic acid which limits its decomposition to the active oxidizing radicals, which leads to lower conversion of sulfur-containing compounds to the corresponding sulfoxides and sulfones [54]. At the high values of n_o/n_s , S_r

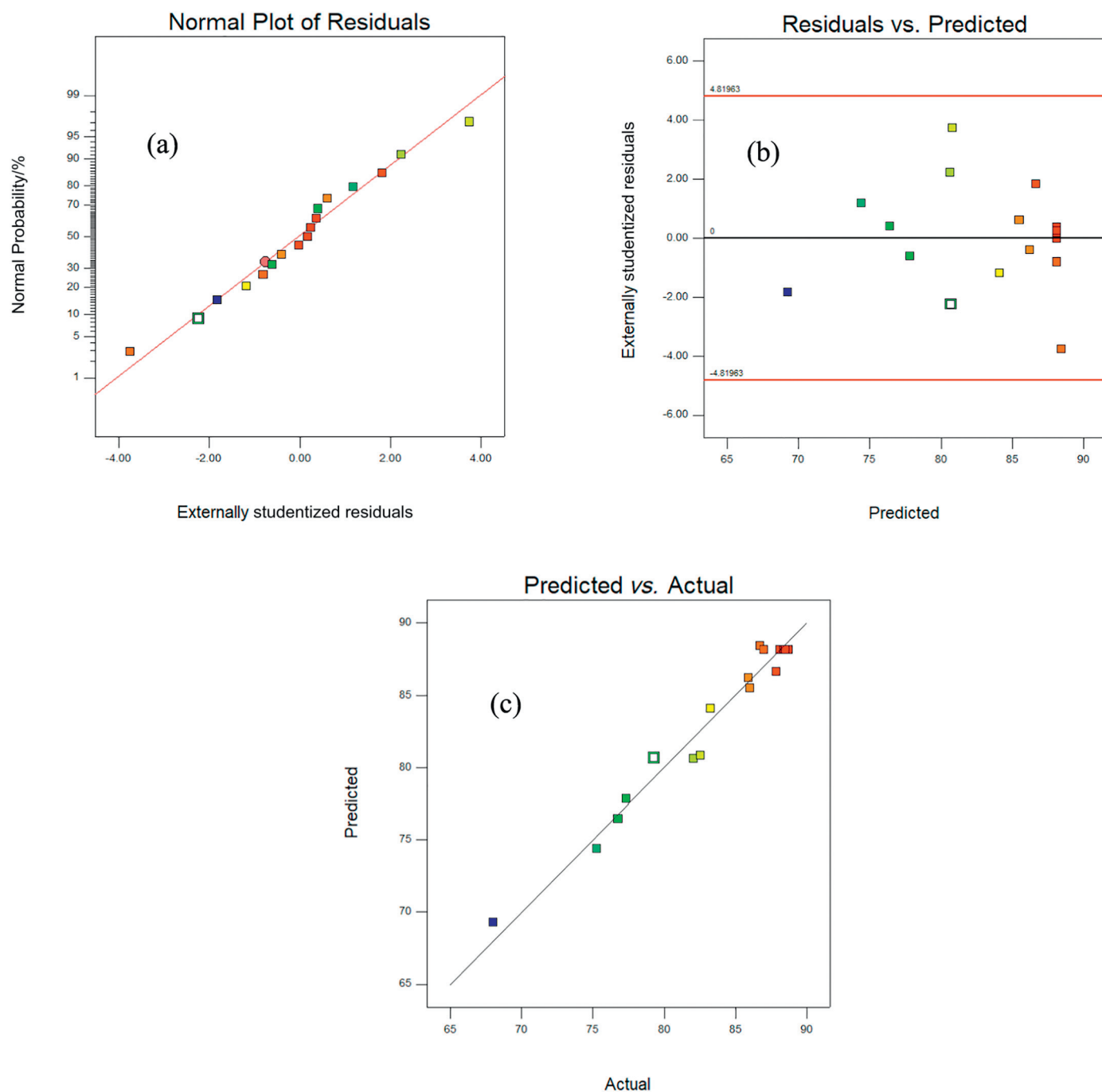


Fig. 2. Evaluation of the proposed correlation by RSM for sulfur removal of diesel; (a) normal distribution of the residuals; (b) residuals vs predicted responses; (c) predicted vs actual values.

increases and reaches a steady state condition by increasing n_a/n_s . According to the reversible reaction of the peroxyformic acid generation, the slight variation of S_r at the high values of n_o/n_s and n_a/n_s can be attributed to reaching the equilibrium concentrations of hydrogen peroxide, formic acid, and peroxyformic acid in the oxidation reaction.

