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Immobilization of ethylene sulfide in aminated cellulose for removal of the divalent cations

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ABSTRACT

Cellulose (Cel) was first chemically modified with thionyl chloride to increase its reactivity. In the next step CelCl was reacted with ethylenediamine (CelEn) and subsequently reacted with ethylene sulfide to obtain a solid substance, CelEnEs. The modification reactions were confirmed by elemental analysis, TG, XRD, ^{13}C NMR and FTIR. The chemically modified biopolymer CelEnEs had an order of divalent metal sorption of $Pb^{2+} > Cd^{2+} > Ni^{2+} > Co^{2+} > Cu^{2+} > Zn^{2+}$, and the maximum adsorption capacities were found to be 6.282 ± 0.023, 5.783 ± 0.015, 5.561 ± 0.017, 4.694 ± 0.013, 1.944 ± 0.062 and 1.733 ± 0.020 mmol g^{-1}, respectively. The equilibrium data were fitted to Langmuir, Freundlich and Temkin models, and in general, the experimental data best fit the Freundlich model. This newly synthesized biopolymer proved to be a chemically useful material for cations removal from aqueous solution.

1. Introduction

The mere presence of a variety of metals such as copper, cadmium, lead, nickel and chromium in an aquatic environment is of great concern because they are toxic and do not biodegrade in nature. These metal ions may show acute toxicity to aquatic organisms and terrestrial life and cause remarkable adverse physiological effects in humans and animals. From this perspective, the need to reduce or eliminate these pollutants and minimize their adverse effects has lead to a significant increase in recent decades in the number of investigations aimed at controlling these metals in the environment (Santana, Vieira, da Silva Filho, Melo, & Airoldi, 2010).

Currently, research has become more focused on developing new materials that have the ability to remedy this problem. Many studies use natural or synthetic materials whose roles during synthesis and in the process of removing the cations pollutants follow the requirements of green chemistry, which aims to reduce waste and optimize the wastewater treatment processes (Airoldi, 2008; Staudinger, 1920).

When seeking new materials, a natural source is undoubtedly the most exploited and becomes more attractive when the isolation process is less expensive, especially when it is used as we have found or when very few processing operations are necessary. Additionally, certain chemical modifications enhance the utility of their surfaces (Airoldi, 2008).

In recent years, polymers that have attracted more interest such as cellulose, which comes from a variety of sources, and chitin, which is derived from crustaceans, mollusks, insects, fungi and other organisms (Airoldi, 2008; Staudinger, 1920).

Cellulose is the most abundant biopolymer and represents approximately 1.5×10^{12} tons of the total production of biomass per year. It is considered a source of almost inexhaustible raw material for environmentally safe and biocompatible products (Staudinger, 1920).

The molecular structure of cellulose consists of a carbohydrate polymer generated by repeating β-D-glucopyranose units, which are covalently linked by acetal functionalities between the equatorial OH group on carbon atom 4 (C4) and carbon atom 1 (C1), hence the name β-1,4-glucan. As a result, cellulose possesses an extensive linear chain polymer with a large number of hydroxyl groups (three groups per anhydroglucose unit (AGU)) and a thermodynamically preferred conformation 4C1 (a bond between carbons 4 and carbon 1).

Pure cellulose has very few applications compared to the diversity of applications of its changed form (Jorge & Chagas, 1988). That is why chemical changes are made; one of the main objectives for introducing structural modification is to increase its adsorption capacity for heavy metals in aqueous and non-aqueous media (Kamel, Hassan, & El-Sakhawy, 2006). Moreover, chemical modifications can be used to vary several other properties of cellulose, such as hydrophobicity or hydrophilicity, elasticity,

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adsorptivity, microbial resistance and heat and mechanical resistance (McDowall, Gupta, & Stannett, 1984).

Chemical modification of a polysaccharide surface follows the same principles as those established for other media, such as silica gel. However, the hydroxyl groups on cellulose are less reactive and the start of a chemical modification takes place at the primary hydroxyl found on carbon 6, which may occur through several different routes. However, modifications may also occur on in the secondary hydroxyl groups present on carbons 2 and 3. The major modifications of cellulose occur through halogenation, oxidation, etherification and esterification (Martin, Sánchez-Chaves, & Arranz, 1999).

This study aimed to synthesize a new cellulose derivatives by incorporating ethylene sulfide into the polysaccharide chain through reaction of an available amino group, which was present from a previously reaction with ethylenediamine, that required prior chlorine anchoring to increase the reactivity of the cellulose surface. The derivative's capacity for adsorbing divalent cations from aqueous solution was studied using batchwise studies, and three models, the Langmuir, Freundlich and Temkin, were used to evaluate the obtained new isotherms after linear adjust.

2. Experimental

2.1. Materials

The microcrystalline cellulose (Cel) (Aldrich) was previously dried at a 373 K under vacuum for 24 h to remove any physically adsorbed water (Martin et al., 1999). Ethylenediamine (Vetec), thionyl chloride ($SOCl_2$) (Chemiker), N,N-dimethylformamide (Vetec) and ethylene sulfide (Vetec) were used in the cellulose modification reactions. The nitrates of the divalent heavy metals (Vetec) were used in the adsorption process with deionized water.

