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Chitosan–cyanuric chloride intermediary as a source to incorporate molecules—Thermodynamic data of copper/biopolymer interactions

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ABSTRACT

The reaction of a chitosan–cyanuric chloride (ChC) intermediate with ethylenediamine (d) and diethylenetriamine (t) molecules yielded the new biopolymers ChCd and ChCt, which were characterized by elemental analysis, thermogravimetry, X-ray diffractometry, scanning electron microscopy and infrared and C^{13} nuclear magnetic resonance spectroscopies. The precursor chitosan (Ch) and all derivatives adsorb copper from aqueous solution at 298 ± 1 K, determined using a batchwise procedure. The results were fitted to a modified Langmuir equation. The ability to adsorb copper is dependent on the availability of the basic nitrogen atoms attached to the pendant biopolymer chains in the order ChCt > ChCd > ChC > Ch, as given by the values 2.84 ± 0.03, 2.62 ± 0.05, 2.55 ± 0.04 and 2.09 ± 0.03 mol g^{-1}, respectively. The same interactive process was also followed through calorimetric titration at 298.15 ± 0.20 K. The net thermal effects were also adjusted to a modified Langmuir equation to give the thermodynamic data at the solid/liquid interface. The exothermic enthalpic values were −28.98 ± 0.05, −32.77 ± 0.04, −60.60 ± 0.03 and −56.41 ± 0.05 kJ mol^{-1} for the biopolymers Ch, ChC, ChCd and ChCt, respectively. The spontaneity of the systems is shown by the negative ΔG values, −21.1 ± 0.1, −22.1 ± 0.1, −22.1 ± 0.1 and 23.4 ± 0.1 kJ mol^{-1} for the same sequence. The negative entropic values −26 ± 1, −36 ± 1, −129 ± 1 and −111 ± 1 J mol^{-1} K^{-1} indicate an ordering of solvent as complexation occurred. The thermodynamic data demonstrate the capability of these biopolymers for cation removal from aqueous solutions, being new derivative biomaterials that may act as useful agents to renew an ecosystem.

1. Introduction

Chitin is the second most abundant polysaccharide in nature, next to cellulose, and widely distributed as a component of the skeletal structure of crustaceans, insects and cell wall fungi [1,2]. The copolymer chitosan is composed of β(1 → 4) linked 2-amino-2-deoxy-D-glucose and 2-acetamido-2-deoxy-D-glucose, normally obtained by purified chitin deacetylation with concentrated alkali at high temperature and frequently commercialized in powder or flake forms [3–5].

The biopolymer chitosan has increasing applications, including in a variety of areas for practical uses as illustrated for pharmaceutical and biomedical engineering, paper production, textile finishes, wastewater treatment and heavy metal chelation [6,7]. This biopolymer has excellent properties for transition metal adsorption, mainly due to the presence of the active amino groups bonded directly to the polymeric backbone. However, its adsorbent capacity depends on the degree of deacetylation, the nature of the metal ion and the pH of the solution [8–10]. The presence of a high amount of reactive primary amino groups distributed on the polymeric matrix, expressed by the high degree of deacetylation, offers innumerous chemical modification capabilities with tosyl, alkyl and carboxyl groups, as well as sulfonation, Schiff base formation, and immobilization of complexing agents [1,8].

Chemical modification of the polymer surface through the introduction of new pendant chains bonding directly to amino or hydroxyl on carbon-6, enables the formation of different new biopolymers. When the chitosan pendant chains have basic atoms an increase in adsorption capacity and selectivity toward metal ions from solutions can be observed [8,11]. Various investigations demonstrate the effectiveness of chitosan and also its derivatives in the uptake of cations such as cadmium [12,13], copper [14–18], zinc [19,20], and nickel [12,21] and the uptake of oxyanions as well complexed metal ions. The ability of such polymers for adsorption is closely related to their principal characteristics: high hydrophilicity owing to large number of hydroxyl and primary amino groups that presents activity as adsorption sites and to the flexible structure of the polymeric chitosan chain to adjusting suitable configurations for complexation with metal ions [22].

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With the intent to improve the biopolymer for other useful applications, the present investigation deals with the enhancement in chitosan reactivity, to yield new synthethic biopolymers with centers available to complex cations. The chosen agent to fulfill this design is the linking triazine agent cyanuric chloride that is explored in a variety of reactions, including air-oxidised active carbon surface, whose available hydroxyl centers can anchor transition metal complexes through ether linkages [23] and also various derivatives that have been used for many potential drugs, having antihypertensive, antimicrobial and calcium-channel blocking activities [24].

In general, the majority of biopolymers have been studied from the structural point of view, but the thermodynamics involving species binding on biopolymers from solutions are very rare, due to the complexities of the systems, as well as the experimental difficulties. However, calorimetric techniques have been contributed to the understanding of adsorption phenomena at the solid/liquid interface [25–28].

When the triazine agent forms a bridge between chitosan and the desired incorporated linear diamine molecule, due to the available halide, the pendant chains are enriched with the increase in basic centers, which can remove cations from aqueous solution. The nitrogen atom basic center/copper interaction at the solid/liquid interface can be calorimetrically followed and from the net quantitative thermal data, the thermodynamics for this cation removal can be obtained, as now reported for this system.

2. Experimental

2.1. Materials

Powdered chitosan, with a degree of deacetylation of 78%, determined from infrared spectroscopy [28], was obtained from crab extraction and supplied by Primex Ingredients A.S. (Norway). Cyanuric chloride (Acros), ethylenediamine (Aldrich), diethylenetriamine (Aldrich), toluene (Synth), ethanol (Synth), potassium hydrogen phthalate (Riedel-de Haën), potassium chloride (Synth), sodium hydroxide (Synth), hydrochloric acid (Synth), and copper nitrate (Vetec) were all analytical reagent grade and were used without purification.