Fig. 3b shows the interactions between n_o/n_s and R_t with S_r . As it can be seen, at any value of n_o/n_s , S_r initially increases and then slightly decreases by increasing R_t . Increasing R_t causes the components react sufficiently. In addition, increasing R_t leads to more cavitation that creates more fine emulsions in the reaction medium resulting in the higher conversion of the sulfur-containing compounds that leads to more S_r . Fig. 3b shows the slope of S_r surface is negative when R_t is longer than 20 min due to the possibility of the oxidant decomposition [4].

Fig. 3c illustrates the interactions between n_a/n_s and R_t with S_r . It is observed that, at any value of n_a/n_s , increasing R_t leads to an increase in S_r up to a maximum point and then decreases it slightly. Reduction of S_r at high residence time is related to the decomposition of the oxidant.

3.4. The choice of appropriate conditions for the oxidation of diesel

As can be observed in Fig. 3, there is no unique maximum value for the sulfur removal, however, its value is appropriate in a vast spectrum of the operating conditions (Table 7).

According to the Table 7, the predicted S_r is about 88% for the all conditions. Therefore, it is reasonable to consider the operating cost of

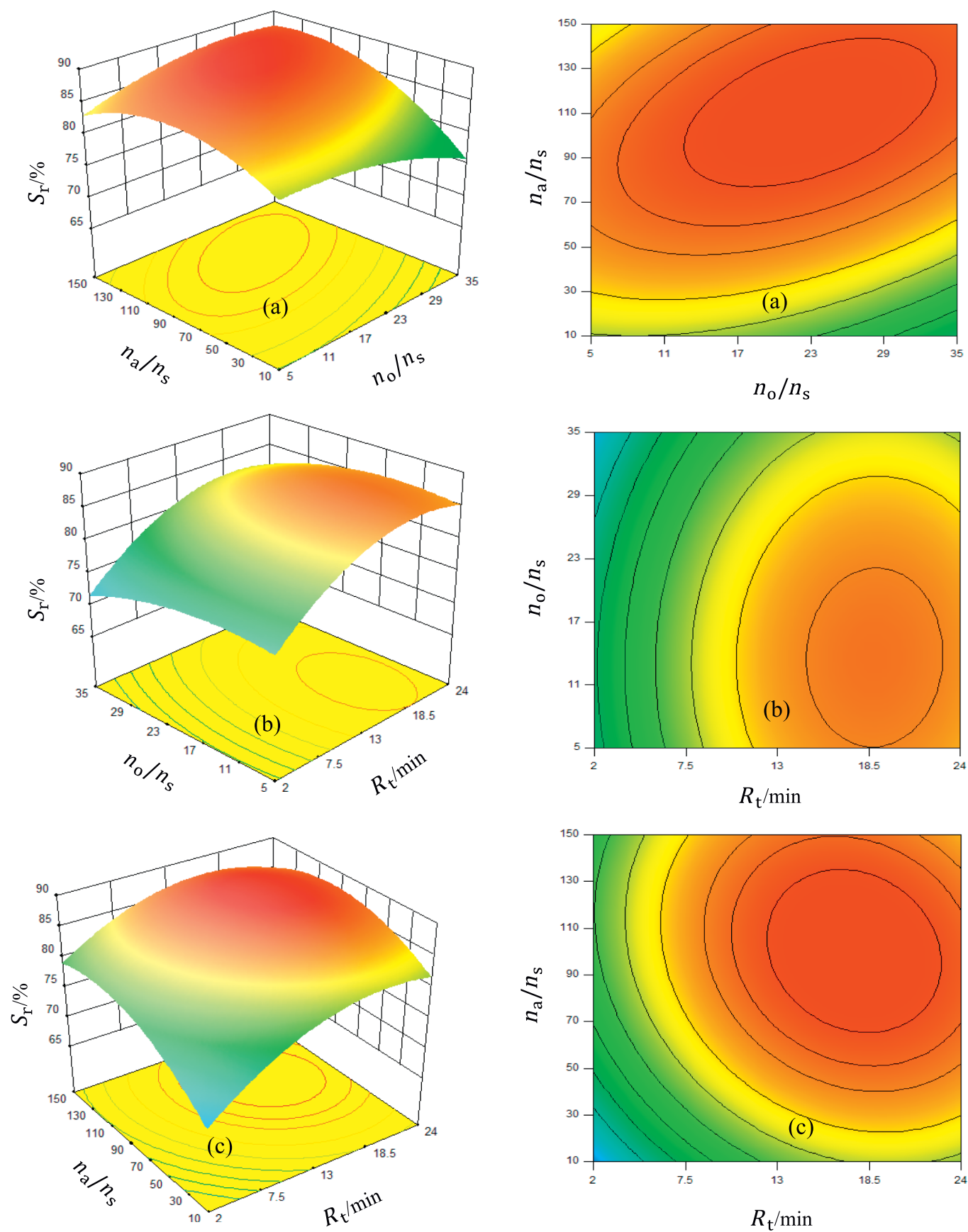


Fig. 3. Response surface plots of S_T (%) as a function of; (a) n_a/n_s and n_o/n_s , (b) n_o/n_s and R_t (min), and (c) n_a/n_s and R_t (min) and contour plots corresponding to the response surface plots (other oxidation conditions: $T = 50\text{ }^\circ\text{C}$, and ultrasound power = 360 W) (extraction conditions: ambient temperature; solvent: dimethylformamide with the volume ratio of solvent to fuel = 1; no. of extraction stages = 1, mixing time = 30 min).

