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ORIGINAL ARTICLE

Removal of Cd (II) from water using the waste of jatropha fruit (*Jatropha curcas* L.)

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Abstract The aim of this work was to evaluate the removal of Cd (II) from water using three biosorbents originated from the biomass of jatropha (bark, endosperm, and endosperm + tegument). For that, batch tests were performed to verify the effect of solution pH, adsorbent mass, contact time, initial concentration of Cd (II), and the temperature of the process. The adsorption process was evaluated by the studies of kinetics, isotherms, and thermodynamics. The ideal conditions of solution pH were 5.5 and 8 g L^{-1} of adsorbent mass of biosorbents by solution volume, with an equilibrium time of 60 min. According to the Langmuir model, the maximum adsorption capacity for bark, endosperm, and bark + endosperm of jatropha was, respectively, 29.665, 19.562, and 34.674 mg g^{-1}, predominating chemisorption in monolayers. The biosorbents presented potential for the remediation of waters contaminated with Cd (II).

Keywords Agro-industrial waste · Natural adsorbents · Remediation of water resources · Cadmium

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Introduction

Metal pollution caused by the modern anthropic activities in the industry, agricultural, and mining sectors is causing a great concern worldwide (Galunin et al. 2014). As everybody knows, toxic metals are the main pollutants of the highly relevant water resources and environment (Li et al. 2014).

Among the toxic metals, cadmium (Cd) has a very high toxic potential, and it is perhaps the seventh most dangerous chemical element in the world (ATSDR 2008). Cadmium has several uses of which the most important are batteries, pigments, plastics, and agricultural pesticides (Yavuz et al. 2007). The metal may also be frequently found as a contaminant substance in agricultural fertilizers and in wastes from zinc, copper, and lead-mining activities (ICdA 2001). Mining and casting are the main sources of Cd in water (drain water, waste water, discharge reservoir, and run-off rain water in mining areas), welding operations, application of contaminated fertilizers, treatment plants of urban, and industrial drainage, and deposits and earth fillings with dangerous residues (ATSDR 2013).

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Cadmium has a high accumulative capacity in the human body and harms the cardiovascular (heart and blood vessels), gastro-intestinal (digestive), neurological (nervous system), kidney (urinary system and kidneys), reproduction, and respiratory (from the nose to the lungs) systems, coupled to devastating effects during the development of the organs. In fact, it is one of the most powerful carcinogenic agents (ATSDR 2013; Zhang et al. 2014).

Several strategies, mainly chemical and physical precipitation, ionic exchange, extraction by solvents, bio-accumulation by aquatic plants or micro-organisms, and filtration by membranes and adsorption, have been deployed to remove metal contaminants from water solutions (Li et al. 2014; Jimenez 2004; Bessbousse et al. 2008; Ali et al. 2013).

Although activated carbon is the main adsorption material, its high production costs have a negative impact on its ranking in contaminant removal on a large scale (Santhi et al. 2010). The employment of alternative materials for the production of adsorbents is increasing the object of research, where the main sources of prime matters are agro-industrial wastes (Valdman et al. 2001). It should be underscored that the use of agro-industrial wastes is advantageous due to low costs, lack of any treatment, and derivation from renewable sources.

The jatropha (*Jatropha curcas* L.), commonly known as Barbados nut, is an oil-producing plant for the production of biodiesel in several countries worldwide (FACT 2010). Great amounts of vegetal wastes, currently with low usage, are generated after oil extraction from the seeds (Ye et al. 2009). The possible usage of residues as an adsorbent of toxic compounds, such as Cd, may increase the value of the species's productive chain and may de-contaminate the environment through an economical sustainability of its cultivation.

The current research evaluates the removal capacity of Cd^{2+} from water solutions by three biosorbents obtained from the jatropha biomass (bark, endosperm, and endosperm + peel) in different experimental conditions (adsorbent mass, solution's pH, contact time, and initial concentration of Cd^{2+} in the solutions) by the adsorption process, determining kinetic, equilibrium, and thermodynamic parameters of the adsorptive process. The three evaluated adsorbents were also compared with a commercial adsorbent.

Materials and methods

Obtaining and preparing the adsorbent materials

The adsorbent materials (biosorbents) evaluated were produced from the biomass of jatropha fruit harvested from

plants cultivated at the experimental farm of the Universidade Estadual do Oeste do Paraná (Unioeste) at Pato Bragado PR Brazil. Fruit harvest occurred in 4-year-old plants, and their cultivation occurred without any sort of fertilization. Harvested jatropha fruits were dried in the shade for 45 days and stored for later use.

The three adsorbent materials were produced from different types of waste of the jatropha fruit: the bark of the plant produced the first adsorbent (adsorbent C); the second adsorbent (adsorbent E) was obtained from the cake after oil extraction from the endosperm of the jatropha seeds; and the third adsorbent (adsorbent E + T) was obtained from the cake after the oil extraction of the endosperm coupled to the peel of the jatropha seeds. Although the peel of jatropha fruit is not used for biodiesel production, it was evaluated, since it is the first residue material produced in fruit processing. The chemical extraction generally used in jatropha oil extraction (extraction by solvents) produces wastes similar to adsorbent E, whereas the mechanical extraction of oil from the jatropha seeds (pressing) produces a residue similar to that used for the adsorbent E + T (FACT 2010). Consequently, the three adsorbents simulated true conditions for the re-use of the residues of the activity.

After drying, the jatropha fruits were divided into the three above-mentioned prime matters. The latter were ground and sieved in a 14–60 mesh granulometry and then dried in forced air buffer at 60 °C for 48 h. In the case of adsorbents E and E + T, vegetal oil was extracted by the Soxhlet method for 4 h after the dehydration of the prime matters (IUPAC 1988). Drying followed in a buffer at 80 °C for 24 h for the total evaporation of the solvent (*n*-hexane) used in the extraction of vegetal oil.

Characterization of biosorbents

The three adsorbents evaluated in the current assay were characterized by their functional groups, their morphology, by the quantification of their surface loads and the metals in their structure. The biosorbents' functional groups were performed by infrared spectra with a Shimadzu Infrared Spectrophotometer FTIR-8300 Fourier Transform, in the region between 400 and 4000 cm^{-1}, with 4 cm^{-1} resolution. Spectra were obtained by transmittance with potassium bromide pellets (KBr).

The morphology of the biosorbents was characterized by a Scanning Electron Microscope (SEM) in a microscope FEI Quanta 200 at 30 kV. Procedure comprised samples placed on a double surface carbon adhesive tape fixed on a sample support, followed by gold metallization up to a thickness of approximately 30 nm with a Baltec Scutter Coater SCD 050.

Surface loads were quantified by determining the point of zero charge (pH$_{PCZ}$) of the adsorbents. In fact, pH$_{PCZ}$ is

the pH in which the adsorbents' equilibrium of surface loads is nil. Procedure consisted in adding, for each material, 50 mg of biosorbent mass to 50 mL of potassium chloride water solutions (KCl, Vetec, 99 %) at 0.05 and 0.5 mol L^{-1}, with the initial pH rates ranging between 2.0 and 9.0, and adjusted to hydrochloric acid (HCl, Vetec, 37 %) or sodium hydroxide (NaOH, Vetec, 99 %) solutions at a concentration of 0.1 mol L^{-1}. After stirring for 24 h (200 rpm) in each solution, the final pH rates were calculated. A graph on the variations of the initial pH related to the final pH was produced. The point of nil rate of pH variation corresponded to pH$_{PCZ}$ (Mimura et al. 2010).

A nitroperchloride digestion of the materials was performed for the initial quantification of the metals in the biosorbents structure with the posterior determination of potassium (K), calcium (Ca), magnesium (Mg), copper (Cu), iron (Fe), manganese (Mn), zinc (Zn), cadmium (Cd), lead (Pb), and chromium (Cr) concentrations by flame atomic absorption spectrometry (FAAS).