2.2. Equipment and measurements

Carbon, hydrogen and nitrogen elemental analysis were performed on a Perkin Elmer model PE 2400 elemental analyzer. Infrared spectra of the samples were obtained as KBr pellets by accumulating 32 scans on a Bomem Spectrophotometer, MB-series, in the 4000–400 cm^{-1} range, with 4 cm^{-1} of resolution, by applying Fourier transformation. Solid state ^{13}C NMR spectra of the samples were obtained on a Bruker AC 300/P spectrometer. The CP/MAS technique was used. The measurements were obtained at 75.47 MHz frequencies, with magic angle spinning of 4 kHz with pulse repetition of 5 s and contact times of 1 ms. X-ray diffraction patterns were obtained on a Shimadzu XD-3A diffractometer (35 kv, 25 mA), in the 2θ form over the 1.5–50° range with nickel-filtered CuKα radiation, with a wavelength of 0.154 nm. Thermogravimetric curves were obtained on a Shimadzu TGA 50 apparatus, under an argon atmosphere at a flow rate of 30 $cm^3\ s^{-1}$, with a heating rate of 0.167 $K\ s^{-1}$. The amount of cation adsorbed was determined by the difference between the initial concentration in the aqueous solution and that found in the supernatant, by using an ICP-OES Perkin Elmer 3000 DV apparatus. For each experimental point, the reproducibility was checked by at least one duplicate run. Scanning electron microscopy (SEM) data were obtained from detection of the secondary electron images on a JEOL JSM 6360LV scanning electron microscope, operating at 20 kV. The samples were fixed onto a double-faced carbon tape adhered to a gold support and carbon-coated in a Bal-Tec MD20 instrument.

2.3. Synthesis of chemically modified chitosan

A sample of 20.0 g of chitosan (Ch) was suspended in 200 cm^3 of toluene, followed by the slow addition of 27.60 g (0.150 mol) of cyanuric chloride (C) at 373 K, under mechanical stirring. After stirring at the same temperature for 24 h, the material (ChC) obtained from this reaction was washed exhaustively with ethanol. The solid was then separated by filtration and dried under vacuum at 333 K for 12 h.

In a second step, a sample of 10.0 g ChC was reacted with 7.0 cm^3 (0.105 mol) of ethylenediamine (d) under reflux with mechanical stirring for 24 h. The material (ChCd) obtained from the reaction was washed with ethanol, separated by filtration and dried under vacuum at 333 K for 12 h. Another sample of 10.0 g of ChC was reacted with 17.0 cm^3 (0.157 mol) of diethylenetriamine (t) under reflux and with mechanical stirring for 24 h. The new biopolymer (ChCt) obtained from this reaction was washed with ethanol, separated by filtration and dried under vacuum at 333 K for 12 h. The immobilization of the ethylenediamine and diethylenetriamine on ChC is outlined in Fig. 1.

2.4. Copper adsorption

The capacity of the chemically modified chitosan to extract copper from aqueous solution was determined in duplicate runs, using a batch process with aqueous solutions of divalent copper nitrate, using a mass of approximately 20 mg of chitosan or of each chemically modified chitosan suspended in 25.0 cm^3 of the copper solutions with concentrations ranging from 0.70 to 7.0 mmol dm^{-3}. The suspensions were shaken for 4 h in an orbital bath at 298 ± 1 K. At the end of this process, the solid was separated by decantation, aliquots of the supernatant were removed and the amounts of copper were determined by ICP-OES. The adsorption capacities (N_f) were calculated by Eq. (1), where N_f is the number of moles adsorbed on raw or chemically modified chitosan, n_i and n_s are the number of moles of copper cation in the initial and the supernatant solutions after reaching equilibrium, respectively, and m is the mass of the adsorbent used in each adsorption process [29].

$$N_f = \frac{n_i - n_s}{m} \tag{1}$$

To evaluate the results obtained from the isotherms of adsorption and to determine the mole fraction of the ion in solution, the data were adjusted to the Langmuir model [30], assuming that a monolayer of cation formed on the biopolymer, expressed by Eq. (2)

$$\frac{C_s}{N_f} = \frac{1}{N^s b} + \frac{C_s}{N^s}, \tag{2}$$

where C_s (mmol dm^{-3}) is the concentration of supernatant copper cation in equilibrium, N_f (mmol g^{-1}) is the number of moles adsorbed, N^s (mmol g^{-1}) is the maximum adsorption capacity of copper per gram of biopolymer, which is related to the number of adsorption sites, and b is a constant related to chemical equilibrium at the solid/liquid interface. The N^s and b values for each adsorption process were obtained from the angular and linear coefficients, respectively, of the linearized form of the adsorption isotherms, by considering C_s/N_f versus C_s plots, using the method of least squares.

