



# Influence of diesel acidification on dibenzothiophene removal: A new desulfurization practice



Yahya S. Al-Degs<sup>a</sup>, Mohammad A. Al-Ghouti<sup>b,\*</sup>

<sup>a</sup> Department of Chemistry, The Hashemite University, P.O. Box 150459, Zarqa, Jordan

<sup>b</sup> Department of Biological and Environmental Sciences, College of Arts and Sciences, Qatar University, State of Qatar, P.O. Box 2713, Doha, Qatar

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## ABSTRACT

Commercial diesel is often loaded with organosulphur compounds including hard-to-remove dibenzothiophene DBT and other derivatives. Following uncommon and simple procedure, dibenzothiophene was selectively removed upon diesel acidification by acetic acid prior to activated carbon adsorption. Initially, competitive adsorption tests from synthetic fuel proved that dibenzothiophene is preferentially removed over di/tri and tetra-aromatic hydrocarbons upon fuel acidification by 5% (*by vol.*) acetic acid. The efficacy of the proposed method was further validated by removing dibenzothiophene from commercial diesel containing 2578 ( $\pm 15$ ) mg kg<sup>-1</sup>. The removal of DBT from complex diesel has increased from 27% to 55% upon acidification by 5% acetic acid. Acidity value of the treated diesel is within the regulated limit giving more chance for the new procedure for practical applications.

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## 1. Introduction

The existence of organosulphur 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 and attracted attention many researchers from different specialities [1–3]. OSC are present in most fractions of crude oil distillation, the higher boiling fractions (>270 °C) like diesel contain more sulphur 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 diesel [3]. Commercially, hydrosulfurization is the most adopted S-cleaning method from diesel [4]. Recently, oxidative desulfurization and adsorptive desulfurization were applied for removing OSC from diesel and other fuels [5]. The earlier reported methods are either of high cost or even not efficient for removing hardly adsorbable BT and DBT from diesel, hence, this initiated many researches to find alternative solutions for removing OSC [2,6]. Selective removal of OSC including BT and DBT from diesel using metal-loaded zeolite [7], natural aluminosilicates [8,9], and treated activated carbon [10,11] was reported.

The challenge of using commercial activated carbon in desulfurization is the difficulty of removing OSC among other diaromatic/triaromatic compounds which often present in large amounts in diesel [12,13]. Accordingly, selective adsorbents for OSC from diesel are required [2]. For effective OSC removal from diesel, special carbons of acidic nature and high micro and mesopore volumes are recommended [2,13].

In this work, uncommon desulfurization procedure for selective removal of DBT from diesel is proposed. Using model fuel, competitive adsorption of dibenzothiophene, naphthalene, anthracene and chrysene are investigated before and after acidification by acetic acid. The proposed method is further evaluated by removing dibenzothiophene from commercial diesel. Acid value of the treated diesel is monitored to be within the safe limits.

## 2. Experimental

### 2.1. Activated carbon and commercial diesel

A coal-based activated carbon was supplied by Gainland Chemical Company (GCC, UK). Physicochemical tests in our laboratory revealed that the adsorbent has a large 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 pH<sub>ZPC</sub> (pH at zero point of charge) 9.3. A 200 g sample was sieved and the particle size 300–500 μm was collected, washed with distilled water and dried at 105 °C. A 100-litre diesel sample (0.840 g/

\* Corresponding author. Tel.: +974 44036451; fax: +974 44034531.

E-mail address: [mohammad.alghouti@qu.edu.qa](mailto:mohammad.alghouti@qu.edu.qa) (M.A. Al-Ghouti).

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 organosulphur compounds OSC expressed as mgS kg<sup>-1</sup> was accurately made using X-ray fluorescence analyser (SLFA-2100/2800 X-ray Fluorescence Sulphur-in-Oil Analysers, Horiba, USA). Dibenzothiophene DBT (a major organosulphur compound) was targeted in diesel using gas chromatography as outlined in our earlier work [14].

## 2.2. Adsorption isotherms and selectivity studies using model fuel

Competitive adsorption behaviour of DBT in the presence of (naphthalene NAP, anthracene ANT and chrysene CHR) was carefully studied using synthetic diesel following the common concentration–variation procedure. Eight mixtures of the solutes (DBT, NAP, ANT, and CHR) at different levels were prepared using synthetic fuel (98.0 g of equal masses of *n*-hexane/*n*-heptane) with a final volume of 140.0 ml. For each solute in the mixtures, the concentration range was taken from 100 to 4000 mg/kg which corresponds to 0.54–21.71, 0.56–22.47, 0.44–17.52, and 0.78–31.20 mmol/kg for DBT, ANT, CHR, and NAP, respectively. For each mixture, 1.00 (±0.01) g of activated carbon was added and the mixtures were closed and agitated using a thermostated shaker (GFL, Germany) at 25 °C for 300 min which is necessary to reach equilibrium. At the end of shaking time, the particles of activated carbon were removed by filtration, and the equilibrium concentrations of DBT, NAP, ANT, and CHR were quantified using gas chromatography as outlined in the literature [14]. The surface concentration of a certain solute  $q_e$  (mmol/g-carbon) was estimated as:

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

where  $C_o$ ,  $C_e$ ,  $m_1$  and  $m_2$  are the initial concentration (mmol/kg-fuel), equilibrium concentration (mmol/kg-fuel), mass of fuel (kg), and carbon mass (g), respectively. Washing of the adsorbent and preparation of acid solutions were carried out using distilled water and ethanol, respectively.

