

Adsorption behaviors of the aminated chitosan adsorbent

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Abstract—Using inverse suspension technology, a novel aminated chitosan adsorbent with higher adsorption ability for metal cations and metal anions was prepared. Through cross-linking amination reaction, the content of amidocyano-gen of aminated chitosan adsorbent was enhanced four times than that of chitosan cross-linked adsorbent. As can be seen from the results, the adsorption ability of the novel aminated chitosan adsorbent for Ni^{2+} and Cr(VI) was enhanced remarkably. When the initial concentration of metallic ion was 1,000 mg/L, the adsorption capacity of the novel aminated chitosan adsorbent for nickel citrate and Cr(VI) was up to 30.2 mg/g and 28.7 mg/g, respectively. And the adsorption capacity of the novel aminated chitosan adsorbent for Ni^{2+} was still higher. So the new aminated chitosan adsorbent offers not only a higher uptake for metal cations but also a better adsorption capacity for metal anions.

Key words: Heavy Metallic Anion, Adsorption, Chitosan, Cross-linking, Aminated

INTRODUCTION

With economic and technological development, environmental pollution is a common problem worldwide. Environmental pollution has become more and more serious, especially regarding heavy metal ions. Heavy metals, mainly from industrial activities such as plating, metallurgy, and dyeing industries, are a serious threat to human beings and the environment, due to their toxicity and persistence after being released into the natural environment. The amount of heavy metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Se, V, and Zn) produced from metal industries, agricultural activities, and waste disposal has increased dramatically. Many conventional adsorbents are used for removal of toxic metals, such as activated carbon [1], cellulose [2,3] and zeolite [4]. With the development of technology, many novel methods are used for adsorption, such as removal of phenolic compounds by electro-assisted process [5], absorption of NO_2 with chemical reaction in a falling raindrop [6], absorption of CO_2 into w/o emulsion with aqueous alkaline liquid droplets [7]. As a fungible method for traditional treatment technology, biosorption technology has been extensively applied in the removal of heavy metal ions from wastewater. Many researches on the biosorption for heavy metal ions have been carried out. Many new kinds of bioadsorbent [8,9] have been developed such as mycelium adsorbent [10], surface molecular imprinting adsorbent [11-14], surface coated mycelium adsorbent [15], chitosan adsorbent [16], imprinting chitosan adsorbent [17,18] and so on.

Most of the adsorbents have higher adsorption capacity for heavy metal cations, but less for metal anions [19]. Except for the form of metal cations, many heavy metals exist as a form of anions such as nickel citrate, Cr(VI) . The toxicity of Cr(VI) is 100 times higher than that of Cr(III) . So it is necessary to study bioadsorption for heavy metal anions.

Chitosan has many $-\text{NH}_2$ and $-\text{OH}$ groups that can chelate heavy metal ions, providing higher adsorption capacity and better selectivity [20]. The alkalinescence of chitosan, which has close relation to the adsorption capacity, will be reduced after reaction with cross-linking agents. The alkalinescence can be improved through chemical modification of chitosan to increase the adsorption capacity for heavy metal ions. Many researches have been carried out on the preparation of chitosan derivatives of anions, such as carboxymethylated derivations, but few on that of chitosan amino derivatives [21]. And many studies are about the adsorption behaviors of adsorbent for anionic dye. Zongyao Pu et al. [22] found that the adsorption ability of cellulose fiber for heavy metal ions was improved after being treated through carbamate reaction and the removal ratio could reach 90%. As for the adsorption behaviors of adsorbent for metal anion, there are few studies.

On the basis of former researches, the hydroxylpropyl group and amino group were introduced into the structure of chitosan in this paper. A new aminated chitosan adsorbent with higher adsorption ability for metal cations and metal anions was prepared. The content of amino groups in the structure and alkalinescence of chitosan were obviously improved.

The adsorption behaviors of the mycelium adsorbent, chitosan adsorbent, the mycelium surface imprinting adsorbent and aminated chitosan adsorbent for nickel citrate and Cr(VI) were investigated and compared. The effects of heavy metal concentration and citrate acid concentration on the adsorption behavior were studied.

MATERIALS AND METHODS

1. Materials

Chitosan was obtained from shrimp shells with 90% degree of deacetylation and provided by our lab. Epichlorohydrine, dimethylsulfoxide, glutaraldehyde, fluid-wax, 1,6-Hexanediamine, acetic acid, petroleum ether, acetone, $\text{NiSO}_4 \cdot \text{H}_2\text{O}$, K_2CrO_4 and triammonium citrate were of analytical grade and obtained from the Chemical Reagent Company of Beijing. Tween-20 was of analytical grade and obtained from Hong Kong.

