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Biosorption of Cu (II) and Zn (II) with açaí endocarp *Euterpe oleracea* M. in contaminated aqueous solution

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ABSTRACT. Current analysis investigates the capacity of the açaí endocarp (*Euterpe oleracea* M.) as a biosorbent for the removal of Cu^{2+} and Zn^{2+} in monoelementary water solutions. The best conditions for the ion adsorption process were pH of the solution at 4.0; 8 g L^{-1} of the biosorbent mass per volume of solution; best equilibrium time at 60 min. The application of kinetic models suggests that chemosorption may be the main limiting stage for metal ion adsorption. In the case of adsorption isotherms, Langmuir´s model had the best adjustment for biosorption and indicated adsorption in monolayers. A strong interaction of metals with the surface of the adsorbent was indicated due to low elution rates. Thermodynamic parameters showed that the biosorption process was spontaneous and endothermal. Results demonstrated that the use of the açaí endocarp as biosorbent is an alternative for the remediation of Cu^{2+} and Zn^{2+} contaminated waters since it is a natural, low-cost and highly available material.

Keywords: adsorption process, kinetic parameters, isotherms; thermodynamic parameters.

Biossorção de Cu (II) e Zn (II) utilizando o endocarpo de açaí *Euterpe oleracea* M. em solução aquosa contaminada

RESUMO. O presente estudo investiga o potencial do endocarpo de açaí (*Euterpe oleracea* M.) como um biossorvente para a remoção de Cu^{2+} e Zn^{2+} em soluções aquosas monoelementares. As melhores condições para o processo de adsorção dos íons foram: pH da solução de 4,0 e 8 g L^{-1} de massa biossorvente por volume da solução e o tempo de equilíbrio de 60 min. A aplicação de modelos cinéticos sugere que a quimiossorção pode ser a principal forma de adsorção dos íons metálicos. No caso das isotermas de adsorção, o modelo de Langmuir teve o melhor ajuste para a biossorção e indicou adsorção em monocamadas. Como as taxas de eluição foram baixas, sugere-se que há uma forte interação de metais com a superfície dos adsorventes. Os parâmetros termodinâmicos mostraram que o processo de biossorção foi espontâneo e endotérmico. Os resultados demonstraram que a utilização do endocarpo de açaí como biossorvente pode ser uma alternativa para a reabilitação de Cu^{2+} e Zn^{2+} em águas contaminadas, uma vez que o material é natural, de baixo custo e de elevada disponibilidade.

Palavras-chave: processo de adsorção, parâmetros cinéticos, isotermas, parâmetros termodinâmicos.

Introduction

Heavy metals, highlighted among the several contaminating factors of water resources, are actually toxic, contaminating and non-biodegradable elements released in the water medium chiefly as products of industrial and agricultural activities. Even in small concentrations, these elements are highly dangerous to the environment and public health (Gautam, Mudhoo, Lofrano, & Chattopadhyaya, 2014). Due to intense pollution and contamination, water constantly requires new de-pollutant technologies so that it could be used and reused as a resource (Mimura, Vieira, Martelli, & Gorgulho, 2010).

Several methods, such as coagulation, flocculation, ion exchange, separation by membranes and chemical precipitation, have been employed to remove metal ions from water solutions. However, their main disadvantages are high costs and technical limitations. The interest in the development of alternative low cost and efficient technologies is highly relevant. In fact, biosorption is an emergent, competitive and sustainable technology (Gonçalves et al., 2013a; 2013b; Rubio et al., 2013a; 2013b; Coelho et al., 2014, Schwantes et al., 2015a; 2015b; Nacke et al., 2016).

Agro-industrial wastes are frequently used as biosorbents to remove metal ions from monoelementary water solutions. Their main advantages as biosorbents replacing conventional ones comprise high availability and low costs. In fact, cheap residues or wastes with low economical values are actually used. Quintáns-Fondo et al. (2016) report that biosorbents are more relevant when they are derived from agro-industrial wastes since their volume may cause serious environmental problems.

The açaí palm tree (*Euterpe oleracea* Mart.) is a native Brazilian tropical palm distributed in the northern and northeastern regions of Brazil, whose market potential mainly lies in the juice extracted from the fruit (Nascimento, Cicero, & Novembre, 2010). Since its agro-industrial processing generates great amounts of wastes, with approximately 80% of the fruit´s total volume made up of the endocarp (Pacheco-Palencia, Duncan, & Talcott, 2009), the use of waste as biosorbent is a sustainable alternative.

Current assay investigates the potentiality of the use of the açaí stone as biosorbent in the removal of metal ions Cu^{2+} and Zn^{2+} from fortified mono-elementary water solutions to simulate the contamination of water bodies by these metal ions.

Material and methods

Preparation and characterization of the biosorbent

The experimental stages of current research were performed at the Laboratory of Environmental and Instrumental Chemistry of the Agrarian Sciences Center of the Universidade Estadual do Oeste do Paraná (Unioeste), campus Marechal Cândido Rondon, Paraná State, Brazil.

