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Herbert Nacke, Affonso Celso Gonçalves Jr., Marcelo Angelo Campagnolo, Gustavo Ferreira Coelho*, Daniel Schwantes, Marcelo Gonçalves dos Santos, Dionir Luiz Briesch Jr., Juliano Zimmermann

Adsorption of Cu (II) and Zn (II) from Water by *Jatropha curcas* L. as Biosorbent

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Abstract: The objective of this work was to evaluate the removal of Cu^{2+} and Zn^{2+} in water by means of the adsorption process using three biosorbents derived from jatropha biomass (bark, endosperm and endosperm + seed coat). The experiments were performed in batch and evaluated the effect of solution pH, adsorbent mass, contact time, different initial concentrations of the metals Cu^{2+} and Zn^{2+}, and the temperature of the solution during the adsorptive process. By kinetics, the adsorption isotherms and thermodynamics the mechanisms that control the adsorptive process were evaluated. The optimal conditions for the realization of the adsorptive process for both metals were: solution pH of 5.0 and 8 g L^{-1} of adsorbent mass per volume of solution, with a contact time between adsorbent and adsorbate of 60 min. According to the Langmuir model, the maximum adsorption capacities for the bark, endosperm and endosperm + seed coat of Jatropha were, respectively, for Cu^{2+} 11.541, 20.475 and 22.910 mg g^{-1}, and for Zn^{2+} 14.852; 15.888 and 14.674 mg g^{-1}, with the predominance of chemisorption in monolayer. The three biosorbents derived from the biomass of Jatropha have potential for the remediation of water contaminated with Cu^{2+} and Zn^{2+}.

Keywords: Agroindustrial residues, natural adsorbents, remediation of water resources, copper, zinc.

1 Introduction

Heavy metals are chemical species which may cause severe damage to the planet´s entire ecosystem. Since they are not biodegradable, they accumulate during the years within the environment and in living beings [1]. The contamination of water resources by heavy metals is highly relevant due to the fact that they dissolve within this matrix and immediately become available to the living beings in the ecosystem. The intake of contaminated water by humans and animals affects the entire food chain [2]. Further, since drinkable water is becoming scarcer, concern on the contamination of water resources with heavy metals is a highly serious affair.

Although copper (Cu) and zinc (Zn) are classified as heavy metals and are toxic in large quantities, in lower amounts they are essential micronutrients for living beings. The elements are widely used in human activities. Mining, metal casting, high tech industries, agriculture and cattle-raising are the main sources of contamination by Cu [3]. In the case of Zn, the main activities that produce contaminated residues are steel work, mining, petrochemical industries, agriculture and cattle-raising [4,5].

In Brazil there are several reports of contamination of water and soil by Cu and Zn. Gonçalves Jr., et al., [5] studied the contamination of Brazilian soils by fertilizers, and found very high levels of toxic metals and micronutrients, above what was reported by the manufacturer. Mineral exploitation, in the State of Amapá, has impacted the soil and water of this region with high levels of heavy metals, among Cu and Zn [6]. Pompêo et al., [7] reported high

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***Corresponding author: Gustavo Ferreira Coelho:** University Center Dynamic of Cataracts, Educacional College of Medianeira, Paraná, Brasil, Rua Rio Branco, 1820, Zip code: 85884-000, E-mail: gf_coelho@yahoo.com.br

Herbert Nacke: University Center Dynamic of Cataracts, Foz do Iguaçu, Paraná, Brasil, Rua Castelo Branco, 349, Zip code: 85852-010

Affonso Celso Gonçalves Jr.,: 2State University of West Paraná, Center for Agricultural Sciences, Marechal Cândido Rondon, Paraná, Brazil. Rua Pernambuco, 1777, CEP 85960-000

Marcelo Angelo Campagnolo, Marcelo Gonçalves dos Santos, Dionir Luiz Briesch Jr., Juliano Zimmermann: State University of West Paraná, Center for Agricultural Sciences, Marechal Cândido Rondon, Paraná, Brazil. Rua Pernambuco, 1777, CEP 85960-000

Daniel Schwantes: Pontifical Catholic University of Paraná, Environmental Enginerring, Polytechnic School – Toledo, Brazil. União Avenue, 500, CEP: 85902-532

concentrations of Cu (1157 mg kg^{-1}) and Zn (223 mg kg^{-1}) in sediments of the Guarapiranga reservoir on the city of São Paulo. Also found high levels of heavy metals in the river Tietê, in São Paulo, mainly Zn [8]. Santos et al., [9] reported the predominance of metal such as Cu and Zn in sediments of the Lagoa Mirim, in the state of Rio Grande do Sul, bordering Brazil and Uruguay. Marengoni [10] found the bioaccumulation of heavy metals in mussel in the reservoirs of the hydroelectric plant of Itaipu State of Parana Brazil. It can be seen that contamination by Cu and Zn is a problem found in almost all regions of Brazil.

High Cu concentrations may cause epilepsy, melanoma, rheumatic arthritis, gastric ulcer, necrosis in the liver, kidney problems and loss of taste in humans [11,12]. When large amounts of Zn are taken, the element affects the respiratory, gastrointestinal and blood system causing nauseas, vomiting, diarrhea, skin rashes, anemia and sterility [13-14].

There are currently several procedures for heavy metal removal, especially adsorption, chemical and physical precipitation, ion exchange, filtrating membranes, flotation, electro-chemical treatment and coagulation-flotation [15]. However, most methods are characterized by high operational costs, low selectivity, incomplete removal of contaminants and the production of great amounts of residues with consequent technical and economical limitations mostly when the metal concentration in waste water is low (< 100 ppm) [16]. Natural adsorbents are advantageous since these materials are low-cost, highly efficient and easily applicable due to their adaption to different conditions of pH, temperature, pressure and agitation [17]. The development of alternative adsorbent materials featuring low costs, high availability, feasibility and high adsorption capacities is required [18].

The jatropha (*Jatropha curcas* L.) is a perennial species with a high production of vegetal oil for the manufacture of biodiesel worldwide [19]. The process main waste is the pie from seeds used in oil extraction, with low applicability. In fact, it is mainly employed as fertilizer or as biomass for the production of biogas, both with low commercial value [20]. According to Evangelista [21] the productivity of Jatropha can be 6000 kg ha^{-1} of seed. This makes it possible to produce more than 2000 kg ha^{-1} of oil, generating 4000 kg ha^{-1} of residue.

