



Use of rice straw as biosorbent for removal of Cu(II), Zn(II), Cd(II) and Hg(II) ions in industrial effluents

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ABSTRACT

Adsorption experiments were carried out using waste rice straw of several kinds as a biosorbent to adsorb Cu(II), Zn(II), Cd(II) and Hg(II) ions from aqueous solutions at room temperature. To achieve the best adsorption conditions the influence of pH and contact time were investigated. The isotherms of adsorption were fitted to the Freundlich equation. Based on the experimental data and Freundlich model, the adsorption order was Cd(II) > Cu(II) > Zn(II) > Hg(II) on the rice straw. This quick adsorption process reached the equilibrium before 1.5 h, with maximum adsorptions at pH 5.0. Thermodynamic aspects of the adsorption process were investigated. The biosorbent material was used in columns for the removal of ions Cu, Zn, Cd and Hg of real samples of industrial effluent and its efficiency was studied.

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1. Introduction

The industrial activities represent an important pollutant source nowadays, mainly concerning the addition of heavy metals in the soil. This is contributing to a significant increase on the concentrations of those ions in waters, representing an important source of contamination of the aquatic bodies, especially when it is considered that such ions can be disseminated through the food chain [1].

Heavy metal contamination exists in aqueous waste streams from diverse industries such as metal plating, mining, tanneries, painting, car radiator manufacturing, batteries, as well as agricultural sources where fertilizers and fungicidal sprays are intensively used. Cu, Zn, Hg and Cd are harmful wastes produced by industry that pose a risk of contaminating groundwater and other water resources. Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders [2–11]. For example, cadmium causes serious renal damage, anemia, hypertension and itai-itai [2].

The reduction of the pollutant to an acceptable level is necessary when toxic metals are present in the aquatic system [12]. Adsorption and ion exchange processes are the most useful methods to

remove them. These methods explore the availability of different kinds of adsorbents associated with convenient procedures for obtaining high efficiency [13,14]. A large number of different adsorbent materials containing a variety of attached chemical functional groups have been reported for this purpose. For instance, activated carbon is the most popular material, however, its high cost restricts its large-scale use [15,16].

In recent years, special attention has been focused on the use of natural adsorbents as an alternative to replace the conventional adsorbents, based on both the environmental and the economical points of view [15,16]. Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have potential as inexpensive sorbents. Due to their low cost, when these materials the end of their lifetime, they can be disposed of without expensive regeneration. The abundance and availability of agricultural by-products make them good sources of raw materials for natural sorbents.

In Brazil there are extensive plantations of rice in the southern area of the country. The annual production of rice in Brazil is of approximately 11.1 million tons [17]. The rice straw, an agriculture residue, represents 45 % of the volume of the production of rice and in Brazil this residue is used in processes of energy generation.

In this paper, rice straw was treated with NaOH solution to produce a carbonaceous adsorbent. The capacity of the produced adsorbent to remove Cu(II), Zn(II), Cd(II) e Hg(II) from aqueous solution was tested.

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2. Materials and methods

2.1. Chemicals

All the chemicals used were of analytical grade. Stock solutions of Cu(II), Zn(II), Cd(II) and Hg(II) were prepared in miliQ_{plus} water using copper chloride (CuCl₂·2H₂O), zinc chloride (ZnCl₂), cadmium chloride (CdCl₂·H₂O) and mercury chloride (HgCl₂). All the working solutions were prepared by diluting the stock solution in miliQ_{plus} water. The water used in all experiment has quality miliQ_{plus}.

2.2. Biosorbent preparation

The rice straw was given kindly by School Farm of the State University of Londrina, UEL. The natural material was washed with water three times and it was dried to 60 °C. Soon afterwards the rice straw was triturated and the particles were sieved to obtain a fraction with particles size between 0.05 and 0.10 mm which was used in this work. This material passes starting from here to be named as RS.

