

## Diesel Oil Upgradation by Ultrasound Irradiation: A Study on the Effects of Main Operational Parameters

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The main objective of this work is to upgrade a diesel oil sample from Shiraz Oil Refining Co. (SORC) to reduce the sulfur content, as well as to break the kinematic viscosity of the feedstock. Effects of several operating parameters including volume of hydrogen peroxide/acetic acid as an oxidant mixture, amounts of tetraoctylammonium bromide as a phase transfer agent (PTA) and phosphotungstic acid as a transition metal catalyst (TMC) and time were first screened using two-level factorial design and then optimized with the Box-Behnken scheme. It was shown that the kinematic viscosity cannot be substantially reduced due to the low power generated by the ultrasonicator. In addition, irradiation time has the least effect on desulfurization efficiency of the oil among the parameters studied in this work. Moreover, results showed that at optimal conditions of 13.17 ml hydrogen peroxide, 17.26 ml acetic acid, 0.15 g PTA and 1.5 g catalyst, a sulfur removal of 60.75% is attained which in turn could be increased to more than 68% by using a single-stage extraction step in the wake of the main ultrasound-assisted oxidative desulfurization (UAOD) process.

**Keywords:** Ultrasound-assisted oxidative desulfurization, Viscosity reduction, Two-level factorial, Box-Behnken, Diesel oil

### INTRODUCTION

During the recent few decades, a huge deal of attempt has been made to make human kind less dependent to fossil fuels by replacing them with new sources such as solar energy; however, the entire global system is still significantly based on the traditional sources of energy. This has turned crude into the most political commodity worldwide. Naturally, there is constantly an enthusiastic attention towards improving technologies in crude oil refining.

Organic sulfur compounds (OSCs) are inseparable characteristics of crude and its derivatives especially transportation fuels such as gasoline and diesel which are the most popular [1]. During crude oil refining, a multitude of these compounds such as benzothiophene (BT) and dibenzothiophene (DBT) still remain intact in the final products [2]. When combusted, OSCs are converted into

sulfur oxides ( $\text{SO}_x$ ) and sulfate particulate matter (PM) which in turn are responsible for air pollution and acid rains [2-4].

On the other hand, over the years, environmental regulations have become stricter to defeat global warming. For instance, European Union has set a maximum sulfur content of 10 ppmw for diesel fuels standard as of 2010 [5]. Hydrosulfurization (HDS) is traditionally a well-known industrial process for deep desulfurization in which hydrogen gas reacts with sulfur content of the fuel in the presence of expensive metallic catalysts to produce  $\text{H}_2\text{S}$ . This, of course, needs high temperature (300-400 °C) and high pressure (20-100 atm) as well as large reactors with long reactional time, resulting in high operational costs [6,7]. Besides, it has been established that HDS fails to remove refractory aromatic sulfur components such as thiophene, BT and DBT because of their low reactivity [7,8].

New alternative techniques are, therefore, emerging to remove these stubborn components; however, they are yet

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far from being commercialized in large scale. One promising method is oxidative desulfurization (ODS) process which is basically carried out under mild conditions without any need to hydrogen gas [9,10].

Technically, ODS is a two-stage process: oxidation of OSCs to sulfones and sulphoxides followed by liquid-liquid (L-L) extraction or alternatively solid adsorption stage to remove the oxidized sulfur-containing compounds [11-12]. Common solvents for the L-L extraction are polar non-miscible acetonitrile and methanol, whereas activated alumina and activated carbon are frequently used for adsorption.

It is well known that irradiation of ultrasound waves to homogenous and heterogeneous systems practically improves the chemical reaction and mass transfer rates in the interfacial regions [13]. These are sound like waves with frequencies above 20 kHz which are generally above the normal hearing range for humans. Ultrasonic waves can be generated from electrical, electromagnetic, mechanical or thermal energy sources [14].

The effect of ultrasonication involves formation, growth and implosive collapse of bubbles in liquids caused by cavitation. This produces local hot spots with effective temperature of *ca.* 5000 K, pressure of *ca.* 1000 atm, and heating and cooling rates above  $10^{10} \text{ K s}^{-1}$  while maintaining the stability and chemical characteristics of the working fluid. The extraordinary physical and chemical conditions can be begot in otherwise cold liquids which are favorable to produce active intermediates such as alkyl radicals and hydrogen radicals allowing the reaction to proceed instantaneously. For a liquid-liquid heterogeneous reaction system such as oxidative desulfurization of diesel, ultrasound helps improve the interfacial area through emulsification. Intense microturbulence created by the cavitation bubbles disrupts the aqueous/organic interface and creates very fine emulsions between phases. This improves the interfacial area available for reaction, increases the effective local concentration of reactive species, and enhances the mass transfer in the interfacial region which leads to a remarkable increase in oxidative desulfurization reaction rate [2,8,9,15-18].

Akbari *et al.* [10] applied the Central Composite Design scheme of RSM (response surface method) to optimize the process parameters in an ultrasound-assisted system with

solid  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalyst for oxidative desulfurization of model diesel fuel. They came to a conclusion that ultrasound improves the activity of the catalyst by modification of its textural properties, reducing the catalyst particles as a result of fragmentation phenomena along with providing a good dispersion of catalyst particles and oxidant. It was also noted that ultrasound irradiation helps removal of impurities from catalyst surface.

Choi *et al.* [3] studied the effects of different factors such as ferrate catalyst concentration on sulfur reduction of model BT and DBT sulfurs in a UAOD system in order to optimize the operating parameters supposed to be utilized in a real-life process.

Duarte *et al.* [9] optimized a number of UAOD process variables in sulfur reduction of both model S compounds and diesel oil. They also investigated the reuse of reagents in the process and compared the outcomes with those of a process without ultrasound, proving the significant role of ultrasonication in improving the efficiency of oxidative desulfurization.

