Assessment of chemically modified sugarcane bagasse for lead adsorption from aqueous medium

V. C. G. Dos Santos, C. R. T. Tarley, J. Caetano and D. C. Dragunski

ABSTRACT

This study evaluated the adsorption capacity of chemically modified sugarcane bagasse with citric acid (B-CA), sodium hydroxide (B-S) and citric acid and sodium hydroxide (B-CAS) for Pb^{2+} ion adsorption in aqueous medium. Infrared spectroscopy (FT-IR) was used to characterise the materials, where the chemical modification was confirmed by the presence of carboxylate groups created at 1,730 cm^{-1} peak. All assays related to Pb^{2+} ion adsorption onto adsorbent, i.e. equilibrium time between Pb^{2+} ions and adsorbate (24 h), as well as Pb^{2+} ion concentration, were performed in batch system. The initial and final Pb^{2+} ion concentration after shaking time was determined by Flame Atomic Absorption Spectrometry (FAAS). Isotherm adsorptions were applied to Langmuir and Freundlich linear models and maximum adsorption capacity (MAC) of materials towards Pb^{2+} ions was calculated in function of modifications. A significant improvement regarding Pb^{2+} ion adsorption after the bagasse treatment with citric acid, in which MAC was 52.63 $mg\,g^{-1}$, was observed. The adsorptions followed the behaviour described by the Langmuir linear model and its kinetics follow the behaviour described by the pseudo-second-order equation.

Key words | adsorption, lead, sugarcane bagasse

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INTRODUCTION

Constant demographic growth and industrial development of several regions associated with consumption, production and exploitation of resources, as fossils and minerals, have resulted in more effluents containing heavy metals. When thrown away without previous treatment, most of these materials are highly mobile, bioaccumulative in the food chain and harmful to fauna, flora and human health (Rodrigues *et al.* 2006; Albertini *et al.* 2007; Sousa *et al.* 2007). Even in small amounts, metallic ions cause a series of diseases; for instance, Pb^{2+} ions can cause serious circulatory problems (Schvartsman 1991; Shaik *et al.* 2006).

Heavy metals potentially pollute the soil directly because of their availability to plants, contamination of superficial plants due to erosion and contamination of subsurface water. Therefore, regarding the destination of these elements in the soil, it is essential to evaluate the environmental impact (Oliveira *et al.* 2002).

Pollution of groundwater, or water tables, by heavy metals is presently one of the main environmental concerns. Heavy metals have a cumulative impact on the human body, and may cause several types of intoxication and even death. When groundwater is contaminated, it certainly reaches the population through the water system service (Gavrilescu 2004).

Lead intoxication may cause a disease called Saturnism, also associated with low height in children. A literature study has shown that children in a contaminated area were chronically exposed to lead in the air, in the dust of their living and leisure areas, and even in their diets, and then exposed to some toxicity of the central nervous system (Dietrich *et al.* 2004; CONAMA 2005).

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Thus, through regulation No. 357, on March 17, 2005, CONAMA (The Brazilian National Council of the Environment) established that the maximum lead concentration level for drinking water is 0.01 mg L^{-1}, the same value set by WHO (World Health Organization) (CONAMA 2005).

It is known that conventional treatment methods of effluents contaminated by heavy metals, such as rainfall, ionic exchange, electrochemical treatment, flocculation, ozonisation, and filtration, are many times restricted because they are technically or economically not viable. Because of the expensive and long detention time, the implementation of these techniques is difficult, especially when the metals are dissolved in great volumes of water. Another relevant point of these treatments is the production of solid residues that are kept and stored, becoming another serious problem (Ferreira *et al.* 2007; Romera *et al.* 2007; Sousa *et al.* 2007; Karnitz Júnior *et al.* 2009; Karnitz Júnior *et al.* 2010).

Adsorption is an alternative treatment method that is very efficient and used to remove toxic metals (Sousa *et al.* 2007). It is considered one of the most important phenomena on the surface, where there is an accumulation of a determined element or substance in the interface between two phases, i.e. between the solid surface and the adjacent one (Sousa *et al.* 2007; Dahiya *et al.* 2008; Yan & Viraraghavan 2008).

Alternative adsorption methods for effluent treatment have been developed using natural materials. The most used adsorbing agents from natural materials include, besides compost materials, agricultural products, wood, algae, microorganisms. They can retain metallic ions through adsorption, and are better than conventional methods because they are economically viable and come from renewable sources. The adsorption properties of these materials may increase significantly after chemical treatment. For example, it was verified that there was a significant increase of the biomass capacity to retain metallic ions when soybean hulls were submitted to treatments with alkaline solution (NaOH), followed by a modification with citric acid at high temperatures (Annadurai *et al.* 2002; Tarley & Arruda 2003; Tarley & Arruda 2004; Pérez-Marín *et al.* 2007; Feng *et al.* 2009; Karnitz Júnior *et al.* 2009; Karnitz Júnior *et al.* 2010).

