Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1085906

57 (2016) 17738–17747
August

Taylor & Francis
Taylor & Francis Group

Evaluation of kinetic and thermodynamic parameters in adsorption of lead (Pb^{2+}) and chromium (Cr^{3+}) by chemically modified *macadamia* (*Macadamia integrifolia*)

Naiza Vilas Boas[a], Juliana Casarin[a], Gislaine Passarella Gerola[a],
César Ricardo Teixeira Tarley[b], Josiane Caetano[c], Affonso Celso Gonçalves Jr.[d],
Douglas Cardoso Dragunski[a,c,*]

[a]*Diretoria do Instituto de Ciências Exatas, Agrárias, Tecnológicas e Geociências, Universidade Paranaense, UNIPAR, Praça Mascarenhas de Moraes, Umuarama PR 87502-210, Brazil, Tel. +55 44 36212828; emails: naizavilasboas@hotmail.com (N. Vilas Boas), Fax: +55 45 3379 7002; email: juh_casarin@hotmail.com (J. Casarin), gislainepassarela@hotmail.com (G. Passarella Gerola), Tel. +55 45 3379 7142; Fax: +55 45 3379 7002; email: dcdragunski@gmail.com (D. Cardoso Dragunski)*

[b]*Departamento de Química, Universidade Estadual de Londrina, UEL, Londrina, PR 86051-990, Brazil, Tel. +55 43 33714276; email: tarley@uel.br*

[c]*Centro de Engenharias e Ciências Exatas, Universidade Estadual do Oeste do Paraná, UNIOESTE PR, Toledo PR85903-000, Brazil, Tel. +55 45 33797142; email: caetanojosi@gmail.com (J. Caetano)*

[d]*Centro de Ciências Agrárias, Universidade Estadual do Oeste do Paraná, UNIOESTE PR, Marechal Cândido Rondon PR 85960-000, Brazil, Tel. +55 45 32847924*

Received 2 December 2013; Accepted 18 August 2015

ABSTRACT

This study aimed to analyze the efficiency of *in natura* and chemically modified with sodium hydroxide *macadamia* mesocarp as alternative adsorbents for removal of Pb^{2+} and Cr^{3+} from aqueous medium. The effect of chemical modification on the *in natura macadamia* mesocarp with respect to chemical structure and morphological feature were verified by Fourier transform infrared spectroscopy, scanning electronic microscopy, and zero point charge. The best adsorption occurred when pH ranged from 4.0 to 5.0. The adsorbent–adsorbate equilibrium time was found to be at 200 min and followed the pseudo-second-order kinetic model. The maximum adsorption capacity of the modified mesocarp for Pb^{2+} and Cr^{3+} was found to be 91.40 and 81.63 mg g^{-1}, respectively. The thermodynamic parameters indicated an increase of the system spontaneity after the modification, corroborated by the negative values of Gibbs' energy. Besides greater adsorption, the modified material also had greater ion desorption, approximately 94% for Pb^{2+} and 70% for Cr^{3+}, and may be reutilized as a retention filter for metals in the future.

Keywords: Biosorption; Heavy metals; *Macadamia integrifolia*; Modified chemically

1. Introduction

The contamination by toxic metal has been increasing in the past decades due to the industrial activities that are needed to supply the demand for new products [1]. Companies that manufacture leather, electroplating industries that produce stainless steel, and textile industry are among the industries that are liable for this kind of contamination due to their

---

*Corresponding author.

residues containing Pb^{2+} and Cr^{3+}. As a result, soil, water, and sediment can be contaminated by these metals [2,3]. Lead is recognized worldwide as a poisonous metal to human health and can cause several effects on the central nervous system, blood pressure, kidneys, and the reproductive system [4–6]. So, the guidelines for the maximum allowed of Pb^{2+} in natural water samples (Class 1) established by CONAMA (National Council for the Environment—Brazil, 2005) is 1.0 μg L^{-1}, while the United States Environmental Protection Agency (US EPA) recognize Pb^{2+} as a primary contaminant in drinking water, being not allowed any concentration of this element in water [5,7]. Cr^{3+} is considered an essential nutrient that can potentiate insulin action and therefore influences carbohydrate, lipid, and protein metabolism [8]. However, when high concentration of Cr^{3+} is absorbed by human organism, it may become toxic. Besides, when introduced to the environment, they quickly react with organic compounds, spreading easily and causing more contamination [9].

Therefore, several methods to treat industrial effluents containing metal ions have been used including reverse osmosis, chemical precipitation, filtration, ion exchange, phytoremediation, electrodialysis, and coagulation. However, the applicability of these methods generally is limited due to incomplete ion removal, capital and high operational costs, low selectivity, toxic residue generation, or other residual products that are difficult to remove [10,11]. Adsorption at solid/solution interfaces is certainly one of the most effective, inexpensive, and simplest techniques for removing transition metal ions from aqueous media [12]. This phenomenon occurs by adsorbate transport from the bulk solution to the adsorbent surface controlled by diffusion or adsorption process. The diffusion can take place across the liquid film surrounding the sorbent particles or through the sorbent pores [13,14]. The most solid adsorbent materials involves active coal, zeolite, and silica gel, but these materials have high cost, making researchers seek for alternative byproducts from agriculture such as rice hull, coconut shell, hazelnut shell, nutshell, cottonseed shell, grape stem, tree barks, sawdust, nut skin, peanut skin, and sugarcane bagasse [15,16]. The utilization of these materials has been satisfactory for the removal of pollutants in aqueous flows, especially for heavy and dyeing metal ions [17,18]. *macadamia* shell is one of the alternative agro industrial materials that can be used in the future because its byproduct corresponds to 77% of the fruit and it has been studied only for the active coal preparation for adsorption [19].