Preparation of strengthened solutions and experimental conditions

All Cd^{2+} solutions in the current assay were obtained by diluting Cd nitrate salt [Cd(N$_2$O$_6$).4H$_2$O], purchased from Sigma-Aldrich®, grade P.A., purity higher than 99 % and diluted in ultrapure water type I.

All adsorption tests were done by triplicate in batches of 125 or 50 mL Erlenmeyer's flasks. After each test, the solutions were filtered with quality filter paper (Unifil) to separate biosorbent and liquid solution. Aliquots of liquid solution were retrieved to determine the amount of Cd^{2+} by FAAS.

Effect of adsorbent mass and pH of solution on the adsorption process

Experiments with mass quantity and pH were performed to obtain the ideal quantity of adsorbent mass to be employed and the best pH condition of the solution during the adsorption process. Different mass quantities (0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 g) for each biosorbent were tested in different Cd^{2+} solutions with four pre-defined pH conditions (4.0, 5.0, 6.0, and 7.0). Furthermore, pH rates were adjusted with HCl (Vetec, 37 %) or NaOH (Vetec, 99 %) solutions, at 0.1 mol L^{-1} concentration. At this stage, stirring speed (200 rpm), stirring time (1.5 h), temperature of solutions (25 °C), and Cd^{2+} concentration in the solutions (10 mg L^{-1}) were constant.

After the batch tests, the solutions were filtered with quality filter paper (Unifil) to separate the biosorbent and

the liquid solution. The filter paper did not influence in the results, because it was used the same kind of filter paper for all samples. The quantity of Cd^{2+} in the solution was determined. Cd^{2+} removal percentage from the solutions could be obtained from the results by Eq. (1):

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

where %R is the removal percentage of the metal by the biosorbent; C_{eq} is the concentration of Cd^{2+} in equilibrium (mg L^{-1}); and C_0 is the initial concentration of Cd^{2+} in the solution (mg L^{-1}).

All the experiments were conducted in laboratory and in controlled environment, and concentrations were determined by FAAS using the Cd certified standards.

Effect of contact time between adsorbent and adsorbed and the kinetics of adsorption

After defining mass quantity (0.4 g) and ideal pH (5.5), tests evaluated the effect of contact time between adsorbent and adsorbed (5, 10, 20, 40, 60, 80, 100, 120, 140, and 160 min). Stirring speed (200 rpm), temperature of solutions (25 °C), and Cd^{2+} concentrations in the solutions (10 mg L^{-1}) were kept constant, whilst the solutions' pH was adjusted with HCl (Vetec, 37 %) or NaOH (Vetec, 99 %) solutions at 0.1 mol L^{-1}. Amount adsorbed in the equilibrium gave rise to the rate obtained for the concentration in equilibrium by Eq. (2):

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

where Q_{eq} is the quantity of Cd^{2+} adsorbed per unit of adsorbent in equilibrium (mg g^{-1}); m is the biosorbent's mass used (g); C_0 is the initial concentration of Cd^{2+} in the solution (mg L^{-1}); C_{eq} is the Cd^{2+} concentration in the solution in equilibrium (mg L^{-1}); and V is the volume of the solution employed (L).

Results were employed to explain the kinetic mechanism that controls the adsorption process by means of the pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion models.

Effect of the initial concentration of the adsorbate in the adsorptive process

The analysis of the effect of different initial concentrations of Cd^{2+} in solution (5, 20, 40, 60, 80, 100, 120, 140, 160, and 200 mg L^{-1}) was performed with ideal conditions of the biosorbents' mass (0.4 g), pH of solution (5.5), and contact time (60 min). The solutions' stirring speed (200 rpm) and temperature (25 °C) were constant during the procedure. Furthermore, pH of the solutions was

adjusted with HCl (Vetec, 37 %) or NaOH (Vetec, 99 %) solutions at 0.1 mol L^{-1} concentration.

Equations (1) and (2), respectively, provided the removal percentage of Cd^{2+} (%R) and the amount adsorbed in equilibrium (Q_{eq}). The latter parameter is used to obtain adsorption isotherms which were linearized by the mathematical models of Langmuir, Freundlich, and Dubinin–Raduschkevich (D–R).

In the current assay, the comparison of Cd^{2+} removal capacity between jatrophas's adsorbents and a commercial adsorbent was undertaken by experiments within the same conditions for biosorbents, or rather, activated coal P.A. Synth®, widely used in the removal of pollutants in water matrixes (Oliveira et al. 2008).

Another procedure consisted in determining the structural components in the biosorbents after the adsorptive process. Samples of biosorbents were removed after adsorption process and submitted to IR spectrometric techniques within the same conditions, as described in "Characterization of biosorbents".

Desorption assay

Tests were performed with masses obtained after experiments involving different initial concentrations of Cd^{2+} to evaluate the Cd^{2+} desorption of biosorbents compared with commercial adsorbent (activated coal). Masses were obtained by filtering solutions in equilibrium coupled to drying in buffer at 60 °C for 24 h. Each biosorbent mass was then placed in contact with 50 mL of HCl solution (Vetec, 37 %) at 0.1 mol L^{-1}, followed by the stirring of the solutions at 200 rpm, at 25 °C for 60 min. After determining the concentration of Cd^{2+} desorbed in solution, the desorption percentage was calculated by Eq. (3):

$$\%D = \left(\frac{c_{eq(des)}}{c_{eq(ads)}}\right) \times 100 \tag{3}$$

where %D is the percentage of Cd^{2+} desorption by the biosorbent; and $C_{eq(des)}$ (mg L^{-1}) and $C_{eq(ads)}$ (mg L^{-1}) are, respectively, the concentrations of desorbed and adsorbed Cd^{2+} in equilibrium by the biosorbent.

Effect of temperature in the adsorption process (thermodynamics)

Tests at different solution temperatures (15, 30, 45, and 60 °C) were performed with the Cd^{2+} initial concentration the highest removal percentages for the three biosorbents (80 mg L^{-1} for biosorbent C, 120 mg L^{-1} for biosorbent E, and 80 mg L^{-1} for biosorbent E + T). During this stage, the solutions' pH (5.5), biosorbent mass (0.4 g), stirring speed (200 rpm), and contact time between biosorbent and solution (60 min) were kept constant.

Data were used to determine thermodynamic parameters and to investigate the adsorption process. Gibbs's free energy (ΔG) (Eq. 4), enthalpy (ΔH), and entropy (ΔS) (Eq. 5) were calculated (Sari et al. 2007; Gonçalves et al. 2008):

$$\Delta G = -RT \ln K_d \tag{4}$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{5}$$

where K_d is the ratio Q_{eq}/C_{eq}; R is the universal constant of gases (8.314 J mol^{-1} K^{-1}); T is the temperature (K) used in adsorption tests; and ΔH and ΔS rates were obtained by $\ln K_d$ as a function of $1/T$.

Results and discussion

Characterization of biosorbents

Figure 1 shows the IR spectra of the three biosorbents under the analysis in the current assay, with vibrations at bands 760, 1062, 1370, 1542, 1650, 2900, and 3400 cm^{-1}.

