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Tunable functional hydrogels formed from a versatile water-soluble chitosan



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ABSTRACT

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Keywords: Water-soluble chitosan Hydrogel Tunable Formation Function A versatile water-soluble chitosan (WSC) was applied to construct two kinds of controllable functional hydrogels. Magnetic beads were prepared by physical cross-linking WSC with sodium alginate, soaking particles with ferrous chloride and being subjected to self-oxidation. Magnetic character of the beads was tunable by simply changing the initial concentration of ferrous ions. The beads could bind compounds that contained different charges. Their adsorption capacities for coomassie brilliant blue, rhodamine and hemoglobin were 1, 0.5 and 2.3 mg/g respectively. Another kind of functional hydrogel was prepared through radical cross-linking reaction between WSC and a macromonomer (PVAM) derived from well-defined polyvinyl alcohol. The dynamic mechanical thermal analysis and thermogravimetric analysis results revealed that the mechanical strength and thermal stability of this hydrogel depended on the structure of PVAM. The capability to bind heavy metal ions of the hydrogel also relied on the structure of PVAM. The adsorption capacities of the hydrogels for Cu²⁺ and Pb²⁺ could reach 20.3 and 60.1 mg/g respectively.

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1. Introduction

As natural polysaccharides are non-toxic, biocompatible, biodegradable and renewable, they have widely applied in different fields [1–3]. Among them, chitosan is the derivative of chitin, which is the second abundant natural polysaccharide, and has received increasing attention. Its backbone bears a lot of amino groups, which enables this biopolymer to form polycation in dilute acid [4,5]. However, chitosan is not soluble in neutral and alkali aqueous medium [6]. On the other hand, chitosan can form chemical or physical hydrogels. Chitosan-based hydrogels exhibit many unique physicochemical properties and have been widely utilized in biomedical applications and other fields [7–9]. Covalent crosslinking of chitosan is usually carried out through the reaction between chitosan and a compound that contains two or more reactive functional groups such as epichlorhydrine or glutaraldehyde. One issue is these cross-linking reagents are generally considered as toxic. Moreover, most of the amino groups on the chitosan chains have been consumed [10]. To overcome these problems, physical cross-linking strategy or modified chemical route may be desirable

http://dx.doi.org/10.1016/j.ijbiomac.2016.01.006 0141-8130/© 2016 Elsevier B.V. All rights reserved. for preparing chitosan-based hydrogels to widen their potential applications.

By taking advantage of the electrostatic interaction between cationic chitosan and an anionic polyelectrolyte such as sodium alginate or maleic starch half-ester acid, physical chitosan-based hydrogels are easily to be formed [11,12]. Such a gelation approach is performed in mild condition and efficient. Physical chitosan-based hydrogels can be obtained in another way. Poly(vinyl alcohol) (PVA) is a water soluble synthetic polymer that exhibits excellent properties including biodegradability, biocompatibility and capacity of forming physically cross-linked hydrogel under mild condition [13,14]. We synthesized a chitosan-g-PVA with controllable graft percent and formed physically cross-linked hydrogel through freezing-thawing its aqueous solution [15].

In spite of this, we think there is room for further functionalizing physical chitosan-based hydrogel to impart more characters. On the other hand, to develop a non-toxic cross-linker for preparing chemical chitosan-based hydrogels is also meaningful. Herein, we present a strategy to obtain functional chitosan-based hydrogels through either chemical or physical approach. The adopted water-soluble chitosan (WSC) is an amphoteric polyelectrolyte and an unsaturated macromonomer simultaneously [16], which enables us to facilely prepare physical or chemical chitosanbased hydrogels. We physically cross-linked WSC with sodium alginate and soaked WSC-SA gel with ferrous chloride, which pro-

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vided us magnetic hydrogel particles after being oxidized in basic medium. We also chemically cross-linked WSC with a PVA-based macromonomer derived from well-defined poly(vinyl alcohol). Then, we attempted to modulate the properties of chitosan-based hydrogels by simply varying the initial concentration of ferrous ions or the structure of PVAM. To our best knowledge, such an idea is seldom reported. The experimental results indicate our intension and the adopted approaches are feasible.

2. Experimental

2.1. Materials

Water-soluble (WSC, chitosan the percentage of -CO-CH=CH-COOH was 19.6%) was prepared in our lab via the esterification reaction between chitosan (minimum 90% deacetylation, viscosity average molecular weight was 2.1×10^6) and maleic anhydride [16]. Sodium alginate (SA, number average molecular weight was ca. 3.3×10^4) was dried before use. PVA-based macromonomer (PVAM) derived from well-defined poly(vinyl alcohol), PVA maleic half-ester, was prepared in the light of literature [17]. Ferrous chloride, sodium hydroxide (NaOH), potassium persulphate (KPS), ethylene diamine tetraacetic acid (EDTA), xylenol orange, lead nitrate, copper sulfate, coomassie brilliant blue G-250 (CB, molecular weight was 854), rhodamine B (Rh, molecular weight was 479) and hemoglobin (HB, molecular weight was ca. 6.7×10^4) were all analytical grade reagents purchased domestically and used as received.

2.2. Formation of tunable magnetic WSC-SA hydrogel beads

WSC-SA hydrogel beads were fabricated according to the literature [18]. Briefly, a predetermined amount of WSC and SA was respectively dissolved in distilled water to obtain homogeneous aqueous solutions. Then WSC solution of 20 mg/mL was added into 2 wt% SA solution drop by drop. The formed WSC-SA beads were kept in the SA solution for 24 h, filtered, rinsed with distilled water to remove the remained SA solution, and dried at 40 °C for 24 h.

