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Ethylenesulfide as a useful agent for incorporation on the biopolymer chitosan in a solvent-free reaction for use in lead and cadmium removal

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Abstract In this work 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. ChEs was used in studies of lead and cadmium adsorption from aqueous solution, using the batchwise method and calorimetric studies were accomplished to those interactions, through the calorimetric titration technique. The obtained results show that the modified Ch, ChEs is a material, that besides presenting the advantages of being a biopolymer, it showed a good adsorption capacity of the lead and cadmium cation metallic, that are extremely poisonous and harmful to the environment. The results of the calorimetric titration showed that the related thermodynamic parameters to those adsorptions shown favorable thermodynamic data.

Keywords Chitosan · Modification · Ethylenesulfide · Adsorption · Calorimetry

Introduction

Chitosan (Ch) is a linear copolymer constituted by $\beta(1 \rightarrow 4)$ 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 [1, 2]. It is usually obtained trough alkaline deacetylation from chitin that is a natural occurrence polymer made up of acetylglucosamine units, which are widely found in the exoskeleton of shellfish and crustaceans, such as crab, lobsters, and shrimps [3], being the second more abundant polysaccharide of the planet [4] and defeated only by cellulose. Cellulose, chitin, and Ch have related structures and occur in nature, being among the most abundant materials in the world [5, 6]. Chitosan is extensively exploited due to its innumerous advantages, since besides its chemical behavior Ch exhibits also physical and biological properties as non toxicity, biocompatibility, and biodegradability. When the biopolymeric Ch 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 areas such as agriculture, medicine, food, industry, pharmaceutical technology and so on become possible technological applications [7]. A point toward these modifications is the Ch sorption capacities studies, detaching its behavior with divalent cations [8].

This investigation deals with the incorporation of ethylenesulfide (Es) molecule in the polysaccharide chain through the reaction of the available amino group. An environmentally friendly solvent-free reaction was explored and the activity in sorbing divalent lead and cadmium from aqueous solution was studied through the proposed model. The cation/basic center interactions at the solid/liquid interface were also followed calorimetrically, and the set of thermodynamic data involved in these interactive processes was determined.

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Experimental

Chemicals

Chitosan powder (Primex) with a degree of deacetylation of 82 %, determined through infrared spectroscopy was utilized [9]. Ethylenesulfide (Aldrich) reagent was incorporated on Ch in a solvent-free reaction. Lead and cadmium nitrate solutions were used in the sorption process in deionized water.

Chemical reaction

To a sample of Ch (2.0 g) in an appropriate flask protected from humidity, Es in excess (5.6 cm^3) was added in the absence of solvent, at 328 K, under 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 [8].

Characterizations

The contents of carbon, sulfur, and nitrogen 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 to 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. 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 sorbed was determined using a Perkin Elmer 3000 DV ICP-OES apparatus.

Sorption experiments

An amount of 20 mg of the ChEs were 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}, for 4 h at 298 ± 1 K [10, 11]. The essays were accomplished in pH 6.1, since in acidic pH, lower than 4.0, raw Ch is soluble, and the same occurs to the modified material. Besides in such conditions the proton ions compete with the cations in binding to basic centers of the modified Ch. 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 Chs, 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 [12, 13].

$$N_f = (n_i - n_s)/m. \tag{1}$$

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.

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

Calorimetric titration

The interactive effect between the cations in solution and the basic centers attached on the modified Ch, ChEs, were measured through calorimetric titrations on a LKB 2277 instrument [14, 15], 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 [14–16]. Thus, the resulting thermal effect is given by the following equation:

$$\sum Q_{res} = \sum Q_{tit} - \sum Q_{dil}. \tag{3}$$

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, $\Delta_{mono}H$, can be determined:

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

where $\sum X$ is the sum of the mole 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.

Results and discussion

Elemental analysis

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 Es 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 and the sulfur content was 6.37 mmol g^{-1}. Based in this ratio, the reaction comprised in the described processes is schematically represented in Fig. 1. In addition, there is the possibility of the Es molecule in reacting with the hydroxyl groups on the biopolymer in a similar manner to its reaction with an inorganic silica polymer. However, the greater probability is reacting with the amino groups [17], in agreement with its greater reactivity. This new modified material has as active groups for sorption process besides the remaining amino groups, the introduced sulfur groups, whose last have a great affinity for cations such as lead and cadmium.

