Adsorption of Cu(II), Cd(II), and Pb(II) from aqueous single metal solutions by succinylated mercerized cellulose modified with triethylenetetramine

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ABSTRACT

This study describes the preparation of two new chelating materials derived from succinylated mercerized cellulose (cell 1). Cell 1 was activated through two different methods by using diisopropylcarbodiimide and acetic anhydride (to form an internal anhydride) and reacted with triethylenetetramine in order to obtain cell 2 and 4. New modified celluloses were characterized by mass percent gain, concentration of amine functions, elemental analysis, and infrared spectroscopy. Cell 2 and 4 showed degrees of amination of 2.8 and 2.3 mmol/g and nitrogen content of 6.07% and 4.61%, respectively. The capacity of cell 2 and 4 to adsorb Cu^{2+}, Cd^{2+}, and Pb^{2+} ions from single aqueous solutions were examined. The effect of contact time, pH, and initial concentration of metal ions on the metal ions uptake was also investigated. Adsorption isotherms were well fitted by the Langmuir model. The maximum adsorption capacity of cell 2 and 4 were found to be 56.8 and 69.4 mg/g for Cu^{2+}; 68.0 and 87.0 mg/g for Cd^{2+}; and 147.1 and 192.3 mg/g for Pb^{2+}, respectively.

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1. Introduction

Effective removal of toxic metals, in connection with a comprehensive wastewater treatment strategy is one of the largest topics of present research. The increased awareness on the toxicity of metals prompted the implementation of strict regulations for its disposal. Modern metal removal technologies such as ion exchange, reverse osmosis, and membrane systems are being used to produce effluents of better quality while allowing for the recovery and reuse of metals, which provides some economic and environmental advantages (Brierly, 1990; Navarro, Sumi, Fujii, & Matsumura, 1996).

The chemical modification of natural or synthetic polymers is an elaborate experimental task that results in improvements in the original surface properties of the materials for uses in technological applications. Such endeavors are directly connected to the development of new surfaces that may be used to adsorb metal ions from water and wastewater. These new materials are successful for this purpose when the pristine solid presents covalently attached organic molecules that display basic centers to coordinate metal ions from aqueous (Ruiz, Petrucelli, & Airoldi, 2006) or non-aqueous solutions (Lazarin & Airoldi, 2006). Normally, the principal interest of these investigations examines, in the first stage, the functionalization model before choosing the desired series of metal ions for removal under controlled conditions. The aim

is to combine the properties of these materials by including the desired functional groups into the original structure (Babel & Kurniawan, 2003; Da Silva Filho, de Melo, & Airoldi, 2006).

From the viewpoint of the chemical potential of some natural or synthetic materials for useful applications, sugarcane bagasse, sawdust, and cellulose and others have been explored. Cellulose is regarded as the most abundant and renewable biopolymer in nature and is available at low cost (Gurgel, Karnitz Júnior, Gil, & Gil, 2008a, Gurgel, Freitas, & Gil, 2008b). It displays active potential hydroxyl groups available to react under appropriate conditions. However, the stability of the chain-forming acetal groups toward various reagents, mechanical and thermal load is limited (Klemm, Heublein, Fink, & Bohn, 2005). Thus, a variety of appropriate groups of organic ligands could be used to modify the cellulose surface through low-cost chemical processes such as amines, carboxylic acids, and thiols, to produce materials with higher metal ion exchange capacity (Da Silva Filho et al., 2006).

Removal of heavy metal ions from aqueous solution by various modified adsorbents has been performed by many researchers (Wan Ngah & Hanafiah, 2008). Some types of chemicals used for activation and modification of biopolymers and their maximum adsorption capacities (Q_{max}) are shown in Table 1.

Gurgel (2008a) proposed in a previous study the mercerization treatment as a way of increasing the fibers specific surface area and to make the hydroxyl groups of cellulose macromolecules more easily accessible for the modification with succinic anhydride (succinylation). As a result of this proposal, they obtained succinylated mercerized cellulose with a higher mass gain (107.4%) and

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Table 1
Summary of some modified adsorbents for removal of heavy metal ions from aqueous solution.

Adsorbent	Activating agent	Modifying agent	Metal ion	Q_{max} (mg/g)[a]	b (L/mg)	Reference
Cellulose (CelNN)	Phosphorous oxychloride	Ethylenediamine	Cu^{2+}	104.2	–	Torres, Faria, and Prado (2006)
			Ni^{2+}	30.8	–	
			Zn^{2+}	69.3	–	
Cellulose (Celen)	Thionyl chloride	Ethylenediamine	Cu^{2+}	90.2	0.025	Da Silva Filho et al. (2006)
			Ni2+	89.0	0.019	
			Zn^{2+}	73.1	0.003	
			Co^{2+}	118.5	0.026	
Chitosan (CCTS)	Epichlorohydrin	Triethylenetetramine	Pb^{2+}	559.4	0.011	Tang et al. (2007)
Sugarcane bagasse (MSB 5)	1,3-diisopropilcarbodiimide	Ethylenediamine	Cu^{2+}	139	0.173	Karnitz Júnior et al. (2007)
			Cd^{2+}	164	0.068	
			Pb^{2+}	189	0.125	
Sugarcane bagasse (MSB 6)	1,3-diisopropilcarbodiimide	Triethylenetetramine	Cu^{2+}	133	0.014	Karnitz Júnior et al. (2007)
			Cd^{2+}	313	0.004	
			Pb^{2+}	313	0.121	
Mercerized cellulose (Cell 6)	Pyridine	Succinic anhydride	Cu^{2+}	153.9	3.095	Gurgel et al. (2008a)
			Cd^{2+}	250.0	1.818	
			Pb^{2+}	500.0	5.000	
Mercerized Sugarcane bagasse (MMSCB 2)	Pyridine	Succinic anhydride	Cu^{2+}	185.2	0.307	Gurgel et al. (2008b)
			Cd^{2+}	256.4	1.700	
			Pb^{2+}	500.0	0.952	

