

Removal of toxic metals using endocarp of açai berry as biosorbent

Affonso Celso Gonçalves Jr, Daniel Schwantes,
Marcelo Angelo Campagnolo, Douglas Cardoso Dragunski,
César Ricardo Teixeira Tarley and Arthur Kinkas dos Santos Silva

ABSTRACT

The effectiveness of açai endocarp as biosorbent for removal of Cd^{2+} , Pb^{2+} and Cr^{3+} from single solute solutions was analyzed. The biomass of açai endocarp was characterized by scanning electron microscopy, infrared spectroscopy and determining the point of zero charge. The optimum conditions for adsorption process were obtained at solution pH 6.0 for Cd(II) removal, pH 5.0 for Pb(II) removal, and, pH 4.0 for Cr(III). Furthermore, the average optimum efficiency of biosorbent in the optimum conditions was 8, 20 and 12 g of biosorbent per litre of contaminant solution, respectively, for Cd(II), Pb(II) and Cr(III). The best dynamic equilibrium time was reached at 60 min and Langmuir's model had the best fit for Cd(II) and Cr(III) biosorption, indicating a monolayer adsorption. Freundlich's model exhibited the best fit for Pb(II) ion. Elution rates were low, indicating a strong metal interaction with the adsorbent's surface. Thermodynamic parameters showed a spontaneous and endothermic process in the case of Cd(II) and Pb(II) ions, but not for Cr(III) ion, which appears to be an exothermic process. Results show that the use of the açai biosorbent may be a promising alternative for the remediation of polluted water, due to its low cost and highly availability.

Key words | adsorption, *Euterpe oleracea* Mart., metal remediation, natural adsorbent, water treatment

Affonso Celso Gonçalves Jr (corresponding author)

Arthur Kinkas dos Santos Silva
Center for Agricultural Sciences,
State University of Western Paraná,
Pernambuco street, 1777, CEP 85960-000,
Marechal Cândido Rondon – Paraná,
Brazil
E-mail: affonso133@hotmail.com

Daniel Schwantes
Department of Engineering and Exact Sciences,
Federal University of Paraná,
Palotina Sector – Pioneiro Street, 2153,
CEP: 85950-000
Palotina – Paraná,
Brazil

Marcelo Angelo Campagnolo
Environmental Engineering, Polytechnic School –
Toledo,
Pontifical Catholic University of Paraná,
União Avenue, 500, CEP: 85902-532,
Toledo – Paraná,
Brazil

Douglas Cardoso Dragunski
Department of Chemistry,
State University of Western Paraná,
College street, 645, CEP 85903-000,
Toledo - Paraná,
Brazil

César Ricardo Teixeira Tarley
Department of Chemistry,
Londrina State University,
Celso Garcia Cid Highway, CEP 86050-482,
Londrina – Paraná
Brazil

INTRODUCTION

Among the several contaminating elements of water resources, heavy metals are dangerous compounds derived from the inadequate storage of non-treated industrial waste. They are priority contaminants due to their toxicity and to their mobility in surface or underground waters, constituting a serious environmental and public health issue. Cadmium (Cd), lead (Pb), chromium (Cr) and other metals are highly toxic in human physiology, causing several diseases and disorders (Bulgariu & Bulgariu 2012).

There are several methods for the removal of these contaminants, such as chemical and physical precipitation, ionic exchange, extraction by solvents, bio-accumulation by aquatic plants or micro-organisms, and filtration by membranes. The adsorption process is one of the most promising for metal remediation (Witek-Krowiak 2012).

Activated carbon is one of the most frequently used adsorbents, although at high costs of production (Santhi *et al.* 2010). The main characteristics of this material are high surface area,

high porosity and surface reactivity, which are excellent characteristics for an adsorbent material. The high cost of production is due to the dependence on controlled burning of biomass with low oxygen content at temperatures of 800 to 1,000 °C, i.e., with great energy expenditure to obtain a small amount of carbon mass (Peireira et al. 2008), which is the main reason for not using it in large scale adsorption processes.

With this in mind, biosorption is a method with a significant contribution for the removal of chemical contaminants (Febrianto et al. 2009).

Biosorption is the natural capacity of biomass to adsorb dissolved components, i.e., the removal of contaminants in the environment, such as from aqueous solutions. Main requirements for the selection of adequate biosorbents are adsorption and regeneration capacity, kinetic and thermodynamic parameters, costs and availability of adsorbent material (Witek-Krowiak 2012).

The search for new adsorbents has been focused on biomaterials, because they are of high availability, biodegradable, economically viable and derived from renewable resources. In general, these materials are locally and easily available in large amounts in the agroindustry. Therefore, they are usually cheap and have little or no economic value (Barreiro et al. 2014; Quintáns-Fondo et al. 2016); i.e., these materials are wastes with no industrial or agricultural use, with their accumulation being in many cases a problem.

Another advantage of the use of such adsorbents is that the content of these materials is lignin, cellulose and other organic species, which include functional groups such as carboxylic groups, phenolic groups, amides, and others, which usually are indicative of good adsorbent materials (Feng et al. 2011).

The 'açazeiro' (*Euterpe oleracea* Mart.) is a tropical, perennial palm tree, common in Brazil, which occurs in the North and Northeast, belonging to the Arecaceae family (Gonçalves et al. 2016). This plant can reach heights of more than 25 meters, with trunks of 9 to 16 centimeters in diameter. Its fruits, the main product of this palm, are rounded, with one to two centimeters in diameter and an average weight of 0.8 to 2.3 grams. The endocarp is bulky and hard, constitutes about 80% of the total volume of the fruit, and is covered by fibrous layers, which are rich in cellulose, hemicellulose and lignin (Pacheco-Palencia et al. 2009), which can be excellent composition characteristics for biosorption of metallic ion processes.

About 216 thousand metric tons of *Euterpe oleracea* berries, commonly known as açai berries, are produced only in Brazil every year, mainly in the Amazon region. The consumption of açai in the northern region of Brazil is generally combined with other regional foods or in the form of ice cream, creams, porridge, jellies and liqueurs,

leaving the endocarp, which does not generate any benefit, with no industrial or agricultural use (Gonçalves et al. 2016).

Açai berries have already been shown to have excellent characteristics for Cu(II) and Zn(II) removal from polluted waters (Gonçalves et al. 2016); however, studies examining the use of this adsorbent for toxic metals are not yet available in literature.

The current study investigates the potential use of the endocarp of the açai berry as a biosorbent in the removal of Cd(II), Pb(II) and Cr(III) from water. The study also deals with the characterization of the adsorbent material by surface morphology, determination of functional groups and of point of zero charge, the evaluation of kinetic, equilibrium and thermodynamic factors of adsorption of metal ions, elution and comparisons with a commercial adsorbent.