The *macadamia* tree (*Macadamia integrifolia* Maiden and Betche) belongs to the Proteaceae botanical family, native from the tropical jungles of Australia [20]. From the several *macadamia* genera that produce edible nuts, only *M. tetraphylla* and *M. integrifolia*, which better adapts to the tropics, are commercially relevant [21]. The *macadamia* fruit is a follicle made of the carpel (exocarp and mesocarp), shell (endocarp), and nut (embryo). The nut is still little known in Brazil, but very much appreciated in the international market. The nut oil is mainly used by the cosmetics and pharmaceutical industries. It has been relevant to the food industry because it has high nutritional value and can be eaten raw or roasted [22].

Thus, the aim of the present research was to study the applicability of *in natura* and chemically modified with sodium hydroxide *macadamia* mesocarpas alternative adsorbents for Pb^{2+} and Cr^{3+} adsorption from aqueous medium. The chemical modification of natural adsorbent was performed in order to improve its adsorption capacity.

2. Materials and methods

2.1. Reagents

All the chemical products used in this study were of analytical grade. The solutions of Cr^{3+} from $Cr(NO_3)_3$ and Pb^{2+} from $Pb(NO_3)_2$ (Vetec, 99%) were prepared with deionized water. The solutions of 0.1 mol L^{-1} hydrochloric acid (HCl) (F. Maia, 37%) were used to adjust the pH of solutions. Solution of 0.1 mol L^{-1} sodium hydroxide (NaOH) (F. Maia, 97%) was utilized to modify the mesocarp and to adjust the pH of solutions.

2.2. Adsorbent and chemical modification

The *in natura* mesocarp (M-Nat) was obtained in the region of Umuarama, PR, Brazil, grounded and sieved (Bertel sieve, 24 mesh). This material was submitted to chemical modification with sodium hydroxide (M-NaOH), using 20.0 mL of sodium hydroxide solution at 0.1 mol L^{-1} concentration for each gram of the material. The mixture was agitated for 2 h and the supernatant was discarded. Next, the residue was washed with deionized water until the rinsing water reached pH close to 7.0; then, it was dried at 55°C for 24 h. This procedure was done to remove any impurity that could interfere in the effluent quality, increase the porosity of material, as well as to create new chemical groups available to adsorb metal ion, as already has been documented [23].

2.3. Characterization of adsorbents

The adsorbents were characterized utilizing Fourier Transform Infrared (FTIR) spectroscopy;

potential of zero pH_{pcz} and scanning electronic microscopy (SEM). Infrared transmission spectra were recorded in the 400–4,000 cm^{-1} using a FTIR-8,300 FTIR spectrophotometer from Shimadzu (Kyoto, Japan) at 4 cm^{-1} resolution and using the conventional KBr pellet. The zero charge potential (pH_{pcz}) was determined to calculate pH where the surface charge of the material surface is zero. Therefore, 0.5 g of *in natura* residue (M-Nat) and modified residue (M-NaOH) were agitated with 50.0 mL of KCl solution at 0.1 mol L^{-1} at different pH values (2.0, 3.0, 4.0, 5.0, 7.0, and 8.0). After 24 h, the final pH of supernatant was measured. Finally, a pH_{final} (supernatant) × $pH_{initial}$ plot was constructed. Micrographs were obtained to observe the morphological features of the byproducts (M-Nat; M-NaOH). The samples were deposited on a double-sided carbon adhesive tape fixed in a tin sample support. Afterwards, the samples were coated with gold until the coating was 30 nm thick, utilizing a Baltec Scutter Coater SCD 050 (Germany). The images were obtained using a scanning electron microscope, FEI Quanta 200 (Netherlands), 30 kV.

2.4. Adsorption experiments

2.4.1. Adsorption as a function of pH

After the characterization, the materials were evaluated as adsorbents for Pb^{2+} and Cr^{3+} using batch procedure [24]. The first studied factor that play important role on the adsorption was the pH. The experiment was carried out in triplicate by stirring 50.0 mL of Pb^{2+} or Cr^{3+} solutions at 700.0 mg L^{-1} concentration with 0.5 g of *macadamia* mesocarp (M-Nat or M-NaOH) during 24 h. The sample pH was ranged from 2.0 to 6.0. After the stirring time the mixture was filtrated and the Pb^{2+} or Cr^{3+} concentrations in the supernatant was determined by flame atomic absorption spectrometry (GBC 932 plus). Then, the amount of adsorbed metal per gram of residue (q_{eq}) was determined using the Eq. (1).

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

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

2.4.2. Adsorption kinetics

To carry out Pb^{2+} or Cr^{3+} adsorption kinetic studies for *macadamia* mesocarp (M-Nat or M-NaOH), 50.0 mL of solutions at 700.0 mg L^{-1} concentration under optimized pH (pH 5.0), were stirred with 0.5 g of adsorbents at room temperature for 15 up to 500 min. The samples were then filtrated and analyzed using a GBC 932 plus flame atomic absorption spectrometer.

2.4.3. Adsorption isotherms

The maximum adsorption capacities of adsorbents with respect to Pb^{2+} or Cr^{3+} were determined from experimental isotherms. The experiments were carried out in closed polyethylene flasks at room temperature using 0.5 g of each adsorbent added to 50.0 mL of 100.0–1000.0 mg L^{-1} Pb^{2+} or Cr^{3+} solutions at pH 5.0. The mixture was stirred for 8.0 h under pH 5.0. The mixtures were filtrated and the solutions were analyzed in a flame atomic absorption spectrometer, model GBC 932 plus.

2.5. Thermodynamic studies

Thermodynamic parameters related to the energy changes associated with the adsorption process between the adsorbate and adsorbent including ΔH (enthalpy variation), ΔS (entropy variation), and ΔG (variation of Gibbs' energy) were also determined. Therefore, at pH 5.0, 0.5 g of adsorbents were stirred with 50.0 mL of Pb^{2+} or Cr^{3+} solutions at 700.0 mg L^{-1} concentration in the range of 10–80°C for 8 h. Again, the mixtures were filtrated and the solutions were analyzed in a flame atomic absorption spectrometer (GBC 932 plus).

