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Ethylenesulfide as a useful agent for incorporation into the biopolymer chitosan in a solvent-free reaction for use in cation removal

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ABSTRACT

Chitosan (Ch) was chemically modified with ethylenesulfide (Es) under solvent-free conditions to give (ChEs), displaying a high content of thiol groups due to opening of the three member cyclic reagent. Elemental analysis showed a decrease in nitrogen content. This result indicated the incorporation of two ethylenesulfide molecules for each unit of the polymeric structure of the precursor biopolymer. Infrared spectroscopy, thermogravimetry, and ^{13}C NMR in the solid state demonstrated the effectiveness of the reaction, with signals at 30 ppm for ChEs due to the change in the methylene group environment. Divalent metal uptake by chemically modified biopolymer gave the order Cu > Ni > Co > Zn, reflecting the corresponding acidity of these cations in bonding to the sulfur and the basic nitrogen atoms available on the pendant chains. The equilibrium data were fitted to Freundlich, Temkin, and Langmuir models. The maximum monolayer adsorption capacity for the cations was found to be 1.54 ± 0.02, 1.25 ± 0.03, 1.13 ± 0.01, and 0.83 ± 0.03 mmol g^{-1}, respectively. The Langmuir model best explained the cation–sulfur bond interactions at the solid–liquid interface. The thermodynamics for these interactions gave exothermic enthalpic values of -43.02 ± 0.03, -28.72 ± 0.02, -26.27 ± 0.04, and -17.32 ± 0.02 kJ mol^{-1}, respectively. The spontaneity of the systems is given by negative Gibbs free energies of -31.2 ± 0.1, -32.7 ± 0.1, -31.7 ± 0.1, and -32.2 ± 0.1 kJ mol^{-1}, respectively, in spite of the unfavorable negative entropic values of -39 ± 1, -13 ± 1, -18 ± 1, and -49 ± 1 J K^{-1} mol^{-1} due to solvent ordering in the course of complexation. This newly synthesized biopolymer is presented as a chemically useful material for cation removal from aqueous solution.

1. Introduction

Properties, such as abundance, biodegradability, non-toxicity, biocompatibility, biodegradability, bioactivity, and low cost are useful features for choosing biopolymers for valuable applications and they have recently received significant attention, not only because they are renewable, but also because they are more environmental friendly than conventional polymers.[1–3] Cellulose, chitin, and chitosan have related structures and occur in nature, being among the most abundant materials in the world.[4,5]

Among these biopolymers, chitin is natural, abundant, and suitable for developing novel types of materials containing different functions.[6,7] It is biodegradable and is the second most abundant polysaccharide on earth, after cellulose. It is a non-toxic biopolymer made up of acetylglucosamine units, which are widely found in the exoskeleton of shellfish and crustaceans, such crab, lobsters, and shrimps.[8]

Chitosan is a linear copolymer constituted by β-(1→4) linking 2-acetamido-2-deoxy-β-D-glucopyranose and 2-amino-2-deoxy-β-D-glucopyranose units obtained through N-deacetylation of chitin under strongly basic conditions. From the structural viewpoint, available amino (NH_2) and hydroxyl (OH) groups present single-pairs of electrons, even though the N-deacetylation is almost never complete.[9] Chitin and chitosan have similar polymeric structures, differing in the amount of acetylated units, as represented by the degree of deacetylation (DD), which is a useful parameter related to this property.[10,11] There is no formal nomenclature for this classification; however, it is expected that chitosan shows a DD value higher than 50%.[12,13]

The more available reactive amino groups on chitosan enable this polysaccharide to substitute chitin in the course of investigations, as an easily synthesized derivative from natural sources, demonstrating a facility for adsorption, in addition to other attractive physical properties.[14–16] On the other hand, when the biopolymeric chitosan is submitted to chemical modification, this is a promising route to yield new biomaterials. Through the inclusion of desirable pendant molecules covalently bonded to the main chain, some characteristic properties are changed and, consequently, many other interesting

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areas such as agriculture, medicine, food, industry, and pharmaceutical technology, become possible for technological applications.[17]

In the course of studying the applicability of chitosan and derivatives in many research fields in recent years, little attention has been focused on the study of these biopolymers using solvent-free reactions. The absence of solvent is an excellent reaction alternative, as it leads to an environmental friendly process for acquisition of new polysaccharides, with less expensive methodology. As is known, environmental contamination is a serious problem that is related to possible serious consequences, including contamination of water from various sources. Many traditional treatments have been applied to regenerate contaminated waters from distinct species, including heavy metals. These include ion-exchange, electrodeposition, membrane separation, and adsorption procedures.[2,18]

From these applied methodologies to purify effluents, adsorption seems to be a reliable alternative and many adsorbents have been proposed for this purpose.[19] Various natural or synthetic materials have been tested, and chitosan is being greatly exploited due to its advantages when compared, for example, with active carbon, which is the most intensively used material.[8] Indeed, the success of chitosan is closely related to its binding capacity for cations, mainly using the available amino groups. Thus, chitosan has been explored as one of the most popular adsorbents for metal removal from aqueous solution, because it was proven to have better chelating power than other biopolymers.[19] However, the extent of adsorption depends on its source, its deacetylation degree, the nature of the cation, and the pH of solution.