10 g of triturated RS was dispersed in 50 mL of HNO₃ solution 1.0 mol L⁻¹ and left agitating for 1 h at the room temperature. The material was filtered and washed with water until the removal of the excess of acid in the material. After that, the material was dispersed in 100 mL of a NaOH solution 0.75 mol L⁻¹ and was left under agitation for 1 h at the room temperature. The rice straw again was filtered and washed exhaustively with water. The material was dried at 60 °C. Biosorbent obtained in this process will be called this point ahead modified rice straw, MRS.

2.3. Biosorbent analysis

2.3.1. Surface area and average pore volume

N₂ adsorption isotherms were determined on an ASAP 2010 apparatus at liquid nitrogen temperature. Initially the sample was degassed at 100 °C for 48 h. The specific surface area of the material was obtained using the MP method [18] and the average pore volume was obtained using the Horvath-Kavazoe approximation [19].

2.3.2. FT-IR spectra

The infrared spectra were obtained as KBr pellets (1 wt%) and the equipment used was a Shimadzu FT-IR 3300 spectrophotometer with 4 cm⁻¹ resolution, using 200 cumulative scans.

2.3.3. Scanning electron microscopy (SEM)

The SEM images were obtained by the dispersion of the sample on double-faced conducting tape fixed on a graphite support. The sample was covered with a conductive film of gold. The electronic microscope used was a JEOL JSM T-300.

2.3.4. Thermogravimetry (TG)

The thermogravimetric curves of the materials were obtained in an DuPont model 9900 Thermoanalyzer equipment warming the samples with a speed of 10 °C min⁻¹, under flow of argon gas.

2.4. Adsorption studies

2.4.1. pH variation

The maximum adsorption capacity was determined by the batch method at pH values varying between 2 and 6, shaking the suspension for 1.5 h at a temperature of 25 ± 1 °C. The desired pH was adjusted with sodium hydroxide or hydrochloric acid solutions. In a typical experiment 300 mg of the adsorbent were suspended in 50.0 mL of the cation solution 2.88 × 10⁻³ mol L⁻¹ at the desired pH

and the mixtures were orbitally stirred at 25 ± 1 °C for 2 h. At different periods of time, aliquots of supernatant were withdrawn for metal analysis. The amount of metal adsorbed on the adsorbent surface (N_f) was calculated by applying the equation $N_f = (N_i - N_s)/m$, where N_i and N_s are the initial and the amount (mmol) of the metal ion which remained in solution after adsorption procedure, respectively, and m is the mass (g) of the solid in each flask. The metal ions were analyzed by complexometric EDTA titration using an appropriate indicator [20,21].

2.4.2. Batch adsorption

The rice straw adsorption capacity for individual metals was studied at the optimum pH 5.0 using the batch procedure. For this determination, about 300 mg of the adsorbent was immersed in 50.0 mL of the metal solutions, whose concentrations varied between 2.90 × 10⁻³ and 30.70 × 10⁻³ mol L⁻¹. The mixtures were orbitally shaken in a thermostated water bath with constant speed for 1 h. After the prescribed contact time, the aliquots of supernatant withdrawn were analyzed as stated before.

2.5. Statistical analysis

Comparisons between means were performed using ANOVA and Student-Newman-Keuls test (S. N. K. test) at a significance level of $p < 0.05$.

3. Results and discussion

3.1. Characterization of the biosorbent

The rice straw is constituted basically by cellulose, hemicellulose, lignin, extractives, water and mineral ash which is in large amount SiO₂. The lignin is promptly available to interact with cations, by firstly exchanging with protons and subsequently by chelating with the metallic ion.

The surface area and pore volume for RS and MRS obtained were 50 m² g⁻¹, 0.22 cm³ g⁻¹ and 160 m² g⁻¹, 0.43 cm³ g⁻¹, respectively.

