Artigo

Removal of Metals Ions from Aqueous Solution Using Modified Sugarcane Bagasse

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Remoção de Íons Metálicos em Solução Aquosa Utilizando Bagaço de Cana de Açúcar

Resumo: O presente estudo descreve a preparação de bagaço de cana-de-açúcar quimicamente modificado com ácido cítrico bem como a adsorção de íons Cu (II), Cr (III) e Pb (II) a partir de soluções aquosas pelo bagaço de cana *in natura* e quimicamente modificado. Análises de adsorção em sistema de batelada foram realizadas em função do tempo de contato com a concentração de adsorvente. A espectrometria de absorção atômica com chama foi utilizada para mensurar as concentrações de íons. Neste sentido, dados experimentais de adsorção foram ajustados aos modelos lineares de Langmuir e Freundlich, e a capacidade máxima de adsorção foi estimada para íons de cobre em função de modificações. As modificações químicas foram obtidas a 1.730 cm^{-1} de pico nos espectros de infravermelho, referindo-se aos grupos carboxilato. O tempo necessário para que a adsorção atingisse o equilíbrio foi de 24 horas e a cinética apresenta comportamento descrito pela equação de pseudo-segunda ordem. Neste contexto, uma significativa melhoria na adsorção de íons foi observada após a modificação do bagaço, de acordo com o modelo linear da Isoterma de Langmuir, apontando capacidade máxima de adsorção para íons Cu (II), Pb (II) e Cr (III) entre 6,87 e 31,53 mg.g^{-1}, 11,63 a 52,63 mg.g^{-1} e 21,87 a 22,08 mg.g^{-1}, respectivamente.

Palavras-chave: Adsorção; bagaço de cana modificado; íons metálicos; cinética; parâmetros termodinâmicos.

Abstract

This work describes the preparation of sugarcane bagasse chemically modified with citric acid and evaluated adsorption of Cu(II), Cr(III) and Pb(II) ions from aqueous solutions by sugarcane bagasse *in natura* and chemically modified. Adsorption analyses in batch system were carried out in function of contact time with the adsorbent and adsorbate concentration. Flame atomic absorption spectrometry was used to determine the ions concentrations. Adsorption experimental data were fitted to Langmuir and Freundlich linear models, and the maximum adsorption capacity was estimated for copper ions in function of modifications. The chemical modifications were confirmed at 1.730 cm^{-1} peak in infrared spectra, referring to the carboxylate groups. The required time for the adsorption to reach equilibrium was 24 h and the kinetics follows the behavior described by the pseudo-second order equation. Besides, a significant improvement of the ions adsorption has been observed after the bagasse modification, according to Langmuir isotherm linear model, showed maximum adsorption capacities for Cu(II), Pb(II), and Cr(III) ions ranging from 6.87 to 31.53 mg.g^{-1}, 11.63 to 52.63 mg.g^{-1}, and 21.87 to 22,08 mg.g^{-1}, respectively.

Keywords: Adsorption; modified sugarcane bagasse; metals ions; kinetics; thermodynamic parameters.

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1. Introduction

Removing pollutants from water and wastewater has grown with rapid industrialization, as well as increase in environmental pollution caused by metals ions. That is of great concern because could causing the deterioration of some ecosystems and can reach the food chain, accumulating in

living tissues and would probably cause various diseases and disorders.[1-4]

Conventional methods that have been used to remove metals ions from various industrial effluents usually include chemical precipitation, flocculation, membrane separation, ion exchange, evaporation, and electrolysis and are often costly or ineffective, especially in removing of these ions in dilute solution. Because of this, the development of efficient and low-cost separation processes is therefore of utmost importance.[2-3, 5]

In recent years, there has been considerable interest in the use of biological materials, including algae, bacteria, fungi, agricultural by-products and residues as adsorbents to remove metals ions from aqueous solution by adsorption. Among these materials, agricultural by-products and biomass are relatively cheap and exhibit very high adsorption capacities.[6-7] To the choosing of appropriate adsorbent are taken into consideration mainly the parameters as sorption capability, regeneration ability, kinetic parameters, price and market availability. The maximum sorption capability is the most important parameter that characterizes each sorbent.[3]

