Adsorption for Metal Ions of Chitosan Coated Cotton Fiber

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ABSTRACT: A kind of adsorbent for metal ions, cotton fiber coated by high loading of chitosan (SCCH) was prepared. Its structure was characterized by elemental analysis, scanning electronic microscopy (SEM), Fourier transform infrared spectrum (FTIR), and wide-angle X-ray diffraction (WAXD). The adsorption properties of SCCH for Cu^{2+}, Ni^{2+}, Pb^{2+}, Cd^{2+}, such as saturated adsorption capacities, static kinetics, and isotherm were investigated. The adsorption for Ni^{2+}, Pb^{2+}, and Cd^{2+} was controlled by liquid film diffusion, but by particle diffusion for Cu^{2+}. The adsorption process for Cu^{2+}, Ni^{2+}, Cd^{2+} could be described with Langmuir or Freundlich equation, but only with Freundlich equation for Pb^{2+}. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2321–2327, 2008

Key words: chitosan coated cellulose; adsorption; heavy metal ions

INTRODUCTION

Contamination of aquatic media by heavy metals is a serious environmental problem, mainly because of discard of industrial waste. Most of heavy metals must be removed from the contaminated water before discharge, as they are considered persistent, unbiodegradable, and toxic. Many methods, such as chemical precipitation,[1] ion exchange,[2] membrane filtration,[3] electrolytic method,[4] and solvent extraction[5] etc. have been used to treat such effluents, but most of them are either expensive or incapable of removing trace level of heavy metal ions. Adsorption is one of promising approach for this purpose, especially using low-cost natural materials.

Biopolymers, useful for heavy metals adsorption, have recently received a great deal of attention because of the fact that they represent renewable resources and are more environmental friendly than traditional materials, and among them can be emphasized the chitosan, a polymer derived from chitin by *N*-deacetylation, which can be widely found in the exoskeleton of shellfish and crustaceans as the second most abundant natural biopolymers next to cellulose. Chitosan has excellent properties for the adsorption of metal ions, principally because of the presence of amino and hydroxyl groups in the polymer matrix, which can interact with metal ions in solution by complexation reactions.[6–9] In addition, since the deacetylated amino groups in chitosan can be protonated, the polycationic properties of the polymer can be expected to contribute to the charged interactions with anionic substances. It has been reported to have high potential for adsorption of anionic dyes,[10] organic acids,[11] and proteins[12] etc. Polycationic chitosan has other versatile properties such as flocculation,[13] scale inhibition ability,[14] and antibacterial activity.[15] Comparing with traditional polyanionic resins, as a polycationic polymer, chitosan exhibits much higher adsorption selectivity for some heavy metal ions because of its chelating or coordination adsorption mechanism for metal ions but not ion exchange of polyanionic resins. Therefore, chitosan is very useful to treat waste water. However, the applications of chitosan are limited due to its degradability[16] and loss in acidic environment.[17] Although crosslinking process has been found to effectively improve the chitosan stability,[18] the crosslinking reduces the density of the functional groups on the modified material. Recently, chitosan attached to polymer have been shown to be useful for metal ions extraction, which may increase the stability of chitosan.[19] Cellulose, which can be easily obtained in nature, is the most abundant material with good hydrophilicity. Moreover, cellulose, with good reaction properties, is not dissoluble in water and most of organic solvents. Therefore, various researches were focused on preparing many kinds of cellulose derivatives with good adsorption properties towards heavy metal ions.[20–23] Li and Bai[24] prepared chitosan-cellulose hydrogel beads by blending cellulose with chitosan as adsorbent for Cu^{2+}. It was

found that the introduction of cellulose into chitosan improved the chemical stability of chitosan-cellulose beads in solutions with pH value down to 1. Liu et al.[25] prepared a new cotton fiber with a chitosan coating (CCCF) with the maximum contents (1.8%) of chitosan by the oxidation of a cotton thread and treatment with a solution of chitosan. In this article, we prepared the Schiff base-type chitosan coated cotton fiber (SCCH) with higher loading of chitosan, and applied it in adsorbing for Cu^{2+}, Ni^{2+}, Pb^{2+}, and Cd^{2+}.

