Sulfur removal of gas oil using ultrasound-assisted catalytic oxidative process and study of its optimum conditions

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(*Received 31 December 2012 • accepted 25 May 2013*)

Abstract−Ultrasound-assisted oxidative desulfurization process (UAOD) was applied to reduce sulfur compounds of gas oil containing various types of sulfur content. The environmental regulation requires a very deep desulfurization to eliminate the sulfur compounds. UAOD is a promising technology with lower operating cost and higher safety and environmental protection. For the first time the typical phase transfer agent (tetraoctyl-ammonium-bromide) was replaced with isobutanol because using isobutanol is much more economical than TOAB, imposing no contamination. The reaction was carried out at optimal point with various temperatures, in single-, two- and three step-procedures, investigating the effect of gradual increase of H_2O_2 and TOAB being used instead of isobutanol. Total sulfur concentration in oil phase was analyzed by ASTM-D3120 method. The highest removal of about 90% for gas oil containing 9,500 mg/kg of sulfur was achieved in three-steps during 17 minutes of process at 62 ± 2 °C when 180.3 mmol of H_2O_2 was used and extraction carried out by methanol.

Key words: Ultrasound-assisted Oxidative Desulfurization, Gas Oil, Oxidant, Catalyst, Isobutanol

INTRODUCTION

Sulfur compounds are one of the main pollutants in petroleum and a significant percentage of these compounds are conveyed to fuels during refining processes [1]. While the fuel is used in combustion engines, sulfur compounds are transformed into sulfur oxides (SO_x) which are released to atmosphere, cause acid rain, and imperil public health [2]. Sulfur compounds in petroleum fractions also have a poisoning effect on catalysts and increase the corrosion of refining equipment and combustion engines [1]. Sulfur compounds affect the quality of petroleum products by decreasing the American Petroleum Institute (API) gravity.

Nowadays, environmental regulations have been issued to control the sulfur levels in gas oil and diesel fuel. It is necessary to produce ultra-low sulfur fuels, so desulfurization of petroleum fractions becomes an essential part of refining processes [3-8]. Hydrodesulfurization (HDS) is the present industrial technique to eliminate sulfur compounds from diesel oil [9,10]. This technique has to be operated under special conditions, such as use of high temperature (about 400 °C), high hydrogen pressure (up to 100 atm), large amount of active metal catalysts (e.g., CoMo and NiMo), large reactor and long residence time that cause high operation costs [3,9,11-13]. The conventional HDS process is effective for removing mercaptans, thioethers, sulfides and disulfides, but it has exposed some restriction related to elimination of thiophene, benzothiophen (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) [14-22].

Consequently, some progressive desulfurization technologies have been developed. Among these alternative processes, the oxidative desulfurization (ODS) process has obtained great attention as an efficient and promising technique of desulfurization [2,3,5,9,10,14, 23,24]. It has two main advantages compared to the HDS process. The supreme advantage of ODS is that it can be performed in the liquid phase under very mild conditions, such as relatively low temperature and pressure [9,25]. The second significant quality of ODS is that it converts refractory thiophenic compounds to the sulfoxides and/or sulfones, which are highly polar and can be easily and selectively removed by solvent extraction or adsorption [26,27].

Ultrasound-assisted oxidative desulfurization (UAOD) is a new method that causes the oxidation reaction to be carried out quickly, economically and safely. UAOD process occurs under ambient temperature and atmospheric pressure and permits selective removal of sulfur compounds from hydrocarbons of fuels [3].

The oxidizing of the sulfur compounds, which can happen in the bulk of the oxidants and fuel mixture or at their interface, needs good dispersion of two phases (aqueous and oil). The ultrasonic waves produce cavitation bubbles, leading to creating a fine emulsion between two phases [12,28].

It is evident that ultrasonic irradiation can considerably advance the reaction efficiency, because of acoustic cavitation bubbles in the liquid. Ultrasound waves can cause the formation, growth and implosive collapse of bubbles, producing extreme local conditions such as high temperature (up to 5,000 K), high pressure (up to 1,000 atm) and extreme liquid jets arising from the violent collapse of each bubble [29-34]. These conditions increase the surface activity of catalysts by improved micro-mixing, allowing the reaction to progress rapidly [29,35]. Effective factors in the UAOD process are ultra-

sonic frequency and power, oxidants, catalysts, phase-transfer agent, time, extractant and adsorbent [35-37]. Phase transfer agents (PTA) are surface-active species that lower surface tension and permit easy formation of micro bubbles under ultrasound [28]. Some important phase transfer includes quaternary ammonium salts (QAS) such as tetraoctylammonium bromide and/or fluoride [3,38] as cationic surfactants. The QAS especially can function as a phase transfer agent and deliver the anion into organic phase or interfacial region, thus facilitating the oxidation of organic sulfur compounds [38]. However, we used isobutanol as PTA because QAS is the external material that must be separated at the end of the process, but isobutanol is a hydrocarbon and gas oil also includes hydrocarbons in the carbon chain range of C_9-C_{28}, so isobutanol does not act like a contaminant. The other advantage of isobutanol is its economical domination.

Diesel fuel is one of the most significant transportation fuels that is widely used in industries and powerhouses for generating energy. Diesel fuels are complex mixtures of alkanes, cycloalkanes, and aromatic hydrocarbons with carbon numbers in the range of C_9-C_{28} and with a boiling-range of 150-390 °C [39]. Although diesel oil is a versatile fuel and desulfurization is an essential step of its production and purification process, there have been just few studies in the literature regarding application of UAOD for desulfurization of diesel oil till now.

A proper experimental design should be used to study effects of parameters and their interactions with a minimum number of experiences. For this goal, response surface methodology (RSM) was used to design experiments. RSM applies mathematical and statistical techniques for analysis of problems in which response is dependent on several variables and the objective is modeling or optimization of this response. In the present study, the application of ultrasonic waves to develop the oxidation and removal of sulfur compounds from gas oil was investigated. UAOD process was utilized under relatively mild conditions and by using the trace metal catalysts under phase transfer conditions. For the first time the typical phase transfer agent (tetraoctyl ammonium bromide) was replaced with isobutanol. Effects of operational parameters such as amount of hydrogen peroxide, time and concentration of catalyst on the UAOD process were studied [35-38,40-43]. The optimum condition for the sulfur removal reaction was determined by response surface method. Subsequently, at the obtained optimal point, various temperature values, multistep procedure, tetraoctyl ammonium bromide usage and the effect of gradual increase of H_2O_2 were all tested.

