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Preparation and characterization of highly mesoporous spherical activated carbons from divinylbenzene-derived polymer by $ZnCl_2$ activation

Zhaolian Zhu, Aimin Li [*], Lei Yan, Fuqiang Liu, Quanxing Zhang

State Key Laboratory of Pollution Control and Resource Reuse, Jiangsu Engineering and Technology Research Center for Organic Toxicant Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210093, China

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Abstract

Highly mesoporous spherical activated carbons (SACs) were prepared from divinylbenzene-derived polymers by $ZnCl_2$ activation; the effects of activation temperature and retention time on the yield and textural properties of the resulting SACs were studied. SACs thus prepared were characterized by N_2 adsorption, X-ray diffraction (XRD), scanning electron microscopy (SEM), and aqueous adsorption assays. All the SACs were generated with high yield (>54%) and high mesopore fraction (around 80%). SEM and XRD analyses of SAC28 verified the presence of the disordered micrographite stacking with developed mesoporosity. Compared with conventional activated carbons, SAC28 prepared in our study exhibited a comparable adsorption capacity of 190 mg g^{-1} for bisphenol A and even more excellent capacity of 330 mg g^{-1} for phenol. Bisphenol A preloading significantly reduced the adsorption capacity of SAC28 for phenol due to both reduction of adsorption sites and pore blockage.

Keywords: Spherical activated carbon; Chemical activation; Characterization; Pore structure; Pore size distribution

1. Introduction

In recent years, carbon materials have found many new applications such as catalyst supports, battery electrodes, double-layer capacitors, gas storage, biomedical engineering, and adsorbents for bulky molecules [1–6]. Carbon materials of such applications usually possess high mesoporosity (2–50 nm) thereby allowing efficient adsorption of molecules and ions that are too large to enter micropores. It has been reported that the pore size and pore size distributions of activated carbons have a strong effect on the adsorption of organic compounds [7]. Mesopores are generally required for activated carbons applied in liquid-phase adsorption due to the larger size of liquid molecules. They not only contribute significantly to adsorption via the mechanism of capillary condensation, but also alleviate pore obstruction and maintain a fast kinetic adsorption rate as the main transport arteries for the adsorbate [7–9]. As a result, the presence of mesopores in the activated carbon can significantly enhance their adsorption capacities, especially for large adsorbates [7,10–13].

As such, considerable recent interest has been triggered in the synthesis of mesoporous activated carbons. Many methods have been described to prepare mesoporous carbons, such as activation to high burn-off degrees [14], combination of physical and chemical activation [15], catalytic activation in the presence of transition metals or rare metals [13,16], carbonization of polymer blends and organic gels [17,18], and template carbonization [19–22]. Despite these successes in the laboratory, most of these methods are not ready for large-scale preparation of mesoporous carbon, either because of the complicacy of the process, expensive raw materials, low yield or poor mechanical properties of the products.

Among these methods, $ZnCl_2$ activation is one of the most effective methods for producing mesoporous carbons due to its high activating capability and relatively low cost [23–25]. In this process, the starting materials are first impregnated with concentrated $ZnCl_2$ solution at a high $ZnCl_2$-to-raw material ratio, and then pyrolyzed at a moderate temperature from 500 to 800 °C. The remaining $ZnCl_2$ can widen the pore size by localized decomposition of the organic matter, which results in

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[*] Corresponding author. Fax: +86 25 85572627.
E-mail address: liaimin@nju.edu.cn (A. Li).

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the formation of mesopores. Meanwhile, $ZnCl_2$ can inhibit the tar formation and enhance the carbon yield.

Activated carbon fibers (ACFs) and granular activated carbons (GACs) are two kinds of the most widely used activated carbon materials. However, spherical activated carbons (SACs) have received considerable recent attention for their various potential advantages over ACFs and GACs such as extremely low resistance to liquid diffusion, higher adsorption efficiency, better mechanical properties, and more resistance to abrasion [26]. Pitch [27], oil agglomerated bituminous coals [28], phenolic resin [26], ion exchange resin [29,30], styrene–divinylbenzene copolymers [31], and acrylonitrile–divinylbenzene copolymer [32] have been used to prepared SACs by physical activation or catalytic activation. To the best of our knowledge, preparation of highly mesoporous SACs from divinylbenzene-derived polymers by $ZnCl_2$ activation has not been described.

The aim of this paper is to prepare and characterize highly mesoporous SACs from divinylbenzene-derived polymers by $ZnCl_2$ activation. The preparation conditions affecting the yield and textural properties (specific surface area, pore volume and pore size distribution) were investigated. The textural properties of SACs were characterized by N_2 adsorption, XRD, SEM and aqueous adsorption assays.

