



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

Leandro Vinícius Alves Gurgel^a, Rossimiriam Pereira de Freitas^b, Laurent Frédéric Gil^{a,*}

^a Departamento de Química, Instituto de Ciências Exatas e Biológicas, Universidade Federal de Ouro Preto, 35400-000, Ouro Preto, Minas Gerais, Brazil

^b Departamento de Química, Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, 31270-901, Belo Horizonte, Minas Gerais, Brazil

ARTICLE INFO

Article history:

Received 26 February 2008

Received in revised form 10 May 2008

Accepted 20 May 2008

Available online 8 June 2008

Keywords:

Mercerization

Modified sugarcane bagasse

Succinylation

Adsorption

Heavy metals

ABSTRACT

This work describes the preparation of new chelating material from mercerized sugarcane bagasse. The first part treats the chemical modification of non-mercerized sugarcane bagasse (SCB) and twice-mercerized sugarcane bagasse (MMSCB) with succinic anhydride. Mass percent gains (mpg) and degrees of succinylation (DS) of succinylated non- and twice-mercerized sugarcane bagasse 1 (SCB 1 and MMSCB 1) were calculated. MMSCB 1 exhibited an increase in mpg and DS of 49.2% and 0.9 mmol/g in relation to SCB 1. SCB 2 and MMSCB 2 were obtained by treatment of MMSCB 1 and SCB 1 with bicarbonate solution to release the carboxylate functions and characterized by FTIR. The second part evaluates and compares the adsorption capacity of SCB 2 and MMSCB 2 for Cu²⁺, Cd²⁺ and Pb²⁺ ions in an aqueous single metal solution. Adsorption isotherms were developed using Langmuir model. MMSCB 2 exhibited an increase in Q_{\max} for Cd²⁺ (43.6 mg/g) and Pb²⁺ (83.3 mg/g) in relation to SCB 2.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

Heavy metal ions are known to be toxic and carcinogenic to living organisms (Clement, Eiceman, & Koester, 1995; MacCarthy, Klusman, Cowling, & Rice, 1995). Their presence in the aquatic environment has been of great concern because of their toxicity and non biodegradable nature. Some metal ions are cumulative poisons, capable of being assimilated and stored in the tissues of organisms, causing noticeable adverse physiological effects (Gupta & Ali, 2000).

The removal of toxic metal ions from water is a very difficult task due to the high cost of treatment methods (Weng & Huang, 1994). There are various methods for the removal of toxic metal ions from aqueous solutions: reverse osmosis, ion exchange, precipitation, electro dialysis, adsorption, etc. Among these methods, adsorption is by far the most versatile and widely used for the removal of different pollutants (Gupta & Ali, 2004).

Brazil is the world leading producer of sugarcane for both the alcohol and the sugar industries. These industries produce a large amount of sugarcane bagasse. According to the last official survey from CONAB, an agency from the Brazilian Ministry of Agriculture, the national production of sugarcane in 2007/2008 was 527 million

tons, the largest of all times. On average, 280 kg of sugarcane bagasse containing 50% moisture are produced by ton of sugarcane. In those industries, bagasse is burned in order to produce energy for sugar mills, but the leftovers are still significant (Karnitz Júnior et al., 2007). The remaining bagasse still continues to be a menace to the environment and a suitable utilization of this residue is an important target to be pursued (Sun, Sun, Zhao, & Sun, 2004). Sugarcane bagasse is constituted mainly of cellulose (40–50%), polyoses (25–30%), and lignin (20–25%) (Caraschi, Campana, & Curvelo, 1996).

Hassan and El-Wakil (2003) have reported the use of amidoximated bagasse (Am-B) for adsorption of some heavy metal ions such as Cu(II), Hg(II), Ni(II), Cr(III), and Pb(II) from aqueous solutions. Adsorption studies were performed at different pHs, contact times, metal ion concentration, and temperatures. The maximum milligrams of metal ions adsorbed per gram of AM-B were 672, 156, 137, and 47 for Hg²⁺, Cr³⁺, Cu²⁺, and Ni²⁺, respectively.

Nada and Hassan (2006) have recently reported the chemical modification of bagasse fibers with the aim to prepare lignocellulosic materials for removal of heavy metal ions from wastewater. Different reactions were used to modify bagasse fibers and to produce the following materials: oxy-bagasse, succinylated bagasse, and carboxymethylated bagasse. Adsorption studies were performed to evaluate the ability of these cation exchangers to remove heavy metal ions. The maximum milligrams of metal ions adsorbed

* Corresponding author. Tel.: +55 31 3559 1717; fax: +55 31 3551 1707.
E-mail address: laurent@iceb.ufop.br (L.F. Gil).

per gram of oxy-bagasse, succinylated bagasse, and carboxymethylated bagasse were 233, 88, 394, and 200; 170, 113, 321, and 88; 392, 460, 504, and 465, for Cu^{2+} , Ni^{2+} , Cr^{3+} , and Fe^{3+} , respectively.

Karnitz Júnior et al. (2007) have recently reported the use of sugarcane bagasse modified with succinic anhydride (MSB 2) for removal of Cu(II), Cd(II) and Pb(II) from aqueous solutions. The authors have reported that the hydroxyl and phenolic groups in sugarcane bagasse could be easily converted to carboxylic groups by using succinic anhydride. Adsorption studies to determine the maximum adsorption capacity (Q_{max}) of MSB 2 towards each heavy metal were developed. The results were analyzed by Langmuir and Freundlich models. MSB 2 exhibited a maximum adsorption capacity of 114 mg/g for Cu^{2+} , 196 mg/g for Cd^{2+} and 189 mg/g for Pb^{2+} according to Langmuir model.

Gurgel, Karnitz Júnior, Gil, and Gil (2008) reported the use of modified non- and mercerized cellulose with succinic anhydride for removal of Cu(II), Cd(II) and Pb(II) from aqueous solutions. The authors reported the effect of mercerization in the increase of the fibers specific surface area and in their reactivity. The mercerization makes the hydroxyl groups of the cellulose macromolecules more accessible and decreases the cellulose crystallinity index by 7%. Modified mercerized cellulose exhibited an increase in the mass percent gain and in the concentration of carboxylic functions in relation to modified non-mercerized cellulose by 68% and 2.8 mmol/g, respectively. Adsorption studies to determine the maximum adsorption capacity (Q_{max}) of modified celluloses for metals ions were developed. The results were analyzed by Langmuir model. Modified mercerized cellulose exhibited an increase in the adsorption maximum capacity of 30.4 mg/g for Cu^{2+} , 86.0 mg/g for Cd^{2+} and 205.9 mg/g for Pb^{2+} in relation to modified non-mercerized cellulose.

