

# Preparation of biosorbents from the Jatoba (*Hymenaea courbaril*) fruit shell for removal of Pb(II) and Cd(II) from aqueous solution

Isis P. A. F. Souza · André L. Cazetta · Osvaldo Pezoti · Vitor C. Almeida

Received: 25 November 2016 / Accepted: 26 October 2017 / Published online: 12 November 2017  
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**Abstract** In this study, the biosorption properties of Jatoba (*Hymenaea courbaril*) fruit shell for removal of Pb(II) and Cd(II) ions from aqueous solutions, and its potential as a low-cost biosorbent for water treatment, were investigated. The Jatoba fruit shell (JB<sub>in</sub>) was subjected to different treatments with heated water (JB<sub>H<sub>2</sub>O</sub>) and sodium hydroxide (JB<sub>NaOH</sub>) to modify its surfaces and improve its adsorption properties. The chemical modification of the surfaces of the resulting materials was confirmed by analyzing the compositions and structural features of the raw material and the chemically treated materials using SEM, FTIR, <sup>13</sup>C NMR, and pH<sub>pzc</sub>. The ability of the biosorbents to remove the metal ions was investigated with batch adsorption procedures. The adsorption data were then examined in detail by applying adsorption models of Langmuir, Freundlich, and Dubinin-Radushkevich. The results showed that the experimental data were best described by the Langmuir model for the Pb-JB<sub>in</sub> and Cd-JB<sub>NaOH</sub> systems, the Freundlich model for the Pb-JB<sub>H<sub>2</sub>O</sub> and Pb-JB<sub>NaOH</sub> systems, and the Dubinin-Radushkevich model for Cd-JB<sub>in</sub> and Cd-JB<sub>H<sub>2</sub>O</sub> systems. The maximum adsorption capacities of JB<sub>NaOH</sub> obtained using the Langmuir model reached values of 30.27 and 48.75 mg g<sup>-1</sup> for Cd(II) and Pb(II), respectively. The adsorption

kinetic studies showed that the pseudo-second-order model was the best fitted to the experimental data, and adsorptions for Pb-JB<sub>H<sub>2</sub>O</sub> and Cd-JB<sub>H<sub>2</sub>O</sub> are controlled by intraparticle diffusion mechanism.

**Keywords** Biosorption · Heavy metals · Jatoba (*Hymenaea courbaril*) · Fruit shell

## Introduction

Industrial development in a country almost always promotes the living standard and the economic wealth of its population. However, as it has been seen time and time again over decades, the industrial growth of a country can also lead to undesired environmental problems, especially associated with the industrial wastes generated by various industrial chemical processes. Depending on the industry type (chemical, textile, and metallurgical), industrial effluents may contain significant concentrations of heavy metals and/or organic compounds (Chakravarty et al. 2010; Palin et al. 2016). And such industrial effluents that oftentimes are discarded to the environment without any treatment and control, as has been done in many countries, particularly pose the most significant environmental damages and health risks.

Many industrial effluents possess heavy metals that are cumulative and non-biodegradable in the environment; they can thus severely contaminate rivers and streams and harm aquatic life (Taşar et al. 2014). Among the elements, heavy metals, lead, and cadmium are considered the most toxic and to cause problems to

I. P. A. F. Souza · A. L. Cazetta · O. Pezoti · V. C. Almeida (✉)

Laboratory of Environmental and Agrochemistry, Department of Chemistry, Universidade Estadual de Maringá, Av. Colombo 5790, Maringá, Paraná 87020-900, Brazil  
e-mail: vcalmeida@uem.br

human health even at extremely low concentrations. Notably, lead poisoning can impair the nervous system, gastrointestinal tract, kidney, and reproductive system (Palin et al. 2016) whereas cadmium poisoning can cause renal and carcinogenic disorders, pulmonary insufficiency, bone lesions, cancer, anemia, and hypertension (Jain et al. 2015).

Hence, several physicochemical methods have been in development for removal of such heavy metals from wastewaters. The most commonly considered methods include extraction, ion exchange, chemical precipitation, membrane separation, and adsorption (Witek-krowiak et al. 2011). Biosorption, which uses waste materials from renewable sources as adsorbents, has been emerging as an efficient and promising method for the removal of pollutants from wastewaters. Moreover, the method is considered as clean, efficient, and inexpensive (Mahmood-ul-Hassan et al. 2015), besides being biological and relatively more benign for environmental control (Jain et al. 2015). The effectiveness of a given biosorbent to remove pollutants may be measured by the ability of the active sites on its surfaces to bind and pull out the pollutant species from solutions (Pavan et al. 2006).

Recently, several agro-industrial residues have been evaluated as low-cost biosorbent materials for the removal of heavy metals from aqueous solutions. These materials include banana stalk, corn cob, sunflower head (Mahmood-ul-Hassan et al. 2015) peanut shell (Witek-krowiak et al. 2011), fruit wastes (Kelly-Vargas et al. 2012), rice straw and bran (Ding et al. 2012; Zafar et al. 2015), papaya seeds (Gilbert et al. 2011), and ginger residue (Kumar and Ahmand 2011) which have also been successfully employed for removal of pollutants.

With the aim of finding new renewable sources, which can be used as efficient adsorbent materials for heavy metal ions in solutions, herein we investigated Jatoba (*Hymenaea courbaril*) fruit shells as biosorbents. The Jatoba tree is originally found in Brazil's Amazon and Atlantic forest regions. The tree is often planted in areas of heterogeneous reforestation and afforestation, and in places such as parks and gardens as it grows very easily. Jatoba fruit possesses indehiscent pods of hard shell, presenting dimensions of 8 to 15 cm in length, 3 to 5 cm in width, and 4 to 6 cm in thickness, with each fruit containing about two to four seeds. The fruit has a hard shell, weighing up to 66% of the fruit's total weight. Each seed is surrounded by a yellow pulp, which when dried is edible and is often consumed with regional

dishes as well as cakes, breads, and hot cereals (Silva et al. 2001). Additionally, the use of Jatoba fruit and its stem bark for treatment of gastritis, ulcers, and diarrhea and as anti-inflammatory agent has been reported in the literature (Grandi et al. 1989; Boniface et al. 2017). Thus, besides promoting an appropriate means for the disposition of Jatoba fruit wastes, the present work aims to make useful biosorbents from Jatoba fruit's shell, studying different treatments of modification, and apply them in removal of Pb(II) and Cd(II) ions from aqueous solutions. To prepare the most effective biosorbent from Jatoba fruit's shell, the latter was treated with basic solution and boiled water, and the adsorption property of each material was investigated. The modification techniques may reduce organic components of the raw material such as cellulose, hemicellulose, and tannins, which create a high chemical oxygen demand when used as adsorbent material, and increase surface active sites for adsorption (Pezoti et al. 2016).

## Materials and methods

### Raw material

Jatoba fruits were collected from native trees of the countryside of Santa Fe City, Parana State, Brazil. First, the shells were separated from the fruits, and then washed with a copious amount of tap water, followed by a copious amount of distilled water, and dried in an oven at 100 °C for 12 h. Subsequently, the resulting material was ground using a knife mill (Marconi brand, model MA048) and submitted for granulometric separation. The resulting samples with particle diameters of 250 to 425 µm were properly stored for posterior studies.

### Preparation of biosorbents

Different biosorbents were prepared from Jatoba fruit peels by washing with distilled water ( $JB_{in}$ ), boiling in distilled water ( $JB_{H_2O}$ ), and boiling in 0.1 mol L<sup>-1</sup> NaOH solution ( $JB_{NaOH}$ ). Typically, 100 g of the raw material was placed in 2 L of boiled distilled water and/or basic solution. The mixtures were magnetically stirred and separated from the solutions, after 2 h of contact time. The biosorbent obtained from the treatment under basic solution ( $JB_{NaOH}$ ) was properly rinsed with distilled water until the wash water reached to a pH

value of close to 7.0. Then, all the biosorbents were dried at 105 °C for 24 h, and stored for further use.

