

## A novel desulfurization practice based on diesel acidification prior to activated carbon adsorption

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**Abstract**—Commercial diesel is often rich with organosulfur compounds and a value of 7,100 mgS/kg was recently reported. As confirmed by chromatographic analysis, about 36% of sulfur compounds are originated from dibenzothiophene. Following uncommon desulfurization method, organosulfur compounds were efficiently removed upon diesel acidification by organic acids prior to activated carbon adsorption. Protonation of S-containing compounds has enhanced their uptake by activated carbon. Competitive adsorption of di/tri/tetra-aromatics and dibenzothiophene from synthetic fuel proved that the later solute was preferentially removed against other aromatics upon fuel acidification. Results showed that 48% of organosulfur compounds were eliminated upon adding acetic acid to a final content of 3% *by vol.*. Principal component analysis indicated that acid content and carbon mass are the most significant factors on organosulfur compounds removal: %Removal=5.8 (Acid Content)+6.3 (Mass)–0.02 (PD)–0.90 (Temp). The practical efficiency of the proposed method was demonstrated by removing organosulfur compounds from commercial diesel.

Keywords: Diesel Acidification, Organosulfur Compounds, Dibenzothiophene, Activated Carbon, Adsorption

### INTRODUCTION

The presence of organosulfur compounds (OSC) in diesel and gasoline fuels can cause toxic emissions and inefficient performance of exhaust catalysts [1,2]. Accordingly, efficient removal of OSC from diesel is an interesting research area that has attracted the attention of many researchers over the scientific community [1–3]. OSC are present in most fractions of crude oil distillation and higher boiling fractions (>270 °C) like diesel contain relatively more sulfur compounds of higher molecular weight [1]. Thiophene (T), benzothiophene (BT), dibenzothiophene (DBT) and their alkyl derivatives are the most abundant forms of OSC in diesel [2,3]. Particularly, BT and DBT are making more than 50% of OSC in some diesel samples [3]. Commercially, hydrodesulfurization is the most applied method for removing OSC from diesel [4]. Recently, oxidative desulfurization and adsorptive desulfurization were applied for removing OSC from diesel and other fuels [5]. The earlier methods are either of high cost or even not efficient for removing BT and DBT from diesel, hence, this initiated many researches to find another solutions for OSC removal [2,6]. Selective removal of OSC including BT and DBT from diesel using metal-loaded zeolite [7], natural aluminosilicates [8], and unmodified and modified activated carbons [9–11] was reported in the literature. Effective removal of H<sub>2</sub>S (and NH<sub>3</sub>) by activated-carbon-coated electrode was reported recently and this material would be used for removing S-compounds

from complex diesel matrix [9]. The high specific surface area, modifiable surface, high density of functional groups, and developed porosity make activated carbon (AC) a suitable adsorbent for OSC [12].

Adsorptive desulfurization by many adsorbents is a cost-effective process for OSC removal at ambient temperature and pressure [12]. The challenge of using AC for diesel desulfurization is the difficulty of removing OSC among other diaromatic/triaromatic compounds which often are present in large amounts [12,13]. Accordingly, selective adsorbents are required for effective adsorptive desulfurization process [2]. For effective OSC removal from diesel, activated carbon of acidic nature and higher micro/mesopore volumes are recommended [2,13].

We followed an uncommon experimental pathway for sake of OSC removal from diesel. Instead of surface modification to improve selectivity, diesel is acidified in preparation for OSC removal by activated carbon. Herein, acidification of diesel by different organic acids is adopted to improve OSC removal and avoid surface modification of the adsorbent. For this purpose, common organic acids (acetic acid, formic acid, oxalic acid and citric acid) were added to diesel for improving OSC removal from complex diesel matrix. Initially, influence of fuel (synthetic fuel) acidification on competitive adsorption of three aromatics and dibenzothiophene DBT was studied. Experimental factors affecting OSC removal were studied including acid type, acid content, diesel-to-carbon ratio, particle diameter, and temperature. Acid value of the treated diesel was also monitored. Kinetics of OSC adsorption from acidified diesel was investigated under different experimental factors. Kinetic data are presented with different models to elucidate adsorption mechanism upon acidification.

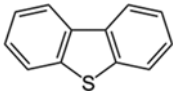
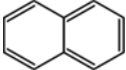
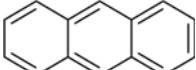
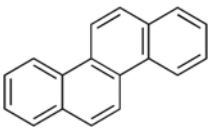
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**Table 1. Composition of synthetic fuel in the experimental adsorption test**

Compound	Structural formula	Concentration range		wt%
		mg/kg	mmol/kg	
Dibenzothiophene <b>DBT</b> C <sub>12</sub> H <sub>8</sub> S (184.3 g/mol)		100-4000	0.54-21.74	0.01-0.40
Naphthalene <b>NAP</b> C <sub>10</sub> H <sub>8</sub> (128.2 g/mol)		100-4000	0.78-31.25	0.01-0.40
Anthracene <b>ANT</b> C <sub>14</sub> H <sub>10</sub> (178.2 g/mol)		100-4000	0.56-22.47	0.01-0.40
Chrysene <b>CHR</b> C <sub>18</sub> H <sub>12</sub> (228.3 g/mol)		100-4000	0.43-17.54	0.01-0.40
<i>n</i> -Hexane		Solvent		49.20-49.98
<i>n</i> -Heptane		Solvent		49.20-49.98