Flores *et al.* [19] investigated the effects of hydrogen peroxide concentration along with the reagent volumetric ratio and catalyst type on the UAOD of heavy fuel oil.

Gopinath *et al.* [20] assessed the effect of ultrasound waves on properties of heavy gas oil. In their experiments wherein no additive was used, they were able to reach 11% and 7% removal in nitrogen and sulfur heteroatoms, respectively. They also managed to break the feedstock viscosity as high as 5%. In addition, a mechanism for radical reactions, initiated during ultrasound treatment, was presented.

Mei *et al.* [18] evaluated the efficiency of the UAOD method on sulfur removal from both DBT model sulfur and diesel oil which could gain as high as 99% at ambient conditions. They also came up with a mechanism wherein the combined effect of catalyst, phase transfer agent and ultrasonication was modeled.

Chen *et al.* [21] performed the UAOD process with diesel and pyrolysis oil recovered from waste tires. They optimized the effects of various operating parameters including the amount of transitional metal catalyst and sonication time, and compared the sulfur removal efficiency of a solvent extraction versus a solid adsorption process following the main oxidation desulfurization treatment,

concluding that the latter exhibits higher efficiency on the oxidized oil.

Gunnerman [22] suggested a method in which ultrasound waves in the frequency and intensity range of preferably 1-100 MHz and 50-100 watts/cm<sup>2</sup>, respectively, were irradiated to an emulsion of fuel oil and aqueous solution like water with appropriate amounts of additives such as transition metal catalyst and phase transfer agent. The boiling point distribution of the treated oil when recovered was shifted 13.9-16.6 °C downward in comparison to the starting material.

In this work, the effects of a number of operating parameters in a process which aimed to simultaneously remove the sulfur content and to reduce the kinematic viscosity of a diesel oil sample from a local refinery (SORC) are elucidated. This is performed using a Design Expert v.7.0.0 software to, at first, plan and, then, analyze the results of the experiments in a process in which a combination of hydrogen peroxide and acetic acid is used as an oxidant mixture, tetraoctylammonium bromide as a phase transfer agent and phosphotungstic acid as a metal catalyst. This is followed by an attempt to obtain the optimum value for each process variable. Under the optimized conditions, the effect of a complementary liquid-liquid extraction step using caustic soda as a solvent is also investigated.

## EXPERIMENTAL

### Reagents and Materials

The feedstock under study was diesel oil with sulfur content of 5044 ppmw donated by Shiraz Oil Refining Company that its specifications are summarized in Table 1. The oxidizing reagent was chosen as a combination of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30% vol.) and glacial acetic acid (CH<sub>3</sub>COOH, 1.05 kg l<sup>-1</sup>) which were both purchased from Merck Chemicals (Darmstadt-Germany). In order to promote the kinetic of the oxidative desulfurization reaction, tetraoctylammonium bromide (TOAB, (C<sub>8</sub>H<sub>17</sub>)<sub>4</sub>N<sup>+</sup>Br<sup>-</sup>) as a phase transfer agent and phosphotungstic acid (H<sub>3</sub>[P(W<sub>3</sub>O<sub>10</sub>)<sub>4</sub>]<sup>\*</sup>xH<sub>2</sub>O) as a transition metal catalyst were also provided by Merck Chemicals (Darmstadt-Germany) and employed in the experiments. Ultra-pure water (Pars Chemical, Tehran-Iran) was used for cleaning the ultrasonic probe, reactor and the separation funnel. All chemicals were

of analytical grade and used without further purification. For the extraction step, 20 °Bé (166.7 g l<sup>-1</sup>) caustic soda (NaOH) prepared from pure soda (Pars Chemical, Tehran-Iran) was used as a solvent.

### Instruments

UAOD experiments were carried out using a Q-700 ultrasonic processor with 20 kHz output frequency and 700 W maximum power (Qsonica LLC, Newtown-USA). The sonicator was equipped with a titanium probe tip (12.7 mm in diameter and 254 mm in length) directly immersed into the liquid mixture. A 150 ml three-neck glass reactor was used for all experiments, whereas a 250-ml glass separation funnel was employed in the L-L extraction step. The sulfur concentration in the organic phase was determined by an X-ray sulfur meter (Model RX-360SH, Tanaka Scientific LTD, Tokyo-Japan) using energy dispersion fluorescence (EDXRF) method prescribed in ASTM D-4294-03 standard. Kinematic viscosity measurements were also made using a visco bath (Model ME-18V, Julabo GmbH, Seelbach-Germany).

### Methodology

In each test, firstly, an appropriate volume of diesel oil containing pre-determined amount of PTA and TMC was added to the glass reactor. Next, the specified volumes of hydrogen peroxide and acetic acid were added to the oil phase so that the total working volume of the mixture was kept at 100 ml. Here, the organic acid acts as an oxidation-promoter agent [23]. The mixture was then irradiated by ultrasound waves set at 40% amplitude for a certain period of time. The probe tip was immersed 20 mm below the liquid level inside the reactor. The temperature of the mixture was maintained at constant value of 50 °C using a 3-litre water bath in which the whole reactor body was immersed. A thermometer was inserted through one neck into the reactor to monitor the operating temperature.