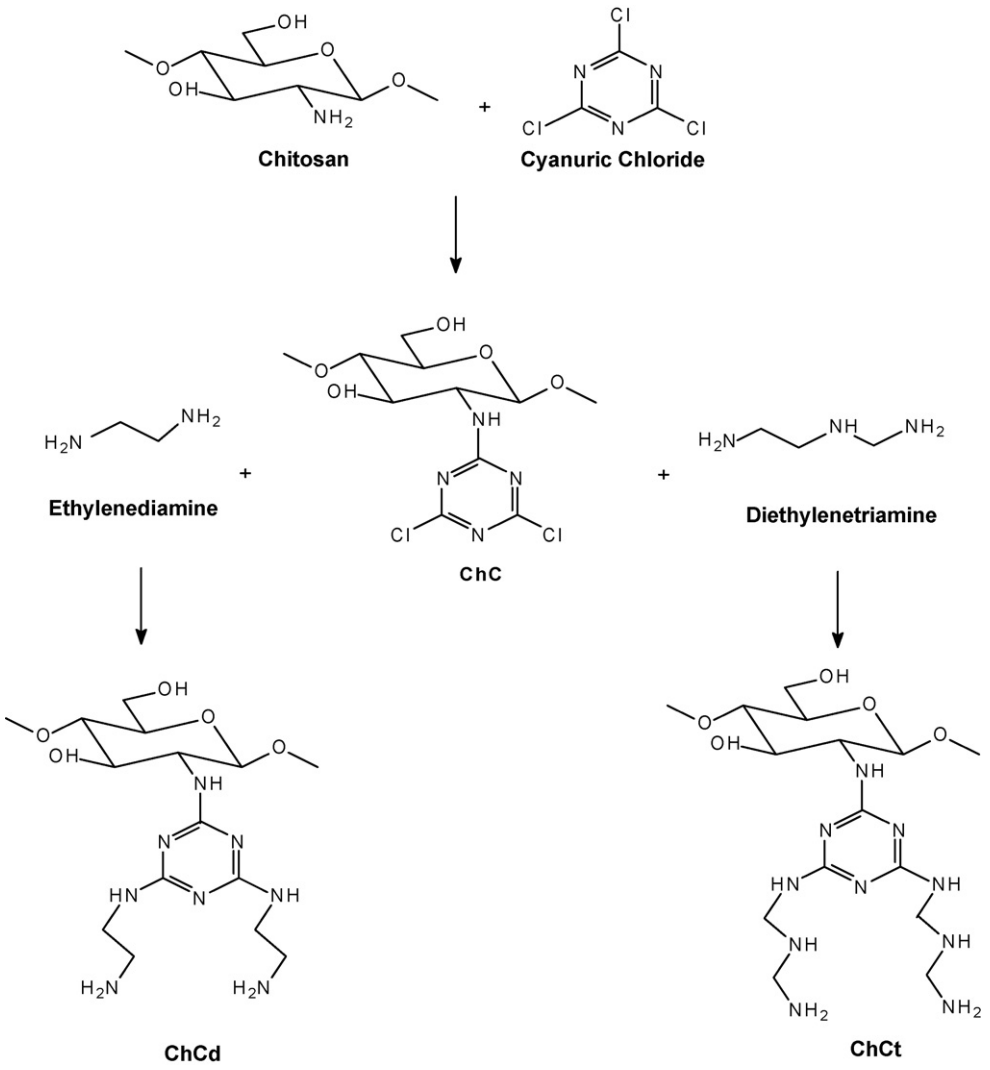

Fig. 1. Schematic drawing for chemical structures of ChCd and ChCt.

2.5. Calorimetric titration

The thermal effects involved in the interaction of copper ion with the biopolymers were measured through a titration method, using a Thermometric 2277 (Thermal Activity Monitor) precision calorimetric system [27]. For each operation, a sample of nearly 20 mg of chitosan or chemically modified chitosan was suspended in 2.0 cm^3 of water under stirring and thermosted at 298.15 ± 0.20 K. The titration was followed by adding successively 10 μL increments of the titrant that consisted of 0.10 mol dm^{-3} copper nitrate solution. The thermal effect of the titration, Q_t (J), was determined after each increment of titrant. Under the same experimental conditions, the corresponding thermal effect of the dilution of the cation solution was obtained in the absence of any biopolymer, Q_d (J). Under such conditions, the net thermal effect of adsorption $\sum Q_r$ (J) was obtained through Eq. (3)

$$\sum Q_r = \sum Q_t - \sum Q_d. \tag{3}$$

The change in enthalpy associated with cation/biopolymer interaction can be determined by adjusting the adsorption data to a modified Langmuir equation to calculate the integral enthalpy involved in the formation of a monolayer per unit mass of adsorbent $\Delta_{mono}H$ [31,32]

$$\frac{\sum X}{\sum \Delta H} = \frac{1}{(K-1)\Delta_{mono}H} + \frac{X}{\Delta_{mono}H}, \tag{4}$$

where $\sum X$ is the sum of the mole fraction of the cation in solution after adsorption, with X being obtained for each point of titrant addition by using the modified Langmuir equation; ΔH (J/mol), the integral enthalpy of adsorption per gram of the matrix, was obtained by dividing the thermal effect resulting from adsorption by the number of moles of the adsorbate and K is the proportionality constant, which also includes the equilibrium constant. Using the angular and linear values from the $\sum X/\sum \Delta H$ versus $\sum X$ plot enables the calculation of the $\Delta_{mono}H$ value. The enthalpy of adsorption ΔH could then be calculated by means of Eq. (5)

$$\Delta H = \frac{\Delta_{mono}H}{N^s}. \tag{5}$$

From K values, the free Gibbs energies were calculated by the expression

$$\Delta G = -RT \ln K \tag{6}$$

and the entropy value can be calculated through

$$\Delta G = \Delta H - T\Delta S. \tag{7}$$

Table 1
Percentages and amounts of nitrogen (N), carbon (C), hydrogen (H), chlorine and the molar ratio (C/N) for chitosan and the chitosan derivatives.

