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Full Length Article

Construction of horizontal stratum landform-like composite foams and their methyl orange adsorption capacity

Jiajia Chen, Xiaowen Shi, Yingfei Zhan, Xiaodan Qiu, Yumin Du, Hongbing Deng*

Hubei International Scientific and Technological Cooperation Base of Sustainable Resource and Energy, Hubei Key Lab of Biomass Resource Chemistry and Environmental Biotechnology, School of Resource and Environmental Science, Wuhan University, Wuhan, 430079, China

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ABSTRACT

Chitosan (CS)/rectorite (REC)/carbon nanotubes (CNTs) composite foams with good mechanical properties were successfully fabricated by unidirectional freeze-casting technique. The morphology of the foam showed the well-ordered porous three-dimensional layers and horizontal stratum landform-like structure. The holes on the layers looked like the wings of butterfly. Additionally, the X-ray photoelectron spectroscopy and energy-dispersive X-ray spectroscopy results indicated the successful addition of CNTs and REC. The intercalated REC with CS chains was confirmed by small-angle X-ray diffraction. The surface structure of the foams was also analyzed by Raman spectroscopy. The adsorption experiments showed that when the mass ratio of CS to REC was 10:1 and CNTs content was 20%, the composite foam performed best in adsorbing low concentration methyl orange, and the largest adsorption capacity was 41.65 mg/g.

1. Introduction

During the past decade, porous materials have drawn much attention for their extensive applications such as tissue engineering [1], drug delivery [2], environmental protection [3,4] and so on. Lots of methods have been performed to construct porous materials, among those methods, unidirectional freeze-casting technique (UDFC) stands out because it is friendly to environment, simple to operators, and controllable to designers [5]. As a promising and versatile technique, UDFC introduces neither chemical reactions nor any other compounds during the preparation process [6,7]. Actually, it is the simplest way to prepare oriented foams so far. During UDFC, a slurry is poured into a mold and then frozen with a uniaxial thermal gradient created by liquid nitrogen or other thermostat. Ice crystals grow along the uniaxial thermal gradient, push the particles or polymers to the gap of grown ice crystals. After the sublimation of the ice crystals, the pores are left as the replica of the ice crystals [8]. Water, which is environment-friendly and economically feasible, is often chose as the solvent. The removal of it can be easily realized by freeze-drying, so that the potential complications (including byproducts or the chemical processes used to remove template) can be avoided [9].

As we know, porous materials with high surface area to volume and well-ordered architectures are good candidates for adsorbents [3,10]. However, the majority of the foams prepared by UDFC were reported to apply to tissue engineering [1] and biological field [11,12], only a few studies focused on the adsorption of contaminant. In general, azo dye wastewater is hard to degrade because of its high chroma, high content of organic compounds, and complexity of the components [13,14]. In addition, azo dyes are known to be toxic, mutagenic and carcinogenic [15]. Hence, it is necessary and important to remove them before discharging. Nowadays, several methods have been reported, but most of conventional methods are either technically complicated or economically unfavorable [16], and the adsorption treatments are still dominant.

For environmental pollutants adsorption, the candidates derived from nature are more preferable. In many studies, organic, inorganic and composite aligned porous materials have been exploited by UDFC, such as alumina [17,18], silicate cement [19], hydroxyapatite [1], poly(vinyl alcohol) [2], gelatin [11], chitin [20], chitosan-gelatin/graphene oxide [21] and so on.

Chitosan (CS), famous for its non-poisonous, biocompatibility, biodegradability, and adsorption properties, has been employed in UDFC [22]. CS-based composites composed of two or more distinct components will produce new properties in structure or function that pure CS does not have, or boost the excellent properties of pure CS material to obtain unprecedented performances [9,23]. Rectorite (REC), a kind of layered silicate, has been reported with remarkable

* Corresponding author.
E-mail addresses: hbdeng@whu.edu.cn, alphabeita@yahoo.com (H. Deng).

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intercalation/exfoliation properties. The polymer chains could be intercalated into its interlayer to enhance the interlayer spacing [24]. As a result, REC was often used to mix with polymer, such as lysozyme [25], poly(lactic acid) [26] and CS [27]. Carbon nanotubes (CNTs) with the hollow structures as well as their large specific surface area are used as ideal absorbent. Their adsorption of inorganic and organic contaminants has been proved by experimental studies [28,29]. Hence, it will be meaningful to prepare ordered porous CS foams with incorporation of REC and CNTs.

Based on above considerations, a series of CS/REC/CNTs foams were fabricated via UDFC in this study. The morphology, composition, structure, surface area, and adsorption capacity of the foams on methyl orange (MO) were examined. Furthermore, the effect factors such as initial pH, adsorbent dose, adsorption time and initial concentration of MO were discussed.

2. Experimental details

2.1. Materials

Chitosan (CS, medium molecular weight) was supplied by Sigma Aldrich Chemical Reagent Co. Ltd. Rectorite (Ca^{2+}-REC) was purchased from Hubei Mingliu Inc., China. Carbon nanotubes (CNTs) were provided by Nanotech Port Co. Ltd., Shenzhen, China. Analytical reagent acetic acid and methyl orange (MO) were purchased from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. All aqueous solutions were prepared using purified water with a resistance of 18.2 MΩ cm.

