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ORIGINAL ARTICLE

Chemical modification of Chitosan for metal ion removal

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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.

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; 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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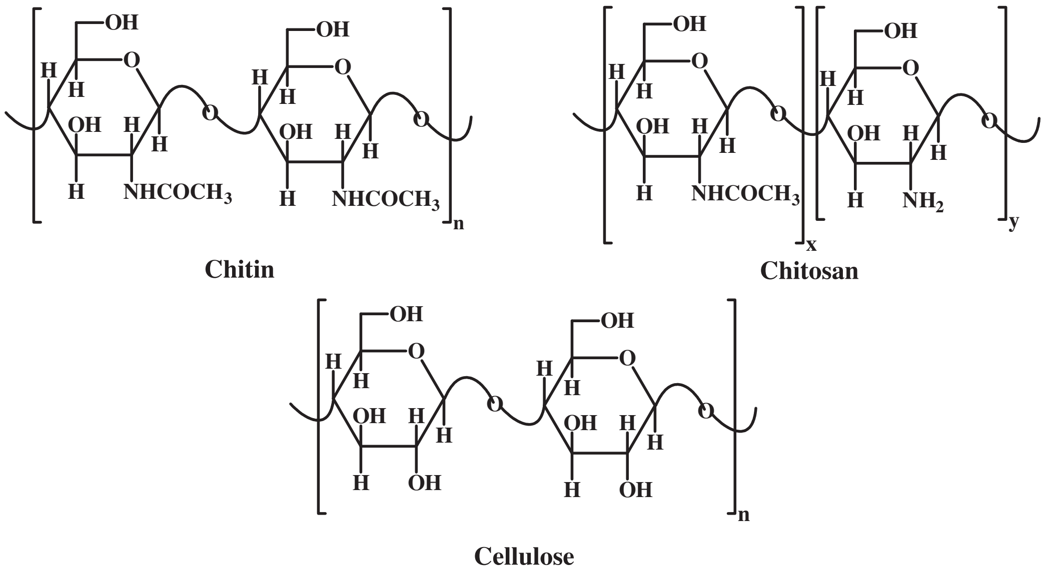


Figure 1 Chemical structure of cellulose, Chitin and Chitosan.

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 °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.

Table 1 Water uptake of the uncrosslinked and crosslinked Chitosan derivatives.

	Chitosan	Benzaldehyde	Salicylaldehyde	Cinnamaldehyde	Glucose	Maltose	Starch
Uncrosslinked	178	132	146	128	216	228	195
Crosslinked	156	114	120	113	186	193	172

2.4. Characterization of the modified Chitosan

Modified Chitosan derivatives were characterized by using FT-IR spectroscopic analysis. Besides, salicylaldehyde-modified Chitosan was reacted with $FeCl_3$ solution to test the presence of phenolic hydroxy group in the aldehyde residue. Unsaturation in the case of cinnamaldehyde-modified Chitosan was tested by using both bromine water and $KMnO_4$ solutions. Molisch's and iodine tests were applied for the carbohydrate- and starch-modified Chitosan, respectively.

2.5. Determination of water uptake of Chitosan derivatives

A sample of 0.5 g of Chitosan derivative was immersed in distilled water at 37 °C for 72 h. The weight of the swollen samples was determined after removal of the surface liquid with lint-free tissue paper. The water uptake was then calculated according to the following Eq. (1) and the results obtained have been summarized in Table 1.

$$W_u = [(W_f - W_o)/W_o] \times 100 \tag{1}$$

where W_u, W_f and W_o are water uptake, final weight and initial weight of the sample, respectively.

2.6. Treatment of the modified Chitosan with solutions of metal ions

A sample of 0.1 g of Chitosan derivative was treated with 50 ml of 0.1 M $FeCl_3$ and $CuSO_4$ solutions, separately. The metal ion concentration has been determined before and after the treatment using ICP-OES. The difference in the amount of metal ion was considered as a function of the metal ion uptake of the investigated derivative. Eq. (2) was used to calculate the polymer capacity in mg/g polymer and the results obtained are summarized in Table 2.

$$C = W_a/W_p \tag{2}$$

where C is the polymer capacity of metal ion in mg/g, W_a is the absorbed amount of metal ion in mg, and W_p is the weight of blend in grams.

Table 2 The capacity "C" of the crosslinked and uncrosslinked Chitosan derivatives using $FeCl_3$ and $CuSO_4$ solutions.