2. Experimental

2.1. SACs preparation

Divinylbenzene-derived spherical polymers (SPs) were synthesized essentially as described [33]. Briefly, styrene (126 g), divinylbenzene (74 g), dibenzoyl peroxide (2 g), and liquid paraffin (100 g) were mixed in a round-bottomed flask. Subsequently, 1200 g of 1 wt% gelatin solution was added. Polymerization was performed with stirring at 80 °C for 12 h. When the reaction was completed, SPs were filtered and rinsed with hot deionized water at 80 °C, and extracted with acetone for 8 h before being dried under vacuum at 60 °C.

The resulting SPs were mixed with $ZnCl_2$ solution (30 wt%) and incubated at 80 °C for 24 h. After that, SPs were filtered and dehydrated at 110 °C for 6 h before being placed in a quartz combustion boat and loaded into a horizontal cylindrical furnace (i.d. = 80 mm) under N_2 flow ($150\ \mathrm{cm^3\,min^{-1}}$). The samples were heated up to 600–900 °C at a heating rate of $10\,^\circ\mathrm{C\,min^{-1}}$ and maintained at the desired activation temperature for 1–3 h. The samples prepared at temperatures of 600, 700, 800, and 900 °C for 2 h were designated as SAC26, SAC27, SAC28, and SAC29, respectively, and those at 800 °C for 1 and 3 h as SAC18 and SAC38. The resultant SACs were washed sequentially with 0.5 N HCl solution at 80 °C and boiling water to remove excess $ZnCl_2$ before being dried at 110 °C for 24 h and stored in a desiccator for characterization.

2.2. SACs characterization

The specific surface area (S_{BET}) and pore structural parameters of SACs were determined from the adsorption–desorption isotherm of nitrogen at −196 °C (Micromeritics ASAP2010). The S_{BET} was calculated by the BET equation, micropore volume (V_{mi}) and micropore specific surface (S_{mi}) area were obtained using the t-plot method, and pore size distribution (PSD) was determined using the BJH model [34]. The total pore volume (V_{t}) was obtained by converting the nitrogen adsorption amount at a relative pressure of 0.98 to the liquid nitrogen volume. The mesopore volume (V_{me}) was calculated by subtracting V_{mi} from V_{t}.

The morphology of SAC28 was examined in an SEM (Hitachi S-4300). The SAC28 was coated with platinum by a platinum sputtering device for clear visibility of the surface morphology. The stacking structure of aromatic carbon layers of SAC28 was analyzed with an X-ray diffractometer (ARL-X'TRA, Cu$K\alpha$ radiation at 40 kV and 30 mA, $\lambda = 0.15406$ nm) and the X-ray patterns were recorded for 2θ from 5 to 60° at a scan rate of $0.02^\circ\ \mathrm{min^{-1}}$.

2.3. Aqueous adsorption characteristics

SAC28 was used to study the aqueous adsorption characteristics by single solute adsorption and preloading adsorption assays with two ubiquitous organic contaminants of different molecular sizes, phenol and bisphenol A (BPA), as adsorbates. The adsorption assays were carried out using a batch equilibration technique in a 250 ml flask. In the single solute adsorption assays, each flask was filled with 0.025 g SAC28 and 100 ml of either BPA or phenol solution at known concentration gradients from 50 to 90 $\mathrm{mg\,L^{-1}}$ for BPA and 70–150 $\mathrm{mg\,L^{-1}}$ for phenol. The flasks were shaken in a temperature-controlled shaker at a constant temperature (25 °C) and agitation speed (140 rpm) for 4 days to attain equilibrium.

In the BPA preloading assays, 0.025 g of SAC28 was exposed to BPA with an initial concentration of 70 $\mathrm{mg\,L^{-1}}$ for 4 days, then filtered and subjected to contact with single solute phenol solution at a concentration gradient from 70 to 150 $\mathrm{mg\,L^{-1}}$. After additional 4 days of contact, the samples were taken for analysis. In the phenol preloading assays, SAC28 was exposed to single solute phenol solution with an initial concentration of 100 $\mathrm{mg\,L^{-1}}$. After 4 days of contact, the phenol-loaded SAC28 was filtered and subjected to contact with single solute BPA solution at 50–90 $\mathrm{mg\,L^{-1}}$ for additional 4 days. All the flasks were shaken at the same conditions as that for the single solute adsorption assays. All the tests were repeated with a conventional activated carbon PICA I1000 (PICA) for the needs of comparison. The equilibration adsorption period is 6 days for PICA.

The concentrations of phenol and BPA were determined by HPLC (Waters 600, Waters Corp.) using a 30:70 ratio of CH_3OH:deionized water and the effluents were monitored at 275 nm. Phenol calibration curve with the linear range of 3.0–100 $\mathrm{mg\,L^{-1}}$ and bisphenol A calibration curve with the linear range of 1.8–60 $\mathrm{mg\,L^{-1}}$ were first established. Each sample determination was repeated at least once. The adsorption capacity was calculated according to $Q_{\mathrm{e}} = (C_0 - C_{\mathrm{e}})V/W$, where C_0 and C_{e} are the initial and equilibrium concentrations ($\mathrm{mg\,L^{-1}}$), respectively; V is the volume (L) and W the weight (g) of activated carbon.