Chinese J. Chem. Eng., **10** (6) 650－652 (2002)

Adsorption of Heavy Metal Ions by Adsorbent from Waste Mycelium Chitin*

SU Haijia(苏海佳)[a], WANG Lijuan(王丽娟)[b] and TAN Tianwei(谭天伟)[a,]**

[a]Department of Biochemical Engineering，Beijing University of Chemical Technology, Beijing 100029, China

[b]Science & Technology Development Department, SINOPEC, Beijing 100029, China

Abstract The adsorption properties of chitin adsorbent from mycelium of fermentation industries for the removal of heavy metal ions were studied. The result shows that the chitin adsorbent has high adsorption capacity for many heavy metal ions and Ni^{2+} in citric acid. The influence of pH was significant：When pH is higher than 4.0, the high adsorption capacity is obtained，otherwise H^+ ion inhibits the adsorption of heavy metal ions. The comparison of the chitin adsorbent with some other commercial adsorbents was made, in which that the adsorption behavior of chitin adsorbent is close to that of commercial cation exchange adsorbents, and its cost is much lower than those commercial adsorbents.

Keywords mycelium chitin, adsorbents, heavy metal ions

1 INTRODUCTION

Chitosan contains large amount of amino (N_2H—) or hydroxyl (—OH) which can adsorb many heavy metal ions such as Ni^{2+}, Zn^{2+} and Cu^{2+}, which often cause serious toxicity to human and other forms of life. Chitosan is natural polymer, and doesn't cause additional pollution to envir-onment[1,2]. Now chitosan comes from the deaceylation of chitin, which is a major component of arthropod and crust-acean shells, such as lobsters, shrimps or crabs. So its preparation is limited by season and the process is very complex, which results in its high cost. This has motivated many workers to search for cheaper substitutes. Puranik and Paknikar reported that *Streptoverticillium cinnamoneum* could be used to adsorb lead and zinc ions[3]. Fourest and Roux studied that fungal mycelium adsorbed heavy metal ions[4]. Since chitin is the second abundant biopolymer in the nature next to cellulose, widely distributed in mycelium biomass cell walls of fermentation industries, its simple prepa-ration, and effectiveness in the uptake of heavy metal ions, chitin appears more attractive. In this paper, the adsorption capacity of heavy metal ions by mycelium chitin from *Penicillin chrysoganum* was studied. The parameters such as pH, metal ion concentration and the citric acid concentration were discussed. On the basis of adsorption capacity and its cost, chitin adsorbent was found to be effective compared with chitosan and some commercial adsorbents.

2 MATERIALS AND METHODS

2.1 Chemicals

$NiSO_4 \cdot 6H_2O$ and Ni^{2+} in citric acid, $ZnSO_4$, $CuSO_4$ and $Cr_2(SO_4)_3 \cdot 3H_2O$ are analytic grade, Strongly acidic cation exchange 001×7, weakly acidic cation exchange D152 were supplied by the Chemical Plant of Nankai Univeisity, D-751 chelated resin and anion resin Amberlite IRA-400(A-400) and weakly basic anion resin 201×7 were supplied by Rohm and Hass Shanghai Chemical Industry Co., Ltd. Chitosan powder from shrimp shells was prepared in our laboratory with 90% degree of deacetylation.

2.2 Mycelium chitin adsorbent pretreatment

In this work, chitin adsorbent from waste biomass of *Penicillin chrysoganum* in fermentation industries was offered by Dongchen Biochemical Engineering Company of Dongying City , Shandong Province. The pretreatment of mycelium chitin is as follows: Chitin adsorbent was washed with enough deionized water to pH 7.0, then was dried in 60°C and blended. Finally the dry adsorbent was sized by a 300-mesh sieve for further use.