Sample	C (%)	H (%)	N (%)	Cl (%)	C/N	N (mmol g^{-1})	Cl (mmol g^{-1})
Ch	40.43	7.06	7.69	–	5.29	5.47	–
ChC	40.27	6.83	7.81	0.96	5.16	5.50	0.27
ChCd	41.40	7.69	9.98	0.71	4.12	7.07	0.20
ChCt	39.75	6.84	9.89	0.72	4.02	7.06	0.20

3. Results and discussion

3.1. Characterization

Carbon, hydrogen, nitrogen and chlorine elemental analysis results for chitosan and for all modified polymers as well as the C/N relationship are summarized in Table 1. These listed results show an increase in the amount of nitrogen in the ChCd and ChCt biopolymers, 7.07 and 7.06 mmol g^{-1}, respectively, when compared with the precursor chitosan, 5.47 mmol g^{-1}. These values are in agreement with the incorporation of both ethylenediamine and diethylenetriamine molecules as pendant chains onto the chitosan polymeric backbone.

The infrared spectra of the precursor chitosan and all derivatives are shown in Fig. 2. The unmodified chitosan spectrum was very similar to those previously reported [33], presenting a series characteristic bands, such as: (i) a broad band at 3421 cm^{-1} attributed to OH stretching frequency, which overlaps the amino stretching band in the same region, (ii) the band at 1590 cm^{-1} assigned to NH bending (amide II) and (iii) a small band near 1652 cm^{-1} that corresponds to C=O stretching (amide I). By comparing this spectrum with those obtained for the chemically modified chitosans: ChC, ChCd and ChCt, clear evidence of modification can be observed. These spectra showed a displacement and enlargement of the original band around 1590 cm^{-1} related to the N—H deformation band, indicating the involvement of the amine groups when the pendant chains are included in the polymeric backbone.

The thermogravimetric curves for chitosan and the chemically modified chitosans are shown in Fig. 3. The thermal decomposition profiles are similar in raw chitosan and its derivatives, suggesting that the thermal degradation occurred in two stages. The first stage, observed for all chitosans in the 307–380 K range is attributed to loss of physically adsorbed water originally bonded on the surface. The second mass loss for the biopolymers occurred in a well-established temperature range: 464–709 for Ch, 474–715 for ChC, 490–723 for ChCd and 464–806 K for ChCt. This step of mass loss has been previously attributed to the corresponding thermal decomposition of the biopolymers, with vaporization and elimination of volatile products [34]. These mass loss values reflect the characteristic of the synthesized polymeric materials. Two well-defined peaks are clearly shown in the derivative curves in Fig. 4. These results also reflect that the chemically modified chitosans present thermal stability similar to that of the precursor chitosan.

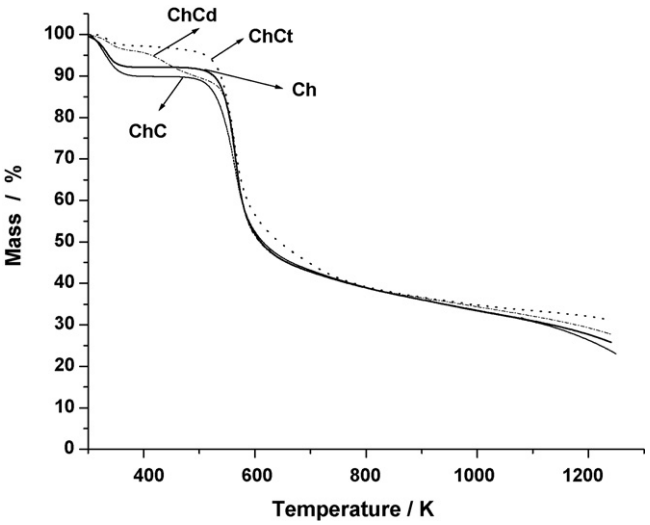

Fig. 3. Thermogravimetric curves for Ch, ChC, ChCd and ChCt.

Nuclear magnetic resonance of carbon nucleus in the solid state is a valuable technique to clarify structural features, not only of the components of the main linear skeleton, but also those involving the moieties bonded as pendant chains on the polymer. The ^{13}C NMR spectra for all chitosans are shown in Fig. 5. The inserted skeleton structure of the biopolymer indicates the labeled carbon atoms. For chitosan a sequence of five well-formed distinct peaks are shown in Fig. 5a, assigned to C1, C2, C4, C6 and C3/5 at 105, 57, 83, 60 and 75 ppm, respectively. In addition, two other signals at 23 and 175 ppm are attributed to methyl and carbonyl groups associated with the monomeric form remaining from chitin, due

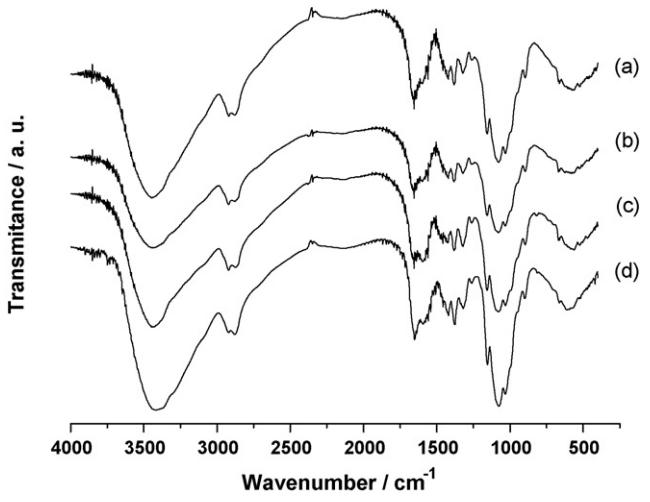

Fig. 2. Infrared spectra of chitosan (a), ChC (b), ChCd (c) and ChCt (d) biopolymers.

