Preparation and Characterization of Cellulose-Coated Chitosan Beads with Improved Strength and Acid Resistivity

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ABSTRACT: A new chitosan bead was successfully prepared by simply dropping acidic chitosan solution into 0.5 wt % alkaline cellulose solution. The X-ray photoelectron spectroscopy analysis and the scanning electron microscope observation indicate that thin layer of cellulose was coated on the chitosan bead to have strong interaction with inner chitosan. Therefore, the bead reveals porous microstructure of regenerate cellulose in the surface. Owing to the cellulose coating, the bead displays improved mechanical properties and acid resistance. The adsorption of Fe^{3+} onto the new chitosan beads was investigated in detail, and the results show that the cellulose coating has little influence on the adsorption of the chitosan. Therefore, this study provides a novel method to expand the application of chitosan by coating with an acid-insensitive polymer. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: cellulose; chitosan bead; coating; improved mechanical properties and acid resistance; adsorption

INTRODUCTION

By deacetylation of chitin, a natural biopolymer widely available from seafood processing waste, chitosan (CS) is obtained to provide abundant-free amino groups. CS has great potential to prepare affinity or adsorptive materials based on the large amount of functional groups such as amino and hydroxyl groups in the repeat unit of the biopolymer, which could adsorb, chelate, or interact with metal ions and bioactive molecules. In addition, the biodegradability, biocompatibility, and nontoxicity of the biopolymer have attracted more and more attention to prepare CS-based novel materials with various functions. For example, CS-based materials were widely reported to be applied as adsorbents of heavy metal ions,[1–5] drug-delivery systems,[6] and DNA-delivery systems.[7] However, the application of CS materials has been greatly restricted by the low mechanical strength and poor acid resistance of pure CS.[8] To make full use of the amino groups of CS, the poor mechanical property of pure CS is often overcome by blending it with other polymers,[9–17] by coating it on strong supports,[18–23] or by crosslinking.[24,25] Those methods usually consume some functional groups or decrease the amount of CS to reduce the adsorption capacity of CS.

In this study, it is aimed to improve the mechanical strength and the acid resistance of CS but without loss of its adsorption capacity. Hence, acidic CS solution was dropped into cellulose 6/5 wt % NaOH/thiourea solution to cover the obtained CS bead with a layer of cellulose, which is a stronger biopolymer and is expected to strengthen the CS material. It has been reported that cellulose and CS are compatible owing to strong interaction between the two biopolymers with similar molecular architecture.[15,16,23] Meanwhile, porous regenerate cellulose films were always obtained when casting the cellulose NaOH/urea[26] or NaOH/thiourea[27] aqueous solution in any coagulant. Therefore, it is hoped that the porous microstructure of the coating cellulose layer would not affect the adsorption capacity of the

inner CS, and the strong interaction between the two polymers would benefit the improvement in acid resistance of the inner CS. The morphology and microstructure of the obtained CS bead were studied by scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS), and the porous cellulose coating has been characterized. The mechanical properties of the material were tested, and the weight loss of the beads was determined to test their acid resistance. Moreover, Fe^{3+} was used as ion representative to study the adsorption behavior of the cellulose-coated new CS bead.

EXPERIMENTAL

Materials

CS with a degree of deacetylation of 90% was purchased from Jinan Haidebei Marine Bioengineering (Shandong, China). Its viscosity–average molecular mass (M_η) was determined in 0.1 mol/L CH_3COONa/0.2 mol/L CH_3COOH buffer at 30°C to be 1.44×10^5 g/mol according to $[\eta] = 6.589 \times 10^{-3}M^{0.88}$.[23] Cotton linter with M_η of 10.1×10^4 g/mol and α-cellulose content of over 95% was purchased by Hubei Chemical Fiber Group (Xiangfan, China). Other chemical reagents purchased from commercial sources in China were analytical grade and were used without further purification.

