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Adsorption of heavy metal ion from aqueous single metal solution by chemically modified sugarcane bagasse

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Abstract

This work describes the preparation of new chelating materials derived from sugarcane bagasse for adsorption of heavy metal ions in aqueous solution. The first part of this report deals with the chemical modification of sugarcane bagasse with succinic anhydride. The carboxylic acid functions introduced into the material were used to anchor polyamines, which resulted in two yet unpublished modified sugarcane bagasse materials. The obtained materials were characterized by elemental analysis and infrared spectroscopy (IR). The second part of this reports features the comparative evaluation of the adsorption capacity of the modified sugarcane bagasse materials for Cu^{2+}, Cd^{2+}, and Pb^{2+} ions in aqueous single metal solution by classical titration. Adsorption isotherms were studied by the Freundlich and Langmuir models.
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1. Introduction

Water pollution is a major environmental problem faced by modern society (Baird, 1995) that leads to ecological disequilibrium and health hazards (Kelter et al., 1997). Heavy metal ions such as copper, cadmium, lead, nickel, and chromium, often found in industrial wastewater, present acute toxicity to aquatic and terrestrial life, including humans. Thus, the discharge of effluents into the environment is a chief concern. The methods commonly used to remove toxic heavy metal from municipal and industrial wastewater are based on the adsorption of ions onto insoluble compounds and the separation of the sediments formed. Many efforts have been made recently to find cheaper pollution control methods and materials (Panday et al., 1985; Ali and Bishtawi, 1997; Acemioğlu and Alma, 2001).

The new material world trends point to the importance of using industrial and agricultural residues as production starting materials. Reusing and recycling these residues can minimize the environmental problems associated with their build-up and reduce the use of noble starting materials. This trend has contributed to the reconsideration of the use of traditional biomaterials such as natural lignocellulosic fibers to substitute synthetic polymers, for example, since in many cases they have a better performance.

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 and although it is burned to produce energy for sugar mills, leftovers are still significant. Thus, on account of the importance of

bagasse sugar as an industrial waste, there is a great interest in developing chemical methods for recycling it. Sugarcane bagasse has around 50% cellulose, 27% polyoses, and 23% lignin (Caraschi et al., 1996). These three biological polymers have many hydroxyl and/or phenolic functions that can be chemically reacted to produce materials with new properties (Xiao et al., 2001; Navarro et al., 1996).

Despite the many studies of the chemical modification of cellulose published around the world in this area (Gurnani et al., 2003; Gelleresed and Gatenholm, 1999), only a few have investigated the modification of bagasse sugar (Krishnan and Anirudhan, 2002; Orlando et al., 2002).

This work describes the preparation and the evaluation of new chelating materials from sugarcane bagasse to adsorb heavy metal ions in aqueous solution. In a preliminary study, it has been chosen to study the adsorption of Cu^{2+}, Cd^{2+}, and Pb^{2+}. The first part of this work describes the modification of sugarcane bagasse with succinic anhydride to introduce carboxylic functions to sugarcane bagasse and the chemical introduction of commercial linear polyamine via the formation of amide functions. It is well known that polyamines have powerful chelating properties, mainly towards ions such as Cu^{2+}, Zn^{2+}, and Pb^{2+} (Bianchi et al., 1991; Martell and Hancock, 1996).

The second part of this work evaluates the adsorption of Cu^{2+}, Cd^{2+}, and Pb^{2+} onto three modified sugarcane bagasses (MSBs) from aqueous single metal ion solutions by classical titration. The results were analyzed by the Langmuir and Freundlich models (Ho et al., 2005).

2. Methods

2.1. Materials

Polyamines ethylenediamine 3 and triethylenetetramine 4 were used in this work. Succinic anhydride, 1,3-diisopropylcarbodiimide (DIC), and triethylenetetramine, from Aldrich, were used without purification. Ethylenediamine and dimethylformamide were distilled before use. Pyridine was refluxed with NaOH and distilled.

2.2. Sugarcane bagasse preparation

Sugarcane bagasse was dried at 100 °C in an oven for approximately 24 h and next fiber size was reduced to powder by milling with tungsten ring. The resulting material was sieved with a 4-sieve system (10, 30, 45, and 60 mesh). Then, the material was washed with distilled water under stirring at 65 °C for 1 h and dried at 100 °C. Finally, it was washed anew in a sohxlet system with n-hexane/ethanol (1:1) as solvent for 4 h.