This work describes the preparation and evaluation of two materials from sugarcane bagasse to adsorb heavy metal ions in aqueous solutions. The first material was prepared by modification of sugarcane bagasse with succinic anhydride (SCB) and the second was prepared by mercerization of sugarcane bagasse with an aqueous NaOH solution (20 wt%) followed by reaction with succinic anhydride (MMSCB). The adsorption studies of Cu^{2+} , Cd^{2+} and Pb^{2+} from aqueous single metal ion solutions by SCB and MMSCB were developed at different times, pHs, and metal ion concentration.

2. Experimental procedure

2.1. Materials

Sugarcane bagasse, a waste material of sugar-alcohol industry, was collected from an alcohol factory at Ouro Preto, Brazil. 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. Sugarcane bagasse preparation

Integral sugarcane bagasse was first dried under sunlight. The fibers were manually broken into small pieces and subsequently dried at 90 °C in an oven for 24 h. Sugarcane bagasse was powdered by a mill with tungsten rings. The powder was sieved in a 6-sieve system (10, 30, 45, 60, 100 and 200 mesh). The fraction of 200 mesh was chosen for the accomplishment of the experiments. This fraction was treated with distilled water under constant stirring at 60–70 °C for 1 h to eliminate residual sugars and separated by single filtration. Afterwards, it was washed with EtOH 95% and dried at 90 °C in an oven. Finally, it was washed again in a Soxhlet apparatus with hexane-ethanol (1:1, v/v) for 24 h to eliminate extractives. During this process small fractions of lignin ex-

tracted during pulverization are also solubilized. Then, it was dried at 90 °C in an oven and stored in desiccator.

2.3. Sugarcane bagasse mercerization

Sugarcane bagasse (SCB) (7.5 g) was treated with 350 mL of aqueous NaOH solution (20 wt%) at 25 °C for 16 h under constant stirring in order to obtain mercerized sugarcane bagasse (MSCB). MSCB was treated again using the same procedure described above in order to obtain twice-mercerized sugarcane bagasse (MMSCB). In the end of each treatment, the alkali was separated of bagasse by filtration in sintered filter, washed with distilled water up to pH 7 and acetone. The mercerized products (MSCB and MMSCB) were then dried at 90 °C in an oven for 1 h and stored in desiccator. The mass percent loss (mpl) was calculated at the end of each treatment.

2.4. Synthesis of SCB 1 and MMSCB 1

Sugarcane bagasse (SCB) (5 g) was reacted with succinic anhydride (15 g) under pyridine reflux (50 mL) for 24 h in order to obtain modified sugarcane bagasse 1 (SCB 1). The twice-mercerized sugarcane bagasse (MMSCB) (5 g) was reacted with succinic anhydride (25 g) under pyridine reflux (150 mL) for 4 h in order to obtain modified twice-mercerized sugarcane bagasse 1 (MMSCB 1). The modified materials (SCB 1 and MMSCB 1) were separated by filtration in sintered filter, washed in sequence with: solution of acetic acid in methylene chloride (1 mol/L), ethanol 95%, distilled water, chloridric acid solution (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 gains (mpg) and degrees of succinylation were calculated.

2.5. Synthesis of SCB 2 and MMSCB 2

SCB 2 and MMSCB 2 were obtained by treatment of SCB 1 and MMSCB 1 with saturated sodium bicarbonate solution in a 250 mL Erlenmeyer for 30 min under constant stirring. Soon afterwards, the materials were separated by filtration in sintered filter and washed with distilled water and acetone. Finally SCB 2 and MMSCB 2 were dried in an oven at 80 °C and stored in a desiccator.

2.6. Materials characterization

2.6.1. Determination of Crystallinity Index (CI)

The crystalline structures of SCB, MSCB and MMSCB were analyzed by wide-angle X-ray diffraction in a Shimadzu XRP-6000 X-ray diffractometer. The samples were prepared by powdering, laid on an aluminium sample holder (35 × 55 × 3 mm) and analyzed under plateau conditions. Mg-filtered $\text{Fe K}\alpha$ radiation ($\lambda = 1.9374 \text{ \AA}$) 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 materials were determined by the resolution of wide-angle X-ray diffraction curves. The determination of CI was taken from the method of Jayme and Knolle (Krässig, 1993). Amorphous halos were drawn by Microcal™ ORIGIN™ program for the determination of h_{am} and h_{cr} . CI was calculated by Eq. (1)

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

where h_{cr} (crystalline height) is the crystalline scatter of the 002 reflection at 2θ of 28.4° for cellulose I or 10 $\bar{1}$ reflection at 2θ of 25.0° for cellulose II and h_{am} (amorphous height) is the amorphous

reflection at 2θ of 22.7° for cellulose I or 20.2° for cellulose II, respectively (Krässig, 1993).

2.6.2. 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^{-1} resolution from 500 to 4000 cm^{-1} and 32 scans per sample.

2.7. Characterization of SCB 1 and MMSCB 1

2.7.1. Mass percent loss (mpl)

The mass percent loss (mpl) after each treatment of sugarcane bagasse (SCB) with NaOH 20 wt% was calculated according to Eq. (2)

$$\text{mpl (\%)} = \left(\frac{m_i - m_f}{m_i} \right) * 100 \quad (2)$$

where m_i is the mass of sugarcane bagasse before and m_f is the mass of the sugarcane after treatment.

2.7.2. Mass percent gain (mpg)

The mass percent gain (mpg) was calculated according to Eq. (3)

$$\text{mpg (\%)} = \left(\frac{m_{\text{mod}} - m_{\text{unmod}}}{m_{\text{unmod}}} \right) * 100 \quad (3)$$

where m_{mod} is the mass of modified bagasse and m_{unmod} is the mass of unmodified bagasse.

2.7.3. Degree of succinylation (DS)

The degree of succinylation of SCB 1 and MMSCB 1 was determined by measuring the quantity of introduced acid functions. The concentration of carboxylic functions per gram of material was determined by retro-titration. For this, amounts of 0.1000 g of SCB 1 and MMSCB 1 were treated with 100.0 mL of an aqueous NaOH solution (0.01 mmol/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 mmol/L) (Gurgel et al., 2008; Karnitz Júnior et al., 2007). The concentration of carboxylic functions was calculated using Eq. (4).

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

where C_{NaOH} is the concentration of NaOH solution (mmol/L), C_{HCl} is the concentration of HCl solution (mmol/L), V_{NaOH} is the volume of NaOH solution (L), V_{HCl} is the volume of HCl spent in the titration of excessive non-reacted base (L) and m_{mat} is the material mass (g).

