



# Effect of oxidative modification of coal tar pitch-based mesoporous activated carbon on the adsorption of benzothiophene and dibenzothiophene



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## ABSTRACT

This work examines the effect of modification of coal tar pitch-based mesoporous activated carbon (MC) by  $\text{HNO}_3$  oxidation on the liquid-phase adsorption of benzothiophene (BT) and dibenzothiophene (DBT) in the model fuel oil. The pore structure and surface properties of the MC samples were characterized by  $\text{N}_2$  adsorption, SEM, FT-IR and Boehm titration. The results show that after oxidative modification, the specific surface area decreased, while the mesopore ratio and the density of the surface oxygen-containing groups increased remarkably. Moreover, the average pore sizes of MCs were not changed. The oxidative modification considerably enhanced the adsorption capacity toward BT and DBT by 1.3 times and 0.9 times, respectively. The improved adsorption performance upon the  $\text{HNO}_3$  oxidation can be attributed mainly to an increase in the acidic oxygen-containing functional groups. The higher the concentration of nitric acid and the oxidation temperature were, the more the amounts of surface acidic oxygen-functional groups were, and thus the higher the amounts adsorbed of BT and DBT on corresponding carbon were. The resulting oxidized MC afforded a maximum capacity of 53.0 mg DBT and 32.8 mg BT  $\text{g}^{-1}$  of MC follow saturation kinetics with respect to the total acidity on the surface of the MC. The competitive adsorption effects of naphthalene and phenanthrene against DBT on the oxidized MCs are obvious, and the effect of phenanthrene is greater than that of naphthalene. The MCs could be easily regenerated by washing with toluene. The regenerated adsorbent afforded 98%, 95% and 91% of the initial adsorption capacity after the first three regeneration cycles, respectively.

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## 1. Introduction

Sulfur in transportation fuels remains a major source of  $\text{SO}_x$  which contributes to air pollution and acid rain [1]. Thus, the threshold limit for sulfur in fuel oil is expected to be regulated on a global level to zero in the future. Most of the sulfur removed from petroleum currently is achieved by the catalytic hydrodesulfurization (HDS) process. HDS is highly efficient at removing thiols, sulfides and disulfides, but it is less effective for aromatic thiophenes, especially the alkyl-dibenzothiophenes. Operation at higher temperature and pressure is inevitably required to remove these recalcitrant sulfur species. This brings forth a number of problems including high investment, high operating cost, reduction of the catalyst cycle length, and increase in the hydrogen consumption due to the hydrogenation of olefins and aromatics presented in fuels [2]. Consequently, several alternative approaches have been used, such as biodesulfurization [3], selective adsorption [4], extraction by ionic-liquid [5] and oxidative desulfurization (ODS) [6].

The adsorption desulfurization is one of the most promising desulfurization approaches because the adsorption process can be performed at ambient temperature and pressure [7]. Recently, mesoporous carbons (MCs) have been expected to be used as selective membrane [8], catalyst supports [9], biological reaction [10], sensors [11], electrochemistry [12], selectivity adsorption [13], and so on, owing to their highly ordered mesopore structure, large specific surface area and pore volume. However, the adsorption capacity of the MCs is not only related to the pore size and specific surface area, but also related to the surface chemical properties of the MCs [14]. In the meantime, none of adsorption desulfurization of fuel oil by cheap coal tar pitch-based MCs has been reported. Therefore, it is a highly desired goal to develop cheap MCs with improved adsorption capacity, high selectivity and regenerability. In the present work coal tar pitch-based mesoporous carbons were studied for adsorption of BT and DBT in the model fuel oil. The adsorbents were prepared by using nanosized silica as the hard template, followed by nitric acid oxidation. The structural order and textural properties of the MCs have been characterized by nitrogen adsorption, Fourier transform infrared (FT-IR), scanning electron microscopy (SEM) and Boehm titration. The effects of such factors as the pore structure and surface chemical properties on the adsorption efficiency of BT and DBT by the

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**Table 1**  
Porous structure parameters of MCs under different modification conditions.

Concentration of nitric acid (%)	Oxidation temperature (°C)	Oxidation time (h)	$S_{\text{BET}}$ ( $\text{m}^2 \cdot \text{g}^{-1}$ )	$V_{\text{mic}}$ ( $\text{mL} \cdot \text{g}^{-1}$ )	$V_{\text{total}}$ ( $\text{mL} \cdot \text{g}^{-1}$ )	Mesopore portion (%)
35	60	3	262.00	0.00074	1.7654	72.08
65	60	3	230.35	0.01303	1.0308	63.86
85	60	3	233.14	0.01499	0.8836	75.66
85	40	3	186.27	0.01464	0.6236	87.27
85	40	3	202.93	0.01159	0.7237	84.69
85	80	3	170.02	0.01172	0.5667	77.77
85	60	1	207.86	0.01565	0.7609	82.73
85	60	5	189.55	0.01439	0.5974	86.53

MCs have been studied. Competitive adsorption of naphthalene and phenanthrene has been performed to investigate the adsorption selectivity of the MCs, and regeneration was evaluated.