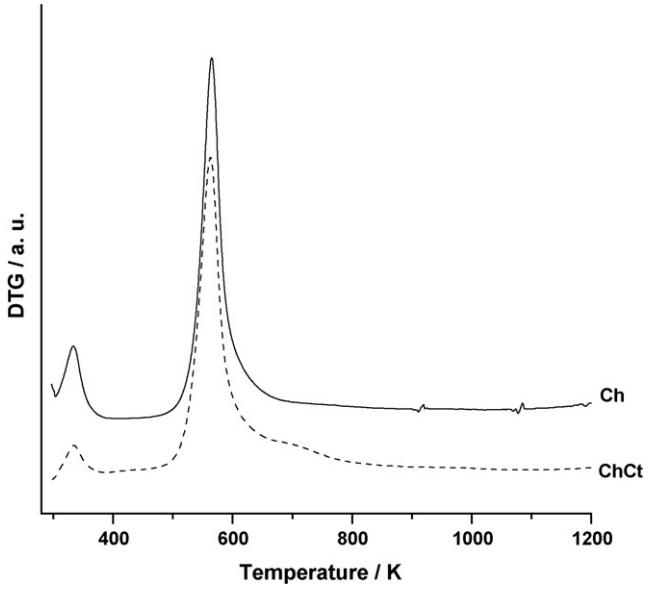

Fig. 4. DTG curves for Ch and ChCt.

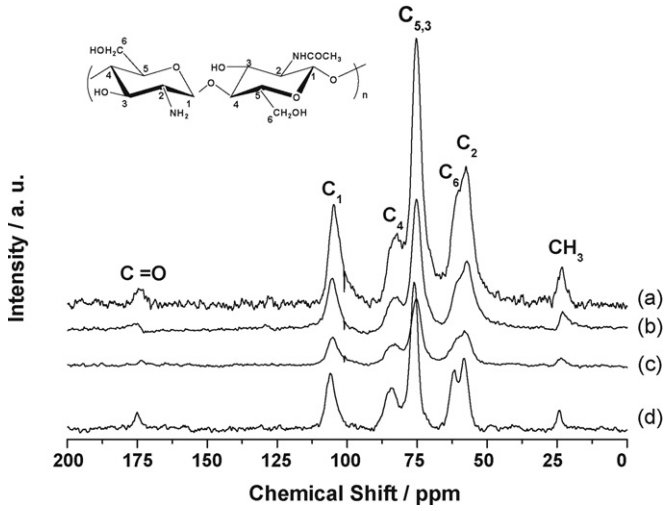

Fig. 5. Solid state ^{13}C NMR of Ch (a), ChC (b), ChCd (c) and ChCt (d).

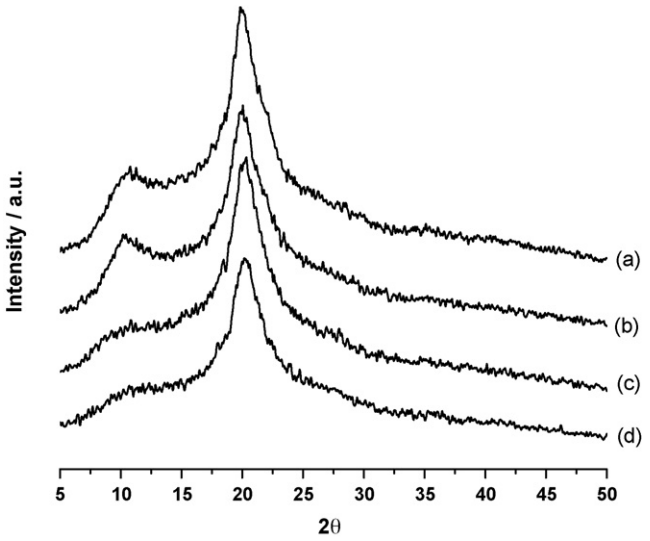

Fig. 7. X-ray diffraction patterns of chitosan Ch (a), ChC (b), ChCd (c) and ChCt (d).

to the incomplete deacetylation of the original biopolymer [35]. As expected, the spectra for all chemically modified chitosans are very similar to the precursor spectrum. A slight difference was observed for ChCd, in which the C2 peak overlaps the C6 signal after incorporating ethylenediamine, as shown in Fig. 5c. However, these peaks are well separated after the reaction with diethylenetriamine, as shown in Fig. 5d.

The scanning electron microscopic images for chitosan and all three chemically modified biopolymers are shown in Fig. 6. By comparing these images, that related to chitosan in Fig. 6a demonstrates that the raw chitosan seems to have a smooth surface morphology. As expected, as cyanuric chloride is attached to the biopolymer a rougher morphology is observed as shown in Fig. 6b. On contrast both ChCd and ChCt biopolymer surfaces, as shown in Fig. 6c and d, did not exhibit the same structure as ChC, with a relatively homogeneous aspect and smooth surface morphology, after immobilization of ethylenediamine or diethylenetriamine.