EXPERIMENTAL

Materials

Chitosan with degree of deacetylation 90% was purchased from Yuhuan Halobios Company (Zhejiang province, China). Cotton fiber with fineness of 25 tex was obtained from Ruitai Textile Group. (Shandong province, China). Glacial acetic acid, dehydrated alcohol and all other reagents were of analytical grade.

Instruments

Infrared spectra (IR) were recorded on a MAGNA-IR 550 spectrophotometer, Nicolet, the US. Wide-angle X-ray diffraction (WAXD) was performed using a D/max-2500vpc X-ray power diffractometer, Rigaku, Japan. Elemental analysis was conducted using an Elementar Vario EL β model elemental analyzer, Elementar, Germany. The concentration of metal ions was determined using a 932B-model atomic adsorption spectrometer (AAS), GBC, Australia. The morphology of the samples was characterized using a JSM-5600LV scanning electronic microscope (SEM), JOEL, Japan.

Preparation of chitosan coated cotton fiber

Ten grams of fragmental cotton fiber (about 1 cm in length) was immersed in a solution of 13 g of sodium periodate in 500 mL deionized water. The mixture was then stirred at 60°C for 5 h in a light-proof condition. Then, 10 mL of ethylene glycol was added into the solution above to terminate the reaction. The fragmental cotton fiber was filtered, washed firstly with 1 : 1 (v/v) ethanol-water solution, then with deionized water to remove the oxidant, and dried under vacuum at 60°C. Thus, the oxidized fiber (ODC) was obtained. The method[26,27] for determination of aldehyde group contents is based on the following quantitative chemical reaction:

$$-CHO + NH_2OH\,HCl = -CHNOH + HCl + H_2O.$$
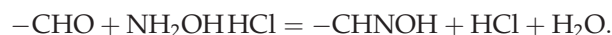
During the reaction in methanol, the released hydrochloric acid was titrated with sodium hydroxide-methanol solution. The contents (mmol g^{-1}) of aldehyde group are calculated according to following equation:

$$H = \frac{(V_2 - V_1) \times C_{HCl}}{W}$$

where V_2 (mL) and V_1 (mL) are the volume of the HCl solution; C_{HCl} is the concentration of HCl solution; and W(g) is the weight of oxidized cellulose. The contents of aldehyde groups of ODC prepared were determined to be 2.058 mmol g^{-1}.

A chitosan solution was prepared by stirring a dispersion of chitosan (2.0 g) in 0.4% (v/v) aqueous acetic acid solution (200 mL) for 1 h at 60°C. 0.5 g of ODC was immersed in the chitosan solution with constant stirring for 8 h at 65°C. The solid product was filtered and washed with 0.4% (v/v) acetic acid solution and deionized water, respectively. After dried at 60°C in vacuum, the final product Schiff base-type chitosan coated cellulose (SCCH) was obtained. Element analysis (%) of SCCH: N, 0.526; C, 41.68; H, 6.002.

Adsorption of SCCH

Adsorption equilibrium

In a thermostat-cum-shaking assembly, batch adsorption experiments were carried out by shaking 0.1 g of resin with 25 mL of an aqueous solution of metal ions of the desired concentration, pH, and temperature in 50 mL flask. The concentration of metal ions before and after adsorption was deter-
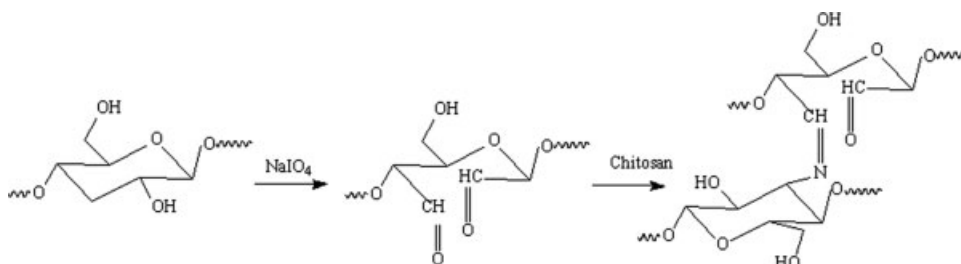
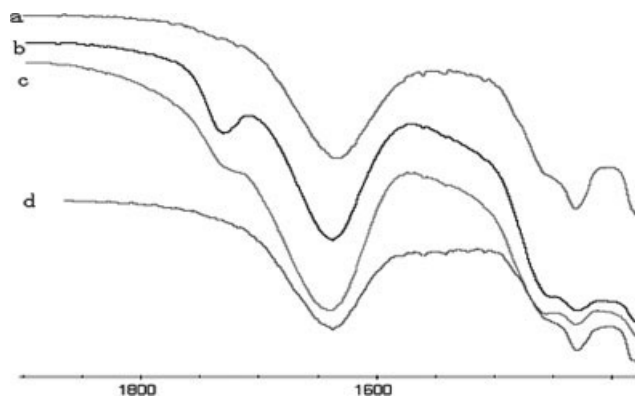**Scheme 1** The synthesis route of SCCH.

