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Adsorption of Cu(II), Cd(II) and Pb(II) from aqueous single metal solutions by succinylated twice-mercerized sugarcane bagasse functionalized with triethylenetetramine

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ABSTRACT

This study describes the preparation of two new chelating materials, MMSCB 3 and 5, derived from succinylated twice-mercerized sugarcane bagasse (MMSCB 1). MMSCB 3 and 5 were synthesized from MMSCB 1 using two different methods as described by Gurgel and Gil (2009). In the first method MMSCB 1 was activated with 1,3-diisopropylcarbodiimide and in the second with acetic anhydride (to form an internal anhydride) and later both were reacted with triethylenetetramine in order to obtain MMSCB 3 and 5. New obtained materials were characterized by mass percent gain, concentration of amine groups, FTIR, and elemental analysis. MMSCB 3 and 5 showed mass percent gain of 19.9 and 57.1%, concentration of amine groups of 2.0 and 2.1 mmol/g, and nitrogen content of 5.8 and 4.4%. The capacity of MMSCB 3 and 5 to adsorb Cu²⁺, Cd²⁺, and Pb²⁺ from aqueous single metal ion solutions was evaluated at different contact times, pHs, and initial metal ion concentrations. Adsorption isotherms were well fitted by Langmuir model. Maximum adsorption capacities of MMSCB 3 and 5 for Cu²⁺, Cd²⁺, and Pb²⁺ were found to be 59.5 and 69.4, 86.2 and 106.4, 158.7 and 222.2 mg/g, respectively.

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1. Introduction

The removal of toxic metals from wastewater is a matter of great interest in the field of water pollution, which is a serious cause of environmental degradation (Chen and Chai, 2008). Heavy metals such as lead, copper, cadmium, zinc, and nickel are among the most common pollutants found in industrial effluents. Even at low concentrations, these metals can be toxic to organisms, including humans (Sheng et al., 2004). The selective adsorption and separation of metal ions from an aqueous waste have received increasing importance in environmental evaluation and protection in recent years. Nowadays, the solid phase extraction (SPE) is being utilized for preconcentration of heavy metals due to its flexibility,

economy, environmental friendliness and safety (Hou et al., 2007).

Ion exchange resins, which can be completely regenerated, can be used for thousands of cycles before they need to be replaced. They have shown excellent metal ion separation and are widely used for removing heavy metal ions from wastewater (Chen et al., 1988). A large range of special chelating polymers have been prepared in recent years (Ojeda et al., 2006). Chelating resins are generally efficient in the removal and recovery of heavy metal ions because of their physical and chemical stabilities. Many studies covering a vast number of different chelating moieties immobilized on various synthetic and natural polymeric networks have been reported (Malakul et al., 1998).

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An efficient adsorbing material should consist of a stable and insoluble matrix, which has active groups (typically organic groups) that interact with heavy metal ions (Hou et al., 2007). Sugarcane bagasse is an excellent matrix because it is inexpensive when compared to other matrixes such as cellulose pulp, epoxy resins, chitosan, and synthetic polymers. Besides, owing to the increase of ethanol production in countries such as Brazil, tons and tons of sugarcane bagasse are being produced. According to the last official survey from National Company of Supply – CONAB, an agency from the Brazilian Ministry of Agriculture, the national production of sugarcane in 2008/2009 was 558 million tons, the largest of all times. On average, 280 kg of sugarcane bagasse containing 50% moisture are produced by ton of sugarcane. In the industries of sugar and ethanol, bagasse is burned to produce energy, whereas the leftovers are still significant. The remaining bagasse still continues to be a menace to the environment and a more suitable and economic utilization may be the production of bioethanol or ethanol of second generation and resins to treat wastewater effluents. Sugarcane bagasse is constituted mainly of cellulose (40–50%), polyoses (25–30%), and lignin (20–25%) (Gurgel et al., 2008b).

Removal of heavy metal ions from aqueous solutions by various modified adsorbents has been performed by a number of research groups in the world. Some adsorbents modified with triethylenetetramine, a polyamine of prime interest in this work are shown in Table 1.

Gurgel et al. (2008b) proposed in a previous work the study of mercerization treatment as a way of increasing the fiber specific surface area and making sugarcane bagasse hydroxyl groups more easily accessible for modification with succinic anhydride. As a result of this study, succinylated twice-mercerized sugarcane bagasse (MMSCB 1) was obtained with a higher mass percent gain (138.8%) and concentration of

carboxylic groups (6.5 mmol/g). In the present study, we have described the preparation of two new chelating materials containing amine groups from succinylated twice-mercerized sugarcane bagasse (MMSCB 1) with the aim of adsorbing Cu^{2+} , Cd^{2+} , and Pb^{2+} from aqueous solutions as a continuation of the study of Gurgel et al. (2008b). Carboxylic groups from MMSCB 1 were modified with triethylenetetramine through two different synthesis routes according to methodology described by Gurgel and Gil (2009). Gurgel and Gil (2009) used succinylated mercerized cellulose (cell 1) as model compound to accomplish similar reactions proposed here due to cellulose to be a homopolymer, and, therefore, easier to be characterized than sugarcane bagasse. In the first synthesis route MMSCB 1 was activated with 1,3-diisopropylcarbodiimide (DIC) and in the second with acetic anhydride. In both synthesis routes after the activation step the activated materials were modified with triethylenetetramine in order to produce MMSCB 3 and 5. Adsorption studies of Cu^{2+} , Cd^{2+} , and Pb^{2+} from aqueous single metal solutions by MMSCB 3 and 5 were carried out using different contact times, pHs, and initial metal ion concentrations. The results were evaluated by Langmuir model (Rosen, 1989; Ho et al., 2005) and compared to the results obtained for cell 2 and 4 (succinylated mercerized celluloses modified with triethylenetetramine, see Table 1) that were synthesized as model compounds in our previous work (Gurgel and Gil, 2009).