Magnetic WSC-SA hydrogel beads were controllably prepared by adopting the strategy we reported [19]. Twenty milligrams of dried WSC-SA particles were mixed with 20 mL ferrous chloride solution of different concentration in a beaker. The mixture was sealed and kept for 24 h. Subsequently, NaOH aqueous solution was added until pH of the medium of the mixture was 13. Then the mixture was exposed to the air at room temperature for 10 min. The resultant beads were filtered, washed with distilled water and dried at 40 °C for 24 h.

2.3. Controlled preparation of WSC-PVA hydrogels

WSC-PVA hydrogels were prepared by a common radical crosslinking reaction. Briefly, 10 mL WSC aqueous solution of 0.1 g/mL was mixed with 10 mL PVAM aqueous solution of 0.2 g/mL. The chemical cross-linking reaction between WSC and PVAM was conducted at 60 °C for 3 h by initiating the mixture with KPS. The formed light brown gel was removed directly, washed with distilled water, and dried.

2.4. Characterizations of WSC-based hydrogels

The magnetic character of the WSC-SA beads was examined with a vibrating sample magnetometer (VSM, Lakeshore Model 735). Powdered WSC, PVAM and WSC-PVA gel was mixed with dry KBr and compressed into disk respectively. Then, Fourier transform infrared (FTIR) spectra of the samples were recorded using a Nexus 470 FTIR spectrometer. Thermogravimetric analysis (TGA) of the WSC-SA beads and WSC-PVA hydrogels were performed with a TA V2.4F thermoanalyzer, which was conducted over the temperature range from 20 to 800 °C with a programmed temperature increment of 10 °C/min under N₂ atmosphere. The storage modulus (E') and loss modulus (E'') of the WSC-PVA hydrogels were determined using a DMA/SDTA861e dynamic mechanical thermal analysis (DMTA) instrument (Mettler Toledo Co., Switzerland), which was performed over the temperature range from 0 to 100 °C with heating speed of 5 °C/min at 1 Hz.

2.5. Adsorption property of WSC-SA hydrogel beads

CB, Rh and HB were employed as model substances to investigate the complexation capacity of WSC-SA beads for the compounds that borne different charges. Twenty milligrams of the magnetic beads were placed into a bottle that contained 10 mL CB, Rh or HB solution of 0.02 mg/mL and maintained at ambient temperature for 24 h, respectively. The beads were removed and the absorbencies of the remained solutions were measured with a UV2450 UV-vis spectrophotometer at 465, 554 and 405 nm respectively. The concentration change of CB, Rh and HB could be obtained from the linear relationship between concentration (C) and absorbency (A), which were A = 34.5155C - 0.0115 $(R^2 = 0.9989)$ for CB, A = 85.2642C - 0.00173 ($R^2 = 0.9998$) for Rh and $A = 7.3835C - 0.0131 (R^2 = 0.9989)$ for HB respectively. The adsorption capacities Q(mg/g) of the beads were calculated according to the formula $Q = (C_0 - C)V/W_0$, where C_0 and C(mg/mL) were the initial and equilibrium concentration of CB, Rh and HB in the solution respectively, V was the volume (mL) of solution, and W_0 was the initial dry weight of WSC-SA beads (g).

2.6. Adsorption property WSC-PVA hydrogels

Adsorption tests were carried out by placing ca. 25 mg dry WSC-PVA gel in 20 mL solution of 0.1 mg/mL Pb²⁺ or Cu²⁺ and kept at 37 °C for 24 h. A certain amount of solution was sampled, mixed homogeneously with 1 mL xylenol orange or 3 mL EDTA, as chelator of lead and copper ions respectively, and 2 mL buffer solution of pH5.8. The concentration of Pb²⁺ or Cu²⁺ was analyzed with a UV-2450 UV–Vis spectrophotometer at 575 and 730 nm respectively. The adsorption capacities Q (mg/g) of the samples were calculated according to the formula $Q = (C_0 - C)V/W_0$, where C_0 and C (mg/mL) were the initial and equilibrium concentration of the metal ions in the solution respectively, V was the volume (mL) of solution, and W_0 was the initial dry weight of WSC-PVA gel (g).

3. Results and discussion

3.1. Controllable magnetic WSC-SA hydrogel beads

WSC is easily to be physically cross-linked with SA to obtain WSC-SA beads [18]. Some amino groups are probably remained in the backbone of WSC after the ionic complexation between two polyelectrolytes. In addition, there are carboxyl groups on both WSC and SA chains. Therefore, WSC-SA beads are possible to combine substances that contain different charges. In order to examine this conjecture, WSC-SA beads were immersed in solution containing negatively charged CB, positively charged Rh or amphoteric HB respectively. As shown in Fig. 1, the adsorption capacities of the beads toward CB, Rh and HB are 1.0, 0.5 and 2.3 mg/g respectively. In other words, WSC-SA beads are able to bind electrolytes containing positive or negative charges.

The charged groups contained in the WSC-SA beads are sufficient to bind metal ions [18]. Thus, we can apply this character to further functionalize the beads. By introducing ferrous ions into the beads through ionic interaction and transforming them into

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