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Bio-inspired functionalization of microcrystalline cellulose aerogel with high adsorption performance toward dyes

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ABSTRACT

As one of the materials from natural resources, the functionalization and application of cellulose attract increasing concerns. In this work, we reported a facile method to prepare the bio-inspired functionalization of microcrystalline cellulose (MCC) aerogel through polydopamine (PDA) coating, which was realized via the self-polymerization of dopamine in the MCC/LiBr solution followed by the freeze-drying technology. The morphological characterization showed that the pore morphologies of the compounded aerogel were influenced by the content of PDA. Adsorption measurements toward methylene blue (MB) showed that the compounded aerogel had high adsorption ability. Moreover, the compounded MCC/PDA aerogel exhibited excellent adsorption selectivity and it exhibited high efficiency to remove MB from different solutions, such as the mixed solution with anionic dyestuffs, the mixed solution with cationic dyestuffs and the mixed solution with common salt (NaCl). The high adsorption ability and excellent adsorption selectivity endows the compounded MCC/PDA aerogel with great potential applications in wastewater treatment.

1. Introduction

Emission of organic dyestuffs is one of the most important sources that result in the increasingly serious water pollution. Attaching importance to wastewater treatment to reduce the emission of such pollutants is the essential way to weaken the water pollution. To date, various treatment methods, such as physical, chemical and biological schemes, have been developed to remove dyestuffs from wastewater (Madrakian, Afkhami, Ahmadi, & Bagheri, 2011). Among those methods, adsorption technology through using various adsorbents, such as porous membranes (Zhu et al., 2016), microspheres (Fu et al., 2015) and aerogels (Wei et al., 2017), is particularly regarded as an easy-operation technology with relatively low cost, high recyclability and high-efficiency. Due to their extremely low density, high porosity and high adsorption capacities, aerogels have attracted much attention of researchers (Dai et al., 2016). Many kinds of aerogels, such as carbon-based aerogels (Sun, Xu, & Gao, 2013), polymer-based aerogels (Luong, Lee, & Nam, 2008) and ceramic-based aerogels (Melone et al., 2013), have been developed to remove the dyestuffs from wastewater. It is worth noting that there are many kinds of dyestuffs, such as neutral, anionic and cationic dyestuffs. In actual industrial processes, different kinds of dyestuffs are possibly simultaneously present in the wastewater and therefore, removal of these dyestuffs becomes very complicated. Obviously, the removability toward dyestuffs is determined by the selective adsorption abilities of the aerogels. It is believed that developing new kind of aerogels with high selectivity toward a certain dyestuff is significant, which is not only favorable for the understanding of the adsorption mechanism but also favorable for the reclamation of a certain dyestuff. However, less work has been done to investigate the adsorption selectivity of aerogels.

As a material which can be obtained from natural resources, cellulose and its derivatives attract increasing concerns of researchers. Cellulose-based aerogels have extremely high structure stability due to the strong hydrogen-bonding interaction between molecules (Wei et al., 2017), which is apparently different from the other aerogels, such as graphene oxide aerogels that have extremely high hydrophilicity and usually experience the structure collapse in wastewater, which results in the second pollution problem. However, it is worth noting that the intrinsic adsorption ability of the cellulose is rather low. This indicates that the other adsorbents must be incorporated with cellulose or the cellulose must be further modified so that it can be used as the adsorbents of dyestuffs (Wei et al., 2017). For example, Feng, Nguyen, Fan, and Hai (2015) developed a facile and cost-effective synthesis method to prepare the biocompatible cellulose aerogel using recycled cellulose fibers and Kymene crosslinker. Their results confirmed that after being coated with methyltrimethoxysilane (MTMS) via chemical

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vapor deposition, the recycled cellulose aerogels exhibited extremely high super-hydrophobicity and excellent oil adsorption ability. Chen et al. (2017) fabricated a cellulose sponge with multipore structure. In their work, amphiphilic molecular brushes of polyethylene glycol with short perfluorinated end caps (F-PEG) were grafted on cellulose sponge. The results showed that the modified cellulose sponge exhibited high flux and separation efficiency simultaneously.

Polydopamine (PDA) is one of the nature-inspired materials and it is widely obtained in mussel adhesive proteins. PDA can be obtained through the self-polymerization of dopamine (DA) in aerobic atmosphere under alkaline situation or at high temperature and it owns many functional groups, such as catechol, amine and imine (Fu et al., 2016). During the self-polymerization process, PDA can be easily deposited on various surfaces of materials, leading to the apparent changes of the surface characteristics and microstructure (Yan, Huang, Miao, Tjiu, & Liu, 2015). Therefore, PDA exhibits great potential applications in many fields, such as chemical, biological, medical and materials science areas (Dong et al., 2014; Wang, Huang, & Jiang, 2017; Yan et al., 2015). For example, Wang et al. (2017) introduced the derivative of PDA with brush-like long-chain tailed structure on the surface of the anatase TiO_2 nanowires to improve the interfacial compatibility between components. Dong et al. (2014) prepared a series of sub-nano thick PDA layer coated graphene oxide (GO) composites. Adsorption measurements demonstrated that the PDA/GO composites showed excellent adsorption ability toward the dyes with an Eschenmoser structure. Yan et al. (2015) prepared the free-standing poly (vinyl alcohol)/poly(acrylic acid) membranes with PDA coating. The prepared membranes exhibited high adsorption performance toward organic dyestuff. In our previous work (Ma et al., 2017), DA was co-electrospun with poly(vinylidene fluoride) (PVDF) and then the self-polymerization of PDA was triggered in Tris − HCl buffer solution. A thin layer of PDA was successfully coated on the hydrophobic PVDF electrospun fibers and consequently, the fiber membrane exhibited largely enhanced hydrophilicity, excellent adsorption ability and oil/water separation ability.

