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Preparation and characterization of a novel xanthated chitosan

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Abstract

A novel xanthated chitosan derivative was prepared by the chemical reaction of CS_2 under alkaline conditions. Spectroscopic studies like FTIR, ^{13}C NMR, TGA and XRD, SEM, and EPR were used for its characterisation. The chemically modified chitosan (CMC) was evaluated for its adsorption properties for Cr(VI). For a 100 mg/L solution of Cr(VI), the uptake of Cr(VI) by CMC at pH 3, was found to be much enhanced (71 mg/L) compared to the control chitosan (49 mg/L). The CMC can be a potential adsorbent for tannery wastewater treatment.

Keywords: Chitosan; Cross-linked; Glutaraldehyde; Xanthation

1. Introduction

Chitosan is a natural, cationic aminopolysaccharide copolymer of glucosamine and *N*-acetylglucosamine, obtained by the alkaline, partial deacetylation of chitin, which originates from shells of crustaceans such as crabs and prawns (Muzzarelli, 1977). Chitosan is a non-toxic, hydrophilic, biodegradable, biocompatible, mucoadhesive, and anti-bacterial, biopolymer which has led to a very diverse range of its applications (Lehr, Bouwstra, Schacht, & Junginger, 1992). It has attracted tremendous attention as novel functional materials and potentially important renewable agricultural resource, and has been widely applied in the fields of agriculture, medicine, pharmaceuticals, cosmetic, and food industries, environmental protection, and biotechnology in the last 20 years (Kurita, 1998). The presence of a large number of amine groups on the chitosan chain increases the adsorption capacity of chitosan (Evans, Davids, MacRae, & Amirbahman, 2002; Lu, Yao, Wu, & Zhan, 2001; Wu, Tseng, & Juang, 2000).

Several methods have been used to modify raw chitosan flake either physical or chemical modifications (Guibal, Dambies, Milot, & Roussy, 1999; Yang, Zhuang, & Tan, 2002). Physical modifications (Onsoyen & Skaugrud, 1990) may increase the sorption properties: gel formation decreases the crystallinity of the sorbent and involves an expansion of the porous network. Chemical modifications also offer a wide spectrum of tools to enhance the sorption properties of chitosan for metals. Both hydroxyl and amine groups of chitosan can be chemically modified. They may increase the chemical stability of the sorbent in acid media and, especially, decrease the solubility in most mineral and organic acids. They also increase its resistance to biochemical and microbiological degradation (Guibal et al., 1999; Yang & Yuan, 2001). Cross-linking on chitosan is a convenient and effective way on improving its physical and mechanical properties for practical usages. Various reagents, including glutaraldehyde (Goissis et al., 1999; Guibal, Milot, & Tobin, 1998; Hsien & Rorrer, 1997), sulfuric acid (Huang, Pal, & Moon, 1999), epoxy compound (Wei, Hudson, Mayer, & Kaplan, 1992), and dialdehyde starch (Schmidt & Baier, 2000) etc. have been used as cross-linking agents for chitosan. Glutaraldehyde has been frequently used to cross-link chitosan and to stabilize it in acidic solutions whereby the reaction occurs through a