The wide and strong band in 3400 cm^{-1} for the three biosorbents may be attributed to the vibration lengthening of the hydroxyl bonds (O–H) usually found in carbohydrates, fatty acids, proteins, lignin units, cellulose, and absorbed water (Stuart 2004; Garg et al. 2008; Gonçalves et al. 2010; Han et al. 2010; Feng et al. 2011). Vibration lengthening in 2900 cm^{-1} may be related to C–H bonds in alkane groups and aliphatic acids (Barbosa 2007; Iqbal et al. 2009). Bands in 1650, 1542, and 1370 cm^{-1} may be attributed to the vibration lengthening of C–O-type bonds found in starch and carboxyl groups (Han et al. 2010). Moreover, vibration in 1650 cm^{-1} may also be provided by C = O-type bonds, which constitutes carbonyl and carboxylate groups in lignocellulose compounds (Jacques
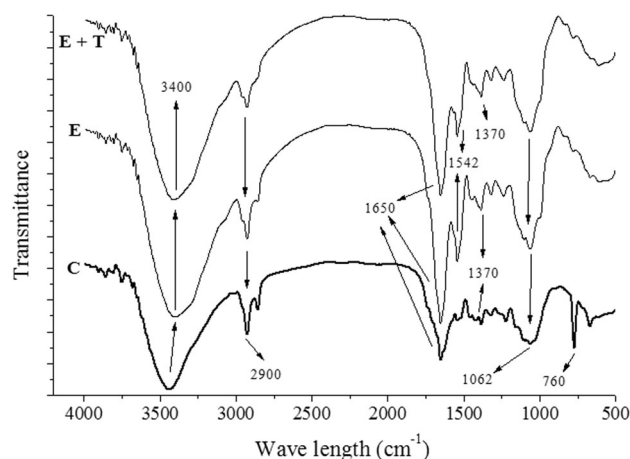

Fig. 1 IR spectra of biosorbents: jatropha bark (C), endosperm (E), and endosperm + peel (E + T)

et al. 2007; Tongpoothorn et al. 2011). Bands in 1542 and
1370 cm^{-1} may also occur due to C = C bonds of aro-
matic compounds (Pavan et al. 2008). It should be under-
scored that 1370 cm^{-1} band may be provided by the
vibration of C–H-type bonds of celluloses, hemicelluloses,
and lignin (Smith 1999). Vibration lengthening in
1062 cm^{-1} may be related to C–O-type bonds in lignin and
in phenols, which contains carboxyl groups that make
available adsorption sites for metallic ions (Pascoal-Neto
et al. 1995; Guo et al. 2008; Barka et al. 2010). Band in
760 cm^{-1} for biosorbent from jatropha peel shows the
probable presence of nitrogen (N) with bio-bondings
(Barka et al. 2010).

Proteins, lignin, cellulose, hemicellulose, lignocellu-
loses and the hydroxyl, carboxyl, and carbonyl and phenol
groups are the main compounds capable of forming bonds
with metallic ions in the structure of biosorbents obtained
from jatropha biomass (Kurniawan et al. 2006; Demirbas
2008). As a rule, vegetal-derived materials are mainly
constituted by cellulose, hemicellulose, and lignin (Pehli-
van et al. 2009). It should be underscored that the results in
IR spectra for the three biosorbents are similar to those
reported by Tongpoothorn et al. (2011) and Prola (2013)
who also experimented with the biomass of jatropha fruit
biomass for the production of biosorbents.

SEM-produced evaluation of adsorbents' morphology
(Fig. 2) showed that the three materials had a highly
irregular morphology which indicated a porous surface.
Materials with such characteristics generally have a high
specific surface, which provides good adsorption capacity.

Results obtained from the determination of the biosor-
bents' surface loads (pH$_{PCZ}$) in the two KCl concentrations
(0.05 and 0.5 mol L^{-1}) revealed that the load equilibrium
is nil when pH rates lay between 5 and 6 (Fig. 3). Or rather,
equilibrium between positive and negative loads is zero in
such pH conditions. When the solution's pH is lower than
pH$_{PCZ}$, positive surface loads predominate on the biosor-
bents' surface due to the protonation of the latter. On the
other hand, when pH rates of solutions are higher than
pH$_{PCZ}$, the predominant surface loads are negative and
cation adsorption occurs (Mimura et al. 2010). Further-
more, pH$_{PCZ}$ rates for the three biosorbents are close to

those reported by Namasivayam et al. (2007), with pH$_{PCZ}$
equal 7.2 for the jatropha peel.

The quantification of metal concentrations in biosor-
bents prior to deployment (Table 1) showed that Cd^{2+}
concentrations were lower than the quantification limit of
the method used (FAAS). In fact, the above results were
expected, since plants rarely accumulated toxic substances
in their reproductive structures (Shtangeeva et al. 2011).

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

Evaluation of pH influence on the adsorption process
(Fig. 4) demonstrated that Cd^{2+} adsorption capacity by
biosorbents jatropha bark (C) and jatropha endo-
sperm + peel (E + T) was only slightly affected by the
variations of this factor. In the case of the jatropha endo-
sperm (E), a greater Cd^{2+} removal occurred when the
solution's pH lay between 4.0 and 5.0.

Moreover, the pH affects the qualities of the adsorbents,
functional groups, and the ionic state of the metal species.
In fact, it is an important factor to be taken into account in
metal ions adsorption (Hossain et al. 2012). As a rule, a
strong competition occurs in acid pH by the active sites of
the adsorbent between the excess of H$^+$ ions and the metal
ions in the solution. On the other hand, the adsorption's
bond sites may not be activated with an alkaline pH. There
is the possibility of the complexation and precipitation of
the metals in the solution, with less contact between the
adsorbent and the adsorbed and, consequently, a low
adsorption (Sari et al. 2007; Demirbas 2008). The co-re-
lationship between results in the determination of pH$_{PCZ}$
and pH tests revealed 5.5 as the best rate for the adsorption
process.

Results on the influence of mass quantity of biosorbents
(Fig. 4) show that a high Cd^{2+} removal rate occurs as from
0.2 g, and remains relatively stable up to 1.2 g. Since this
experimental stage was performed at a low Cd^{2+} concen-
tration in the solution (10 mg L^{-1}), the best mass quantity
was 0.4 g, which warranted an effective removal of the
metal in the subsequent stages. Since studies on the
biosorbent mass were performed in 50 mL solutions, the

Fig. 2 SEM-produced images
of biosorbents jatropha bark
(a.1 = 1200× and
a.2 = 2400×), endosperm
(b.1 = 1200× and
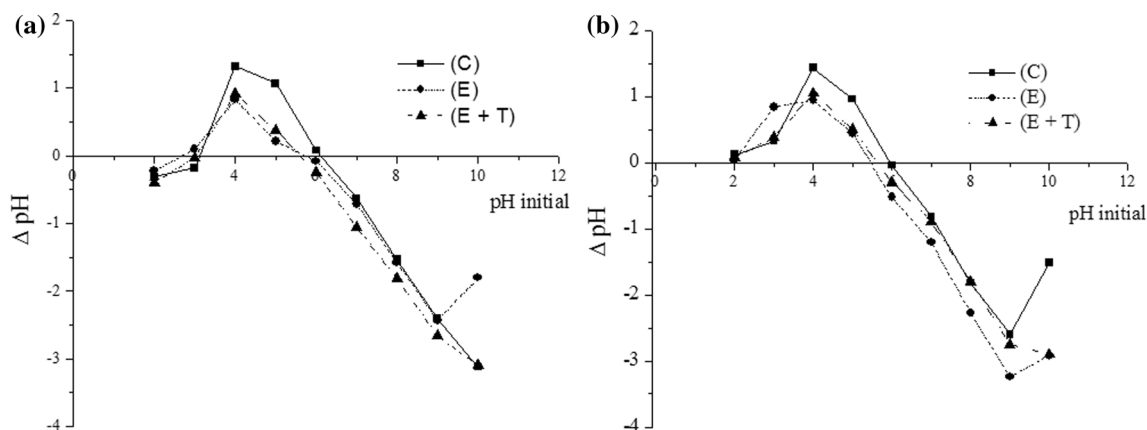b.2 = 2400×), and
endosperm + peel
(c.1 = 1200× and
c.2 = 2400×)
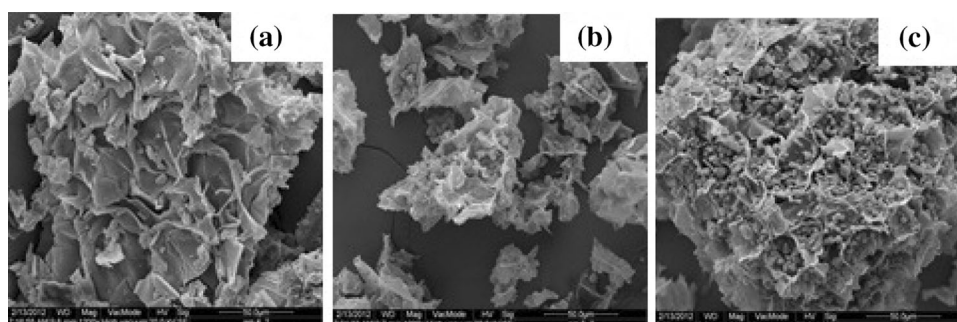
Fig. 3 Point of zero charge (pH_{PCZ}) in KCl 0.05 mol L^{-1} (**a**) and 0.5 mol L^{-1} (**b**) of the biosorbents jatropha bark (C), endosperm (E), and endosperm + peel (E + T)