Since there is a need to acquire natural low-cost adsorbents and to expand the productive chain of the species with aggregated value similar to the main residue, current investigation develops and evaluates three natural adsorbents (biosorbents) from the jatropha biomass (rind, endosperm and endosperm+peel) to remove Cu^{2+} and Zn^{2+} by the adsorption process in different experimental conditions (adsorbent mass; solution´s pH; contact time; initial concentration of metals in the solutions). Kinetic and equilibrium parameters, the thermodynamics of the adsorption process and the comparison of the three biosorbents with a commercial adsorbent were determined.

2 Materials and Methods

2.1 Obtaining and preparing the adsorbent materials

Adsorbent materials (biosorbents) evaluated were produced from the biomass of the jatropha fruit from plants cultivated in the experimental farm of the Universidade Estadual do Oeste do Paraná (UNIOESTE) in Pato Bragado PR Brazil. No fertilization occurred during the whole cultivation period and the fruits were collected on the fourth year of cultivation. Jatropha fruits were collected, dried in the shade for 45 days and stored in a dry room.

The three adsorbents were produced from different types of the jatropha fruit wastes: fruit rind (adsorbent C), pie from the oil extraction from seed endosperms (adsorbent E) and the pie from the oil extraction from endosperm and seed peel (adsorbent E+T). Although the rind of the jatropha fruit is not used for the extraction and production of biodiesel, it is a waste product and the first co-product in the species’ fruit processing. The production of adsorbent E simulated the waste product in the chemical extraction of the jatropha oil (extraction by solvents), whereas adsorbent E + T is similar to the waste product produced by the mechanical extraction of seed oil (pressing) [22].

The production of adsorbents comprised the division of the fruits harvested into rind, seeds without the skin (the endosperm only) and seeds with skin and endosperm. The material was ground, sieved with 14–60 mesh granulometry, and dried in a forced air buffer at 60°C for 48 h. In the case of adsorbents E and E+T, after dehydration of prime matter, vegetal oil extraction was undertaken by Soxhlet-type system for 4 h, followed by more drying in a buffer at 80°C for 24 h for total solvent evaporation (n-hexane) used in the extraction of vegetal oil.

2.2 Characterization of the biosorbents

The functional groups of the three adsorbents, visualization of their morphology and the amount of their surface loads and of the metals in their structure were determined to characterize the adsorbents.

The biosorbents functional groups were analyzed by IR spectra with Shimadzu Infrared Spectrophotometer FTIR- 8300 Fourier Transform, at the region between 400 and 4000 cm^{-1} and resolution 4 cm^{-1}. Spectra were obtained by transmittance with potassium bromide (KBr) tablets.

Scanning electron microscopy (SEM), using microscope FEI Quanta 200 at 30 kV, visualized the adsorbents morphology. Samples were first placed on a double-side carbon adhesive band on a support and gold metallization was performed at a thickness of approximately 30 nm, by metallizer Baltec Scutter Coater SCD 050. The point of zero charge (pH_{PCZ}) with regard to pH determined the amount of surface load of the adsorbents, where the balance of the material´s surface charges is null [23].

The initial amount of metals in the biosorbent structure was undertaken by nitroperchloride digestion by determining K, Ca, Mg, Cu, Fe, Mn, Zn, Cd, Pb and Cr with flame mode atomic absorption spectrometry (FAAS).

2.3 Preparation of strengthened solutions and experimental conditions

All Cu^{2+} and Zn^{2+} solutions in current assay were prepared by the dilution of nitrate salts [$Cu(NO_3)_2 \times 3H_2O$ and $Zn(NO_3) \times 6H_2O$] from Sigma-Aldrich®, P.A. grade, purity higher than 99%, diluted in ultrapure water type I.

All adsorption experimental tests were performed in triplicate. Batch system employed 125 mL^{-1} and 50 mL-Erlenmeyer flasks for the solution. After each test, solutions were filtered with quality filter paper (Unifil) to separate the biosorbent from the liquid solution. Aliquots of the liquid solution were retrieved to determine Cu^{2+} or Zn^{2+} amounts by FAAS.

2.4 Effect of adsorbent mass and solution´s pH in the adsorption process

The effect of the adsorbent´s mass and solution´s pH on the adsorption process was undertaken with simultaneous experiments involving the two factors. Different amounts of adsorbent mass (0.2; 0.4; 0.6; 0.8; 1.0 and 1.2 g) were tested in different Cu^{2+} or Zn^{2+} solutions with pH between 4.0 and 7.0. Further, pH rates were adjusted with HCl (Vetec, 37%) or NaOH (Vetec, 99%) solutions at a concentration of 0.1 mol L^{-1}. At this stage, agitation speed (200 rpm), agitation time (1.5 h), temperature of solutions (25°C) and Cu^{2+} or Zn^{2+} concentration in the solutions (10 mg L^{-1}) were kept constant.

Removal percentages of Cu^{2+}, Zn^{2+} or solutions were calculated by Eq. 1:

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

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

2.5 Effect of contact time between adsorbent and adsorbed in adsorption kinetics

Due to results in studies on mass and pH (optimized mass 0.4 g and optimized pH 5.0), tests were undertaken to evaluate the effect of contact time between the adsorbent and the adsorbed (5, 10, 20, 40, 60, 80, 100, 120, 140 and 160 min). Speed agitation (200 rpm), temperature of solutions (25°C) and the concentration of Cu^{2+} or Zn^{2+} in the solutions (10 mg L^{-1}) were kept constant at this stage. Solutions pH was adjusted with HCl (Vetec, 37%) or NaOH (Vetec, 99%) solutions at 0.1 mol L^{-1}.

The amount adsorbed in equilibrium was calculated by Eq. 2 from the rate obtained for the concentration in equilibrium.

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

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

Foregrounded on results of contact time tests, studies on kinetic mechanism that control the adsorption process were performed with pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion models.

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

Studies on the effect of different initial concentrations of Cu^{2+} or Zn^{2+} in solutions (5, 20, 40, 60, 80, 100, 120, 140, 160 and 200 mg L^{-1}) were performed with the best mass conditions of the biosorbents (0.4 g), solution´s pH (5.0) and contact time (60 min). Agitation speed (200 rpm) and temperature of solutions (25°C) were constant during procedure. Solution´s pH was adjusted to HCl (Vetec, 37%) or NaOH (Vetec, 99%) at concentration 0.1 mol L^{-1}.