Characterization of biosorbents

The biosorbents obtained above were characterized by pH<sub>pzc</sub>, FTIR spectroscopy, scanning electronic microscopy (SEM), and <sup>13</sup>C nuclear magnetic resonance (NMR <sup>13</sup>C) spectroscopy. pH<sub>pzc</sub> was determined following the methodology described by Prahas et al. (2008). pH<sub>pzc</sub> corresponds to the condition which is pH<sub>initial</sub> = pH<sub>final</sub> or ΔpH = 0. FTIR spectra were obtained in the range between 4000 and 400 cm<sup>-1</sup> (resolution of 4 cm<sup>-1</sup> and acquisition rate of 20 scans min<sup>-1</sup>), using a Bomem MB100 spectrometer. Pellets were prepared mixing 1 mg of sample with 500 mg KBr (Merck) in an agate mortar, and then pressed at 5 t cm<sup>-2</sup> for 5 min. The morphologies of the materials were examined from their SEM images obtained by using a Shimadzu model SS-550 Superscan instrument. The preparation of the samples for imaging was carried out by depositing gold (Au) over the samples using a Shimadzu sputter coater IC-50 ion in 3 cycles of 5 min at a current of 60 mA. Solid-state <sup>13</sup>C NMR spectra were acquired by using cross-polarization magic angle spinning (CP/MAS) technique with a Mercury Plus 300 (Varian) NMR instrument, operating at a resonant frequency of

75.5 MHz and at 20 °C. The surface areas of materials were determined using a Quantachrome, NOVA 1200e surface area and pore size analyzer. The BET surface areas were calculated from the mathematical model proposed by Brunauer–Emmett–Teller (BET), and results were 2.07, 2.61, and 4.64 m<sup>2</sup> g<sup>-1</sup> for JB<sub>in</sub>, JB<sub>H2O</sub>, and JB<sub>NaOH</sub> biosorbents, respectively.

Biosorption experiments

The biosorption studies were carried out using standard solutions of metal ions, prepared from their corresponding salts: lead nitrate (Pb(NO<sub>3</sub>)<sub>2</sub>, Merck) and cadmium nitrate (Cd(NO<sub>3</sub>)<sub>2</sub>, Merck). The working solutions were prepared by diluting the standard solutions with distilled water. For each adsorption experiment, 25.0 mL of heavy metal ion solution of known concentration was placed in contact with 0.125 g of biosorbent (dosage = 5.0 g L<sup>-1</sup>) in polypropylene tubes, and subjected to agitation (at 180 rpm) at room temperature. After different contact times, aliquots of solutions were sampled and properly stored in glass recipients for further analysis. The determination of heavy metal concentrations was performed by flame atomic absorption spectrometry (FAAS).

The effect of pH on the materials' sorption properties toward heavy metals was carried out using

**Table 1** Non-linear models of isotherm and kinetic

Model	Equation
Isotherm	
Langmuir	$q_e = \frac{Q_m K_a C_e}{1 + K_a C_e}; R_L = \frac{Q_m K_a C_e}{1 + K_a C_e}$
Freundlich	$q_e = K_F C_e^{1/n_F}$
Dubinin–Radushkevich	$q_e = Q_m \exp\left(-K_{DR} \left[RT \ln\left(1 + \frac{1}{C_e}\right)\right]^2\right)$ $E = \frac{1}{\sqrt{2} B_{DR}}$
Kinetic	
Pseudo-first-order	$q_t = q_e [1 - e^{-k_1 t}]$
Pseudo-second-order	$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$
Intraparticle diffusion	$q_t = K_{id} \cdot \sqrt{t} + C_i$

*Q<sub>m</sub>* maximum adsorption capacity, *K<sub>a</sub>* Langmuir constant, *R<sub>L</sub>* separation factor, *K<sub>F</sub>* and *n<sub>F</sub>* Freundlich constants, *K<sub>DR</sub>* Dubinin–Radushkevich constant, *E* mean free energy, *K<sub>1</sub>* and *K<sub>2</sub>* rate constants for the pseudo-first- and pseudo-second-order adsorption, respectively, *h<sub>0</sub>* initial adsorption rate, *K<sub>id</sub>* intraparticle diffusion constant (mg g<sup>-1</sup> h<sup>-0.5</sup>), *C<sub>i</sub>* boundary layer thickness (mg g<sup>-1</sup>)

500.0-mg L<sup>-1</sup> solutions after adjusting their pH in the range of 2.0 to 6.0, with nitric acid and sodium hydroxide solutions. The mixtures, containing the biosorbent and aliquot of heavy metal solution, were agitated for 120 min at room temperature.

The biosorption kinetic studies were carried out using heavy metal ion solutions with a concentration of 500 mg L<sup>-1</sup> at pH 5.50 and 4.00 for Pb(II) and Cd(II), respectively. The systems were kept under agitation in the interval between 5 and 360 min. The concentration

of heavy metal on biosorbents at a given time,  $t$  ( $q_t$ , mg g<sup>-1</sup>), was calculated from Eq. 1:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (1)$$

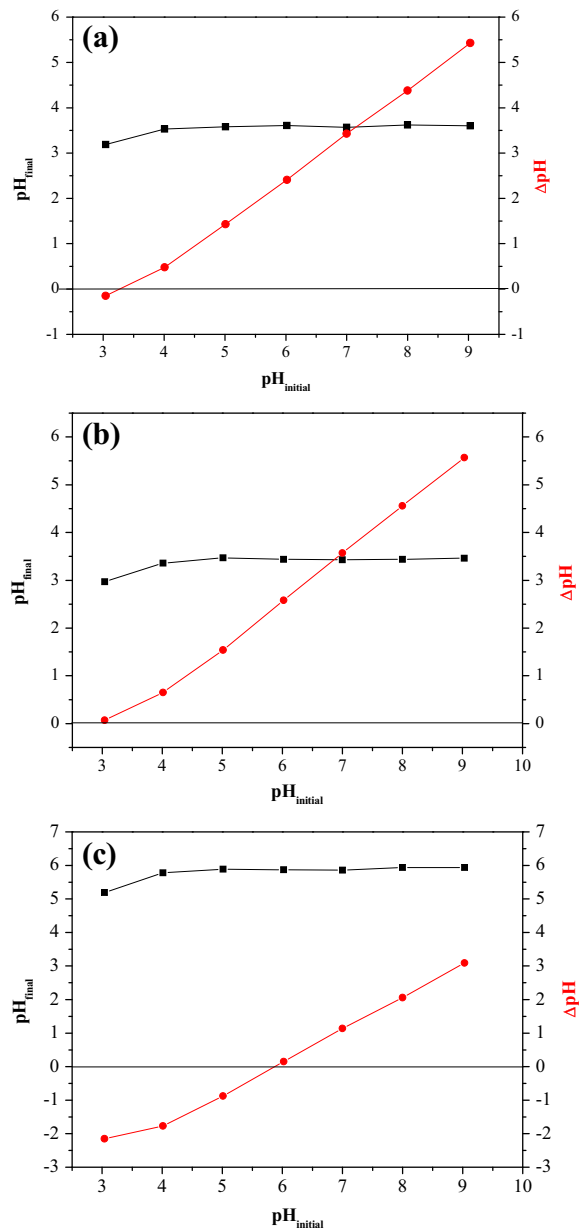
where  $C_0$  is the initial concentration (500.0 mg L<sup>-1</sup>),  $C_t$  is the heavy metal concentration in solution at any time (mg L<sup>-1</sup>),  $V$  is the solution volume (L), and  $W$  is the biosorbent mass (g).

Equilibrium studies of the biosorption processes were performed using heavy metal ion solutions with concentrations ranging from 50.0 to 800.0 mg L<sup>-1</sup> at pH 5.5 and 4.0 for Pb(II) and Cd(II), respectively, and an agitation time of 180 min. The adsorption capacity of biosorbents to retain heavy metal ions ( $q_e$ , mg g<sup>-1</sup>) was then calculated by using Eq. 2:

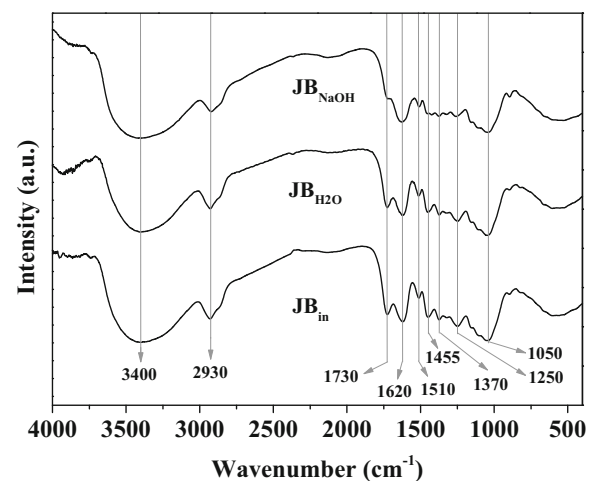
$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

where  $C_0$  and  $C_e$  correspond to initial and final equilibrium concentrations, respectively,  $V$  is the solution volume (L), and  $W$  is the biosorbent mass (g).

