Available online at www.sciencedirect.com
ScienceDirect
Carbohydrate Research 341 (2006) 2842–2850
Carbohydrate
RESEARCH

Preparation of ethylenediamine-anchored cellulose and determination of thermochemical data for the interaction between cations and basic centers at the solid/liquid interface

Edson C. da Silva Filho, Júlio C. P. de Melo and Claudio Airoldi*

Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13084-971 Campinas, São Paulo, Brazil

Received 15 August 2006; received in revised form 30 August 2006; accepted 4 September 2006
Available online 4 October 2006

Abstract—Cellulose was first modified with thionyl chloride, giving 99% substitution at C6, and then reacted with ethylene-1,2-diamine to produce 6-(2′-aminoethylamino)-6-deoxy-cellulose. From the 8.5% of nitrogen incorporated in the polysaccharide backbone, the amount of ethylene-1,2-diamine anchored per gram of modified cellulose was determined to be 3.03 ± 0.01 mmol. This chemically immobilized surface was characterized by FTIR, TG, ^{13}C NMR, and SEM techniques. The available basic nitrogen centers covalently bonded to the biopolymer skeleton were studied for copper, cobalt, nickel, and zinc adsorption from aqueous solutions and the respective thermal adsorption effects were determined by calorimetric titration. The ability to adsorb cations gave a capacity order of $Co^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$ with affinities of 1.91 ± 0.07, 1.32 ± 0.07, 1.31 ± 0.02, and 1.08 ± 0.04 mmol/g, respectively. The net thermal effects obtained from calorimetric titration measurements were adjusted to a modified Langmuir equation and the enthalpy of the interaction was calculated to give the following exothermic values: -20.8 ± 0.05, -11.72 ± 0.03, -7.32 ± 0.01, and -6.27 ± 0.02 kJ/mol for Co^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+}, respectively. With the exception of the entropic value for copper, the other thermodynamic data for these systems are favorable for cation adsorption from aqueous solutions at the solid/liquid interface, suggesting the use of this anchored biopolymer for cation removal from the environment.

Keywords: Cellulose; Ethylene-1,2-diamine; Adsorption; Calorimetry; Metals

1. Introduction

The chemical modification of natural or synthetic polymers is an elaborate experimental task resulting in improvements in the original surface properties of the materials for use in academic and technological applications. Such endeavors are directly connected to the development of new surfaces that may be used to adsorb organic molecules as well as for cation pre-concentration from wastewater. These new materials are successful for this purpose when the pristine solid presents covalently attached organic molecules that display basic centers to coordinate cations from aqueous[1] or non-aqueous solutions.[2] Normally, the principal interest of these investigations examines, in the first stage, the functionalization model before choosing the desired series of cations for removal under controlled conditions. The goal is to combine the properties of these materials by including the desired functional groups into the original structural framework.[3]

From the viewpoint of the chemical potential of some natural or synthetic materials for useful applications, amorphous silica gel,[4] chitosan,[5] fruit peel,[6] crystalline lamellar talc-like,[7] clay-like[8] or inorganic phosphate,[9] and others have been explored. However, the richest natural raw material, cellulose, has been less exploited. This is despite the fact that this polysaccharide is encountered everywhere in nature, displays active potential functional groups available to react under appropriate conditions, displays changes in the surface after convenient immobilization, and can embody a diversity of functionalities. For modification, hydroxyl groups are

---

* Corresponding author. Fax: +55 19 35213023; e-mail: airoldi@iqm.unicamp.br

0008-6215/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carres.2006.09.004

available in the main skeleton and also in the branched chain, which is the most reactive position in the functionalization process.[10,11]

The applicability of such materials depends upon the availability of the active functions attached to the pendant chains covalently bonded to a given framework. As the original structure is changed into a surface, the hydrophilic character of the new material transforms its properties, leading eventually to a more hydrophobic behavior. Thus, these kinds of modified surface agents comprise a variety of organic molecules displaying amines,[12] ketones,[13] carboxylic acids,[14] or thiol functions,[15] and also inorganic groups such as phosphates[9] or oxides.[16] Moreover, in general more than one functional basic center attached to the pendant molecule covalently bonded to the framework structure[5] is desired.

The chosen methods of synthesizing the new materials and the respective proposed applications depend on the origin of the material associated with its specific use. Generally, the purpose of such reactions is to obtain an increase in application properties that improves the precursor matrix. Convenient methods can transform these new materials for catalysis,[17] or for pre-concentration of trace chemical species in solution,[18] for use as stationary phases in chromatography,[19] or into ion-exchangers,[20] sensors[21] and for use in cation adsorption operations.[7–9]

One of the most explored applications for these kinds of materials is cation adsorption on a solid support, chemically functionalized or not, which has been intensively investigated in these last decades for heavy cation removal from aqueous and non-aqueous effluents, for example, fluviatic water and commercial ethanol.[2,18,22]

The simple presence of metals as extra components in nature, in a variety of forms, has encouraged finding a solution to this problem, especially when discharges of these metals directly to soil or to ground water are increased. The discharge of domestic, industrial, and agricultural residues is a pollutant source, which can reach not only potable water, but also the alimentary chain, thus affecting the entire ecosystem. The toxicity of metals in aquatic organisms has awakened and focused biological interest. The adsorption of trace metals by natural materials can perform an important role in the determination of species in aqueous systems. Therefore, these concerns are part of an organized society that is preoccupied with the welfare of the community and any material is welcome to apply for such applications.[3]

The present investigation deals with the chemical modification of cellulose, by incorporating the ethylene-1,2-diamine moiety as a pendant chain covalently bonded to the main polymeric framework. These basic nitrogen centers can adsorb cations from aqueous solution. Thus, the interaction between the metal and the basic center at the solid/liquid interface was followed by calorimetry to detail this interactive process.

2. Experimental

2.1. Materials

Cellulose (Merck), thionyl chloride (Chemika), *N*,*N*-dimethylformamide (Synth), ammonium hydroxide (Aldrich), ethylene-1,2-diamine (Aldrich), and cation nitrates (Vetec) were all reagent grades and were used without prior purification.