Metal removal percentages (%R) and amount adsorbed in equilibrium (Q_{eq}) were obtained respectively by Eqs. 1 and 2. The latter parameter was employed for the adsorption of isotherms which were linearized by Langmuir, Freundlich and Dubinin-Raduschkevich´s mathematical models

Experiments in current assay were undertaken to compare the removal capacity of Cu^{2+} or Zn^{2+} by the adsorbents with a commercial adsorbent. The experiments were performed in the same conditions used to obtain isotherms from the biosorbent activated coal P.A. Synth®, widely used in the removal of pollutants in water.

Adsorption metals were determined after the adsorption process for a better understanding of the structural components of the adsorbents involved in the adsorption of metals in solution. Biosorbent samples were removed after the adsorption process and IR spectrometry techniques were applied in the same conditions described in 2.2.

2.7 Desorption

Desorption capacity of the metals Cu^{2+} and Zn^{2+} from the biosorbents and from the commercial adsorbent (activated coal) was evaluated with adsorbents masses, posterior to the experiments involving the metals different initial concentrations. After filtered the solutions in equilibrium, the adsorbent masses were separated and dried in a buffer at 60°C for 24 h and placed in contact with 50 mL of HCl solution (Vetec, 37%) at 0.1 mol L^{-1}, followed by agitation of the solutions at 200 rpm at 25°C for 60 min. Desorption percentage was calculated from the concentrations of the desorbed metals of the mass of adsorbents by Eq. 3:

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

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

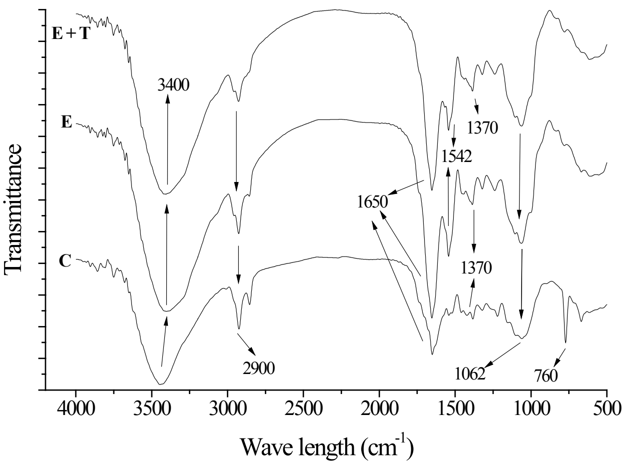

Figure 1: Infra-red spectra of biosorbents: jatropha rind (C), endosperm (E) and endosperm + peel (E+T).

3 Results and Discussion

3.1 Characterization of biosorbents

Functional groups in the three biosorbents evaluated in current assay by IR spectra demonstrate vibrations at bands 760, 1062, 1370, 1542, 1650, 2900 and 3400 cm^{-1}.

A wide and strong band in the three adsorbents within the 3400 cm^{-1} region may be attributed to vibration lengthening by the hydroxyl bonds (O-H) found in carbohydrates, fatty acids, proteins, lignin units, cellulose and absorbed water [24-28]. Vibration lengthening within the 2900 cm^{-1} region derives from C-H type-bonds which are common in alkane and aliphatic groups [29]. Bands within the 1650, 1542 and 1370 cm^{-1} regions are probably related to vibration lengthening of C-O-type bonds found in starch and carboxyl groups [27], whereas vibrations within the 1650 cm^{-1} region are linked to C=O-type bonds found in carbonyl and carboxyl groups, which partly constitute ligno-cellulose compounds [30]. Bands within 1542 and 1370 cm^{-1} regions may be related to C=C-type bonds of aromatic compounds [31]. Bands within the 1370 cm^{-1} region may be due to vibration of C-H-type bonds occurring in cellulose, hemicelluloses and lignin. Vibration lengthening may also be found in the 1062 cm^{-1} region, derived from C-O-type bonds provided by compounds such as lignin and phenols of the carboxyl groups, which are known to make available adsorption sites for metal ions [27]. The jatropha rind (C) demonstrated a vibration lengthening in the 760 cm^{-1} region and may be attributed to nitrogen (N) with bioligands [32].

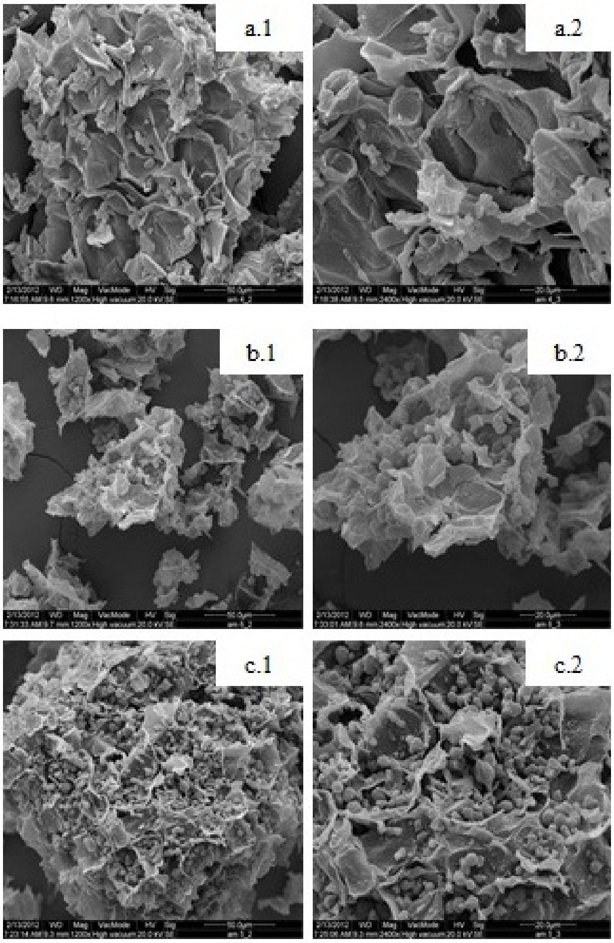

Figure 2: SEM images of biosorbents jatropha rind (a.1 = 1200x and a.2 = 2400x); endosperm (b.1 = 1200x and b.2 = 2400x); endosperm + peel (c.1 = 1200x and c.2 = 2400x).

IR spectra results of the three biosorbents evaluated in current assay show that protein, lignin, cellulose, hemicelluloses, lignocelluloses, the hydroxyl, carboxyl and carbonyl groups and phenols are the main compounds that make possible the links with metal ions in solutions [17]. Since the adsorbents are vegetal-derived, the main compounds in their structure are cellulose, hemi-cellulose and lignin. When results of current assay are compared to those by other authors, one may underscore that in their assays on jatropha biomass, Tongpoothorn et al. [30] arrived at similar results to those in current analysis on the characterization of IR functional groups.