Table 7The values of the independent variables and the predicted S_r by RSM for the selected items with higher S_r .

Num	R_t /min	n_s/n_s /mol·mol ⁻¹	n_o/n_s /mol·mol ⁻¹	Gas oil volume /ml	Formic acid volume /ml	Oxidant volume /ml	Predicted S_r /%
1	13	80	20	89.83	23.09	12.08	88.14
2	14.85	65.92	12.66	96.39	20.42	8.20	87.77
3	20.57	63.43	5.77	100.59	20.50	3.90	87.08
4	19.78	62	19.90	93.78	18.68	12.54	87.89
5	16	54.47	8.24	101.59	17.78	5.63	86.90
6	10.90	81.26	17.26	90.77	23.70	10.53	87.24
7	21.02	86.55	8.74	93.50	26	5.49	88.11
8	23.87	79.35	18.17	90.77	23.14	11.08	87.90
9	21.85	77.75	32.80	85.02	21.24	18.74	86.66
10	17.02	94.23	9.49	91.47	27.69	5.84	88.67
11	14.38	87.87	29.38	84.47	23.85	16.68	88.11
12	13.04	74.76	16.33	92.59	22.24	10.17	87.86
13	15.04	73.58	26.07	88.55	20.93	15.52	87.74
14	13.70	75.44	20.52	90.57	21.95	12.49	88.07

oxidation stage as a criterion for selecting the best condition between 14 situations listed in Table 7. The operating costs during the continuous-flow oxidation stage essentially consist of the consumed chemical cost (formic acid 85 wt% and hydrogen peroxide 35 wt%) and the cost of electricity, associated with the ultrasound irradiation.

The costs in the continuous-flow UAOD cost model are shown in Table 8.

The operating cost of the continuous-flow UAOD system per liter of the oxidized diesel is calculated as follows:

$$C_t = C_m + C_l \quad (5)$$

Where:

$$C_m = 0.05 \times C_a + C_o = (4.697 \times V_a + 73.348 \times V_o)/V_d \quad (6)$$

Table 8

The unit costs of the chemicals and electrical energy

Operating cost data	Operating cost
Electrical energy	0.12 USD·(kW·h) ⁻¹
Formic acid 85 wt%	0.70 USD·kg ⁻¹
Hydrogen peroxide 35 wt%	0.60 USD·kg ⁻¹