Fig. 1 shows the FT-IR absorption spectra of RS and MRS. In spectra RS the absorption bands at 3400–3300 cm⁻¹ are assigned to the O–H stretching mode (ν OH) of cellulose and lignin in macromolecular association [22,23]. The weak bands at 2930 cm⁻¹ are assigned to the C–H stretching mode (ν CH) indicating material of

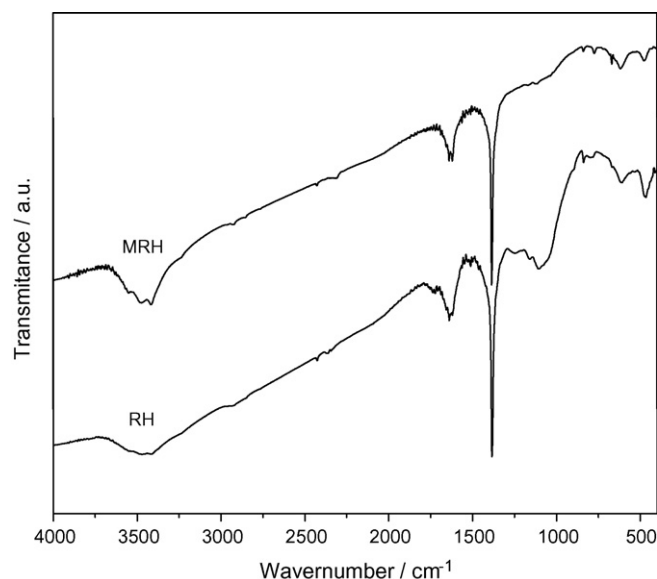


Fig. 1. FT-IR spectra of RS and MRS.

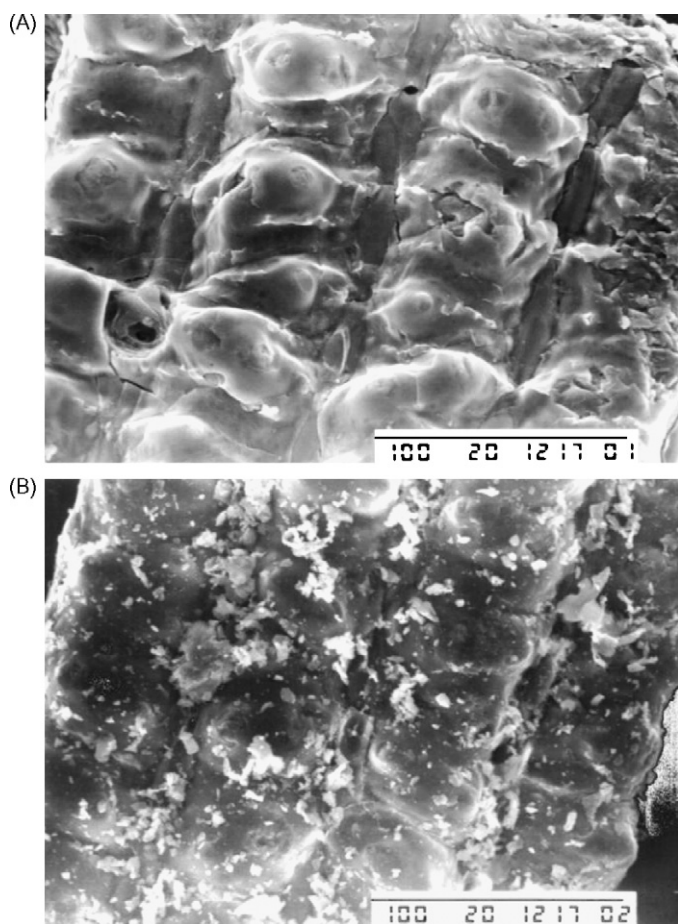


Fig. 2. Image SEM of RS (A) and MRS (B).

the aliphatic nature [23]. The absorption bands at $1800\text{--}1300\text{ cm}^{-1}$ are characteristics of $\nu\text{C}=\text{C}$ in aromatics ring [24]. The absorptions at 1080 and 460 cm^{-1} are attributed to Si-O stretching and Si-O bending indicating of the silica presence [25–28]. The spectra MRS presents a very similar profile to the RS while the absorptions at 1080 and 460 cm^{-1} attributed of the silica, decreased considerably. This fact suggests that a portion of silica was removed. The modified profile of the absorption at $3400\text{--}3300\text{ cm}^{-1}$ suggests that after the chemical treatment of RS, with removal of the silica, the groups $-\text{OH}$ acids became more exposed in the material probably resulting in interactions between them and water molecules with more defined frequencies.