Polymer	Uncrosslinked		Crosslinked	
	$FeCl_3$	$CuSO_4$	$FeCl_3$	$CuSO_4$
Salicylaldehyde	22.9	24.6	20.5	23.2
Cinnamaldehyde	16.8	19.2	15.5	18.9
Benzaldehyde	16.1	16.7	15.6	15.8
Acetyl	13.4	15.6	13.2	14.9
Carbohydrate	11.7	15.2	12.6	16.6

3. Results and discussion

3.1. Characterization of the aldehyde-modified Chitosan

The aldehyde-modified Chitosan derivatives have been characterized by using both chemical and spectroscopic techniques. Chemical tests proved the modification of Chitosan with the concerned aldehydes in the case of using salicylaldehyde and cinnamaldehyde. Salicylaldehyde-modified Chitosan showed positive phenolic hydroxyl group test when reacted with ferric chloride solution while cinnamaldehyde-modified Chitosan showed positive unsaturation test when reacted with both bromine water and potassium permanganate solutions where the color has been discharged in both the cases. Also all the aromatic aldehyde-modified Chitosan showed a smoky flame when burnt due to the aromatic residues in the aldehyde moiety.

FT-IR spectroscopy was used for characterization to elucidate the changes that occur in the chemical structure. FT-IR spectrum of the obtained products showed the characteristic absorptions of Chitosan at 1089 cm^{-1} for C–O–C bonds, 1559 cm^{-1} for free NH_2 groups and 1658 cm^{-1} for the residual acetamido groups that remain after deacetylation of Chitin during the production process of Chitosan. In addition, there is absorption at 2938 cm^{-1} attributed to C–H bonding. In addition to the absorption related to the modifying residues, absorption at 1620 cm^{-1} and 3150 cm^{-1} is shown for the aromatic moiety and phenolic hydroxyl group, respectively, in case of salicylaldehyde. Also absorption at 1600 cm^{-1} was observed for the olefinic double bonds in case of cinnamaldehyde-modified Chitosan (Fig. 2).

3.2. Characterization of the acid-modified Chitosan

Chitosan has been re-acetylated by chemical modification with acetic anhydride and has been characterized by using FT-IR spectroscopic analysis. It showed no big difference from the original Chitosan used in the chemical modification due to almost similar functional groups in both. However, there are some important differences between Chitosan and its re-acetylated derivative such as the ability to absorb water and to uptake ions of heavy metals. Hence, characterization of the product may help in proving the achievement of the modification.

Conversion of Chitin into Chitosan enhances the solubility in slightly acidic aqueous solutions due to the regeneration of free amino groups during the hydrolysis process of Chitin. Besides, flexibility of the chains will be obviously enhanced. It contributes mainly in the gel forming nature of Chitosan opposite to Chitin, which has slight attractive forces for water to diffuse into the polymer matrix and hence a lower ability to uptake water and consequently to absorb ions of heavy metals. However, re-acetylation of Chitosan affects mainly hydrophilicity of the matrix and availability of the free amino groups to take part in the chelation process with different metal ions due to site separation.

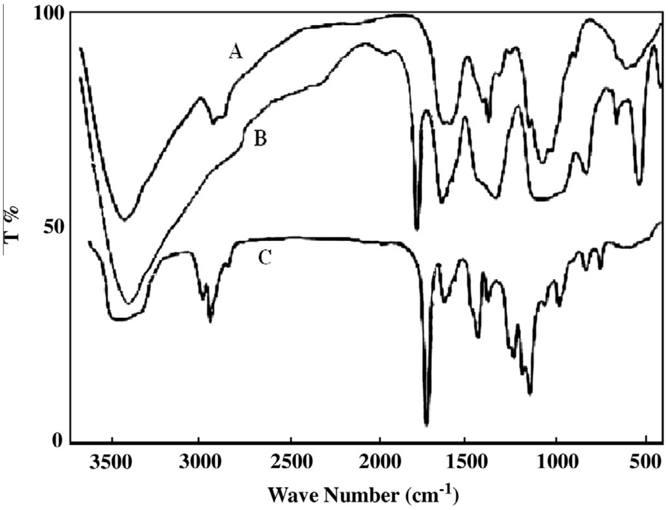


Figure 2 FTIR spectra of (A) Chitosan, (B) salicylaldehyde modified Chitosan and (C) cinnamaldehyde modified Chitosan.

3.3. Characterization of the blended Chitosans

Blended Chitosan has been characterized by using both chemical and spectroscopic ways. Carbohydrate-modified Chitosan showed positive Molisch's test and gave violet color with iodine in the case of starch-modified Chitosan. Also, Chitosan showed different colors after blending with different carbohydrates. FT-IR spectroscopic analysis showed the absorption characteristic for Chitosan as previously mentioned above beside the absorption related to the carbohydrate included in the blend.