The adsorbent´s morphological evaluation by SEM (Fig. 2) demonstrates that the three materials have a very irregular morphology and, thus, a porous surface. Materials with these characteristics generally have a high specific surface which provides them a good adsorption capacity.

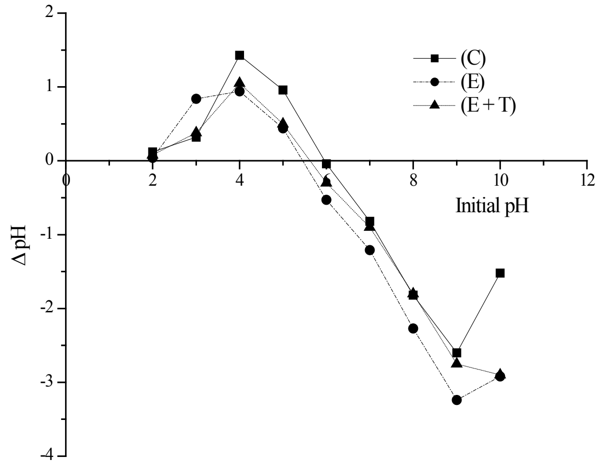

Figure 3: Point of zero charge (pH_{PCZ}) in 0.5 mol L^{-1} of biosorbents jatropha rind (C); endosperm (E); endosperm + peel (E + T).

The determination of surface loads (pH_{PCZ}) of biosorbents shows that in the two concentrations of KCl (0.05 and 0.5 mol L^{-1}), the point of zero charge lies between pH 5.0 and pH 6.0 (Fig. 3). Equilibrium between positive and negative charges is zero in the pH interval. When the solution´s pH is less than pH_{PCZ}, positive surface charges predominate on the biosorbents´ surface due to its protonation, whereas the predominant surface charges are negative in pH rates of solution higher than pH_{PCZ}, benefitting cation adsorption [23].

Table 1 shows that Cu^{2+} and Zn^{2+} are present in the structure of the three biosorbents prior to their employment. This may be due to the fact that they are micronutrients and their presence in the plants structure is normal since they are part of the organisms metabolism.

3.2 Effect of adsorbent mass and solution´s pH in the adsorption process

Results of pH influence on the adsorption process (Fig. 4) show that the removal of Cu^{2+} and Zn^{2+} by biosorbent obtained from jatropha rind (C) was only slightly affected by the solution´s pH, whereas pH variation in the case of biosorbents E and E+T provided significant differences in the removal of the two metals. In spite of such differences, the three adsorbent materials obtained the highest Cu^{2+} and Zn^{2+} removal rates when initial pH of the solution was equal to 5. When results obtained in the determination of pH_{PCZ} and pH tests are co-related, pH 5.0 was selected as the best for the adsorption process of Cu^{2+} and Zn^{2+} for the three biosorbents.

Furthermore, pH affects the adsorption process because it changes the quality of the adsorbent surface, functional

Table 1: Initial concentration of metals in the three biosorbents under analysis.

Biosorbent	K	Ca	Mg	Cu	Fe	Mn	Zn	Cd	Pb	Cr
	g kg^{-1}			mg kg^{-1}						
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 rind; E: endosperm; E + T: 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; Cr = 0.01.