Another important parameter are kinetic parameters because allow to determine the rate at which metal ions are transferred from the solution to the adsorbent surface and are accumulated during the sorption process.[3] The residence time of a solute on the adsorbent surface is important to determining whether the process will go completion or not and also to estimate the total adsorption. The evaluation of adsorption rate and maximum sorption capability are valuable information about the interactions during the sorption and have therefore attracted the interests of almost all involved in experimenting with adsorption on solid surfaces. They are also an important tool for the theoretical evaluation and interpretation of thermodynamic parameters.[3, 8-9]

Recently many studies are being developed with the aim of using sorption processes to treatment effluents containing metals ions especially using agricultural by-products and waste with sorbent.[3,10] Khormaei *et al.,* used sour orange residue to biosorption Copper from aqueous solutions.[10] Gurgel *et al.,* investigated the effect of chemical modified in cellulose to adsorption of Cu(II), Cd(II), and Pb(II) from aqueous single metal solutions.[5] Witek-Krowiak *et al.,* observed the biosorption of heavy metals from aqueous solutions onto peanut shell.[3] Kwon *et al.,* scoria used in the removal of divalent heavy metals and arsenic (III) from aqueous solution.[11] Mohammad *et al.,* used the potential of physic seed hull of *Jantropha curcas* L. as an adsorbent for the removal of metal ions from aqueous solution.[12]

The objective of this paper is investigate the possible use of sugarcane bagasse as an alternative adsorbent material for Cu(II), Pb(II) and Cr(III) ions removal from aqueous solutions. The Langmuir and Freundlich equations were used to fit the equilibrium isotherm. The adsorption capacity was determined using various kinetic models. The dynamic behavior of the adsorption was investigated on the effect of concentration and temperature. The thermodynamic parameters were also evaluated from the adsorption measurements.

2. Experimental

2.1. Reagents

Analytical grade chemical reagents were used throughout the experiment. Standard solutions of 1.000 mg.L^{-1} from copper, lead and chromium were prepared singly from copper nitrate [Cu(NO$_3$)$_2$ Vetec, 99 %], lead nitrate [Pb(NO$_3$)$_2$ Vetec, 99 %], chromium nitrate ninth-hydrate [Cr(NO$_3$).9H$_2$O, Vetec, 99 %] and necessary dilutions were done with deionized water. 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.

2.2. Equipments

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 (1mg sample/100mg KBr) and put in a pastillator, then 4.000 to 400 cm^{-1} spectral range was analysed. A Flame Atomic Absorption Spectrometer (FAAS) (GBC 932 plus), equipped with deuterium lamp for background correction and a single-element hollow cathode lamps and air-acetylene burner was used for the determination of Pb (II), Cu (II) and Cr(III) ions, at their respective wavelengths 217,0 nm; 327,4 nm and 357,9 nm, was used for metal quantification For quantification all samples were previously diluted in Milli-Q water.

2.3. 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.

2.3.1. Modification with citric acid (B-CA)

The modification 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 55C, and after 24 h the temperature was raised to 120˚C and kept for 90 min. Later the bagasse was washed with deionized water (60–80˚C) and dried at 55˚C for 24 h.[13]

2.4. Adsorption study

2.4.1. Effect of contact time on adsorption profile

In order to check the effect of chemical modification on bagasse, the material (B-CA) were compared with *in natura* bagasse (B-N). The adsorption experiments were performed with each material and ions, singly, it using to 50 mL of solutions with initial concentration of 1.000 mg.L^{-1} were agitated with 0.5 g of bagasse in an orbital shaker. Ten aliquots of 500 mL aliquots were collected from supernatant in a time interval ranging from 15 to 1.440 min and transferred to volumetric flask of 50 mL whose volume was adjusted up with deionised water. The amount of chromium 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 and was calculated according to Equation (1):[3, 14]

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

where C_0 and C_{eq} are the initial metal concentration and in equilibrium of the solution (mg.L^{-1}), respectively, V is the solution volume (mL), and M the bagasse mass (g).

2.4.2. Adaptions isotherms

Study of the metal ion retention properties of the composites was carried, for this solutions of each ions (Cu(II), Pb(II) and Cr (III)) at different concentrations were prepared, ranging from 100 to 1.000 mg.L^{-1}. After, 50 mL of solutions of ions were shaken individually with 0.5 g of each material (B-CA and B-N) in an orbital shaker for 24 h. Next, the mixtures were filtrated and the solutions were analyzed by FAAS. At the end of this step, was calculated using the Equation (1), the amount of adsorbed metal per gram of bagasse and a plot of q_{eq} in function of C_{eq}.