2.3. Synthesis of MSBs 1 and 2

Washed and dried sugarcane bagasse (5.02 g) was treated with succinic anhydride (12.56 g) under pyridine reflux (120 mL) for 18 h. The solid material was filtered, washed in sequence with 1 M solution of acetic acid in CH_2Cl_2, 0.1 M solution of HCl, ethanol 95%, distilled water, and finally with ethanol 95%. After drying at 100 °C in an oven for 30 min and in a desiccator overnight, MSB 1 (7.699 g) was obtained with a mass gain of 53.4%. MSB 2 was obtained by treatment of 1 with saturated $NaHCO_3$ solution for 30 min and afterwards by filtering using sintered filter and washing with distilled water and ethanol.

2.4. Synthesis of MSBs 5 and 6

The process used to introduce amine functions was the same as that used to prepare MSB 5 and 6. MSB 1 was treated with 5 equiv of 1,3-diisopropylcarbodiimide (DIC) and 6 equiv of polyamine in anhydrous DMF at room temperature for 22 h under stirring. After filtration, the materials were washed with DMF, a saturated solution of $NaHCO_3$, distilled water, and finally with ethanol. Next, they were dried at 80 °C in an oven for 30 min and in a desiccator overnight.

2.5. Kinetic study of metal ion adsorption of MSBs 2, 5, and 6

Experiments with each material and metal ion were performed to determine the adsorption equilibrium time from 10 to 90 min in 10 min intervals. The amount of 100 mg MSB was placed in a 250-mL Erlenmeyer with 100.0 mL metal ion solution with concentration of 200 mg/L under stirring. The experiments were done at pHs 5.8 for Cu^{2+}, 7.0 for Cd^{2+}, and 6.2 for Pb^{2+}, optimal values to obtain the best adsorption. To adjust pH values, was added NaOH solution (0.01 mol/L) into metal solutions with MSB. After filtration, metal ion concentration was determined by EDTA titration.

2.6. pH study of metal ion adsorption of MSBs 2, 5, and 6

Experiments with each material and metal ion were performed to determine the effect of pH on ion adsorption. An amount of 100 mg MSB was placed into a 250-mL Erlenmeyer with 100.0 mL of metal ion solution 200 mg/L under stirring. pH was calibrated with HCl or NaOH solutions (0.1–1.0 mol/L). The reaction times used were 30 min (MSB 2) or 40 min (MSB 5 and 6) for Cu^{2+} and Cd^{2+}, and 40 min (MSB 2) or 50 min (MSB 5 and 6) for Pb^{2+}. Metal ion concentration was determined after filtration by EDTA titration. No significative variation of pH was observed at the end of each experiment.

2.7. Adsorption isotherms of MSBs 2, 5, and 6

Experiments were performed for each material and metal ion to determine adsorption isotherms. In each experiment, 100 mg of MSB was placed into a 250-mL Erlenmeyer with 100.0 mL of metal ion solution in specific concentrations (between 200 mg/L and 400 mg/L) under stirring. Each experiment was performed at the pH of

larger ion adsorption during the time necessary for equilibrium (Tables 3 and 4). After filtration, the metal ion concentration was determined by EDTA titration.

2.8. Characterization of the new obtained materials

MSB **1**, **2**, **5,** and **6** were characterized by IR spectroscopy in a Nicolet Impact 410 equipment with KBr. Elemental analyses were accomplished in Analyzer 2400 CHNS/O Perkin Elemer Series II.

3. Results and discussion

3.1. Synthesis of MSBs 1, 2, 5, and 6

The synthesis route used to prepare MSBs **1**, **2**, **5,** and **6** are presented in Scheme 1. Prewashed sugarcane bagasse was succinylated for various periods of time. The degree of succinylation of the bagasse fibers was determined by measuring the quantity of acid function. The results are shown in Fig. 1. The concentration of carboxylic functions per mg of bagasse was determined by retro titration. For this, MSB **1** was initially treated with an excess solution of NaOH (0.01 mol/L) for 30 min. Soon afterwards the material was filtered and the obtained solution was titrated with an HCl solution (0.01 mol/L). The highest degree of succinylation was reached after 18-h reaction. Using this reaction time, sugarcane bagasse was succinylated to produce MSB **1,** which presented a weight gain of 54% and a concentration of carboxylic acid function per mg of 3.83×10^{-6} mol. Next, MSB **1** was treated with a saturated NaHCO$_3$ solution to produce MSB **2**.