[a] The values of Q_{max} and b were obtained by Langmuir model.

degree of succinylation (6.2 mmol/g). In the present study, we have described the preparation of two new chelating materials containing amine groups from succinylated mercerized cellulose (cell 1) to adsorb Cu^{2+}, Cd^{2+}, and Pb^{2+} ions as continuation of the study of Gurgel et al. (2008a). The carboxylic acid functions from cell 1 were modified with triethylenetetramine through two different pathways. The first material (cell 2) was prepared by reaction of cell 1 with 1,3-diisoproylcarbodiimide (DIC) and later with triethylenetetramine (Karnitz Júnior et al., 2007). The second material (cell 4) was prepared using a new method developed in our laboratory that uses the carboxylic acid functions contained in cell 1 to form an internal carboxylic acid anhydride (cell 3) that could be opened by triethylenetramine. Adsorption studies of Cu^{2+}, Cd^{2+}, and Pb^{2+} from aqueous single metal solutions by cell 2 and 4 were performed at different contact times, pHs, and metal ion concentration. The results were evaluated by Langmuir model.

2. Experimental

2.1. Materials

Grade 3MM Chr cellulose chromatography paper (Cat. No. 3030-861) and grade quantitative filter paper (Cat. No. 1441-150) for Instrumental Analysis were purchased from Whatman Company, Maidstone, England. N,N′-dimethylformamide (DMF) was purchased from TEDIA (CAS:68-12-2). 1,3-Diisopropylcarbodiimide (DIC) and triethylenetetramine were purchased from Aldrich (Cat. No. D12,540-7; 112-24-3, respectively). $CuSO_4 \cdot 5H_2O$, $Pb(NO_3)_2$, $CdCl_2 \cdot 2.5H_2O$ were purchased from SYNTH (Brazil). Dimethylformamide was treated with 4 Å molecular sieves (MERCK) and soon afterwards distilled under reduced pressure.

2.2. Synthesis of cellulose 2 (cell 2)

Succinylated mercerized cellulose (cell 1) was prepared and characterized using the methodology described by Gurgel et al. (2008a). Cell 1 (3.0 g and 7.2 mmol/g of carboxylic acid functions) was washed with acetone and dried at 80 °C in an oven for 1 h, and soon afterwards it was reacted with 9.0 mL (3 equiv.) of diisopropylcarbodiimide (DIC) in presence of anhydrous dimethylformamide (DMF) (51 mL) at 25 °C for 1 h under magnetic stirring in order to activate carboxylic acid functions. Afterwards, 13.6 mL (5 equiv.) of triethylenetetramine was added to the reactional mixture. The

material was reacted for more 3 h in order to obtain cellulose 2 (cell 2). The reaction mixture was filtered through a sintered glass funnel, and washed in sequence with DMF, ethanol 95%, distilled water, saturated bicarbonate solution, distilled water, ethanol 95%, and then with diethyl ether. Cell 2 was dried and stored in a desiccator overnight. The mass percent gain (mpg) was calculated.

2.3. Synthesis of cellulose 4 (cell 4)

Succinylated mercerized cellulose (cell 1) (3.0 g, 7.2 mmol/g of carboxylic acid functions) was reacted with 80 mL (30 equiv.) of acetic anhydride at 100 °C under magnetic stirring for 24 h in order to obtain cellulose 3 (cell 3). The reaction mixture was filtered through a sintered glass funnel, washed with dried diethyl ether, and stored in a desiccator. Cell 3 (3.0 g) was reacted with 13.8 mL (5 equiv.) of triethylenetetramine in presence of anhydrous dimethylformamide (DMF) (51 mL) at 25 °C for 3 h in order to obtain cellulose 4 (cell 4). The reaction mixture was separated, elaborated, and stored in a desiccator as described in Section 2.2. The mass percent gain (mpg) was also calculated.

2.4. Characterization of celluloses 2, 3, and 4

2.4.1. Mass percent gain (mpg)
The mass percent gain (mpg) was calculated according to Eq. (1):

$$mpg\ (\%) = \left(\frac{m_f - m_i}{m_i}\right) * 100 \qquad (1)$$

where m_f and m_i are masses of materials after and before the modification, respectively.

2.4.2. Degree of amination
The degree of amination could be determined through measuring the amount of introduced amine function. For such, the concentration of amine functions *per* gram of celluloses 2 and 4 was determined by back titration. Two 0.1000 g samples of cell 2 and 4 were treated with 100.0 mL of an aqueous HCl standard solution (10 mmol/L) in a 250-mL Erlenmeyer for 1 h under mechanic stirring. Soon after the mixtures were separated through single filtration and three 25.00 mL samples were titrated to the phenolphthalein end-point with aqueous NaOH standard solution (10 mmol/L) (Gurgel et al., 2008a, 2008b; Karnitz Júnior et al.,

2007). The concentration of amine functions was calculated by Eq. (2):

$$C_{NH,NH_2} = \left[\frac{(C_{HCl} * V_{HCl}) - (4 * C_{NaOH} * V_{NaOH})}{m_{modified\ cell}} \right] \quad (2)$$

where C_{HCl} (mmol/L) is the concentration of HCl standard solution, C_{NaOH} (mmol/L) is the concentration of NaOH standard solution, V_{HCl} (L) is the volume of HCl solution, V_{NaOH} (L) is the volume of NaOH solution spent in the titration of unreacted acid's excess, and $m_{modified\ cell}$ is the mass (g) of cellulose 2 or 4.