Biosorbent material (açaí endocarps) was obtained from the municipality of Curionópolis in the southeastern mesoregion of Pará, Brazil. Açaí endocarps were dried in a buffer (Biopar S36 BD) at 65 ± 2°C for 48 hours, ground in a Wiley knife mill (Marconi MA 048) and sieved in a 20 - 48 mesh Bertel sieve for the standardization of the particles. The biosorbent material did not undergo any chemical modification in the course of the experiments. The chemical, structural and morphological characteristics of the biosorbent were investigated, coupled to its point of zero charge (pH_{PZC}).

The nitroperchloride digestion of samples of the biosorbent material determined the initial concentrations of the metal ions Cu^{2+} and Zn^{2+} in the biosorbent *in natura*, coupled to K, Ca, Mg, Fe, Mn, Cd, Pb and Cr. Further, the concentration of these elements by flame atomic absorption spectrometry (FAAS) was determined with standard curves for the metals.

Spectroscopy analyses were undertaken in the infra red region (FT-IR) by Shimadzu Infrared Spectrophotometer FTIR- 8300 Fourier Transform at the region between 400 and 4000 cm^{-1},with resolution 4 cm^{-1}, to determine the functional groups in the biosorbent. The morphology of the biosorbent´s surface was analyzed by scanning electron microscopy (SEM), FEI Quanta 200, at 30kV. The above determinations were performed in a joint study with the Chemical Department of the State University of Londrina, Londrina, Paraná State, Brazil.

The point of zero charge (pH_{PZC}) was determined by adding 50 mg of the biosorbent in 50 mL of a water solution of potassium chloride (KCl, Vetec, 99%) at 0.5 mol L^{-1} for initial pH ranging between 2.0 and 9.0, adjusted with solutions of hydrochloric acid (HCl, Vetec, 37%) and sodium hydroxide (NaOH, Vetec, 99%), at concentration 0.1 mol L^{-1}. After 24 hours stirring in a Dubnoff thermostat bath (Marconi MA 035) at 25°C and at 200 rpm, final pH rates were given in a graph with initial pH variations as a function of final pH. Therefore, pH_{PCZ} is the point of zero rate of pH variation (Mimura et al., 2010).

Determination of best conditions for the adsorption process

Mono-elemental solutions of the metal ions Cu^{2+} and Zn^{2+} were prepared from salts of copper nitrate [$Cu(NO_3)_2$ $3H_2O$ A.R. ≥ 99%] and zinc nitrate [$Zn(NO_3)_2$ $6H_2O$ A.R. ≥ 99%]. At the end of each adsorption test, all concentrations of metals were determined by FAAS.

Some tests were conducted to warrant optimal conditions for adsorption, since factors such as amount of adsorbent, pH of solution, contact time and temperature influence the metal removal by adsorption from the aqueous medium. For mass tests, increasing amounts of the adsorbent material (0 to 1200 mg) were used at three pH levels (4.0, 5.0 and 6.0), adjusted with standard solutions of HCl or NaOH (0.1 mol L^{-1}). The masses were placed in 125 mL-Erlenmeyer flasks together with fixed volumes of 50 mL of each aqueous solution and 10 mg L^{-1} of metals. These flasks were stirred for 90 min under constant temperature (25ºC) and stirring (200 rpm) in a thermostat Dubnoff water bath. Samples were then filtered through quantitative paper to determine the final concentration of metals by FAAS.

The adsorbed amount was calculated from rates obtained for the final concentration (Equation 1).

$$Q = \frac{(C_0 - C_f)}{m} V \qquad (1)$$

where:

Q is the amount of ions adsorbed per unit of adsorbent at equilibrium (mg g^{-1});
m is the mass of adsorbent used (g);
C_0 is the initial concentration of the ion in the solution (mg L^{-1});
C_f is the final concentration of the ion in the solution (mg L^{-1});
V is the volume of solution used (L).

The removal percentage of metal ions was calculated by Equation 2:

$$\%R = 100 - \left(\frac{C_f}{C_0} x\, 100\right) \qquad (2)$$

where:

%R is the removal percentage of the ion by the adsorbent;
C_f is the final concentration of the ion (mg L^{-1});
C_0 is the initial concentration of the ion in the solution (mg L^{-1}).

So that the equilibrium time for the adsorption process could be determined, 400 mg of the adsorbent were added to 125 mL-Erlenmeyer flasks, plus 50 mL of respective monoelemental solutions fortified with 10 mg L^{-1} Cu^{2+} and Zn^{2+}, at pH 4.0. The samples were then removed at timed intervals (from 5 to 180 min) and filtered through quantitative paper to determine the final concentration of metals by FAAS.

So that the kinetic mechanism that controls the adsorption process may be evaluated, the pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion models were applied to data obtained in the contact time adsorbent/adsorbed tests.

Adsorption isotherms

Further, 400 mg of the adsorbent were added to 125 mL-Erlenmeyer flasks with 50 mL of the mono-elemental solution containing the metal ions Cu^{2+} (pH 4.0) or Zn^{2+} (pH 4.0) with increasing concentrations, 5 - 200 mg L^{-1}, for the construction of adsorption isotherms.