2.5.1. Elution/desorption

In order to assess the reuse of adsorbents, desorption experiment was performed. Thus, 0.5 g of adsorbents were stirred with 50.0 mL of solutions of Pb^{2+} or Cr^{3+} at 100 mg L^{-1} concentration during 8 h. Then, the solutions were filtrated and the ion concentration was analyzed. Afterwards, the *macadamia* residues were washed in deionized water repeatedly and dried for 24 h in an air oven at 50°C. The desorption process was carried out by adding 25.0 mL of 0.1 mol L^{-1} HCl to the *macadamia* residues previously dried and submitted to stirring for 24 h. The liquid was filtrated and analyzed in a GBC 92-plus model flame atomic adsorption spectrometer and, through the results; the percentage of desorbed metal was obtained.

For all experiments, the mean and standard deviation were calculated using the software Biostart 5.0.

3. Results and discussions

3.1. Characterization of adsorbents

The profile of infrared spectra for M-Nat and M-NaOH byproducts were very similar and are shown in Fig. 1. The main absorption signals were observed at 3,402, 2,920, 1,740, 1,650, 1,151, and 1,054 cm^{-1}. The presence of strong broad band at 3,402 cm^{-1} is attributed to the OH vibration and the peak at 2,920 cm^{-1} corresponds to the vibrational stretching of (C–H) linking. The peaks located at 1,730 and 1,640 cm^{-1} are characteristics of carbonyl group stretching from aldehydes and ketones [25]. The peak at 1,151 cm^{-1} indicates the C–O stretching. The strong bands at 1,054 cm^{-1} confirmed the presence of polysaccharides [26]. The absence of signal at 1,740 cm^{-1} for M-NaOH byproduct indicates the hydrolysis of carbonyl groups by NaOH addition [27].

After the modification, there was no emergence of new functional groups, besides the ones that already existed in *in natura* material, except for a change in the peak shape at 1,421 cm^{-1}, referring to carbonyl groups [23].

The micrographs of adsorbents are shown in Fig. 2. According to the images of *in natura* mesocarp (Fig. 2(a) and (b)), few cracks can be observed in the material when compared to the modified mesocarp ones (Fig. 2(c) and (d)). The morphological modification of mesocarp surface was due to hydrolyses of some functional groups present in the material. Similar results have been observed after chemical treatment of by product from agricultural using sodium hydroxide [27].

The pH_{final} (supernatant) × $\text{pH}_{\text{initial}}$ plot is shown in Fig. 3 and makes possible to determine the point of zero charge representing the pH value, at which the electric charge density on the material surface is zero. As can be observed, the value of pH_{pcz} became constant at 6.0 and 7.7 for *in natura* mesocarp (M-Nat) and modified mesocarp (M-NaOH), respectively. Thus, when the pH solution is lower than the pH_{pcz}, there is predominance of positive superficial charge in the residue, and when the pH is higher than the pH_{pcz}, the superficial liquid charge is negative. It can be noticed that, after the modification with sodium hydroxyl, there was a significant increase of the superficial charge value of the material; this can be attributed to the sodium hydroxide on the shell, even after the material had been washed until the rinsing water had pH 7.0 [24].

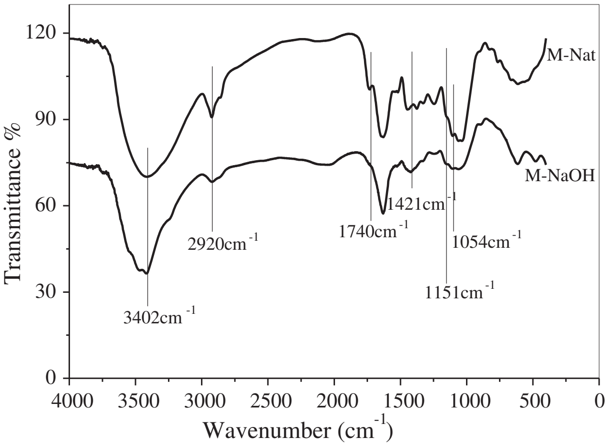

Fig. 1. Infrared spectrum of *macadamia* mesocarp: M-Nat (*in natura* mesocarp), M-NaOH (mesocarp modified with sodium hydroxyl).

3.2. Adsorption experiments

3.2.1. Adsorption as a function of pH

The values of q_{eq} in function of pH for the residues (M-Nat and M-NaOH) are represented in Fig. 4. After the modification, a significant improvement on metal ion adsorption was observed, mainly for Pb^{2+} ion. This occurred owing to the availability of new binding sites that are able to interact with metal. It was also verified that metal ion adsorption was lower in acid medium due to the protonation of binding sites, which makes the analyte adsorption less effective. The best adsorption of both metal ions on M-NaOH was found to be in the range 4.0–5.0. It is important to stress out that although the value of pH_{pcz} for M-NaOH was found to be 7.7, the best Pb^{2+} and Cr^{3+} adsorption occurred at pH 5.0. Thus, the adsorption phenomena may be explained not only by electrostatic interactions, but also by other processes as complex formation with metal ions. Thus, pH 5.0 was chosen to carry out the other adsorption experiments. Furthermore, at pH 6.0, the Pb^{2+} and Cr^{3+} salts can be cconverted to hydroxide species [24].

3.2.2. Adsorption kinetics

The Fig. 5 shows the adsorption kinetics built at optimized pH (pH 5.0).

As one can see from Fig. 5, the equilibrium time was reached at 200 min, which is considerably lower than other adsorbents such as sugarcane bagasse and *Saccharomyces cerevisiae* with 24 h and 48 h, respectively [24,28].

To describe the adsorption kinetic behavior of the adsorbents towards Pb^{2+} and Cr^{3+}, kinetic models including pseudo-first-order, pseudo-second-order, Elovich, and intra particle diffusion were applied to the experimental data [28–33].