2.2. Equipment and measurements

The content of chlorine, sulfur and nitrogen of the precursor cellulose and the chemically modified biopolymer were determined through elemental analysis on a Perkin Elmer, model 2400, elemental analyzer. The FTIR spectra of the samples as KBr pellets (1% sample) were obtained by accumulating 36 scans on a MB-series Bomem Spectrophotometer in the range of 4000–400 cm^{-1}, with 4 cm^{-1} of resolution. Solid-state ^{13}C NMR spectra of the samples were obtained on an INOVA Varian spectrometer, using the CP/MAS technique, with pulse repetitions of 5 s and contact times of 1 ms; the measurements were recorded at 75.47 MHz, with magic angle spinning of 4 kHz. The x-ray diffraction patterns were obtained on a Shimadzu XD-3A diffractometer (35 kV, 25 mA), with a scan rate of 5° min^{-1} in the 2θ = 5–50° range and nickel-filtered Cu Kα radiation, with a wavelength of 0.154 nm. The 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} and 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, and by determining the difference between the initial concentration in the aqueous solution and that found in the supernatant after the adsorption process. The reproducibility was checked by performing at least one duplicate run for each experimental point.

2.3. Chemical reaction

2.3.1. Cellulose chlorination

A 10.0 g sample of cellulose (Cel) previously activated at 353 K for 12 h was suspended in 200.0 cm^3 of N,N-dimethylformamide (DMF). The 35.0 cm^3 of thionyl chloride ($SOCl_2$) was slow added with mechanical stirring at 353 K. After the addition was complete, the stirring was continued at the same temperature for an additional 4 h. The cellulose chloride (CelCl) obtained from this reaction was washed with several aliquots of a dilute ammonium hydroxide solution and the supernatant after each treatment was removed to restore the pH to neutral. To complete the washing step, the suspension was exhaustively treated with distilled water and acetone to ensure the DMF removed. The solid was then isolated by filtration and dried under vacuum at room temperature (Kobayashi, Sakamoto, & Kimura, 2011; Martin et al., 1999).

2.3.2. Functionalization with organic molecules

The synthesis was performed without solvent under reflux for 4 h with 1.0 g of chlorinated cellulose (CelCl) and 5.0 cm^3 of ethylenediamine. At the end of the reaction, the solid was separated from the liquid by vacuum filtration and washed with deionized water to remove the excess reagent, and then, it was dried under vacuum at 353 K for 24 h. The material obtained was named CelEn (Kobayashi, Uyama, & Ohmae, 2001).

In the final step, 1.0 g of CelEn was reacted with 2.83 cm^3 of ethylene sulfide, and the mixture was kept under reflux with constant stirring for 4 h at 328 K. Subsequently, the material was filtered and washed with water to remove the unreacted ethylene sulfide, dried under vacuum at room temperature and named CelEnEs.

2.4. Adsorption experiments

The obtained solid, CelEnEs, was suspended in several metal salt solutions to evaluate its adsorptive capacity. All of the experiments were performed in duplicate, using a batch process in which approximately 20.0 mg of the chemically modified biopolymer (CelEnEs) was introduced into a series of polyethylene flasks containing 25.0 cm^3 of a metallic cations solution. The concentrations of the cation solutions ranged from approximately 7.0×10^{-4} to 7.0×10^{-2} mol dm^{-3}.

The time chosen for the adsorption procedure 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 by filtration and aliquots were taken to determine the amount of remaining cations by ICP-OES.

The amount of cations adsorbed in the experiment (mmol g^{-1}) was calculated using Eq. (1), where N_f is the number of moles adsorbed onto the modified cellulose, n_i and n_s are the number of moles in the initial solution and the supernatant after equilibrium, respectively, and m is the mass of the adsorbent used in each adsorption process (da Fonseca et al., 2004).

$$N_f = \frac{n_i - n_s}{m} \quad (1)$$

The experimental data were fit to three isotherm models: (i) the Langmuir model, which assumes that the sorption sites have similar energies and are gradually saturated in a monolayer behavior, (ii) the Freundlich model establishes the same sorption process occurs in a multilayer condition and (iii) the Temkin model assumes both of the previously described possibilities but that the solutes adsorb on the surface at the same time.

The parameters related to each model were obtained by linearly fitting the data according to the linear equation that corresponds to each model. Therefore, the parameters for the Langmuir isotherm are N_s the number of moles needed for the formation of the monolayer, and b, a constant related to the equilibrium constant, obtained from the linear fit of the experimental data to the modified Langmuir equation (Eq. (2)) (Langmuir, 1918).

$$\frac{C_s}{N_f} = \frac{1}{N_s b} + \frac{C_s}{N_s} \quad (2)$$

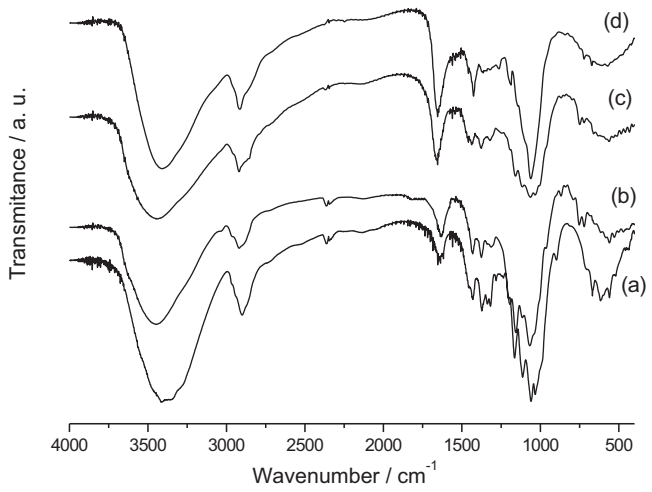

Fig. 1. Infrared spectra of pure cellulose (a), chlorinated cellulose (b), cellulose + ethylenediamine (c) and CelEn + ethylene sulfide (d).