Fig. 2 shows the image SEM of RS (A) and MRS (B) materials. It can be observed that the irregular superficial layer of protective silica and natural resins present in RS were largely removed with the chemical treatment in MRS. The removal of the superficial layer was not total, because it is possible to observe to several free fragments on MRS. The appearance of perforations in the material indicates the leaching of structural substances that might have generated or exposed the active sites in MRS.

Thermogravimetric curves of RS (curve A) and MRS (curve B) are shown in Fig. 3. The TG curves show that the materials until $100\text{ }^\circ\text{C}$ present a loss of 3 wt% corresponding to the humidity. In the range between 200 and $500\text{ }^\circ\text{C}$ occurs a loss of 77 wt% in RS and of 90 wt% in MRS due to two different processes, belonging probably one of them to the oxidation of the aliphatic organic matter and the other to the oxidation of the aromatic organic matter. In RS (curve A) of $500\text{--}970\text{ }^\circ\text{C}$ a residue of 20 wt% stays constant. In MRS (curve B) of 500 up to $970\text{ }^\circ\text{C}$ a residue of 7 wt% stays constant. These residues were identified as silica for FT-IR.

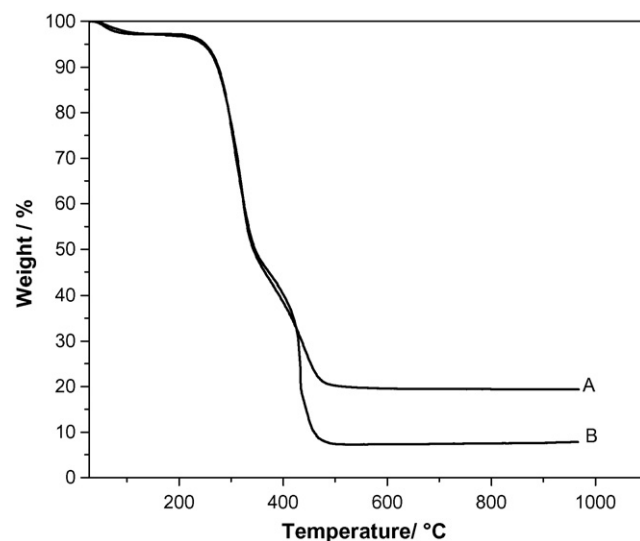


Fig. 3. Thermogravimetric curves of RS (curve A) and MRS (curve B).

3.2. Determination of equilibrium time

The adsorption data for metal uptake versus contact time for a fixed adsorbent amount are shown in the Fig. 4. The maximum capacity of adsorption of MRS for the Cu(II) , Zn(II) , Cd(II) and Hg(II) ions were 0.128 , 0.132 , 0.133 and 0.110 mmol g^{-1} , respectively. According to these data, equilibrium is achieved at round 45, 15, 20 and 60 min for Cu(II) , Zn(II) , Cd(II) and Hg(II) respectively, at 1.0 mmol L^{-1} solutions. However, to be sure of the best adsorption conditions at higher concentration levels and to obtain equilibrium at the solid/liquid interface, all the experiments were carried out with 1.5 h of contact time. This short time period required to attain equilibrium suggests an excellent affinity of the adsorbent for these metals from aqueous solution.

3.3. Effects of pH

The extractability of the cations from the solution phase is pH dependent. The effectiveness of the process can be expressed by the quantity adsorbed (mmol g^{-1}) versus pH plot for the cations