2.2. Instrumentation

The amount of ethylene-1,2-diamine anchored onto the cellulose surface was calculated based on nitrogen percentage, determined through elemental analysis on a Perkin Elmer, model 2400, elemental analyzer. Infrared spectra of the samples in KBr pellets were obtained by diffuse reflectance by accumulating 250 scans on a Bomem Spectrophotometer, MB-series, 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 a Bruker AC 300/P spectrometer at rt. For each run, approximately one gram of each solid sample was compacted into a 7 mm zirconium oxide rotor. The measurements were obtained at frequencies of 75.47 MHz with a magic angle spinning of 4 Hz. To increase the signal-to-noise ratio, the CP/MAS technique was used, with pulse repetition of 2 s for both nuclei and contact times of 1 and 2 ms, respectively. The thermogravimetric curves in an argon atmosphere were obtained on a TA instrument, coupled to a model 1090 B thermobalance, using heating at a rate of 0.167 K/s, under a flow of 30 mL/s, varying from rt to 1273 K, with an initial mass of approximately 10 mg of solid sample. 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 ICPOES Perkin Elmer 3000 DV apparatus. For each experimental point, the reproducibility was checked by at least one duplicate run. Secondary electron images were acquired with a JEOL JSM 6360LV scanning electron microscope, operating at 20 kV. The samples were fixed onto a double-faced carbon tape adhered to an aluminum support and carbon-coated in a Bal-Tec MD20 instrument.

2.3. Synthesis of 6-chloro-6-deoxycellulose

A sample of 10 g cellulose (Cel) previously activated at 353 K for 12 h was suspended in 200 mL of *N*,*N*-dimethylformamide (DMF), followed by the slow addition of 35 mL of thionyl chloride ($SOCl_2$) at 353 K, under mechanical stirring. After the addition was complete, stirring was continued at the same temperature for another 4 h. The cellulose chloride (CelCl) obtained from this reaction was washed with several aliquots of dilute ammonium hydroxide solution and the supernatant after each treatment was removed to bring the pH to neutral. To complete the washing, the suspension was exhaustively treated with distilled water. The solid was then separated by filtration and dried in vacuum at rt.[23]

2.4. Synthesis of 6-(2′-aminoethylamino)-6-deoxy-cellulose

A sample of 1.0 g CelCl was reacted with 5.0 mL of ethylene-1,2-diamine (en) under reflux and with mechanical stirring for 3 h. The solution was filtered through a sintered glass filter and the solid (Celen) was dried in vacuum at rt for 24 h.

2.5. Adsorption

The capacity of the chemically modified cellulose to extract cations from aqueous solution was determined in duplicate, using a batch process with divalent copper, cobalt, nickel, and zinc nitrates, by using a mass (m) of ~30 mg of Celen suspended in 25.0 mL of an aqueous solution with concentrations of each metal varying from 0.10 to 5.0 mmol/L. The suspensions were shaken for 4 h in an orbital bath at 298 ± 1 K. This required time was previously established as close to 2.5 and 4 h was chosen to ensure maximum adsorption. At the end of this process, the solid was separated by centrifugation during 10 min at 2300 rpm. Aliquots of the supernatant were removed by a pipet and the cations were determined by ICPOES. The adsorption capacities (n_f) were calculated by considering the number of moles: $n_f = (n_i - n_s)/m$, where n_i and n_s are the initial and supernatant number of moles.[9]

The adsorption at the solid/liquid interface demands a competition between the solvent (solv) bonded to the chemically modified cellulose (Celen) that is gradually displaced by the solute in solution to reach the equilibrium, Eq. 1

$$\mathrm{Celen}_{(\mathrm{solv})} + \mathrm{M}^{2+}_{(\mathrm{solv})} = \mathrm{Celen} \cdot \mathrm{M}^{2+}_{(\mathrm{solv})} + \mathrm{solv} \tag{1}$$

The ratio between the number of moles of metal in solution at equilibrium and the number of moles of metal adsorbed on the surface is used to obtain the modified Langmuir isotherm, Eq. 2

$$\frac{C_s}{n_f} = \frac{C_s}{n^s} + \frac{1}{n^s b}, \tag{2}$$

where C_s (mol/L) is the concentration of supernatant cations in the equilibrium, n_f (mol/g) is the number of moles adsorbed, and n^s (mol/g) is the maximum amount of solute adsorbed per gram of Celen, which is related to the number of adsorption sites, and b is a constant. 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 (g/L) versus C_s, using the method of least squares.

2.6. Calorimetric titration

The thermal effect evolved from the interaction between the cation and the basic center anchored on pendant groups at the solid/liquid interface was measured by calorimetry on a LKB 2277 calorimeter.[1] For each operation, a sample of functionalized cellulose, varying from 15.0 to 50.0 mg, was suspended in 2.0 mL of water under stirring at 298.15 ± 0.20 K. The thermostated solutions of the cations, in the 0.054–0.199 mol/L range, were incrementally added to the calorimetric vessel and the thermal effect of the titration $Q_t(J)$ was determined. Under the same experimental conditions, the corresponding thermal effect of the dilution of the cation solution was obtained in the absence of the support $Q_d(J)$. The thermal effect of the hydration of Celen in water was determined as before.[1] 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/matrix 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 $\Delta_{\mathrm{mono}}H$[12,24]

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

where $\sum X$ is the sum of the mole fraction of the cation in solution after adsorption, and X is 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 (ΔH) 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 $\Delta_{\mathrm{mono}}H$ value. The enthalpy of adsorption ΔH could be calculated by means of expression 5