Infrared spectroscopy

The pristine Ch possesses characteristic bands that are 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 vibrations 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 [17], appear at around 1655 and 1380 cm^{-1}, and are attributed to C=O stretching and CH deformation bands. The band at 1320 cm^{-1} is related to aliphatic CH 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 Ch showed small changes when compared to the original matrix, which may be explained by considering the difficulty in seeing the SH 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} region. A clear illustration for the effectiveness of the chemical modification process came from the CH:CH_2 ratio of 5:1 for the precursor Ch, which changes to 5.5 in the final biopolymer [18, 19].

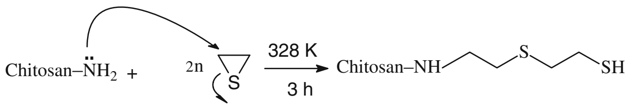

Fig. 1 The chemical reaction for Es incorporated on Ch

NMR spectroscopy

The ^{13}C NMR spectra for Ch and the chemically modified biopolymer are shown in Fig. 2. Raw Ch 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 Fig. 2a. The spectrum of chemically modified Ch is shown in Fig. 2b, 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 Es 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 Fig. 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 [20].

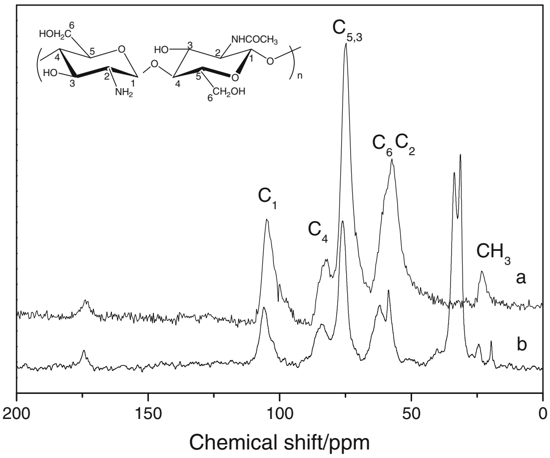

Fig. 2 ^{13}C NMR spectra in the solid state for natural Ch (*a*) and chemically modified Ch, ChEs (*b*)

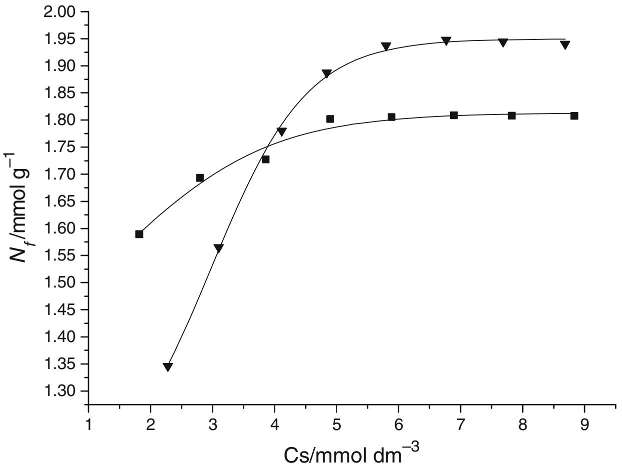

Fig. 3 Langmuir isotherms for lead (*filled square*) and cadmium (*filled inverted triangle*) sorption with chemically modified Ch, ChEs, at 298 ± 1 K

Adsorption isotherms

The isotherm of the chemically modified Ch, ChEs, with divalent cations, lead and cadmium, is illustrated in Fig. 3. This data from the adsorption isotherms gave maximum values of 1.94 mmol g^{-1} ± 0.02 and 1.81 mmol g^{-1} ± 0.03 for divalent cadmium and lead, respectively. These values are higher when compared to the other sorption cation values showed in the previous study [8], demonstrating higher effectiveness and affinity of Es in such cation removal. The mechanism of sorption can involve interactions that can be interpreted due to the transference of cation from solution to the basic centers of the modified Ch molecule (ChEs), by complexation of the cations through the available Es groups. The affinity between the sulfur atom and the cation will determine the adsorption capacity. The chemically modified Ch has less free amino content in comparison to the precursor biopolymer, to be able to chelate the metallic cations; however, it has additional sulfur centers that can be used as pendant chains, increasing the available basic centers for cation complexation. Based on these structural features it is suggested that the use of Es as modifier agent, in a solvent-free reaction, allows achieving some advantages, by increasing the adsorption capacity of the resulting polymeric biopolymer. Thus, it was found that the chemically modified Ch presented the following order of adsorption for divalent cations: Cd > Pb, 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 [10].