Taking all these into consideration, attempts to look for new adsorbent materials that are technically and economically viable are focused on biomaterials. The term "biosorption" has been used to describe the property of retaining metallic ions in aqueous solutions, and it is considered promising for the removal of heavy metals from industrial effluents (Rodrigues *et al.* 2006; Ferreira *et al.* 2007; Karnitz Júnior *et al.* 2009; Karnitz Júnior *et al.* 2010).

Biosorption results from the electrostatic interaction and also from the complex formations among metallic ions and functional groups present in biomasses, when they have chemical affinity to the metal. The identification of these functional groups is of paramount importance to determine the responsible mechanisms for metal links in the structure of these materials. Functional groups such as carboxylate, phosphate and amino are considered responsible for the biosorption process (Rodrigues *et al.* 2006; Khormaei *et al.* 2007; Lei *et al.* 2008).

Chemical modifications have been made in the structures of some agro-industrial residues in order to enhance the adsorption capacity of materials (Gurgel *et al.* 2008; Karnitz Júnior *et al.* 2009). According to Gurgel & Gil (2009), by reacting cellulose with succinic anhydride, the adsorption capacity of this material increases considerably with the inclusion of negative sites on the polymer chain.

The use of sugarcane bagasse as adsorption biomass, besides being economically viable for industries that need to treat effluents, will also be very valuable to alcohol and sugar mills as they are responsible for the production of large amounts of residues. Most of them are processed to feed furnaces because there is an excess of sugarcane bagasse, corresponding to 8% in auxiliary distilleries and 12% in independent ones. Thus, sugarcane bagasse can be considered an agro-industrial residue, and an environmentally friendly destination for these materials would be their use for the removal of metal ions from aqueous effluents (Pérez-Marín *et al.* 2007; Karnitz Júnior *et al.* 2009; Karnitz Júnior *et al.* 2010). Thus, in the present study, we demonstrated the feasibility of chemically modified sugarcane bagasse as a new biosorbent candidate for the adsorption of Pb^{2+} ions.

EXPERIMENTAL

Reagents

Analytical grade chemical reagents were used throughout the experiment. Lead standard solutions of 1,000 mg L^{-1}

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were prepared from lead nitrate salt ($Pb(NO_3)_2$ Vetec, 99%), and appropriate dilutions were made in deionised water (MILLIPORE, Bedford, MA, USA). Solutions of 0.1 mol L^{-1} NaOH (F. Maia, 97%), 0.1 mol L^{-1} HCl (F. Maia, 37%) and 1.2 mol L^{-1} citric acid were used.

Equipment

A BOMEM (model MB-102) FT-IR infrared spectrometer was used to elucidate the functional groups present in the adsorbents. Bagasse samples were proportionally macerated with KBr crystals (1 mg sample/100 mg KBr) and put in a pastillator, then 4,000 to 400 cm^{-1} spectral range was analysed. A Flame Atomic Absorption Spectrometer (FAAS) (GBC 932plus), equipped with deuterium lamp for background correction and a hollow cathode lamp as radiation source for lead, was used for metal quantification.

Adsorbent preparation – sugarcane bagasse modification

Sugarcane bagasse produced by the Santa Terezinha Mill, in the town of Ivate-PR, Brazil, was used for the experiments. It was ground and sieved (Bertel sieve, 200 mesh) to obtain a more homogeneous particle size. Next, the material was submitted to three chemical modifications.

Modification using NaOH (B-S)

The first treatment of sugarcane bagasse was performed by using a NaOH solution. For this task, 20 mL of 0.1 mol L^{-1} NaOH was added for each gram of the material; the mixture was agitated for 2 h and the supernatant was discarded. Then, the material was washed with deionised water and dried at 55°C for 24 h (Rodrigues *et al.* 2006).

Modification using citric acid (B-CA)

The second treatment was performed by using citric acid, where a 1.2 mol L^{-1} citric acid solution was added to the material at 8.3 mL g^{-1} of bagasse ratio. Next, the mixture was agitated for 30 min and the supernatant discarded. The bagasse was dried at 55°C, and after 24 h the temperature was raised to 120°C and kept for 90 min. Then, the bagasse was washed with deionised water (60–80°C) and dried at 55°C for 24 h (Rodrigues *et al.* 2006).