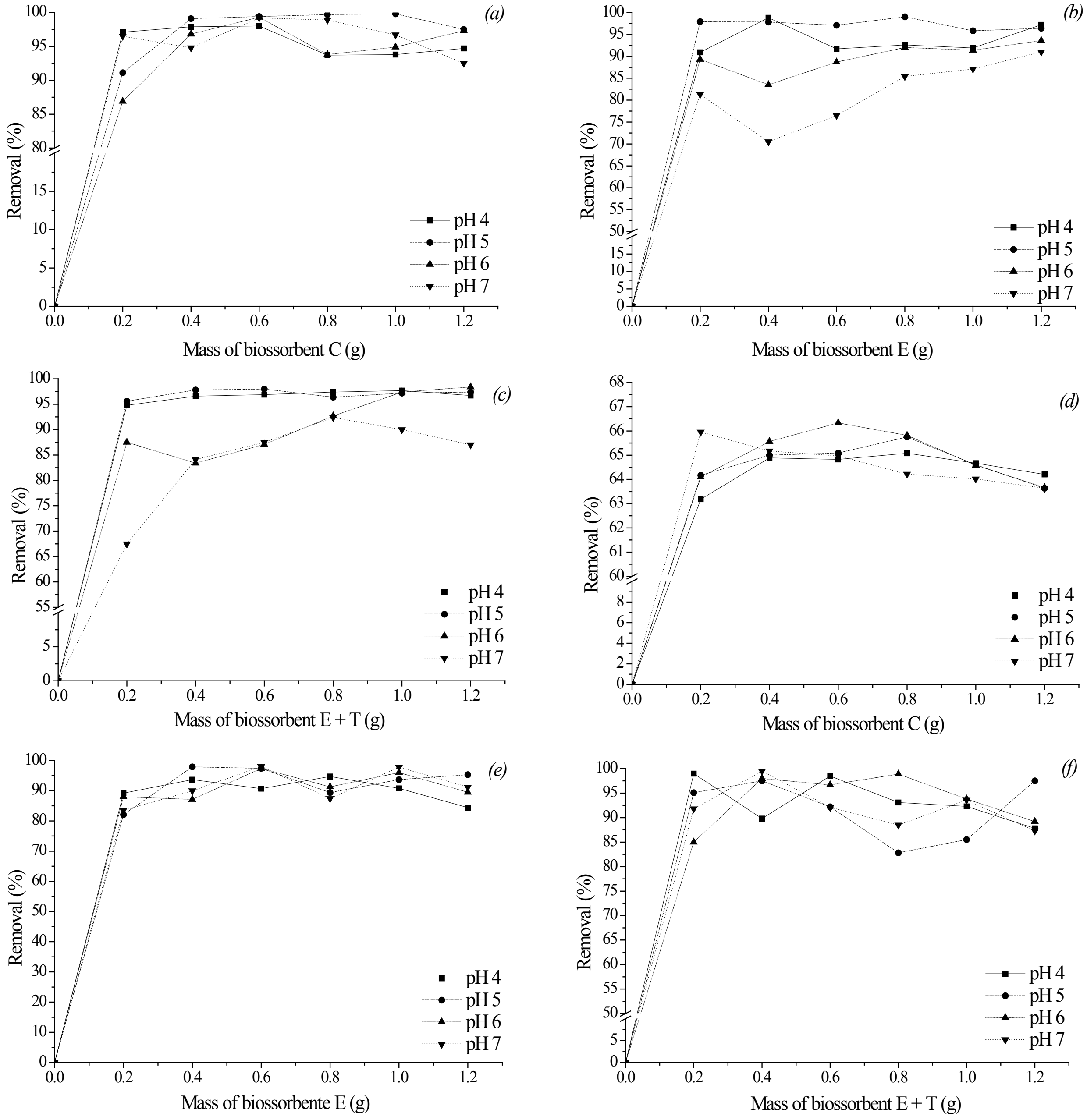

Figure 4: Effect of mass of jatropha rind (*a* for Cu^{2+} and *d* for Zn^{2+}); endosperm (*b* for Cu^{2+} and *e* for Zn^{2+}); endosperm + peel (*c* for Cu^{2+} and *f* for Zn^{2+}) in the removal of metals from solutions with different pH rates (C_0: 10 mg L^{-1}; t: 90 min; 200 rpm; 25°C).

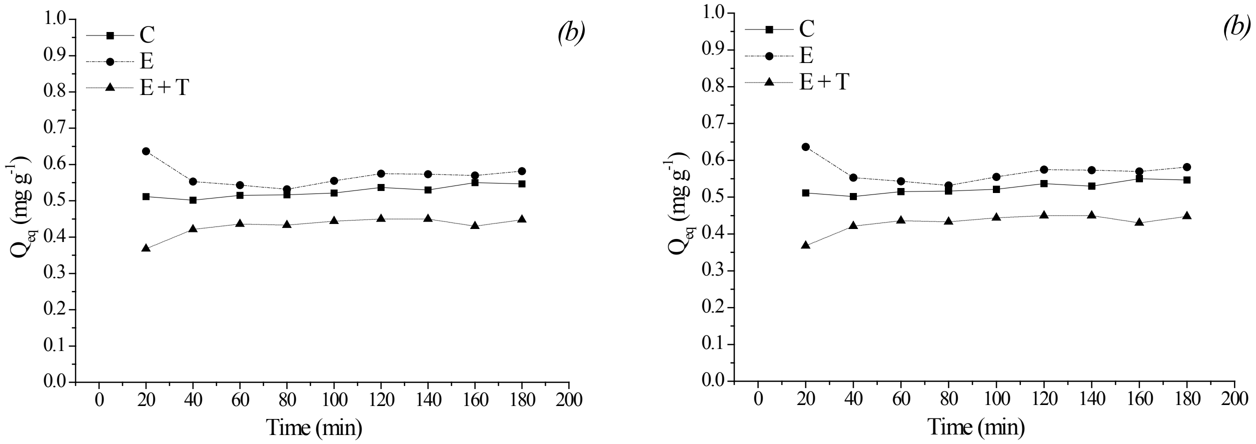

Figure 5: Adsorbed quantity of Cu^{2+} (a) and Zn^{2+} (b) due to different contact times for the biosorbents jatropha rind (C), endosperm (E) and endosperm + peel (E+T) (t: 5 at 180 min; C_0: 10 mg L^{-1}; m: 8 g L^{-1}; pH: 5,0; 200 rpm; 25°C).

groups and ion condition of the metal species [33]. As a rule, there is a strong competition by the adsorbent´s active sites in acid pH between excess H^+ ions and metal ions in the solution. On the other hand, complexation and precipitation of metals in solution occur in base pH, with low contact between adsorbent and adsorbed and the inactivation of the adsorbent´s linking sites [17].

With regard to the influence of the amount of biosorbent mass (Fig. 4), one may perceive that in the case of Cu^{2+} and Zn^{2+}, when initial pH of the solution is 5.0, a 0.4 g mass is sufficient to obtain the highest rates in metal removal. There is no adsorption increase with an increase in mass amount. Since studies on the effect of adsorbents´ mass are undertaken with 50 mL solutions, the proportion of mass per volume in L has been calculated and 0.4 g in 50 mL were found to correspond to 8.0 g L^{-1}.

The adsorbent´s mass quantity used in the adsorption process alter all the surface area of the adsorbent material and the number of available adsorption sites where a mass increase provides an increment in the two characteristics and thus a greater removal of the adsorbed [34]. However, an increase in mass quantity will increase the removal of the adsorbate in the solution up to the determined point. A decrease in the removal of the adsorbate generally occurs above this limit due to the formation of the adsorbent´s aggregates in empty active sites within these aggregates provided by their lack of contact with the metal ions in the solution [35-37].

Mean Cu^{2+} removal rates by the three biosorbents under analysis were 96, 91 and 92% for jatropha rind (C), endosperm (E) and endosperm + peel (E+T), respectively, whereas in the case of Zn^{2+} mean rates were 65, 92 and 92% for jatropha rind (C), endosperm (E) and endosperm + peel (E+T), respectively.

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

The effect of contact time between the three biosorbents and solutions contaminated by Cu^{2+} or Zn^{2+} (Fig. 5) demonstrates that equilibrium is obtained after 60 min. No relevant variations are extant in the quantity adsorbed (Q_{eq}) after this period for the two metals. In fact, 60 min were determined to be the best contact time between biosorbents and Cu^{2+} or Zn^{2+} solutions.

Best contact time between adsorbent and adsorbate, which defines the minimum period required for equilibrium within the adsorption system to obtain maximum removal of Cu^{2+} or Zn^{2+} by the biosorbents studied in current research, is short. As a rule, longer contact time, sometimes up to 180 min, are necessary to obtain high removal rates [38-40]. The faster the effective removal of the adsorbate by the adsorbent, the better will be the material. In fact, it guarantees higher feasibility and potential use in decontamination processes in batch or continuous flow systems.

Besides determining minimum time for the removal of the adsorbate, studies on the effect of contact time provides important information related to the mechanisms that control the adsorption process, determined by adsorption kinetics. The pseudo-first and second, Elovich and intraparticle diffusion mathematical models were employed for these parameters, shown in Tables 2-5.

