Chitosan(Chitin)/Cellulose Composite Biosorbents Prepared Using Ionic Liquid for Heavy Metal Ions Adsorption

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Chitosan(chitin)/cellulose composites as biodegradable biosorbents were prepared under an environment-friendly preparation processes using ionic liquids. Infrared and X-ray photoelectron spectra indicated the stronger intermolecular hydrogen bond between chitosan and cellulose, and the hydroxyl and amine groups were believed to be the metal ion binding sites. Among the prepared biosorbents, freeze-dried composite had higher adsorption capacity and better stability. The capacity of adsorption was found to be Cu(II) (0.417 mmol/g) > Zn(II) (0.303 mmol/g) > Cr(VI) (0.251 mmol/g) > Ni(II) (0.225 mmol/g) > Pb(II) (0.127 mmol/g) at the same initial concentration 5 mmol L^{-1}. In contrast to some other chitosan-type biosorbenrts, preparation and component of the biosorbent were obviously more environment friendly. Moreover, adsorption capacity of chitosan in the blending biosorbent could be fully shown. © 2009 American Institute of Chemical Engineers *AIChE J,* 55: 2062–2069, 2009
Keywords: ionic liquid, chitosan, cellulose, biosorption, heavy metals

Introduction

The heavy metals in wastewater may cause long-term risk to ecosystem and human.[1] There were various methods available for removing the toxic metal ions, such as chemical precipitation, ion exchange, solvent extraction and membrane processes, but from the view of stricter environment-protection requirement, these methods usually involved higher cost to deal with the pollution due to more chemicals introduced in the process.[2] Recently, biosorption using non-living biomass is becoming a promising clean technique for heavy metal removal from industrial effluents,[3] and these biological materials are inexpensive.[4] The biosorption process is provided with high efficiency, low operating costs, and minimization of chemical volume and biological sludge need to be further handled.[5] Most biopolymers are nontoxic, hydrophilic, biocompatible, and biodegradable.[6] In the numerous biosorbents, cellulose and chitin are two of most abundant materials in nature.[7] Chitosan is prepared by partially deacetylating acetamido groups from chitin.[8] Although both chitin and chitosan are excellent metal ligands, disadvantages for biosorption were also found. For example, common chitin flake is a crystallized polymer with higher crystallinity,[9] and it is found that chitin flake has low adsorption because metal ions can only be adsorbed onto the amorphous region of crystals.[10] On the other hand, when powder of chitin and chitosan is used, it will become difficult to be separated after adsorption.[11] Chitosan is easily soluble in dilute acidic solutions, and its mechanical properties are also not suitable for adsorption.[12] In view of the above problems, the physical or chemical modification will be necessary before chitin and chitosan are available as bisorbents. As a common method, some cross-linking stabilizing agents were used to decrease the solubility, overcome swelling behavior and enhance mechanical strength.[13] In additional, polymer

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blending was also used to decrease crystallinity of chitin[9] and enhance the mechanical and chemical properties of chitosan.[14]

With higher requirement of environment, the use of renewable feedstocks, less hazardous and degradable chemical arouse public attentions,[15] and traditional biosorption technology is facing challenges. For example, a 6-wt % NaOH/5 wt % thiourea aqueous solution with 5% H_2SO_4 was used to prepare cellulose/chitin biosorbent,[9] and the mixed solvents were toxic, and not easily recovered and reused. Some cross-linking agents of biosorbents, such as glutaric dialdehyde, ethylene glycol glycidyl ether, were poisonous and nonbiodegradable, and it was also reported that the cross-linking agents could react with amino groups of chitosan, and the adsorption capacity decreased greatly.[16] As a potential environment-friendly solvent, room temperature ionic liquid (IL) has received intense scrutiny.[17] They have also been successfully applied in the area of separation science.[18] In our previous works, IL-based liquid-liquid[19] extraction and liquid-solid[20] extraction for separating metal ions were studied. As a novel solvent, IL has low vapor pressure and unique solvation ability.[21] For example, 1-butyl-3-methylimidazolium chloride ([Bmim][Cl])[22] and 1-allyl-3-methylimidazolium chloride ([Amim][Cl])[23] could be used to dissolve cellulose and other biomasses, and some simple method was also used to recover and reuse these water soluble ILs.[24] The regenerated cellulose was manufactured into different structural forms[25] and showed better mechanical performance.[23] Some cellulose composites have been developed by the IL dissolution and regeneration process, such as the immobilization of enzymes,[26] physical encapsulation of macromolecules,[27] synthesis of TiO_2 nanowires on cellulose fibre.[28] In additional, chitin and chitosan can also be dissolved, regenerated, and functionalized through the IL processing.[29] To our knowledge, no preparation of biosorbents for metal ions adsorption based on IL has been reported. Thus, we reported herein the preparation of chitosan(chitin)/cellulose biosorbents using IL and their adsorption capacities for heavy metal ions.