Preparation of novel CS beads

CS was dissolved in 2 wt % acetic acid aqueous solution to prepare a 3 wt % solution at room temperature. A 0.5 wt % cellulose solution was prepared according to our previous study.[23] Briefly, the cotton linter was immersed in 6/5 wt % NaOH/thiourea mixture aqueous solvent, and then the mixture was stored under −12°C for over 8 h. Following, it was stirred vigorously for 1 h, and centrifuged at 4000 rpm for 25 min. Then, the upper layer of transparent solution was obtained with the cellulose concentration of 0.5 wt %.

It is expected that cellulose would be precipitated at the surface of a CS bead to form a coating, which would improve the strength and acid resistivity of the CS bead. Therefore, the CS solution was dropped into the cellulose solution by using a syringe, and then stirred for 1 h. The obtained CS beads (CS1) were washed vigorously and thoroughly with running water, and then with distilled water. Pure CS beads (CS0) were also prepared by directly dropping CS solution into 6/5 wt % NaOH/thiourea aqueous solution. The diameter of the prepared CS beads in wet state is in the range of 4–6 mm, and is about 1 mm after dried.

Characterization of the CS beads

X-ray photoelectron spectra (XPS) of the beads were measured with a Quantum 2000 spectrometer (Physical Electronics, Chanhassen, MN, USA) with a monochromated AlKα X-ray radiation. The samples were air dried at ambient temperature for 48 h.

The wet beads were frozen in liquid nitrogen, immediately snapped, and then freeze dried under vacuum. The surface and the inner part of the beads were coated with a thin layer of gold (about 2 nm) to observe their microstructures by using a SEM (LEO 1530, LEO, Germany).

It is hard to measure the mechanical properties of the small CS beads. Hence, CS films were prepared by similar manners as those of CS beads, and the mechanical properties of the obtained CS films could represent those of CS beads. The CS films were prepared by casting 3 wt % CS solution onto glass substrate, then coagulating in 0.5 wt % cellulose solution, or in 6/5 wt % NaOH/thiourea aqueous solution for some time. After being washed and dried, the tensile strength (σ_b) and breaking elongation (ε_b) of the CS films were measured on an universal testing machine (WDS-5, Tianshui, Tianshui Hongshan Test Machine, Gansu, China) according to ISO 527-2, 1993 (E) at a speed of 5 mm/min.[23]

The acid resistance of the CS beads was investigated by the weight loss ratio (WLR) of the CS beads after immersion in HCl solution (pH = 2) for desired time, which was defined as

$$WLR = \frac{(W_0 - W_1)}{W_0} \times 100\% \qquad (1)$$

where W_0 is the original weight of the dry beads and W_1 is the weight of the dry beads after immersion in HCl solution.

Adsorption of the CS beads

The Fe^{3+} solution was prepared by dissolving $FeCl_3$ in deionized water, and the desired pH of the solution was adjusted by addition of HCl or NaOH aqueous solution. The wet CS beads were immersed into the Fe^{3+} solution with lightly stirring for adsorption at room temperature, and the remained Fe^{3+} was measured by an UV–Vis spectrophotometer (Beckman DU-7400, Fullerton, CA, USA) at a wavelength of 510 nm after chelating with ammonium rhodanate.[5] The adsorption amount $(q_e,$ mmol/g) of the metal ions was calculated by

$$q_e = \frac{(c_0 - c_e) * V}{W} \qquad (2)$$

where V is the volume of Fe^{3+} solution (L), W is the weight of the CS beads in dry state (g), c_0 and c_e are

the initial concentration and the final concentration of Fe^{3+}, respectively.