The Langmuir parameters can be expressed in terms of a dimensionless separation factor, R_L, which indicates the shape of the isotherm, as defined by Eq. (3) (Hall, Eagleton, Acrivos, & Vermeulen, 1966; Weber & Chakravorti, 1974), it can be evaluated.

$$R_L = \frac{1}{1 + bC_s} \quad (3)$$

The Freundlich model is based on the idea that metal ions are infinitely accumulated on the surface of the adsorbent. The Freundlich equation used to obtain the sorption parameters (da Silva Filho, Barros Júnior, Santana, de Melo, & Airoldi, 2011; da Silva Filho, da Silva, et al. 2011; da Silva Filho, Monteiro, Sousa, & Airoldi, 2011) is given by the expression:

$$\log N_f = \frac{1}{n_F} \log C_s + \log K_F \quad (4)$$

K_F is a constant related to the adsorption capacity, and n_F is a constant related to the intensity of adsorption and the spontaneity of adsorption when this value is greater than one. Another model used to evaluated this same equilibrium was the Temkin model (Vieira et al., 2011), in which N_f is calculated as:

$$N_f = \frac{1}{n_T} \ln K_T + \frac{1}{n_T} \ln C_S \quad (5)$$

where n_T represents the reactivity of the energetic sites on the biomaterial and K_T is a constant related to the chemical equilibrium at the solid/liquid interface.

3. Results and discussion

3.1. Infrared spectroscopy

The infrared spectra of cellulose and its chemically modified derivatives are shown in Fig. 1. The spectrum of pure cellulose (Fig. 1(a)) indicates the presence of OH groups because bands that appear in the region between 3400 and 3300 cm^{-1}, which is related to the stretching vibrations of the OH ring and the side chains (—CH—OH) and (—CH_2—OH). Another vibration in the spectrum of cellulose appears at approximately 2900 cm^{-1}, which corresponds to the stretching of the methylene groups. The absorption in the region between 3000 and 2800 cm^{-1} was assigned only to the —CH groups because the ratio found for CH to CH_2 was 5:1 in the structure of cellulose (Franco, Senso, Oliveros, & Minguillon, 2001; Loescher, Ruckstuhl, & Seeger, 1998; Silva Filho, Melo, & Airoldi, 2006).

The spectrum of pure cellulose displayed a band at 1639 cm^{-1}, which corresponds to the deformation vibration (δ OH) of the hydroxyl groups in its structure. In the region between 1500 and 1200 cm^{-1}, several bands appear that correspond to the deformation of the primary and secondary OH groups, and the stretching bands of the CO groups are seen between 1200 and 1000 cm^{-1}. The bands within the region below 1000 cm^{-1} are assigned to the absorption of the alcohol groups (Franco et al., 2001; Loescher et al., 1998; Silva Filho et al., 2006).

By comparing the spectrum that corresponds to the chlorinated cellulose (Fig. 1(b)) with that of pure cellulose, the presence of bands 753 and 709 cm^{-1} were observed. These bands correspond to the carbon–chlorine stretch (ν C—Cl), thus confirming the effectiveness of the chlorination reaction. The decrease in the intensity of the bands from 1500 to 1200 cm^{-1} is due to substitution of the hydroxyl group on carbon 6 after reaction with thionyl chloride. This resul proved that chlorination reaction was successful. Another significant change occured with the shift of the band at 896 cm^{-1} observed wiht pure cellulose, to 868 cm^{-1} for chlorinated cellulose. This band corresponds to the C—OH stretching (Franco et al., 2001; Loescher et al., 1998; Silva Filho et al., 2006).By analyzing the spectrum of the ethylenediamine derivative of cellulose (Fig. 1(c)) and that of pure cellulose, a difference is noticed, like in the spectrum of chlorinated cellulose (CelCl), because of the band at 2837 cm^{-1}, which corresponds to the stretching vibration of the methylene groups (—CH_2). In raw cellulose, the CH:CH_2 ratio was 5:1 and the correspondent vibration did not appear. However, after immobilization with ethylenediamine the ratio changes to 5:3 and the band for this stretching is observed. Another significant vibration at 1658 cm^{-1}, which correspond to deformation of the amino group (δ NH), and the hydroxyl groups this vibration is also shifted after chlorination (da Silva Filho, Barros Júnior, 2011; da Silva Filho, da Silva, et al. 2011; da Silva Filho, Monteiro, et al. 2011; Franco et al., 2001; Linder, Bergman, Bodin, & Gatenholm, 2003; Lin-Vien, Colthup, Fateley, & Grasselli, 1991; Pavia, Basser, & Morrill, 1996; Schwanninger, Rodrigues, Pereira, & Hinterstoisser, 2004; Silvertein, Bassler, & Morrel, 1991).

In the chlorinated cellulose's spectrum, the vibrations in the region between 1500 and 1200 cm^{-1} are reduced, which correspond to the substitution of OH groups by chlorine and subsequently by ethylenediamine. The band at 896 cm^{-1} observed for raw cellulose was shifted to 868 cm^{-1} after chlorination and it disappeared after the reaction with ethylenediamine, thus reducing the prevalence of the alcohol groups present in this region. It may also be noted that the bands present in the spectrum of chlorinated cellulose at 752 and 709 cm^{-1} greatly reduced in intensity, but did not disappear; these based are due to the presence of chlorine in the cellulose structure, which were still present because they were not all replaced even after immobilization with ethylenediamine.