Table 1 Initial concentrations of metals in the three biosorbents under the analysis

Biosorbent	K g kg^{-1}	Ca	Mg	Cu mg kg^{-1}	Fe	Mn	Zn	Cd	Pb	Cr
C	36.10	12.75	5.93	6.70	268.00	196.00	23.00	<0.005	<0.01	<0.01
E	25.03	13.50	8.83	37.00	107.00	54.00	95.00	<0.005	<0.01	<0.01
E + T	26.68	15.92	8.35	31.33	107.00	94.00	64.00	<0.005	<0.01	<0.01

C jatropha bark, *E* jatropha endosperm, *E + T* jatropha endosperm + peel; FAAS quantification limits: K = 0.01; Ca = 0.005; Mg = 0.005; Cu = 0.005; Fe = 0.01; Mn = 0.01; Zn = 0.005; Cd = 0.005; Pb = 0.01; and Cr = 0.01

proportion of mass per volume in L was calculated, in which 0.4 g in 50 mL corresponded to 8.0 g L^{-1}.

Since mass variation in the adsorption process modifies the surface area of the adsorbent material and the number of active sites available for adsorption (Ofomaja 2010; Vaghetti et al. 2008) increase in mass causes an increase in these two characteristics. However, when a very high mass quantity is employed, a decrease in adsorbate removal may occur, since there is a reduction of the total surface area of the biosorbent due to the formation of aggregates and the occurrence of empty active sites within the aggregates caused by their reduced of contact with the metal ions in the solution (Montanher et al. 2005; Ho and Ofomaja 2006; Kumar and Porkodi 2007).

Average Cd^{2+} removal rates by biosorbents under the analysis were, respectively, 86, 74, and 82 % for the jatropha bark (C), endosperm (E), and endosperm + peel (E + T).

Study on the effect of contact time between adsorbent and adsorbate and adsorption kinetics

An analysis of contact time between adsorbent and adsorbed explains the minimum period required for equilibrium within the adsorption system. The current assay shows that the results for this factor (Fig. 5) demonstrate that after a

60-min contact, the system commences a dynamic equilibrium, with no great variation in the absorbed quantity (Q_{eq}) after this interval. The best contact time between biosorbents and Cd^{2+} solution is 60 min. The above corroborates results by Garg et al. (2008) when they studied Cd^{2+} adsorption in jatropha cake.

The required 60 min to obtain maximum Cd^2+ removal may be a short time. Longer contact periods are usually needed for high removal rates which may reach 180 min (Guo et al. 2008; Argun and Dursun 2008; Witek-Krowiak et al. 2011; Coelho et al. 2014; Meneghel et al. 2013a; Rubio et al. 2013a). It should be underscored that a quick and effective removal of solution contaminants is highly important and desirable for biosorbents. In fact, it is an asset for their viability and potential in de-contamination processes in batch or continuous flow systems.

Studies on contact time between adsorbent and adsorbed clarify the mechanisms that control the adsorption process and determined by the adsorption kinetics. A study on the adsorption kinetics by well-known and well-established models, namely, the pseudo-first, pseudo-second, Elovich, and intraparticle models. Figure 6 and Tables 2 and 3 show the application results of the models.

Studies on the diffusion models deal with the rate of the coefficient of determination (R^2) for the acceptance or rejection of the model, or rather, the closer the model is to 1.00, the better the model adjusts itself. In the case of the
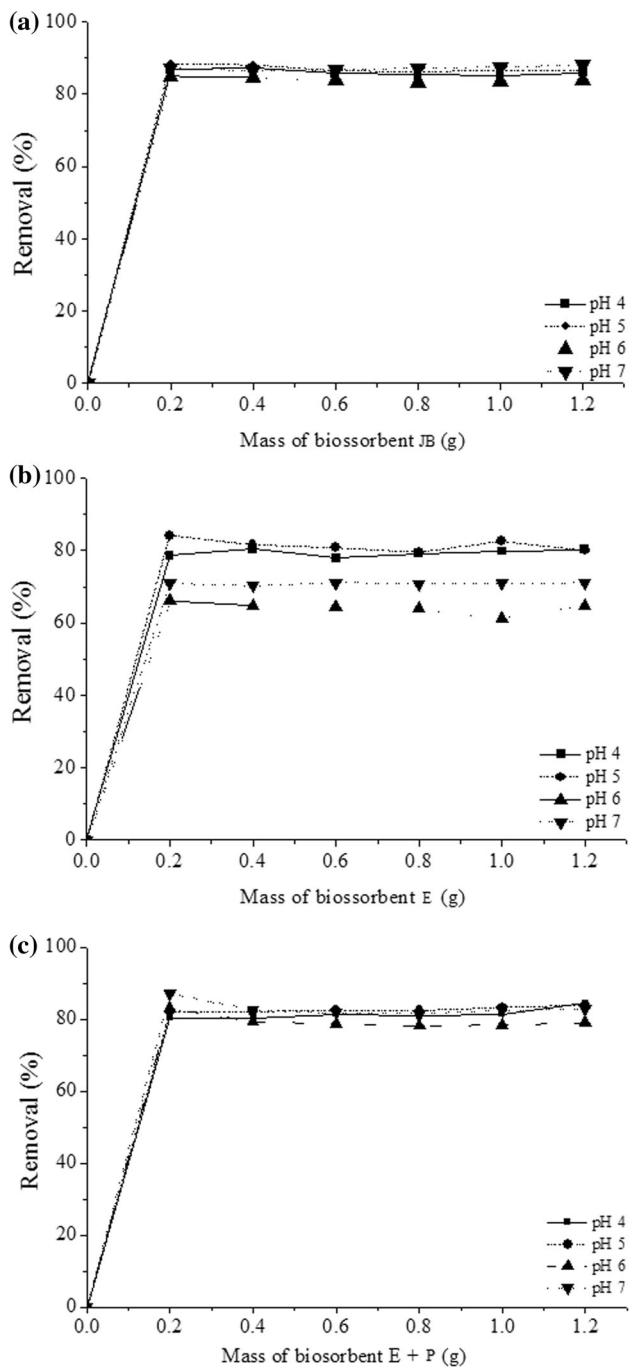
Fig. 5 Adsorbed quantity of Cd^{2+} according to different contact times for the biosorbents jatropha bark (C), endosperm (E), and endosperm + peel (E + T) (t 5–180 min, C_0 10 mg L^{-1}, m 8 g L^{-1}, pH 5.5, 200 rpm, and 25 °C)

When the parameters given by the kinetic model of the pseudo-first order (Table 2) are evaluated, it may be seen that the model does not adjust itself adequately for the three biosorbents (R^2 rates are low and calculated Q_{eq} rates were not close to those of the experimental Q_{eq} rates). Consequently, there is no predominance of physiosorption in the adsorption process, since the pseudo-first-order model indicates this kind of adsorption.