EXPERIMENTAL METHOD AND MATERIAL

1. Reagent and Material

Gas oil with sulfur content of 9,500 mg/kg (from atmospheric

Table 1. Properties of the Tabriz refinery gas oil

Parameter	Unit	Specification
Density at 15 °C	g/cm³	0.82-0.86
Total sulfur	mg/kg	9500
FBP	°C	385
Flash point	°C	106
Pour point	°C	(-6)-(-2)

gas oil unit of Tabriz refinery) was used as feedstock throughout this work. Table 1 summarizes the properties of the gas oil.
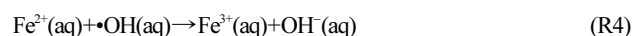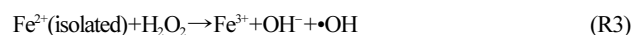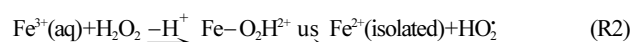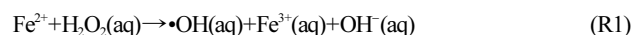
In this study, hydrogen peroxide (H_2O_2 30% (v/v)), glacial acetic acid ($C_2H_4O_2$, 99%, 1.05 kg/l), isobutanol ($C_4H_{10}O$, 0.802 g/cm³), methanol (CH_3OH, 0.79 kg/l) and $FeSO_4$ were used in the UAOD process. Merck Company (Darmstadt, Germany) supplied all of the above materials.

2. Apparatus

We used an ultrasound apparatus (UP400S, 24 kHz and 400 W of nominal power) manufactured by Hielscher. An ultrasonic probe with a 0.5 in. threaded end titanium tip was immersed into approximately 30 ml of reaction mixture, where it was able to produce ultrafine emulsion by introducing high intensity ultrasound irradiation to the system. The wave generator in this study was set at 100% of the nominal power of 400 W. Temperature of all experiments was controlled with water bath at 62±2 °C.

3. Mechanism

The mechanism of oxidation reaction of sulfur compounds and degradation of organic contamination has been reported in some researches in US- Fe^{2+} ion - H_2O_2 system. In aqueous phase the reaction kinetics is assumed to be the first-order reaction; however, the exact reaction mechanism is very complex. The degradation of organic contaminants occurred in the presence of hydroxyl radicals. The decomposition of hydrogen peroxide to hydroxyl radicals was accelerated by the effect of the ultrasound waves in combination with $FeSO_4$ catalyst [13,36,37,40,44,45].

$$Fe^{2+}+H_2O_2(aq) \rightarrow \bullet OH(aq)+Fe^{3+}(aq)+OH^-(aq) \tag{R1}$$

$$Fe^{3+}(aq)+H_2O_2 \xrightarrow{-H^+} Fe-O_2H^{2+} \xrightarrow{us} Fe^{2+}(isolated)+HO_2^\bullet \tag{R2}$$

$$Fe^{2+}(isolated)+H_2O_2 \rightarrow Fe^{3+}+OH^-+\bullet OH \tag{R3}$$

$$Fe^{2+}(aq)+\bullet OH(aq) \rightarrow Fe^{3+}(aq)+OH^-(aq) \tag{R4}$$

$$\bullet OH+H_2O_2 \rightarrow HO_2\bullet+H_2O \tag{R5}$$

$$Fe^{3+}+HO_2\bullet \rightarrow Fe^{2+}+O_2+H^+ \tag{R6}$$

The schematic reaction mechanism of desulfurization reaction in ultrasound (Fe^{2+}) system is illustrated in Fig. 1 [40].

4. Experimental Method

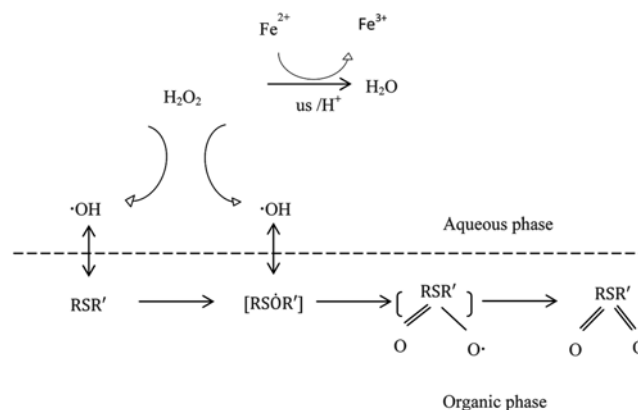The experiments were performed according to the following procedure:

Fig. 1. Possible reaction pathways for the sulfur compounds oxidation reaction in ultrasound (Fe^{2+}) system.

1) Preparing the mixture of gas oil, isobutanol, acetic acid, $FeSO_4$ solution and H_2O_2, respectively.

2) Using ultrasonic waves for creation of ultra-fine emulsion by UP400S.

3) Separating aqueous and oil phases by conic glass.

4) Extracting the oil layer (the upper one) for three times with methanol.

In this work, experiments were designed by response surface methodology. Reactions for sulfur removal with the UAOD process were carried out combining different mixtures of hydrogen peroxide (30% w/w) in the amount range of 15.6-180.3 mmol and constant volume of glacial acetic acid into the glass sono-reactor containing 25 ml of gas oil. Hydrogen peroxide was used as the oxidant agent. In addition, isobutanol and $FeSO_4$ were added as phase transfer agents (PTA) and catalyst, respectively. $FeSO_4$ was applied in the trace range between 25 to 525 ppm.

Ferrous ion (from $FeSO_4$) was added into the reactor in the form of aqueous solution. In this set of experiments, the pH value of the aqueous phase was adjusted by acetic acid because the activity of catalyst is dependent on acidity of the solution and its value should be kept less than 3 [3].

The reaction time was considered from 1.6 to 18.4 min. All of the experiments were performed at atmospheric pressure. After ultrasound treatment, oil and aqueous phases were separated (in less than 1 minute). The treated oil phase contained the sulfones produced by the oxidation reaction. Organosulfur compounds are commonly polar and can simply be extracted by liquid-liquid extraction using solvent such as methanol. As a usual necessity the solvent must have high polarity and be insoluble in the oil [7,12,26,27,46].