2.4.3. FTIR analysis

The samples were prepared by mixing 1 mg of material with 100 mg of spectroscopy grade KBr. The infrared spectra were recorded by Nicolet Impact 410 FTIR spectrometer with detector at 4 cm^{-1} resolution from 500 to 4000 cm^{-1} and 32 scans per sample. The spectra were analyzed by Microcal^{TM} Origin^{TM} software for identification of main characteristic bands of the introduced functions.

2.4.4. Elemental analysis

The samples were previously washed with acetone in a sintered glass funnel and dried at 80 °C for 1 h. Then, they were analyzed by a CHNS/O Perkin Elmer Series II. The analyses were made in duplicate for each sample.

2.5. Effect of contact time on the metal ions adsorption onto celluloses 2 and 4

The metal ion uptake capacities were measured as a function of time to determine the optimum contact times for the adsorption of Cu^{2+}, Cd^{2+}, and Pb^{2+} ions on cell 2 and 4. The contact times used in the present study were from 10 to 40 min for cell 2 and 4. Samples of 50 mg of cell 2 and 4 were placed in 250-mL Erlenmeyer flasks with 50.00 mL of metal ion solution at a fixed concentration (200 and 200 mg/L for Cu^{2+}, 210 and 200 mg/L for Cd^{2+}, and 290 and 280 mg/L for Pb^{2+} for cell 2 and 4, respectively). Solubility product constants (Ksp) and concentration of metal ion solutions for copper, cadmium, and lead were used to calculate the maximum pH where these ions cannot occur as hydrolyzed species to ensure that only Cu^{2+}, Cd^{2+}, and Pb^{2+} would be adsorbed. Therefore, pHs were only taken to 5.4 for Cu^{2+}, 7.0 for Cd^{2+}, and 6.0 for Pb^{2+} after the addition of cell 2 or 4 to each metal ion solution. Erlenmeyer flasks were kept under constant stirring. The pH values were being measured during the experiments. Variations about 0.1 U of pH were found in relation to values of pH initially adjusted. Then, pH values were corrected by addition of drops of aqueous NaOH and/or HCl solutions (0.01–1.0 mol/L) to the mixtures. At the end of the experiments the measured equilibrium pH values were taken into account.

At the end of the experiments, the mixtures were separated by single filtration using Whatman quantitative filter paper No. 41 for instrumental analysis. In order to determine metal ion concentration, three 10.00 mL samples of each solution were titrated. The concentration of Cu^{2+} ions was determined by direct titration with standard EDTA solution (2 mmol/L) at pH 10 using Murexide as indicator. The concentration of Cd^{2+} and Pb^{2+} ions was determined by back titration of an excess of standard EDTA solution (3 mmol/L) with an aqueous Mg^{2+} standard solution (2.5 mmol/L) at pH 10 using Erichrome Black T as indicator (Gurgel et al., 2008a, 2008b).

2.6. Effect of pH on the metal ions adsorption onto celluloses 2 and 4

Experiments were performed to determine the effect of pH on the adsorption process of Cu^{2+}, Cd^{2+}, and Pb^{2+} ions on cell 2 and 4. Samples of 50 mg of cell 2 and 4 were placed in 250-mL Erlenmeyer flasks with 50.00 mL of metal ion solution at a fixed concentration (100 and 100 mg/L for Cu^{2+}, 210 and 200 mg/L for Cd^{2+}, and 290 and 280 mg/L for Pb^{2+} for cell 2 and 4, respectively). The pH range studied for cell 2 and 4 was from 1.8 to 5.7 and 2.0 to 5.5 for Cu^{2+}, from 2.6 to 5.7 and 2.5 to 5.7 for Pb^{2+}, and from 2.6 to 5.8 and 2.0 to 5.9 for Cd^{2+}, respectively. The range of pH values were chosen on basis of the literature data (Gurgel et al., 2008a, 2008b; Karnitz Júnior et al., 2007). The pHs were adjusted by addition of drops of aqueous NaOH and/or HCl solutions (0.1–1.0 mol/L), and then the Erlenmeyers flasks were kept under constant stirring. The adsorption equilibrium times used in this study were those obtained from Section 2.5. The pH values were being measured during the experiments. Variations about 0.1 U of pH were also found in relation to values of pH initially adjusted. Then, pH values were corrected as described earlier. At the end of the experiments the measured equilibrium pH values were also taken into account. The concentration of Cu^{2+}, Cd^{2+}, and Pb^{2+} ions was also determined by titration as described previously.

2.7. Effect of initial concentration and adsorption isotherms

The effect of initial concentration on metal ion uptake capacities was investigated by variation of initial concentrations of the metal ions at optimum pHs values and equilibrium times obtained from Sections 2.5 and 2.6. Samples of 50 mg of cell 2 and 4 were placed in 250-mL Erlenmeyer flasks with 50.00 mL of metal ion solution at predetermined concentrations from 60 to 140 and 70 to 120 mg/L for Cu^{2+}, from 80 to 180 and 80 to 180 mg/L for Cd^{2+}, and from 150 to 320 and 170 to 320 mg/L for Pb^{2+} for cell 2 and 4, respectively. The pHs were adjusted by addition of drops of aqueous NaOH and/or HCl solutions (0.1–1.0 mol/L), and then the Erlenmeyers flasks were kept under constant stirring. Some variations about 0.1 U of pH were also found during the experiments. The pH values were also corrected as described earlier. The concentration of Cu^{2+}, Cd^{2+}, and Pb^{2+} ions was also determined by titration as described previously.

