

# Adsorption of Cu(II), Cd(II), and Pb(II) from aqueous single metal solutions by cellulose and mercerized cellulose chemically modified with succinic anhydride

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## Abstract

This work describes the preparation of new chelating material from mercerized cellulose. The first part treats the chemical modification of non-mercerized cellulose (cell 1) and mercerized cellulose (cell 2) with succinic anhydride. Mass percent gains (mpg) and degree of succinylation (DS) of cell 3 (from cell 1) and cell 4 (from cell 2) were calculated. Cell 4 in relation to cell 3 exhibited an increase in mpg and in the concentration of carboxylic functions of 68.9% and 2.8 mmol/g, respectively. Cells 5 and 6 were obtained by treatment of cells 3 and 4 with bicarbonate solution to release the carboxylate functions and characterized by FTIR. The second part compares the adsorption capacity of cells 5 and 6 for Cu<sup>2+</sup>, Cd<sup>2+</sup>, and Pb<sup>2+</sup> ions in an aqueous single metal solution. Adsorption isotherms were developed using Langmuir model. Cell 6 in relation to cell 5 exhibited an increase in  $Q_{max}$  for Cu<sup>2+</sup> (30.4 mg/g), Cd<sup>2+</sup> (86.0 mg/g) and Pb<sup>2+</sup> (205.9 mg/g).

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## 1. Introduction

The importance of heavy metal pollution control has increased significantly in recent decades (Goel et al., 2005). Toxic metals such as Cu(II), Cd(II) and Pb(II) have become an ecotoxicological hazard of prime interest and increasing significance owing to their tendency to accumulate in the vital organs in humans and animals. They do not degrade into harmless end products in the metabolism and accumulate in the food chain, thereby posing a great danger to living organisms (Çay et al., 2004).

Conventional methods that have been used to remove heavy metal ions from various industrial effluents usually include chemical precipitation, flocculation, membrane

separation, ion exchange, evaporation, and electrolysis, and are often costly or ineffective, especially in removing heavy metal ions from dilute solutions (Ng et al., 2002; Bayramoglu et al., 2002).

Cellulose is regarded as the most abundant and renewable biopolymer in nature, and is one of the promising raw materials available in terms of cost for the preparation of various functional materials (Zugenmaier, 2001; Saito and Isogai, 2005). It is a linear homopolymer of ( $\beta$ 1  $\rightarrow$  4) linked  $\beta$ -D-glucopyranose units (Glc) aggregated to form a highly ordered structure due to its chemical constitution and spatial conformation (Klemm et al., 1998). It is known to crystallize in at least four polymorphic forms, commonly known as celluloses I, II, III and IV (Marchessault and Sarko, 1967). Three hydroxyl groups in each Glc are able to interact with one another forming intra and intermolecular hydrogen bonds (Oh et al., 2005). Hydrogen bonds in

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cellulose substrates can be modified by physical and/or chemical transformations for various applications. Typically, treatment with an aqueous NaOH solution at a specific concentration (~10 wt%) causes the transformation of cellulose I into cellulose II within the crystalline domains (Dinand et al., 2002; Jähn et al., 2002; Klemm et al., 1998). However, the concentration of NaOH for complete transformation depends on the type of cellulose being treated (Oh et al., 2005).

During mercerization, the alkali penetrates the cellulose fiber and causes a rearrangement of the crystal packing of chains from native cellulose I, with chains aligned in parallel, to cellulose II, where the chains are antiparallel (Beatriz et al., 2006; Zugenmaier, 2001). This change is irreversible and normally accompanied by a decrease in crystallinity (Buschle-Diller and Zeronian, 1992; Nishimura and Sarko, 1987) and a reduction in the degree of polymerization due to hydrolysis of the glycosidic bonds. Mercerization also increases the specific surface area of the fiber, making the hydroxyl groups of cellulose macromolecules more easily accessible (Pusic et al., 1999).