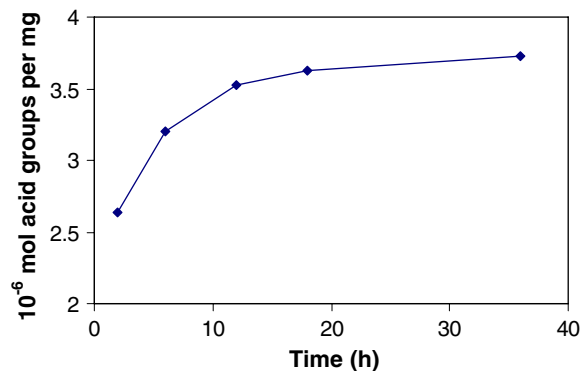Starting from MSB **1**, two polyamines were introduced: ethylenediamine **3** and triethylenetetramine **4**. The methodology used to introduce the polyamines was the same for the two MSBs **5** and **6**, as shown in Scheme 1. Concentrations of 2.4×10^{-6} mol (**5**) and 2.6×10^{-6} mol (**6**) of amine function per mg of material were determined by back titration with excess HCl solution. The introduction of the amine functions was also verified by IR spectroscopy (Table 1) and elemental analysis (Table 2).

Fig. 1. Quantity of acid function as a function of succinic anhydride treatment time.

3.2. Characterization of MSBs 1, 5, and 6

Characterization of carboxylated MSB **1** was accomplished by IR spectroscopy. The spectrum of unmodified sugarcane bagasse and MSB **1** are presented in Fig. 2. The spectrum of MSB **1** displayed two strong bands at 1740 and 1726 cm^{-1} in relation to that of unmodified sugarcane bagasse. This demonstrated the presence of two types of carbonyl functions, one relative to carboxylic acid and another relative to the ester. The acid and ester IR bands indicate that succinic anhydride acylated the
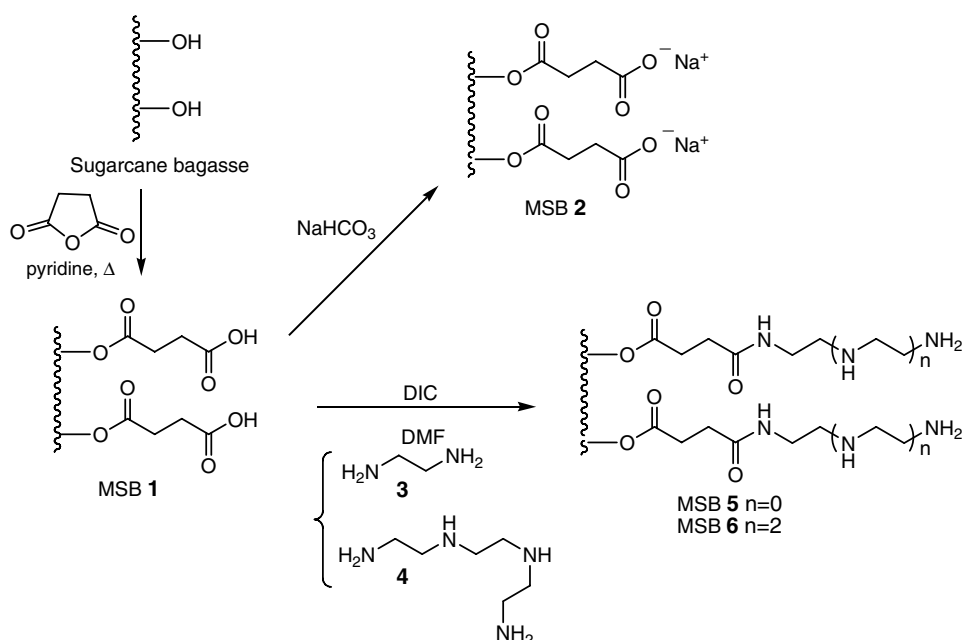
Scheme 1. Synthesis route used to obtain MSBs **1**, **2**, **5**, and **6**.