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

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

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

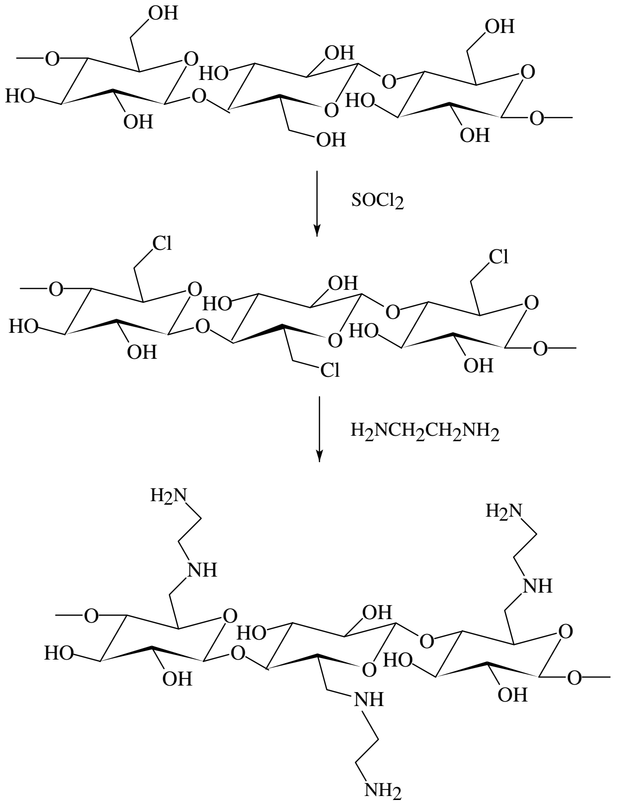
and the entropy value can be calculated through

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

3. Results and discussion

3.1. Characterization

From the reaction of cellulose with thionyl chloride, the polysaccharide was chlorinated with high degree of substitution of 0.99 ± 0.01, which occurred on C6, preferentially,[24] as shown in Scheme 1. This new substituted biopolymer was chemically modified with ethylene-1,2-diamine, giving a polymer with 8.5% nitrogen, as determined by elemental analysis. Based on this value, the corresponding amount of nitrogen content in the organic chains covalently bonded to the backbone structure was calculated as 6.06 ± 0.02 mmol per gram of the biopolymer, which is equivalent to 3.03 ± 0.01 mmol of ethylene-1,2-diamine per gram of polymer, as shown in Scheme 1. This degree of immobilization differs from an earlier synthesis, when the agent of chlorination was thionyl chloride[23] but the immobilization method used water as a solvent to obtain 1.25 mmol/g. In a recent publication, phosphorus oxychloride in xylene was used and 0.813 mmol/g of ethylene-1,2-diamine was anchored.[25] An explanation for the higher degree of immobilization obtained in the present investigation is related to the absence of solvent in Celen syntheses, an innovative feature in the experimental procedure, as recommended by Green Chemistry principles.[26]



Scheme 1. Syntheses of 6-chloro-6-deoxycellulose (CelCl) from the reaction of cellulose (Cel) with thionyl chloride ($SOCl_2$) and subsequent reaction with ethylene-1,2-diamine to yield 6-(2′-aminoethylamino)-6-deoxy-cellulose (Celen).

The infrared spectra of the crude cellulose and its modified biopolymers are shown in Figure 1. The chlorinated cellulose (Fig. 1b) showed the appearance of two new bands at 709 and 752 cm^{-1}, which correspond to the stretching vibration of the C–Cl bond, from the branched part of the original polymer. The displacement and decreasing size of the band originally observed in the cellulose at 894 cm^{-1}, shown in Figure 1a, shifted to 865 cm^{-1} in the CelCl compound (Fig. 1b) and disappeared in Celen (Fig. 1c). This fact corroborates the substitution of the hydroxyl groups by chlorine atoms in this reaction. The appearance of a new band at 2844 cm^{-1} is also observed in Figure 1c.

The vibration at 2844 cm^{-1} is assigned to C–H stretching of the symmetric CH$_2$ group, of the 2′-aminoethylamino moiety. The displacement of the band at 1632 cm^{-1}, which corresponds to the bending of O–H bonds, and also the angular deformation of the N–H amine band at 1659 cm^{-1} are unequivocal proof that confirm ethylene-1,2-diamine immobilization on the cellulose surface.[27,28]

The thermogravimetric curves for cellulose and the chemically modified celluloses are shown in Figure 2. Cellulose in Figure 2a gave only one event in the decomposition process covering the interval of temperature from 536 to 647 K, corresponding to a mass loss of 92%. The chlorinated biopolymer in Figure 2b gave a mass loss in the 386–430 K range, which correlated to the water physically adsorbed onto the surface. The second step, between 438 and 534 K, with a mass loss of 23% corresponded to the displacement of the HCl molecule, as the condensation of hydroxyl groups on carbons 2 and 3 occurred. The last event in this process, from 521 K, can be interpreted as cellulose fiber

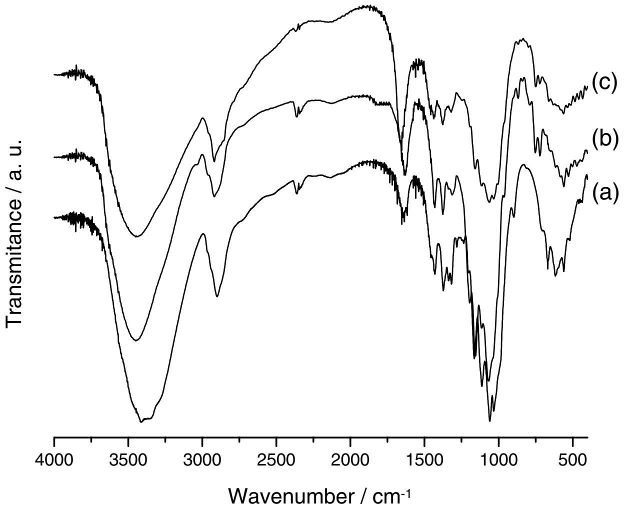


Figure 1. Infrared spectra of the Cel (a), Cel–Cl (b), and Celen (c).

