



Adsorptive removal of benzothiophene from model fuel, using modified activated carbons, in presence of diethylether



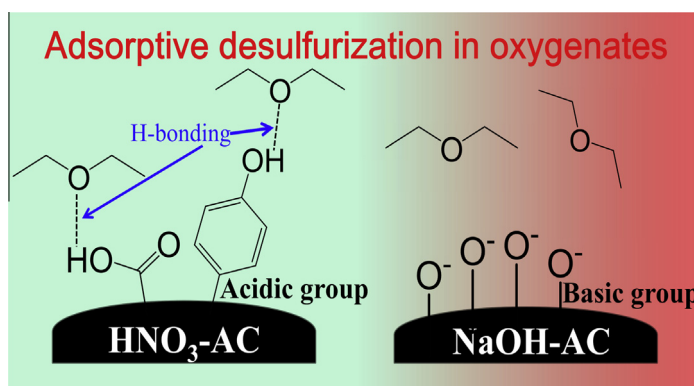
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HIGHLIGHTS

- Acid or base-treated carbons can be efficiently used in adsorptive desulfurization.
- Acid-treated carbons showed significant resistance to oxygenates.
- The resistance to oxygenates might be due to hydrogen bonding.

GRAPHICAL ABSTRACT



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ABSTRACT

The adsorptive removal of benzothiophene (BT) over three activated carbons (ACs) was carried out using a model fuel containing various concentrations of diethylether (DEE) as a typical example of an oxygenate additive for fuel. ACs treated with either an acid or a base improved the adsorptive removal of BT from solutions without any DEE, showing the beneficial effect of functional groups on the ACs on the adsorption of BT. DEE generally decreased the adsorption of BT in adsorptive removal with ACs. However, an acid-treated AC gave relatively better performances in the BT adsorption (when DEE was present) than virgin AC and a base-treated AC. Therefore, treatment of ACs with an acid is suggested as a way of improving BT adsorption, even in the presence of oxygenates such as DEE. Moreover, the small decrease in the performance of the acid-treated AC in BT adsorption in the presence of DEE may be explained by hydrogen bonding between the O and HO- group of DEE and the AC, respectively.

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1. Introduction

Sulfur is a pollutant in fossil fuels, and it should be removed because it causes severe environmental pollution through toxic emissions during power generation. The contents of sulfur-containing compounds (SCCs) such as thiophene, benzothiophene (BT), dibenzothiophene (DBT), and dimethyldibenzothiophene in

commercial diesel or gasoline should be reduced to extremely low levels in order to avoid air pollution from sulfur oxides and catalyst deactivation. EU and US regulations state that the level of sulfur in fossil fuels should not be more than 10 and 15 $\mu\text{g/g}$ (ppm), respectively [1–7]. Furthermore, ultralow sulfur contents (<60 $\mu\text{g/kg}$, ppb) are mandatory for fuel cell applications, since SCCs destroy fuel cell systems by sulfur poisoning [7].

Hydrodesulfurization, oxidation, and adsorption have been widely studied as desulfurization methods [1–8]. There is currently great interest in developing adsorbents based on porous solids for

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selective removal of SCCs under ambient conditions since adsorption is one of the most competitive techniques, particularly for ultralow sulfur contents [7]. Porous adsorbents including activated carbons (ACs) [9–23], zeolites [24–27], mesoporous materials [28–30] and metal–organic frameworks [31–36] have been investigated for SCC adsorption from liquid fuels. Among proficient porous solids, carbonaceous materials are interesting, because of their high specific surface areas, broad ranges of porosity, and cost effectiveness. The pore size distributions of ACs are wider than those of zeolitic materials, therefore not only small SCCs but also bulky ones can be adsorbed effectively without steric hindrance [17]. Moreover, it has been reported that modified ACs show enhanced sulfur adsorption [14–19]. ACs with oxygen-containing functional groups on their surfaces were reported to adsorb SCCs via oxygen–sulfur interactions [19,20]. Selective and enhanced adsorption of slightly basic SCCs onto acidic AC surfaces (modified) through acid–base interactions has also been reported [15,20]. ACs loaded with metal oxides were also found to adsorb BT and DBT more selectively than virgin carbons, through favorable interactions between SCCs and the incorporated metal oxides [23].

Considerable attention has been paid to developing cleaner-burning fuels in order to reduce toxic emissions. Recently, various fuel additives have been considered to be attractive solutions for increasing engine power and reducing dust [37,38]. The reformulation of fuels can include the addition of oxygen-containing materials to the fuel. It has been reported that many oxygenates are effective in reducing emissions of particulate matter from diesel engines [37]. Therefore, it is important to identify suitable oxygenated fuel additives, including alcohols, esters, ketones, and ethers, to improve fuel performances. However, the presence of oxygenates decreases the adsorptive desulfurization (ADS) efficiency [39]. Moreover, simultaneous adsorption of SCCs and oxygenates onto porous adsorbents can also reduce the adsorption capacities of the adsorbents for SCCs. It is therefore also very important to develop special adsorbents and appropriate adsorption conditions for the selective adsorption of SCCs in the presence of oxygenates.

