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RESEARCH PAPER

Carbon foams produced from lignin-phenol-formaldehyde resin for oil/water separation

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Abstract: Carbon foams for oil/water separation were synthesized using lignin-phenol-formaldehyde (LPF) resin as the carbon source and polyurethane (PU) foam as the template. Lignin was extracted from sedge grass and was used to replace 25 wt% of the phenol to prepare a LPF resin in an alkaline medium. The carbon foams exhibit unique properties such as open macropores, low bulk density, good water repellency and efficient oil absorption. The absorption capacities of the carbon foams are 12 to 41 times their own weight for a wide range of oils and organic solvents. The foams can be recycled by directly burning the oil within their pores and absorption capacity remains above 83% after 10 absorption test cycles, indicating that the carbon foams are promising oil sorbents with a good recyclability.

Key Words: Carbon foam; Lignin; Biomass; Resin; Oil/water separation

1 Introduction

Carbon foams are lightweight materials with high mechanical strength, low thermal expansion coefficient, adjustable thermal conductivity and large external surface area, which make them suitable materials for energy storage, catalyst supports and filters, et al. [1-3]. Since the first development of carbon foam from thermosetting organic polymers, advances in finding new precursors as well as the preparation of carbon foam from coal, mesophase pitch and, polyimide , etc. have been described [3-9]. For example, carbon foams were successfully prepared from polyimide with urethane foam as the template, and their applications for an adsorbent of ambient water vapor and a substrate of photocatalyst anatase TiO_2 were experimentally confirmed [3]. Recently, the utilization of biomass for the synthesis of carbon foams has received great attention due to the scarcity of fossil energy. For example, Molina-Sabio et al. reported that the pyrolysis of lignocellulosic material such as olive stones produced a swelling of the particle and eventually led to the formation of carbon foam [8]. Unfortunately, most cells in the resultant carbon foam derived from the biomass were irregular and uncontrollable due to the expansion mechanism. The production of carbon foam with controlled pores using renewable biomass as the carbon sources is challenging [10]. Nature provides an enormous variety of biomass resources including vegetal biomass and agricultural residues. Sedge grass, a very common annual plant in China, is often exploited as a raw material in the pulping industry. During pulping process, lignin is produced in million tons per year as a waste material or a low value byproduct. Fortunately, some researches have found that lignin instead of toxic phenol has successfully been used to produce phenol-formaldehyde (PF) resin owing to their similar phenolic structures [11, 12]. The lignin-phenol-formaldehyde (LPF) resin will be the potential sources for the carbon foams based on the low cost and little toxicity of lignin.

Oil/water separation is a worldwide problem because of the increasing industrial oily wastewater as well as the frequent oil spill accidents [7, 13]. These issues have inspired the recent scientific research in the field of material science, with numerous studies aiming at the development of new materials for oil/water separation. So far, superhydrophobic and superoleophilic meshes, films, aerogels or membranes have been used as filters that allow oil to penetrate through them and keep water on their surfaces [13-15]. Recently, a novel composite material based on commercially available polyurethane (PU) foams functionalized with colloidal superparamagnetic iron oxide nanoparticles and polytetrafluoroethylene has been reported, which can be used efficiently to separate oil from water [16]. Herein, we demonstrate an approach to the synthesis of carbon foams using LPF resin as the carbon source and PU foam as the template. The oil/water separation for the obtained carbon foams have been investigated.

2 Experiamental

2.1 Lignin extraction from sedge grass

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Lignin was extracted from sedge grass using the similar method according to the reference [17]. Typically, 10 g grass with a length about 1 cm was impregnated in a mixture of formic acid (FA), acetic acid (AA) and water (3:5:2 *v*/*v*/*v*, 100 mL) at 60 ^{o}C for 1 h, and the resulting mixture was heated at 107 ^{o}C for 3 h under strong stirring. After cooled to room temperature, the mixture was filtered. The filtrate was distilled at 118 ^{o}C to reclaim the liquid mixture. Finally, lignin was precipitated by adding water to the residual liquor, filtered and dried at 40 °C.

2.2 Synthesis of the carbon precursor

LPF resin was prepared under the basic condition according to the literature [18, 19]. Typically, 1.5 g lignin and 4.6 g phenol were mixed in a 5.5 mL NaOH solution (20 wt%) and stirred for 20 min [20]. After that, 37 wt% formalin (9.5 mL) was added, and the mixture was heated at 71 ^{o}C for 1 h and collected.