In this study, the oxidized gas oil was extracted with methanol three times, and each time the solvent/oil ratio was kept at 4 : 5 (v/v). In each step, 20 ml of methanol was used and the oil/solvent mixture was shaken at room temperature for 2 minutes. In general, efficiency of desulfurization increases and the sulfur containing of gas oil decreases with the rising either solvent/oil ratio or extraction time.

After extraction step, by using a glass separator funnel, oil and solvent phases were separated. Finally, sulfur concentration of oil phase was determined with ASTM 3120 method. The solvent phase was sent to the waste treatment section of our research institute and refined. The procedure for separation of sulfur from was performed by utilizing ionic membranes.

The ultrasound-assisted oxidative process produces heat and does not need an extra heat source. The temperature effect on the oxidative reaction under ultrasound was investigated in the range of 20 to 90 °C in some studies. The upper limit is the boiling point of the most volatile component of the mixture. There are two limitations for increasing the temperature:

1) Destruction of hydrogen peroxide at high temperatures (i.e., more than 80).

2) Evaporation of light components of the gas oil.

The reaction is faster at higher temperatures. This performance can be explained by an increase in the oxidation reaction rate of sulfur-containing compounds present in gas oil due to the strong dependence of reaction rate on the reaction temperature [12,41,42]. On the other hand, the creation of effective cavitation and the intensity of cavitation collapse are weakened with the rising temperature. In this study, the temperature was set to be 62±2 °C.

Table 2. Experimental values and levels of variables

Variable	Levels and values			
Time (min)	1.591	5	10	15	18.409
H_2O_2 (mmol)	15.582	48.97	97.94	146.910	180.298
Catalyst (ppm)	25	126.349	275	423.651	525

5. Experimental Design

In response surface methodology (RSM) problems, the form of the relationship between the response and variables is usually unknown. Therefore, it is important to find a suitable approximation for the relationship between response and independent variables. At first, a first-order polynomial (i.e., Eq. (1) is employed. If the response is well modeled by this linear function of the independent variables, then the function is chosen for prediction and optimization.

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \cdots + \beta_k x_k + \varepsilon \tag{1}$$

If there is curvature in the system, then a higher degree polynomial must be used, such as the second-order model,

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i<j} \sum \beta_{ij} x_i x_j + \varepsilon \tag{2}$$

where y is the response variable of sulfur removal, $x_1, \ldots, x_i$ are coded parameters, β_0 is the interception term, $\beta_1, \ldots, \beta_i$ are regression coefficients of linear effects; β_{ii} the regression coefficients of squared effects; β_{ij} the regression coefficients for interaction effects and ε is error. For this study, the second-order model was satisfactory enough for analysis of sulfur removal efficiency. It is unlikely that a polynomial model will be a completely true approximation over the entire space of the independent variables, but for a relatively small region of variables of this research, it works quite well. The levels of the independent variables and their variation limits for gas oil sulfur removal efficiency of this work are presented in Table 2.

RESULT AND DISCUSSION

1. Model of Response Surface

We applied central composite design (CCD), which is a useful form of RSM, to optimize the parameters of desulfurization using ultrasonic process. Based on CCD, a relationship between the response and variables was obtained and expressed by the following second-order polynomial equation (Eq. (3)):

$$
\begin{aligned}
\text{Sulfur removal (\%)} = &\ 60.7298 + (0.8151 \times \text{Time}) + (1.8047 \times H_2O_2) \\
&- (1.9599 \times \text{Catalyst}) - [3.7466 \times (\text{Time})^2] \\
&- [3.7215 \times (H_2O_2)^2] - [2.2811 \times (\text{Catalyst})^2] \\
&- (1.2146 \times \text{Time} \times H_2O_2) \\
&- (6.5728 \times \text{Time} \times \text{Catalyst}) \\
&- (8.0661 \times H_2O_2 \times \text{Catalyst})
\end{aligned} \tag{3}
$$

The observed results and predicted values for sulfur removal are presented in Table 3.

Table 4 shows the results of the second-order response surface model of sulfur removal. Analysis of variance (ANOVA) is required to test the significance and suitability of the predicted model. As shown in Table 5, the F-test of the regression model produced very low P-value, which means that the obtained model has high impor-

Table 3. Experimental design and observed and predicted response values for the central composite design

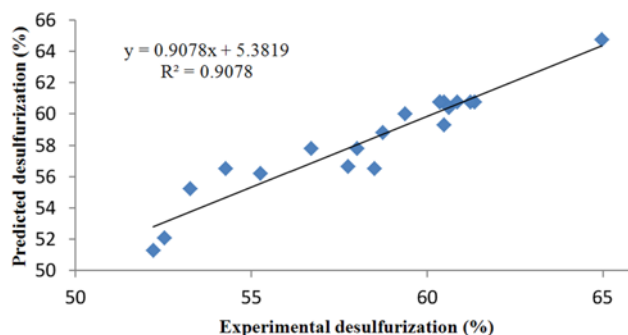| Run	Coded levels			Real values			Sulfur removal (%)	
	Time[a]	H_2O_2[b]	Catalyst[c]	Time	H_2O_2	Catalyst	Observed	Predicted
1	1	0	0	18.409	97.94	275	56.71	57.80
2	−0.595	0.595	0.595	5	146.91	423.651	57.76	56.61
3	0	1	0	10	180.298	275	58.76	58.81
4	0.595	0.595	−0.595	15	146.91	126.349	64.97	64.75
5	−0.595	−0.595	0.595	5	48.97	423.651	60.50	59.31
6	0.595	−0.595	−0.595	15	48.97	126.349	58.01	57.76
7	0	0	0	10	97.94	275	61.37	60.73
8	0	0	0	10	97.94	275	60.37	60.73
9	0	0	0	10	97.94	275	60.90	60.73
10	−0.595	−0.595	−0.595	5	48.97	126.349	52.23	51.29
11	0	0	0	10	97.94	275	60.50	60.73
12	0	0	−1	10	97.94	25	60.62	60.41
13	0	0	1	10	97.94	525	54.29	56.49
14	−1	0	0	1.591	97.94	275	55.26	56.17
15	0	−1	0	10	15.582	275	53.27	55.20
16	0	0	0	10	97.94	275	61.24	60.73
17	0.595	0.595	0.595	15	146.91	423.651	52.55	52.07
18	0	0	0	10	97.94	275	60.37	60.73
19	−0.595	0.595	−0.595	5	146.91	126.349	59.38	59.99
20	0.595	−0.595	0.595	15	48.97	423.651	58.51	56.49