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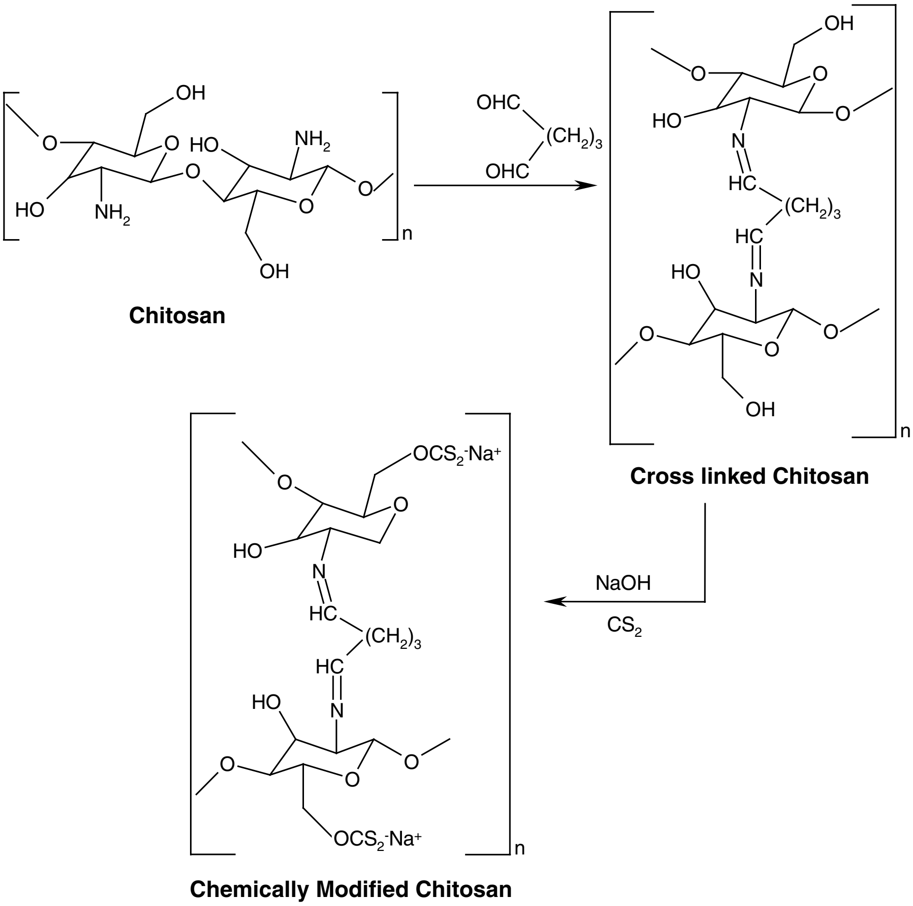
Schiff's base reaction between aldehyde groups of glutaraldehyde and some amine groups of chitosan. Although cross-linking may reduce the adsorption capacity, it enhances the resistance of chitosan against acid, alkali and chemicals. The chemically modified chitosan has a bright future and their development is practically boundless. For a breakthrough in utilization, chemical modification to introduce a variety of functional groups is a key point. For this purpose, more fundamental studies on chemical modification will be required. Although the chemical modification of cellulose is well studied and is still an active field, not much work has been reported on the chemical modification of chitin and chitosan.

Carbon dioxide and carbon disulfide have been utilized for polymer synthesis, both by their direct (co)polymerizations and polymerizations of monomers synthesized from them. Carbon disulfide, which also exists in the troposphere, has long been used as a sulfur source in organic chemistry and a solvent for various polymers, such as cellulose in industrial processes. Carbon disulfide finds use as a starting material for a variety of useful chemicals for agricultural, medicinal, and pharmaceutical applications. Sulfur compounds are very efficient at chelating metals and especially precious metals, according to Hard and Soft acid theory used by Pearson for the prediction of complexation reactions (Chanda & Rempel, 1990). Introducing sulfur chelating moieties gives a dual structure to the polymer: chelating and ion exchange capability. Since sulphur has a very strong affinity for most heavy metals, the metal–sulphur complex is very stable in basic conditions. Sorbents with donor N and more especially S atoms in their functional groups are thus performing resins. Muzzarelli and Tanfani produced dithiocarbamate chitosan by reaction of chitosan with carbon disulfide (Muzzarelli & Tanfani, 1982). Xanthation of carbohydrate materials, particularly starch, has been reported to assist removal of metals from aqueous solutions (Lokesh & Tare, 1989; Tare & Chaudhari, 1987). The xanthated rice straw was first used for removal of iron, copper, and chromium from synthetic and electroplating industry waste (Changgeng, 1991). The characterization of xanthated straw and the mechanism(s) of heavy metal removal (Kumar, Rao, & Kaul, 2000) have been studied. In this paper, sulphur groups were introduced onto glutaraldehyde cross-linked chitosan through a chemical reaction, and its characteristics of chromium adsorption were compared to that of control chitosan.

The chemical structure and physical properties of chitosan derivatives were characterized by FTIR, ^{13}C NMR, TGA, and XRD. SEM-EDAX techniques were also used to characterize chemical modifications of the sorbent.



Scheme 1. Xanthation of chemically modified chitosan.

2. Materials and methods

2.1. Materials

The sample of pure chitosan (Sigma) from crab shells was used; the degree of deacetylation was 85%. Chitosan was ground to fine powders (>140 mesh) and dried under vacuum at room temperature. Glutaraldehyde and carbondisulfide were purchased from Sigma–Aldrich and used without further purification. Potassium chromate (BDH chemicals), sodium hydroxide (BDH chemicals) and hydrochloric acid (merck) were used. All the inorganic chemicals used were of analytical grade. All the reagents were prepared in Millipore milli-Q deionised water.

