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Synthesis and Characterization of Modified Chitosan Through Immobilization of Complexing Agents

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Summary: The complexation agents 2[-bis-(pyridylmethyl)aminomethyl]-4-methyl-6-formyl-phenol (BPMAMFF) and 2-[2-(hydroxybenzyl)-2-(pyridylmethyl)aminomethyl]-4-methyl-6-formyl-phenol (HBPAMFF) were immobilized on chitosan biopolymer in order to obtain new adsorbent materials for metal ions. The chitosan derivatives were characterized by IR spectroscopy, DSC, TGA, and CHN analysis. The characterization study proved that the chitosan surface was chemically modified with both complexing agents and however, it is expected that these modifications improve the selectivity for metal ions specific in relation to the chitosan.

Keywords: characterization; chitosan; complexation agents; modification; selectivity

Introduction

Chitosan (CHS) is produced from chitin, one of the most abundant biopolymers in nature, which is obtained from crustacean shells such as crabs, shrimps, and prawns.[1–3] CHS biopolymer has a very diverse range of applications, as in the biomedical field,[4] in cosmetic, food, and textile industries, and in water treatment,[5,6] due mainly to their properties such as biocompatibility, biodegradability, non-toxicity, and adsorption ability, and also to the possibility of structural modification of the polymer matrix.[7]

Chitosan has been well described as an excellent natural adsorbent for metal ions due to the high content of primary amino groups in the chain, which can act as coordination sites[1,8,9] and enable a variety of chemical modifications.[2,10] The modification of the polymer surface through the immobilization of ligands or complexation agents onto CHS matrix may improve their adsorption properties.[10,11]

The theory of hard and soft acids and bases (HSAB), as defined by Pearson, describes the ability of ions to interact or coordinate with ligands of the same kind (soft-soft and hard-hard) and shows that this effect is governed primarily by the charge and size of the metal ion. Therefore, the selectivity for a specific metal ion depends on the complexation agent which is introduced into the polymer chain.[12]

The purpose of this study was to modifiy chemically the CHS biopolymer surface through immobilization of complexation agents 2[-bis-(pyridylmethyl)aminomethyl]-4-methyl-6-formyl-phenol(BPMAMFF)and 2-[2-(hydroxybenzyl)-2-(pyridylmethyl)-aminomethyl]-4-methyl-6-formyl-phenol (HBPAMFF) and to characterize the new adsorbent materials.

Experimental Part

Materials

The CHS with a 90% degree of deacetylation was obtained from Purifarma (Brazil). The BPMAMFF ligand was prepared through the reaction of 2-chloro-methyl-4-methyl-6-(formyl)phenol with bis-(2-pyridylmethyl)amine.[13,14] The HBPAMFF ligand was synthesized through the reaction

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of 2-chloro-methyl-4-methyl-6-(formyl)-phenol with 2-(hydroxybenzyl)-2-(pyridyl-methyl)amine.[15] All other reagents were of analytical grade.

Instrumentation

The elemental analysis (CHN) was carried out using a Carlo Erba model EA 1110 CHNS/O analyzer.

IR spectra were obtained from KBr pellets, using a spectrophotometer with Fourier Transform System, 2000 FT-IR-Perkin Elmer.

DSC and thermogravimetric analysis (TGA) were carried out with a DSC-50 Shimadzu and a TGA-50 Shimadzu, respectively. In DSC analysis, the scanning was carried out within a temperature range of 25–500 °C, with a heating rate of 10 °C · min^{-1}, under a nitrogen atmosphere.

Preparation of Chitosan Derivatives

The CHS was dispersed in methanol in a ratio of 1.5 mol of both BPMAMFF and HBPAMFF ligands per mol of glucosamine, and then the systems were maintained under agitation for 16 h and in reflux for 18 h. Figure 1 shows the structures of the Schiff bases formed in the reactions with CHS; both obtained products, the CHS-BPMAMF and the CHS-HBPAMF, had an intense yellow color. After the reaction, the