After the sonication step, the mixture was allowed to settle for 1 min to separate the organic phase from aqueous phase. The interface between the two phases is quite distinctive, thereby making it possible to easily remove the aqueous phase. This was done using a simple separation funnel. In the extraction step, the oil phase was brought into contact with (1:1 v/v) 20 °Bé caustic solution inside a

**Table 1.** Specifications of the Feed Diesel Oil

Row	Specification	Unit	
1	Specific Gravity @ 16 °C	-	0.8470
2	IBP (Initial Boiling Point)	°C	257
3	Temperature at 5%	°C	279
4	Temperature at 10%	°C	284
5	Temperature at 20%	°C	292
6	Temperature at 30%	°C	301
7	Temperature at 40%	°C	309
8	Temperature at 50%	°C	319
9	Temperature at 60%	°C	332
10	Temperature at 70%	°C	343
11	Temperature at 80%	°C	359
12	Temperature at 90%	°C	376
13	Temperature at 95%	°C	387
14	FBP (Final Boiling Point)	°C	391
15	Kinematic Viscosity @ 40 °C	cSt	3.96
16	Color	-	0.5
17	Flash Point	°C	125
18	Total Sulfur	ppmw	5044
19	Cetane Index	-	55
20	Water Content	vol. %	< 0.05

separatory funnel in two minutes. The treated diesel oil was then collected as the final product and its total sulfur content and kinematic viscosity were measured and compared to those of the feedstock in order to determine the sulfur removal efficiency,  $Y$ , and viscosity reduction percentage,  $v_R$ , in each test run, which are calculated according to Eqs. (1) and (2), respectively. For more accuracy, each test run was repeated twice and the arithmetic mean value of two measurements, with a relative standard deviation lower than 5 %, was reported as the final data point.

$$Y = \frac{\text{Sulfur Content in Feedstock} - \text{Sulfur Content in Treated Product}}{\text{Sulfur Content in Feedstock}} \times 100 \quad (1)$$

$$v_R = \frac{\text{Feedstock Viscosity (at 40 °C)} - \text{Treated Product Viscosity (at 40 °C)}}{\text{Feedstock Viscosity (at 40 °C)}} \times 100 \quad (2)$$

### Experimental Design

**Screening analysis.** In order to get an idea of the effects

**Table 2.** Process Variables and Their Working Ranges

Parameter	Coded designation	Type	Range and Levels		
			-1	0	1
H <sub>2</sub> O <sub>2</sub> Vol. (ml)	X <sub>1</sub>	Numeric	0.00	15.00	30.00
Acetic Acid Vol. (ml)	X <sub>2</sub>	Numeric	0.00	15.00	30.00
PTA Wt. (g)	X <sub>3</sub>	Numeric	0.00	0.15	0.30
Catalyst Wt. (g)	X <sub>4</sub>	Numeric	0.00	1.44	2.88
Time (min)	X <sub>5</sub>	Numeric	5.00	7.50	10.00

of process parameters on the target variables; *i.e.*, sulfur removal efficiency and kinematic viscosity reduction, also known as "Responses", a two-level factorial screening analysis was designed using a Design Expert v.7.0.0. software. Screening identifies the significant factors using only two levels for each parameter. In other words, the parameters namely, hydrogen peroxide and acetic acid volumes, PTA and catalyst weights and time are designated two levels of -1 and 1 as coded values for minimum and maximum extremes in each parameter range, respectively. This gives 16 test runs for a total of five parameters. Additionally, three repetitive "mid-point" runs were added in which each parameter was designated the middle value in its relative working range. Moreover, the mid-point runs, also known as "Center Points", were included not only to acquire the values of target variables within experimental ranges of parameters but also to check for the repeatability of the tests. This gives a total of 19 runs.

Basically, the screening analysis helps find the parameters which have the least effect on the response [24]. In this vein, the least effective factor is omitted in order to obtain a less complex optimization process designed based on the remaining four independent variables.

**Response surface method.** Response surface method is one of the relevant multi-variable techniques that can deal with experimental design, statistical modeling and process optimization. It is used to examine the relation between a set of quantitative variables or factors. The Box-Behnken design (BBD) scheme is one of the most popular RSMs that

is well suited for fitting complicated systems and regularly works well for process investigation and optimization [25]. This method also allows a reasonable amount of information for sensitivity analysis, while not involving an unusually large number of test points.

The intriguing response, *i.e.*, sulfur removal efficiency "Y" can be expressed as a quadratic function in terms of independent factors, as stated in Eq. (3):

$$Y = \beta_0 + \sum_{i=1}^4 \beta_i X_i + \sum_{i=1}^4 \beta_{ii} X_i^2 + \sum_{i=1}^4 \sum_{j=i+1}^4 \beta_{ij} X_i X_j + \varepsilon \quad (3)$$

where, X<sub>i</sub>s (i = 1, 2, 3 and 4) are the input (independent) factors influencing the predicted response, Y (including hydrogen peroxide volume, acetic acid volume, PTA weight and the catalyst weight). β<sub>0</sub>, β<sub>i</sub>, β<sub>ii</sub> and β<sub>ij</sub> are the offset term, linear coefficient, quadratic effect and the cross product coefficient, respectively, and are obtained by the least square method and ε is also referred as the statistical (unanticipated) error.

The input parameters were designated three levels as -1, 0 and 1 for low, middle and high values, respectively, resulting in a total number of 27 runs, 3 of which were repetitive center points.

