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Colloids and Surfaces A: Physicochem. Eng. Aspects 277 (2006) 69–74
COLLOIDS AND SURFACES A
www.elsevier.com/locate/colsurfa

Synthesis and properties of diethylene triamine derivative of chitosan

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Received 22 September 2004; received in revised form 29 August 2005; accepted 29 August 2005
Available online 7 February 2006

Abstract

A novel diethylene triamine derivative of chitosan (CTSN) was synthesized via the reaction of diethylene triamine and epoxy activated chitosan. The product contains amino functional groups, secondary amine and polar hydroxyl groups in its skeleton. Its structure was characterized by elemental analysis, infrared spectra analysis, and X-ray diffraction analysis. The results are in agreement with the expectations. The static adsorption properties for Pd^{2+}, Ag^{+}, Ni^{2+}, Cu^{2+}, Co^{2+}, and Cd^{2+} were studied. Experimental results demonstrated that CTSN had higher adsorption capability for metal ions. Specifically, the adsorption capacities for Ag^{+} and Pd^{2+} were 1.29 and 1.15 mmol/g, respectively. With the coexistence of Cu^{2+} and Ni^{2+}, higher adsorption selectivity of CTSN for Ag^{+} ion was found. The selectivity coefficients were $K_{Ag^+/Cu^{2+}} = 11.73$ for CTSN and $K_{Ag^+/Cu^{2+}} = 3.2$ for crosslinked chitosan (CCTS). The adsorption capacity for Ag^{+} was greatly influenced by pH.

Keywords: Chitosan; Diethylene triamine; Metal ions; Adsorption

1. Introduction

Chitosan is a biocompatible polysaccharide obtained from deacetylation of chitin. It can be used to remove metal ions from solutions efficiently. Various chemical modifications [1–4] on its reactive amino and hydroxyl groups can enhance its stability in acidic medium, especially decrease the solubility in mineral and organic acid [5]. They also enhance the ability of resistance to biochemical and microbiological degradation [6] and increase adsorption capacity and adsorption selectivity for different metal ions [7,8]. The complexation and interaction of metal ions with chitosan and its derivatives have been discussed recently [9,10]. The recovery of metal ions in diluted waste water has also been widely studied [11,12].

Most amino compounds disappear quickly and are hard to recover from solution after used, which limits their applications. If amino compounds are mediated in chitosan skeleton to form double structures of chitosan and amino compounds, the derivatives of chitosan containing more amino groups will have stronger adsorption character owing to the original and newly introduced amino groups. Adsorption selectivity and stability may be enhanced as well [13–16]. These chitosan derivatives will have wide applications in separation and concentration of metal ions and heavy metal ions from solution.

This study is involved with the introduction of diethylene triamine into chitosan backbone through the reaction of an intermediate of epoxy activated chitosan and diethylene triamine. The chitosan-benzaldhyde was synthesized via Schiff-base reaction between amino groups in chitosan and benzaldhyde. After the activation of chitosan-benzaldhyde by epichlorohydrin to give epoxy chitosan-benzaldhyde, epoxy-activated chitosan-benzaldhyde was obtained by the reaction of epoxy chitosan-benzaldhyde and diethylene triamine. A new diethylene triamine derivative of chitosan was obtained after the removal of Schiff base with dilute hydrochloride solution. This removal prevented the loss of amino binding sites by reaction with aldehyde from decreasing adsorption on metal ions. Its structure was confirmed by elemental analysis, infrared spectra analysis and X-ray diffraction. The adsorption and selectivity for metal ions were also investigated.

2. Experimental

2.1. Materials

Chitosan (CTS) with a degree of deacetylation of 81.2% (amino content) [17] was prepared by *N*-deacetylation of

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doi:10.1016/j.colsurfa.2005.08.053

chitin from shrimp shells and then after passage through a 200 mesh sieve. Benzaldhyde and epichlorodydrin were reagent-grade without further purification. Crosslinked chitosan (CCTS) was prepared following a procedure reported previously [18].

The chosen metal salts $AgNO_3$, $Ni(NO_3)_2{\cdot}6H_2O$, $CdCl_2{\cdot}6H_2O$, $PdCl_2$, $Cu(NO_3)_2$, $Sr(NO_3)_2$, and $CoCl_2{\cdot}2.5H_2O$ were analytical-reagent-grade. All solutions were prepared with distilled deionized water.

