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Synthesis and characterization of a new vic-dioxime derivative of chitosan and its transition metal complexes

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Abstract

In this study, a new chitosan derivative including vic-dioxime was synthesized by adding anti-monochloroglyoxime to chitosan (CS) at heterogeneous medium. The vic-dioxime-chitosan (v-DOCS) was characterized by elemental analysis (C, H, N), FT-IR and ^{13}C CP–MAS NMR spectroscopy. The degree of substitution (DS) of v-DOCS was evaluated by ^{13}C CP–MAS NMR spectroscopy and found to be 13.57%. As a result of the solubility test, unlike chitosan, v-DOCS were not dissolved in the aqueous solution of acetic acid. Metal complexes of v-DOCS with Co (II) and Cu (II) were synthesized and characterized by FT-IR and atomic absorption spectroscopy (AAS). Surface characterizations of CS, v-DOCS and v-DOCS–Copper (II) were performed by scanning electron microscope (SEM). Thermal behaviors of the synthesized compounds were investigated by TG-DTA analysis.

Keywords: Vic-dioxime; Chitosan; Metal complexes; Thermal analysis

1. Introduction

Chitin is the most important natural polysaccharide after cellulose, which is isolated from a variety of sources; predominantly marine, such as the shells of several crustaceans, krill and squid pen, but it also forms part of the exoskeleton of insects and is present in the cell walls of fungi.

Chitosan is a natural, cationic aminopolysaccharide copolymer of glucosamine and *N*-acetylglucasamine, obtained by the alkaline, partial *N*-deacetylation of chitin (Muzzarelli, 1977). Chitosan is insoluble in water, but it dissolves in aqueous solutions of organic acids as acetic, formic, citric, besides inorganic acids, as diluted hydrochloric acid resulting in viscous solutions (Rinaudo, Pavlov, & Desbrières, 1999). This biopolymer has application ranging from cosmetics, artificial skin, photography, medicine, food and nutrition, ophthalmology and wastewater treatment (Kurita, 1998; Mathur & Narang, 1990; Ravi Kumar, 2000).

The free amino groups of chitosan enable a variety of chemical modifications and substitution processes like carboxyalkylation, acylation, sulfation, Schiff's base, enzymatic substitution, metal chelation, cyanoethylation, nitration, phosphorylation, etc. (Binsu, Nagarale, Shahi, & Ghosh, 2006; de Britto & Assis, 2006; Ji et al., 2007; Prashanth & Tharanathan, 2007). Therefore, these modifications offer a wide spectrum of tools to enhance the sorption properties of chitosan for metals. 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, Dambies, Milot, & Roussy, 1999; Yang & Yuan, 2001). It has been reported that, chitosan can be chemically modified at very high degrees of substitution (DS > 1) by homogenous reactions but at low levels by heterogeneous reactions (typically up to DS > 0.3). Although very high DS can be achieved when chitosan is dissolved in acidic solutions, many studies

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indicate that functionalization, even under mild conditions, dramatically reduces the molecular weight of the chitosan (Macquarrie & Hardy, 2005).

On the other hand, the synthesis of vic-dioximes and their different derivatives have been the subject of study for very a long period of time. The chemistry of transition metal complexes with dioxime ligands has been studied (Serin & Bekaroğlu, 1983; Gök, Kantekin, & Degirmencioglu, 1993) and has also been the subject of several reviews (Chakravorty, 1974; Schrauzer, 1976; Thomas & Underhill, 1972). The presence of mildly acidic hydroxyl groups and slightly basic nitrogen atoms cause vicinal dioximes to become amphoteric ligands which form corrin type square-planar, square-pyramidal and octahedral complexes with transition metals such as nickel (II), cobalt (II) and cobalt (III) as central atoms (Kurtoglu & Serin, 2002). Vic-dioximes and their metal complexes are of current interest for their physicochemical properties, reactivity patterns and potential applications in many important chemical processes in the areas of medicine (Dilworth & Parrott, 1998), bioorganic systems, catalysis, electrochemical, electro optical sensors and semiconducting properties (Wolkert & Hoffman, 1999). Besides, much work has been reported on the vic-dioxime derivatives which synthesized by the reactions of anti-monochloroglyoxime with primary amine compounds (Kurtoglu & Serin, 2002; Serin, Oksal, & Serindağ, 1992).