The ethylene sulfide cellulose's spectrum (Fig. 1(d)) shows only a few changes in relation to the spectrum of cellulose modified with ethylenediamine, because it is difficult to identify SH stretching bands (a weak band that is observed near 2550 cm^{-1}) in an infrared spectrum. However, it is possible to see that the band at 2837 cm^{-1} seems to be broader, because the ratio between the methylene groups increades to 5:7 (CH:CH_2) after the incorporation of ethylene sulfide.

3.2. X-ray diffraction

An X-ray diffraction technique and ^{13}C nuclear magnetic resonance, were used to qualitatively determine the crystallinity of the materials after modifications, and to determine which region, the most or least crystalline (or amorphous), experienced changes. Fig. 2(a) shows the XRD pattern of the cellulose starting material.

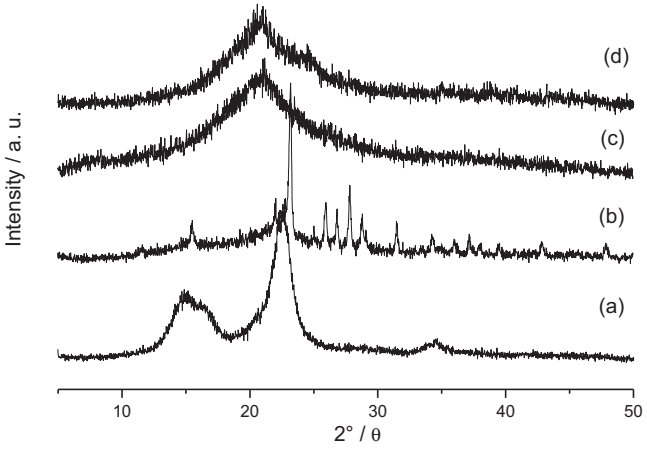

Fig. 2. X-ray diffraction patterns of microcrystalline cellulose (a), chlorinated cellulose (b), CelEn (c) and CelEnEs (d).

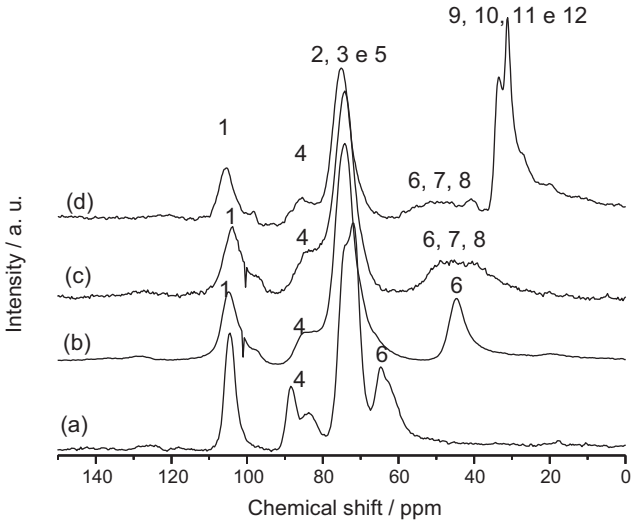

Fig. 3. Solid state ^{13}C NMR spectra of pure cellulose (a), chlorinated cellulose (b), CelEn (c) and CelEnEs (d).

Three very distinct planes can be observed 101, 002 and 040, which are characteristic of microcrystalline cellulose (da Silva Filho, de Melo, da Fonseca, & Airoldi, 2009).

The functional groups present in the cellulose structure are presented differently with respect to the reactivity coming from the diversified interactions (chemical or physical) suffered by each group. The strong physical intramolecular interactions between the hydroxyl groups decrease in intensity as the occurrence of reactions with the cellulose surface decreased because the anchored groups allow for the existence of these interactions with only some of the hydroxyl groups on the material, causing a non-uniform distribution (O'Sullivan, 1997).

Crystallinity is an important parameter in determining a hydroxyl group's availability to interact with solvent molecules and reagents (Klemm, Heublein, Fink, & Bohn, 2005). In crystalline regions because the intermolecular interactions are more intense and the arrangement more ordered, the availability of the hydroxyl groups to be available for a chemical reaction is minimized. In the non-crystalline regions these interactions are less intense and the arrangement is not as ordered; therefore, the hydroxyls are more accessible to solvents or reagents.The XRD pattern of chlorinated cellulose is illustrated in Fig. 2(b), where it was observed that the material is much more crystalline than pure cellulose, and it acquired new plans that are not yet identified or indexed. Chlorination is a process in which there is replacement of a hydroxyl by a chlorine atoms. Hydrogen bonds are established from electronics shares between the pendants hydroxyl groups or between the hydroxyl and the ring oxygens. Chlorine atoms covalently linked to the biopolymer provide three electron pairs that can form hydrogen bonds. Therefore, as chlorine atoms replace the hydroxyl groups, new hydrogen bonds with different characteristics are formed between the chlorine atoms and the unreacted hydroxyls' hydrogens. These bonds create a chemically modified biopolymer, with different features because of the new crystalline arrangement in the chains.