Experimental

Chemicals

Microcrystalline cellulose was purchased from Shanghai Hengxin Chemical Reagent Co. Chitin and chitosan (with a deacetylation degree of 90%) were purchased from Sinopharm Chemical Reagent Co. The IL used in this study was [Bmim][Cl], which was prepared and purified as described previously.[30,31] Analysis of [Bmim][Cl] by ^{1}H-NMR resulted in a spectrum containing the following peaks: δ 0.88(3H, t), 1.24(2H, m), 1.75(2H, m), 3.87(3H, s), 4.18(2H, t, J = 3.2 Hz), 7.77(1H, s), 7.85(1H, s), 9.45(1H, s), and the corresponding ^{13}C-NMR was δ 13.21, 18.69, 31.33, 35.63, 48.31, 122.21, 123.49, 136.71. All other reagents used were of analytical grade and purchased from commercial sources.

Procedure

^{1}H- and ^{13}C-NMR spectra were obtained in dimethyl sulfoxide with a Bruker AV 400 NMR spectrometer. A model pHs-3C pH meter, calibrated daily with 4.01 and 6.86 standard buffer solutions, was used for measuring pH values of the aqueous phase. The solubility of $[Bmim]^+$ in aqueous phase was measured using a Shimadzu UVmini-1240 UV-visible spectrophotometer. The freeze-drying of biosorbent was conducted by a Sihuan LGJ-10 freeze drier. Infrared (IR) spectra were measured with a Bruker Vector 22/N spectrometer. The surfaces of biosorbents were examined using FEI XL 30 Environmental Scanning Electron Microscopy. X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCLAB MKII. The concentrations of metal ions in aqueous phase were determined with Inductively Coupled Plasma Spectroscopy (Thermo iCAP 6000 ICP-OES).

Biosorbent preparation

The chitin, chitosan, cellulose, and IL were dried at 70°C for 24 h in a vacuum oven before use to avoid the interference from air and water. Preparation of the biosorbents was achieved by dissolving 1:2 chitosan(chitin)/cellulose into [Bmim][Cl] using microwave pulse heating for 6min. Care was taken to avoid the chitosan(chitin)/cellulose pyrolysis during the dissolution process. The obtained clear and viscous solution (6%) was introduced dropwise into water bath using a 1.6-mm diameter syringe needle. Then the hydrogel beads were collected and extensively rinsed with deionized H_2O until the rinsing water have no characteristic UV adsorption at 211 nm,[32] which meant the remanent [Bmim][Cl] in bead was almost removed. Finally, the chitosan(chitin)/cellulose beads were dried at 70°C for use. The biosorbents so prepared were reasonably spherical in shape. However, shrinkage was found to be obvious during the air drying process. To ameliorate the preparation process, freeze-drying was conducted in a vacuum freeze dryer for 8 h at −40°C. By this means, no obvious shape change of the biosorbents was observed.

Adsorption experiments

Adsorption experiments were conducted to evaluate adsorption capacities of the biosorbents. The biosorbent (0.1 g) was added into a conical flask (50 mL), and the flask was sealed with a cap to minimize evaporation. The mixture was stirred by a magnetic stirrer (180 rpm) for 12 h at 25°C, and the adsorption equilibrium was achieved. For desorption experiment, the biosorbent loaded with metal ion was placed in the hydrochloric acid or ethylenediaminetetraacetic acid (EDTA) and stirred at 180 rpm for 2 h at 25°C. The amounts of adsorption (q), desorption ratio (D_s) were defined as the following equations:

$$q = (C_0 - C_e) \times V/M \tag{1}$$

Where q was the amount of metal ion adsorbed onto the biosorbent (mmol g^{-1}), C_0 and C_e were the initial and final concentration of metal ion (mmol L^{-1}), V was the volume of metal ion solution (L), M was dry weight of the biosorbents (g).

$$D_s = C'_e/(C_0 - C_e) \times 100\% \tag{2}$$

C_0 was the initial metal ion concentration (mmol L^{-1}), C_e was the equilibrium metal ion concentration (mmol L^{-1}), C'_e was