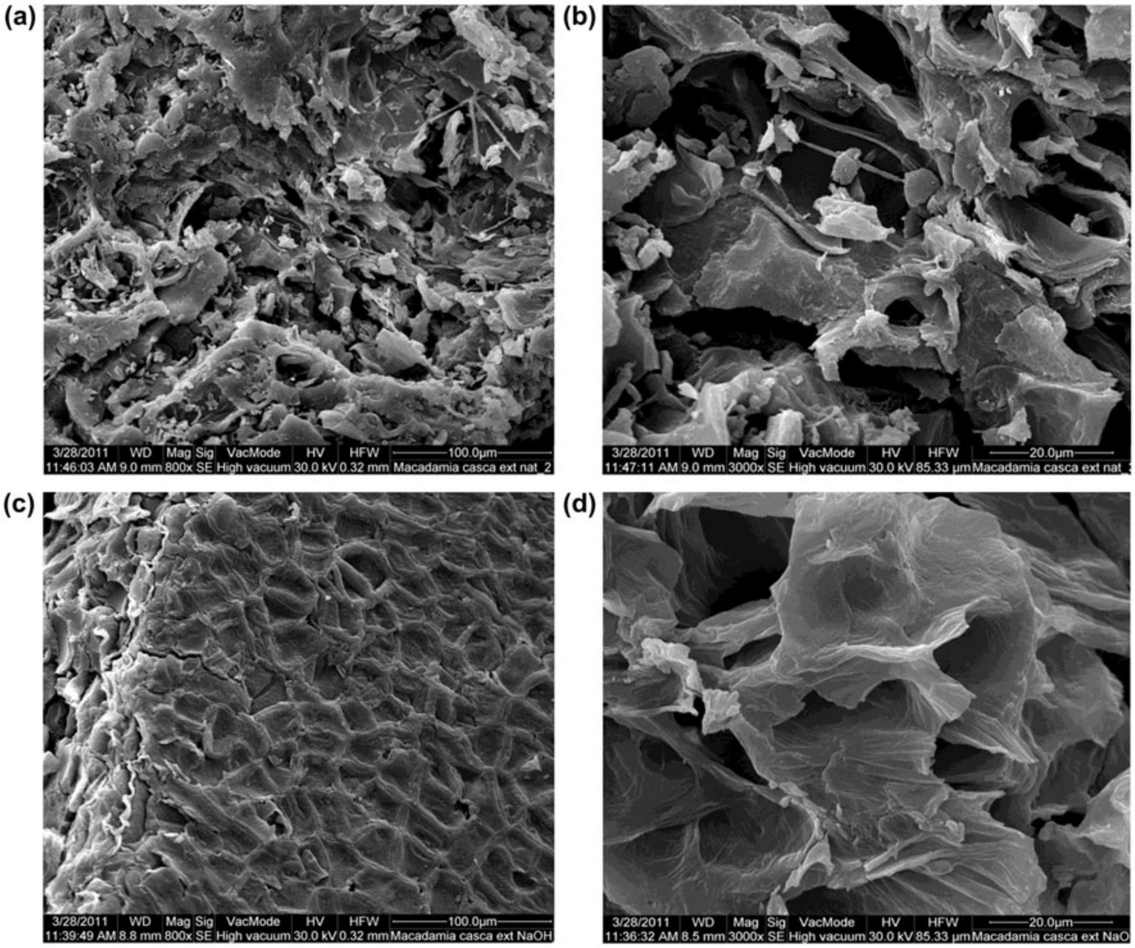

Fig. 2. Mesocarp micrographs: *in natura* (a and b); modified with NaOH (c and d). Images a and c were magnified 800×, and images b and d, 3000×.

The kinetic parameters for pseudo-second-order models are presented in Table 1. It can be observed that the mesocarp for both metal ions follows the pseudo-second-order models since better regression coefficient were obtained ranging from 0.98 to 0.99, this model, indicates that the adsorption speed is proportional to the lower adsorption rate processes. Besides, it can be verified that the calculated values of q_{eq} for the pseudo-second-order model were very similar to the experimental values, indicating that this model would be the most compatible to this adsorption. The other models had regression coefficient below the 0.95.

3.2.3. Adsorption isotherms

The isotherms of adsorption were used to describe the relationship between the amount of adsorbate taken up by the adsorbent (q_e) and the adsorbate concentration remaining in the solution after the system attained the equilibrium (C_e), in this case 200 min. Fig. 6 shows the isotherms of residues (M-Nat and M-NaOH) carried out at room temperature.

We can see that the adsorption capacity of M-NaOH-Pb^{2+} is higher than that of M-NAT-Pb^{2+}, so does Cr^{3+}, this may be due to insertion of negative groups in the residue, with maximum adsorption capacity of 90.0 to the $Pb^{2+}$and 80.0 mg g^{-1} to the Cr^{3+}. There are several isotherm models to analyze experimental adsorption equilibrium data. In this work, the models of Langmuir, Freundlich, Dubinin–Radushkevich (D–R), and Temkin, were applied [34–38].

Analyzing the values of Table 2, where the adsorption isotherm parameters are represented, it was verified, based on regression coefficients, that Langmuir model is the best isotherm for both metal ion Pb^{2+} and Cr^{3+} on residues (M-Nat and M-NaOH). The other models had determination coefficient below of the

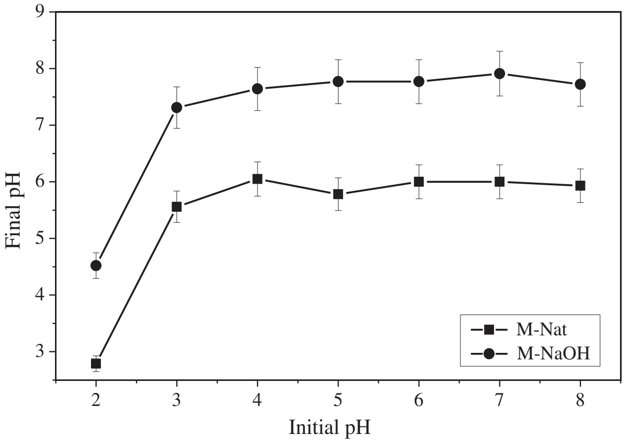

Fig. 3. Values of initial and final pH obtained in the experiment of pH_{pcz} measurement of potassium chloride (KCl) at 0.1 mol L^{-1}. M-Nat (*in natura* mesocarp), M-NaOH (mesocarp modified with sodium hydroxide).Temperature: 25°C.

