Carbohydrate Polymers 136 (2016) 95–100

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Green and facile fabrication of carbon aerogels from cellulose-based waste newspaper for solving organic pollution

Shenjie Han[a], Qingfeng Sun[a,b,*], Huanhuan Zheng[a], Jingpeng Li[a], Chunde Jin[a,b,*]

[a] *School of Engineering, Zhejiang Agricultural and Forestry University, Lin'an 311300, PR China*
[b] *Key Laboratory of Wood Science and Technology, Zhejiang Province, PR China*

ARTICLE INFO

Article history:
Received 17 May 2015
Received in revised form 7 September 2015
Accepted 10 September 2015
Available online 11 September 2015

Keywords:
Waste biomass
Carbon aerogel
Hydrophobicity
Absorption
Recyclability

ABSTRACT

Carbon-based aerogel fabricated from waste biomass is a potential absorbent material for solving organic pollution. Herein, the lightweight, hydrophobic and porous carbon aerogels (CAs) have been synthesized through freezing–drying and post-pyrolysis by using waste newspaper as the only raw materials. The as-prepared CAs exhibited a low density of 18.5 mg cm^{-3} and excellent hydrophobicity with a water contact angle of 132° and selective absorption for organic reagents. The absorption capacity of CA for organic compounds can be 29–51 times its own weight. Moreover, three methods (e.g., squeezing, combustion, and distillation) can be employed to recycle CA and harvest organic pollutants. Combined with waste biomass as raw materials, green and facile fabrication process, excellent hydrophobicity and oleophilicity, CA used as an absorbent material has great potential in application of organic pollutant solvents absorption and environmental protection.

1. Introduction

With the rapidly increasing exploitation, transportation and storage of oils and toxic organic solvents, oil and toxic chemical spills/leaks accidents have resulted in severe energy, environmental, and ecological problems all around the world (Gui et al., 2011; Wu et al., 2014). For example, on April 20, 2010, the Gulf of Mexico oil spill accident caused widespread contamination and pollution of coastal waters and living environment, let alone the tremendous loss of a variety of valuable resources (Burns, Olin, Woltmann, Stouffer, & Taylor, 2014; Li, Samad, Polychronopoulou, Alhassan, & Liao, 2014). Among the existing strategies used for oil recovery currently, sorption is considered as an economical choice because of its simplicity and high efficiency (Adebajo, Frost, Kloprogge, Carmody, & Kokot, 2003). Traditional oil sorbent materials were classified as natural organic materials, inorganic mineral products, synthetic polymers and polymer-based composites (Bayat, Aghamiri, Moheb, & Vakili-Nezhaad, 2005; Li et al., 2014; Wu et al., 2014). However, natural organic materials demonstrate poor selectivity and low sorption capacity. The reserve of inorganic mineral products is limited and the used products are difficult to recycling. Synthetic polymers and polymer-based composites degrade very slowly and may introduce other types of containments during the cleanup procedure (Wu et al., 2014). Therefore, there is a demand to synthesize new sorbent materials with high absorption capacity and low production cost.

Recently, carbon-based aerogels, such as carbon fiber aerogel (Wu, Li, Liang, Chen, & Yu, 2013), carbon micro belt aerogel (Bi et al., 2014), graphene/CNT hybrid foam (Dong et al., 2012), carbon nanotube (CNT) sponges (Gui et al., 2010), and spongy graphene aerogel (Zhao, Ren, & Cheng, 2012), used as oil sorbents have been extensively investigated because they have three-dimensional (3D) structures and outstanding physical properties (e.g., low apparent density, high electrical conductivity, porosity, large specific surface area, and surface hydrophobicity) (Li et al., 2014). Those unique physical properties make them ideal candidates for the removal of oil or hydrophobic organic solvents from water by improving absorption capacity and facilitating selective absorption. Nevertheless, the expensive/toxic precursors, complicated fabrication technologies, and expensive equipment involved in their preparations dramatically hamper their large-scale production for practical applications (Wu et al., 2014). Therefore, there is a growing demand for exploring a green, facile and environmentally friendly pathway to massive production of carbon-based aerogels with high sorption capacity, good selectivity, and low cost for oil spills and chemical leaks.

Nowadays, the production of carbon-based materials from waste biomass has attracted intensively increasing attention due to its low cost, sustainability, nontoxicity to humans, etc. (Bi et al.,

---

* Corresponding authors at: School of Engineering, Zhejiang Agricultural and Forestry University, Lin'an 311300, PR China.
E-mail address: qfsun@zafu.edu.cn (Q. Sun).

http://dx.doi.org/10.1016/j.carbpol.2015.09.024
0144-8617/

2013; Feng, Nguyen, Fan, & Duong, 2015; Wu et al., 2013; Zhang, Liu, Cui, & Chen, 2014). However, the generation of acidic waste and the use of a large amount of chemicals during the preparation process will improve production cost and restricting their industrial applications. Waste newspaper, contributes to about 7% municipal solid waste, is a typical waste biomass material and a low-cost cellulosic material (Subhedar, Babu, & Gogate, 2015). Its abundance makes it a promising raw material for fabricating carbon-based aerogel. Herein, in this study, the lightweight, hydrophobic and porous carbon aerogels were made by a freezing-drying method and post-pyrolysis route using waste newspaper as the raw material. Importantly, the obtained CA can absorb various organic solvents. Compared with other carbon-based aerogels, the absorption capacity of CA is 29–51 times its own weight. Considering the high performance, cheap raw materials, and green synthetic method, CA is believed to have great potential for removing petroleum products and toxic organic solvents.