METHODS

Preparation and characterization of biosorbent

Endocarps of the açai berry used in the current experiment as biosorbent material were obtained from the southeastern municipality of Curionópolis, state of Pará, Brazil. The material was prepared by drying açai endocarps in an oven (Biopar S36 BD) at 65 ± 2 °C for 48 h, after which it was ground in a Wiley mill (Marconi MA 048) and sieved through 20–48 mesh for the standardization of particle size.

To determine the original concentrations of the metal ions Cd^{2+} , Pb^{2+} and Cr^{3+} in biosorbent *in nature* as well as potassium (K), calcium (Ca), magnesium (Mg), copper (Cu), iron (Fe), manganese (Mn) and zinc (Zn) (AOAC International 2005) nitroperchloric digestion was performed and the elemental composition as determined by FAAS – flame atomic absorption spectrometry (Welz & Sperling 1999).

Biosorbent surface morphology was analyzed by an FEI Quanta 200 scanning electron microscope (SEM) at 30 kV. Infrared spectroscopy analyses determined the functional groups in the biosorbent before and after the adsorption process. A Shimadzu FTIR-8300 Fourier transform infrared spectrophotometer was employed in the 400 and 4,000 cm^{-1} region, with 4 cm^{-1} resolution. Structural characterization of the biosorbent under saturation conditions was performed to verify alterations of functional groups.

The point of zero charge (pH_{PZC}) was determined according to the methodology proposed by Mimura et al. (2010). The procedure to define the zero load point, i.e., the pH at which the surface of the solid has a neutral charge, was determined by preparing a solution of KCl in the concentration of 0.5 mol L^{-1} with

initial pH values from 2.0 to 8.0 by adjustment with NaOH and HCl at 0.1 mol L^{-1} . Then, 0.4 g of each adsorbent was added to 40 mL of solution and kept under constant stirring for 24 hours. Subsequently the final pH was measured. By plotting the values of ΔpH versus initial pH, we obtain the point of intercept of the curve with the x-axis, which corresponds to the material pH_{PZC} .

Preparation of contaminated solutions and optimal conditions of adsorption

Contaminated single solute solutions with metal ions Cd(II), Pb(II) and Cr(III) were prepared from salts (Sigma-Aldrich) of cadmium nitrate [$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ P.A. (para análise; Portuguese analysis grade) $\geq 99\%$], lead nitrate [$\text{Pb}(\text{NO}_3)_2$ P.A. $\geq 99\%$] and chromium nitrate III [$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ P.A. $\geq 99\%$], respectively, diluted in type I ultrapure water produced by a Puritech Permuton[®] system.

All adsorption tests were performed in triplicate and performed in batch systems; concentrations of metal ions were determined by FAAS (Welz & Sperling 1999), stirring in Erlenmeyer flasks of 125 mL at 200 rpm, with 50 mL of contaminated single solute solutions.

Three pH conditions (4.0; 5.0; 6.0) were studied, for three basic reasons: according to pHPZC result (5.09), because adsorption of cations is theoretically favored by values above the pHPZC ; also because of the pH of normal band of wastewaters, which is in many cases about 4.0 to 6.0; and also to avoid chemical precipitation of the metals in solution, which usually occurs at pH rates higher than 7.0.

The pH of contaminated solutions was adjusted with NaOH (Vetec, 99%) or HCl (Vetec, 37%) at a concentration of 0.1 mol L^{-1} . Increasing quantities of biosorbent mass, varying between 200 and 1,200 mg, were employed.

Shaking speed (200 rpm) and period (1.5 h), temperature (25°C) and the concentration of metal ions in the solutions (10 mg L^{-1}) were maintained constant. After batch tests in a Dubnoff thermostated bath (Marconi MA 035), solutions were filtered through quality filter paper (Unifil) to separate the biosorbent and liquid solution, followed by the determination of metal ion concentrations in the solution. Removal percentage was calculated from results according to Equation (1):

$$\%R = 100 - \left(\frac{C_{\text{eq}}}{C_0} 100 \right) \quad (1)$$

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

For kinetics studies, the optimal conditions obtained in the previous tests were employed. Shaking periods comprised intervals between 5 and 180 min. The constant experimental conditions for Cd(II) adsorption were 400 mg of adsorbent (8 g L^{-1}) at solution pH 6.0; for Pb(II) 1,000 mg of adsorbent (20 g L^{-1}) at solution pH 5.0; and for Cr(III) adsorption test 600 mg of adsorbent was used (12 g L^{-1}) at solution pH 4.0. After stirring, solutions were filtered and the concentrations of metal ions were calculated. The balanced adsorbed quantity was calculated from the rate obtained by the concentration in equilibrium (Equation (2)).

$$Q_{\text{eq}} = \frac{(C_0 - C_{\text{eq}})}{m} V \quad (2)$$

where Q_{eq} is the quantity of ions adsorbed per unit of adsorbent in equilibrium (mg L^{-1}); m is the adsorbent mass used (g); C_0 is the initial ion concentration in the solution (mg L^{-1}); C_{eq} is the ion concentration in the solution in equilibrium (mg L^{-1}); V is the volume of the solution employed (L).

The obtained results were linearized by the mathematical models of pseudo-first order, as described by Ho & McKay (2004), pseudo-second order (Ho & McKay 1999), Elovich, as described by Ho & McKay (2004), and intraparticle diffusion, as described by Yang & Al-Duri (2005).

Adsorption isotherms (equilibrium studies)

The optimal conditions obtained in the previous tests were employed in the isotherms tests. In all batch experiments the same conditions were kept. Initial concentrations of metal ions ranged between 5 and 200 mg L^{-1} . The obtained results were linearized by Langmuir's (Langmuir 1916), Freundlich's (Freundlich 1906) and Dubinin-Radushkevich's (Dubinin & Radushkevich 1947) models.

Elution (possibility of the adsorbent reuse)

The elution process was performed after the isotherm tests, using the obtained mass added with 50 mL of HCl (0.1 mol L^{-1}) with constant shaking at 200 rpm. The biosorbent material was then separated by filtration.

Study on the effect of temperature in the adsorption process (thermodynamics)

Five temperature values ranging between 15 and 55°C were tested to verify the effect of temperature in the adsorption process, using 50 mL of contaminant solution

at 50 mg L⁻¹ concentration of metal ion, The experimental conditions were, for Cd(II) adsorption, 400 mg of adsorbent (8 g L⁻¹) at solution pH 6.0; for Pb(II), 1,000 mg of adsorbent (20 g L⁻¹) at solution pH 5.0; and for Cr(III) adsorption test, 600 mg of adsorbent (12 g L⁻¹) at solution pH 4.0. All these experiments were performed with 60 min of contact time between adsorbent/adsorbate, according to the obtained optimum results.

The obtained values of Q_{eq} were employed in the estimative of thermodynamic parameters ΔG (Gibbs free energy), ΔH (enthalpy) and ΔS (entropy), as equations described by Sari *et al.* (2007), which indicate, respectively, the spontaneity of the adsorption process, endothermic or exothermic reactions, and the disorder of the process.