The available amino and hydroxyl groups in the biopolymer chitosan can be potentially modified to yield new products that usually increase the number of reactive sites to act as chelating centers to adsorb metals, dyes or others species.[20] However, the reactive free active primary amino group also opens the possibility to exploit the chemical reactions involving this group. The hydroxyl groups on carbons 3 and 6 of the ring can also react, to provide even more interesting chemical modifications of this biopolymer.[21]

Taking into account the rigidness of the polymeric chain, resulting in a material insoluble in common solvents, chitosan being soluble only in mineral or some dilute organic acids,[5] investigations are needed to give new biopolymers that enhance solubility. On the other hand, from the viewpoint of the adsorption methodology, chemical modifications, such as a crosslinking process, can be expected to reduce dissolution in acidic media, but with a disadvantage of decreasing sorption capacity.[22,23]

With the aim of synthesizing new chitosan derivatives the present investigation deals with the incorporation of ethylenesulfide molecule in the polysaccharide chain through the reaction of the available amino group. This nucleophilic amino center reacts with the three member cyclic reagent to place pendant chains with sulfur and nitrogen basic sites onto the original structure. An environmentally friendly solvent-free reaction was explored and the activity in adsorbing divalent cations from aqueous solution was studied through various proposed models. The cation–basic center interactions at the solid $\neq$ liquid interface were also followed calorimetrically and the set of thermodynamic data involved in these interactive processes was determined.

2. Experimental

2.1. Materials

Chitosan (Ch) powder (Primex) with a degree of deacetylation of 82%, determined through infrared spectroscopy, after treating the biopolymer with an alkaline solution.[24] Ethylenesulfide (Es) (Aldrich) reagent was incorporated on chitosan in a solvent-free reaction. Zinc, nickel, cobalt, and copper nitrate solutions were used in the adsorption process in deionized water.

2.2. Equipment and measurements

The carbon, sulfur, and nitrogen content of the precursor chitosan and of the chemically modified biopolymer were determined through elemental analysis on a Perkin Elmer, model 2400, elemental analyzer. FTIR spectra of the samples as KBr pellets were obtained by accumulating 32 scans on a Bomem Spectrophotometer, MB-series, in the 4000–400 cm^{-1} range, with 4 cm^{-1} of resolution. Solid-state ^{13}C NMR spectra of the samples were obtained on a Bruker AC 300/P spectrometer, using the CP–MAS technique, with pulse repetitions of 5 s and contact times of 1 ms; the measurements were at 75.47 MHz, with magic angle spinning of 4 kHz. X-ray diffraction patterns were obtained on a Shimadzu XD-3A diffractometer (35 kv, 25 mA), in the $2\theta = 1.5–50°$ range, with nickel-filtered Cu Kα radiation, having a wavelength of 0.154 nm. Thermogravimetric curves were obtained using a Shimadzu TGA 50 apparatus, under an argon atmosphere at a flow rate of 1.67 $cm^3\ s^{-1}$, with a heating rate of 0.167 K s^{-1}. The amount of cation adsorbed was determined using a Perkin Elmer 3000 DV ICP-OES apparatus, considering the difference between the initial concentration in the aqueous solution and that found in the supernatant after the adsorption process. The reproducibility was checked through at least one duplicate run for each experimental point.

2.3. Chemical reaction

To a sample of chitosan (2.0 g) in an appropriate flask protected from humidity, ethylenesulfide in excess (5.6 cm^3) was added in absence of solvent, with magnetic stirring. After 3 h, the solid was separated by filtration and extensively washed with deionized water. The isolated solid, hereafter named ChEs, was dried at 328 K in an oven.

2.4. Adsorption experiments

The new biopolymer (ChEs) was suspended in several metal salt solutions to evaluate its adsorptive capacity. All experiments were performed in duplicate, using a batch process in which nearly 20 mg of the chemically modified biopolymer was introduced into a series of polyethylene flasks containing 10.0 cm^3 of metallic cation solution having concentrations ranging from 7.0×10^{-4} to 7.0×10^{-3} mol dm^{-3}. With the purpose to obtain the time to reach isotherm saturation, kinetic experiments were previously assayed using similar cation solutions. For this determination the amount of cation removal as a function of time well defined a plateau at 4 h.[25] However, the time chosen was 6 h to ensure the best equilibrium condition and the suspensions were stirred in an orbital bath at 298 ± 1 K. The supernatant solutions were separated from the solid through decantation and aliquots were taken to determine the amounts of cation remaining by ICP-OES. The amount of the cation adsorbed in the experiment (mmol g^{-1}) was calculated by Eq. 1, where N_f is the number of moles adsorbed on modified chitosans, n_i and n_s are the number of moles in the initial solution and the supernatant after equilibrium, and m is the mass of the adsorbent used in each adsorption process.[26]

$$N_f = (n_i - n_s)/m \qquad (1)$$

To determine the maximum adsorption capacity, N_s, the experimental data related to the number of moles in the supernatant at each point of the titration, C_s, and the N_f obtained were fitted to a modified Langmuir equation (Eq. 2), b being a constant related to the chemical equilibrium at the solid/liquid interface.

