Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1088475

57 (2016) 17616–17623
August

Optimization analysis of mixing-assisted oxidative desulfurization of model sulfur compounds using commercial ferrate(VI)

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Received 6 February 2015; Accepted 13 August 2015

ABSTRACT

Mixing-assisted oxidative desulfurization of benzothiophene (BT) and dibenzothiophene (DBT) was investigated using commercial ferrate(VI). The effect of operating parameters such as temperature (50–70°C), agitation speed (7,600–14,000 rpm), and mixing time (10–30 min) were examined in relation to sulfur reduction. Optimization experiments were carried out using Box–Behnken design under response surface methodology to evaluate the significance of operating variables. Results show that optimum sulfur reduction of 84.35% for BT could be attained at 15.42 min, 12,198 rpm, and 52.22°C. Moreover, a 93.68% sulfur reduction for DBT could be achieved at 14.43 min, 8,704 rpm, and 51.26°C. Using the optimized conditions, diesel oil was oxidized and showed a sulfur reduction of 58.03 and 93.15% for BT and DBT, respectively.

Keywords: Benzothiophene; Box–Behnken design; Dibenzothiophene; Ferrate; Mixing-assisted oxidative desulfurization

1. Introduction

Petroleum and its fractions contain high amount of sulfur compounds where a significant portion would be transferred to fuels during the refining process [1]. Untreated diesel oil contains an approximate 1,000–1,500 ppm of organic sulfur compounds (OSCs), which are mainly composed of alkylbenzothiophenes (BTs) and alkyldibenzothiophenes (DBTs) [2,3]. Upon combustion, OSCs are converted into sulfur dioxide (SO_2) and particulate matter that leads to the formation of cloud condensation nuclei and acid rain [4]. Moreover, SO_2 causes poisoning of catalytic converters by occupying the sites designated for CO and NO_x reduction [5]. Therefore, environmental regulations in US and Europe have become more stringent and constituted a limited sulfur content in diesel of <10 ppm in 2011 [5–7]. Furthermore, Taiwan Environmental Protection Administration has reduced the sulfur level in diesel from 350 to 50 ppm in 2007 [2].

Currently, hydrodesulfurization (HDS) is utilized for the desulfurization of liquid fuels in petroleum refineries [8]. HDS is a hydrotreatment process where hydrogen is used to break up the bonds of

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sulfur-containing compounds to form hydrogen sulfide and hydrocarbons [1]. The process is highly effective in removing disulfides, sulfides, and thiols, but has difficulty in removing refractory polyaromatic sulfur compounds such as BT, DBT, and their derivatives [7]. These compounds have high resistance to hydrogenation and would require the use of a modified catalyst under severe reaction conditions, which translates to higher costs [9–12].

An alternative process called oxidative desulfurization (ODS) has the ability to operate under mild conditions without the consumption of hydrogen. The process involves selective oxidation of the divalent sulfur of BT and DBT via electrophilic addition reaction of oxygen atoms that forms sulfoxides and sulfones, which are easily removed from diesel by adsorption, distillation, or solvent extraction [13,14]. Previous studies on various oxidants of sulfur compounds such as H_2O_2, [3,8,10,15,16], Cu/titanium silicate-1 [9], H_2O_2–acetic acid [1,17], and *tert*-butyl hydroperoxide [18,19] have been reported.

In ODS, the oxidation efficiency can be enhanced through the application of an ultrasonicator [1–3,5,10], of which the method is called an ultrasound-assisted oxidative desulfurization (UAOD). However, the disadvantage of using UAOD is its difficulty to upscale in industries and high capital cost due to high energy utilization and addition of a sono-reactor, amplifier, and function generator, respectively [20]. In the study of Lu et al. (2014), an alternative process was investigated using a high-shear mixer that showed promising desulfurization efficiency that matches that of an ultrasonicator [20]. Nevertheless, there are limited studies in utilizing a high-shear mixer in ODS and no study has yet shown its use in conjunction with the Fe(VI) oxidation system.

Ferrate or Fe(VI), in the form of K_2FeO_4, has an estimated standard half-cell reduction potential of +2.20 and +0.72 V in acidic and basic media, respectively [21]. The oxidation potential of K_2FeO_4 in acidic medium is considered to be the strongest in comparison to $KMnO_4$, O_3, Cl_2, ClO_2, H_2O_2, and hypochlorite [13,22]. Moreover, K_2FeO_4 is an environmentally friendly oxidant since reduction of Fe(VI) would yield nontoxic Fe(III) compounds. A recent study has investigated the use of Fe(VI) in the ODS of BT and DBT in acidic medium [13]. However, there are limited optimization studies in utilizing a high-shear mixer with ODS in conjunction with the Fe(VI) oxidation system that are available in literature.