The flasks were shaken at 200 rpm in a water bath at 25°C for 60 min. After stirring, samples were filtered through qualitative filter paper to determine the concentration of metal ions in solution by flame atomic absorption spectrometry. The amount of metal ions adsorbed at equilibrium by the adsorbent (Q_{eq}) was calculated by Equation 1.

Adsorption isotherms were linearized by the mathematical models of Langmuir, Freundlich and Dubnin-Radushkevich.

Elution

Following the adsorption isotherms, the adsorbent was separated from the solution by filtration with quantitative filter paper, washed with ultrapure water and oven-dried at 60°C for 24 hours. The mass of the adsorbent obtained after drying was placed in contact with 50 mL HCl solution (0.1 mol L^{-1}) for 60 min, under constant temperature and stirring. Further, the samples were filtered again to determine the final concentrations of metals.

The desorption percentage was calculated by Equation 3:

$$\%D = \left(\frac{C_{eq(des)}}{C_{eq(ads)}}\right) 100 \qquad (3)$$

where:

$C_{eq(des)}$ (mg L^{-1}) and $C_{eq(ads)}$ (mg L^{-1}) are the concentrations of desorbed Cd^{2+}, Pb^{2+} and Cr^{3+} and the adsorbed concentration of metals in equilibrium by the adsorbents.

Comparative study between the proposed biosorbent and a commercial adsorbent

Experimental tests with powdered activated coal P.A. (Synth) were performed to compare the potential of the biosorbent (açaí endocarps) with that of a commercial adsorbent (activated coal) in their efficaciousness to remove metal ions. The same conditions used in the adsorption and elution isotherms of the biosorbent were employed. It should be underscored that activated coal is an effective adsorbent widely used on the market (Debrassi, Largura, & Rodrigues, 2011).

Effect of temperature on the adsorption process

The influence of temperature on adsorption was investigated to evaluate the thermodynamic parameters and the nature of the process. Consequently, 400 mg of the material were placed into 125 mL-Erlenmeyer flasks, plus 50 mL of Zn^{2+} or Cu^{2+} solution adjusted at pH 5.0 and 4.0, respectively. Samples were stirred at 200 rpm at different temperatures (15, 25, 35, 45 and 55°C). The parameters of Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were calculated with the results obtained (Sari, Tuzen, Citak, & Soylak, 2007).

Results and discussion

Characterization of the biosorbent

Table 1 shows results of metal concentrations in the biosorbent. Cu and Zn results showed concentrations of 14.53 and 9.50 mg kg^{-1}, respectively. No concentrations of the metal ions Cd, Pb and Cr were detected.

Table 1. Determination of initial concentrations of metals in the biosorbent açaí endocarp.

K g kg^{-1}	Ca g kg^{-1}	Mg g kg^{-1}	Cu mg kg^{-1}	Fe mg kg^{-1}	Mn mg kg^{-1}	Zn mg kg^{-1}	Cd mg kg^{-1}	Pb mg kg^{-1}	Cr mg kg^{-1}
4.39	9.01	0.98	14.53	65.07	172.63	9.50	< 0.005	< 0.01	< 0.01

LQ (quantification limits): K = 0.01; Ca = 0.005; Mg = 0.005; Cu = 0.005; Fe = 0.01; Mn = 0.01; Zn = 0.005; Cd = 0.005; Pb = 0.01; Cr = 0.01.

Figure 1 shows the infrared spectra of the biosorbent açaí endocarp (*Euterpe oleracea* Mart.). Analysis of bands in the biosorbent indicates that the large and strong band 3342 cm^{-1} may be attributed to the vibration lengthening of the O-H Bond which characterizes the vibration stretching of the hydroxyl groups in cellulose, lignin and water adsorbed on the adsorbent´s surface (Gonçalves Jr., Nacke, Fávere, & Gomes, 2010; Han et al., 2010).

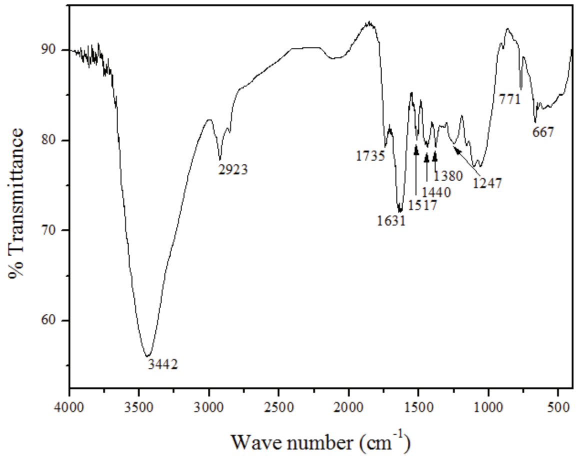

Figure 1. Infrared spectra for the biosorbent açaí endocarp (*E. oleracea*).