Table 1
Main IR spectrum bands observed in MSBs **1**, **5**, and **6**

MSB	Main bands observed (cm^{-1})
1	1740, 1726
5	1745, 1650, 1635, 1575, 1423, 1060
6	1738, 1651, 1635, 1560, 1400, 1159, 1060

Table 2
Elemental analysis of MSBs **1**, **2**, **5**, and **6**

	C (%)	H (%)	N (%)
Sugarcane bagasse	43.98	6.02	0.13
MSB **1**	45.41	5.62	0.10
MSB **2**	38.04	5.14	0.01
MSB **5**	44.01	6.51	2.21
MSB **6**	46.88	6.65	3.43

Fig. 3. IR spectrum (KBr) of MSB **5**.

Fig. 2. IR spectrum (KBr) of unmodified sugarcane bagasse and MSB **1**.

Fig. 4. IR spectrum (KBr) of MSB **6**.

hydroxy group of bagasse to generate an ester bond with consequent release of a carboxylic acid functional group.

The spectra of MSBs **5** and **6** (Figs. 3 and 4, respectively) showed three new strong bands at 1550–1650 cm^{-1} (see data in Table 1) corresponding to the presence of amide and amine functions, and one band at 1060 cm^{-1} corresponding to C–N stretch. The bands at 1635 and 1650 cm^{-1} (Fig. 3) correspond to the axial deformation of the carbonyl of the amide function and the angular deformation of the N–H bond of the amine function. The band at 1575 cm^{-1} corresponds to the angular deformation of the N–H bond of the amide function. The band at 1159 cm^{-1} (Fig. 4) corresponds to the asymmetric stretch of C–N–C bond.

The main bands observed in all MSBs are presented in Table 1.

MSB elemental analysis data presented in Table 2 show a modification in the carbon and hydrogen composition of MSB **1** and a larger proportion of nitrogen as the number of amine functions in the used polyamine increases.
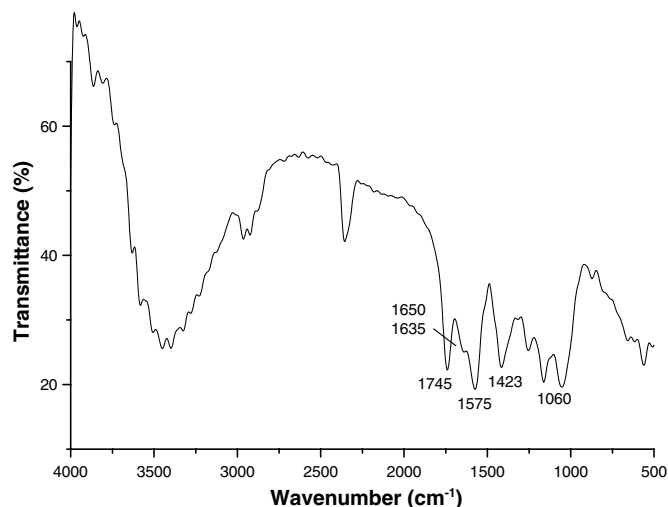
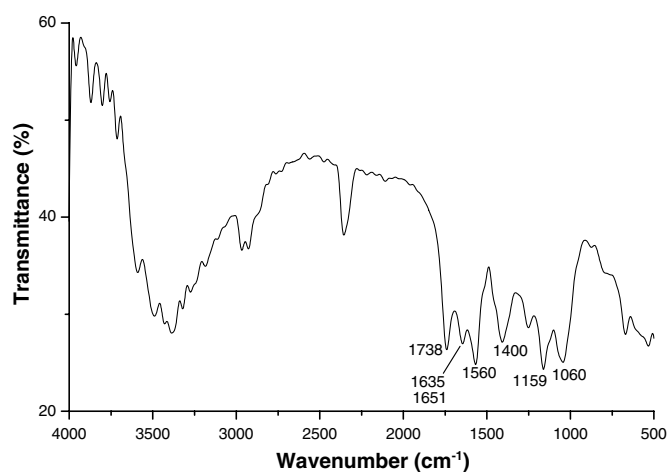### 3.3. Study of adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} on MSBs **2**, **5**, and **6**

The study of the MSB adsorption properties was accomplished for each material and metal ion. A kinetic study and an adsorption study as a function of pH were first carried out.