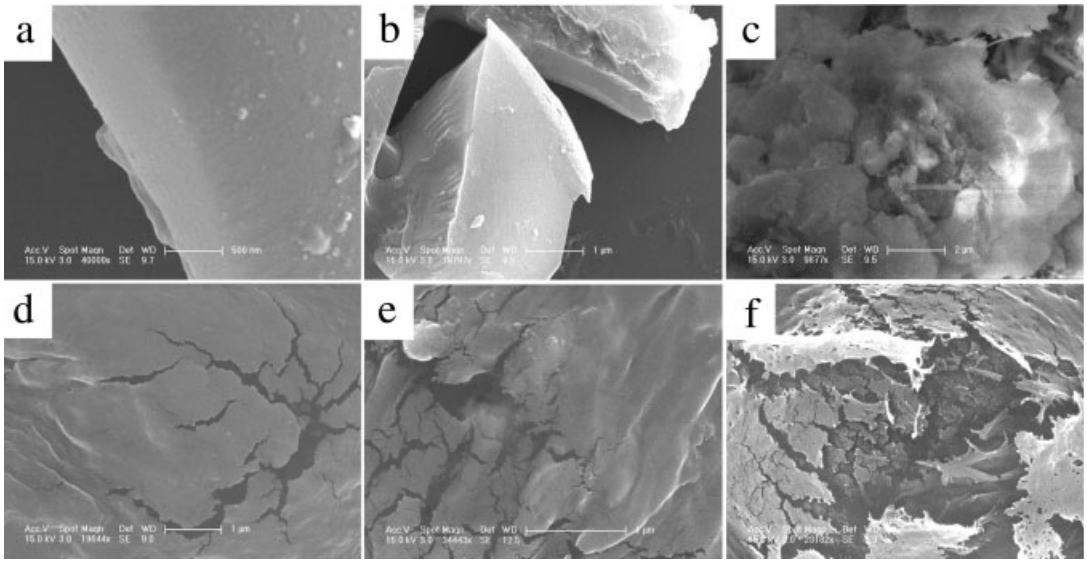


Figure 1. Scanning electron microscopic images of pure cellulose (a), pure chitin (b), pure chitosan (c), dried chitin/cellulose biosorbent (d), dried chitosan/cellulose biosorbent (e), and freeze-dried chitosan/cellulose biosorbent (f).

the equilibrium metal ion concentration in elution medium (mmol L^{-1}). The volume of adsorption and desorption solution were all 10 mL.

Results and Discussion

Microstructure of biosorbents

To examine microstructure of the chitosan(chitin)/cellulose biosorbents, scanning electron microscopic images of pure chitin, pure chitosan, pure cellulose, and the prepared biosorbents were compared. As could be seen in Figures 1d–f, the hydrit biosorbents displayed some microporous structures, which was quiet different to those of pure cellulose, chitin, and chitosan. The morphology implied larger surface areas of the biosorbents and preferable blending of the biopolymers. Actually, the porous structures could be attributed to ILs template effect during preparation. Recent investigations[26,28] revealed that the solubility of cellulose and chitosan(chitin) in [Bmim][Cl] was easily up to 10%. To increase pore volume of biosorbents, 6-wt % chitosan(chitin)/cellulose/[Bmim][Cl] solutions were used in this study. The resulting biosorbents were found to possess enough mechanical strength during the adsorption and desorption processes. As shown in Figure 1, the microporous structures in freeze-dried chitosan/cellulose biosorbent (Figure 1f) were obviously more than those in dried chitin/cellulose biosorbent (Figure 1d) and dried chitosan/cellulose biosorbent (Figure 1e), the difference could be attributed to the different drying means of freeze-drying and drying. In contrast to drying, freeze-drying was an advanced dehydration methods, which contributed to give heat sensitive material higher porosity, wider pore size distribution, lower bulk density, and less shrinkage.[33] It was worth commenting that the diameter of freeze-dried chitosan/cellulose biosorbent (Figure 1f) was obviously bigger than those of dried chitin/cellulose biosorbent (Figure 1d) and dried chitosan/cellulose biosorbent (Figure 1e). Undoubtedly, the larger surface area contributed to the adsorption process.