2. Experimental

2.1. Materials

Sugarcane bagasse, a biomass waste material from the sugar-alcohol industry, was collected from an alcohol factory at Ouro Preto, Minas Gerais, Brazil. Succinic anhydride,

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)	b (L/mg)	Source
Chitosan (CCTS)	Epichlorohydrin	Triethylenetetramine	Pb^{2+}	559.4	0.011	Tang et al. (2007) ^a
Sugarcane bagasse (MSB 6)	1,3-diisopropylcarbodiimide	Triethylenetetramine	Cu^{2+}	133	0.014	Karnitz Júnior et al. (2007) ^a
			Cd^{2+}	313	0.004	
			Pb^{2+}	313	0.121	
Mercerized sugarcane bagasse (MMSCB 2)	Pyridine	Succinic anhydride	Cu^{2+}	185.2	0.307	Gurgel et al. (2008b) ^a
			Cd^{2+}	256.4	1.700	
			Pb^{2+}	500.0	0.952	
PSMP-TETA (resin4)	–	Triethylenetetramine	Cu^{2+}	51	–	Qu et al. (2005)
			Cd^{2+}	34	–	
			Pb^{2+}	186	–	
Macroporous epoxy resin (epoxy-TETA resin)	–	Triethylenetetramine	Cu^{2+}	126	–	Hou et al. (2007)
Macroporous chloromethylpolystyrene (PS-TETA)	–	Triethylenetetramine	Cu^{2+}	101.7	–	Sun et al. (2007)
Mercerized cellulose (cell 2)	1,3-diisopropylcarbodiimide	Triethylenetetramine	Cu^{2+}	56.8	0.310	Gurgel and Gil (2009) ^a
			Cd^{2+}	68.0	0.930	
			Pb^{2+}	147.1	0.360	
Mercerized cellulose (cell 4)	Acetic anhydride	Triethylenetetramine	Cu^{2+}	69.4	0.652	Gurgel and Gil (2009) ^a
			Cd^{2+}	87.0	1.027	
			Pb^{2+}	192.3	0.776	

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

pyridine and acetic anhydride were purchased from VETEC (Brazil). *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). $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ were purchased from SYNTH (Brazil). Grade quantitative filter paper (Cat. No. 1441-150) for instrumental analysis was purchased from Whatman Company. Pyridine was refluxed with NaOH lentils overnight and distilled. Dimethylformamide was treated with 4 Å molecular sieves (MERCK) overnight and distilled under reduced pressure.

2.2. Sugarcane bagasse preparation

Integral sugarcane bagasse (B) was first dried under sunlight. The fiber and medulla fractions were broken into small pieces and subsequently dried at 90 °C in an oven for 24 h. Sugarcane bagasse was reduced to powder by milling with tungsten ring mill. The powder was sieved in a six-sieve system (10, 30, 45, 60, 100 and 200 mesh). The fraction from 100 to 200 mesh was collected and washed with distilled water under constant stirring at 60–70 °C for elimination of residual sugars, separated by single filtration, 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) for 4 h to eliminate extractives and small fractions of lignin extracted from milling process. It was dried at 90 °C in an oven and stored in desiccator.

2.3. Synthesis of MMSCB 3

Succinylated twice-mercerized sugarcane bagasse (MMSCB 1) was prepared and characterized according to the methodology described by Gurgel et al. (2008b). MMSCB 1 was washed with acetone and dried at 80 °C in an oven for 1 h and left to cool in a desiccator. MMSCB 1 (3.0 g, 6.5 mmol/g of carboxylic acid functions) was reacted with 9 mL (58 mmol, 3 equiv.) of 1,3-diisopropylcarbodiimide (DIC) in the presence of anhydrous dimethylformamide (DMF) (51 mL) at 25 °C for 1 h under constant magnetic stirring in order to activate carboxylic acid functions. After 1 h of reaction, 13.6 mL (91 mmol, 5 equiv.) of triethylenetetramine was added to reactional medium. The mixture was then reacted for a further 3 h in order to obtain MMSCB 3. MMSCB 3 was separated by filtration in a sintered glass funnel, washed in a row with DMF, ethanol 95%, distilled water, saturated sodium bicarbonate solution, distilled water, ethanol 95% and then dried diethyl ether. After drying under a vacuum for 30 min at 25 °C, MMSCB 3 was left to cool in a desiccator and weighted. The mass percent gain (mpg) was calculated (Gurgel et al., 2008a,b).

2.4. Synthesis of MMSCB 5

Succinylated twice-mercerized sugarcane bagasse (MMSCB 1) was prepared and characterized according to the methodology described by Gurgel et al. (2008b). MMSCB 1 was washed with acetone and dried at 80 °C in an oven for 1 h and left to cool in a desiccator. MMSCB 1 (3.0 g, 6.5 mmol/g of carboxylic functions) was reacted with 55 mL (585 mmol, 30 equiv.) of

acetic anhydride in a reflux system at 100 °C under constant stirring for 24 h in order to obtain MMSCB 1's anhydride (MMSCB 4). MMSCB 4 was separated by filtration in a sintered glass funnel, washed with dried diethyl ether and stored in a desiccator after drying under a vacuum for 30 min at 25 °C. MMSCB 4 was reacted with 13.6 mL (58 mmol, 5 equiv.) of triethylenetetramine in the presence of 51 mL of anhydrous dimethylformamide (DMF) at 25 °C for 3 h in order to obtain MMSCB 5. MMSCB 5 was separated by filtration using sintered glass funnel, elaborated, and stored in a desiccator as described in Section 2.3. The mass percent gain (mpg) was also calculated (Gurgel et al., 2008a,b).

2.5. Characterization of modified materials

2.5.1. Mass percent gain

The mass percent gain (mpg) of MMSCB 3 and 5 was calculated according to Eq. (1):

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

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

2.5.2. Degree of amination

The degree of amination of MMSCB 3 and 5 was determined by measuring the quantity of introduced amine groups. The concentration of amine groups per gram of MMSCB 3 and 5 was determined by back titration. Two 0.1000 g samples of MMSCB 3 and 5 were treated with 100.0 mL of an aqueous HCl standard solution (0.01 mol/L) in a 250-mL Erlenmeyer for 1 h under constant stirring. Soon after the suspensions were separated by single filtration and three aliquots (25.0 mL) of each obtained solution were titrated with aqueous NaOH standard solution (0.01 mol/L) (Karnitz Júnior et al., 2007; Gurgel et al., 2008a,b; Gurgel and Gil, 2009). The concentration of amine groups was calculated by Eq. (2):

$$C_{\text{NH}_2} = \left[\frac{(C_{\text{HCl}} * V_{\text{HCl}}) - (4 * C_{\text{NaOH}} * V_{\text{NaOH}})}{m_{\text{modified material}}} \right] \quad (2)$$

where C_{HCl} is the concentration of HCl solution (mmol/L), C_{NaOH} is the concentration of NaOH solution (mmol/L), V_{HCl} is the volume of HCl solution (L), V_{NaOH} is the volume of NaOH spent in the titration of unreacted excess of acid (L) and $m_{\text{modified material}}$ is the mass of MMSCB 3 or 5 (g).