The adsorption mechanism of Fe^{3+} onto the CS beads is analyzed by using the Langmuir adsorption equation[28] as

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max}b}\frac{1}{c_e} \qquad (3)$$

and the Freundlich adsorption equation[28] as

$$\ln q_e = \frac{1}{n}\ln c_e + \ln K_F \qquad (4)$$

where q_{max} is the maximum adsorption amount at monolayer coverage (mmol/g) and b is the Langmuir adsorption equilibrium constant (L/mg). K_F and $1/n$ are the Freundlich characteristic constants.

RESULTS AND DISCUSSION

Microstructures of the CS beads

XPS is usually used to identify the existence of an element within 10 nm depth of a surface, and to characterize its chemical environment variation. The XPS spectra of pure CS beads (CS0) and the cellulose-coated beads (CS1) are shown in Figure 1, which are the narrow scans of N 1s, O 1s, and C 1s, respectively. The peak centered around 398.1 eV for CS0 is attributed to nitrogen (N 1s) of amide and amine in CS chain.[29] The N 1s peak of CS1 is weaker than that of CS0 to suggest lower amount of N at the surface of the CS1 bead. This result indicates coating of cellulose over CS bead during preparation, because the coating cellulose layer does not have N element. Meanwhile, the peaks at 530.9 and 535.5 eV for O 1s of CS0 are assigned to the electrons of C=O=C or C=O=H and C=O groups, respectively. The peaks at 284.2 and 287.7 eV for C 1s of CS0 are attributed to the alkyl carbon (C=C) or C=O and C=O groups,[20,21] respectively. After coating with cellulose, the intensities of those peaks of CS1 at 535.5 eV for O 1s and at 287.7 eV for C 1s, which belong to C=O groups of CS,[30] decrease evidently as the variation of N 1s. It is, therefore, believed that the CS beads are coated with layer of cellulose with the thickness of about 10 nm. Moreover, the N 1s peak of CS1 is found to shift to a higher binding energy of around 398.9 eV, and the O 1s peak of CS1 at 530.9 eV shifts to 531.4 eV. The binding energy shifts suggest chemical environment variations of N and O atoms within the surface layer, indicating strong interaction between coated cellulose and CS molecules, which might be a new hydrogen bonding between the two polymers.[23,31]
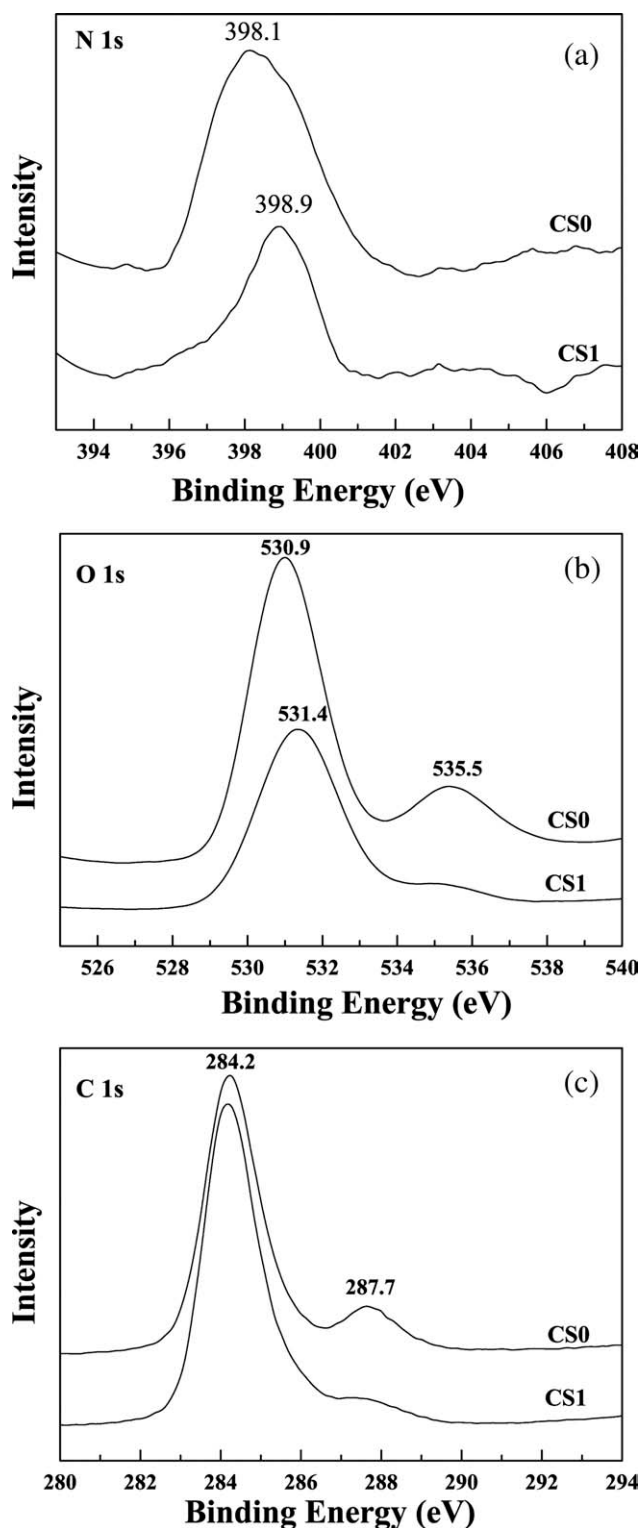