2.2. Analysis

Infra red (IR) spectra were recorded on a Perkin-Elmer infra red spectrophotometer using KBr pellets. X-ray diffraction (XRD) was carried out on Isodebeyxlex 2002 X-ray powder diffractometer and thermal gravimetric analysis (TGA) was carried out on Perkin-Elmer TGA-7 at a heating rate of 10 °C per min under nitrogen atmosphere. scanning electron microscopy (SEM) was done on EDAX, FEI Quanta 200 machine.

Dissolved Cr(VI) was determined by the spectrophotometric method at 540 nm using diphenyl carbazide method (APHA) after suitable dilutions. Total chromium concentrations in solution were assessed by Aanalyst 400 Perkin-Elmer Atomic Absorption Spectrophotometer. The measurements were done at wavelength 357.9 nm with a slit width of 0.7 nm using air-acetylene flame. Experimental samples were filtered using Whatman 0.45 mm filter paper and the filtrates were analyzed after suitable dilutions.

2.3. Preparation of chitosan beads

Chitosan gel beads were prepared by the method reported by Guibal et al. (1998). Chitosan was dissolved in acetic acid (4%, w/w) solution at a final concentration of 4% (w/w). The viscous solution was dropped into an alkaline sodium hydroxide solution (2 M) through a dropper (2.0 mm, internal diameter), the beads were collected after 16 h in the coagulating bath (NaOH) and then rinsed with demineralized water until pH no longer varied. The diameter of the beads was 4–5 mm and the water content was ~95%.

2.4. Chemical modification of the chitosan beads

Glutaraldehyde was used as cross-linking agent in this study. Cross-linked chitosan beads (CLC) were prepared as described earlier (Becker, Schlaak, & Strasdeit, 2000). Methanol wet beads (ca. 56 g, 12 mmol of monomeric units) were suspended in methanol (100 ml), and a 25% aqueous glutaraldehyde solution (0.46 ml, 1.2 mmol) was added. After stirring at room temperature for 6 h, the product was filtered and extensively rinsed with distilled water.

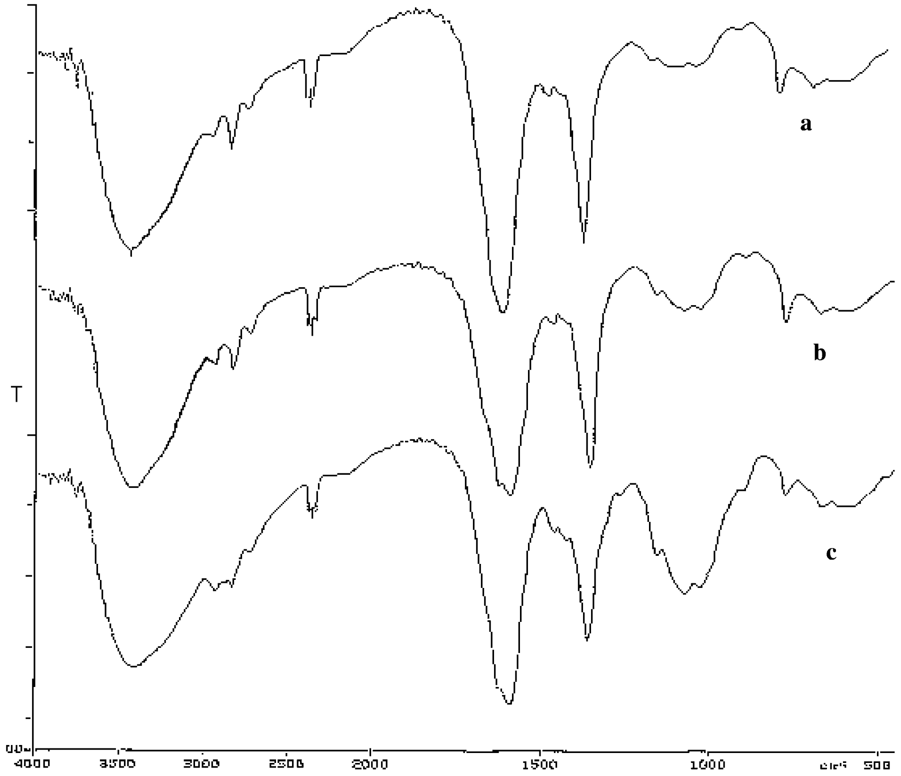


Fig. 1. IR of (a) chitosan, (b) CLC, and (c) CMC.

