Adsorptive desulfurization of dibenzothiophene from fuels by rubber tyres-derived carbons: Kinetics and isotherms evaluation

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ABSTRACT

The aim of this work was to investigate the utilization of waste rubber tyres as a low cost adsorbent for adsorptive desulfurization of dibenzothiophene from fuels, as a double cleaning process. Thus, rubber tires were converted into activated carbon by pyrolysis, activation and chemical treatment with 4 M HNO_3 for 3 h at 90 °C for the enhancement of surface functionalities. The effects of temperature and time on the yield of carbons were investigated. The optimized pyrolysis time and temperature yielded carbon with average BET surface area of 493 m^2/g, a pore volume of 0.77 cm^3/g, and pore size of about 6 nm. The adsorbent was also characterized by thermogravimetric analysis and differential scanning calorimetry. X ray diffraction pattern indicates that the sample showed a broad diffraction peak at 2θ values around 25° (0 0 2) and 43° (1 0 0). Fourier transform infrared spectrum showed peaks centered at 3430 cm^{-1}, 1720 cm^{-1} and 1640 cm^{-1} indicating the presence of hydroxyl and carboxylic groups on the carbon surface. The adsorbent was evaluated for the adsorptive desulfurization of dibenzothiophene. Pareto chart was used to investigate the effect of the experimental parameters. Adsorption kinetics and isotherm studies were performed, and the adsorption data fitted well to pseudo second-order model and Freundlich isotherm model. The adsorbent after adsorption was characterized by scanning electron microscopy equipped with an energy-dispersive X-ray spectroscopy.

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1. Introduction

Rubber tires have become an indispensable part of our transportation system. The tire industry has been continuously developing, and the overall use of the product has increased dramatically. One billion rubber tires were generated worldwide, according to a report by world business council for sustainable development (WBCSD, 2008). Substantial amounts of these non-biodegradable products end up in the landfills at the termination of their use, posing serious environmental, land management and health related impacts. The basic

management alternatives employed to curtail the impacts are to burn, retread, vulcanize and reclaim the tires.

Various thermochemical processes such as gasification, combustion, and pyrolysis are used to curtail the impacts of these materials. However, pyrolyzing these waste materials, despite their recalcitrant nature is believed to be a viable management alternative, because it leads to the production useful raw materials such as gases, liquid hydrocarbon fuels, and solid carbon black for industrial purposes (Ariyadejwanich et al., 2003; Martinez et al., 2013; Antoniou et al., 2014). The carbon black is considered one of the most important products

since it accounts for 30–40% weight of the rubber tyres and it is used for activated carbon production.

Activated carbon (AC) is amorphous and possesses a microcrystalline structure with large surface area and high porosity. The physical production of AC from rubber tyres involves carbonization of the tyres followed by physical or chemical activation of the material formed (Srinivasakannan and Abu Bakar, 2004). In carbonization, the rubber tyres are subjected to pyrolysis at a temperature ≤800 °C under controlled conditions of the atmosphere and heat. At this stage, the elemental composition of the rubber tyres used will be decomposed, leaving behind only the aggregates of carbon that are randomly linked together forming residual pores which are used for adsorption. The activation of the material formed by pyrolysis involves modification at 800 °C to 900 °C in a controlled atmosphere. This will improve the surface area of the AC (Williams and Brindle, 2003; Cunliffe and Williams, 1993). Studies on the utilization of this form of adsorbent (AC from rubber tyres) focus more on the removal of dyes, pesticides, and heavy metals from waste water (Zabaniotou et al., 2014; Saleh and Al-Saadi, 2015; Saleh et al., 2015).

The removal of sulfur is an important step in the refining of crude oil since the combustion products of sulfur compounds are the main reason for acid rain and environmental pollution. In addition, sulfur poisons catalysts and corrode refining equipment. Hence, ppb levels of sulfur contaminants are required to achieve a commercially viable operation life. Those problems are the reasons for an ongoing effort to lower the legal limits of sulfur in various kinds of petroleum products. In Germany, transportation fuels with a residual sulfur content of more than 10 ppm are taxed to encourage refiners to further reduce their diesel sulfur content to 10 ppm wt. In the US, the Environmental Protection Agency (EPA) has mandated 15 ppm wt, highway diesel since 2006 (Triantafyllidis and Deliyanni, 2014).