$$\frac{C_s}{N_f} = \frac{1}{N_s b} + \frac{C_s}{N_s} \tag{2}$$

The Freundlich equation used to obtain the adsorption parameters[27] is given by the expression:

$$N_f = K_f C_s^{1/n_f} \tag{3}$$

where n_f represents the reactivity of energetic sites of the material and K_f is a constant related to the chemical equilibrium at the solid/liquid interface. Another equation is given by the Temkin model,[27] in which N_f is calculated through Eq. 4:

$$N_f = \frac{1}{n_T}\ln K_T + \frac{1}{n_T}\ln C_s \tag{4}$$

For comparing these models, three statistical tools have been used. The first one adjusts the correlation coefficient (r) obtained by means of linear regression of each equation, with a scaling factor derived by the division of each individual deviation with the standard deviation of the corresponding variable. These data were calculated using the ORIGIN® *7.5 software* program. Another tool is the sum of the squares of the errors (SSE), as shown in Eq. 5, and it is obtained from the sum of the squares of the difference between the experimental and the calculated N_f for each point of isotherm for each model:[27]

$$SSE = \sum_{i=1}^{m}(N_{f_{\mathrm{exp}_i}} - N_{f_{\mathrm{calc}i}})^2 \tag{5}$$

The last statistical tool used to verify the efficiency and adjustment of the models was the standard error (*SE*), calculated through the square root of the product of *SSE*, multiplying by a factor related to the division between the unit and the difference between the number of points in each isotherm and the parameters in each model.[27] The mathematical equation that represents this tool is shown in Eq. 6:

$$SE = \sqrt{\frac{1}{m-p}\sum_{i=1}^{m}(N_{f_{\mathrm{exp}_i}} - N_{f_{\mathrm{calc}i}})^2} \tag{6}$$

where $N_{f_{\mathrm{exp}}}$ is the number of experimentally adsorbed moles, $N_{f_{\mathrm{calc}}}$ is the number of calculated moles from each model, m is the number of points present in each isotherm and p is the number of parameters in each equation.

2.5. Calorimetric titration

The interactive effect between the cations in solution and the basic centers attached on the modified chitosan, ChEs, were measured through calorimetric titrations on a LKB 2277 instrument,[28] where three independent titrations must be carried out to complete the thermodynamic cycle: (i) the thermal effect due to ChEs interaction with cations (Q_{tit}), (ii) hydration of the solid biopolymer (Q_s), and (iii) dilution of cation solutions (Q_{dil}). For Q_{tit} experimental titration, the metallic solution is added to a suspension of nearly 20 mg of each biopolymer sample in 2.0 cm^3 of water, under stirring at 298.15 ± 0.20 K. Increments of 10.0×10^{-3} cm^3 of divalent cation solution were added to the biopolymer to obtain the thermal effect of interaction (Q_{tit}). The thermal effect of hydration of the suspended solid samples in water was null.[28] Thus, the resulting thermal effect is given by the following equation:

$$\sum Q_{res} = \sum Q_{tit} - \sum Q_{dil} \tag{7}$$

After adjusting the adsorption data to a modified Langmuir equation it is possible to determine the enthalpy associated with the cation/biopolymer interaction and the enthalpy of the formation of a monolayer per unit of mass of adsorbent, $\Delta_{\mathrm{mono}}H$, can be determined through:

$$\frac{\sum X}{\sum \Delta H} = \frac{1}{(K-1)\Delta_{mono}H} + \frac{X}{\Delta_{mono}H} \tag{8}$$

where $\sum X$ is the sum of the mole fractions of the cation solution after adsorption. X is obtained for each point of titrant addition; ΔH (J/mol), the enthalpy of adsorption per gram of adsorbent, is obtained by dividing the thermal effect resulting from adsorption by the number of moles of adsorbate and K is the proportionality constant, which also includes the equilibrium constant. From the angular and linear values of the $\sum X/\sum \Delta H$ versus $\sum X$ plot it is possible to calculate the $\Delta_{mono}H$ value. Then, the enthalpy of adsorption, ΔH, can be calculated through Eq. 9

$$\Delta H = \frac{\Delta_{mono}H}{n_s} \tag{9}$$

From K values, the Gibbs free energies (ΔG) were calculated through:

$$\Delta G = -RT\ln K \tag{10}$$

and the entropy (ΔS) can be calculated through:

$$\Delta G = \Delta H - T\Delta S \tag{11}$$

3. Results and discussion

3.1. Elemental analysis

The success of the reaction between Es and the non-bonded electron pair on the chitosan amino group is due to a typical nucleophilic attack of the basic nitrogen atom on the strained electrophilic carbon atom of the three-membered ring reagent. Consequently, the electrons of the bond between carbon and sulfur of the reagent are transferred to sulfur, with the opening of the ring. The excess of the charge on the sulfur atom attacks an adjacent hydrogen atom, once bonded to nitrogen, to form a sulfur–hydrogen bond to give a final neutral product. Again the non-bonded electron pair in the pendant chain has the ability to react identically as before with another molecule of the reagent to elongate the chain.[29] It could be supposed that this reaction will continue to consume more reagent, however, elemental analysis demonstrated the inclusion of only two molecules, as given by the results listed in Table 1.

