

Synthesis of Sulfhydryl Chitin and Its Adsorption Properties for Heavy Metal Ions

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ABSTRACT: This article discusses the preparation of the water-insoluble adsorbent sulfhydryl chitin (s-chitin), by treatment of the chitin with sulfhydryl acetic acid in the presence of sulfuric acid as a catalyst. Its structure was confirmed by elemental analysis, FTIR spectra analysis and near-IR spectra analysis. We also investigated the adsorption properties of sulfhydryl chitin for Cu^{II}, Cd^{II}, Pb^{II}, Cr^{III}, and Ni^{II}. Based on the research results of adsorption capacity, the effect of pH value on adsorption, adsorption kinetics experiments, and selective adsorption experiments were observed. It has been shown that the s-chitin has much better adsorption for Pb^{II}, Cu^{II}, and Cd^{II} than chitin itself. The adsorption capacities of s-chitin for Pb^{II}, Cu^{II}, and Cd^{II} were 108.3, 94.7, and 57.1 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 Cu^{II}, Cd^{II}, and Pb^{II} could be eluted by diluted chlorhydric acid. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 151–155, 2000

Key words: sulfhydryl chitin; adsorption property; heavy metal ions

INTRODUCTION

Chitin is a natural polysaccharide, and its structure is similar to cellulose; it is insoluble in water and common organic solvents. Chitosan is an important derivate of chitin, obtained by deacetylation; it is soluble in dilute acetic acid. Marsri et al.¹ pointed out in 1974 that chitin and chitosan may be good adsorbents for removing heavy metal ions from water. But as chitin has little adsorption capacity for heavy metal ions, chitosan is soluble in an acid solution, leading to degradation. These properties strongly restrict any practical application of chitin and chitosan. In recent years the study of the removal of metal ions from

aqueous solution, either for pollution control or for raw material recovery, has been of increasing importance. Many attempts to prepare adsorbents from chitosan and chitosan derivatives have been reported.^{2,3} Qu Rongjiun and coworker⁴ have synthesized a series chitosan derivatives, and Yoshinari Inukai et al.⁵ have also synthesized many chitosan derivatives to obtain novel adsorbents with a high selectivity for semimetals. Szosland and East⁶ made many attempts to prepare fibers from chitin and some chitin derivatives, such as dibutrylchitin.

The objective of this work was to prepare a new [derivate] from chitin: sulfhydryl chitin. The major advantages of this material are not only its greater adsorption capacity than chitin but also its insolubility in an acid solution. The synthesis of s-chitin was carried out by treatment of chitin with sulfhydryl acetic acid in the presence of sulfuric acid as a catalyst.

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By elemental analysis, FTIR spectra analysis, and near IR spectra analysis, it was shown that s-chitin contained the sulfhydryl group. The synthesis of s-chitin will be described in detail elsewhere. This investigation concerns the adsorption properties of s-chitin with respect to Cu^{II} , Cd^{II} , Cr^{III} , Pb^{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 40-mesh granular membrane. Sulfhydryl acetic acid was of chemical reagent grade. Other reagents used were of analytical reagent grade. Stock solution (2.5 mg/mL) of Cu^{II} , Cd^{II} , Pb^{II} , Ni^{II} , and Cr^{III} were prepared by dissolving appropriate quantities of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cr}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 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 Tmlmpact 410 FTIR spectrometer; Bran Luebbe Nir 500 near IR spectrometer; and 360M atomic absorption spectrometer.

Preparation of Sulfhydryl Chitin

Added to a 250-mL flask were 100 mL sulfhydryl acetic acid and 1 g sulfuric acid as catalyst. Then chitin (5 g) was added with stirring. The reaction was allowed to proceed at 40°C under heterogeneous conditions with stirring. After 24 h, the reaction stopped. The solid products were recovered by filtration and washed with distilled water to remove excess sulfhydryl acetic acid and sulfuric acid until the filter solution was neutral; then products were washed with a little amount of ethanol. The products were collected by filtration and dried in a drying oven at 35°C. The yields were 92–96%. The products had to be free from sunshine and moisture upon storage.