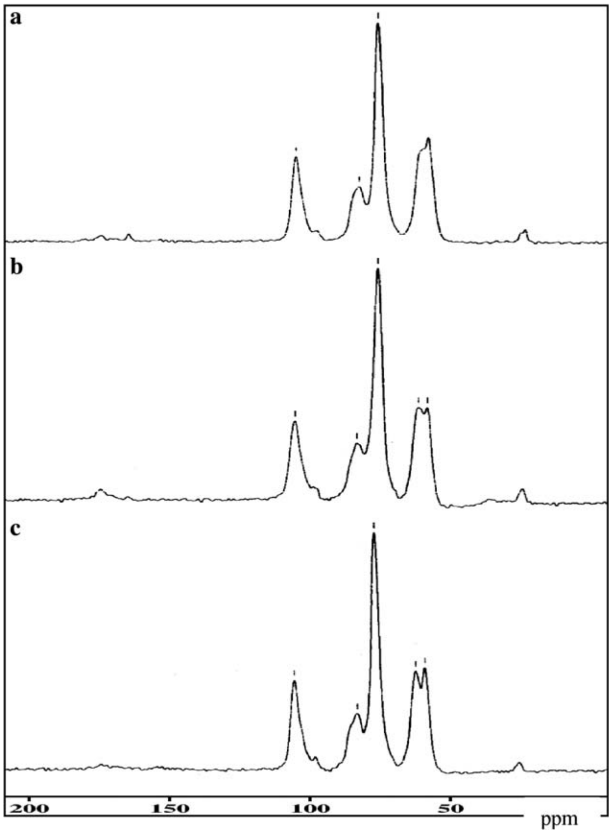


Fig. 2. ^{13}C spectrum of (a) chitosan, (b) CLC, and (c) CMC.

Procedure reported by Hirano, Usutani, and Midorikawa (1997) was followed for the preparation of chemically modified chitosan (Scheme 1). CLC beads (5 g) were treated with 25 ml of 14% NaOH and 1 ml CS_2 and the mixture was stirred at room temperature for 24 h. The obtained orange product, cross-linked chemically modified chitosan beads (CMC) were washed thoroughly with water and stored in methanol and used for further experiments.

3. Results and discussion

3.1. Characterization of CMC with respect to chitosan and CLC

3.1.1. IR

Fig. 1a shows the basic characteristics of chitosan at: 3429 cm^{-1} (O–H stretch), 2828 cm^{-1} (C–H stretch), 1596 cm^{-1} (N–H bend), 1154 cm^{-1} (bridge-O-stretch), and 1081 cm^{-1} (C–O stretch) (Brugnerotto et al., 2001; Shigemasa, Matsuura, Sashiwa, & Saimoto, 1996). The IR spectrum of the chitosan showed strong peaks at 1030, 1076, and 1261 cm^{-1}, characteristic peaks of a saccharide structure (due to O–H bending, C–O stretching, and C–N stretching). The strong peak around 3429 cm^{-1} could be assigned to the axial stretching vibration of O–H superimposed to the N–H stretching band, and inter hydrogen bonds of the polysaccharide. The strong peaks in the range 3400–3200 cm^{-1} correspond to combined peaks of hydroxyl and intramolecular hydrogen bonding. Primary amines also show sharp absorption at 3500 and 3400 cm^{-1} arising from the asymmetric and symmetric stretching of 2 N···H bonds, but the peaks appear broad here due to the contributed peaks of O···H stretching and hydrogen bonds. The C···H stretching vibration of the polymer backbone is manifested through strong peak at 2828 cm^{-1}. Acetyl groups absorb in the range 1300–1100 cm^{-1}, as seen in Fig. 1. The peaks in the fingerprint region of the spectrum are given by ethereal bonds, where the symmetric stretch of C···O···C is found around 1010–1040 cm^{-1}. For cross-linked chitosan (Fig. 1b) an additional peak at 1624 cm^{-1} can be observed, which corresponded to stretching vibrations of C=N bond. This peak indicated the formation of Schiff's base as a result of the reaction between carbonyl group of glutaraldehyde and amine group of chitosan chains.

