

Preparation and Adsorption Properties for Metal Ions of Chitin Modified by L-Cysteine

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ABSTRACT: A new adsorbent for heavy metal ions, cys-chitin, was produced by modifying chitin in THF with L-cysteine in the presence of sulfuric acid as a catalyst. Its structure was confirmed by elemental analysis and FTIR spectra analysis. The adsorption properties of cys-chitin for Cu^{II}, Cd^{II}, Pb^{II}, Zn^{II}, and Ni^{II} were investigated. The effect of pH value on adsorption and adsorption kinetics was examined. The results indicate that the cys-chitin has much better adsorption for Cd^{II}, Pb^{II}, and Zn^{II} than chitin itself. The

adsorption capacities of cys-chitin for Cd^{II}, Pb^{II}, and Zn^{II} were 214.6, 351.5, and 107.0 mg/g, respectively. It also had good adsorption properties for heavy metal ions. The adsorption capacities were also affected by the acidity of medium. The adsorbed Cd^{II}, Pb^{II} could be eluted by diluted nitric acid. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2575–2579, 2003

Key words: adsorption; modification; polysaccharides

INTRODUCTION

Chitin is an amino polysaccharide, and its structure is similar to cellulose; chitosan is an important derivative of chitin, obtained by deacetylation. Marsri et al.¹ reported that chitin and chitosan might be good adsorbents for removing heavy metal ions from water, either for pollution control or for raw material recovery. Successive reports show that chitin has little adsorption capacity for heavy metal ions due to its deacetylated amino groups, and that although chitosan's adsorption capacity is great, it is soluble in acid solution, even in acescent solution. These properties strongly restrict any practical application of chitin and chitosan in the fields as ion exchangers and chelating agents. In recent years, so many efforts have been focused on modifying chitin to obtain novel adsorbents.^{2,3} Yang and Shao⁴ modified chitin by sulhydryl acetic acid to introduce sulhydryl groups into chitin.

The objective of this work was to prepare a new derivative from chitin: cys-chitin. The synthesis of cys-chitin was carried out by treating chitin in THF with L-cysteine in the presence of sulfuric acid as a catalyst. Thus, free amino groups and sulhydryl groups were introduced into chitin. The major advantages of this resulting derivative are its greater adsorption capacity than chitin, and its insolubility in an acid solution to make it tractable.

By elemental analysis and FTIR spectra analysis, it was shown that cys-chitin contained the sulhydryl groups. We have examined various factors influencing the reaction and established efficient preparative procedures. This investigation concern the adsorption properties of cys-chitin with respect to Cu^{II}, Cd^{II}, Pb^{II}, Zn^{II}, and Ni^{II}. Their adsorption capacities, the effect of the pH value, and other properties are reported here.

EXPERIMENTAL

Materials and reagents

Chitin was supplied by Nantong Water Products Institute, Nantong, People's Republic of China. Additionally, it was ground through a granulating machine and then sent through a 100-mesh granular membrane. L-Cysteine and other reagents used were of analytical reagent grade. Stock solution (25 mg/mL) of Cu^{II}, Cd^{II}, Pb^{II}, Zn^{II}, and Ni^{II} were prepared by dissolving appropriate quantities of CuCl₂ · 2H₂O, Cd(NO₃)₂ · 4H₂O, Pb(NO₃)₂, ZnCl₂, and NiCl₂ · 6H₂O in 200 mL distilled water, respectively, and 20 mL concentrated nitric acid was added; the solution was diluted to 1 L with distilled water.

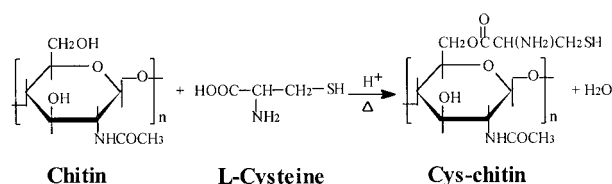
Instrument and apparatus

Instruments used were: model PHS-3C pH-meter; Carlo Erba 1106 elemental analysis instrument; Nicolet Impact 410 FT-IR spectrometer; 360M atomic absorption spectrometer.

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Preparation of cys-chitin

Added to a 250-mL flask were 50 mL THF and 10 mL sulfuric acid as catalyst. Then L-cysteine (10 g) and chitin (5 g) were added with stirring. The reaction was allowed to proceed at 50°C under heterogeneous conditions with magnetic stirring. After 72 h, the reaction stopped. The solid products were recovered by filtration and washed with distilled water to remove excess L-cysteine and sulfuric acid until the filter solution was neutral; then products were washed with ethanol to remove remaining L-cysteine. The products were collected by filtration and dried in a vacuum drying oven at 35°C. The yields were 90–95%. The products must be kept from sunshine and moisture. The chemical reaction can be described as follows:



Structural characterization of product

Chitin and cys-chitin powders were ground with IR-grade potassium bromide in an agate mortar; the IR spectra were recorded with a Nicolet Impact 410 FTIR spectrometer. Elemental analysis of Chitin and cys-chitin were carried out with a Carlo Erba 1106 elemental analysis instrument.