Some aldehydes have been attached to chitosan to act as ligands for transition metals, where the metal is complexed via N, O or N, N coordination, respectively (Hardy, Hubert, Macquarrie, & Wilson, 2004; Wang, Sun, & Xia, 2003). In both cases, the activity of the bidentate ligand–metal complex was considerably better than the direct chitosan–metal complex (Macquarrie & Hardy, 2005).

Up to now, there are no studies on vic-dioxime derivatives of chitosan. In this paper, we aimed to synthesize a new chitosan derivative from anti-monochloroglyoxime and the high molecular weight chitosan under heterogeneous reaction medium. In addition, we studied the synthesis of metal complexes (Cu^{2+}, Co^{2+}) of vic-dioxime-chitosan derivative.

2. Experimental

2.1. Materials

Chitosan with high molecular weight was purchased from Aldrich (Cat. No. 41,941-9, >75% deacetylated, Brookfield viscosity 800,000 cpi) having a 24.84% degree of acetylation (DA) as determined by CP–MAS ^{13}C NMR spectrometer. Chloralhydrate and hydroxylammonium chloride were supplied by Merck to synthesize the anti-monochloroglyoxime as described by Brintzinger and Titzmann (1952), Ponzio and Baldracco (1930). Cu^{2+} and Co^{2+} ions were used as their acetates salts. All other chemicals were analytically pure and used without further purification.

2.2. Instrumentation

Infrared (IR) spectra were measured on a Perkin-Elmer RX-1 FT-IR spectrophotometer using KBr pellets (4400–400 cm^{-1}). Elemental analyses were carried out with LECO-CHNS-932 (at METU Central Laboratory). Vic-dioxime-chitosan (v-DOCS) was characterized by using solid-state ^{13}C NMR spectra, which were obtained by using cross-polarization (CP) and magic angle spinning (MAS), with Bruker 300 MHz Ultrashield spectrometer. The surface morphology of chitosan and derivatives were examined by scanning electron microscope (SEM). The samples observed by using a JEOL JSM 5500 scanning electron microscope with double sided carbon tape at an accelerating voltage of 10 kV. Thermogravimetric analyses (TG-DTA) of the samples were performed with DuPont 951 thermal analyzer under a dynamic N_2 atmosphere at a heating rate of 10 °C min^{-1}. Metal analyses were carried out by atomic absorption spectroscopy (AAS) Perkin-Elmer 3100 in a solution prepared by decomposition of the complexes with HNO_3 followed by dilution with deionized water.

2.3. Synthesis of vic-dioxime-chitosan (v-DOCS)

Five grams of anti-monochloroglyoxime was dissolved in methanol (99.9%) and then was added dropwise to the suspension of swelled chitosan in methanol under a nitrogen atmosphere and with stirring at 25 °C. The mixture was stirred for 24 h, the color changed from white to yellow. Then it was filtered, washed several times with methanol, ethanol and distilled water and dried in the oven (Scheme 1).

2.4. Synthesis of vic-dioxime-chitosan metal complexes

2.4.1. Cobalt (II) complex (v-DOCS–Co)

v-DOCS (1.05 g) was suspended in methanol and stirred at 60 °C and then a hot solution of $Co(AcO)_2{\cdot}4H_2O$ (0.55 g) in methanol (20 ml) was added drop wise. The mixture was stirred for 10 h. The complex (Scheme 2) was filtered from por 3 gooch crucible and washed with methanol, ethanol and water, then dried in the vacuum oven.