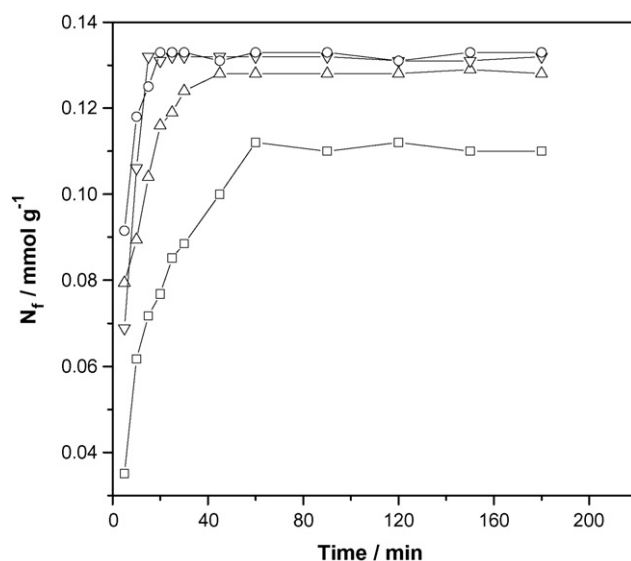


Fig. 4. Contact time for $1.0 \times 10^{-3}\text{ mol L}^{-1}$ of copper (\square), zinc (Δ), cadmium (∇) and mercury (\circ) chloride adsorption from aqueous solution at $25 \pm 1\text{ }^\circ\text{C}$.

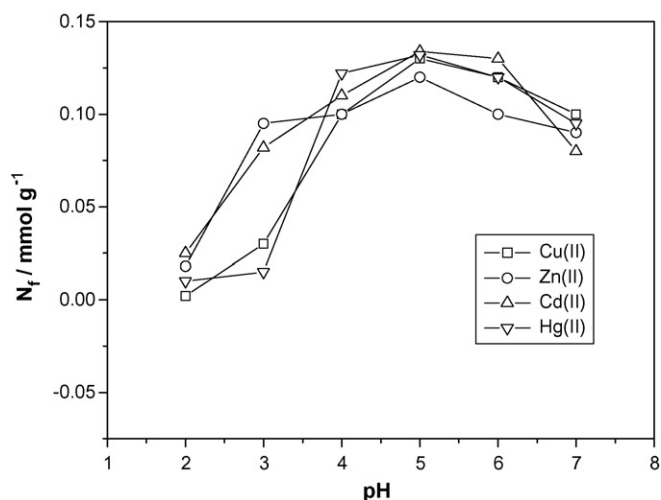
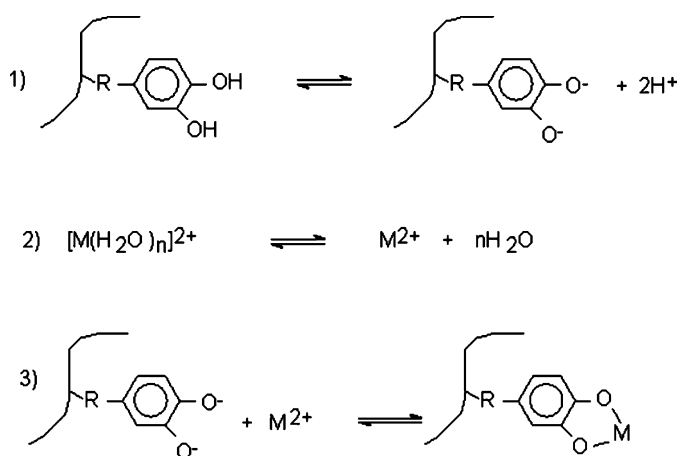


Fig. 5. Effect of pH on $1.0 \times 10^{-3} \text{ mol L}^{-1}$ of copper, zinc, cadmium and mercury chloride adsorption from aqueous solution at $25 \pm 1^\circ \text{C}$.

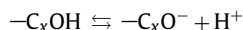
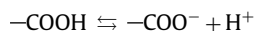
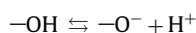
involved, as represented in Fig. 5 for divalent copper, zinc, cadmium and mercury. From the corresponding data for each metal, an increase in pH corresponds to an increase in adsorption, reaching the maximum capacity at pH 5. On higher pH values a slight decrease of adsorption for Cu(II), Zn(II), Cd(II) and Hg(II) was observed. The metallic ions (Cu, Zn and Cd) could be suffering hydrolysis, starting at pH higher than 5, forming $\text{Cu}(\text{OH})^+$, $\text{Zn}(\text{OH})^+$ and $\text{Cd}(\text{OH})^+$ species, which promotes a reduction of the adsorption capacity, due to the diminution of the formal charge of the metallic ion. In the case of Hg(II) in solution, these ions are extensively hydrolysed and the specie formed is HgO, and require acidification to prevent the formation of polynuclear hydroxo-bridged species or the precipitation of basic salts [29]. This specie does not present electrostatic interaction with the active site of the rice straw. Based on the results a mechanism is proposed for metallic ion uptake by rice straw is depicted on the Scheme 1.