To gain insight into the interaction between adsorbates and biosorbents, and to obtain the parameters that can provide information about adsorption mechanisms, the models of Langmuir (1916; Pezoti et al. 2016), Freundlich (Freundlich 1906; Pezoti et al. 2014), and Dubinin–Radushkevich (1960; Gautam et al. 2014) were applied. In addition, for evaluation of the adsorption dynamic in relation to time, kinetic models of



**Fig. 1**  $pH_{pzc}$  of  $JB_{in}$  (a),  $JB_{H_2O}$  (b), and  $JB_{NaOH}$  (c)



**Fig. 2** FT-IR spectra of  $JB_{in}$ ,  $JB_{H_2O}$ , and  $JB_{NaOH}$

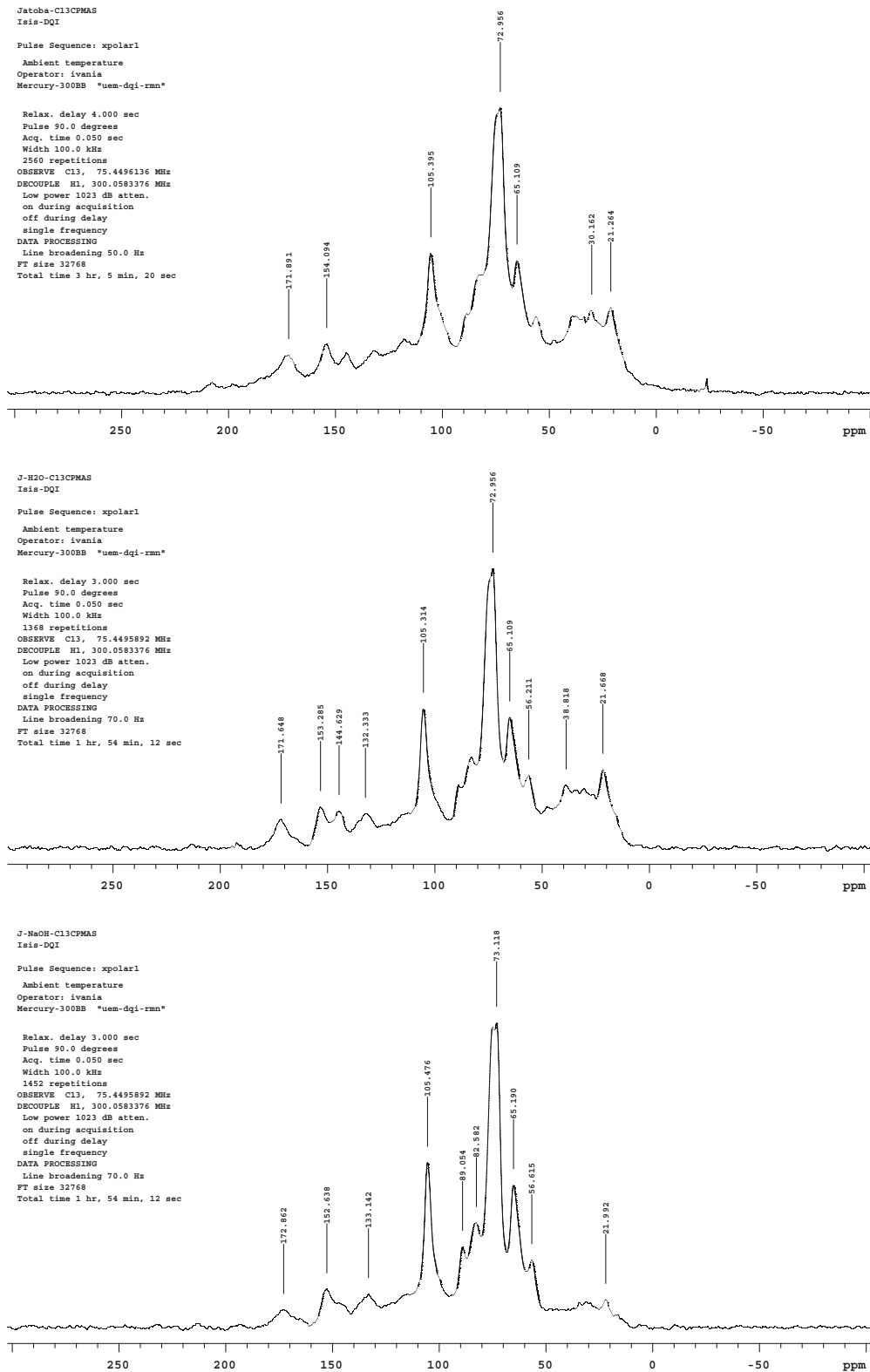


Fig. 3 <sup>13</sup>C NMR spectra of JB<sub>in</sub>, JB<sub>H<sub>2</sub>O</sub>, and JB<sub>NaOH</sub>

pseudo-first order (Lagergren 1898; Salem and Awwad 2014) and pseudo-second order (Pezoti et al. 2014) and intraparticle diffusion (Ofomaja 2010) were employed. Equations of models are shown in Table 1.

The kinetic and isotherm models were fitted to the experimental data, using Origin 6.1® software. The selections of mathematic models, which explain the adsorption processes, were performed by analysis of determination coefficients ( $R^2$ ) and variation from the normal standard deviation ( $\Delta q_e$ ). The  $\Delta q_e$  values were calculated applying Eq. 3:

$$\Delta q_e = 100 \sqrt{\frac{\sum \left[ \frac{(q_{e,exp} - q_{e,cal})}{q_{e,exp}} \right]^2}{N-1}} \quad (3)$$

where  $N$  is the data number and  $q_{e,exp}$  and  $q_{e,cal}$  ( $\text{mg g}^{-1}$ ) are values of experimental and calculated adsorption capacities, respectively.

### Desorption procedure

Desorption experiments were carried out after biosorption assays. Typically, the biosorbents were loaded with the heavy metal (Pb(II) and Cd(II) ions using the same condition for the equilibrium studies (biosorbent dosage of  $5.0 \text{ g L}^{-1}$  and Pb(II) and Cd(II) solutions with concentrations of  $100.0$  and  $200.0 \text{ mg L}^{-1}$ , respectively). The materials obtained after filtration were then washed with distilled water to remove any non-adsorbed species and dried at  $40 \text{ }^\circ\text{C}$  for 24 h. Then,  $0.125 \text{ g}$  of biosorbents was placed in contact with  $25.0 \text{ mL}$  of  $\text{HCl } 0.1 \text{ mol L}^{-1}$  and/or  $\text{NaOH } 0.1 \text{ mol L}^{-1}$  and stirred for 2 h. The concentrations of the heavy metal ions in the liquid phase were determined, and percentages of the metal ions removed were then calculated.

## Results and discussion

### Characterization of biosorbents

The  $\text{pH}_{\text{pzc}}$  values of sorbent materials can provide important information about the possible biosorption mechanisms occurring on the material. Figure 1 shows plots constructed from the  $\text{pH}_{\text{final}}$  values and  $\Delta\text{pH}$  vs.  $\text{pH}_{\text{initial}}$  values for biosorbents  $\text{JB}_{\text{in}}$ ,  $\text{JB}_{\text{H}_2\text{O}}$ , and  $\text{JB}_{\text{NaOH}}$ . The results indicate that the  $\text{pH}_{\text{pzc}}$  values of  $\text{JB}_{\text{in}}$ ,  $\text{JB}_{\text{H}_2\text{O}}$ , and  $\text{JB}_{\text{NaOH}}$  were found to be 3.4, 3.0, and 6.0, respectively. It

is known that biosorption processes of heavy metals are favored in pH values higher than those of  $\text{pH}_{\text{pzc}}$ , where the surface of the biosorbent material is negatively charged. This negative surface of the material enables metal ions to anchor on it, favoring the biosorption processes. On the other hand, at pH values lower than those of  $\text{pH}_{\text{pzc}}$ , the functional groups present on the biosorbent surfaces are protonated and can generate a positive liquid charge, which can repel metal ions and create an unfavorable biosorption process (Salem and Awwad 2014).