According to Farooq et al. (2011), the pseudo-first-order model does not usually provide adjustment for most biosorption systems. The above has been reported in other research works that evaluated Cd^{2+} removal capacity from water solutions by biosorbents (Coelho et al. 2014; Meneghel et al. 2013a; Rubio et al. 2013a).

The pseudo-second-order model had the best adjustment among the kinetic models for the three biosorbents. In fact, all R^2 rates were excellent (1.000 for C and E and 0.999 for E + T), whereas the rates of calculated Q_{eq} (1.033 mg g^{-1} for C, 1.106 mg g^{-1} for E, and 0.965 mg g^{-1} for E + T) were close to those by the experimental Q_{eq} rates (0.998 mg g^{-1} for C, 1.074 mg g^{-1} for E, and 0.927 mg g^{-1} for E + T) (Table 2). The adsorption process among Cd^{2+} ions and the actives sites of the three biosorbents occurred by chemical adsorption through valence and electron sharing (Oliveira et al. 2008; Feng et al. 2011; Ho and Mckay 1999).

Since R^2 results for the Elovich model (Table 2) were very low, the kinetic model proved to be non-adjustable and, consequently, could not be used for adsorption kinetics. As a rule, the Elovich kinetic model had better adjustments in systems that involve the chemosorption of gases in solid surfaces without the products' desorption (Tseng et al. 2003). However, several researchers are employing the model to explain the adsorption process of metal species in biosorbents, since their parameters

Fig. 4 Effect of mass of the jatropha bark (a), endosperm (b), and endosperm + peel (C) in the removal of Cd^{2+} from solutions with different pH rates (C_0 10 mg L^{-1}, t 90 min, 200 rpm, and 25 °C)

pseudo-first- and pseudo-second-order models, Q_{eq} rates obtained by the models should be compared with the experimental Q_{eq} rates and the average of Q_{eq} rates in the contact time test (Febrianto et al. 2009). The experimental Q_{eq} rates for biosorbents bark (C), endosperm (E), and endosperm + peel (E + T) of the jatropha were, respectively, 0.998, 1.074, and 0.927 mg g^{-1} (Table 2).
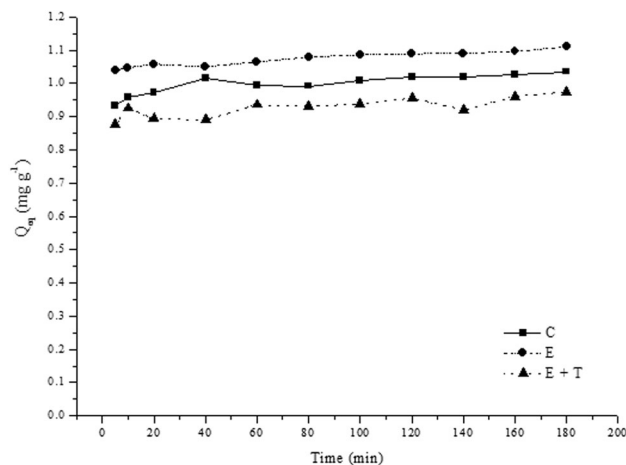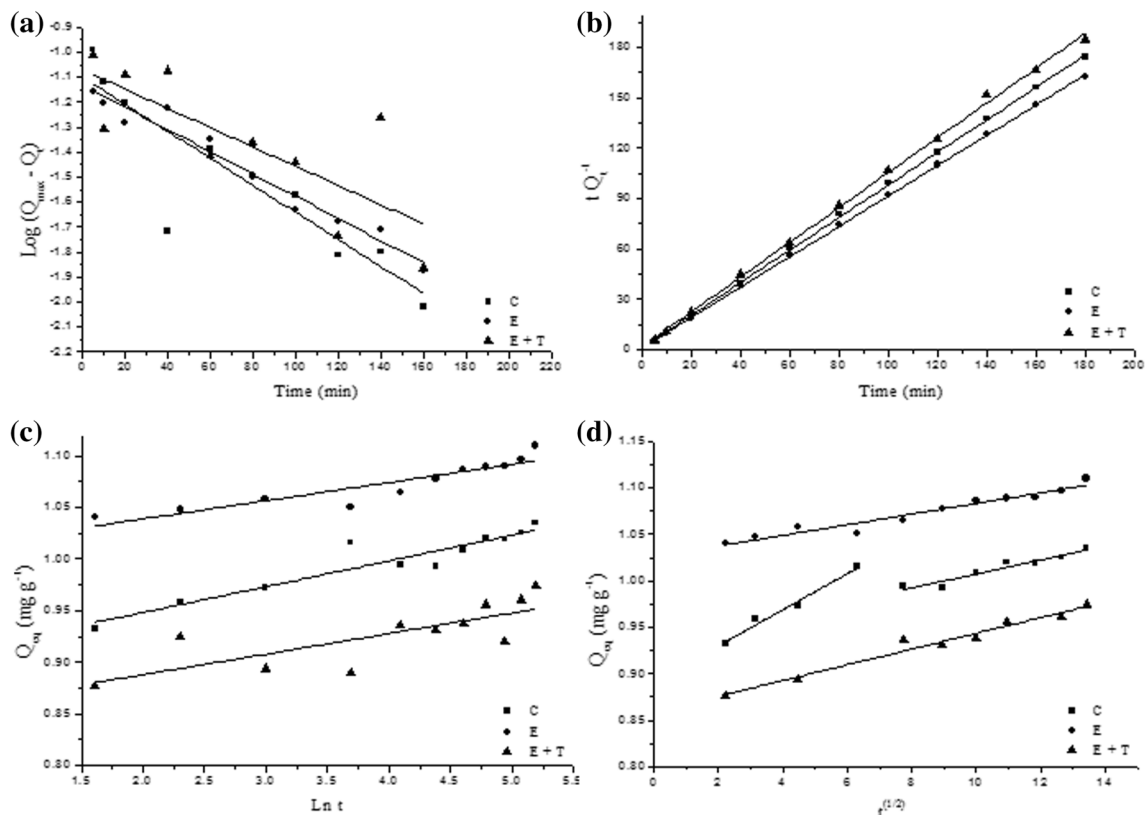
Fig. 6 Linearization of Cd^{2+} adsorption kinetics by the biosorbents jatropha bark (C), endosperm (E), and endosperm + peel (E + T) for the pseudo-first-order (**a**), pseudo-second-order (**b**), Elovich (C), and intraparticle diffusion (**d**) models (t 5–180 min, C_0 10 mg L^{-1}, m 8 g L^{-1}, pH 5.5, 200 rpm, and 25 °C)

(A and B) may be used to interpret and understand the initial rate of the adsorption process and the sites involved in the adsorption process (Hossain et al. 2012).

Intraparticle diffusion is another model for the explication of adsorption kinetics. It is largely applied for adsorbents with porous morphology and large specific surface. The evaluation of the model employs R^2 rates and C_i rate which shows whether the straight line generated by the application of the model passes or not on the origin of axes of Q_{eq} vs $t^{1/2}$. In this case, the straight line passes on the origin axes when C_i rate is equal to zero. The above shows that the intraparticle diffusion is the bordering stage of the adsorption process (Rocha 2012).

Results from the application of the intraparticle diffusion model (Table 3) show that linearization for biosorbent C provided two straight lines, with relatively satisfactory R^2 rates, whereas a single straight line was generated for biosorbents E and E + T. Since the three materials had C_i rates different from zero, intraparticle diffusion is not the limiting stage of the adsorption process, which may be monitored by diffusion and by external transport with surface adsorption (Vadivelan and Kumar 2005; Gundogdu et al. 2009). C_i rate also indicates the thickness of the limit layer of adsorption. Consequently, the higher its rate, the

greater is the amplitude of the surface diffusion in the limiting stage of the process, especially biosorbent E in this particular case (Melo 2009).

