



Synthesis of ethylenediamine modified chitosan and evaluation for removal of divalent metal ions



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ABSTRACT

Selective modification of chitosan has been achieved by incorporating ethylene-1,2-diamine molecule in a regioselective manner using N-phthaloylchitosan and chloro-6-deoxy N-phthaloylchitosan as precursors. The present modification results in additional nitrogen centres which function as potential binding sites during adsorption of metal ions. The derivative ethylene-1,2-diamine-6-deoxy-chitosan and its phthaloylated precursor have been evaluated for divalent metal ion removal. The former is found to have higher capacity for adsorption due to the presence of additional $-\text{NH}_2$ group. The samples exhibited highest affinity for Cu and least for Zn. About 80% of the adsorbed metal ions could be stripped in a solution of pH 1.2. The interaction between acidic metal centres and basic nitrogen centres on surface of the adsorbent appears to govern adsorption. Intrachain and interchain co-ordinate bonding involving NH and NH_2 groups is proposed to be the mechanism of formation of metal-adsorbent complex. The adsorption process is described by Langmuir model.

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1. Introduction

Environmental pollution has always been a serious issue, especially regarding heavy metal ions. Heavy metals are considered to be the most dangerous polluting agents in water. The danger is due to their bioaccumulation and non-biodegradability (Nica, Bura, Gergen, Harmanescu, & Bordean, 2012).

Adsorption is one of the most economical, effective and widely used methods for the removal of toxic metals from aqueous environments. The great advantage of this method over others is the low generation of residues, easy metal recovery and the possibility of reuse of the adsorbent. Studies have been carried out to develop more effective and selective adsorbent materials, which are abundant in nature and require minimal processing in order to the decrease cost (Ng, Cheung, & McKay, 2003; Vasconcelos, Guibal, Laus, Vitali, & Favere, 2009).

The application of biopolymers as adsorbents is an emerging technique and is of interest in studies on the removal of metal ions from aqueous solutions. Special attention has been given to the biopolymer, chitosan (Findon, McKay, & Blair, 1993). Chitosan has a large capacity for the fixation of molecules such as pesticides, proteins, and dyes. The free amino function of chitosan gives it a better ability to chelate ions of transition metals than other natural polymers such as cellulose and its derivatives. The chelating properties

are utilized for water treatment and particularly to recover metals (Muzzarelli, 2011). It has been found that cross linking reduces the adsorption capacity of the chitosan. The main reason for the loss of adsorption capacity is the involvement of amine groups in the cross-linking reaction (Ngah, Endud, & Mayanar, 2002). The ability of chitosan to capture metal ions can be enhanced by suitable modification of the molecule. The amino and two hydroxyl groups on each glucosamine in the repeating unit of chitosan can act as reactive sites for chemical modification. Several such studies have been reported in the literature on the enhancement of adsorption ability of chitosan and adsorption selectivity (Ramesh, Hasegawa, Sugimoto, Maki, & Ueda, 2008; Zhou, Wang, Liu, & Huang, 2009; Guo et al., 2005).

In the present investigation, modification of Cts has been attempted by substitution of ethylenediamine molecule at C-6 position in highly regioselective manner. This modification has been carried out with an idea of enhancing the metal binding capacity of the compound due to the presence of additional 'N' centres incorporated during modification.

2. Experimental

2.1. Materials

Chitosan (Cts) was purchased from Sigma-Aldrich (India). Phthalic anhydride, N,N'-dimethylformamide (DMF), thionylchloride (SOCl_2), ethylene-1,2-diamine (En), hydrazine hydrate, N-methyl-2-pyrrolidone (NMP), copper sulphate, lead

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nitrate, nickel sulphate, zinc sulphate, potassium chloride and hydrochloric acid were all reagent grade and purchased from Spectrochem (India). The reagents were used without prior purification.

2.2. Synthesis

2.2.1. Synthesis of *N*-phthaloylchitosan (PtCts)

Phthaloyl chitosan was synthesized according to a previous method (Torii, Ikeda, Shimojoh, & Kurita, 2009). A sample of 1.0 g chitosan was reacted with 4.04 g of phthalic anhydride in 20-mL of DMF/water (95/5) at 120 °C with stirring under nitrogen. The mixture turned into a viscous dispersion in about 1.5 h and then to a gelatinous mass in 2 h. The reaction was continued and after 8 h, the mixture was cooled to room temperature and the product was precipitated in 500 mL of ice water. The solid product, represented as PtCts, was washed with methanol and dried to give 1.62 g (90%) of white powdery material.

2.2.2. Synthesis of chloro-6-deoxy-*N*-phthaloylchitosan (PtCtsCl)

A sample of 2.0 g of PtCts was dispersed in 25-mL of DMF and stirred for 2 h at 80 °C on a water bath. 0.9-mL SOCl₂ was added and the mixture was further maintained under stirring at 80 °C. After 2 h, the mixture was cooled to room temperature, the yellow powdery product, designated as PtCtsCl, was filtered, washed with acetone and dried.