Table 2 lists the process parameters and their ranges under study. "Zero" dosage was set as a minimum for reagents in order to investigate the effect of absence of each

**Table 3.** Design Arrangement and Experimental Results for Screening Analysis

Run	Factor $X_1$	Factor $X_2$	Factor $X_3$	Factor $X_4$	Factor $X_5$	$Y$ (%) <sup>a</sup>	$\nu_R$ (%) <sup>b</sup>
1	30.00	0.00	0.00	2.88	10.00	23.51	8.39
2	30.00	30.00	0.30	0.00	5.00	18.64	7.21
3	0.00	30.00	0.30	2.88	5.00	23.63	20.08
4	30.00	30.00	0.30	2.88	10.00	24.28	4.35
5	0.00	0.00	0.00	0.00	10.00	0.00	3.92
6	0.00	0.00	0.30	2.88	10.00	0.00	0.31
7	0.00	30.00	0.00	2.88	10.00	23.37	18.50
8	30.00	0.00	0.30	2.88	5.00	36.83	0.39
9	0.00	30.00	0.30	0.00	10.00	25.00	17.32
10	15.00	15.00	0.15	1.44	7.50	51.53	8.07
11	0.00	0.00	0.00	2.88	5.00	0.00	1.70
12	15.00	15.00	0.15	1.44	7.50	52.12	8.07
13	30.00	30.00	0.00	0.00	10.00	12.63	6.99
14	30.00	30.00	0.00	2.88	5.00	16.22	1.77
15	30.00	0.00	0.30	0.00	10.00	8.41	1.77
16	0.00	0.00	0.30	0.00	5.00	0.00	1.92
17	0.00	30.00	0.00	0.00	5.00	27.65	3.15
18	15.00	15.00	0.15	1.44	7.50	53.35	4.92
19	30.00	0.00	0.00	0.00	5.00	7.33	1.13

<sup>a</sup>Sulfur removal efficiency defined as in Eq. (1). <sup>b</sup>Viscosity reduction percentage defined as in Eq (2).

material on the target variables.

## RESULTS AND DISCUSSION

### Screening Section

The experimental plan for screening analysis and measured target responses are detailed in Table 3. Basically, low observed sulfur reduction is typical of diesel oil in comparison to pure model sulfurs such as BT or DBT. This

is chiefly due to the fact that the former is actually a combination of different sulfur compounds that makes oxidation by the UAOD process difficult in practice [3]. The test runs, in which hydrogen peroxide and acetic acid volumes are simultaneously zero, are naturally considered to have zero sulfur removal, whereas for cases in which only hydrogen peroxide is absent in the reaction medium, some sulfur removal is expected due to the fact that acid by itself can play an additional role as an extraction solvent for the

**Table 4.** Summarized ANOVA Results for Screening

Source	Sum of squares <sup>a</sup>	df <sup>b</sup>	Mean square <sup>c</sup>	F-Value	p-Value	
Model	2058.01	13	158.31	258.24	<0.0001	<i>Significant</i>
Curvature	3433.26	1	3433.26	5600.54	<0.0001	<i>Significant</i>
Residual	2.45	4	0.61			
Lack of Fit	0.73	2	0.36	0.42	0.7033	<i>Not Significant</i>
Pure Error	1.72	2	0.86			
Total	5493.72	18				

<sup>a</sup>Sum of squares =  $\sum_{i=1}^n (y_i - y_m)^2$ ; where:  $y_i$  is the  $i$ th observation,  $n$  is the number of observations and  $y_m$  is the mean of  $n$  observations. <sup>b</sup>df =  $n - 1$ . <sup>c</sup>Mean square = Sum of squares/df.

sulfur-containing compounds [26].

Results of kinematic viscosity reveal that the maximum reduction in viscosity is around 20.1%. Therefore, it is safe to state that the current process fails to break (reduce) the feedstock viscosity to a significant amount. This is due to the low power of ultrasonic waves generated by the sonicator [22]. Hence, the kinematic viscosity is checked out of the target variables list, and the sulfur removal efficiency is considered the sole response of the experiment. Table 4 summarizes the results for the analysis of variance (ANOVA) to validate the defined screening model.

Generally, a high  $F$ -value or "F-statistic" shows that most of the variations in the response can be described by the predicted model, while a "Significance Probability" or  $p$ -value less than 0.05 indicates that the model and model terms are statistically significant [3]. Therefore,  $p$ -value of a variable is an indication for its significance level in the predicted model so that the smaller its  $p$ -value, the more significant the variable is, and *vice versa*. Here, the  $p$ -values of  $X_1$  through  $X_5$  are 0.0001, <0.0001, 0.0011, 0.001 and 0.0139, respectively. Comparing the  $p$ -values of the parameters, it is safe to say that the response function is the least sensitive to  $X_5$  (time). Moreover, the  $p$ -values for cross interactions of time with the other four parameters are notably high, making it the least effective candidate among all independent variables. Therefore, the parameter of time

was considered insignificant and could be safely ignored.

Table 4 also demonstrates that the predicted model for sulfur removal enjoys curvature which has to be further investigated in the RSM analysis. The high values of the coefficients of determination  $R^2 = 0.9988$  and Adjusted  $R^2 = 0.9949$  prove that the screening predictions are highly reliable.

In Fig. 1a, normal probability is plotted against studentized residuals. The deviation between the experimental and model-predicted values are defined as residuals. The residual points in the figure are appropriately located close and along the straight line which basically implies the normal distribution of errors and high accuracy of model predictions.

Figure 1b shows the experimental data points on sulfur removal compared with the predicted values. Results demonstrate a close proximity of the two series of data, indicating the validity of the regression model. Consequently, the RSM analysis was set to the minimum extreme (5 min) while the time remained constant for the whole set of runs.

