Research article

Pore size dependent molecular adsorption of cationic dye in biomass derived hierarchically porous carbon

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ABSTRACT

Hierarchically porous carbon adsorbents were successfully fabricated from different biomass resources (softwood, hardwood, bamboo and cotton) by a facile two-step process, i.e. carbonization in nitrogen and thermal oxidation in air. Without involving any toxic/corrosive chemicals, large surface area of up to 890 m^2/g was achieved, which is comparable to commercial activated carbon. The porous carbons with various surface area and pore size were used as adsorbents to investigate the pore size dependent adsorption phenomenon. Based on the density functional theory, effective (E-SSA) and ineffective surface area (InE-SSA) was calculated considering the geometry of used probing adsorbate. It was demonstrated that the adsorption capacity strongly depends on E-SSA instead of total surface area. Moreover, a regression model was developed to quantify the adsorption capacities contributed from E-SSA and InE-SSA, respectively. The applicability of this model has been verified by satisfactory prediction results on porous carbons prepared in this work as well as commercial activated carbon. Revealing the pore size dependent adsorption behavior in these biomass derived porous carbon adsorbents will help to design more effective materials (either from biomass or other carbon resources) targeting to specific adsorption applications.

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1. Introduction

Porous materials are of great interest due to their large surface area and tunable pore structure and have found wide applications in various fields such as ion exchange (Kusakabe et al., 1998), adsorption (Kyriakopoulos and Doulia, 2006; Liu et al., 2014; Meng et al., 2015; Zhao et al., 2015), energy production/storage (Chen et al., 2017; Dutta et al., 2014; Kyriakopoulos et al., 2016) and catalysis (Ji et al., 2015, 2016; Liu et al., 2010). The International Union of Pure and Applied Chemistry categorized pores into micropores (<2 nm), mesopores (2—50 nm) and macropores (>50 nm) according to their pore size (Sing, 1982).

Porous materials can be fabricated by different techniques, such as physical/chemical activation (Alabadi et al., 2015; Anoop Krishnan et al., 2011; Williams and Reed, 2006), phase separation (Nakanishi and Tanaka, 2007), template method (Lee et al., 2006; Tang et al., 2015), etc. Activation is a process that converts

carbonaceous source materials such as coconut husk (Babel and Kurniawan, 2004; Hasany and Ahmad, 2006), wood (Acharya et al., 2009; Wang et al., 2009) and coal (Ahmadpour and Do, 1996; Chingombe et al., 2005) into microporous materials by using activating agents. Depending on the nature of activating agents, the process can be classified as physical (Ahmadpour and Do, 1996; Rodríguez-Reinoso and Molina-Sabio, 1992) or chemical activation (Chen et al., 2015a; Diao et al., 2002; Tsai et al., 1998). Activated carbon can achieve surface area ranging from 500 to 3000 m^2/g with major micropores and non-uniform pore size distribution. As for template method, the monomers or polymer precursors are firstly impregnated/infiltrated into the pores of the template, after which, cross-linking and carbonization processes are carried out in sequence. After removing template, the monomer or polymer precursor becomes the continuous carbon framework and the space pre-occupied by the template is transferred into pores in the products (Lee et al., 2000; Qiang et al., 2014). The porous carbon produced from template method features uniform pore size. For both methods, either high energy consumption, complicated process, or toxic/corrosive chemicals are required, which is undesirable facing the energy and environmental challenges nowadays.

Taking advantage of rich-carbon nature, converting lignocellulosic biomass (raw resources such as wood, cotton or treated resources including cellulose, lignin, tannin and starch) into porous carbon seems a promising approach. For example, wood biomass has been processed into shape controlled hierarchical porous carbon by flash heating method (Kurosaki et al., 2008). In recent years, researchers have successfully fabricated porous carbon materials from different biomass resources such as winter melon (Li et al., 2014), shiitake mushroom (Cheng et al., 2015), banana peel (Lv et al., 2012), bamboo (Hameed et al., 2007) *etc*. More than that, our previous work demonstrated a facile two-step process to produce high surface area porous carbon from softwood by selectively removing lignin without using any toxic chemicals (Chen et al., 2015b). It is worthwhile to find out whether this method can be applied to produce high surface area porous carbon from different biomass resources.

Adsorption is a surface-based process that targeted atoms, ions or molecules are adhered to adsorbent surface. Porous materials with high surface area are required to achieve large adsorption capacity. However, adsorbents with large surface area sometimes give poor adsorption capacity (Chen et al., 2015a). In fact, besides the surface area, pore size distribution and size of the adsorbate molecule also affect the adsorption capacity. In previous studies, researchers related and compared the adsorption capacity directly with total surface area regardless of their pore size distribution, adsorbent size, *etc*., which fails to interpret the adsorption phenomenon precisely (Chen et al., 2015a). Some researchers mentioned the concept of "effective surface area" in adsorption, however, the exact definition of "effective surface area" was not clearly defined (Malik, 2003; Wan et al., 2015; Zare et al., 2015). Until now, rare work has been reported to correlate the adsorption capacity with effective specific surface area, pore size distribution and adsorbate molecule size. Not even to mention the attempt of constructing a model to quantify the adsorption contributed by effective and ineffective surface area. A clearly defined model will enable systematic analysis and prediction of adsorption capacity and can even help to design materials with desirable properties towards various adsorption applications.