Table 1 Number of moles adsorbed (N_f), parameters of the Langmuir (n^s and K) and correlation coefficients (r) for the interaction of divalent metals with chemically modified Ch (ChEs) at 298 ± 1 K

Metals	N_f/mmol g^{-1}	n^s/mmol g^{-1}	K	r
Cd	1.94 ± 0.02	2.47	198789	0.9927
Pb	1.81 ± 0.03	2.12	327747	0.9989

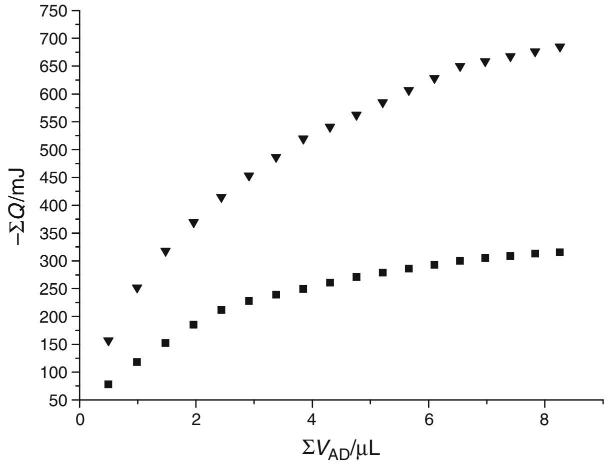

Fig. 4 The resulting thermal effects of the sorption isotherms of the divalent cations: Cd^{2+} (*filled inverted triangle*) and Pb^{2+} (*filled square*) on chemically modified Ch surface, ChEs, at 298.15 ± 0.20 K

The parameters obtained from the linearized Langmuir model for divalent metal sorption on ChEs are listed in Table 1. From these data it is observed that cadmium is the cation having the highest adsorption in comparison to the lead cation, although both cations possess an excellent linear coefficient for the Langmuir model.

Calorimetric titration

The thermal effects obtained when cation nitrates interacted with ChEs were determined in separate calorimetric experiments as shown in Fig. 4. The enthalpic data are exothermic for both studied cations interactions and the magnitude of the values presented follows the order Cd > Pb as reflected by the sorption values as shown in Table 2. The negative free energy values indicate that a spontaneous process of complexation of both cations by ChEs has occurred, as previously observed [8, 19, 20]. All systems presented negative entropic values, which are also consistent with previously reported results. These values suggest that 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 Ch chains [20].

Table 2 Thermodynamic values for interaction of the divalent cations with chemically modified Ch (ChEs) at the solid/liquid interface at 298.15 ± 0.20 K

Metals	$-\Delta_{mono}H$/J g^{-1}	$-\Delta H$/kJ mol^{-1}	ln K	$-\Delta G$/kJ mol^{-1}	$-\Delta S$/J mol^{-1} K^{-1}
Cd^{2+}	158.75 ± 0.03	64.27 ± 0.02	12.2	30.2 ± 0.1	114 ± 1
Pb^{2+}	124.90 ± 0.02	58.91 ± 0.02	12.7	31.5 ± 0.1	91 ± 1

Conclusions

The synthesis of a new chemically modified Ch possessing a SH bonding in its chain using Es in the absence of solvent was efficiently performed, according to such characterization methods as elemental analysis and carbon nuclear resonance spectroscopies. The chemically modified biopolymer adsorbed metallic cations giving the values 1.94 mmol g^{-1} ± 0.02 and 1.81 mmol g^{-1} ± 0.03 for Cd and Pb, 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 a good model to obtain the adsorption parameters as showed by the correlation coefficients.

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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