2.7.1. Coordination number (CN)

The coordination number can be calculated through the relationship between the degree of amination or concentration of amine functions and the adsorption maximum capacity obtained from Langmuir isotherm. It could predict how many amine groups are coordinating a metal ion, and therefore, it would be possible to describe the interaction between cell 2 and 4 and metal ions adsorbed better, as well as the differences between the two kinds of prepared ligands. The coordination number was calculated by Eq. (3):

$$CN = \frac{C_{NH-NH_2}}{(Q_{max}/M(M^{2+}))} \quad (3)$$

where C_{NH-NH_2} is degree of amination or concentration of amine functions (mmol/g), Q_{max} is the adsorption maximum capacity (mg/g) obtained from Langmuir isotherm for Cu^{2+}, Cd^{2+}, and Pb^{2+}, and $M(M^{2+})$ is the molar mass of the metal ion studied (mg/mmol).

2.7.2. Gibbs free energy

According to Liu (2006), Gibbs free energy ($\Delta G°$) for an adsorbent with relatively low adsorption capacity to adsorbate can be calculated as defined by Eq. (4):

$$\Delta G° = -RT * \ln K \quad (4)$$

where R is the gas constant 8.3144 J/K·mol, T (K) is the temperature, and K (L/mmol) is the equilibrium constant.

3. Results and discussion

3.1. Synthesis of celluloses 2 and 4

The synthesis route used to obtain cell 2 and 4 is shown in Fig. 1. The carboxylic acid functions presented in cell 1 were used to synthesize cell 2 and 4. In the first pathway, diisopropylcarbodiimide (DIC) was used as a coupling agent to activate the carboxylic acid carbonyl to introduce the triethylenetetramine through formation of an amide bond. In the second pathway, acetic anhydride, a much cheaper reagent than DIC, was used to prepare cell 3 through formation of an internal carboxylic acid anhydride. Cell 1's anhydride function could be opened by triethylenetetramine to obtain a similar compound to cell 2 (cell 4). The opening of the anhydride by triethylenetetramine forms an amide bond, and consequently releases a carboxylic acid and amine groups. The mass percent gains, concentration of amine functions and nitrogen percentages are shown in Table 2.

Compared to cell 2, cell 4 showed an increase of 58.8% in the mass percent gain, but it also showed a small decrease of 0.5 mmol/g and of 1.46% in the concentration of amine functions and in the nitrogen content, respectively. Considering, therefore, the obtained results, it is possible to conclude that the second synthesis route used for the preparation of cell 4 was efficient and represents an alternative form to anchor amine functions onto succinylated cellulose fibers to form a new chelating material.
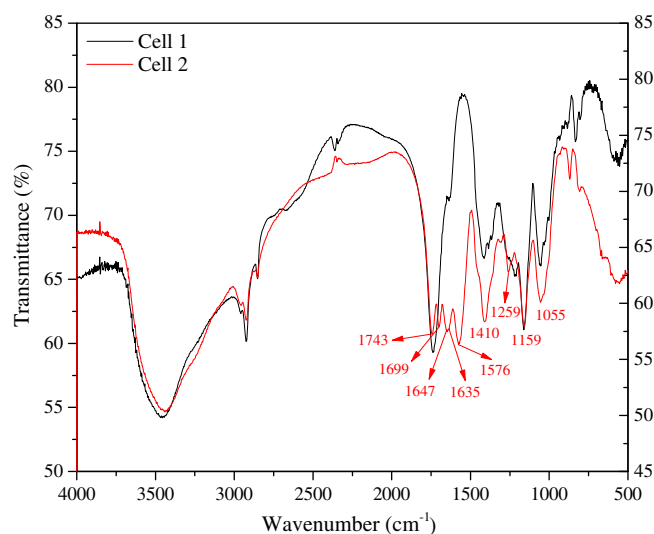
3.2. FTIR characterization

The characterization of celluloses 2, 3, and 4 was accomplished by FTIR spectroscopy. Fig. 2 shows FTIR spectra of cell 1 and 2, and Fig. 3a and b shows FTIR spectra of cell 1 and 3, and cell 1 and 4. As depicted in Fig. 2, the major changes can be noticed in FTIR spectrum of cell 2 in relation to cell 1 are the arising of bands at 1699, 1647, 1635, 1410, 1259, 1159, and 1055 cm^{-1}. The bands at 1699 and 1647 cm^{-1} correspond to stretching of carbonyl group (C=O) of primary amide (amide I). The band at 1635 cm^{-1} corresponds to deformation vibration of —NH_x in plane. The band at 1576 cm^{-1} corresponds to deformation vibration of groups —NH— of amines. The bands at 1410, 1259, and 1159 cm^{-1} correspond to deformation vibration of C—N, and the band at 1055 cm^{-1} corresponds to asymmetric stretching of C—N—C.

Carboxylic acid anhydrides show two bands of stretching in the carbonyl region. These two bands result from modes of asymmetric and symmetric stretching of C=O group. Normally, the separation of these bands is 60 cm^{-1}, but this difference can be between 35 ad

Table 2
Type of material, mass gains percent, concentrations of amine functions and percentages of nitrogen.

