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Adsorption of Cd^{2+} and Cu^{2+} on Ion-Exchange Beads from Cellulose/Alginic Acid Blend

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Adsorption of Cd^{2+} and Cu^{2+} on Ion-Exchange Beads from Cellulose/Alginic Acid Blend

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ABSTRACT

Our previous work has proved that mechanical properties of a blending alginate with cellulose was significantly enhanced in a wet state and maintained its biodegradability. In this article, ion-exchange beads were prepared from cellulose and alginate in 6 wt% NaOH/4 wt% urea aqueous solution by using an emulsion phase separation method. The structure and morphology of the beads were characterized by scanning electron microscope (SEM) and Fourier transform infrared (FTIR) spectra, and the adsorption behaviors to Cd^{2+} and Cu^{2+} ions were measured by atomic absorption spectrometry (AAS). The effects of pH, adsorption time, ion concentration, temperature, and reusability of the beads on the adsorbed amount of Cd^{2+} and Cu^{2+} ions in aqueous solution were investigated by a batch method. The results indicated that the beads had a spherical shape, with $\sim$4–20 μm of diameter and relatively high

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ion-exchange capacity (3.81 mmol g^{-1}). The combined action of Cd^{2+} and Cu^{2+} ions on beads generally was found to be antagonistic. The selectivity of the beads for the adsorption of Cd^{2+} ions was higher than that of Cu^{2+} ions. The adsorbed amount was given to a maximum for Cd^{2+} ions at pH 2.2, and for Cu^{2+} ions at pH 3.2. The adsorbed amount of the beads reached the values of 0.7 and 0.5 mmol g^{-1} for Cd^{2+} and Cu^{2+} ions, respectively. The beads could be regenerated by using 1 mol L^{-1} HCl aqueous solution, up to 95% recovery, and the adsorption–desorption cycles, performed over 10 times, maintained the adsorption capacity, indicating a good reusability.

Key Words: Cellulose; Alginic acid; Ion-exchange beads; Metal ions; Adsorption; Environmental friendly material.

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INTRODUCTION

A variety of industries are responsible for the release of heavy metal ions into the environment through their wastewaters.[1,2] Ion-exchange resins and chelating resins from the synthetic polymer based on petroleum have been widely used as commercial sorbents to collect toxic metals, precious metals, base metals, and radionuclides from the aqueous solutions.[3] However, the polymer-based products are discarded, to appear in the environment; nonbiodegradable plastics have become a serious threat to the environment throughout the world. Natural polymers such as alginate, chitosan, chitin, and cellulose as environmentally friendly materials have attracted much attention, because they are renewable, biodegradable, and biocompatible, and will be the main chemical resources in the future. Alginic acid is a linear multiblock copolymer from blocks of β-(1 $\rightarrow$ 4)-D-mannuronic acid and α-(1 $\rightarrow$ 4)-L-guluronic acid, as well as alternating copolymers from these two monomer units.[4] The carboxyl groups could be available for characteristic co-ordination bonding with metallic ions and are accompanied by the displacement of protons.[5] An application of alginate gel particles is based on the affinity toward certain ions and the ability to bind these ions selectively and cooperatively.[6] The selectivity of alginate gel as adsorbing aging for divalent metals has been reported, indicating a high selectivity for Cu^{2+} ions compared with Ca^{2+} ions,[7] a high adsorption capacity of 55.83 g kg^{-1} for Cd^{2+} ions,[3] a more strongly absorbability of Cu^{2+} ions (14.23 mg g^{-1}) for Ca-alginate gels[8] and a higher biosorption capacity of Cd^{2+} ions (35.1 $\pm$ 1.2 mg g^{-1}) for pure alginate beads.[9]

Cellulose and wood are abundant in nature are produced in a sustainable way, and offer many possibilities for use.[10] By using a blend of cellulose and alginate to prepare new material, not only can the strength of alginate gel be

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increased, but also the biodegradability can be maintained. In our laboratory, cellulose/alginic acid ion-exchange membranes have been prepared by a coagulating mixture of a cellulose cuoxam and alginate aqueous solution[11] and a mixture of cellulose and alginate in 6 wt% NaOH/4 wt% urea aqueous solution.[12] The blend membranes of cellulose/alginic acid exhibited significantly good mechanical properties, owing to a strong electrostatic interaction caused by the occurring intermolecular hydrogen bonds between two polymers and the formation of a Ca^{2+} bridge.[11–13] Moreover, the cellulose/alginic acid ion-exchange membranes were satisfactory for the adsorption of Cd^{2+} and Sr^{2+} ions.[14] In this article, we attempted to prepare ion-exchange beads by blending alginate and cellulose in a 6 wt% NaOH/4 wt% urea aqueous solution by using a emulsion phase separation method, to study the effects of pH, adsorption time, ion concentration, and temperature on an adsorbed amount of the beads for Cd^{2+} and Cu^{2+} ions.