X-ray diffraction patterns for all biopolymers presented a common intense peak as shown in Fig. 7. Chitosan presented poor crystallinity, as indicated by the presence of two broad peaks at 10.58 and 20.0° [35]. The chemically modified biopolymers, incorporating ethylenediamine and diethylenetriamine in the ChC precursor, show for further decreases in the crystalline nature for the ChCd and ChCt biopolymers, as shown in Fig. 7c and d. The crystallinity associated with chitosan is closely related to the intra and intermolecular hydrogen bond system involved in all polymeric chains to maintain their stability. However, as the molecules

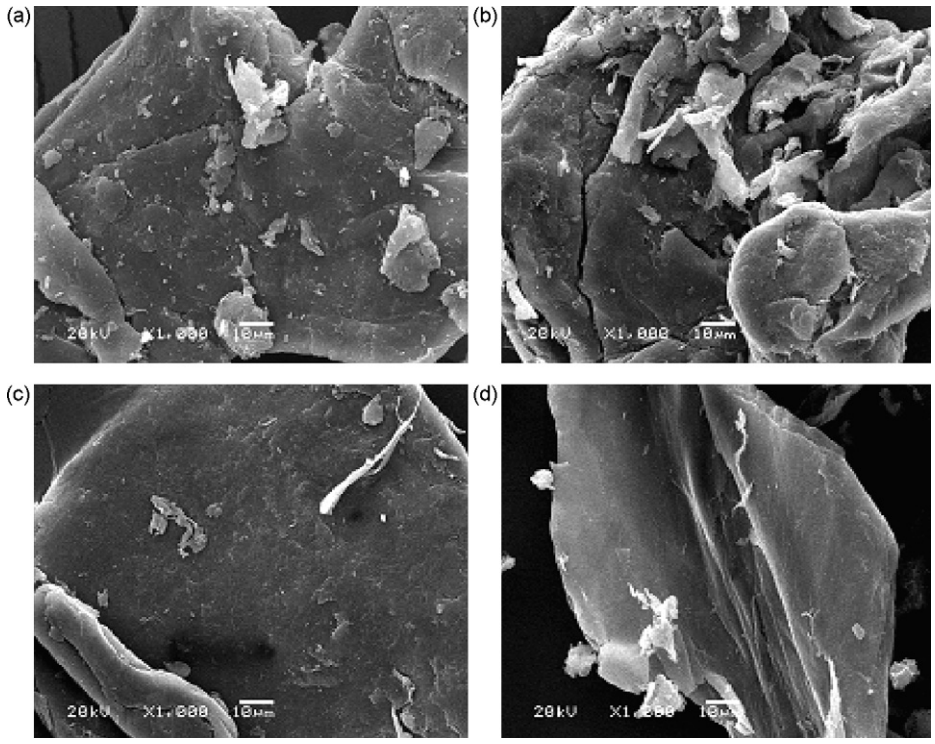

Fig. 6. SEM images of Ch (a), ChC (b), ChCd (c) and ChCt (d).

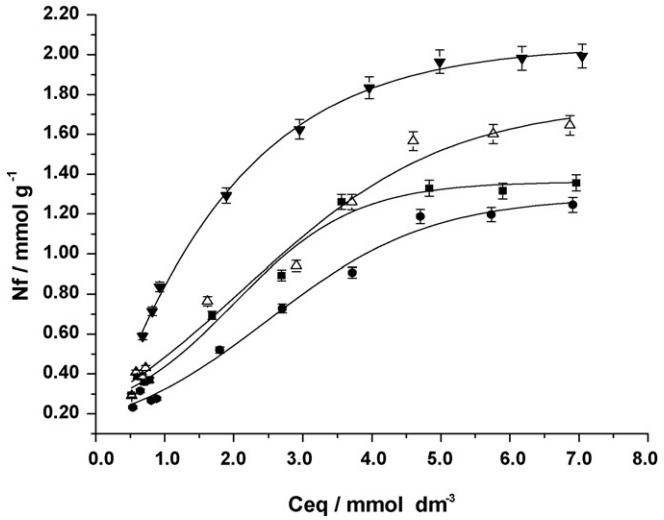

Fig. 8. Adsorption isotherms of Cu^{2+} on the Ch (■), ChC (●), ChCd (△) and ChCt (▼) surfaces at 298 ± 1 K.

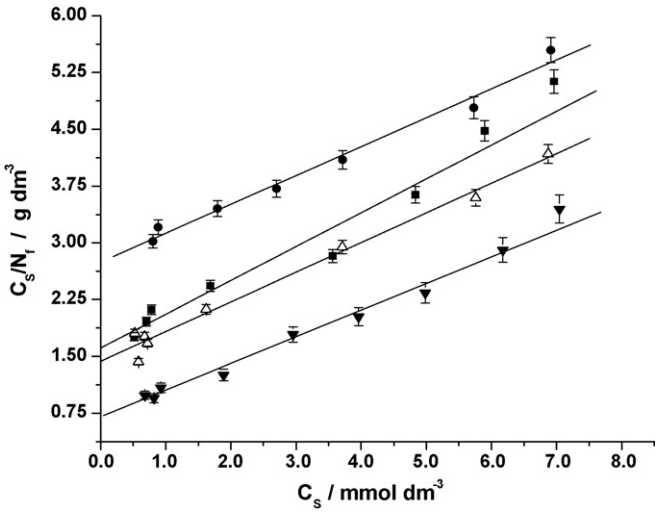

Fig. 9. Linearized Langmuir isotherm of Cu^{2+} on the Ch (■), ChC (●), ChCd (△) and ChCt (▼) surfaces at 298 ± 1 K.

are introduced in the polysaccharide backbone, a change in the crystalline arrangement could be expected, especially from loss of hydrogen bonding [36].

3.2. Adsorption isotherms

The biopolymer chitosan presents the ability to extract metals from aqueous solutions, mainly by using its favorable nitrogen atom, as part of the amino group, covalently bonded to the polymeric structure, containing a pair of free electrons to coordinate cations [22]. The effectiveness of such adsorption for metal ions depends, mainly, on the availability of the amine groups, which is directly related to the degree of acylation. Thus, the basic amine nitrogen center attached to chitosan pendant groups has the ability to form chelate compounds, mainly with cations with similar characteristics [37]. In this process, the free electron doublet on nitrogen is responsible for the adsorption of the metal, which may co-exist with anionic species, depending on the speciation of the cation [38]. For example, for copper, which is one of the most studied cations, it is proposed in many cases that the amine group on chitosan is essential to establish a defined $[NH_2]/[Cu^{2+}]$ ratio. On the other hand, the presence of a second coordination center, the hydroxyl group on carbon 3, must be considered for participation. However, another possibility is related to the participation of two distinct monomers of the same or different chains to embrace the same cation to form stable complexes [28].