Measurement of content of sulfhydryl group

The content of the sulfhydryl group was determined by iodimetry. The procedure is as follows: 0.25 g cys-chitin was accurately weighted in a 50-mL iodine flask; then 15 mL distilled water, 2.5 mL acetic acid, and 0.5 g potassium iodide were added. When potassium iodide was completely dissolved, 10 mL potassium iodate (0.003 mol/L) was added. The flask was then put in ice water for 5 min. Then the I₂ produced was titrated with 0.03 mol/L sodium thiosulfate as a volumetric solution until the yellow color vanished. The content of the sulfhydryl group was calculated by the following equation:

$$[\text{SH}] \% = \frac{\left[6 \times 10 - \frac{M_2 V_2}{M_1} \right] M_1 \times 33.07}{W \times 10} \quad (1)$$

where M_1 , M_2 are the concentration of KIO₃ and Na₂S₂O₃, respectively (mol/L); V_2 is the volume of Na₂S₂O₃ (mL); and W is the weight of cys-chitin (g).

Measurement of specific surface area

The specific surface area was determined by dye adsorption method.³ Cys-chitin or chitin (0.1000 g) was equilibrated with 10 mL aqueous solution containing 16.0 mg/L methylene blue. The mixture was shaken for 2 h and then stored for 2 days at 25°C. The concentrations of methylene blue before and after adsorption were determined by the absorbance at 665 nm, and their adsorption capacities of methylene blue were calculated. Because 1 mg methylene blue can cover 2.45 m² surface area of adsorbent, we obtained the following result of specific surface area: chitin: 4.62 m²/g; cys-chitin: 4.51 m²/g (no marked difference between them).

Adsorption capacity (Q)

Chitin or cys-chitin (0.1000 g) was equilibrated with 10 mL of a 25 mg/mL stock metal ion solution. The pH value was adjusted to 5.0 for Cu^{II}, Pb^{II}, to 6.0 for Zn^{II}, and to 6.5 for Cd^{II}, and Ni^{II}, respectively. The solution was shaken for 9 h and stored for 12 h at 25°C. The concentrations of metal ions before and after adsorption were determined by atomic absorption (Q); Q was calculated by the following equation:

$$Q = \frac{V(C_0 - C)}{W} \quad (2)$$

where V is the volume of metal ion (mL); W is the weight of the adsorbent (g); C_0 is the concentration of metal ions before adsorption (mg/mL); C is the concentration of metal ions after adsorption (mg/mL); and Q is the adsorption capacity (mg/g).

Adsorption kinetics

Prescribed standard procedures were used to investigate the adsorption kinetic properties of cys-chitin for heavy metal ion.³ Cys-chitin samples (0.1000 g) were added to several portions of solution containing a single metal ion, respectively. The metal ion solutions were adjusted to desired pH value. These solutions were stored at 25°C. After a time interval of 30 min, the present adsorption capacity of one solution were determined. Thus, the adsorption kinetic curves of cys-chitin for metal ions were obtained.

TABLE I
The Result of Elemental Analysis (%)

Samples	N	C	H	S
Chitin	6.45	43.71	5.98	0
Cys-chitin	6.90	43.16	6.00	1.98

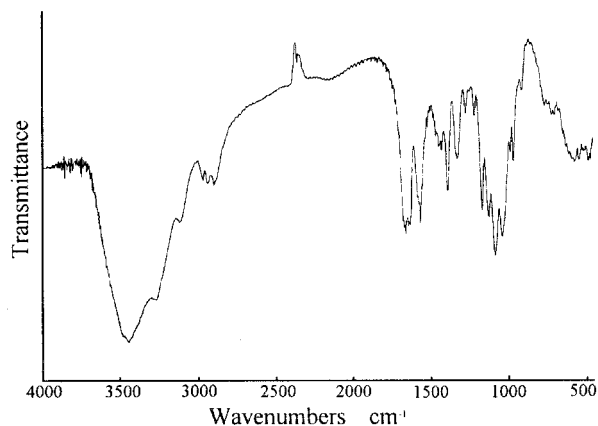


Figure 1 FTIR spectra of chitin.

Effect of pH value on adsorption

Cys-chitin samples (0.1000 g) were equilibrated with 10 mL of 25 mg/mL metal-ion solution at 25°C. The pH value range for the test was 2.0–8.0.