3.4. Characterization of crosslinked Chitosans

Crosslinked Chitosan derivatives have been characterized by FT-IR spectroscopy where all samples showed an absorption similar to those without crosslinking. However, there are some differences between the crosslinked Chitosan derivatives and the non-crosslinked ones in the light of resolution of the absorption bands and the higher noisy in the base line of the spectrum in case of the crosslinked products resulted in variable environment around the functional groups. On the other hand, the chemical tests used for characterization of non-crosslinked products showed similar results. Also, it is noticeable that the crosslinked products showed lower solubility represented by the higher gelation percent in addition to the color changes due to the presence of C=N bond formed during crosslinking (Schiffman and Schauer, 2007).

3.5. Determination of water uptake of modified Chitosan derivatives

Water uptake of the crosslinked Chitosan derivatives was determined at 37 °C after equilibration in distilled water. The preliminary tests lead to the equilibrium time required for complete swelling and was shorter than 60 h. Therefore, the experiments were carried out considering the water uptake cal-

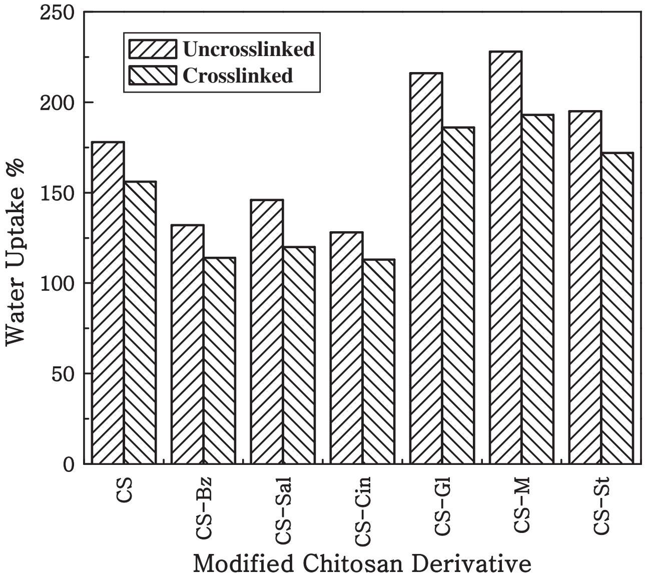


Figure 3 Water uptake of the uncrosslinked and crosslinked Chitosan derivatives.

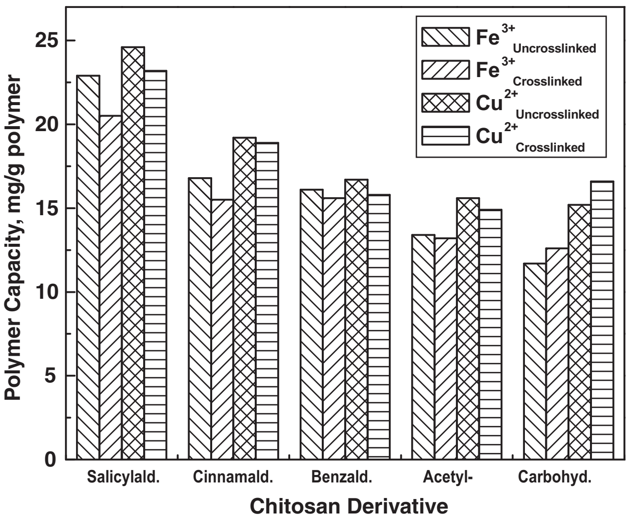
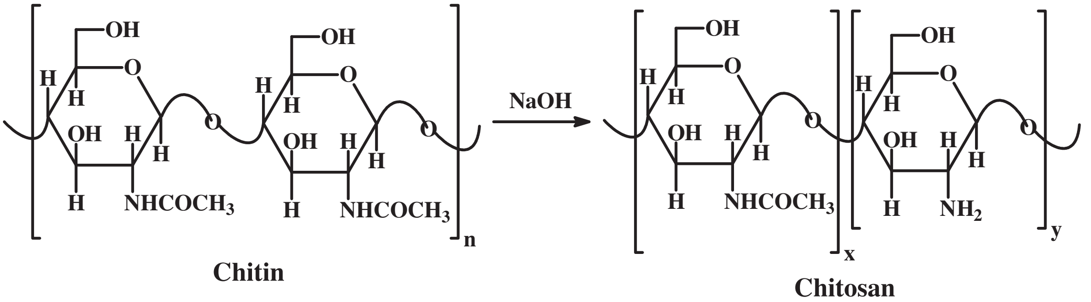


Figure 4 Polymer capacity of modified Chitosan derivatives of $FeCl_3$ and $CuSO_4$.