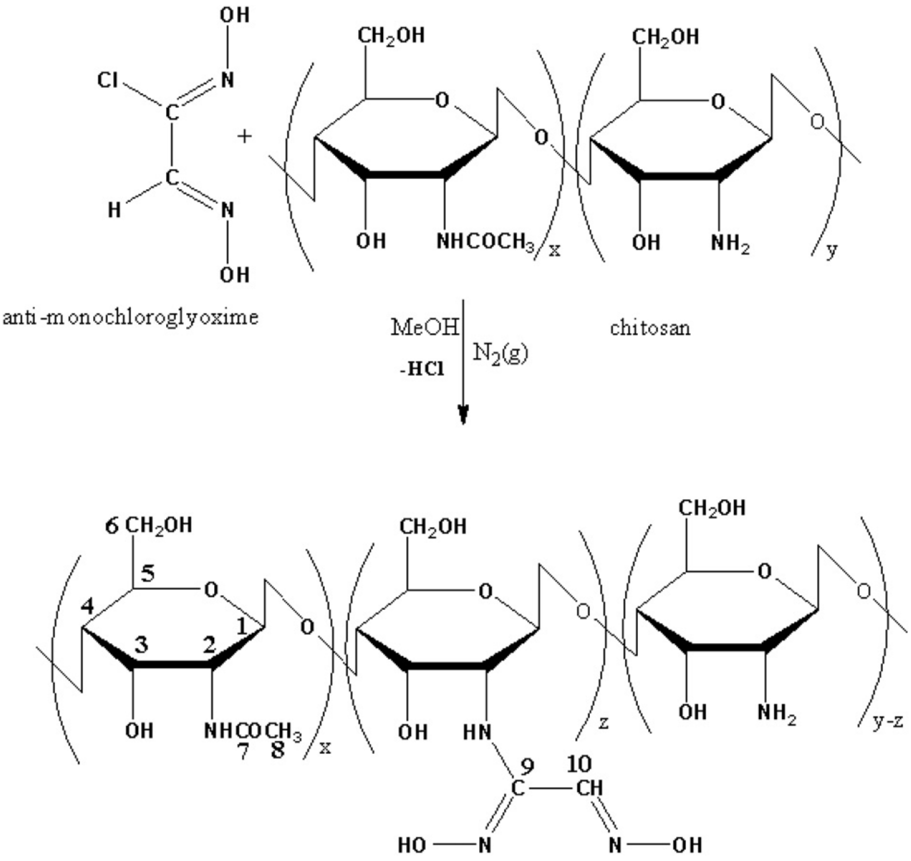
2.4.2. Copper (II) complex (v-DOCS–Cu)

A similar procedure as that for v-DOCS–Co was followed with 1.03 g of v-DOCS and 0.50 g of $Cu(AcO)_2{\cdot}H_2O$ (Scheme 2).

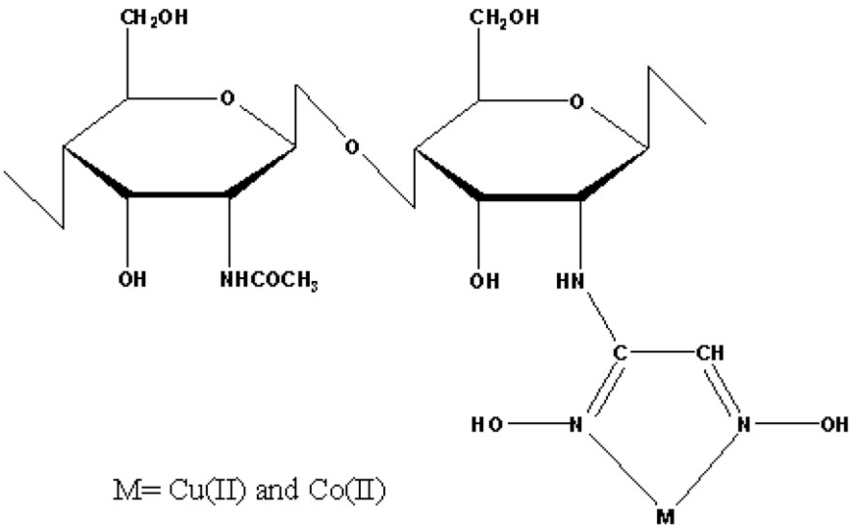
3. Results and discussions

3.1. Solubility

Solubility of chitosan is related to the DA, the ionic concentration, the pH, the distribution of acetyl groups along the chain, the intra-chain H bonds involving the hydroxyl



Scheme 1. The synthesis of vic-dioxime-chitosan (v-DOCS).