2.3 Adsorption experiment

50 ml of heavy metal ion solution (metal ion concentra-tion 50—1000 $mg \cdot L^{-1}$) was added into a 150 ml flask. The initial pH was regulated to pH 4.0—5.0 by 1 $mol \cdot L^{-1}$ NaOH or 1 $mol \cdot L^{-1}$ HCl. 0.15 g of dry adsorbent was added and the suspension was stirred at 40℃ and 150 $r \cdot min^{-1}$ for 24 h. The uptake (Q) of the metal ion can be calculated by

$$Q=(c_0-c_e)V/W \quad (mg \cdot g^{-1})$$

where c_0, c_e are the initial and equilibrium concentrations of metal ion in solution ($mg\ L^{-1}$); W is the mass of the adsorbent (dry, g); and V is the volume of solution(L).

2.4 Metal ion analyses

The metal ion Cu^{2+} was analyzed with absorption spectrophotometer according to Ref.[5]. Ni^{2+} and Zn^{2+} were determined by Ref.[6]. Cr^{3+} was assayed by colorimetry[7].

3 RESULTS AND DISCUSSION

3.1 Adsorption heavy metal ions by mycelium chitin adsorbent

3.1.1 *Influence of initial pH*

The pH is an important parameter for adsorbing heavy

Received 2002-05-10, accepted 2002-09-23.

* Supported by National Natural Science Foundation of China(No. 29976004 and 20136020) and Fok Ying-tung Education Foundation(No. 71067).

** To whom correspondence should be addressed.

metal ions. Under the acidic condition, high H^+ concentr-ation can decrease the adsorption of metal ions because high H^+ concentration inhibits the adsorption of heavy metal ions through binding functional groups of biomass chitin adsorbent. But when pH is higher than 7.0, some metal ions will precipitate. Fig.1 shows that, with increasing pH, the adsorption capacity gradually increases to the maximum (except Ni^{2+}). And the initial optimal range of pH for sorption of metal ions are as follows: Cu^{2+} 4.5 to 5.5; Ni^{2+} 5.0 to 6.0; Zn^{2+} 4.0 to 6.0; Cr^{3+} 5.0 to 6.0. The initial pH in subsequent experiment is the optimal value (except in Figs.1and 2).

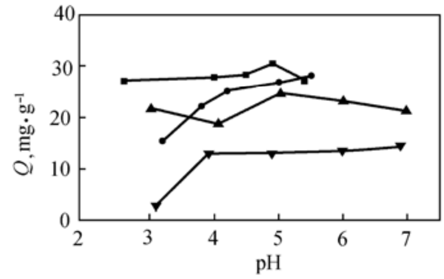


Figure 1 The effect of pH to metal ion

(The initial metal ion concentration in the solution is 200 mg·L^{-1})

■ Cu^{2+}; ● Cr^{3+}; ▲ Ni^{2+}; ▼ Zn^{2+}

3.1.2 *Comparison of chitin with chitosan adsorbent*

The comparison of adsorption properties of chitin with chitosan resins is shown in Fig.2. When pH is lower than 4.0, chitosan resins will be dissolved by acid solution, which causes the low adsorption capacity of chitosan. When pH is higher than 4.0, the chitosan has higher adsorption capacity than that of chitin adsorbent. But the chitin adsorbent has high stability in acidic solution and its cost is relatively low. So the mycelium chitin is still considered to be an effective adsorbent for treatment of wastewater.

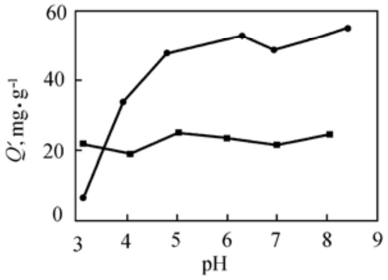


Figure 2 The effect of pH to Ni^{2+}

(The initial metal ion concentration in the solution is 200 mg·L^{-1})

■ mycelium chitin; ● mycelium chitosan

3.1.3 *Effect of initial metal ion concentration*

The dilute solution of heavy metal ions often need the tertiary treatment, so the adsorption properties of heavy metal ions in dilute solution should be studied. The relati-onship of adsorption capacity with the initial concentr-ation of metal ion in solution is shown in Fig.3. The result shows that when the initial concentration of metal ion is high, the adsorption capacity for different adsorbents will be improved, and when the initial concentration of metal ion is lower than 400 mg·L^{-1}, the adsorption capacity will increase quickly; but at high concentration (> 400 mg·L^{-1}), the adsorption capacity gradually rises to a fixed value.