2.5.3. FTIR analysis

The samples were prepared by mixing 1 mg of material with 100 mg of spectroscopy grade KBr. The FTIR spectra were recorded using Nicolet Impact 410 FTIR spectrometer with a detector at 4 cm^{-1} resolution from 500 to 4000 cm^{-1} and 32 scans per sample. The spectra were analyzed by Microcal™ Origin™ software in order to identify the main characteristic bands after modification of the materials.

2.5.4. Elemental analysis

The samples were previously washed with acetone in a sintered glass funnel and dried at 80 °C in an oven for 1 h. Samples were analyzed using a CHNS/O Perkin Elmer Series II equipment. The analyses were made in duplicate for each sample.

2.6. Effect of contact time on metal ions adsorption onto MMSCB 3 and 5

The loading of MMSCB 3 and 5 with Cu^{2+} , Cd^{2+} , and Pb^{2+} was measured as a function of time in order to determine adsorption equilibrium time. Adsorption equilibrium time is one of the parameters for economical wastewater treatment plant applications (Kadirvelu and Namasivayam, 2003). The contact times used in this study were from 10 to 40 min for MMSCB 3 and 5. Samples of 50 mg of MMSCB 3 and 5 were placed in a 250-mL Erlenmeyer flasks with 50.0 mL of metal ion solution of known concentration (200 and 200 mg/L for Cu^{2+} , 200 and 200 mg/L for Cd^{2+} , 295 and 300 mg/L for Pb^{2+} for MMSCB 3 and 5, respectively). Solubility product constants (K_{sp}) and concentration of metal ion solutions for copper, cadmium, and lead were used to calculate the maximum pH where these ions may not occur as hydrolyzed species. Solubility product constants for $\text{Cu}(\text{OH})_2$, $\text{Cd}(\text{OH})_2$, and $\text{Pb}(\text{OH})_2$ used were 6.0×10^{-20} (Pauling, 1970), 7.2×10^{-15} (Lide, 2009), and 1.43×10^{-20} (Lide, 2009). Calculated maximum pH for Cu^{2+} , Cd^{2+} , and Pb^{2+} considering concentrations mentioned above were 5.64, 8.30, and 5.50. This procedure is necessary to ensure that only Cu^{2+} , Cd^{2+} , and Pb^{2+} would be adsorbed. The pHs were only taken to 5.6 for Cu^{2+} , 6.0 for Cd^{2+} , and 5.5 for Pb^{2+} after addition of MMSCB 3 or 5 to each metal ion solution. Then, Erlenmeyer flasks were kept under constant stirring. The pH values were being measured along the experiments. Variations about 0.1 units of pH were found with respect to values of pH initially adjusted. These variations were corrected by the addition of drops of aqueous NaOH or HCl solutions (0.01–1.0 mol/L) to the suspensions. At the end of the experiments measured equilibrium pH values were taken into account.

The suspensions were separated by single filtration using Whatman quantitative filter paper No. 41 for instrumental analysis. In order to determine metal ion concentration, three 10.0 mL aliquots of each solution were titrated. The concentration of Cu^{2+} ions was determined by direct titration with 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 excess standard EDTA solution (3 mmol/L) with aqueous Mg^{2+} standard solution (2.5 mmol/L) at pH 10 using Erichrome Black T as indicator. A buffer of $\text{NH}_3/\text{NH}_4^+$ was used to adjust pH to 10 in the titrations (Karnitz Júnior et al., 2007; Gurgel et al., 2008a,b; Gurgel and Gil, 2009).

2.7. Effect of pH on metal ion adsorption onto MMSCB 3 and 5

Experiments with each material and metal ion were performed to determine the effect of pH on metal ion adsorption onto MMSCB 3 and 5. Samples of 50 mg of MMSCB 3 and 5 were placed in a 250-mL Erlenmeyer with 50.0 mL of metal ion solution of known concentration (200 and 200 mg/L for Cu^{2+} , 200 and 200 mg/L for Cd^{2+} , 295 and 300 mg/L for Pb^{2+} for MMSCB 3 and 5, respectively), under constant stirring. The pH range studied for MMSCB 3 and 5 was from 2.6 to 5.6 and 2.6 to 5.6 for Cu^{2+} ; 2.5 to 6.2 and 2.2 to 6.1 for Cd^{2+} ; 2.1 to 5.5 and 2.3 to 5.5 for Pb^{2+} , respectively. These values were chosen on the basis of the literature data (Karnitz Júnior et al., 2007; Gurgel et al., 2008a,b; Gurgel and Gil, 2009). The pHs were adjusted by the addition of

drops of aqueous HCl or NaOH solutions (0.01–1.0 mol/L). Erlenmeyer flasks were kept under constant stirring. The contact times used in this study were those obtained from the effect of contact time (Section 2.6). Variations about 0.1 units of pH were also found along the experiments with respect to values of pH initially adjusted. At the end of the experiments the pH of the suspensions were measured and taken into account in the data analyses. The concentration of Cu^{2+} , Cd^{2+} , and Pb^{2+} was also determined as described earlier in Section 2.6.

2.8. Effect of initial concentration and adsorption isotherms of MMSCB 3 and 5

The effect of initial metal ion concentration on metal ion uptake capacities of MMSCB 3 and 5 was carried out by varying the initial concentration of the metal ions solutions in order to obtain adsorption isotherms. Adsorption equilibrium times and pHs of greatest adsorption used in these experiments were those obtained from Sections 2.6 and 2.7. Samples of 50 mg of MMSCB 3 and 5 were placed in 250-mL Erlenmeyer flasks with 50.0 mL of metal ion solution at predetermined concentrations from 70 to 120 and 85 to 135 mg/L for Cu^{2+} ; 100 to 200 and 110 to 210 mg/L for Cd^{2+} ; 130 to 280 and 220 to 370 mg/L for Pb^{2+} for MMSCB 3 and 5, respectively. The pHs were adjusted by the addition of drops of aqueous NaOH or HCl solutions (0.1–1.0 mol/L). Variations of 0.1 units of pH were also found and corrected as described in Sections 2.6 and 2.7. The concentration of Cu^{2+} , Cd^{2+} , and Pb^{2+} was also determined by titration. Metal ion equilibrium concentrations determined by titration were used to calculate equilibrium adsorption capacities as described by Eq. (3)

$$q_e = \frac{[(C_i - C_e) \times V_m]}{m_{\text{ads}}} \quad (3)$$

where q_e (mg/g) is the equilibrium adsorption capacity, C_i (mg/L) is the initial metal ion concentration, C_e (mg/L) is the metal ion equilibrium concentration, V_m (L) is the volume of the metal ion solution, and m_{ads} (g) is the mass of adsorbent.

