Materials and Design 107 (2016) 26–32

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Synthesis of carbon fiber aerogel from natural bamboo fiber and its application as a green high-efficiency and recyclable adsorbent

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ARTICLE INFO

Article history:
Received 31 May 2016
Received in revised form 2 June 2016
Accepted 5 June 2016
Available online 6 June 2016

Keywords:
Bamboo fiber
Carbon fiber aerogel
Superhydrophobic
Recyclable
Green adsorbent

ABSTRACT

We report an eco-friendly and inexpensive pyrolysis route to produce lightweight and superhydrophobic carbon fiber aerogel (CFA) by using cheap natural bamboo fiber as raw material. When used as an adsorbent, CFA can effectively and rapidly adsorb organic liquid from wastewater and didn't allow any water adsorption. CFA can adsorb an extensive range of organic liquids. The adsorption efficiency can reach up to 23–51 times the weight of original CFA. In addition, CFA shows excellent recyclability, and remained high adsorption efficiency even after five cycles through burning, squeezing, or extracting. In view of the lightweight feature, good adsorption selectivity, substantial adsorption efficiency, excellent adsorption recyclability, and easily-operated cost-effective preparation technique, consequently, we believe that such natural bamboo fiber-derived CFA holds potential for environmental remediation. More importantly, this work provides a good example to expand high-value applications of low-cost biomass resources.

1. Introduction

The increasing seriousness of environmental pollution arising from oil spills, chemical leaks and industrial organic wastewater discharge has become an important issue demanding prompt solution. Extensive researches have been carried out to develop novel high-performance absorbent materials. For instance, Hrubesh et al. [1–3] fabricated different types of hydrophobic silica aerogels, which effectively removed organic liquids from aqueous solutions and mixtures. Zheng et al. [4] reported hybrid aerogels composed of polyvinyl alcohol and cellulose nanofibril. After being treated with methyltrichlorosilane, the superhydrophobic and superoleophilic aerogels not only exhibited excellent absorption performance for various types of oils or organic solvents (44–96 g g^{-1}), but also exhibited a good scavenging capability for heavy metal ions. Zhai et al. [5] synthesized superhydrophobic poly(vinyl alcohol)/cellulose nanofibril aerogel microspheres, whose crude oil absorption and organic solvent uptake capacity can reach up to 116 and 140 times of their own weight, respectively. In recent decades, with the increasing emphasis on green chemistry, natural sustainable and biodegradable resources have attracted huge research interest. Several investigations have been undertaken for removal of organic pollutants from wastewater by using different biomass materials or their derivatives. For instance, Rashwan and Girgis [6] reported a kind of activated carbons derived from pyrolysis of rice straw. The activated carbons exhibited high adsorption capacities of 139 mg g^{-1} for methylene blue, 154 mg g^{-1} for congo red, 59 mg g^{-1} for phenol, and 149 mg g^{-1} for *p*-nitrophenol. Recently, Srinivasan and Viraraghavan [7] used walnut shell media to treat with various oils. It was found that adsorbed oil could be recovered from walnut shell media by applying pressure. The oil sorption capacities of 0.3–0.74 g g^{-1} were obtained. More recently, Venkatanarasimhan and Raghavachari [8] synthesized eco-friendly nanocomposite materials based on mild epoxidation of natural rubber and magnetite nanoparticles. The magnetically recoverable materials could adsorb 7 g of petrol per gram without any mass loss. In addition, some other similar bioadsorbents based on biomass materials (e.g., pine bark [9], avocado kernel seeds [10], passion fruit peel [11], bamboo [12], and orange peel [13]) have been widely reported.

As one of the main components of plants, cellulose is a kind of typical hydrophilic carbohydrate polymer generated from repeating β-D-glucopyranose molecules that are covalently linked through acetal functions between the equatorial OH group of C4 and the C1 carbon atom (β-1, 4-glucan), as shown in Fig. 1. However, the strong hydrophilicity of cellulose is not beneficial to adsorb hydrophobic liquids like most organic solvents and oils. Therefore, prior to the use as adsorbents for organic liquids, these natural hydrophilic bioresources generally need to be subjected to hydrophobic treatment (e.g., acetylation [14],

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http://dx.doi.org/10.1016/j.matdes.2016.06.015
0264-1275/

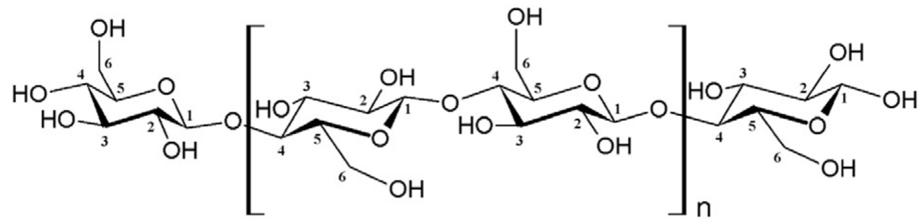

Fig. 1. Chemical structure of cellulose.

esterification [15] and silanization [16]) for grafting oleophilic groups. Also, some nanomaterial coatings (e.g., TiO_2) have been verified to facilitate construction of a low-energy and hydrophobic surface [17]. Recently, an easily-operated pyrolysis process is highly regarded. The process makes contribution to the transformation from hydrophilic cellulose-based materials to hydrophobic carbon products by destroying hydrophilic groups [18,19]. Especially, the micromorphology changed little before and after the pyrolysis [20]. Compared with the aforementioned traditional chemical modifications, the pyrolysis technique is relatively easier to operate and more environmentally friendly; and no poisonous chemicals are needed. Although several reports [19, 21] have adopted pyrolysis technique to fabricate carbon-based adsorbents using cellulose-based materials as raw materials (like bacterial cellulose), it is still worth to develop cheaper and widely available natural biomass materials as feedstocks to fabricate novel high-performance carbon products.