3. Results and Discussion

3.1. Adsorbent characterization

Figure 1 shows the infrared spectra of modified and *in natura* sugarcane bagasse. After the bagasse modification with citric acid (Figure 1 C), the presence of carboxylate groups at 1.730 cm^{-1} was observed. Such result corroborates the study done by Rodrigues *et al.*,[13] that verified the occurrence of carboxylic groups in Paraju sawdust after treatment with NaOH and citric acid. The carboxylic groups present *in natura* adsorbents are usually weak acids and make negative sites in medium moderately acid, the interaction of cations in solution becomes easier. These groups are usually weak acids, depending on the pH become negative sites that facilitate cation interaction in solution. According to Rodrigues *et al.*,[13] Ozsoy and Kumbur[6] and Feng *et al.*,[7] the adequate pH for these sites to become more reactive is usually around pH 5. Therefore, pH 5 was chosen to be used throughout the experiments and was maintained at 5 with the addition of hydrochloric acid or sodium hydroxide 0.1 mol.L^{-1}.
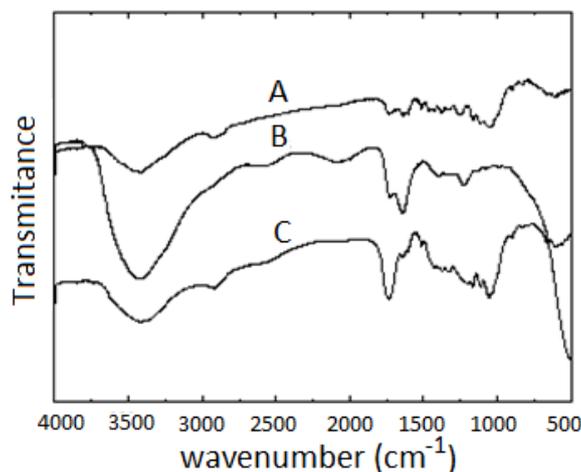

Figure 1. Infrared spectrum for B-N (A), citric acid (B) and B-CA (C)

3.2. Effect of contact time on adsorption profile

Figure 2 show the metals ions adsorption in the B-CA and B-N materials in function of shaking time. The highest adsorption was observed for the lead, followed of cuper and chromium for B-CA material, and preliminarily, it was observed that the chemical modification improved the adsorbing properties of the bagasse. Regarding the shaking time, it was observed that, for all experiments, the system tends to

reach equilibrium around 500 min, however, a slight increase on adsorption was verified around 1.440 min (24 h). Pergher *et al.,* obtained equilibrium after a period around 12 h.[15] Ghorbel-Abid, Galai and Trabelsi-Ayadi obtained system equilibrium in around 20 h.[16]
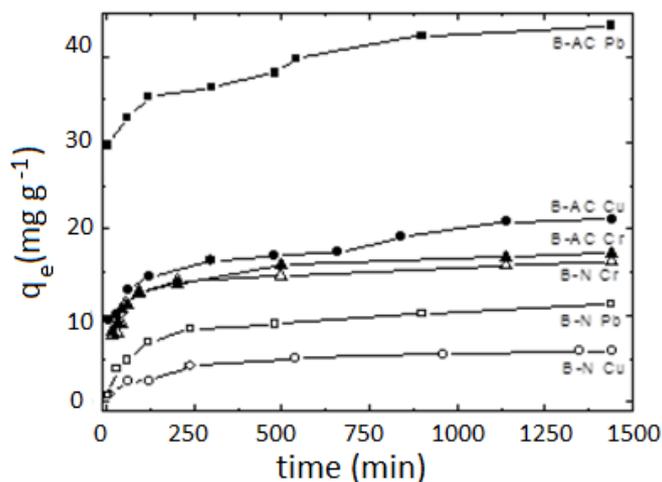

Figure 2. Adsorption of Cu(II), Pb(II) and Cr(III) in B-CA and B-N in function of time

From data presented in Figure 2, it was possible to characterize the kinetics for each adsorbent, using pseudo-first and pseudo-second order kinetic models. The pseudo-first order kinetics follows the Lagergren model expressed by Equation 2:[7-9, 17-18]

$$\log\left(q_{eq} - q_t \right) = \log q_{eq} - \frac{K_1 \, x \, t}{2.303} \qquad (2)$$

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. Comparing the experimentally obtained values for q_{eq} the calculated by Equation 2, it was observed that they were not close (Table 1). Besides, r^2 values are distant from 1, suggesting that adsorption does not follow a first-order reaction.