Effect of pH on adsorption

As well known, chitin and chitosan were always applied for adsorbing heavy metal ions in industrial effluents. However, they had some drawbacks unsuitable for adsorption, such as the higher crystallinity of chitin[9] and dissolution of chitosan in acidity solution.[15] To overcome these disadvantages, cellulose was used as biological support to blend chitin and chitosan in this study. As a toxic heavy metal ion, the pollution by nickel always comes from industrial processes.[34] However, less study on Ni(II) adsorption had been mentioned. Thus, we examined herein validity of the biosobents by Ni(II). Because insoluble nickel hydroxide starts precipitating at higher pH values,[35] initial pH values of the solutions were conducted at lower than 7.

As depicted in Figure 2, adsorption of Ni(II) by the biosorbents was strongly affected by aqueous phase acidity. The effect could be attributed to more protons available to protonate amine groups at higher acidity, accordingly, the numbers of binding sites in chitosan(chitin) for adsorption were reduced. In addition, the adsorption amounts of dried chitosan/cellulose biosorbent were obviously higher than those of dried chitin/cellulose biosorbent. As a result, two conclusions could be achieved. First, the chitin and cellulose in dried chitin/cellulose biosorbent had lower adsorption capacities for Ni(II). It was because the adsorption capacity of chitin was lower than that of chitosan, chitin was not further studied in this article. Second, chitosan resulted in the higher adsorption amounts. Moreover, the adsorption amounts of chitosan/cellulose biosorbent prepared by freeze-drying were obviously higher than those prepared by drying due to the larger surface area. Although the adsorption capacity of pure chitosan biosorbent was better than that of freeze-dried

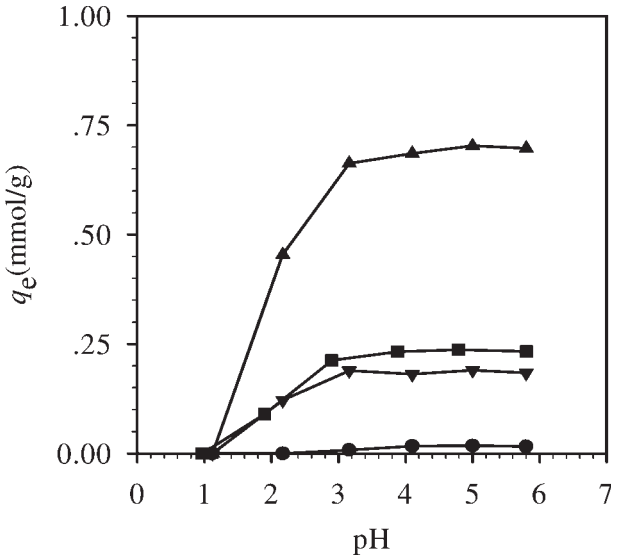


Figure 2. Effect of pH on q_e of dried chitin/cellulose biosorbent (●), dried chitosan/cellulose biosorbent (▼), freeze-dried chitosan/cellulose biosorbent (■), and dried chitosan biosorbent (▲). Ni(II) = 0.5 mmol/L.

chitosan/cellulose biosorbent, its mechanical strength was poor in aqueous phase. The dried chitosan biosorbent was found to be dissolved at pH = 1 aqueous phase, and became sticky and deformed at pH up to 2 and 3. Furthermore, chitosan biosorbent prepared by freeze-drying came to be fragments during adsorption since their worse mechanical strength. Obviously, the disadvantages revealed that pure chitosan was still unfit for adsorption even prepared by the IL dissolution and regeneration process. Compared with the pure chitosan biosorbents, chitosan/cellulose biosorbent was in good condition at all pH scope. The contrast revealed that cellulose could reinforce chemical stability of chitosan. In addition, the chitosan/cellulose biosorbent was composed of chitosan and cellulose at a ratio of 1:2, i.e., the chitosan accounted for third quality of the biosorbent. As could be seen in Figure 2, the q_e of dried chitosan biosorbent was nearly three times bigger than that of freeze-dried chitosan/cellulose biosorbent, which indicated clearly that the adsorption capacity of chitosan in the blending biosorbent could be full shown. Because its better stability and adsorption capacity, freeze-dried chitosan/cellulose biosorbent was further studied in this article.

IR spectra

To better understand material formation and adsorption mechanism, IR spectra were resorted to compare chitosan, cellulose, freeze-dried chitosan/cellulose biosorbent, and Ni(II)-loaded freeze-dried chitosan/cellulose biosorbent.