### RSM Section

Table 5 illustrates the experimental design of the utilized RSM along with the observed response values. Here, a quadratic model is employed for correlating the

**Table 5.** Design Arrangement and Experimental Results for RSM Analysis

Run	Factor $X_1$	Factor $X_2$	Factor $X_3$	Factor $X_4$	Y (%)
1	0.00	0.00	0.15	1.44	0.00
2	15.00	0.00	0.15	2.88	11.54
3	30.00	15.00	0.00	1.44	7.83
4	0.00	15.00	0.00	1.44	18.04
5	15.00	30.00	0.00	1.44	24.23
6	15.00	30.00	0.15	0.00	11.85
7	30.00	15.00	0.15	0.00	4.52
8	15.00	15.00	0.15	1.44	62.89
9	0.00	15.00	0.15	0.00	18.46
10	15.00	30.00	0.30	1.44	21.95
11	15.00	30.00	0.15	2.88	20.95
12	30.00	15.00	0.30	1.44	6.68
13	0.00	15.00	0.15	2.88	21.05
14	15.00	0.00	0.00	1.44	12.47
15	30.00	0.00	0.15	1.44	18.36
16	0.00	15.00	0.30	1.44	21.61
17	15.00	0.00	0.30	1.44	12.53
18	30.00	15.00	0.15	2.88	12.65
19	15.00	15.00	0.00	2.88	17.49
20	15.00	15.00	0.15	1.44	61.24
21	15.00	15.00	0.30	0.00	19.77
22	30.00	30.00	0.15	1.44	15.94
23	0.00	30.00	0.15	1.44	37.95
24	15.00	15.00	0.00	0.00	10.43
25	15.00	15.00	0.30	2.88	21.83
26	15.00	0.00	0.15	0.00	17.45
27	15.00	15.00	0.15	1.44	58.68

**Table 6.** ANOVA Results for RSM

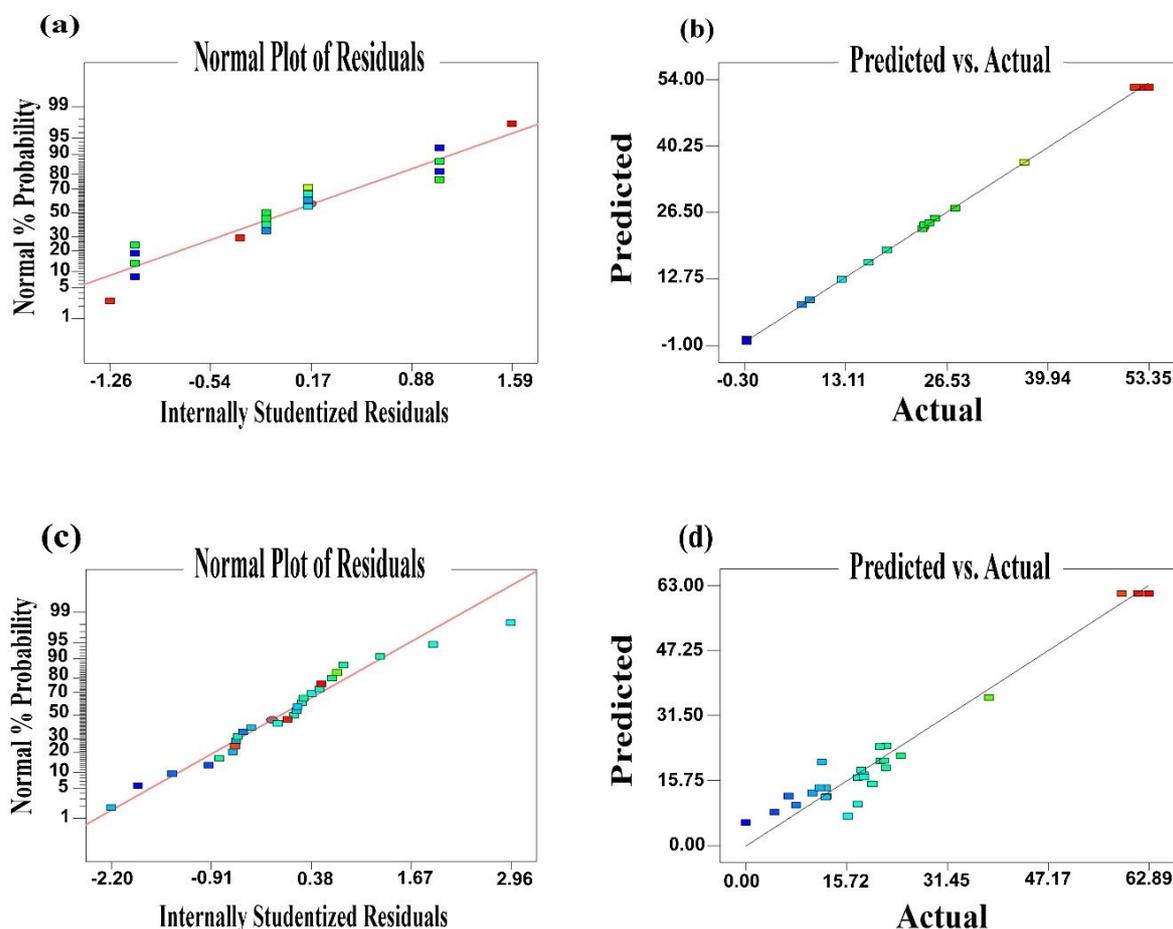
Source	Sum of squares	df	Mean square	F-Value	p-Value	
Model	6471.49	14	462.25	19.36	<0.0001	<i>Significant</i>
$X_1$	217.86	1	217.86	9.13	0.0106	
$X_2$	305.22	1	305.22	12.79	0.0038	
$X_3$	16.05	1	16.05	0.67	0.4281	
$X_4$	44.20	1	44.20	1.85	0.1986	
$X_1X_2$	407.43	1	407.43	17.07	0.0014	
$X_1X_3$	5.57	1	5.57	0.23	0.6378	
$X_1X_4$	7.67	1	7.67	0.32	0.5812	
$X_2X_3$	1.37	1	1.37	0.06	0.8148	
$X_2X_4$	56.33	1	56.33	2.36	0.1504	
$X_3X_4$	6.25	1	6.25	0.26	0.6182	
$X_1^2$	2982.53	1	2982.53	124.95	<0.0001	
$X_2^2$	2325.57	1	2325.57	97.42	<0.0001	
$X_3^2$	2622.96	1	2622.96	109.88	<0.0001	
$X_4^2$	2830.03	1	2830.03	118.56	<0.0001	
Residual	286.44	12	23.87			
Lack of fit	277.44	10	27.74	6.17	0.1475	<i>Not significant</i>
Pure error	9.00	2	4.50			
Total	6757.93	26				

experimental data points. The results for the RSM ANOVA are presented in Table 6, where the level of confidence is assumed to be 0.05.