Scheme 2. The structure of v-DOCS–metal complexes.

groups and the molecular weight. Solubilization of chitosan occurs by protonation of the —NH_2 group on the C-2 position of the D-glucosamine repeat unit, whereby the polysaccharide is converted to a polyelectrolyte in acidic media (Rinaudo, 2006).

The synthesized biopolymer (v-DOCS) was insoluble in aqueous solutions of organic acids and common solvents like acetone, ethanol, toluene, CH_2Cl_2 and DMF. This case can be explained by the decrease in number of —NH_2 groups of chitosan due to the insertion of anti-monochloroglyoxime on the N atoms of the primary amino groups (Scheme 1). Also, the v-DOCS–metal complexes were insoluble in the same solvents. Therefore, this property of the complexes is important for easy separation from the reaction mixture while used as catalysts.

3.2. Elemental analyses

Carbon, hydrogen and nitrogen elements analyses results of chitosan powder and vic-dioxime-chitosan were given in Table 1. The results show that, nitrogen content was increased after the chemical modification of chitosan because of the high percent of nitrogen (32%) in glyoxime. Therefore, it can be easily understood the reason of the decreases in the ratio C/N for v-DOCS. The results of atomic absorption spectroscopy with respect to percent of metals by weight for v-DOCS–metal complexes compounds were also given in Table 1. These results suggest that, the values of metal content of metal complexes can be in a satisfaction range (8.15% and 10.35% for v-DOCS–Co and v-DOCS–Cu, respectively) (Chang, Wang, Zha, & Wang, 2004).

3.3. FT-IR analysis

The infrared spectrum of the chitosan (Fig. 1a) showed strong peak at 3390 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; C—H stretching at 2879 cm^{-1}; bands due to the CS—NHAc (acetyl) units (with C=O stretching) at 1655 cm^{-1}, (with N—H bending) at 1579 cm^{-1}, (with C—N stretching coupled with N—H plane deformation) at 1420 cm^{-1} and symmetrical angular deformation of CH_3 at 1376 cm^{-1}; C—N stretching of the amino groups of at 1320 cm^{-1}; C—O—C stretching vibration at 1030 cm^{-1}; and the specific bands of the β(1–4) glycoside bridge at 1154 and 896 cm^{-1} (Mansouri et al., 2004; Tian, Liu, Hu, & Zhao, 2004).

Fig. 1b shows the FT-IR spectrum of the anti-monochloroglyoxime. The main absorption vibration bands were observed as 3100–3440 cm^{-1} (broad, O—H), 2890 cm^{-1} (C—H), 1638 cm^{-1} (—C=N—) and 900 cm^{-1} (N—O).

It can be seen that, the FT-IR spectra of anti-monochloroglyoxime and chitosan were almost the same. Therefore, it is not easy to interpret the chemical modification of chitosan with anti-monochloroglyoxime by using FT-IR spectral data. Nevertheless, there are some important differences at the FT-IR spectrum of v-DOCS (Fig. 1c); broadening at 3000–3500 cm^{-1} due to the O—H absorption of the glyoxime and the decrease of $—NH_2$ absorption peak of CS at 1605 cm^{-1}, implies that the substitution took place on the N atoms under this experimental condition. In addition, the differences at 2800–2900, 1350–1400 and 500–700 cm^{-1} region at FT-IR spectrum of CS, might be attributed to the insertion of anti-monochloroglyoxime group to the chitosan.