As depicted in Figures 3a, b, the —OH stretching vibrations for chitosan and cellulose located at 3436 cm^{-1} and 3343 cm^{-1} were slightly broadened and shifted to 3413 cm^{-1} in the biosorbent (Figure 3c). The phenomena indicated that stronger intermolecular hydrogen bonds in the freeze-dried chitosan/cellulose beads were found between chitosan and cellulose. A comparison of the spectra of Figures 3c, d revealed characteristic changes of the hydroxyl groups shift from 3413 cm^{-1} to 3344 cm^{-1} after adsorption, the changes suggested that there were strong interactions of Ni(II) with hydroxyl group. In addition, the peaks at 1652 cm^{-1} (Amide I) and 1599 cm^{-1} (Amide II) (—NH bending vibration in $—NH_2$), 1430 cm^{-1} (—NH deformation vibration in $—NH_2$), 895 cm^{-1} (—CN stretching vibration) were weakened after the adsorption. All these changes related to nitrogen indicated the amine groups were involved in the adsorption process. The vibration band located at 615 cm^{-1} was believed to be caused by the Ni(II)—N adsorption.

XPS spectra

To further investigate the adsorption mechanism, XPS spectra were used to analyze the biosorbents before and after adsorbing Ni(II).

Figure 4 showed the typical results of XPS spectra for freeze-dried chitosan/cellulose biosorbents before (1) and after nickel adsorption (2). First, no chloric ion could be detected by the spectra (Figure 4a), which indicated no [Bmim]Cl was left in the biosorbent. Second, there was one peak in the N 1s spectrum at a binging energy (BE) $\sim$ 398.4 eV (Figure 4b1), and a peak was observed at a BE $>$ 400.05 eV (Figure 4b2). The shifts might be explained as a lone pair of electrons in the nitrogen atom was donated to the shared bond between N and Ni(II), accordingly, the electron cloud density of nitrogen atom was reduced. The BEs of O 1s electron decreased from 532.1eV (Figure 4c1) to 531.55eV (Figure 4c2) might be explained as the electronic density around O and N atoms decreased because the electron was migrated to Ni(II). Third, an obvious peak occurred at the BE of $\sim$856ev (Figure 4d2), which represented the oxidation state +2 for the Ni 2p orbital. The peak provided direct evidence of the adsorbed Ni(II). The XPS results indicated that Ni(II)—O and Ni(II)—N coordinate bonds were formed, i.e., the NH_2 group and OH group were involved during the adsorption process. The mechanism was in good

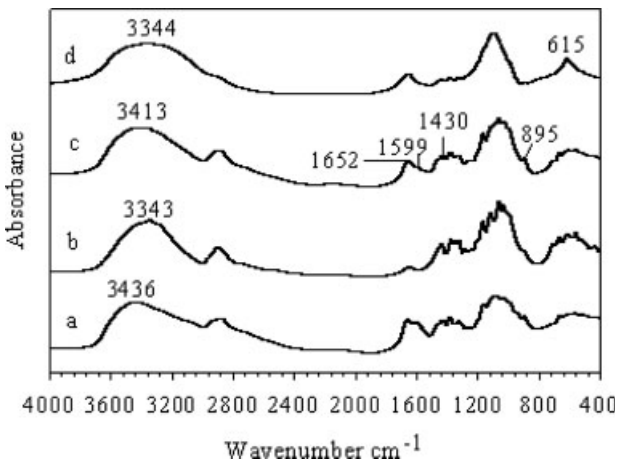


Figure 3. FTIR spectra of chitosan (a), cellulose (b), freeze-dried chitosan/cellulose biosorbent (c), and Ni(II)-loaded freeze-dried chitosan/cellulose biosorbent (d).

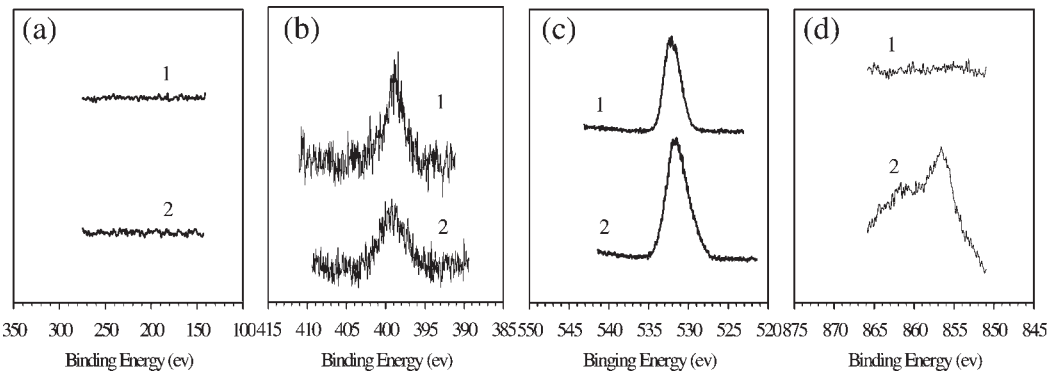


Figure 4. XPS spectra of Cl 1s (a), N 1s (b), O 1s (c), and Ni 1s (d) on the chitosan/cellulose biosorbent before (1) and after (2) Ni(II) adsorption.

agreement with that resulted from IR, thus, a scheme of the preparation and adsorption process could be given as follows (Scheme 1).