2.8. Kinetic study of metal ion adsorption for SCB 2 and MMSCB 2

Experiments with each material and metal ion were performed to determine the adsorption equilibrium time. The interval times used were 10–40 min. An amount of 100 mg for SCB 2 and MMSCB 2 were placed in a 250 mL Erlenmeyer with 100.0 mL of metal ion solution at fixed concentrations (200 mg/L and 250 mg/L for Cu^{2+} ; 520 mg/L and 370 mg/L for Cd^{2+} ; 500 mg/L and 590 mg/L for Pb^{2+} for SCB 2 and MMSCB 2, respectively) under constant stirring. The experiments were done at pHs 5.4 for Cu^{2+} , 7.0 for Cd^{2+} , and 6.0 for Pb^{2+} , optimal values to obtain the best adsorption. Significant pH variations were noticed during each experiment, but pH values were kept constant by adding up an aqueous NaOH solution (0.01–0.1 mol/L) to the metal solutions with each material.

After single filtration, the concentration of Cu^{2+} ions was determined by direct titration with EDTA (2 mmol/L) at pH 10 using Murexide as indicator.

In the case of Pb^{2+} and Cd^{2+} ions, the concentration was determined by retro-titration. In this procedure, an excess of EDTA solution of known concentration (3 mmol/L) is added up to an aliquot containing Pb^{2+} and Cd^{2+} ions to be analyzed. These ions are complexed by EDTA and consequently they do not precipitate with the addition of a buffer ($\text{NH}_3/\text{NH}_4^+$) of pH equal to 10. In this pH the EDTA excess can be determined by titration with an aqueous Mg^{2+} solution (2.5 mmol/L) using Erichrome Black T as an indicator (Jeffery, Bassett, Mendham, & Denney, 1989). Then, the concentration of Pb^{2+} and Cd^{2+} ions can be obtained through a simple calculation according to Eq. (5)

$$C_{\text{M}^{2+}} = \left[\frac{(C_{\text{EDTA}} * V_{\text{EDTA}}) - (C_{\text{Mg}^{2+}} * V_{\text{Mg}^{2+}})}{V_{\text{M}^{2+}}} \right] * MM_{\text{metal}} \quad (5)$$

where $C_{\text{M}^{2+}}$ is the metal ion concentration (mg/L), C_{EDTA} and V_{EDTA} are the concentration (mmol/L) and the volume (mL) of EDTA, $C_{\text{Mg}^{2+}}$ and $V_{\text{Mg}^{2+}}$ are the concentration (mmol/L) and the volume (mL) of Mg^{2+} solution, $V_{\text{M}^{2+}}$ is the volume of the aliquot (mL) analyzed and MM_{metal} is the molar mass of Lead or Cadmium (mg/mmol).

2.9. pH study of metal ion adsorption for SCB 2 and MMSCB 2

Experiments with each material and metal ion were performed to determine the effect of pH on metal ion adsorption. An amount of 100 mg for SCB 2 and MMSCB 2 was placed in a 250-mL Erlenmeyer with 100.0 mL of metal ion solution at fixed concentrations (200 and 250 mg/L for Cu^{2+} ; 520 and 370 mg/L for Cd^{2+} ; 490 and 570 mg/L for Pb^{2+} for SCB 2 and MMSCB 2, respectively) under constant stirring. The pH range studied for SCB 2 and MMSCB 2 was from 2.1 to 5.4; 2.5 to 5.6 for Cu^{2+} ; 2.4 to 6.1; 2.4 to 6.1 for Cd^{2+} ; 2.5 to 5.4; 2.6 to 5.5 for Pb^{2+} , respectively. The pH was adjusted with an aqueous HCl or NaOH solutions at 0.01–1.0 mol/L. The reaction times used were those obtained from the kinetic study.

There were significant pH variations during the experiments, but they were corrected by adding up an aqueous NaOH or HCl solution (0.01–0.1 mol/L) to the metal solutions with each material. After single filtration, the metal ions concentration was determined by titration as described earlier.

2.10. Adsorption isotherms for SCB 2 and MMSCB 2

Experiments were performed for each material and metal ion to determine adsorption isotherms. In each experiment, 100 mg for SCB 2 and MMSCB 2 were placed into a 250 mL-Erlenmeyer with 100.0 mL of metal ion solution at specific concentrations from 160 to 290 mg/L and 180 to 230 mg/L for Cu^{2+} ; 210 to 310 mg/L and 250 to 350 mg/L for Cd^{2+} ; 430 to 580 mg/L and 500 to 650 mg/L for Pb^{2+} for SCB 2 and MMSCB 2, respectively, under constant stirring. Each experiment was performed using the time and the pH of the greatest ion adsorption obtained from kinetic and pH studies, respectively.

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

2.10.1. Coordination number

The coordination number was calculated according to Eq. (6)

$$\text{CN} = \frac{C_{\text{COOH}}}{Q_{\text{max}}/MM_{\text{metal}}} \quad (6)$$

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

3. Results and discussion

3.1. X-ray diffraction and FTIR analysis for SCB, MSCB and MMSCB

The treatment of lignocellulosic materials such as sisal, cotton linters and sugarcane bagasse with aqueous NaOH solution and the removal of lignin and polyoses together with the rearrangement of chain crystal packing from cellulose I in cellulose II have been reported by Ass, Ciacco, and Frollini (2006) and López et al. (2000), regarding position shifts and peak intensities in diffractogram and FTIR spectra. Reactions such as the inclusion of alkali and water in cellulose and the splitting and formation of new inter and intramolecular hydrogen bonds have also been reported by Fengel (Fengel, 1992, 1993a, 1993b; Fengel & Strobel, 1994), regarding the absorbance variations and wave number shifts in FTIR spectra.

X-ray diffraction curves for SCB, MSCB and MMSCB are shown in Fig. 1. When SCB is submitted to the first treatment with aqueous NaOH solution, hydrolysis reactions of lignin and polyoses occur, consuming a larger amount of alkali and hindering access of hydroxide ions to cellulose. SCB before of the alkaline treatment has shown typical reflections of the polymorphic form attributed to cellulose I (native cellulose), i.e., at Bragg angles of 28.4° (002 plane), 26.1° (021), 20.6° (10 $\bar{1}$), 18.6° (101). After the first treatment a significant mass loss of 52.6% was noticed due to amorphous cellulose fraction, lignin and polyoses hydrolysis and cellulose transformation from cellulose I to cellulose II. This transformation can be proven by appearance of reflections at Bragg angles typical of cellulose II, namely at 2 θ 25.0° (10 $\bar{1}$) and 27.5° (002) for MSCB and MMSCB.