Band 2923 cm^{-1} refers to the vibration lengthening of C-H bonds of the alkane groups, whereas the 1735 cm^{-1} band may be attributed to the carbonyl groups of the aldehyde and ketone functions occurring in lignins and holocellulose (Figure 1). Bands 1631, 1517 and 1440 cm^{-1} may be attributed to the vibration lengthening of C-O bonds of amides and carboxyl groups (Han et al., 2010) and 1247 cm^{-1} band may be associated with the stretching of C-O in phenols (Han et al., 2010). Further, bands with wave lengths less than 800 cm^{-1} may be attributed to N with bio-bonds (Barka, Abdennouri, Boussaoud, & Makhfouk, 2010), whereas 771 and 667 cm^{-1} bands may be attributed to the vibration lengthening of the C-N bond (Salem & Awwad, 2011). The literature also demonstrates that the açaí endocarp is rich in cellulose and lignin (Pacheco-Palencia et al., 2009), corroborating results obtained.

Figure 2 shows SEM images amplified 150 (a), 1200 (b) and 12000 (c) times. The images show that the biosorbent´s surface has a fibrous and irregular aspect with significant empty spaces. Since the lamellar structure features fissures and pores on the surface, the endocarp has favorable conditions for the adsorption of metal ions

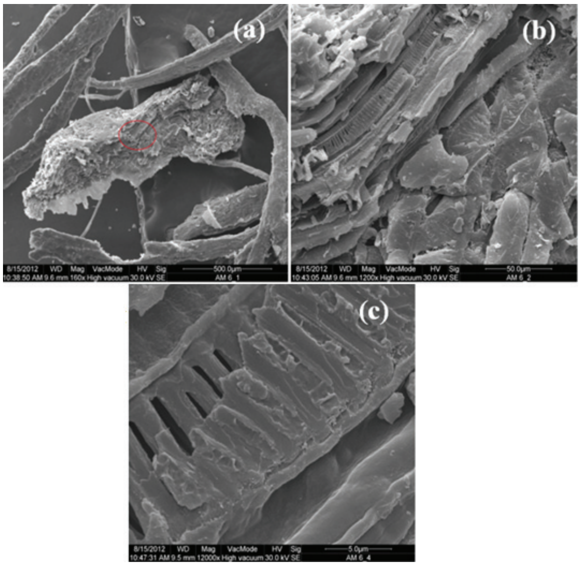

Figure 2. SEM images of the biosorbent açaí endocarp (*E. oleracea*.) amplified 150 (a), 1200 (b) and 12000 (c) times.

Result for the biosorbent´s pH$_{PZC}$ indicates that the pH which is equivalent to a point between negative and positive charges for the biosorbent lies at 5.09, and thus cation adsorption should be favored by higher pH rates (Mimura et al., 2010).

Determination of best conditions for the adsorption process

Figure 3 demonstrates that in the case of Cu^{2+} and Zn^{2+} the removal percentage was higher when pH was equal to 4.0 and 5.0. According to Özer, Özer, & Özer (2004), the dominant species of copper in the pH range between 3.0 and 5.0 is Cu^{2+} and $CuOH^{+}$; above pH 6.3, Cu is in insoluble form as $Cu(OH)_2$; Zn^{2+} above pH 5.0 has low solubility and down a high solubility (Araújo, Bertagnolli, Silva, Gimenes, & Barros, 2013). The later pH rate was thus chosen for later tests.

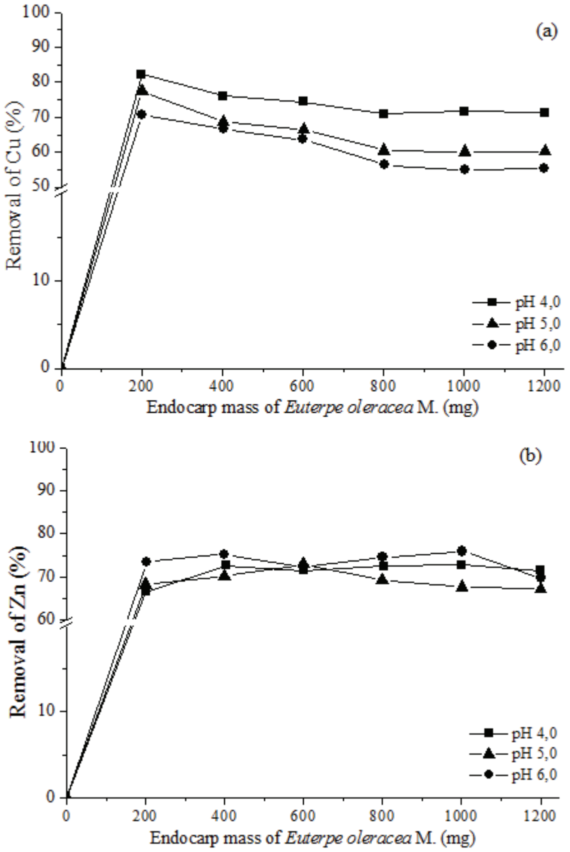

Figure 3. Effect of adsorbent mass and pH of the solution in % of Cu^{2+}(a) and Zn^{2+} (b) removal for the biosorbent açaí endocarp (*E. oleracea* Mart.).