The nitrogen content in the chemically modified biopolymer, 3.28 mmol g^{-1}, decreased when compared to the precursor biopolymer, 5.49 mmol g^{-1}, and this fact is in agreement with the incorporation of one ethylenesulfide molecule in the available amino groups bonded to the polymeric structure, followed by another molecule of **Es** bonding to the first to give a S/N molar ratio of 1.94. Based on this ratio, the reaction comprised in the described processes is schematically represented in Figure 1. In addition, there is the possibility of the ethylenesulfide molecule reacting with the hydroxyl groups on the biopolymer in a manner similar to its reaction with an inorganic silica polymer. However, the greater probability is reaction with the amino groups,[30] in agreement with its greater reactivity, to give the stable –NH-group.

3.2. Infrared spectroscopy

The infrared spectra of chitosan and its chemically modified biopolymer are shown in Figure 2. Pure chitosan possesses characteristic bands: C–H stretching around 2900 cm^{-1} and a broad intense band near 3400 cm^{-1} due to O–H and N–H stretching. The band at 1320 cm^{-1} is related to aliphatic CH bending vibra-

Table 1
Percentages of carbon (C), nitrogen (N), and sulfur (S), the respective number of moles for chitosan (Ch) and chemically modified chitosan (ChEs) and the molar ratio (S/N) for ChEs

Sample	C (%)	N (%)	S (%)	C (mmol g^{-1})	N (mmol g^{-1})	S (mmol g^{-1})	S/N
Ch	40.43	7.69	–	33.69	5.49	–	–
ChEs	40.49	4.59	20.39	33.74	3.28	6.37	1.94

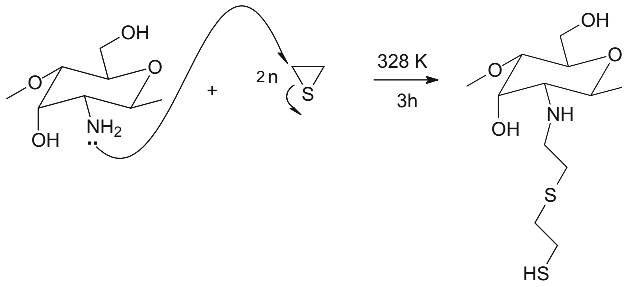

Figure 1. Synthesis of ChEs under solvent-free conditions.

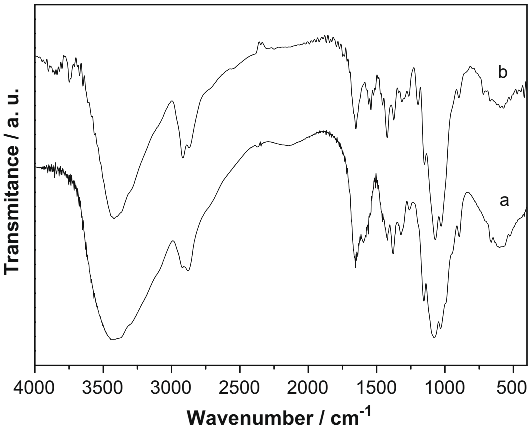

Figure 2. Infrared spectra of chitosan (a) and chemically modified chitosan, ChEs (b).

tions and those between 2920 and 2850 cm^{-1} correspond to the stretching vibrations of the same groups. Bands corresponding to the acetamide group, remaining from chitin, due its incomplete deacetylation,[11] appear at around 1655 and 1380 cm^{-1}, and are attributed to C=O stretching and C–H deformation bands. The band at 1320 cm^{-1} is related to aliphatic C–H bending vibrations and those between 2920 and 2850 cm^{-1} correspond to the stretching vibrations of the same groups. The bands in the 1200–800 cm^{-1} region are associated with the pyranosidic ring, reflecting C–O–C and β glycosidic linkages as well as the C–O bond related to primary and secondary alcohols. The spectra of the chemically modified chitosan showed small changes when compared to the original matrix, which may be explained by considering the difficulty in seeing the S–H band in the infrared spectrum. Nevertheless this band can be seen, although with difficulty, in the region around 2550 cm^{-1}. It is also possible to observe a change in bands that belong to the methylenic groups in the 2700 and 3000 cm^{-1} regions. A clear illustration for the effectiveness of the chemical modification process came from the CH:CH_2 ratio of 5:1 for the precursor chitosan, which changes to 5.5 in the final biopolymer.[31]

3.3. X-ray diffraction

Poor crystallinity was observed from X-ray diffraction patterns as shown in Figure 3 for chitosan, indicating the presence of two broad peaks around 9° and 20°, as previously reported.[24] The chemically modified chitosan (ChEs) did not present a significant change in terms of crystallinity, but the peak at 9° disappeared. This behavior can be attributed to the intra- and intermolecular hydrogen bonds that drive the crystallinity related to the stability to maintain the polymeric chains. In the present case, the chemically modified biopolymer incorporated ethylenesulfide in the precursor chitosan. Then, the crystallinity associated with chitosan is closely related to the ability of this reagent to disrupt these sets of bonds in all polymeric chains and also the bulkier precursor substitution on it, during the course of the reaction.[32,33] As a general rule, the new chemically modified chitosan decreases in crystallinity in comparison with the precursor biopolymer, as it is also clearly demonstrated in this investigation.