Cellulosic fibers generally has very few functional groups that are capable of anchoring metals. Hence, many attempts have been made to utilize cellulose as a metal scavenger through some derivatizations. Some of these attempts are based on the introduction of groups with capacity chelating as carboxylate and amine groups (Navarro et al., 1996, 1999, 2001) or on the oxidation catalytic of cellulose (Isogai and Kato, 1998; Tahiri and Vignon, 2000; Saito and Isogai, 2005). Some investigations also have shown that the succinylation reaction is an alternative that can be used to introduce carboxylic functionality into cellulose (Zhang et al., 1994; Gellerstedt and Gatenholm, 1999; Gellerstedt et al., 2000; Mallon and Hill, 2002).

Karnitz Júnior et al. (2007) introduced carboxylic functions in sugarcane bagasse via succinylation reaction to impart for it capacity to adsorb heavy metals ions. Sugarcane bagasse is least expensive than cellulose, however cellulose has considerably more hydroxyl groups that can be modified compared to sugarcane bagasse. Therefore, cellulose should present a large degree of succinylation and consequently a large adsorption capacity than sugarcane bagasse, what can make cellulose use viable.

This study describes the preparation and evaluation of two adsorbent materials from cellulose to adsorb heavy metal ions in aqueous solutions. The first material was prepared by modification of non-mercerized cellulose (cell 1) using succinic anhydride (Karnitz Júnior et al., 2007) as the acylating agent and the second was prepared by initial mercerization of cellulose using an aqueous NaOH solution to increase the reactivity of the material with succinic anhydride.

The first part of this work describes the reaction of non-mercerized and mercerized cellulose with succinic anhydride. This reaction allows the introduction of carboxylic functions to cellulose via formation of ester functions. The second part evaluates the adsorption of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$

and  $\text{Pb}^{2+}$  into modified celluloses from aqueous single metal ion solutions by classical titration. The results were analyzed by the Langmuir model (Ho et al., 2005).

## 2. Methods

### 2.1. Materials

Grade 3MM Chr cellulose chromatography paper (Cat. No. 3030-861) was purchased from the Whatman Company, Maidstone, England. Succinic anhydride and pyridine were purchased from VETEC (Brazil).  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  were purchased from SYNTH (Brazil). Pyridine was refluxed with NaOH overnight and distilled.

### 2.2. Cellulose mercerization

Cellulose (3MM, Whatman) (cell 1) (7.5 g) was treated with 200 mL of NaOH solution 20 wt% at 25 °C for 16 h with constant stirring. The alkali-cellulose was filtered in sintered filter, washed with distilled water up to pH 7 and then acetone. The mercerized product (cell 2) was dried at 90 °C in an oven for 1 h and stored in a desiccator.

### 2.3. Synthesis of celluloses 5 and 6

Cellulose (3MM, Whatman) (cell 1) washed with acetone and dried at 90 °C in an oven for 1 h (10.9 g) was reacted with succinic anhydride (32.6 g) under pyridine reflux (169 mL) for 24 h in order to obtain cellulose 3 (cell 3). The mercerized product (cell 2) (8.4 g) was reacted with succinic anhydride (25.2 g) under pyridine reflux (169 mL) for 24 h to obtain cellulose 4 (cell 4). The modified celluloses (cells 3 and 4) were filtered in sintered filter, washed in sequence with: solution of acetic acid in methylene chloride (1 mol/L), ethanol 95%, distilled water, a solution of chloridric acid (0.01 mol/L), distilled water and finally with acetone. After drying at 80 °C in an oven for 1 h and in a desiccator overnight the mass percent gain (mpg) was calculated.

In order to liberate carboxylate functions for a better chelating function than the carboxylic group, cells 5 and 6 were prepared by treatment of cells 3 and 4 with a saturated sodium bicarbonate solution for 30 min under constant stirring and afterwards by filtering using sintered filter and afterward washed with distilled water and then acetone. Finally, celluloses 5 and 6 were dried in an oven at 80 °C and stored in a desiccator.

### 2.4. Characterization of celluloses

#### 2.4.1. Determination of crystallinity index (CI)

The crystalline structures of cellulose samples (cells 1 and 2) were analyzed by wide-angle X-ray diffraction in a Shimadzu XRP-6000 X-ray diffractometer. These cellulose samples prepared by powder were laid on an aluminum

sample holder (35 × 55 × 3 mm) and analyzed under plateau conditions. Mg-filtered Fe K $\alpha$  radiation ( $\lambda = 1.9374$  Å) generated at a voltage of 40 kV and current of 30 mA was utilized, with a scan speed of 2°/min from 7° to 40°.