As can be seen, the fibrous rice straw containing cellulose, hemicellulose and lignin (phenol groups) loses two protons per each mol of divalent cation (the fibrous materials contains several phenol groups which were withdrawn from the scheme for simplicity) at the first step. In the second step the hydrated metallic ion loses its hydration waters. In the third step the fibrous material uptakes the non-solvated metallic ion. At pH lower than 5, the first step of the adsorption procedure is hindered, diminishing the adsorption of the divalent metallic ions. The functional groups like $-\text{OH}$ and fiber



Scheme 1. Reaction that takes place for divalent ion uptake by rice straw.

carbonaceous C_xOH are dissociated at various pH values depending on their respective acidic dissociation constants and consequently take part in surface complexation/exchange of metal cations [30].



It should be stressed that, the maximum metal uptake at pH 5 allows this low-cost natural adsorbent be used for metallic ion removal from natural waters without requiring pH adjustments [31]. In this way the rice straw is a heterogeneous material formed by several types of site capable to interact with the metallic ions during the process of adsorption.

3.4. Adsorption data

The isotherms of adsorption for these divalent cations, represented by number of moles per gram of the adsorbent at $25 \pm 1^\circ \text{C}$, under optimum contact times and pH values, are shown in Fig. 7.

Two equilibrium isotherm equations were used to find out the relation between the equilibrium concentrations of the adsorbate in the liquid phase and in the solid phase. These isotherms [32,33] are:

a) Freundlich isotherm:

$$q_e = K_f C_e^n,$$

where C_e and q_e are respectively the concentration of the adsorbate divalent cation at equilibrium in the liquid phase and q_e is the corresponding concentration of the adsorbate in the solid phase, K_f and n being Freundlich coefficients.

b) Langmuir isotherm:

$$\frac{C_e}{q_e} = \frac{1}{(nq_m)} + \left(\frac{1}{q_m}\right) C_e,$$

where n and q_m are Langmuir coefficients representing the equilibrium constant for the adsorbate--adsorbent equilibrium and the monolayer capacity, respectively.

The linear Freundlich and Langmuir plots are obtained by plotting (i) $\log q_e$ vs. $\log C_e$ and (ii) C_e/q_e vs. C_e , respectively, from which the adsorption coefficients could be evaluated. The Langmuir equation is also used to obtain R_L , the dimensionless equilibrium parameter or the separation factor [34,35] from the expression:

$$R_L = \frac{1}{(1 + bC_0)},$$

where C_0 is the initial concentration of the adsorptive. For favorable adsorption, $0 < R_L < 1$; while $R_L > 1$, $R_L = 1$ and $R_L = 0$, respectively, describe unfavorable, linear and irreversible adsorption [36–38].

The experimental data didn't adjust appropriately to the model of Langmuir and therefore only the values parameters and correlations coefficients of Freundlich equations of experimental data are shown in the Table 1. For the analysis of the K_f values is revealed that the order of adsorption was $\text{Cd} > \text{Cu} > \text{Zn} > \text{Hg}$. Table 1 shows that there are three different strips of adsorption on rice straw. The metal more adsorbed was Cd^{2+} , following for Cu^{2+} and Zn^{2+} and finally the metal less adsorbed was Hg^{2+} , and these values were different statistically amongst themselves ($p < 0.05$, test S. N. K.). The differentiated behavior of adsorption of Hg^{2+} on the rice straw

Table 1
The values of parameters and correlation coefficients of Freundlich equation.