3.4. NMR spectroscopy

The ^{13}C NMR spectra for chitosan and the chemically modified biopolymer are shown in Figure 4. Raw chitosan presented characteristic chemical shifts at 105, 55, 85, and 60 ppm, related to the C1, C2, C4, and C6 carbons, respectively, as well as the signal at 75 ppm attributed to C3 and C5 carbon atoms. The signals at 22 and 175 ppm are attributed to methyl and carbonyl groups from the original chitin, due to the expected incomplete deacetylation process, as clearly indicated in the biopolymer structure in Figure 4a. The spectrum of chemically modified chitosan is shown in Figure 4b, in which peaks in the 30–50 ppm region suggest different chemical environments for CH_2 groups. Such different environments are due to the contribution of the ethylenesulfide molecules in the new polymeric structure. A significant modification was found in the peaks related to C6 and C2 carbon atoms, which were completely separated in the ChEs structure, as shown in Figure 4b. The displacement occurs for one of the carbons present in the 50 and 70 ppm region, proving that the reaction occurred in the amino group located on C2 carbon atom, due to the fact that this group is more reactive than the hydroxyl group on the C6 carbon atom.[34]

3.5. Thermogravimetry

The thermal degradation profiles are quite similar for original and the derivative, but comparing the thermogravimetric curves

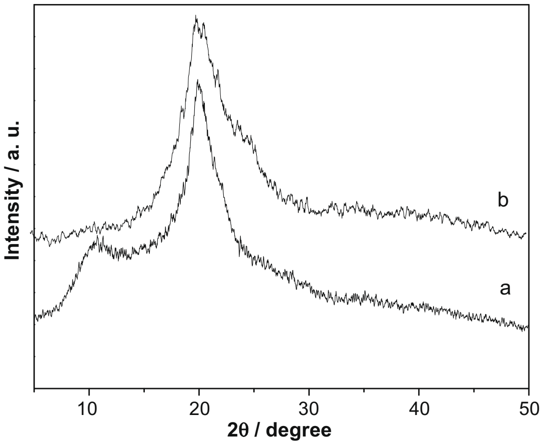

Figure 3. X-ray diffraction patterns of chitosan (a) and chemically modified chitosan, ChEs (b).

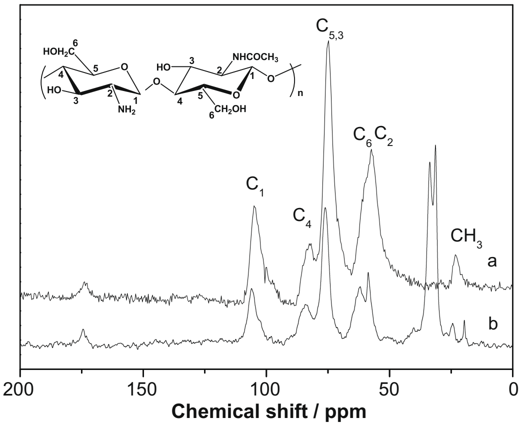

Figure 4. ^{13}C NMR spectra in the solid state for natural chitosan (a) and chemically modified chitosan, ChEs (b).

it is possible to observe that chitosan continues its degradation up to 1200 K, while the modified chitosan showed a relative stability from 700 K. The thermogravimetric curves are shown in Figure 5 and the decomposition suggested that the thermal degradation occurred in two stages, results that corroborate with the defined well-established peaks in the derivative curves, as shown in Figure 6. The first stage is attributed to loss of adsorbed water that is observed at 337 K for chitosan and at 323 K for the derivative. The second mass loss for chitosan and the modified biopolymer occurred at 569 K. These values represent the maximum mass loss temperature of the synthesized polymeric materials and were obtained from the first derivative curves. These results reflect that the chitosan is a little more stable than the synthesized derivative at temperatures lower than 600 K. However, this behavior changed above this temperature, suggesting that the chemically modified material has improved thermal stability, because this material presented a lower mass loss than the precursor chitosan.[33]

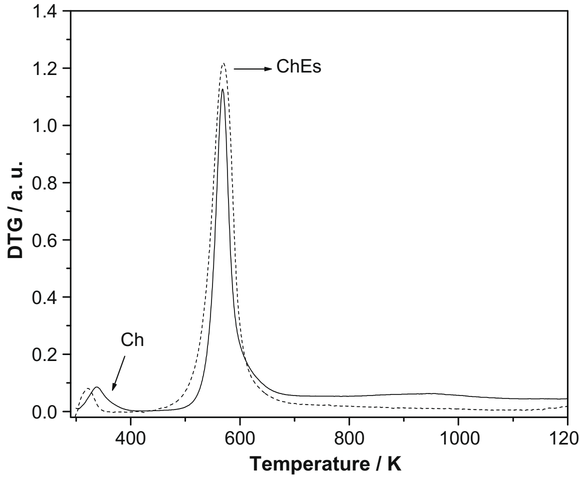

Figure 6. Thermogravimetric derivative curves of chitosan (a) and chemically modified chitosan, ChEs (b).