The crystalline allomorphs of cellulose were determined by the resolution of wide-angle X-ray diffraction curves. The determination of CI is taken from the method of Jayme and Knolle (Krässig, 1993). Amorphous halos were drawn by the Microcal™ ORIGIN™ program for the determination of  $h_{am}$  and  $h_{cr}$ . CI was calculated by

$$CI = 1 - \frac{h_{am}}{h_{cr}} = 1 - \frac{h_{am}}{(h_{tot} - h_{am})}, \quad (1)$$

where the crystalline scatter of the 002 reflection at  $2\theta$  of 28.4° for cellulose I or 101 reflection at  $2\theta$  of 25.0° for cellulose II (crystalline height,  $h_{cr}$ ) with the height of the amorphous reflection at  $2\theta$  of 22.7° of cellulose I or 20.2° for cellulose II (amorphous height,  $h_{am}$ ), respectively (Krässig, 1993).

#### 2.4.2. FTIR analyses

The samples were prepared mixing 1 mg of material with 100 mg of spectroscopy grade KBr. The FTIR spectra were recorded using Nicolet Impact 410 equipment with detector at 4 cm<sup>-1</sup> resolution from 500 to 4000 cm<sup>-1</sup> and 32 scans per sample.

### 2.5. Characterization of succinylated celluloses

#### 2.5.1. Mass percent gain

The mass percent gain (mpg) was calculated according to

$$\text{mpg (\%)} = \left( \frac{m_{\text{mod}} - m_{\text{unmod}}}{m_{\text{unmod}}} \right) * 100, \quad (2)$$

where  $m_{\text{mod}}$  is the mass of the modified cellulose and  $m_{\text{unmod}}$  is the mass of the unmodified cellulose.

#### 2.5.2. Degree of succinylation

The degree of succinylation of the celluloses was determined by measuring the quantity of introduced acid function. The concentration of carboxylic functions per gram of modified cellulose was determined for retro titration. For this, an amount of 0.1000 g of cells 3 and 4 were treated with 100.0 mL of an aqueous NaOH solution (0.01 mol/L) in a 250-mL Erlenmeyer for 1 h under constant stirring. Soon thereafter the materials were separated by single filtration and three aliquots (25.0 mL) of each obtained solution were titrated with an aqueous HCl solution (0.01 mol/L) (Karnitz Júnior et al., 2007). The concentration of carboxylic functions was calculated by:

$$C_{\text{COOH}} = \left[ \frac{(C_{\text{NaOH}} * V_{\text{NaOH}}) - (4 * C_{\text{HCl}} * V_{\text{HCl}})}{m_{\text{cell}}} \right], \quad (3)$$

where  $C_{\text{NaOH}}$  is the concentration of the NaOH solution (mmol/L),  $C_{\text{HCl}}$  is the concentration of the HCl solution

(mmol/L),  $V_{\text{NaOH}}$  is the volume of the NaOH solution (L),  $V_{\text{HCl}}$  is the volume of HCl spent in the titration of the excess of the base non-reacted (L) and  $m_{\text{cell}}$  is the cellulose mass (g).

### 2.6. Kinetic study of metal ion adsorption of cells 5 and 6

Experiments with each material and metal ion were performed to determine the adsorption equilibrium time. The interval times used were from 5 to 105 min for cell 5 and from 5 to 30 min for cell 6. An amount of 100 mg from cells 5 and 6 were placed in a 250-mL Erlenmeyer with 100.0 mL of metal ion solution at fixed concentrations (200 mg/L and 300 mg/L Cu<sup>2+</sup>; 200 mg/L and 280 mg/L Cd<sup>2+</sup>; 300 mg/L and 500 mg/L Pb<sup>2+</sup> for cells 5 and 6, respectively) under constant stirring. The experiments were done at pHs 5.4 for Cu<sup>2+</sup>, 7.0 for Cd<sup>2+</sup>, and 6.0 for Pb<sup>2+</sup>, as optimal values to obtain the best adsorption. Significant pH variations were observed during each experiment, but pH values were maintained constant adding up an aqueous NaOH solution (0.01–0.1 mol/L) to the metal solutions with each cellulose.