Figure 1 The IR spectra of: (a) cotton fiber: (b) ODC: (c) SCCH: (d) SCCH reduced with NaBH$_4$.

mined by an AAS. The amount of adsorbed metal ions was calculated according to the eq. (1): $Q = V(C_0 - C)/W$, where C_0 and C (mmol mL^{-1}) is the initial and equilibrium concentration of metal ions, respectively; V(mL) is the volume of solution, and W(g) is the dry weight of SCCH.

Adsorption kinetics

The batch kinetics experiments were performed in a similar step to 1.4.1. At present time intervals the amount of adsorption at time t, Q_t (mmol g^{-1} chitosan) was obtained as follows: $Q_t = V(C_0 - C_t)/W$, where C_0 (mmol mL^{-1}) and C_t (mmol mL^{-1}) are the concentration in the solution at time $t = 0$ and at time t, respectively; V(mL) is the volume of the solution , and W(g) is the weight of chitosan used.

RESULTS AND DISCUSSION

Synthesis and characterization of SCCH

Infrared spectra analysis

The SCCH was synthesized as shown in Scheme 1. The FTIR spectra of cotton fiber, SCCH, and ODC were shown in Figure 1. From (a,b) in Figure 1, it could be seen that the main difference between cotton fiber (a) and ODC (b) was the appearance of characteristic absorption peaks of C=O stretch vibration at around 1730 cm^{-1} in the spectrum of (b).
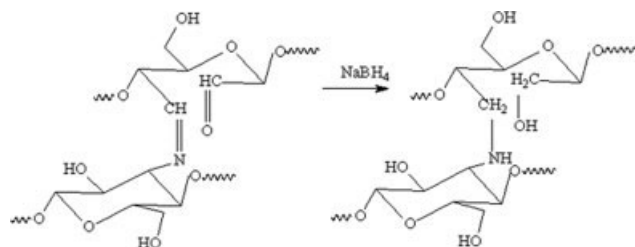
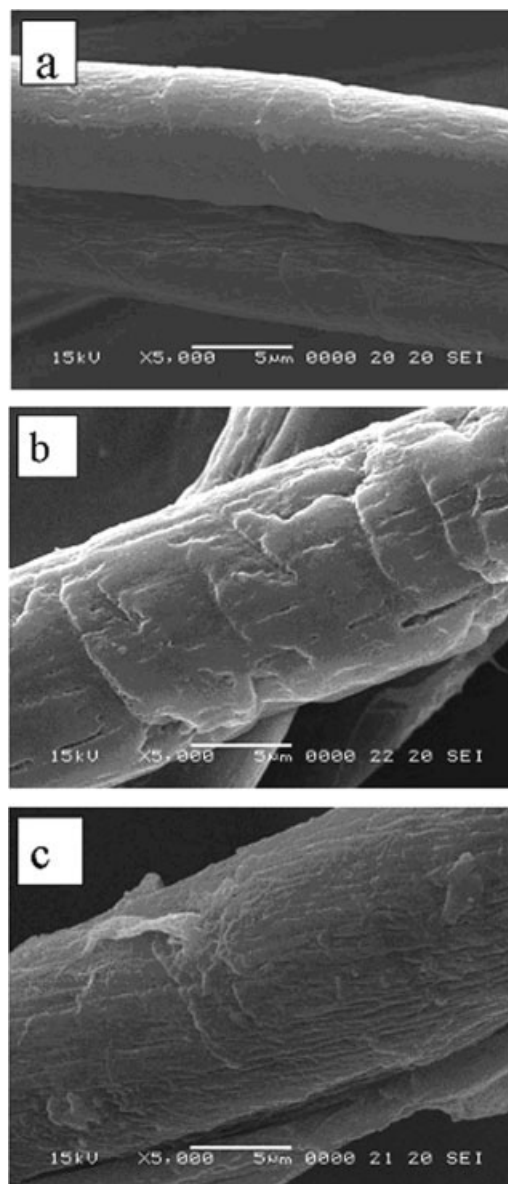**Scheme 2** The reaction route of SCCH reduced with NaBH$_4$.