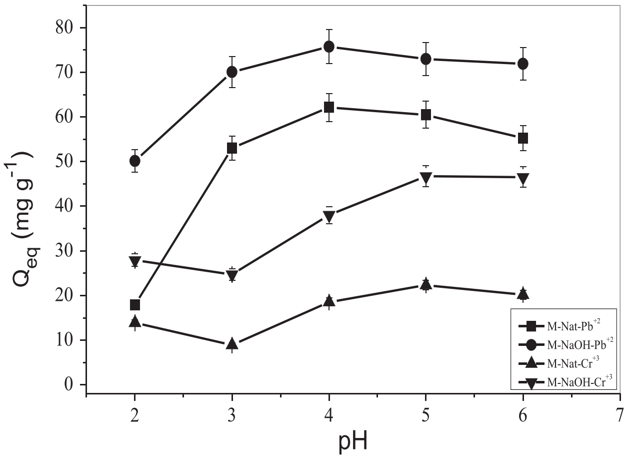

Fig. 4. Effect of the pH on Pb^{2+} and Cr^{3+} adsorption in *macadamia* mesocarp: M-Nat (*in natura* mesocarp), M-NaOH (mesocarp modified with sodium hydroxide). Experimental conditions: metal ion concentration at 700 mg L^{-1}, agitation time: 24 h, temperature: 25°C.

values for Langmuir. Thus, the maximum adsorption capacity (q_m) were found to be 91.4 and 81.6 mg g^{-1} for Pb^{2+} and Cr^{3+}, respectively, when using the modified mesocarp (M-NaOH). were calculated, and after Pb^{2+} ion modification, it had the greatest adsorbed amount of 91.40 mg g^{-1}, when compared to Cr^{3+} (81.63 mg g^{-1}). These values are close to the maximum adsorption measured experimentally. Pb^{2+} was mostly adsorbed onto materials in comparison to Cr^{3+} probably due to its higher electronegativity and ionic radius [39].

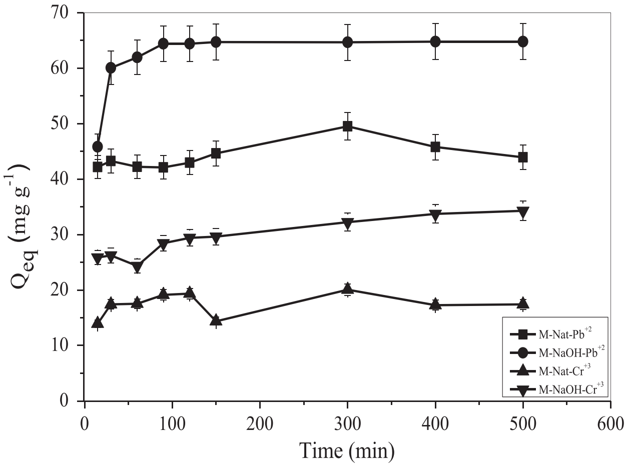

Fig. 5. Amounts of adsorbed Pb^{2+} and Cr^{3+} per gram of residue (q_{eq}) in function of time (minutes). M-Nat (*in natura* mesocarp), M-NaOH (mesocarp modified with sodium hydroxide). Experimental conditions: metal ion concentrations at 700 mg L^{-1}, pH 5 and temperature: 25°C.

In Table 3 is presented the maximum adsorption capacity of residue M-NaOH used as alternative adsorbent. By seeing this Table, it is noted that adsorption capacity of proposed adsorbent with respect to Pb^{2+} and Cr^{3+} is higher when compared with other natural adsorbents.

3.2.4. *Adsorption thermodynamics*

After obtaining the maximum adsorption capacity, adsorption experiments in function of temperature were performed to obtain the energies involved in process (enthalpy (ΔH), entropy (ΔS), and Gibbs' free energy (ΔG)). Using the graphic of $\ln K_d$ vs. $1/T$, the value ΔH ($-\Delta H/R$) was calculated from the angular coefficient of the straight line, which provided $T\Delta S$ ($\Delta S/R$), according to Eq. (2):

$$\ln K_d = \left(\frac{\Delta S}{R}\right) - \left(\frac{\Delta H}{R}\right)\frac{1}{T} \tag{2}$$

where K_d is the adsorbate distribution coefficient (L g^1) which corresponds to the ratio between q_{eq} and C_{eq}, T is the temperature in Kelvin (K), R is the universal gas constant (8.314 J K^{-1} mol^{-1}). With the calculated values of enthalpy and entropy, it is possible to determine ΔG values, Eq. (3), which refer to the adsorption spontaneity, that is, the more negative ΔG value of is the more spontaneous adsorption is:

$$\Delta G = \Delta H - T\Delta S \tag{3}$$

Table 1
Kinetic parameters obtained through the linearization of pseudo-second-order model, for Pb^{2+} and Cr^{3+}, utilizing the adsorbents: M-Nat (*in natura* mesocarp), M-NaOH (mesocarp modified with sodium hydroxide)

		Samples			
		M-Nat-Pb^{2+}	M-NaOH-Pb^{2+}	M-Nat-Cr^{3}	M-NaOH-Cr^{3+}
pseudo-second-order $\frac{t}{q_t} = \frac{1}{K_2 q_{eq}^2} + \frac{t}{q_{eq}}$	K_2 (10^{-3}) (g mg^{-1} min^{-1})	0.16	5.35	0.08	1.51
	q_{eq} (mg g^{-1})	45.49	64.79	17.70	35.11
	R^2	0.99	0.99	0.98	0.99
	$q_{eq\ exp}$ (mg g^{-1})	49.53	65.27	20.06	38.41

Notes: q_t is the amount of adsorbed metallic ions (mg g^{-1}) in t time (min); q_{eq} is the amount of adsorbed metal per gram of residue (mg g^{-1}); K_2 is the pseudo-second-order constant (g mg^{-1} min^{-1}); R^2 coefficient of determination.