After single filtration, the concentration of ions Cu<sup>2+</sup> was determined by direct titration with EDTA at pH 10 using murexide as an indicator, and in the case of Cd<sup>2+</sup> and Pb<sup>2+</sup> ions, the concentration was determined by retro titration of an excess of EDTA solution with Mg<sup>2+</sup> at pH 10 using Erichrome Black T as an indicator. A buffer NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup> was used to adjust the pH in the titrations.

### 2.7. pH study of metal ion adsorption of cells 5 and 6

Experiments with each material and metal ion were performed to determine the effect of pH on metal ion adsorption. An amount of 100 mg from cells 5 and 6 were placed in a 250-mL Erlenmeyer with 100.0 mL of metal ion solution at a fixed concentration (200 mg/L and 300 mg/L Cu<sup>2+</sup>; 200 mg/L and 280 mg/L Cd<sup>2+</sup>; 300 mg/L and 500 mg/L Pb<sup>2+</sup> for cells 5 and 6, respectively) under constant stirring. The pH range studied for cells 5 and 6 was from 1–6 to 2–5.5 for Cu<sup>2+</sup>; 2–6 and 2.5–5.5 for Pb<sup>2+</sup>; 1.5–8 and 3–8 for Cd<sup>2+</sup>, respectively. The pH was adjusted with HCl or NaOH solutions at 0.01–1.0 mol/L. The reaction times used were obtained from the kinetic study. After single filtration, the metal ion concentration was determined by titration and the pH variations observed were corrected during each experiment as described earlier.

### 2.8. Adsorption isotherms of cells 5 and 6

Experiments were performed for each material and metal ion to determine adsorption isotherms. In each experiment, 100 mg from the cell was placed into a 250-mL Erlenmeyer with 100.0 mL of metal ion solution at specific concentrations from 120 to 540 mg/L under constant stirring. Each experiment was performed at the pH of the

greatest ion adsorption during the time necessary for equilibrium.

After single filtration, the metal ion concentration was determined by titration described earlier.

### 2.8.1. Coordination number

The coordination number was calculated according to

$$CN = \frac{C_{\text{COOH}}}{Q_{\text{max}}/MM_{\text{metal}}} \quad (4)$$

where  $C_{\text{COOH}}$  is the concentration of carboxylic functions (mmol/g),  $Q_{\text{max}}$  is the maximum adsorption capacity (mg/g) obtained by the Langmuir model for  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  and  $MM_{\text{metal}}$  are the mass molars of the metals (mg/mmol).

## 3. Results and discussion

### 3.1. X-ray diffraction and FTIR analyses of cells 1 and 2

Various reactions such as the inclusion of alkali and water in cellulose and the splitting and formation of new inter and intramolecular hydrogen bonds have been reported by Fengel (1992, 1993a,b) and Fengel and Strobel (1994), regarding the absorbance variations and wave number shifts in the FTIR spectra.

In the presence of NaOH, the crystallites composed of parallel cellulose chains incorporate hydrated sodium and hydroxide ions, forming alkyl cellulose (Shibazaki et al., 1997). Solvation of the cellulose I chains increases their mobility, allowing them to rotate about their axes to produce the antiparallel structure typical of cellulose II (Kroon-Batenburg and Kroon, 1997).

In the present study, the diffraction patterns of cell 1 showed reflections typically attributed to cellulose I, i.e. at Bragg angles of  $28.4^\circ$  (002 plane),  $26.1^\circ$  (021),  $20.6^\circ$  ( $10\bar{1}$ ),  $18.6^\circ$  (101). Cell 2, on the other hand, produced reflections at Bragg angles typical of cellulose II, namely at  $2\theta$   $25.0^\circ$  ( $10\bar{1}$ ),  $27.5^\circ$  (002) (Figure not shown).

By the transformation of cellulose I into cellulose II, many characteristic bands were shifted at the peak maximum or the absorbance was changed. The bands at 1431, 1371, 1317, 1282, 1236, 1202, 1163, 1032, 983 and  $897\text{ cm}^{-1}$  are shifted to 1421, 1376, 1315, 1278, 1227, 1200, 1160, 1022, 993 and  $894\text{ cm}^{-1}$ , respectively. Including the shift of O–H and C–H stretching vibrations ( $3348 \rightarrow 3446$ ,  $2901 \rightarrow 2892\text{ cm}^{-1}$ ), all the bands were influenced by the transformation related to the change of intra and intermolecular bonds (Oh et al., 2005) (Figure not shown).