Figure 1 XPS narrow scans of N 1s, O 1s, and C 1s for CS0 and CS1.

Figure 2 shows the SEM images of the surfaces and the parts close to surface of CS0 and CS1. It is clear that the surface and the inner part of pure CS beads (CS0) display smooth and dense microstructure. After coating with cellulose, the bead exhibits
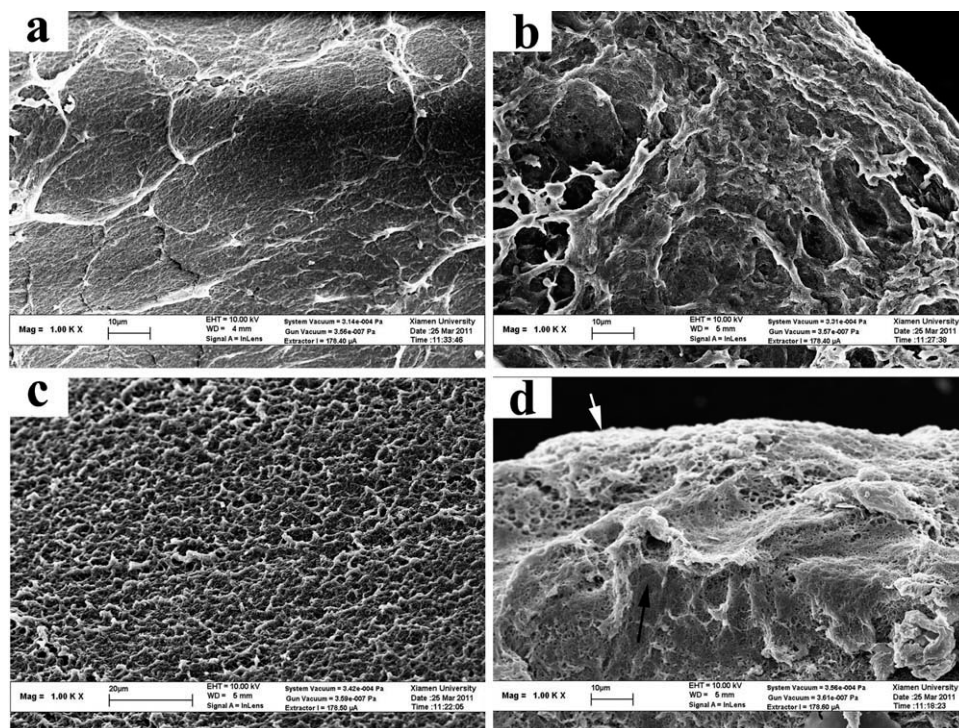
Figure 2 SEM images of the surfaces (left) and the parts close to surface (right) of CS0 (a, b) and CS1 (c, d). The white arrow in (d) indicates cellulose coating and the black arrow shows the CS beneath the cellulose coating.