These data are supported by the solid state ^{13}C NMR spectra, shown in Fig. 3(b), confirming the depolymerization and crystallization of the amorphous part of cellulose, and the disappearance of the amorphous peaks at C4 and C6 for the chlorinated cellulose. From these two simultaneous analyses, the change in crystallinity is observed (da Silva Filho, Santana, Melo, Oliveira, & Airoldi, 2010).

The diffractogram of cellulose modified with ethylenediamine shows that the material completely loses its crystallinity. When ethylenediamine is reacted with the chlorinated cellulose, the inter and intramolecular interactions present in the material, which are responsible for much of its organization and lead to its crystalline arrangement, are disrupted due to structural disorder, and the material becomes amorphous. The XRD pattern of the CelEnEs solid, showed that the final material exhibits the same amorphous behavior of the cellulose modified with ethylenediamine.

3.3. ^{13}C NMR spectroscopy

The spectrum of pure cellulose is presented in Fig. 3(a), which displays the monomer and the carbon numbering on the side. In addition all of the signs that represent the chemical shifts assigned to its six carbons are show and correspond to a monomer unit of the biopolymer. The carbon that has the largest shift is carbon 1 (C1) at 104 ppm, which is bonded to two oxygen atoms. Another shift is observed at 88 ppm, which is attributed to C4, which is connected to only one oxygen atom and is responsible for binding 1,4-β-glucoside (Suflet, Chitanu, & Popa, 2000). A chemical shift occurs at 74 ppm that is attributed to carbons 2, 3 and 5, which have similar chemical environments because they are all secondary carbons, attached to —CH and hydroxyl groups. The C6 carbon has the lowest chemical shift, because it is a primary carbon attached to a hydroxyl and the —CH_2 present in cellulose (Kobayashi et al., 2011; Martin et al., 1999; Staudinger, 1920).

The spectrum of chlorinated cellulose (Fig. 3(b)) shows significant changes in relation to the pure compound's spectrum. The C1 peak shifts from 104 to 103 ppm, the C4 peak shifts from 88 to 83 ppm and for C2, C3 and C5 carbons appears in the same region. A nucleophilic attack occurs at the C6 carbon by thionyl chloride, causing displacement of the hydroxyl and a chemical shift of its peak from 65 to 44 ppm. This shift confirms the chlorine immobilization that forms the chlorinated cellulose because the chlorine has greater electronegativity than the hydroxyl groups, and causes a smaller chemical shift.

The CelEn spectrum is shown in Fig. 3(c), and by comparing it with the spectrum of chlorinated cellulose, the only difference from chlorinated cellulose is observed at the C6 peak. The average chemical shift remains approximately the same, but there is peak broadening because this chemical shift now corresponds to three carbons, which are carbon 6 (already existing in cellulose) and carbons 7 and 8 that originated from ethylenediamine.

The spectrum of the ethylene sulfide cellulose derivative (Fig. 3(d)) shows several differences when compared to the spectrum of its precursor (CelEn). Two very close chemical shifts approximately 30 ppm and 32 ppm were observed, that are

Table 1
Percentages of chlorine, nitrogen and sulfur in the matrices: chlorinated cellulose (CelCl), cellulose + ethylenediamine (CelEn) and CelEn + ethylene sulfide (CelEnEs), number of mols of nitrogen (n_N) and sulfur (n_S).

Matriz	Cl (%)	N (%)	n_N (mmol g^{-1})	S (%)	n_S (mmol g^{-1})
CelCl	17.58 ± 0.10	–	–	–	–
CelEn	7.54 ± 0.09	8.50 ± 0.03	6.06 ± 0.02	–	–
CelEnEs	–	6.42 ± 0.12	4.59 ± 0.09	17.21 ± 0.03	5.38 ± 0.01

attributed to the two additional carbons from the addition of ethylene sulfide, and these carbons appear at a lower chemical shift region than the others because of sulfur's low electronegativity.

3.4. Elemental analysis

Elemental analysis is essential because it allows for the determination of the amount of groups anchored to the cellulose matrix, and helps to again a better understanding of how immobilization occurs. In addition to the percentages of immobilized chlorine, nitrogen and sulfur, Table 1 shows the number of moles of nitrogen and sulfur for each matrix, where these last values are (together with other characterization techniques such as ^{13}C NMR) extremely important for defining the form of immobilization of the anchored groups on cellulose.

The ratio between the number of moles of nitrogen and sulfur showed a value close to 1 (nN/nS = 0.85), indicating that the relationship between nitrogen and sulfur in the final material is approximately to 1:1. This result coupled with the ^{13}C NMR results leads to the proposed structure for CelEnEs illustrated in ^{13}C NMR figure. The CelEnEs spectrum showed two peaks with chemical shifts near 30 and 32 ppm that were not observed in the spectrum of CelEn to the two carbon from ethylene sulfide molecule.