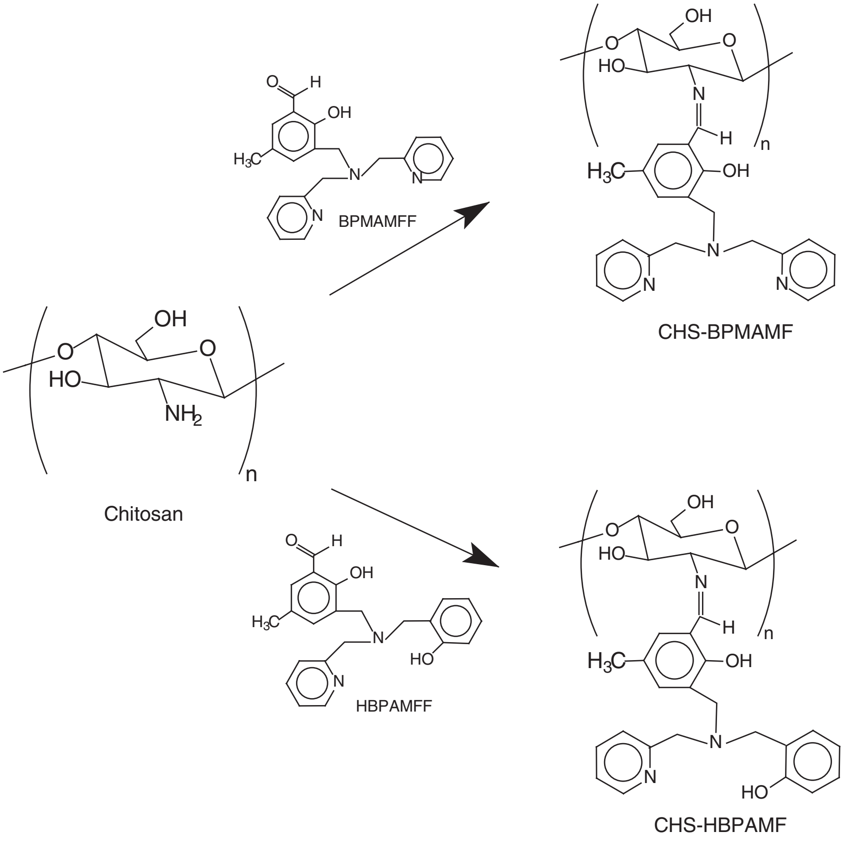

Figure 1.
Structures of chemically modified chitosan with BPMAMFF and HBPAMFF ligands.

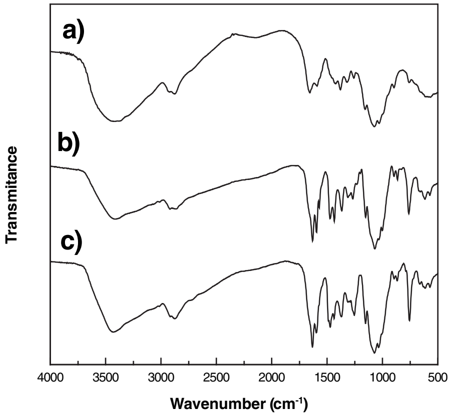

Figure 2.
IR spectra of (a) CHS, (b) CHS-BPMAMF, and (c) CHS-HBPAMF.

new materials were filtered and washed with methanol and distilled water to remove, and then dried in a vacuum.

Results and Discussion

The characterization of the new adsorbent materials was carried out through IR, DSC, TGA, and CHN analysis. The CHS-BPMAMF derivative was also evaluated in a previous work.[16]

IR Analysis

In the IR spectra of CHS (Figure 2) the characteristic vibrational bands for this polymer were observed, at 1 660 cm^{-1} which is attributed to the C=O absorption of the –NHC=O structure, 1 599 cm^{-1} to the NH$_2$ deformation, 1 075 cm^{-1} to the –C–O stretching of primary alcohols, and 3 373 cm^{-1} to the –OH stretching. In IR spectra of the modified CHS (Figure 2) the appearance of bands related to the ligands through comparison with the spectrum of primitive CHS can be observed. The bands located in the region at 900–650 cm^{-1}, as well as characteristics bands at 1 600–1 300 cm^{-1}, indicate that the new polymeric structures had aromatic rings, suggesting the chemical modifications of CHS, whereas these bands are absent in the spectrum of the polymer. The bands observed at 763 and 862 cm^{-1} (CHS-BPMAMF) and at 756 and 867 cm^{-1} (CHS-HBPAMF) correspond to the angular deformation of aromatic C–H, and those at 1 434, 1 469, and 1 595 cm^{-1} (CHS-BPMAMF) and at 1 436, 1 472, and 1 597 cm^{-1} (CHS-HBPAMF) are associated to the C=C stretching of the aromatic rings. At 1 269 cm^{-1} (CHS-BPMAMF) and at 1 254 cm^{-1} (CHS-HBPAMF) bands related to the C–O stretching of the phenol of the ligands are found out, and those at 1 151 cm^{-1} (CHS-BPMAMF) and 1 152 cm^{-1} (CHS-HBPAMF) are attributed to stretching of the C–N bond of the tertiary aliphatic amine. The absence in both IR spectra of modified CHS of a band in the region at 1 680 cm^{-1}, attributed to the carbonyl group of the ligands, such as the appearance of new intense bands at 1 631–1 632 cm^{-1} associated to the stretching of the imine bond C=N formed, proves the chemical modifications of CHS.[17]

Table 1.
CHN analysis of chitosan and derivatives.