homogenous microporous structure in the surface, which is similar as mesh network structures of the regenerate cellulose films prepared from the NaOH/thiourea or the NaOH/urea solvent system.[23,26] It is easily conceived that when acidic CS solution was dropped into the cellulose solution, the neighboring cellulose molecules would be immediately precipitated from the NaOH/thiourea solvent system because of the rapid neutralization reaction. With the ongoing of the neutralization reaction, gelation of CS molecules would occur to form CS bead, which would be covered by the precipitated cellulose. In other words, the precipitated cellulose was just a layer of cellulose, which was regenerated in acid to coat the CS bead. Therefore, the microstructure of the surface of the CS1 bead would be similar as those of cellulose films regenerated from acid coagulants,[26] as shown in Figure 2(c). Moreover, the regenerated cellulose would bond CS firmly owing to the strong interaction between the two polymers, resulting in homogeneous interface between the coating cellulose layer and the CS inner core [Fig. 2(d)].

Properties of the beads

As it is difficult to characterize the strength of the CS beads, the mechanical properties of the CS films prepared in the same manners as those of CS beads were measured to represent those of CS beads.

Three to five specimens for each film were tested in parallel to measure their ensile strengths (σ_b) and breaking elongations (ε_b), which are shown in Figure 3. The σ_b and ε_b of the film coagulated in NaOH/thiourea aqueous solution for 10 min were measured to be about 11.7 MPa and 1.4%, respectively. When the CS film was prepared by coagulating in cellulose solution, the tensile strength and elongation at break of the films were improved markedly. With increase of coagulation time, the
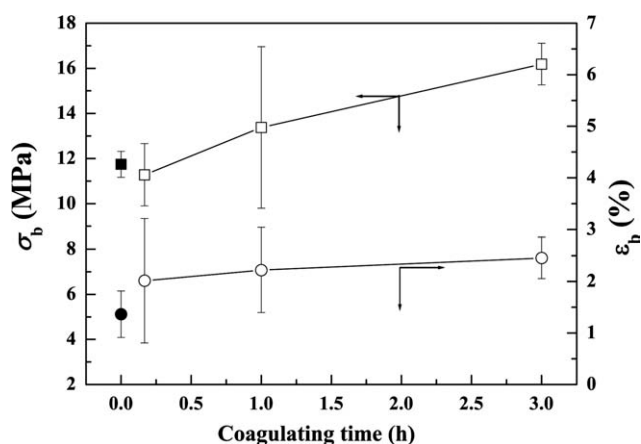

Figure 3 The dependencies of tensile strength (σ_b, square) and elongation at break (ε_b, circle) on the coagulation time for the CS films. The full symbols represent the mechanical properties of CS film prepared by coagulating in 6/5 wt % NaOH/thiourea aqueous solution for 10 min.

TABLE I
The WLRs of CS0 and CS1 When They Were Immersed in HCl Solution (pH = 2)

	Time				
	10 min	30 min	2 h	3 h	5 h
CS0	9.0	11.4	17.3	18.3	19.9
CS1	6.2	6.1	6.4	8.8	8.2

strength of the obtained film increased, indicating increasing amount of cellulose coating on the CS film. This result implies that the CS bead could be strengthened by coating of cellulose. It is evidenced by the experimental fact that the pure CS beads were very brittle to be easily broken when stirring in aqueous medium, whereas the cellulose-coated beads of CS1 were stable under the same condition.