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EXPERIMENTAL

Materials and Reagents

The cotton linters (cellulose I) were purchased from Hubei Chemical Fiber Group, Ltd. (Xiangfan, China). The viscosity-average molecular weight (M_η) of the cotton linter was determined to be 1.03×10^5, according to $[\eta] = 3.85 \times 10^{-2}\ M_w^{0.76}$ (mL g^{-1}) in cadoxen at 25 ± 0.1°C by viscometry.[15] The sodium alginate was purchased from the Branched Factory of Shanghai Chemical Reagent Co. (Shanghai, China). The intrinsic viscosity $[\eta]$ of sodium alginate in a 0.09 mol L^{-1} NaCl/0.01 mol L^{-1} NaF aqueous solution was measured at 25 ± 0.1°C, and the M_η of the sodium alginate was calculated to be 3.65×10^5, according to $[\eta] = 2.0 \times 10^{-3}\ M_w$ (mL g^{-1}).[16] The nonionic surfactant, based on a polyoxyethylene sorbitan monolaurate such as Span-80, was obtained from the Shanghai Chemical Reagent Co. (Shanghai, China).

All of the solutions were prepared from deionized water and analytical grade reagents. The stock solutions (500 mg L^{-1}) of Cd^{2+} and Cu^{2+} were prepared by dissolving the desired amounts of cadmium chloride ($CdCl_2 \cdot 2.5H_2O$) and copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), respectively, in deionized water acidified with 10 mL of corresponding concentrated acid. The 0.01 mol L^{-1} HCl aqueous solution and acetate–sodium acetate buffers were used to adjust pH in the range from 2 to 7. The 1 mol L^{-1} HCl aqueous solutions was used as an eluant for regeneration of the beads.

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Preparation of Ion-Exchange Beads

A 4 wt% cellulose solution and a 4 wt% alginate solution in 6 wt% NaOH/4 wt% urea aqueous solution were prepared according to our previous work.[12] The cellulose solution and alginate solution were blended by a weight ratio of 1 : 4. The mixture solution was stirred for 15 min, then centrifuged, and degassed. The beads were prepared by the emulsion phase separation method. Briefly, the mixture solution was dispersed in liquid petrolatum containing 5% Span-80, and the reaction was performed isothermally at 45 ± 0.2°C in a 1-L capacity flask. By using a mechanical stirrer at a speed of 500 rpm for 2 hr, the liquid petrolatum system formed a water-in-oil (w/o) emulsion. Thereafter, a mixture of 200 mL 5% $CaCl_2$ aqueous solution and 100 mL chloroform was added, in drops, to the above system, and the dispersion was stirred for 2 hr to form spherical beads. The beads were collected by filtration, washed with 5% $CaCl_2$ aqueous solution three times. The ion-exchange beads were completely converted to the H^+ form by treating with excess 0.1 mol L^{-1} HCl ethanol solution in a column. The beads were washed with ethanol–water for up to 2 hr to remove free hydrogen ions from the beads, until there was no change in pH, and then the beads were washed with acetone three times and dried at 45°C to a constant weight.

Characterization

The surface of the beads were coated, under vacuum with gold, then they were observed and photographed by using a scanning electron microscopy (SEM) with a Hitachi S-570 SEM (Hitachi, Japan).

The beads were crushed to fine powder prior to analysis by using a Nicolet 170SX Fourier transform infrared (FTIR) spectrometer. KBr was used as the embedding medium to make disks containing the samples.

The water content in the wet beads was measured as follows. The 0.5 g of dry beads were soaked completely in distilled water in a fritted column at ambient temperature for 12 hr, and then the supernatant was removed by centrifugation at 5000 rpm for 40 min and weighted. The beads were vacuum dried at 45°C for 12 hr and weighed. The degree of swelling (S_{H_2O}) of the beads was calculated by [17]

$$S_{H_2O} = \frac{w_w - w_d}{w_d} \times 100\% \quad (1)$$

where w_w and w_d are the weight (g) of the wet beads at the equilibrium swelling state and the dry beads, respectively.

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The measurement of weight loss of the beads in solution were carried out in 1 mol L^{-1} HCl aqueous solution and 4% volume per volume (v/v) H_2SO_4 aqueous solution to evaluate the stability of the cellulose/alginate acid ion-exchange beads during adsorption tests. The weight loss of the beads (w_L) during adsorption treatments was calculated by[8]

$$W_L = \frac{w_o - w_f}{w_f} \times 100\% \quad (2)$$

where w_o and w_f are the weight (g) of the dry beads before and after each test.

