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Preparation and Adsorption Property of Chitosan Derivative Bearing β-Cyclodextrin and Schiff-Base

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Chitosan derivative bearing β-cyclodextrin and Schiff-base was prepared by modification of chitosan with glutaric diketone, followed by reaction with epichlorohydrin and β-cyclodextrin. The derivative was characterized by IR and XRD spectra. Adsorption property of the chitosan derivative was investigated. It can adsorb metallic ions and phenolic compounds simultaneously.

Keywords: chitosan derivative; preparation; β-cyclodextrin; glutaric diketone

1 Introduction

Chitosan, a natural polymer obtained by N-deacetylation of chitin from the shell of crab or shrimp, has both hydroxyl and amino groups that can be modified easily. A range of research on the use of chitosan has been discussed for wastewater treatment, as the supporter of catalyzer, and in pharmaceutical preparation (1–3).

Currently, another interesting study is focused on the host-guest chemistry and the representative host is cyclodextrin. Cyclodextrin is cyclic oligosaccharides consisting of six to eight glucose units joined by α-1,4-glycosidic linkages. The interior cavity of cyclodextrin molecule is under hydrophobic circumstance whereas the exterior is highly hydrophilic. This characteristic enables cyclodextrin to entrap various kinds of guest molecules, which apparently must satisfy a single requirement, namely a steric hindrance, compatible with the size of the cavity. Cyclodextrin was applied extensively in the adsorptive separation, pharmaceutics, and environmental protection (4–6).

Due to the special properties of chitosan and cyclodextrin, chitosan derivatives, bearing cyclodextrin, have also drawn the attention of researchers and some water-soluble and insoluble polymers have been synthesized (7–10). In those studies, chitosan is merely modified by cyclodextrin or its derivative. Our interest is to modify the amino and hydroxyl groups of chitosan simultaneously to make it has the multi-functions such as adsorption of inorganic and organic compounds at the same time. Thus, in this paper, chitosan derivative bearing β-cyclodextrin and Schiff-base was prepared and characterized, and its adsorption property of heavy metallic ions and phenolic compounds were investigated.

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2 Experimental

2.1 Reagents

Chitosan was obtained commercially and was used without any further purification. β-Cyclodextrin was provided by Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. It was recrystallized twice and dried in vacuum at temperature of 383 K before use. Glutaric diketone, epichlorohydrin, dimethyl sulphoxide (DMSO) and others are all analytical reagents. The redistilled water was used throughout.

2.2 Instruments

IR spectra (recorded in KBr on Nicolet AVATAR FT-IR spectrophotometer, USA) and XRD spectra (recorded with Rigaku D/MAX-RB X-Ray Diffracter, Japan, using Cu-Kα as X-ray resource with Ni as filter) were used to characterize the chitosan derivative. The content of metallic ions and phenolic compounds were investigated by Optima 4300DV ICP (Perkin-Elmer, USA) and Agilent 8453A UV-Visible Spectroscopy (Agilent, USA), respectively.

2.3 General Method for the Preparation of Chitosan Derivative

The synthesis of chitosan derivative include three steps:

1. 5.6 g of glutaric diketone was added to the suspension which contained 5.0 g of swelled chitosan (a) and 50 ml of methanol. The mixture was heated at 343 K for 24 h with stirring and reflux. After being cooled to the room temperature, the mixture was filtered and the chitosan-supported Schiff-base was washed with substantial water, then with acetone and ethanol, respectively.
2. Chitosan-supported Schiff-base was added to the solution consisting of NaOH aqueous (25 ml, 0.4 mol/l) and DMSO (25 ml), and was stirred at 313 K. To this suspension, 15 ml of epichlorohydrin was added dropwise within 2 h. The mixture was stirred for an additional hour and was then filtered. The epihydrin functionalized chitosan-supported Schiff-base was washed with ample water and acetone.
3. 75 ml of 0.1 mol/l NaOH was added to the mixture of epihydrin functionalized chitosan-supported Schiff-base and β-cyclodextrin (1:1, g/g), and heated at 333 K for 4 h with stirring. The suspension was filtered and a chitosan derivative bearing cyclodextrin and Schiff-base was washed with water and acetone, and dried in vacuum at 313 K for 24 h.