With a few exceptions (the bands at 3348, 2901, 1371, 1202,  $897\text{ cm}^{-1}$ ), many of the bands at 1431, 1317, 1282, 1236, 1163, 1032,  $897\text{ cm}^{-1}$  were decreased. The absorbances of the bands at 1337, 1114, 1058 and  $713\text{ cm}^{-1}$  were decreased by the transformation.

### 3.2. The change of CI by transformation

Treatment of cellulose with NaOH changes the CI as well as the crystal system of the cellulose. The CIs of cells 1 and 2 obtained from the X-ray diffraction curves were 99% and 92%, respectively. The CI of cell 2 decreased up to 7% by treatment with 20 wt% of NaOH.

### 3.3. Synthesis of cells 3, 4, 5 and 6

The synthesis route used to prepare cells 3, 4, 5 and 6 is shown in Fig. 1. Non-mercerized cellulose (cell 1) and mercerized cellulose (cell 2) were reacted with succinic anhydride for 24 h. The mass percent gain (mpg) was calculated according to Eq. (2). The degree of succinylation of the cellulose fibers was determined by measuring the quantity of acid function. The concentration of carboxylic functions per gram of modified cellulose was determined by retro titration (Eq. (3)). The results are shown in Table 1.

The treatment of cellulose with a 20 wt% NaOH solution reduced the value of IC by 7%, increased the mass gain percent of cell 3 in relation to cell 4 from 38.8% to 107.4% and the concentration of carboxylic functions from 3.4 to 6.2 mmol/g (Table 1). These results are a consequence of the alkaline treatment that transforms crystalline cellulose from cellulose I into cellulose II. These two forms exist because the hydroxymethyl group ( $-\text{CH}_2\text{OH}$ ) can adopt two distinct conformations, resulting in two ways of packing the chains in the microcrystal. In cellulose I, whose

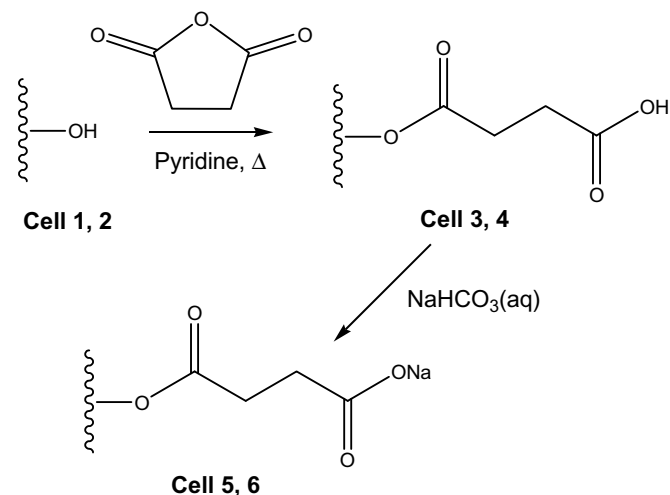


Fig. 1. Synthesis route used to obtain cells 3, 4, 5 and 6.

Table 1  
Type of cellulose, mass gain percent and concentration of carboxylic functions

Material	Type of cellulose	Crystallinity index (%)	mpg (%)	$C_{\text{COOH}}$ (mmol/g)
Cell 3	I	99	38.5	3.4
Cell 4	II	92	107.4	6.2

chains are orientated in parallel, the  $-\text{CH}_2\text{OH}$  groups of adjacent chains have the same conformation, while the antiparallel structure of cellulose II occurs when adjacent chains have these groups in different positions (Pusic et al., 1999). This rearrangement of the crystal packing increases the chains' separation, providing easier access to the hydroxyl groups of cellulose and reducing packing efficiency, thereby facilitating penetration of succinic anhydride and promoting a higher degree of substitution and more uniform succinylation, due to a greater number of hydroxyl groups available for reaction, justifying the larger mpg and  $C_{\text{COOH}}$  of cell 4 in relation to cell 3.