The ion-exchange capacity (A_R) was measured by titration. According to the definition of the active ion-exchange capacity,[18] A_R was determined and calculated by

$$A_R = \frac{q_{ion}}{w_d} \quad (3)$$

where q_{ion} and w_d are the amounts (mmol g^{-1}) of ion-exchange groups and the weight (g) of the dry beads, respectively. A total of 0.2 g beads with the H^+ form were placed into a 250-mL ground-glass stoppered conical flask, and 50 mL of standard 0.1 mol L^{-1} NaOH aqueous solution was added to a conical flask, stirring by using a magnetic stirrer for about 12 hr. After equilibration, 10 mL aliquots of the supernatant solution was back-titrated to the methyl orange end point with a standard 0.1 mol L^{-1} HCl aqueous solution. The A_R value of the beads was calculated from the amounts of the hydroxide ion.

Determination of Adsorbed Amount

The metal ion concentrations of Cd^{2+} and Cu^{2+} ions were determined by atomic absorption spectrophotometer (AAS) with 180-80 Polarized Zeeman AAS (Hitachi, Japan) equipped with an air–acetylene flame at wavelengths 228.8 and 324.8 nm (air and acetylene flow rate: 10 and 2 L min^{-1}, respectively). The pHs of the solutions were measured by a S-10B pH meter (Xiaoshan Scientific Apparatus Co., China) equipped with a calomel electrode and a glass electrode (Shanghai Dian Guang Device Works, China).

The adsorbed amount, metal ions combining capacity (q), was measured by the batch equilibration technique in a polyethylene bottle. The weighed beads were soaked in metal ion solutions and shaken by a magnetic stirrer at different experimental conditions. After equilibration was completed, the supernatant solution was collected for metal ions determination. The

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concentration of metal ions adsorbed on the beads was determined from the liquid phase mass balance. The q was calculated by

$$q = \frac{Q}{w_d} \tag{4}$$

where Q and w_d are the amounts (mmol) of metal ions up-take on the beads and the weight (g) of the dry beads, respectively.

RESULTS AND DISCUSSION

Physical Properties and Structure of Beads

The physical properties of the ion-exchange beads are summarized in Table 1. The data indicate that the blend beads exhibited relatively good ion-exchange capacity, similar to that of alginate gel[3] and higher than cellulose/alginic acid blend membranes at the same component.[19] Moreover, the ion-exchange beads studied here have more lower weight loss than pure alginate,[8] indicating that the beads have excellent physical and mechanical properties compared with pure alginate due to blending with cellulose, resulting in a strength of the beads in a wet state.

Representative SEM photographs of the beads are shown in Fig. 1. The beads had a spherical shape, with approximately 4–20 μm of diameter. Figure 2 shows the FTIR spectra of cellulose, alginic acid, the cellulose/alginate ion-exchange beads, and the beads combined with Cd^{2+} and Cu^{2+} ions. Usually, cellulose has the characteristic absorption at 3430 and 1635 cm^{-1}. However, the alginic acid has a strong band of characteristic absorption at 1740 cm^{-1}, which could be indicative of the free carboxyl group of the

Table 1. Comparison of physical properties of the ion-exchange beads.

	Values	
Properties	Cellulose/alginic acid	Alginic acid
Particle size (μm)	2–20	
Ion-exchange capacity (mmol g^{-1})	3.81 2.78[19]	3.78[3]
Swelling degree in water (%)	700	
Weight loss in water (%)	0.96	4.14[8]
Weight loss in 1 mol L^{-1} HCl (%)	2.74	
Weight loss in 4% H_2SO_4 (% v/v)	5.86	33.41[8]