Ion	Freundlich		
	$K_f \times 10^3$	n	R^2
Cu ²⁺	2.7 ± 0.2	4.1 ± 0.4	0.9125
Zn ²⁺	2.3 ± 0.1	3.9 ± 0.1	0.9214
Cd ²⁺	4.2 ± 0.1	7.4 ± 0.1	0.9353
Hg ²⁺	1.2 ± 0.4	2.7 ± 0.5	0.9218

Table 2
Thermodynamic adsorption parameters.

Ion	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)
Cu ²⁺	8.9 ± 0.1	-7.9 ± 0.1	-56.5
Zn ²⁺	8.3 ± 0.4	-33.5 ± 0.2	-140.0
Cd ²⁺	9.8 ± 0.9	-5.4 ± 0.6	-51.2
Hg ²⁺	7.1 ± 0.3	-9.7 ± 0.3	-56.7

can be explained by the strong interference of the size of the particle of the material adsorbent used on the process of adsorption, as it can be observed by the data of the literature [39,40]. The lower adsorption value observed for Hg²⁺ it can also be presumably due to the stronger interaction of Hg²⁺ with Cl⁻ species in solution phase. Hg²⁺ can form stable species such as HgCl⁺ and HgCl₂ in solution phase while for Cu²⁺, Cd²⁺ and Zn²⁺ this interaction is negligible. As all of the ions present $n > 1$ values one can suppose that the adsorption sites on surface of the rice straw are heterogeneous nature.

3.5. Effects of temperature

The variation of sorption with temperature was studied from 15 and 45 °C for each toxic metal ion under the optimized conditions selected and the data are shown in Fig. 6. The thermodynamic parameters for the adsorption process, ΔH , ΔS and ΔG , were evaluated using the equation [41,42]:

$$\ln K_d = \Delta S/R - \Delta H/RT,$$

where K_d , known as the distribution coefficient of the adsorbate, is equal to (q_e/C_e) . The plot of $\ln K_d$ vs. $1/T$ (with T in K) is linear with the slope and the intercept giving values of ΔH and ΔS , respec-

Table 3
AAS result of wastewater real samples before and after treatment with the biosorbent.

Sample	Metal ion	C_{initial} (mg L ⁻¹)	C_{final} (mg L ⁻¹)	Adsorption amount (mg g ⁻¹)	Removal ratio (%)
1	Cu	2.54	nd*	2.54	100.0
	Zn	2.62	0.01	2.61	99.6
	Cd	4.50	nd	4.50	100.0
	Hg	8.02	nd	8.02	100.0
2	Cu	2.10	nd	2.10	100.0
	Zn	1.83	nd	1.83	100.0
	Cd	3.96	0.01	3.95	99.7
	Hg	6.00	nd	6.00	100.0
3	Cu	1.97	nd	1.97	100.0
	Zn	2.38	0.01	2.37	99.6
	Cd	4.00	nd	4.00	100.0
	Hg	7.07	nd	7.07	100.0
4	Cu	2.01	nd	2.01	100.0
	Zn	1.98	0.01	1.97	99.5
	Cd	4.16	nd	4.16	100.0
	Hg	5.80	nd	5.80	100.0
5	Cu	1.87	nd	1.87	100.0
	Zn	2.25	0.01	2.24	99.6
	Cd	5.07	nd	5.07	100.0
	Hg	6.78	nd	6.78	100.0

* nd = not detected.

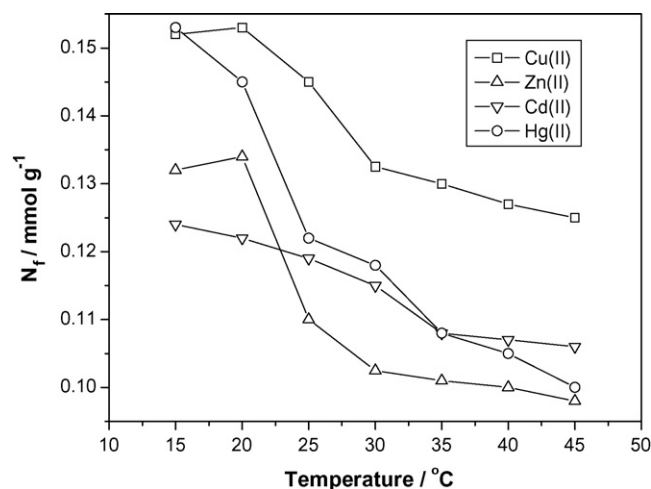


Fig. 6. Effect of temperature on 1.0×10^{-3} mol L⁻¹ of copper, zinc, cadmium and mercury chloride adsorption from aqueous solution at 25 ± 1 °C.