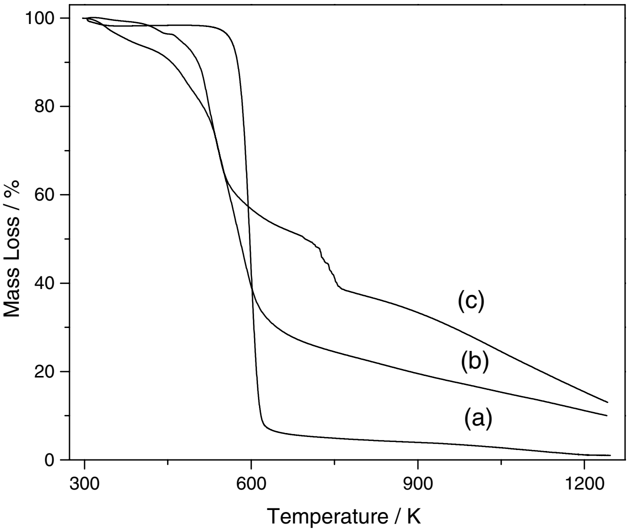


Figure 2. Thermogravimetric curves of Cel (a), Cel–Cl (b), and Celen (c).

decomposition. The decomposition of immobilized biopolymer Celen, shown in Figure 2c, is very similar to the stages shown by CelCl, with an initial mass loss of 4% from 320 to 363 K, attributed to the physisorbed water. The second decomposition event occurred in the 364–563 K range, with a mass loss of 34%, corresponding to the loss of the immobilized ethylene-1,2-diamine molecule together with condensation of the hydroxyl groups on carbons 2 and 3. The third decomposition step, starting from 564 K, also correlated with the loss of cellulose fiber, giving an amount of 48%. Based on the quantitative amount of mass loss, a distinct behavior for these decomposition processes can be observed, by presenting the sequence expressed as Celen < CelCl < Cel. These values are in agreement with the fact that Celen is the most thermally stable matrix, followed by CelCl and finally by Cel.[29]

The ^{13}C NMR spectra in the solid state for these three matrices are shown in Figure 3. For the Cel spectrum in Figure 3a, a set of five distinct peaks were present, C1 at 104 ppm, C4 at 88 ppm, C2, C3, and C5 at 74 ppm, and C6 at 65 ppm. For CelCl, significant changes in the chemical shifts for C4 and C6 are observed, which are present at 82 and 44 ppm, respectively (Fig. 3b). For Celen, in Figure 3c, a change in chemical shift for C6 is observed as compared to the spectrum in Figure 3b. In addition, enlargement of this peak is found, which is the result of the presence of C6, C7, and C8, where the central chemical shift for this peak is located at 42 ppm.[27,28,30]

The SEM images for Cel, CelCl, and Celen are shown in Figure 4. The first image in Figure 4a demonstrates that the biopolymer cellulose presents a porous and fibrous morphology. These characteristics remained in the chloride cellulose, as shown in Figure 4b, but the rugosity decreased in comparison to the original cellulose matrix. However, the porosity as well as the fibrous aspects decreased significantly in the anchored cellulose in Figure 4c, when compared with the original and chloride matrices.

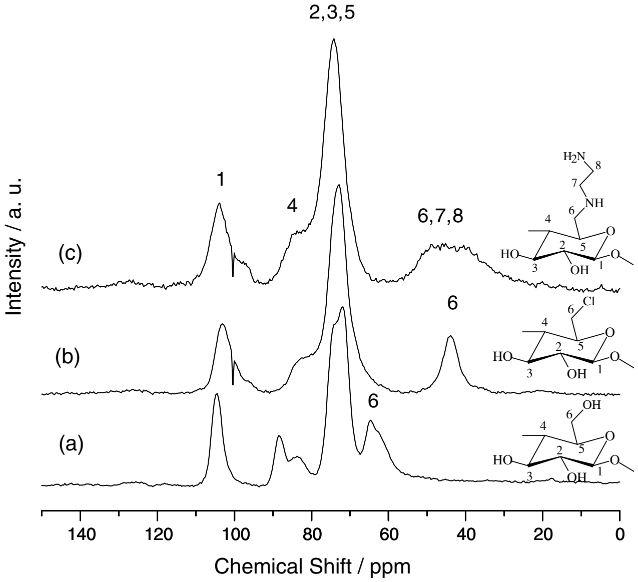


Figure 3. Solid state ^{13}C NMR of Cel (a), Cel–Cl (b), and Celen (c).

3.2. Adsorption isotherms

For effectiveness between the divalent cations Cu^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} and Celen, the main characteristics of the biopolymer should be considered. Thus, the available amine groups covalently bonded to the cellulose backbone have the ability to act as sorbents to these cations from aqueous solution, due to the complexing ability of these basic centers at the solid/liquid interface.[9,12,31,32]

The isotherms of cation adsorption with Celen biopolymer are shown in Figure 5. The isotherm and its linearized form for the modified Langmuir equation (Eq. 2) for cobalt adsorption, represented by C_s/n_f as a function of C_s, given in Figure 6, enables the calculation of the linear and angular data from the straight line, to obtain n^s and b values, as listed in Table 1.

Based on the data listed in Table 1 and the isotherms presented in Figure 5, the n_f values for the complexed cations by the pendant groups suggest the following adsorption order: $Co^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$. This same sequence was previously observed when glycidoxypropyltrimethoxysilane is anchored to silica gel, followed by 1,3-propanodiamine incorporation, using a heterogeneous route in the synthesis.[12] However, the values were lower, nearly half of those obtained in the present case.

For the extraction of cations from aqueous solution using chemically modified surfaces containing the ethylene-1,2-diamine moiety, copper is the most explored.