When the applicability of all the kinetic models employed in the current research is taken into account, it may be perceived that chemosorption occurs in the adsorption process between Cd^{2+} ions and the three biosorbents. An exchange of electrons effectively occurs between the adsorbent and the adsorbed in such an adsorption, with a strong bond between the two components, mainly with the occurrence of polar covalent bonds (Melo 2009). Chemical adsorption with big bond forces between the adsorbate and the active sites of the adsorbent is a relevant characteristic, since it is desirable that in the de-contamination of water, the contaminants are strongly adhered to the adsorbent and do not return easily to the solution.

Effect of the initial concentration of the adsorbate in the adsorption process

Removal percentages

It should be underscored that in the evaluation of Cd^{2+} removal percentages by biosorbents (Table 4), the highest removal

Table 2 Kinetic parameters for the pseudo-first-order, pseudo-second-order, and Elovich models in the study of Cd^{2+} adsorption by the biosorbents jatropha bark (C), endosperm (E), and endosperm + peel (E + T)

Kinetic models	Biosorbent		
	C	E	E + T
Pseudo-first order			
K_1 (min^{-1})	−0.012	−0.010	−0.009
Q_{eq} (cal.) (mg g^{-1})	0.079	0.073	0.084
R^2	0.757	0.958	0.546
Q_{eq} (exp.) (mg g^{-1})	0.998	1.074	0.927
Pseudo-second order			
K_2 (g mg^{-1} min^{-1})	0.674	0.657	0.554
Q_{eq} (cal.) (mg g^{-1})	1.033	1.106	0.965
R^2	1.000	1.000	0.999
Q_{eq} (exp.) (mg g^{-1})	0.998	1.074	0.927
Elovich			
A (mg g^{-1} h^{-1})	0.898	1.004	0.848
B (g mg^{-1})	0.025	0.018	0.020
R^2	0.883	0.833	0.557

C jatropha bark, E jatropha endosperm, E + T jatropha endosperm + peel, K_1 constant speed of the first order, Q_{eq} quantities of adsorbed substance retained per gram of the adsorbent in equilibrium, K_2 speed constant of the second order, A constant indicating the speed of the initial chemosorption, B number of adequate sites for adsorption related to the extension of surface cover and chemosorption energy, R^2 coefficient of determination

Table 3 Kinetic parameters for the intraparticle diffusion model in the analysis of Cd^{2+} adsorption by biosorbents jatropha bark (C), endosperm (E), and endosperm + peel (E + T)

Biosorbent	Parameters	SL A	SL B
C	K_{id} (g mg^{-1} min$^{-1/2}$)	0.019	0.008
	C_i (mg g^{-1})	0.891	0.932
	R^2	0.968	0.919
E	K_{id} (g mg^{-1} min$^{-1/2}$)	0.006	–
	C_i (mg g^{-1})	1.030	–
	R^2	0.935	–
E + T	K_{id} (g mg^{-1} min$^{-1/2}$)	0.008	–
	C_i (mg g^{-1})	0.859	–
	R^2	0.965	–

C jatropha bark, E endosperm, E + T endosperm + peel, K_{id} intraparticle diffusion constant, C_i suggests thickness of the limit layer effect, R^2 coefficient of determination

rates of the metal by the three biosorbents were obtained within the concentration interval between 60 and 100 mg L^{-1}. Among the three biosorbent materials, the jatropha endosperm (E) had the lowest removal rates, with approximately 70 % of Cd^{2+} in the solution at a concentration of 200 mg L^{-1}. On the other hand, bark (C) and endosperm + peel (E + T) had a removal capacity of approximately 90 % of the metal at the above-mentioned concentration.

In spite of the differences in removal percentages, the three materials had a similar behavior with an increase in Cd^{2+} concentrations, with an initial increase of removal rate and later a decrease of the parameter. A decrease in the

removal of adsorbates due to an increase of the initial concentration is due to a greater occupation of the adsorption sites in the adsorbent material. The competition for these active sites may even increase, followed by a decrease in the adsorption efficiency (Puranik and Paknikar 1999; Singha and Das 2011). An increase in the concentration of the adsorbate does not provide a higher removal rate due to the saturation of active sites and a greater competition for the sites. There is consequently a lower removal rate when compared to the initial concentration.

The comparison between the removal percentages of the three biosorbents and the removal percentage of a

Table 4 Removal percentage of Cd^{2+} by biosorbents jatropha bark (C), endosperm (E), endosperm + peel (E + T), and by activated carbon (AC)

Adsorbent	C_0 (mg L^{-1})									
	5	20	40	60	80	100	120	140	160	200
C	85.86	91.75	92.14	93.63	94.22	93.48	92.58	90.54	88.81	89.51
E	66.44	75.76	86.81	89.85	91.61	90.07	85.94	82.63	78.08	70.17
E + T	74.28	88.87	93.41	94.88	94.64	94.18	94.37	94.08	91.52	89.97
AC	96.91	98.67	98.71	98.69	98.15	97.85	97.01	95.05	91.95	84.35

C jatropha bark, E endosperm, E + T endosperm + peel, AC activated carbon, C_0 initial concentration

commercial adsorbent (activated coal) shows that the latter has a Cd^{2+} removal capacity which is higher than adsorbents, especially with regard to endosperm + peel (E + T), as from 160 mg L^{-1}, higher than activated coal. Removal efficiency of metallic contaminants in liquid solutions by activated coal is very well known, since it is actually a high capacity adsorbent. Comparison with this material is relevant to show the efficiency of the biosorbents under the analysis. Or rather, the biosorbents analyzed are capable of removing Cd^{2+} from water solutions.

It should be underscored that biosorbent materials from jatropha biomass did not undergo any modification or chemical activation, whereas activated carbon was obtained by these processes which is the main cause for its high cost (Girods et al. 2009). The use of waste materials with a good removal capacity of contaminants without modification or activation is highly desirable, since there is a decrease in the main impairments of the process, or rather, effluent treatment costs or contaminated resources.

Results as removal percentages of the metal Cd^{2+} from contaminated solutions were employed to obtain the amount of metal in the solutions after the adsorption process. Rates were then compared with those listed by Brazilian law resolution of CONAMA n. 357/2005 and n. 430/2011 and Ordinance n. 2914/2011 of the Ministry of Health (Brasil 2005, 2011a, b), respectively, 0.01, 0.20, and 0.005 mg L^{-1} of Cd^{2+}. The lowest Cd^{2+} concentrations in the solutions after the adsorption process with regard to bark, endosperm, and endosperm + peel were, respectively, 0.71, 1.68, and 1.29 L^{-1}. According to the Brazilian legislation, the solution was still contaminated. It should be emphasized that the initial concentrations of Cd^{2+} were high and that the contaminated solution was processed only once. Consequently, further adsorption could have decontaminated the solutions.

Adsorption isotherms

Adsorption isotherms are the relationship between the amount of adsorbed ions per adsorbent mass and the concentration of the solution in dynamic equilibrium (Witek-

Krowiak et al. 2011). The coefficients obtained in linearization are highly relevant for the interpretation of data derived from the adsorption process.

The three biosorbents under the analysis and activated carbon provided the isotherms of group L of Langmuir (Fig. 7), with the curve turned downwards due to a decrease in the availability of active sites when the adsorbate concentration increased (Witek-Krowiak et al. 2011). The above isotherm also provided maximum adsorption capacity by mathematical models, such as that by Langmuir (Montanher et al. 2005).