3.6. Adsorption isotherms

The ability of chitosan in extracting metallic cations has been previously reported. Copper ion has been much employed in these adsorption assays, as it is normally adsorbed by the natural biopolymer from aqueous solution at neutral pH.[24] The isotherm of the chemically modified chitosan, ChEs, with divalent cations were fitted to Langmuir, Temkin, and Freundlich models, as illustrated for copper in Figure 7. It is well established that chitosan has the ability to bind cations through the electron pairs available on the nitrogen atom in the free amino groups,[35] however studies involving other cations have also been performed.[2] The present data from the adsorption isotherms gave maximum values of 1.54 ± 0.02, 1.25 ± 0.03, 1.13 ± 0.01, and 0.83 ± 0.03 mmol g^{-1} for divalent copper, cobalt, nickel, and zinc, respectively, as shown in Table 2. These values are higher when compared with raw chitosan,[11] which gives 0.28 ± 0.05, 0.20 ± 0.03, 0.21 ± 0.01, and 0.14 ± 0.07 mmol g^{-1} for this sequence of cations and the same powder adsorbent, indicating identical decreased order. On the other hand, it is not easy to compare the values due to difference in chitosan source, the degree of deacetylation and also the form found. For example, for the same powder form, approximately values of 0.70,[36] 0.25,[37] 0.30,[38] and 0.15[39] mmol g^{-1} were determined. For chitosan chemically modified with thiourea, the sulfur attached to pendant chain acts as donor atom to give 0.78 and 0.30 mmol g^{-1} for copper and nickel, demonstrating higher effectiveness of ethylenesulfide in cation removal.

The modifier agent ethylenesulfide promotes a reaction with the free amino group of the chitosan providing a sulfur basic center in the resulting biopolymer that is also available to interact with

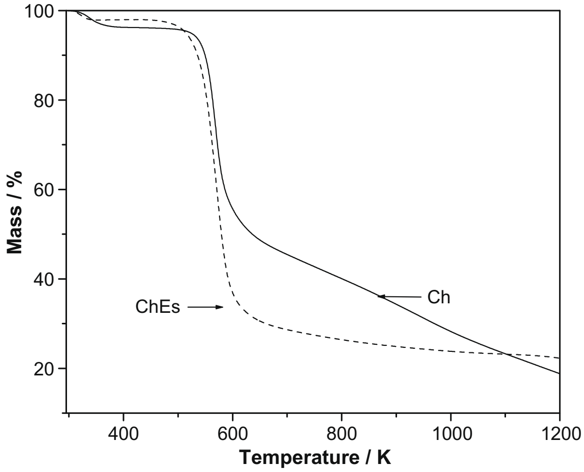

Figure 5. Thermogravimetric curves of chitosan (a) and chemically modified chitosan, ChEs (b).

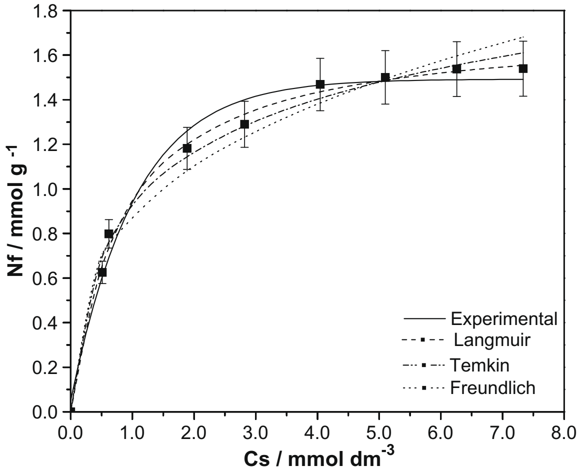

Figure 7. Adjustment of the data to Langmuir, Freundlich, and Temkin isotherms for copper adsorption with chemically modified chitosan, ChEs, at 298 ± 1 K.