[a] (min)

[b] (mmol)

[c] (ppm)

Table 4. Analysis of variances (ANOVA) for sulfur removal (%)

Source of variations	Freedom degrees	Sum of squares	Adjusted mean square	F-value	P-value
Regression	9	197.652	21.9613	10.94	0.000
Residuals	10	20.071	2.0071		
Total	19	217.723			

Table 5. Estimated regression coefficients and corresponding t values and P values

Term	Parameter estimate	Standard deviation	t-value	P-value
β_0	60.7298	0.5778	105.105	0.000
β_1	0.8151	0.6447	1.264	0.235
β_2	1.8047	0.6447	2.799	0.019
β_3	−1.9599	0.6447	−3.040	0.012
β_{11}	−3.7466	1.0555	−3.549	0.005
β_{22}	−3.7215	1.0555	−3.526	0.005
β_{33}	−2.2811	1.0555	−2.161	0.056
β_{12}	−1.2146	1.4167	−0.857	0.411
β_{13}	−6.5728	1.4167	−4.639	0.001
β_{23}	−8.0661	1.4167	−5.694	0.000

Model of UAOD process

$y = 0.9078x + 5.3819$
$R^2 = 0.9078$

Fig. 2. Predicted versus experimental values of sulfur removal (%).

employed to realize the pattern of interactions among the parameters. For each coefficient, larger magnitude of t-value along with smaller P-value indicates higher significance of that coefficient. In Table 5, it is clear that the importance of time and interaction between time and H_2O_2 was not significant.

The regression model had a high value of coefficient of determination (R^2=90.8%). The R^2-value provides a scale of variability in the observed response values by the independent variables and their interactions.

Fig. 2 has a comparison between calculated and experimental values of the response, confirming that the experimental values are in good agreement with the predicted values.

tance. The student's t-test was applied to recognize the importance of the regression coefficients of parameters. In addition, P-values were

Table 6. Optimal operating conditions maximizing desulfurization of gas oil

Time (min)	H_2O_2 (mmol)	Catalyst (ppm)	Sulfur removal (%)	
			Observed	Predicted
16.97	180.298	25.0	67.7%	69.1%

The response surface and contour plots of the predicted responses, while one variable is kept at constant value and the others vary, were obtained by the Minitab software and used to assess the relationships between the process variables and outputs for desulfurization of gas oil. Results of the optimization are shown in Table 6.

2. The Effect of H_2O_2 as an Oxidant Agent

The most significant part of an ODS process is the utilization of an oxidant. Hydrogen peroxide is the best common oxidant in the UAOD process. One of its advantages is that it does not pollute environment and its only byproduct is water. In oxidative process, H_2O_2 should decompose to produce free hydroxyl radicals. Each mole of liquid H_2O_2 makes one mole of hydroxyl radical. Catalyst ($FeSO_4$) could accelerate this reaction. Hydroxyl radical acts as oxidant for oxidation of sulfur components and can oxidize sulfides to sulfoxide and sulfons easier and faster than hydrocarbon compounds, then sulfur component can be oxidized selectively [17,47-49]. In this study, for investigating the effect of H_2O_2, different amounts of that in the range of 15.6 to 180.3 mmol were tested and results are shown in Figs. 3 and 4. As the amount of H_2O_2 increased, the amount of

released free radicals increased and then the yield of sulfur removal became better. However, according to economic considerations, H_2O_2 should not be used inconsiderably. In addition, it is important to minimize the use of oxidizing reagents and the consequent chemical residues.

According to Fig. 3, the interaction between H_2O_2 and catalyst was so important but as shown in Fig. 4, the interaction between H_2O_2 and time was not so significant.

3. The Effect of Time

One of the advantages of the UAOD process is that it demands a short time period. Desulfurization processes such as HDS and ODS need much time, but the UAOD process can be carried out in a short time (less than 20 minutes). In this study, the effect of process time was investigated in the range of 1.6 to 18.4 minutes. Results are presented in Figs. 4 and 5. It seems that the effect of increasing time is very important on the gas oil treatment. The yield of sulfur removal was increased with increase in the time. However, according to the figures, it is clear that after the optimum value of time, increase in time was not so effective for desulfurization and amount of sulfur removal did not change. Actually, the increase in time is beneficial for this process, but for reducing the operational cost it is necessary to find optimum time.

4. The Effect of $FeSO_4$

In ODS of diesel fuels, reaction rate constants can be greatly increased by adding metal ions as catalyst and using ultrasound. These can also reduce the apparent activation energy. The rate of reaction can be improved by using ultrasonic waves to destabilize the boundary layer between solid catalysts and reagents and mixing the homogeneous catalysts and reagent. The decomposition rate of hydrogen
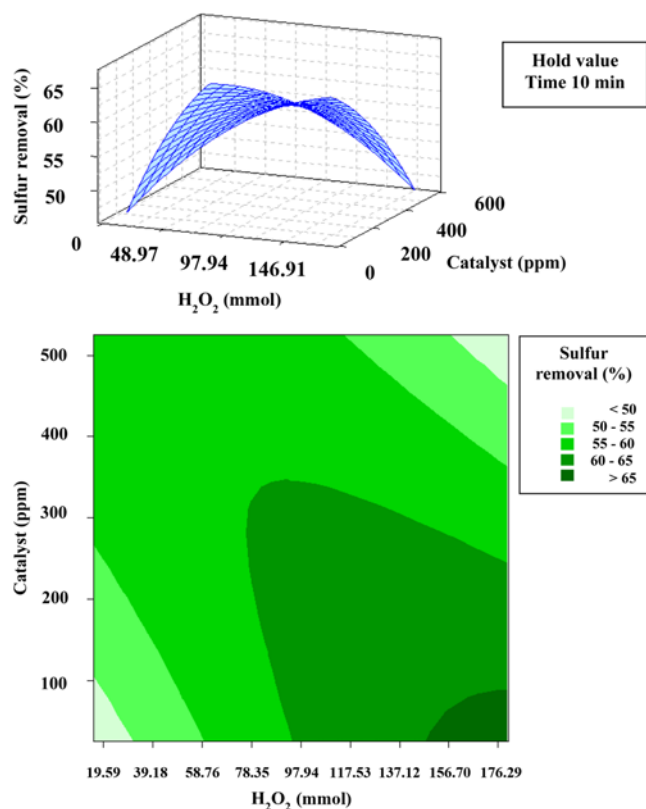