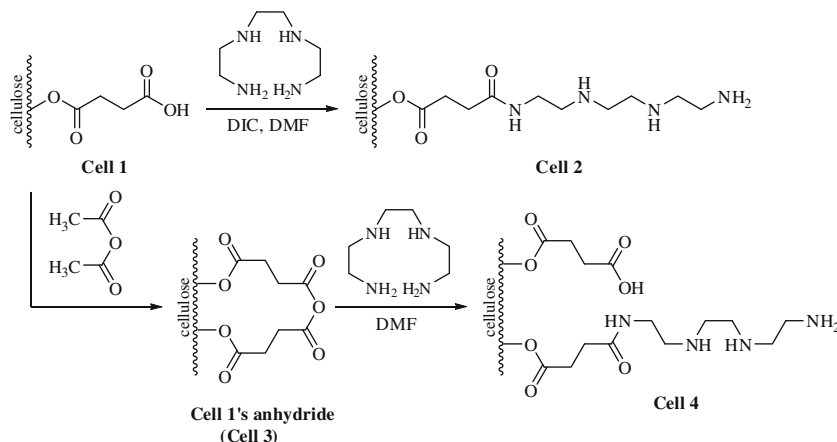| Material	Mpg (%)	C_{NH-NH_2} (mmol/g)	N (%)
Cell 2	33.6	2.8 ± 0.0	6.07 ± 0.01
Cell 4	92.4	2.3 ± 0.0	4.61 ± 0.21

Fig. 2. FTIR spectra of cell 1 and 2.

90 cm^{-1} (Nakanishi, 1962). As depicted in Fig. 3a, the most relevant change can be noticed in FTIR spectrum of cell 3 in relation to cell 1 is the arising of bands at 1824 and 1751 cm^{-1}. The arising of these bands confirms the formation of the anhydride function in cell 3.

As depicted in Fig. 3b, the major changes can be noticed in FTIR spectrum of cell 4 in relation to cell 1 are the arising of bands at 1695, 1647, 1576, 1419, 1254, 1153, and 1053 cm^{-1}. The assignment for these bands is the same discussed above for cell 1 and 2, which proves the formation of the amide bond.

3.3. Adsorption studies of Cu^{2+}, Cd^{2+}, and Pb^{2+} onto celluloses 2 and 4

3.3.1. Effect of contact time

Metal ion adsorption capacities were investigated as a function of time to determine the adsorption equilibrium time for the adsorption of heavy metal ions on cell 2 and 4. The experiments
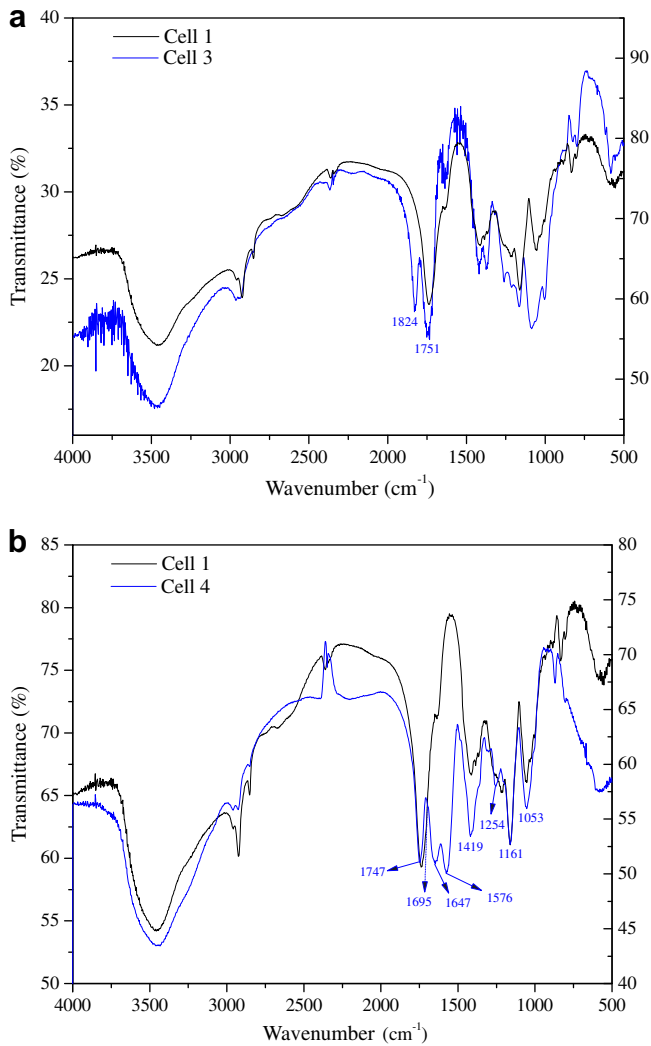

Fig. 1. Synthesis route used to obtain cell 2 and 4.

Fig. 3. FTIR spectra of (a) cell 1 and 3, (b) cell 1 and 4.