Based on the criteria explained in the previous section and according to the  $F$  and  $p$ -values of 19.36 and <0.0001, respectively, it is well concluded that the quadratic model is statistically remarkable.

As can be seen in Table 6, parameters and interactions

including  $X_1$ ,  $X_2$ ,  $X_1X_2$ ,  $X_1^2$ ,  $X_2^2$ ,  $X_3^2$  and  $X_4^2$  are significant model terms ( $p$ -value < 0.05). Therefore, the response can be well presented using the mentioned terms; however, in order to sustain the hierarchy of the proposed model,  $X_3$  and  $X_4$  are retained and only  $X_1X_3$ ,  $X_1X_4$ ,  $X_2X_3$ ,  $X_2X_4$  and  $X_3X_4$  interactions are excluded from the quadratic response. The coefficients of determination are obtained as  $R^2 = 0.9462$  and Adjusted  $R^2 = 0.9177$ . The final correlation concerning



**Fig. 1.** Model evaluation for screening: (a) Normal probability of the residuals, (b) Predicted vs. actual sulfur removal efficiency and for RSM: (c) Normal probability of the residuals, (d) Predicted vs. actual sulfur removal efficiency.

the response,  $Y$ , to the independent variables is given as in Eq. (4):

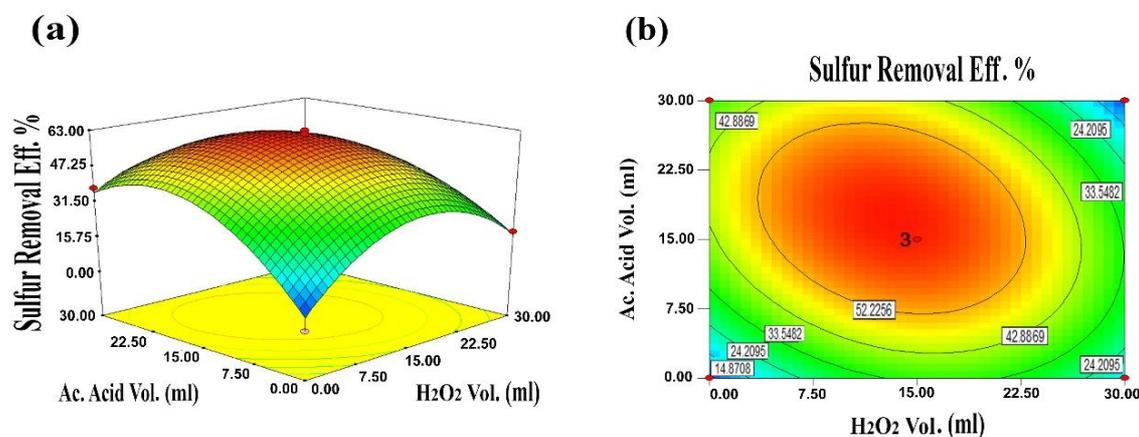
$$Y (\text{Sulfur removal}\%) = 60.94 - 4.26X_1 + 5.04X_2 + 1.16X_3 + 1.92X_4 - 10.09X_1X_2 - 23.65X_1^2 - 20.88X_2^2 - 22.18X_3^2 - 23.04X_4^2 \quad (4)$$

in which  $X_1$ ,  $X_2$ ,  $X_3$  and  $X_4$  are the coded parameters. Basically, the sign and the coefficient value of each term show increasing or decreasing effects on the response. As noted in Eq. (4), the proximity of the coefficients of  $X_3$  and  $X_4$  to unity, 1.16 and 1.92, respectively, confirms the low importance of these parameters on removal efficiency. This

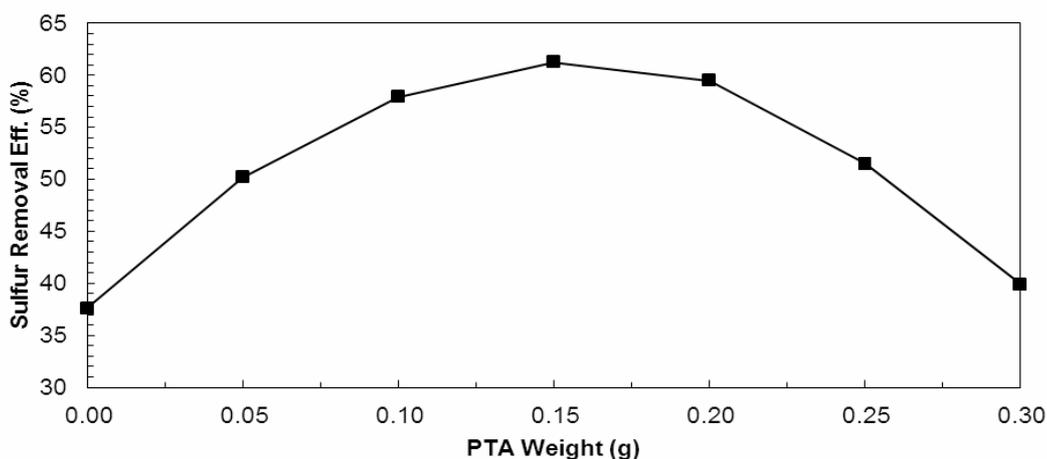
is, of course, due to the promoting role of PTA and TMC in the oxidative desulfurization reaction of diesel oil used as the feedstock [27-30].