## EXPERIMENTAL

### 1. Activated Carbon and Diesel

The employed carbon is a coal-based material supplied by Gainland Chemical Company (GCC, UK). The selected adsorbent is an effective adsorbent as indicated from the provided properties: specific surface area 985 m<sup>2</sup>/g, pore volume 0.52 cm<sup>3</sup>/g, average pore diameter 2.1 nm, surface acidity 0.57 mmol/g, surface basicity 0.83 mmol/g, and p*H*<sub>zpc</sub> (pH at zero point of charge) 9.3. A 200 g sample was sieved into different particle sizes (150-300, 300-500, and 500-800 μm) and the fractions were washed with distilled water and dried at 105 °C. A 100-liter diesel sample (0.840 g/cm<sup>3</sup> at 25 °C) was collected from a local fuel station. The sample was carefully filtered and kept in a closed polyethylene barrel before use. The total concentration of organosulfur compounds OSC expressed as mgS/kg was accurately made using X-ray fluorescence analyzer (SLFA-2100/2800 X-ray Fluorescence Sulfur-in-Oil Analyzers, Horiba, USA) in accordance with the standard test method for sulfur in petroleum products by wavelength dispersive X-ray fluorescence Spectrometry (ASTM D2622) [14]. As a significant organosulfur compound, dibenzothiophene DBT was targeted in the diesel using gas chromatography (GC). Before chromatographic analysis of complex diesel, standards of DBT ranging from 100 to 5,000 mgDBT/kg were prepared using S-free-*n*-hexane. Chromatographic separation of DBT was accomplished as follows: After injecting the sample, the temperature of GC column (HP-5 siloxane 5%, 15 m×0.53 mm i.d., 1.5 μm film thickness) was carefully programmed as follows: Initially, the temperature was maintained at 120 °C for 2 min then gradually increased by 10 °C/min up to 180 °C. The temperature was further increased to 290 °C with the rate of 12.0 °C/min. Helium gas of high purity was employed as carrier gas and injection temperature was fixed at 290 °C. Injection volume was 2.5 μL. Commercial diesel was diluted using *n*-hexane before chromatographic analysis. A linear calibration graph of DBT was created by plotting peak area vs. solute concentration.

### 2. Diesel Acidification by Different Organic Acids

1.0 M of acetic, formic, oxalic and citric acids were prepared

using ethanol. Different diesel/acid mixtures were prepared by adding appropriate amounts of the acid to end up with final levels of 1-5% *by vol*. The mixtures were carefully agitated in preparation for adsorption tests. All chemicals were obtained from Sigma®. Washing of adsorbents and preparation of acid solutions was by using distilled water and ethanol, respectively.

### 3. Adsorption Isotherms and Selectivity Studies Using Model Diesel

The competitive adsorption behavior of DBT against other aromatics that often present in diesel was studied using synthetic or model diesel system. Table 1 summarizes the experimental conditions adopted in the study.

Competitive adsorption tests were carried out using concentration variation method as follows: 1.0 g of dried activated carbon (300-500 μm diameter) was added to 140 mL model fuel (98.0 g) in 250 mL volumetric flask. The mixture was closed and agitated using a thermostated shaker (GFL, Germany) at 25 °C for 300 min, which is necessary to reach equilibrium. The test was conducted for eight solutions covering the ranges of solutes given in Table 1. At the end of the shaking period, the particles of activated carbon were removed by filtration, and then the equilibrium concentration of Dibenzothiophene (DBT), naphthalene (NAP), anthracene (ANT), and chrysene (CHR) was quantified using GC. The earlier GC protocol (section 2.1) was adopted to separate organic solutes from their mixtures with some modifications. For each solute, five standard solutions ranging from 100 to 5,000 mg/kg were prepared using *n*-hexane and injected in GC as described in section 2.1. Quantitative analysis of solutes in new samples was by using pre-constructed calibration graphs (concentration vs. peak area) for each solute. Surface concentration of a certain solute *q<sub>e</sub>* (mg/g) was estimated as:

$$q_e = \frac{(C_o - C_e) \times m_1}{m_2} \quad (1)$$

where *C<sub>o</sub>*, *C<sub>e</sub>*, *m<sub>1</sub>* and *m<sub>2</sub>* are the initial concentration (mg/kg), equilibrium concentration (mg/kg), mass of model diesel (kg), and carbon mass (g), respectively.

#### 4. Equilibrium and Kinetic Studies of OSC Adsorption from Commercial Diesel

Single-point adsorption test was adopted in this work. A 20.0 mL diesel sample was added to accurately weighted AC mass and the mixture was agitated for 300 min at a fixed temperature. The equilibrium time (300 min) was determined earlier from separate measurements. After that, diesel was filtered and analyzed for OSC in accordance to ASTM D2622 [14]. Effect of carbon mass, particle diameters, and temperatures on OSC removal was studied following the earlier experimental steps. Kinetic experiments were conducted at different particle diameters and temperatures. In all kinetic tests, 1,000 cm<sup>3</sup> diesel (containing 3% *by vol.* acid) and 50.0 g AC (L/S ratio 20 mL/g) were stirred mechanically at 250 rpm using Heidolph instrument (Heidolph, RZR1, Germany). For temperature studies, a thermostated water bath was used to stabilize temperature during OSC removal. Aliquots of diesel (1.0 mL) were taken at pre-selected intervals over the period 0-300 min. The samples were filtered and analyzed for total sulfur content (mgS/kg). The following equation was used to estimate %Removal of OSC:

$$\% \text{Removal} = \frac{(C_o - C_e)}{C_o} \times 100\% \quad (2)$$

where,  $C_o$  and  $C_e$  are the initial and equilibrium OSC concentrations, respectively. Equilibrium surface concentration  $q_e$  and surface concentration at time  $t$  were estimated from Eq. (1).

### RESULTS AND DISCUSSION

#### 1. Chromatographic Analysis of Aromatics, Dibenzothiophene and Diesel

Before analyzing the chromatographic results, the X-ray fluorescence analysis showed that the total concentration of OSC (given as total S) was 7100 ( $\pm 5$ ) mgS/kg. This level is extremely high when compared to the regulated value for diesel. According to the local standards, OSC content is twenty-times higher than the regulated value for commercial diesel (350.0 mgS/kg) [15]. The proposed chromatographic method was effective for separating aromatic hydrocarbons/DBT and for quantification of DBT, ANT, and NAP in complex diesel. Gas chromatographs are shown in Fig. 1.