Fig. 3. Response surface and contour plots for sulfur removal efficiency as a function of H_2O_2 amount and catalyst concentration.
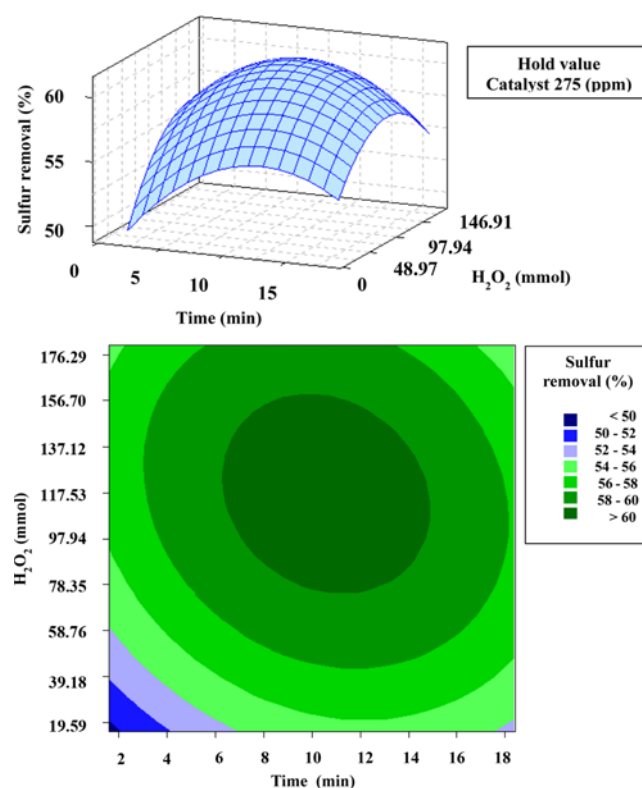

Fig. 4. Response surface and contour plots for sulfur removal efficiency as a function of time and H_2O_2 amount.
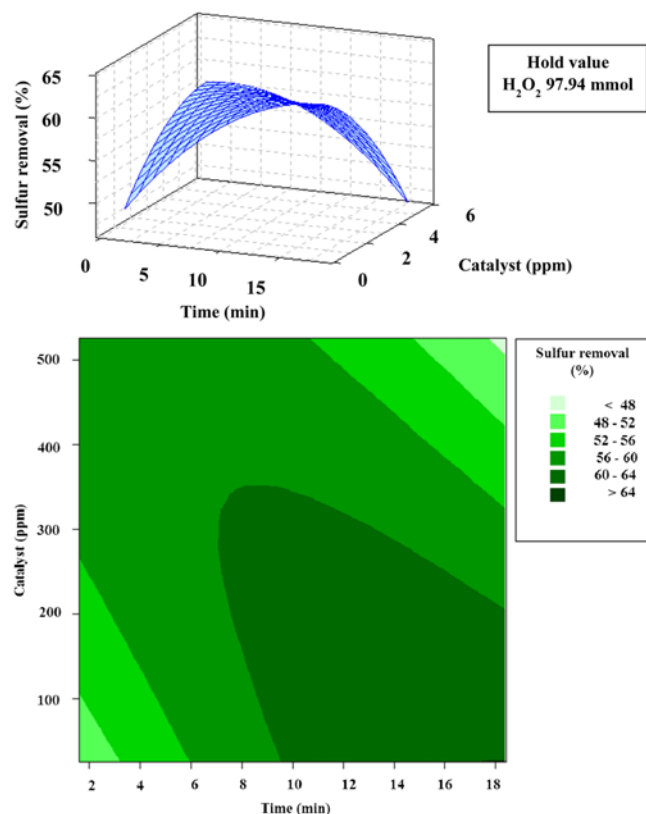
Fig. 5. Response surface and contour plots for sulfur removal effi-
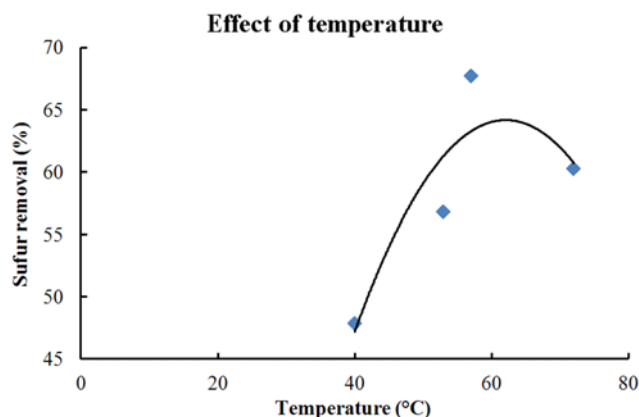ciencyas a function of time and catalyst concentration.

Fig. 6. Effect of temperature at optimum point (time: 16.97 min,
hydrogen peroxide amount: 180.3 mmol and catalyst amount:
25 ppm).

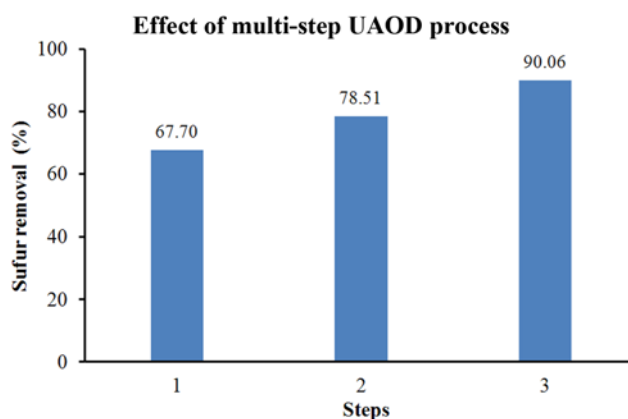
Fig. 7. Effect of multi-step UAOD process at optimum point (time:
16.97 min, hydrogen peroxide amount: 180.3 mmol and cata-
lyst amount: 25 ppm).

peroxide into hydroxyl radicals, when the reaction was catalyzed
by metal ions, was reported to be related to the aqueous phase pH
[51,52]. The effect of the aqueous phase pH on the catalytic activity
of the metal ion was studied by performing oxidation reactions of
gas oil with hydrogen peroxide under constant aqueous phase pH
values. On the basis of mechanism of oxidation reaction by metal
ions, high degradation efficiencies for a wide range of contaminants
have been achieved by using ferric ion. Because of high dependency
of iron species on pH values, these studies have been performed at
acidic pH [52].