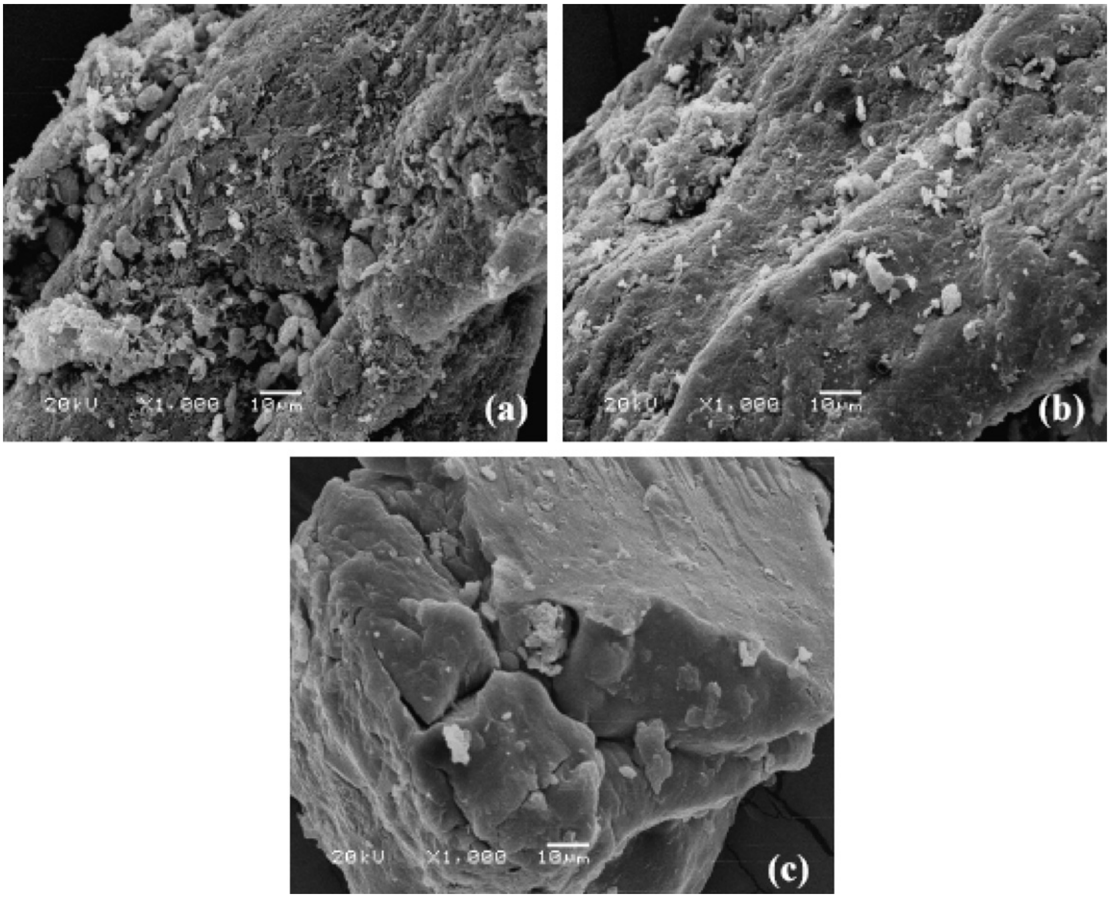


Figure 4. SEM photographs of Cel (a), Cel–Cl (b), and Celen (c), the bar represents 10 μm.

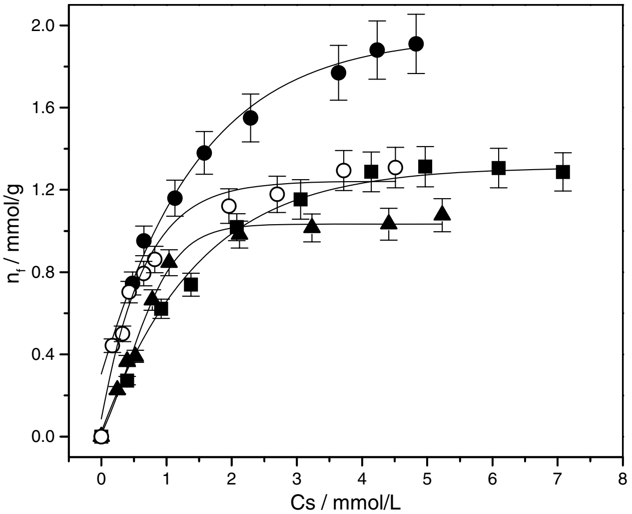


Figure 5. Adsorption isotherms of the divalent cations: Cu^{2+} (■), Co^{2+} (●), Ni^{2+} (▲), and Zn^{2+} (○) on the Celen surface at 298 ± 1 K.

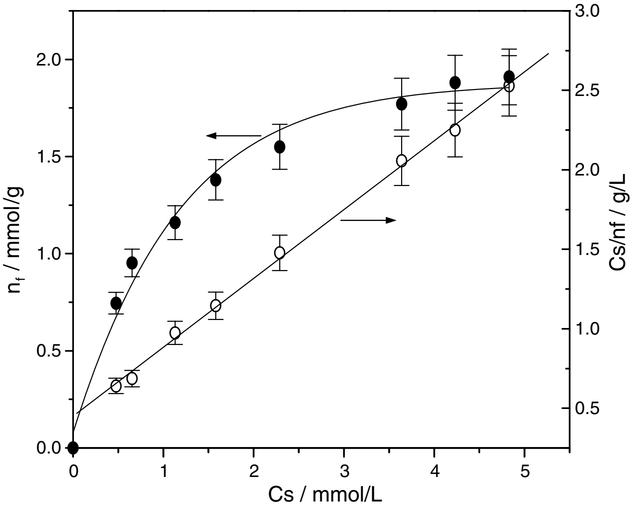


Figure 6. Adsorption isotherm of Co^{2+}(●) and the linearized Langmuir isotherm (○) on Celen surface at 298 ± 1 K.