## 2.3. Effect of acidification by organic acids on DBT removal from model fuel

Acidification of model fuel or commercial diesel by organic acids was carried out as following: 1.0 M of acetic, formic, oxalic and citric acids were prepared in ethanol. Different fuel/acid mixtures were prepared by adding appropriate volumes of the acid to fuel to end up with the desired level (1–5% by vol). The fuel-acid mixtures were carefully agitated before use in adsorption tests. All chemicals were obtained from Sigma®. The influence of fuel acidification on aromatics removal was studied following the experimental procedures that outlined in Section 2.2.

## 2.4. Effect of acidification of commercial diesel on dibenzothiophene: a practical study

The proposed desulfurization practice was evaluated by monitoring DBT removal from commercial diesel containing 2578 mgDBT/kg. Typically, 140 mL of acidified diesel was agitated with 1.0 g activated carbon (300–500 μm) for 300 min at 25 °C. Control experiments were carried out side-by-side but without adding any acid to the fuel. The final DBT content and other aromatics were quantified as mentioned in Section 2.1.

## 3. Results and discussion

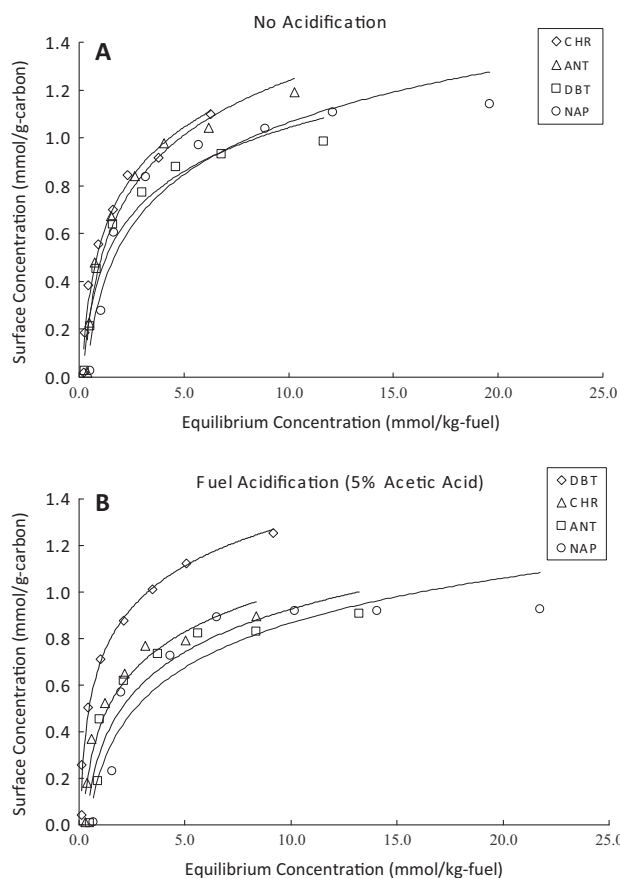
### 3.1. Level of organosulphur compounds and dibenzothiophene in commercial diesel

X-ray fluorescence analysis showed that the total concentration of OSC was 7100 (±10) mgS/kg. This level is extremely high when compared to the regulated limits [14]. Based on the chromatographic analysis, the content of DBT was 2578 (±15) mg/kg and this amount contributes to 36% of total sulphur in the fuel. Indeed, a large fraction of OSC in diesel is originated from DBT and the selective removal of this problematic compound is necessary.

### 3.2. Influence of fuel acidification on DBT adsorption: selectivity studies

Aromatic compounds are making a good fraction of diesel and they are negatively compete with dibenzothiophenes adsorption [2,12]. In this work, a new practice for selective removal of DBT was proposed by diesel acidification using organic acids. To have a better insight, competitive adsorption of DBT, NAP, ANT, and CHR by carbon in the absence and presence of 5% (by vol.) acetic acid was studied using model fuel and the results are shown in Fig. 1. Selectivity factors and the parameters of Langmuir model are also summarised in Table 1.

As indicated in Fig. 1, the isotherms have typical L2 shapes according to the Giles and Smith classification [16]. In Fig. 1,



**Fig. 1.** Competitive adsorption of cyclic aromatics and DBT from model diesel before and after diesel acidification by 5% by vol. acetic acid. Conditions: fuel:carbon ratio 140 ml/g, temperature 25 °C, shaking time 300 min, and concentration ranges of solutes 100–4000 mg/kg which corresponds to 0.54–21.71, 0.56–22.47, 0.44–17.52, and 0.78–31.20 mmol/kg for DBT, ANT, CHR, and NAP, respectively.

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