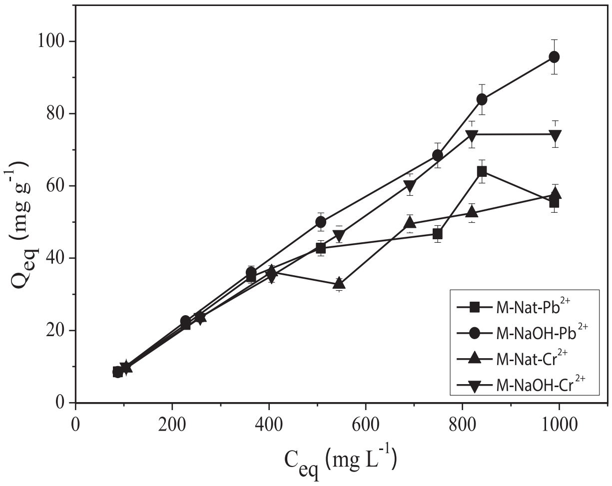

Fig. 6. $Pb^{2+}$and Cr^{3+}adsorption isotherm. M-Nat (*in natura* mesocarp), M-NaOH (mesocarp modified with sodium hydroxide). Experimental conditions: agitation time of 8 h, pH 5 and temperature: 25°C.

The values of enthalpy, entropy, and Gibbs' free energy are shown in Table 4. It was possible to verify that after the residue modification, there was a decrease of ΔG value to make the process more favorable. In addition, for "in natura" residues, the values were also negative, indicating spontaneity of this system.

All the enthalpy (ΔH) values were negative for this adsorption, indicating that adsorption has exothermal nature; besides, it was verified that it became more negative after the modification, which can be explained by the increase between adsorbent and adsorbate [40], in accordance to the data of B_1, obtained in Temkin isotherm. For entropy (ΔS), it was also observed that the values were negative, demonstrating that a certain metal ordering occurred on the mesocarp surface [41–44] mainly when the residue was modified. Thus, it was verified that, the system was more spontaneous, exothermal and more ordered after the modification, corroborating a greater adsorption capacity (Table 2).

3.2.5. Elution/desorption

In order to check the reuse of the residues for the adsorption of Pb^{2+} and Cr^{3+}, desorption experiments (Table 5) were carried as expected, higher adsorption

Table 2
Isotherms of Langmuir models for Pb^{2+} and Cr^{3+} adsorption in *macadamia*: M-Nat (*in natura* mesocarp), M-NaOH (mesocarp modified with sodium hydroxide)

		Samples			
		M-Nat-Pb^{2+}	M-NaOH-Pb^{2+}	M-Nat-Cr^{3+}	M-NaOH-Cr^{3+}
Langmuir $\frac{C_{eq}}{q_{eq}} = \frac{1}{q_m b} + \frac{C_{eq}}{q_m}$	q_m (mg g^{-1})	55.89	91.40	59.17	81.63
	b (L mg^{-1})	0.07	0.01	0.01	6.63
	R^2	0.97	0.84	0.86	0.90

Notes: q_{eq} is the amount of adsorbed metal per gram of residue (mg g^{-1}); b is a constant that indicates the adsorption intensity; q_m is the capacity measurement that indicates the maximum adsorption intensity; C_{eq} is the concentration in equilibrium of the solution (mg L^{-1}).

Table 3
Comparison among different biosorbents for Cr^{3+} and Pb^{2+}

Adsorbents	pH	Mass (g)	q_m (mg g^{-1}) Cr^{3+}	pH	Mass (g)	q_m (mg g^{-1}) Pb^{2+}	Refs.
Sugarcane bagasse	5	0.50	41.81	5	0.50	52.63	[12,24]
Peanut shell	4	0.20	3.34	4	0.20	4.59	[15,16]
Orange peel	5	0.50	75.64	5	0.50	84.50	[19]
Lichen (Parmelinatiliaceae)	5	4.00	52.10	5	4.00	75.80	[21]
Mesocarp-NaOH	5	0.50	81.63	5	0.50	91.40	This study

Table 4
Thermodynamic parameters, enthalpy (Δ*H*), entropy (Δ*S*), and Gibbs' free energy (Δ*G*) for Pb^{2+} and Cr^{3+} adsorption in M-Nat (*in natura* mesocarp), M-NaOH (mesocarp modified with NaOH)

Sample	ΔG^a (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (JK^{-1} mol^{-1})
M-Nat-Pb	−13.80	−19.62	−19.51
M-NaOH-Pb	−18.15	−66.15	−161.07
M-Nat-Cr	−13.39	−23.80	−34.94
M-NaOH-Cr	−16.28	−26.87	−35.55

Notes: Experimental conditions: metal ion concentration at 700 mg L^{-1}, agitation time of 8 h, pH 5.
[a]Values calculated at 25˚C.

