



# Ultra-deep desulfurization of diesel fuel via selective adsorption over modified activated carbon assisted by pre-oxidation



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## ARTICLE INFO

### Article history:

Received 18 September 2016

Received in revised form

14 May 2017

Accepted 20 May 2017

Available online 25 May 2017

### Keywords:

Adsorption  
Desulfurization  
Activated carbon  
Modification  
Sulfone

## ABSTRACT

Commercial adsorbents were tested for removing the dibenzothiophene sulfone (DBTO) from a model diesel fuel and organosulfur oxidized products (sulfones) from a real diesel fuel under ambient conditions. Activated carbons treated by concentrated H<sub>2</sub>SO<sub>4</sub> at high temperature showed increasing adsorption capacity and affinity towards DBTO. On the basis of adsorption tests and the characterization by BET, base titration, SEM, XPS, Visible-Raman and FTIR, the acidic-oxygenated groups incorporated to the surface act as adsorption sites for selective adsorption of sulfone. The specific interaction may be formed through the acid-base interaction involving the S=O group. Activated carbon treated by steam at 900 °C and followed by concentrated H<sub>2</sub>SO<sub>4</sub> at 250 °C displayed significantly enhanced DBTO adsorption performance and a sulfur capacity of 5.8 mg S/g adsorbent for removing organosulfur compound from a real diesel to less than 10 ppmw.

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## 1. Introduction

Deep desulfurization of liquid hydrocarbon fuels has become an increasingly important subject worldwide. The sulfur content in the transportation fuels is a very serious environmental concern. Globally, more and more stringent law has been enacted to limit the sulfur content in the transportation fuels worldwide. So world oil-refinery industry must meet these increasingly stringent regulations on the sulfur contents in the transportation fuels, especially in the diesel fuel due to its higher sulfur content. China government already reduced the limit of the sulfur concentration in diesel to 15 ppmw in 2014. In US, regulations have been set at 10 ppmw sulfur in diesel fuel from 2017. Conventional hydrodesulfurization technology (HDS) is very difficult to remove those refractory sulfur-containing compounds such as dibenzothiophene (DBT) and its derivatives, achieving an ultra-low sulfur level for diesel fuel. An

estimate showed that in order to reduce the sulfur level in diesel from 300 to less than 10 ppm, the HDS reactor volume needed to be increased by a factor of 15 at 600 psi, or by a factor of 5 at 1000 psi. This makes HDS an inappropriate solution for treating the whole (100 wt%) fuel in order to convert the fuel mass of less than 0.3 wt% (sulfur compounds). Thus, new technologies for deep desulfurization have been explored to meet the urgent needs to produce clean diesel fuel in recent years. Deep desulfurization via selective adsorption at ambient conditions is regarded as one of the most promising alternative strategy to replace the conventional HDS technology. The major challenge for adsorption desulfurization from the diesel fuel is to find an adsorbent that selectively adsorbs the aromatic sulfur compounds, but does not adsorb the co-existing aromatic hydrocarbons. This is because the aromatic sulfur compounds and aromatic hydrocarbons have some common features due to the presence of aromatic ring.

Many kinds of materials are promising adsorbent candidates for the removal of organic sulfur containing compounds from the transportation fuels. Xiong et al. reported BN mesoporous nano-wires as adsorbent for the adsorptive desulfurization (Xiong et al., 2015, 2016a,b). This material displayed outstanding adsorptive

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desulfurization activity for DBT ( $65.4 \text{ mg S g}^{-1}$  adsorbent). The significant enhancement of adsorption desulfurization performance of BN mesoporous nanowires was ascribed to the large number of low coordinated atoms along the nanowire surface and mesopores, which could cause an interaction with DBT. The doped oxygen atoms further strengthen the interaction. Danmaliki et al. prepared the activated carbon from waste rubber tires (Danmaliki and Saleh, 2016). The activated carbon was evaluated for adsorptive desulfurization of dibenzothiophene. It was found that the equilibrium adsorption is best fitted to the Freundlich isotherm model. Tan et al. reported magnetically responsive core–shell microspheres,  $\text{Fe}_3\text{O}_4@\text{C}$  as the adsorbent for the removal of aromatic sulfur and nitrogen compounds.  $\text{Fe}_3\text{O}_4@\text{C}$  are capable of removing thiophene ( $0.483 \text{ mmol g}^{-1}$ ), benzothiophene ( $0.476 \text{ mmol g}^{-1}$ ), indole ( $0.463 \text{ mmol g}^{-1}$ ), and quinoline ( $0.297 \text{ mmol g}^{-1}$ ) efficiently under ambient conditions (Tan et al., 2016). Shimoyama and Baba, (2016) reported thiophene adsorption on phosphorus- and nitrogen-doped graphites. It was found that phosphorus-doped graphite had an adsorption ability that was 10–20 times larger than that of nitrogen-doped graphite, indicating that the adsorptive desulfurization property of carbon largely depends on dopant atoms. Haji and Erkey reported the carbon aerogel as the adsorbent for the DBT removal (Haji and Erkey, 2003). It was found that the carbon aerogel with the larger average pore size had a higher sulfur adsorption rate and a higher capacity for DBT. Zhou et al. reported the carbon materials as the adsorbent for the multi-ring sulfur compounds removal (Zhou et al., 2006). It was found that the adsorption of multi-ring sulfur compounds on carbon materials obeyed the Langmuir isotherm and an increase in the oxygen-containing functional groups on the surface appeared to enhance sulfur adsorption capacity. Ania and Bandosz (2005) showed the importance of pore sizes and surface chemistry of AC for the adsorption of DBT from liquid phase. They proposed that the higher uptake might be linked to the large volume of narrow micropores and introduction of surface functional groups enhanced the adsorption performance of AC for DBT. Sano et al. reported AC as adsorbent for the sulfur removal (Sano et al., 2005). It was found that AC having higher surface area and surface polarity showed the higher total capacity for adsorption of sulfur species.