Desorption of adsorbed heavy metal ions

After a solution containing 1 mg/mL single metal ion was slowly passed through an adsorption column of cys-chitin (diam. 10 × 120 mm), the adsorption column was eluted with distilled water. The water eluting solution was collected for determining the concentration of metal ion by atomic absorption spectrometry and also for calculating the percentage of adsorption. Nitric acid (0.5 mol/L) was then used as desorption solution, the outflow of which was used to determine the concentration of metal ions and to calculate the percentage of desorption.

The deterioration of cys-chitin

The deterioration of the cys-chitin was investigated by the change in the adsorption capacity. First, the ad-

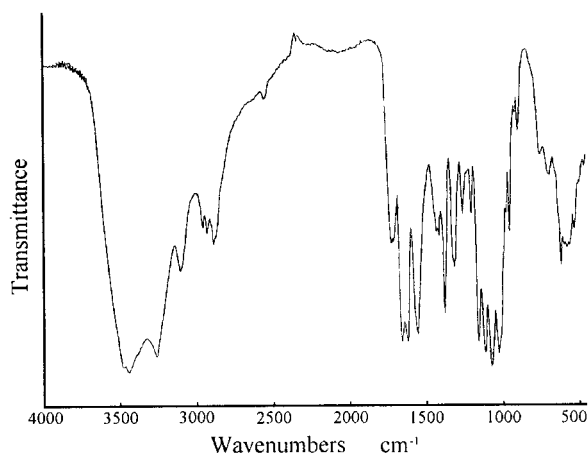


Figure 2 FTIR spectra of cys-chitin.

TABLE II
Adsorption Capacities of Chitin and Cys-Chitin for Metal Ions (mg/g)

Adsorbents	Cu ^{II}	Ni ^{II}	Pb ^{II}	Cd ^{II}	Zn ^{II}
Chitin	57.9	21.3	132.4	108.0	46.9
Cys-chitin	86.1	11.2	351.5	214.6	107.0

sorption capacity for metal ions was determined, and nitric acid (0.5 mol/L) was used to make metal ions desorped from cys-chitin. Then distilled water was used to wash this adsorption until the solution was neutral, thus obtaining regenerated adsorbent. This regenerated adsorbent was used to determine the adsorption capacity for metal ions again, then desorped and washed. The cys-chitin was adsorbed-regenerated six times with these procedures.

RESULTS AND DISCUSSION

Preparation of cys-chitin

The influence of reaction temperature is evident between room temperature and 80°C. We found that the content of sulfhydryl group in the samples prepared under much milder condition at room temperature and 35°C was almost zero. The degradation of chitin backbones took place when the reaction temperature was above 60°C, so the reaction was proceeded at 50°C.

Because esterification cannot be run in aqueous solution, we carried out the reaction in organic solvents, such as tetrahydrofuran (THF), dioxane, *N,N*-dimethylformamide (DMF), cyclohexane. We found that the reaction is efficiently conducted only in THF.

Sulfuric acid was used not only to be a catalyst but to help L-cysteine dissolve in THF. Too much sulfuric acid may cause degradation of chitin backbones.

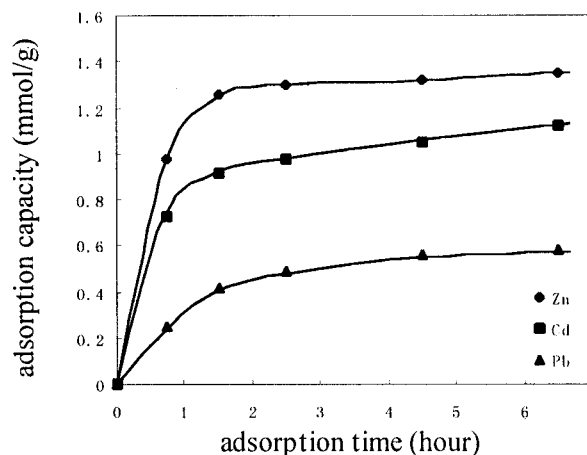


Figure 3 The kinetic curves of cys-chitin in adsorption for Zn^{II}, Cd^{II}, and Pb^{II}.

TABLE III
The Relation between pH value and Adsorption Capacities (mg/g)

Metal Ions	pH Value							
	2.0	4.0	5.0	5.5	6.0	6.5	7.0	8.0
Pb ^{II}	0	144.1	351.5	334.4	313.8	↓	↓	↓
Zn ^{II}	0	60.1	105.7	102.5	107.0	102.8	78.2	/
Cd ^{II}	0	90.1	143.0	174.6	184.6	214.6	198.8	193.9
Cu ^{II}	17.8	59.3	86.1	84.1	79.4	61.6	/	/

Characterization of cys-chitin

Table I shows that the content of N in cys-chitin is a little higher than that of chitin, and that the content of S in cys-chitin is 1.98. Iodimetry used to measure the content of the sulfhydryl group in cys-chitin showed it range from 1.5–2.2%. These results confirm that L-cysteine and chitin have reacted to create cys-chitin.