Comparative study between proposed biosorbent and a commercial adsorbent

Açai endocarp was evaluated in comparative studies with powdered activated carbon (Synth, Diadema, São Paulo state, Brazil) in the same experimental conditions. For this purpose the isotherm studies were undertaken.

Description of employed models

Table 1 shows all mathematical models employed in the current research, all of them in the used linear form.

RESULTS AND DISCUSSION

Characterization of the biosorbent

No Cd²⁺, Pb²⁺ or Cr³⁺ metal ions were detected in the evaluated biosorbent. Figure 1 shows the SEM images at an enlargement of 150× (a) and 12,000× (b).

Analysis of the images reveals that the biosorbent's surface is fibrous, irregular and with significant voids. It also shows a laminar structure with fissures and pores on the surface, which indicates that the material has rather favorable morphology for the adsorption of contaminants.

Before adsorption (Figure 2(a)) a large and strong 3,342 cm⁻¹ biosorbent band is observed, attributed to the vibration lengthening of the O-H link. The band characterizes vibration stretching of the hydroxyl group in cellulose, lignin and water adsorbed at the surface of the adsorbent (Feng *et al.* 2011). The 2,923 cm⁻¹ band refers to the vibration lengthening of C-H links of alkane groups, whereas the 1,735 cm⁻¹ band may be attributed to carbonyl groups of

aldehyde and ketone functions in lignin and holocellulose (Pastore *et al.* 2004). Bands 1,631, 1,517 and 1,440 cm⁻¹ may be attributed to the vibration lengthening of C-O links of starches and carboxylic groups (Han *et al.* 2010). The 1,247 cm⁻¹ band may be associated with C-O stretching in phenols (Han *et al.* 2010). Wave length bands less than 800 cm⁻¹ may be attributed to N with bio-links (Barka *et al.* 2010), whilst 771 and 667 cm⁻¹ bands may be attributed to the vibration lengthening of the C-N link (Salem & Awwad 2011).

After the adsorption process (Figure 2(b)) there is a decrease in the intensity of the vibrations due to chemical reactions related to the adsorption process. In this way, bands still exist in the material after the biosorption process, suggesting the presence of alkane groups, carbonyl groups, aldehyde, ketone, carboxylic groups, phenols, and others which are constituents of lignin and cellulose macromolecules. Moreover, the literature shows that açai endocarp is rich in lignin and cellulose (Pacheco-Palencia *et al.* 2009), corroborating the obtained results.

The possible functional groups found in adsorbent materials suggest that the physical adsorption may be favored, with physical interaction between these groups and metals.

Results for pHPZC of the biosorbent are shown in Figure 3. According to Santhi *et al.* (2010), cation adsorption must be favored by solution pH values higher than the pHPZC, which in this study is 5.09.

Effect of adsorbent mass and pH of contaminated solution in the adsorption process

Figure 4 exhibits some results for ideal adsorption conditions. In the case of Cd(II), removal percentage was higher, on average 90%, at pH 6.0. Similar results were obtained in studies employing *Crambe abyssinica* seeds pie (Rubio *et al.* 2013) as biosorbents. As the solution's pH increased, removal efficiency increased too.

Moreover, 400 mg of biosorbent mass in studies on Cd(II) was used, equivalent to 8 g of biosorbent per litre of water solution, since higher removal percentage were not found with mass increase. Similar results were obtained when biosorbent consisted of a *Moringa oleifera* seeds pie (Meneghel *et al.* 2013a).

Removal percentage of Pb(II) (Figure 4) was similar no matter the evaluated pH value (4.0, 5.0 or 6.0), although pH 5.0 was selected in later studies, because Pb may precipitate or complex into other forms in pH rates higher than 5.0 and thus affect the adsorptive

Table 1 | Mathematical linear models used for kinetic, equilibrium and thermodynamic studies*Kinetic linear models*

Pseudo-first order model (Ho & McKay 2004)	$\log(Q_{eq} - Q_t) = \log Q_{eq} - \left(\frac{K_1}{2.303}\right)t$	Q_{eq} and Q_t (mg g ⁻¹): quantities of adsorbate retained per gram of adsorbent in equilibrium and in time (t); K_1 (min ⁻¹): the rate constant of pseudo-first order.
Pseudo-second order model (Ho & McKay 1999)	$\frac{t}{Q_t} = \frac{1}{K_2 Q_{eq}^2} + \frac{1}{Q_{eq}} t$	K_2 (g mg ⁻¹ min ⁻¹): the rate constant of pseudo-second order.
Elovich model (Ho & McKay 2004)	$Q_{eq} = A + B \ln t$	A: the speed of initial chemisorption (mg g ⁻¹ h ⁻¹); B: number of suitable sites for adsorption, which is related to the extent of surface coverage and the activation energy of chemisorption (g mg ⁻¹).
Intraparticle diffusion model (Yang & Al-Duri 2005)	$Q_{eq} = K_{id} t^{1/2} + C_i$	K_{id} : intraparticle diffusion constant (g mg ⁻¹ min ^{-1/2}); C_i : suggests the thickness of the boundary layer effect (mg g ⁻¹); t: time.

Equilibrium linear models

Langmuir model (Langmuir 1916)	$\frac{1}{Q_e} = \frac{1}{C_m} + \frac{1}{K_L C_m C_e}$ $\frac{C_{eq}}{q_{eq}} = \frac{1}{q_m b} + \frac{C_{eq}}{q_m}$	C_e or C_{eq} : concentration at equilibrium; Q_e or q_{eq} : amount adsorbed at equilibrium per unit of mass of the adsorbent; K_L or $q_m b$ and C_m : reflect properly the nature of the adsorbent material and can be used to compare the performance of adsorption; C_m or q_m : maximum capacity of adsorption; K_L or $q_m b$: adsorbent-adsorbate interaction forces.
Freundlich model (Freundlich 1906)	$\log q_{eq} = \log K_f + \left(\frac{1}{n}\right) \log C_{eq}$	C_{eq} : concentration on balance; q_{eq} : amount adsorbed at equilibrium per unit of mass of adsorbent; K_f and n : the two parameters of Freundlich.
Dubinin-Radushkevich model (Dubinin & Radushkevich 1947)	$\ln Q_{eq} = \ln Q_d - B_d \varepsilon^2$ $\varepsilon = RT \ln \left(1 + \frac{1}{C_{eq}}\right)$	Q_{eq} : amount of adsorbed ion per unit mass of the adsorbent (mol g ⁻¹); Q_d : adsorption capacity (mol L ⁻¹); B_d : coefficient related to the energy of sorption (mol ² J ⁻²); ε : potential of Polanyi. R: universal gas constant (kJ mol ⁻¹ K ⁻¹); T: temperature (K); C_{eq} : liquid phase equilibrium concentration (mol L ⁻¹).