Isotherms obtained in the experiments with increases in the initial Cd^{2+} concentrations were linearized by the Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) mathematical models to determine the adsorption capacity of the biosorbents and the main parameters that involve the adsorption process (Fig. 8). With regard to linearization, the applicability of the mathematical model is evaluated by the rate of the coefficient of determination (R^2). Consequently, linearization results (Table 5) show that Langmuir's model had the best adjustment in the case of the three biosorbents and suggested that Cd^{2+} adsorption by these materials occurred predominantly in monolayers (Montanher et al. 2005). On the other hand, activated coal had the highest R^2 rate by Freundlich's adjustment model (0.991). However, Langmuir's model also provided a satisfactory R^2 rate (0.984).

When Q_m rates, or rather, the highest adsorption capacity by Langmuir's model, are evaluated, the biosorbents from the jatropha bark (C) and endosperm + peel (E + T) showed higher rates than those by activated carbon (C = 29.665, E + T = 34.674, and AC = 22.692 mg g^{-1}). Contrastingly, jatropha endosperm (E) had the lowest adsorption capacity when compared to the three materials (E = 19.562 mg g^{-1}), albeit very close to activated carbon. Results also showed that the adsorbent materials under the analysis had a high potential for Cd^{2+} adsorption. Since adsorption process conditions were optimized to evaluate the biosorbents, activated carbon could have a higher maximum adsorption under different conditions.

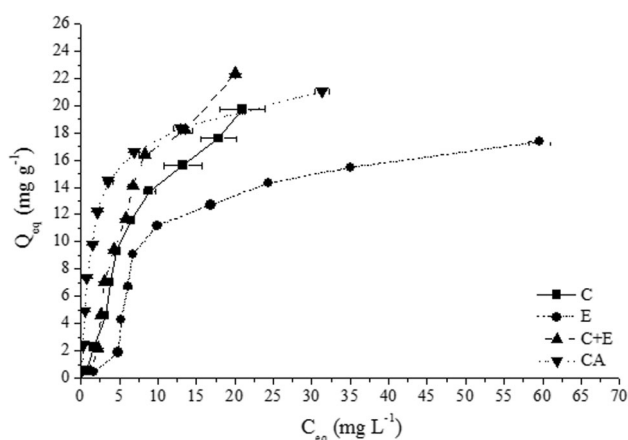Rates for Langmuir's parameter R_L for the three biosorbents and activated carbon showed that the

Fig. 7 Isotherms of Cd^{2+} adsorption by biosorbents jatropha bark (C), endosperm (E), and endosperm + peel (E + T) and by activated coal (AC) (C_0 5–200 mg L^{-1}, m 8 g L^{-1}, t 60 min, pH 5.5, 200 rpm, and 25 °C)

adsorption process was positive, since they lay between intervals 0 and 1 (Lin and Juang 2002).

Although Freundlich model's R^2 rates are lower than those by Langmuir's model, they are relatively close to 1.0, which show that the adsorption process may occur in multilayers. Consequently, the biosorbents evaluated the present adsorption in mono- and in multilayers, with more than one adsorption site type interacting with the adsorbate (Montanher et al. 2005; Gonçalves et al. 2012).

When Freundlich's parameter n (reactivity of the adsorbent's active sites) are higher than 1, highly energetic sites exist in the material and they are the first to be occupied by the metals (Sodré et al. 2001). All three biosorbents' n rates are lower than 1, or rather, highly energetic sites are not extant. The above corroborates the best adjustment of Langmuir's model which shows the existence of equal energy active sites in all the material.

In the case of Dubinin–Radushkevich's (D–R) mathematic model, R^2 rates may be taken as satisfactory and permit the use of the parameters associated with the model

to explain the Cd^{2+} adsorption process by the three biosorbents and by activated coal.

Sorption average energy of (E), free energy involved in the transference of 1 mol of the solute of the solution for the adsorbent surface, defines whether adsorption is physical or chemical (Wan Ngah and Hanafiah 2008). In fact, E rates between 1.0 and 8.0 kJ mol^{-1} indicate a physical adsorption, whereas rates higher than 8.0 kJ mol^{-1} indicate a chemical adsorption process (Romero-González 2005; Fávere et al. 2010). Consequently, biosorbents from jatropha endosperm (E) and from endosperm + peel (E + T) and activated coal have E rates higher than 8.0 kJ mol^{-1}, and thus the predominance of chemical adsorption in the adsorption process. Once more the above corroborates the best adjustment of Langmuir's model, since chemical adsorption occurs in monolayers (Montanher et al. 2005). Since E rate equivalent to 7.603 kJ mol^{-1} was obtained for the jatropha bark (C), physical adsorption was predominant. However, it should be underscored that the rate was close to 8.0 kJ mol^{-1} and that the D–R model had the lowest R^2 rate for the biosorbent. Consequently, there is no absolute certainty that the Cd^{2+} adsorption process in jatropha active was a physical adsorption.

When maximum adsorption capacity (Langmuir's Q_m) of the biosorbents under the analysis is compared with other biosorbents (Table 6), the materials of the current assay had the best adsorption capacities, and only lower than jatropha cake analyzed by Garg et al. (2008). In fact, they prove to be excellent materials for the removal of Cd^{2+} in solutions.

Characterization of adsorbent's functional groups after the adsorption process

So that the functional groups in the structure of the biosorbents after the Cd^{2+} adsorption process could be characterized, their determination was performed by IR spectrometry. Spectra (Fig. 8) showed that functional
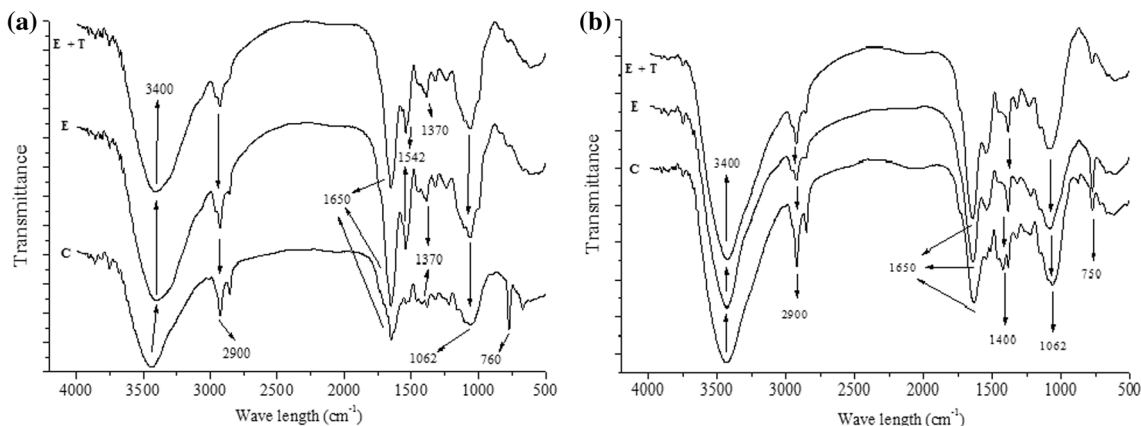

Fig. 8 IR spectra of the biosorbents jatropha bark (C), endosperm (E), endosperm + peel (E + T) before (**a**) and after Cd^{2+} adsorption process

Table 5 Parameters obtained from the linearization of isotherms by Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) mathematical models for the Cd^{2+} adsorption process for biosorbents

Model	Parameter	Adsorbent			
		C	E	E + T	CA
Langmuir	Q_m	29.665	19.562	34.674	22.693
	K_L	0.013	0.022	0.009	0.005
	R_L	0.281	0.186	0.346	0.506
	R^2	0.972	0.998	0.980	0.984
Freundlich	K_f	1.220	3.480	1.676	4.400
	n	0.218	0.214	0.362	3.331
	R^2	0.948	0.966	0.933	0.991
D–R	Q_d	0.104×10^{-1}	0.004×10^{-1}	0.022×10^{-1}	0.004×10^{-1}
	E	7.603	13.269	9.676	16.807
	R^2	0.944	0.977	0.947	0.979