Figs. 3 and 5, illustrate that the amount of catalysts has an opti-
mum point. If more than the optimum amount is used, undesired
adverse reactions will progress and the efficiency of the desulfur-
ization process will reduce.

5. Determination of Optimal Point by Response Surface Meth-odology and Minitab

The optimum condition for the sulfur removal reaction was deter-
mined by response surface method with results shown in Table 6.
According to these results, the highest achievable sulfur removal
yield in this experimental design is at 17 minutes, with maximum
amount of hydrogen peroxide and minimum concentration of $FeSO_4$
solution. The experimental sulfur removal percentage at the optimal
point was 67.7%, which is in good agreement with the predicted
value of the model (Table 6).

6. Experimental Results of the Optimal Point

6-1. Effect of Temperature

The sulfur removal reaction was carried out in optimal point at
different process temperatures of 40 °C, 53 °C, 57 °C and 72 °C. The

results (Fig. 6) demonstrate that temperature increase leads to high-
er desulfurization efficiency with maximum sulfur removal yield
achieved at 62 °C. Actually, increasing the temperature leads to the
accelerated oxidative reaction rate. More growth of temperature
beyond 62 °C results in decrease of the sulfur removal efficiency.
This is believed to be a result of hydrogen peroxide decomposition
and volatile compounds evaporation that occurs at temperatures
over 62 °C.

6-2. Multistep Procedure

To study the efficiency of employing a multistep procedure instead
of a single step one, the UAOD process was performed at deter-
mined optimum condition in single-, two- and three step procedures.
At the end of each step, the desulfurized gas oil was extracted by
methanol. The results are shown in Fig. 7. As it can be observed,
the single step procedure resulted in 67.7% sulfur removal; how-
ever, the two-step one improved desulfurization efficiency up to
78.51%, and the three-step procedure reached a 90% sulfur removal
yield. Using multistep procedures in the conditions can lead to better
result with less material and time.

6-3. Tetraoctyl Ammonium Bromide as Phase Transfer Agent

In this study, for the first time isobutanol was replaced with com-
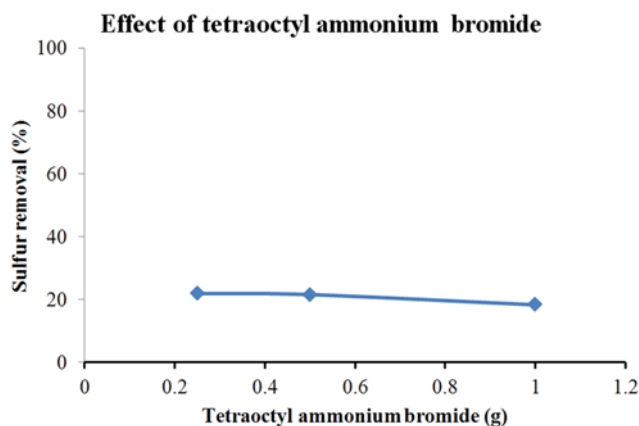monly used phase transfer agent tetraoctyl ammonium bromide.

Fig. 8. Effect of tetraoctyl ammonium bromide at optimum point (time: 16.97 min, hydrogen peroxide amount: 180.3 mmol and catalyst amount: 25 ppm).

Fig. 10. Effect of gradual increasing of H_2O_2 at optimum point (time: 16.97 min, hydrogen peroxide amount: 180.3 mmol and catalyst amount: 25 ppm).
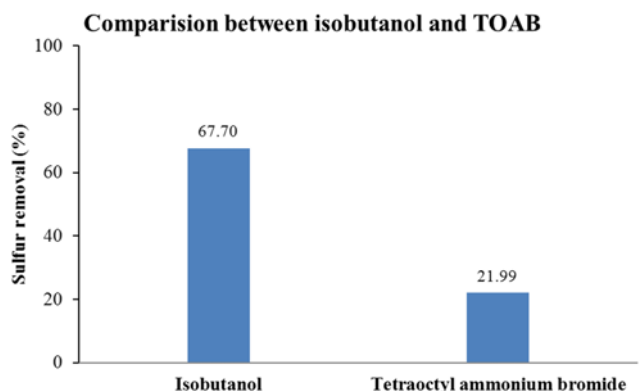

Fig. 9. Comparison between isobutanol and tetraoctyl ammonium bromide at optimum point (time: 16.97 min, hydrogen peroxide amount: 180.3 mmol and catalyst amount: 25 ppm).

Fig. 11. Effect of type of mixing instrument at optimum point (time: 16.97 min, hydrogen peroxide amount: 180.3 mmol and catalyst amount: 25 ppm).

To investigate the effect of this replacement on desulfurization efficiency, the process was carried out separately with these two phase transfer agents and the results were compared. The appropriate amount of tetraoctyl ammonium bromide for the process was determined by Fig. 8. This figure shows the effect of the amount of used tetraoctyl ammonium bromide on desulfurization efficiency. It was found that a higher amount of phase transfer agent leads to lower sulfur removal yield. The results of altering phase transfer agent are given in Fig. 9, which shows 67.7% and 21.99% sulfur removal for isobutanol and tetraoctyl ammonium bromide, respectively.

The commonly used tetraoctyl ammonium bromide is a type of quaternary ammonium salts (QAS) which is an external contamination that requires an extra separation step at the end of the process. However, isobutanol is a hydrocarbon that can be burnt as fuel. Furthermore, the other advantage of isobutanol is its cost, which is pretty much cheaper than tetraoctyl ammonium bromide.