These peaks show a greater intensity than the ethylenediamine carbon peaks, confirming that these carbons are in greater quantities and the ratio ofethylene sulfide to ethylenediamine is 2:1. This result confirms the N/S ratio obtained from the elemental analysis results because ethylenediamine contains two nitrogen atoms and ethylene sulfide contains on sulfur atom, and their relationship

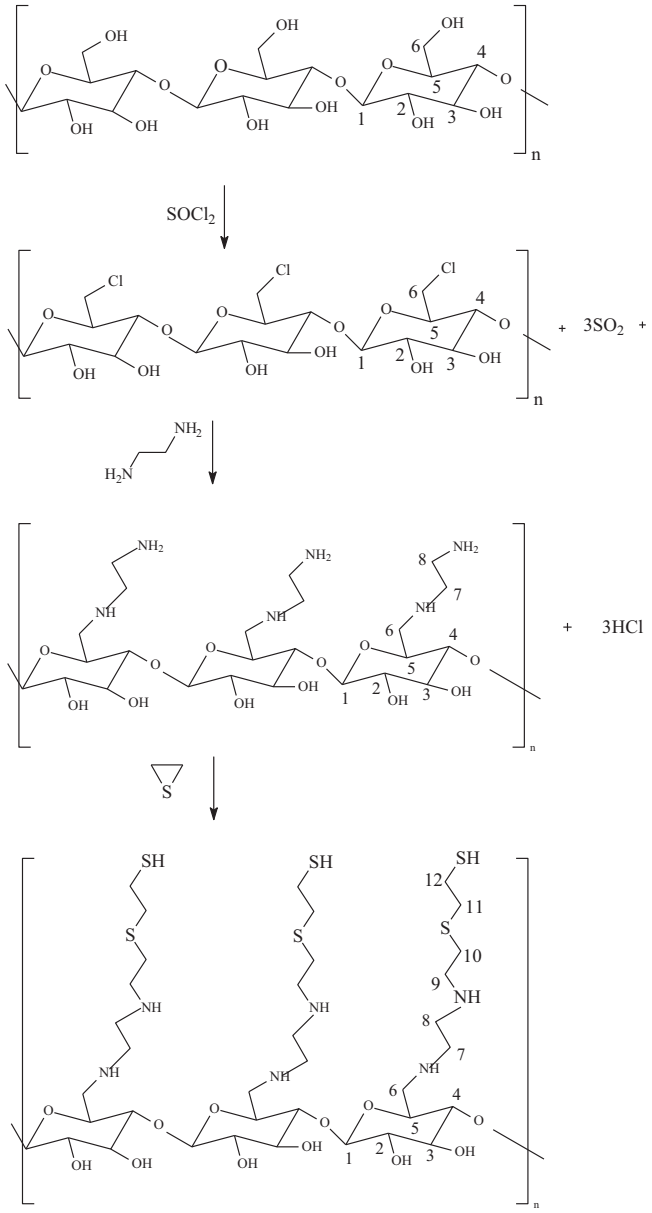

Fig. 4. Proposed structure for the immobilization of the organic molecules on the cellulose.

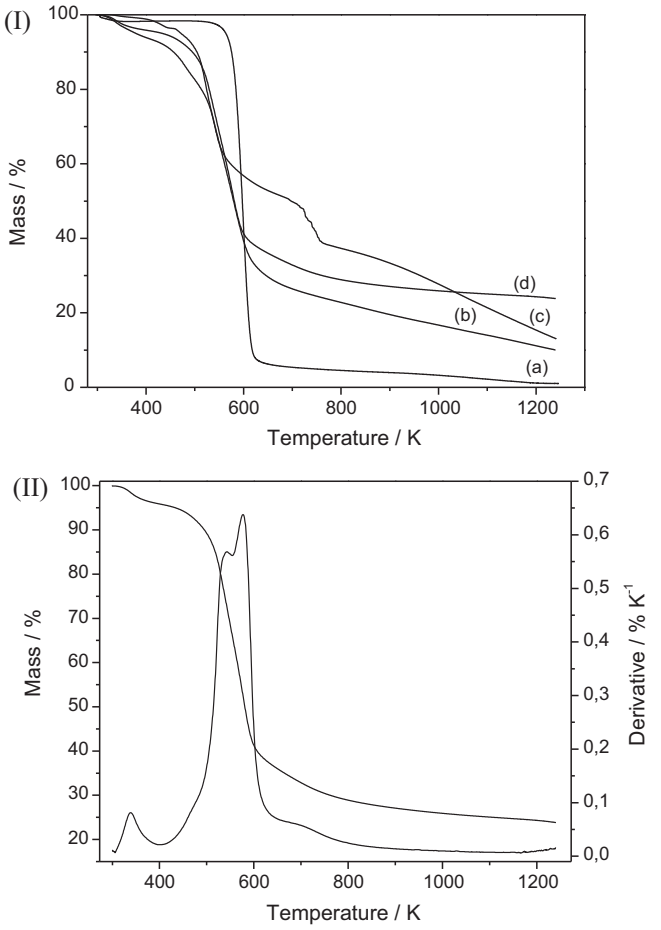

Fig. 5. Thermogravimetric curves of pure cellulose (Ia), chlorinated cellulose (Ib), CelEn (Ic) and CelEnEs (Id) and the thermogravimetric curve and its derivative of CelEnEs (II).