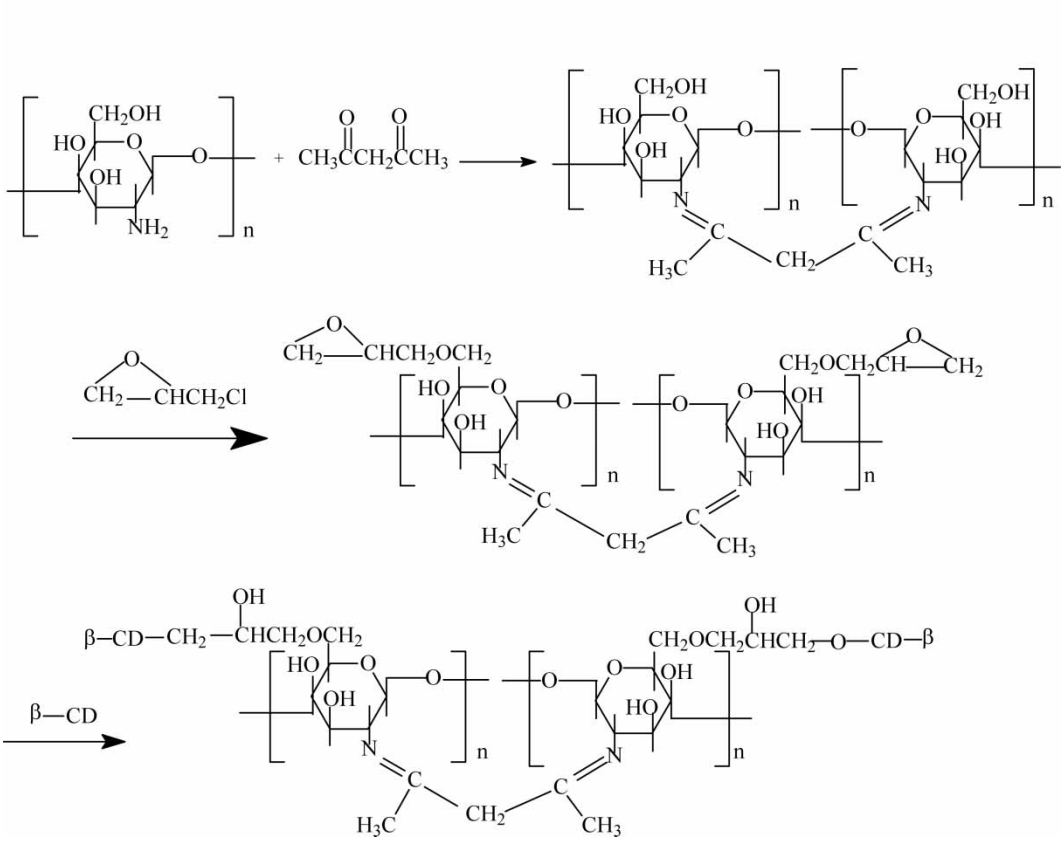
The synthesis routine is described in Scheme 1.

3 Results and Discussion

3.1 Characterization of Chitosan Derivative

Compared with the IR spectrum of chitosan, new absorption bands appear at 1567 cm^{-1} and 749 cm^{-1} after it is modified by glutaric diketone, which belong to -C═N group and -CH_2 group, respectively. When chitosan-supported Schiff-base is functionalized by epichlorohydrin, no band of the -C-Cl group appeared, which indicates that the reaction of epichlorohydrin with chitosan-supported Schiff-base is a process of dechlorination. The absorption band of chitosan derivative bearing cyclodextrin and Schiff-base at 3429 cm^{-1} has a little shift and the peak area increases, apparently after β-cyclodextrin is immobilized to epihydrin functionalized chitosan-supported Schiff-base.

XRD spectra were shown in Figure 1. Chitosan has the diffractive band at 10°, 20° and 29°. When glutaric diketone is bonded to chitosan, the diffractive peak at 29° shows an obvious decrease. There is also a new peak which appeared at 6° when the chitosan-supported



Sch. 1. The routine of synthesis of chitosan derivative.

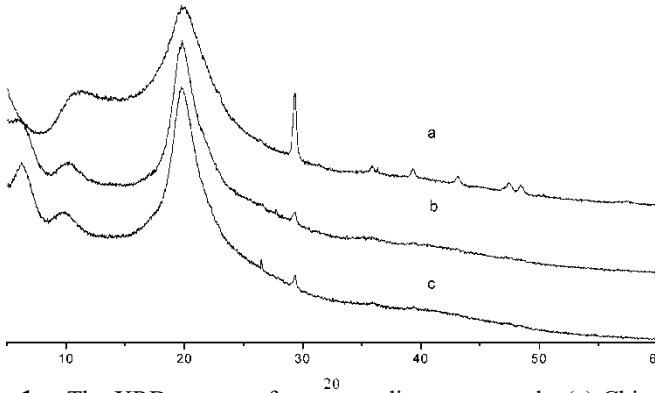


Fig. 1. The XRD spectra of corresponding compounds. (a) Chitosan, (b) chitosan-supported Schiff-base, (c) chitosan derivative bearing β-cyclodextrin and Schiff-base.

Schiff-base was modified by β-cyclodextrin. Furthermore, the diffractive peaks of the chitosan derivative bearing cyclodextrin and Schiff-base at 20° and 6° become sharper than that of chitosan-supported Schiff-base. This is mainly because the -OH groups of β-cyclodextrin enhance the hydrogen bonds of chitosan, although the configuration of chitosan is changed when it is modified by glutaric diketone and β-cyclodextrin.

3.2 Adsorption Properties of Chitosan Derivative

Due to the special structure of the synthesized chitosan derivative, its property for adsorption of metallic ions and phenolic compounds was determined. The adsorption capacity of the chitosan derivative was calculated according to the following equation:

$$Q_e = \frac{V(C_0 - C_e)}{m}$$

where Q_e is the equilibrium adsorption capacity. C_0 and C_e are the initial and equilibrium concentration of solute, respectively. V is the volume of solution, and m is the mass of the chitosan derivative.

The result shown in Table 1 shows that the synthesized chitosan derivative can adsorb the metallic ions and phenolic compounds, simultaneously. Thus, it can be used as a novel adsorbent in the treatment of wastewater to remove harmful substancse such as heavy metallic ions and small organic compounds.

Table 1. The adsorption capacity for metallic ions and phenolic compounds

Metallic ion	Cu^{2+}	Pb^{2+}	Cr^{3+}	Al^{3+}
Adsorption capacity (mg/g)	38.45	43.21	15.16	19.86
Phenolic compound	Phenolic	p-Dioxy benzene	o-Dioxy benzene	m-Dioxy benzene
Adsorption capacity (mg/g)	1.82	23.17	6.27	6.11

4 Conclusions

The chitosan derivative bearing β-cyclodextrin and Schiff-base was prepared by the chitosan reaction with glutaric diketone, functionalized with epichlorohydrin and followed with β-cyclodextrin. The polymer was characterized by IR and XRD spectra. Investigation shows it can adsorb metallic ions and phenolic compounds simultaneously.

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