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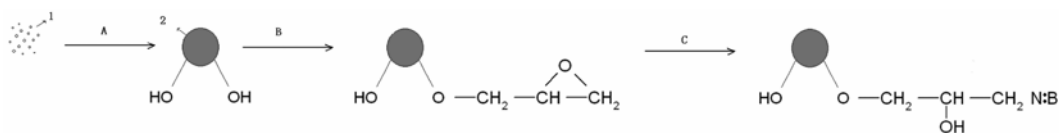


Fig. 1. A sketch of the preparation process of the aminated chitosan adsorbent.

1. Chitosan power, 2. Chitosan sphere, A. Cross-linked reaction, B. Activated reaction, C. Aminated reaction

2. Analysis of Metal Ions

The metal ion Ni^{2+} and Cr^{6+} were analyzed with adsorption spectrophotometer according to the method presented in Ref. [23,24], respectively.

3. Preparation of the Adsorbent

3-1. Preparation of the Chitosan Cross-linked Adsorbent [25]

Chitosan (dry weight) was dissolved in acetic acid solution (2% (v/v)) to give a chitosan solution of 2% (v/v). Then Tween-20 and fluid-wax were added into this solution, and the mixture was stirred at room temperature. The glutaraldehyde solution (18.75% (v/v)) was added into the above mixture and reacted for 1 h at 40 °C. Finally, the product was washed in turn by petroleum ether, acetone and water. The chitosan cross-linked adsorbent was filtered by using filter paper and dried at 60 °C (see Fig. 1A).

3-2. Preparation of the Activated Chitosan Adsorbent

NaOH (0.4 mol/L), DMSO and H_2O were added into the swelling chitosan cross-linked adsorbent, and the mixture was stirred. Epichlorohydrin was slowly added into the mixture and allowed to carry out for 1 h at 40 °C. Then the product was washed by acetone and water until the pH=7.0, and dried at 60 °C (see Fig. 1B).

3-3. Preparation of the Aminated Chitosan Adsorbent.

H_2O and 1,6-hexanediamine were added into the activated chitosan adsorbent. Then the mixture was stirred at 60 °C and allowed to react for 2 h. After the temperature fell to room temperature, the product was washed by water until the pH=7.0, and dried (see Fig. 1C).

4. Mensuration of the Concentration of Amidocyanogen on the Aminated Chitosan Adsorbent

0.1 g adsorbent was added into 20.0 cm^3 HCl solution of 0.05 mol/L. And the mixture was stirred for 1 h, 15.0 ml supernatant was titrated through 0.05 mol/L NaOH; using phenolphthalein as indicator the concentration of amidocyanogen can be calculated according to the following equation:

$$C_{\text{NH}_2} = (N_1 V_1 - N_2 V_2 \times 20/15) / W \quad (1)$$

Where, C_{NH_2} is the concentration of amidocyanogen, N_1 is the concentration of HCl solution; V_1 is the volume of HCl solution; N_2 is the concentration of NaOH solution; V_2 is the volume of NaOH solution; W is the weight of the adsorbent.

5. Adsorption of Metal Ions

0.15 g bioadsorbent, such as mycelium, chitosan, mycelium surface molecular imprinted adsorbent and aminated chitosan adsorbent, was added into 50.0 cm^3 nickel citrate solution or 50.0 cm^3 Cr^{6+} solution (the concentrations of metal ions were 50 mg/L, 100 mg/L, 150 mg/L, 200 mg/L, 500 mg/L, 1,000 mg/L). Then the mixture was stirred for 12 h at room temperature. Finally, the concentration of metal ion in solution was mensurated.

RESULTS AND DISCUSSION

Table 1. The concentration of amidocyanogen of the aminated mycelium surface modified adsorbent

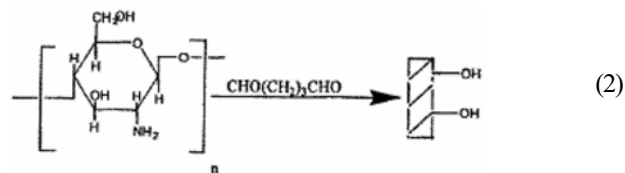
	Chitosan cross-linked adsorbent	Activated adsorbent	Aminated adsorbent
The concentration of amidocyanogen mmol/g	0.6	0.3	2.5