Thermodynamic lineal models

Gibbs free energy parameter (Sari et al. 2007)	$\Delta G = -RT \ln K_d$	K_d : ratio of the quantity adsorbed per unit of adsorbent (Q_{eq}) and solution concentration in equilibrium (C_{eq}); R: universal gas constant (8.314 J mol ⁻¹ K ⁻¹); T: temperature used in the experiment (K). The values of ΔH and ΔS were obtained from the graph of $\ln K_d$ as a function of $1/T$.
Enthalpy and entropy parameters (Sari et al. 2007)	$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$	

process. Pb may have different forms at different pH conditions. In water solutions with pH < 6, the Pb ions may become Pb(II) and/or Pb(OH)⁺. The formation of Pb(II) hydrolysis products occurs in pH > 6.0 conditions and may lead towards polymerization (Reddy et al. 2010). The use of 1,000 mg, the equivalent of 20 g of biosorbent per litre of contaminated solution was selected with regard to the ideal mass of the biosorbent in terms of Pb(II) removal.

Another study using *Moringa oleifera* showed that the pH range between 3 and 6 showed maximum removal of Pb, higher than 98%, agreeing with the previously results (Tavares et al. 2015). Further, a mass of 600 mg was decided

upon, or rather, the equivalent of 12 g of biosorbent per litre of contaminated solution.

There was a variation in removal percentage for pH conditions under analysis for Cr(III) (Figure 4(c)). Therefore, pH 4.0 was selected due to a higher removal percentage of Cr(III) at this value.

Kinetics of adsorption

Figure 5 provides the results on the quantity of metal ions Cd(II), Pb(II) and Cr(III) adsorbed per mass unit of the adsorbent açai endocarp according to time.

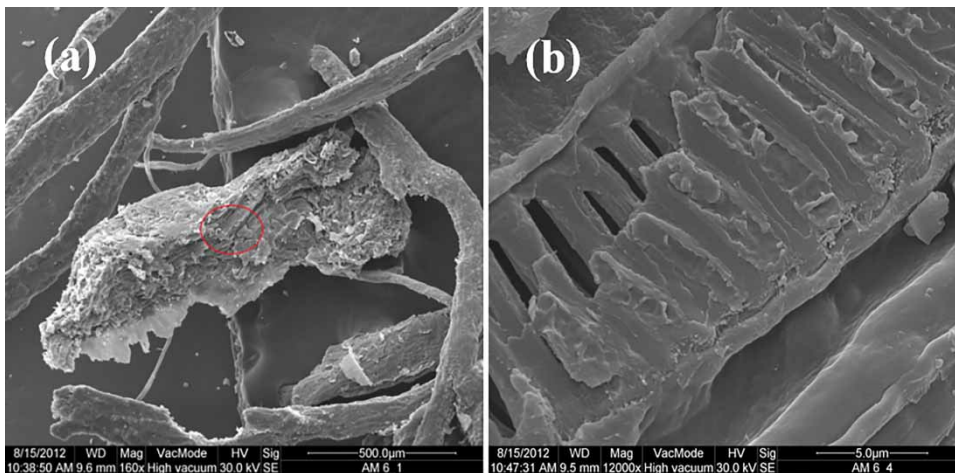


Figure 1 | SEM images of the biosorbent açai endocarp (*Euterpe oleracea* Mart.) amplified by 150× (a) and 12,000× (b).

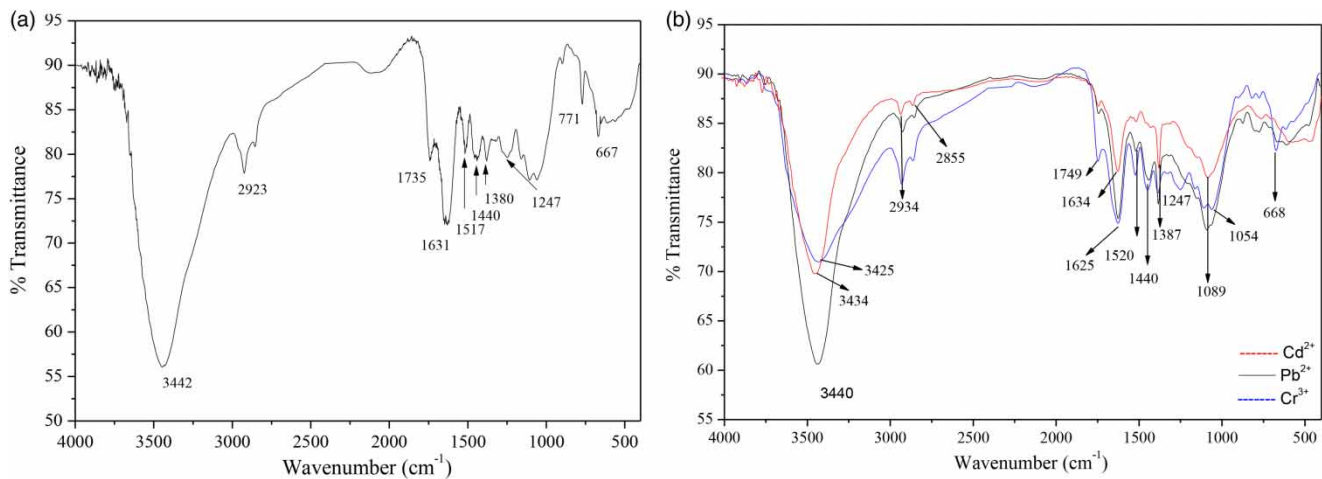


Figure 2 | Spectra in the IR region before (a) and after (b) adsorption of ions Cd²⁺, Pb²⁺ and Cr³⁺ for the biosorbent açai endocarp (*Euterpe oleracea* Mart.).

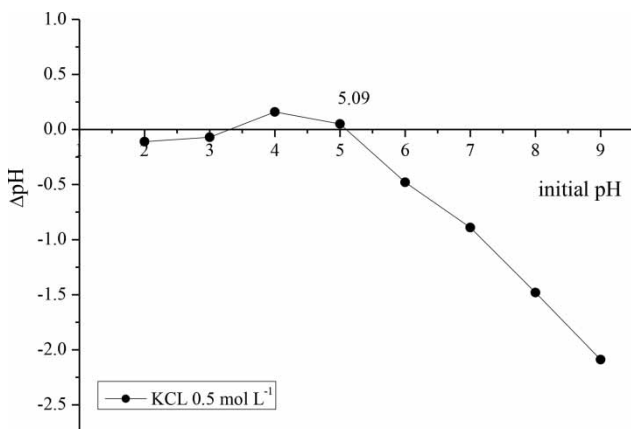


Figure 3 | Graph of point of zero charge (pH_{pzc}) for the biosorbent açai endocarp (*Euterpe oleracea* Mart.).

Results show an increase in adsorption rates over time; after 60 min the adsorption process enters into dynamic equilibrium, reaching the higher adsorption capacity.