2.9. Coordination number (CN)

The coordination number can be obtained from the relationship between the concentration of amine groups and adsorption maximum capacity. Coordination number refers to the number of ligand atoms surrounding the central atom, where most metal cations engage in coordinations of 2, 4, 6, and 8, with 4 and 6 being the most common. In the case of polymers these values may be lower owing to steric effects (Davis et al., 2003). CN can be very useful to understand the interaction between MMSCB 3 and 5 and metal ions adsorbed, as well as the differences between the two kinds of prepared ligands with respect to adsorption capacities. CN was calculated according to Eq. (4):

$$\text{CN} = \frac{C_{\text{NH-NH}_2}}{Q_{\text{max}}/M(M^{2+})} \quad (4)$$

where $C_{\text{NH-NH}_2}$ is the concentration of amine groups (mmol/g), Q_{max} is the maximum adsorption capacity (mg/g) obtained by Langmuir model for Cu^{2+} , Cd^{2+} and Pb^{2+} and $M(M^{2+})$ is the molar mass of the metal ion studied (mg/mmol).

2.10. Gibbs free energy

According to Liu (2006), Gibbs free energy (ΔG°) can be calculated as defined by Eq. (5):

$$\Delta G^\circ = -RT \times \ln K \quad (5)$$

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

For an adsorbent with relatively low adsorption capacity to adsorbate, i.e. M_{AB} can be reasonably approximated by M_B , and the equilibrium constant that is defined as, $K = b(M_A M_B) / M_{AB}$, reduces to $K \approx b M_A$, where b (L/g) is the Langmuir constant, M_{AB} (g/mol) is the molar mass of binding complex, M_A (g/mol) is the molar mass of metal studied, and M_B (g/mol) is the molar mass of the adsorbent.

3. Results and discussion

3.1. Synthesis and characterization of MMSCB 3 and 5

The synthesis route used to prepare MMSCB 3 and 5 is shown in Fig. 1. Carboxylic acid groups of MMSCB 1 were used as a way to graft triethylenetetramine on modified sugarcane bagasse matrix. In the first route, diisopropylcarbodiimide (DIC), a coupling reagent, was used to activate carboxylic acid carbonyl groups of MMSCB 1 in order to introduce triethylenetetramine units, whereas in the second route, acetic anhydride, a dehydrating reagent less expensive and toxic than DIC was used to the same purpose. In both cases triethylenetetramine was grafted to MMSCB 1 through formation an amide bond. However the second route is a reaction that involved two steps. In the first step, carboxylic acid groups were converted into internal carboxylic anhydride groups and in a second step these groups were converted into amide groups, releasing amine and carboxylic acid groups as can be seen from Fig. 1. The mass percent gains, concentration of amine groups and nitrogen percentages are shown in Table 2.

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

Material	Mpg (%)	$C_{\text{NH-NH}_2}$ (mmol/g)	N (%)
MMSCB 3	19.9	2.0 ± 0.0	5.8 ± 0.1
MMSCB 5	57.1	2.1 ± 0.1	4.4 ± 0.2
Cell 4	92.4	2.3 ± 0.0	4.6 ± 0.2

Compared to MMSCB 3, MMSCB 5 exhibited an increase of 37.2% and 0.1 mmol/g in the mass percent gain and concentration of amine groups. However, MMSCB 5 showed a decrease of 1.4% in the nitrogen content.

The second synthesis route used in this work to obtain MMSCB 5 was first developed by our research group for amination of modified mercerized cellulose (cell 1) that contained a high concentration of carboxylic acid groups (Gurgel and Gil, 2009). In the work of Gurgel and Gil (2009) grade 3MM cellulose chromatography paper was selected as a starting material due to its purity, being its derivatives easier of being characterized by FTIR and CHN than lignocellulosic polymers such as sugarcane bagasse. Whether we compare MMSCB 5 with cell 4 (succinylated mercerized cellulose modified with triethylenetetramine) it is possible to notice that there is a small difference in the concentration of amine groups and nitrogen content as can be seen from Table 2. Considering these results it is possible to conclude that second synthesis route can be applied to any lignocellulosic modified with carboxylic acid groups since the starting material contains a high concentration of carboxylic acid groups. The high concentration of carboxylic acid groups is necessary to minimize steric effects ensuring the formation of internal carboxylic anhydride groups.

3.2. FTIR characterization

Characterization of MMSCB 3, 4, and 5 was accomplished by FTIR spectroscopy. FTIR spectra of MMSCB 1 and 3,

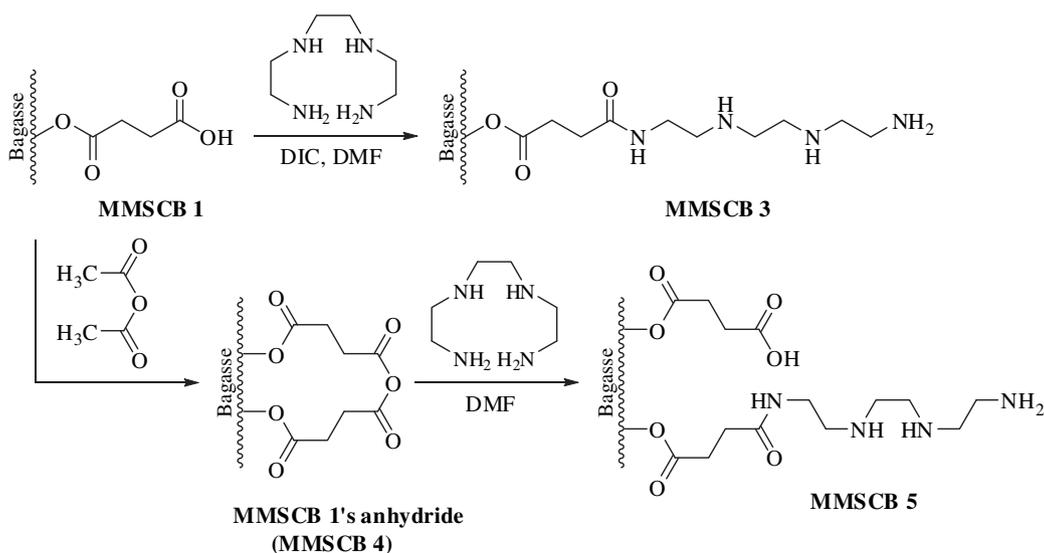


Fig. 1 – Synthesis route used to obtain MMSCB 3 and 5.