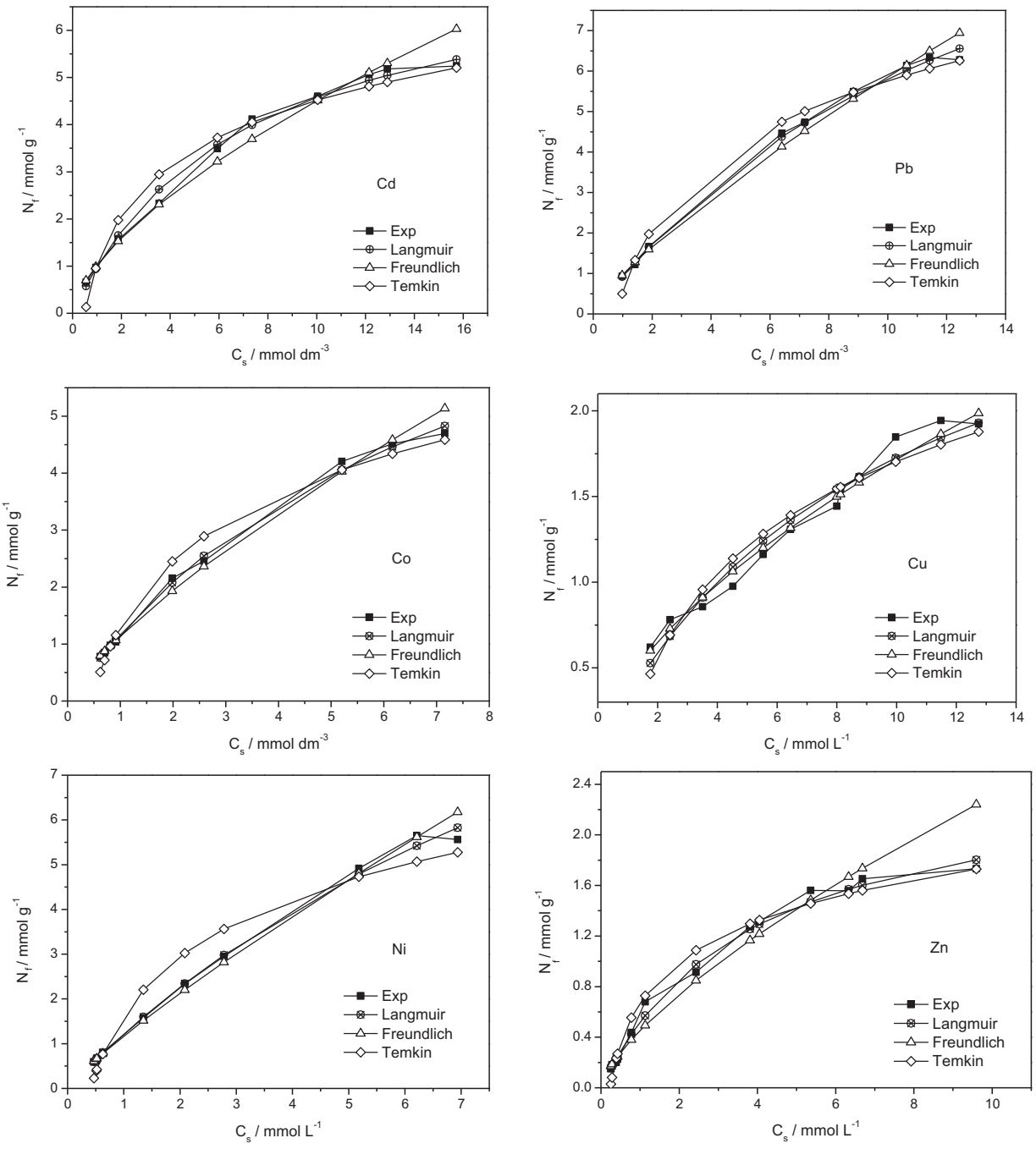

Fig. 6. Adsorption isotherms of the CelEnEs surface with Cd^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+} and Zn^{2+}, presented with Langmuir, Freundlich and Temkin adjustments at 298 ± 1 K.

is close to 1:1. Therefore, it appears that two ethylene sulfide molecules are reacting with each immobilized ethylenediamine, as shown in Fig. 4.

3.5. Thermogravimetry

The thermogravimetric curves of cellulose and the chemically modified celluloses are shown in Fig. 5(I). The curve derived for CelEnEs is shown in Fig. 5(II), where the temperatures of mass loss can be observed. For pure cellulose (Fig. 5(Ia)) the curve showed a single decomposition event in the temperature range of 563–647 K, corresponding to a total mass loss of 92%. However, it is clear that 2 wt% is freed up to 343 K, corresponding to physisorbed water, and that cellulose does not completely decomposed within the temperature range described above because up to 1273 K over 5 wt% is released (Kim & Kuga, 2001; Tashiro & Shimura, 1982).

For the chlorinated cellulose (Fig. 5(Ib)), the decomposition occurs in three stages, but the first event was not taken into account because of the thermal stability and because physisorbed water is removed from the biopolymer, between 386 and 430 K. The second decomposition event occurs between 438 and 534 K resulting in a mass loss of 23%, which corresponds to HCl output and condensation of the hydroxyl groups present on carbons 2 and 3 with water output. The third event corresponds to the decomposition of the organic support that occurs at temperatures greater than521 K (da Silva Filho et al., 2010).

The TG curves representing the cellulose matrix with ethylenediamine (Fig. 5(Ic)) and cellulose modified with ethylenediamine

Table 2
Parameters of Langmuir equation (N_s and b), Freundlich (n_F and K_F) and Temkin (n_T and K_T), correlation coefficient (R) and dimensionless separation factor R_L for the interaction of CelEnEs and cations at 298 ± 1 K.