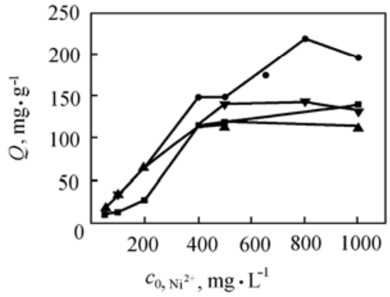


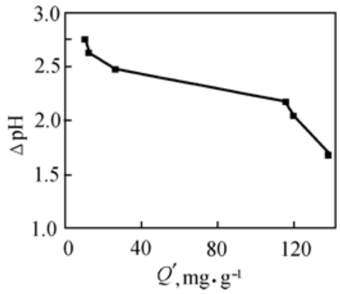
Figure 3 The comparison of some adsorption resins

(The initial pH is 5.0)

■ mycelium chitin; ● D152; ▲ 001×7; ▼D751

3.1.4 *Relationship of adsorption capacity with the change of pH (ΔpH)*

The relationship of adsorption capacity with ΔpH can be seen from Figs.4 and 5, where ΔpH is the change of pH in the initial and final solution. The higher the adsorption capacity of chitin, the lower the change of pH. The reason is that when Ni^{2+} ion concentration becomes higher, a large amount of functional groups (—NH_2) will combine with Ni^{2+} ions, the adsorption of H^+ ion will be inhibited (see Figs.4 and 5).



Figue 4 Adsorption capacity and changement of pH on chitin

(The initial pH is 5.0)

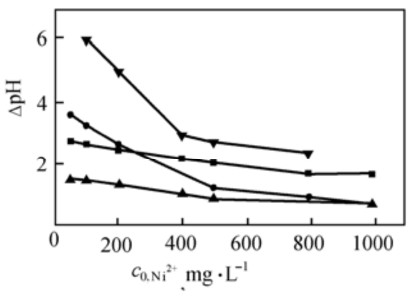


Figure 5 The change of pH on the different adsorbents

■ chitin; ● D152; ▲ 001×7; ▼ D751

3.2 Effect of competing parameter

3.2.1 *Effect of citric acid concentration*

During the production of terblock polymer styrene-ethylene/butylenes-styrene (SEBS), the citric acid was used to extract Ni^{2+} and Al^{3+} to separate catalyst. Ni^{2+} and Al^{3+} are founded very difficult to separate due to citric acid chelation.

It can be seen from Fig.6, with the increasing of citric acid concentration, the adsorption capacity of chitin resin and cation exchanger D152 rapidly drops to zero; but the adsorption capacity of chelated resin D-751 slowly falls to a stabilized level. On the contrary, the adsorption capacity of anion resin 201×7 is the worst without citric acid. In the 0.5% citric acid solution, the adsorption capacity of anion resin 201×7 is rapidly enhanced from 2.0 mg· g^{-1} to 27.8 mg· g^{-1}, and then slowly decreases with the increasing of concentration of the citric acid. At the same time, the effect of citric acid concentration for anion resin becomes weaker than that of chitin resin and cation exchanger D152, the reason is that they have different ion exchange mechanism. Therefore, we can conclude that the adsorpt-ion behavior of chitin adsorbent is similar to that of cation exchange resin.

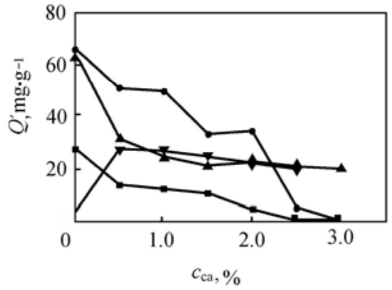


Figure 6 The effect of citric acid on Q
■ mycelium chitin; ● D152; ▲ D751; ▼ 201×7

3.2.2 *Effect of Ni^{2+} ion concentration in citric acid solution*

The system is in the citric acid solution in which the concentration of citric acid is 0.5% (by mass). The adsorpt-ion capacity of chitin will be promoted by a higher con-centration of Ni^{2+}, which can be seen from Fig.7, but its im-provement of the adsorption capacity is lower than that without citric acid. When the concentration of Ni^{2+} is lower, the influ-ence of citric acid seems not so considerable.