Structural Characterization of Product

Chitin and s-chitin were ground with IR grade KBr in an agate mortar; the IR spectra were recorded with a Nicolet [Tmlmpact] 410 FTIR spectrometer. Elemental analysis of chitin and s-chitin were carried out with a Carlo Erba 1106 elemental analysis instrument. The near IR spectra of chitin and s-chitin were carried out by a Bran Lubbe near IR spectrometer, model Nir 500.

Measurement of Content of Sulfhydryl Group

The content of the sulfhydryl group was determined by iodimetry. The procedure is as follows: 0.25 g s-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 I_2 produced was titrated with 0.03 mol/L sodium tithisulfate as a volumetric solution until the yellow color vanished. Then the content of the sulfhydryl group was calculated by the following equation:

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

where M_1 , M_2 are the concentration of KIO_3 and $\text{Na}_2\text{S}_2\text{O}_3$, respectively (mol/L); V_2 is the volume of $\text{Na}_2\text{S}_2\text{O}_3$ (mL); and W is the weight of s-chitin (g).

Adsorption Capacity (Q)

Chitin or s-chitin (0.1000 g was equilibrated with 10 mL of a 2.5 mg/mL stock metal ion solution. The pH value was adjusted to 7.0 for Cu^{II} , Pb^{II} , Cd^{II} , Ni^{II} and to 6.0 for Cr^{III} , 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:

Table I The Result of Elemental Analysis (%)

Samples	N	C	H
Chitin	6.30	30.77	5.45
S-Chitin	5.10	37.37	5.52

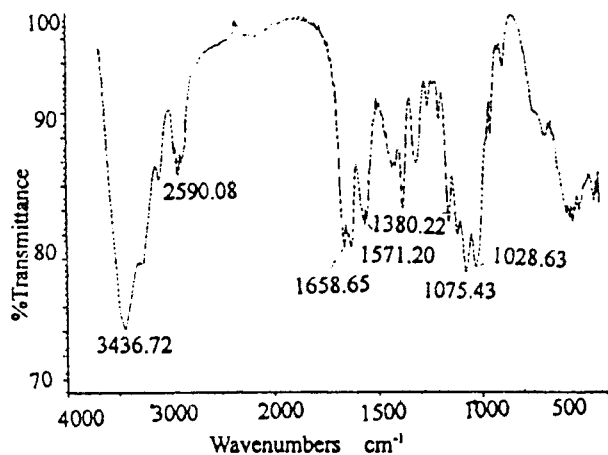


Figure 1 FTIR spectra of chitin.

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

where V is the volume of metal ion solution (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 Versus Time

According to the procedures described above, adsorption versus time of the s-chitin for heavy metal ions were investigated with the solution containing either single metal ion. All the metal ion solutions were adjusted to the desired pH values. Subsequently, the metal solutions were

added to s-chitin (0.1000 g), which was previously transferred into a 1000-mL flask. Mixing started immediately after addition of the tested metal ion solutions to the samples. After a time interval of 10 min, 1.0-mL aliquots of the tested solutions were collected and centrifuged to separate any remaining s-chitin. The actual concentration of metal ions in solution was determined by atomic absorption spectroscopy (AAS). In this case, the amounts of added metal ions did not exceed the saturation adsorption capacity of the s-chitin for these metal ions.

Effect of pH Value on Adsorption

S-chitin samples (0.1000 g) were equilibrated with 5 mL of 2.5 mg/mL metal solutions at 25°C. The pH value range for the test was 2.0–8.0.

Selective Adsorption Experiment

The s-chitin sample (0.1000 g) was equilibrated with an appropriate metal-ion mixing solution at 25°C. The other steps were similar to those for the determination of adsorption capacity. Then the ratio of selective adsorption was calculated.

Desorption of Adsorbed Heavy Metal Ions

An appropriate metal-ion solution was slowly flowed into an adsorption column of s-chitin ($\Phi 10 \times 120$ mm). Then the adsorption column was eluted with deionized water, collected eluting solution. From this we determined the concentration of metal ions by AAS and calculated the percentage of adsorption. After that we used an