6-4. Effect of Increasing Hydrogen Peroxide Gradually

It seems that it's better to add the hydrogen peroxide gradually because of the undesirable adverse reactions with catalyst ($FeSO_4$). So the sulfur removal reaction was carried out in the optimal point in two states. First, hydrogen peroxide was increased immediately at the beginning of the reaction time and in the second one it was
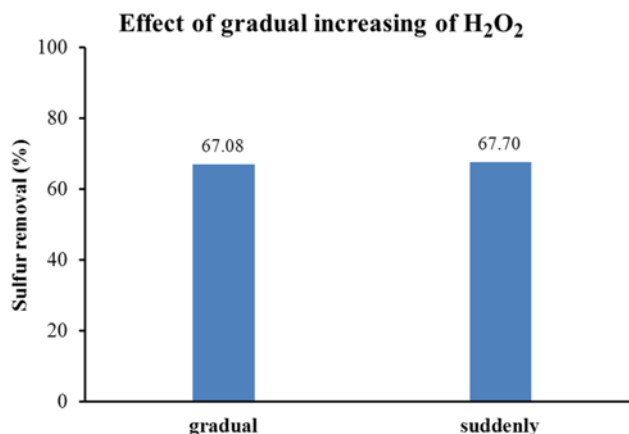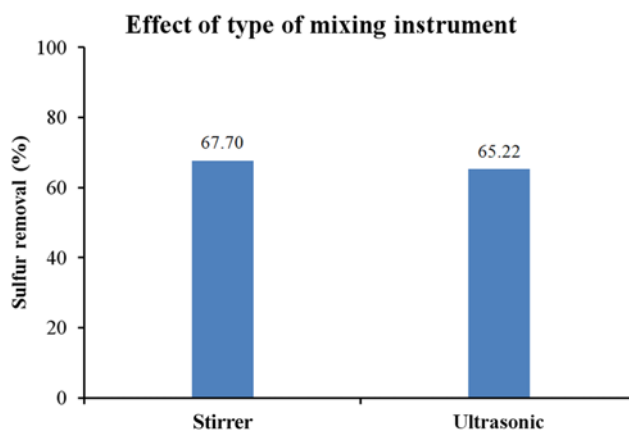
increased gradually by micro pump during the desulfurization process. At first the micro pump calibration equation was found and accordingly the flow rate of hydrogen peroxide was determined. Results are shown in Fig. 10. It can be seen that there are no significant changes in sulfur removal yield, because of the catalyst optimum amount, which is well selected for both states.

6-5. Effect of Ultrasound Wave at Extraction Step

The extraction process is the final and also a very important step in desulfurization technology. The efficiency of this process must be high enough to ensure all the desulfurized gas oil is recovered. The extraction process in this study was carried out by a liquid-liquid extraction using (methanol) as the solvent. This process is quite simple but requires an efficient mixing of the immiscible phases so that the maximum interface and subsequently maximum mass transfer take place between the phases. As indicated before, ultrasound waves and cavitation process supply a superior mixing condition which can be used at extraction step as well.

Gas oil extraction at the end of UAOD process was carried out at optimum point in two methods. In this section ultrasound waves and stirrer were used for extraction step. The results are shown in Fig. 11. According to that, these two methods had the same result.

According to the selected time and volume of methanol for the extraction step, oxidized sulfur component reached its maximum value for both methods.

CONCLUSION

Ultrasound irradiation combined with hydrogen peroxide as oxidant, $FeSO_4$ as catalyst, acetic acid as pH adjuster and methanol as extraction solvent were utilized to reduce the sulfur amount of gas oil. The effective factors studied in this work were time, amount of H_2O_2 and volume of catalyst solution, which was all adjusted in experimental design. Subsequently at the obtained optimal point, various temperature values, multistep procedure, tetraoctyl ammonium bromide usage and the way of increasing hydrogen peroxide were all tested. An increase in sulfur removal was observed when the amount of either H_2O_2 or time was increased, but it is important to minimize the use of oxidizing reagents and time because of economic considerations. Sulfur removal was of higher efficiency when catalyst solution volume was lower.

At the optimum point temperature increase leads to higher desulfurization efficiency with maximum sulfur removal yield achieved at 62 °C. More growth of temperature beyond 62 °C results in decrease of the sulfur removal efficiency.

Using multistep procedures improves the sulfur removal of gas oil. In this study, the three-step procedures of desulfurization of gas oil achieved 90% efficiency.

For the first time, isobutanol was used as phase transfer agent instead of quaternary ammonium salts (QAS). Because it has economical domination, it does not act like contaminant and additionally has more efficiency in sulfur removal.

There are no significant changes in sulfur removal yield between increasing hydrogen peroxide immediately at the beginning of the reaction time and increasing it gradually by micro pump during the process. So it shows the amount of catalyst is well-selected for both states.

At the end of ultrasound irradiation at the optimal point, there were no changes between using ultrasound waves and stirrer for extraction step.

The highest sulfur removal of about 67.7% for gas oil containing 9,500 mg/kg of sulfur was obtained during 17 minutes of the process at 62±2 °C when 180.3 mmol of H_2O_2 was used and extraction steps were done by methanol.

The UAOD process allowed great efficiency for sulfur removal in mild conditions such as atmospheric pressure and low temperature, in comparison with conventional methods; thus, the operating cost was lower and the safety was higher. There is a high potential for further improvements in the UAOD process of gas oil desulfurization and more studies should be done.