2.2. Preparation of CS/REC/CNTs blend suspensions

2% CS solution was prepared by dissolving CS powder into 1% acetic acid solution with constant agitation for 3 h at room temperature. Then REC and CNTs were added into the obtained CS solution successively, kept stirring for 4 days. The mass ratio of CS to REC was adjusted at 10:1 and 5:1, and the concentrations of CNTs were kept at 0, 5, 10 and 20% of total solute, respectively. The concentrations of all solutions were expressed in wt/wt%.

2.3. Foams fabrication

The prepared suspensions were poured into polyethylene molds with a diameter of 5.2 cm, then the molds were surrounded by styrofoam to avoid the heat transfer between the prepared suspension and outside air. Afterwards, the molds were controlled to contact with liquid nitrogen slowly in a certain rate. As the liquid nitrogen evaporated, the suspension was unidirectionally frozen from bottom to the top. After that, the samples were freeze dried for 48 h. As the solvent sublimated, the formation of the porous structure occurred. These composite foams were recorded as $[(CS/REC)_{10:1}]$-0%CNTs, $[(CS/REC)_{10:1}]$-5%CNTs, $[(CS/REC)_{10:1}]$-10%CNTs, $[(CS/REC)_{10:1}]$-20%CNTs, $[(CS/REC)_{5:1}]$-5%CNTs, $[(CS/REC)_{5:1}]$-10%CNTs and $[(CS/REC)_{5:1}]$-20%CNTs.

2.4. Characterizations

The morphology of the foams was observed by Field emission scanning electron microscopies (FE-SEM) (Zeiss, Germany). Energy-dispersive X-ray (EDX) spectroscopies and field emission transmission electron microscopy (FE-TEM) images were obtained by JEM-2100 (HR, JEOL, Japan). The surface elemental composition of samples was identified by X-ray photoelectron spectroscopy (XPS) using an axis ultra DLD apparatus (ESCALAB 250Xi, Thermo Fisher Co., USA). Fourier transform infrared (FT-IR) spectra were recorded by using Nicolet170-SX (Thermo Nicolet). A DXR Raman microscope (Thermo Electron Co., USA) was utilized with a 785 nm excitation laser. The X-ray diffraction was evaluated using a diffractometer type D/max-rA (Rigaku Co., Japan) with Cu target and Ka radiation (λ= 0.154 nm) at 40 kV. The scanning rate was 5°/min and 1°/min, the scanning scope of 2θ was 6–60° and 2–9°, for wide-angle X-ray diffraction (WAXRD) and small-angle X-ray diffraction (SAXRD), respectively. The Brunauer-Emmett-Teller (BET) surface area data and nitrogen adsorption-desorption isotherms were measured by a surface area and pore size analyzer (Quantachrome NOVA 4200e) at 77 K and a relative pressure (P/P_0) range of 0.005–0.99. Textural profile analysis of composite foams was performed on a Texture Analyser (TA-XT. Plus, Stable Micro Systems, UK) equipped with probe P/36R.

The water adsorption of the composite foams was measured by putting them into deionized water till equilibration, and calculating according to the following equation:

$$\text{Water absorption } (\%) = \frac{M_t - M_0}{M_0} \times 100\% \quad (1)$$

where M_0 (g) and M_t (g) are the weight of the composite foams before and after immersing into deionized water, respectively.

2.5. Adsorption experiments

The MO dye solution was prepared by dissolving the powder with known weight in deionized water. Batch adsorption experiments were carried out to study the effects of parameters (initial pH, adsorbent dose, adsorption time and the initial concentration of MO). The adsorption capacity (Q_e) and removal percentage was calculated according to the following equations:

$$Q_e = \frac{C_0 - C_e}{m} V \quad (2)$$

$$\text{Removal percentage } (\%) = \frac{C_0 - C_e}{C_0} \times 100\% \quad (3)$$

where C_0 and C_e (mg/L); are the initial and equilibrium concentrations of MO solution, respectively. Q_e (mg/g) is the adsorption capacity of adsorbent for MO. V (mL) is the volume of MO solution, and m (mg) is the mass of the adsorbent.

3. Results and discussion

3.1. Morphology investigation of the foam

The FE-SEM images were showed in Fig. 1. Obviously, the porous materials with a well-patterned and multilayered films were developed successfully. The beautiful continuous parallel layers could be observed in Fig. 1a and the edge of the layer was similar with a sharp knife, which was analogous to the structure of the horizontal stratum landform. The completely horizontally straight-lined layers remarkably testified that the layers' construction process via UDFC occurred expeditiously and efficiently. Undoubtedly this kind of porous structure could increase the surface area to volume of the foam. Interestingly, the intervals between the multilayers were different from each other and their average diameter was 18.31 ± 8.16 μm (Fig. 1a'). The inhomogeneous distribution of the layers indicated that UDFC process still possessed some uncontrollability. In another word, during the rapid freezing process, the direction of the layers could be controllable, but the distance between the layers was resigned. We speculated that the fine structure regulation could be achieved by adjusting the parameters of the initial solutions and the freeze-casting process, and the construction mechanism of the interesting layers would be investigated next.

Fig. 1b presents the vertical section of the porous materials, and the lamellar structure with holes looked like the wings of a