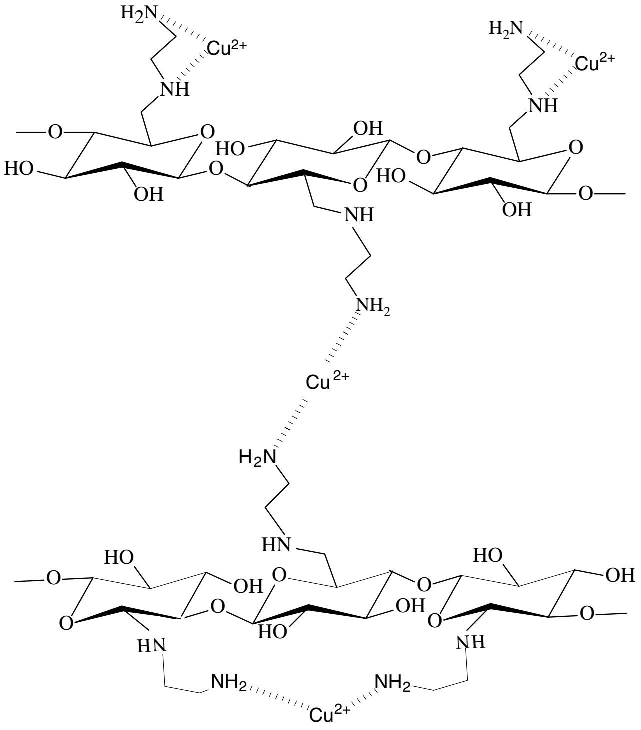
Nevertheless, by considering the available data, Celen, with an n_f value of 1.91 ± 0.07 mmol/g for cobalt, is the most efficient matrix, in comparison to crysotile,[31] phyllosilicate,[33] and hydroxyapatite[9] materials, with values of 0.35, 1.07, and 1.18 mmol/g, respectively. For copper, these same matrices adsorbed 1.02, 2.25, and 1.11 mmol/g, showing that only phyllosilicate gave higher value than the 1.32 ± 0.07 mmol/g obtained with

Table 1. Number of moles adsorbed (n_f), maximum adsorption capacity (n^s), constant (b), and correlation coefficient (r) for the interaction of divalent metal (M) nitrates with Celen at 298 ± 1 K

M	n_f (mmol/g)	n^s (mmol/g)	b	r
Cu	1.32 ± 0.07	1.42 ± 0.09	1592	0.9868
Co	1.91 ± 0.07	2.01 ± 0.12	1516	0.9871
Ni	1.08 ± 0.04	1.24 ± 0.05	1120	0.9934
Zn	1.31 ± 0.02	1.36 ± 0.07	225	0.9886

Celen. Both nickel and zinc cations are less studied; however, for the last cation, a lower value of 0.85 mmol/g for a barium phosphate surface was obtained, in comparison with 1.31 ± 0.02 mmol/g for Celen. As observed, the biopolymer Celen presented a larger cation adsorption capacity, suggesting its use in preconcentration and separation, especially for cobalt. Such interactions can be interpreted due to the transference of cation from solution to the basic centers of the anchored ethylene-1,2-diamine molecule, by complexation of the cations through the available amine groups.

The advantage of the modified biopolymer described here, compared with those previously investigated,[23,25] is related to the large number of basic centers attached to the pendant chains. Also, the adsorption values are higher and the results were obtained in neutral pH, which was kept essentially constant during the complete titration. To illustrate the possible cation complexation on this surface, the structures are proposed as shown in Scheme 2.



Scheme 2. Possible structures for copper complex formation on the Celen surface.

3.3. Calorimetric titration

The resulting thermal effects due to the interaction of copper nitrate with Celen polysaccharide are obtained by considering the deduction of the dilution effect in water from the total thermal effect, applying Eq. 3. The effects of the thermodynamic cycle for this series of interactions involving a suspension (susp) of Celen in aqueous (aq) solution with metallic cations can be represented by the following calorimetric reactions:

$$\mathrm{Celen_{(susp)}} + \mathrm{M^{2+}_{(aq)}} = \mathrm{Celen}\cdot\mathrm{M^{2+}_{(susp)}} \qquad Q_{\mathrm{tit}} \qquad (8)$$

$$\mathrm{Celen_{(susp)}} + n\mathrm{H_2O} = \mathrm{Celen}\cdot n\mathrm{H_2O_{(susp)}} \qquad Q_{\mathrm{hid}} \qquad (9)$$

$$\mathrm{M^{2+}_{(aq)}} + n\mathrm{H_2O} = \mathrm{M^{2+}}\cdot n\mathrm{H_2O_{(aq)}} \qquad Q_{\mathrm{dil}} \qquad (10)$$

$$\mathrm{Celen_{(susp)}} + \mathrm{M^{2+}_{(aq)}} = \mathrm{Celen}\cdot\mathrm{M^{2+}_{(susp)}} \qquad Q_{\mathrm{r}} \qquad (11)$$

The net thermal effect obtained for the calorimetric titration ($\sum Q_r = \sum Q_t - \sum Q_d$), as given by Eq. 11, was experimentally represented as isotherms in Figure

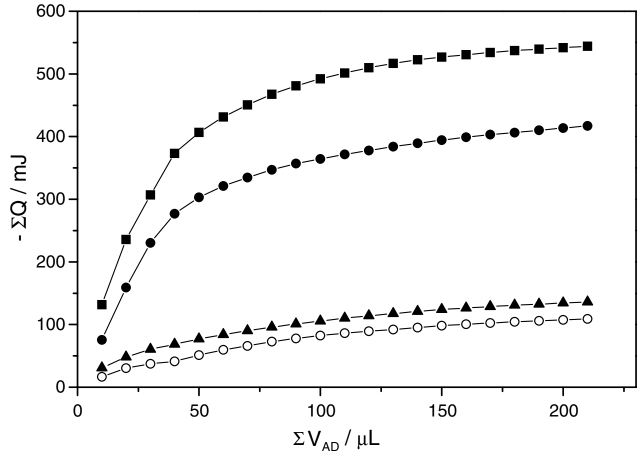


Figure 7. The resulting thermal effects of the adsorption isotherms of the divalent cations: Cu^{2+} (■), Co^{2+} (●), Ni^{2+} (▲), and Zn^{2+} (○) on the Celen surface at 298.15 ± 0.20 K.