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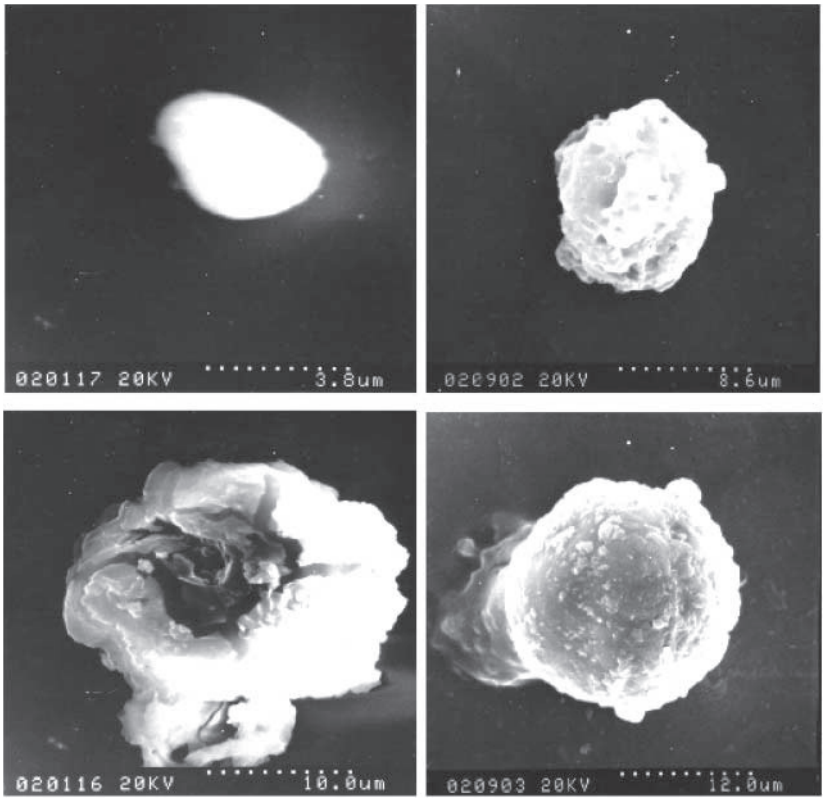

Figure 1. Scanning electron micrographs of the ion-exchange beads.

alginate acid, whereas, the bands at 1630 and 1425 cm^{-1} were assigned to the presence of the salified carboxyl group. In detail, 1630 and 1425 cm^{-1} were assigned to the antisymmetric and symmetric COO^- stretching vibration of the salified carboxyl group, respectively.[20,21] After blending, the –OH stretching vibration bands at around 3440 cm^{-1} of the blend beads were broadened and shifted to a lower wave number, compared with cellulose and alginic acid, indicating that a strong intermolecular hydrogen bond occurred between cellulose and alginic acid, which agreed with the relatively low W_L of the beads in Table 1. The results supported the conclusion that the blend beads had more strength than pure alginic acid. In view of the spectrum, the peaks of the beads adsorbed with Cd^{2+} and Cu^{2+} ions at 1627 and 1640 cm^{-1} significantly strengthened, owing to the ionized carboxyl of alginic acid.[20] Moreover, the peak at 1627 cm^{-1} for Cd^{2+} ions was stronger than that at

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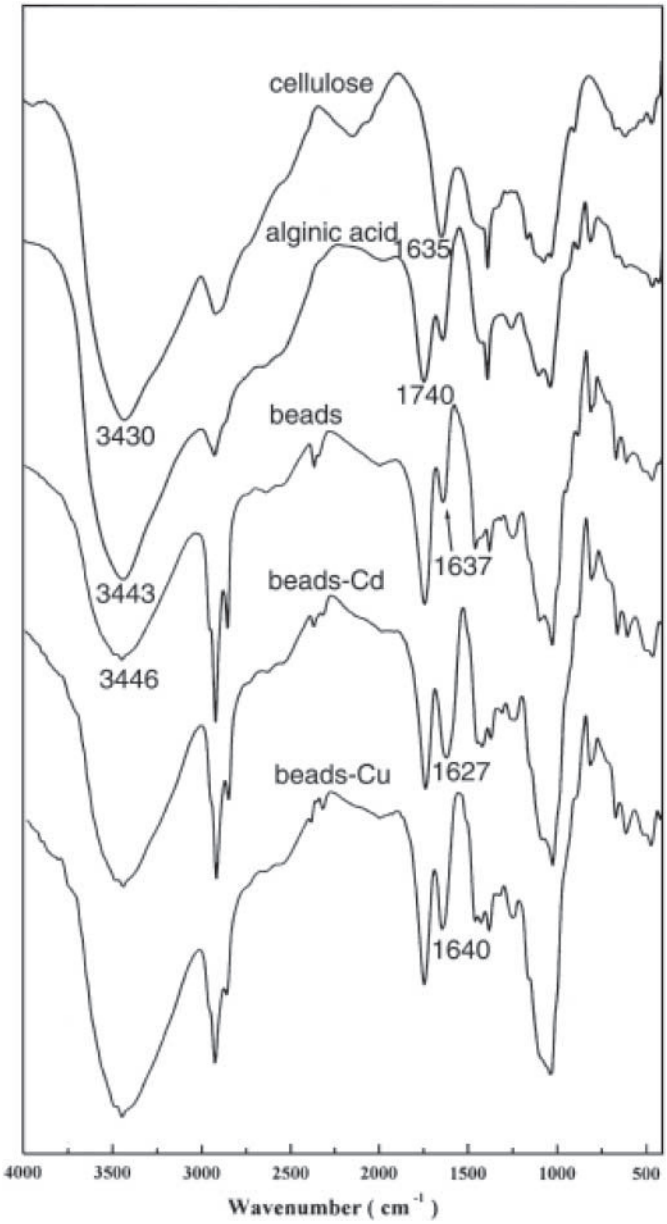

Figure 2. The FTIR spectra of the cellulose, alginic acid, blend beads, and beads containing Cd^{2+} and Cu^{2+} ions, respectively.