### 3.3.1. Characterization of cells 5 and 6

Characterization of carboxylated cells 5 and 6 was accomplished by FTIR spectroscopy. Fig. 2 shows the FTIR spectra of cells 1 and 5 (a), and cells 2 and 6 (b). As depicted in Fig. 2, the three major changes noticed in FTIR spectrum for cell 5 in relation to cell 1, and cell 6 in relation to cell 2 are: (1) the arising of a band at

$1735\text{ cm}^{-1}$  for cell 5 and of a strong band at  $1743\text{ cm}^{-1}$  for cell 6, corresponding to asymmetric and symmetric stretching of ester C–O; (2) the arising of a band at  $2923\text{ cm}^{-1}$  for cells 5 and 6 corresponding to asymmetric stretching  $\text{CH}_2$  due the introducing of the succinic group; (3) the arising of bands at  $1568$  and  $1413\text{ cm}^{-1}$  for cell 5 and of strong bands at  $1579$  and  $1413\text{ cm}^{-1}$  for cell 6, corresponding to asymmetric and symmetric stretching due to presence of carboxylate ion, respectively.

The ester and carboxylate IR bands indicate that succinic group was introduced via formation of the ester bond with consequent release of a carboxylic functional group.

### 3.4. Study of adsorption of $\text{Cu}^{2+}$ , $\text{Cd}^{2+}$ and $\text{Pb}^{2+}$ in cells 5 and 6

The studies of the adsorption properties cells 5 and 6 were accomplished for each material and metal ion. A kinetic study and adsorption study as a function of pH were first carried out.

#### 3.4.1. Effect of contact time

The adsorption equilibrium time experiments were carried out for different contact times with a fixed adsorbent quantity (100 mg) with 100.0 mL of metal ion solution at a pH of 5.0 for  $\text{Cu}^{2+}$  and 7.0 for  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ , at a fixed concentration. The adsorption of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions increased with contact time up. The equilibrium time was achieved after 20 and 10 min for  $\text{Cu}^{2+}$ ; 10 and 10 min for  $\text{Cd}^{2+}$ ; 10 and 10 min for  $\text{Pb}^{2+}$  for cells 5 and 6, respectively. The adsorption equilibrium times mentioned above were chosen for pH and concentration dependent experiments.

#### 3.4.2. The pH effect

The removal of metal ions from aqueous solutions by adsorption is dependent on the solution pH and, since it affects adsorbent surface charge, the degree of ionization, and the species of adsorbates. Adsorption of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  in cells 5 and 6 as a function of pH is shown in Fig. 3a and b. The adsorption of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  increased as pH increased. The maximum removal of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  was observed at pHs 5.0, 8.0 and 5.0 for cell 5 and at pHs 5.6, 6.0, 5.4 for cell 6, respectively.

#### 3.4.3. Adsorption isotherms

Adsorption isotherms describe how adsorbates interact with adsorbents and are important in optimizing the use of the latter. The widely used Langmuir isotherm (Langmuir, 1918) has been successfully applied in many real adsorption processes and is expressed as