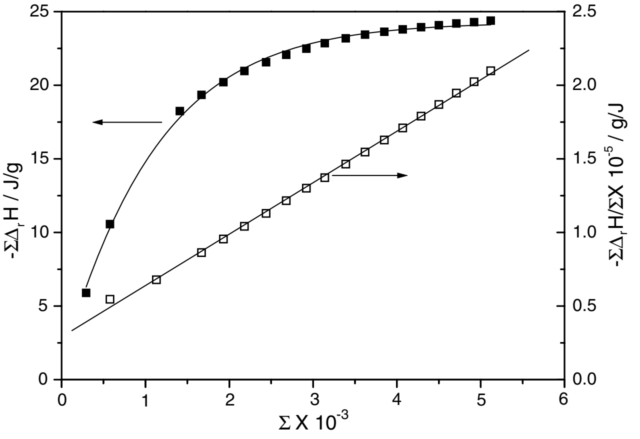


Figure 8. Isotherm from calorimetric titration of Cu^{2+} (■) and this linearized form (□) on the Celen surface at 298.15 ± 0.20 K.

Table 2. Thermodynamic values ($\Delta_{\mathrm{mono}}H$, ΔH, ΔG, and ΔS) for the interaction of divalent metal (M) nitrates on the Celen surface at 298.15 ± 0.20 K

M	$-\Delta_{\mathrm{mono}}H$ (J/mol)	$-\Delta H$ (kJ/mol)	$\ln K$	$-\Delta G$ (kJ/mol)	ΔS (J/mol K)
Cu	29.13 ± 0.97	20.81 ± 0.05	7.37	18.3 ± 0.1	−8 ± 1
Co	23.55 ± 0.10	11.72 ± 0.03	7.32	18.2 ± 0.1	22 ± 1
Ni	9.07 ± 0.09	7.32 ± 0.01	7.02	17.4 ± 0.1	28 ± 1
Zn	8.52 ± 0.19	6.27 ± 0.02	5.42	13.4 ± 0.6	24 ± 2

7. One example of linearization involving copper adsorption is shown in Figure 8. From Eq. 4 and the linearized data for all cations, the enthalpy of interaction, $\Delta_{\mathrm{int}}H$, can be obtained for all processes, which enable calculation of the molar enthalpy, Eq. 5. From the equilibrium constant the Gibbs free energy was calculated from Eq. 6 and combined with the enthalpic value, the entropy can also be calculated by Eq. 7. These values are listed in Table 2. All enthalpic data are exothermic in nature, which contrasts with previous results with an identical immobilized agent.[25] The magnitude of the values presented follow the order $\mathrm{Cu}^{2+} > \mathrm{Co}^{2+} > \mathrm{Ni}^{2+} > \mathrm{Zn}^{2+}$, which is the same sequence as observed for this bidentate pendant moiety bonded on silica gel[34] and in other systems[35,36] where the copper complex formed always gave a higher value. The negative free energy changes indicate spontaneous processes of complexation with the same order of enthalpies, as also previously observed for anchored organic molecules on silica gel.[37] With the exception of copper, all other systems presented positive entropic values, which are also consistent with the occurrence of favored reactions. These entropic values suggested that, during complex formation, the expected desolvation disturbed the original structure of the solvent, by causing a disorganization of the system with a consequent increase in entropy. On the other hand, another contribution to the entropic value comes from the displacement of the water molecules hydrogen-bonded to nitrogen centers attached to the pendant chains, as the complexation is in progress,[38] to form the final rearrangement in structure as proposed in Scheme 2. Although the entropic value for copper complexation is unfavorable, all other thermodynamic data are in agreement with the adsorption of those cations at the solid/liquid interface, suggesting an application for this anchored polysaccharide in cation removal.

4. Conclusions

The ethylene-1,2-diamine chelating group was successfully anchored onto the apparently unreactive biopolymer cellulose. The effectiveness of such surface modification depends on a prior chlorination reaction. The present investigation explored this feature to lead to an effective surface with a high degree of hydroxyl substitution on C6 of the polymeric cellulose structure. The high degree of chloride content, which is much higher than those previously obtained, governs the potentiality of the next step. Under such conditions, the desired molecule is covalently bonded through the attack of the nucleophile nitrogen basic centers in ethylene-1,2-diamine to yield the final product 6-(2′-aminoethylamino)-6-deoxy-cellulose. This new synthetic surface, with anchored pendant chains containing basic nitrogen atoms that are potentially centers for cation removal, is a promising material to be applied for this operation, with good sorption capacity for the divalent cations with ability in adsorbing $\mathrm{Co}^{2+} > \mathrm{Cu}^{2+} > \mathrm{Zn}^{2+} > \mathrm{Ni}^{2+}$. For cobalt, the sorption capacity for this polymer is higher than other matrices containing an ethylene-1,2-diamine moiety, suggesting the use of Celen in pre-concentration and separation processes. The quantitative interactions between the cation and the nitrogen basic centers at the solid/liquid interface were followed by calorimetry and gave favorable thermodynamic data, such as exothermic enthalpy, negative Gibbs free energy and positive entropy. These thermodynamic values suggest the application of this material, available worldwide, to improve the environment.

Acknowledgements

The authors are indebted to FAPESP for financial support and a fellowship to ECSF and are also indebted to CNPq for a fellowship to C.A.