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1640 cm^{-1} for Cu^{2+} ions. This suggests that the Cd^{2+} ions have a stronger loading capacity than Cu^{2+} ions on the beads.

Dependence of *q* on pH

The effects of pH on the adsorption of Cd^{2+} and Cu^{2+} ions for single adsorption in an aqueous solution are shown in Fig. 3. This indicated that the *q* values of Cd^{2+} ions were much larger than that of Cu^{2+} ions, and the maximum lies at pH of 2.2 for Cd^{2+} ions and 3.2 for Cu^{2+} ions in the tests. As seen from the results obtained for the same metal ions in the literature,[3,8,22] the general trend is that the metal up-take increases when the pH increases. However, in this work, the adsorption of Cd^{2+} and Cu^{2+} ions on the blend beads decreased with an increase of pH. This can be explained that the ionic strength of the buffer solution increased with the increase of pH values. The ionic strength of the buffer solution increased from 0.01 to 0.76 mol kg^{-1} with

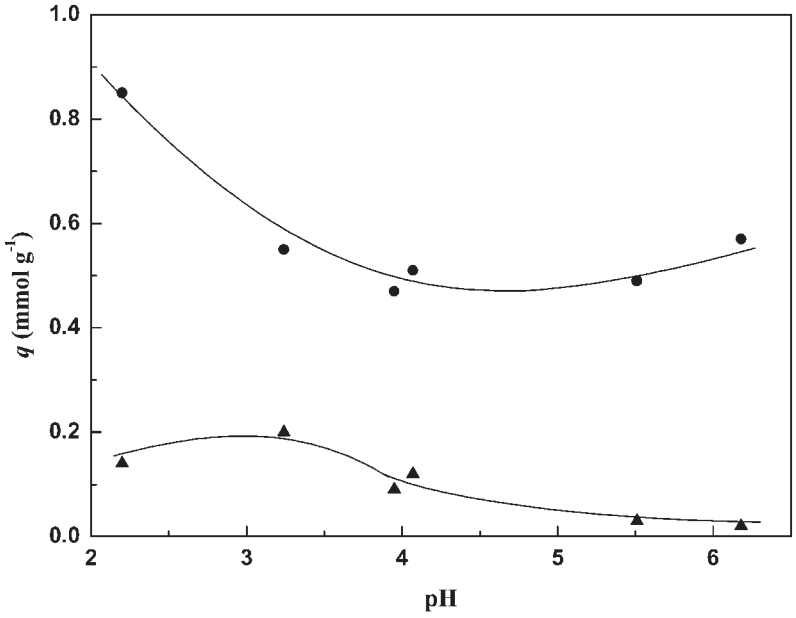

Figure 3. Effect of pH on *q* of Cd^{2+} (●) and Cu^{2+} (▲) ions for single adsorption in 100 mL aqueous solution containing 140 mg L^{-1} Cd^{2+} and Cu^{2+} ions, respectively. (Temperature, 25°C; beads' concentration, 1.0 g L^{-1}; agitation rate, 200 rpm; adsorption time, 2 hr.)

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the increase of pH from 2.2 to 6.2, and the effect of ionic strength on the adsorption could not be negligible.[14] The reduction of the adsorption of Cd^{2+} or Cu^{2+} ions on the blend beads is due to the competitive adsorption of Na^{+}.

Dependence of *q* on Absorption Time

Figure 4 shows the adsorption time of Cd^{2+} and Cu^{2+} ions up-take on the beads containing 140 mg L^{-1} Cd^{2+} and Cu^{2+} ions. The saturation levels were obtained at 10 min. After this period, the concentration of adsorbed metal ions did not significantly change for Cu^{2+} ions within 24 hr, while increasing after 12 hr for Cd^{2+} ions. The amounts of Cd^{2+} ions up-take on ion-exchange beads continued to increase after the equilibrium stage, suggesting that chemisorptions, a subsequent slow up-take, is responsible for much of the Cd^{2+} ions up-take. The process of absorbing Cu^{2+} ions on the beads was a physical