pK_{a1}, pK_{a2}, pK_{a3}, and pK_{a4} of triethylenetetramine is equal to 3.32, 6.67, 9.20, and 9.92, respectively. Adsorption capacities were found to be low at lower pH values, and high at larger pH values. At lower pHs the carboxylate and amine functions are closely associated with hydronium ions (H_3O^+) and restricted the approach of metal cations as a result of the repulsive force, and consequently they cannot bind the metal ions in solution. When the pH is increased, the adsorption surface becomes deprotonated, and therefore, electrostatic attraction from carboxylate groups and electron-pair donor from amine groups is likely to increase (Garg, Kaur, Jawa, Sud, & Garg, 2008; Srivastava et al., 2008). Therefore, these functional groups take part in metal ion uptake process by complexation reaction and the adsorbed amount consequently increases. The optimum pH values at which the maximum removal of Cu^{2+}, Cd^{2+}, and Pb^{2+} ions could be achieved were found to be 5.8, 6.0, and 5.7, and 5.5, 6.0, and 5.8 for cell 2 and 4, respectively. The calculated pH for Cu^{2+} adsorption was 5.4 as mentioned in Section 2.5, and the optimum pH value was found to be 5.8. At pH 5.8 hydrolyzed species of copper as $Cu(OH)^+$ may occur. The presence of hydrolyzed species as $Cu(OH)^+$ may decrease substantially the copper adsorption (Hasan, Ghosh, Viswanath, & Boddu, 2008). As can be seen from the Fig. 4a and b, this behavior was not observed. Therefore, for all of the following experiments, these optimum pH values were used.
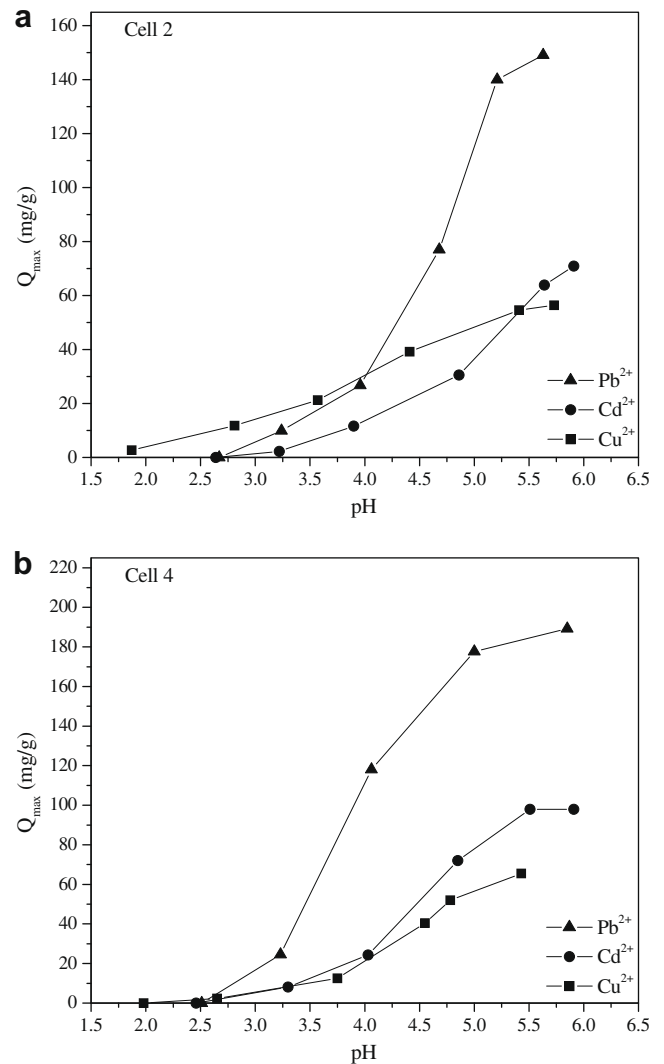
were performed using a fixed adsorbent quantity (50 mg) and 50.0 mL of metal ions solution at pH 5.4 for Cu^{2+}, 7.0 for Cd^{2+}, and 6.0 for Pb^{2+}, at fixed concentration. The adsorption equilibrium time was attained in 20 and 10 min for Cu^{2+}, 20 and 10 min for Cd^{2+}, and 30 and 20 min for Pb^{2+} for cell 2 and 4, respectively (figure not shown). These adsorption equilibrium times were used for pH and concentration-dependent experiments.

3.3.2. Effect of pH

The pH of the solution affects the adsorptive process through protonation and deprotonation of functional groups of the active sites of the adsorbent surface. Therefore, pH variation affects the kinetics and equilibrium characteristics of the adsorption process (Srivastava, Mall, & Mishra, 2008; Ünlü & Ersoz, 2006). The effect of pH on adsorption capacities of heavy metal ions was investigated by varying the initial pHs of the solutions with different pH intervals which depend on the metal ions studied. The equilibrium pH values obtained from these experiments were considered to evaluate the variation of metal ion uptake with pH, which is shown in Fig. 4a and b. As the introduced ligand groups in cell 2 are amine groups and in cell 4 are carboxylate and amine groups, it is possible to correlate the pK_as of these introduced chemical compounds in cell 2 and 4 with the pH and this way to predict the form of the ligand on the metal ion solution. According to Dean (1999) the pK_{a1} and pK_{a2} of succinic acid is equal to 3.5 and 4.5 and

Fig. 4. Adsorption of metal ions onto cell 2 (a), and 4 (b) as a function of pH.

3.3.3. Adsorption isotherms

Adsorption isotherms describe how adsorbates interact with adsorbents. Langmuir isotherm models the monolayer coverage of the adsorption surface. This model assumes that adsorption occurs at specific homogeneous adsorption sites within the adsorbent, and intermolecular forces decrease rapidly with the distance from the adsorption surface. The Langmuir model is based on the assumption that all the adsorption sites are energetically identical and adsorption occurs on a structurally homogenous adsorbent. The widely used Langmuir isotherm (Langmuir, 1918) has found successful application in many real adsorption processes and is expressed as shown by Eq. (5):

$$q_e = \frac{Q_{max} * b * C_e}{1 + b * C_e} \tag{5}$$

which can be rearranged to obtain a linearized form

$$\frac{C_e}{q_e} = \frac{1}{Q_{max} * b} + \frac{C_e}{Q_{max}} \tag{6}$$

where q_e (mg/g) is the equilibrium adsorption capacity, Q_{max} (mg/g) is the maximum amount of the metal ion per unit weight of the modified cellulose to form complete monolayer coverage on the surface bound at high equilibrium metal ion concentration C_e (mg/L) and b (L/mg) is Langmuir constant related to the binding sites affinity. Q_{max} represents the practical limiting adsorption capacity when the surface is fully covered with metal ions, assisting the comparison of adsorption performance, and b indicates the adsorption reaction bond energy between metal ion and cell 2 and 4.