Modification using NaOH and citric acid (B-CAS)

For the last treatment, sugarcane bagasse was treated with NaOH and later with citric acid solution. For this procedure, 20 mL of 0.1 mol L^{-1} NaOH solution was added to each gram of the material; the mixture was agitated for 2 h and the supernatant discarded; then the material was washed with deionised water and dried at 55°C, for 24 h. After that, a 1.2 mol L^{-1} citric acid solution was added to the material at 8.3 mL g^{-1} of bagasse ratio, followed by shaking for 30 min. The supernatant was discarded and the bagasse was dried at 55°C and after 24 h the temperature was increased to 120°C and kept for 90 min. Finally, the bagasse was washed with deionised water (60–80°C) and dried at 55°C for 24 h.

Adsorption study

Effect of contact time on adsorption profile

Lead solutions were prepared using lead nitrate salt ($Pb(NO_3)_2$, Vetec, 99%). In order to check the effect of chemical modification on bagasse, the three materials (B-S, B-CA and B-CAS) were compared with *in natura* bagasse (B-N). Thus, 50 mL of Pb solutions with initial concentration of 1,000 mg L^{-1} were agitated with 0.5 g of bagasse in an orbital shaker. Further, 500 μL aliquots were collected in a time interval ranging from 15 to 1,440 min and transferred to volumetric flask of 50 mL whose volume was made up with deionised water. The amount of Pb^{2+} ion in each aliquot was determined by FAAS. Corrections were made for each aliquot regarding amount of material. The amount of metal adsorbed per gram of bagasse (q_{eq}) was calculated as a function of time. It was calculated according to Equation (1):

$$q_{eq} = \frac{(C_0 - C_{eq}) * V}{M} \quad (1)$$

where C_0 and C_{eq} are, respectively, the initial and final concentrations of Pb^{2+} ion, V is the solution volume and M the bagasse mass (g).

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Adsorption isotherms

Solutions of Pb^{2+} were prepared in different concentrations ranging from 100 up to 1,000 mg L^{-1}. Aliquots of 50 mL of Pb^{2+} solutions were shaken with 0.5 g of each material (B-S, B-CA, B-CAS and B-N) in an orbital shaker for 24 h and the pH was kept constant at 5 with the addition of NaOH or HCl. Next, the mixtures were filtrated and the supernatant was analysed by FAAS. At the end of this step, that amount of adsorbed metal per gram of bagasse was calculated, where a plot of q_{Equation} (mg g^{-1}) in function of C_{Equation} (mg L^{-1}) was built.

RESULTS AND DISCUSSION

Characterisation of adsorbent

Figure 1 shows the infrared spectrum of the materials. After chemical modification of bagasse with citric acid (Figure 1C, D), the presence of carboxylic groups represented by stretching vibrations at 1,730 cm^{-1} was observed. These characteristic vibrations are absent in Figure B, where the modification was done only with NaOH. These same groups can be observed for the citric acid spectrum (Figure 1E). Comparing the spectrum A (without modification) and C (modified with NaOH and citric acid), there is a peak with good intensity in the region of 1,730 cm^{-1}, thus confirming the insertion of carboxylic groups. This result corroborates the study carried out by Rodrigues *et al.* (2006), wherein the presence of carboxylic groups was confirmed in the structure of Paraju sawdust celluloses after chemical treatment with NaOH and citric acid. Depending on the pH, these groups become negative sites that facilitate cation interaction in solution. Therefore, according to Rodrigues *et al.* (2006), Sousa *et al.* (2007) and Feng *et al.* (2009), higher adsorption of metal ions on natural adsorbents containing carboxylic groups commonly takes place at pH 5.0. Thus, it was chosen as the best value for adsorption experiments.

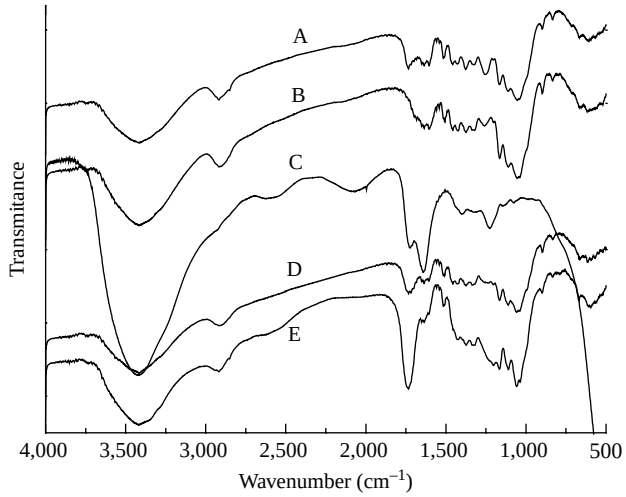

Figure 1 | Infrared spectrum for B-N (A) and B-S (B); B-CA (C); B-CAS (D) and also just citric acid (E).