The biosorbents are constituted mainly of macromolecules of cellulose surrounded by hemicelluloses and lignin molecules. The main functional groups that may exist on the biosorbent surfaces are hydroxyl, carbonyl, carboxylic, and phenolic. Figure 2 shows FTIR spectra of biosorbents obtained. As can be seen, the spectra have a strong band at  $3400 \text{ cm}^{-1}$ , which can be attributed to stretching of O–H and N–H bonds characteristic of phenolic compounds, carboxylic acids, and alcohol, amide, and amine groups (Chakravarty et al. 2010; Salem and Awwad 2014). The band at  $2930 \text{ cm}^{-1}$  can be assigned to C–H stretching methyl groups. The peaks at  $1730$  and  $1620 \text{ cm}^{-1}$  can be assigned to C–O stretching vibration of ester and carboxyl groups (Nagy et al. 2014; Rangabhashiyam and Selvaraju 2015). Additionally, bands between  $1651$  and  $1421 \text{ cm}^{-1}$  can be attributed to the vibrational stretching of the C–O bond of amide and carboxylic groups, whereas the peak at  $1250 \text{ cm}^{-1}$  may be assigned to C–O stretching of phenols and carboxylic acids (Nagy et al. 2014). The band at  $1058 \text{ cm}^{-1}$  has been attributed to C–O stretching, suggesting the presence of lignin (Palin et al. 2016). According to the results, it can be seen that the  $\text{JB}_{\text{NaOH}}$  spectrum showed changes when compared to other materials. The peaks at  $1730$ ,  $1455$ ,  $1400$ , and  $1250 \text{ cm}^{-1}$  decreased significantly, which suggests that the performed treatment could have removed amide and carboxylic compounds, as well as phenolic compounds.

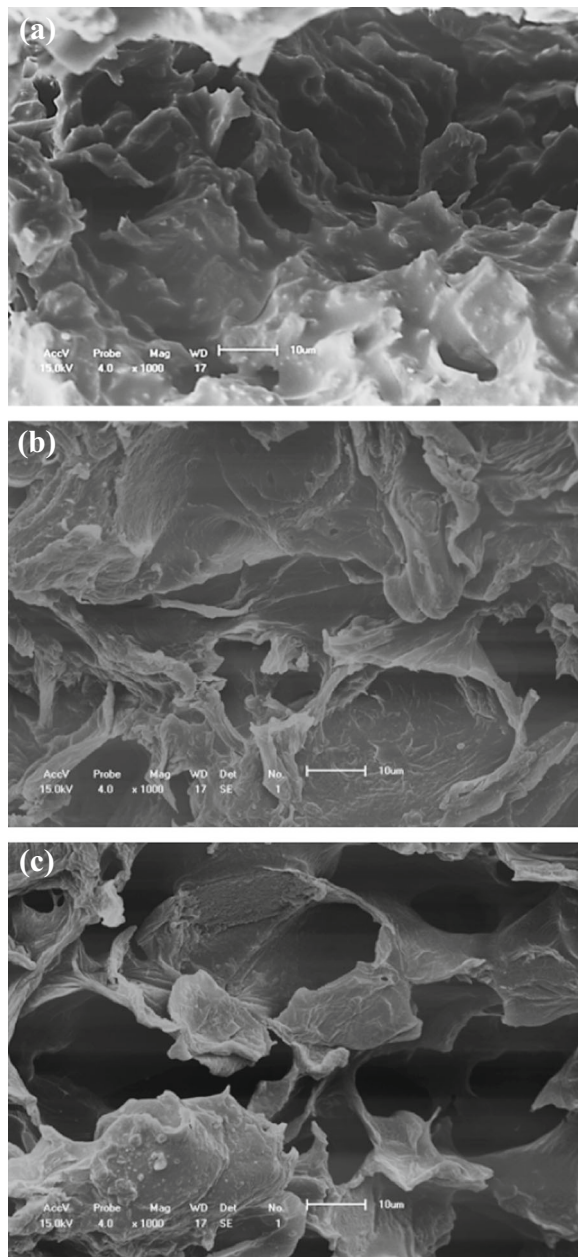
The  $^{13}\text{C}$  NMR analyses have been used for identification of functional groups present in hemicellulose, lignin, and cellulose structures. Figure 3 shows  $^{13}\text{C}$  NMR spectra for biosorbents herein obtained. According to the results, it is possible to identify characteristic peaks of the functional groups present in the biosorbent structure, including the peak at  $21 \text{ ppm}$  that can be attributed to acetyl and methyl groups of hemicelluloses, and the peak at  $56 \text{ ppm}$  that can be assigned to methoxy groups of lignin (Fu et al. 2015). The peaks at  $65$  and  $73 \text{ ppm}$  were attributed to aliphatic carbon 6 (C6) of crystalline cellulose, and to carbons 2 (C2), 3 (C3), and 5 (C5) of the cellulose, respectively,



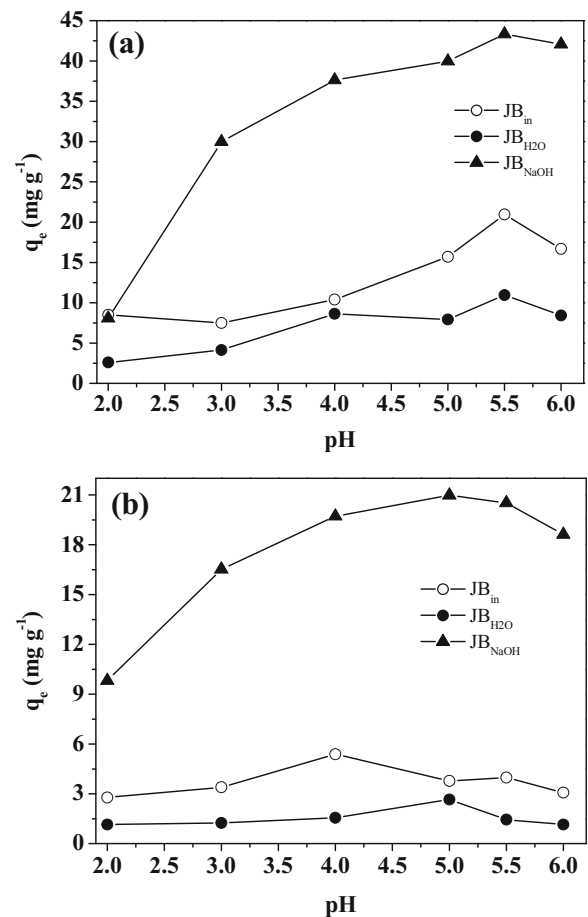
while the peak at 105 ppm was assigned to carbon 1 (C1) of the anomeric cellulose. The peaks in the range of 82 to 89 ppm have been assigned to C4 of the amorphous and crystalline cellulose, respectively (Cao et al. 2016). At lower intensity, the peaks are observed from 135 ppm which indicates the presence of aromatic lignin (Fu et al. 2015). The spectra of JB<sub>in</sub> and JB<sub>H<sub>2</sub>O</sub> showed peaks at 38 ppm corresponding to amide and carboxylate groups, which is not observed in the case of JB<sub>NaOH</sub>, indicating

that the chemical modification carried out with NaOH alters the surface composition of material. This result is consistent with those obtained from the FTIR spectra.

Figure 4 shows the SEM images of JB<sub>in</sub> (Fig. 4a), JB<sub>H<sub>2</sub>O</sub> (Fig. 4b), and JB<sub>NaOH</sub> (Fig. 4c). As can be observed from Fig. 4, the biosorbents show a heterogeneous structure with cavities and cracks on its surfaces, which are distributed from unorganized forms (De Souza et al. 2012; Peláez-Cid et al. 2013). The SEM image of JB<sub>NaOH</sub> (Fig. 4c) shows more cracks and pores in comparison with the images of JB<sub>in</sub> and JB<sub>H<sub>2</sub>O</sub> (Fig. 4a, b), indicating that the chemical modification promotes changes on surface features of the material, possibly due to removal of phenolic compounds present in the precursor, as can be seen in FTIR spectra, and increasing the values of the BET surface area. This alteration in the surface characteristic of the JB<sub>NaOH</sub> is in accordance with results of <sup>13</sup>C NMR and FTIR analyses.