Figure 2 SEM of photomicrographs of: (a) cotton fiber; (b) ODC; (c) SCCH.

From Figure 1 (c), it was obvious that the characteristic absorption peaks of C=O shifted to 1716 cm^{-1} after ODC was treated with chitosan, suggesting that the Schiff base (C=N double bond) formed between the aldehyde group and chitosan.

To further confirm the presence of C=N, SCCH was immersed into deionized water, and then excessive amount of NaBH$_4$ was added into the mixture with constant stirring at ambient temperature. The resulting fiber was washed with deionized water, and then dried in vacuum (see Scheme 2). The IR spectrum (d) of reduced SCCH was shown in Figure 1. The disappearance of absorption peak at 1716 cm^{-1} suggested that the C=N was reduced successfully by NaBH$_4$. The aforementioned IR analytic results confirmed the formation of the Schiff base in SCCH.
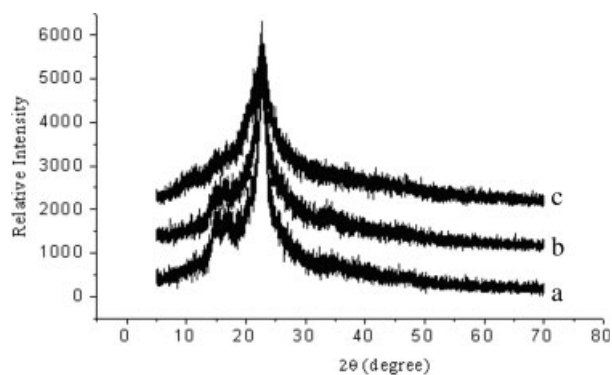
Figure 3 The wide-angle X-ray diffraction patterns of (a) cotton fiber; (b) ODC; (c) SCCH.

SEM analysis

The SEM images of cotton fiber, ODC and SCCH were shown in Figure 2. It could be seen that the surface of cotton fiber (a) was smoother than that of ODC (b) and SCCH (c), the surface of ODC became rough with some different-depth longitudinal stripes generation, indicating that the cotton fiber was suffered from corrosion of sodium periodate in the process of oxidation. On the other hand, from Figure 2(c), it could also be observed that the surface of SCCH became smooth with regular compact stripes after the ODC was treated with chitosan, indicating that after treatment with chitosan, the surface of ODC was covered with a layer of chitosan.

WAXD analysis

Figure 3 showed the WAXD patterns of cotton fiber, ODC, and SCCH. It could be seen from Figure 3(a) that the WAXD patterns the characteristic peaks of cotton fiber appeared at $2\theta = 15.5°$ and $2\theta = 22.5°$, which represented the crystallization and noncrystallization regions. In Figure 3(b), the peaks at $2\theta = 15.5°$ of ODC decreased slightly, which was attributed to the deformation of the strong hydrogen bond in the ODC because of the oxidation of hydroxyl groups into aldehyde groups. ODC giving a lower crystallinity than cotton fiber indicated that it was considerably more amorphous than cotton fiber. From Figure 3(c),

it could be seen that the peaks at $2\theta = 15.5°$ disappeared completely, indicating that the formation of Schiff base between ODC and chitosan made the crystal structure further disorder.

Adsorption properties of SCCH

Saturated adsorption

The batch saturated capacities experiments were performed in a similar step to 1.4.1 with 25 mL $0.01M$ aqueous solution of metal ions. The experiment results of the saturated adsorption of SCCH for Cu^{2+}, Ni^{2+}, Pb^{2+}, and Cd^{2+} were shown in Table I. It was evident from Table I that the sequence of the saturated adsorption for four kinds of metal ions was as follows: $Pb^{2+} > Cu^{2+} > Ni^{2+} \approx Cd^{2+}$, which implied that SCCH had better adsorption selectivity for Pb^{2+} and Cu^{2+} than for Ni^{2+} and Cd^{2+}. The difference in adsorption selectivity might be contribute to the formation of complex compounds with different stability and structures between metal ions and chelating groups (such as —OH, —NH$_2$ and —C=N).