The complete isotherms for copper adsorption with the original chitosan and all derivatives are shown in Fig. 8. The curves represent the number of moles of cation adsorbed per gram of the biopolymer, N_f, against the concentration of the solute in the supernatant, C_s, with a fit obtained through Eq. (1). As observed, copper gives a plateau region that progressively saturates the biopolymer surfaces. The N_f values for the copper complexed by pendant groups suggest the following adsorption order: ChCt > ChCd > Ch > ChC. The linearized form from the isotherms for the modified Langmuir equation, Eq. (2), for such adsorption, represented by C_s/N_f as a function of C_s, is shown in Fig. 9. This enables the calculation of the linear and angular data from the straight line, to obtain N^s and b values, as listed in Table 2. The maximum adsorption capacity, N^s, is an important parameter to express the ability for cation/basic center interactions, as given by the values 2.09 ± 0.02, 2.52 ± 0.02, 2.62 ± 0.04 and 2.84 ± 0.01 mmol g^{-1} for Ch, ChC, ChCd and ChCt, respectively. These values suggest that when the amines are incorporated in chitosan to give ChCd and ChCt biopolymers, the efficiency of the adsorption process increases in comparison to the precursor biopolymer. This process shows that these new synthesized biomaterials present the largest capacity for cation adsorption due to transference of cation from solution to the basic centers of the anchored ethylenediamine and diethylenetriamine molecules, by cation complexation through the increase by two or three available basic nitrogen atoms on the amine chains. These results clearly confirm the importance of the presence of free amine groups on chemically modified chitosan surface to extract cations from an aqueous solution in heterogeneous conditions.

3.3. Calorimetric titration

The resulting thermal effects obtained from copper nitrate interaction with precursor chitosan and their derivatives were determined in separate calorimetric experiments by considering the deduction of the dilution effect in water from the total thermal effect, as given by Eq. (3). The effects of the complete thermodynamic cycle for this series of interactions involving a suspension (sp) of biopolymers (Biopol) in aqueous (aq) solution with copper ion are represented as follows:

$$\text{Biopol}_{(sp)} + n\text{H}_2\text{O} = \text{Biopol}\cdot n\text{H}_2\text{O}_{(sp)}; \quad Q_h, \tag{8}$$

$$\text{Cu}^{2+}{}_{(aq)} + n\text{H}_2\text{O} = \text{Cu}^{2+}\cdot n\text{H}_2\text{O}_{(aq)}; \quad Q_d, \tag{9}$$

$$\text{Biopol}_{(sp)} + \text{Cu}^{2+}{}_{(aq)} = \text{Biopol}\cdot\text{Cu}^{2+}{}_{(sp)}; \quad Q_i \tag{10}$$

$$\text{Cu}^{2+}\cdot n\text{H}_2\text{O}_{(aq)} + \text{Biopol}\cdot n\text{H}_2\text{O}_{(sp)} = \text{Biopol}\cdot\text{Cu}^{2+}{}_{(sp)} + 2n\text{H}_2\text{O}; \quad Q_r \tag{11}$$

Table 2
Number of moles adsorbed (N_f), maximum adsorption capacity (N^s), constant (b), and correlation coefficient (r) for the interaction of Cu^{2+} with raw chitosan and its derivatives at 298 ± 1 K.

Sample	N_f (mmol g^{-1})	N^s (mmol g^{-1})	b	r
Ch	1.36 ± 0.04	2.62 ± 0.02	0.31	0.9904
ChC	1.25 ± 0.05	2.09 ± 0.02	0.14	0.9926
ChCd	1.64 ± 0.02	2.55 ± 0.04	0.27	0.9943
ChCt	1.99 ± 0.02	2.84 ± 0.01	0.35	0.9910

Table 3
Thermodynamic values for copper nitrate–biopolymer interactions at the surface at 298.15 ± 0.20 K.

Sample	$-\Delta_{mono}H$ (J g^{-1})	$-\Delta H$ (kJ mol^{-1})	ln K	$-\Delta G$ (kJ mol^{-1})	$-\Delta S$ (J mol^{-1} K^{-1})
Ch	11.10 ± 0.07	28.98 ± 0.05	8.5	21.1 ± 0.1	26 ± 1
ChC	16.04 ± 0.09	32.77 ± 0.04	8.9	22.1 ± 0.1	36 ± 1
ChCd	29.18 ± 0.10	60.60 ± 0.03	8.9	22.1 ± 0.1	129 ± 1
ChCt	22.81 ± 0.08	56.41 ± 0.05	9.4	23.4 ± 0.1	111 ± 1

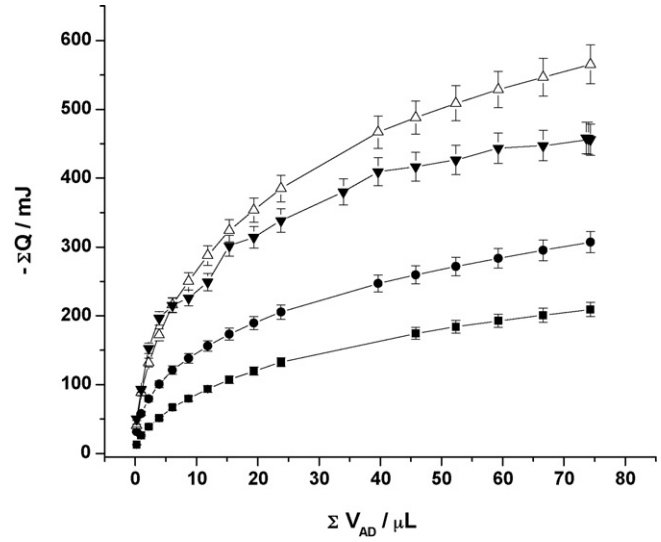

Fig. 10. The resulting thermal effects of the adsorption isotherms of Cu^{2+} on the Ch (■), ChC (●), ChCd (△) and ChCt (▼) surfaces at 298.15 ± 0.20 K.