Table 9

The costs of the chemical consumption and electrical energy consumption

No.	Cost of formic acid consumption /cent	Cost of oxidant consumption /cent	Cost of electrical energy consumption /cent	Operating cost /cent
1	1.21	9.86	2.61	13.67
2	0.99	6.24	2.77	10.01
3	0.96	2.84	3.68	7.48
4	0.94	9.81	3.80	14.54
5	0.82	4.06	2.85	7.73
6	1.23	8.51	2.16	11.90
7	1.31	4.31	4.05	9.66
8	1.20	8.96	4.73	14.89
9	1.17	16.17	4.63	21.97
10	1.42	4.68	3.35	9.45
11	1.33	14.49	3.07	18.88
12	1.13	8.05	2.54	11.72
13	1.11	12.85	3.06	17.02
14	1.14	10.12	2.72	13.98

$$C_l = 18 \times R_t/V_d \quad (7)$$

where C_m is the cost of the chemical consumption and C_l is the cost of electrical energy consumption related to the ultrasound irradiation. In addition, C_a and C_o are the costs of formic acid 85 wt% and hydrogen peroxide 35 wt%, respectively. According to our preliminary evaluation, 95% of the formic acid in the oxidation reaction is recoverable, although hydrogen peroxide cannot be recovered due to thermal decomposition. Therefore, 5% makeup for formic acid is considered at this stage for the cost analysis. In addition, V_a , V_o , and V_d are the volumes of formic acid 85 wt%, hydrogen peroxide 35 wt%, and diesel, respectively.

As can be observed, increasing R_t increases the cost of electrical energy consumption by ultrasound irradiation.

The costs of chemical consumption in the oxidation stage and electrical energy consumption related to the ultrasound irradiation per liter of oxidized diesel were given in Table 9. As can be seen, the main part of the operating costs during the continuous-flow oxidation process is the cost of hydrogen peroxide.

According to Tables 7 and 9, the highlighted items had less hydrogen peroxide consumption and operating cost, as a result were selected as appropriate conditions for further oxidation testing.

Continuous-flow oxidation experiments were performed to ensure the accuracy of S_r of the highlighted items under the appropriate

operating conditions proposed by RSM (Table 7). Table 10 represents the sulfur removal of diesel for the highlighted items. The obtained values reveal that the proposed model obtained by RSM can fit the experimental data well.

Table 10Flow rate of oxidized diesel and S_r for the highlighted items

Num	Flow rate of oxidized diesel/ ml·min ⁻¹	S_r /%
2	6.49	83.91
3	4.89	83.80
5	6.32	86.52
6	8.33	85.18
7	4.45	84.89
10	5.37	85.15
12	7.10	86.09

As can be seen in Tables 9 and 10, experiment No. 5 has resulted in the lowest operating cost, while the S_r and flow rate of the oxidized diesel are high. In addition, for this experiment, the difference between actual and predicted S_r was at the lowest level. Therefore, the condition of experiment No. 5 was selected as the best condition.

As mentioned, to reduce the operating costs during the continuous-flow oxidation process, it was necessary to use the lowest amount of the chemical. To investigate the reduction of chemical consumption, the ratio of formic acid to oxidizing agent was kept constant while the ratio of the hydrocarbon phase to the aqueous phase (formic acid 85 wt% and hydrogen peroxide 35 wt%) was changed. Therefore, the values of 4.34, 6, 7, 8 and 10 were selected for the volume ratio of the hydrocarbon phase to the aqueous phase and the volume ratio of the formic acid to hydrogen peroxide was equal to the optimum value of 3.16, where R_t was 16 min. Table 11 shows the reactants volume, operating cost of oxidation stage, flow rate of the oxidized diesel, and S_r using different volume ratios of the hydrocarbon to aqueous phases.

Table 11Reactants volume, operating cost of oxidation stage, flow rate of oxidized diesel, and S_r using different volume ratios of the hydrocarbon to aqueous phases

Volume ratio of the hydrocarbon to aqueous phases	Diesel volume/ ml	Formic acid volume/ ml	Oxidant volume/ ml	Operating cost /cent	Flow rate of oxidized diesel/ ml·min ⁻¹	S_r /%
4.34	101.59	17.78	5.63	7.73	6.32	86.52
6	107.14	13.57	4.29	6.23	6.67	85.04
7	109.38	11.87	3.76	5.67	6.81	83.51
8	111.11	10.55	3.34	5.25	6.92	82.94
10	113.64	8.63	2.73	4.66	7.07	84.38

