



Engineering sodium alginate-based cross-linked beads with high removal ability of toxic metal ions and cationic dyes

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ARTICLE INFO

Keywords:

Sodium alginate
Poly (2-acrylamido-2-methylpropane-1-sulfonic acid)
Cross-linked beads
Wastewater treatment

ABSTRACT

Sodium alginate (SA) beads with ultrahigh adsorption capacity were prepared *via* hydrogen bonds between SA and 2-acrylamido-2-methylpropane-1-sulfonic acid (AMPS), and the AMPS was then post-cross-linked to manufacture SA/PAMPS beads. The equilibrium adsorption capacities of methylene blue (MB) and Pb²⁺ for the SA/PAMPS10 beads were 2977 and 2042 mg/g, respectively. Although the SA beads exhibited higher equilibrium adsorption capacities of MB and Pb²⁺ than those of the SA/PAMPS10 beads, the SA/PAMPS10 beads had better mechanical property and higher stability. The pseudo-second-order kinetic model and the Langmuir isotherm described the adsorption processes of the SA/PAMPS10 beads for MB well. In addition, the SA/PAMPS10 beads could be reused with stable adsorption capacity for at least three cycles. The beads also had excellent performances on absorbing methylene violet and other heavy metal ions (Cu²⁺, Cd²⁺ and Ni²⁺). Therefore, the SA-based beads with high adsorption capacity might be good candidates for industrial pollutant treatments.

1. Introduction

Sodium alginate (SA), a biological polymer derived from sea algae, is one of abundant natural polymers with good properties such as the low cost and non-toxic properties (LeRoux, Guilak, & Setton, 1999). It is a natural polysaccharide consisted of β -D-mannuronic acid (M) and α -L-guluronic acid (G) (Dragnet, Østgaard, & Smidsrød, 1990). The M and G units are organized in MG, MM and GG blocks, and the proportions of these blocks are varied with the source of the polymers (Rocher, Siaugue, Cabuil, & Bee, 2008). Moreover, SA has high density of carboxyl groups (Gok & Aytas, 2009; Sheng, Ting, Chen, & Hong, 2004) and hydroxyl groups (Daemi & Barikani, 2012; Ionita, Pandele, & Iovu, 2013), and can be modified with specific functional groups, such as sulfonic groups. For instance, a novel SA supported tetrasodium thiacalix[4]arene tetrasulfonate nanogel was prepared (Lakouraj, Mojerlou, & Zare, 2014); SA grafted poly (acrylic acid-co-2-acrylamido-2-methyl-1-propane sulfonic acid)/attapulgit hydrogels were used for wastewater treatment (Zhu, Zhang, Tang, & Kou, 2014). In general, sulfonic group modified SA can be prepared into hydrogels and applied to wastewater treatment.

Hydrogels can hold a large amount of water while maintaining the structure when they swelled in water (Jeon, Bouhadir, Mansour, & Alsberg, 2009). They are formed by cross-linking polymer chains by

hydrogen bonds, covalent bonds, Van der Waals interactions, and/or physical entanglements (Bryant & Anseth, 2002). Due to their unique properties, hydrogels are widely applied in drug delivery system (Qiu & Park, 2001), biomedical engineering (Bell & Peppas, 1995) and water treatment (Chen, Liu, Jin, Nie, & Zhou, 2017), etc. It has been reported that SA-based hydrogels can be used to remove dyes and heavy metal ions (Wang, Kang, & Wang, 2013; Wang, Wang, & Wang, 2013). For example, Ag₂O/SA supramolecular hydrogel was prepared as a film photocatalyst to remove organic dyes (Ma et al., 2017), the preparation method was simple but the adsorption capacity was not high. SA-based organic/inorganic superabsorbent composite hydrogel was prepared with a high adsorption capacity (Thakur, Pandey, & Arotiba, 2016), however, it required a relatively complex preparation process. Therefore, it is still a big challenge to prepare SA-based adsorbents with ultrahigh adsorption capacity *via* a simple approach so far.

For the application of adsorbents, bead-shaped hydrogels are more widely used than bulk hydrogels due to the controllable size and spherical shape, which avoid attrition losses. The main method for preparing bead-shaped SA hydrogels is ionic cross-linking. However, ionic cross-linking process sacrifices the carboxyl groups in SA. To prepare SA-based beads with high adsorption capacities but not sacrificing the carboxyl groups is challenging for the removal of toxins in industry. By combining hydrogen bonds, Van der Waals interactions,

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and/or physical entanglements, as well as covalent bonds, bead-shaped hydrogels could be prepared without losing functional groups. In our previous work, Lu et al. (2015) fabricated SA beads by the combination of phase inversion method and post-crosslinked reaction with glutaraldehyde (GA) in acetone without engaging carboxyl groups comparing with ionic cross-linked process. However, acetone is not an eco-friendly solvent. In addition, the treatment and recovery of acetone in industry will cost extra money compared to water phase process. Therefore, preparing SA beads in organic free solvent and without consuming carboxyl groups is desired.

Herein, 2-acrylamido-2-methylpropane-1-sulfonic acid (AMPS) solution was used as the coagulant, and the SA solution was dropped into the coagulant bath to form SA beads by hydrogen bonds. Subsequently, the SA/PAMPS beads with interpenetrating polymer network were obtained by post-cross-linking of the AMPS in the beads. The introduction of sulfate groups into SA beads would expand the range of application compared to our previous work (Lu et al., 2015). We hypothesize that the mechanical property and stability of the SA/PAMPS beads could be improved via the post-cross-linking of AMPS. Furthermore, the proposed method might be used to prepare SA-based beads in a large scale, and provide the beads with a high adsorption capacity, which was useful for the removal of toxic such as cationic dyes and heavy metal ions.