Scheme 1 Chemical modification of Chitin into Chitosan.

culation after equilibration in distilled water for 72 h. The weight of swollen samples was determined after removal of the surface liquid with lint-free tissue paper. Water uptake was then calculated according to the following Eq. (1):

$$W_u = [(W_f - W_o)/W_o] \times 100 \quad (1)$$

where, W_u, W_f and W_o are water uptake, final weight and initial weight of the sample, respectively.

From the results shown in Table 1 and represented in Fig. 3 there is an obvious difference between Chitosan before and after the modification where the water uptake decreased by chemical modification from 178% to 156%, which is close to the previously cited value (Mohy Eldin et al., 2008). Among the modified Chitosan derivatives, salicylaldehyde-modified Chitosan showed the highest one (146%) while the benzaldehyde- and cinnamaldehyde- modified Chitosans were lower in water uptake (132% and 128%, respectively) and relatively similar especially after crosslinking (114% and 113%, respectively).

On the other hand, carbohydrate blended Chitosan showed higher water uptake than Chitos3an. This can be attributed to the more hydrophilic nature of carbohydrate residues in comparison with the modifying aldehydes. It was difficult for the uncrosslinked Chitosans to determine the water uptake in a similar way due to the gel nature of the water-treated products. Most of the factors affecting the equilibrium swelling properties represented here as water uptake are related to mobility restriction of chains between crosslinks and the polymer composition (Kossmehl et al., 1994).

3.6. Treatment of modified Chitosans with solution of metal ions

The Chitosan derivatives have been investigated to be used for metal ion uptake applications using $FeCl_3$ and $CuSO_4$ aqueous solutions as representative examples for metal ions. The polymer capacity in mg/g shown in Table 2 and Fig. 4 was determined by Eq. (2) and considered as a characteristic for the polymer efficiency for metal ion uptake process for both crosslinked and uncrosslinked derivatives. Table 2 shows remarkably that crosslinked derivatives are of higher capacity than the uncrosslinked ones. This can be attributed to the ease of diffusion of metal ions into the aqueous phase, which is more favored in the uncrosslinked derivatives due to their relatively higher swelling ability in aqueous media (Scheme 1).

It is also noticeable that all the modified Chitosan products showed good ability to uptake metal ions from their aqueous solutions. The modified Chitosan with aldehydes showed better metal ion uptake while carbohydrate modified Chitosan showed lower capacity. This may be due to the higher ability of carbohydrate to be leached out of the Chitosan matrix as a result of its higher solubility in water.

On the other hand, crosslinking of Chitosan derivatives reflected in obvious decrease in such capacity as the solubility and swelling ability of the derivatives of Chitosan decrease. This behavior can be attributed to the chain mobility restrictions caused by crosslinking and hence the limited swelling ability of the Chitosan derivative matrices in water. This holds true for the Chitosan derivatives chemically modified with aldehydes and carboxylic acid. In case of carbohydrate modified Chitosan derivatives, the polymer capacity of the metal ions increases by crosslinking. This can be explained by the fact that the crosslinking process hinders the chain mobility and consequently the matrix swelling ability. Therefore, the blended carbohydrate moieties are no longer able to leach out the matrix and still play its role in the metal ion uptake process. This leads to a higher polymer capacity after crosslinking than that before crosslinking.

Some investigators report opposite observations when they use W_p in Eq. (2) as the weight of the polymer sample after the uptake experiment in which W_p will be smaller leading to misleading results as the effective mass of the polymer is quite different in the two cases.

4. Conclusion and recommendations

From the current study, it can be concluded that the chemical modification of Chitosan with the different organic compounds and polymeric materials can lead to promising materials in the light of their application directions. These conclusions can be summarized in the following points:

- Chemical modification of Chitosan is available and easy to perform after considering its special conditions while conducting the experiments.
- The aldehyde-modified Chitosan can be used in the metal ion uptake application exemplified by waste water treatment.
- Crosslinking of chemically modified Chitosan derivatives decreases the ability of the derivatives to uptake metal ions.
- Carbohydrate-modified Chitosan showed good metal ion uptake in both crosslinked and uncrosslinked forms.

- Crosslinked carbohydrate-modified Chitosan is preferable in the metal uptake process over the uncrosslinked ones as the later leach some carbohydrate into the medium causing contamination.

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