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ORIGINAL ARTICLE

Chemical modification of Chitosan for metal ion removal



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KEYWORDS

Chemical modification; Chitosan; FT-IR spectroscopy; Water uptake; Metal ion removal; Characterization **Abstract** In the current work some modification reactions have been conducted to modify Chitosan with some organic compounds, such as aldehydes and organic acids. On the other hand, different blends of Chitosan with some carbohydrates were prepared to obtain Chitosan derivatives of certain physical and chemical properties. The obtained products have been characterized with the necessary chemical and spectroscopic techniques. The efficiency of the obtained modified materials has been investigated for separation of metal ions and for water uptake.

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1. Introduction

Chitosan is the only pseudonatural cationic polymer and thus, it finds many applications that follow from its unique character (flocculants for protein recovery, depollution, etc.). It is largely used in different applications as solutions, gels, or films and fibers (Rinaudo, 2006). Solution properties of Chitosan depend on its average degree of acetylation (DA) and the distribution of the acetyl groups along the main chain in addition to the molecular weight (Kubota and Eguchi, 1997;

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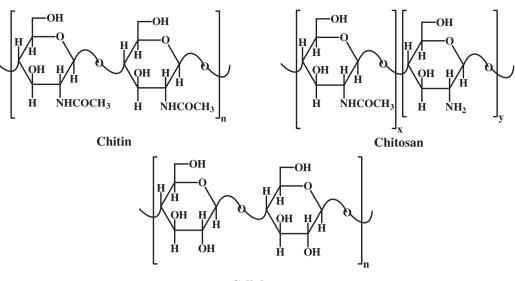
Aiba, 1991; Rinaudo and Domard, 1989). Deacetylation, usually done in the solid state, gives an irregular structure due to the semicrystalline character of the initial polymer. The role of protonation of Chitosan in the presence of acetic acid (Rinaudo et al., 1999a) and hydrochloric acid (Rinaudo et al., 1999b) on solubility is shown by the dependence of the degree of ionization on pH and pK of the acid.

Chitosan is known to have good complexing ability through specific interactions of the $-NH_2$ groups with heavy metals (Muzzarelli, 1973). Examination of complex formation mechanism with copper in dilute solution proposed two different complexes depending on pH and the copper content (Rhazi et al., 2002). Chelation depends on the physical state of Chitosan (powder, gel, fiber, film) and better chelation is obtained for greater degrees of deacetylation of Chitin. Thus, chelation is related to the content and distribution of the $-NH_2$ groups (Kurita et al., 1979) as well as DP of the oligo-Chitosan (Rhazi et al., 2002). Chitosan differs from cellulose where Chitosan has NH_2 group in C-2 position instead of OH group in cellulose (Fig. 1). The main reaction easily performed

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Cellulose

Figure 1 Chemical structure of cellulose, Chitin and Chitosan.

involving the C-2 position in Chitosan is the quaternization of the amino group or a reaction in which an aldehydic function reacts with $-NH_2$ by reductive amination (Sashiva et al., 2003).

Medical applications of Chitosan and its derivatives are of great interest in addition to cosmetics and the pharmaceutical and biomedical applications that probably offer greatest promise (Thanou and Junginger, 2005; Ravi Kumar et al., 2004). Drug delivery applications include oral, nasal, transdermal and parenteral administration of drugs, implants and gene delivery and have been recently discussed (Illum and Davis, 2005; Kanke et al., 1999). Chitosan gels and layer-by-layer polyelectrolyte capsules are often used for the controlled release of drugs or proteins (Abdelaal et al., 2007).

The current work is aiming to modify Chitosan with some aldehydes, acids and carbohydrates. After that the obtained products have been characterized and tested towards their water and metal uptake applications.

2. Experimental

All chemicals are purchased by Aldrich unless otherwise mentioned. Chitosan (CS) of M.Wt. 10,000.00 was used. Characterization of the obtained materials were achieved in the department including FT-IR Spectroscopy using Perkin– Elmer FT-IR Spectrometer, thermal analysis using Shimadzu Thermal Analyzer and determination of the concentration of metal ions using ICP-OES instrument.

2.1. Chemical modification of Chitosan

2.1.1. Modification with aldehydes

Chitosan (0.5 g) was suspended in the least amount of distilled water for 1 h. Few drops of acetic acid were added and sonicated for a further 2 h until complete solubility was obtained. The aldehyde (0.5 g) was added drop-wise while stirring. The

mixture was stirred for a further 3 h. A pale yellow material was formed and separated by filtration. The obtained product has been dried in vacuum at 40 $^{\circ}$ C for 24 h.

2.1.2. Modification with acids

CS (0.5 g) was suspended in the least amount of distilled water for 1 h. Few drops of acetic acid was added and sonicated for a further 2 h until homogeneity was obtained. About 2 ml of acetic anhydride was dropwise added while stirring and the reaction mixture was stirred for a further 30 min. The reaction mixture was heated for 1 h and then an aqueous sodium hydroxide solution was added carefully after cooling to adjust the medium at pH ~ 8.5. The formed pale yellow material was filtered off and dried in vacuum at 40 °C for 24 h.

2.2. Preparation of the Chitosan blends

A solution of Chitosan (0.5 g) was prepared as mentioned and about 1 g of the carbohydrate material was dissolved – or suspended in the case of starch – in distilled water and dropwise added while stirring. The reaction mixture was stirred for a further 30 min at room temperature, then poured carefully on a flat surface and left for drying at ambient temperature. The obtained product has been collected and dried in vacuum for 24 h at 40 °C. Glucose, maltose and starch were used as representatives for monosaccharides, disaccharides and polysaccharides, respectively.

2.3. Crosslinking of Chitosan derivatives

Modified Chitosan products were crosslinked by adding glutaraldehyde to the swollen Chitosan derivative in water followed by stirring for 15 min. The products were isolated by decantation of all water-soluble and liquid materials and were dried at 40 °C in a vacuum oven for 24 h. Download English Version:

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