Cations	Models									
	Langmuir				Freundlich			Temkin		
	N_S	b	R	R_L	n_F	K_F	R	n_T	K_T	R
Cu^{2+}	3.93	106	0.9904	0.43	1.65	1145	0.9909	1.40	1091	0.9686
Co^{2+}	9.65	135	0.9947	0.51	1.14	1310	0.9972	0.60	2189	0.9898
Ni^{2+}	6.78	81	0.9959	0.64	1.17	1173	0.9984	0.53	2407	0.9751
Zn^{2+}	2.48	259	0.9935	0.29	1.41	453	0.9877	2.14	4199	0.9900
Pb^{2+}	13.93	72	0.9910	0.53	1.28	970	0.9974	0.44	1264	0.9927
Cd^{2+}	7.75	145	0.9923	0.31	1.55	1021	0.9958	0.66	1971	0.9821

and ethylene sulfide (Fig. 5(Id)) show that as subsequent reactions are performed, the material presents a higher thermal stability. In other words, as the immobilization of the organic groups in cellulose occurs, the polymer becomes more thermally stable and consequently, a smaller loss of mass is observed. The following order of degradation can be observed, CelEnEs < CelEn < CelCl < Cel (Kim & Kuga, 2001).

3.6. Adsorption isotherms

When compared to other natural or synthetic supports, the CelEnEs biopolymer displays an enormous ability to extract metals from an aqueous solution, because it nitrogen and sulfur atoms provide free electrons that are highly reactive adsorption sites that can effective coordinate metal cations (Inoue, Yoshizuca, & Ohto, 1999). Based on previous studies (da Silva Filho, Barros Júnior, 2011; da Silva Filho, da Silva, et al. 2011; da Silva Filho, Monteiro, et al. 2011; Sousa, da Silva Filho, & Airoldi, 2009) and because of these structural features, it was suggested that the use of ethylene sulfide as a modifying agent in a solvent-free reaction would advantageously, increas the adsorption capacity of the resulting biopolymer (Lopes, Sousa, & Airoldi, 2008).

Fig. 6 shows the adsorption isotherms of Pb^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+} and Zn^{2+} on the CelEnEs surface, at room temperature, and the isotherms calculated from the Langmuir, Freundlich and Temkin models. The curves represent the moles of cations adsorbed per gram of biopolymer, N_f, versus the concentration of solute in the supernatant, C_s. The experimental data were obtained using Eqs. (2), (4) and (5).

The N_f values showed the following adsorption order, $Pb^{2+} > Cd^{2+} > Ni^{2+} > Co^{2+} > Cu^{2+} > Zn^{2+}$, whose maximum adsorption capacities were found to be 6.282 ± 0.023, 5.783 ± 0.015, 5.561 ± 0.017, 4.694 ± 0.013, 1.944 ± 0.062 and 1.733 ± 0.020 mmol g^{-1}, respectively.

The adsorption order observed does not reflect the well-known Irving–Williams series (Machado, Lopes, Sousa, & Airoldi, 2009) for which the expected order would be: Cu > Ni > Co > Zn. Copper is less preferred by the cellulose biopolymer than nickel and cobalt, because they exhibit favorable complexation equilibrium constants. This results suggest that the complexation process of this modified cellulose shows poor copper retention. However, the adsorption value for this metal is high compared to others supports.

The linearized form of the isotherms for the modified Langmuir equation, and the Freundlich and Temkin models allows for the linear and angular data to be calculated from the straight line to obtain the N_s and b values for the Langmuir model, the n_F and K_F values for the Freundlich model and the n_T and K_T values for the Temkin model. These parameters are shown in Table 2.

The results for the Langmuir linear correlation coefficients were good, but the Freundlich correlation coefficient values were higher and closer to 1 compared to the other models. The Freundlich model showed the best linear fit for all of the cations except zinc. Another to confirmed that the Freundlich model provides the best fit for the experimental data observe the change in correlation coefficients as the amount of adsorption is increased, in other words, as the adsorption capacity of the material increased, the correlation coefficients for this model also increased and approached linearity. Therefore, it can be proposed that the multilayer was formed as the adsorption capacity increased.

The R_L values showed that all of the systems are favorable (da Silva Filho et al., 2009) despite not having a very good fit for the Langmuir model. Another important parameter is the n_f value because when it takes on values greater than 1, it indicates that the process is spontaneous. Because the obtain data had an n_F parameter with values >1 and showed the best linear fit, we can conclude that the processes are spontaneous.

These results clearly confirm the importance of incorporating free amine and sulfur groups onto a chemically modified cellulose surface to extract cations from an aqueous solution in heterogeneous conditions.

4. Conclusions

The synthesis of a new chemically modified cellulose possessing S—H bonds in its chain using ethylene sulfide, in the absence of solvent was efficiently performed. The synthesized products were analyzed by elemental analysis, carbon nuclear resonance spectroscopy and infrared spectroscopy to confirm the presence of the functional groups. X-ray diffraction showed that the final material exhibits the same amorphous behavior as cellulose modified with ethylenediamine. The chemically modified biopolymer CelEnEs showed the following order for divalent metal uptake $Pb^{2+} > Cd^{2+} > Ni^{2+} > Co^{2+} > Cu^{2+} > Zn^{2+}$; this order reflects the corresponding acidity of the cations. The adsorption ability of each metal cation is associated with its intrinsic parameters that determine their affinity for the modified surface. Three physicochemical models were applied to the experimental isotherms, and it was concluded that the Freundlich model showed, as demonstrated by the linear correlation coefficients, the best linear fit for almost all of the cations. The adorption's results suggest that this modified biopolymer could be utilized for the removal of divalent cations from an environment contaminated with heavy metals.

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