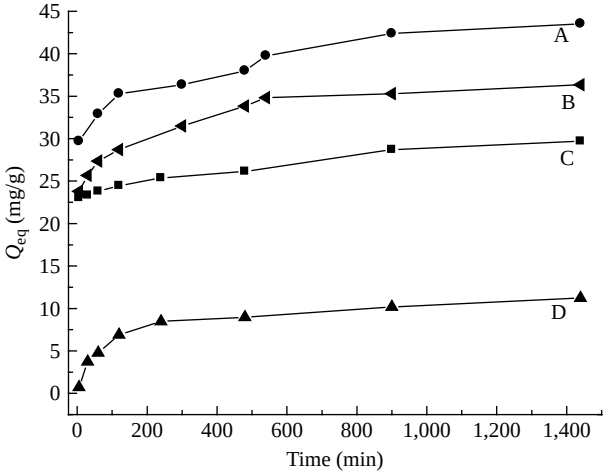

Figure 2 | Pb adsorption kinetics in B-CA (A), B-CAS (B), B-S (C) and B-N (D).

Effect of contact time on adsorption profile

The adsorption kinetics of Pb^{2+} ion on B-S, B-CA, B-CAS and B-N is represented in Figure 2. As can be verified, higher amounts of Pb^{2+} ion were adsorbed by modified materials (B-S, B-CA, B-CAS) than by unmodified material (B-N), attesting the effective chemical modification of the materials. A brief evaluation of these data shows that uptake of Pb^{2+} ions on sugarcane bagasse chemically modified with citric acid is higher than for other materials. Such a result is a consequence of the insertion of carboxylic groups on the material surface, making the physical attraction to Pb^{2+} ion easier. These data corroborate those observed in the infrared spectra (Figure 1). The reached equilibrium time was around 1,440 min (24 h) for all materials.

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This value is lower than in the adsorption of Pb^{2+} ion on Saccharomyces cerevisiae (48 h) (Ferreira *et al.* 2007). Therefore, the adsorption process using bagasse can be considered efficient.

In order to characterise the kinetics for each adsorbent, pseudo-first-order and pseudo-second order kinetic models were applied. Pseudo-first-order kinetic models follow Lagergren model, expressed by Equation (2) (Doğan *et al.* 2004; Noeline *et al.* 2005; Özcan *et al.* 2005; Pérez-Marín *et al.* 2007; Feng *et al.* 2009).

$$\log(q_{eq} - q_t) = \log q_{eq} - \frac{k_1 \times t}{2.303} \quad (2)$$

where q_t is the adsorbed amount of metallic ions (mg g^{-1}) in t time (min) and k_1 is the pseudo-first-order constant (min^{-1}). Through linear and angular constant of log graphic ($q_{eq} - q_t$) in function of time, q_{eq} and k_1 can be calculated, respectively. As observed in Table 1, q_{eq} values obtained experimentally do not fit those calculated through Equation (2). Besides, r^2 values are distant from 1, suggesting that adsorption does not follow a first-order reaction. The pseudo-second-order model for the metal adsorption kinetics in different sugarcane bagasse is presented by Equation (3) (Doğan *et al.* 2004; Noeline *et al.* 2005; Özcan *et al.* 2005; Pérez-Marín *et al.* 2007; Feng *et al.* 2009).

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}} \quad (3)$$

where k_2 is the pseudo-second order constant (g mg^{-1} min^{-1}) obtained by calculation of linear coefficient and q_{eq} is calculated through angular coefficient (Figure 3). Experimental calculated values of q_{eq}, k_2 and r^2 are shown in Table 1.

It can be verified, using data presented in Table 1, that q_{eq} values (cal.) are close to the experimental model according to the pseudo-second-order kinetic model, and the values obtained for the linearity coefficient are near 1. Besides, r^2 values for this model are superior to the ones obtained for the pseudo-first-order model. Also, it was verified that q_{eq} values for this model (pseudo-second-order) are close to the experimentally obtained values, confirming that this adsorption occurs according to pseudo-second-order kinetics, and that the adsorption is controlled by a chemical adsorption.

Adsorption isotherms

After determination of equilibrium time of Pb^{2+} ions established by the interaction between solid and liquid phases, i.e. 24 h, the adsorption isotherms were built. In Figure 4, Pb^{2+} ion adsorption in B-S, B-CA, B-CAS and B-N bagasses is shown in function of $C_{Equation}$ (mg L^{-1}) by the Pb adsorption amount $q_{Equation}$ (mg g^{-1}). As observed, the sugarcane bagasse treated with citric acid (B-CA) showed higher adsorption towards Pb^{2+} ions than the other materials. This treatment provided a considerable increase of adsorption of *ca.* three-fold higher than natural bagasse (B-N). In a similar study, Tarley & Arruda (2003) showed a value of $q_{Equation}$ (9.20 mg g^{-1}) for Pb^{2+} ions onto *Luffa cylindrica*, a natural adsorbent. This result is lower than the one for B-CA (52.63 mg g^{-1}), indicating that this material is considered a promising adsorbent for this metal.