A reasonable elution time was reported for DBT (7.74 min) as indicated from Fig. 1(a). A linear calibration graph was reported for DBT over the concentration range 100-5,000 mg/kg. Peak Area =  $41.0 C_{DBT} + 5982.4$  ( $R^2 = 0.9993$ ). The estimated detection limit ( $3\sigma$ ) and limit of quantification ( $10\sigma$ ) were 23.0 and 75.9 mg/kg, respectively. The earlier chromatographic procedure (that employed for DBT) was found applicable for separating all aromatics along with DBT as depicted in Fig. 1(b). All solutes were separated using HP-5 siloxane column with retention times of 1.01, 7.88, 8.45, and 14.11 min for NAP, DBT, ANT and CHR, respectively. The late elution of CHR was attributed to its higher molar mass among other solutes. Direct GC analysis of diesel ended up with highly overlapped peaks with high intensities and unstable baseline; however, chromatographic output was obtained when raw diesel was diluted 25-times with *n*-hexane (Fig. 1(c)). As indicated from Fig. 1(c), NAP, DBT, and ANT were reasonably identified in diesel. The estimated peak area of DBT signal was 30331, which is equivalent to 593 mgDBT/

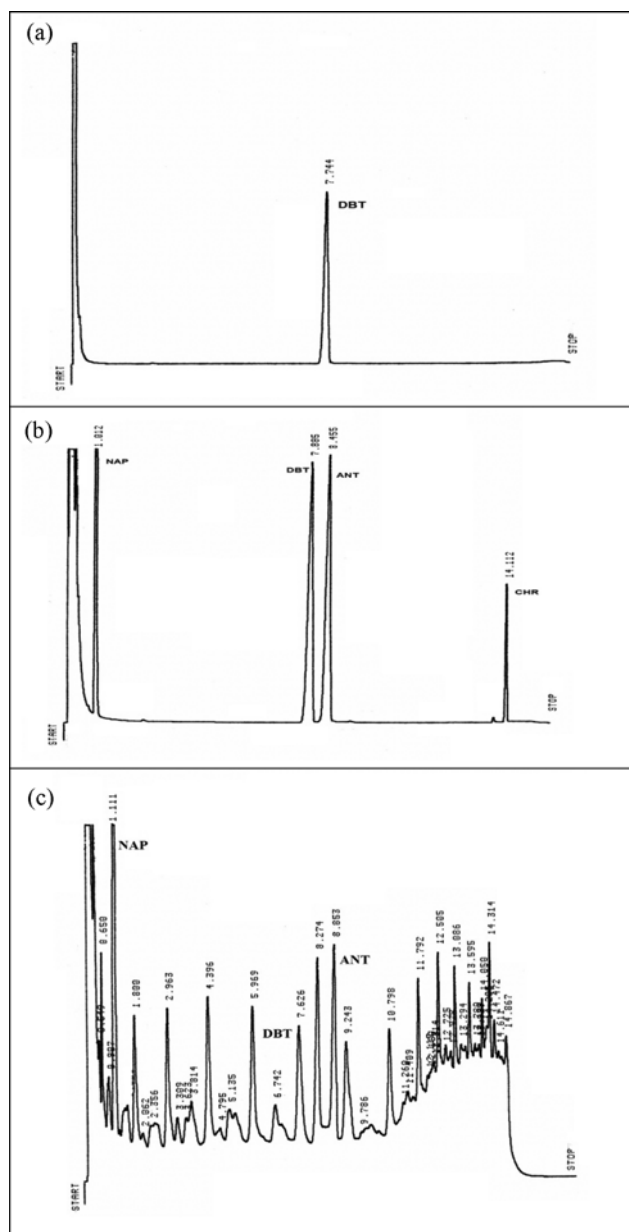


Fig. 1. GC chromatograms of DBT (1,000 mg/kg) (A); Aromatics and DBT (2,000 mg/kg) (B); Commercial Diesel (diluted with *n*-hexane 1 : 25) (C), as obtained by the proposed analytical procedure.

kg or 103.1 mgS/kg. Taking dilution factor in account, the level of sulfur content due to DBT is 2577.5 mgS/kg and this makes 36% of total OSC in diesel. Indeed, a large fraction of OSC in diesel is present as DBT and elimination of this hardly adsorbable compound is necessary at this stage. The content of NAP and ANT in diesel was estimated from their corresponding areas and found to be 4.33% and 2.45%, respectively. Note that the identity of NAP, ANT and DBT in diesel was also confirmed by analyzing spiked-diesel mixtures. Quantification of CHR was not carried out due to poor solute separation (peak appeared at 14.31 min) and unstable baseline as shown in Fig. 1(c). Indeed, diesel is composed of complex paraffins, cyclic hydrocarbons and OSC mixture, and identification of

each single component is a hard analytical task. The most important part in GC analysis is the detection and accurate quantification of DBT in complex diesel.

## 2. Adsorption of Aromatic Hydrocarbons and DBT and Fuel Acidification: Selectivity Studies

Aromatic compounds form a large fraction of diesel and negatively compete with OSC adsorption by AC [2,12]. Adsorptive removal of OSC is a promising method as it can be accomplished at ambient temperature and pressure and reduces unwanted OSC to a very low level [16]. To achieve the best selectivity and capacity for DBT or OSC removal, acidic surfaces of activated carbon are created for attracting more S-containing compounds [2,17]. However, in this work we proposed a different procedure for selective removal of OSC by diesel acidification using organic acids before desulfurization step. As will be shown later, adding acetic acid to diesel improved OSC removal to a large extent. To have a better picture, competitive adsorption of DBT, NAP, ANT, and CHR by AC in the presence and absence of acetic acid (5%) was studied using model fuel (Fig. 2). Running competitive adsorption tests is possible due to the accurate separation and quantification of the solutes as outlined in the earlier section. Competitive adsorption tests were conducted at comparable molar concentration ranges of the solutes as shown in Fig. 2. Adsorption isotherms are shown in Fig. 2 and modelling outputs and selectivity factors are summarized in Table 2.