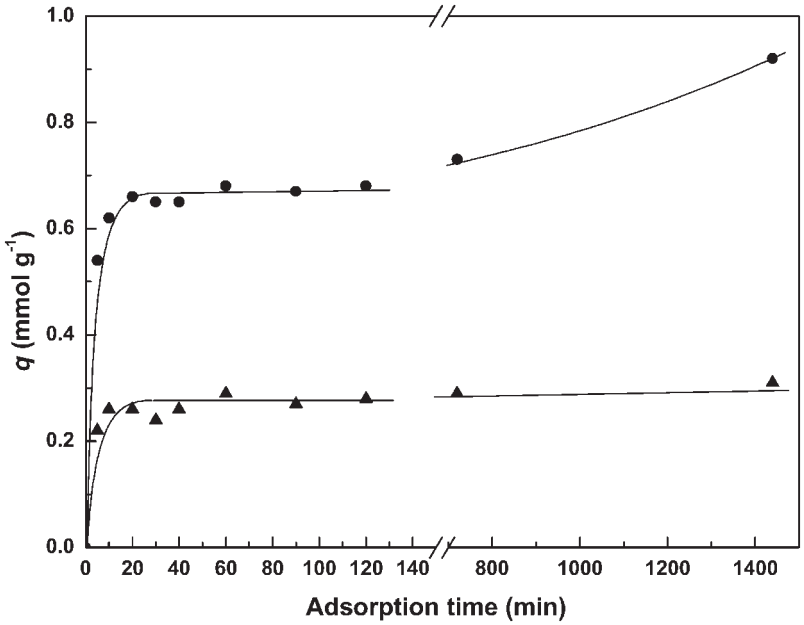

Figure 4. Effect of adsorption time on *q* of Cd^{2+} (●) and Cu^{2+} (▲) ions for adsorption in initial 250 mL aqueous solution containing 140 mg L^{-1} Cd^{2+} and Cu^{2+} ions, respectively. (Temperature, 25°C; beads' concentration, 0.5 g L^{-1}; agitation rate, 200 rpm; pH, 2.6 for Cd^{2+} ions and 3.0 for Cu^{2+} ions, respectively.)

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sorption reaction, so the adsorption amounts of Cu^{2+} ions hardly changed after the equilibrium stage.[23]

Dependence of q on Initial Ion Concentration

The adsorption capacities of the ion-exchange beads as a function of the initial concentrations of Cd^{2+} and Cu^{2+} ions in the aqueous phase are shown in Fig. 5. The adsorption capacity of the beads first increased with the initial concentrations of Cd^{2+} and Cu^{2+} ions, and then reached a saturation values when the ion concentrations increased to 100 and 220 mg L^{-1}, respectively. The adsorption capacities of Cd^{2+} and Cu^{2+} ions combining on the beads were 0.7 and 0.5 mmol g^{-1}, respectively.

To determine whether the ion-exchange beads could be modeled by using adsorption isotherms, the two most commonly used sorption isotherms (the Langmuir and Freundlich models) for adsorption of Cd^{2+} and Cu^{2+} ions were

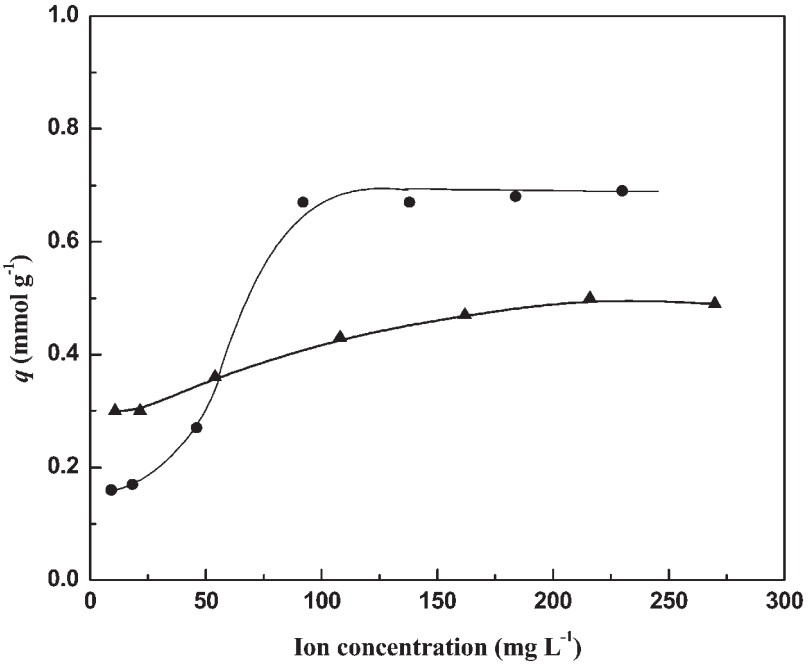

Figure 5. Effect of Cd^{2+} (●) and Cu^{2+} (▲) ion concentration on q in 250 mL aqueous solution. (Temperature, 25°C; beads concentration, 0.5 g L^{-1}; agitation rate, 200 rpm; pH, 2.6 for Cd^{2+} ions and 3.0 for Cu^{2+} ions, respectively.)