Adjustment and applicability evaluation of diffusion models was performed by observing the coefficient of determination (R^2) rate; the closer to 1.00, the best will be the model´s adjustment. On the other hand, Q_{eq} rates obtained by models with experimental Q_{eq} rates (average

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

Kinetic models	Biosorbent		
Pseudo-first order	C	E	E + T
K_1 (min^{-1})	-0.040	-0.024	-0.066
Q_{eq} (cal.) (mg g^{-1})	0.235	0.091	0.407
R^2	0.982	0.826	0.891
Q_{eq} (exp.) (mg g^{-1})	0.247	0.224	0.462
Pseudo-second order			
K_2 (g mg^{-1} min^{-1})	0.464	0.806	-0.606
Q_{eq} (cal.) (mg g^{-1})	0.280	0.236	0.460
R^2	0.992	0.997	0.999
Q_{eq} (exp.) (mg g^{-1})	0.247	0.224	0.462
Elovich			
A (mg g^{-1} h^{-1})	0.060	0.148	0.330
B (g mg^{-1})	0.043	0.017	0.033
R^2	0.763	0.948	0.786

C: jatropha rind; E: endosperm; E + T: endosperm + peel; K_1: speed constant of the first order; Q_{eq}: adsorbate amounts retained per adsorbent gram in equilibrium; K_2: speed constant of the second order; A: constant indicating speed of initial chemo-sorption; B: number of adequate sites for adsorption, related to extension of surface coverage and activation energy of chemo-sorption; R^2: coefficient of determination.

Table 3: Kinetic parameters for pseudo-first order and pseudo-second order and Elovich models for the analysis of Zn^{2+} adsorption by biosorbents jatropha rind (C), endosperm (E) and endosperm + peel (E+T).

Kinetic models	Biosorbent		
Pseudo-first order	C	E	E + T
K_1 (min^{-1})	-0.016	-0.027	-0.006
Q_{eq} (cal.) (mg g^{-1})	0.088	0.146	0.155
R^2	0.830	0.822	0.878
Q_{eq} (exp.) (mg g^{-1})	0.526	0.431	0.569
Pseudo-second order			
K_2 (g mg^{-1} min^{-1})	0.410	0.717	0.657
Q_{eq} (cal.) (mg g^{-1})	0.556	0.453	0.582
R^2	0.998	0.998	0.997
Q_{eq} (exp.) (mg g^{-1})	0.526	0.431	0.569
Elovich			
A (mg g^{-1} h^{-1})	0.387	0.279	0.406
B (g mg^{-1})	0.031	0.035	0.034
R^2	0.876	0.818	0.825

C: jatropha rind; E: endosperm; E + T: endosperm + peel; K_1: speed constant of the first order; Q_{eq}: adsorbate amounts retained per adsorbent gram in equilibrium; K_2: speed constant of the second order; A: constant indicating speed of initial chemo-sorption; B: number of adequate sites for adsorption, related to extension of surface coverage and activation energy of chemo-sorption; R^2: coefficient of determination.

of Q_{eq} rates from the contact time test) were compared in the case of pseudo-first and pseudo-second order models [41]. Experimental Q_{eq} rates from biosorbents rind (C), endosperm (E) and endosperm + peel (E + T) of jatropha in Cu^{2+} removal from the solutions were 0.247; 0.224 and 0.462 mg g^1 (Table 2) respectively, whilst in the case of Zn^{2+} amounts were 0.526; 0.431 and 0.569 mg g^1 (Table 3).

The kinetic model of the pseudo-first order in the case of Cu^{2+} (Table 2) and Zn^{2+} (Table 3) did not adjust itself adequately for the three biosorbents (R^2 rates were low and Q_{eq} rates were not close to experimental Q_{eq}). Consequently, the adsorption process of the metals with the three biosorbents did not occur by physiosorption since the pseudo-first order model indicated this type of adsorption. It should be also mentioned that the pseudo-first order model did not have any adjustment for most adsorption systems between biosorbents and metal ions [42].

The evaluation of adjustment of the pseudo-first order model best explained the kinetics of the adsorption process of the metals Cu^{2+} and Zn^2 by the three biosorbents under analysis. In fact, the three adsorbent materials showed R^2 rates close to 1.00 (biosorbent C: 0.992 for Cu^{2+} and 0.998 for Zn^{2+}; biosorbent E: 0.997 for Cu^{2+} and 0.998 for Zn^{2+}; biosorbent E+T: 0.999 for Cu^{2+} and 0.997 for Zn^{2+}) and Q_{eq} rates similar to experimental Q_{eq} (Tables 2 and 3). Results suggest that the adsorption process between Cu^{2+} and Zn^{2+} ions and the active sites of the three biosorbents occur by chemical adsorption, through valence forces and sharing of electrons [28,43].

R^2 rates in the Elovich model were low (Tables 2 and 3) and their adjustment was not acceptable. According to Tseng et al. [44], the adjustment of the Elovich kinetic model occurs with higher frequencies in systems that involve chemisorption of gases on solid surfaces without the de-sorption of the products, with low applicability for systems involving the adsorption of metal ions in biosorbents.

Results for the application of intraparticle diffusion (Table 4 and 5) also demonstrate that diffusion is not a limiting stage of the Cu^{2+} and Zn^{2+} adsorption process by the three biosorbents. In other words, intraparticle

Table 4: Kinetic parameters for the intraparticle diffusion model in the study on Cu^{2+} adsorption by biosorbents jatropha rind (C), endosperm (E) and endosperm + peel (E+T).

Biosorbent	Parameters	Straight line A	Straight line B
C	K_{id} (g $mg^{-1}min^{-1/2}$)	0.027	0.002
	C_i (mg g^{-1})	0.050	0.247
	R^2	0.986	0.374
E	K_{id} (g $mg^{-1}min^{-1/2}$)	0.003	--
	C_i (mg g^{-1})	0.196	--
	R^2	0.713	--
E + T	K_{id} (g $mg^{-1}min^{-1/2}$)	0.014	-0.003
	C_i (mg g^{-1})	0.0363	0.507
	R^2	0.890	0.426

C: jatropha rind; E: endosperm; E+T: endosperm + peel; K_{id}: intraparticle diffusion constant; C_i: thickness of the limit layer effect; R^2: coefficient of determination.

Table 5: Kinetic parameters for the intraparticle diffusion model in Zn^{2+} adsorption by biosorbents jatropha rind (C), endosperm (E) and endosperm + peel (E+T).

Biosorbent	Parameters	Straight line A
C	K_{id} (g $mg^{-1}min^{-1/2}$)	0.006
	C_i (mg g^{-1})	0.466
	R^2	0.943
E	K_{id} (g $mg^{-1}min^{-1/2}$)	0.010
	C_i (mg g^{-1})	0.034
	R^2	0.819
E + T	K_{id} (g $mg^{-1}min^{-1/2}$)	0.007
	C_i (mg g^{-1})	0.049
	R^2	0.932

C: jatropha rind; E: endosperm; E+T: endosperm + peel; K_{id}: intraparticle diffusion constant; C_i: thickness of the limit layer effect; R^2: coefficient of determination.

diffusion and external transport occur through adsorption on the surface [45].