The individual calorimetric titration experiments were carried out in duplicate and as the experimental thermal effect of hydration (Q_h) of the biopolymer was null, the net thermal effect was obtained by considering the thermal effects of dilution and interaction, from the calorimetric titration, as given by $\sum Q_r = \sum Q_i - \sum Q_d$, represented by Eq. (11). The isotherms are shown in Fig. 10. An example of linearization involving cation adsorption on ChCd is shown in Fig. 11. By applying Eq. (4) and the linearized data for all biomaterials, the enthalpy involved in the formation of a monolayer, $\Delta_{mono}H$, can be obtained for all processes, which enables calculation of the molar enthalpy, Eq. (5). From K values the free Gibbs energy was calculated from Eq. (6) for cation–basic center interactions on all chitosan surfaces and the missing thermodynamic entropic value was calculated from enthalpic and free Gibbs energy values through the Eq. (7). These values are listed in Table 3. The enthalpic data are exothermic for the all biopolymers and the magnitude of the values presented follows the order ChCd > ChCt > ChC > Ch. This behavior is associated with the availability of the free amino groups to interact with cations in solution at the solid/liquid interface. The negative free energy changes indicate that a spontaneous process of complexation of the copper by chitosan, presenting similar values for chitosan and their derivative forms, as previously observed [26]. All systems presented negative entropic values, which are also consistent with previously reported results [27,28,33]. The negative entropic values suggest that copper–biopolymer interactions cause an ordering of the system upon complexation. On the other hand, a disorder in solvent behavior causes an increase in entropy; however, the chemically modified biopolymers have the ability to order the solvent molecules of the system as the complexation process is in progress. These negative entropic values also suggest that the presence of cations bonding available amine groups in one or different polymeric chains may order the random coil disposition of the chains [27]. Although this process is less entropically favorable, the net result must be compensated by the more favorable enthalpic value, to give a negative free Gibbs energy.

It is worth mentioning that earlier enthalpic (−41.27 ± 1.57 kJ mol^{-1}) and entropic (−15 ± 1 kJ^{-1} mol^{-1}) values [28] obtained with unmodified chitosans differ from the present data. This fact can be associated with different chitosan sources, having different chitin deacetylations and, commercial product, which also reflect in 0.12 and 1.36 mmol g^{-1} maximum copper adsorption values, respectively.

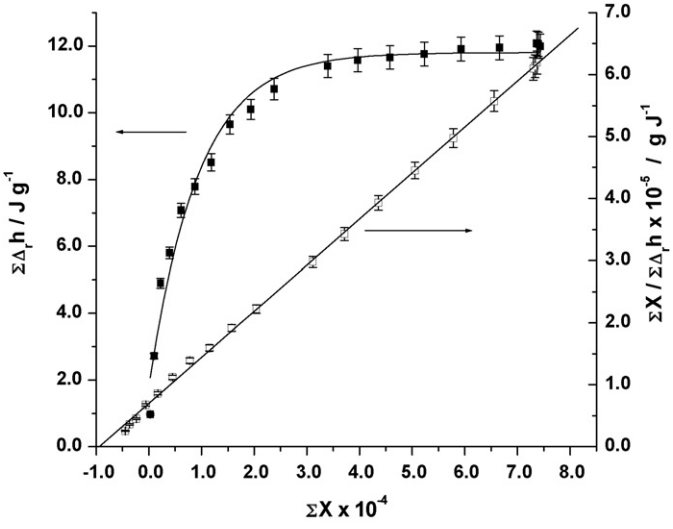

Fig. 11. Isotherm from calorimetric titration of Cu^{2+} (■) and its linearized form (□) on the ChCd surface at 298.15 ± 0.20 K.

4. Conclusions

The chemical modification of chitosan through reaction with ethylenediamine and diethylenetriamine resulted in new adsorbents, which were successfully characterized, having pendant chains attached to the main biopolymer skeleton. The effectiveness of such surface modification depends on a prior reaction to incorporate cyanuric chloride as intermediate biomaterial. The efficiency of the precursor chitosan, the intermediate and those containing diamines for copper ion adsorption was investigated using the batch process. The adsorption isotherms and the calorimetric titration curves confirmed that, in general, chitosan derivatives are more effective than the original chitosan in interacting with the copper cation. This pronounced interaction effect is reflected in exothermic enthalpic values that increase with the availability of basic nitrogen atoms on the pendant chains. The negative free Gibbs energy for copper–biopolymer interactions demonstrated favorable processes for copper–nitrogen basic atom complexes, with unfavorable entropic values for such interactions, indicating also an increase in the order of the final system. The copper adsorption capacity is mainly due to the availability of nitrogen on the chitosans, which is more effective in those biopolymers with increased amounts of amino groups, as clearly demonstrated with ethylenediamine and diethylenetriamine molecule incorporation on the biopolymer.

Finally, these results suggest that the chemically modified chitosans can be successfully employed for copper removal from wastewater or industrial effluents.

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