REFERENCES

1. J. G. Speight, *Handbook of petroleum product analysis*, Wiley-Interscience (2002).
2, F. M. Collins, A. R. Lucy and C. Sharp, *J. Mol. Catal. A: Chem.*, **117**, 397 (1997).
3. H. Mei, B. W. Mei and T. F. Yen, *Fuel*, **82**, 405 (2003).
4. Y. Nie, C.-X. Li and Z.-H. Wang, *Ind. Eng. Chem. Res.*, **46**, 5108 (2007).
5. C. Song, *Catal. Today*, **86**, 211 (2003).
6. C. Song and X. Ma, *Appl. Catal. B: Environ.*, **41**, 207 (2003).
7. V. Ukkirapandian, V. Sadasivam and B. Sivasankar, *Petroleum Science and Technology*, **26**, 423 (2008).
8. K. Yazu, Y. Yamamoto, T. Furuya, K. Miki and K. Ukegawa, *Energy Fuels*, **15**, 1535 (2001).
9. I. V. Babich and J. A. Moulijn, *Fuel*, **82**, 607 (2003).
10. F. Zannikos, E. Lois and S. Stournas, *Fuel Process. Technol.*, **42**, 35 (1995).
11. M. F. Ali, A. Al-Malki, B. El-Ali, G. Martinie and M. N. Siddiqui, *Fuel*, **85**, 1354 (2006).
12. A. Deshpande, A. Bassi and A. Prakash, *Energy Fuels*, **19**, 28 (2004).
13. M. Te, C. Fairbridge and Z. Ring, *Appl. Catal. A: Gen.*, **219**, 267 (2001).
14. A. Attar and W. H. Corcoran, *Ind. Eng. Chem. Product Res. Development*, **17**, 102 (1978).
15. H. Farag, *J. Colloid Interface Sci.*, **348**, 219 (1996).
16. J. Gui, D. Liu, Z. Sun, D. Liu, D. Min, B. Song and X. Peng, *J. Mol. Catal. A: Chem.*, **331**, 64 (2010).
17. M. R. Hoffmann, I. Hua and R. Hochemer, *Ultrasonics Sonochemistry*, **3**, S163 (1996).
18. M. Houalla, D. H. Broderick, A. V. Sapre, N. K. Nag, V. H. J. de Beer, B. C. Gates and H. Kwart, *J. Catal.*, **61**, 523 (1980).
19. X. Ma, K. Sakanishi, T. Isoda and I. Mochida, *Energy Fuels*, **9**, 33 (1995).
20. X. Ma, K. Sakanishi and I. Mochida, *Ind. Eng. Chem. Res.*, **35**, 2487 (1996).
21. F. van Looij, P. van der Laan, W. H. J. Stork, D. J. DiCamillo and J. Swain, *Appl. Catal. A: Gen.*, **170**, 1 (1998).
22. L. Vradman, M. V. Landau and M. Herskowitz, *Catal. Today*, **48**, 41 (1999).
23. E. Ito and J. A. R. van Veen, *Catal. Today*, **116**, 446 (2006).
24. S. Otsuki, T. Nonaka, N. Takashima, W. Qian, A. Ishihara, T. Imai and T. Kabe, *Energy Fuels*, **14**, 1232 (2000).
25. M. Breysse, G. Djega-Mariadassou, S. Pessayre, C. Geantet, M. Vrinat, G. Perot and M. Lemaire, *Catal. Today*, **84**, 129 (2003).
26. P. De Filippis and M. Scarsella, *Energy Fuels*, **17**, 1452 (2003).
27. L. F. Ramirez-Verduzco, F. Murrieta-Guevara, J. L. Garcia-Gutierrez, R. S. Martin-Castanon, M. d. C. Martinez-Guerrero, M. d. C. Montiel-Pacheco and R. Mata-Diaz, *Petroleum Science and Technology*, **22**, 129 (2004).
28. Y. T. Shah, A. B. Pandit and V. S. Moholkar, *Cavitation reaction engineering*, Kluwer Academic/Plenum Publishers (1999).
29. G. Cravotto and P. Cintas, *Angewandte Chemie International Edition*, **46**, 5476 (2007).
30. E. B. Flint and K. S. Suslick, *Science*, **253**, 1397 (1991).
31. R. Gopinath, A. K. Dalai and J. Adjaye, *Energy Fuels*, **20**, 271 (2005).
32. T. J. Mason and J. P. Lorimer, *Applied sonochemistry: The uses of power ultrasound in chemistry and processing*, Wiley-VCH (2002).
33. K. S. Suslick, *Science*, **247**, 1439 (1990).
34. K. S. Suslick, Y. Didenko, M. M. Fang, T. Hyeon, K. J. Kolbeck, W. B. McNamara, M. M. Mdleleni and M. Wong, *Philosophical Transactions of the Royal Society of London. Series A: Mathematical, Physical and Engineering Sciences*, **357**, 335 (1999).
35. T.-C. Chen, Y.-H. Shen, W.-J. Lee, C.-C. Lin and M.-W. Wan, *J.*

Cleaner Production, **18**, 1850 (2010).

36. Y. Dai, Y. Qi, D. Zhao and H. Zhang, *Fuel Process. Technol.*, **89**, 927 (2008).

37. V. S. Sutkar and P. R. Gogate, *Chem. Eng. J.*, **155**, 26 (2009).

38. M.-W. Wan and T.-F. Yen, *Appl. Catal. A: Gen.*, **319**, 237 (2007).

39. C. Song, *Chemistry of diesel fuels*, Taylor & Francis (2000).

40. Y. Dai, D. Zhao and Y. Qi, *Ultrasonics Sonochemistry*, **18**, 264 (2011).

41. A. M. Dehkordi, M. A. Sobati and M. A. Nazem, *Chinese J. Chem. Eng.*, **17**, 869 (2009).

42 F. b. A. Duarte, P. b. A. Mello, C. A. Bizzi, M. A. G. Nunes, E. M. Moreira, M. S. Alencar, H. N. Motta, V. L. Dressler and R. M. M. Flores, *Fuel*, **90**, 2158 (2011).

43. P. d. A. Mello, F. d. A. Duarte, M. A. G. Nunes, M. S. Alencar, E. M. Moreira, M. Korn, V. L. Dressler and r. M. M. Flores, *Ultrasonics Sonochemistry*, **16**, 732 (2009).

44. H. Farag, *Energy Fuels*, **20**, 1815 (2006).

45. A. Rehorek, M. Tauber and G. Gbitz, *Ultrasonics Sonochemistry*, **11**, 177 (2004).

46. F. Al-Shahrani, T. Xiao, S. A. Llewellyn, S. Barri, Z. Jiang, H. Shi, G. Martinie and M. L. H. Green, *Appl. Catal. B: Environ.*, **73**, 311 (2007).

47. E. L. Bier, J. Singh, Z. Li, S. D. Comfort and P. J. Shea, *Environ. Toxicol. Chem.*, **18**, 1078 (1999).

48. K. Makino, M. M. Mossoba and P. Riesz, *J. Phys. Chem.*, **87**, 1074 (1983).

49. C. Petrier, M.-F. Lamy, A. Francony, A. Benahcene, B. David, V. Renaudin and N. Gondrexon, *J. Phys. Chem.*, **98**, 10514 (1994).

50. D. W. Sundstrom, B. A. Weir and H. E. Klei, *Environ. Progress*, **8**, 6 (1989).

51. O. Bortolini, F. Di Furia, G. Modena R. Seraglia, *J. Organic Chem.*, **50**, 2688 (1985).

52. B. G. Kwon, D. S. Lee, N. Kang and J. Yoon, *Water Res.*, **33**, 2110 (1999).