Table 2
Number of moles adsorbed (N_f), parameters of the Langmuir (n_s and K_L), Freundlich (n_F and K_F), and Temkin (n_T and K_T) equations, correlation coefficients (r), sum of the squares of the errors (*SSE*), and standard errors (*SE*) for the interaction of divalent metals with chemically modified chitosan (ChEs) at 298 ± 1 K

Model	Parameters	Metal			
		Cu	Co	Ni	Zn
N_f	–	1.54 ± 0.02	1.13 ± 0.01	1.25 ± 0.03	0.83 ± 0.3
Langmuir	n_s	1.73	1.29	1.34	0.90
	K_L	1194	1449	2763	2876
	r	0.9993	0.9990	0.9988	0.9986
	SSE	0.01	0.01	0.03	0.02
	SE	0.04	0.03	0.07	0.05
Freundlich	n_F	3.08	3.14	3.45	4.24
	K_F	881	720	882	625
	r	0.9900	0.9880	0.9500	0.9145
	SSE	0.02	0.01	0.06	0.02
	SE	0.05	0.04	0.10	0.06
Temkin	n_T	2.91	3.82	4.06	6.85
	K_T	14,828	17340	43784	81755
	r	0.9740	0.9754	0.9106	0.8828
	SSE	0.05	0.01	0.10	0.04
	SE	0.09	0.01	0.13	0.08

cations. The affinity between the sulfur atom and the cation will determine the adsorption capacity. As observed, ChEs showed lower affinity for zinc and higher for copper cations, which behavior is observed with the majority of the chemically modified aminated chitosans for both cations.[11,19]

The chemically modified chitosan has less free amino content in comparison to the precursor biopolymer, to be able to chelate the metallic cations; however, as any reagent with additional centers can be attached as pendant chains, increasing the available basic centers for cation complexation. Based on these structural features it is suggested that the use of ethylenesulfide as modifier agent, in a solvent-free reaction, allows achieving some advantages, by increasing the adsorption capacity of the resulting polymeric biopolymer.[33] Thus, it was found that the chemically modified chitosan presented the following order of adsorption for divalent cations: Cu > Ni > Co > Zn, due to favorable complexation equilibrium constant, as it is predicted by Irving–Williams series. During such interaction the cations are bonded to the basic center attached on pendant chains to form cation/biopolymer complex at the solid/liquid interface.[25]

The parameters obtained from the linearized Langmuir, Freundlich, and Temkin models for divalent metal adsorption on ChEs are listed in Table 2. From these data it is observed that copper is the cation having the highest adsorption, although the others possess an excellent linear coefficient for the Langmuir model. For the Freundlich and Temkin models the adjustment showed lower values of the linear correlation coefficients when compared to the Langmuir model. Observing the experimental adsorption curves, it can be seen that these curves behave as typical Langmuir type 2L isotherms, in the classification of Giles, showing curves with concavity, that is, possessing an acclivity followed by a plateau. These types of curves represent monolayer formation.[40]

Considering the appraised statistical parameters *SSE* and *SE*, the values obtained for Freundlich and Temkin models are small as the linear fits are very low. The parameters obtained for the Langmuir model were larger than those for the other two models, and the linear adjustment was very satisfactory. The Langmuir model is, in general, the best model to describe the experimental curves. All n_F values are larger than 1, indicating the existence of favorable systems for all cations.[27]

3.7. Calorimetric titration

The thermal effects obtained when cation nitrates interacted with ChEs were determined in separate calorimetric experiments. The net quantitative effects for each biopolymer–cation interactions were obtained after subtracting the cation dilution effect, as given by Eq. 7. These thermal effects from the complete thermodynamic cycle for this series of interactions involve a suspension (sp) of biopolymers (Biop) in aqueous (aq) solution with divalent cation (M^{2+}) and are represented as follows:

$$\mathrm{Biop}_{(\mathrm{sp})} + \mathrm{M}^{2+}_{(\mathrm{aq})} = \mathrm{Biop}\cdot\mathrm{M}^{2+}_{(\mathrm{sp})};\quad Q_t \tag{12}$$

$$\mathrm{Biop}_{(\mathrm{sp})} + n\mathrm{H_2O} = \mathrm{Biop}\cdot n\mathrm{H_2O}_{(\mathrm{sp})};\quad Q_h \tag{13}$$

$$\mathrm{M}^{2+}_{(\mathrm{aq})} + n\mathrm{H_2O} = \mathrm{M}^{2+}\cdot n\mathrm{H_2O}_{(\mathrm{aq})};\quad Q_d \tag{14}$$

$$\mathrm{Biop}\cdot n\mathrm{H_2O}_{(\mathrm{sp})} + \mathrm{M}^{2+}\cdot n\mathrm{H_2O} = \mathrm{Biop}\cdot\mathrm{M}^{2+}_{(\mathrm{sp})} + 2n\mathrm{H_2O};\quad Q_r \tag{15}$$

The great advantage of the calorimetric titration for this heterogeneous system is the simultaneous determination of equilibrium and enthalpies data, after adjusting the net thermal effects to a mathematical model. Through these values, the Gibbs free energy and the entropy for this system can also be calculated. For the present case, the net thermal effect obtained from the calorimetric titration is given by the expression $\sum Q_r = \sum Q_t - \sum Q_d$, based on Eq. 15. The respective isotherms for cations interacting with the chemically modified chitosan, ChEs is shown in Figure 8. One example of linearization involving cobalt adsorption in ChEs is shown in Figure 9. By applying Eq. 8 and the linearized data for all biopolymers, the enthalpy involved in the formation of a monolayer, $\Delta_{mono}H$, can be obtained for each process, which enables the calculation of the molar enthalpy, as given in Eq. 9. From the K value the Gibbs free energy was calculated from Eq. 10 for cation–basic center interactions and the thermodynamic entropy was calculated from the enthalpic and Gibbs free energy values through Eq. 11 and the complete set of values are listed in Table 3.