**Fig. 4** SEM images of JB<sub>in</sub> (a), JB<sub>H<sub>2</sub>O</sub> (b), and JB<sub>NaOH</sub> (c)



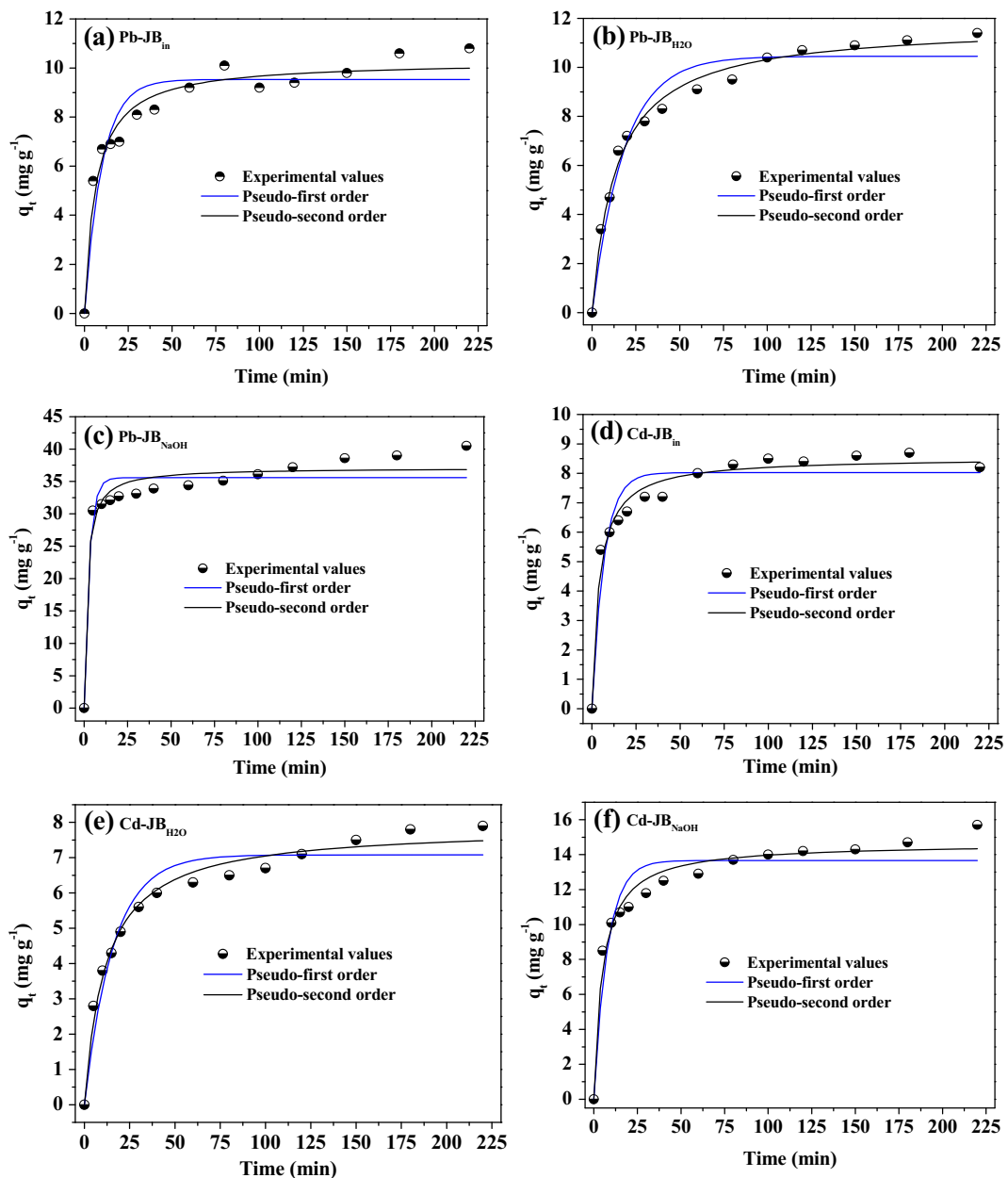
**Fig. 5** Effect of solution pH on biosorption of Pb(II) (a) and Cd(II) (b) on JB<sub>in</sub>, JB<sub>H<sub>2</sub>O</sub>, and JB<sub>NaOH</sub>

## Adsorption studies

## Effect of pH

Figure 5 shows the effect of pH on the ability of the biosorbent to remove Pb(II) and Cd(II) ions from aqueous solutions. According to the results, the pH effect on biosorption is more evidenced for  $\text{JB}_{\text{NaOH}}$ , which shows

the highest  $q_e$  values. These highest values of heavy metal removal for  $\text{JB}_{\text{NaOH}}$  prove the influence of chemical treatment performed. The  $q_e$  of  $\text{JB}_{\text{NaOH}}$  increases with pH until values of about 5.5, which was 5.6 and 2.1 times higher than those found at pH 2.0, for biosorption of Pb(II) and Cd(II), respectively. It was observed that at high pH values, solutions show lowest hydrogen ion concentrations, consequently producing a smaller



**Fig. 6** Non-linear fits of pseudo-first-order and pseudo-second-order models to biosorption kinetics of systems Pb- $\text{JB}_{\text{in}}$  (a), Pb- $\text{JB}_{\text{H}_2\text{O}}$  (b), Pb- $\text{JB}_{\text{NaOH}}$  (c), Cd- $\text{JB}_{\text{in}}$  (d), Cd- $\text{JB}_{\text{H}_2\text{O}}$  (e), and Cd- $\text{JB}_{\text{NaOH}}$  (f)



competition between hydrogen ions and metal ions by the adsorption sites on the biosorbents, leading to improvement in biosorption capacities. Additionally, the pH values that lead to greater removal of heavy metal ions by JB<sub>NaOH</sub> were found to be lower than those of pH<sub>pzc</sub>, under conditions in which the biosorbent surface is protonated. This suggests that the modification from chemical treatment improved the material’s porosity, and consequently its biosorption capacity. The BET surface area value of JB<sub>NaOH</sub> is 2.24 times higher than that of JB<sub>in</sub> and 1.77 higher than that of JB<sub>H2O</sub>. The results obtained herein agree with those in other studies involving biosorption of metal ions. Palin et al. (2016) studied the biosorption of Pb(II) by quebracho tannin resin, and they observed that the best removal occurs at pH 5.0. Using rice straw as biosorbent, Ding et al. (2012) obtained the best adsorption of ion Cd(II) in pH about 5.0.

*Adsorption kinetic*

With the aim of understanding the adsorption dynamic of heavy metal ions on the materials, pseudo-first- and pseudo-second-order models and intraparticle diffusion model were fitted to the experimental data, and the results are shown in Fig. 6. It can be observed from the figures that the equilibriums were established in about 75 min for all biosorbents. The kinetic parameters obtained from the fits of models to the experimental data for adsorption of Pb(II) and Cd(II) ions on different biosorbents are listed in Table 2. According to results for both heavy metals, the pseudo-second-order model presented highest values of R<sup>2</sup> and lowest values of Δ<sub>qe</sub>, when compared with the values observed for the

pseudo-first-order model. The pseudo-second-order model may be considered a special kind of Langmuir kinetic, which assumes that the concentration of adsorbate is constant in relation to time and the total number of available binding sites depends on the adsorbed amount at equilibrium (Gupta and Bhattacharyya 2011). As shown in Table 2, R<sup>2</sup> and Δ<sub>qe</sub> values ranged from 0.9612 to 0.9906 and 2.94 to 6.47, respectively, for the adsorption of Pb(II) on different JB biosorbents. For adsorption of Cd(II), the values of parameters R<sup>2</sup> and Δ<sub>qe</sub> ranged from 0.9728 to 0.9844 and 3.72 to 4.04, respectively. Additionally, it is possible to observe that the values of q<sub>e,exp</sub> and q<sub>e,cal</sub> were close to each other, confirming the best fit of the pseudo-second-order model to experimental data. These results are in agreement with works reported in the literature on the adsorption of Pb(II) and Cd(II) on other biosorbents (Huang and Liu 2013; Palin et al. 2016).