Further, 400 mg of biosorbent mass were employed in the case of Cu^{2+} and Zn^{2+}, or rather, the equivalent of 8 g of biosorbent per liter of water solution. In fact, an increase in mass did not significantly alter removal percentage, although a decrease occurred. According to Kumar and Porkodi (2007), a high rise in the quantity of the adsorbent may trigger a decrease in the adsorption of metal ions, due to the reduction of the biosorbent´s total surface area when the aggregates are formed.

Influence of contact time between adsorbent and adsorbed by adsorption kinetics

Results showed that although there was an initial increase in the quantity of adsorbed ions Cu^{2+} and Zn^{2+} over time, only slight variations occurred after 60 min, indicating that the system tended towards dynamic equilibrium. The ideal dynamic equilibrium time for later tests was set at 60 min (Figure 4).

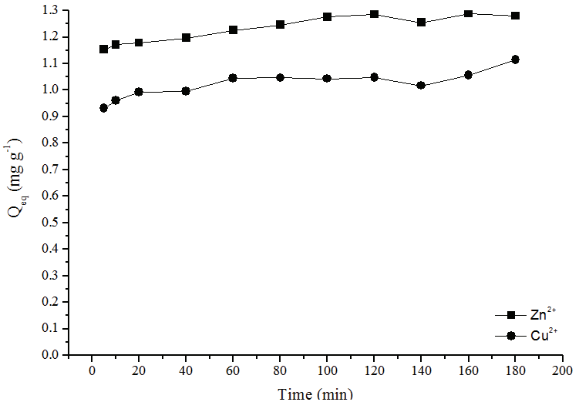

Figure 4. Effect of time (min) on the quantity of adsorbed ions (mg g^{-1}) of Cu^{2+} and Zn^{2+} for the biosorbent açaí endocarp (*E. oleracea*).

Pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion models were employed for a better analysis of Cu^{2+} and Zn^{2+} kinetic adsorption. Table 2 gives the kinetic parameters by the models for the biosorption process of the metal ions Cu^{2+} and Zn^{2+} with biosorbent açaí endocarp.

Results in Table 2 demonstrate that the pseudo-first order model, which indicates the predominance of physiosorption, is not applicable since R^2 rates (0.874 and 0.902) do not represent the best adjustment. Moreover, there is no proximity between Q_{eq} calc (0.157 and 0.148) and Q_{eq} exp (1.023 and 1.234) rates (Febrianto et al., 2009).

Table 2. Kinetic parameters from the study on Cu^{2+} and Zn^{2+} adsorption by biosorbent açaí endocarp (*E. oleracea*) for pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion models.

	Pseudo-first order			Pseudo-second order			Elovich		
	K_1 (min^{-1})	$Q_{eq\,(cal.)}$ (mg g^{-1})	R^2	K_2 (g mg^{-1} min^{-1})	$Q_{eq\,(cal.)}$ (mg g^{-1})	R^2	A (mg g^{-1} h^{-1})	B (g mg^{-1})	R^2
Cu^{2+}	-0.007	0.157	0.874	0.381	1.081	0.997	-22.189	25.570	0.943
Zn^{2+}	-0.009	0.148	0.902	0.409	1.293	0.999	-26.494	24.672	0.934

	Intraparticle diffusion						
	K_{id} (g mg^{-1} min$^{-1/2}$)		C_i (mg g^{-1})		R^2		$Q_{eq(exp.)}$ (mg g^{-1})
	A	B	A	B	A	B	
Cu^{2+}	36.140	48.762	31.459	40.778	0.989	0.368	1.023
Zn^{2+}	55.540	40.592	61.613	40.520	0.911	0.411	1.234

K_1: velocity constant of the first order; Q_{eq}: amounts of adsorbates retained per gram of adsorbent in equilibrium; K_2: velocity constant of the second order; A: constant indicating the velocity of initial chemo-sorption; B: number of sites which are adequate for adsorption, related to the coverage extension of surface and the activation energy of chemo-sorption; R^2: coefficient of determination; $K_{id:}$ constant of intraparticle diffusion: C_i: suggests thickness of the limiting layer´s effect; R^2: coefficient of determination.

Best results for R^2 (0.997 and 0.999) obtained by the pseudo-second model and the proximity between Q_{eq} calc (1.081 and 1.293) and Q_{eq} exp (1.023 and 1.234) rates reveal the chemical characteristics of the biosorption process for the removal of Cu^{2+} and Zn^{2+} with regard to the biosorbent açaí endocarp. Similar results have been reported by Liu et al. (2013) in studies on biosorbents for Cu^{2+} and Zn^{2+} removal.

Results by the Elovich model (Table 2) demonstrate that R^2 rates are greater than 0.90 (0.943 and 0.934). Consequently, the model partially explains the biosorption process of the metal ions Cu^{2+} and Zn^{2+}. Hossain, Piyatida, Silva, and Fujita (2012) reported that R^2 rates between 0.914 and 0.970 represented moderate adjustments and thus the Elovich model may not be satisfactory to explain the studied adsorption phenomenon. Further, the above results confirm data obtained by the pseudo-second order model and indicate predominance of chemosorption (Liu et al., 2013).