Table 1
Elemental analysis of CS, v-DOCS and v-DOCS–metal complexes

Sample	Color	Element (%)				
		Metal	C	H	N	C/N
CS	White	–	42.35	7.06	8.23	5.15
v-DOCS	Yellow	–	39.61	6.28	9.88	3.67
v-DOCS–Co	Brown	8.15				
v-DOCS–Cu	Green	10.35				

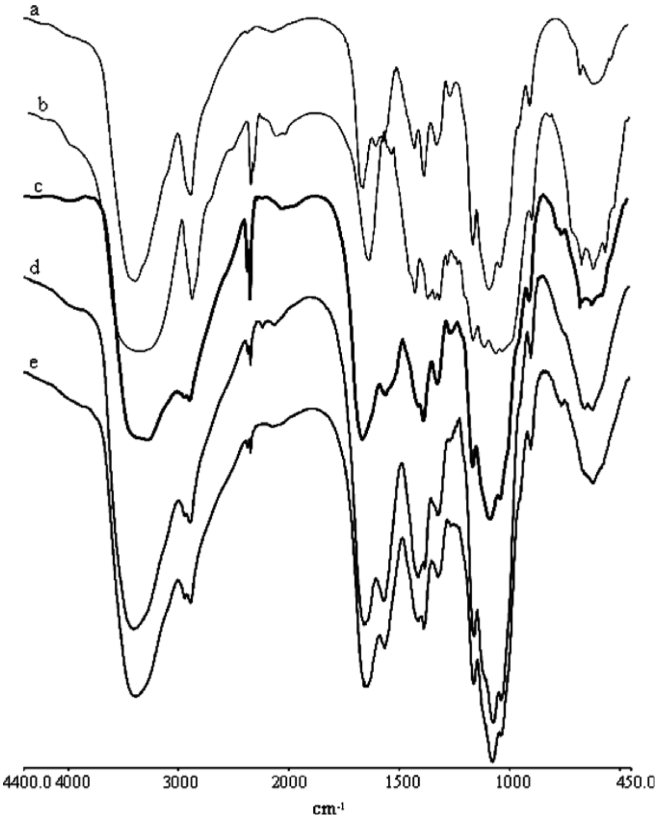


Fig. 1. The FT-IR spectra of CS (a), anti-monochloroglyoxime (b), v-DOCS (c), v-DOCS–Co (d) and v-DOCS–Cu (e).

On the other hand, at the FT-IR spectra of v-DOCS–metal complexes; v-DOCS–Co (Fig. 1d) and v-DOCS–Cu (Fig. 1e), the broad bands at 500–700 cm^{-1} region of v-DOCS spectrum become sharp and new peaks were observed especially at 600–620 cm^{-1} region which might be explained by the metal-N coordination.

3.4. CP–MAS ^{13}C NMR analysis

The solubility properties of v-DOCS act as an important role in the characterization part. It was studied with solid state ^{13}C NMR to characterize the structure and to identify degree of acetylation (DA) and degree of substitution (DS) of v-DOCS because of the insoluble property. The analysis of CP–MAS ^{13}C NMR spectrum (Fig. 2) of v-DOCS, shows that peaks at 98.1, 75.2, 70.0, 69.2, 53.7 and 50.0 ppm are attributed to C-1, C-4, C-5, C-3, C-6 and C-2, respectively. Also it shows that the peaks attributed to acetyl carbons at 169.8 ppm (C=O) and 18.7 ppm ($—CH_3$). In addition, new peaks were observed at

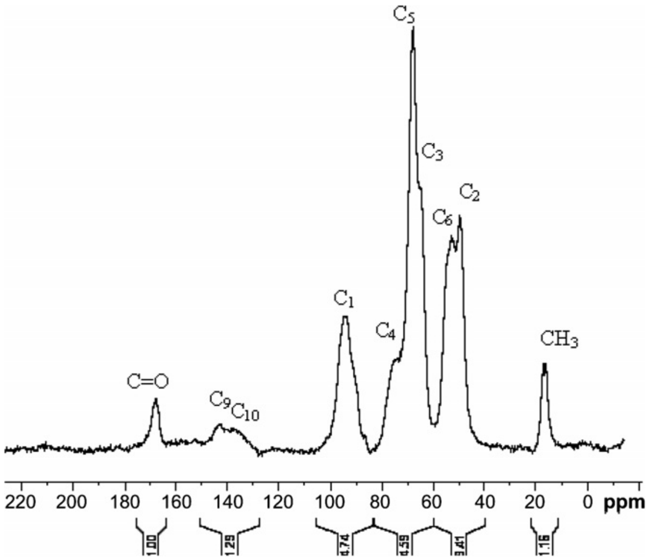


Fig. 2. ^{13}C CP–MAS NMR spectrum of v-DOCS.

