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Influence of acidic and basic treatments of activated carbon derived from waste rubber tires on adsorptive desulfurization of thiophenes

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ABSTRACT

This work reports on the influence of treatment conditions on the waste tire-derived activated carbon for adsorptive desulfurization. The rubber tires were carbonized and activated. The obtained activated carbon (AC) was treated with HNO_3 or NaOH at a temperature range of 30–90 °C. The morphology and surface properties of AC were characterized by surface pH, Boehm's titration, N_2 adsorption–desorption isotherms, Fourier-transform infrared spectroscopy, X-ray diffraction, and scanning electron microscope. The AC sample, treated with HNO_3 at 90 °C, possess the highest surface oxygen containing functional groups (2.39 mmol/g), surface area (473.35 m^2/g) and pore volume (0.70 cm^3/g) and the more adsorption capacity to the refractory sulfur compounds. The Boehm's titration experiments indicated that the amount of surface oxygen containing functional groups on the surface of the acid-treated AC increases with treatment temperatures. Acid-treated AC at 90 °C proves to be optimum for adsorptive desulfurization with the order of dibenzothiophene > benzothiophene > thiophene.

1. Introduction

Combustion of fossil fuels is associated with the release of toxic gases that pose serious environmental and health related impacts. Sulfur and its refractory compounds found in fossil fuels are extremely reactive. They cause catalyst poisoning and corrode refining equipment. In order to reduce air pollution and technological problems, EU and US have enacted laws to regulate sulfur emissions to 10 and 15 ppm respectively [1,2]. Various technologies are currently in use to lower the organic sulfur compounds in fuels, these methods include: hydrodesulphurization (conventional method), oxidative desulfurization, ionic liquids desulfurization, adsorptive desulfurization and biodesulfurization [3–6]. Of all these technologies, adsorptive desulfurization, one of the most promising technologies is receiving much attention because of its facile and mild operating conditions. Much attention is focused on the development of porous adsorbents such as activated carbon, zeolites, alumina, and zirconia that are cheap, easily regenerated and possesses high selectivity for sulfur compounds [7–11].

The surface areas and porosities of AC are greatly influenced by the parent material and the method employed in the production. Better adsorption capacities and adsorption rates of AC are directly linked to larger surface areas and pore size distributions [12]. Mesoporous and microporous volumes of AC also play a crucial role in the adsorption of larger molecules. In general, the selective adsorption of inorganic molecules on the surface of AC directly depends on the amount of oxygen containing complexes. The oxygen containing complexes are mostly created using dry or wet oxidation methods [13–15]. Adsorptive capability of AC modified with HNO_3 at 120 °C was increased significantly and modification using HNO_3 even at high temperatures showed a promising result in the removal of thiophenes from oil [16,17].

The aim of this work was to produce AC from end of life tires as a free-of-cost source, and to treat the AC using HNO_3 and NaOH at various temperatures. The influence of acid/base treatment of AC for the removal of thiophenes was examined. The adsorption performance of the AC was evaluated.

2. Experimental

2.1. Development of the adsorbent

Waste rubber tires were cleaned by removing the iron wires from the tire. Then, the waste rubber was cut into small pieces and thoroughly washed with deionized water, and then dried in an oven at 110 °C. The elemental analysis of the waste rubber indicated their initial elemental composition as 82.3 carbon, 9.2 oxygen, 0.7 nitrogen, 2.8 sulfur, 3.8 silicon and 1.2 silicon and silicon with different wt. %.

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The granules were heated up to 300 °C to separate the black tire crude oil, distilled diesel oil and produced oil. Pyrolysis was carried out in a muffle furnace at 500 °C for 5 h to isolate the ash and carbon black from pyro-gas and other oils, followed by treatment with hydrogen peroxide solution to oxidize all adhering organic impurities. The material was washed with deionized water and dried in vacuum oven at 110 °C overnight. The char was then placed in the stainless tube, inserted into the furnace, heated under nitrogen flow through the sample bed at 200 ml/min at 20 °C/min to 900 °C and a holding time of 5 h. Then the reactor was cooled down to room temperature before the sample was removed, and kept in an oven overnight, then grounded to small particles using pestle and mortar.

The produced black granules were sieved and the powdered carbon with a particle size of < 0.1 mm was used to allow good surface contact with acid or base reagent solution. Chemical activation was conducted on the prepared material using 4 M HNO_3 and 4 M NaOH at three different temperatures respectively (30, 60, and 90 °C) and a duration of 3, 6 and 12 h. Then, the mixture was filtered and the obtained activated carbon (AC) was washed with deionized water and dried overnight.

It should be mentioned that increasing the refluxing time from 3 h to 12 h has an overall net negative effect on the removal of the refractory sulfur compounds (see supporting information file, section S3.1.). Therefore, 3 h refluxing time was selected.