With regard to the intraparticle diffusion model, there is an increase in K_{id} rates related to straights lines A and B for the metal ion Cu^{2+}, whereas these rates decrease for metal ion Zn^{2+}, which showed that the diffusion rate was lower in the latter phase, mainly due to the decrease in active sites for the adsorption of this metal ion. However, in the case of Cu^{2+} and Zn^{2+}, the rates of C_i for the two lines are different from zero, and thus mathematically they do not cross the axes origin. The above indicates that the diffusion model is not the limiting stage of the kinetic process (Han et al., 2010).

Adsorption isotherms

Table 3 shows that the highest percentages of metal ions Cu^{2+} and Zn^{2+}, or rather, 74 and 72% and 73 and 71%, respectively, were removed by the biosorbent açaí endocarp at low concentrations (5 and 20 mg L^{-1}). However, as the initial concentration of the ions in the solution increased, there was a decrease in the efficiency of the biosorbent removal, respectively with 14 and 16% removals for the highest concentration used (200 mg L^{-1}). According to Singha and Das (2011), the decrease in removal efficiency was due to the saturation of adsorption active sites, with more and more ions in the solution, as the initial concentration of the metal ions in the solution increased.

When removal percentages of the metal ions Cu^{2+} and Zn^{2+} are compared, the mean removal efficiency rates by the biosorbent and by activated coal were 39.71 and 40.30% and 88.35 and 82.70% respectively. It should be underscored that, although the removal efficiency by activated coal is higher, the biosorbent used is a natural material, low cost and highly available, whereas coal is a product requiring chemical modifications with high production costs. According to Witek-Krowiak and Reddy (2013), great availability and low costs are the main advantages of agro-industrial wastes as biosorbents to replace conventional ones.

Adsorption isotherms describe the relationship between the amount of ions adsorbed per mass of adsorbent related to the concentration of the solution in dynamic equilibrium (Witek-Krowiak & Reddy, 2013). The equilibrium isotherms should be investigated to better understand the adsorption process. Figure 5 shows the equilibrium isotherms for the adsorption process of the metal ions Cu^{2+} and Zn^{2+} by the biosorbent açaí endocarp and by activated coal.

According to their behavior, the adsorption isotherms may be classified in classes and subgroups, following Giles, Macewan, Nakhwa, and Smith (1960). Figure 5 shows that adsorption isotherms for the biosorbent (Figure 5a) and for activated coal (Figure 5b) have a convex behavior, typical of Class L (Langmuir), with an initial downward curve due to the decrease of the availability of active sites, with high removal capacity in the lowest concentrations, but with a trend towards equilibrium in the highest concentrations.

Results in Table 4 show that Langmuir´s model has the best adjustment for the biosorption of ions Cu^{2+} and Zn^{2+}, with a coefficient of determination (R^2) equal to 0.999. In the case of adsorption of the metal ions by activated coal, Langmuir´s model has the best adjustment ($R^2 = 0.999$). Since Langmuir´s model had the best data adjustment for the biosorbent and for activated coal, the adsorption process occurred in monolayers (Gonçalves Jr. et al., 2010).

Table 3. Removal percentage of metal ion Cu^{2+} and Zn^{2+} by biosorbent açaí endocarp (BAE) and activated coal (AC) increasing initial concentrations (C_0).

		C_0 (mg L^{-1})									
Metalic ion	Adsorbent A	5	20	40	60	80	100	120	140	160	200
		% Removal									
Cu^{2+}	BEC	74.44	72.22	59.47	43.93	35.19	30.02	25.31	22.64	19.31	14.58
	AC	99.27	99.76	99.76	99.88	99.64	94.88	83.69	77.29	72.06	57.30
Zn^{2+}	BEC	73.50	71.51	58.67	47.31	38.07	31.21	26.18	22.46	19.46	15.57
	AC	99.20	99.33	98.58	96.44	92.83	83.33	76.72	68.05	62.50	50.00

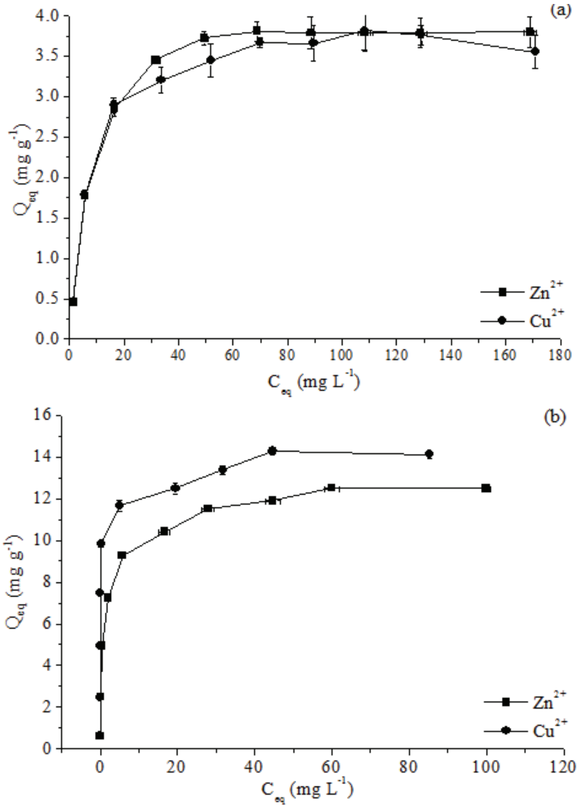

Figure 5. Isotherms of adsorption equilibrium of the metal ions Cu^{2+} and Zn^{2+} on the biosorbent açaí endocarp (*E. oleracea*) (a) and activated coal (b).