$$q_e = \frac{Q_{\text{max}} b C_e}{1 + b C_e} \quad (5)$$

which can be rearranged to obtain a liner form

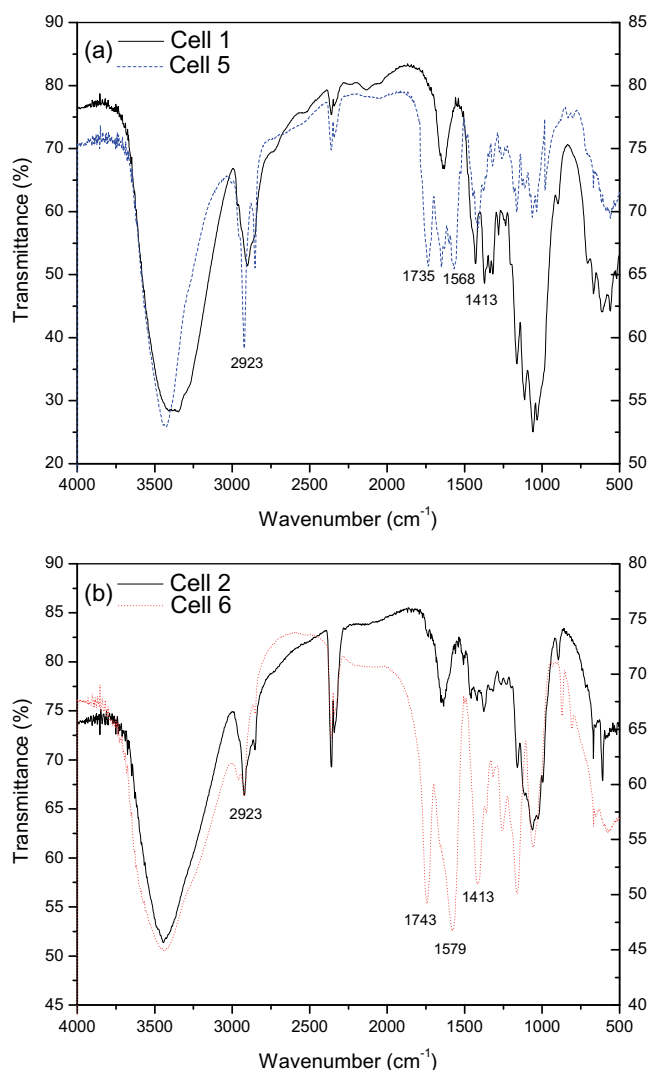


Fig. 2. FTIR spectrum of cells 1 and 5 (a) and cells 2 and 6 (b).

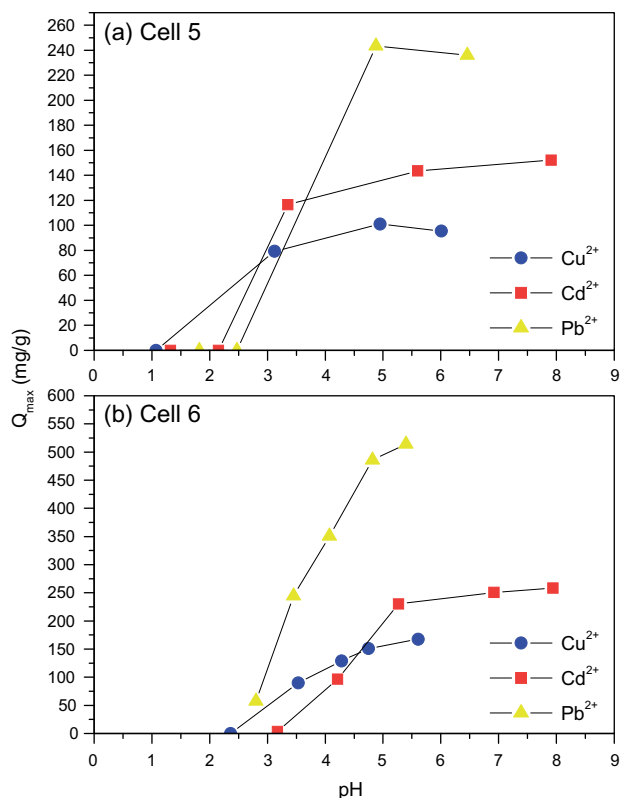


Fig. 3. Adsorption of metal ions in cells 5 (a) and 6 (b) as a function of pH.

$$\frac{C_e}{q_e} = \frac{1}{Q_{max}b} + \frac{C_e}{Q_{max}} \quad (6)$$

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 cell to form a complete monolayer coverage on the surface bound at high equilibrium metal ion concentration  $C_e$  (mg/L) and  $b$  (L/mg) is the Langmuir constant related to the affinity of binding sites.  $Q_{max}$  represents the practical limiting adsorption capacity when the surface is fully covered with metal ions, assisting in the comparison of adsorption performance, and  $b$  indicates the bond energy of the adsorption reaction between metal and material.

A linearized plot of  $C_e/q_e$  versus  $C_e$  is obtained from the model shown in Fig. 4a and b.  $Q_{max}$  and  $b$  were computed from the slopes and intercepts of different straight lines representing cells with different metal ions (Table 2).

The high correlation coefficients of the linearized Langmuir equation indicate that this model can explain metal ion adsorption by the modified celluloses satisfactorily.