MMSCB 1 and 4, and MMSCB 1 and 5 are shown in Figs. 2 and 3a,b, respectively. As can be seen from Fig. 2, the most relevant changes that can be noticed in FTIR spectra of MMSCB 3 in relation to MMSCB 1 are the appearance of bands at 1701, 1645, 1570, 1410, 1261, 1163 and 1057 cm^{-1} . The bands at 1701 and 1645 cm^{-1} correspond to stretching of carbonyl group (C=O) of primary amide (amide I). The band at 1570 cm^{-1} corresponds to deformation vibration of groups -NH- of amines. The bands at 1410, 1261 and 1163 cm^{-1} correspond to deformation vibration of C-N, and the band at 1057 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 in the modes of asymmetric and symmetric stretching of the group C=O. Normally, the separation of these bands is of 60 cm^{-1} , whereas this difference may be from 35 to 90 cm^{-1} according to anhydride type (Nakanish, 1962; Gurgel and Gil, 2009).

As depicted in Fig. 3a, the most relevant change noticed in FTIR spectra of MMSCB 4 in relation to MMSCB 1 is the appearance of bands at 1820 and 1741 cm^{-1} . These bands confirm the MMSCB 1's anhydride formation (MMSCB 4).

As depicted in Fig. 3b, the most relevant changes noticed in the FTIR spectra of MMSCB 5 in relation to MMSCB 1 is the appearance of bands at 1701, 1645, 1570, 1410, 1255, 1161 and 1055 cm^{-1} . The characterization and assignment of these bands is the same shown for MMSCB 3, which proves the formation of amide bond.

3.3. Adsorption study of Cu^{2+} , Cd^{2+} and Pb^{2+} onto MMSCB 3 and 5

The studies of adsorption properties of MMSCB 3 and 5 were accomplished for each material and metal ion. Adsorption capacity of MMSCB 3 and 5 was first evaluated as a function of contact time and pH of the solution. The results obtained from the effect of contact time and pH were used to study the effect of initial metal ion concentration and build adsorption isotherms.

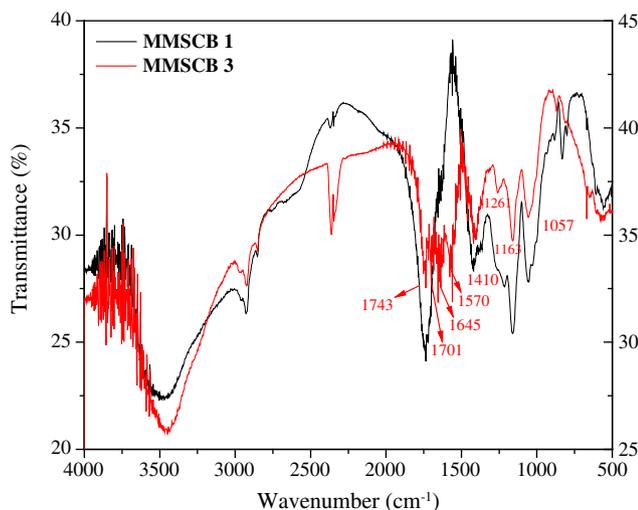


Fig. 2 – FTIR spectra of MMSCB 1 and 3.

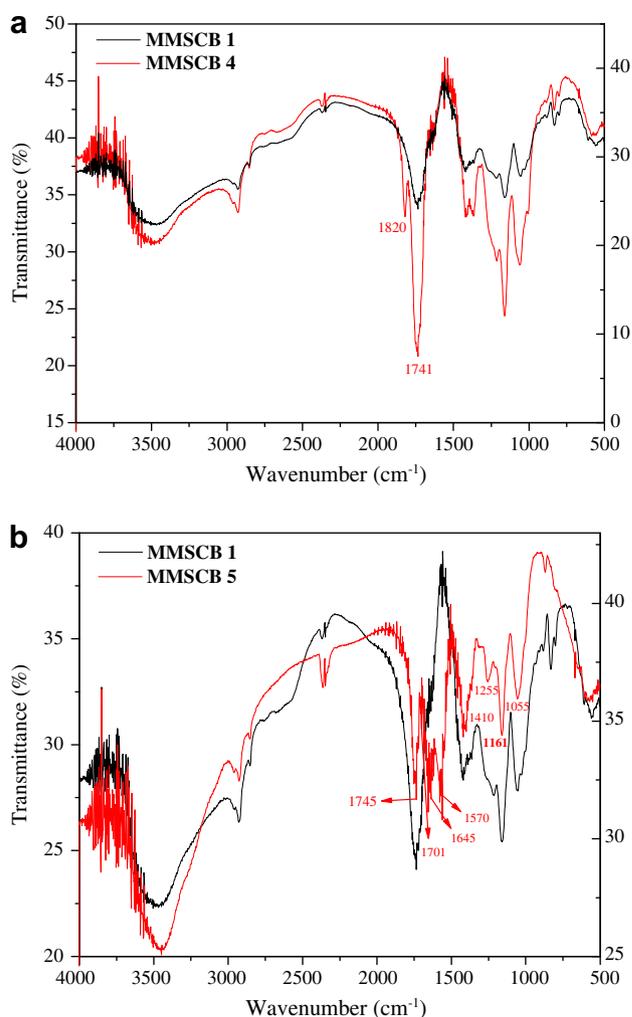


Fig. 3 – FTIR spectra of (a) MMSCB 1 and 4 and (b) MMSCB 1 and 5.

3.3.1. Effect of contact time

Adsorption experiments were performed to investigate the effect of contact time on metal ion uptake and determine adsorption equilibrium time for MMSCB 3 and 5. Samples of 50 mg of MMSCB 3 or 5 were placed into Erlenmeyer flasks containing 50.0 mL of each metal ion solution of known concentration at pH 5.6, 6.0, and 5.5 for Cu^{2+} , Cd^{2+} , and Pb^{2+} , respectively. Adsorption equilibrium time was attained after 20 min for both MMSCB 3 and 5 and metal ions (figure not shown). Adsorption equilibrium time (20 min) was used for pH and concentration-dependent experiments.