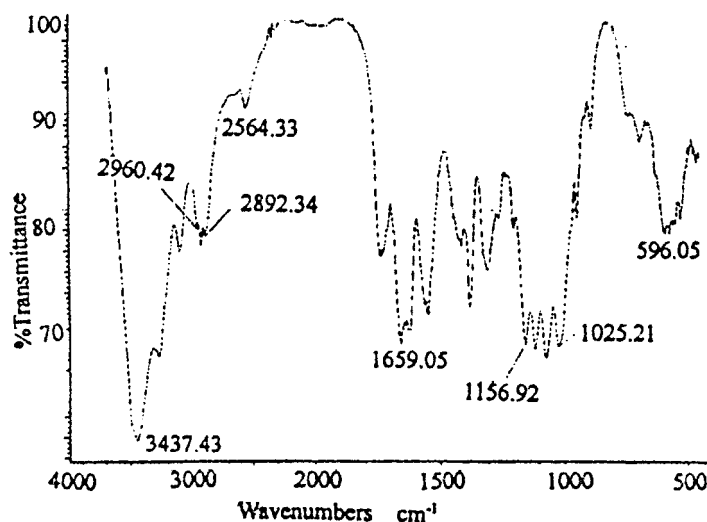


Figure 2 FTIR spectra of s-chitin.

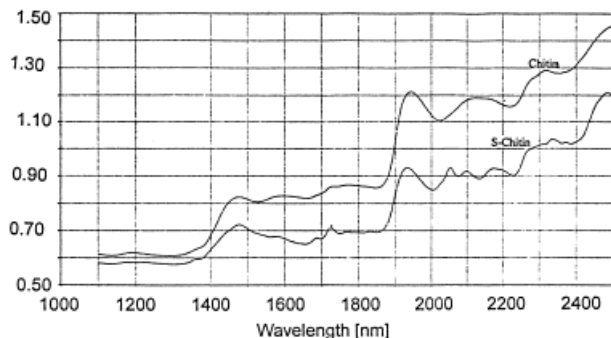


Figure 3 Near-IR spectra of chitin and s-chitin.

appropriate concentration of [chlorohydric] acid as a desorption solution, collected all outflow solution, determined the concentration of metal ions, and calculated the percentage of desorption.

RESULTS AND DISCUSSION

Characterization of S-Chitin

From Table I, it can be seen that the N content of s-chitin is much lower than that of chitin, showing that sulfhydryl acetic acid and chitin have reacted, creating s-chitin.

The ITIR spectra of chitin and s-chitin are presented in Figures 1 and 2. In the spectra of s-chitin, new absorptions appeared at around 2564.33 cm^{-1} and 1738.38 cm^{-1} . Adsorption appeared at around 2564.33 cm^{-1} that corresponded to the —SH group, while the absorption that appeared at 1738.38 cm^{-1} corresponded to the R—O—CO—R group.

The near-IR spectra of chitin and s-chitin are presented in Figure 3. In the spectrum of s-chitin there was a new absorption appearing at around 1733 nm, which shows that the s-chitin contains the —SH group.

With iodimetry, we measured the content of the sulfhydryl group in s-chitin many times; the content value range was 1.6–2.1%.

Adsorption Capacities of Heavy Metal Ions

The adsorption capacities for metal ions is important for assessment of the ability of the material

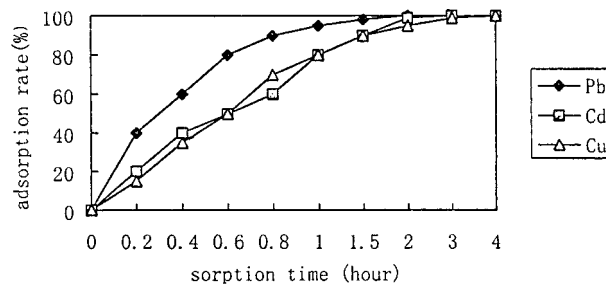


Figure 4 Adsorption versus time of s-chitin.

under study to serve as an adsorbent. More than one heavy metal ion is adsorbed by the s-chitin because of the combining several functional groups. The capacities of chitin and s-chitin for heavy metals are reported in Table II. From Table II, we can see that s-chitin has a large adsorption capacity for Pb^{II} , Cd^{II} , and Cu^{II} .

Adsorption Versus Time and Effect of pH Value on Adsorption

Figure 4 shows the curves of adsorption versus time of s-chitin for Pb^{II} , Cd^{II} , and Cu^{II} . From Figure 4, we can see that adsorption speeds of s-chitin for Pb^{II} , Cd^{II} , and Cu^{II} are fast. After 2 h the adsorption percentages of Pb^{II} , Cd^{II} , and Cu^{II} reach to 99%, 97%, and 95%, respectively. The adsorption speeds of s-chitin followed the sequence: $\text{Pb}^{\text{II}} > \text{Cd}^{\text{II}} > \text{Cu}^{\text{II}}$.