Adsorption isotherm

The Langmuir isotherm described the monolayer coverage of adsorbate over specific homogeneous sites within an adsorbent.[36]

$$q_e = q_{max} b C_e / (1 + b C_e) \tag{3}$$

Where C_e was the equilibrium concentration (mmol L^{-1}), q_e was the amount of metal ion adsorbed at specified equilibrium (mmol g^{-1}), q_{max} and b were the Langmuir constants related to adsorption capacity and adsorption energy. Linear form of the Langmuir model could be described by the equation:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max} \mathrm{b}} \frac{1}{C_e} \tag{4}$$

In this study, Langmuir isotherm was applied to analyze relationship between Ni(II) concentration and adsorption capacity of the biosorbents. The uptake isotherms of nickel ions by the biosorbents were obtained in a wide range of initial nickel concentrations varying from 3 to 13 mmol L^{-1}, and the pH value was adjusted to nearly 5.30.

As shown in Figure 5, experimental data of the biosorbents were well fitted by the Langmuir plots. The chitosan/cellulose biosorbents prepared by drying was more accordant with the Langmuir isotherm than those prepared by freeze-drying with a correlation coefficient 0.993 *vs.* 0.985. Moreover, q_{max} value of the freeze-dried biosorbent was estimated to be 0.68 mmol g^{-1}, which was larger than 0.621 mmol g^{-1} of the dried biosorbent.

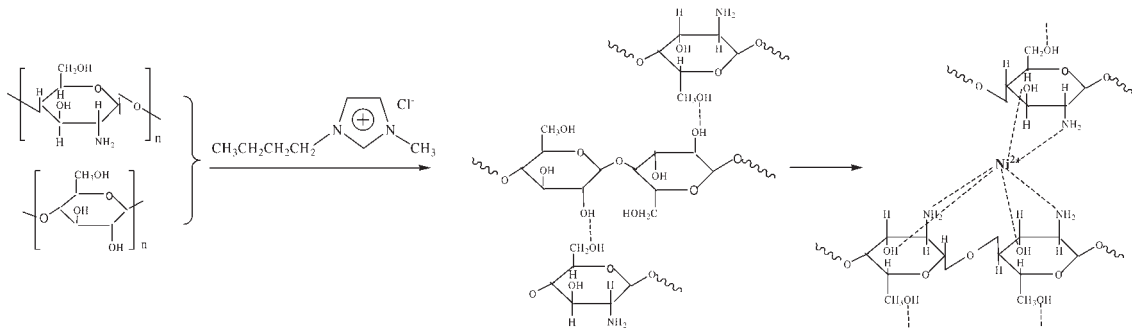
Freundlich isotherm suggested that sorption energy exponentially decreased on the completion of sorptional centers of an adsorbent and described heterogeneous systems.[37]

$$q_e = K_f C_e^{1/n} \tag{5}$$

Where C_e was the equilibrium metal ion concentration in solution (mmol L^{-1}), q_e was the amount of metal ion adsorbed at specified equilibrium (mmol g^{-1}). K_f and $1/n$ were the Freundlich constants characteristics of the system, indicating the adsorption capacity and adsorption intensity, respectively. A linear form of the Freundlich model could be obtained by taking logarithms of Eq. 6.

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{6}$$

As can be seen in Figure 6, the Freundlich model fitted well in C_e range of the biosorbents. Because the correlation coefficient of freeze-dried biosorbent (R^2 = 0.991) was



Scheme 1. Schematic diagrams of freeze-dried chitosan/cellulose biosorbent and its adsorption for Ni(II).