142.9 ppm and 138.2 ppm as different from CP–MAS ^{13}C NMR spectrum of chitosan which have acetyl groups (DA > 0) (Capitani, De Angelis, Crescenzi, Masci, & Segre, 2001). These new peaks were assigned to glyoxime carbons; NH—C=NOH (C-9) and H—C=NOH (C-10), respectively (Babahan, Anıl, & Sarıkavaklı, 2006).

The degree of acetylation (DA) was evaluated from the relative integrals of methyl groups (1.19) compared to the carbon integrals ($\sum(\text{C1} - \text{C6})/6$; $28.74/6 = 4.79$) of the polysaccharidic backbone. The result was found as $(1.19/4.79) * 100 = 24.84\%$ confirmed the values given by supplier (Aldrich, DA < 25). On the other hand, the degree of substitution (DS) of v-DOCS was calculated from the relative integrals of glyoxime carbons ($1.29/2 = 0.65$) compared to the carbon integrals of the polysaccharidic backbone as $(0.65/4.79) * 100 = 13.57\%$. Although the vic-DOCS derivative of chitosan was synthesized by heterogeneous reaction, the DS value (13.57%) was found almost in the same range (26% and 12%) with the chitosan derivatives which obtained from homogenous medium (Gomes, Gomes, Batista, Pinto & Silva, 2007). Eventually, this result seems to be significant due to the synthesis conditions (heterogeneous). In addition, it is estimated that the polymer backbone was not distorted and the chemical modification occurred without any degradation because of the case reported in the literature (Macquarrie & Hardy, 2005).

3.5. SEM

The SEM images of the surface morphology of CS, v-DOCS and v-DOCS–Copper are shown in Fig. 3. CS has a smooth surface (Fig. 3a), but v-DOCS have not a smooth surface (Fig. 3b) as well as CS surface due to the chemical modification. In contrast, the surface of v-DOCS–Cu (Fig. 3c and d) does not exhibit the same structure as v-DOCS. This difference may be assigned to the metal sites which coordinated to v-DOCS.

3.6. Thermal properties

The thermal stability and degradation behavior of CS, v-DOCS and v-DOCS–metal complexes were studied by TG-DTA under nitrogen atmosphere. The TG-DTA curves of CS, v-DOCS, v-DOCS–Co and v-DOCS–Cu were given in Figs. 4–7, respectively. Also, Table 2 shows the thermal degradation values of CS, v-DOCS, v-DOCS–Co and v-DOCS–Cu. According to the TG