Natural bamboo fiber, as a type of cellulose fibers, comes from an abundant and renewable resource (namely bamboo) at low cost, which ensures a continuous fiber supply and a significant material cost saving. Some researches [22,23] show that the bamboo fiber is alike bast fibers in chemical composition; that is, cellulose constitutes the major portion (73.83%), and other components include hemicellulose (12.49%), lignin (10.15%), pectin, tannin, pigment, etc. Moreover, owing to loose structure and existence of disordered non-cellulose substances, bamboo fiber has a larger moisture regain capability than that of cotton, ramie and flax fibers. Also, bamboo fiber has high water-retention rate. Therefore, these characteristics indicate that bamboo fiber is a favorable potential adsorbent material. Nevertheless, the weak organic liquids sorption property, poor hydrophobicity, and unsatisfactory recyclability impose great restrictions on its application in adsorption and separation of organic pollutants from wastewater. Therefore, in the present work, we report a simple synthesis of carbon fiber aerogel (CFA) from inexpensive sustainable and degradable natural bamboo fiber via an eco-friendly pyrolysis technique. The changes in morphology, chemical components, crystal structure, and water wettability were investigated before and after the pyrolysis treatment by using scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) analysis, Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), and water contact angle (WCA) tests. When used as adsorbents, the adsorption efficiency of CFA towards various common organic solvents and oil was measured. In addition, the adsorption selectivity and recyclability were also evaluated.

2. Materials and method

2.1. Materials

Natural bamboo fiber was rinsed several times by deionized water, and then dried in vacuum at 60 °C for 24 h. All other chemicals were of analytical grade and used without further purification.

2.2. Preparation of carbon fiber aerogel (CFA)

A piece of dried bamboo fiber was put into a cylindrical quartz container, and then the container was placed into a tubular furnace. Prior to the pyrolysis treatment, the air in the tubular furnace and sample was completely removed by vacuum pumping followed by ventilating nitrogen gas for 15 min. After that, the sample was heated to 500 °C at a heating rate of 5 °C min^{-1}, and this temperature was maintained for 1 h; then, the temperature was raised to 1000 °C at 5 °C min^{-1} and remained for 2 h to allow for complete pyrolysis. Thereafter, the temperature decreased to 500 °C at 5 °C min^{-1}, and finally decreased naturally to the room temperature, and the following CFA was obtained. The whole pyrolysis process was conducted under the protection of nitrogen.

2.3. Adsorption property of CFA for oil and organic solvents

A typical adsorption test contains following steps: CFA was firstly weighed before the test, and subsequently placed in contact with an organic solvent or oil until the aerogel was completely filled with the liquid (about 3 min for organic solvents and 10 min for oil), and finally taken out for weight measurement. To avoid the effects of evaporation of adsorbates, especially for those with low boiling points and strong volatility, the weight measurement must be done quickly. The adsorption property was characterized by adsorption efficiency, which was calculated by dividing the wet weight of the samples after the adsorptions by the initial weight. The adsorption recyclability was assessed by repeating the aforementioned adsorption process for five times and monitoring the changes of adsorption efficiency. The adsorbates were removed by three methods, i.e., combusting for cheap flammable and toxic liquid pollutants, squeezing for low-cost and low-viscosity solvents, and extracting for expensive and high-viscosity solvents (residual extraction agent in CFA was removed by burning).

2.4. Characterizations

The morphology was observed by SEM (HITACHI, TM3030) operating at 15.0 kV. Elemental analysis was conducted by an EDX spectrometer. FTIR spectra were recorded on a FTIR instrument (Nicolet 6700, Thermo Fisher Scientific., USA) in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}. The crystal structures were characterized by XRD (Rigaku D/MAX 2200) operating with Cu Ka radiation (λ = 1.5418 Å) at a scan rate (2θ) of 4 min^{-1} ranging from 5° to 40°. WCA was measured on a Powereach JC2000C contact angle analyzer. The Brunauer–Emmet–Teller (BET) surface area and pore property of CFA were determined from N_2 adsorption–desorption experiments at 196 °C using an accelerated surface area and porosimetry system (3H-2000PS2 unit, Beishide Instrument S&T Co., Ltd). Meanwhile, the pore volume and pore-size distribution were estimated by the Barrett–Joyner–Halenda (BJH) method.

3. Results and discussion

3.1. Characterizations of CFA by SEM, EDX, XRD and FTIR

The SEM image in Fig. 2a shows the microstructure of the natural bamboo fiber. As shown, the long fibers are intertwined leading to the formation of three-dimensional (3D) networks. The 3D porous frame provides congenital condition for adsorption [24]. The average size (d)