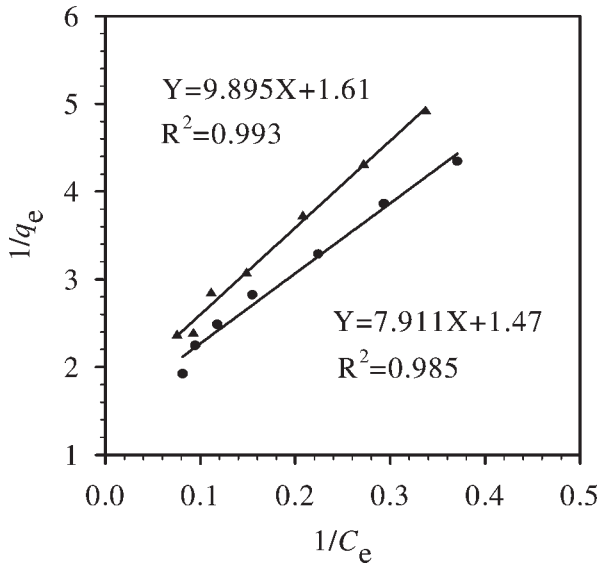


Figure 5. Langmuir adsorption isotherms of dried (▲) and freeze-dried (●) biosorbents.

higher than that of dried biosorbent (R^2 = 0.985), the Freundlich equation was more applicable to describe the sorption data of the freeze-dried biosorbents.

Desorption characteristics

Desorption character was an important factor for evaluating potential application value of the biosorbent. As mentioned earlier, adsorption capacity of the freeze-dried chitosan/cellulose biosorbent was strongly affected by acidity, which offered a possibility for desorption. Thus, desorption of Ni(II) was carried out by HCl at 25°C. To optimize concentration of HCl required for quantitative stripping of the loaded Ni(II), serial experiments were carried out with varying HCl solution concentration from 0.01 to 0.1 mol L^{-1}. As shown in Figure 7, the uploaded Ni(II) could also be effectively desorbed by EDTA, which could be attributed to the higher complexation ability of EDTA with Ni(II) than that of the biosorbent.

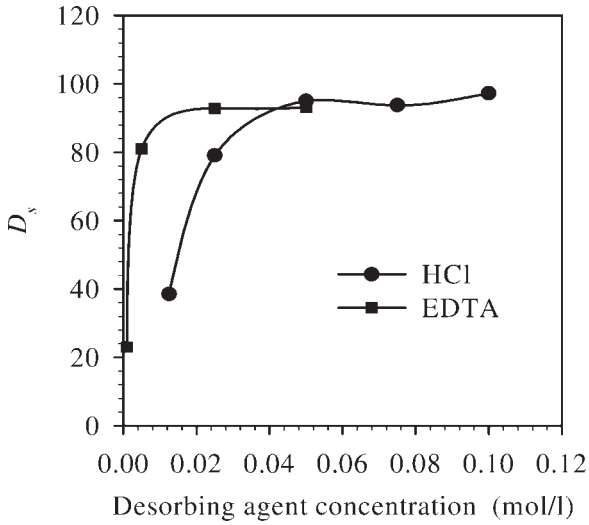


Figure 7. Desorption of Ni(II) by HCl and EDTA.

Competitive adsorption behavior of the heavy metal ions

To confirm validity of the freeze-dried chitosan/cellulose biosorbent to heavy metal ions, the dependence of q value of Pb(II), Zn(II), Ni(II), Cr(VI), and Cu(II) on the adsorption time was studied. As Figure 8 revealed, the Cr(VI) ions were more rapidly adsorbed on the biosorbent for 4 h, and equilibrium times of other metal ions approximately amount to 10 h. In addition, adsorption capacities of biosorbent to the adsorbates were also different, quantitatively, more Cu(II) (0.417 mmol/g) ions were adsorbed than Zn(II) (0.303 mmol/g), than Cr(VI) (0.251 mmol/g), than Ni(II) (0.225 mmol/g), and finally Pb(II) ions (0.127 mmol/g). Although chitosan content and adsorption condition were

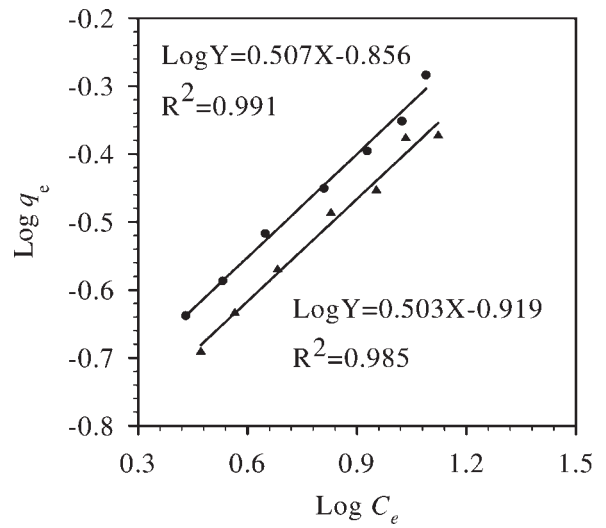


Figure 6. Freundlich adsorption isotherms of dried (▲) and freeze-dried (●) biosorbents.