A linearized plot of C_e/q_e versus C_e is obtained from the model and is shown in Fig. 5a and b. The parameters Q_{max} and b are computed from the slopes and intercepts of different straight lines representing the interaction of cell 2 and 4 with different metal ions. These calculated values are shown in Table 3.

As it can be seen from Table 3, the experimental data were well correlated to the Langmuir model. Then, it can be concluded that Langmuir model could very well explain the adsorption process of Cu^{2+}, Cd^{2+}, and Pb^{2+} ions onto cell 2 and 4. Cell 4 in relation to cell 2 exhibited larger maximum adsorption capacity (Q_{max}) and stability constant (b) for the adsorption process of Cu^{2+}, Cd^{2+}, and Pb^{2+} ions. In order to explain this further it is necessary to consider the coordination chemistry of ligand groups contained in cell 2 and 4.

During the chelation process, a metal ion forms a coordination bond with electron pair of negatively charged oxygen atom in carboxylate groups to satisfy its primary valence, as well as, with unshared electron pair of nitrogen atom in polyamine to satisfy its secondary valence. Compared to cell 2, cell 4 contains a smaller concentration of amine functions, and therefore, it is possible to conclude that less carboxylic groups were modified by triethylenetetramine in this material. Then, cell 4 contains a higher concentration of carboxylate groups negatively charged than cell 2, which allows it to work as a better ion exchanger material in addition to its chelation abilities. The amine ligand, on the other hand, relies on a great extent on its coordination capabilities for metal binding. Hence, external sources of anions are necessary to neutralize any positive charge introduced by adsorbed cations (Navarro et al., 1996; Navarro, Sumi, & Matsumura, 1999; Navarro, Tatsumi, Sumi, & Matsumura, 2001). This chemical makeup probably provides to cell 4 a larger maximum adsorption capacity of Cu^{2+}, Cd^{2+}, and Pb^{2+} ions in relation to cell 2.

Cell 2 in relation to cell 4 exhibited a lower stability constant (b) for adsorption process of Cu^{2+}, Cd^{2+}, and Pb^{2+} ions. The bond energy between cell 4 and adsorbed metal ions is larger than cell 2 due to the presence of carboxylate functions in cell 4 that probably help to stabilize better the bond between metal ion and cell 4.
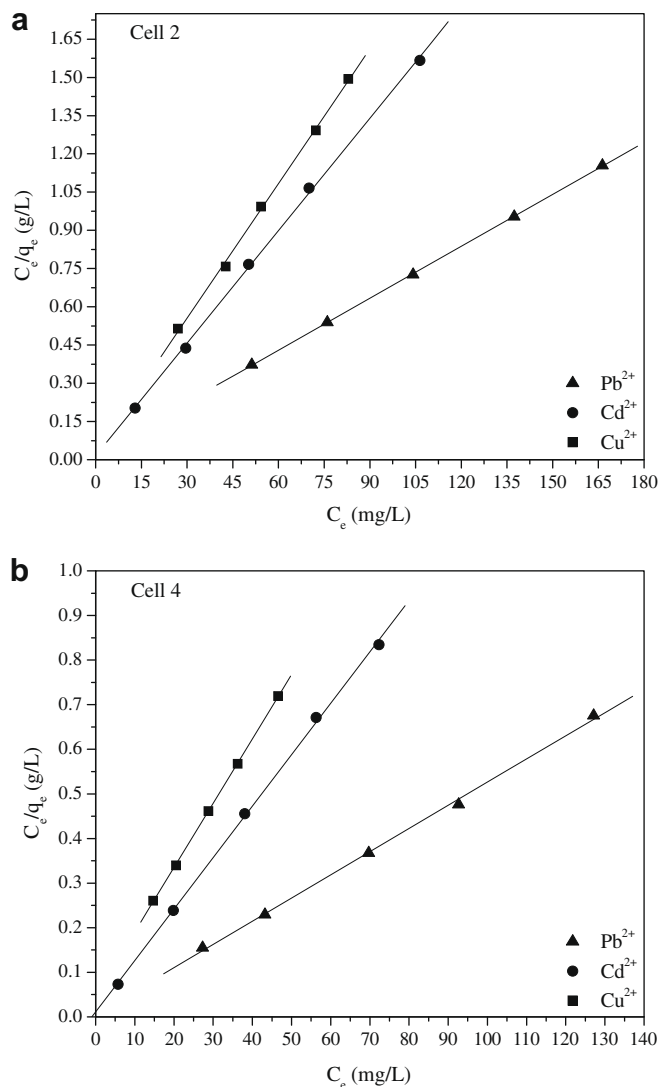
Fig. 5. Langmuir isotherm of cell 2 (a), and 4 (b).

Cell 2 in relation to cell 4 showed a larger coordination number (CN). Starting from these results it is possible to conclude that the presence of carboxylate functions reduces CN.

Cell 4 also showed larger $\Delta G°$ values in relation to cell 2. As $\Delta G°$ can indicate the spontaneity degree of the adsorption process, it is possible to conclude that adsorption process between cell 4 and metal ions is more energetic favorable in relation to cell 2. These $\Delta G°$ values also indicate that the type of adsorption involved is chemical adsorption.

