Preparation of micro-nanofibrous chitosan sponges with ternary solvents for dye adsorption

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ABSTRACT

Chitosan has been widely used to adsorb the contaminants in wastewater owing to its unique chemical structure. However, it is difficult to improve its adsorption performance by fabricating fibrous chitosan sponge with nanofiber or microfiber due to its strong hydrogen bond inside the molecular chain. In this study, different from traditional binary acetic acid/water solvents, ternary solvents comprised with acetic acid/water/tetrahydrofuran, along with quench temperature of −196 ℃ were adopted to prepare three dimensional chitosan sponge with micro-nanofibrous structure. The chitosan micro-nanofibrous sponge showed substantially improved adsorption capacity of Acid Blue-113 (687 mg/g) compared with the chitosan sponge (176.5 mg/g) prepared with binary acetic acid/water solvents and quench temperature of −20 ℃. The adsorption of Acid Blue-113 onto chitosan micro-nanofibrous sponges was a chemical process, which fitted the pseudo-second-order and Langmuir isotherm models. The results indicated that microstructure modification was an effective and facile way to improve the chitosan adsorption capacity. The pure chitosan micro-nanofibrous sponge could be considered as an ideal dye adsorbent from wastewater.

1. Introduction

Chitosan, derived by the alkaline deacetylation of chitin, is a linear copolymer of D-glucosamine and *N*-acetyl-D-glucosamine (Guo, Anderson, Bozell, & Zivanovic, 2016; Yang, Li, Huang, Yang, & Li, 2016). Due to its low cost, biodegradability, nontoxicity and multiple reactive functional groups (Esquerdo, Cadaval, Jr, Dotto, & Pinto, 2014; Li et al., 2016, 2013), chitosan has been extensively used in fields of agriculture, food, cosmetics, biomedicine and wastewater treatment (Cheung, Ng, Wong, & Chan, 2015; Gul et al., 2016; Muxika, Etxabide, Uranga, Guerrero, & de la Caba, 2017; Zhang, Zeng, & Cheng, 2016).

Chitosan could adsorb organic pollutants effectively as its amine and hydroxyl groups serve as coordination sites to form charge neutralized complexes. Pietrelli et al. used raw chitosan to study the adsorption capacities for acid, basic, reactive, and direct dyes. The results showed that chitosan exhibited good adsorption capacities for all dyes, especially for the acid dyes because of its high reactive protonated amine group (Pietrelli, Francolini, & Piozzi, 2014). Dotto and Pinto reported chitosan powder adsorption capability food yellow 3 could be up to 295 mg/g (Dotto & Pinto, 2011a). These previous researches indicated that chitosan might serve as a promising material to remove dyes from wastewater.

Pure chitosan powder is not a cost effective absorbent. Further studies focused on the chemical modification or physical modification were conducted to improve its adsorption capacity (Maity & Ray, 2018). For example, succinyl was grafted onto chitosan as adsorbent to remove Remacryl Red TGL, the adsorption capacity raised from 431 mg/g by the pure chitosan to 1401 mg/g by the chemically modified chitosan (Kyzas, Siafaka, Pavlidou, Chrissafis, & Bikiaris, 2015). Although chemical modification can improve its adsorption efficiency, the complex process, environmental waste in the production and rising cost limit the development of chitosan derivative adsorbents. Relatively speaking, physical modification is simple and cost effective. Chitosan can be easily prepared in various forms, such as fiber, particle, membrane, bead, gel, and sponge (Chedly et al., 2017; Li et al., 2018; Shakeri, Salehi, & Rastgar, 2017). No matter what forms are prepared, the final aim of physical modification is to increase the ratio of adsorption area to weight. Pure chitosan powder with particle size of 70 ± 5 μm was utilized to remove acid blue 9, the adsorption capacity were only 210 mg/g (Dotto & Pinto, 2011b). Li et al. prepared pure chitosan nanofibrous membranes by electrospinning for removal of Acid Blue-113 (AB113). The chitosan nanofibrous membranes showed an excellent dye adsorption capacity of 1377 mg/g when the average fiber diameter was 86 nm (Li et al., 2018). These results suggested that physical modifications could also improve the adsorption capacity significantly. However, electrospinning is difficult to fabricate three-

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dimensional sponge with controlled pore size (Kaya et al., 2016; Mahmoodi & Mokhtari-Shourijeh, 2015; Sedghi, Shaabani, Mohammadi, Samadi, & Isaei, 2017; Yu, Li, Zhang, & Williams, 2017). Moreover, electrospinning of pure chitosan is low productive because cationic chitosan has strong hydrogen bond inside the molecular chain, which limits the future application in the commercial scale (Lemma, Bossard, & Rinaudo, 2016; Ma & Liu, 2017; Sedghi et al., 2017).