The adsorption isotherms were adjusted to Langmuir and Freundlich linear models, Equations (4) and (5), respectively.

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{q_{m^b}} + \frac{C_{eq}}{q_m} \quad (4)$$

Table 1 | Kinetic parameters of the pseudo-first and pseudo-second-order model for Pb^{2+} adsorption

		Kinetic in pseudo-first-order			Kinetic in pseudo-second-order		
Adsorbent	$q_{Equation}$ (exp.) (mg g^{-1})	$k_1(10^{-3})$	$q_{Equation}$ (cal.) (mg g^{-1})	r^2	$k_2(10^{-3})$	$q_{Equation}$ (cal.) (mg g^{-1})	r^2
B-N	11.23	2.30	7.19	0.871	0.96	11.62	0.996
B-S	29.70	1.99	6.95	0.951	1.40	29.75	0.998
B-CA	43.53	2.50	13.65	0.940	0.61	44.05	0.997
B-SCA	36.33	2.76	10.99	0.948	1.00	37.03	0.999

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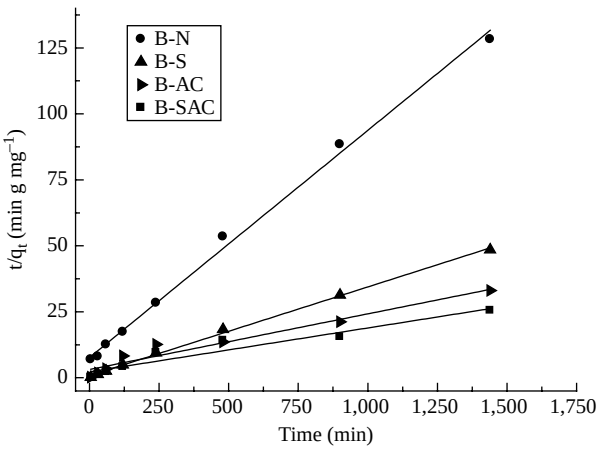

Figure 3 | Pseudo-second-order kinetic graphic for Pb adsorption in modified and *in natura* sugarcane bagasse.

where, b is a constant that indicates adsorption intensity; q_m is the capacity measurement that indicates the maximum adsorption intensity.

$$\log q_{eq} = \log k_f + \left(\frac{1}{n}\right)\log C_{eq} \quad (5)$$

where, k_f can indicate the ion adsorption in the adsorbent and n indicates, quantitatively, the reactivity of adsorbent energetic sites (Sodré *et al.* 2001).

The Langmuir model establishes that adsorption is considered similar to the one in chemical reaction nature; it is also observed that there is no interaction among adsorbed molecules themselves, only between them and the adsorbent. Molecule adsorption on the solid surface of the adsorbent is limited to one single layer (monolayer). On the other hand, the Freundlich model establishes that the amount of adsorbed ions onto adsorbate follows an exponential distribution of adsorption values (Özacar & Şengil 2003; Doğan *et al.* 2004; Dahiya *et al.* 2008; Gonçalves *et al.* 2008).

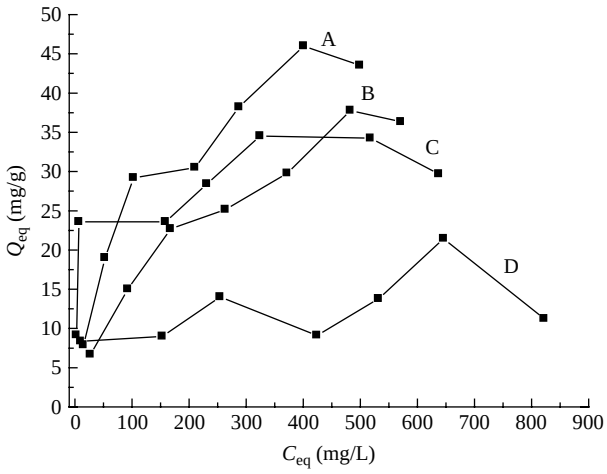

Figure 4 | Pb adsorption isotherms in B-AC (A), B-CAS (B), B-S (C) and B-N (D).

In Table 2, it can be observed that there was a better adjustment of data for the Langmuir model, and it will be used to analyse the parameters involved in this adsorption.

According to Sodré *et al.* (2001), the Langmuir adsorption model has been widely used to estimate adsorption capacity of several chemical elements and species, and their principal advantage over other isotherms is allowing quantification of the adsorption capacity of chemical species (q_m) and evaluating a constant related to linking energy (b).