3.3.2. Effect of pH

One of the crucial parameters that affect the adsorption of Cu^{2+} , Cd^{2+} , and Pb^{2+} is the pH. The dependence of metal ions removal on pH is related to both surface functional groups present on the adsorbent and the metal ion form in solution (Sheng et al., 2004). MMSCB 3 is a weakly basic ion exchanger, and MMSCB 5 is an amphoteric one that contains both acidic and basic functional groups as can be seen from Fig. 1. According to Navarro et al. (2001), it is expected that MMSCB 5

works as an ion exchanger in addition to its chelating ability owing to the presence of negatively charged oxygen atoms ($\text{COO}^- \text{Na}^+$) in relation to MMSCB 3. At low pH, functional groups of MMSCB 3 and 5 are closely associated with hydronium ions (H_3O^+) and restricted the approach of metal cations as a result of the repulsive force. Based on these results, the effect of pH on adsorption capacities of Cu^{2+} , Cd^{2+} , and Pb^{2+} was investigated by varying the initial pH of the solutions with different pH intervals, which depend on the metal ion studied. The equilibrium pH values obtained from these experiments were taken into account to evaluate the variation of metal ion uptake with pH, which is shown in Figs. 4a,b. As can be seen from Figs. 4a,b, adsorption capacities were found to be low at lower pH values, and high at larger pH values. At lower pH values, the higher concentration of hydrogen ions effectively leads to fewer ligands being available for metal ions binding (Sheng et al., 2004). The typical dependence of metal ion uptake on pH suggests that the weak carboxyl acid groups (succinic acid, pK_a s equal to 3.5 and 4.5) (Dean, 1999) and weak basic amine groups (triethylenetetramine, pK_a s equal to 3.32, 6.67, 9.20, and 9.92) (Dean, 1999) of MMSCB 3 and 5 may be protonated or partially

protonated. Due to this, it is expected that at lower pH values the binding sites are occupied by protons and that there is a competition between hydronium and metal ions for the free binding sites.

Increasing pH (i.e., fewer H_3O^+), adsorption surfaces becomes deprotonated, resulting in more ligand groups available for metal ion binding, and electrostatic attraction from carboxylate groups and free electron-pairs from amine groups is likely enhanced. Therefore, more amine functional groups take part on metal ion uptake by complexation reaction or chelating and adsorbed amount consequently increases. Therefore, it is expected that at high pH values where the concentration of protons is very low, carboxylic groups from MMSCB 5 work as ion exchangers, where sodium ions are released in the solution while metal ions are sorbed, and amine groups work in compleximetric mode, where metal ions are chelated forming a coordinate-type interaction. For the amine groups, an external source of anions is necessary to neutralize any positive charge introduced by adsorbed cations in order to maintain the electroneutrality in the liquid phase as well discussed by Navarro et al. (2001). Some observations regarding the enhancement of metal ion adsorption capacity of nitrogen-type chelating resins by certain anions are well documented. Sengupta et al. (1991) has provided an exhaustive evaluation of the effects of anions such as nitrate on capacity, operating pH and metal ion recovery from chelating resins with nitrogen donors (DOW 2N and DOW 3N).

As can be seen from Figs. 4a,b, maximum removal of Cu^{2+} , Cd^{2+} , and Pb^{2+} was attained at pH 5.6, 6.2 and 6.0 for MMSCB 3 and 5.8, 6.1, 5.9 for MMSCB 5, respectively. These pH values were taken into account for all of the following experiments.

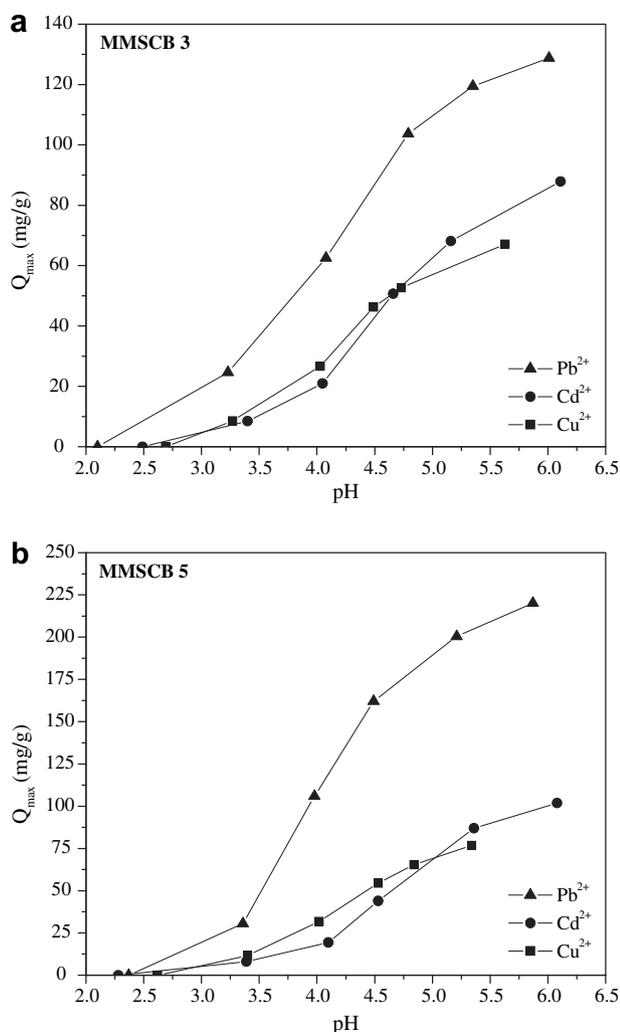


Fig. 4 – Adsorption of metal ions onto MMSCB 3 (a) and 5 (b) as a function of pH.

3.3.3. Adsorption isotherms

Adsorption isotherms describe how adsorbates interact with adsorbents. Langmuir adsorption isotherm has traditionally been used to quantify and contrast the performance of different biosorbents. Langmuir isotherm was originally developed to describe the gas-solid phase adsorption of activated carbon. In its formulation, binding to the surface was primarily by physical forces, i.e. electrostatic or London-van der Waals forces and implicit in its derivation was the assumption that all sites possess equal affinity for the adsorbate. Its use was extended to empirically describe equilibrium relationships between a bulk liquid phase and a solid phase.

Langmuir adsorption isotherm theory (Langmuir, 1918; Rosen, 1989; Davis et al., 2003) is based on five assumptions: (1) adsorption is limited to the formation of a monolayer, or the number of adsorbed species does not exceed the total surface sites; (2) the energy of adsorption is independent, on the other hands, all surface sites have the same energy or equal affinity for the adsorbate; (3) both solute and solvent have equal molar surface areas; (4) both surface and bulk phases exhibit ideal behavior, e.g. no solute-solute or solute-solvent interaction in either phase; and (5) it assumes that all sites are initially free and does not consider any reverse reaction of a displaced ion, such as protons, with the site. Eq. (6) is the general form of Langmuir equation and Eq. (7) is a linearized and rearranged form of the Eq. (6) (Rosen, 1989; Ho et al., 2005).