1. Mensuration of the Concentration of Amidocyanogen

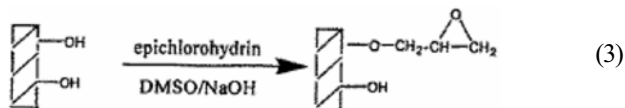
The amine contents of chitosan cross-linked adsorbent, activated chitosan adsorbent and amine-modified chitosan adsorbent were determined by acid-base titrimetric analysis, respectively, and the results are shown in Table 1. As can be seen from the results, the amine content of chitosan cross-linked adsorbent was lower. The reason is that amine groups were not influenced through the cross reaction between chitosan and glutaraldehyde, which can be seen from Eq. (2). As can be seen from Table 1, the amine content was only half of that active reaction. However, it can be seen that amine groups were not influenced by activation reaction from Eq. (3). The reason is probably that the decrease of the alkalinescence of the adsorbent results in a decrease of amine content. As can be seen from Eq. (4), amine groups were introduced into chitosan through amine reaction, so the amine content of amine-modified chitosan adsorbent was the highest, which was four times higher than that of chitosan, resulting in the improvement of alkalinescence of amine-modified chitosan.

The equations of the reaction are as follows [25]:

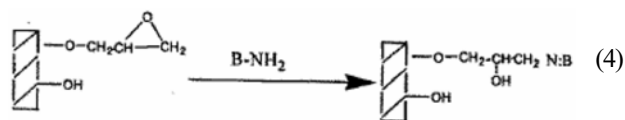
(1) Glomeration reaction:



(2) Activation reaction:



(3) Amination reaction:



Major changes of the absorption peak can be found at 3,500-3,100 cm^{-1} and 1,350-1,000 cm^{-1} . Characteristic absorption peaks of amine