After modifications of the sugarcane bagasse structure, there was a considerable increase in the maximum adsorption capacity, mainly for B-CA. Regarding values for b, adsorption intensity, it was verified that, before and after the treatment, there was a great metal affinity by the bagasse, and the highest value was for the treatment with NaOH. After the treatment, there was an improvement in r values (linear correlation) for Langmuir isotherm. According to Sodré *et al.* (2001), when n values (Freudlich isotherms) are different from 1, the energetic site distribution tends to vary with adsorption density.

Comparing the q_m value obtained in the present study to the others that have already been determined, such as pinups cork (3.33 mg g^{1}), Betonies clay (6.00mg g^{-1}), apple residues (8.00 mg g^{1}) and natural luffa *Luffa cylindrica* (9.20 mg g^{1}), it was verified that modified sugarcane bagasse presented higher values than the ones reported, confirming that it will be a promising adsorbent for this metal (Tarley & Arruda 2003).

Table 2 | Langmuir and Freundlich isotherm constants for Pb^{2+} adsorption on B-CA, B-CAS, B-S and B-N

	Langmuir			Freundlich		
Adsorbent	q_m (mg g^{-1})	b (L mg^{-1})	r^2	k_f (mg g^{-1})	n	r^2
B-N	11.63	0.087	0.932	0.16	0.143	0.325
B-S	30.68	0.101	0.983	0.46	0.178	0.939
B-CA	52.63	0.011	0.989	4.33	0.479	0.661
B-SCA	35.09	0.007	0.995	5.18	0.559	0.980

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Thermodynamic parameters

Thermodynamic parameters for adsorption ΔH (enthalpy), ΔS (entropy) and ΔG (Gibbs energy) were calculated from Equations (6) and (7):

$$\Delta G = -\mathrm{RT} \ln k_d \quad (6)$$

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

where, k_d corresponds to the ratio between q_{eq} and C_{eq}, R is the gas constant and assumes the value of 8.314 $\mathrm{JK^{-1}\,mol^{-1}}$, T is the experiment temperature expressed in Kelvin (K). Enthalpy and other parameters (Table 3) were obtained from graphic construction of $\ln k_d$ versus $1/T$, from Van't Hoff Equation.

When presenting a negative value of Gibbs free energy (ΔG), a favourable interaction is indicated, and as a consequence a more spontaneous system will be observed (Gonçalves *et al.* 2008; Guerra *et al.* 2008). Besides measuring the strength that guides a determined reaction, Gibbs energy also indicates how far the initial state of the system is from the equilibrium.

After the bagasse modification, it was possible to observe a negative increase in values of ΔG, when compared to unmodified bagasse. Thus, it was verified that alterations in the bagasse made metal adsorption more energetically favourable, mainly for adsorption of bagasse modified with citric acid, corroborating its higher adsorption capacity.

Values of ΔH for adsorption of modified bagasse with citric acid were close to values referring to chemical adsorption (40 $\mathrm{kJ\,mol^{-1}}$), corroborating data from the pseudo-second-order kinetics. Negative values of enthalpy indicate that this adsorption has exothermal nature, but it is noted that lower than zero values for entropy demonstrate that certain ordering of those metals on the adsorbent surface occurred. Thus, it can be observed that adsorption is ruled by enthalpy factors rather than entropic ones.

Table 3 | Thermodynamic parameters obtained from bagasse adsorption

Adsorbent	k_d	ΔG ($\mathrm{kJ\,mol^{-1}}$)	ΔH ($\mathrm{kJ\,mol^{-1}}$)	ΔS ($\mathrm{JK^{-1}mol^{-1}}$)
B-N	13.67	−6.48	−17.37	−37.00
B-S	6.61	−6.68	−9.39	−9.00
B-CA	87.23	−11.08	−39.53	−95.00
B-SCA	63.63	−10.29	−31.74	−72.00

Table 4 | Adsorption–desorption of Pb^{+2} values, initial concentration of 934 $\mathrm{mg\,L^{-1}}$

Adsorbent	Concentration adsorbed ($\mathrm{mg\,L^{-1}}$)	Concentration desorbed ($\mathrm{mg\,L^{-1}}$)	% Desorption
B-N	112.3	70.6	62.9
B-S	297.0	226.1	76.1
B-CA	435.3	421.5	96.8
B-SCA	363.3	246.1	67.7

Lead desorption

In order to assess desorption of Pb^{2+} ions adsorbed onto materials and its reuse, an acid solution was investigated as eluent. This assay was carried out by loading the bagasse with a known amount of Pb^{2+}, followed by washing with 150 mL milli-Q water and drying for 24 h in an oven at 50°C. After this period, the bagasse was soaked in a 0.1 $\mathrm{mol\,L^{-1}}$ HCl solution for Pb^{2+} recovery. Then, the resulting concentration was determined and the desorbed Pb^{2+} percentage was verified; the obtained values are shown in Table 4 (Feng *et al.* 2009).