In this study, the adsorption of BT in the presence of diethylether (DEE) as an oxygenate was performed using porous adsorbents based on ACs. ACs treated with nitric acid and sodium hydroxide were also used in the adsorption experiments to check the effect of acid/base treatment of the AC on the adsorption of BT in the presence of DEE [40,41].

2. Experimental

2.1. Materials

Granular AC (2–3 mm, Duksan, Lot No.: A102171, CAS No.: 7440–44–0) and phenolphthalein (99%) were purchased from the Duksan Pure Chemicals Co., Ltd. *n*-Octane (97.0%), sodium hydroxide (NaOH, 93.0%) and anhydrous sodium carbonate (Na₂CO₃, 99.0%) were obtained from the Daejung Chemicals. BT (C₈H₆S, 98%), methyl orange (C₁₄H₁₄N₃NaO₃S, 85%) and sodium bicarbonate (NaHCO₃, 99.7%) were purchased from the Sigma Aldrich Co. DEE (C₂H₅OC₂H₅, 99.0%) and nitric acid (HNO₃, 60%) were obtained from the OCI Chemicals. All the chemicals used in this study were analytical grade and used without further purification.

2.2. Preparation and analysis of adsorbents

An exact amount of AC (1 g) was transferred to glass vials containing 10 mL of 4 M HNO₃ or NaOH aqueous solution and stirred magnetically for 24 h at room temperature. The mixture was filtered and washed thoroughly with deionized water until neutral. Finally, the wet solids were transferred to a vacuum oven (to avoid

air contact) and dried overnight at 100 °C. The adsorbents were denoted by HNO₃-AC and NaOH-AC for HNO₃- and NaOH-treated samples, respectively.

The XRD patterns of ACs were obtained with a diffractometer (D2 Phaser diffractometer, Bruker, Cu K α radiation). The XRD patterns were calibrated with the (012) diffraction of α -alumina which was applied as an internal standard. The nitrogen adsorption isotherms of the adsorbents were obtained using a surface area and porosity analyser (Micromeritics, Tristar II 3020) after evacuation at 150 °C for 12 h, and the Brunauer–Emmett–Teller surface areas and total pore volumes were calculated using the obtained nitrogen adsorption isotherms. The pore size distributions of the adsorbents were calculated with the Barrett–Joyner–Halenda equation.

2.3. Adsorption experiments

Stock solutions of BT (1000 mg/g) were prepared by dissolving BT in *n*-octane or *n*-octane: DEE mixture (98:2 vol% or 95:5 vol%). BT solutions containing different concentrations of BT (50–1000 mg/g) were prepared by successive dilutions of the stock solutions with *n*-octane and DEE. The BT concentrations were determined using a high-performance liquid chromatography (Waters e2695 Separations Module) equipped with a photo diode detector.

Before adsorption, the adsorbents were dried overnight under vacuum at 100 °C and kept in a desiccator. The adsorbents were placed in BT solutions with fixed BT concentrations. The BT solutions containing the adsorbents were mixed well by magnetic stirring and kept for a fixed period of time (1–24 h) at a constant temperature of 25 °C. After adsorption for a predetermined time, the solution was separated from the adsorbent using a syringe filter (polytetrafluoroethylene, hydrophobic, 0.5 μ m), and the BT concentration was measured. The maximum adsorption capacity was calculated using the Langmuir adsorption isotherm (see the [Supplementary data](#)) after adsorption for 24 h under various conditions. A dimensionless constant, R_L , also known as the separation factor or equilibrium parameter, was calculated (see the [Supplementary data](#)) to understand the adsorption process better.

2.4. Analyses of functional groups in ACs

The contents and types of surface oxygen groups with acidic and basic properties in ACs were estimated by Boehm titration after slightly modifying the experimental conditions in a literature [42]. Exact amounts of AC (0.5 g) were separately added to three beakers containing 50 mL of 0.1 M NaOH, Na₂CO₃, or NaHCO₃ to determine the concentrations of acidic sites on the adsorbents. The solutions containing the ACs were mixed well by magnetic stirring for 24 h at a constant temperature of 25 °C. Finally, the solid samples were filtered-off and the concentrations of acidic sites were calculated after titrating the obtained solution with 0.1 M HCl aqueous solution. The Boehm titration procedure [42] used in this study is summarized in [Supplementary data](#). A similar procedure was followed to measure the concentration of basic sites. For this, the AC was soaked in 0.1 M HCl solution and the final solution was titrated with 0.1 M NaOH. Methyl orange and phenolphthalein were used as indicators in the titrations.

3. Results

3.1. Properties of adsorbents

As shown in [Fig. S1 \(Supplementary data\)](#), the XRD patterns of the ACs used were similar to those previously reported results

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