Therefore, the pseudo-second order model (Equation 3) was applied for the kinetics of metal adsorption.[7-9, 18-19]

$$\frac{t}{q_t} = \frac{1}{K_2 q_{eq}^2} + \frac{t}{q_{eq}} \qquad (3)$$

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 and calculated values of q_{eq}, K_2 and r^2 are shown in Table 1.
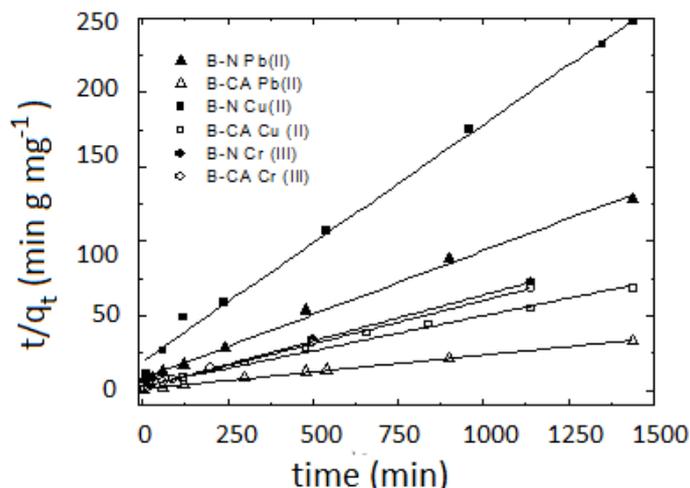
Figure 3. Pseudo-second-order kinetic graphic for Pb(II), Cu(II) and Cr(III) adsorption in modified and *in natura* sugarcane bagasse

Table 1. Kinetic parameters of the pseudo-first and pseudo-second-order model for metals ions adsorption

Material/íons	q_{eq} (exp.) (mg.g^{-1})	Pseudo-first-order kinetic			Pseudo-second-order kinetic		
		K_1	q_{eq} (cal.)(mg.g^{-1})	r^2	K_2	q_{eq} (cal.)(mg.g^{-1})	r^2
B-N Pb(II)	11.23	2.30×10^{-3}	7.19	0.8710	0.96×10^{-3}	11.62	0.9960
B-N Cu(II)	6.87	2.30×10^{-3}	7.56	0.8180	1.30×10^{-4}	6.29	0.9960
B-N Cr(III)	16.21	2.58×10^{-3}	6.33	0.8899	2.13×10^{-3}	16.10	0.9992
B-CA Pb(II)	43.53	2.50×10^{-3}	13.65	0.9400	0.61×10^{-3}	44.05	0.9970
B-CA Cu(II)	31.53	2.30×10^{-3}	11.56	0.8770	7.39×10^{-4}	21.28	0.9890
B-CA Cr(III)	17.20	2.67×10^{-3}	7.10	0.9540	1.87×10^{-3}	17.15	0.9990

Taking into account the values of correlation coefficient for pseudo-first-order and pseudo-second-order kinetic models, it can be verified that the second one fits for experimental data very well. The theoretical q_{eq} values are equivalent to those observed for experimental q_{eq} values, suggesting that the biosorption followed a pseudo-second-order model. Besides, the value of r^2 (linear correlation) around 1 for the pseudo-second-order confirms that the adsorption kinetics is controlled by this order and that there is a strong interaction between adsorbent and adsorbate. The pseudo-second-order kinetic suggests that chemisorption is responsible of metals ion adsorption.[18-19]