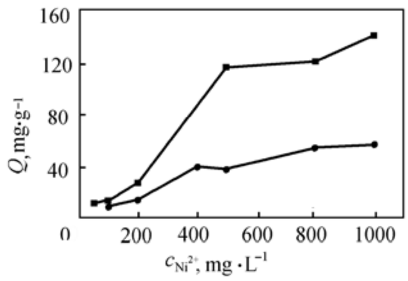


Figure 7 The effect of the citric acid on Q for chitin
■ without citric acid; ● citric acid(0.5%)

We can find from Fig.8 that the changing tendency of ΔpH is contrary to the system without citric acid. Therefore, H^+ ion was easier adsorbed than that without citric acid. The main reason is that the citric acid is a weak acid, the more Ni^{2+} in citric acid was formed, the more dissociated H^+ ion was obtained, which strongly inhibits the adsorption of metal ions.

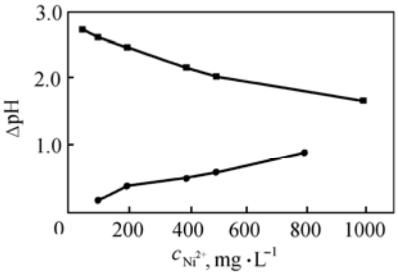


Figure 8 The effect of the citric acid on ΔpH for chitin adsorption
■ without citric acid; ● citric acid(0.5%)

4 CONCLUSIONS

The waste biomass of penicillin industry has high adsorption capacity for many heavy metal ions and Ni^{2+} in citric acid. So chitin adsorbent has great potential in wastewater treatment due to its low cost as compared with commercial adsorbents.

pH is a very important parameter which influences adsorption of heavy metal ions, and H^+ ion inhibits the adsorption of heavy metal ions when pH>4.0. The adsorption behavior of chitin adsorbent is similar to that of commercial anion resins.

NOMENCLATURE

c_{ca}	citric acid concentrations (by mass), %
$c_{e,M}$	equilibrium concentrations of metal ion M in solution, mg· L^{-1}
c_{0M}	initial concentrations of metal ion M in solution, mg· L^{-1}
$c_{Ni^{2+}}$	concentration of metal ion Ni^{2+} in solution, mg· L^{-1}
$c_{0,Ni^{2+}}$	initial concentrations of metal ion Ni^{2+} in solution, mg· g^{-1}
Q	uptake or adsorption capacity of the metal ion, mg· g^{-1}
Q'	adsorption capacity of Ni^{2+}, mg· L^{-1}
V	volume of solution, L
W	mass of the adsorbent(dry), g

REFERENCES

1 Chen, T., Wang, S.X., "Adsorption studies of Cr^{3+} by chitosan", *Ion Exchange and Adsorption,* **13**(5), 466—471 (1997). (in Chinese)

2 Findon, A., Mckay, G., "Transport studies for the sorption of copper ions by chitosan", *Environ. Sci. Health,* **28**(1), 173—185 (1993).

3 Puranik, P.R., Paknikar, K.M., "Bioseperation of lead and zinc from solutions using *Streptoverticillium cinnamoneum* waste biomass", *Biotechnol*., **55**(2), 113—124 (1997).

4 Fourest, E., Roux, J.C., "Heavy metal biosorption by fungal mycelium by-products: Mechanisms and influence of pH", *Appl. Microbiol. Bio-technol*, **37**, 399—403 (1992).

5 Ma, B.X., "Photometric analysis of Cu with SCO", *Chinese J. Analytical Chemistry*, **2** (2), 53—56 (1974). (in Chinese)

6 Luo, Z.M., Ceng, P. N., "Reaction between Zincon and Zn with Tween-80 existent and its applications", *Chinese. J. Phys. Chem. Measurement*, **25**(5), 274—276 (1989).

7 State Environmental Protectional Administration, Analysis of Water and Wastewater, China Environment and Science Press, Beijing, 156—161 (1989). (in Chinese)