When mercerized sugarcane bagasse (MSCB) was submitted to the second treatment with aqueous NaOH solution, a mass loss of 14.5% was noticed. This mass loss is attributed to residual lignin hydrolysis of the first treatment and hydrolysis of glycosidic bonds of cellulose chains. An increase of the amorphous fraction of materials was also observed, characterized by an increase of the region intensity at 2 θ from 5° to 15° for MMSCB (see Fig. 1).

FTIR spectra in the 3500–640 cm⁻¹ region are shown in Fig. 2a and b for SCB, MSCB and MMSCB. The treatment of SCB with NaOH transforms cellulose I into cellulose II, and produces a large removal of lignin and polyoses and also hydrolysis of amorphous cellulose fraction. By this transformation of cellulose I into cellulose II, many characteristic bands are shifted at the maximum peak, and absorbance is changed as shown in Table 1. The bands at 1631, 1427, 1165, 1053, 1038, 991 and 897 cm⁻¹ are shifted to 1637, 1419, 1159, 1062, 1026, 996 and 894 cm⁻¹, respectively. Including the shift of O-H and C-H stretching vibrations (3411 → 3444 cm⁻¹ and 2900 → 2892 cm⁻¹), all the bands are influenced by the trans-

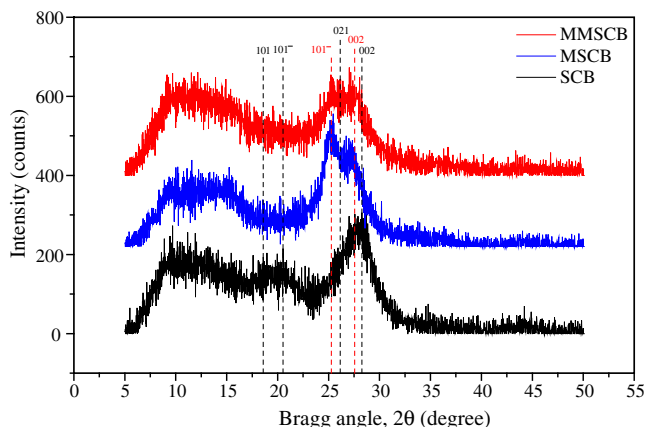


Fig. 1. Wide-angle X-ray diffraction curves for SCB, MSCB and MMSCB.

formation related to the change of intra and intermolecular bonds (Ho, Chiu, & Wang, 2005).

By treatment with aqueous NaOH solution, characteristic bands of lignin disappear, and/or the absorbance is changed as can be noticed in Fig. 2a and b. We can notice that the large removal of lignin can be attributed to the disappearance of bands at 1604, 1514 e 1252 cm⁻¹ (López et al., 2000) corresponding to aromatic skeletal vibrations and C=O stretch, and of bands at 1325 and 1111 cm⁻¹ corresponding to phenolic OH, syringil and condensed guaiacyl rings vibration. The absorbance of the band at 1377 cm⁻¹ that corresponds to deformation vibration of C-H has decreased due to large removal of lignin (Schwanninger, Rodrigues, Pereira, & Hinterstoisser, 2004).

3.2. The change of CI by transformation

The crystallinity index (CI) for SCB, MMSCB and MMSCB obtained from X-ray diffraction curves, as shown in Fig. 1, are 88.6, 94.9 and 77.7%, respectively. The first treatment of SCB with aqueous NaOH solution removed a large amount of lignin, polyoses and amorphous cellulose fraction, allowing a better packing of cellulose chains and increasing CI (Ass et al., 2006). On the second treatment, due to large removal of lignin and polyoses, the hydroxide ions could act directly on cellulose fibers, promoting decrease of crystallinity and increase of the material's amorphous fraction.

3.3. Synthesis of SCB1, MMSCB 1, SCB 2 and MMSCB 2

The synthesis route used to prepare SCB 1, MMSCB 1, SCB 2 and MMSCB 2 is shown in Fig. 3. SCB and MMSCB were reacted with succinic anhydride for 24 and 4 h, respectively. The reaction with succinic anhydride (succinylation) allows the introduction of carboxylic functions to materials through formation of ester functions. The mass percent gains (mpg) were calculated according to Eq. (3). The succinylation degrees of materials were determined by measuring the acid function introduced. The concentration of carboxylic functions per gram of modified materials was determined by retro-titration [Eq. (4)]. The results are shown in Table 2.

The two treatments of SCB with aqueous NaOH 20 wt% solution reduced CI by 10.9%, removed large amount of lignin and polyoses, converted cellulose I into cellulose II and increased the mass percent gain of MMSCB 1 in relation to SCB 1 from 89.6% to 138.6% and the concentration of carboxylic functions from 5.6 to 6.5 mmol/g (Table 2). As the role of the lignin and polyoses is to unit the bundles of cellulose fiber, their removal facilitates penetration of reagents, making the hydroxyl groups of cellulose macromolecules more easily accessible and making the transformation of cellulose I into cellulose II possible. This rearrangement resulting from alkaline treatment increases the chains separation, reducing packing efficiency and thereby facilitates the penetration of succinic anhydride. As a consequence, MMSCB exhibited a larger succinylation capacity than SCB.

3.3.1. Characterization of SCB 2 and MMSCB 2

The characterization of carboxylated materials was accomplished by FTIR spectroscopy. Fig. 4 shows the FTIR spectra for SCB and SCB 2 (a), MMSCB and MMSCB 2 (b).

As depicted in Fig. 4, the major changes that can be noticed in FTIR spectrum for SCB in relation to SCB 2, and for MMSCB in relation to MMSCB 2 are: (1) the arising of bands at 2925 for SCB 2 and MMSCB 2, corresponding to asymmetric stretching of CH₂ due to introduction of the succinyl group; (2) the arising of bands at 1577 and 1419 cm⁻¹ for SCB 2 and at 1570 and 1417 cm⁻¹ for MMSCB 2, corresponding to asymmetric and symmetric stretching due to presence of carboxylate ion and (3) the arising of two strong bands, the first for SCB 2 at 1743 cm⁻¹ and the second for MMSCB 2