Considering the percentage found for desorption, it is verified that B-CA material is also significant in the desorption process, as well as in adsorption, where the desorbed concentration is higher than the others. The desorbed percentage can be considered satisfactory for a possible reutilisation of these materials for new adsorption phases. The precision assessed in terms of repeatability based on relative standard deviation (RSD) was evaluated for the modified bagasse with citric acid, and the RSD was found to be 2% for four cycles involving adsorption and desorption.

CONCLUSION

Chemical modification of sugarcane bagasse was made in this study in order to introduce carboxylic groups to improve Pb^{2+} ion adsorption. The modifications were verified by spectroscopy in the infrared region, when a band around 1,730 $\mathrm{cm^{-1}}$ peak area indicated the presence

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of the carboxylic group. Through experiments and calculations, it was possible to check that sugarcane bagasse, after chemical treatment, had an improvement on its adsorbent properties, mainly the bagasse modified only with critic acid. The adsorption process follows the adsorption model of Langmuir isotherm, and lead adsorption in aqueous solution follows pseudo-second-order kinetics. Chemical modification of sugarcane bagasse, besides increasing adsorbent properties, also made the system energetically more favourable as shown by Gibbs free energy values, and the process was considered exothermal with disorder decrease. It was also verified that, after the modifications, there was an improvement in lead desorption, indicating that this material can be reused.

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REFERENCES

Albertini, S., Carmo, L. F. & Prado-Filho, L. G. 2007 Use of sawdust and pulp from cane as adsorbents of cadmium. *Ciência Tecnologia Alimentos.* **27**(1), 113–118.

Annadurai, A., Juang, R. S. & Lee, D. J. 2002 Adsorption of heavy metals from water using banana and orange peels. *Water Sci. Technol.* **47**(1), 185–190.

Dahiya, S., Tripathi, R. M. & Hegde, A. G. 2008 Biosorption of heavy metals and radionuclide from aqueous solutions by pre-treated arca shell biomass. *J. Hazard. Mater.* **150**, 376–386.

Dietrich, K. N., Ware, J. H., Salganik, M., Radcliffe, J., Rogan, W. J., Rhoads, G. G., Fay, M. E., Davoli, C. T., Denckla, M. B., Bornschein, R. L., Schwarz, D., Dockery, D. W., Adubato, S. & Jones, R. L. 2004 Effect of chelation therapy on the neuropsychological and behavioral development of lead-exposed children after school entry. *Pediatrics* **114**, 19–26.

Doğan, M., Alkan, M., Türkyılmaz, A. & Özdemir, Y. 2004 Kinetics and mechanism of removal of methylene blue by adsorption onto perlite. *J. Hazard. Mater.* **109**, 141–148.

Feng, N., Guo, X. & Liang, S. 2009 Adsorption study of copper (II) by chemically modified orange peel. *J. Hazard. Mater.* **164**, 1286–1292.

Ferreira, J. M., Silva, F. L. H., Alsina, O. L. S., Oliveira, L. S. C., Cavalcanti, E. B. & Gomes, W. C. 2007 Equilibrium and kinetic study of Pb^{2+} biosorption by *Saccharomyces cerevisiae*. *Química Nova.* **30**, 1188–1193.

Gavrilescu, M. 2004 Removal of heavy metals from the environment by biosorption. *Eng. Life Sci.* **4**, 219–232.

Gonçalves, M., Oliveira, L. C. A. & Guerreiro, M. C. 2008 Magnetic niobia as adsorbent of organic contaminants in aqueous medium: effect of temperature and pH. *Química Nova.* **31**, 518–522.

Guerra, D. L., Airoldi, C., Lemos, V. P., Angélica, R. S. & Viana, R. R. 2008 Application of Zr/Ti-PILC in the adsorption process of Cu(II), Co(II) and Ni(II) using adsorption physico-chemical models and thermodynamics of the process. *Química Nova.* **31**, 353–359.

Gurgel, L. V. A. & Gil, L. F. 2009 Adsorption of Cu(II), Cd(II), and Pb(II) from aqueous single metal solutions by succinylated mercerized cellulose modified with triethylenetetramine. *Carbohydr. Polym.* **77**, 142–149.

Gurgel, L. V. A., Karnitz Júnior, O., De Freitas, R. P. & Gil, L. F. 2008 Adsorption of Cu(II), Cd(II), and Pb(II) from aqueous single metal solutions by cellulose and mercerized cellulose chemically modified with succinic anhydride. *Bioresour. Technol.* **99**, 3077–3083.