In the case of the mathematical parameters of Langmuir´s model, maximum adsorption quantity (Q_m) rates of the biosorbent (3.997 and 3.929) for the Cu^{2+} and Zn^{2+} ions were lower than Q_m rates by activated coal (14.166 and 12.631). However, in the case of the constant related to the interaction forces adsorbent/adsorbed (b or K_L), rates were higher for the biosorbent (0.448 and 0.274) when compared to those for activated coal (0.004 and 0.011). Therefore, the relation between the studied biosorbent and the metal ions is higher when compared with that of activated coal. The above reveals that in the adsorption process the ions are closely bonded to the adsorption sites of the biosorbent.

According to Sodré, Lenzi, and Costa (2001), in the linearization by Freundlich, the parameter *n* indicates the reactivity of the adsorbent´s active sites. When *n* rates are over 1, there is a strong indication of highly energetic sites, which suggests that they are the first to be occupied by the metals. Such behavior has been registered (Table 4) for the biosorbent and for activated coal in the case of the metal ions under analysis.

With regard to the D-R mathematical model, mean sorption energy (E) shows whether the adsorption process is physical or chemical. Rates between 1 and 8 kJ mol^{-1} indicate physical adsorption, whereas rates above 8 kJ mol^{-1} demonstrate a chemical adsorption process (Wan & Hanafiah, 2008). *E* rates in Table 4 demonstrate that, in the case of the biosorbent and activated coal, the adsorption process is a chemical one.

Elution

Elution rates for the metal ions Cu^{2+} and Zn^{2+} were low for the biosorbent (41.77 and 36.83%) and for the activated coal (44.76 and 54.77%). Results suggest that adsorption is a chemical process since, according to Namasivayam, Prabha, and Kumutha (1998), low elution rates indicate that the metal ion is strongly bonded with the adsorbent´s active sites by chemical links. Therefore, the reuse of these adsorbent metals for new adsorption processes in this case is not feasible. There is a possibility of using different concentrations for HCl solution, or still, new regenerating solutions such as nitric acid (HNO_3) or sulfuric acid (H_2SO_4) for better elution results.

It should be underscored that, due to results given and the high availability and low costs of the biosorbent material, burning was the best disposal of the material after the biosorption process.

Structural characterization of the biosorbent after the adsorption process

Adsorbent infrared spectra after adsorption isotherm experiments were performed again to evaluate the behavior of Cu2+ ions and Zn2+ to the functional groups of the adsorbent (Figure 6).

Figure 6 shows the spectra of the IR region prior to (6a) and after (6b) the adsorption process of the metal ions Cu2+ and Zn2+ by the biosorbent açaí endocarp.

Table 4. Parameters of Langmuir, Freundlich and Dubinin-Radushkevich mathematical models for the biosorbent açaí endocarp (*E. oleracea*) and for activated coal in the adsorption of ions Cu^{2+} and Zn^{2+}.

		Langmuir's constants				Freundlich's constants			D-R parameters		
		Q_m (mg g^{-1})	*b ou* K_L (L mg^{-1})	R_L	R^2	K_f (mg g^{-1})	*n*	R^2	*Qd* (mol g^{-1})	*E*(kJ mol^{-1})	R^2
CCC	Cu^{2+}	3.997	0.448	0.011	0.999	0.680	2.610	0.809	0.000	11.456	0.877
	Zn^{2+}	3.929	0.274	0.018	0.999	1.361	4.282	0.833	0.000	11.223	0.891
CA	Cu^{2+}	14.166	0.004	0.588	0.999	4.817	3.275	0.749	0.000	16.396	0.740
	Zn^{2+}	12.631	0.011	0.322	0.999	3.317	2.820	0.891	0.000	13.710	0.943

Q_m: maximum adsorption capacity; *b* or K_L: constant related to the interaction forces adsorbent/adsorbed; R_L: Langmuir´s constant; R^2: coefficient of determination; K_f: related to adsorption capacity; *n*: related to the solid´s heterogeneity; Q_d: maximum adsorption capacity; *E*: mean sorption energy.

There were no modifications when the functional groups in the structure of the saturated biosorbent were analyzed, showing that there were still bands in the material prior to the biosorption process, which represented functional groups indicating lignin and cellulose. The absence of bands 771 and 667 cm^{-1} should be underscored and proves that the functional groups in these bands (N with biobonds) are not part in the biosorption process.