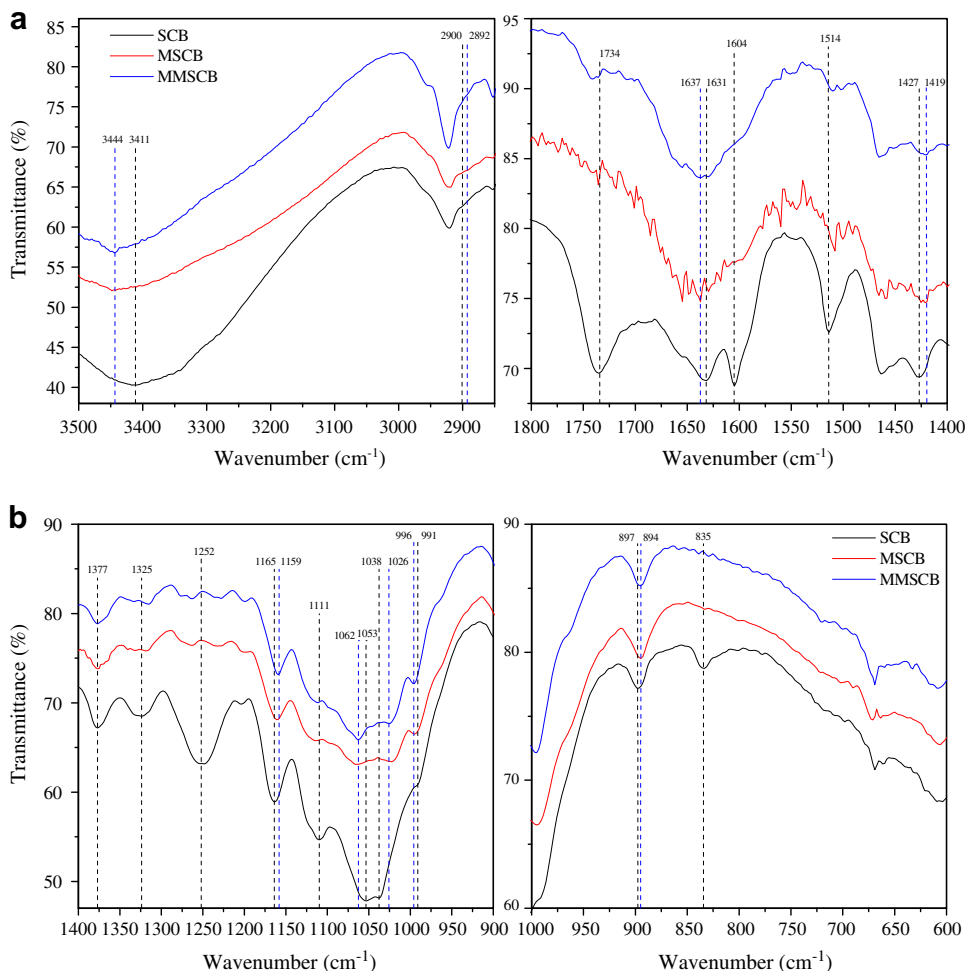


Fig. 2. FTIR spectra for SCB, MSCB and MMSCB (a) from 3500 to 1400 cm^{-1} and (b) from 1400 to 600 cm^{-1} .

Table 1
Band characteristics of FTIR spectra related to transformation (cellulose I \rightarrow cellulose II) by NaOH treatment^a

Characteristics	ν (cm^{-1}) related to the crystal system		$\Delta\nu$ (cm^{-1})/absorbance change	Assignment ^b
	Cellulose I	Cellulose II		
Peak Shift	3352	3447	+95/–	γ OH (hydrogen bonded)
	2901	2892	–9/–	γ CH
	1431	1419	–12/ ∇	δ CH ₂ (sym) at C-6
	1373	1376	+3/ ∇	δ C-H
	1319	1317	–2/ ∇	δ CH ₂ (wagging) at C-6
	1282	1278	–4/ ∇	δ C-H
	1236	1228	–8/ ∇	δ COH in plane at C-6
	1202	1200	–2/–	δ COH in plane at C-6
	1165	1162	–3/ ∇	γ COC at β -glucosidic linkage
	1032	1019	–13/ ∇	γ CO at C-6
	983	993	+10/ Δ	γ CO at C-6
	897	894	–3/ Δ	γ COC at β -glycosidic linkage γ COC, γ CCO, and γ CCH at C5 and C-6
Absorbance change	1337	1337	∇	δ COH in plane at C-2 or C-3
	1263	1263	Δ	δ COH in plane at C-2 or C-3
	1114	1114	∇	γ ring in plane
	1058	1058	∇	γ CO at C-3 γ C-C
	713	713	∇	δ COH out plane (cellulose I β)
	668	668	Δ	δ COH out of plane

^a Data from Oh et al. (2005).

^b Key to symbols: γ , stretching; δ , bending; Δ , increase; ∇ , decrease.

at 1741 cm^{-1} , corresponding to asymmetric and symmetric stretching of ester groups C–O due to introduction of the succinyl group.

The ester and carboxylate IR bands indicate that succinyl groups were introduced *via* formation of ester bonds with consequent release of carboxylic functional groups.

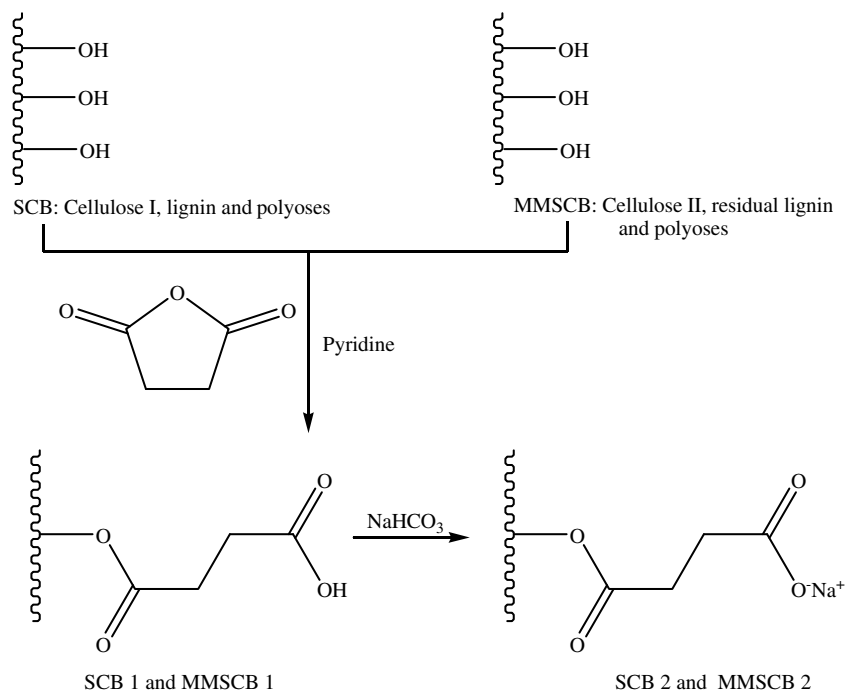


Fig. 3. Synthetic route used to obtain SCB 1, MMSCB 1, SCB 2 and MMSCB 2.

