Preparation of highly developed mesoporous activated carbon fiber from liquefied wood using wood charcoal as additive and its adsorption of methylene blue from solution

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HIGHLIGHTS

- A new method for preparing mesoporous activated carbon fibers was introduced.
- ACF with 2604.7 m^2/g specific surface area and 1.433 cm^3/g total pore volume.
- 86.8% pore volume was from the contribution of the small mesopores of 2–4 nm.
- The effects of wood charcoal on the formed mesoporous were investigated.

ARTICLE INFO

ABSTRACT

Activated carbon fiber (C-WACF) with super high surface area and well-developed small mesopores were prepared by liquefied wood and uses wood charcoal (WC) as additive. The characterization and properties of C-WACF were investigated by XRD, XPS and N$_2$ adsorption. Results showed the pore development was significant at temperatures >750 °C, and reached a maximum BET surface area (2604.7 m^2/g) and total pore volume (1.433 cm^3/g) at 850 °C, of which 86.8% was from the contribution of the small mesopores of 2–4 nm. It was also found that the mesopore volume and methylene blue adsorption of C-WACF were highly increased as the temperature increases from 750 to 850 °C. Additionally, the reduction of graphitic layers, the obvious changes of functional groups and the more unstable carbons on the surface of C-WACF, which played important roles in the formation of mesopores, were also observed.

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1. Introduction

As a new type of activated carbon, activated carbon fiber (ACF) has an excellent adsorptive property due to large specific surface area, pore volume, and uniform microporosity, and has been widely applied for purification, separation or catalysis (Soheil et al., 2009). Currently, ACF is mainly prepared from phenolic resin, polyacrylonitrile (PAN), or pitch fibers. With the increase of fossil resources shortage and environmental awareness, some biomass-based ACF were prepared from renewable sources, such as wood, bamboo, Kenaf, jute, cotton-stalk, etc. (Uraki et al., 2001; Asakura et al., 2004; Phan et al., 2006; Kunbin et al., 2010; Yang et al., 2011; Dongna et al., 2014). However, most ACF were mainly micropore, which cannot meet some special demands, such as adsorption of bulky molecules from solution and catalyst supports for

macromolecule reaction. And it has been also reported that mesoporous ACF was better than microporous in the view of the cyclic voltammetry and capacitance (Kowalczyk et al., 2003). So, it is desired to increase the mesopore and macropore content in ACF and explore its new applications.

Besides open pores on the surface of the fiber and narrow pore size distribution as normal ACF does, mesoporous ACF, or ACF abound with mesopores, features high specific surface area, large pore size and pore volume, great adsorption speed and high adsorption capacity (Foo et al., 2012). Various methods have been reported for the preparation of mesoporous ACF, such as polymer blending method, catalytical method, and re-activation method (Ozaki et al., 1997; Guillermo et al., 2003; Yanqiu et al., 2011). The activation reaction takes place in the immediate vicinity of metal/oxide particles, resulting in the formation of mesopores by pitting holes into the carbon matrix. Some transition and rare earth metal compounds as catalyst, including yttrium acetylacetonate, cobalt, cerium oxide and so on, were used to improve the development of mesopores and macrospores in ACFs (Hong et al., 2000;

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Yihong et al., 2004). But it was difficult to eliminate the catalyst from the mesoporous ACF matrix. In addition, carbon black as additive was added to the precursor for the development of mesopores during activation (Yinzhi et al., 1998), and some catalytic gasification (e.g. CO_2, steam, or air) was used to prepare mesoporous activated carbon fiber using pure or mixed gas (Joanna et al., 2011). Mesoporous ACF as the above reported ACF has limited application because of the lower mesoporosity percentage, the higher loading or cost.

Wood charcoal (WC) with amorphous carbon has a large number of pore structures, and is inexpensive because of easily obtaining from wood resources (Ahmendna et al., 2000). When WC is added into the matrix, the structure of the fiber matrix could be disrupted and become loose. It is expected that activated reaction could become readily in the interface between WC particles and the fiber matrix (Eltekov et al., 1994). Except for release gas, the separation of WC and the matrix has also assisted the formation of mesopore in ACF due to their different extent of shrinkages during activation (Yinzhi et al., 1998). In addition, some mesopore in ACF matrix could also be formed by re-activation of WC in the process of carbonization and activation, and WC is not required to be removed after activation. Therefore, WC as additive will play an important role for the mesopore formation of ACF.