2. Materials and methods

2.1. Materials

The waste newspaper procured locally was shredded mechanically into small pieces. Its composition based on the dry substrate was: 50.1% cellulose, 16.8% hemicellulose, 18.1% lignin, 6.8% ash and 5.9% moisture. The composition was determined by using the standard method described by National Renewable Energy Laboratory (NREL) (Sluiter et al., 2008). All other chemical reagents and deionized water were of laboratory grade and used as received.

2.2. Preparation of carbon aerogels from waste newspaper

0.90 g of waste newspaper scraps were poured into 30 mL of DIW and soaked for three days. Then the mixture was subjected to agitate acutely under vigorous magnetic stirring to form a uniform mixture called waste newspaper pulp (WNP). The WNP was freeze dried to generate WNP fiber aerogel. After that, the obtained WNP fiber aerogels were transferred into a tubular furnace (OTF1200X, Hefei Kejing Materials Technology Co., Ltd, China) for pyrolysis. In order to remove the air trapped in the WNP fiber aerogel completely, the furnace was evacuated before introducing argon gas, followed by evacuating the furnace again. After that, the furnace was heated up to 400 °C at a heating 2 °C min^{-1}, kept this temperature for 1 h, then heated to 900 °C at 5 °C min^{-1} and held at this temperatures for 2 h to assure complete pyrolysis, cooled to 400 °C at 5 °C min^{-1}, finally, cooled to room temperature (16 °C) naturally to yield black and low-density CAs.

2.3. Sorption of organic solvents and oils by the CAs

A series of oils and organic reagents were employed to study the sorption capacity of the CAs. In the present study, the sorption experiments were conducted at room temperature (16 ± 2 °C). The CAs were weighed and placed in contact with the oil or organics solutions until the CAs were filled with the oil or organic reagents completely. The wet CA used for oil sorption removed from the solution, lifted up for 30 s to allow the surface residual liquid to drip away, and then weighed. To avoid evaporation of absorbed organic liquids, especially for those with low boiling points, weight measurements of CAs after organic reagents sorption should be done quickly. The sorption capacity of the CA was calculated using the following formula:

$$Q_t = \frac{m_t - m_o}{m_o} \qquad (1)$$

where Q_t (g/g) is the sorption capacity of the CA at a certain time t (s), m_t (g) is the weight of the CA after sorption, and m_o (g) is the initial weight of the CA.

2.4. Characterizations

The changes in the macroscopic appearance of the composite aerogels before and after pyrolysis were observed through visual examination. The morphologies of the WNP fiber aerogels and the CAs were characterized by a scanning electron microscopy (SEM, S-3400N, Kyoto, Japan) at an accelerating voltage of 12.5 kV. The as-obtained samples were subjected to gold sputtering prior to electron microscopy to give the necessary conductivity. The surface wettability of CA was evaluated by contact angle measurement, using a contact angle analyzer (JC2000C) at ambient temperature. The average value of five measurements performed at different surface locations was reported as the contact angle. The volume of the water droplets fixed at 5 μL and the water contact angle was determined 10 s after the water droplet was deposited on the surface of the CAs. The FTIR spectra were recorded on a Fourier Transform infrared instrument (Nicolet Magna-IR 560, Thermo Scientific) in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}. All the raw materials and the CAs were ground into powder by a fiber microtome and then blended with KBr before pressing the mixture into ultrathin pellets. The XRD patterns of the raw materials and the CAs were measured by X-ray diffraction (XRD, Rigaku, D/MAX 2200) operating with Cu Kα radiation (γ = 1.5418 Å) at a scan rate (2θ) of 2°/min with the accelerating voltage of 40 kV and the applied current of 30 mA ranging from 5° to 50°.

3. Results and discussion

3.1. Synthesis and characterizations of CAs

The fabrication process of CA illustrated in Fig. 1. Typically, a certain amount of waste newspaper pieces were immersed in DIW for three days. Then, they were broken down into a mixture of cellulose through strong agitation under vigorous stirring, and the resulting mixture was called WNP. Then the WNP was subjected to freeze-drying to manufacture the WNP fiber aerogel, the size and shape of which can be controlled by using various shapes of containers. The resulted WNP fiber aerogels were pyrolyzed at 900 °C for 2 h at a low pressure (∼0.5 mbar) under argon atmosphere to generate the black and lightweight CAs (see Section 2.2 for details). In this study, the WNP fiber aerogel had a diameter of 35.48 mm (Fig. 1c), and decreased to 26.23 mm (Fig. 1d) after pyrolysis, and the volume of obtained CA is only 35.4% of that of the original WNP fiber aerogel.

Scanning electron microscope (SEM) images show that the WNP fiber aerogels and the CAs are porous and interconnected 3D networks (Fig. 2). The most fiber lengths of the WNP fiber aerogels are up to a few centimeters or even longer (Fig. 2a and b). High-magnification SEM image and diameter distributions image exhibit that the width of belt fibers is about 11.86 μm (Fig. 2c and d). In contrast, the fibers after pyrolysis in CAs were cross-linked with each other tightly (Fig. 2e and f) and the most fiber lengths were almost unaltered. Furthermore, the fibers of CAs show a reduced size of ∼3.76 μm (Fig. 2g and h).

As shown in Fig. 3a, the CA, has a weight of 9.84×10^{-2} g, is lightweight and has a low density of ∼18.5 mg cm^{-3} calculated based on Archimedes' principle. The WNP fiber aerogel, consists of a large amount of cellulose, can absorb water effectively due to the hydrophilic character of cellulose. On the contrary, the CA is hydrophobic. The water repellency of the CA highlighted in Fig. 3b, water droplet exhibit typical spherical shape on the CA surface,