In this study, ODS of model compounds such as BT and DBT using Fe(VI) has been investigated. A Box–Behnken design under response surface methodology has been utilized for system optimization and to examine the effect of different operating parameters such as temperature, agitation speed, and mixing time. The effectiveness of mixing-assisted oxidative desulfurization (MAOD) using Fe(VI) on commercial diesel is evaluated using optimized conditions.

2. Experimental

2.1. Materials

Model sulfur compounds such as BT (97% purity) and DBT (99% purity) were purchased from Acros Organics (Taiwan) and Alfa Aesar (Taiwan), respectively. Toluene was acquired from Merck (USA) and glacial acetic acid was obtained from Panreac (Taiwan). Chemicals such as tetraoctylammonium bromide, aluminum oxide, and potassium ferrate (90% purity) were obtained from Sigma-Aldrich (Wisconsin, USA). Commercial diesel oil with sulfur content of 1426.8 ppm was provided by Taichin Global Company (Taichung, Taiwan).

2.2. Batch MAOD experiments

Model compounds such as BT and DBT were dissolved in toluene to produce a stock solution with initial sulfur concentration of 500 ppm. Experiments were carried out in a 50-mL round glass reactor. In a typical batch experiment, a predetermined volume of model compound, Fe(VI), and tetraoctylammonium bromide as the phase-transfer agent (PTA) were mixed using the optimal conditions based on a previous study [23]. The PTA aids the emulsification between organic and aqueous phases. Then, adjustment of pH in the reactor system was carried out using a 0.1 N glacial acetic acid until pH 4 was achieved. The mixture system was agitated using a high-shear mixer (T25 Digital Ultra-Turrax) under varying temperature, agitation speed, and mixing time. After the reaction, the mixture is cooled down and the oil phase was separated using centrifugation.

2.3. Statistical analysis using Box–Behnken method

In the present work, sulfur removal of BT and DBT using MAOD was optimized using Box–Behnken method under response surface methodology. A full experimental design methodology has been carried out to test the three operating parameters. Table 1 illustrates the independent variables and their respective values. The general form of the quadratic equation used in the optimization process is given by Eq. (1):

Table 1
The levels and experimental range of independent variables in an MAOD system

Factors	Levels		
	Low (−1)	Medium (0)	High (+1)
Mixing time (min), X_1	10	20	30
Agitation speed (rpm), X_2	7,600	10,800	14,000
Reaction temperature (℃), X_3	50	60	70

$$Y = \beta_0 + \sum \beta_a X_a + \sum \beta_b X_a^2 + \sum \beta_{ab} X_a X_b \tag{1}$$

where Y is the predicted response, β_0 is the coefficient of intercept, β_a refers to the linear coefficient, β_b is the square coefficient, and β_{ab} refers to the interaction effects. The experimental results were examined using analysis of variance (ANOVA) and Design Expert 7.1.4 software. The statistical analysis of the model and its coefficients were determined using the p-test and F-test.

2.4. Instrument analysis

Various sulfur compounds were analyzed quantitatively using a gas chomatograph (Agilent Gas Chomatograph, 7890A, California, USA) equipped with sulfur chemiluminescence detector and fused silica capillary HP-5 MS column with a thickness of 0.25-mm film (J&W, Scientific, USA). For analysis of BT, the oven temperature was initially set at 100℃ for 3 min, heated at a rate of 20℃/min up to 180℃, and retained for 3 min. Meanwhile, the DBT column temperature settings were set at 150℃ to reach 280℃ using heating rate of 20℃/min for 1 min. An X-ray fluorescence sulfur-in-oil analyzer (SLFA-2100 Horiba) was used in determining the sulfur content of diesel oil.

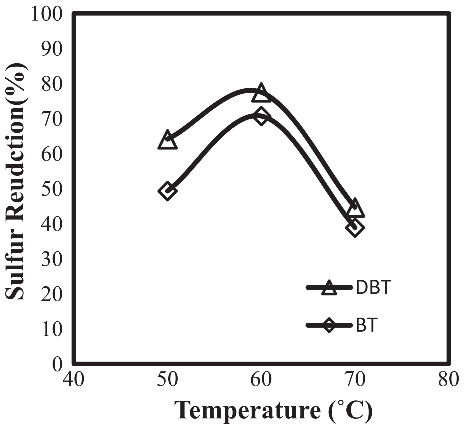

Fig. 1. Effect of temperature on sulfur reduction of BT and DBT using an MAOD system.

