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Aqueous phase adsorption of different sized molecules on activated carbon fibers: Effect of textural properties

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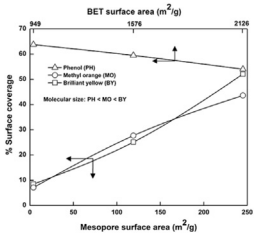
HIGHLIGHTS

- Rayon-based ACFs with different textural properties were prepared as adsorbents.
- ACFs were tested for the adsorption of different sized molecules (BY, MO, PH).
- Surface coverage by BY and MO increased with increasing mesopore surface area.
- Adsorption of small PH molecules primarily depended on micropore volume.

GRAPHICAL ABSTRACT



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ABSTRACT

The effect that the textural properties of rayon-based activated carbon fibers (ACFs), such as the BET surface area and pore size distribution (PSD), have on the adsorption of differently sized molecules, namely, brilliant yellow (BY), methyl orange (MO) and phenol (PH), was investigated in the aqueous phase. ACF samples with different BET areas and PSDs were produced by steam-activating carbonized fibers for different activation times (0.25, 0.5, and 1 h). The samples activated for 0.25 h were predominantly microporous, whereas those activated for relatively longer times contained hierarchical micro-mesopores. The adsorption capacities of the ACFs for the adsorbate increased with increasing BET surface area and pore volume, and ranged from 51 to 1306 mg/g depending on the textural properties of the ACFs and adsorbate size. The adsorption capacities of the hierarchical ACF samples followed the order BY > MO > PH. Interestingly, the number of molecules adsorbed by the ACFs followed the reverse order: PH > MO > BY. This anomaly was attributed to the increasing molecular weight of the PH, MO and BY molecules. The equilibrium adsorption data were described using the Langmuir isotherm. This study shows that suitable textural modifications to ACFs are required for the efficient aqueous phase removal of an adsorbate.

1. Introduction

Activated carbon fibers (ACFs) possess outstanding properties (large BET surface areas and pore volumes), which make them an excellent gas/liquid phase adsorbent for various pollutants

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(Bandosz, 2006). The ease of adding textural and surface modifications to ACFs makes them suitable candidates for many adsorption and catalytic applications (Cal et al., 1997; Xu et al., 2006; Bikshapathi et al., 2011; Talukdar et al., 2014). The adsorption characteristics of ACFs primarily depend on their textural properties, such as the BET surface area, pore volume and pore size distribution (PSD). The physical properties of the adsorbate molecules, such as their size, structure, polarity, and so on, also play a vital role in adsorption.

ACFs are inherently microporous materials with large BET surface areas, which makes them ideal for adsorbing small molecules that can easily travel through the microporous channels in a material. The adsorption performance of ACFs may, however, be lacking in large molecules, especially in the liquid phase, when the material is used without suitable textural modification. The efficient adsorption of large molecules requires creating sufficient mesopores in the ACFs (Hsieh and Teng, 2000; Tanthapanichakoon et al., 2005; Kim et al., 2006). The adsorption capacity also depends on the molecular size and weight of the adsorbate. In this context, more small molecules than large molecules may adsorb on the same adsorbent. However, the adsorption capacity of the adsorbent may be higher for molecules with relatively high molecular weights despite fewer molecules adsorbing in the pores. The number of adsorbed molecules depends on the PSD of the adsorbent, which affects its adsorption capacity. Study shows that adsorbents with relatively broad PSD exhibited higher adsorption capacities, although they contained lower mesopore volumes (Shen et al., 2003).

Producing ACFs with large BET areas and controlled PSDs is not trivial. The proper activation conditions (time, temperature, and activating agents such as CO_2 and steam) and precursor materials are required to produce ACFs for a particular application (Huang, 2009). Phenolic resins and viscous rayon precursor-based ACFs have been used to successfully remove hydrocarbons in the gaseous phase (Huang et al., 2002; Rong et al., 2003; Gaur et al., 2006). However, whereas the effect that the textural properties of phenolic resin-based ACFs have on the adsorption of differently sized molecules has been investigated in the aqueous phase (Pelekani and Snoeyink, 2000, 2001; Li et al., 2002; Chakraborty et al., 2011), viscous rayon-based ACFs have not been studied in detail. Pastor et al. (1999) and Rodriguez-Reinoso et al. (2000) performed heat treatment studies of viscous rayon-based fibers. However, their applications were not explored. From this perspective, the adsorption characteristics of viscous rayon-based ACFs in the aqueous phase require exploration.