As indicated in Fig. 2, typical L2 shapes (or Langmuir) were obtained based on Giles and Smith classification for the isotherms [18,19]. In Fig. 2, the surface concentration (y-axis) is sharply increased at lower solute concentration and then a gradual removal is observed at higher concentrations. In the current system, adsorption of aromatics and DBT by activated carbon (with and without fuel acidification) proceeded until a monolayer was accomplished and multilayer layer formation was mostly achieved. In L2 isotherms, a high adsorption is often observed at lower solute concentration. Activated carbon is effective for aromatics and DBT uptake at lower levels (100–1,500 mg/kg), but at higher levels (1,500–4,000 mg/kg), large amounts of aromatics are left over in the fuel. Similar adsorption isotherms were reported for DBT uptake by porous activated carbon [12,13]. L2-type isotherms are often observed in ionic-sol-

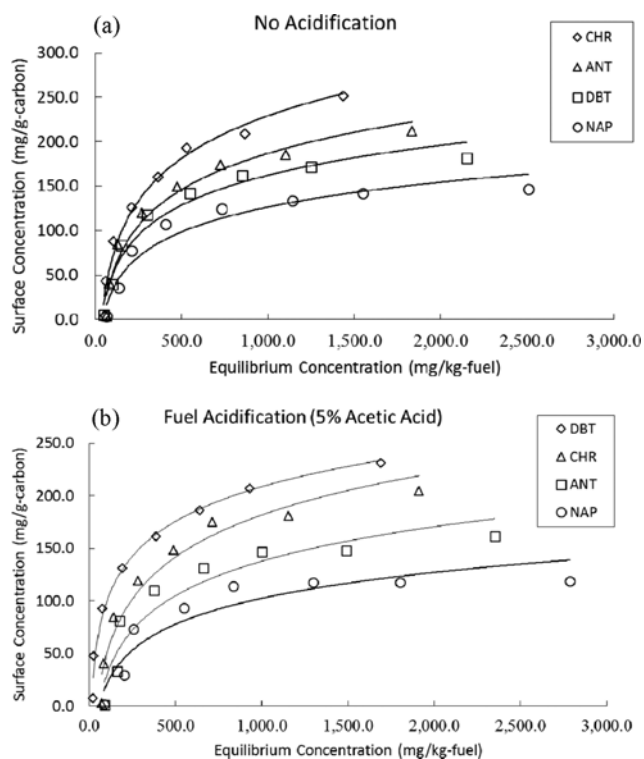


Fig. 2. Competitive adsorption of aromatic hydrocarbons and DBT before and after diesel acidification by 5% acetic acid. Conditions: fuel : carbon ratio 98.0 g·g<sup>-1</sup>, 25 °C, shaking time 300 min, and concentration ranges 100–4,000 mg/kg (Lines represent Langmuir fitting).

ute adsorption (e.g., metal cations and charged dye molecules) with weak competition with solvent molecules [18,19]. Accordingly, the favorable interaction of aromatics and DBT (mechanisms involving  $\pi$ - $\pi$  or S interactions) with poor competition of aliphatic solvent molecules has ended up with isotherms of L2 shape. As noted from experimental isotherms, fuel acidification by acetic acid has improved DBT removal among other aromatics. Further modelling of adsorption data by Langmuir and Freundlich equations and determination of selectivity factors were performed and the results

Table 2. Modeling competitive adsorption of aromatics hydrocarbon and DBT and selectivity factors

No acidification								
Solute	Langmuir model				Freundlich model			Selectivity factor
	$Q_{max}$ (mg/g)	$Q_{max}$ (mmol/g)	$K_L$ g/mmol	PRESS	$K_F$	$n$	PRESS	
NAP	166.7	1.30	622	45.3	15.62	0.25	177.3	1.00
ANT	238.1	1.33	858	39.6	20.89	0.34	110.3	1.43
DBT	203.4	1.10	720	36.1	17.30	0.29	88.3	1.22
CHR	307.3	1.35	952	55.2	22.13	0.39	144.7	1.84
Fuel acidification								
NAP	126.6	0.99	845	62.4	14.34	0.21	153.7	1.00
ANT	175.4	0.98	817	41.2	18.36	0.26	108.4	1.39
DBT	255.3	1.39	1140	63.0	24.55	0.37	111.3	2.02
CHR	227.3	0.99	908	56.7	21.33	0.33	96.4	1.79

are summarized in Table 2.

Langmuir and Freundlich equations were tested for modelling competitive adsorption of NAP, ANT, DBT, and CHR from model fuel, and the models were selected due to their popularity and their ability for handling competitive adsorption systems [19]. Langmuir model is simply presented as [19]:

$$q_e = \frac{Q_{max} K_L C_e}{1 + K_L C_e} \quad (3)$$

where  $q_e$  (mg/g<sub>carbon</sub>),  $C_e$  (mg/kg<sub>fuel</sub>),  $Q_{max}$  (mg/g<sub>carbon</sub>), and  $K_L$  (g·mmol<sup>-1</sup>) are the equilibrium surface concentration, the equilibrium solute concentration in fuel, the amount of solute adsorbed at saturation, and a constant related to the heat of adsorption [19]. The Freundlich model takes the general form [20]:

$$q_e = K_F C_e^n \quad (4)$$

where  $K_F$  and  $n$  are the model parameters that indicate adsorption affinity and adsorption intensity, respectively [20]. The degree of fitness, i.e., model to the experimental data, was assessed by finding prediction error sum of squares PRESS which is estimated as [21]:

$$\sum_{i=1}^n (q_{e,i \text{ pred}} - q_{e,i \text{ exp}})^2 \quad (5)$$

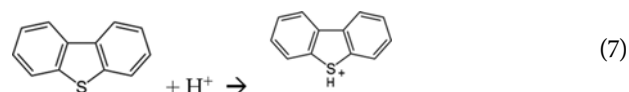
where  $q_{e, \text{pred}}$  and  $q_{e, \text{exp}}$  are the predicted and the experimental adsorption values, respectively.  $n$  is the number of experimental data. The parameters of both models were estimated following a non-linear fitting mathematical procedure using data-solver which is available in Excel<sup>®</sup>. On the other hand, selectivity factor was estimated from the maximum adsorption values ( $Q_{max}$ ) of competing solutes as follows:

$$\text{Selectivity factor} = \frac{Q_{max-\text{solute}}}{Q_{max-\text{NAP}}} \quad (6)$$

NAP was selected as a reference solute as it showed lower adsorption among other solutes.