Here we report on a facile and eco-friendly method to prepare a new kind of compounded aerogel based on microcrystalline cellulose (MCC) and PDA through self-polymerization of PDA in the solution of MCC/LiBr followed by the freeze-drying technology. It is expected that the functionalization of MCC through PDA coating not only endows the MCC aerogel with high adsorption ability but also maintains the high mechanical stability of the MCC aerogel. Adsorption measurements toward methylene blue (MB) in different conditions demonstrate that the compounded MCC/PDA aerogel is a suitable candidate as an efficient adsorbent with high adsorption capacity and selectivity toward the cationic dyestuffs.

2. Experimental part

2.1. Materials

Microcrystalline cellulose (MCC, with a trade name of C10583) and dopamine (DA) were purchased from Aladdin Chemical Reagent Co. (Shanghai, P.R. China). LiBr was supplied by Changzheng Chemical Reagent Co. Company (Chengdu, P.R. China).

2.2. Preparation of the compounded MCC/PDA aerogels

First, a certain amount of LiBr was dissolved in the distilled water to prepare the LiBr/water solution with a concentration of 60 wt%. Then, a certain amount of dopamine was dissolved in the LiBr/water solution at room temperature. And then, a certain amount of MCC (50 mg) was dissolved in the DA/LiBr/water solution and the temperature of the mixed solution was enhanced up to 120 °C. After being continuously stirred for 30 min, MCC was completely dissolved in the mixed solution and simultaneously the self-polymerization of PDA was triggered. Subsequently, the mixture was transformed into a water bath set at room temperature. After being statically placed for about 3 min, the mixture changed into gel. The gel was immersed into the deionized water for about 3 days and in this process, the gel was periodically taken out and the solution was changed by the fresh distilled water. After that, the MCC/PDA hydrogel was obtained. Subsequently, the hydrogel was pre-frozen in the atmosphere of liquid nitrogen vapor for about 30 min, and then it was transferred into a freeze-drying machine FD-1A-50 (Boyikang, China) set at a temperature of − 50 °C and a pressure of 20 Pa for 48 h. Finally, the compounded MCC/PDA aerogel was obtained. In this work, a series of the compounded MCC/PDA aerogels with different PDA contents were prepared. The contents of PDA in the compounded MCC/PDA aerogels were varied from 0 to 67 wt%. The sample notation is defined as PDA-*x*, where *x* represents the content of PDA in the compounded MCC/PDA aerogel. For example, PDA-67 means that the content of PDA in the aerogel is 67 wt%. For comparison, the pure MCC aerogel was also prepared through the completely same processing procedures.

2.3. Microstructure characterization

The morphologies of the aerogels before and after adsorbing MB were characterized using a scanning electron microscope (SEM) Fei Inspect (FEI, the Netherlands) operated at an accelerating voltage of 20 kV. Before SEM characterization, all the samples were sputter-coated with a thin layer of gold.

The specific surface areas (Brunauer-Emmett-Teller (BET) area) of the aerogels were measured by nitrogen adsorption-desorption at 77 K through using a Quantachrome Instrument 2S1-MP-9 (USA).

The chemical characteristics of aerogels before and after adsorbing MB were investigated using a Fourier transform infrared spectroscope (FTIR) iS50 (Thermo Nico-let, USA), and the measurements were carried out in a transmission mode with a resolution of 4 cm^{-1}.

2.4. Adsorption behavior measurements

The adsorption ability toward MB by the compounded MCC/PDA aerogel was evaluated by measuring the amount of MB which was adsorbed by aerogel from the MB/H_2O solution in 48 h. The detailed procedures can be described as follows. First, aerogel sample of about 20 mg was immersed into 50 mL MB/H_2O solution with a concentration of 50 mg/L, and the container was placed in a thermostatic shaker (Jiang Su, P.R. China) which was operated at 200 rpm. After being treated for 48 h, the aerogel was taken out and the residual amount of MB in the solution was detected using the UV–Vis spectroscope UV-1800PC (SPEC-TROPHOTOMETER, Japan) in a wavelength range of 400–800 nm. The detecting wavelength was 663 nm. The variation of adsorption capacity of aerogel sample with increasing adsorption time was also evaluated through the following procedures. The aerogel sample of about 20 mg was immersed into 80 mL MB/H_2O solution with a concentration of 50 mg/L. About 4 mL MB solution was periodically collected for UV–vis testing.

The equilibrium adsorption capacity (q_e) and the adsorbed MB amount (q_t) at adsorption time *t* were calculated using the following equations:

$$q_e = \left(\frac{C_0 - C_e}{m}\right)V \tag{1}$$

$$q_e = \left(\frac{C_0 - C_t}{m}\right)V \tag{2}$$

Where $C_0$and $C_e$represent the initial and equilibrium concentration (mg/L) of MB solution before and after adsorbing by the compounded MCC/PDA aerogel, respectively, $m$and Vrepresent the mass (g) of the MCC/PDA hybrid aerogel and the volume (mL) of MB solution, respectively, and $C_t$represents the MB concentration in the solution at