According to the results of elemental analysis of 0.526% nitrogen content in SCCH, the contents of amino groups and chitosan were calculated to be 0.376 mmol g^{-1} and 6.049%, respectively. The corresponding adsorption capacities of per gram of chitosan and per nitrogen atom for Cu^{2+}, Pb^{2+}, Ni^{2+}, Cd^{2+} were shown in Table I. Form Table I, it could be seen that the adsorption of Cu^{2+} and Pb^{2+} exceeded one heavy ion per nitrogen atom, which could be explained by the fact that among the three kinds of groups —OH also exhibited chelating capability to metal ions besides-NH$_2$ and —C=N. Compared with the data reported in literature,[28] the utilization ratio of chitosan in SCCH was much larger than that of pure chitosan, which is just one of the aims of the chitosan coated cotton fiber was prepared.

Adsorption kinetics of SCCH

The adsorption kinetics curves of SCCH for Cu^{2+}, Pb^{2+}, Ni^{2+}, and Cd^{2+} were shown in Figure 4. It was seen that it need different time to reach adsorption equilibrium for different metal ions. The adsorption equilibriums were established in about 5 h for

TABLE I
The Saturated Adsorption of SCCH (pH = 6.3–6.5; $T = 25°C$) ($n = 4$)

Metal ions	Cu^{2+}	Pb^{2+}	Ni^{2+}	Cd^{2+}
Saturated adsorption (mmol g^{-1} SCCH)[a]	0.3902 ± 0.0187	0.4911 ± 0.0196	0.1303 ± 0.0045	0.1407 ± 0.0056
Corresponding adsorption capacities (mmol g^{-1} chitosan)	6.45 (2.33[b])	8.09 (1.79[b])	2.15	2.31
Corresponding adsorption capacities (ions/nitrogen atom)	1.04 (0.38[b])	1.31 (0.29[b])	0.35	0.37

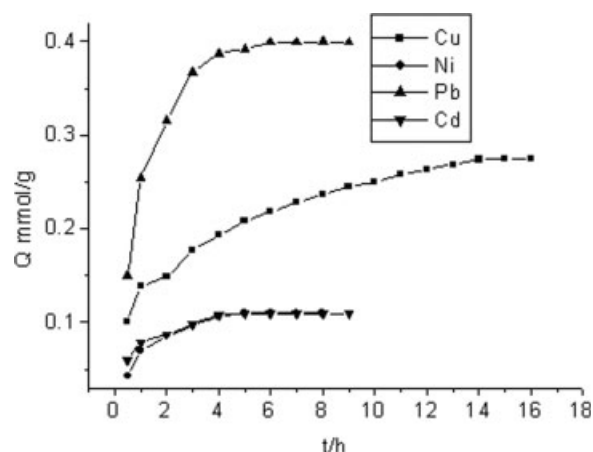[a] Average of four runs $\pm$ S.D.
[b] The values in parentheses were from Ref. 28.

Figure 4 The relationship between adsorption amount and time (25°C, pH = 6.5).

Cd^{2+} and Ni^{2+}, and 6 h for Pb^{2+}, and 15 h for Cu^{2+}, respectively.

The data of the kinetics in Figure 4 were analyzed by the procedure given by Reichenberg[29] and Helfferich.[30] The following equations were used:

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \left[\frac{-D_i t \pi^2 n^2}{r_0^2} \right] \quad \text{or}$$