2. Experimental

2.1. Materials

Sodium alginate (SA, 200 ± 20 MPa.s) powder, methylene blue (MB), Congo red (CR), methylene violet (MV) and amaranth red (AR) were received from Chengdu Kelong Chemical Reagent. 2-Acrylamido-2-methylpropane-1-sulfonic acid (AMPS, 98%), N,N'-methylenebis (acrylamide) (MBA, 97%), ammonium persulfate (APS), and the salts of heavy metal ions (Cu^{2+} , Pb^{2+} , Cd^{2+} and Ni^{2+}) were purchased from Aladdin reagent Co. Ltd. (China). Other reagents were purchased from Aladdin and used without any further purification. Deionized (DI) water was used throughout this study.

2.2. Preparation of SA/PAMPS beads

SA beads were prepared via the formation of hydrogen bonds between SA and AMPS; then SA/PAMPS beads were prepared by the post-cross-linking of AMPS as shown in Scheme 1. Briefly, SA solution (4 wt. %) was prepared by adding 20 g of SA to 480 g of deionized water. Coagulant bath was prepared by adding 100 g of AMPS powder to 400 g of deionized water. The SA solution was dropped into the AMPS solution (20 wt.%) by using a needle at a speed of 30–40 drops/min, and kept in the AMPS solution for 12 h. Then, the beads were soaked in the reaction solution (AMPS, MBA and APS) for another 12 h and protected with an ice bath. The reaction was carried out in an oven at 75°C for 3 h. Then, cross-linked beads were separated from the gel system by adding alcohol and agitating. The cross-linked beads were washed with DI water for four times to remove the soluble chemicals. The details of the sample names and chemical compositions are shown in Table 1 (for example, “SA/PAMPS4” represented the AMPS concentration was 20 wt.% and the MBA concentration was 4 mol% of the AMPS).

2.3. Characterization of SA and SA/PAMPS beads

Fourier transform infrared spectroscopy (FTIR, Nicolet 560, America) was used to characterize the chemical structures of the samples. Generalized 2D correlation FTIR spectra of SA beads were analysed by using two-dimensional correlation spectroscopy software (2DCS). Thermo-gravimetry analysis (TGA) was measured by using a thermogravimeter instrument (TG209F1, Germany) at a heating rate of $10^\circ\text{C}/\text{min}$ under a dry N_2 atmosphere. Scanning electron microscopy

(SEM, JSM-7500F, JEOL) was used for the morphology observation of the beads. The samples were lyophilized, and then immersed into liquid nitrogen, after that the samples were cutting with a razor blade. Thereafter, the beads were coated with a gold layer after attaching to sample supports.

2.3.1. Water uptake

The water uptake (WU) of the beads was determined by using the weight change of the wet beads before and after drying at 60°C for 48 h (Obeid et al., 2014). It could be obtained by using the following Eq. (1) (Zhao, Glavas, Odelius, Edlund, & Albertsson, 2014a; Zhao, Glavas, Odelius, Edlund, & Albertsson, 2014b):

$$WU = (W_e - W_d)/W_d \quad (1)$$

where W_e represents the wet weight of the samples, and W_d represents the dry weight of the samples.

2.3.2. Mechanical property

The mechanical property of the samples was qualitatively determined using a tensile machine (HZ 1004B, Dongguan). A single bead was positioned on a flat platform and was compressed in a vertical direction with a speed at 0.1 mm/min.

2.4. Adsorption experiments

2.4.1. Effect of pH values on MB adsorption

MB was selected as a cationic dye model to investigate the adsorption capacity of the beads. First, two beads were added to 40 mL of MB solution ($800 \mu\text{mol/L}$) at the stirring speed of 120 rpm at room temperature for 48 h. The concentration of the MB was determined by an UV–vis spectroscopy (UV-1750, Shimadzu, Japan) at the wavelength of 631 nm (Zhang et al., 2013). Then, the effect of pH values (range 3–11) on the adsorption was studied, and the pH values were adjusted using 0.1 M NaOH or 0.1 M HCl solution. The adsorption amounts can be obtained by the following Eq. (2) (Lu et al., 2015) :

$$N = (C_0 - C_a) \times V \times M/m_0 \quad (2)$$

where N (mg/g) is the adsorption amounts, C_0 represents the concentration of MB solution before the adsorption while C_a represents the concentration of MB after the adsorption. V (L) is the volume of the MB solution, M (g/mol) is the relative molecular weight of the MB, m_0 (g) is the dry weight of the samples.

2.4.2. Effect of concentrations on MB adsorption

The effect of MB concentrations ($200\text{--}500 \mu\text{mol/L}$) on the adsorption capacity was also investigated. The adsorption procedure was the same as described above; and the adsorption amounts were also calculated by using the Eq. (2).

2.4.3. Adsorption of AR, CR and MV dyes

For other dyes (AR, CR and MV), the testing method and calculation method for adsorption capacities were the same as those of adsorbing MB as mentioned in Section 2.4.1. The adsorption amounts of AR, CR and MV were measured at the wavelengths of 522, 494 and 586 nm, respectively.

2.4.4. Adsorption of heavy metal ions

For the adsorption of heavy metal ions, individual heavy metal ion (Cu^{2+} , Pb^{2+} , Cd^{2+} and Ni^{2+}) solution at a concentration of 40 mmol/L was used. For all the samples, two beads were added to 10 mL of metal ion solution, and agitated at 120 rpm for 48 h at room temperature. Then, the concentration of heavy metal ion was determined by an atomic spectrophotometer (Shimadzu SPCA-626D, Japan). The calculation method of the adsorption capacity was the same as that for MB adsorption.

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