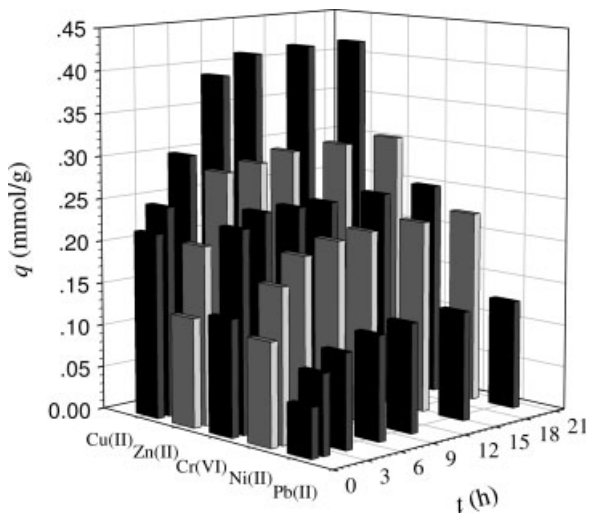


Figure 8. The dependence of q on adsorption time. Cu(II) = Zn(II) = Cr(VI) = Ni(II) = Pb(II)= 0.5 mmol/L.

Table 1. Adsorption Abilities of Some Chitosan-Type Biosorbents

Preparation Method	The Amount of Adsorption (mmol/g)					Adsorption Condition*	Ref.
	Cu(II)	Zn(II)	Cr(VI)	Ni(II)	Pb(II)		
Blended with chitin in NaOH/thiourea with H_2SO_4 as coagulant	0.26				0.27	280 mg/L (Pb); 160 mg/L (Cu); pH = 5.0; 4.5 h	9
Crossed by dibenzo-16-*c*-5 acetate crown ether	0.37			0.01	0.14	0.5 mmol/L; pH = 5.6; 12 h	38
Crossed by 3,5-di-*tert*-butyldibenzo-14-*c*-4 diacetate crown ether	0.49			0.07	0.29		
Treated with 40% NaOH/$NaHB_4$				1.02	0.14	100 mg/L; pH = 4.5; 23 h	39
Crossed by glutaraldehyde	0.56	0.45		0.49	0.17	50 mg/L; pH = 5; 4 h	40
Blended with cellulose by [Bmim][Cl]	0.42	0.3	0.25	0.22	0.13	0.5 mmol/L; pH = 5.8; 10 h	The current study

*Adsorption condition included initial concentration of metal ion, pH, and equilibrium time.

different, q_e and equilibrium time of the freeze-dried chitosan/cellulose biosorbent were similar to those of some other chitosan-type biosorbents as shown in Table 1.

Conclusions

The biosorbents prepared in this study have the following advantages for heavy metal ions adsorption. First, chitin(chitosan) and cellulose are the most abundant biopolymers in nature. Second, preparation of the biosorbents by IL were environment-friendly processes, the IL could be recovered and reused. Moreover, IL took part in temple effect for producing porous networks. Mechanical strength and stability of the biosorbents were indicated to be enough for adsorption. Third, because no cross-linking agent or nondegradable blending polymer was used, the blending chitosan(chitin)/cellulose biosorbents could be biodegradable without secondary pollution. Among the prepared biosorbents, freeze-dried chitosan/cellulose biosorbent was indicated to possess higher adsorption capacity together with better stability, and adsorption capacity of chitosan in the blending biosorbent could be fully shown. Interaction of the two components and the resulting material's adsorption capacity to Ni(II) were confirmed by IR and XPS. The results of applying it for Cr(VI), Cu(II), Zn(II), Ni(II), Pb(II) adsorption proved well validity of the biosorbent for adsorbing heavy metal ions. Although q_e and equilibrium time of the freeze-dried chitosan/cellulose biosorbent were similar to those of the reported chitosan-type biosorbents, preparation and component of the biosorbent were obviously more environment friendly. Its desorption characteristic revealed the potential application value of the biosorbent.

Acknowledgments

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