3.3.1. Effect of contact time

The kinetic study of MSB **2** with Cu^{2+}, Cd^{2+}, and Pb^{2+} ions in aqueous solution is presented in Fig. 5. Adsorption equilibrium was reached after 20 min for Cd^{2+} ions. A time of 30 min was chosen for all studies of MSB **2** with Cd^{2+}. The adsorption equilibrium times chosen for pH and concentration dependent experiments are presented in Table 3.

Similar studies were accomplished for MSBs **5** and **6** for Cu^{2+}, Cd^{2+}, and Pb^{2+}. The results are presented in Table 3.

3.3.2. pH Effect

The removal of metal ions from aqueous solutions by adsorption is dependent on solution pH as it affects adsor-
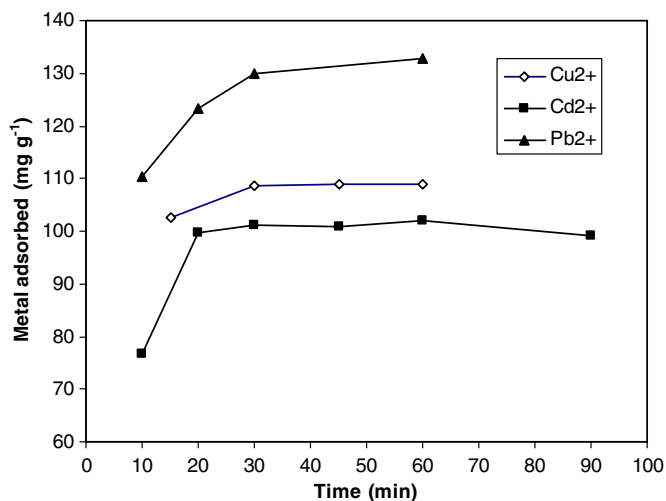
Fig. 5. Effect of contact time on MSB **2** metal ion adsorption.

Table 3
Adsorption equilibrium times of MSBs **2**, **5** and **6**

MSB	Equilibrium time (min)		
	Cu^{2+}	Cd^{2+}	Pb^{2+}
2	30	30	40
5	40	40	50
6	40	40	50

bent surface charge, the degree of ionization, and the species of adsorbates. The study of adsorption of Cd^{2+}, Cd^{2+}, and Pb^{2+} on MSB **2** as a function of pH was accomplished with the reaction times given in Table 3; the results are presented in Fig. 6. The adsorption of the three metal ions increases with the increase in pH. Maximum removal of Cd^{2+} was observed above pH 6 and in the case of Pb^{2+} and Cu^2, above pH 5 and 5.5.

Similar studies were accomplished for MSBs **5** and **6** and Cu^{2+}, Cd^{2+} and Pb^{2+} with similar results, as shown in Table 4.
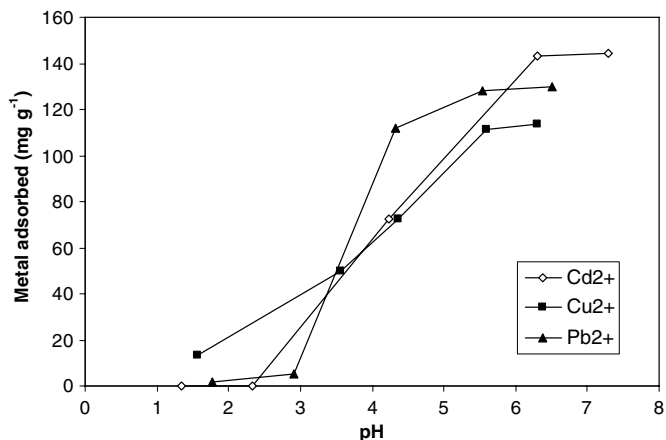

Fig. 6. Adsorption of metal ions on MSB **2** as a function of pH.