References

1. Ruiz, V. O. V.; Petrucelli, G. C.; Airoldi, C. *J. Mater. Chem.* **2006**, *16*, 2338–2346.
2. Lazarin, A. M.; Airoldi, C. *Chem. Mater.* **2006**, *18*, 2226–2232.
3. Babel, S.; Kurniawan, T. A. *J. Hazard. Mater.* **2003**, *B-97*, 219–243.
4. Jal, P. K.; Patel, S.; Muhra, B. K. *Talanta* **2004**, *62*, 1005–1028.
5. Guibal, E. *Prog. Polym. Sci.* **2005**, *30*, 71–109.
6. Pavan, F. A.; Lima, I. S.; Lima, E. C.; Airoldi, C.; Gushiken, Y. *J. Hazard. Mater.* **2006**, *B-137*, 527–533.
7. Sales, J. A. A.; Petrucelli, G. C.; Oliveira, F. J. V. E.; Airoldi, C. *J. Colloid Interface Sci.* **2006**, *297*, 95–103.
8. Jaber, M.; Miché-Brendlé, J.; Michelin, L.; Delmotte, L. *Chem. Mater.* **2005**, *17*, 5275–5281.
9. da Silva, O. G.; da Silva Filho, E. C.; da Fonseca, M. G.; Arakaki, L. N. H.; Airoldi, C. *J. Colloid Interface Sci.* **2006**, *302*, 485–491.

10. Kadla, J. F.; Gilbert, R. D. *Cellul. Chem. Technol.* **2000**, *34*, 197–216.
11. Klemm, D.; Heublein, B.; Fink, H.-P.; Bohn, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 3358–3393.
12. Sales, J. A. A.; Airoldi, C. *Thermochim. Acta* **2005**, *427*, 77–83.
13. Espínola, J. G. P.; Oliveira, S. F.; Lemus, W. E. S.; Souza, A. G.; Airoldi, C.; Moreira, J. C. A. *Colloids Surf., A* **2000**, *66*, 45–50.
14. Castro, G. R.; Alcântara, I. L.; Roldan, P. S.; Bozano, D. F.; Padilha, P. M.; Florentino, A. O.; Rocha, J. C. *Mater. Res.* **2004**, *7*, 329–334.
15. Arakaki, L. N. H.; Espínola, J. G. P.; da Fonseca, M. G.; Oliveira, S. F.; Sousa, A. N.; Arakaki, T.; Airoldi, C. *J. Colloid Interface Sci.* **2004**, *273*, 211–217.
16. Pavan, F. A.; Francisco, M. S. P.; Landers, R.; Gushiken, Y. *J. Braz. Chem. Soc.* **2005**, *16*, 815–820.
17. Abrantes, M.; Gago, S.; Valente, A. A.; Pillinger, M.; Gonçalves, I. S.; Santos, T. M.; Rocha, J.; Romão, C. C. *Eur. J. Inorg. Chem.* **2004**, *24*, 4914–4920.
18. Prado, A. G. S.; Airoldi, C. *Anal. Chim. Acta* **2001**, *432*, 201–211.
19. Silva, C. R.; Airoldi, C.; Collins, K. E.; Collins, C. H. *J. Chromatogr., A* **2006**, *1114*, 45–52.
20. Pehlivan, E.; Altum, T. *J. Hazard. Mater.* **2006**, *134*, 149–156.
21. Fernández-Sanchez, J. F.; Cannas, R.; Spichiger, S.; Steiger, R.; Spichiger-Keller, U. E. *Anal. Chim. Acta* **2006**, *566*, 271–282.
22. Machado, R. S. A., Jr.; da Fonseca, M. G.; Arakaki, L. N. H.; Oliveira, S. F. *Talanta* **2004**, *63*, 317–322.
23. Tashiro, T.; Shimura, Y. *J. Appl. Polym. Sci.* **1982**, *27*, 747–756.
24. Martin, A. I.; Sanchez-Chaves, M.; Arranz, F. *React. Funct. Polym.* **1999**, *39*, 179–187.
25. Torres, J. D.; Faria, E. F.; Prado, A. G. S. *J. Hazard. Mater.* **2006**, *B-129*, 239–243.
26. Warner, J. C.; Cannon, A. S.; Dye, K. M. *Environ. Imp. Asses. Rev.* **2004**, *24*, 775–799.
27. Silvertein, R. M.; Bassler, G. C.; Morrel, T. C. *Spectrometric Identification of Organic Compounds*; Wiley/Interscience: London, 1991.
28. Pavia, D. L.; Basser, G. M.; Morrill, T. C. *Introduction to Spectroscopy*, 2nd ed.; Saunders College: New York, 1996.
29. Kim, U.-J.; Kuga, S. *Thermochim. Acta* **2001**, *369*, 79–85.
30. Atalla, R. H.; VanderHart, D. L. *Solid State Nucl. Magn. Reson.* **1999**, *15*, 1–19.
31. da Fonseca, M. G.; da Silva Filho, E. C.; Machado, R. S. A., Jr.; Arakaki, L. N. H.; Espínola, J. G. P.; Oliveira, S. F.; Airoldi, C. *Colloids Surf., A* **2003**, *227*, 85–91.
32. da Fonseca, M. G.; da Silva Filho, E. C.; Machado, R. S. A., Jr.; Arakaki, L. N. H.; Espínola, J. G. P.; Airoldi, C. *J. Solid State Chem.* **2004**, *177*, 2316–2322.
33. da Fonseca, M. G.; Barone, J. S.; Airoldi, C. *Clays Clay Miner.* **2000**, *48*, 638–647.
34. Airoldi, C.; Gushikem, Y.; Espinola, J. G. P. *Colloids Surf., A* **1986**, *17*, 317–323.
35. Arakaki, L. N. H.; Nunes, L. M.; Simoni, J. A.; Airoldi, C. *J. Colloid Interface Sci.* **2000**, *228*, 46–51.
36. Vieira, E. F. S.; Cestari, A. R.; Simoni, J. A.; Airoldi, C. *Thermochim. Acta* **1999**, *328*, 247–252.
37. Arakaki, L. N. H.; Espínola, J. G. P.; Oliveira, S. F. *Curr. Top. Colloid Interface Sci.* **2001**, *4*, 219–225.
38. Fonseca, M. G.; Airoldi, C. *Thermochim. Acta* **2000**, *359*, 1–9.