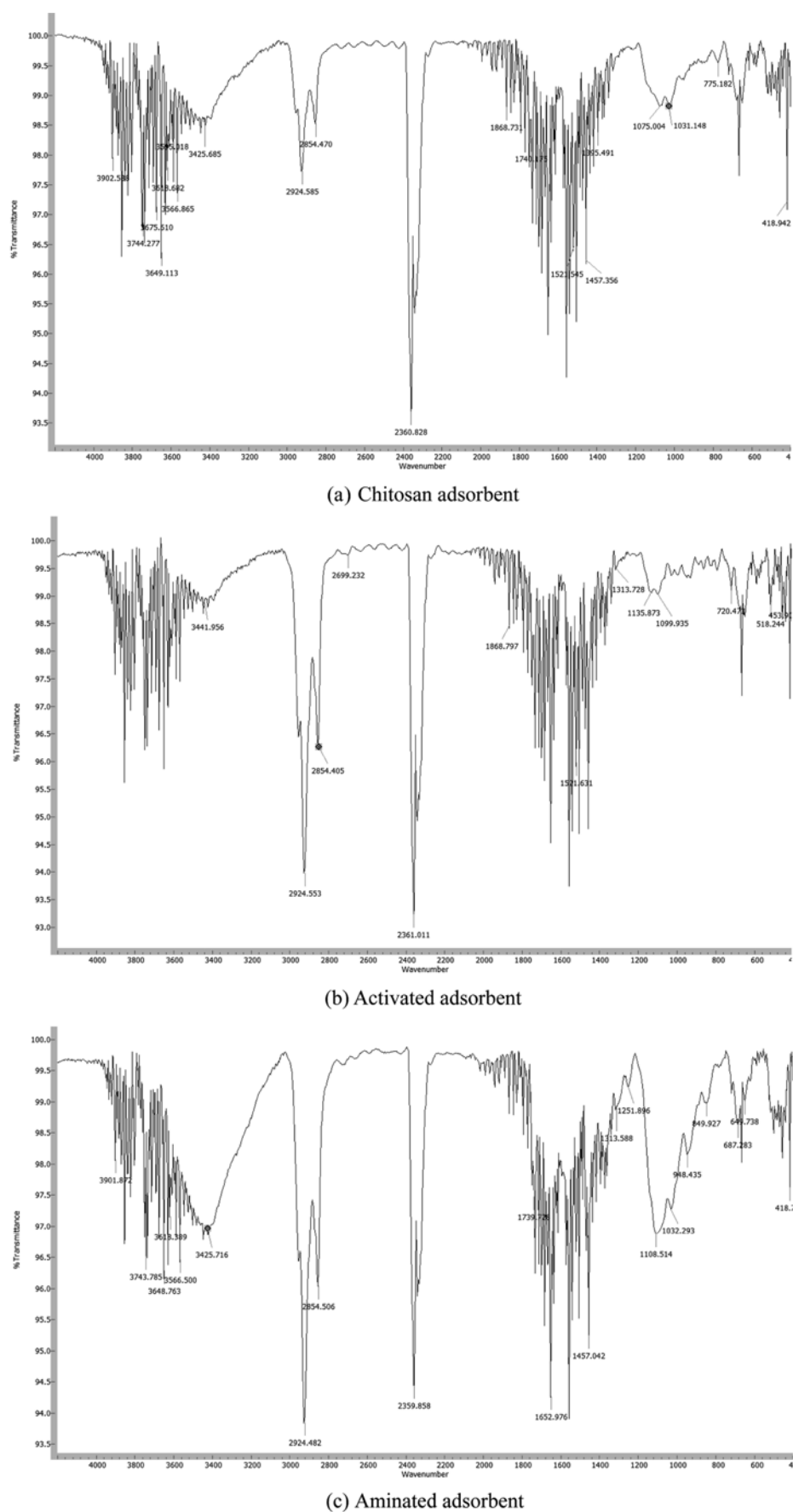


Fig. 2. FTIR spectra of the adsorbents.

are as follows: stretching vibrational absorption of N-H bond is at $3,500\text{--}3,100\text{ cm}^{-1}$, and that of C-N bond is $1,350\text{--}1,000\text{ cm}^{-1}$. As can be seen from Fig. 2(c), strong absorption peaks are observed at $3,500\text{--}3,100\text{ cm}^{-1}$ and $1,350\text{--}1,000\text{ cm}^{-1}$, indicating that the amine content of aminated chitosan adsorbent is enhanced.

2. Effect of Metal Ion Concentration on Adsorption Behavior

The adsorption capacities of mycelium, chitosan, mycelium surface molecular imprinted adsorbent for Cr^{6+} nearly equal zero, and those for nickel citrate were also comparatively low. But with the increase of metal ion concentration in solution, the adsorption capacity of aminated chitosan adsorbent was obviously enhanced. At a metal ion concentration in solution of 50 mg/L , the adsorption capacity of aminated chitosan adsorbent for nickel citrate was 9.2 mg/g , and that for Cr^{6+} was 9.1 mg/g . When metal ion concentration was more than 150 mg/L , the rate of increase become lower. The adsorption capacity of the novel aminated chitosan adsorbent for nickel citrate was up to 30.2 mg/g , and that for Cr^{6+} was up to 28.7 mg/g , when metal ion concentration was up to $1,000\text{ mg/L}$.

3. Effect of the Concentration of the Citric Acid on the Adsorption Behavior

When the concentration of the citric acid was 0% , the adsorption capacity of mycelium surface molecular imprinted adsorbent was highest (37.23 mg/g). This was similar to the inference [10]. The adsorption capacity of aminated chitosan adsorbent was up to 30.24 mg/g , and was a little lower than that of mycelium surface molecular imprinted adsorbent. But when the concentration of the

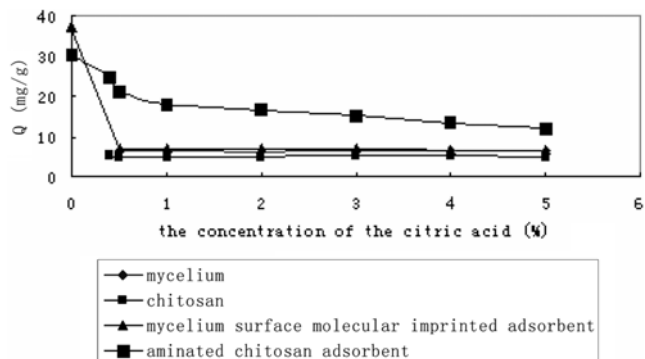


Fig. 4. The influence of the concentration of the citric acid for the adsorption behaviors.

The initial concentration of Ni^{2+} is 200 mg/L .

citric acid was higher than zero, nickel citrate was formed, and the adsorption capacity of mycelium surface molecular imprinted adsorbent decreased rapidly. The adsorption capacity of aminated chitosan adsorbent was three or four times higher than that of mycelium, chitosan and mycelium surface molecular imprinted adsorbent, at a concentration of citric acid of 0.5% (see Fig. 4).