The present study investigated the adsorption characteristics of viscous rayon-based ACFs with different pore textures in the aqueous phase. These pore textures were generated via the heat-treatment of carbon fibers for different times at a constant temperature (850 °C). Brilliant yellow (BY), methyl orange (MO) and phenol (PH), which have molecular weights of 625, 327, and 94, respectively, were used as the adsorbates. These compounds are to be considered large, medium and small, respectively, based on their molecular size. Fig. 1 shows the molecular structures and sizes of these adsorbates (Kim et al., 2006; Zhuang et al., 2009). This study performed a series of adsorption experiments at atmospheric pressure and room temperature, and the resulting isotherms were interpreted using well-developed adsorption models.

2. Experimental

2.1. Materials

Viscous rayon precursor-based carbon fibers (CFs) were purchased in the woven form from Aerospace Materials Private Ltd, Coimbatore, Tamil Nadu (India). BY (purity > 85%), MO (ACS grade, dye content, 85%), and PH (GR grade, purity > 99.5%) were purchased from Sigma-Aldrich. All chemicals were used without further purification.

2.2. Activation of CFs

The physical activation of the CFs was performed using steam as the activating agent in a horizontal tubular reactor inside an electric furnace. The woven CF samples were first cut into small pieces (approximately 4 cm × 5 cm), and approximately 2 g of the samples was placed on a SS mesh. The mesh was then placed inside the reactor. The fiber activation was performed at 850 °C for varying times (0.25, 0.5 and 1 h). The activation temperature was achieved by heating the samples 5 °C/min. N_2 gas was flowed through the reactor at 200 standard cc/min (sccm) to protect the samples from burning. The activation time was measured starting when the activation temperature was reached. A mixture of N_2 and steam was then fed into the reactor. The activated samples were named ACF-0.25h, ACF-0.5h, and ACF-1h throughout this study depending on the activation times.

2.3. Batch adsorption of BY, MO, and PH

Batch tests were performed in 100-mL Erlenmeyer flasks. Stock solutions of 2000 mg/L BY and 1000 mg/L MO and PH were prepared in Milli-Q water without adjusting the pH. Test solutions of the required concentrations were prepared by diluting a fixed volume of the stock solutions. The adsorption tests were performed by mixing a fixed amount (1000 mg/L of solution) of the ACFs in 50-ml solutions with different initial concentrations. The solution-containing flasks were shaken at 150 rpm using an orbital incubator shaker (Mahindra Scientific Instruments Mfg. Co.), and the temperature was maintained at 30 °C. After adsorption for a predetermined time, the adsorbent was separated from the solution using filter paper (Whatman ashless filter paper; grade number 42; diameter: 125 mm). The adsorbate concentrations in the filtrate were determined from their respective maximum wavelength using a UV spectrophotometer (Varian Cary 100). All adsorption experiments were performed in triplicate, and the average values are reported in this study. The equilibrium adsorption capacity (mg/g) of the adsorbents was determined from the mass balance:

$$q_e = \frac{(C_o - C_e)V_{sol}}{m_{ads}} \quad (1)$$

where, C_o and C_e are the initial and equilibrium adsorbate concentrations (mg/L), respectively. V_{sol} is the adsorbate solution volume (50 ml), and m_{ads} is the adsorbent mass (50 mg).

2.4. Surface characterization

The ACF surface morphologies were examined using a field emission scanning electron microscope (FE-SEM) (Gemini Supra 40 VP, Zeiss). The N_2 adsorption-desorption isotherm, BET surface area and PSD of the ACFs were determined by adsorbing N_2 into the samples at its liquid temperature (77 K) using the Autosorb-1C instrument (Quantachrome, USA). Prior to analysis, the samples were degassed at 200 °C under vacuum for 24 h. The BET surface area was calculated from the linear range (P/Po = 0.01–0.1) of the adsorption data (Li et al., 2002; Boudou et al., 2006). Total pore volume was determined from the amount of N_2 adsorbed at a relative pressure near unity (0.9994). Micropore volume (V_{micro}), meso-macropore volume (V_{meso}) and meso-macropore surface area (S_{meso}) were calculated using t-plot (Galarneau et al., 2014). The