As shown in Table 2, cell 6 presented greater adsorption capacity ( $Q_{max}$ ) and larger bond energy between metal and material ( $b$ ) than cell 5 for  $Cu^{2+}$ ,  $Cd^{2+}$  and  $Pb^{2+}$ . The increase of the adsorption capacity ( $Q_{max}$ ) and of the bond energy between metal and material ( $b$ ) of cell 6 in relation to cell 5 for  $Cu^{2+}$ ,  $Cd^{2+}$  and  $Pb^{2+}$  can be explained by the fact that cell 6 presents a larger concentration of carboxylic

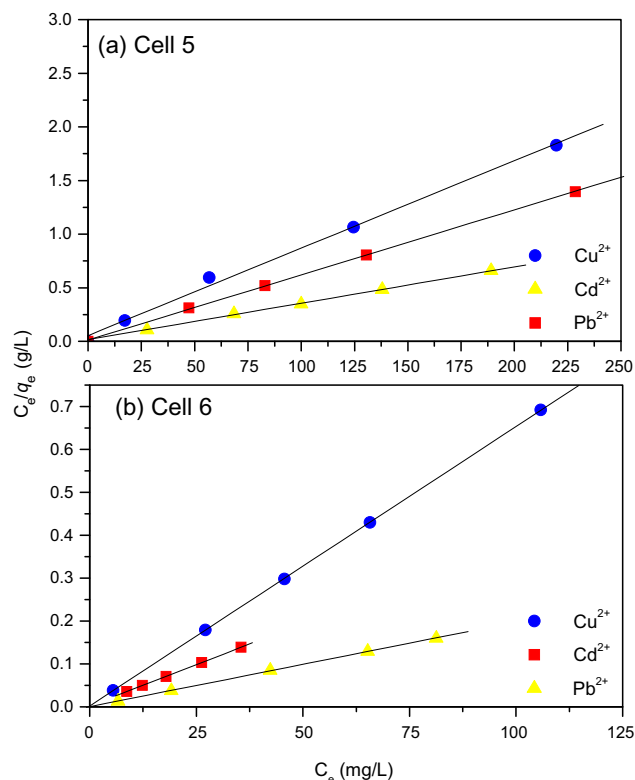


Fig. 4. The Langmuir isotherm of cells 5 (a) and 6 (b).

Table 2

The Langmuir parameters for  $Cu^{2+}$ ,  $Cd^{2+}$  and  $Pb^{2+}$  adsorption

Metal ion	Cell	Langmuir			Coordination number
		$Q_{max}$ (mg/g)	$b$ (L/mg)	$R^2$	
$Cu^{2+}$	5	123.5	0.147	0.9956	1.75
	6	153.9	3.095	1.0000	2.56
$Cd^{2+}$	5	164.0	0.517	0.9997	2.33
	6	250.0	1.818	1.0000	2.79
$Pb^{2+}$	5	294.1	0.207	0.9993	2.40
	6	500.0	5.000	1.0000	2.57

functions than cell 5. This higher concentration of carboxylic functions increases the coordination number of cell 6 in relation to cell 5 for each metal.

#### 4. Conclusions

The mercerization of cellulose increases the separation of polysaccharide chains and reduces the packing efficiency, thereby facilitating the penetration of succinic anhydride. The higher mass gain percent and concentration of carboxylic functions observed during the succinylation for mercerized cellulose in relation to non-mercerized cellulose is due a greater number of hydroxyl groups available for reaction. The modified mercerized cellulose 6 showed a higher adsorption capacity for  $Cu^{2+}$ ,  $Cd^{2+}$  and  $Pb^{2+}$  ions than modified non-mercerized cellulose 5.

Modified mercerized cellulose (cell 6) in relation to modified non-mercerized cellulose (cell 5) presented an increase in the mass gain and concentration of carboxylic functions of 68.9% and 2.8 mmol/g, respectively, and an increase in the adsorption capacity for  $\text{Cu}^{2+}$  (30.4 mg/g),  $\text{Cd}^{2+}$  (86 mg/g) and  $\text{Pb}^{2+}$  (205.9 mg/g), and it demonstrated that metal ion adsorption efficiency was proportional to the number of carboxylic acids introduced.

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