With the increase of the concentration of the citric acid, pH value in the solution decreased gradually; as a result, the competitive adsorption of H^+ caused the adsorption ability of adsorbent for nickel citrate to fall. From Fig. 4, when the concentration of the citric acid was higher than $0.5\% \text{ w/w}$, the adsorption capacity of the aminated chitosan adsorbent also decreased. Therefore, a higher adsorption capacity can be acquired when the concentration of the citric acid is lower than 1% . However, as can be seen from Fig. 4, the aminated chitosan adsorbent will provide higher adsorption capability for both the metal cations and metal anions.

4. Comparison of Different Adsorbents for Metal Ion on Adsorption Behavior

The adsorption behavior of the adsorbents for nickel citrate and Cr^{6+} was compared (see Fig. 5). Chitosan cross-linked adsorbent was made from chitosan by cross-linked reaction.

As shown in Fig. 5(a), the adsorption capacities of the chitosan and mycelium surface molecular imprinted adsorbent for nickel citrate were obviously lower, and only had 5.64 mg/g and 6.89 mg/g , respectively. But the adsorption capacity of the mycelium increased twice or three-folds up to 15.3 mg/g than that of the chitosan and mycelium surface molecular imprinted adsorbent. The reason may be that the functional groups on the chitosan and the mycelium surface molecular imprinted adsorbent are $-\text{NH}_2$ and $-\text{OH}$, which showed lower adsorption ability for $(\text{Nicit})^-$, but the physical adsorption of the mycelium adsorbent makes a contribution to the adsorption of $(\text{Nicit})^-$. Since amidocyanogen was introduced into aminated adsorbent, the concentration of amidocyanogen of aminated adsorbent increased, the adsorption capacity of aminated adsorbent was up to 24.51 mg/g , and is four times than that of chitosan.

The adsorption behaviors of the adsorbents for nickel citrate were compared with the commercial resins (chelated resin D-751, weakly acidic cation exchange D-152, weakly basic anion resin 201×7 , anion resin aberlate IRA-400). The adsorption capacity of aminated adsorbent was closed to that of weakly basic anion resin 201×7 .

As shown in Fig. 5(b), the adsorption capacities of mycelium,

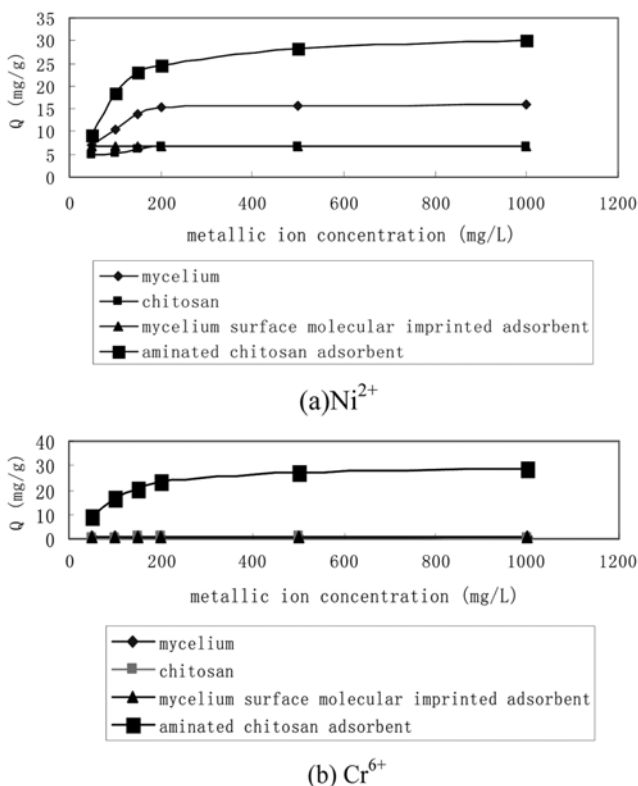
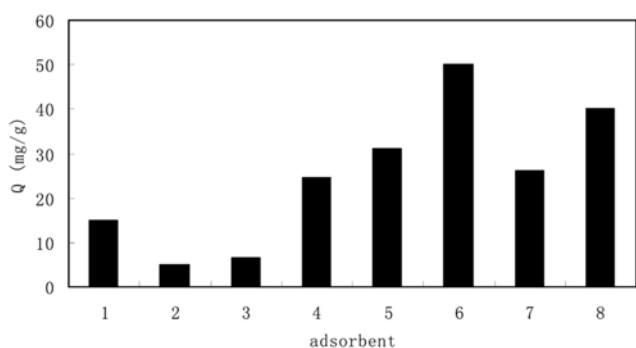


Fig. 3. The influence of the concentration of the metal ion for adsorption behavior.