Table 5
Values of Pb^{2+} and Cr^{3+} adsorption and desorption at initial concentration of 100 mg L^{-1}: M-Nat (*in natura* mesocarp), M-NaOH (mesocarp modified with NaOH). Experimental conditions: agitation time of 8 h, pH 5 and temperature: 25˚C

Adsorbents	Adsorbed concentration (mg L^{-1})	% Adsorption	Desorbed concentration (mg L^{-1})	% Desorption
M-Nat-Pb	74.70	82.46	65.48	87.55
M-NaOH-Pb	87.56	96.66	82.98	94.76
M-Nat-Cr	80.62	85.72	54.87	68.06
M-NaOH-Cr	85.03	95.69	59.80	70.32

was noticed for Pb^{2+}, and Cr^{3+} when using modified mesocarp. As already observed from Langmuir model, the amount of Pb^{2+} adsorbed onto residue M-NaOH was considerably higher. On the other hand, the use of 0.1 mol L^{-1} HCl desorbed Pb^{2+} ions uptaken by the M-NaOH immediately (94.76%), in which indicates that Pb^{2+} is not strongly linked to the matrix, when compared to Cr^{3+}. Thus, ion charges may be a possible explanation for this event, corroborated by significant increases of *b* parameters (Langmuir isotherm) and B_1 (Temkim isotherm) for Cr^{3+}, indicating an increase in the adsorbent–adsorbate interaction, respectively.

4. Conclusions

The *in nature macadamia* byproduct (mesocarp) and especially when modified with sodium hydroxide are alternatives to remove Pb^{2+} and Cr^{3+} from aqueous medium. Through kinetic studies, it was proved that the residues follow pseudo-second-order kinetics for Pb^{2+} as well as Cr^{3+}, indicating a strong adsorbent–adsorbate interaction. Moreover, when using several isotherm models, the experimental data were better adjusted to the model proposed by Langmuir, indicating that adsorption occurred in monolayers. From this isotherm model, the maximum adsorption capacity (q_m) were found to be 91.4 and 81.6 mg g^{-1} for Pb^{2+} and Cr^{3+}, respectively, when using the modified mesocarp (M-NaOH). These data are considerably higher when compared to the q_m of *in natura* residue.

The adsorption process of the residues for both solutions is spontaneous due to the negative values presented by Gibbs' energy. Desorption results were satisfactory, mainly for Pb^{2+} solution, reaching 94.76% of desorption for the modified residue, indicating that the adsorbent and the ion can be reutilized.

Acknowledgments

This study was supported by the UNIPAR and UNIOESTE. The authors would like to thank CNPq (National Council for Scientific and Technological Development) and Araucária Foundation for the financial support and fellowships.

References

[1] J. Li, Q. Lin, X. Zhang, Y. Yan, Kinetic parameters and mechanisms of the batch biosorption of Cr(VI) and Cr(III) onto *Leersia hexandra* Swartz biomass, J. Colloid Interface Sci. 333 (2009) 71–77.

[2] P.B. Szefer, Distribution of trace metals in the Pacific Oyster, *Crassostrea gigas*, and crabs from the east coast of Kyushu Island, Japan, Bull. Environ. Contam. Toxicol. 58 (1997) 108–114.

[3] P. Szefer, J. Geldon, Distribution and association of trace metals in soft tissue and byssus of *Mytella strigata* and other benthal organisms from Mazatlan Harbour, Mangrove Lagoon of the northwest coast of Mexico, Environ. Int. 24 (1998) 359–374.

[4] M.G.A. Korn, J.B. de Andrade, D.S. de Jesus, V.A. Lemos, M.L.S.F. Bandeira, W.N.L. dos Santos, M.A. Bezerra, F.A.C. Amorim, A.S. Souza, S.L.C. Ferreira, Separation and preconcentration procedures for the determination of lead using spectrometric techniques: A review, Talanta 69 (2006) 16–24.

[5] C.R.T. Tarley, F.N. Andrade, H. Santana, D.A.M. Zaia, L.A. Beijo, M.G. Segatelli, Ion-imprinted poly-vinylimidazole-silica hybrid copolymer for selective extraction of Pb(II): Characterization and metal adsorption kinetic and thermodynamic studies, React. Funct. Polym 72 (2012) 83–91.

[6] CONAMA, National Council for the Environment, Resolução CONAMA N˚ 357. Available from: <http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=459>, (2005) (Accessed 07 of December 2012).

[7] USEPA, National Primary Drinking Water Regulations, Available from: <http://water.epa.gov/drink/contaminants/#List>, (2009) (Accessed at 07 December 2012).

[8] M. Tuzen, M. Soylak, Chromium speciation in environmental samples by solid phase extraction on Chromosorb 108, J. Hazard. Mater. B 129 (2006) 266–273.

[9] A. Dube, T. Kowalkowski, R. Zbytniewski, P. KosobuckI, E. Cukrowska, B. Buszewski, Proceedings of the XVth international symposium on physicochemical methods of the mixtures separation, Ars. Separatoria 21 (2000) 14–17.

[10] B. Volesky, Detoxification of metal-bearing effluents: biosorption for the next century, Hydrometallurgy 59 (2001) 203–216.

[11] G. Zhang, R. Qu, C. Sun, C. Ji, H. Chen, C. Wang, Y. Niu, Adsorption for metal ions of chitosan coated cotton fiber, J. Appl. Polym. Sci. 110 (2008) 2321–2327.

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

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

[14] S.Y. Ho, J.C.Y. Ng, G. McKay, Kinetics of pollutant sorption by biosorbents: Review, Sep. Purif. 29 (2000) 189–232.

[15] R.S. Jimenez, S.M. Dal Bosco, W.A. Carvalho, Remoção de metais pesados de efluentes aquosos pela zeólita natural escolecita—Influência da temperatura e do pH na adsorção em sistemas monoelementares (Heavy metals removal from wastewater by the natural zeolite scolecite—temperature and pH influence in single-metal solutions), Quim. Nova, 27 (2004) 734–738.

[16] E. Repo, J.K. Warchoł, A. Bhatnagar, M. Sillanpää, Heavy metals adsorption by novel EDTA-modified chitosan–silica hybrid materials, J. Colloid Interface Sci. 358 (2011) 261–267.