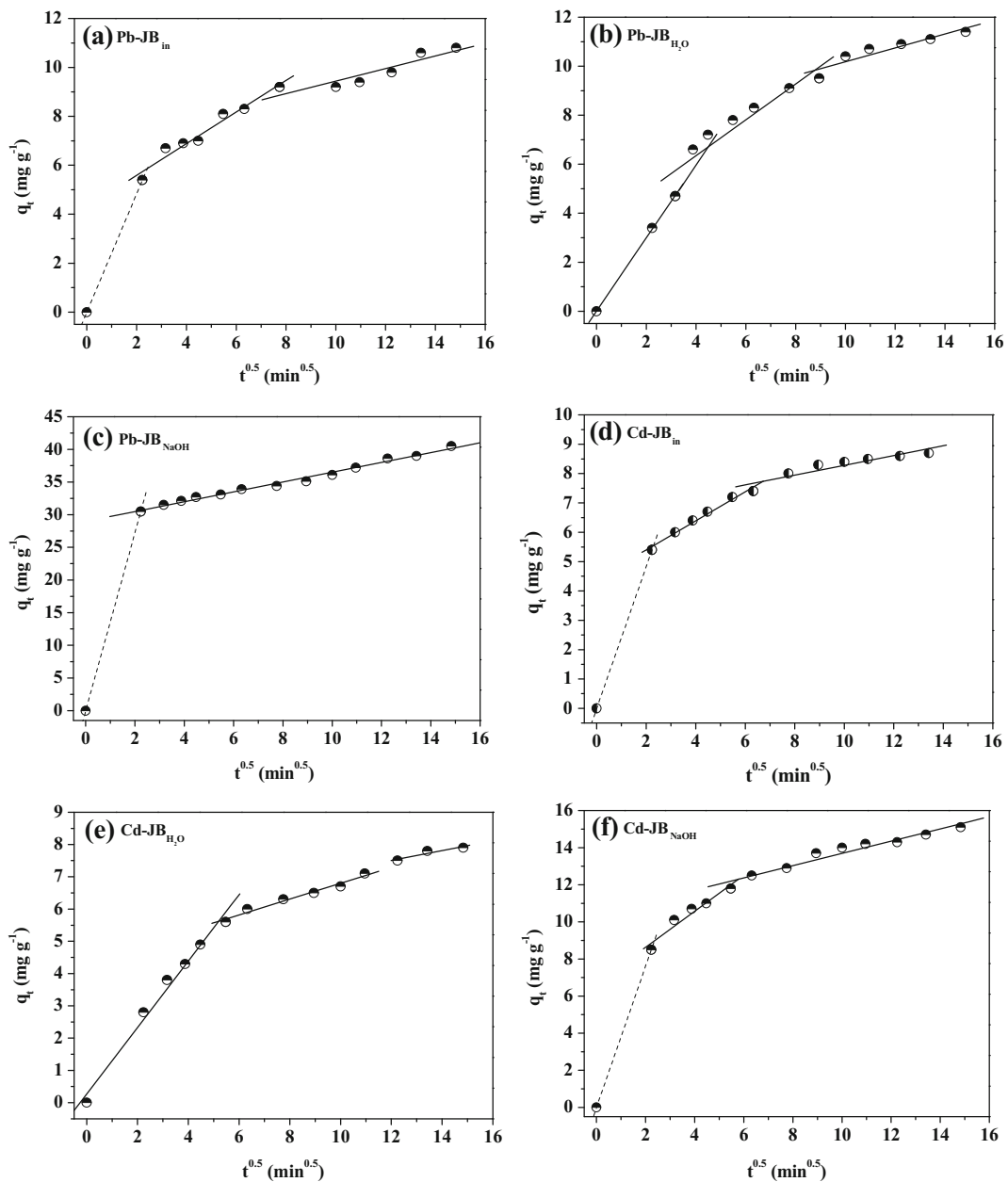
The intraparticle diffusion model has been applied to investigate the occurrence of diffusion mechanism in the biosorption system. The model is represented by linear fits of a graphic of q<sub>t</sub> vs. t<sup>0.5</sup>. Figure 7 shows the intraparticle diffusion model for biosorption kinetics of Pb(II) and Cd(II) for different biosorbents, respectively, and Table 3 presents the calculated parameters. The parameter K<sub>id</sub> is obtained from a straight slope, and the intercept corresponds to the value of C<sub>i</sub>.

Figure 7 shows different fits, indicating that performed treatments promoted significant changes on the surface of biosorbents, which influenced directly on the biosorption mechanisms of Pb(II) and Cd(II) ions. The intraparticle diffusion is considered an important step of the biosorption process, when the straight line of fit passes through the origin (Palin et al. 2016). As can be

**Table 2** Kinetic parameters of biosorption of Pb(II) and Cd(II) on JB<sub>in</sub>, JB<sub>H2O</sub>, and JB<sub>NaOH</sub>

Heavy metal	Biosorbent	q <sub>e,exp</sub>	Pseudo-first-order				Pseudo-second-order			
			q <sub>e,cal</sub>	k <sub>1</sub>	R <sup>2</sup>	Δ <sub>qe</sub>	q <sub>e,cal</sub>	k <sub>2</sub>	R <sup>2</sup>	Δ <sub>qe</sub>
Pb(II)	JB <sub>in</sub>	10.80	9.50	0.10	0.8981	9.65	10.30	0.015	0.9612	5.88
	JB <sub>H2O</sub>	11.40	10.50	0.05	0.9582	7.07	11.80	0.006	0.9906	2.94
	JB <sub>NaOH</sub>	40.50	34.10	0.41	0.9756	8.58	35.40	0.027	0.9897	6.47
Cd(II)	JB <sub>in</sub>	8.20	8.00	0.15	0.9204	8.05	8.50	0.029	0.9772	4.04
	JB <sub>H2O</sub>	7.90	7.10	0.06	0.9421	7.12	7.90	0.010	0.9844	3.72
	JB <sub>NaOH</sub>	15.10	13.70	0.13	0.9104	9.21	14.70	0.010	0.9728	4.92

q<sub>e,exp</sub> maximum amount adsorbed experimentally (mg g<sup>-1</sup>), q<sub>e,cal</sub> maximum amount adsorbed calculated from theoretical model (mg g<sup>-1</sup>), k<sub>1</sub> pseudo-first-order constant (min<sup>-1</sup>), k<sub>2</sub> pseudo-second-order constant (g mg<sup>-1</sup> min<sup>-1</sup>), Δ<sub>qe</sub> normalized standard deviation



**Fig. 7** Intraparticle diffusion model fitted to experimental data of biosorption kinetics of systems Pb-JB<sub>in</sub> (a), Pb-JB<sub>H<sub>2</sub>O</sub> (b), Pb-JB<sub>NaOH</sub> (c), Cd-JB<sub>in</sub> (d), Cd-JB<sub>H<sub>2</sub>O</sub> (e), and Cd-JB<sub>NaOH</sub> (f)

seen from the figures, Pb-JB<sub>in</sub>, Cd-JB<sub>in</sub>, and Cd-JB<sub>NaOH</sub> systems showed graphics with two steps, which are related to processes of gradual biosorption and final equilibrium, respectively. On the other hand, Pb-JB<sub>H<sub>2</sub>O</sub> and Cd-JB<sub>H<sub>2</sub>O</sub> systems showed three steps, where the first step could be attributed to the diffusion of heavy metal from the solution to the external surface of the biosorbent, the second step to intraparticle diffusion,

and the third step to the equilibrium (Gupta and Bhattacharyya 2011). These profiles indicate that intraparticle diffusion is not the rate-limiting step in the biosorption of Pb(II) and Cd(II) on JB<sub>H<sub>2</sub>O</sub>.

The Pb-JB<sub>NaOH</sub> system exhibited a different fit profile of all other materials. The system presented only one step, which can be attributed to the equilibrium state. In this state, a decrease in the diffusion rate of the adsorbate

**Table 3** Intraparticle diffusion parameters of biosorption of Pb(II) and Cd(II) on JB<sub>in</sub>, JB<sub>H2O</sub>, and JB<sub>NaOH</sub>

Heavy metal	Biosorbent	Intraparticle diffusion								
		K <sub>id 1</sub>	K <sub>id 2</sub>	K <sub>id 3</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	R <sup>2</sup> <sub>1</sub>	R <sup>2</sup> <sub>2</sub>	R <sup>2</sup> <sub>3</sub>
Pb(II)	JB <sub>in</sub>	–	0.65	0.26	–	4.30	6.86	–	0.9798	0.9181
	JB <sub>H2O</sub>	1.49	0.73	0.28	0.014	3.43	7.35	0.9998	0.9398	0.9329
	JB <sub>NaOH</sub>	–	–	0.75	–	–	28.96	–	–	0.9947
Cd(II)	JB <sub>in</sub>	–	0.50	0.17	–	4.41	6.62	–	0.9908	0.9295
	JB <sub>H2O</sub>	1.03	0.25	0.21	0.27	4.34	4.88	0.9924	0.9865	0.9630
	JB <sub>NaOH</sub>	–	0.97	0.33	–	6.69	10.39	–	0.9707	0.9735

K<sub>id</sub> intraparticle diffusion constant (mg g<sup>-1</sup> h<sup>-0.5</sup>), C<sub>i</sub> boundary layer thickness (mg g<sup>-1</sup>)