Karnitz Júnior, O., Gurgel, L. V. A., De Freitas, R. P. & Gil, L. F. 2009 Adsorption of Cu(II), Cd(II), and Pb(II) from aqueous single metal solutions by mercerized cellulose and mercerized sugarcane bagasse chemically modified with EDTA dianhydride (EDTAD). *Carbohydr. Polym.* **77**, 643–650.

Karnitz Júnior, O., Gurgel, L. V. A. & Gil, L. F. 2010 Removal of Ca(II) and Mg(II) from aqueous single metal solutions by mercerized cellulose and mercerized sugarcane bagasse grafted with EDTA dianhydride (EDTAD). *Carbohydr. Polym.* **79**, 184–191.

Khormaei, M., Nasernejad, B., Edrisi, M. & Eslamzadeh, T. 2007 Copper biosorption from aqueous solutions by sour orange residue. *J. Hazard. Mater.* **149**, 269–274.

Lei, Z., Yu, T., Ai-zhong, D. & Jin-sheng, W. 2008 Adsorption of Cd(II), Zn(II) by extracellular polymeric substances extracted from waste activated sludge. *Water Sci. Technol.* **58**, 195–200.

National Council on the Environment 2005 *Resol. No. 357* de 17/03/2005 http://www.mma.gov.br/port/conama/legiano1.cfm?codlegitipo=3&ano=2005/ (accessed 10 July 2009).

Noeline, B. F., Manohar, D. M. & Anirudhan, T. S. 2005 Kinetic and equilibrium modeling of lead (II) sorption from water and wastewater by polymerized banana stem in a batch reactor. *Sep. Purif. Technol.* **45**, 131–140.

Oliveira, F. C., Mattiazzo, M. E., Marciano, C. R. & Abreu, Jr. C. H. 2002 Movement of heavy metals in an Oxisol fertilized with municipal solid waste compost. *Pesquisa Agropecuária Brasileira* **37**, 1787–1793.

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Özacar, M. & Şengil, İ. A. 2003 Adsorption of reactive dyes on calcined alunite from aqueous solutions. *J. Hazard. Mater.* **B98**, 211–224.

Özcan, A., Özcan, A. S., Tunali, S., Akar, T. & Kiran, I. 2005 Determination of the equilibrium kinetic and thermodynamic parameters of adsorption of copper (II) ions onto seeds of capsicum annuum. *J. Hazard. Mater.* **B124**, 200–208.

Pérez-Marín, A. B., Zapata, V. M., Ortuño, J. F., Aguilar, M., Sáez, J. & Lloréns, M. 2007 Removal of cadmium from aqueous solutions by adsorption onto orangewaste. *J. Hazard. Mater.* **B139**, 122–131.

Rodrigues, R. F., Trevezoli, R. L., Santos, L. R. G., Leão, V. A. & Botaro, V. R. 2006 Heavy metals sorption on treated wood sawdust. *Engenharia Sanitária Ambiental.* **11**(1), 21–26.

Romera, E., González, F., Ballester, A., Blázquez, M. L. & Muñoz, J. A. 2007 Comparative study of biosorption of heavy metals using different types of algae. *Bioresour. Technol.* **98**, 3344–3353.

Schvartsman, S. 1991 *Intoxicações agudas*, 4th edition. Sarvier, São Paulo, pp. 214–215.

Shaik, A. P., Sankar, S., Reddy, S. C., Das, P. G. & Jamil, K. 2006 Lead-induced genotoxicity in lymphocytes from peripheral blood samples of humans: in vitro studies. *Drug Chem. Toxicol.* **29**(1), 111–124.

Sodré, F. F., Lenzi, E. & Costa, A. C. 2001 Applicability of adsorption models to the study of copper behaviour in clayey soils. *Química Nova.* **24**, 324–330.

Sousa, F. W., Moreira, S. A., Oliveira, A. G., Cavalcante, R. M., Nascimento, R. F. & Rosa, M. F. 2007 The use of green coconut shells as absorbents in the toxic metals. *Química Nova.* **30**(5), 1153–1157.

Tarley, C. R. T. & Arruda, M. A. Z. 2003 Adsorbents natural and potential applications of natural sponge (*Luffa cylindrica*) the removal of lead in wastewater laboratory. *Revista Analítica.* **4**, 26–31.

Tarley, C. R. T. & Arruda, M. A. Z. 2004 Biosorption of heavy metals using rice milling by-products. Characterisation and application for removal of metals from aqueous effluents. *Chemosphere* **54**, 987–995.

Yan, G. & Viraraghavan, T. 2008 Mechanism of biosorption of heavy metals by *Mucor rouxii*. *Eng. Life Sci.* **8**, 363–371.

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