ACF with microporous (WACF) were prepared from liquefied wood in previous study (Dongna et al., 2013). WC and WACF were used wood as their raw materials, so WC and the WACF matrix have a good compatibility. In the present study, ACF with highly developed mesoporous was prepared from liquefied wood filled with WC by steam activation. By comparing with WC and ACF from liquefied wood, the mesoporous development of activated carbon fiber from liquefied wood filled with WC was analyzed by N_2 adsorption. The adsorption characteristics of the obtained samples in the liquid phase were also investigated where methylene blue (MB) was used as representative adsorbates. In addition, in order to understand the relationship between the microstructure, the surface chemistry and mesoporosity, the mesoporous ACF prepared from liquefied wood filled with WC with different degrees of activation were studied by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Materials

Chinese fir (*Cunninghamia lanceolata*) used in this study as a raw material was sourced from Fujian, China. Prior to use, sample was air dried, grounded in high-speed rotary cutting mill and then screened to give the fraction of 0.2 < Dp < 0.8 mm particle size for use in the experiments. A commercial wood charcoal (0.05 < Dp < 0.07 mm) for use in the spinning solution was from Jiaozuo Carbon Corporation, China. All other chemicals in the study were reagent grade and they were used without further purification.

2.2. Preparation of activated carbon fibers

The mixture of 20 g of wood and 120 g of phenol as well as 9.6 g of H_3PO_4, loading in a round bottom flask, was heated in an oil bath at 160 °C for 150 min. The liquefaction of bamboo was obtained. Subsequently, hexamethylenetetramine as synthetic agent was added to the liquefaction medium by 5 wt% (on the weight of liquefaction solution). The obtained mixtures were held for 5 min after heating to 130 °C in 40 min to prepare spinning solution. The spinning solution was placed into a spinning machine, and the spun filaments were prepared by melt-spinning. The spun filaments were cured by soaking in an acid solution HCHO and

HCl (1:1 by volume) as main components at 95 °C for 4 h, washed with distilled water and finally dried at 90 °C for 45 min to obtain the fiber samples.

The activation was carried out in a tubular furnace (GSL1200, SiYang Corp., China) and the fiber samples were heated from room temperature to the final activation temperature with a heating rate of 5 °C/min under N_2 flow of 200 cm³/min. Thereafter these fibers were held at 800 °C for 40 min by introducing a steam flow of 8 g/min and then cooled down to room temperature. The sample was denoted by WACF. WACF filled with WC were prepared by the same procedure as stated above. The only difference was the addition of 1 wt% (on the weight of liquefaction) wood charcoal into the liquefaction medium before spinning. The activation temperature was varied to 700, 750, 800 and 850 °C. The WACF filled with WC samples (C-WACF) were referred as C-WACF-700, C-WACF-750, C-WACF-800, and C-WACF-850, respectively.

2.3. Characterization and analysis methods of ACF

Surface morphology of the samples was examined by the field emission-scanning electron microscopy (NanoSEM430, FEI, Netherlands).

The surface area and the porosity of the samples were determined by N_2 adsorption–desorption isotherm measured at 77 K in a Micromeritics ASAP-2020 apparatus. Before analysis, the samples were degassed at 350 °C for 2 h. The specific surface area (S_{BET}) was calculated by the Brunauer–Emmett–Teller (BET) method using N_2 adsorption isotherm data. The total pore volume (V_{tot}) was evaluated by converting the amount of N_2 adsorbed at a relative pressure of 0.995 to the volume of liquid adsorbate. The micropore area (S_{micro}) and micropore volume (V_{micro}) were obtained by t-plot method. The mesopore area (S_{meso}) and mesopore volume (V_{meso}) were calculated by Barrett–Joyner–Halenda (BJH) method. Pore size distributions were calculated using the Density Functional Theory (DFT) Plus Software (provided by Micromeritics Instrument Corporation), which based on calculated adsorption isotherms for pores of different sizes. This program performs an inversion of the integral equation for the overall adsorption isotherm with respect to pore size distributions.

The X-ray diffraction (XRD) patterns of the samples were obtained with a diffractometer (D/max-2500, Japan Rigaku) using Cu Ka radiation (λ = 0.154 nm, powdery samples) at 40 kV and 100 mA by step-scanning over the range of 5–60° (2θ). In order to examine the differences of microcrystalline structure of samples at various temperatures, the apparent crystallite thickness (L_c), the apparent layer-plane length parallel to the fiber axis (L_a), and the average interlayer spacing d were calculated using the Bragg and Scherrer formula (Huiming et al., 1999). The effective dimension L of the graphitic microcrystallites can be written as (Emmerich et al., 1993):

$$L = \left(\frac{\pi}{4}L_a^2 L_c\right)^{1/3} \tag{1}$$

XPS measurements were carried out on a Kratos Axis UltraDLD multi-technique X-ray photoelectron spectroscopy with a monochromated Al Kα X-ray source ($h\nu$ = 1486.6 eV). XPS survey spectra were recorded with pass energy of 80 eV, and high resolution spectra with pass energy of 40 eV. For calibration purposes, the C 1s electron binding energy corresponding to graphitic carbon was set at 284.5 eV (Cuerda-Correa et al., 2008). Atomic ratios were calculated from the XPS spectra after correcting the relative peak areas by sensitivity factors according to the transmission characteristics of the Physical Electronics SCA. A nonlinear least squares curve-fitting program (XPSPEAK software, Version 4.1) was used for XPS spectral deconvolution.