According to [Witek-Krowiak \(2012\)](#) adsorption kinetics revealed a fast initial removal of metals in solutions, followed by a slower process. In fact, [Figure 5](#) shows a higher adsorption rate in the initial minutes followed by a gradual stabilization. Most active sites of the adsorbent are initially available. Proportionally to their occupation of sites, the molecules in the solution are adsorbed with greater difficulty due to the repulsion forces between the molecules adsorbed in the solid and those still in the solution ([Ibrahim 2010](#)).

According to [Meneghel et al. \(2013b\)](#) the best mathematical adjustment depends on the obtained coefficients of

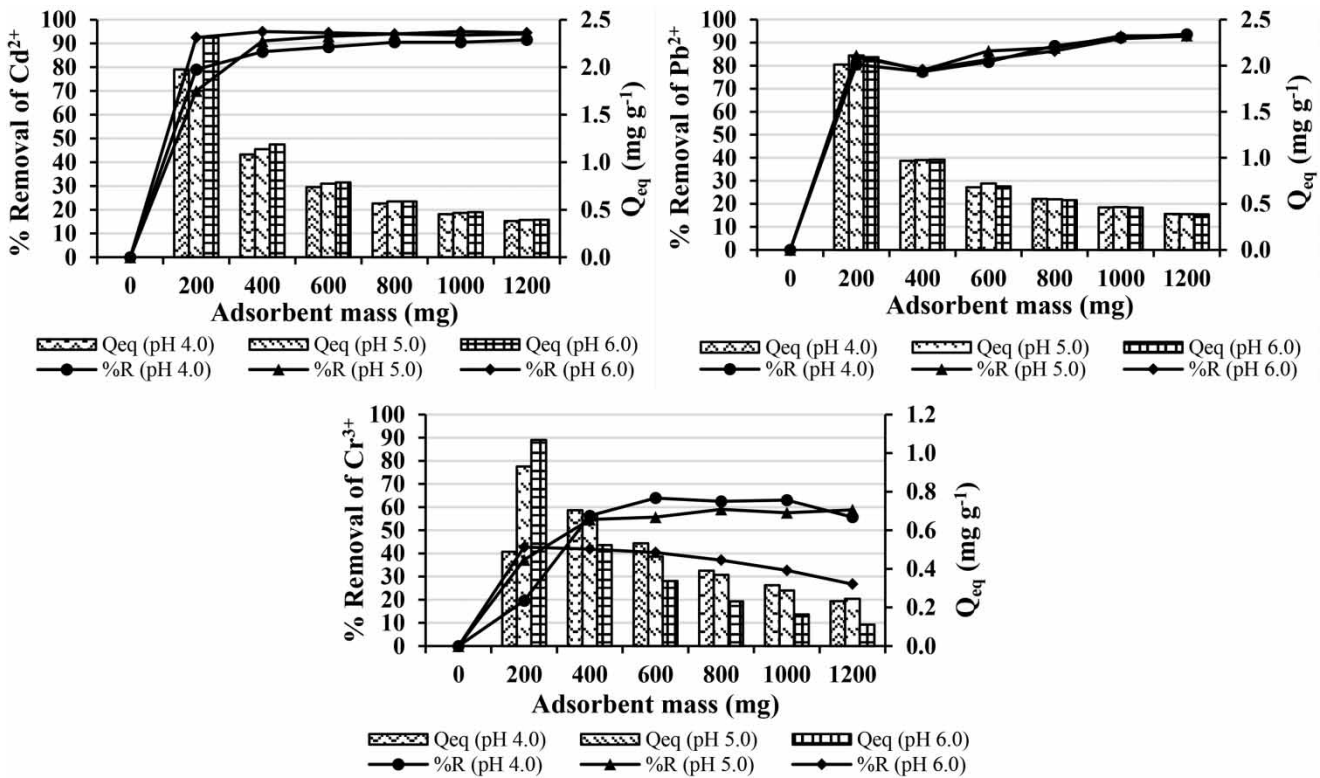


Figure 4 | Effect of the solution's adsorbent mass and pH on the removal percentage and Q_{eq} ($mg\ g^{-1}$) of Cd^{2+} , Pb^{2+} and Cr^{3+} for biosorbent açai endocarp (*Euterpe oleracea* Mart.).

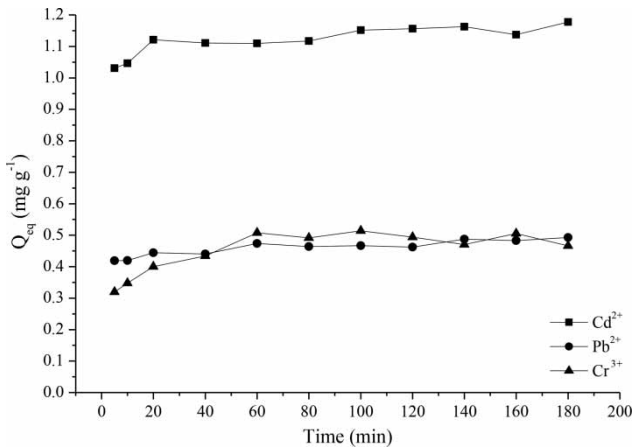


Figure 5 | Effect of time (min) on the quantity of adsorbed ($mg\ g^{-1}$) Cd^{2+} , Pb^{2+} and Cr^{3+} ions by the biosorbent açai endocarp (*Euterpe oleracea* Mart.).

determination (R^2) and the proximity of the quantity adsorbed in equilibrium ($Q_{eq\ calc.}$) to that experimentally obtained ($Q_{eq\ exp.}$), i.e., when R^2 presents values close to 1, and when the values of $Q_{eq\ calc.}$ and $Q_{eq\ exp.}$ are close to each other, the proposed mathematical model represents with fidelity the observed adsorption process. The values of kinetic parameters are shown in Table 2.

The kinetics tests show best fit by the pseudo-second order model, according to the R^2 (0.999; 0.998; 0.994) and proximity between $Q_{eq\ calc.}$ (1.170; 0.491; 0.493) and $Q_{eq\ exp.}$ (1.120; 0.459; 0.450) indicating chemical characteristics in the adsorption process (Ho & McKay 1999).

The models of pseudo-first order, Elovich and intraparticle diffusion do not show satisfactory fit or correlation between Q_{eq} values.

The pseudo-second order kinetics describes well the processes of chemical adsorption, involving donation or exchange of electrons between the adsorbate and the adsorbent, as covalent and ion exchange forces (Ho & McKay 2004); in this type of adsorption, the molecules are not attracted by all the points of the surface of the solid, but specifically to the active centers, in order to form a single layer initially, and other layers can be formed by physisorption (Neta et al. 2012). The obtained results for kinetics studies suggests that chemisorption is the main process that regulates the adsorption of Cd(II), Pb(II) and Cr(III) by *Euterpe oleracea* Mart. biosorbent.