Table 2
Type of material, mass percent gains and concentrations of carboxylic functions

Material	Type of cellulose	Crystallinity index (%)	Mpg (%)	C _{COOH} (mmol/g)
SCB 1	I	88.6	89.6	5.6 ± 0.0
MMSCB 1	II	77.7	138.8	6.5 ± 0.1

3.4. Study of adsorption of Cu²⁺, Cd²⁺ and Pb²⁺ for SCB 2 and MMSCB 2

The studies of adsorption properties for SCB 2 and MMSCB 2 were accomplished for each material and metal ion. At first, a kinetic study and an adsorption study as a function of pH were 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 pH 5.0 for Cu²⁺, 7.0 for Cd²⁺ and 6.0 for Pb²⁺, at fixed concentration. The adsorption of Cu²⁺, Cd²⁺ and Pb²⁺ ions increases with contact time. The equilibrium time was achieved after 10 and 10 min for Cu²⁺; 20 and 10 min for Cd²⁺; 20 and 10 min for Pb²⁺ for SCB 2 and MMSCB 2, 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's pH and, since it affects adsorbent surface charge, on the degree of ionization, and on the adsorbates species. The studies of adsorption of Cu²⁺, Cd²⁺ and Pb²⁺ ions on SCB 2 and MMSCB 2 as a function of the pH are shown in Fig. 5a and b. The adsorption of Cu²⁺, Cd²⁺ and Pb²⁺ ions increases with the increase of pH. The maximum removal of Cu²⁺, Cd²⁺ and Pb²⁺ ions was noticed at pHs 5.4, 6.1 and 5.4 for SCB 2 and at pHs 5.6, 6.1 and 5.5 for MMSCB 2, 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 found successful application in many real adsorption processes and is expressed as:

$$q_e = \frac{Q_{\max} b C_e}{1 + b C_e} \quad (7)$$

which can be rearranged to obtain a linear form

$$\frac{C_e}{q_e} = \frac{1}{Q_{\max} b} + \frac{C_e}{Q_{\max}} \quad (8)$$

where q_e (mg/g) is the equilibrium adsorption capacity, Q_{\max} (mg/g) is the maximum amount of 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 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 and material (Ho et al., 2005).

A linearized plot of C_e/q_e versus C_e is obtained from the model shown in Fig. 6a and b. Q_{\max} and b are computed from the slopes and interceptions of different straight lines representing materials with different metal ions. Table 3 lists the calculated results.

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

As shown in Table 3, MMSCB 2 presented larger adsorption capacity (Q_{\max}) for Pb²⁺ and Cd²⁺ ions than SCB 2. This can be explained by the removal of large amount of lignin promoted by two treatments with aqueous NaOH solution (20 wt%) and by higher degree of succinylation exhibited by the MMSCB 2 in relation to SCB 2. Comparing the coordination number for adsorption of Pb²⁺ and Cd²⁺ ions for MMSCB 2 and SCB 2, the adsorption capacity of

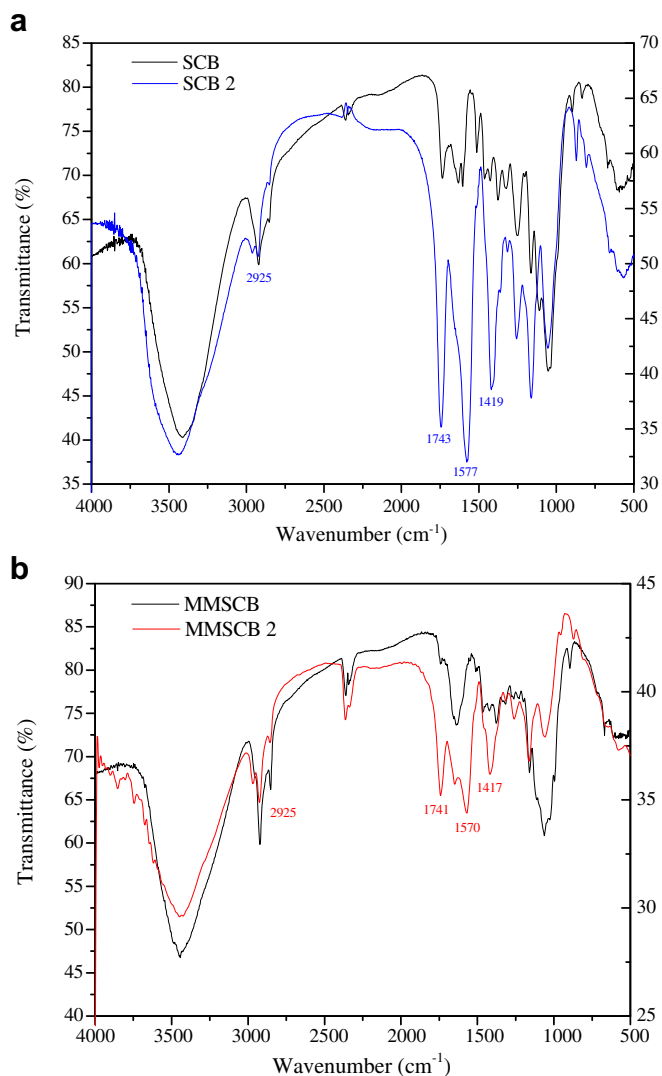


Fig. 4. FTIR spectrum for SCB and SCB 2 (a), MMSCB and MMSCB 2 (b).

these ions is proportional to the concentration of carboxylic functions, while for adsorption of Cu²⁺ the same is not noticed.

The lignin present in SCB 2 has ligand groups of R-OH type (OH phenolic and unsaturated chains OH) which are classified as hard bases and show preferences for complex hard acids such as Cu²⁺ ions, also justifying the smaller maximum adsorption capacity for Pb²⁺ and Cd²⁺ ions presented by SCB 2 in relation to MMSCB 2.

SCB 2 and MMSCB 2 exhibited equal maximum adsorption capacity for Cu²⁺ ions. This is explained by the ligand groups of R-OH type present in lignin. They are classified as hard bases and, therefore, show preferences for complex hard or moderate acids such as Cu²⁺ ions to form complexes with larger stability constant, justifying this result.

These results were compared with those that have reported by Gurgel et al. (2008) for succinylated non- and mercerized cellulose with carboxylate groups (cell 5 and 6, respectively). The Q_{\max} of cell 5 and 6 for Cu²⁺, Cd²⁺ and Pb²⁺ were 123.5 and 153.9 mg/g, 164.0 and 250.0 mg/g, 294.1 and 500.0 mg/g, respectively. Comparing the succinylated mercerized materials, cell 6 and MMSCB 2, MMSCB 2 exhibited larger Q_{\max} for Cu²⁺ and Cd²⁺ than cell 6, and equal Q_{\max} for Pb²⁺. For non-mercerized materials, cell 5 and SCB 2, SCB 2 exhibited larger Q_{\max} for Cu²⁺, Cd²⁺ and Pb²⁺ than cell 5. MMSCB 2 presented the largest Q_{\max} in the materials mentioned.