3. Results and discussions

3.1. Effect of temperature

To examine the performance of Fe(VI) in an MAOD system, the effect of temperature on sulfur reduction was investigated. In Fig. 1, results show that increasing the temperature from 50 to 60℃ caused an increase in sulfur reduction. The formation of Fe(VI)

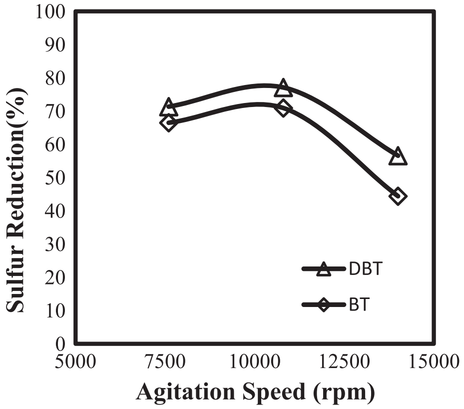

Fig. 2. Effect of agitation speed on sulfur reduction of BT and DBT using an MAOD system.

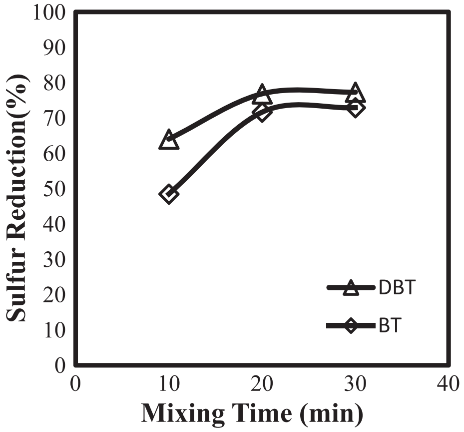

Fig. 3. Effect of mixing time on sulfur reduction of BT and DBT using an MAOD system.

complexes is favorable at high temperature, which leads to better oxidative activity and greater reduction efficiency. Results are similar to a previous study of Sachdeva and Pant (2010) for the ODS of diesel using peroxide [24]. Further increasing the temperature to 70˚C, sulfur reduction was observed to decrease remarkably from 70.92 to 44.40% and 77.10 to 56.60% for BT and DBT, respectively. This could be attributed to lower the Fe(VI) concentration due to its exothermic nature and low thermostability at high temperature [13,25].

3.2. Effect of agitation speed

In Fig. 2, results show that increasing the agitation speed from 7,600 to 10,800 rpm would lead to an increase in sulfur reduction. This is due to the formation of smaller and more uniformly shaped droplets at 10,800 rpm, which would indicate that Fe(VI) would be well dispersed at the interface [6]. Moreover, smaller emulsion droplets reduce the mass-transfer resistance of the system, which results in better oxidative capacity [24]. A drop in sulfur reduction was observed

Table 2
Observed percent (%) sulfur reduction for BT and DBT by Fe(VI) in the MAOD system using BBD experimental design

Run	Mixing time (min)	Agitation speed (rpm)	Temperature (˚C)	%BT reduction	%DBT reduction
1	30	14,000	60	65.48	71.85
2	20	10,800	60	70.92	73.04
3	20	7,600	50	65.58	87.90
4	10	10,800	70	69.65	64.53
5	20	10,800	60	71.64	77.10
6	10	14,000	60	81.57	62.68
7	30	7,600	60	63.63	67.38
8	10	10,800	50	75.80	89.14
9	10	7,600	60	63.77	85.23
10	20	7,600	70	60.94	79.76
11	20	14,000	70	68.22	70.07
12	30	10,800	50	69.65	71.21
13	20	10,800	60	70.70	74.01
14	20	10,800	60	72.82	76.85
15	30	10,800	70	65.14	78.48
16	20	14,000	50	75.80	81.82
17	20	10,800	60	72.06	77.47

Table 3
Results for ANOVA using a quadratic model for percent (%) sulfur reduction of BT and DBT using Fe(VI) in the MAOD system

