



# Regeneration methods to restore carbon adsorptive capacity of dibenzothiophene and neutral nitrogen heteroaromatic compounds



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## HIGHLIGHTS

- Effective regeneration methods to recover adsorption capacity were studied.
- Microporosity plays an important role in the adsorption of N and S compounds.
- Diffusion resistance from micropores restricts carbon regeneration.
- An increase in oxygen functional groups can improve carbon capacity restoration.

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## ABSTRACT

Activated carbon (AC) spent by model diesel fuel was regenerated using thermal, ultrasound and solvent approaches. The variations of physical and chemical properties of AC in the cycles of adsorption and desorption were studied. The results suggest that micropores play a more significant role in the carbon regeneration than mesopores do. The loss of micropores results in a lower capacity of carbon to adsorb S and N heteroaromatic compounds. Toluene extraction retains more porosity and oxygen functional groups of carbon, leading to better recovery than those by the other approaches. The toluene extracted AC can achieve 70% of the fresh capacities after nine cycles' regeneration. Thermal regeneration results in the loss of pores in carbon as well as the decomposition of oxygen functional groups. N,N-dimethylformamide (DMF) residues on regenerated AC samples, which helps with the adsorption of DBT to some extent even though this DMF lowers the carbon porosity. The difficulty in the diffusion of adsorbed sulfur- and nitrogen-containing compounds from the micropores of AC hinders the regeneration process.

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## 1. Introduction

Desulfurization and denitrogenation of diesel fuels is necessary because sulfur (S) and nitrogen (N) compounds are one source of SO<sub>x</sub> and NO<sub>x</sub> that result in environmental issues [1]. Different from the traditional hydrodesulfurization and hydrodenitrogenation approach, adsorptive desulfurization and denitrogenation method can be conducted under mild conditions without the presence of hydrogen gas, which saves both capital and operational costs [2]. Activated carbon (AC) has been studied as the adsorbent in adsorptive removal of S and N compounds because of its superior physical and chemical nature [3,4]. From the viewpoint of economics, regeneration has to be performed in order to repeatedly use the adsorbent. So far limited studies were concerned with the regeneration of diesel spent activated carbons. Bioregeneration was reported in recovering the adsorption capacity of dibenzothiophene

(DBT) spent AC [5]. However, due to the strong interaction between DBT and AC, less than 10% of the adsorbed DBT was desorbed after bioregeneration. Solvent extraction is a frequently reported method in the recovery of the adsorptive capacity of activated carbons [3,4,6]. However, there have been limited reports concerning other regeneration methods.

Thermal treatment is a conventional approach that has already been applied on an industrial scale in restoring spent AC in wastewater treatment [7]. The adsorption capacity of a benzene-spent AC can be completely restored by thermal regeneration at around 800–1000 °C even after six cycles [8]. Ultrasonication is a relatively new technology studied for spent AC regeneration. The cavitation created by ultrasound waves can decrease the surface diffusion activation energy and facilitate the desorption of adsorbed contaminants [9]. Ultrasonication has been successfully used to remove monoaromatic compounds [10,11], p-chlorophenol [12,13] and trichloroethylene [14] from AC. These two approaches have been studied in regenerating diesel spent zeolite-based and activated carbon cloth adsorbents. Calcination at elevated temperatures in oxidative atmosphere can burn the adsorbed S compounds to SO<sub>2</sub> and recover

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the adsorptive sites of metal supported adsorbents [15,16]. The adsorptive capacity for thiophene on the sorbent Cu(I)/zeoliteY was slightly lowered after the regeneration at 350 °C in air [15]. Fallah and Azizian reported that ultrasonication can accelerate the equilibrium of DBT desorption from HNO<sub>3</sub> oxidized activated carbon cloths [17]. In this work, thermal regeneration and ultrasonication were compared with solvent extraction in recovering the adsorption ability of a model diesel spent activated carbon. The effect of a non-aromatic solvent, N, N-dimethylformamide (DMF) was also examined. The factors that influence the regeneration process were investigated as well. Based on these factors, the reasons for why using solvent extraction to regenerate diesel spent AC samples were provided.

## 2. Experimental

### 2.1. Adsorption and regeneration

Successive cycles of adsorption and regeneration experiments were performed alternatively. Adsorption was carried out in a batch mode at ambient temperature and pressure for 24 h, with a stirring rate of 300 rpm. 1 g activated carbon (WV-B 1500, Mead-Westvaco Corporation) was mixed with 28 g model diesel fuel, which composition is listed in Table 1. Ethyl acetate was used in order to dissolve carbazole. The AC to model diesel fuel mass ratio was applied to all the adsorption processes.

Spent AC samples were then regenerated, using three approaches: thermal regeneration, ultrasound regeneration in DMF and solvent extraction in DMF or toluene. These methods are denoted as Thermal, US-DMF, Sol-DMF and Sol-Tol, respectively. Thermal approach was conducted in a 450 °C furnace for 2 h in flowing N<sub>2</sub> (180 ml/min). The temperature and duration were determined based on a preliminary TGA result (not shown in this paper). The regeneration time is 1 h longer than what recommended by Sereydych et al. [18]. In US-DMF, the spent AC sample was ultrasonically treated in DMF using a Model 500 Sonic Dismembrator (Fisher Scientific) at a frequency of 20 kHz. The regeneration lasted for 1 h which was accomplished by 10 even rounds. Solvent regeneration was conducted in DMF or toluene for 22 h using a Soxhlet apparatus. The regenerated AC samples were treated at 300 °C in flowing N<sub>2</sub> to remove any residual solvent before being subjected to adsorption. This adsorption–regeneration cycle was repeated 9 times.