As indicated in Table 2, all aromatics were removed from fuel with different amounts. However, in the absence of acetic acid, the maximum adsorption values were 307.3 and 238.1 mg/g for CHR and ANT, respectively. The adsorption trend of organics was increasing in the following order: NAP<DBT<ANT<CHR. The selectivity factor also confirmed the preferential uptake of CHR with a value of 1.84. The preferential uptake of the large CHR molecule (see Table 1) may reflect the ease of migration of all other solutes inside particles of activated carbon. Besides the developed porous structure of activated carbon, the surface functional groups are involved in complexation and attracting adsorbates from fuel. It is highly possible that  $\pi$ - $\pi$  dispersive interaction between aromatic rings and the graphene sheets of activated carbon has been controlling the overall adsorption process. Moreover, the acid/base mechanism was also involved in removing S-containing molecules. The earlier mechanisms were also theorized in the literature for removing S-containing aromatics and S-free-aromatics from model diesel [12]. As indicated from PRESS values (36.1-55.2), the Langmuir model was more suitable for presenting competitive adsorption of organics. The interesting point in Table 2 is the selective removal of DBT among other organics after fuel acidification by 5% acetic

acid. After acidification, the adsorption trend of solutes was increasing in the following order: NAP<ANT<CHR<DBT. DBT was preferably removed over other organics as also indicated from the selectivity values: 1.0, 1.39, 1.79, and 2.02 for NAP, ANT, CHR, and DBT, respectively. The favorable uptake of DBT upon acidification is attributed to the protonation of S atom, and hence enhancing the electrostatic attraction with the surface of activated carbon. The protonation reaction for DBT prior to surface removal was proposed as follows:



Protonation of other aromatics is not possible and the improved DBT uptake has been reduced uptake of other solutes. A large reduction was observed for ANT; the adsorption capacity was reduced by 26.3% after acidification. The distinguishing uptake of DBT is confirmed by the energy parameter;  $K_L$  was increased from 720 to 1,140 g/mmol after acidification and this large increment was not observed for other solutes. On the other hand,  $K_F$  values indicated the same removal trend of organics by activated carbon: 14.34, 18.36, 21.33, and 24.55 for NAP, ANT, CHR, and DBT, respectively. It seems that the employed adsorbent has a heterogeneous surface with active sites of variable energies as  $n$  values were less than unity in all cases [20]. Relatively speaking, the better performance of the Langmuir model (lower PRESS values than the other model) is a support to the assumption that adsorption of aromatics was accomplished with a minimum competition for active sites. The main conclusion of this part of the study is that DBT (a major component of OSC in many diesels) was preferentially removed among other di, tri and tetra-aromatics after fuel acidification.

### 3. Effect of Diesel Acidification upon OSC Removal from Commercial Diesel: Practical Application

Based on the earlier results, selective removal of DBT from commercial diesel is possible upon diesel acidification by acetic acid. In this, work we have proposed a different strategy to enhance OSC removal from diesel by activated carbon. The strategy is: Instead of modifying the surface of activated carbon, diesel was acidified with different organic acids to enhance the overall desulfurization process. The real application of the proposed strategy will be validated by desulfurization of a real diesel sample. The influence of acid type and content on OSC removal from commercial diesel was studied as shown in Fig. 3 and Table 3.

As indicated in Fig. 3, large improvement in OSC uptake was achieved for all tested acids. The best improvement was observed for acetic and oxalic acids with %Removal values of 40 and 45%, respectively. The significant enhancement in OSC removal indicated the efficiency of the proposed procedure. The proposed acidification method is much simpler when compared to modification procedures that employed for the surface of activated carbon. Yang and co-workers have improved DBT removal by activated carbon after surface modification by heating the surface at 900 °C and then refluxing the surface by concentrated H<sub>2</sub>SO<sub>4</sub> for 4.0 hrs [17]. In a similar study, acid treatment of activated carbon improved thiophene removal but significantly reduced DBT removal from synthetic fuel [22].

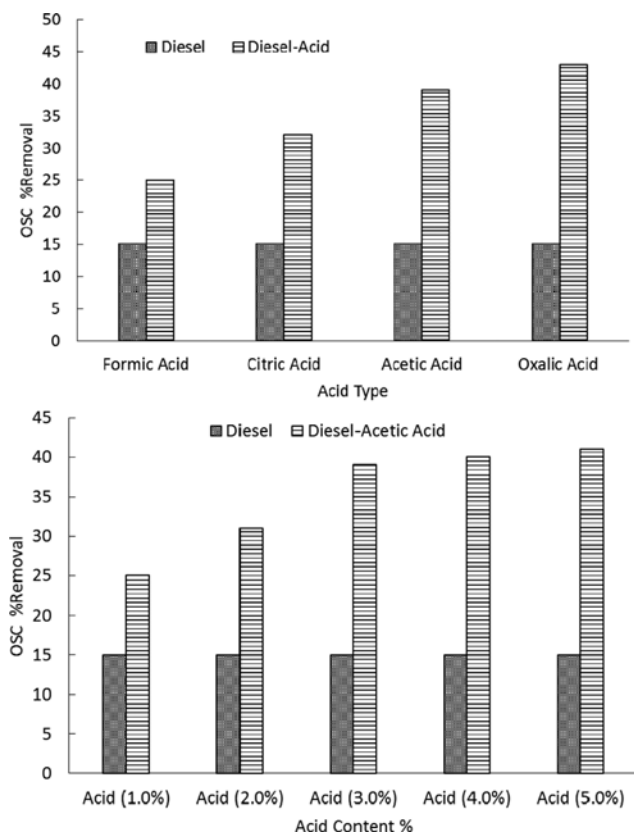


Fig. 3. Effect of acid type (3% by vol.) and content on OSC removal by AC. Conditions: OSC level 7100 ( $\pm 5$ ) mg/kg, diesel 20 mL, AC 1.0 g, particle diameter 300–500  $\mu\text{m}$ , 25  $^{\circ}\text{C}$ , and shaking time 300 min.