Achieving near-zero sulfur levels are technically challenging. Hydrodesulfurization (HDS) has been widely used sulfur abatement technology in refining. Even though the majority of low-sulfur hydrocarbon fuels are derived through HDS, there are limitations like the requirement of large catalyst volumes. In oxidative desulfurization (ODS), an aqueous oxidant reacts with the sulfur contaminant in the fuel phase. The thiophene contaminants are oxidized to sulfones, which are easily removed from the fuel because they are no longer soluble in the fuel phase. With ODS, the sulfur contaminants, that are most resistant to HDS, are reactive under ODS conditions (Sundararaman et al., 2010). However, a major problem with the ODS processes is that it employs an aqueous oxidant (hydrogen peroxide with a catalytic amount of an acid such as acetic acid) that must react with the sulfur contaminants in the fuel phase. Such process has some constraints like the requirements of hours of stirring at elevated temperatures and pressure, the cost of H_2O_2, the generation of water as a byproduct driving the need for molecular efficiency because excessive water in the fuel is detrimental to an engine.

Adsorptive desulfurization, another alternative to HDS, can take the form of H_2S removal after initial HDS, or it can involve direct adsorption of the most recalcitrant compounds (Song et al., 2011; Gaddafi and Saleh, 2016). Direct adsorption of the recalcitrant sulfur compounds is an appealing process because it can be carried out at ambient temperatures and pressures. There has been much recent interest in desulfurization of fuels at ambient temperature and pressure using a variety of adsorbents for selective sulfur removal, such as activated carbon, modified carbons, NaY and other type-Y zeolites, and Ag-doped on mesoporous supports (Song, 2003). However, there are some requirements for sorbents to be used in desulfurization by adsorption, including low-cost and fast adsorption process. The present study, therefore, aims to study the efficiency of rubber-derived activated carbon for adsorptive desulfurization of dibenzothiophene. The work includes an initial optimization study for the production of the best adsorbent, characterization of the synthesized adsorbent, a Pareto chart generated by experimental design using Minitab software to understand the important factors affecting DBT adsorption, and kinetics and isotherm studies.

2.   Experimental

2.1.   Preparation of activated carbons

Pieces of waste rubber tyres were collected from the dumping site, cleaned, thoroughly washed with deionized water, and then dried in an oven at 120 °C for 4 h. Then, they were divided into small chunks for carbonization (to convert organic matter to elemental carbon at high temperature in the absence of oxygen). The dried materials, with an initial mass of 20 g, were subjected to pyrolysis by heating at temperatures ranging from 250 to 550 °C and for different intervals, in inert (nitrogen) atmosphere. Then, to oxidize adhering organic impurities, the obtained materials were treated with hydrogen peroxide solution.

Physical and chemical activation were performed in this study. For physical activation, the obtained material was activated at different temperatures: 400, 500, 600, 700, 800 and 900 °C at a fixed time 5 h in a muffle furnace in a steam as an oxidizing agent. This is followed by chemical activation where the material was treated with 4 M HNO_3 for 3 h at 90 °C to activate and develop oxygen functional groups on the surface of the adsorbent. The adsorbent was washed with deionized water and dried. The following formulas were used for the calculation of percentage yield and recovery percentage:

$$\% \, \text{Yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$$

$$\% \, \text{Recovery} = \frac{\text{amount of pure product recovered}}{\text{amount of crude material used}} \times 100$$

2.2.   Characterization

2.2.1.   BET surface area
The porous structure of the synthesized materials 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), pore volume and pore size distribution of the treated sorbents.

2.2.2.   XRD
The X-ray diffraction pattern of the adsorbent was taken using (Rigaku Miniflex II desktop X-ray diffractometer) using Cu-Kα radiation and an X-ray gun operated at 40 kV (voltage), 200 mA current and λ = 1.54 Å using powdered samples. Data was collected from 2θ = 0–80° at a scan rate of 4°/min to understand the atomic and molecular structure of the adsorbent. The atoms present in the adsorbent were determined and the relative intensities were also taken. The microcrystalline structure of the adsorbent was examined by determining the crystallite