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp[-n^2 Bt],$$

where F is the fractional attainment of equilibrium at time t and is obtained by the expression $F = Q_t/Q_0$, where Q_t is the amount of adsorption at time t and Q_0 is the maximum equilibrium uptake and $B = \frac{\pi^2 D_i}{r_0^2}$ = time constant, where D_i is the effective diffusion coefficient of ion in the adsorbent phase; r_0 is the radius of the adsorbent particle, assumed to be spherical; and n is an integer that defines the infinite series
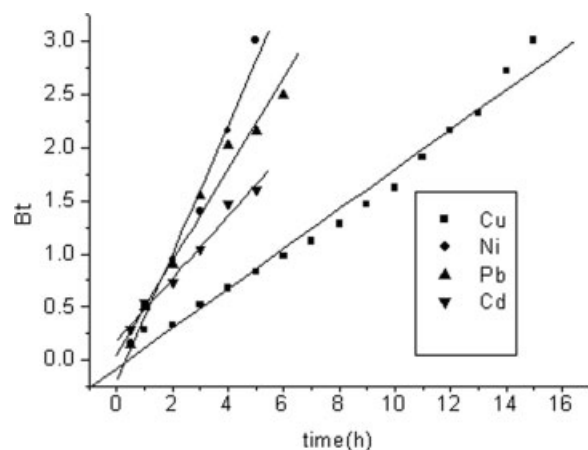
TABLE II
The Bt versus Time (t) Linear Equations, Correlation Coefficients R^2 and Intercept Error

Metal ions	Linear equation	R^2	Intercept error
Cu^{2+}	$Bt = 0.18696t - 0.07229$	0.98948	0.0643
Ni^{2+}	$Bt = 0.60811t - 0.20833$	0.99135	0.12218
Pb^{2+}	$Bt = 0.43223t + 0.07016$	0.98543	0.12085
Cd^{2+}	$Bt = 0.29528t + 0.18287$	0.99141	0.0591

solution. Bt values were obtained for each observed value of F from Reichenberg's table.[29] The results were plotted in Figure 5, and the linear equations and correlation coefficients R^2 were presented in Table II.

The linearity test of Bt versus time plots was employed to distinguish between the film diffusion and particle diffusion controlled adsorption.[31] If the plot of Bt versus time (having slope B) is a straight line passing through the origin, the adsorption rate is governed by particle diffusion mechanism, otherwise, it is controlled by film diffusion. From Figure 5 and Table II, it could be seen that the straight lines for Pb^{2+}, Ni^{2+}, and Cd^{2+} did not pass through the origin, indicating the rate controlling step to be liquid film diffusion mechanism; the straight line for Cu^{2+} almost past through the origin, indicating the rate controlling step not to be liquid film diffusion, but particle diffusion. From the above adsorption kinetics, it was worth noting that the adsorption rates for Cu^{2+} was much slower than that of others. This might be a result that the interaction rate of Cu^{2+} with coordination atoms is faster than that of other metal ions; thus, a copper complex matrix was rapidly formed around the resin particle, which retarded the diffusion of into interior of resin particle. Obviously, the adsorption procedure of SCCH for Cu^{2+} was controlled by particle diffusion, which accorded with the simulation result aforementioned equation given by Reichenberg[29] and Helfferich.[30]
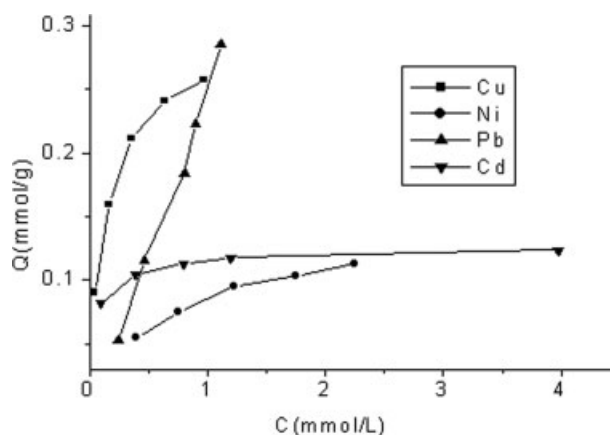

Figure 5 The relationship between Bt and t.

Figure 6 The adsorption of isotherms of SCCH for metal ions (25°C, pH = 6.5).
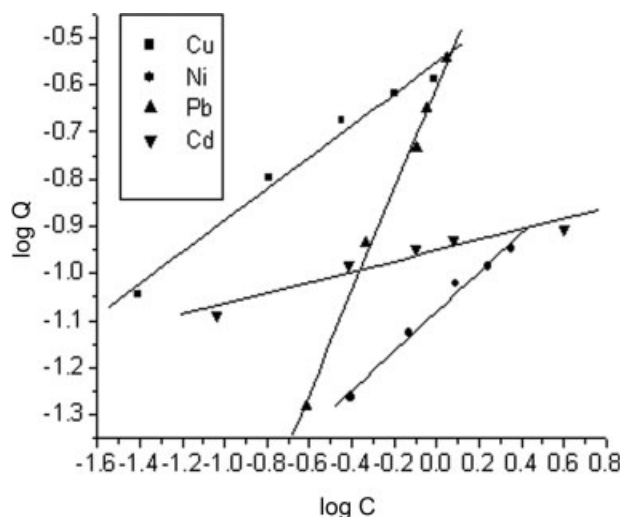
Figure 7 The relationship between log Q and log C.