According to the oxidation reactions of sulfur-containing compounds, the stoichiometric ratio of hydrogen peroxide to sulfur in the oxidation reaction is equal to 2. In the oxidation reaction, the interphase mass transfer limits the overall rate of reactions. Therefore, it is necessary to use the hydrogen peroxide slightly more than the stoichiometric ratio in the reaction medium due to mass transfer limitations and the probability of thermal decomposition of hydrogen peroxide to water and oxygen and peroxyformic acid to water and carbon dioxide [1,11]. If the amount of hydrogen peroxide is much more than the stoichiometric ratio, the excess amount of hydrogen peroxide may be converted to water and oxygen due to thermal decomposition of hydrogen peroxide. Furthermore, as noted above, hydrogen peroxide 35 wt% contains abundant amount of water, and adding the excess hydrogen peroxide 35 wt% to the reaction medium may lead to reduction of the peroxyformic acid concentration, which results in low S_r and high operating cost of the UAOD system. According to Table 11, it can be seen that as the volume

ratio of the hydrocarbon to aqueous phases increases, S_r decreases slightly. In addition, increasing the ratio reduces the operating cost and the oxidant consumption and increases the flow rate of oxidized diesel. Therefore, the volume ratio of the hydrocarbon to the aqueous phase is considered to be equal to 10 (Table 12).

Table 12

Operating conditions for the volume ratio of the hydrocarbon to the aqueous phases of 10

R_t /min	16	Flow rate of diesel /ml·min ⁻¹	7.07
(n_a/n_s) /mol·mol ⁻¹	23.64	Flow rate of formic acid /ml·min ⁻¹	0.54
(n_o/n_s) /mol·mol ⁻¹	3.58	Flow rate of oxidant /ml·min ⁻¹	0.17

Fig. 4 shows the sulfur removal achieved in different processes including the continuous-flow UAOD, direct extraction, continuous-flow UAOD followed by liquid/liquid extraction, and continuous-flow simple mixing oxidation followed by liquid/liquid extraction. The extraction conditions were the same for all above-mentioned processes.

As can be observed in Fig. 4, the sulfur removal in the continuous-flow oxidation process is 22.46%, which is the least value comparing different processes. The continuous-flow oxidation process converts the sulfur-containing compounds into the corresponding sulfoxides and sulfones. The removal of oxidized sulfur-containing compounds in this process is due to partial *in situ* extraction of produced sulfoxides and sulfones into the aqueous phase (*i.e.*, formic acid, water, and hydrogen peroxide) during the oxidation reaction. In addition, 41.30% sulfur removal is achieved using direct extraction. The low sulfur removal in the direct extraction process is due to the fact that the polarity of sulfur-containing compounds in the diesel is low. As a result, the direct extraction process using a polar solvent cannot remove these compounds, effectively. The highest sulfur removal is achieved in the continuous flow UAOD process followed by liquid/liquid extraction. It should be mentioned that the majority of the sulfur-containing compounds in diesel are benzothiophene (BTs), dibenzothiophene (DBTs), and their alkylated derivatives [50,55]. In addition, different studies have reported these compounds can be easily oxidized and converted into the corresponding sulfoxides and sulfones [25,56].

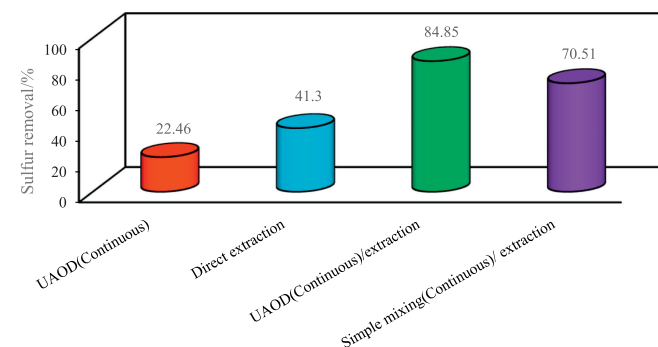


Fig. 4. Comparison of sulfur removal by continuous-flow UAOD, direct extraction, continuous-flow UAOD followed by liquid/liquid extraction, and continuous-flow simple mixing oxidation followed by liquid/liquid extraction processes.