The enthalpic data are exothermic for all studied interactions and the magnitude of the values presented follows the order Cu > Ni > Co > Zn. The larger enthalpic value for copper, when compared to nickel, cobalt, and zinc, has been shown for other systems,[31] as also observed by comparing copper interactions with ChEs and

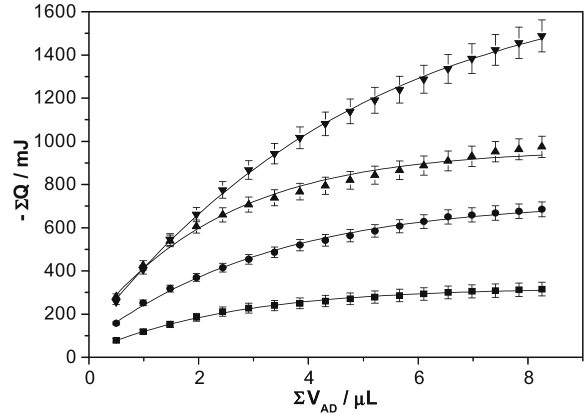

Figure 8. The resulting thermal effects of the adsorption isotherms of the divalent cations: Cu^{2+} (▼), Ni^{2+} (▲), Co^{2+} (●), and Zn^{2+} (■) on chemically modified chitosan surface, ChEs, at 298.15 ± 0.20 K.

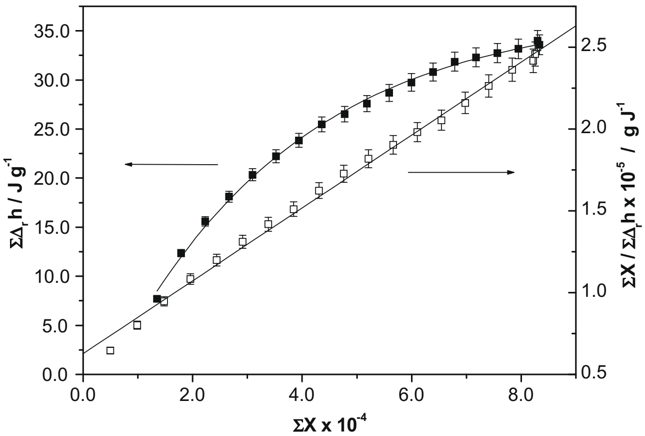

Figure 9. The linearized form of adsorption isotherms for divalent cobalt on chemically modified chitosan, ChEs, at 298.15 ± 0.20 K.

Table 3
Thermodynamic values for interaction of the divalent cations with chemically modified chitosan (ChEs) at the solid/liquid interface 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})
Cu	74.42 ± 0.06	43.02 ± 0.03	12.6	31.2 ± 0.1	39 ± 1
Ni	38.51 ± 0.07	28.72 ± 0.02	13.2	32.7 ± 0.1	13 ± 1
Co	34.01 ± 0.03	26.27 ± 0.04	12.8	31.7 ± 0.1	18 ± 1
Zn	15.58 ± 0.07	17.32 ± 0.02	12.9	32.2 ± 0.1	49 ± 1

with pure chitosan.[33] A larger value of enthalpy for the copper/ChEs interaction was obtained.

The negative free energy values indicate that a spontaneous process of complexation of all cations by ChEs has occurred, as previously observed.[11] All systems presented negative entropic values, which are also consistent with previously reported results.[24] These values suggest that the order in solvent behavior causes a decrease in entropy as the complexation process is in progress. These negative values obtained for entropy also suggest that the presence of cations bonding to available sulfur groups may order the random disposition of the chitosan chains.[34]

4. Conclusions

The synthesis of a new chemically modified chitosan possessing a S–H bond in its chain using ethylenesulfide in the absence of solvent was efficiently performed, according to characterization methods such as elemental analysis and carbon nuclear resonance spectroscopy. X-ray diffraction showed that this modification on chitosan chains yields a biopolymer with a slightly smaller degree of crystallinity. The chemically modified biopolymer adsorbed metallic cations giving the values 1.54; 1.25; 1.13, and 0.83 mmol g^{-1} for Cu, Ni, Co, and Zn, respectively. The adsorption ability for each metal is associated with intrinsic parameters of each cation that determine its affinity for the modified surface. These interactions could be calculated by applying the modified Langmuir equation that showed to be the best model to obtain the adsorption parameters when compared with the Freundlich and Temkin models.

The interactions between the cation and the basic centers of ChEs at the solid/liquid interface followed by calorimetric titrations, showed negative entropies, but favorable thermodynamic values, suggesting the possibility of application of this modified biopolymer for removal of this series of divalent cations from aqueous solutions.

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