Adsorption isotherm

The batch adsorption isotherm studies were conducted in similar manner to the batch adsorption equilibrium studies by varying the metal ions concentration. Figure 6 showed the results of the adsorption isotherm of SCCH for Cu^{2+}, Pb^{2+}, Ni^{2+}, and Cd^{2+} at 25°C and pH = 6.5. It could be seen that within experimental concentration, the adsorption capacities increased with increasing metal ions concentration till the equilibrium was established, and the adsorption capacities of SCCH for Pb^{2+} established fine linear relation.

Two theoretical isotherm models, namely, the Freundlich and the Langmuir equations, have long been used for the interpretation of experimental data related to the binding behavior of ion exchange and affinity adsorbent. It is necessary to determine which theoretical isotherm best fits the data. The experi-
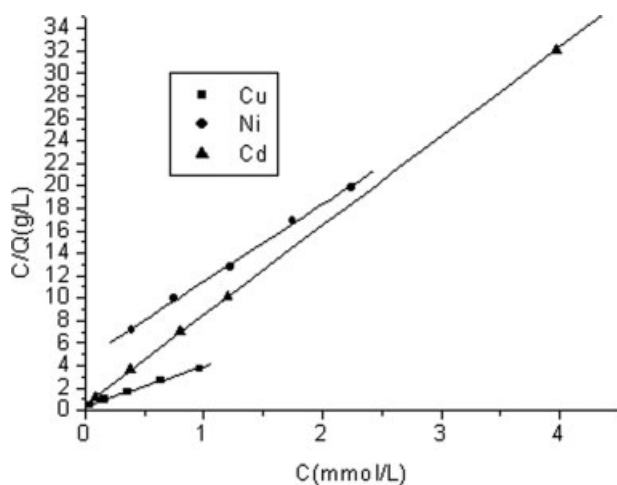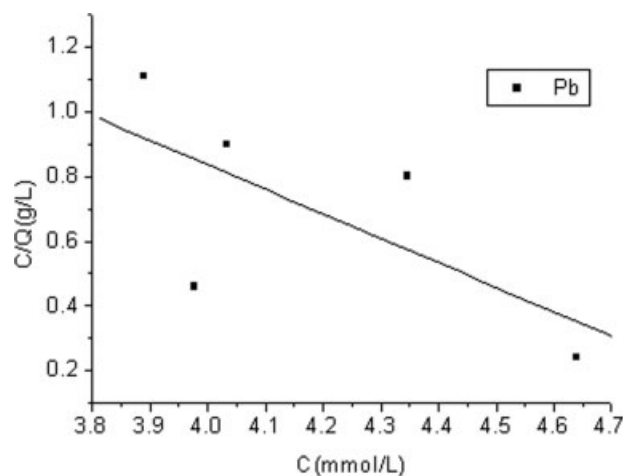

Figure 9 The relationship between C/Q and C.

mental data related to the adsorption of SCCH for the above metal ions were applied to the linear Freundlich and Langmuir equation, which were expressed as the follows respectively: Freundlich equation, $\log Q = \log K + (1/n)\log C$; Langmuir equation, $C/Q = C/Q_0 + 1/(Q_0 \times b)$, where Q is the capacities, mmol g^{-1}; C is the equilibrium or final concentration, mmol mL^{-1}; Q_0 is the maximum adsorption capacities, mmol g^{-1}; b, k, and n are the constants relevant to the adsorption and experience parameters. The results were presented in Figures 7–9. Freundlich and Langmuir parameters were given in Table III. From the Figures 7–9 and the Table III, it was evident that the adsorption of SCCH for Cu^{2+}, Ni^{2+}, Cd^{2+} fitted perfectly to both Freundlich and Langumuir model with correlation coefficients above 0.95; indicating that the adsorption of SCCH for Cu^{2+}, Ni^{2+}, Cd^{2+} might be described with Langmuir or Freundlich equation. However, Figures 7 and 9 showed that the adsorption process for Pb^{2+} could be modeled using Freundlich equation.