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 in turn influences the group structure of the adsorbents, the formation of metal ions, and the interaction between sorbents and metal ions. Therefore, the adsorption dependence on pH for the metal ions was examined in detail. In Table III the results show that these adsorption levels have a similar dependence on the pH value.

For Cu^{II} the degree of adsorption is decreased rapidly in the pH range 1–3. The Cu^{II} ion is scarcely adsorbed below a pH of 2. The degree of adsorption is constant at 99% above a pH of 6. The adsorption percentage for Cd^{II} increases in

Table II Adsorption Capacities of Adsorbents (mg/g)

Adsorbents	Cu^{II}	Cd^{II}	Cr^{III}	Ni^{II}	Pb^{II}
Chitin	27.8	23.4	0.35	1.6	48.9
S-Chitin	94.7	57.1	0.90	1.9	108.3

Table III Effect of pH Value on Adsorption

Metal Ions	pH Value					pH Value				
	2.0	4.0	6.0	7.0	8.0	2.0	4.0	6.0	7.0	8.0
Adsorption Capacity (mg/g)	4.6	46.7	91.2	92.7	94.3	0	49.6	54.2	56.4	57.1

the pH range 2–4, reaching a constant level at a pH > 4. If the pH value is more 8, the metal ion would suffer hydrolytic decomposition. So the controlling pH value range was 6–8.

Selective Adsorption

Table IV shows selective adsorption of s-chitin for the mixture solution of Cd—Cu—Ni—Cr.

From Table IV, it is evident that the adsorption of S-Chitin for Cu^{II} and Cd^{II} is more complete than for Ni^{II} and Cr^{III}. So it can be used to recover Cu^{II} and Cd^{II}.

Elution of Adsorbed Metal Ions

A solution containing 1 mg/mL Cu^{II} flowed through the adsorption column of s-chitin. After adsorption, the remaining concentration of Cu^{II} was 24 µg/mL. The adsorption percentage of Cu^{II} reached 97.6%. Then the Cu^{II} was eluted with distilled water, [chlorhydric] acid (2M), and distilled water in that order. The weight of the eluted was measured Cu^{II}. The elution percentage of Cu^{II} was 97%, and the percentage recovery was 94.7%.

CONCLUSIONS

In this article the adsorption characteristics of s-chitin for heavy metal ions were studied. From the experimental results and analysis above, the following conclusions have been drawn:

Table IV Selective Adsorption for Cu—Cd—Ni—Cr

Metal Ions	Cu ^{II}	Cd ^{II}	Ni ^{II}	Cr ^{III}
Adsorption Capacity	39.2 mg/g	21.0 mg/g	0.2 mg/g	0

Coefficient of selective adsorpting: K(Cu/Cd) = 1.87; K(CU/Ni) = 196; K(Cu/Cr) = ∞.

1. We have for the first time synthesized a new [adsorbent,] sulfhydryl chitin (s-chitin), from chitin.
2. The investigation of s-chitin reveals that its adsorption capacities for Cu^{II}, Pb^{II}, Cd^{II}, Cr^{III}, Ni^{II} are 94.7, 108.3, 57.1, 0.90, and 1.9 mg/g and that of the chitin are 27.8, 48.9, 23.4, 0.35, and 1.6 mg/g, respectively. So the adsorption capacity of s-chitin is much bigger than that of chitin.
3. The adsorption of the heavy metal ions on the s-chitin is strongly dependent on the equilibrium pH value of solution. The metal ions cannot be absorbed by the s-chitin at a lower pH value range. By increasing the pH value, the adsorption percentage for the metal ions exhibited a sudden jump.
4. Adsorption versus time of the s-chitin–metal ion interaction has been found to be rapid and can be [adsorbed] completely after 1–2 h of treatment time in most cases.
5. The adsorbed Cu^{II} on the s-chitin can be eluted by an elution solution in 2M [chlorhydric] acid.

Therefore, it might be an effective tool for the removal and accumulation of the heavy metal ions found in natural water and industrial effluents.

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