Such results demonstrate that the process of metals adsorption is more complex than imagined. The adsorbent material appears to be extremely heterogeneous; the results

Table 2 | Kinetic parameters obtained in the adsorption study of Cd²⁺, Pb²⁺ and Cr³⁺ on açai biosorbent (*Euterpe oleracea* Mart.) for the pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion models

	Pseudo-first order			Pseudo-second order		
	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
Cd ²⁺	-0.017	0.159	0.948	0.488	1.170	0.999
Pb ²⁺	-0.011	0.076	0.876	0.692	0.491	0.998
Cr ³⁺	-0.012	0.157	0.622	0.926	0.493	0.994
Elovich						
	A	B	R ²	Q _{eq} (exp.)		
	(mg g ⁻¹ h ⁻¹)	(g mg ⁻¹)		(mg g ⁻¹)		
Cd ²⁺	-22.438	23.605	0.957	1.120		
Pb ²⁺	-17.155	45.683	0.933	0.459		
Cr ³⁺	-3.175	15.475	0.927	0.450		
Intraparticle diffusion						
	K _{id} (g mg ⁻¹ min ^{-1/2})		C _i (mg g ⁻¹)		R ²	
	Line A	Line B	Line A	Line B	Line A	Line B
Cd ²⁺	111.524	20.657	22.460	105.952	0.865	0.984
Pb ²⁺	40.719	36.000	92.815	109.299	0.789	0.689
Cr ³⁺	68.145	8.715	34.005	118.463	0.960	0.784

K₁: first order velocity constant; Q_{eq}: amounts of adsorbate retained per gram of adsorbent at equilibrium; K₂: rate constant of pseudo-second order; A: constant indicating the initial chemisorption rate; B: number of sites suitable for adsorption, related to the extent of surface coverage and the activation energy of the chemisorption; R²: coefficient of determination; K_{id}: intraparticle diffusion constant; C_i: suggests the thickness of the boundary layer effect.

through the FTIR analysis suggest the occurrence of physical adsorption, and the results observed by the pseudo-second order model suggest the occurrence of chemisorption.

Adsorption isotherms

Isotherms were constructed from data obtained experimentally and linearized according to Langmuir's (Witek-Krowiak 2012), Freundlich's (Witek-Krowiak 2012) and Dubinin-Radushkevich's (D-R) (Farooq et al. 2011) models (Table 3).

Langmuir's and Freundlich's models showed best fit for Cd(II) and Cr(III) biosorption on açai endocarp, with a coefficient of determination of 0.990 and 0.981. According to Fávere et al. (2010), Langmuir's model suggested adsorption in monolayers, and Freundlich's describe a multilayer sorption; in this specific case we observe the occurrence of both, showing that the adsorption mechanism of these metals is complex. Freundlich's showed best fit for Pb(II) (R² = 0.979), indicating multilayer adsorption. In the case of adsorption by activated carbon, Freundlich's showed the

best fit for Cd(II) and Pb(II) (R² = 0.982 and 0.979), whereas Langmuir's showed best fit for Cr(III) (R² = 0.985), indicating multilayers of Cd(II) and Pb(II), while predominance of monolayers of Cr(III).

Langmuir's parameters demonstrate that rates of the highest adsorption quantity (Q_m) for Cd(II), Pb(II) and Cr(III) are higher for activated carbon (Table 3). It may also be perceived in the case of K_L, a constant related to the adsorbent/adsorbed interaction forces, higher values are found for biosorbent than activated carbon. Also, R_L values show that within the conditions in which adsorption tests were developed, the adsorption process was favorable in all cases since rates ranged between 0 and 1 (Lin & Juang 2002).

The parameter 'n' (from Freundlich's) indicates the reaction of the adsorbent's active sites. When 'n' rates are over 1, there is a strong indication of high energetic sites and suggests that they are the first to be occupied by the metals. Consequently, high energetic interaction and reactivity behavior may be observed for all metal ions under analysis in the biosorbent and in activated carbon.

Table 3 | Parameters of Langmuir's, Freundlich's and Dubinin–Radushkevich's models for biosorbent açai (*Euterpe oleracea* Mart.) endocarp in the adsorption of Cd²⁺, Pb²⁺ and Cr³⁺ ions

Parameters	Açai endocarp			Activated coal		
	Cd ²⁺	Pb ²⁺	Cr ³⁺	Cd ²⁺	Pb ²⁺	Cr ³⁺
<i>Langmuir</i>						
Q _m (mg g ⁻¹)	8.130	16.173	1.211	45.998	-18.979	15.047
b or K _L (L mg ⁻¹)	0.226	0.055	8.274	0.001	-0.009	0.006
R _L	0.022	0.084	0.001	0.822	0.222	0.478
R ²	0.990	0.825	0.981	0.830	0.329	0.985
<i>Freundlich</i>						
K _f (mg g ⁻¹)	1.181	0.682	0.231	13.352	31.714	6.152
n	2.418	1.918	2.951	1.296	1.620	3.256
R ²	0.984	0.981	0.979	0.982	0.979	0.964
<i>Dubinin–Radushkevich</i>						
Q _d (mol g ⁻¹)	0.000	0.000	0.000	0.001	0.008	0.000
B _d	-0.003	-0.005	-0.002	-0.004	-0.005	-0.002
E (KJ mol ⁻¹)	12.328	9.704	16.440	10.976	9.960	17.623
R ²	0.798	0.841	0.838	0.728	0.759	0.702

Q_m (mg g⁻¹): maximum adsorption capacity; K_L or b (L mg⁻¹): constant related to adsorbent/adsorbed interaction forces; R_L: Langmuir's constant; R²: coefficient of determination; K_f (mg⁻¹g): related to adsorption capacity; n: related to the solid's heterogeneity; Q_d (mol g⁻¹): maximum adsorption capacity; E (kJ mol⁻¹): average sorption energy.

With regard to D-R's mathematical model, the obtained values of R² indicate low correlation between the experimental data and the mathematical model; in this case the parameter values are underestimated or overestimated, i.e., cannot be used for interpretation of the adsorption process.

Thermodynamics of adsorption

Table 4 gives the values of the estimated thermodynamic parameters ΔG, ΔH and ΔS.

The variation of Gibbs's free energy (ΔG) is related to the spontaneity of the process; enthalpy variation (ΔH) indicates whether the process is endothermic or exothermic; entropy variation (ΔS) is related to the system order after the adsorption process (Sari et al. 2007).

There was a gradual increase in the adsorbed quantity per biosorbent unit for metal ions Cd(II) and Cr(III), demonstrating the influence of temperature on the biosorption process. In the case of Pb(II) a decrease occurred in the adsorbed amount per adsorbent unit with the temperature increase.