C jatropha bark, E endosperm, $E + T$ endosperm + peel, AC activated coal, Q_m maximum adsorption capacity (mg g^{-1}), K_L or b constant related to interaction adsorbent/adsorbed forces (L mg^{-1}), R_L Langmuir's constant, R^2 coefficient of determination, K_f related with adsorption capacity (L mg^{-1}), n related to the heterogeneity of the solid, Q_d maximum adsorption capacity (mol g^{-1}), E average sorption energy (kJ mol^{-1})

Table 6 Comparative study of maximum capacities of Cd^{2+} adsorption by biosorbents

Biosorbent	Q_m (mg g^{-1})	References
Jatropha bark	29.665	Current assay
Jatropha endosperm	19.562	Current assay
Jatropha endosperma + peel	34.674	Current assay
Pinus bark	6.301	Strey et al. (2013)
M. oleifera	7.864	Meneghel et al. (2013a)
C. abyssinica	19.342	Rubio et al. (2013a)
Jatropha cake	86.960	Garg et al. (2008)

Table 7 Average percentages of Cd^{2+} adsorption and desorption for biosorbents jatropha bark (C), endosperm (E), endosperm + peel (E + T), and for activated coal (AC)

Adsorbent	Adsorption (%)	Desorption (%)
C	91.25	59.96
E	81.74	89.31
E + T	91.02	85.79
CA	95.74	71.01

C jatropha bark, E jatropha endosperm, $E + T$ jatropha endosperm + peel, CA activated carbon

groups in the characterization of non-saturated biosorbents with Cd^{2+} were not modified. Or rather, the biosorbents kept their former characteristics, with the participation of the functional groups mentioned in "Characterization of biosorbents" in the Cd^{2+} adsorption process.

Desorption

The evaluation of desorption of the contaminating material removed by the adsorbent is a relevant characteristic to evaluate the adsorbent's renewal capacity for use in sorption/desorption cycles. A good desorption is desirable for the adsorbent due to a better use of the material and low costs in large-scale remediation processes.

Results of Cd^{2+} desorption of the biosorbents and activated coal (Table 7) revealed that the biosorbents from jatropha endosperm (E) and endosperm + peel (E + T) had low desorption rates (E = 89.31 and E + T = 85.79 %), whereas the jatropha bark (C) had the lowest desorption percentage (59.96 %). Activated coal had a desorption rate of 71.01 %. The above rates register that

biosorbent materials have a good desorption rate that provides their recuperation in sorption/desorption systems and Cd^{2+} recuperation after the adsorption process.

Thermodynamics of adsorption

The study on temperature effect in adsorption is an important stage. Temperature changes the adsorption process and acts on its spontaneity and on the forces that interact in the adsorption of the solute in the adsorbent's active sites. The thermodynamics of the adsorption process was performed to evaluate the temperature's influence.

The current assay shows the results of the adsorption process's thermodynamics between the biosorbents and Cd^{2+} ions in the solution (Table 8). Q_{eq} rates (quantity of Cd^{2+} adsorbed by biosorbent mass) increase proportionally to any rise in the temperature of the solution and show that temperature interferes on the biosorption process.

As a rule, a specific literature reports that a temperature increase causes a decrease in adsorption within liquid/solid systems, since higher temperature rates increase solubility

Table 8 Thermodynamic parameters of Cd^{2+} adsorption by the biosorbents jatropha bark, endosperm, and endosperm + peel

Biosorbent	Temp. (°C)	Thermodynamic parameters				
		Q_{eq}	ΔG	ΔH	ΔS	R^2
C	15	5.532	−11.962	−5.870	21.154	0.961
	30	5.617	−			
	45	5.711	−			
	60	5.671	−			
E	15	4.071	−6.828	−5.144	5.845	0.999
	30	4.184	−6.915			
	45	4.340	−7.003			
	60	4.452	−7.091			
E + T	15	5.589	−	−12.008	42.486	0.998
	30	5.702	−			
	45	5.752	−			
	60	5.892	−			

C jatropha bark, *E* endosperm, *E + T* endosperm + peel, Q_{eq} adsorbed quantity of metal ion per adsorbent unit (mg g^{-1}), ΔG variation of Gibbs's free energy (kJ mol^{-1}), ΔH variation of enthalpy (kJ mol^{-1}), ΔS variation of entropy (J mol^{-1})

and consequently a decrease in chemical potential, with less adsorption (Khattri and Singh 2000). Nevertheless, several assays on the use of biosorbents in metal removal demonstrate that temperature rise may cause a desorption increase (Coelho et al. 2014; Meneghel et al. 2013a, b; Rubio et al. 2013b, c).

Negative enthalpy results (ΔH) from the three biosorbents suggest that the adsorption process is exothermal, or rather, the same occurs with energy release (Wan Ngah and Fatinathan 2010).

Other relevant thermodynamic parameter is the variation of Gibbs's free energy (ΔG) which is the main criterion to indicate the spontaneity of a system with constant conditions of temperature and pressure (Crini and Badot 2008). Negative ΔG rates indicate the spontaneous type of the reaction (Wan Ngah and Hanafiah 2008), or rather, the more negative is the ΔG rate, the more energetically favorable is the adsorption process (Debrassi et al. 2011). ΔG results by the three biosorbents were negative at all temperatures, with more negative rates as temperature increased. Biosorbent obtained from jatropha endosperm + peel (E + T) had the most negative results, followed by biosorbent C, which, in its turn, had more negative results than C. Results showed that temperature increase caused an increase in the quantity of adsorbed Cd^{2+} due to a rise in the spontaneity of the adsorption process (Farooq et al. 2011).

Since entropy (ΔS) rates for the three biosorbents were positive, disorder, and the randomness of the solid/solution interface increased during the adsorption process and thus a higher adsorption capacity (Wan Ngah and Fatinathan 2010).

Adsorbents after the adsorption process

One of the main aspects involved in the evaluation of the viability and efficiency of a biosorbent is the possibility of recovering adsorbent material and the metal adsorbed, especially when the metal has high commercial value. The two main strategies for the recovery of the adsorbent and the adsorbate in contaminant removal systems are the regeneration process of the adsorbent (desorption) and incineration which is feasible when the materials employed in the adsorption process are highly available and low cost (Park et al. 2010).

Desorption results in the current assay revealed that biosorbents obtained from jatropha biomass might undergo the regeneration process for further uses which was a desirable characteristic in the current case. Furthermore, according to Coelho et al. (2014), agro-industrial materials may be used in the composition of cement material due to great amounts of silica in materials of organic origin.

Conclusion

Studies on factors that interfere in the adsorption process between biosorbents and Cd^{2+} ions showed that the best conditions comprise solution's pH at 5.5, 8.0 g L^{-1} of biosorbent in the solution, and contact time 60 min.

According to adsorption kinetics results, the three biosorbents adsorbed Cd^{2+} ions by chemosorption, at the best adjustment of the pseudo-second-order model.

Langmuir's mathematical model was the best that adjusted itself in the study on isotherms with regard to the

three biosorbents and thus the predominance of chemosorption by monolayers. Maximum adsorption capacities by Langmuir's model were 29.665, 19.562, 34.674, and 22,693 mg g^{-1}, respectively, for jatropha bark (C), endosperm (E), endosperm + peel (E + T), and activated carbon (CA).

The three biosorbents provided a desorption rate that makes recuperation possible after the adsorption process, and thus, the use in sorption/desorption flows.

Thermodynamic results showed that the Cd^{2+} adsorption process by biosorbents is an exothermal process with an increase in the system's disorder due to adsorption.

Based on results provided by the current assay, the three biosorbents obtained from the jatropha biomass may remove Cd^{2+} from water solutions and may be used as an alternative to usually employed adsorbents in remediation systems of water resources contaminated by the metal.

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