	Conversion of BT			Conversion of DBT		
Source	F-value	p-value	Results	F-value	p-value	Results
Model	43.93	<0.0001	Significant	34.26	<0.0001	Significant
X_1	82.09	<0.0001	Significant	6.81	0.0349	Significant
X_2	156.48	<0.0001	Significant	48.64	0.0002	Significant
X_3	59.40	0.0001	Significant	58.89	0.0001	Significant
$X_1 X_2$	57.76	0.0001	Significant	61.98	0.0001	Significant
$X_1 X_3$	0.60	0.4652	Not significant	86.29	<0.0001	Significant
$X_2 X_3$	1.96	0.2041	Not significant	1.11	0.3273	Not significant
X_1^2	0.33	0.5825	Not significant	22.60	0.0021	Significant
X_2^2	28.32	0.0011	Significant	0.007	0.9374	Not significant
X_3^2	6.21	0.0415	Significant	24.31	0.0017	Significant
Lack-of-fit	2.15	0.2370	Not significant	0.35	0.7946	Not significant
	Adjusted R^2		0.9602	Adjusted R^2		0.9493
	Predicted R^2		0.8179	Predicted R^2		0.8991

at 14,000 rpm due to the formation of whirlpools in the system [6].

3.3. Effect of mixing time

As seen in Fig. 3, increasing the mixing time from 10 to 30 min would cause a corresponding increase in the sulfur reduction from 48.47 to 72.92% for BT and from 64.04 to 77.31% for DBT. At 30 min, there is longer mixing time between the organic and aqueous phases that implies an enhanced formation of emulsion leading to efficient sulfur to sulfone conversion. Sulfur reduction of BT and DBT were observed to slow down gradually until equilibrium is attained at 20 min.

3.4. Experimental design methodology

A total of 17 runs were carried out for the optimization study regarding sulfur reduction of model compounds using the Box–Behken method. Experimental values of sulfur reduction for BT and DBT obtained from optimization experiments are illustrated in Table 2. The sulfur reduction for BT and DBT was observed to be in the range of 60.94–81.57% and 62.68–89.14%, respectively.

In this study, the quadratic model was utilized in attaining the regression equation and correlation of experimental data. In addition, the determination of the response function coefficients (β_0, β_a, β_b, and β_{ab}) for the independent variables (X_1, X_2, and X_3) was done using experimental data. The response surface predictive model for BT and DBT in terms of percent (%) sulfur reduction (Y_1, Y_2) is given as Eqs. (2) and (3):

$$Y_1 = 71.50 - 3.36X_1 + 4.46X_2 - 2.86X_3 - 3.99X_1X_2 - 2.74X_2^2 - 1.29X_3^2 \tag{2}$$

$$Y_2 = 75.72 - 1.58X_1 - 4.23X_2 - 4.66X_3 + 6.75X_1X_2 + 7.97X_1X_3 - 3.97X_1^2 + 4.13X_3^2 \tag{3}$$