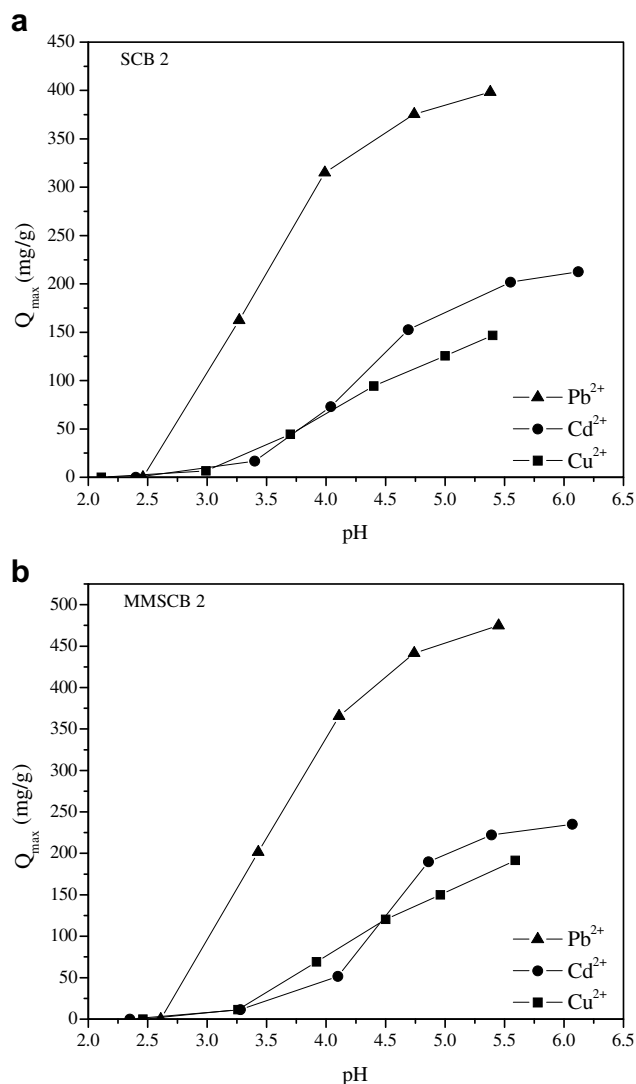


Fig. 5. Adsorption of metal ions on SCB 2 (a) and MMSCB 2 (b) as a function of pH.

This result shows the efficiency of the mercerization in the synthesis of chelating cellulosic materials.

The obtained results were also compared with those reported by Hassan and El-Wakil (2003) and Nada and Hassan (2006) for Cu²⁺ adsorption in aqueous solution. The amidoximated bagasse (Am-B) obtained by Hassan and El-Wakil (2003) adsorbed 137 mg/g of Cu²⁺. The oxy-, succinylated, and carboxymethylated bagasse obtained by Nada and Hassan (2006) adsorbed 233, 170, 392 mg/g of Cu²⁺, respectively. Comparing with obtained materials in this work only oxy- and carboxymethylated bagasse have shown a larger Q_{\max} for Cu²⁺ adsorption.

4. Conclusions

The two alkaline treatments of sugarcane bagasse removed large amount of lignin and polyoses and also the amorphous cellulose fraction, converted cellulose I into cellulose II, decreased the crystallinity index and increased the separation of the cellulose chains. These modifications provided a higher degree of succinylation proven by higher mass percent gain and concentration of carboxylic functions exhibited by modified mercerized sugarcane bagasse MMSCB 1. MMSCB 2 exhibited higher adsorption capacity for Cd²⁺ and Pb²⁺ ions than SCB 2 and equal capacity for Cu²⁺ ion.

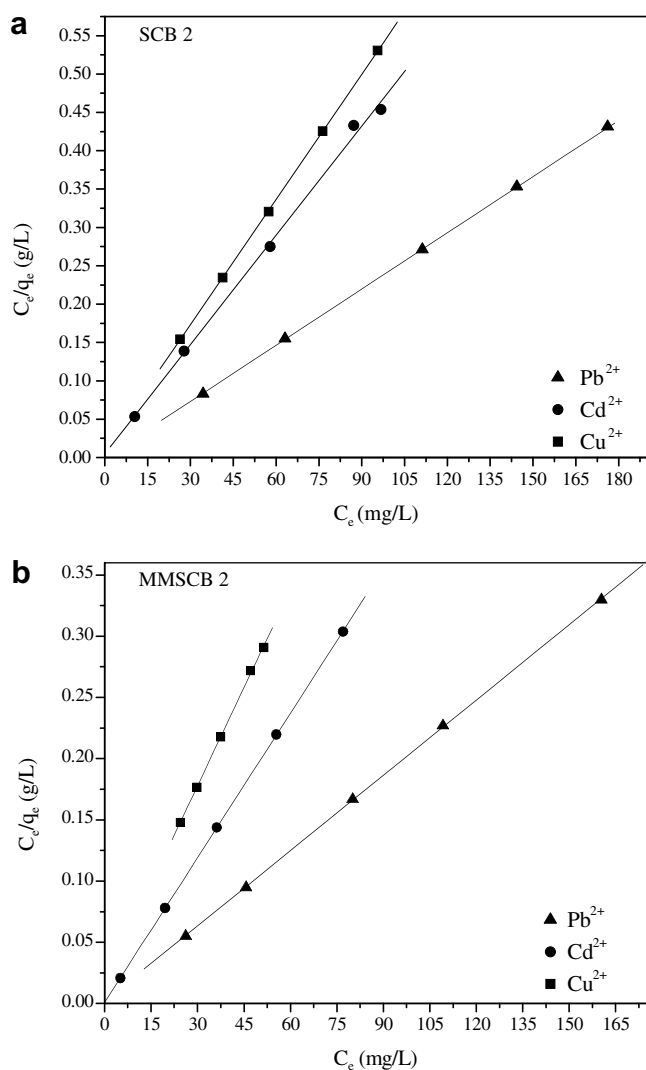


Fig. 6. Langmuir isotherm for SCB 2 (a) and MMSCB 2 (b).