The concentrations of S and N compounds in model diesels were analyzed using a GC-17A gas chromatograph (Shimadzu Corporation) with an FID detector. The regenerated carbon samples in this study are denoted as “AC-MO-regeneration method-C#”, where “#” represents the cycle number. The original activated carbon is denoted as “AC-Fresh”.

### 2.2. Characterization

#### 2.2.1. Nitrogen adsorption–desorption

The specific surface area ( $S_{\text{BET}}$ ), total pore volume ( $V_{\text{Total}}$ ) and micropore volume ( $V_{\text{Micro}}$ ) of AC samples were obtained based on

**Table 1**  
Composition of model diesel fuel.

Component		Concentration	Resource <sup>a</sup>
S compound	Dibenzothiophene	23.8 μmol/g	Alfa Aesar
N compound	Indole	23.8 μmol/g	Acros Organics
	Carbazole	23.8 μmol/g	Sigma–Aldrich
Aromatic compound	Naphthalene	23.8 μmol/g	Fisher Scientific
Paraffin	Dodecane	Balanced	Fisher Scientific
Other	Ethyl acetate	26.5 wt%	Caledon

<sup>a</sup> Chemicals were used as received.

the nitrogen adsorption–desorption isotherms that were recorded by an Autosorb-1 (Quantachrome Instruments) under the liquid nitrogen temperature. The values of these properties were calculated using the software accompanying with the instrument. The multipoint Brunauer–Emmett–Teller (BET) method and the Dubinin–Radushkevich (DR) equations were used to determine  $S_{\text{BET}}$  and  $V_{\text{Micro}}$ , respectively. An outgassing treatment was applied to the AC samples at 200 °C under 10<sup>-5</sup> mbar prior to the examination.

#### 2.2.2. Temperature programmed desorption (TPD)

TPD experiments were performed using an Autosorb-1-c (Quantachrome Instruments). Helium was used as the carrier gas (50 ml/min). 50 mg AC sample was packed in a U-shaped quartz tube. In the analysis, the samples were first dried at 100 °C for 60 min, and then heated at 10 °C/min to 1000 °C. The oxygen functional groups on AC samples decomposed under heating to generate CO<sub>2</sub> and CO, which were monitored by an RGA 200 amu residual gas analyzer (Stanford Research Systems), with the detection limit of 5 × 10<sup>-11</sup> Torr. The TPD curves were deconvoluted using PeakFit v4.12 software, for the analysis of different oxygen functional groups.

#### 2.2.3. Fourier transform infrared spectroscopy (FTIR)

The FTIR characterization was done on a Nicolet 6700 Fourier transform instrument (Thermo Scientific). The AC was ground and pressed into a wafer of 0.1 wt% AC with the addition of KBr. The spectra were collected at room temperature from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup> with 4 cm<sup>-1</sup> resolution.

#### 2.2.4. Thermogravimetric analysis combined with Fourier transform infrared spectroscopy (TGA-FTIR)

Thermogravimetric analysis (TGA) technique was combined with FTIR to investigate the thermal behaviors of AC samples. TGA was carried out using a TGA-Q500 thermal analyzer (TA Instruments). N<sub>2</sub> was used as the carrier gas (50 ml/min in total). 10 mg dried carbon samples were first treated at room temperature for 15 min to remove any contaminants. After being heated to 120 °C at a constant rate (10 °C/min) and kept for 1 h, the samples were heated up to 1000 °C at the same heating rate. The gases released from the TGA furnace went into a TGA-FTIR interface through an insulated transfer line. The temperatures of the transfer line and the analysis cell for FTIR were 200 °C and 225 °C, respectively. FTIR spectra were collected periodically in the mid-infrared (4000–400 cm<sup>-1</sup>) range with a resolution of 4 cm<sup>-1</sup>.

#### 2.2.5. Mechanical property test

The compression tests of AC-Fresh and AC-MO-C9 samples were carried out using a 1332 hydraulic testing machine (Instron). Prior to the test, the carbons were sieved to 20–40 mesh and dried in a 110 °C oven for 48 h. The carbon particles were dispersed in a single layer in a pellet dies (Specac). And then the pellet dies was placed between the platens of the testing machine. The displacement rate was 0.1 mm/min. The maximum load was 2.2 kN.

## 3. Results and discussion

### 3.1. Comparison of three regeneration methods

Fig. 1 shows the adsorption capacities of AC samples for DBT, carbazole and indole in each adsorption–desorption cycle using different regeneration methods. Thermal shows inferior performance while solvent extraction outperforms the other methods. The adsorption capacity decreases with the increase of adsorption–desorption cycle. When AC is regenerated by Thermal and

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