To facilely fabricate three-dimensional fibrous chitosan sponge with controlled pore size, thermal induced phase separation is an ideal technology. Traditionally, chitosan was dissolved in binary solvents (mainly acetic acid/water) and made into three dimensional sponge with sheets up to several hundreds of micrometers, which did not fully exposed chitosan molecule as adsorption site (Anitha et al., 2014; Lou et al., 2016; Maity & Ray, 2018). Phase separation process occurs in a thermodynamically unstable homogeneous polymer solution that tends to separate into a polymer-rich phase and a polymer-lean phase under certain temperature (Ma & Zhang, 1999). During the freeze dry process afterwards, the polymer-rich phase forms fibrous matrix, while the polymer-lean phase transforms into pores (Zhao et al., 2011). Hence, suitable solvent system might be found to modify the phase separation process and the microstructure of chitosan sponge would transform into smaller scale (Wang, Lou, Zhao, & Song, 2016; Xu, Mao, Peng, Luo, & Chang, 2018). In our previous report, by adding dioxane and dimethyl sulfoxide into the acetic acid aqueous solution, the prepared chitosan film presented sheet thickness of several hundreds of nanometers and pore size of 5 μm (Wang, Wang, et al., 2016). It indicated the possibility to modify the microstructure of chitosan sponge by changing the solvent system. We hypothesized that a kind of solvent, which was not a good solvent for chitosan, might promote the formation of microfibers or nanofibers since this solvent inclined to separate into the polymer-lean phase and split the polymer-rich phase into small pieces during the freezing process.

Based on the assumption, we developed a novel ternary solvent system for preparing three dimensional chitosan sponge with micronanofibers, which was beneficial for the enhancement of adsorption capacity. A typical anionic dye of Acid Blue -113 was selected to characterize the adsorption capacity, the kinetics and isotherm models were also discussed.

2. Experimental

2.1. Materials

Chitosan (MW: 200,000, degree of deacetylation: 94.5%, determined by FTIR spectroscopy (Kong, 2012)), tetrahydrofuran (THF), acetic acid (AA) and sodium hydroxide were supplied by Sinopharm Chemicals. AB113 was provided by Huntsman Textile Effects.

2.2. Preparation of pure chitosan sponge

The preparation process of pure chitosan sponge was as follows: chitosan solution was prepared by dissolving chitosan into AA aqueous solution which constructed a binary solvent system under magnetic stirring for 12 h at room temperature. Afterwards, certain THF was added into the dissolved chitosan solution which formed a ternary solvent system and stirred continually for another 12 h. The chitosan solution was divided into glass bottles and frozen at −20 °C for 12 h or at −196 °C for 30 min. The frozen samples were dried in vacuum of 30 Pa for 72 h in a freeze-dryer (FD-1D-80, Boyikang, China). The details of prepared samples are listed in Table 1.

2.3. Characterization

The structural characteristics of chitosan sponges were examined on a scanning electron microscope (SEM, Phenom G2 pure, Netherlands). All samples were vacuum-coated with gold for 180 s before observation.

Table 1
The details of prepared chitosan sponges.

Sample	Chitosan concentration (wt %)	Solvent (AA: water: THF)	Freezing temperature (°C)
S1	0.5	1:99:0	−20
S2	1.0	1:99:0	−20
S3	2.0	1:99:0	−20
S4	0.5	1:89:10	−20
S5	1.0	1:89:10	−20
S6	0.5	1:79:20	−20
S7	0.5	1:59:40	−20
S8	0.5	1:79:20	−196

Fourier transform infrared (FTIR) spectrum was recorded by a Thermo Fisher FTIR spectrometer (Model: Thermo Scientific Nicolet Is50). The wave numbers were scanned in the range of 400 to 4000 cm^{-1}. X-ray diffractometer analysis was obtained by a DX-2700 X-ray diffractometer at an accelerating voltage of 40 kV using Cu-kα radiation (λ = 0.15418 nm).

2.4. Adsorption experiments

The batch adsorption experiments were determined with chitosan sponges prepared by various concentration of chitosan, solvent composition, and freezing temperature. The typical anionic dye of AB113 was selected to evaluate the adsorption capacity. Before adsorption experiments, the chitosan sponges were neutralized by NaOH solution (0.5 mol/L)in order to remove the residual acid in samples. 10 mg of chitosan sponge was put into 100 ml dye aqueous solution with concentration of 125 mg/L (pH = 6.49) for adsorption study. The pH changes during the adsorption process were monitored, while they were in the range of 6.39 to 6.50. All experiments were carried out in a water bath at the temperature of 25 °C. The AB113 concentration was measured by a UV–vis spectrophotometer (Model 721, The Third Analysis Instrument Factory, Shanghai) at wavelength of 565 nm.

The amount of adsorbed dye (q_e) and dye removal efficiency (RE) were calculated by Eqs. (1) and (2), respectively:

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

$$RE(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{2}$$

where C_0 and C_e represent the initial and equilibrium concentration of AB113 (mg/L), respectively, V and m are the volume of dye solution (L) and the weight of chitosan sponges (g), respectively, q_e is the amount of dye adsorbed at equilibrium (mg/g).

2.5. Adsorption kinetics

The pseudo-first-order and pseudo-second-order kinetic models were chosen in order to explicate the adsorption mechanism of AB113 on pure chitosan micro-nanofibrous sponges (Fan et al., 2018; Gatabi, Moghaddam, & Ghorbani, 2016). The pseudo-first-order model can be formulated by Eq. (3),

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{3}$$

The pseudo-second-order model can be formulated by Eq. (4),

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where q_t (mg/g) represents the adsorption capacity of chitosan sample at time t (h), k_1 (h^{-1}) is the pseudo-first-order rate constant, k_2 (g/mg/ h) is the adsorption rate constant of pseudo-second-order, q_e (mg/g) is the theoretical value for the adsorption capacity, t is the adsorption