The values of ΔH indicate an endothermic process for Cd(II) and Pb(II) (8.126 × 10⁻⁶ and 5.204 × 10⁻⁶ J mol⁻¹, respectively) and exothermic process for Cr(III) (-6.679 J mol⁻¹) (Wan Ngah & Hanafiah 2008; Wan Ngah & Fatinathan 2010).

Table 4 | Values of obtained Q_{eq} and thermodynamic parameters of adsorption of Cd²⁺, Pb²⁺, Cr³⁺ on açai biosorbent (*Euterpe oleracea* Mart.)

Metals	Temperature (°C)	Q _{eq}	Thermodynamic parameters			
			ΔG	ΔH	ΔS	R ²
Cd ²⁺	15	3.013	-0.003	0.008	0.011	0.996
	25	3.441	-0.003			
	35	3.522	-0.004			
	45	3.553	-0.004			
	55	3.675	-0.004			
Pb ²⁺	15	2.221	-0.010	0.005	0.034	0.917
	25	2.074	-0.010			
	35	2.044	-0.010			
	45	2.035	-0.011			
	55	2.032	-0.011			
Cr ³⁺	15	0.519	0.013	-6.679	0.046	0.963
	25	0.552	0.014			
	35	0.580	0.014			
	45	0.594	0.015			
	55	0.597	0.015			

Q_{eq}: adsorbed amount of metal ion per unit of adsorbent (mg g⁻¹); ΔG: Gibbs free energy variation (kJ mol⁻¹); ΔH: change in enthalpy (J mol⁻¹); ΔS: change in entropy (J mol⁻¹).

Further, the obtained values of ΔG for Cd(II) and Pb(II) indicate a spontaneous adsorption process, while Cr(III) showed positive values, indicating a non-spontaneous process (Farooq et al. 2011).

The positive values of ΔS confirm that the process has greater randomness in the system (0.01, 0.03 and 0.04 J mol⁻¹, respectively for Cd, Pb and Cr), suggesting, according to Singha & Das (2011) and Sotirelis & Chrysikopoulos (2015), high affinity of the sorbent for the sorbate, which is an excellent result, indicating high affinity of these toxic metals for the studied biosorbent.

Elution

The obtained results indicate low rates for biosorbent recovery, especially when the biosorbent is used for Cr(III) removal (44.5; 45.47 and 1.12% for Cd, Pb and Cr, respectively).

In this way, the obtained data suggest a chemisorption of Cr(III), as in the work of Schwantes *et al.* (2016), which shows that due to the low elution rate there are strong bonds between the metals and the biosorbent material. In this case, the reuse of adsorbent materials for new adsorption processes is not feasible. However, in the case of Cd(II) and Pb(II), the use of different concentrations for HCl solution may be possible or solutions such as nitric acid (HNO₃) or sulfuric acid (H₂SO₄) for better elution results (Sekhar *et al.* 2004).

CONCLUSIONS

Results show that the use of the açai endocarp as biosorbent is an alternative for the recovery of water contaminated by Cd(II), Pb(II) and Cr(III), since the material is natural, low-cost and highly available.

The obtained results indicate that the adsorption is a complex process, especially when biosorbents are employed, which due to their heterogeneity can indicate chemical or physical adsorption of metals, as is the case of the present study.

More studies with the biosorbent of açai endocarp must be conducted, evaluating its potential in removal of other inorganic and organic pollutants from waters.

REFERENCES

- AOAC International 2005 *Official Methods of Analysis*. 18th edn. AOAC International, Gaithersburg, MD, USA.
- Barka, N., Abdennouri, M., Boussaoud, A. & Makhfouk, M. E. L. 2010 Biosorption characteristics of cadmium (II) onto *Scolymus hispanicus* L. as low-cost natural biosorbent. *Desalination* **258** (1–3), 66–71.
- Barreiro, L. C., Manso, L. A., Calviño, D. F., Estévez, M. A., Muñoz, J. C. N., Sanjurjo, M. J. F., Rodríguez, E. Á. & Delgado, A. N. 2014 Pine bark as bio-adsorbent for Cd, Cu, Ni, Pb and Zn: batch-type and stirred flow chamber experiments. *Journal of Environmental Management* **114**, 258–264.
- Bulgariu, D. & Bulgariu, L. 2012 Equilibrium and kinetics studies of heavy metal ions biosorption on green algae waste biomass. *Bioresource Technology* **103**, 489–493.
- Dubinín, M. M. & Radushkevich, L. V. 1947 The equation of the characteristic curve of the activated charcoal. *Proceedings of the National Academy of Sciences. USSR Physical Chemistry Section* **55**, 331–337.
- Farooq, U., Khan, M. A., Athar, M. & Kozinski, J. A. 2011 Effect of modification of environmentally friendly biosorbent wheat (*Triticum aestivum*) on the biosorptive removal of cadmium (II) ions from aqueous solution. *Chemical Engineering Journal* **171** (2), 400–410.
- Fávere, V. T., Riella, H. G. & Rosa, S. 2010 Chitosan-n-2-hydroxypropyl trimethyl ammonium chloride as adsorbent for the removal of the reactive dye from aqueous solutions. *Química Nova* **33** (7), 1476–1481.
- Febrianto, J., Kosasih, A. N., Sunarso, J., Ju, Y. H., Indraswati, N. & Ismadji, S. 2009 Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: a summary of recent studies. *Journal of Hazardous Materials* **162**, 616–645.
- Feng, N., Guo, X., Liang, S., Zhu, Y. & Liu, J. 2011 Biosorption of heavy metals from aqueous solutions by chemically modified orange peel. *Journal of Hazardous Materials* **185** (1), 49–54.
- Freundlich, H. M. F. 1906 Over the adsorption in solution. *The Journal of Physical Chemistry* **57**, 385–471.
- Gonçalves Jr, A. C., Coelho, G. F., Schwantes, D., Rech, A. L., Campagnolo, M. A. & Miola, A. J. 2016 Biosorption of Cu (II) and Zn (II) with açai endocarp *Euterpe oleracea* M. in contaminated aqueous solution. *Acta Scientiarum. Technology* **38** (3), 361–370.
- Han, R., Zhang, L., Song, C., Zhang, M., Zhu, H. & Zhang, L. 2010 Characterization of modified wheat straw, kinetic and equilibrium study about copper ion and methylene blue adsorption in batch mode. *Carbohydrate Polymers* **79**, 1140–1149.
- Ho, Y. S. & McKay, G. 1999 Pseudo-second-order model for sorption process. *Process Biochemistry* **34** (5), 451–465.
- Ho, Y. S. & McKay, G. 2004 Sorption of copper (II) from aqueous solution by peat. *Water Air and Soil Pollution* **158** (1), 77–97.
- Ibrahim, M. N. M. 2010 A novel agricultural waste adsorbent for the removal of lead (II) ions from aqueous solutions. *Journal of Hazardous Materials* **182** (1–3), 377–385.
- Langmuir, I. 1916 The constitution and fundamental properties of solids and liquids. *Journal of the American Chemical Society* **38** (11), 2221–2295.
- Lin, S. H. & Juang, R. S. 2002 Heavy metal removal from water by sorption using surfactant-modified montmorillonite. *Journal of Hazardous Materials* **97** (3), 315–326.
- Meneghel, A. P., Gonçalves Jr, A. C., Rubio, F., Dragunski, D. C., Lindino, C. A. & Strey, L. 2013a Biosorption of cadmium from water using moringa (*Moringa oleifera* Lam.) seeds. *Water, Air and Soil Pollution* **224**, 1383–1396.