3.3. Adsorption isotherms

The adsorption isotherms (Figure 4) were built by setting the equilibrium time between adsorbate and adsorbent at 24 h. It was verified an increments in metals ions adsorption for B-CA regarding the *in natura* bagasse. Similar results have been observed in copper adsorption in Paraju sawdust modified with sodium hydroxide and citric acid[13] and other studies by Han *et al.*[20] The high adsorption efficiency provided by chemical modification can also be assessed by comparison with other natural materials. The results obtained by Sari *et al.,* in which Turkish kaolinite clay war used in the lead adsorption process, showed lower values of q_{eq} than

observed by using B-CA material.[21] The results obtained by Garcia-Reye and Rangel-Mendez with agave bagasse used for chromium adsorption indicate lower qeq values than those observed for B-CAS.[22] Therefore,

commercial activated carbon (CAC) has still been used intensively for removing heavy metals such as lead, chromium, zinc, lithium and mercury.[23]
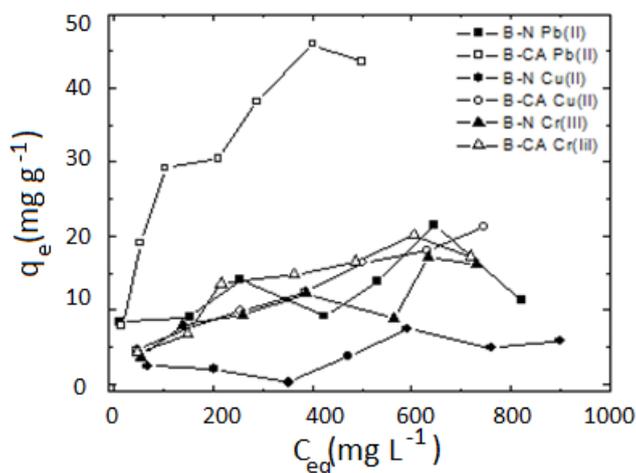

Figure 4. Adsorption isotherms of metals ions on modified and *in natura* sugarcane bagasse

In order to verify the adsorptive behavior of Cr(III) ion, the adsorption isotherms were adjusted to Langmuir and Freundlich linear models, Equations (4) and (5), respectively:

$$\frac{1}{q_{eq}} = \frac{1}{q_m} + \left(\frac{1}{q_m\,K_L}\right)\frac{1}{C_{eq}} \qquad (4)$$

where q_{eq} is the equilibrium Cr(III) concentration on the adsorbent (mg.g^{-1}), C_{eq} the equilibrium Cr(III) concentration in the solution (mg.L^{-1}), q_{max} the monolayer adsorption capacity of the adsorbent (mg.g^{-1})

and K_L the Langmuir adsorption constant (L.mg^{-1}) related to the free energy of adsorption. A plot of $1/q_{eq}$ versus $1/C_{eq}$ for the adsorption gives a straight line of slope $1/(q_{max}K_L)$ and intercept $1/q_{max}$.[9]

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

In which K_f (mg g^{-1}) can indicate the ion adsorption in the biomass and n indicates, quantitatively, the biomass energetic site reactivity.[2, 24-26]

Langmuir model assumes that the forces that act on the adsorption are similar to chemical reactions, also observed that there is no interaction among adsorbed species, only

between them and the adsorbent. The adsorption on the solid surface of the adsorbent occurs in one single layer (monolayers). Freundlich model, on the other hand, was one of the first proposed equations to relate the amount of adsorbed ions to the material concentration in the solution and corresponds to the exponential distribution of adsorption values.[9-10, 17, 27, 28]

In Table 2, are the values estimated for Langmuir and Freundlich isotherm, 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, this model served to estimate the maximum adsorption capacities (q_{max}) where they could not be reached in the experiments.

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_{max}) and evaluating a constant related to linking energy (K_L).[7, 9, 29]

Table 2. Kinetic parameters of the pseudo-first and pseudo-second-order model for metals ions adsorption

Material/ions	Langmuir constants			Freundlich constants		
	q_{max} (mg.g^{-1})	K_L (L.mg^{-1})	r^2	K_f (mg.g^{-1})	n	r^2
B-N Pb(II)	11.63	0.088	0.9320	0.158	0.143	0.3250
B-Ca Pb(II)	52.63	0.011	0.9900	4.325	0.479	0.6610
B-N Cu(II)	6.87	1.20×10^{-2}	0.8720	0.550	2.340	0.5740
B-CA Cu(II)	31.53	2.12×10^{-3}	0.9980	1.180	2.240	0.8510
B-N Cr(III)	21.87	3.70×10	0.9860	3.480	2.610	0.9941
B-CA Cr(III)	22.08	5.36×10^{-3}	0.9940	3.650	1.580	0.9653