From practical view, the cost of the above-mentioned adsorbents material is expensive and most of the evaluation experiments limit to the model solution. Few reports involve the real feedstock. The interaction strength between the sulfur compound and the adsorbent surface is too weak to trap effectively the sulfur compound present in the real fuel, so it is still a challenging subject how to enhance the interaction and increase the adsorption selectivity to meet the practical demands, based on the cheap commercial adsorbent material system.

Here, we report the ultra-deep desulfurization of diesel fuel via selective adsorption over modified activated carbon assisted by pre-oxidation to enhance the adsorption interaction. It generally consists of two steps: 1) pre-oxidation of organosulfur compounds into corresponding sulfones to introduce the  $\text{S}=\text{O}$  group into the molecular structure of the organosulfur compounds; 2) selective adsorption of organosulfur oxidized products (sulfones) from the diesel via the enhanced direct interaction involving the  $\text{S}=\text{O}$  group. In our previous report, selective oxidation of organosulfur compounds in diesel fuel into sulfones has been achieved successfully (Lu et al., 2006). All sulfur-containing compounds in diesel fuel can be selectively oxidized into their corresponding sulfones using hydrogen peroxide as an oxidant at ambient conditions. Liquid–liquid extraction was used to remove the sulfones from the diesel fuel. But significant yield loss and poor sulfones removal ratio had been observed. Improvement of sulfones reduction could be obtained by raising the solvent-to-oil ratio in extraction of oxidative

diesel; however, this will cause a further increase in yield loss.

Several kinds of adsorbents have already been employed for the removal of the sulfones. Collins et al. used silica (Merck Silica Gel 60) to remove the oxidized sulfur compounds (sulfones) from the oxidative diesel (Collins et al., 1997). According to their report, the eluate with sulfur content of 50 ppmw could be obtained. Ryu et al. achieved the reduction of DBT from model solutions by coupling the oxidation of this compound, using an immobilized cytochrome c, to the selective adsorption of the produced sulfone on diatomaceous earth (Ryu et al., 2002). It was found that DBT-sulfone strongly adsorbed on Celite in highly hydrophobic organic solvents. The adsorbed DBT-sulfone could be desorbed from Celite by a simple washing with a less hydrophobic solvent. Sato et al. found that silica gel (Davison silica gel 923) had the highest throughput in reducing the benzothiophene sulfone in model naphtha (Sato et al., 2006). This silica gel could adsorb 5 mg sulfur/g of silica gel. The studies on adsorption of dibenzothiophene sulfone by an imprinted and stimuli-responsive chitosan hydrogel had been reported in the literature (Aburto and Le Borgne, 2004). The major specific adsorption of DBTS by the hydrogel occurred and was due to the stronger ligand-gel interactions. Eternadil and Yen found the acidobasicity of alumina was an important factor for providing adsorption sites for sulfones from fossil fuels (Etemadi and Yen, 2007a,b). The acidic alumina adsorbed 5.7 mg sulfur/g of alumina from an oxidized refractory sulfur compound and is capable of maintaining its capacity at more than 98% after calcining for regeneration. Adsorption of dibenzothiophene sulfone from fuel using chitosan-coated bentonite (CCB) as biosorbent has also been reported (Lu et al., 2016). Ogunlaja et al. reported the adsorptive extraction of sulfones from fuels by using molecularly imprinted chitosan materials (Ogunlaja et al., 2014). It was found that the molecular interactions between imprinted chitosan adsorbent and oxidized sulfur-containing compounds took place via hydrogen bonding. Microporous titania-silica nanocomposite has been used as catalyst-adsorbent for ultra-deep oxidative desulfurization (Bazyari et al., 2016). The titania-silica nanocomposite acts as both a catalyst and adsorbent simultaneously and is capable of removing more than 98% DBT to less than 10 ppm. DBT sulfone is more strongly adsorbed on (001) surface of silica than on (101) surface of anatase titania. A two-step energy-efficient sulfone adsorption separation process has been used for the production of ultralow sulfur diesel (Lim et al., 2012). It confirmed the potential to produce ultralow sulfur diesel with low energy consumption in a continuous separation process. Recently, mesoporous silica (Nanoti et al., 2009) and activated clay (bentonite) has been used for adsorption of sulfone compounds from diesel (Chen et al., 2016). The dynamic sulfur adsorption capacity is calculated to be 4 mg S/g of adsorbent. The acetone is able to completely desorb the sulfones from the adsorbent. In summary, the above-mentioned adsorbent system could be divided into two kinds: For commercial adsorbent such as silica gel, alumina and clay, the cost is cheap, but the capacity and selectivity to sulfones is poor; for novel high performance adsorbent such as biosorbent and nanocomposite, the cost is expensive. So there is still an urgent demand to tailor specific adsorbent with high adsorption capacity and high selectivity for sulfone removal, based on cheap commercial adsorption material.

Carbon materials, particularly activated carbons (AC) are potential adsorbents for the removal of sulfur compounds in the fuel. But the adsorption removal of sulfones over activated carbon adsorbent has few reports in the literature. The aim of this study is to tailor the adsorbent to remove the sulfones from the oxidative diesel, based on the commercial activated carbon adsorbent. It is expected that the acidic-oxygenated groups incorporated to the AC surface could act as adsorption sites for selective adsorption of sulfones and the direct interaction between the adsorbed sulfones

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