The efficiency of formic acid was lower compared to other acids where OSC removal was increased by 26% after acidification. Note that %Removal of OSC using acid-free diesel was 15.1% and this is equivalent to an adsorption value of 18.1 mgS/g. The earlier value is acceptable, taking into account the high content of mono and diaromatics in diesel which strongly compete with OSC adsorption [12,22]. As discussed earlier, enhancement of S-containing aromatics upon fuel acidification is due to protonation of S atom and then increasing electrostatic attraction to the surface. Accordingly, the high OSC uptake observed in oxalic acid is attributed to the high acidity ( $\text{p}K_{\text{a}}=1.25$ ) of the acid, which offers more protonation of OSC molecules. The lower performance of formic acid may be attributed to its lower solubility, and hence ionization in diesel. Due to its lower price and availability, acetic acid was the best candidate for diesel acidification. Fig. 3 and Table 3 also indicate that the content of acetic acid has a strong influence on OSC removal up to 3% by vol. and then, stable removal efficiency ( $\sim 40\%$ ) was observed. In fact, removal efficiency of 40% from diesel containing 7,100 mgS/g clearly indicates the effectiveness of the proposed procedure prior to AC adsorption. Further studies are necessary to measure acid content and other combustion properties of the treated diesel samples, especially after adding organic acids.

#### 4. OSC Removal from Commercial Diesel: Principal Component Analysis of Significant Factors

The combined influence of all experimental factors on OSC re-

Table 3. OSC removal from commercial diesel under different experimental parameters<sup>a</sup>

Parameter	OSC %removal	Adsorption value (mgS/g)
Acetic acid content (% by vol.) <sup>b</sup>		
0.0	15.1	18.1
1.0	26.7	31.8
2.0	32.3	38.5
3.0	39.4	47.0
4.0	40.6	48.4
5.0	41.2	49.1
AC mass <sup>c</sup> g		
0.5	29.2	69.7
1.0	39.5	47.1
1.5	41.3	32.8
2.0	43.4	25.9
Particle diameter <sup>d</sup> $\mu\text{m}$		
150–300	44.7	53.3
300–500	39.5	47.1
500–800	36.7	43.8
Temperature <sup>e</sup> $^{\circ}\text{C}$		
25.0	39.5	47.1
35.0	42.6	50.9
45.0	47.8	57.0

<sup>a</sup>In all tests, volume of diesel and OSC level are 20 mL and 7,100 mg/kg, respectively. The reported values were averaged of 3–4 identical tests with RSD 2–11

<sup>b</sup>AC mass 1.0 g, particle diameter 300–500  $\mu\text{m}$ , temperature 25  $^{\circ}\text{C}$ , and shaking time 300 min

<sup>c</sup>3% by vol. acid, particle diameter (PD) 300–500  $\mu\text{m}$ , temperature 25  $^{\circ}\text{C}$ , and shaking time 300 min

<sup>d</sup>3% by vol. acid, AC mass 1.0 g, temperature 25  $^{\circ}\text{C}$ , and shaking time 300 min

<sup>e</sup>3% by vol. acid, AC mass 1.0 g, particle diameter 300–500  $\mu\text{m}$ , and shaking time 300 min

moval was assessed using principal component analysis (PCA). Instead of studying the influence of each parameter on OSC removal, PCA can provide one general relationship correlating all parameters to OSC removal from diesel. By conducting 16 adsorption tests (Table 3), the influence of acid content, AC mass, particle diameter, and temperature on OSC removal was studied. A matrix of dimension 16 $\times$ 4 (16 experiments and 4 factors) and a response vector 16 $\times$ 1 (containing %Removal values) were generated from Table 3. PCA is a powerful statistical method that often used for factor analysis and modeling complex industrial processes [23]. PCA was carried out by using Matlab<sup>®</sup> [23]. Before applying PCA, the data were mean-centred and the following relation was obtained:

$$\begin{aligned} \text{\%Removal} = & 5.8 (\text{Acid Content}) + 6.3 (\text{Mass}) \\ & - 0.02 (\text{PD}) - 0.90 (\text{Temp}) \end{aligned} \quad (8)$$

The coefficients provided in Eq. (8) reflected the significance of variables on OSC removal, factor of higher coefficient is more sig-

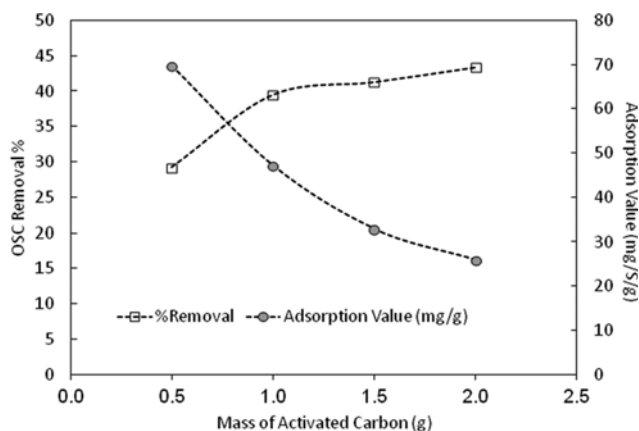


Fig. 4. Influence of AC mass on OSC uptake from diesel at 7,100 mgS/kg.

nificant. The results indicated that acid content and AC mass are being the most significant factors with positive coefficients of 5.8 and 6.3, respectively. It seems that variations in particle diameter and temperature have a slight influence on OSC removal as indicated from the small magnitudes of their coefficients. The main conclusion from PCA is that AC mass is the most significant factor on OSC adsorption, and this is attributed to the high affinity of OSC toward AC particularly after diesel acidification. The assessment of PCA modelling was made by estimating prediction error sum of squares PRESS and correlation coefficient  $r^2$  values. PRESS value was estimated as outlined earlier (Eq. (5)). The magnitudes of  $r^2$  and PRESS values reflected the fair modelling of OSC data by PCA, 0.8211 and 144, respectively. Among the studied experimental variables, mass of adsorbent is a significant variable, considering the high porosity and large surface area of AC. As can be noted in Table 3, both %Removal and adsorption value are going in opposite directions in response to mass of activated carbon. Fig. 4 depicts the relationship between %Removal and adsorption value of OSC as a function with AC mass at 7,100 mgS/kg.