When all models used to understand the kinetics of Cu^{2+} and Zn^{2+} ion adsorption by the three biosorbents are evaluated in the current research, it may be said that the adsorption process occurred by chemiosorption provided by an effective exchange of electrons between the adsorbent and the adsorbed. A strong link between the two components is mainly generated with the occurrence of polar covalent links. The occurrence of chemical adsorption, with greater linking forces between the adsorbed and the active sites of the adsorbent, is a relevant characteristic since in the decontamination of water bodies it is desirable that contaminants strongly adhere to the adsorbent so that they would not return so easily to the solution.

3.4 Effect of the initial concentration of the adsorbed in the adsorption process

3.4.1 Removal percentages

The evaluation of Cu^{2+} removal percentages by biosorbents (Table 6) reveals that the three biosorbents had higher removal rates during the initial concentration interval between 40 and 100 mg L^{-1}. The jatropha rind (C) had the lowest removal rates (maximum 73.72% in 60 mg L^{-1}) when compared to endosperm (E) and endosperm + peel (E+T), which, in their turn, were practically alike. Both biosorbents had the highest Cu^{2+} removal when a 60 mg L^{-1} solution was used (86.47% for E and 86.39% for E+T).

In the case of Zn^{2+}, the three adsorbent material had similar removal rates (Table 6) with a maximum adsorption of the chemical element in the 80 mg L^{-1} solution for biosorbent C (87.30%), 40 mg L^{-1} for the biosorbent E (88.53%) and 40 mg L^{-1} for the biosorbent E+T (91.24%). Highest Zn^{2+} removal rates for the three biosorbents occurred between 20 and 100 mg L^{-1}.

Cu^{2+} and Zn^{2+} removal percentage results show that increase in the metals concentration in the solution causes a decrease in the biosolvents´ adsorption. The above may be explained by a greater occupation of adsorption sites in the adsorbent material. Increase in the competition by the active sites may occur with a decrease in the solution´s efficiency [46].

Cutillas-Barreiro et al. [47] studied the adsorption of Cu and Zn by pine bark in concentrations of up to 3.15 mM. The authors observed removal rates up to 84% for Cu and 83% for Zn. Garrido et al., [48] obtained 100% removal of both metals using 6 and 24 g kg^{-1} of mussel shell (concentrations up to 2.3 mM). When compared to the biosorbents under analysis, the commercial adsorbent (activated coal) showed slightly higher Cu^{2+} and Zn^{2+} removal rates than those of the three materials (Table 6). Since activated coal has a high removal capacity of metal ions in solutions, comparison with the material is basic for the evaluation of the efficiency of the biosorbents analyzed. In spite of the activated coal´s higher performance, the three biosorbents are capable of removing Cu^{2+} and Zn^{2+} from water solutions since these materials did not undergo any transformation process or chemical activation as occurred with activated coal. It should be underscored that production and

Table 6: Cu^{2+} and Zn^{2+} removal percentages by biosorbents jatropha rind (C), endosperm (E), endosperm + peel (E+T) and by activated coal (AC).

Cu										
Adsorbent	**C_0 (mg L^{-1})**									
	5	**20**	**40**	**60**	**80**	**100**	**120**	**140**	**160**	**200**
C	43.60	71.07	73.53	73.72	68.45	65.73	57.56	52.88	47.17	41.15
E	53.59	79.08	81.34	86.47	84.46	83.55	80.40	77.34	73.27	65.82
E + T	63.35	83.43	83.55	86.39	85.52	83.33	81.76	78.00	75.95	69.44
CA	88.36	91.30	90.86	91.92	91.96	93.35	93.63	93.86	94.23	94.97
Zn										
Adsorbent	C_0 (mg L^{-1})									
	5	20	40	60	80	100	120	140	160	200
C	60.33	84.90	84.45	85.92	87.30	84.54	80.66	71.07	58.50	61.44
E	80.39	87.91	88.53	84.78	79.72	75.84	73.41	65.17	57.84	54.47
E + T	79.11	90.45	91.24	87.16	83.41	78.32	75.43	73.69	66.45	64.88
CA	95.93	97.87	90.25	91.33	86.96	82.77	83.50	79.17	76.21	77.42

C: jatropha rind; E: endosperm; E + T: endosperm + peel; AC: activated coal; C_0: initial concentration.

activation of activated coal transforms the material into an adsorbent of the highest quality, although more expensive, consequently causing higher prices in decontamination process [49].

The analysis and production of alternative materials with good capacities for the removal of contaminants without their modification or activation is highly relevant since there will be a significant reduction in costs for the treatment of contaminated affluents or water resources, one of the main impairments in the process.

3.4.2 Adsorption isotherms

Adsorption isotherms provide the amount of ions adsorbed per adsorbent mass in proportion to the concentration of the solution in dynamic equilibrium [16]. Different mathematical models may be used for the linearization of the isotherms and to obtain highly important parameters for the interpretation of data obtained in the adsorption process.

Results for the adsorption isotherms of the three biosorbents under analysis and for activated coal (Fig. 6) showed that, in the case of Cu^{2+} and Zn^{2+}, the three materials revealed isotherms of Langmuir´s L group. In the case of activated coal, removal rates for Cu^{2+} were high in all initial concentrations of the metal, without obtaining the isotherm. In the case of Zn^{2+}, isotherm obtained may also be classified as belonging to Langmuir´s L group. Isotherms of Langmuir L group are mainly characterized by a downward curve, due to the decrease in active sites provided by an increase of adsorbate concentration [50]. The isotherm allows maximum capacity of adsorption by mathematical models such as Langmuir´s [35].

Isotherm linearization was undertaken by Langmuir, Freundlich and Dubinin-Radushkevich´s (D-R) mathematical models to determine the maximum capacity of biosorbent adsorption and the main parameters involved in the adsorption process of the metal analyzed.

Similar to the adsorption kinetics, the adjustment of the mathematical model applied in linearization is evaluated by the rate of the coefficient of determination (R^2). Linearization results (Tables 7 and 8) show that the three biosorbents studied in current assay had the best adjustment by Langmuir´s model. In fact, Cu^{2+} and Zn^{2+} adsorption predominantly occur in monolayers [35]. On the other hand, activated coal had the highest R^2 rate in the adjustment of Freundlich´s model (0.997 for Cu^{2+} and 0.993 for Zn^{2+}) and suggested that, in the case of this material, the adsorption process mainly occurred in multilayers.