The acid resistance of the CS beads was analyzed by determining the WLR of the CS beads after immersed in HCl solution (pH = 2) for a desired time, which are summarized in Table I. The WLR of CS0 was determined to be about 9% after soaked in HCl solution for 10 min, and the value was increased with immersing time to reach about 20% for 5 h. The pure CS beads could not be recovered any more when immersed in the medium for longer time because of the collapse of the beads. The WLR of CS1 is obviously lower than the CS0, and the maximum is found to be <9.0% for 5 h of soaking in HCl solution, suggesting significant improvement in acid resistance of the CS bead. The improvement in acid resistance of the CS bead is thought to be resulted from the cellulose coating, which is insensitive to acid condition. When the CS beads were positioned in HCl solution for some time, the CS beads would be swollen to free some of the polymer chains from the CS beads, resulting in the weight loss. However, the outer cellulose layer of the CS1 bead would restrict the swelling of the inner CS, and suppress the escape of the CS chains. Though the apparent pore size of the cellulose layer is at the level of 200–300 nm [Fig. 2(c,d)], which is much larger than the CS chain dimension, the strong interaction between the two polymers would lead to entanglement of the two kinds of polymer chains to interfere with leaking of the CS chains. Hence, the acid resistance of the CS bead was efficiently improved by coating with a thin layer of cellulose.

Adsorption behaviors

The Fe^{3+} adsorption amounts (q_e, mmol/g) for CS0 and CS1 beads were determined by immersing them into 0.5 mmol/L Fe^{3+} solution at pH = 3, respectively. As shown in Figure 4, the q_e values for both beads increased rapidly, and the adsorption equilibriums were reached within 1 h. However, a little
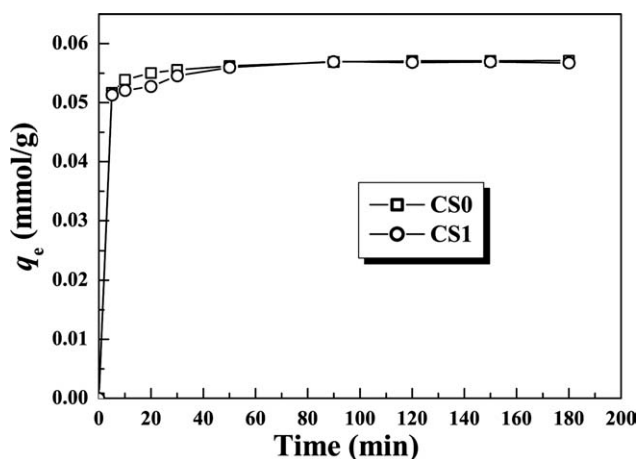

Figure 4 The dependencies of q_e on adsorption time for CS0 and CS1. The c_0 of the Fe^{3+} solution was 0.5 mmol/L with its pH of 3.

adsorption difference in the time range between 10 and 50 min for the beads has been observed to show lower adsorption amount of CS1 than CS0, indicating slight hindrance on the adsorption of CS by the cellulose coating. This is understood that the porous cellulose coating would slow down the diffusion of Fe^{3+} to reach the CS surface. Nevertheless, the dependencies of q_e on adsorption time for both beads display similar profiles, and the equilibrium adsorption capacities of the beads are almost identical, suggesting that the adsorption capacity of CS would not be reduced by the cellulose coating.