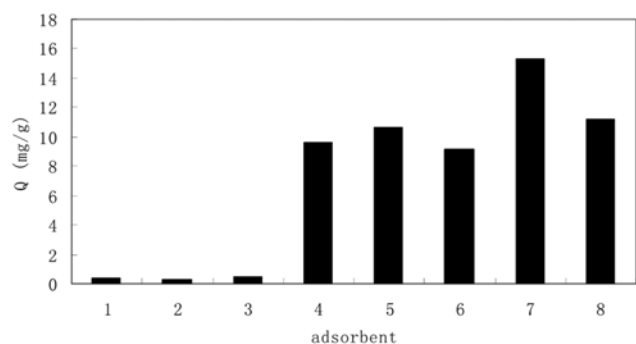
The concentration of the citric acid of (a) is $0.4\% \text{ (w/w)}$.



(a) the adsorption behavior for nickel citrate

The concentration of the citric acid is 0.4% (w/w), the initial concentration of Ni^{2+} is 200mg/L

1: mycelium; 2: chitosan; 3: mycelium surface molecular imprinted adsorbent;
4: aminated adsorbent; 5: chelated resin D-751; 6: weakly acidic cation exchange D-152;
7: weakly basic anion resin 201×7; 8: anion resin aberlate IRA-400

(b) the adsorption behavior for Cr^{6+}

The initial concentration of Cr^{6+} is 50mg/L

1: mycelium; 2: chitosan; 3: mycelium surface molecular imprinted adsorbent;
4: chitosan cross-linked adsorbent; 5: activated adsorbent;
6: aminated adsorbent; 7: D392; 8: D315

Fig. 5. The adsorption behavior of different adsorbents for metallic ion.

chitosan and mycelium surface molecular imprinted adsorbent for Cr^{6+} nearly equal zero. The adsorption capacity of activated adsorbent is up to 10.6 mg/g at the initial Cr^{6+} concentration of 50 mg/L, and is the highest. The adsorption capacity of aminated adsorbent is up to 9.1 mg/g. As can be seen from Fig. 5(b), the adsorption capacities of chitosan cross-linked adsorbent for Cr^{6+} is much higher than chitosan, but amine groups are not influenced during cross-linked reaction. Therefore, the adsorbent mechanism for Cr^{6+} is different from that for $(\text{Nici})^+$. The contributing group is probably not only $-\text{NH}_2$, but also other groups, such as $-\text{OH}$. The reason is that hydroxy groups are introduced into chitosan through amine reaction. Further studies are needed.

The adsorption behavior of the adsorbents for Cr^{6+} was compared with the commercial resins (D392, D315). The adsorption capacity of aminated adsorbent was close to that of resin D315.

CONCLUSION

Using inverse suspension technology, we prepared a novel aminated chitosan adsorbent from chitosan flake. Through cross-linking amination reaction, the content of amidocyanogen of aminated chitosan adsorbent was up to 2.5 mmol/g, and was enhanced four

times more than chitosan cross-linked adsorbent. This new aminated chitosan adsorbent offers not only a higher uptake for metal cations but also a better adsorption capacity for anions. The results showed that the adsorption capacity of the novel aminated chitosan adsorbent for nickel citrate was up to 30.2 mg/g and was enhanced five times that of chitosan cross-linked adsorbent (at the concentration of the citric acid of 0.4% (w/w) and the initial Ni^{2+} concentration of 1,000 mg/L). At the same time, the uptake of the novel aminated chitosan adsorbent for Ni^{2+} was up to 30.24 mg/g (at the initial Ni^{2+} concentration of 1,000 mg/L and no citric acid). When the initial concentration of Cr^{6+} was 1,000 mg/L, the adsorption capacity of novel aminated chitosan adsorbent for Cr^{6+} was up to 28.7 mg/g and was enhanced thirty times more than mycelium, chitosan and the mycelium surface molecular imprinted adsorbent. The reason for that is probably that the adsorbent mechanisms for metal anions (such as Cr^{6+} or nickel citrate) are different from those for metal cations (for example Ni^{2+}), so these need to be further studied.

In this paper, the adsorption capacities of novel aminated chitosan adsorbent for nickel citrate and Cr^{6+} were close to some commercial resins. Since novel aminated chitosan adsorbent is made from chitosan, of which cost is low, the novel adsorbent is cost-effective.

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