## 2. Experimental

### 2.1. Materials

All chemicals including anhydrous ethanol, potassium hydroxide, hydrofluoric acid, nitric acid, n-octane, hydrochloric acid, sodium hydroxide, sodium carbonate, sodium bicarbonate, benzothiophene (BT), dibenzothiophene (DBT), naphthalene (Nap) and phenanthrene (Phe) are analytical pure. Coal tar pitch was supplied by Jining Carbon Group Co., Ltd. A kind of commercial nanosized silica used as the imprinting template was supplied by Anhui Dedicated Nanotechnology Corporation (particle size 20 nm).

### 2.2. Characterization of MC

Nitrogen adsorption isotherms were obtained at 77 K using an accelerated surface area and porosimeter system (SA3100, Micromeritics). The BET equation was used to calculate the specific surface area ( $S_{\text{BET}}$ ). The total volume ( $V_{\text{total}}$ ) was evaluated at  $P/P_0 = 0.95$ , the  $t$ -plot was used to calculate micropore volume ( $V_{\text{mic}}$ ) and the mesopore volume ( $V_{\text{meso}}$ ) was calculated from the pore size ranging from 2 nm to 50 nm. The pore size distributions were calculated by the BJH method. The porous structures and surface morphologies of the samples were observed under scanning electron microscopy (SEM, Nova 400 Nano). FT-IR spectra ( $4000\text{--}500 \text{ cm}^{-1}$ ) were pressed with KBr in the ratio of 1:200.

### 2.3. Boehm titration

The Boehm titration method was used to determine a number of oxygen-containing groups on a sample surface. Thus, a 0.2 g sample of a given activated carbon was weighed carefully and placed into a vial containing 50 mL of a 0.05 mol/L solution of hydrochloric acid, sodium hydroxide, sodium carbonate and sodium bicarbonate, respectively. These vials were then sealed, stirred by shaking for 24 h then filtered. 5 mL of each filtrate with either excess base or acid was titrated with HCl or NaOH. The numbers of different acidic sites were then calculated

assuming that NaOH neutralizes carboxylic, phenolic and lactonic groups,  $\text{Na}_2\text{CO}_3$  neutralizes carboxylic and lactonic groups and  $\text{NaHCO}_3$  neutralizes only carboxylic groups [15].

### 2.4. Preparation and oxidative modification of MCs

MCs were prepared as follows: the nanosized silica particles were dispersed around the powdery coal tar-based mesophase pitch particles ( $m_{\text{pitch}}/m_{\text{silica}} = 3$ ) through strong agitation in the presence of alcohol solvent for 5 h. After the solvent was evaporated, the obtained carbon silica mixture was imprinted at a temperature of 320 °C for 2 h, and then carbonized at 800 °C for 2 h. The carbon silica composite was soaked in mass fraction 40% of HF solution at room temperature for 12 h to eliminate the silica template completely and washed with distilled repeatedly until the filtrate became neutral. Then the samples were dried at 110 °C in a vacuum oven for 24 h to get the MC.

Nitric acid was used for oxidative modification of the MC under mild conditions. The oxidation process was conducted by adding 50 mL of 35%–85%  $\text{HNO}_3$  to 5 g of the MC sample placed in a glass conical flask with a magnetic stirrer. The mixture was kept at 40–80 °C for 1–5 h, and then filtered to remove the solution. The treated MC sample was further washed with the distilled water until the filtrate became neutral. The filter cake was dried at 115 °C in a vacuum oven for 24 h, and then kept in a glass bottle with a cover as the oxidized MC.

### 2.5. Adsorption desulfurization of MCs

A certain amount of dibenzothiophene and benzothiophene was dissolved in n-octane to get a model fuel oil with a sulfur content of 400  $\mu\text{g/g}$  respectively. The procedure for adsorption desulfurization included adding 300 mg of the MC into 10 mL model fuel oil and stirring at a certain reaction temperature for a certain reaction time. Then, the adsorbent was separated from the solution by a filter paper and the solution was subjected to GC-FID analysis. The 100  $\mu\text{g/g}$  naphthalene or 100  $\mu\text{g/g}$  phenanthrene were added into the model fuel oil to study the competitive adsorption of naphthalene and phenanthrene against BT and DBT. After adsorption, the MCs were soaked in toluene for 24 h and then dried at 110 °C for 12 h for regeneration. The desulfurization rate ( $x$ ) and the sulfide capacity ( $q_e$ ) were calculated using the equation  $x = (C_0 - C_e)w / (C_0w) = (C_0 - C_e) / C_0$  and  $q_e = (C_0 - C_e)w / m$ , where  $C_0$  and  $C_e$  are the initial and equilibrium concentrations ( $\mu\text{g/g}$ ) of DBT or

**Table 2**  
Surface groups on the MCs under different modification conditions.

Concentration of nitric acid (%)	Oxidation temperature (°C)	Oxidation time (h)	Carboxylic ( $\text{mmol g}^{-1}$ )	Lactonic ( $\text{mmol g}^{-1}$ )	Phenolic ( $\text{mmol g}^{-1}$ )	Total acidity ( $\text{mmol g}^{-1}$ )
35	60	3	0.08	0.29		0.37
65	60	3	0.47	0.09	0.19	0.75
85	60	3	0.58	0.18	0.02	0.78
85	40	3	2.37	1.20		3.57
85	40	3	2.22	1.29		3.51
85	80	3	3.20	1.85		5.05
85	60	1	1.89	0.59		2.48
85	60	5	2.47	1.44		3.91

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