	Percentage of composition		
	%		
	C	H	N
CHS	40.30	7.49	7.44
CHS-BPMAMF	60.34	6.36	10.06
CHS-HBPAMF	53.75	6.60	7.74

Elemental Analysis

The CHN composition of CHS and modified CHS is given in Table 1. It was found that the chemical modifications increased the percentage of N and C atoms, due to introduction of the BPMAMFF and HBPAMFF ligands into CHS chain.

The degree of substitution (DS) of the ligands to –NH$_2$ group on CHS was calculated by Equation (1), modified with base in the model of Inukai et al.[18]

$$DS = \frac{(a\mathrm{C/N})_\mathrm{m} - (\mathrm{C/N})_\mathrm{o}}{n} \quad (1)$$

where (C/N)$_\mathrm{m}$ is the C/N of the modified CHS, (C/N)$_\mathrm{o}$ is the C/N of the original CHS, and a and n are the number of nitrogen and carbon introduced after CHS modification, respectively. The DS values obtained were 0.60 for CHS-BPMAMF and 0.39 for CHS-HBPAMF.

Thermal Analysis

DSC curves of CHS, CHS-BPMAMF, and CHS-HBPAMF are shown in Figure 3. CHS exhibits a wide endothermic peak at 103 °C, which is originated from a process of dehydration (due to the water contained in the polymer), and an exothermic peak at 305.4 °C, which can be attributed to the thermal decomposition of the polymer. In the thermogram for CHS-BPMAMF a wide exothermic peak can be seen at 306.6 °C, and the CHS-HBPAMF curve shows a wide endothermic peak at 96.8 °C and an exothermic peak at 309.9 °C. In the curves for modified CHS was observed a shift in the exothermic peaks with relation to the CHS was observed, indicating a small change in thermal behavior of the polymer when the ligands were immobilized in the matrix.

In Figure 4, the TGA thermograms for CHS, CHS-BPMAMF, and CHS-HBPAMF can be observed. The TGA curve for CHS shows thermal degradation at 326.2 °C, with a 66.7% loss in polymer mass. During the degradation of modified CHS, a 27.0% (CHS-BPMAMF) and 52.3% (CHS-HBPAMF) loss of material mass occurs at 334.1 and 332.6 °C, respectively.

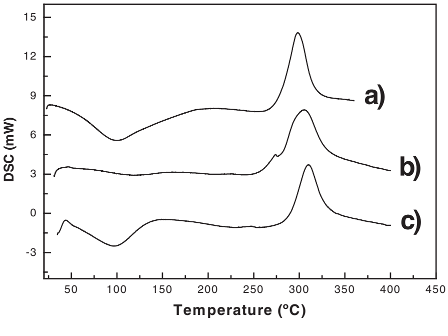

Figure 3.
DSC thermograms for (a) CHS, (b) CHS-BPMAMF, and (c) CHS-HBPAMF.

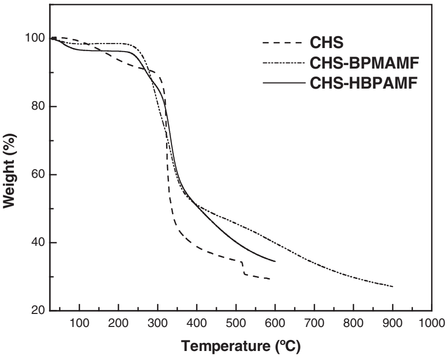

Figure 4.
TGA curves for CHS, CHS-BPMAMF, and CHS-HBPAMF.

From these results, it can be observed that these degradation temperatures were higher than that for CHS. This increase in the thermal stability can be attributed to the presence of imine groups along with the phenolic aromatic rings in both modifications, resulting in rigid structures. Similar effects on thermal stability were also observed for aromatic polymer containing fluorine-polybenzoxazoles in a rigid structure when compared to the polymer containing aliphatic hexafluoroisopropylidene group in the study carried out by Lee and Kim,[19] and for modified CHS with salicylaldehyde and benzoic acid in the study carried out by Cárdenas et al.,[20] where there are also the Schiff base formation and the observation that these compounds are more stable than amides and alkyl amines. This study suggests that the thermal stability of the polymer is influenced by the kind of bond between the CHS and the reactants.

Conclusion

The characterization studies carried out through IR, thermal, and elemental analysis proved the chemical modifications of CHS by immobilization of the complexing agents at the polymer surface. However, it is expected that the modifications improve the characteristics of the polymer as adsorbent for metal ions, such as selectivity and adsorption capacity, and according to the theory of Pearson, it is also expected that the CHS-BPMAMF derivative presents higher adsorption affinity to divalent metal ions and the CHS-HBPAMF derivative to trivalent metal ions.

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