2.2. Boehm's method for surface functional groups

The amount of oxygen surface functional groups (both acidic and basic) was determined according to modified Boehm's method [18]. 0.5 g of raw and treated carbon samples were added to beakers each containing 25 ml of the following 0.05 M solutions: NaOH, Na_2CO_3, $NaHCO_3$ and HCl. The beakers were sealed and shaken for 24 h and then 10 ml of each filtrate was pipetted in an excess of 20 ml 0.05 M HCl for the determination of acidic functional groups or NaOH for the basic functional groups. The filtrate was titrated with 0.05 M NaOH or HCl, respectively, using phenolphthalein indicator and the volume required to reach the endpoint was noted. For Na_2CO_3 reaction bases an excess of 30 ml 0.05 M HCl was added rather than 20 ml due to diprotic property of the base to ensure complete reaction with acid. The number of acidic sites was calculated under the assumption that NaOH neutralizes carboxylic, phenolic, and lactonic groups; Na_2CO_3 neutralizes carboxylic and lactonic groups; and $NaHCO_3$ neutralizes only carboxylic groups. The number of surface basic sites was calculated from the amount of hydrochloric acid required. The following formula was used to calculate the amount of surface acidic and basic groups neutralized with NaOH and HCl respectively [19]:

$$\text{Moles of Carbon functionality} = \frac{([R\ a\ or\ b]\,V_r - ([X]\,V_x - [T]\,V_t))}{m}$$

where $[R\ a \text{ or } b]$ and V_r denote the concentration and volume of the reaction base or acid in mol/L and liters respectively. $[X]$ and V_x denote the concentration and volume of the excess acid or base added to the aliquot. $[T]$ and V_t denote the concentration and volume of the titrant required to reach the endpoint. m stands for the mass of the carbon used in grams.

The amount of surface acidic groups neutralized by Na_2CO_3 and $NaHCO_3$ was calculated using the following formula [20,21]:

$$n_{csf} = \frac{n_{HCl}}{n_B}[B]V_B - ([HCl]V_{HCl} - [NaOH]V_{NaOH})\frac{V_B}{V_a}$$

where n_{csf} denotes the moles of carbon surface functionalities on the surface of the carbon that reacted with base during the mixing step. $\frac{n_{HCl}}{n_B}$ = molar ratio of acid to base $[B]$ and V_B are the concentration and volume of the reaction base mixed with the carbon. [HCl] and V_{HCl} are the concentration and volume of the acid added to the aliquot taken from the original sample. $[NaOH]V_{NaOH}$ is the concentration and volume of the titrant in the back titration. V_a is the volume of the aliquot taken from V_B.

Surface pH of the carbon samples was tested by HI 3512 bench-top pH meter equipped with a graphic LCD display to gain insight about the acidity and basicity of the samples. A suspension of 0.2 g of each sample was added to 10 ml of water and the suspension was stirred overnight to reach equilibrium. The samples were then filtrated and the pH of the each solution was measured.

2.3. Characterization of the adsorbent

The FT-IR spectra of the samples were recorded using Nicolet 6700 spectrometer (Thermo electron, USA) with a resolution of 2.0 cm^{-1} well equipped with deuterated triglycine sulfate detector and an OMNIC program. The experiments were conducted on the powdered samples ground in an agate mortar to produce KBr pellets and spectra were obtained by adding 64 scans and corrected for the background noise. The spectra of the samples were recorded in transmission mode and the wavenumber range of 4000–400 cm^{-1}.

Scanning electron microscopy (SEM) analysis of the treated samples was conducted by using Hitachi model S- 3500 N instrument. Energy dispersive X-ray spectroscopy (EDX) analysis was conducted using Oxford Instrument (England) and X-Max detector to determine the elemental composition of the treated samples.

X ray diffraction patterns of the adsorbents were taken using (Rigaku Miniflex II desktop X-ray diffractometer) using Cu-Kά radiation and an X-ray gun operated at 40 kV (voltage) and 200 mA current. Data was collected from $2\theta = 10°$– 80° at a scan rate of 4°/min.

The porous structure of the AC samples was characterized by adsorption/desorption of nitrogen at (−196 °C) on a Micromeritics ASAP 2020 surface area and porosimetry analyzer (Micromeritics, USA) to determine the surface area (BET) and pore volume of the treated sorbents.

2.4. Adsorption experiment

2.4.1. Batch mode

In a typical run in the batch mode adsorption studies, various amounts, in the range between 0.1 and 0.5 g of adsorbents were introduced into 15 ml of the fuel solution containing thiophene (T), benzothiophene (BT) and dibenzothiophene (DBT) in hexane (85%) and toluene (15%) with initial concentration of 50 ppm each. The sulfur removal efficiency of the AC was calculated using the formula below:

$$x = (C_0 - C_e)/C_0 * 100\% \quad (1)$$

where x x = sulfur removal percentage (%) C_0 = initial concentration of sulfur in model is (ppmw), C_e = final sulfur concentration.

The amount of sulfur compounds adsorbed per unit mass of the adsorbent at equilibrium (q_e mg/g) and at any time t (q_t mg/g) termed as the adsorption capacity was calculated from the formulas:

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (2)$$

$$q_t = \frac{V(C_0 - C_t)}{m} \quad (3)$$

where V (L) is the volume of the liquid phase, C_0 (mg/L) is the initial concentration of the sulfur compounds before they come in contact with the adsorbent, C_e and C_t (mg/L) are the concentration at equilibrium and at any time t, and m (g) is the amount of the adsorbent.

2.4.2. Break-through experiments

Fixed-bed flow system was used to test the simultaneous adsorptive desulfurization of the treated AC samples using a column system.

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