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used here. The Langmuir isotherm[24] has been given by the following expression:

$$q_{eq} = \frac{q_{max} \cdot b \cdot C_{eq}}{1 + b \cdot C_{eq}} \tag{5}$$

where q_{eq} is the amount of metal adsorbed per gram of beads weight (mmol g^{-1}) at the equilibrium, C_{eq} is the residual (equilibrium) metal concentration (mmol L^{-1}) left in solution after binding, q_{max} is the maximum adsorption capacity corresponding to complete monolayer coverage (mmol g^{i-1}), and b is a Langmuir constant related to the affinity of the binding sites for the metals (L $mmol^{-1}$). The Freundlich equation[25] is commonly presented as

$$q = K_F \cdot C_{eq}^{n} \tag{6}$$

where K_F and n are the mono component Freundlich constants, characteristic of the system, indicating, respectively, the adsorption capacity and intensity. The isotherm model constants and correlation coefficients for the adsorption of Cd^{2+} and Cu^{2+} ions on the beads are shown in Table 2. The experimental equilibrium data fits both models well, illustrating the fact that the use of cellulose/alginic acid blend beads as an entrapment matrix for adsorption of Cd^{2+} and Cu^{2+} ions could be modeled with both the Langmuir and Freundlich isotherms.

Dependence of *q* on Temperature

The dependence of an adsorbed amount of the metal ions on temperature is shown in Fig. 6. With an increase of temperature, the adsorption of Cu^{2+} ions decreased, and the optimum adsorption temperature for Cu^{2+} ions was determined to be 20°C. Physical sorption reactions are normally exothermic,

Table 2. Isotherm model constants and correlation coefficients for adsorption of Cd^{2+} and Cu^{2+} ions.

	Langmuir			Freundlich		
Metal ions species	q_{max} (mmol g^{-1})	b (L $mmol^{-1}$)	R^2	K_F (L g^{-1})	n	R^2
Cd^{2+}	0.79	4.56	0.9870	0.58	0.43	0.9789
Cu^{2+}	0.52	5.02	0.9944	0.40	0.21	0.9865

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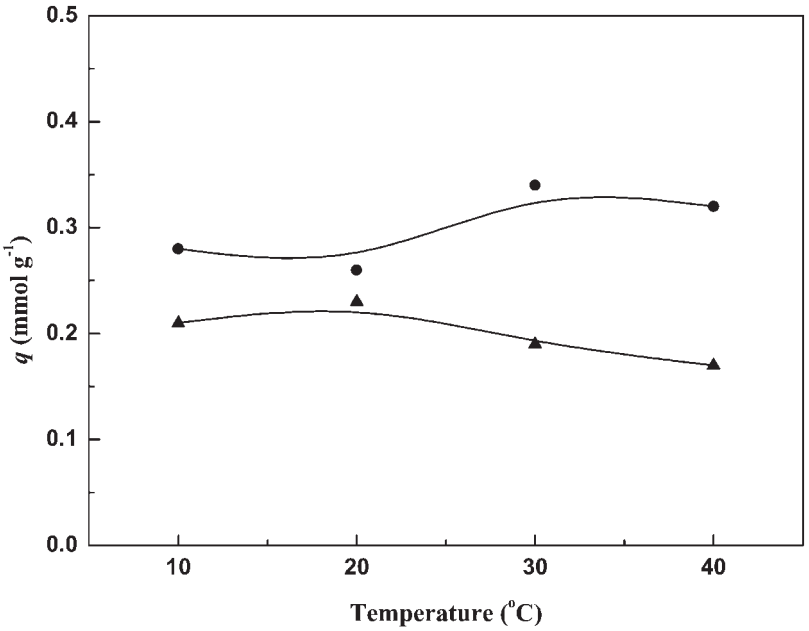

Figure 6. Effect of temperature on q of Cd^{2+} (●) and Cu^{2+} (▲) ions in 50 mL solution containing 140 mg L^{-1} Cd^{2+} and Cu^{2+} ions, respectively. (Beads' concentration, 1.0 g L^{-1}; agitation rate, 200 rpm.)