Table 3

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

Metal ion	Material	Langmuir			Coordination number
		Q_{max} (mg/g)	b (L/mg)	R^2	
Cu^{2+}	SCB 2	185.2	0.540	0.9999	1.85
	MMSCB 2	185.2	0.307	0.9994	2.23
Cd^{2+}	SCB 2	212.8	0.94	0.9972	2.85
	MMSCB 2	256.4	1.700	0.9998	2.85
Pb^{2+}	SCB 2	416.7	1.000	0.9997	2.69
	MMSCB 2	500.00	0.952	0.9999	2.69

In relation to modified non-mercerized sugarcane bagasse (SCB 1), modified mercerized sugarcane bagasse (MMSCB 1) showed an increase in mass percent gain and concentration of carboxylic functions of 49.2% and 0.9 mmol/g, respectively. In relation to modified non-mercerized sugarcane bagasse (SCB 2), modified mercerized sugarcane bagasse (MMSCB 2) presented an increase in adsorption capacity for Cd^{2+} (43.6 mg/g) and Pb^{2+} (83.3 mg/g) and also demonstrated that metal ion adsorption efficiency is pro-

portional to the number of introduced carboxylic acid groups. This result shows the efficiency of the mercerization in the synthesis of chelating cellulosic materials.

Acknowledgements

The authors thank the financial support from the following Brazilian Government Agencies: Fundação de Amparo à Pesquisa do Estado de Minas Gerais – FAPEMIG, Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – CAPES. The authors are also grateful at Universidade Federal de Ouro Preto – UFOP.

References

- Ass, B. A. P., Ciacco, G. T., & Frollini, E. (2006). Cellulose acetates from linters and sisal: Correlation between synthesis conditions in DMAC/LiCl and product properties. *Bioresource Technology*, 97(14), 1696–1702.
- Caraschi, J. C., Campana, S. P., & Curvelo, A. A. S. (1996). Preparação e caracterização de polpas para dissolução obtidas a partir de bagaço de cana-de-açúcar. *Polímeros: Ciência e Tecnologia*, 3, 24–29.
- Clement, R. E., Eiceman, G. A., & Koester, C. J. (1995). Environmental analysis. *Analytical Chemistry*, 67(12), 221R–225R.
- Fengel, D. (1992). Characterization of cellulose by deconvoluting the OH valency range in FTIR spectra. *Holzforchung*, 46(4), 283–288.
- Fengel, D. (1993a). Influence of water on the OH valency range in deconvoluted FTIR spectra of cellulose. *Holzforchung*, 47(2), 103–108.
- Fengel, D. (1993b). In J. F. Kennedy, G. O. Philips, & P. A. Williams (Eds.), *Cellulosics: Chemical, Biochemical and Material Aspects* (pp. 135–140). New York: Ellis Horwood.
- Fengel, D., & Strobel, C. (1994). FTIR spectroscopic studies on the heterogeneous transformation of cellulose I into cellulose II. *Acta Polymerica*, 45(4), 319–324.
- Gupta, V. K., & Ali, I. (2000). Utilisation of bagasse fly ash (a sugar industry waste) for the removal of copper and zinc from wastewater. *Separation and Purification Technology*, 18(2), 131–140.
- Gupta, V. K., & Ali, I. (2004). Removal of lead and chromium from wastewater using bagasse fly ash – A sugar industry waste. *Journal Colloid Interface Science*, 271(2), 321–328.
- Gurgel, L. V. A., Karnitz Júnior, O., Gil, R. P. F., & Gil, L. F. (2008). Adsorption of $\text{Cu}(\text{II})$, $\text{Cd}(\text{II})$, and $\text{Pb}(\text{II})$ from aqueous single metal solutions by cellulose and mercerized cellulose chemically modified with succinic anhydride. *Bioresource Technology*, 99(8), 3077–3083.
- Hassan, M. L., & El-Wakil, N. A. (2003). Heavy metal ion removal by amidoximated bagasse. *Journal of Applied Polymer Science*, 87(4), 666–670.
- Ho, Y. S., Chiu, W. T., & Wang, C. C. (2005). Regression analysis for the sorption isotherms of basic dyes on sugarcane dust. *Bioresource Technology*, 96(11), 1285–1291.
- Jeffery, G. H., Bassett, J., Mendham, J., & Denney, R. C. (1989). *Vogel's textbook of quantitative chemical analysis*. In *Longman Scientific & Technical* (pp. 309–322). New York: Co-published with John Wiley and Sons Inc (326).
- Karnitz Júnior, O., Gurgel, L. V. A., Perin de Melo, J. C., Botaro, V. R., Melo, T. M. S., Gil, R. P. F., et al. (2007). Adsorption of heavy metal ion from aqueous single metal solution by chemically modified sugarcane bagasse. *Bioresource Technology*, 98(6), 1291–1297.
- Krässig, H. A. (1993). *Cellulose: Structure, accessibility and reactivity*. *Polymer monographs* (Vol. 11, pp. 88–90). Yverdon, Switzerland: Gordon and Breach Science Publishers. 100–107, 123–125.
- Langmuir, I. (1918). Adsorption of gases on plain surfaces of glass, mica and platinum. *Journal of the American Chemical Society*, 40, 1361–1403.
- López, R., Poblano, V. M., Licea-Claverie, A., Avalos, M., Alvarez-Castillo, A., & Castaño, V. M. (2000). Alkaline surface modification of sugar cane bagasse. *Advanced Composite Materials*, 9(2), 99–108.
- MacCarthy, P., Klusman, R. W., Cowling, S. W., & Rice, J. A. (1995). Water analysis. *Analytical Chemistry*, 67(12), 525R–582R.
- Nada, A. M. A., & Hassan, M. L. (2006). Ion exchange properties of carbohydrate bagasse. *Journal of Applied Polymer Science*, 102(2), 1399–1404.
- Oh, S. Y., Yoo, D. I., Shin, Y., Kim, H. C., Kim, H. Y., Chung, Y. S., et al. (2005). Crystalline structure analysis of cellulose treated with sodium hydroxide and carbon dioxide by means of X-ray diffraction and FTIR spectroscopy. *Carbohydrate Research*, 340(15), 2376–2391.
- Schwanninger, M., Rodrigues, J. C., Pereira, H., & Hinterstoesser, B. (2004). Effects of short-time vibratory ball milling on the shape of FT-IR spectra of wood and cellulose. *Vibrational Spectroscopy*, 36(1), 23–40.
- Sun, J. X., Sun, X. F., Zhao, H., & Sun, R. C. (2004). Isolation and characterization of cellulose from sugarcane bagasse. *Polymer Degradation and Stability*, 84(2), 331–339.
- Weng, C. H., & Huang, C. P. (1994). Treatment of metal industrial wastewater by fly ash and cement fixation. *Journal of Environmental Engineering*, 120(6), 1470–1487.