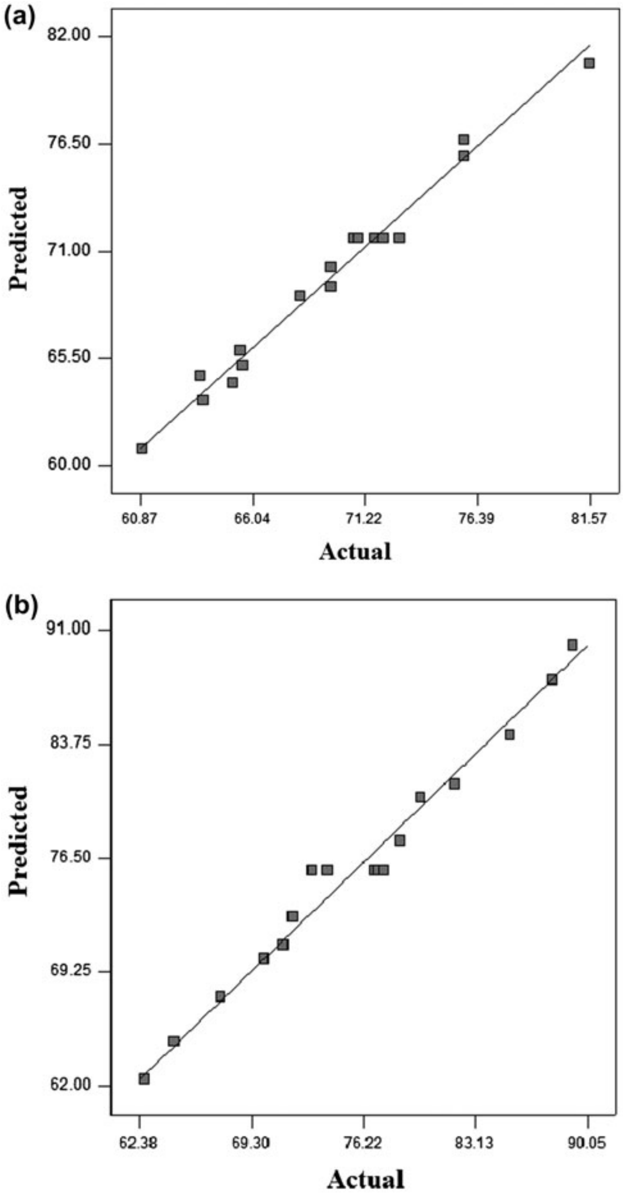

Fig. 4. Plot of actual and predicted values of percent (%) sulfur reduction of (a) BT and (b) DBT.

3.5. Statistical results

Results of ANOVA using the response surface quadratic model for BT and DBT are shown in Table 3. The significance of process parameters and their interaction is determined using the p-value and F-test. A small p-value (<0.05) would indicate statistical significance of the corresponding independent variable. On the other hand, a high F-value would indicate significance of the model terms where most of the variation in response could be explained by the quadratic model equation [26]. In BT reduction, factors and their interaction are considered to be significant except for X_1X_3, X_2X_3, and X_1^2. Specifically, X_1 and X_2 are extremely significant based on their high F-values ($X_1 = 82.09$ and $X_2 = 156.48$) and very low p-values (<0.0001). For DBT reduction, significant variables are determined to be the following: factors X_1, X_2, and X_2 and interacting factors such as X_1X_2, X_1X_3, and X_1^2. Furthermore, the interaction of X_1X_3 is determined to be extremely significant ($p < 0.0001$).