Table 13

Specifications of treated diesel fuel

Characteristic	Content	Test method
Density at 15 °C /kg·m ⁻³	835	ASTM D4052
Kinematic viscosity at 40 °C×10 ⁶ /m ² ·s ⁻¹	4.37	ASTM D445
Flash point /°C	77	ASTM D93
Water content /mg·kg ⁻¹	41	ASTM D6304
Cetane index	56.48	ASTM D4737

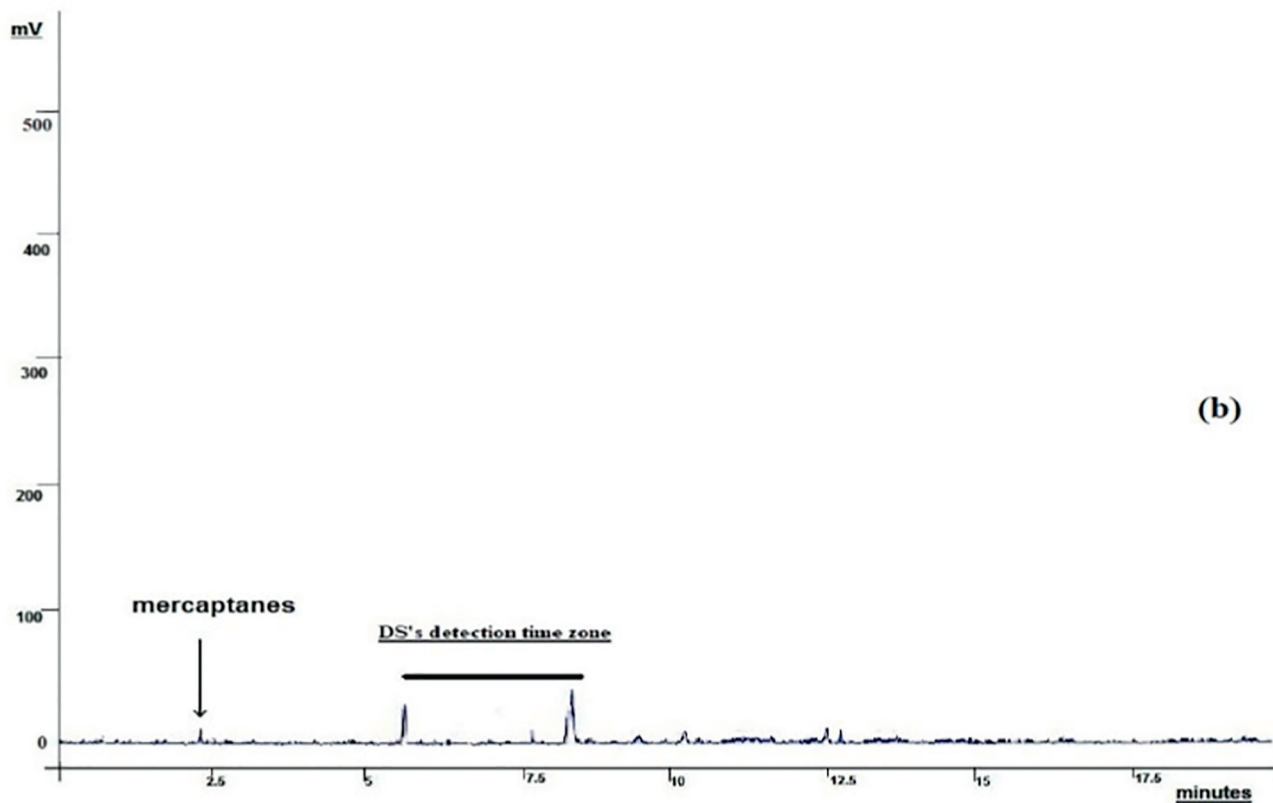
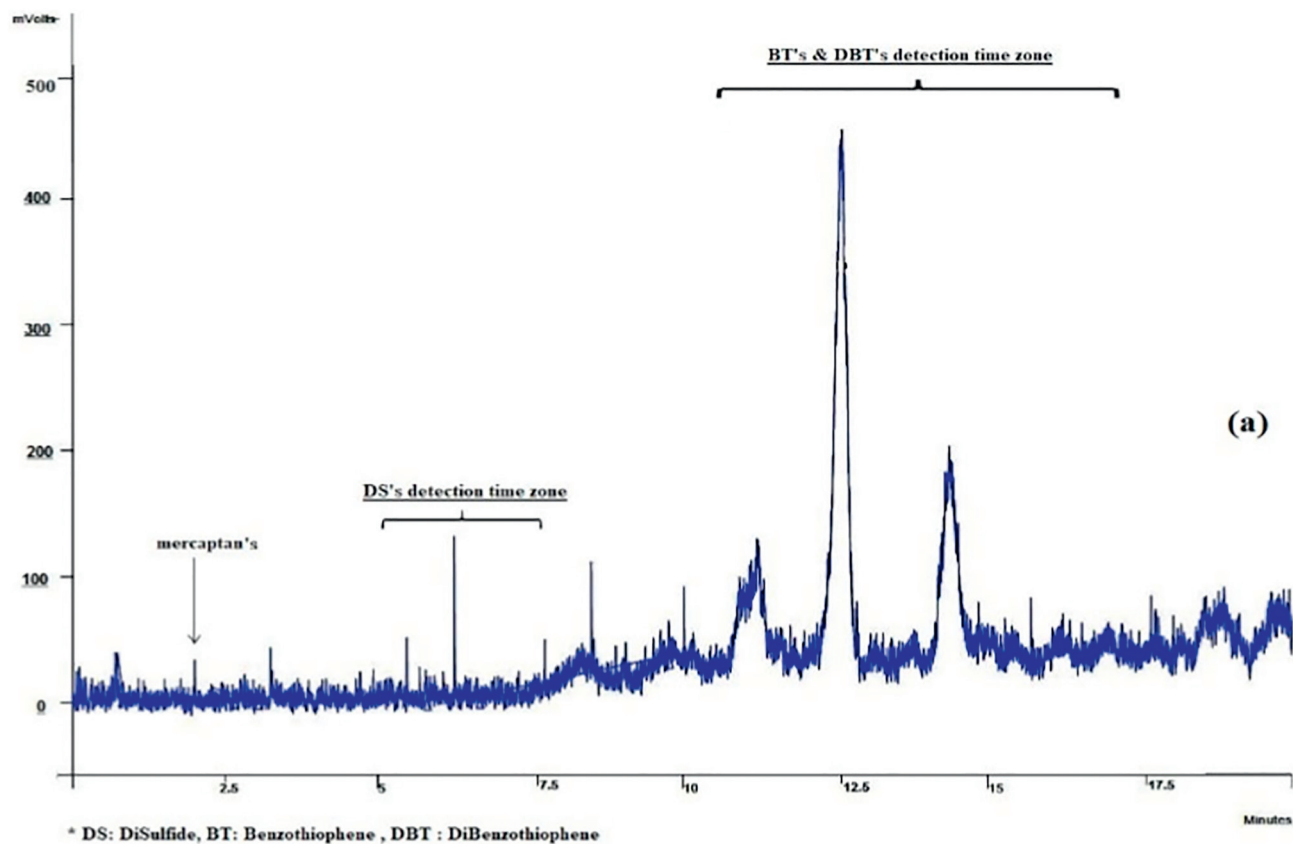