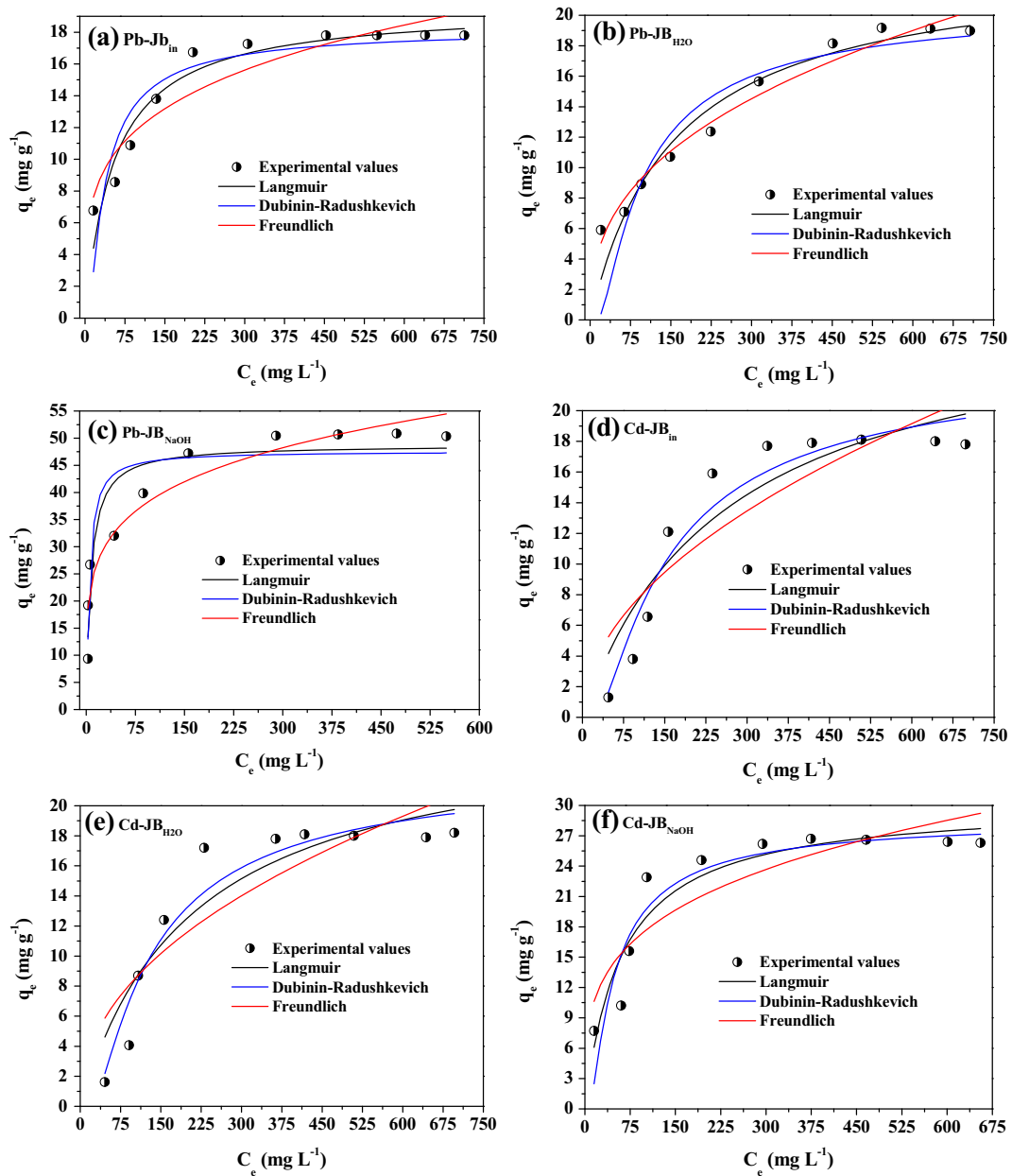
occurs, due to its low concentration in solution (Gao et al. 2013). The Pb-JB<sub>NaOH</sub> system presented a low value of K<sub>id</sub> constant (low slope), added to a high value of C<sub>i</sub>. Additionally, biosorption kinetic (Fig. 7) showed that the system reached equilibrium at a time of about 25 min, indicating a high initial rate of adsorbate transference from the solution to the biosorbent surface. These characteristics demonstrate that the chemical modification of JB shells with NaOH improved the adsorption capacity of the biosorbent, mainly for the Pb(II) ions.

*Adsorption isotherms*

Figure 8 shows experimental data and the non-linear fitting of Langmuir, Freundlich, and Dubinin–Radushkevich models for biosorption of Pb(II) and Cd(II), respectively. The Langmuir model assumes that the adsorption process occurs in monolayer on a surface that exhibits a finite number of sites, which are equally available for interaction with the adsorbate molecule. The empirical model of Freundlich considers that the adsorption process occurs in multilayer on a heterogeneous surface, with non-uniform distribution of energetic sites that present different heats of adsorption. The Dubinin–Radushkevich equation is an empirical model used to distinguish the physical and chemical adsorption of metal ions from the analysis of free energy per molecule of adsorbate, which can be calculated by the use of the B<sub>DR</sub> constant. The adsorption process occurs by chemisorption when 8 < E < 16 kJ mol<sup>-1</sup> and by physisorption when E < 8 kJ mol<sup>-1</sup> (Pezoti et al. 2016).

In Table 4, the biosorption isotherm parameters calculated from non-linear fits are presented. As can be seen, the Langmuir model gives the best fit for the

experimental data of the system Pb-JB<sub>in</sub>, with the highest value of R<sup>2</sup> (0.9313) and lowest value of Δq<sub>e</sub> (14.08). On the other hand, the Freundlich model described the systems Pb-JB<sub>H2O</sub> and Pb-JB<sub>NaOH</sub> better, giving R<sup>2</sup> and Δq<sub>e</sub> values of 0.9733 and 8.81 for JB<sub>H2O</sub> and 0.9190 and 14.37 for JB<sub>NaOH</sub>, respectively. The separation factor (R<sub>L</sub>) calculated from the Langmuir model allows to estimate if the adsorption is favorable or unfavorable. For values 0 < R<sub>L</sub> < 1, the process is favorable; for R<sub>L</sub> > 1, the adsorption is unfavorable; for R<sub>L</sub> = 1, the process is linear; and for R<sub>L</sub> = 0, the adsorption occurs in an irreversible way (Pillai et al. 2013; Pezoti et al. 2016). The initial concentrations of Pb(II) in this study were from 50.0 to 800.0 mg L<sup>-1</sup> for all adsorbents used, and values of R<sub>L</sub> ranged from 0.5 to 0.06 for JB<sub>in</sub>, 0.77 to 0.17 for JB<sub>H2O</sub>, and 0.13 to 8.85 × 10<sup>-3</sup> for JB<sub>NaOH</sub>, indicating that Pb(II) biosorption on different JB biosorbents is favorable. The same behaviors were reported by Yuvaraja et al. (2014) who investigated the biosorption of Pb(II) on *Solanum melongena*. Additionally, the parameters n<sub>F</sub> and 1/n<sub>F</sub> of the Freundlich model provides information related to the intensity and spontaneity of the biosorption process, respectively (Mahapatra et al. 2012; Sivasankar et al. 2012). As shown in Table 4, values of n<sub>F</sub> ranged from 2.57 to 4.99 for Pb(II) biosorption on the different biosorbents, indicating that the process is favorable, which is in concordance with that observed from parameter R<sub>L</sub> of Langmuir. The parameter 1/n<sub>F</sub>, which allows estimation of the surface heterogeneity of material, gives values ranging from 0 to 1. This means that the surface becomes more heterogeneous when its value gets closer to zero. 1/n<sub>F</sub> values ranged from 0.39 to 0.20, indicating high degree of heterogeneity of the JB biosorbents. The Pb-JB<sub>in</sub> and



**Fig. 8** Non-linear fits of Langmuir, Freundlich, and Dubinin–Radushkevich models to biosorption isotherms of systems Pb-JB<sub>in</sub> (a), Pb-JB<sub>H<sub>2</sub>O</sub> (b), Pb-JB<sub>NaOH</sub> (c), Cd-JB<sub>in</sub> (d), Cd-JB<sub>H<sub>2</sub>O</sub> (e), and Cd-JB<sub>NaOH</sub> (f)

Pb-JB<sub>NaOH</sub> systems exhibit the highest values of free energy ( $E$ ) of 9.13 and 25.00 kJ mol<sup>-1</sup>, respectively, indicating that the biosorption of Pb(II) on JB<sub>in</sub> and JB<sub>NaOH</sub> occurs by a chemisorption process. On the other hand, for Pb-JB<sub>H<sub>2</sub>O</sub>, the  $E$  value was 5.00 kJ mol<sup>-1</sup>, indicating that the biosorption may occur by physisorption. Anayurt et al. (2009) investigated the

adsorption of Pb(II) on *Lactarius scrobiculatus* biomass, obtaining a value of  $E = 10.3$  kJ mol<sup>-1</sup>.