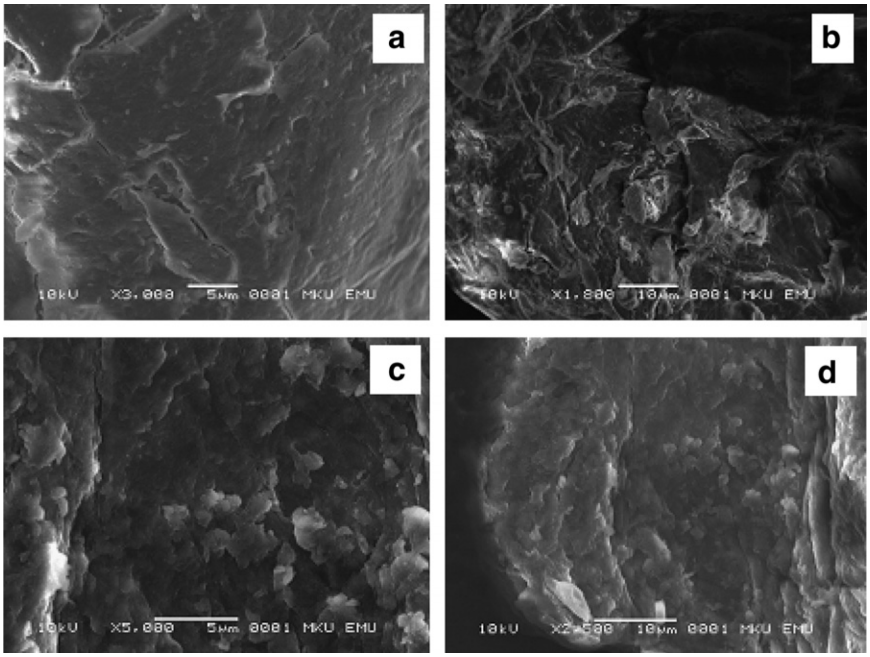


Fig. 3. SEM images of the surface morphologies CS (a), v-DOCS (b), v-DOCS–Cu (c) and as a different size of v-DOCS–Cu (d).

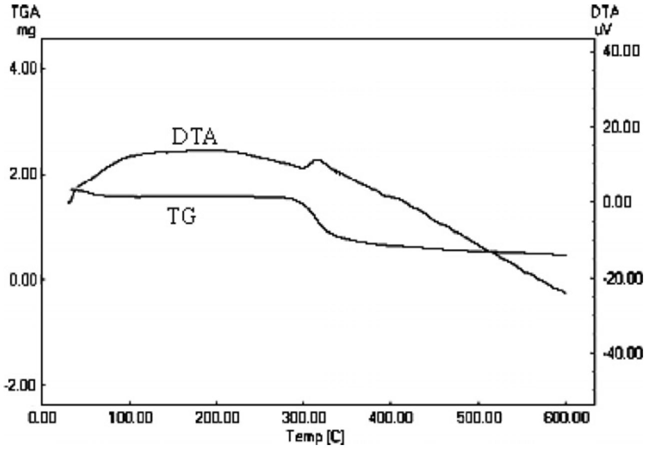


Fig. 4. The TG-DTA curves of CS.

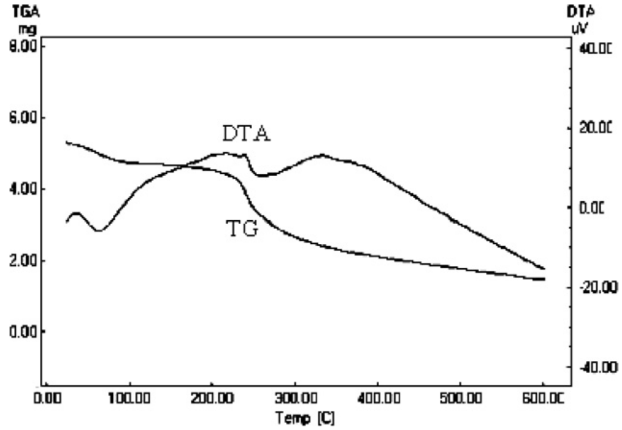


Fig. 5. The TG-DTA curves of v-DOCS.

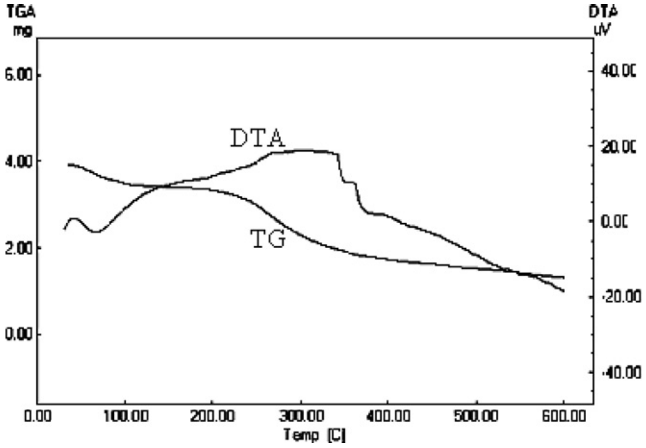


Fig. 6. The TG-DTA curves of v-DOCS–Co.