Fig. 5. GC-SCD chromatograms of untreated and treated diesel samples (a: Untreated diesel, b: treated diesel after oxidation, followed by liquid–liquid extraction) (Oxidation conditions: Reactor residence time = 16 min, n_a/n_s ($\text{mol} \cdot \text{mol}^{-1}$) = 23.64, n_o/n_s ($\text{mol} \cdot \text{mol}^{-1}$) = 3.58, Temperature = 50 °C, ultrasound power = 360 W Extraction conditions: No. of extraction stage = 1, DMF to diesel ratio = 1, mixing time = 30 min, ambient temperature).

In addition to ultrasound irradiation, continuous-flow simple mixing system was applied to oxidize sulfur-containing compounds. The oxidation reaction in this system was also performed in the same conditions as the continuous-flow UAOD process. The chemicals (*i.e.*, diesel and a mixture of formic acid 85 wt% and hydrogen peroxide 35 wt%) were continually introduced into the reactor. The mixture was stirred with 875 rpm stirring rate to oxidize sulfur-containing compounds. In this process, the sulfur removal was obtained 70.51%. This value indicates that in the same conditions, continuous-flow oxidation reaction using ultrasound irradiation leads to more sulfur removal as compared to simple mixing. This can be attributed to the creation of micro-emulsion during bubble-collapse under the ultrasound irradiation.