FTIR spectra of chitin and cys-chitin are presented in Figures 1 and 2. The spectra of cys-chitin showed new peaks at around 2561.38 and 1725.12 cm⁻¹; that at around 2561.38 cm⁻¹ corresponded to the —SH group (ν_{SH}); that at 1725.12 cm⁻¹ corresponded to the ester linkages ($\nu_{C=O}$).

Adsorption capacities of heavy metal ions

A material's adsorption capacity for metal ions is important for assessing its efficiency as adsorbent. More than one heavy metal ion is adsorbed by cys-chitin because of its several functional groups such as —NH₂ groups, —SH groups, and —OH groups. The adsorption capacities of chitin and cys-chitin for heavy metals are listed in Table II. From Table II, we can see that cys-chitin had a larger adsorption capacity for Zn^{II}, Cd^{II}, and Pb^{II}.

Adsorption kinetics and effect of pH value on adsorption

The curves of adsorption kinetics of cys-chitin for Zn^{II}, Cd^{II}, and Pb^{II} (Fig. 3) show rapid adsorption of cys-chitin for Zn^{II}, Cd^{II}, and Pb^{II} in 2 h. The adsorption rate of cys-chitin was Zn^{II} > Cd^{II} > Pb^{II}.

Due to the protonation and deprotonation properties of the acidic and basic groups of the ion exchanger, its adsorption behavior for metal ions is influenced by the pH value, which influences the group structure of adsorbents, the formation of metal ions,

and the interaction between adsorbents and metal ions. The metal ions adsorption dependence on pH was examined in detail. The results are shown in Table III.

With Pb^{II}, Zn^{II}, and Cd^{II}, maxima are observed at neutrality (pH 6–7), whereas Cu^{II} show maximum at 5.0. For these metal ions, the degree of adsorption decreased sharply in the pH range 2.0–5.0. They were scarcely adsorbed below pH 4.0. The pH value over 8.0 may lead to hydrolytic decomposition of the metal ion. Particularly for Pb^{II}, when the pH value of the solution reached 6.5, it became opaque because Pb^{II} was hydrolyzed to produce Pb(OH)₂.

Elution of adsorbed metal ions

Because cys-chitin is insoluble in acid solution, we can use diluted nitric acid to elute the adsorbed metal ions. The results of adsorption and acid elution are showed in Table IV.

Table IV indicates that cys-chitin has good adsorption percentage and desorption percentage for metal ions.

The regeneration of cys-chitin

Very little change in adsorption capacity during the period of reuse, as shown in Table V, indicates that the deterioration of the cys-chitin is little.

CONCLUSIONS

Experimental results of this study on the adsorption characteristics of cys-chitin for heavy metal ions led to the following conclusions:

TABLE IV
Elution of Adsorbed Metal Ions

Metal ions	Concentration of metal ion after adsorbed	Percentage of adsorption	Percentage of acid elution	Percentage recovery
Pb ^{II}	15 μg/mL	98.5%	97.2%	95.7%
Cd ^{II}	21 μg/mL	97.9%	98.0%	95.9%

TABLE V
The Effects of Regeneration Times
on Adsorption Capacities (mg/g)

Metal Ion	Times					
	1	2	3	4	5	6
Pb ^{II}	351.5	350.2	349.8	349.6	349.3	349.0
Cd ^{II}	214.6	212.4	212.4	211.8	211.4	211.1

1. A new adsorbent, cys-chitin, synthesized for the first time from chitin, is insoluble in acid solution.
2. This study shows that cys-chitin's adsorption capacities for Cu^{II}, Cd^{II}, Pb^{II}, and Zn^{II} are 86.1, 214.6, 351.5, and 107.0 mg/g, respectively; while those of chitin are 57.9, 108.0, 132.4, and 46.9 mg/g, respectively; which shows that the adsorption capacity of cys-chitin is higher than that of chitin (there is no marked difference between their specific surface area).
3. Cys-chitin's adsorption for the heavy metal ions is strongly dependent on the equilibrium pH

value of the solution. The metal ions cannot be adsorbed by cys-chitin at a very low pH value range. With the increasing pH value, the adsorption percentage for the metal ions rises sharply.

4. Cys-chitin can rapidly adsorb metal ions in 2 h.
5. The adsorbed metal ions on the cys-chitin can be eluted completely by elution solution of 0.5 mol/L nitric acid.
6. The deterioration of the regenerated cys-chitin for adsorption of heavy metal ions is little.

Therefore, cys-chitin is potentially a powerful tool for removal of heavy metal ions from natural waters and industrial effluents.

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