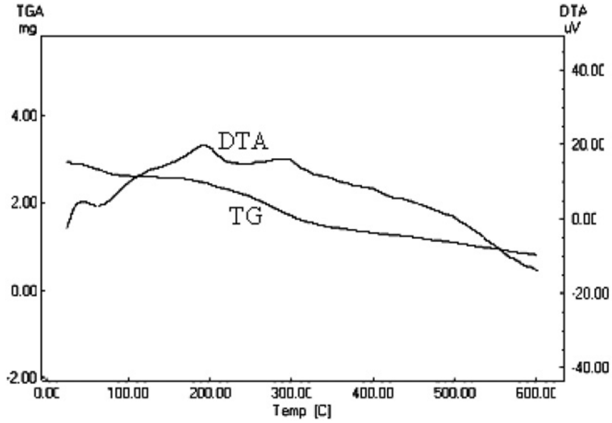


Fig. 7. The TG-DTA curves of v-DOCS–Cu.

Table 2
Thermal degradation values of CS, v-DOCS and v-DOCS–metal complexes

Compound	1st stage, °C (wt loss, %)	2nd stage, °C (wt loss, %)	Carbon residue % (at 600 °C)
CS	40–100 (∼5)	280–400 (∼67)	27.93
v-DOCS	40–140 (∼11)	160–600 (∼61)	27.12
v-DOCS–Co	40–140 (∼15)	200–600 (∼51)	32.99
v-DOCS–Cu	40–140 (∼11)	140–600 (∼60)	28.76

curves of CS and v-DOCS, there are two mass loss stages. The first one; smooth for CS, explained by the water elimination which adsorbed physically to the biopolymer matrix. And the second one; smooth for v-DOCS, might be due to the dehydration of the saccharide rings, depolymerization and decomposition of the polymer (Peniche-Covas, Argüelles-Monal, & San Román, 1993). The value of mass loss at the first stage for v-DOCS was larger (∼11%) than the value of CS (∼5%). This case may be explained by the excess of —OH groups (increase the adsorption of water) of vic-dioxime-chitosan. The main thermal degradation process of the v-DOCS takes place at temperatures lower than the second degradation stage of chitosan, indicating that the vic-dioxime-chitosan polymer is less stable than chitosan. It seems that the instability of the vic-dioxime-chitosan polymer compared with chitosan might be due to the decrease in the number of primary amino groups after the chemical modification process. In comparison with the TG curve of v-DOCS, the TG curves of v-DOCS–metal complexes were showed smoother thermograms because of the coordination to the metal ions. The mass loss about 150–200 °C range for v-DOCS–metal complexes as different from the v-DOCS may be affected by the presence of coordination water (Cazacu, Marcu, Vlad, Rusu, & Avadanei, 2004).

According to the DTA thermograms of the CS (Fig. 4) and v-DOCS (Fig. 5), there were some important differences with respect to the endothermic and exothermic peaks may be caused by the chemical modification. Also, the thermograms of v-DOCS–metal complexes were showed different endothermic and exothermic peaks from v-DOCS because of the metal content. It is well known that for chitosan and its derivatives; the endothermic peaks observe for water vapor elimination and the exothermic peaks observe for decomposition.

4. Conclusions

A new vic-dioxime derivative of chitosan (v-DOCS) was synthesized by heterogenous reaction of chitosan and anti-monochloroglyoxime at room temperature. The degree of substitution (DS) of v-DOCS was evaluated by ^{13}C CP–MAS NMR spectroscopy and found to be 13.57%. The synthesized biopolymer (v-DOCS) was insoluble in aqueous solutions of organic acids and common solvents like acetone, ethanol, toluene, CH_2Cl_2 and DMF. The Co (II) and Cu (II) metal complexes of v-DOCS were synthesized and characterized. Also, metal complexes were not soluble in common solvents. Therefore, the insolubilities of v-DOCS-complexes are important for using as heterogenous catalysts by easy separation from the reaction mixture. According to the TG-DTA analysis, the residue of CS, v-DOCS, v-DOCS–Co and v-DOCS–Cu were found to be 27.93%, 27.12%, 32.99% and 28.76%, respectively, at 600 °C.

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