The dependencies of q_e on the final concentration of Fe^{3+} (c_e) of equilibrium adsorption for CS0 and CS1 at pH = 3 are shown in Figure 5. The adsorption behaviors of both beads exhibit similar tendency. The q_e increases significantly with the increase of c_e, and reaches maximum of about $\sim$ 0.17 mmol/g at c_e around 0.3 mmol/L, indicating saturation adsorption. When c_e is higher than $\sim$ 0.3 mmol/L, it
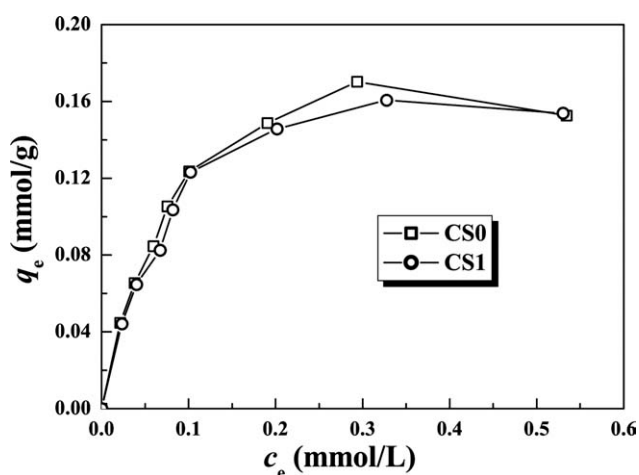

Figure 5 The dependencies of q_e on c_e of equilibrium adsorption for CS0 and CS1 at pH = 3.
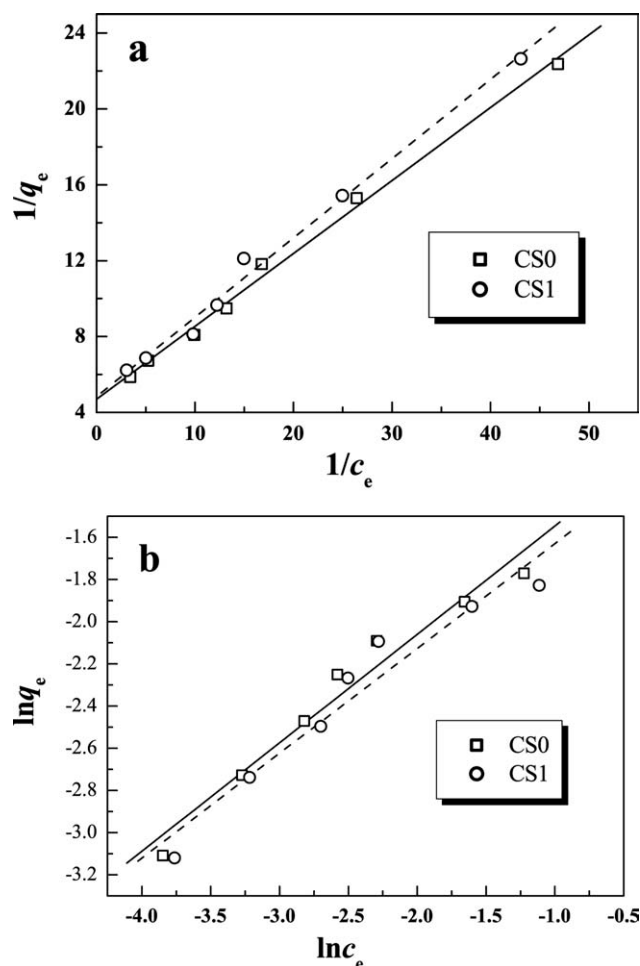
Figure 6 Langmuir isotherms (a) and Freundlich isotherms (b) for the Fe^{3+} adsorption on the CS0 (solid line) and CS1 (dashed line) beads.

is found that q_e decreases slightly, which might be resulted from the inhibited adsorption of CS beads owing to increased ionic strength of the medium.[15,16]

The adsorptions of Fe^{3+} on CS0 and CS1 were modeled by fitting the data points shown in Figure 5 with the Langmuir equation and the Freundlich equation,[28] respectively. Figure 6 shows the Langmuir isotherms and the Freundlich isotherms, and the calculated parameters are summarized in Table II. It is clear that the Fe^{3+} adsorption behaviors for both CS0 and CS1 were better fitted by Langmuir equation (correlation coefficient, $R > 0.99$), indicating monolayer homogeneous adsorption of Fe^{3+} on the CS beads.[16,28] The values of parameter q_{max} give

the maximum adsorption amount at monolayer coverage to be 0.21 mmol/g for both CS0 and CS1. This result suggests that the porous cellulose layer would not influence the adsorption behavior of CS bead, which is consistent with the results mentioned above.