Effect of pH on adsorption

pH is an important parameter for adsorption of chitosan.[32] To examine the effect of pH on the adsorption, the batch pH studies were conducted in similar manner to the batch adsorption equilibrium with pH

Figure 8 The relationship between C/Q and C.

TABLE III
Freundlich and Langmuir Constants for Metal Ions Adsorption on SCCH Resin

Metal ions	Freundlich parameters			Langmuir parameters		
	k	$1/n$	R_F^2	Q_0	b	R_L^2
Cu^{2+}	0.2795	0.33435	0.9903	0.2845	9.115	0.9989
Pb^{2+}	0.2391	1.08463	0.9971	–	–	–
Ni^{2+}	0.0829	0.41816	0.9921	0.1450	1.4750	0.9990
Cd^{2+}	0.1118	0.11286	0.9585	0.1258	13.415	0.9999

TABLE IV
The Relationship Between Adsorption Capacities and pH Value (25°C) of SCCH
(mmol g^{-1}) ($n = 3$)

| pH | Adsorption capacities (mmol·g^{-1})[a] | | | |
	Cu^{2+}	Pb^{2+}	Ni^{2+}	Cd^{2+}
2.0	0	0	0	0
3.0	0	0	0.0861 ± 0.0035	0
4.0	0.0160 ± 0.0008	0.0860 ± 0.0035	0.1135 ± 0.0041	0
5.0	0.0740 ± 0.0021	0.1377 ± 0.0055	0.1135 ± 0.0039	0
6.0	0.2240 ± 0.0089	0.3194 ± 0.0125	0.1139 ± 0.0028	0.0772 ± 0.0050
6.5	0.2850 ± 0.0131	0.4155 ± 0.0150	0.1140 ± 0.0031	0.1237 ± 0.0055
7.8	–	–	–	0.1531 ± 0.0060

[a] Average of three runs ± S.D.

ranging from 2.0 to 7.8. As shown in Table IV, the adsorption amount of SCCH for metal ions was strongly dependant on the pH of the solution. The resin of SCCH had no adsorption for Cu^{2+} at low pH (pH < 3.0) because of the protonation of amine groups, and the adsorption capacities for Cu^{2+} ions increased obviously with the increasing pH ranging from 4.0 to 6.5. At low pH environment (pH < 3), amine groups in SCCH could be easily protonated, which induced an electrostatic repulsion of Cu^{2+}. Therefore, competition adsorption existed between Cu^{2+} and H^{+} for adsorption sites, the adsorption capacity increased with an increase in pH. In addition, amine groups may have chelation with Cu^{2+} by releasing hydrogen ions, as the result of the reaction, high hydrogen ion concentration prevent deeper progress of reaction between amine groups and copper ions. At high pH over 7.8, precipitation of Cu^{2+} hydroxide may occur before adsorption. The adsorption properties of SCCH for other metal ions were similar to that for Cu^{2+}. From this it was considered that amino groups were the main contributors to adsorption for metal ions.

CONCLUSIONS

The SCCH resin synthesized via the reaction between amino groups in chitosan and aldehyde groups in oxidized cotton fiber. Its structure was confirmed by FTIR, elemental analysis, SEM and WAXD analysis. The adsorption of SCCH was investigated. The results showed that the saturated adsorption of SCCH for Cu^{2+}, Pb^{2+}, Ni^{2+}, and Cd^{2+} at 25°C and pH = 6.5 were approximately 0.39, 0.49, 0.13, and 0.14 mmol g^{-1}, respectively. The utilization ratio of chitosan loaded in SCCH is markedly higher than that of pure chitosan. The adsorption for Ni^{2+}, Pb^{2+}, and Cd^{2+} was controlled by liquid film diffusion, but by particle diffusion for Cu^{2+}. The isothermal process for Cu^{2+}, Ni^{2+}, and Cd^{2+} could be described with Langmuir or Freundlich equation, but only with Freundlich equation for Pb^{2+}.

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