Table 4
pH of largest adsorption of MSBs **2**, **5** and **6**

MSB	pH of largest adsorption		
	Cu^{2+}	Cd^{2+}	Pb^{2+}
2	5.5–6.0	6.5–7.5	5.0–6.0
5	5.5–6.0	6.5–7.5	5.0–6.0
6	5.5–6.0	6.5–7.5	5.0–6.0

3.3.3. Adsorption isotherms

The Langmuir (Ho et al., 2005) (Eq. (1)) and Freundlich (Eq. (2)) isotherms were evaluated by adsorption experiments as a function of the initial metal ion concentrations in aqueous solution under equilibrium time and pH conditions given in Tables 3 and 4. The results of each material and metal ion are presented in Fig. 7 (Langmuir) and Fig. 8 (Freundlich) and Table 5.

$$\frac{c}{q} = \frac{1}{Q_{max} \times b} + \frac{c}{Q_{max}} \tag{1}$$

$$\ln q = \ln k + \frac{1}{n} \ln c \tag{2}$$
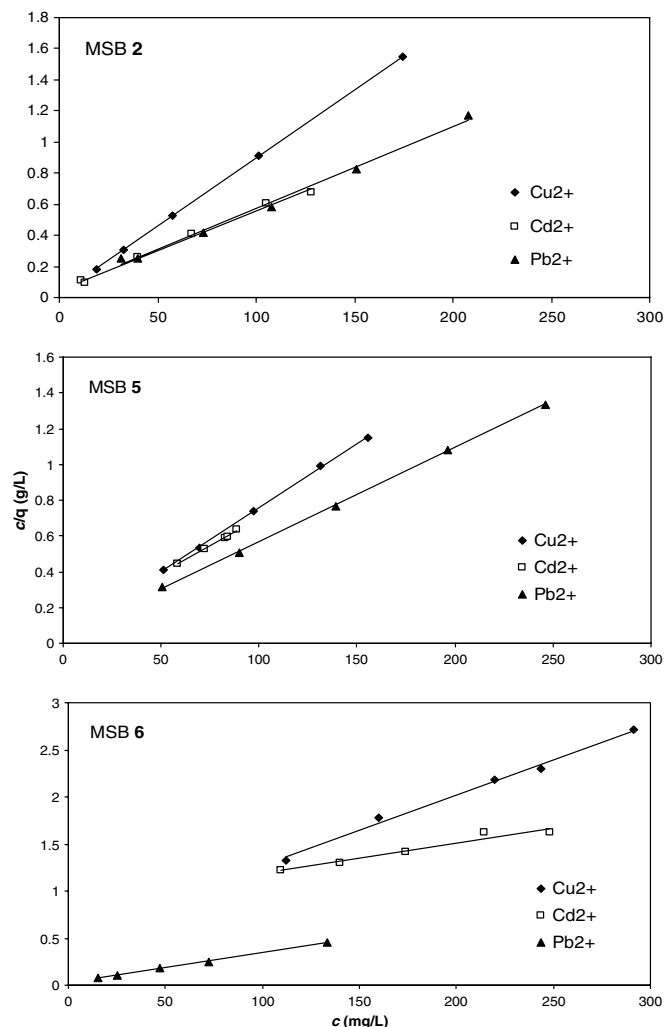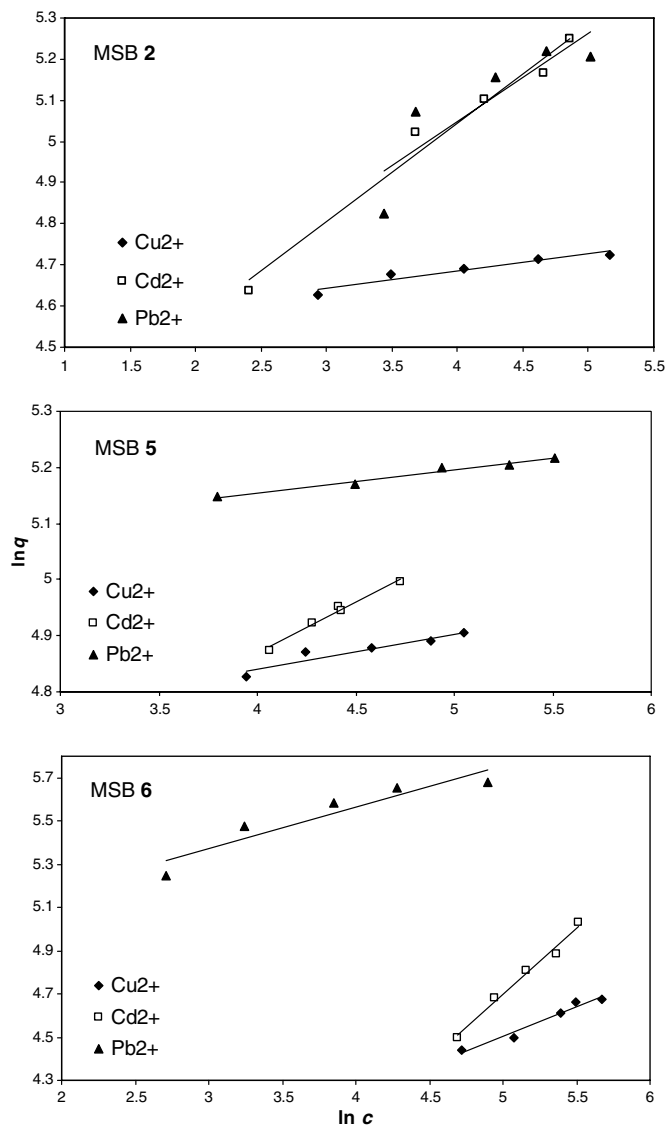