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

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

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 MMSCB 3 or 5 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 ion and material.

Langmuir model also holds for adsorption of one single component onto an adsorbent. Crist et al. (1994) compared the fit of the Langmuir sorption isotherm model with the modified one for multicomponent. The difference between the two approaches is that the original one assumes that all sites are initially free and does not take into account any reverse reaction of a displaced ion, in this case a proton, with the binding site. The differences between the two models were especially pronounced at low metal ion concentrations because of the effect of the reverse reaction involving the displaced ion. Correspondingly, it has been postulated that the original Langmuir model applies only at higher metal ion concentrations where binding of the displaced ion is low. According to Schiewer and Volesky (1995) this deficiency of the simple Langmuir model, however, loses significance for the multicomponent one used in their work since the effect of competing ions, which is high at low metal ion concentrations, is taken into consideration.

The concentrations of metal ions used in this work in order to build adsorption isotherms were from 1.102 to 1.889 and 1.338 to 2.125 mmol/L for Cu^{2+} ; 0.890 to 1.779 and 0.979 to 1.868 mmol/L for Cd^{2+} ; 0.627 to 1.351 and 1.062 to 1.786 mmol/L for Pb^{2+} for MMSCB 3 and 5, respectively. Considering, therefore, these concentrations and taking into consideration that the final pH values were above 5.6 ($[\text{H}_3\text{O}^+] = 2.51 \times 10^{-3}$ mmol/L) for all experiments, we can conclude that simple Langmuir isotherm can be a good approach to predict adsorption capacities of our system.

In the case of MMSCB 3, a weakly basic ion exchanger, and MMSCB 5, an amphoteric ion exchanger that contains both acidic and basic functional groups, as can be seen from Fig. 1, there is more than one type of functional group contributing to the sorption process, each of which has a different affinity for a sorbing metal ion. Despite this fact, Langmuir equation is frequently used to fit experimental data. In this context, b is not truly Langmuir adsorption constant but, rather, a simple fitting parameter because the system does not comply with all the assumptions of the model. However, b may be quite useful as a measure of the biosorption affinity or efficiency of different adsorbents. Gibbs free energy obtained from b parameter can only be used in comparisons where similar assumptions have been complied.

A linearized plot of C_e/q_e versus C_e is obtained from the model and shown in Figs. 5a,b. Q_{\max} and b were computed

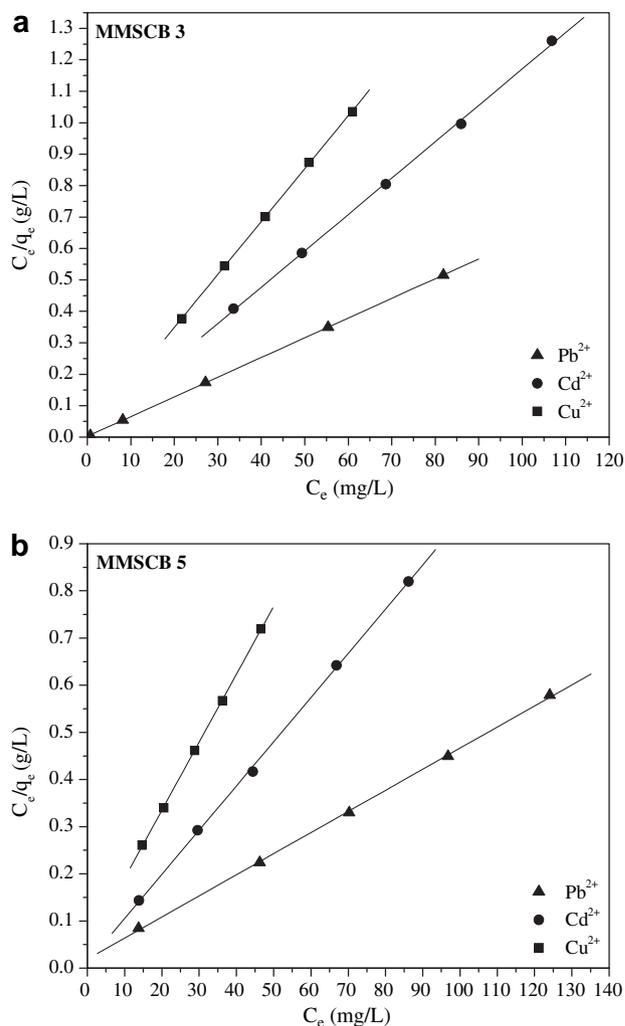


Fig. 5 – The Langmuir isotherm of MMSCB 3 (a) and 5 (b).

from the slopes and intercepts of different straight lines representing MMSCB 3 and 5 with different metal ions (Table 3). The high correlation coefficients obtained by Langmuir model indicate that this model can describe the adsorption of Cu^{2+} , Cd^{2+} and Pb^{2+} onto MMSCB 3 and 5 very well.

MMSCB 5 in relation to MMSCB 3 showed larger maximum adsorption capacity (Q_{\max}) and smaller stability constant (b) for Cu^{2+} , Cd^{2+} and Pb^{2+} . In order to try understanding better these results it is necessary to analyze the nitrogen content, coordination number and maximum adsorption capacity obtained by Langmuir model for MMSCB 3 and 5. As can be seen from Fig. 1, the method used to synthesize MMSCB 5 releases carboxylic acid and amine groups, while for MMSCB 3 the presence of carboxylic groups is due to sites non-modified by DIC and triethylenetetramine. Therefore, considering the nitrogen content of MMSCB 3 (5.8%) and 5 (4.4%) it is possible to conclude that more carboxylic groups are presented in MMSCB 5 than 3. According to Navarro et al. (2001) nitrogen-type chelating resins work in a compleximetric mode, that is, a metal ion binds with participating ligand by coordination-type interaction. Chelating resins containing carboxylate and amine groups are capable to form a coordinate bond with a metal ion using the electron pair of oxygen from carboxylate groups as well as the nitrogen from

Table 3 – The Langmuir parameters for Cu²⁺, Cd²⁺ and Pb²⁺ adsorption.