Due to the chemical modification of chitosan new bands (Fig. 1c) are observed at 1450, 1605, 1210, and 590 cm^{-1}.

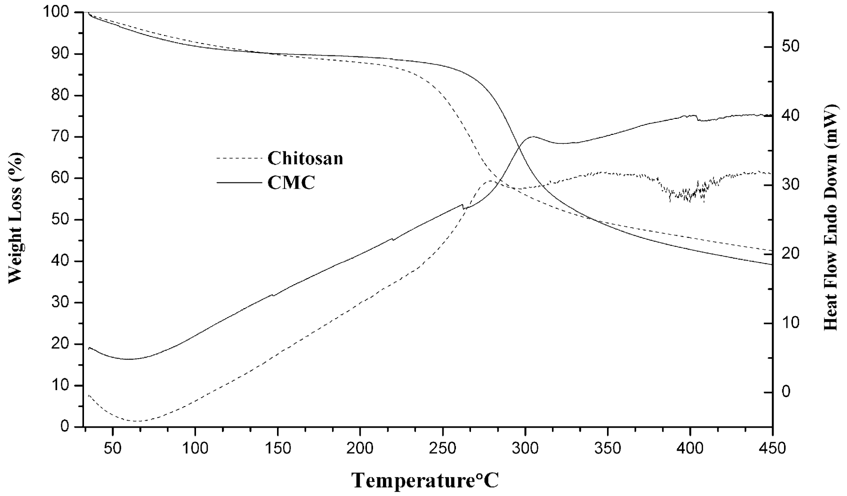


Fig. 3. TGA and DSC of chitosan and CMC.

The major absorption bands characteristic of the xanthate polar groups lie in the region 800–1200 cm^{-1}. Clearly, this region is much more intense for CMC compared to chitosan. The CMC exhibited peaks attributed to $\nu c = s$ at 1010. The peaks for C–S–S and C–O–C symmetric stretching seem to have merged into a broad band at 1073 cm^{-1}. The asymmetric stretching vibration of C–O–C is observed at 1210 cm^{-1}. The very weak vibration for C–S is also observed around 605 cm^{-1}.

3.1.2. ^{13}C NMR spectrum

Liquid-state ^{13}C NMR spectrometry may offer higher resolution and more structural detail than solid-state ^{13}C NMR spectrometry. But this technique may modify the interactions between the polymer and the metal ions. The solid-state method is thus preferable. Moreover, the spectra appear as smooth, unsharpened curves. The analysis of the ^{13}C NMR spectrum (Fig. 2) of chitosan, in solid state spectrometry shows that peaks at 57.9, 61.2, 75.6, 83.3, and 83.5 ppm are attributed to C_2, C_6, C_3, C_5, and C_4, respectively of the pyranose cycle (Domard, Gey, Rinaudo, & Terrassin, 1987) and the anomeric carbons of the *N*-acetyl-D-glucosamine unit are located at 97.3 and 98.2 ppm, respectively.

While several signals, such as C-1 (105.2 ppm), C-2 (57.9 ppm), C-6 (61.1 ppm), are well defined, other signals are controversial and more difficult to interpret. A well defined signal is observed at 75.6 ppm, which could be assigned to C-3. But a large band appears between 87 and 80 ppm, this band can be attributed to the overlapping of the C-4 and C-5 signals. The C-4 signal is usually reported at 79–84 ppm. The broad signal suggests the co-existence of two conformations for chitosan.

Although the differences for the modifications induced by the grafting and modification of chitosan are quite low but are significant enough to deduce the carbon involved in the substitution. Signals are observed at 23.5 and 173.9 ppm, commonly attributed to acetyl groups in the non-deacetylated fraction of chitosan. These signals are assigned to the –CHs and the –C=O of acetyl groups, respectively. Acetyl groups not involved in the grafting step are still present around their original locations: 23.8 and 174 ppm. The C-3 signal is still unchanged at 75.6 ppm whereas the intensity of the C-6 signal which occurs at 60.8 ppm is much increased showing that the xanthation occurred at C-6 rather then at C-3. C-2 signal intensity is significantly reduced and a downfield shift is observed from