so the extent of adsorption generally increases with decreasing temperature. However, with an increase in temperature, the adsorption capacity of Cd^{2+} ions increased. This suggests that chemical sorption plays a dominant role on the whole adsorption process of Cd^{2+} ions on the blend beads, resulting in an increase of adsorption as expected.[23]

Reusability of Beads

To clarify the stability and reusability of the beads, the adsorption–desorption cycles of Cd^{2+} and Cu^{2+} ions were repeated 10 times. The Cd^{2+} and Cu^{2+} ions adsorbed on beads were eluted completely with 1 mol L^{-1} HCl aqueous solution for 10 min. Figure 7 shows the dependence of adsorption capacity of the beads on the regeneration time. Apparently, the adsorption capacities did not change during the repeated adsorption–desorption operations. The results indicated that the ion-exchange beads could be

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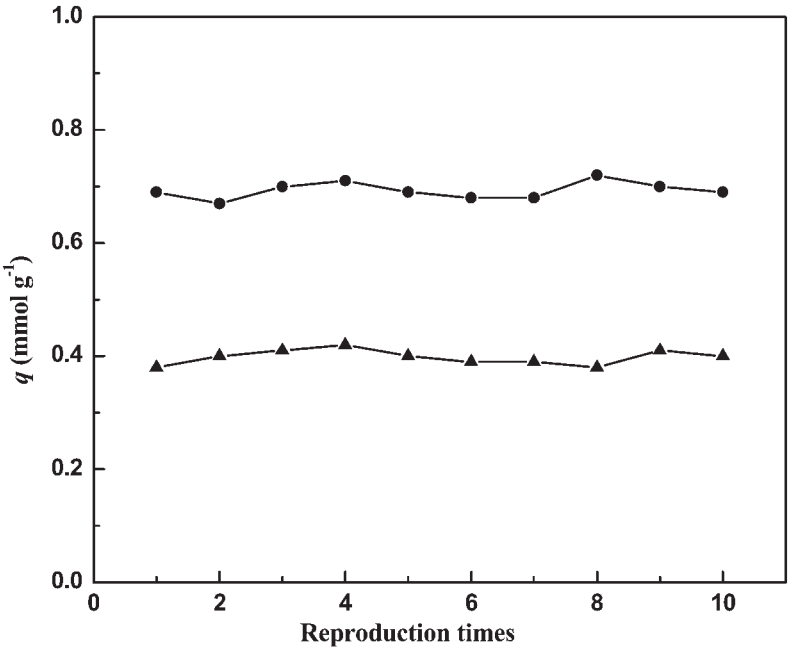

Figure 7. Effect of reproduction times on q of Cd^{2+} (●) and Cu^{2+} (▲) ions in 250 mL aqueous solution containing 200 mg L^{-1} of Cd^{2+} and Cu^{2+} ions, respectively. (Temperature, 25°C; beads' concentration, 0.5 g L^{-1}; agitation rate, 200 rpm; pH, 2.6 for Cd^{2+} ions and 3.0 for Cu^{2+} ions, respectively.)

repeatedly used as heavy metal adsorption for long times, exhibiting good reusability.

CONCLUSIONS

Ion-exchange beads were prepared successfully from cellulose and alginate (1 : 4 by weight) in 6 wt% NaOH/4 wt% urea aqueous solution by using an emulsion phase separation method. The results indicated that the beads exhibited higher ion-exchange capacity with 3.81 mmol g^{-1}; it is possible to foresee a higher adsorption capacity for metal ions. The adsorption amount of Cd^{2+} and Cu^{2+} ions on the beads depended on the pH and the concentration of metal ions in the medium. The combined action of Cd^{2+} and Cu^{2+} ions on the beads generally was found to be antagonistic. Different metal ions have different pH optima, possibly due to the different solution chemistry

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of metal ions. The adsorption capacities of Cd^{2+} and Cu^{2+} ions on the beads were 0.7 and 0.5 mmol g^{-1}, respectively. The selectivity of the beads for adsorption of Cd^{2+} ions was much higher than that of Cu^{2+} ions. The effect of the pH was greater than the effect of the temperature and ion concentration in the medium, and q values were obtained at a maximum of pH 2.2 for Cd^{2+} ions and pH 3.2 for Cu^{2+} ions in our experiment. The leveling off of the adsorption equilibrium was obtained at 10 min. The beads could be regenerated by using a 1 mol L^{-1} HCl aqueous solution and could be reused for long time and still reach up to 95% recovery. By using a blend of cellulose and alginate to prepare beads, it not only can there be an increase in the mechanical properties, but the biodegradability can also be maintained.

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