In a previous study, Gurgel et al. (2008a) synthesized succinylated mercerized cellulose (cell 6) and performed adsorption studies to determine its maximum adsorption capacity for removal of Cu^{2+}, Cd^{2+}, and Pb^{2+} ions from aqueous solution. They employed similar experimental conditions in relation to the present study with respect to the equilibrium time, pH, and metal ion solutions concentration. As can be seen from Table 1, the obtained Q_{max} values for the removal of Cu^{2+}, Cd^{2+}, and Pb^{2+} by cell 6 were 153.9, 250.0, and 500.0 mg/g, respectively. Comparing the results obtained by Gurgel et al. (2008a) with the results obtained in this study (Table 3), it would then be possible to conclude that the addition of amine groups to cell 2 and 4 had a negative impact on the maximum adsorption capacity of these materials.

In order to explain this negative impact it is necessary to consider that the carboxylate groups of cell 6 were used to graft trieth-

Table 3
Langmuir parameters for Cu^{2+}, Cd^{2+}, and Pb^{2+} ions adsorption.

Metal ion	Cell	Langmuir parameters			Coordination number	$\Delta G°$ (kJ/mol)
		Q_{max} (mg/g)	b (L/mg)	R^2		
Cu^{2+}	2	56.8	0.310	0.9988	3.13	−24.3
	4	69.4	0.652	0.9999	2.11	−29.9
Cd^{2+}	2	68.0	0.930	0.9992	4.63	−27.0
	4	87.0	1.027	0.9993	2.97	−27.7
Pb^{2+}	2	147.1	0.360	0.9999	3.94	−26.1
	4	192.3	0.776	0.9984	2.49	−24.3

ylenetetramine on cellulose matrix to synthesize cell 2 and 4. Triethylenetetramine is a polyamine that has four amine groups per molecule. One or more amine groups per unit might react with carboxylic groups from cell 6 which results in the formation of crosslinking along the cell 6 chains. According to Navarro et al. (1999) the crosslinking formation may reduce the mobility of chelating groups and as result, the metal chelating efficiency of the adsorbent for heavy metal ions, which is defined as the ratio of metal adsorbed over the amount of chelating sites. Hsien & Rorrer (1997) and Tang, Zhang, Guo, and Zhou (2007) have made similar observations. They concluded that crosslinking may also reduce the maximum adsorption capacity owing to the consumption of chelating groups.

Besides, it is also necessary to consider the biopolymer mass increase owing to the introduction of triethylenetetramine on cell 6. Whether we consider that two amine groups from triethylenetetramine unit were grafted on cell 6, the molar mass of the modified biopolymer would increase 110 g/mol and this way the concentration of chelating groups would change from 6.2 (—COOH) to 2.5 mmol/g (—NH$_x$—). The experimental results showed that the concentration of chelating functions in cell 6 was found to be 6.2 mmol/g, while in the aminated materials, cell 2 and 4, were found to be 2.8 and 2.3 mmol/g, respectively. Comparing, therefore, the concentration of chelating groups calculated and obtained from the experiments it is possible to conclude there was formation of crosslinking. The maximum adsorption capacity of cell 2 and 4 fell down drastically due to the formation of crosslinking that consumed carboxylate groups that are responsible for the higher adsorption capacity of cell 6 in relation to cell 2 and 4.

The results obtained in this study were also compared with those that have reported by Tang et al. (2007) for triethylenetetramine crosslinked chitosan (CCTS) and Karnitz Júnior et al. (2007) for succinylated sugarcane bagasse modified with triethylenetetramine (MSB 6) (Table 1). The Q_{max} and b obtained from the Langmuir model for CCTS and Pb^{2+} ion was 559.4 mg/g and 0.011 L/mg, and Q_{max} and b for MSB 6 and Cu^{2+}, Cd^{2+}, and Pb^{2+} ions were 133, 313, and 313 mg/g and 0.014, 0.004, and 0.121 L/mg, respectively. CCTS in relation to cell 2 and 4 exhibited larger Q_{max} for Pb^{2+} ions, in contrast CCTS showed much lower stability constant (b) than cell 2 and 4. MSB 6 in relation to cell 2 and 4 also exhibited larger Q_{max} for Cu^{2+}, Cd^{2+}, and Pb^{2+} ions, in contrast cell 2 and 4 showed much larger stability constant (b) than MSB 6.

4. Conclusions

The present study showed that cell 2 and 4 are effective adsorbents for removal of Cu^{2+}, Cd^{2+}, and Pb^{2+} ions from single aqueous solutions. Cell 2 and 4 were obtained with a mass percent gain of 33.6% and 92.4%, concentration of amine functions of 2.8 and 2.3 mmol/g, and nitrogen content of 6.07% and 4.61%.

The developed adsorption studies demonstrated that the optimum pHs for Cu^{2+}, Cd^{2+}, and Pb^{2+} ions adsorption for cell 2 and 4 were found to be 5.8, 6.0, 5.7, and 5.5, 6.0, 5.8, respectively. Equi-

librium adsorption data were very well fitted by Langmuir model. The adsorption maximum capacities of Cu^{2+}, Cd^{2+}, and Pb^{2+} ions for cell 2 and 4 were found to be 56.8; 68.0; and 147.1 mg/g and 69.4; 87.0; and 192.3 mg/g, respectively.

Cell 4 showed a better adsorption capacity for the studied metals than cell 2. In contrast, cell 2 and 4 showed smaller maximum adsorption capacity than cell 6, succinylated mercerized cellulose (Gurgel et al., 2008a), which was used to prepare cell 2 and 4. It was possible to conclude that the introduction of triethylenetetramine on cell 6 had a negative impact on the maximum adsorption capacity of cell 2 and 4 due to crosslinking formation.

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