Figure 7 shows the variation of equilibrium q_e for CS1 on the pH of the feed Fe^{3+} solution. The q_e values were determined to be about 0.23, 0.22, and 0.20 mmol/g when the pHs of the feed were 3.5, 3.0, and 2.5, respectively. It has been found that q_e decreased rapidly to lower than 0.12 mmol/g when the pH of the Fe^{3+} solution decreased to 2.0, at which the CS1 beads were found to be swollen to a large extent and the CS0 beads were collapsed. The q_e decreased to even lower of about 0.09 mmol/g for pH lower than 1.5. The decrease of q_e with pH of the feed Fe^{3+} solution is understood as follows. The amine groups of CS molecules will be protonized to a higher degree with the pH decrease of the feed solution, so that coordination interaction between Fe^{3+} and $-NH_3^+$ or $-NH_2$ would be depressed owing to electrostatic repulsion, resulting in the decrease of adsorption of Fe^{3+} on the beads. When the pH decreased further to lower than 1.5, the q_e decreased to a minimum because of the full protonization of the amine groups of CS molecules. This analysis is supported by the collapse of CS0 beads at pH = 2.0, and by the dissolution of CS0 beads at pH lower than 1.5. This result also indicates the improvement in acid resistance of the CS beads coated by cellulose. At pH higher than 3.5, the Fe^{3+} was found to be hydrolyzing precipitation.

CONCLUSIONS

CS beads coated with cellulose were successfully prepared by simply dropping acidic CS solution into alkaline cellulose solution. Thus, prepared CS beads exhibit porous structure in the surface, which is the microstructure of the covered regenerate cellulose layer. The analyses indicate that strong interaction exists between the cellulose coating and the inner CS. Compared with the pure CS beads, the cellulose-coated CS beads display improved mechanical strength and acid resistance. However, the adsorption behavior of CS has not been reduced by the cellulose coating because of the porous structure of the

TABLE II
Langmuir and Freundlich Isothermal Adsorption Equation Parameters for Fe3+ Adsorption on the CS0 and CS1

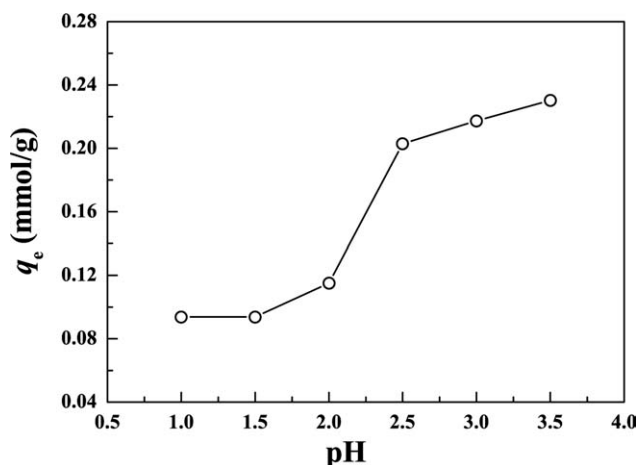| CS bead	Langmuir parameters			Freundlich parameters		
	qmax (mmol/g)	b (L/mmol)	R	1/n	KF (mmol/g)	R
CS0	0.21	12.2	0.9974	0.514	0.356	0.9818
CS1	0.21	11.6	0.9953	0.497	0.322	0.9703

Figure 7 Variation of Fe^{3+} adsorption amount for CS1 on the pH of the feed Fe^{3+} solution ($c_0 = 0.5$ mmol/L).

cellulose layer. Therefore, this study provides an easy way to prepare CS beads with improved strength and acid resistance, which might expand the application of CS materials in the adsorption and separation fields.

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