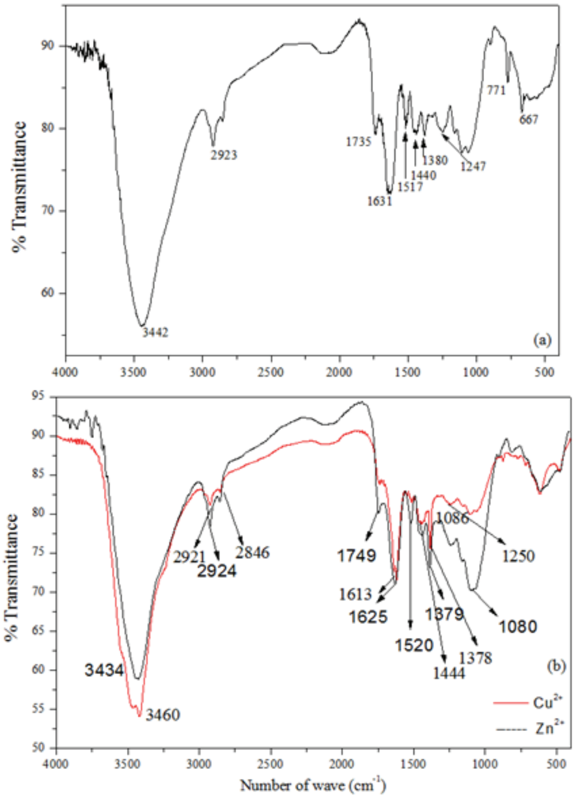

Figure 6. Spectra in the IR region before (a) and after (b) the adsorption of Cu^{2+} and Zn^{2+} ions by the biosorbent açaí endocarp (*E. oleracea*).

Thermodynamics of adsorption

Biosorption mechanism may be determined by thermodynamic parameters such as the variation in Gibbs´ free energy (ΔG), variation in enthalpy (ΔH) and entropy (ΔS) (Witek-Krowiak & Reddy, 2013). Table 5 shows the thermodynamic parameters for the adsorption of Cu^{2+} and Zn^{2+}. When Q_{eq} rates are analyzed, it may be perceived that a rise in temperature causes a decrease in the adsorbed amount per unit of adsorbent, indicating that temperature fails to affect the biosorption process of the metal ions Cu^{2+} and Zn^{2+}.

With regard to thermodynamic parameters, since ΔG rates are negative, they indicate that Cu^{2+} and Zn^{2+} biosorption process is spontaneous and favorable (Debrassi et al., 2011). Further, the ΔH rates are positive (0.004 and 0.005) for the two metal ions, indicating the process endothermal nature (Wan & Hanafiah, 2008).

Table 5. Q_{eq} rates and thermodynamic parameters of Cu^{2+}e Zn^{2+} adsorption on the biosorbent açaí endocarp (*E. oleracea*).

Metal ions	Temperature (°C)	Q_{eq}	Thermodynamic parameters			R^2
			ΔG	ΔH	ΔS	
Cu^{2+}	15	1.214	-0.013	0.004	0.044	0.923
	25	1.156	-0.013			
	35	1.133	-0.014			
	45	0.868	-0.014			
	55	0.654	-0.014			
Zn^{2+}	15	1.617	-0.013	0.005	0.046	0.970
	25	1.345	-0.014			
	35	1.134	-0.014			
	45	1.081	-0.015			
	55	1.124	-0.015			

Q_{eq}: quantity of metal ion adsorbed per adsorbent unit (mg g^{-1}); *ΔG*: variation of Gibbs´ free energy (kJ mol^{-1}); *ΔH*: variation of enthalpy (J mol^{-1}); *ΔS*: variation of entropy (J mol^{-1}).

In the case of the ions Cu^{2+} and Zn^{2+}, the positive rates of ΔS (0.044 and 0.046) suggest an increase in the disorder of the solid-liquid interface. The above indicates an increase in randomness due to the substitution of the solution´s water molecules previously adsorbed by the metal ions (Singha & Das, 2011).

It should be underscored that, although enthalpy was lower than 40 kJ mol^{-1}, characterizing a physical adsorption process (Dos Santos et al., 2010), the best adjustment obtained by the pseudo-second order model (R^2 = 0.997 and 0.999), the rates of the average energy parameter of sorption (E = 11.456 and 11.223) and the low elution percentages (41.77 and 36.83), respectively for metal ions Cu^{2+} and Zn^{2+}, indicate the predominance of the chemical nature of the biosorption process.

Conclusion

The biosorbent´s structural characterization identified the functional groups that showed the existence of lignin and cellulose, whereas the morphological characterization indicated a lamellar structure. Consequently, the biosorbent reveals favorable conditions for the adsorption of the studied metal ions.

The best conditions of the adsorption process for the removal of Cu^{2+} and Zn^{2+} are: solution´s pH at 4.0 and 5.0; the use of 8 g L^{-1} of the biosorbent in the solution and a 60 min contact time.

Evaluated kinetic parameters showed that the biosorbent follows a behavior described by the pseudo-second order model, revealing the chemical process of the biosorption. In the case of adsorption isotherms, Langmuir´s model had the best adjustment and indicated adsorption in monolayers.

Thermodynamic parameters revealed that the biosorption process was spontaneous and endothermic.

The use of açaí endocarp as biosorbent is an alternative method for the remediation of contaminated waters with Cu^{2+} and Zn^{2+}, since the material is natural, low cost and highly available.

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