2.2. Measurements

Infrared spectra were recorded on a Nicolet 5DX Fourier transform infrared spectrophotometer. Wide-angle X-ray diffraction (WAXD) patterns were obtained by using a Rigaku (D/MAX,IIIA) diffraction meter with flat-filtered Cu Kα radiation. Elemental analysis was determined with a Perkin-Elmer automatic instrument. Metal ions concentration was determined with a Hitachi 180–80 atomic absorption spectrometer.

2.3. Preparation of chitosan-benzaldhyde (CTSS)

The amino groups have to be protected in order that the reaction of chitosan and diethylene triamine takes place in the position of C_6 hydroxyl groups. The C_2 amino group in chitosan was protected through the reaction between benzaldhyde and chitosan to form chitosan-benzaldhyde according to the method reported [19]. Chitosan powder (5.0 g) was dissolved in 250 mL 1 wt% acetic acid. The solution was diluted with methanol, and then 25 g of benzaldehyde was slowly added. The mixture was stirred at room temperature for 24 h to obtain transparent gel. The obtained gel was washed by methanol to remove the unreacted benzaldehyde and then dried in vaccum at 60 °C to give the Schiff base benzaldehyde chitosan (CTSS).

2.4. Preparation of epoxy chitosan-benzaldhyde (CTSO)

The CTSS powder was dipped into 250 mL 0.4 M sodium hydroxide solution at 50 °C, and then 30 mL of epichlorohydrin was slowly added. The mixture was stirred for 5 h, cooled, filtered, and washed by distilled water, acetone, and ether in sequence. The filter residue was then dried under infrared light to obtain light yellow powder CTSO 3.2 g [20]. The amount of epoxy group was 2.314 mmol/g, which was determined according to the previous method [21].

2.5. Grafting of diethylene triamine onto chitosan (CTSSN)

Powdered CTSO (0.5 g) was swelling in 30 mL 0.1 M sodium hydroxide solutions at 60 °C. Then 1 g of diethylene triamine was slowly dropped into the solution. The mixture was stirred for 4 h, filtered, and washed by distilled water, alcohol and acetone in sequence. The filter residue was dried under the infrared light and 0.6 g gray white solid powder CTSSN was obtained.

Table 1
Elemental analysis results of chitosan and chitosan derivatives

Compound	Found (%)		
	C	H	N
CTS	39.45	6.21	6.38
CCTS	41.86	6.94	5.79
CTSN	45.94	7.93	16.26

2.6. Preparation of diethylene triamine derivative of chitosan (CTSN)

CTSSN (0.25 g) was dipped into 2% hydrochloride solution for 24 h, filtered and washed by distilled water, alcohol and ether. This filter residue was dried under infrared light to obtain white powder (CTSN, in a yield of 83–85 wt%). A schematic representation of the preparation for CTSN is shown in Fig. 1. The results of elemental analysis of the chitosan derivative are presented in Table 1.

2.7. Metal sorption

Metal ion aqueous solution were prepared from $AgNO_3$, $Ni(NO_3)_2{\cdot}6H_2O$, $CdCl_2{\cdot}6H_2O$, $PdCl_2$, $Cu(NO_3)_2$, $Sr(NO_3)_2$, and $CoCl_2{\cdot}2.5H_2O$. Five milligram of CCTS or CTSN was added into 25 mL aqueous solution of the desired metal ion (30 mg L^{-1}). The mixture was vibrated on the mixer at 20 °C for certain time, and then centrifuged and filtered. The concentrations of metal ions in the original solution and the filtrate were measured by an atomic adsorption spectrophotometer (AAS). The amount of metal ions adsorbed by the adsorbent was calculated as follows:

$$q = \frac{(C_0 - C)V}{mM}$$

where q is the adsorption capacity of adsorbent (mmol metal ion/g adsorbent), V is the volume of solution (mL), C_0 and C are the concentrations of metal ion before and after adsorption (mg L^{-1}), m is the mass of adsorbent (g), and M is the atomic weight of corresponding metal ion.

Adsorption selectivity of the adsorbent was determined by measuring the metal loading capacities with the presence of several metal ions. Five milligram adsorbent was added to the prepared 25 mL solution of metal ions (30 mg L^{-1}). The pH of the solution was adjusted to a certain value and after then the mixture system was stirred for certain time. Finally the solution was centrifuged and filtered. The metal ion concentration in the filtrate was determined by AAS. The selectivity coefficient of adsorbent was calculated as follows [22]:

$$K_{M_1/M_2} = \frac{q_1}{q_2}$$

where q_1 and q_2 are the adsorption capacities of the adsorbent for metal ion M_1 and M_2, respectively (mmol metal ion/g adsorbent).