The normal probability plot in Fig. 1c confirms that the residuals follow a normal and logical distribution. Also, as indicated in Fig. 1d, the model predictions are in good agreement with the observed data points. Both figures prove that the final RSM model is highly reliable for further predictions.

Figure 2 shows the effect of  $\text{H}_2\text{O}_2 + \text{CH}_3\text{COOH}$  volume as the oxidant combination on sulfur removal at constant amounts of PTA and TMC. In Fig. 2a, the 3-D surface plot of sulfur reduction is presented, while its 2-D



**Fig. 2.** Combined effects of H<sub>2</sub>O<sub>2</sub> and CH<sub>3</sub>COOH volumes ( $X_1$  and  $X_2$ ) on sulfur removal efficiency. (a) 3-D surface plot, (b) 2-D projection contour ( $X_3 = 0.15$  g and  $X_4 = 1.44$  g).



**Fig. 3.** Effect of PTA dosage on sulfur removal efficiency ( $X_1 = X_2 = 15$  ml,  $X_4 = 1.44$  g).

projection is illustrated in Fig. 2b for better clarification of this effect.

As shown in the figures, the removal efficiency increases with increasing acetic acid/hydrogen peroxide volume ratio to a maximum amount and then decreases as the ratio is further increased. This behavior is explained by the fact that the oxidation of sulfur-containing compounds with H<sub>2</sub>O<sub>2</sub> + CH<sub>3</sub>COOH is performed through an electrophilic addition reaction of oxygen atoms, *i.e.* H<sub>2</sub>O<sub>2</sub> and CH<sub>3</sub>COOH form peroxyacetic acid which promotes the oxidation of sulfur compounds into corresponding sulfones at the beginning of reaction. As the concentration of acetic

acid is exceeded to a certain value, the stability of peroxycarboxylic acid in the reaction increases. This basically reciprocates the decomposition of peroxycarboxylic acid, and eventually reduces the sulfur removal efficiency [31].

In Fig. 3, the effect of PTA weight on sulfur removal efficiency is depicted, whereas the other parameters including H<sub>2</sub>O<sub>2</sub> and CH<sub>3</sub>COOH volumes and TMC weight are kept constant.

Tetraoctylammonium bromide has large lipophilic cation, which can effectively transfer heteropolymetal anion of the catalyst into organic phase, which in turn accelerates



**Fig. 4.** Turbid layers formed at high amounts of PTA ( $X_3 = 0.3$  g).

the oxidation of sulfur compounds to the corresponding sulfoxides and causes an increase in sulfur reduction [3,32,33]. This is what happens as PTA weight is increased from 0 to 0.15 g in the reaction mixture. As the dosage is further increased to 0.3 g, the mass transfer between hydrophobic (diesel) and hydrophilic (aqueous) phases becomes less effective because of the formation of a highly turbid multilayer interface which leads to a decrease in removal efficiency of sulfur compounds [28].

A photo of thick turbid layers, noted earlier, is presented in Fig. 4. This phenomena likely occurs at high concentrations of PTA in the mixture. Figure 5 also shows the sulfur removal efficiency with respect to catalyst weight,

while the other parameters are kept constant. As can be seen, the sulfur reduction increases with increasing TMC weight on account of the relatively high concentration of catalytically active species. On top of that, as catalyst weight is further increased to 2.88 g, sulfur reduction falls down which can be again attributed to the mass transfer limitations due to large size of the particles and small surface area/unit volume across the organic-aqueous phase interface [8].

#### **Optimization**

In order to obtain the optimum conditions for sulfur removal efficiency, the proposed regression model and

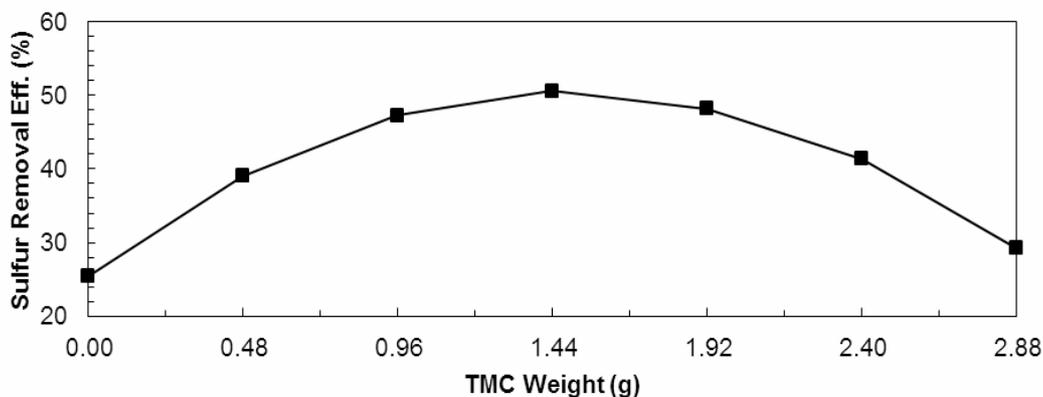


Fig. 5. Effect of TMC weight on sulfur removal efficiency ( $X_1 = X_2 = 15$  ml,  $X_3 = 0.05$  g).