3.4. Thermodynamic parameters

The Gibbs free energy, enthalpy and entropy are factors that must be considered in determining da spontaneity of process, the criterion of spontaneity is given Gibbs free energy change, ΔG. Reactions occur spontaneously at a given temperature if ΔG is a negative quantity.[30]

In order to describe thermodynamic behaviour of the adsorption of metals ions by sugarcane bagasse *in natura* and modification, thermodynamic parameters including the change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were calculated using equations 6 and 7:

$$\Delta G = -RT \ln K_d \qquad (6)$$

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

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 J.K^{-1}.mol^{-1}, T is the experiment temperature expressed in Kelvin (K).[21, 30-31]

Enthalpy and the other parameters (Table 3) were obtained from the graphic construction of $\ln K_d$ versus 1/T, from Van't Hoff equation. Distribution coefficient (K_d) indicates the capability to retain the molecules and also the extent of its movement in a solution phase, being a useful parameter for comparing the adsorptive capacities of different adsorbent materials for any particular ion, when measured under same experimental conditions.[31]

Table 3. Thermodynamic parameters obtained from bagasse adsorption

Material/ion	K_d	$\Delta G(kJ.mol^{-1})$	$\Delta H(kJ.mol^{-1})$	$\Delta S(J.K^{-1}.mol^{-1})$
B-N Pb(II)	13.67	-6.48	-17.370	-37.000
B-CA Pb(II)	87.23	-11.08	-39.530	-95.000
B-N Cu(II)	4.36	-3.47	-20.020	-55.540
B-CA Cu(II)	14.76	-6.34	11.820	60.940
B-N Cr(III)	17.21	-7.00	-42.148	-117.887
B-CA Cr(III)	23.85	-7.81	-5.839	6.611

After the bagasse modification, it was possible to verify a negative increase in the values of ΔG, when compared to the bagasse without modification. Such result shows that the modifications made in the surface of bagasse to a more energetically favorable adsorption, corroborating the higher adsorption capacity. Besides, after the modification, there was an inversion in the system enthalpy and entropy. In cooper adsorption, the enthalpy after the modification became endothermic and there was an increase in the system disorder, therefore, the process spontaneity after the modification was governed by the disorder increase. After modification in the bagasse it was also an increase in negative ΔG adsorption of other ions (lead and chromium), besides being a process exothermic with increasing order.

3.5. Desorption study

The assay to evaluate the ions desorption from materials was carried out by loading the bagasse with known amount of copper (1.000 $mg.L^{-1}$), 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 $mol.L^{-1}$ HCl solution for ions recovery. The obtained values are expressed in Table 4.[7]

Whereas 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 B-N. Desorbed percentage can be considered satisfactory for a possible reutilization of this material for new adsorption phases. The precision of repeatability based on relative standard deviation (RSD) was evaluated for the modified bagasse with citric acid, whereas the RSD was found to be 2 % for four cycles involving adsorption and desorption.

Table 4. Adsorption–desorption of metals ions values, initial concentration of 1.000 mg.L^{-1}

Material/ion	Adsorbed amount (mg.L^{-1})	Desorbed amount (mg.L^{-1})	Desorption %
B-N Pb(II)	112.30	70.60	62.90
B-CA Pb(II)	435.30	421.50	96.80
B-N Cu(II)	58.20	37.14	63.82
B-CA Cu(II)	211.60	199.91	94.67
B-N Cr(III)	125.90	80.60	64.02
BCA Cr(III)	172.00	124.50	71.38

4. Conclusion

In this study, chemical modification of sugarcane bagasse was carried out aiming to introduce carboxylate groups to improve the adsorption of Cu(II), Pb(II) and Cr(III). The modifications were confirmed by infrared data with band around 1.730 cm^{-1} indicated the presence of the carboxylic group. Significant increase on adsorption capacity was verified after modification, with predominance of sugarcane bagasse modified with citric acid. The adsorption process fitted the Langmuir linear model very well and the ions adsorption in aqueous solution followed the pseudo-second order kinetics. In addition, the chemical modification of the sugarcane bagasse made the system more energetically favorable, as demonstrated by the values of Gibbs free energy. The copper adsorption process was considered endothermic with disorder increase and ions other the process was considered exothermal with disorder decrease. Finally, it was also verified that, after the modifications, there was an improvement in the ions desorption, indicating that this material can be reutilized.

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