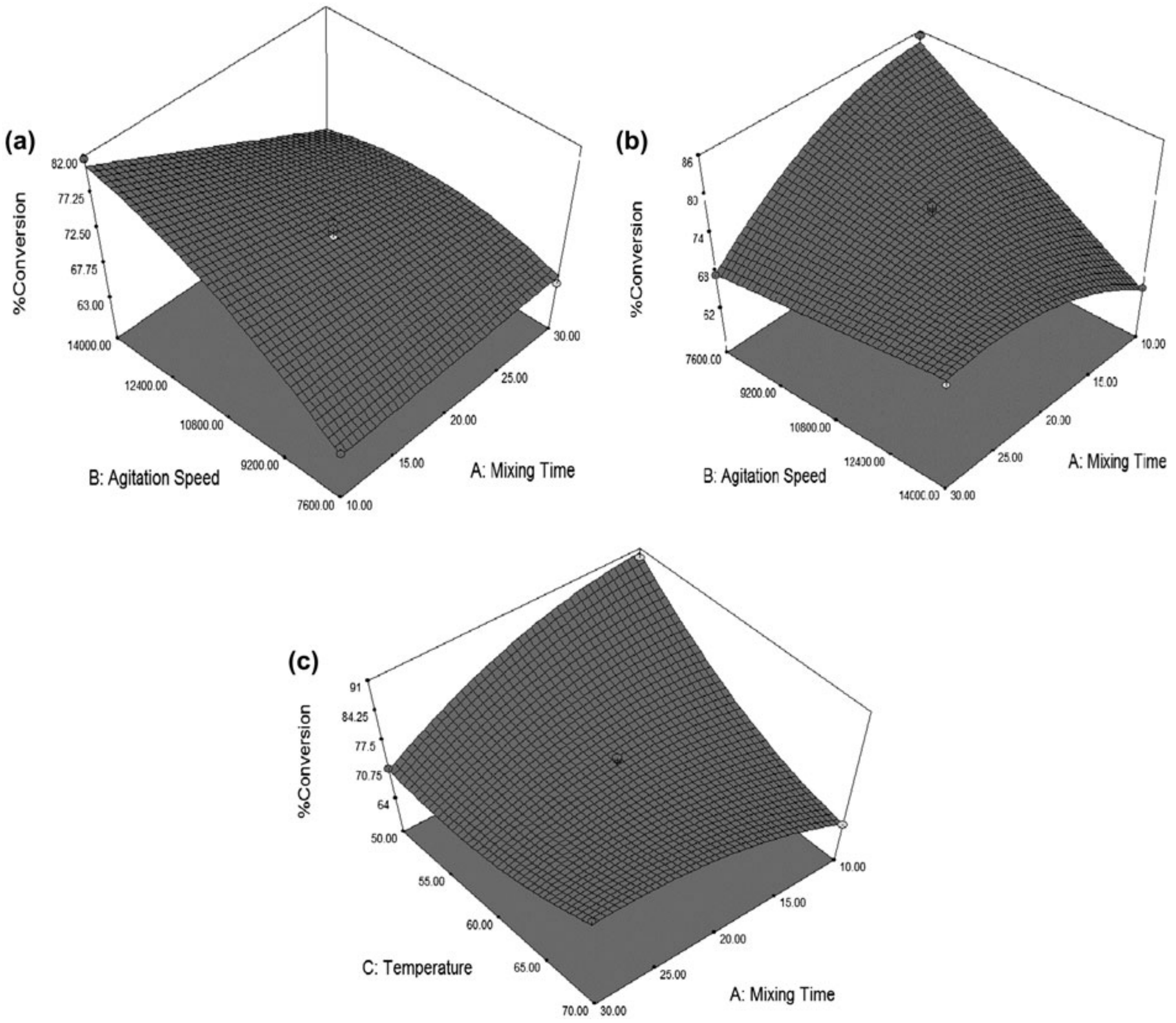

Fig. 5. 3-D surface plot of sulfur reduction as a function of (a) mixing time and agitation speed for BT, (b) mixing time and agitation speed for DBT, and (c) mixing time and temperature for DBT.

The adjusted correlation coefficient of BT ($R^2 = 0.9602$) and DBT ($R^2 = 0.9493$) confirms that the model is highly adequate in predicting the range of experimental variables. Moreover, the model is sufficient in navigating the design space that could be utilized in the optimization of BT and DBT.

Fig. 4 illustrates the plot of actual and predicted values of percent (%) sulfur reduction for BT and DBT, where a good agreement is observed. This indicates reliability and goodness-of-fit of the model. In Fig. 5, the 3-D response surface plots of sulfur reduction as a function of two parameters: mixing time and agitation speed for BT (Fig. 5(a)) and DBT (Fig. 5(b)), and mixing time and temperature for DBT (Fig. 5(c)).

3.6. Optimization and validation

Using the model, optimum conditions were determined to be 15.42 min, 12,198 rpm, and 52.22°C for BT with a predicted sulfur reduction of 82.09%. On the other hand, a 91.71% sulfur reduction for DBT would be attained at 14.43 min, 8,704 rpm, and 51.26°C.

To verify the accuracy and reliability of the model, three confirmatory runs were carried out using the optimum conditions. The mean sulfur reduction of BT and DBT is 84.35 and 93.68%, respectively. This indicates that the model used is adequate for the optimization study since the experimental data are in good agreement with the predicted results. Throughout the study, it was observed that DBT has a better sulfur reduction capacity than BT, which is attributed to higher value of the apparent rate constant and electron density of DBT [27].

3.7. Application to real diesel oil

Diesel oil with an initial sulfur content of 1428.60 ppm was treated in an MAOD system using optimum conditions. The sulfur reduction in diesel oil of 58.03% for BT and 93.15% for DBT was attained. Lower sulfur reduction of BT was observed, which is attributed to other background sulfur compounds present in diesel that could compete for the oxidative capacity of Fe(VI).

4. Conclusion

In this study, the sulfur reduction of model compounds such as BT and DBT using Fe(VI) in an MAOD system was investigated. Sulfur reduction of BT and DBT was observed to increase with increasing temperature, agitation speed, and mixing time. Response surface methodology with Box–Behnken method was utilized in predicting responses for all experimental regions. Results from ANOVA show that mixing time and agitation speed have significant effects on the reduction of BT and DBT. Moreover, interaction between mixing time and temperature has a significant effect on DBT reduction. The optimum sulfur reduction of 82.09 and 91.71% was attained using the following conditions: 15.42 min, 12,198 rpm, and reaction 52.22°C for BT and 14.43 min, 8,704 rpm, and 51.26°C for DBT. Diesel oil was treated using the optimum conditions where sulfur reduction of 58.03 and 93.15% was attained for BT and DBT, respectively.

Acknowledgments

The authors would like to acknowledge the National Science Council, Taiwan (NSC 100-2221-E-041-005) for the financial support.

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