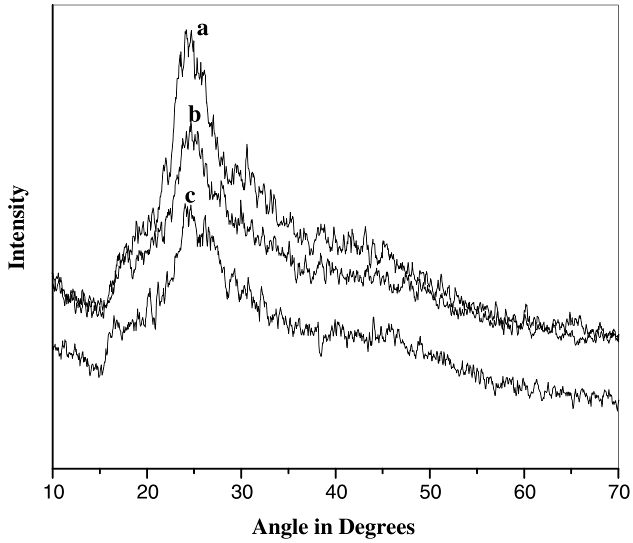


Fig. 4. XRD of (a) chitosan, (b) CLC, and (c) CMC.

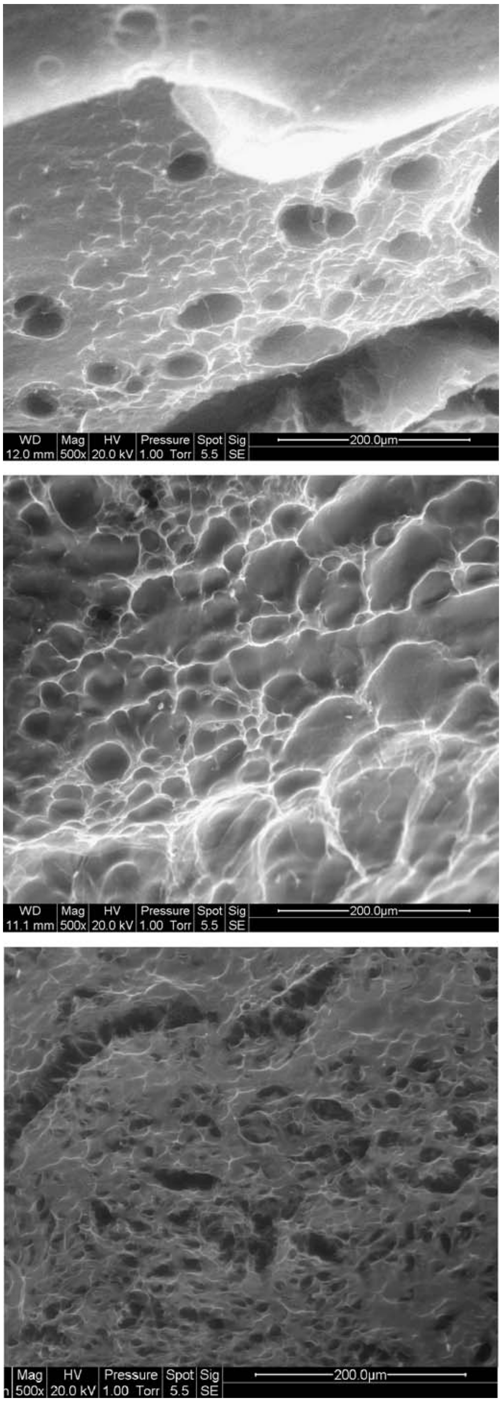


Fig. 5. SEM of chitosan, CLC, and CMC.

57.4 to 55.1 ppm. At the same time C-2′ (substituted form) appears by superposition or juxtaposition near the C-6 signal (61.8 ppm). The mixed C-4 and C-5 band appears reduced and undefined between 85 and 80 ppm. The C-l band seems to be unchanged at around 105 ppm. Such observations would indicate that substitution occurs without significant depolymerization.