In this work, hierarchically porous carbons were fabricated from different biomass resources, spruce-pine-fir (softwood), maple (hardwood), bamboo and cotton, by using a facile two-step (carbonization and thermal oxidation) method. The surface area and pore size can be controlled by simply changing the oxidation temperature and duration. Methylene blue was used as probing molecule to study the pore size dependent adsorption phenomenon relating the total surface area and effective surface area of these porous carbon materials. Moreover, a simple model that quantifies the adsorption capacity contribution from effective and ineffective surface area was proposed and verified. The relationship among adsorption capacity, effective specific surface area and adsorbate molecular size was analyzed in both macroscale and molecular level.

2. Materials and methods

2.1. Materials

Spruce-pine-fir (SPF), maple was purchased from Home Depot, bamboo skewers were purchased from Dave's supermarket, and cotton was obtained from commercially available T-shirt made of 100% cotton. Methylene blue (MB) was purchased from Fisher Scientific. Commercial active carbon (AC) was provided by Cabot Corporation (HDB M-1951). All chemicals were used as received without further treatment. Deionized water (Millipore) was used in all the experiment.

2.2. Synthesis of porous carbon

Biomass derived porous carbon was prepared in two consecutive thermal treatment steps: carbonization and thermal oxidation. In the first step, the four different biomasses were carbonized in N_2 atmosphere at 800 °C for 2 h with a heating rate of 5 °C min^{-1}. The carbonized products are named as X-800 (X = S, M, B and C), where the S, M, B and C are abbreviation of SPF, maple, bamboo and cotton, respectively. Then the carbonized biomasses were further oxidized in air at different temperatures (300–370 °C) for different times (1–7 h), and the products were named as X-temp-time, where X is the abbreviation of biomass species, temp and time are the oxidation temperature and time used during the process. For example, M-340-5 indicates carbon obtained from maple by oxidizing M-800 at 340 °C for 5 h. All samples were grinded into fine particles with diameter between 10 and 50 μm for the adsorption test, the morphology of grinded particles is provided in Fig. S1.

2.3. Adsorption isotherms

For adsorption isotherm, 10 mL MB aqueous solutions with different initial concentrations were mixed with 1.0 g/L porous carbon adsorbent. The pore size dependent adsorption study is performed in neutral solution without adjusting pH values. To investigate the adsorption capacity at different pH conditions, the solution pH was adjusted by HCl or NaOH from 1 to 12. The mixture was magnetically stirred at 25 °C for 12 h to ensure equilibrium has been reached. After that, the mixture was separated by filtration and the remaining MB solution was collect for analysis. A linear standard curve relating the UV–Vis adsorption peak intensity at 665 nm and MB concentration was constructed, refer to our previous work (Chen et al., 2015a, 2016). Based on this standard curve, the concentration of MB solution after adsorption test can be easily determined by measuring UV–Vis peak intensity at 665 nm.

2.4. Characterization

Microstructure of carbonized and oxidized materials was characterized by scanning electron microscopy (SEM, JEOL-7401), the atomic percentage of oxygen in porous carbon was obtained by Energy Dispersive X-ray Spectroscopy. N_2 adsorption-desorption isotherm was performed at −196 °C and CO_2 adsorption was performed at 0 °C on a surface analyzer (Micromeritics Tristar II 3020). Before test, samples were degassed at 100 °C for 12 h using a Micromeritics FlowPrep 060 degas system. Specific surface area (SSA) was calculated by using two different methods. One is Brunauer-Emmet-Teller (BET) method, where SSA is calculated from N_2 adsorption-desorption isotherm. The other is nonlocal density function theory (NLDFT), where the SSA is calculated from combined N_2 and CO_2 adsorption data by using a slit pore model that is provided by MicroActive Software (Version 4.00). SSA obtained from these two different methods were named as BET-SSA and DFT-SSA, respectively. Zeta potential of porous carbon was measured by Nano-ZS90 (Malvern) in the pH range of 1–12. Size of MB cation was measured as 1.40 × 0.60 × 0.18 nm (x × y × z) by using Chem3D software. The energy of MB cation was minimized by MM2 force field method (Allinger, 1977) to ensure it's in most stable state. UV–Vis spectra of MB solution were characterized by a UV-1800 Shimadzu spectrophotometer.

3. Results and discussion

3.1. Microstructure of biomass

Natural wood, the most abundant renewable resources on