Investigation of the adsorption of Cd(II) ions indicated that the Dubinin–Radushkevich model showed the best fit for systems Cd-JB<sub>in</sub> and Cd-JB<sub>H<sub>2</sub>O</sub>, with the highest  $R^2$  value (0.9436 and 0.9369, respectively) and lowest  $\Delta q_e$  value (13.93 and 15.07, respectively). For

**Table 4** Parameters of Langmuir, Freundlich, and Dubinin–Radushkevich models

Heavy metal	Biosorbent	Langmuir				Freundlich				Dubinin–Radushkevich				
		$Q_m$	$K_a$	$R^2$	$\Delta q_e$	$K_F$	$n_F$	$R^2$	$\Delta q_e$	$Q_m$	$B_{DR}$	$E$	$R^2$	$\Delta q_e$
Pb(II)	JB <sub>in</sub>	19.60	0.020	0.9313	14.08	3.92	4.13	0.8923	11.34	18.29	0.006	9.13	0.8330	20.47
	JB <sub>H2O</sub>	23.58	0.006	0.9401	17.94	1.58	2.57	0.9733	8.81	20.88	0.020	5.00	0.8332	25.15
	JB <sub>NaOH</sub>	48.75	0.140	0.8944	17.33	15.39	4.99	0.9190	14.37	47.62	0.0008	25.00	0.8780	17.59
Cd(II)	JB <sub>in</sub>	27.21	0.004	0.8774	22.14	0.74	1.96	0.7935	29.44	23.39	0.030	4.08	0.9436	13.93
	JB <sub>H2O</sub>	25.68	0.005	0.8737	20.81	1.00	2.16	0.7808	27.83	22.76	0.020	5.00	0.9369	15.07
	JB <sub>NaOH</sub>	30.27	0.016	0.8980	15.21	5.10	3.72	0.7998	22.31	28.80	0.008	2.50	0.8601	17.21

$Q_m$  maximum amount adsorbed ( $\text{mg g}^{-1}$ ),  $K_a$  Langmuir constant related with adsorption affinity ( $\text{L mg}^{-1}$ ),  $K_F$  Freundlich constant related with capacity of adsorption ( $\text{mg g}^{-1}$ ),  $n_F$  Freundlich constant related with intensity of adsorption,  $B_{DR}$  Dubinin–Radushkevich constant related with the free energy of adsorption ( $\text{mol}^{-2} \text{kJ}^{-2}$ ),  $E$  free energy of adsorption ( $\text{kJ mol}^{-1}$ )

system Cd-JB<sub>NaOH</sub>, the Langmuir model presented the best fit to experimental data, with  $R^2$  of 0.8980 and  $\Delta q_e$  of 15.21. The separation factor ( $R_L$ ) ranged between 0.83 and 0.24 for JB<sub>in</sub>; 0.80 and 0.20 for JB<sub>H2O</sub>, and 0.53 and 0.072 for JB<sub>NaOH</sub>, indicating that the biosorption of Cd(II) on different materials is favorable. The  $R_L$  values were also evaluated by Pillai et al. (2013) and Awwad and Salem (2014), which showed the biosorption of Cd(II) on loquat (*Eriobotrya japonica*) leaves and xanthated nano banana cellulose, respectively. As shown in Table 4, for systems Cd-JB<sub>in</sub>, Cd-JB<sub>H2O</sub>, and Cd-JB<sub>NaOH</sub>, the values of  $n_F$  ranged between 1.96 and 3.72, characteristic of a favorable process, such as that observed from  $R_L$  values. Additionally, the values of  $1/n_F$  range between 0.51 and 0.27, indicating that the modification of the JB biosorbents increases the degree of heterogeneity of the surface of the materials. The values of biosorption free energy ( $E$ ) (Table 4) for Cd(II) ranged from 2.50 to 5.00  $\text{kJ mol}^{-1}$ , demonstrating that the physical interaction between biosorbent and adsorbate is favorable. Chakravarty et al. (2010) studied the biosorption of Cd(II) on heartwood powder of *Areca catechu* biosorbent and verified from the Dubinin–Radushkevich model that the adsorption process followed a physisorption mechanism.

The adsorption capacity ( $Q_m$ ) obtained for the materials based on the Langmuir model (Table 4) demonstrated that there was an increase in the biosorption capacity of Pb(II) after the treatment with heat water (JB<sub>H2O</sub>) and NaOH (JB<sub>NaOH</sub>), reaching values of 19.60 and 48.75  $\text{mg g}^{-1}$ , respectively. The results of Cd(II) biosorption showed that  $Q_m$  values for JB<sub>in</sub> and JB<sub>H2O</sub> were similar, and JB<sub>NaOH</sub> showed the highest value corresponding to 30.27  $\text{mg g}^{-1}$ .

In Table 5, the values of  $Q_m$  reported in literature for different biosorbents toward adsorption of Pb(II) and Cd(II) are compiled. As can be seen, the values of  $Q_m$  obtained in the present study are in agreement with the values reported in the literature, indicating that the Jatoba fruit shell can result in a good biosorbent.

*Desorption*

Desorption studies were carried out to verify the regeneration of biosorbents. Table 6 shows desorption results

**Table 5** Comparison of biosorption maximum capacities of Cd(II) and Pb(II) on different biosorbents

Biosorbent	$Q_m$ ( $\text{mg g}^{-1}$ )		
	Cd(II)	Pb(II)	Reference
<i>A. bisporus</i>	6.98	–	Nagy et al. 2014
<i>L. piperatus</i>	6.60	–	Nagy et al. 2014
Peanut shell	–	38.91	Taşar et al. 2014
Banana stalk	3.66	20.89	Mahmood-ul-Hassan et al. 2015
Corn cob	13.57	29.17	Mahmood-ul-Hassan et al. 2015
Sunflower head	11.40	22.64	Mahmood-ul-Hassan et al. 2015
<i>Jatropha curcas</i> L.	21.97	–	Jain et al. 2015
Sugarcane bagasse	–	30.71	Palin et al. 2016
JB <sub>NaOH</sub>	30.27	48.75	Present work
JB <sub>H2O</sub>	25.68	23.58	Present work
JB <sub>in</sub>	27.21	19.60	Present work

**Table 6** Desorption of Pb (II) and Cd(II) from the JB<sub>in</sub>, JB<sub>H<sub>2</sub>O</sub>, and JB<sub>NaOH</sub> biosorbents

Adsorbate	Desorption (%)					
	HCl			NaOH		
	JB <sub>in</sub>	JB <sub>H<sub>2</sub>O</sub>	JB <sub>NaOH</sub>	JB <sub>in</sub>	JB <sub>H<sub>2</sub>O</sub>	JB <sub>NaOH</sub>
Pb(II)	99.9	97.7	99.5	34.3	23.8	26.1
Cd(II)	98.8	92.5	99.6	19.3	27.3	2.20

of Pb(II) and Cd(II) from the JB<sub>in</sub>, JB<sub>H<sub>2</sub>O</sub>, and JB<sub>NaOH</sub> biosorbents. According to results, the use of HCl 0.1 mol L<sup>-1</sup> as eluent removed more than 92% of heavy metal ions uptaken by the biosorbents studied, indicating the efficiency of this procedure. On the other hand, NaOH (0.1 mol L<sup>-1</sup>) solution showed low removal of heavy metal ions with values less than 35%. Therefore, under acid conditions, hydrogen ions substitute the heavy metal ions uptaken through the ion exchange mechanism (Gautam et al. 2014). The greater efficient of HCl solution when comprising NaOH solution as eluent of heavy metal uptake on biosorbents was also observed in other studies reported in literature (Pillai et al. 2013; Gautam et al. 2014).

## Conclusion

We have demonstrated the use of Jatoba fruit's shell as an effective biosorbent for removal of heavy metal ions from aqueous solutions. By comparing various materials, including those chemically treated, it was found that the NaOH-treated Jatoba fruit's shell (JB<sub>NaOH</sub>) not only showed different surface characteristics compared to the original material, according to analyses of SEM, FTIR, <sup>13</sup>C-NMR, and pH<sub>pzc</sub>, but also improved adsorption properties toward heavy metal ions compared with the latter. The biosorption equilibrium studies of Pb(II) and Cd(II) showed that the Langmuir model had the best fit for the Pb-JB<sub>in</sub> and Cd-JB<sub>H<sub>2</sub>O</sub> systems, the Freundlich model for Pb-JB<sub>H<sub>2</sub>O</sub> and Pb-JB<sub>NaOH</sub>, and the Dubinin–Radushkevich model for Cd-JB<sub>in</sub> and Cd-JB<sub>H<sub>2</sub>O</sub>, indicating the heterogeneity on the surface of biosorbents. The biosorption maximum capacity values of Langmuir ranged from 19.60 to 48.75 mg g<sup>-1</sup> for Pb-JB systems and from 25.68 to 30.27 mg g<sup>-1</sup> for Cd-JB systems. The pseudo-second-order kinetic model presented the best fit for all systems studied. Additionally, kinetic studies

showed that the intraparticle diffusion is not rate-limiting for the biosorption of heavy metal ions and that the process involves different mechanisms. These results indicate that the JB shell may be applied as biosorbent for removal of heavy metals, such as Cd(II) and Pb(II) from aqueous solutions.

**Acknowledgments** The authors acknowledge the financial support provided by CAPES.

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