2.2.3. Synthesis of ethylene-1,2-diamine-6-deoxy-*N*-phthaloylchitosan (PtCtsEn)

A sample of 1 g of PtCtsCl was dispersed in 50-mL of DMF and stirred for 2 h at 80 °C on a water bath. 5 mL of En was added and the mixture was further heated at 80 °C. After 2 h, the mixture was cooled to room temperature, the product, designated as PtCtsEn, was filtered, washed with water and dried.

2.2.4. Synthesis of ethylene-1,2-diamine-6-deoxy-chitosan (CtsEn)

A sample of 0.21 g of PtCtsEn was dispersed in 15 mL of NMP. To the mixture 15 mL of aqueous hydrazine monohydrate (4 M) was added, and the mixture was stirred at 100 °C for 4 h under nitrogen. The product, designated as CtsEn, was filtered, washed with alcohol and dried.

2.3. Characterization

The infrared spectra of the samples, PtCtsCl, PtCtsEn and CtsEn were recorded in KBr pellets on a Shimadzu FTIR spectrometer, model IR-PreStige-21.

TGA was performed with a Shimadzu DTG-60 thermogravimetric analyser. The samples were heated from 0 to 600 °C at the heating rate of 10 °C min⁻¹ under nitrogen atmosphere.

Scanning electron micrographs of the samples before and after adsorption of metal ions were recorded on a JEOL-JSM 5800LV scanning electron microscope under a voltage of 20 kV.

The concentration of metal ions in aqueous solutions were determined in mg L⁻¹ using Atomic Absorption Spectrometer, GBC 932 plus, calibrated with standard metal ion solutions.

2.4. Adsorption, desorption and competitive adsorption studies

2.4.1. Adsorption studies

The capacity of the ethylenediamine modified chitosan materials to extract metal ions from aqueous solution was determined in duplicate, using a batch process with three divalent metal ions, namely, copper(Cu), lead(Pb), and zinc(Zn). About 10 mg of PtCtsEn or CtsEn was suspended in 25.0 cm³ of an aqueous solution

with concentrations of each metal varying from 5 to 20 mg L⁻¹. After 2 h the suspensions were centrifuged. Aliquot of the supernatant was appropriately diluted and concentration of the metal ion was determined by AAS. The absorption capacity of the material is determined using Eq. (1).

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where q_e is the equilibrium adsorption capacity (mg g⁻¹); C_0 and C_e are the initial and equilibrium liquid phase solute concentration (mg L⁻¹), respectively; V is the liquid phase volume (L) and W is the amount of the adsorbent (g). The capacity of the parent compound Cts to extract the above three metal ions was also determined in duplicate, using the metal ion solution of 20 mg L⁻¹, for comparison.

2.5. Desorption

To evaluate the reusability of sorbent materials, PtCtsEn or CtsEn, adsorption experiments were followed by desorption. The adsorption experiments were carried out by suspending about 10 mg of PtCtsEn or CtsEn in 25-mL of metal salt solutions of initial concentration 20 mg L⁻¹. After 2 h, the metal ion adsorbed sample was separated by centrifugation, washed with water and dried. For desorption studies, 10 mg of adsorbed sample was suspended in 25-mL of stripping solution of pH 1.2 (0.2 M KCl and 0.2 M HCl) and stirred for 2 h at room temperature. The suspension was centrifuged. Aliquot of the supernatant was appropriately diluted and the concentration of the desorbed metal ions was determined by AAS.

The percentage of desorption was calculated using Eq. (2).

$$\text{Desorption (\%)} = \frac{\text{amount of metal ion desorbed}}{\text{amount of metal ion adsorbed}} \times 100 \quad (2)$$

2.6. Competitive adsorption

Competitive adsorption studies were done by suspending 10 mg of PtCtsEn or CtsEn samples in 25 mL of the mixture containing 20 mg L⁻¹ of each metal ion, Cu, Pb and Zn. After stirring at room temperature for 2 h the suspension was centrifuged and aliquot of the supernatant was appropriately diluted and concentration of the three metal ions in the supernatant solution was determined by AAS. The amount of metal ions competitively adsorbed was calculated using the Eq. (1).

3. Results and discussion

3.1. Synthesis of PtCtsEn and CtsEn

The synthesis of CtsEn has been accomplished by sequential modification of Cts by 4 reaction steps following the traditional synthetic methodology adopted for derivatisation of polysaccharides such as cellulose and chitosan (Da Silva Filho, De Melo, Da Fonseca, & Airoidi, 2009; Takagai, Shibata, Kiyokawa, & Takase, 2011). As shown in Scheme 1, the selective modification by ethylenediamine group at the C-6 position has been achieved in a highly regioselective manner using *N*-phthaloylchitosan and chloro-6-deoxy-*N*-phthaloylchitosan as precursors. Phthaloylation of chitosan is proved a convenient technique for protecting the amino functionality and also for solubilisation of Cts in organic solvents (Kurita, Ishizeki, Fujisaki, & Iwakura, 1982; Nishimura, Kohgo, Kurita, & Kuzuhara, 1991). On protection of the amino group at C-2 position of chitosan, regioselective substitution of the hydroxyl group at C-6 position with 'Cl' has been achieved by reaction with SOCl₂. As 'Cl' is known to be a good leaving group for the nucleophilic substitution reaction, the chloro-6-deoxy-*N*-phthaloyl

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