3.1.3. TGA

The thermal stability and degradation behavior of chitosan, CLC, and CMC were evaluated by TGA under nitrogen atmosphere. From the TGA and DTG curves shown in Fig. 3, the differences between the samples can be noted (graph for CLC is not shown in the figure). Chitosan, CLC, and CMC degrade in two stages. The first stage begins at about 100 °C for all the materials with weight loss of 5–10% due to loss of residual or physically adsorbed water on membranes surfaces. The second stage exhibited a rapid weight loss at 160–450 °C reaching a maximum at 235 °C for chitosan, 256 °C for CLC and 268 °C for CMC. The second degradation stage of CMC and CLC takes place at higher temperatures than the corresponding stage of the chitosan indicating that chitosan is less stable than CMC or CLC. The weight loss for chitosan (162–360 °C), CLC (190–425 °C), CMC (197–443 °C) was 40%, 45%, and 50%, respectively. The DTG curves reveal interesting and more accurate differences of the thermal behavior of the chitosan and CMC than the TGA curves. The DTG peak of CMC presents its maximum value at about 305 °C, while the maximum value of this peak for chitosan curve is observed at about 278 °C showing the increase in the thermal stability of the CMC over chitosan.

3.1.4. XRD

X-ray diffraction profiles of chitosan and its graft copolymer are shown in Fig. 4. The strongest reflection appears at $2\theta = 22°$, which correspond to crystal forms II (Dung, Rinaudo, & Desbriers, 1994). Compared with chitosan, CLC shows a less intense peak at 2θ. For CMC this peak further broadens showing a decrease in the crystallinity of the substituted chitosan. Introduction of substituents into polysaccharide structures should disrupt the crystalline structure of chitosan, especially by the loss of the hydrogen bonding. The crystallinity of chitosan polymer could play a restrictive role on metal sorption capacity. The crystallinity parameter of chitosan is a key-parameter in the accessibility to internal sites for both water and metal ions. Many studies have shown that decreasing the crystallinity results in an improvement in metal ion sorption properties (Kurita, Sannan, & Iwakura, 1979).

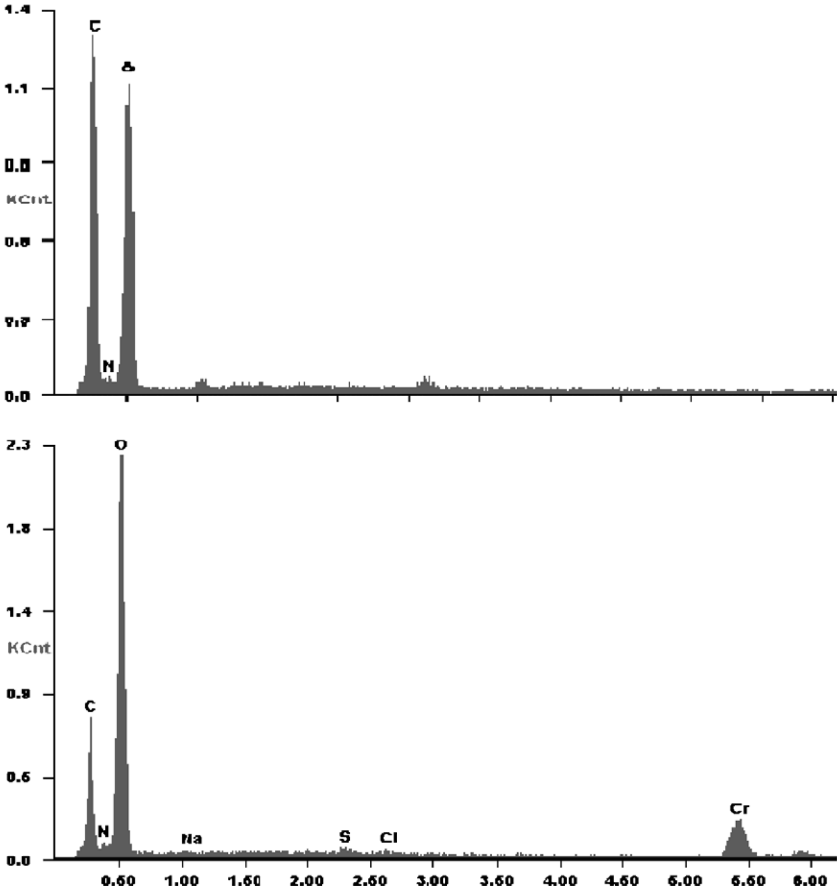


Fig. 6. EDX spectrum of chitosan and CMC.

3.1.5. SEM

The surface morphology of chitosan characterized by ESEM indicates a microporous and fibrous structure. Cross-linking considerably modifies chitosan morphology, and also its physical, chemical and biodegradable characteristics, which varies with respect to the nature of the synthetic side chains incorporated. SEM observations (Fig. 5) of CLC revealed microvoids in the form of honeycomb as well as fingerlike macrovoids. The fibrous nature of chitosan was totally modified when it was chemically modified, wherein distinct morphological differences were discernible in the surface topography. CMC showed apparently isolated and irregularly distributed pores, which are supposed to be formed due to the increase of effective diffusion surface area derived from pore formation.