- Meneghel, A. P., Gonçalves Jr, A. C., Strey, L., Rubio, F., Schwantes, D. & Casarin, J. 2013b Biosorption and removal of chromium from water by using moringa seed cake (*Moringa oleifera* Lam.). *Quimica Nova* **36**, 1104–1110.
- Mimura, A. M. S., Vieira, T. V. A., Martelli, P. B. & Gorgulho, H. F. 2010 Utilization of rice husk to remove Cu^{2+} , Al^{3+} , Ni^{2+} and Zn^{2+} from wastewater. *Quimica Nova* **33** (6), 1279–1284.
- Neta, J. J. S., Silva, C. J., Moreira, G. C., Reis, C. & Reis, E. L. 2012 Removal of the reactive blue 21 and direct red 80 dyes using seed residue of *Mabea fistulifera* Mart. as biosorbent. *Revista Ambiente & Água* **7**, 104–119.
- Pacheco-Palencia, L. A., Duncan, C. E. & Talcott, S. T. 2009 Phytochemical composition and thermal stability of two commercial acai species, *Euterpe oleracea* and *Euterpe precatoria*. *Food Chemistry* **115**, 1199–1205.
- Pastore, T. C. M., Santos, K. O. & Rubim, J. C. 2004 Spectrocolorimetric study on the effect of ultraviolet irradiation of four tropical hardwoods. *Bioresource Technology* **93** (1), 37–42.
- Peireira, E., Oliveira, L. C. A., Vallone, A., Sapag, K. & Pereira, M. 2008 Preparation of activated carbon at low carbonization temperatures: utilization of FeCl_3 as an alternative activating agent. *Quimica Nova* **31** (6), 1296–1300.
- Quintáns-Fondo, A., Ferreira-Coelho, G., Paradelo-Núñez, R., Nóvoa-Muñoz, J. C., Arias-Estévez, M., Fernández-Sanjurjo, M. J., Álvarez-Rodríguez, E. & Núñez-Delgado, A. 2016 F sorption/desorption on two soils and on different by-products and waste materials. *Environmental Science and Pollution Research International* **23**, 1–10.
- Reddy, D. H., Seshaiyah, K., Reddy, A. V., Rao, M. M. & Wang, M. C. 2010 Biosorption of Pb^{2+} from aqueous solutions by *Moringa oleifera* bark: equilibrium and kinetics studies. *Journal of Hazardous Materials* **174**, 831–838.
- Rubio, F., Gonçalves Jr, A. C., Meneghel, A. P., Tarley, C. R., Schwantes, D. & Coelho, G. F. 2013 Removal of cadmium from water using by-product *Crambe abyssinica* Hochst seeds as biosorbent material. *Water Science and Technology* **68**, 227–233.
- Salem, N. M. & Awwad, A. M. 2011 Biosorption of Ni(II) from electroplating wastewater by modified (*Eriobotrya japonica*) loquat bark. *Journal of Saudi Chemical Society* **18** (5), 379–386.
- Santhi, T., Manonmani, S. & Smitha, T. 2010 Removal of malachite green from aqueous solution by activated carbon prepared from the epicarp of *Ricinus communis* by adsorption. *Journal of Hazardous Materials* **179**, 178–186.
- Sari, A., Tuzen, M., Uluözlü, Ö. D. & Soylak, M. 2007 Biosorption of Pb(II) and Ni(II) from aqueous solution by lichen (*Cladonia furcata*) biomass. *Biochemistry Engineering Journal* **37**, 151–158.
- Schwantes, D., Gonçalves Jr, A. C., Coelho, G. F., Campagnolo, M. A., Dragunski, D. C., Tarley, C. R. T., Miola, A. J. & Leismann, E. A. V. 2016 Chemical modifications of cassava peel as adsorbent material for metals ions from wastewater. *Journal of Chemistry* **2016**, 15.
- Sekhar, K. C., Kamala, C. T., Chary, N. S. & Anjaneyulu, Y. 2004 Removal of heavy metals using a plant biomass with reference to environmental control. *International Journal of Mineral Processing* **68** (1–4), 37–45.
- Singha, B. & Das, S. K. 2011 Biosorption of Cr(VI) ions from aqueous solutions: kinetics, equilibrium, thermodynamics and desorption studies. *Colloids and Surfaces B: Biointerfaces* **84**, 221–232.
- Sotirelis, N. P. & Chrysikopoulos, C. V. 2015 Interaction between graphene oxide nanoparticles and quartz sand. *Environmental Science & Technology* **49**, 13413–13421, doi: 10.1021/acs.est.5b03496.
- Tavares, F. O., Pinto, L. A. M., Santos, T. R. T., Vieira, M. F., Bergamasco, R. & Vieira, A. M. S. 2015 Avaliação do uso da *Moringa oleifera* como biosorvente na remoção de chumbo de águas contaminadas (Evaluation of the use of *Moringa oleifera* as a biosorbent of lead from contaminated waters). *Blucher Chemical Engineering Proceedings* **2**, 1084–1091.
- Wan Ngah, W. S. & Fatinathan, S. 2010 Adsorption characterization of Pb(II) and Cu(II) ions onto chitosan-tripolyphosphate beads: kinetic, equilibrium and thermodynamic studies. *Journal of Environmental Management* **91** (4), 958–969.
- Wan Ngah, W. S. & Hanafiah, M. A. K. M. 2008 Biosorption of copper ions from dilute aqueous solutions on base treated rubber (*Hevea brasiliensis*) leaves powder: kinetics, isotherm, and biosorption mechanisms. *Journal of Environmental Sciences* **20** (10), 1168–1176.
- Welz, B. & Sperling, M. 1999 *Atomic Absorption Spectrometry*. Wiley-VCH, Weinheim, Germany.
- Witek-Krowiak, A. 2012 Analysis of temperature-dependent biosorption of Cu^{2+} ions on sunflower hulls: kinetics, equilibrium and mechanism of the process. *Chemical Engineering Journal* **192**, 13–20.
- Yang, X. & Al-Duri, B. 2005 Kinetic modeling of liquid-phase adsorption of reactive dyes on activated carbon. *Journal of Colloid and Interface Science* **287** (1), 25–34.

First received 20 March 2017; accepted in revised form 9 January 2018. Available online 24 January 2018