Fig. 7. The Langmuir isotherms of MSBs **2**, **5,** and **6**.

Fig. 8. The Freundlich isotherms of MSBs **2**, **5**, and **6**.

Table 5
The Langmuir and Freundlich parameters for Cu^{2+}, Cd^{2+} and Pb^{2+} adsorption

Metal ion	MSB	Langmuir			Freundlich		
		Q_{max} (mg/g)	b (L/mg)	r^2	k (mg/g)	n	r^2
Cu^{2+}	**2**	114	0.431	1	91.6	23.9	0.9193
	5	139	0.173	0.9998	98.3	15.8	0.9061
	6	133	0.014	0.9927	22.8	3.64	0.9635
Cd^{2+}	**2**	196	0.103	0.9934	59.4	4.16	0.9773
	5	164	0.068	0.9957	62.8	5.49	0.9834
	6	313	0.004	0.9528	5.15	1.63	0.9856
Pb^{2+}	**2**	189	0.110	0.9945	66.0	4.66	0.7579
	5	189	0.125	0.9999	147	24.51	0.981
	6	313	0.121	0.9994	121	5.21	0.877

where q (mg/g) is the concentration of adsorbed metal ions per gram of adsorbent, c (mg/L) is the concentration of

metal ion in aqueous solution at equilibrium, Q_{max} and b are the Langmuir equation parameters and k and n are the Freundlich equation parameters.

High correlation coefficients of linearized Langmuir and Freundlich equations indicate that these models can explain metal ion adsorption by the materials satisfactorily. Therefore, both models explained metal ion adsorption by MSBs **2**, **5**, and **6** as can be observed in Table 5, with the exception of the Freundlich model for Pb^{2+} adsorption by MSB **2**.

The Langmuir isotherm parameter Q_{max} indicates the maximum adsorption capacity of the material, in other words, the adsorption of metal ions at high concentrations. It can be observed in Table 5 that MSB **5** presents the largest Cu^{2+} adsorption capacity while MSB **6** adsorbs Cd^{2+} and Pb^{2+} the best. Langmuir parameter b indicates the bond energy of the complexation reaction of the material with the metal ion. It can be observed that MSB **2** presents the largest bond energy for Cu^{2+} and Cd^{2+}, while three materials do not differ significantly for Pb^2.

The Freundlich isotherm parameter k indicates the adsorption capacity when the concentration of the metal ion in equilibrium is unitary, in our case 1 mg/L. This parameter is useful in the evaluation of the adsorption capacity of metal ions in dilute solutions, a case closer to the characteristics of industrial effluents. The values of k of MSB **2** and **5** are much similar for Cu^{2+} and Cd^{2+} and much higher than that for MSB **6**. This shows the superiority of both materials in the adsorption of these metal ions in low concentrations. MSB **5** has a higher k value for Pb^{2+} when compared to those of the other materials.