tively. These values could be used to compute ΔG from the Gibbs relation, $\Delta G = \Delta H - T\Delta S$ at constant temperature. All these relations are valid when the enthalpy change remains constant in the temperature range.

Of the thermodynamic point of view the data in Table 2 and of the Fig. 6 shows that the adsorption process of the metals ions on rice straw was exothermic and that occurs a decrease of the entropy probably associated to the organization of the metal adsorbed on surface of the adsorbent.

3.6. Application of the biosorbent studied for wastewater treatment

The five real samples from wastewater of a battery industry were analyzed with atomic adsorption spectrophotometer (AAS) at their respective wavelength. The results before and after treatment are given in Table 3. It is seen that the biosorbent displays high removal efficiency towards Cu, Zn, Cd and Hg.

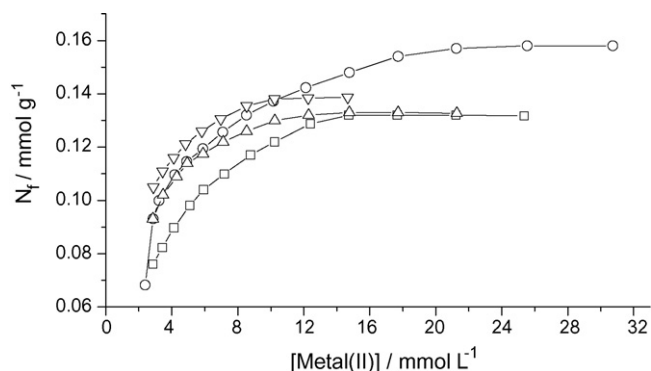


Fig. 7. Isotherm of adsorption for copper (□), zinc (○), cadmium (Δ) and mercury (▽) chloride at 25 ± 1 °C and optimum contact times and pH values.

3.7. Elution and regeneration

The column with a bed depth of 10 and 0.8 cm was selected for this study. The real sample inside the column was pumped at a flow rate of 5.5 mL min^{-1} . Desorption was carried out by 0.01 mol L^{-1} HCl solution through the bed in the downward direction at a flow rate of 3.5 mL min^{-1} . The regenerations were carried in the counter-current mode, that is, in the downflow mode. Counter-current operation generally reduces regeneration cost and regenerant volume and increases effluent quality [43]. Elution efficiency (%) was calculated by dividing the total adsorption capacity in the second run by the total adsorption capacity in the first run. The regenerated biosorbent showed uptake capacity comparable to the fresh one over fifteen cycles with standard deviation of $\pm 2\%$.

4. Conclusion

The rice straw is an attractive adsorbent for divalent Cu(II), Zn(II), Cd(II) and Hg(II) removal from aqueous solutions in a very rapid adsorption process. The maximum adsorption capacities vary with pH values, being higher at pH 5.0, which was experimentally fixed at 25 ± 1 °C for all adsorptions, and the values obtained were 0.128, 0.132, 0.133 and $0.110 \text{ mmol g}^{-1}$ for Cu(II), Zn(II), Cd(II) and Hg(II), respectively, using batch adsorption system.

The rice straw demonstrates a great ability for extracting metallic ions from simulated industrial effluent contaminated individually with Cu(II), Zn(II), Cd(II) or Hg(II) solutions. Use of biosorbent in columns for the removal of metallic ions demonstrated high efficiency for industrial effluents contaminated with Cu, Zn, Cd and Hg.

Of the thermodynamic point of view the adsorption process of the poisonous metals ions on rice straw was exothermic with a decrease of the entropy associated to the organization of the metal adsorbed on surface of the adsorbent.

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