3.5. Effect of UAOD process on treated diesel fuel properties

Table 13 illustrates properties of the treated diesel fuel with UAOD process followed by liquid–liquid extraction. Comparison of density, kinematic viscosity, flash point, water content, and cetane index in Table 1 for untreated diesel and Table 13 for treated diesel indicate that UAOD treatment do not change the diesel specifications, adversely.

Fig. 5 shows the GC-SCD chromatograms of the untreated diesel and treated diesel using UAOD followed by extraction with DMF.

Fig. 5a shows the analysis of the untreated diesel sample with total sulfur content of 2760 mg·kg⁻¹. As can be seen, the main sulfur-containing compounds in the diesel are benzothiophene (BTs), dibenzothiophene (DBTs), and their alkylated derivatives [50,55]. As it is shown in Fig. 5b, the peaks of sulfur-containing compounds are diminished in the treated diesel. In other word, it can be concluded that the present UAOD system is an efficient process for the removal of different sulfur-containing compounds (especially thiophenic compounds) from diesel.

Rahimi *et al.* [1] studied the desulfurization of a diesel fuel with total sulfur content of 1550 mg·kg⁻¹ using a chemical system including formic acid and hydrogen peroxide 35 wt% in a double-stage continuous-flow UAOD system. They concluded that the appropriate amount of n_a/n_s and n_o/n_s were 69.53 and 23, respectively, which resulted in 79.87% sulfur removal. In the present work, as shown in Tables 11 and 12, 84.38% sulfur removal was achieved where n_a/n_s and n_o/n_s were 23.64 and 3.58, respectively. Therefore, in this study, higher sulfur removal is achieved using significantly lower chemical consumption as compared to the results reported by Rahimi *et al.* [1].

4. Conclusions

In this study, a continuous-flow ultrasound-assisted oxidative desulfurization (UAOD) followed by liquid–liquid extraction process was applied for removal of the sulfur-containing compounds of diesel. The chemical system including formic acid 85 wt% and hydrogen peroxide 35 wt%, as the catalyst and oxidant, respectively, was used to oxidize the sulfur-containing compounds. DMF was applied as the extraction solvent to remove the sulfur-containing compounds. An experimental design using response surface methodology based on Box–Behnken design was implemented to investigate the effects of the independent parameters (residence time, formic acid to sulfur molar ratio, and oxidant to sulfur molar ratio) on the sulfur removal in the continuous-flow UAOD process. In addition, an evaluation of the operating cost of oxidation stage was made to select the best experimental conditions. The results indicated that the appropriate value for the sulfur removal was 86.52%, in which the independent oxidation parameters were as follows: residence time of 16 min, formic acid to sulfur molar ratio of 54.48, and oxidant to sulfur molar ratio of 8.23.

Moreover a series of experiments were carried out in different ratios of hydrocarbon phase to aqueous phase in order to reduce the chemical consumption in the oxidation stage. Sulfur removal of 84.38% was achieved where formic acid to sulfur and the oxidant to sulfur molar ratios were equal to 23.64 and 3.58, respectively. These values are

significantly lower comparing the corresponding values reported in the literature for the same oxidation system.

Nomenclature

C_a	Cost of purchasing the formic acid 85 wt%, cent
C_i	Cost of electrical energy consumption related to ultrasound irradiation, cent
C_m	Cost of the chemical consumption, cent
C_o	Costs of purchasing the hydrogen peroxide 35 wt%, cent
C_t	Operating cost of the continuous-flow UAOD system per liter of oxidized diesel, cent
C.V.	Coefficient of variation
n_a/n_s	Formic acid to sulfur molar ratio, mol·mol ⁻¹
n_o/n_s	Oxidant to sulfur molar ratio, mol·mol ⁻¹
R^2	Squared correlation coefficient
R^2_{adj}	Adjusted squared correlation coefficient
R_t	Residence time, min
S_f	Total sulfur content of the treated fuel, mg·kg ⁻¹
S_i	Total sulfur content of the feedstock, mg·kg ⁻¹
S_r	Sulfur removal, %
T	Oxidation temperature, °C
t	Sonication time, min
V_a	Volume of formic acid 85 wt%, ml
V_d	Volume of diesel, ml
V_o	Volume of hydrogen peroxide 35 wt%, ml
β_i	Linear regression coefficients
β_{ii}	Quadratic regression coefficients
β_{ij}	Interaction coefficients
β_o	Intercept coefficient (offset)
ε	Error

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