As shown in Fig 4, increasing AC dosage from 0.5 to 2.0 gram has improved %Removal from 29 to 44%, while adsorption value has significantly reduced from 70.0 to 25.0 mgS/g. Even though %Removal was increased by mass, the actual adsorbed amount of OSC per unit mass of adsorbent is decreased. At higher dosages, more active sites are available for OSC uptake. It has been pointed out that the intersection point in Fig. 4 would present a balance between %Removal and extent of surface adsorption [24]. In Fig. 4, the intersection point is observed at 0.8 g, which is close to the mass selected in adsorption studies.

##### 5. Thermodynamics of OSC Removal by Activated Carbon

As indicated in Table 3, OSC removal was studied at different temperatures, which enables one to estimate thermodynamic parameters of the process. The following equation was used to find enthalpy  $\Delta H^\circ$  and entropy  $\Delta S^\circ$  of OSC removal by AC [25]:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

R is the ideal gas constant  $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ . Equilibrium distribution value  $K_d$  was estimated at different temperatures as follows:

$$K_d = \frac{C_s}{C_L} \quad (10)$$

where,  $C_s$  and  $C_L$  present OSC surface concentration (mg/g) and concentration in diesel (mg/mL), respectively. Plotting  $\ln K_d$  vs.  $1/T$  generated the following linear equation:

$$\ln K_d = -806.4 (1/T) + 5.28 \quad (r^2 = 0.9461).$$

The estimated  $\Delta H^\circ$  and  $\Delta S^\circ$  were 6.7 kJ/mol and 43.9 J/k-mol, respectively. The earlier values proved that OSC removal was an endothermic process and occurred with a net increase in the entropy of the entire system. Moreover, OSC removal is a spontaneous process at 25 °C with  $\Delta G^\circ$  value of -4.6 kJ/mol. Physical and chemical adsorption processes are classified to a certain extent based on the magnitude of  $\Delta H$ . It is accepted that bonding strengths of <84 kJ/mol are typically for those of physical adsorption type bonds. Chemisorption bond strengths can range from 84 to 420 kJ/mol [26]. Based on the earlier discussion, OSC removal by AC seems to be a physical adsorption process.

##### 6. Acidity of Desulfurized Diesel

Organic acids in diesel can cause corrosive wear of the fuel system. Significant wearing was observed for high sulfur diesel [27]. With the introduction of biodiesel fuel, there is some indication that organic acids could potentially increase, leading to more wearing [27]. Accordingly, acidity value of diesel fuel is an important index to be monitored after desulfurization taking into account the role of organic acids in the current process. A standard analytical procedure was adopted to test the level of acidity in all treated samples [28]. In all samples, the acidity value ranged from 0.09 to 0.6 mg/g, and 85% of tested samples have acidity less than 0.5 mg/g. The recommended acidity value of automotive fuels like diesel should not be higher than 0.5 mg/g [28,29]. Based on the earlier discussion, acidity value in most treated samples was lower than the regulated value, giving more applicability of the proposed procedure. It is essential to carry out other physicochemical tests, including density, viscosity, cetane number, water content, flash point, and higher heating value for treated diesel samples.

##### 7. Effect of Diesel Acidification on Adsorption Rate of OSC: Kinetic Studies

The earlier equilibrium studies confirmed the high selectivity for DBT removal and efficient OSC uptake from diesel under the influence of acetic acid. However, detailed kinetic studies are also important for assessing the practical application of the proposed method. For practical purposes and for more simplification, removal of OSC is often treated as a "single-component" adsorption, which facilitates presenting data by different kinetic models [10]. Kinetic data were modelled using reaction-based models due to the fast removal of OSC by AC. For reaction-based models, adsorption of OSC is considered reversible with equilibrium being established between the solution and the solid phase. For non-dissociating molecular adsorption OSC by AC, pseudo-first-order model is presented as [5]:

$$q_t = q_e (1 - e^{-k_f t}) \quad (11)$$

In pseudo-second-order model, OSC uptake at time  $t$  is presented as [5]:

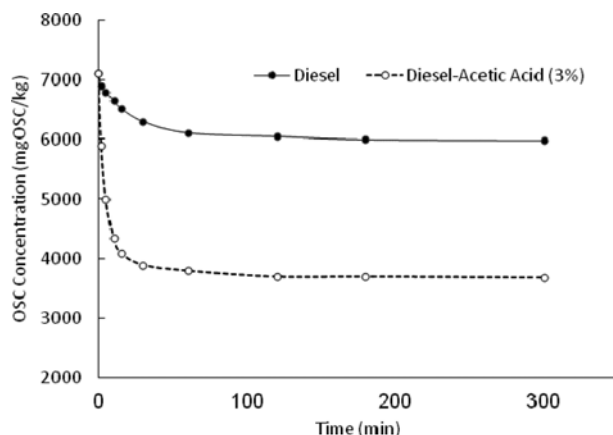


Fig. 5. Adsorption-time plot of OSC presented by pseudo-second order model. Filled circles: diesel (no acid added) and at 25 °C. Empty circles: diesel (3% by vol acetic acid) and at 45 °C. In both tests, particle diameter 300-500 µm, diesel 1,000 mL and AC mass 50.0 g.

$$q_t = tk_2 q_e^2 / (1 + tk_2 q_e) \quad (12)$$

where  $q_e$ ,  $q_t$ ,  $k_1$ ,  $k_2$ , and  $t$  are surface concentration at equilibrium (mgS/g), surface concentration at time  $t$  (mgS/g), pseudo-first-order rate constant ( $\text{min}^{-1}$ ), pseudo-second-order rate constant ( $\text{kg mg min}^{-1}$ ), and reaction time (min). The correlation of models to kinetic data was made by estimating PRESS as outlined earlier. Kinetic data and modelling results are presented in Fig. 5 and Table 4.