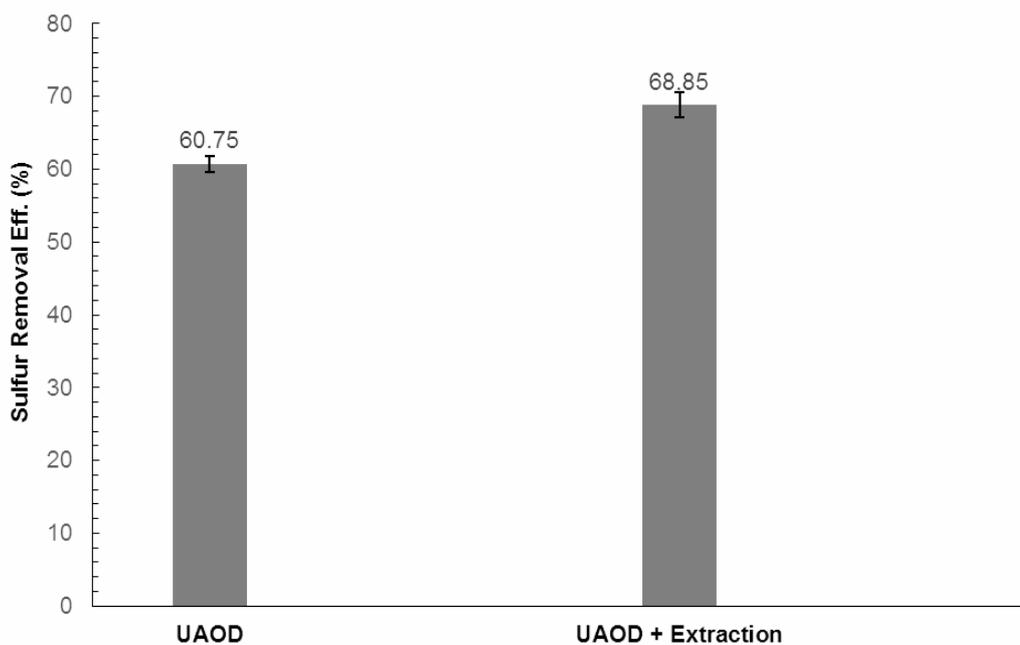


Fig. 6. Single-stage extraction effect with caustic soda on sulfur removal efficiency at optimum conditions ( $X_1 = 13.17$  ml,  $X_2 = 17.26$  ml,  $X_3 = 0.15$  g and  $X_4 = 1.5$  g).

response surface plots were evaluated. Results give a sulfur removal of 61.63% achievable using 13.17 ml hydrogen peroxide, 17.26 ml acetic acid, 0.15 g PTA and 1.5 g of catalyst. Here, the RSM optimization technique is developed by Derringer and Suich which makes use of the concept of desirability functions. The general approach is to

first convert the response, here sulfur removal efficiency, into a desirability function  $d(Y)$  which varies over the range of zero to unity. If the response is at its goal, then  $d(Y) = 1$ , and if the response is outside the acceptable region,  $d(Y) = 0$ . If the response is maximized, as in this case, then desirability function  $d(Y)$  is structured as an exponential

**Table 7.** Validation Tests under Optimized Conditions

Run	Sulfur removal Eff. (%)	Absolute error (%)
Optimized	61.63	-
Observed 1	62.85	1.94
Observed 2	59.12	4.25
Observed 3	60.29	2.22
Observed Avg. <sup>a</sup>	60.75	1.45

$${}^a \text{Observed Avg.} = \frac{\sum_{i=1}^3 \text{Observed } i}{3}$$

function in terms of the response  $Y$ . The maximum value for overall desirability  $D$ , which is equal to  $d(Y)$  in a single response analysis, is solved to give the optimum process parameters [34].

Under the suggested optimized conditions, three replicate tests were performed independently to check the model validation. Results are given in Table 7.

#### UAOD Followed by Extraction

Under optimum conditions obtained for the UAOD process, the treated product was further washed by 20 °Bé caustic soda, also known as a common solvent in industrial L-L extraction processes. Figure 6 shows that under the same optimized conditions, a single-stage extraction step can practically improve the removal efficiency up to 68.85%. This is chiefly due to the fact that the remaining oxidized compounds in the oil phase are highly polar after ultrasonication. Therefore, a subsequent extraction step with a polar solvent is a convenient way to remove sulfones from the oil phase [35].

Under reproducibility conditions, where test results are obtained with the same method on identical test items in different laboratories and with different operators using different equipment, sulfur removal in UAOD + extraction experiment was reported to be 72.92% for the second trial. However, eliminating systematic errors and minimizing random errors (which together compose the experimental errors) through proper calibration and operation of equipment, in turn, promotes good reproducibility of

results [3].

## CONCLUSIONS

This study was devoted to investigate the upgradation of diesel oil with using ultrasound irradiation process. The raw feedstock's total sulfur content and kinematic viscosity were reported as 5044 ppmw and 3.96748 cSt, respectively. In this vein, the effects of five operating parameters namely, oxidant volume, acid volume, PTA weight, catalyst weight and time were studied on sulfur removal (UAOD) and viscosity reduction of the diesel oil. Using a screening analysis, kinematic viscosity and time were ignored from the dependent and independent variables, respectively. Firstly, because the proposed process could not significantly reduce the viscosity, and secondly, time had the least effect on the target sulfur removal efficiency.

Response surface methodology with the Box-Behnken scheme was utilized to further investigate the effects of four remaining parameters on removal efficiency. It was found that oxidant and acid volumes have significant effects, while PTA and catalyst weights are not significant on sulfur removal since they have more of a promoting role in the main oxidation reaction. The optimal conditions of 13.17 ml volume of hydrogen peroxide, 17.26 ml volume of acid, 0.15 g PTA and 1.5 g catalyst resulted in 60.75% sulfur removal from the diesel oil feed. It is evident from the results that the removal efficiency can be improved to 68.85% using a single stage extraction with a polar solvent,

because it can notably wash away relatively polar oxidized sulfur compounds from the bulk of the oil. This work supports the fact that the novel UAOD method and its operating parameters can be manipulated to attain high conversions for potential application on industrial scale.

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