3.1.6. EDX

EDX analysis was employed to confirm the presence of sulphur in CMC. EDX spectra of virgin chitosan bead and CMC bead are presented in Figs. 6(a) and (b). As shown in Fig. 6(a), in the case of virgin chitosan bead, the characteristic peak of sulphur did not show. However, peaks for carbon, oxygen and nitrogen appeared. In the case of CMC bead, the peak for sulphur was clearly visible.

3.2. Adsorption of chromium by CMC

To 20 ml of an aqueous solution of metal ion, were added 5 g of chitosan adsorbent. After shaking in rotary shaker for 16 h at room temperature, the mixture was centrifuged and filtered. The Cr(VI) concentration in the filtrate was determined by Atomic Absorption Spectrometer. Since adsorption of metal ion by CMC was pH sensitive, the amount of Cr(VI) adsorbed was calculated at different pH values (Fig. 7). The uptake of metal ions for 50 mg/L Cr(VI) solution by CMC showed a rise as the pH increased from 2 (8 mg/L) to 3 (32 mg/L). Then with further increase in pH, the amount of Cr(VI) adsorbed decreased. The pH_{zpc} of the chitosan prepared from crab shells is reported to be 6.2 (Muzzarelli, 1977). Below pH_{zpc} of chitosan, sorbent is positively charged with the protonated amino group whereas the sorbate is negatively charged (Cr(VI) exists as $HCrO_4^-$). In view of an electrostatic interaction between the sorbent–sorbate systems, it was decided to maintain the pH at 3 in further experiments.

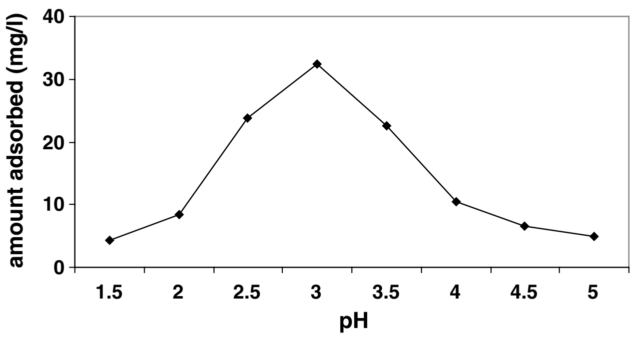


Fig. 7. Effect of pH on adsorption of Cr(VI) by CMC.

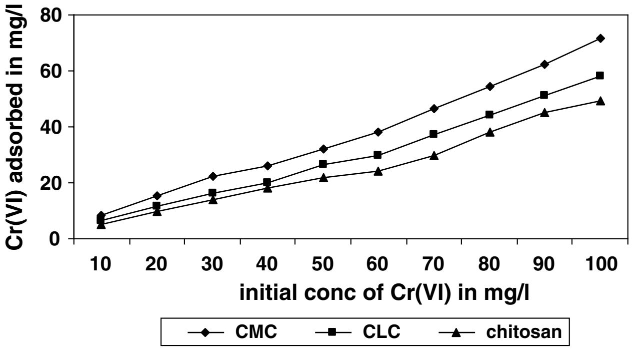


Fig. 8. Amount of Cr(VI) adsorbed for chitosan, CLC, CMC at different initial concentrations of Cr(VI).

Fig. 8 shows the adsorption behavior of chitosan, CLC, and CMC for different initial concentrations of Cr(VI). It was evident that the uptake of Cr(VI) ions by CMC (71 mg/L) was found to be significantly higher than that with CLC (58 mg/L) or plain chitosan (49 mg/L) for 100 mg/L Cr(VI) solution. This study demonstrates the potential use of CMC in the removal of Cr(VI) and other transition metal ions.

4. Conclusions

In this work, a novel chitosan derivative was prepared by chemical reaction with CS_2 under alkaline conditions. It was characterized and evaluated for its adsorption capacity for Cr(VI). The introduction of sulphur group onto chitosan is of importance in enhancing the adsorption properties of plain chitosan. Such chemically modified *Xanthated chitosan* might find potential use as adsorbent in tannery wastewater treatment.

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