Metal ion	MMSCB	Langmuir isotherm parameters				R ²	Coordination number	ΔG° (kJ/mol)
		Q _{max} (mg/g)	Q _{max} (mmol/g)	b (L/mg)	b (L/mmol)			
Cu ²⁺	3	59.5	0.936	1.366	86.8	0.9999	2.14	–28.22
	5	69.4	1.092	0.310	19.7	0.9999	1.92	–24.25
Cd ²⁺	3	86.2	0.767	0.835	93.85	0.9993	2.61	–27.04
	5	106.4	0.947	0.817	91.83	0.9995	2.22	–26.68
Pb ²⁺	3	158.7	0.766	2.520	522.12	1	2.61	–29.59
	5	222.2	1.072	0.236	48.9	0.9996	1.95	–23.62

polyamine. However, in contrast with polyamine, carboxylate groups also contain negatively charged oxygen atoms, which allow their corresponding resin to work as an ion exchanger in addition to their chelation abilities. Therefore, starting from the conclusions that have been made by Navarro et al. (2001) it is possible to conclude that the presence of more carboxylic groups in MMSCB 5 than 3 improved the maximum adsorption capacity of MMSCB 5 in relation to MMSCB 3 and reduced the number of ligand atom necessary to chelate a metal ion (CN) as can be seen from Table 3.

Compared to MMSCB 5, MMSCB 3 showed larger stability constant (*b*) for adsorption of Cu²⁺, Cd²⁺ and Pb²⁺, that is, the bond energy between ligand sites of MMSCB 3 and metal ions was larger than MMSCB 5. The same behavior was not noticed for cell 2 and 4 (succinylated mercerized celluloses modified with triethylenetetramine, see Table 1 or Gurgel and Gil, 2009) where the presence of more carboxylate groups in cell 4 helped to stabilize better the bond between metal ion and ligand sites (Gurgel and Gil, 2009). This suggests that some dissimilarity in coordination complexes formed in these adsorbents. Owing to these materials have been synthesized from different matrixes, MMSCB 3 and 5 from modified twice-mercerized sugarcane bagasse and cell 2 and 4 from modified mercerized cellulose, our data may not permit a more precise analysis.

MMSCB 3 also showed larger ΔG° values in relation to MMSCB 5 as can be seen from Table 3. This suggests that the adsorption of Cu²⁺, Cd²⁺, and Pb²⁺ onto MMSCB 3 is more spontaneous and energetically favorable than MMSCB 5. This ΔG° values also suggest that the type of adsorption involved is chemical adsorption.

3.3.4. Comparisons of results with literature

In a previous study, Gurgel et al. (2008b) synthesized succinylated twice-mercerized sugarcane bagasse (MMSCB 2) and performed adsorption studies to evaluate the adsorption capacity for removal of Cu²⁺, Cd²⁺, and Pb²⁺ from aqueous solutions. They employed similar experimental conditions in relation to the present study with respect to the equilibrium time, pH, and metal ion solutions. As can be seen from Table 1, Q_{max} values for removal of Cu²⁺, Cd²⁺, and Pb²⁺ by MMSCB 2 were 185.2, 256.4, 500.0 mg/g, respectively. Comparing the results obtained by Gurgel et al. (2008b) with the results obtained in this study (Table 3) it is possible to conclude that the addition of amine groups to produce MMSCB 3 and 5 had a negative impact on the maximum adsorption capacity of these materials. Similar results were obtained and discussed by Gurgel and Gil (2009). They concluded that this negative impact on Q_{max} of these materials was mainly due to the formation of

crosslinking. As the methodology proposed by Gurgel and Gil (2009) was applied in this study for modification of succinylated twice-mercerized sugarcane bagasse we believe that the same effect was responsible to reduce the maximum adsorption capacity of MMSCB 3 and 5 in relation to MMSCB 2.

Compared to cell 2 and 4 (succinylated mercerized celluloses modified with triethylenetetramine, see Table 1), MMSCB 3 and 5 showed larger Q_{max} values for adsorption of Cu²⁺, Cd²⁺, and Pb²⁺. In relation to Langmuir constant, MMSCB 3 exhibited larger *b* values than cell 2, whereas cell 4 exhibited larger *b* values than MMSCB 5. MMSCB 3 and 5 showed smaller CN than cell 2 and 4. This suggests some differences between the compleximetric modes of these materials.

The results obtained in this study were also compared with those that have been reported by Qu et al. (2005) for resin4, PSMP modified with triethylenetetramine, Hou et al. (2007) for macroporous epoxy-TETA resin, Sun et al. (2007) for PS-TETA, Tang et al. (2007) for triethylenetetramine crosslinked chitosan (CCTS), Karnitz Júnior et al. (2007) for succinylated sugarcane bagasse modified with triethylenetetramine (MSB 6) and Gurgel and Gil (2009) for succinylated mercerized celluloses modified with triethylenetetramine 2 and 4 (cell 2 and 4) (Table 1). MMSCB 3 and 5 showed smaller Q_{max} for Pb²⁺ than CCTS, whereas MMSCB 3 and 5 exhibited larger *b* for Pb²⁺ than CCTS. MMSCB 3 and 5 also showed smaller Q_{max} for Cu²⁺, Cd²⁺, and Pb²⁺ than MSB 6. In contrast MMSCB 3 and 5 presented larger *b* than MSB 6. Epoxy-TETA resin and PS-TETA exhibited larger Q_{max} for Cu²⁺ than MMSCB 3 and 5. MMSCB 5 showed larger Q_{max} for Cu²⁺, Cd²⁺, and Pb²⁺ than resin4.

4. Conclusions

MMSCB 3 and 5 are effective adsorbents for removal of Cu²⁺, Cd²⁺, and Pb²⁺ from aqueous single metal solutions. MMSCB 3 and 5 were obtained with a mass percent gain of 19.9 and 57.1%, concentration of amine groups of 2.0 and 2.1 mmol/g, nitrogen content of 5.8 and 4.4%.

Adsorption studies were developed and evaluated. These studies demonstrated that pH for greatest adsorption of Cu²⁺, Cd²⁺, and Pb²⁺ for MMSCB 3 and 5 were found to be 5.6, 6.2 and 6.0 and 5.8, 6.1, 5.9, respectively. Equilibrium adsorption data were well fitted by Langmuir model. Maximum adsorption capacities for removal of Cu²⁺, Cd²⁺, and Pb²⁺ by MMSCB 3 and 5 were found to be 59.5 and 69.4, 86.2 and 106.4, 158.7 and 222.2 mg/g, respectively.

Compared to MMSCB 3, MMSCB 5 showed better adsorption capacity for the studied metal ions. In contrast, the

starting material, MMSCB 2, exhibited larger Q_{\max} than MMSCB 3 and 5. We conclude that the introduction of triethylenetetramine on succinylated twice-mercerized sugarcane bagasse (MMSCB 2) had a negative impact on Q_{\max} of MMSCB 3 and 5 owing to crosslinking formation.

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