[17] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, Water Res. 33 (1999) 2469–2479.

[18] Y.H. Wan, S.H. Lin, S.H. Juang, Removal of heavy metals from aqueous solutions using various low-cost adsorbents, J. Hazard. Mater. 102 (2003) 291–302.

[19] S.M. Tam, M.J.J.R. Antal, Preparation of activated carbons from *macadamia* nut shell and coconut shell by air activation, Ind. Eng. Chem. Res. 38 (1999) 4268–4276.

[20] F.A. Silva, J.R.A. Marsaioli, G.J. Maximo, M.A.A.P. Silva, L.A.G. Gonçalves, Microwave assisted drying of *macadamia* nuts, J. Food Process Eng. 77 (2006) 550–558.

[21] L. Cedeno, C. Carrero, Antracnosis en plántulas de *macadamia* causada por *Glomerella mingulata* (Macadamia seedlings anthracnose caused by Glomerella mingulata), Interciencia 27 (2002) 559–562.

[22] L.D. Pimentel, The culture of Macadamia, Jaboticabal, São Paulo, Brasil, 2007.

[23] R.F. Rodrigues, R.L. Trevezoli, L.R.G. Santos, V.A. Leão, V.R. Botaro, Adsorption of heavy metals on sawdust treated with nitric acid, Eng. Sanit. Ambient 11 (2006) 21–26.

[24] V.C.G. Dos Santos, C.R.T. Tarley, J. Caetano, D.C. Dragunski, Copper ions adsorption from aqueous medium using the biosorbent sugarcane bagasse in natura and chemically modified, Water Air Soil Pollut. 216 (2010) 351–359.

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

[26] A. Özcan, A.S. Özcan, S. Tunali, T. Akar, I. Kiran, Determination of the equilibrium kinetic and thermodynamic parameters of adsorption of copper(II) ions onto seeds of *Capsicum annuum*, J. Hazard. Mater. 124 (2005) 200–208.

[27] C.R.T. Tarley, S.L.C. Ferreira, M.A.Z. Arruda, Use of modified rice husks as a natural solid adsorbent of trace metals: Characterization and development ofan on-line preconcentration system for cadmium and lead determination by FAAS, Microchem. J. 77 (2004) 163–175.

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

[29] M. Doğan, M. Alkan, Z.A. Türkyilma, Y. Özdemir, Kinetics and mechanism of removal of methylene blue by adsorption onto perlite, J. Hazard. Mater. 109 (2004) 141–148.

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

[31] S.Y. Ho, Y.G. Mckay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.

[32] F.F. Sodré, E. Lenzi, A.C. Costa, Applicability of adsorption models to the study of copper behaviour in clayey soils, Quim. Nova 24 (2001) 324–330.

[33] M. Gonçalves, L.C.A. Oliveira, M.C. Guerreiro, Magnetic niobium as adsorbent of organic contaminants in aqueous medium: Effect of temperature and pH, Quim. Nova 31 (2008) 518–522.

[34] E.A. Ofomaja, Equilibrium studies of copper ion adsorption onto palm kernel fibre, J. Environ. Manage. 91 (2010) 1491–1499.

[35] M.H. Kalavathy, T. Karthikeyan, S. Rajgopal, L.R. Miranda, Kinetic and isotherm studies of Cu(II) adsorption onto H_3PO_4 activated rubber wood Sawdust, J. Colloid. Interface Sci. 292 (2005) 354–362.

[36] K.K.P. Porpino, M.C.S. Barreto, K.B. Cambuim, J.R.C. Filho, I.A.S. Toscano, M.A. Lima, Fe(II) adsorption on *Ucides Cordatus* crab shells, Quim. Nova 34 (2011) 6.

[37] C.O. Ijagbemi, M. Baek, D. Kim, Adsorptive performance of un-calcined sodium exchanged and acid modified montmorillonite for Ni^{2+} removal: Equilibrium, kinetics, thermodynamics and regeneration studies, J. Hazard. Mater. 174 (2010) 746–755.

[38] M.I. Temkin, V. Pyzhev, Kinetic of ammonia synthesis on promoted iron catalyst, Acta Phys-chim. Sin. 12 (1940) 327–356.

[39] B.Y.M. Bueno, M.L. Torem, F. Molina, L.M.S. de Mesquita, Biosorption of lead(II), chromium(III) and copper(II) by *R. opacus*: Equilibrium and kinetic studies, Miner. Eng. 21 (2008) 65–75.

[40] P. Atkins, J. Paula, Físico-Química, eightth ed., vol. 1, LTC, Rio de Janeiro, Brasil, 2012.

[41] E. Malkoc, Y. Nuhoglu, Determination of kinetic and equilibrium parameters of the batch adsorption of Cr (VI) onto waste acorn of *Quercus ithaburensis*, Chem. Eng. Process. 46 (2007) 1020–1029.

[42] V.C.G. Santos, A.P. Salvado, D.N.C. Peraro, C.R.T. Tarley, J. Caetano, D.C. Dragunski, Highly improved chromium(III) uptake capacity in modified sugarcane bagasse using different chemical treatments, Quim. Nova 35 (2012) 1606–1611.

[43] A.P.A. Salvado, L.B. Campanholi, J.M. Fonseca, C.R.T. Tarley, J. Caetano, D.C. Dragunski, Lead(II) adsorption by peach palm waste, Desalin. Water Treat. 48 (2012) 335–343

[44] C.L. Massocatto, E.C. Paschoal, N. Buzinaro, T.F. Oliveria, C.R.T. Tarley, J. Caetano, A.C. Gonçalves Jr., D.C. Diniz, D.C. Dragunski, Preparation and evaluation of kinetics and thermodynamics studies of lead adsorption onto chemically modified banana peels, Desalin. Water Treat. 51 (2013) 5682–5691.