2.3 Synthesis of the carbon foams

The carbon foams were prepared using LPF resin as the carbon source and PU foam as the template. The PU foam was firstly put into 10 wt% NaOH solution at 50 ^{o}C, then treated for 1h to obtain a high open-cell template (designated as PU* foam) [21]. In a typical synthetic procedure, the LPF solution mentioned in section 2.2 was coated into the PU* foams with a size of 2.4 (L) × 1.2 (W) × 1.0 (H) cm^3. The air bubbles inside the PU* foam scaffolds were removed by frequently squeezing the scaffolds with a glass rod during the infusion of the solution. Solidification was carried out at 180 ^{o}C for 80 min in an oven for the further thermopolymerization. The obtained sample named as PU*/LPF composite was puce in color. Calcination of PU*/LPF composite was carried out at 950 ^{o}C for 2 h with a heating rate of 2 ^{o}C min^{-1} under N_2 flow to remove the template. The as-made macroporous material was carbon foams.

The densities of the carbon foams were tailored by varying the reaction conditions including the amount of LPF impregnation, temperature and time of LPF solidification. The carbon foams with a bulk density of 20.6-29.4 mg cm^{-3} were obtained by the following procedures: (a) solidification of LPF resins in PU template at 180^{o} for 40-120 min; (b) solidification of LPF resins coated onto PU template at 120-210^{o} for 80 min; (c) impregnation of 41.5-47.0 mg LPF resins onto the PU template at 180^{o} for 80 min.

2.4 Oil and solvent absorption of carbon foams

The absorption capacities of the carbon foams were obtained with different densities for various oils. Organic solvents including normal hexane (0.66 g cm^{-3}), diesel oil (0.84 g cm^{-3}), vegetable oil (0.90 g cm^{-3}), and ethylene glycol (1.11 g cm^{-3}) were also measured. Pristine carbon foams with a cubic shape were placed inside the mixtures of solvents and oils for a fixed time (e.g. 20 s), then picked out to measure their absorption capacities. The absorption was very fast and typically reached saturation within a few seconds by immersing the foams into the liquid mixtures. The foam weights after and before the absorption were recorded, then the absorption amount (Q_m, g g^{-1}) of the carbon foam for different oils and organic solvents was calculated according the following formula [15].

$$Q_m=(m_1-m_0)/m_0 \qquad (1\text{-}1)$$

Where, m_0 is the weigh before absorption and m_1 the weigh after absorption.

The feasibility of cleaning an oil-contaminated water by means of the carbon foams was carried out using distilled water and vegetable oil (0.90 g cm^{-3}) colored by red dye.

The morphology and structures of the as-obtained products were examined using a scanning electron microscope (SEM, JSM-6360LV), Fourier transform infrared (FTIR) analysis (Bruker TENSOR 27 FTIR spectrometer) and thermogravimetric analysis (TGA, Perkin-Elmer Diamond TG analyzer).

3 Results and disscussion

The acid-insoluble lignin is extracted from grass with a yield of about 14 wt% in this case. The resultant grass-lignin is brown in powders (shown in the inset of Fig. 1), and its typical IR spectrum is shown in Fig. 1. Various bands in the spectrum are identified as corresponding to -OH (at wavenumber of 3 430 cm^{-1}), methoxyl (2 842 cm^{-1}), aliphatic CH (3 000–2 860 cm^{-1}) as well as aromatic ring modes (1510 cm^{-1} and 1 600 cm^{-1}). The broad band of the hydroxyl stretching is not used for the complete structural elucidation of the complex lignin molecule. The band at 2 842 cm^{-1} represents the symmetric CH_3 stretch of the methoxyl group and the one at 1 028 cm^{-1} is due to the C–O stretch for both O–CH_3 and C–OH. A strong band assigned to ester group C=O stretching is also observed at 1 715 cm^{-1}. The most characteristic bands of lignin are at 1 510 cm^{-1}, 1 600 cm^{-1} (aromatic ring vibrations) and 1 460 cm^{-1} (CH deformation and aromatic ring vibrations), which are in accordance with the reported work [17]. The absence of the aromatic acetoxy band (signal at 1 743 cm^{-1}) in the lignin spectrum indicates that free phenolic OH groups are not esterified during the extraction, which provides some activated sites for the further synthesis of LPF resin[17].

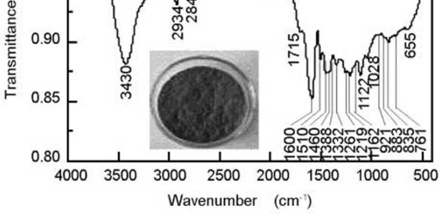

Fig. 1 FT-IR spectrum of grass-lignin, inset is its photograph.