As indicated in Fig. 5, the adsorption rate of OSC increased as indicated from steeper slopes at the earlier stages of interaction, and then the process slowed down and stabilized at 180 min. The residual concentration of OSC at 300 min was found to be varied by ~1.5% than the one obtained at 180 min. So, a contact time of 180 min is reasonable for the system to reach a quasi-equilibrium situation. The high removal rate at early stages is attributed to adsorption by low-energy active sites. At later stages of the process, filling of the remaining high-energy active sites is difficult [5]. Comparable adsorption values were obtained from equilibrium and kinetic

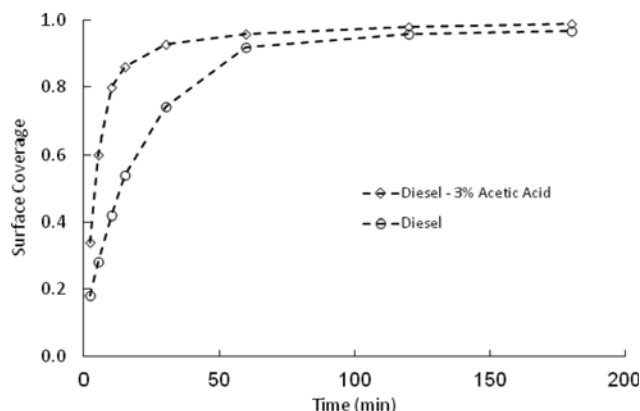


Fig. 6. Effect of acidification on kinetic OSC removal from diesel. Conditions: particle diameter 300-500 µm, diesel 1,000 mL and AC mass 50.0 g, and 25 °C. Surface Coverage =  $q_t/q_{300 \text{ min}}$ ,  $q_t$  and  $q_{300 \text{ min}}$  represented surface concentration at time  $t$  and 300 min, respectively.

studies (as indicated in Tables 3 and 4), and this is attributed to the similar experimental conditions for both tests. Diesel acidification has increased both adsorption capacity and removal rate of OSC by AC. Surface coverage  $\theta$  was monitored before and after acidification as shown in Fig. 6.

Surface coverage at time  $t$  was taken as  $q_t/q_{300 \text{ min}}$  assuming full surface coverage at 300 min. During the early stages of interaction (30 min), 90% of the surface was filled compared to 75% after diesel acidification as indicated in Fig. 6. Accordingly, adsorption rate of OSC was significantly increased after addition of acetic acid. Surface coverage was also estimated for other kinetic tests and the results showed that more than 60% of the surface was filled within 15 min upon adding acetic acid to oil phase. The estimated  $\theta$  values (at 10 min) at 25, 35, 45 °C were 0.56, 0.66 and 0.79, respectively. The earlier results indicated that faster adsorption was accomplished at higher temperatures where 79% of the surface was filled within 10 min at 45 °C. The faster rate is attributed to the decrease in diesel viscosity and hence higher molecular diffusivity of OSC at higher temperatures. Removal rate of OSC is controlled by

Table 4. Parameters of pseudo-first and second order models with PRESS values for OSC removal from commercial diesel<sup>a</sup>

Parameters	Pseudo-first order					Pseudo second order			
	$q_e$ Exp.	$q_e$ Model	$k_1$	$r^2$	PRESS	$q_e$ Model	$k_2$	$r^2$	PRESS
Temperature <sup>b</sup> , °C									
25.0 °C	46.8	51.5	0.05	0.7795	48.4	46.7	0.01	0.9535	1.5
35.0 °C	50.6	53.8	0.06	0.7683	45.4	50.0	0.03	0.8741	8.1
45.0 °C	57.4	59.6	0.07	0.8923	22.6	58.2	0.01	0.9211	10.4
Particle diameter <sup>c</sup> , µm									
150-300 µm	53.8	52.7	0.05	0.8996	19.1	53.2	0.06	0.9619	3.2
300-500 µm	47.3	51.4	0.04	0.7685	44.1	46.9	0.01	0.9741	0.8
500-850 µm	43.6	44.7	0.08	0.8892	17.6	44.0	0.04	0.9102	11.6

<sup>a</sup>In all tests, 1,000 mL diesel (7,100 mgS/kg and 3% by vol acetic acid) and 50.0 g AC were used

<sup>b</sup>Particle diameter 300-500 µm

<sup>c</sup>Temperature 25 °C



many factors including molecular sizes of OSC, concentration and affinity to AC, diffusion coefficient, pore size distribution of adsorbent, and agitation speed [5,12]. To study the dominating mechanism for OSC adsorption, two models were tested and the results are summarized in Table 4. The published research showed that reaction-based models (pseudo-first and second-order) and diffusion-based models (external and internal diffusion) are applicable for modelling OSC kinetics by different adsorbents including alumina, zeolite and activated carbon [5,10]. As indicated in Table 4, the pseudo-second-order model was more applicable for presenting OSC kinetics compared to the pseudo-first-order model as inferred from error-indicator values. Moreover, pseudo-second-order was more reliable for prediction adsorption values. As already known, the rate constant is a temperature independent parameter and hence, the observed variations in  $k_2$  may reflect the complex nature of adsorption process. In a related study, the pseudo-second order model was found excellent for presenting OSC (DBT) adsorption by alumina [5]. Based on kinetic analysis, OSC adsorption was accomplished in two main stages. Stage 1, AC surface was occupied by OSC in a short time due to diesel acidification. Stage 2, another slower step was started where OSC migrated within the pores of the adsorbent and the whole system reached equilibrium within 60 min due to efficient mechanical agitation. In fact, diesel acidification by 3% *by vol.* acetic acid is a promising procedure where OSC level is reduced from 7,100 to 3,700 mg/kg within 60 minutes of interaction as indicated in Fig. 5. Moreover, the better presentation of kinetic data by pseudo-second order model was also depicted in Fig. 5.

## CONCLUSIONS

A novel desulfurization procedure was proposed by adding organic acid to diesel prior to adsorption by activated carbon. Oxalic and acetic acids showed the best desulfurization results. OSC removal was found independent on the amount of acetic acid over the range 3-5%. Competitive adsorption studies of di/tri/tetra-aromatics and DBT from synthetic fuel revealed that adding organic acids has improved DBT removal among other solutes. PCA indicated the significance of AC mass and acid content on OSC removal compared to other factors. Thermodynamic analysis showed that OSC removal is a spontaneous process at 25 °C. Diesel acidification by acetic acid has increased OSC adsorption rate where 90% of the surface is occupied within 30 min compared to 75% without acidification. Kinetic data were best fitted to pseudo-second-order model. Acid value of treated diesel was within the regulated limit; however, more analysis related to diesel combustion properties is recommended after desulfurization.

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