These results were compared with those of Vaughan et al. (2001) for a commercial macroreticular chelating resin with thiol functional groups, Duolite GT-73. The Q_{max} of Duolite GT-73 for Cu^{2+}, Cd^{2+}, and Pb^{2+} were 62 mg/g, 106 mg/g, and 122 mg/g, respectively. Duolite GT-73 exhibited Q_{max} lower than those of MSBs (Table 5).

4. Conclusions

Through a fast, effective, and cheap methodology, it was possible to devise a strategy to introduce chelating functions (carboxylic acid and amine) to sugarcane bagasse. Modified sugarcane bagasses presented a good adsorption capacity for Cu^{2+}, Cd^{2+}, and Pb^{2+} ions with maximum adsorption capacity observed for MSB **6**. It has been demonstrated that metal ion adsorption efficiency is proportional to the number of amine functions introduced into the material. MSB **2**, which contained only carboxylate functions, showed an efficiency similar to that of MSB **5**, a material of much more complex synthesis.

Acknowledgements

References

Acemioğlu, B., Alma, M.H., 2001. Equilibrium studies on adsorption of Cu(II) from aqueous solution onto cellulose. Journal of Colloid and Interface Science 243, 81–83.

Ali, A.A., Bishtawi, R., 1997. Removal of lead and nickel ions using zeolite tuff. Journal of Chemical Technology and Biotechnology 69, 27–34.

Baird, C., 1995. Environmental Chemistry. W.H. Freeman and Company, New York.

Bianchi, A., Micheloni, M., Paoletti, P., 1991. Thermodynamic aspects of the polyazacycloalkane complexes with cations and anions. Coordination Chemistry Reviews 110, 17–113.

Caraschi, J.C., Campana, S.P., Curvelo, A.A.S., 1996. Preparação e Caracterização de Polpas Obtidas a Partir de Bagaço de Cana de Açúcar. Polímeros: Ciência e Tecnologia 3, 24–29.

Gellerested, F., Gatenholm, P., 1999. Surface properties of lignocellulosic fibers bearing carboxylic groups. Cellulose 6, 103–121.

Gurnani, V., Singh, A.K., Venkataramani, B., 2003. 2,3-Dihydroxypyridine-loaded cellulose: a new macromolecular chelator for metal enrichment prior to their determination by atomic absorption spectrometry. Analytical and Bioanalytical Chemistry 377, 1079–1086.

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, 1285–1291.

Kelter, P.B., Grundman, J., Hage, D.S., Carr, J.D., Castro-Acuña, C.M., 1997. A discussion of water pollution in the United States and Mexico; with High School Laboratory Activities for the analysis of lead, atrazine, and nitrate. Journal of Chemical Education 74, 1413–1421.

Krishnan, K.A., Anirudhan, T.S., 2002. Removal of mercury(II) from aqueous solutions and chlor-alkali industry effluent by steam activated and sulphurised activated carbons prepared from bagasse pith: kinetics and equilibrium studies. Journal of Hazardous Materials 92, 161–183.

Martell, A.E., Hancock, R.D., 1996. Metal complexes in aqueous solutions. Plenum, New York.

Navarro, R.R., Sumi, K., Fujii, N., Matsumura, M., 1996. Mercury removal from wastewater using porous cellulose carrier modified with polyethyleneimine. Water Research 30, 2488–2494.

Orlando, U.S., Baes, A.U., Nishijima, W., Okada, M., 2002. Preparation of chelating agents from sugarcane bagasse by microwave radiation as an alternative ecologically benign procedure. Green Chemistry 4, 555–557.

Panday, K.K., Gur, P., Singh, V.N., 1985. Copper(II) removal from aqueous solutions by fly ash. Water Research 19, 869–873.

Vaughan, T., Seo, C.W., Marshall, W.E., 2001. Removal of selected metal ions from aqueous solution using modified corncobs. Bioresource Technology 78, 133–139.

Xiao, B., Sun, X.F., Sun, R., 2001. The chemical modification of lignins with succinic anhydride in aqueous systems. Polymer Degradation and Stability 71, 223–231.