Rates for Langmuir´s parameter Q_m (Tables 7 and 8), maximum adsorption capacity, show that in the case of Cu^{2+}, the biosorbents produced from jatropha rind (C), endosperm (E) and endosperm + peel (E+T), provided 11.541; 20.475 and 22.910 mg g^{-1}, respectively as maximum adsorption capacity, whereas in the case of Zn^{2+} the biosorbents showed a removal capacity of 14.852; 15.888 and 14,674 mg of the metal per g of biosorbent. Q_m rate obtained for Zn^{2+} adsorption by activated coal (18.591 mg g^{-1}) were higher than those for biosorbents. It should however

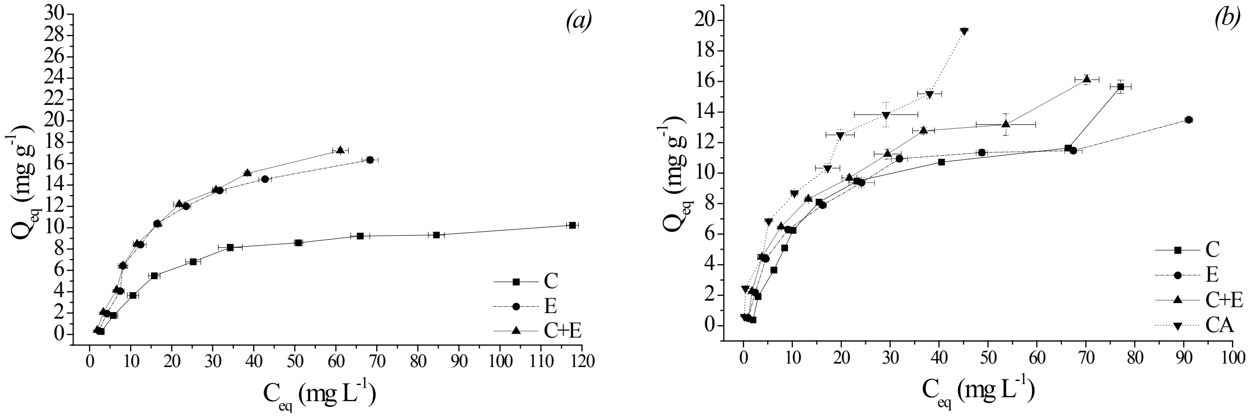

Figure 6: Adsorption isotherms of Cu^{2+} (*a*) and Zn^{2+} (*b*) by biosorbents jatropha rind (C), endosperm (E), endosperm + peel (E+T) and activated coal (AC) (C_0: 5 to 200 mg L^{-1}; m: 8 g L^{-1}; t: 60 min; pH: 5.5; 200 rpm; 25°C).

be underscored that the material underwent chemical activation and thus had a high adsorption capacity.

Evaluation of Langmuir´s parameter R_L for the three biosorbents in the metals evaluated show that the adsorption process is positive since they may be found within the interval of 0 and 1 [51].

Although Freundlich´s mathematical model provided inadequate R^2 rates, the parameter *n* may be used as an indicator of reactivity of the adsorbent´s active sites. In this case, *n* rates higher than 1 suggest highly energetic sites in the material, which are the first to be occupied by metal ions. Consequently, results by the three biosorbents for parameter *n* demonstrate active sites, for Cu^{2+} and Zn^{2+}, with relatively weak and similar energy, occupied without any specific preference by the metal ions. The above corroborates the best adjustment by Langmuir´s model with the best adjustment when actives sites with equal energy throughout the material (monolayer) occur.

Similar to Freundlich´s model, the parameters of Dubinin-Radushkevich´s mathematical model (D-R) may also be employed to explain the mechanisms of the adsorption process of the metals under analysis. The adsorption process of Cu^{2+} by the three biosorbents has chemical characteristics since E rates are higher than 8.0 kJ [52] when average sorption energy (E) mol^{-1} is taken into account. The latter corresponds to the free energy involved in the transference of 1 mol of the solution´s solute to the adsorbent´s surface and thus indicates whether adsorption has physical or chemical features [53]. The same occurred for Zn^{2+} adsorption by adsorbents from jatropha endosperm (E) and from jatropha endosperm + peel (E+T). Jatropha rind (C) had E rate equal to 7.551 kJ mol^{-1}, which characterizes physical adsorption, contrastingly to results in previous studies. However, the biosorbent´s R^2 is relatively low (0.950) and E is close to 8.0 kJ mol^{-1}. Consequently, there is no certainty that Zn^{2+} adsorptive process in jatropha active sites occurs by physical adsorption.

Table 7: Parameters from isotherm linearization by Langmuir, Freundlich and Dubinin-Radushkevich (D-R) mathematical model for Cu^{2+} adsorption process by biosorbents jatropha rind (C), endosperm (E), endosperm + peel (E+T) and for activated coal (AC).

Model	Parameter	Adsorbent		
		C	E	E + T
Langmuir	Q_m	11.541	20.475	22.910
	K_L	0.127	0.041	0.039
	R_L	0.038	0.110	0.115
	R^2	0.997	0.999	0.998
Freundlich	K_f	2.570	2.296	2.073
	n	0.097	0.197	0.196
	R^2	0.874	0.944	0.963
D-R	Q_d	0.002 x 10^{-1}	0.006 x 10^{-1}	0.002 x 10^{-1}
	E	12.520	10.660	8.220
	R^2	0.938	0.962	0.950

C: jatropha rind; E: endosperm; E + T: endosperm + peel; Q_m (mg g^{-1}): maximum capacity of adsorption; K_L or b (L mg^{-1}): constant related to the interactivity forces adsorbent/adsorbed; R_L: Langmuir´s constant; R^2: coefficient of determination; K_f (L mg^{-1}): related to adsorption capacity; n: related to the solid´s heterogeneity; Q_d (mol g^{-1}): maximum capacity of adsorption; E (kj mol^{-1}): mean sorption energy.

Maximum capacity of Cu^{2+} and Zn^{2+} adsorption (Langmuir´s Q_m) by biosorbents in current analysis was also compared to other biosorbent materials (Table 6). The three biosorbents from jatropha residues had better

Table 8: Parameters obtained in isotherm linearization by Langmuir, Freundlich and Dubinin-Radushkevich (D-R) mathematical models for Zn^{2+} adsorption process by biosorbents jatropha rind (C), endosperm (E), endosperm + peel (E+T) and for activated coal (AC).

Model	Parameter	Adsorbent			
		C	E	E + T	CA
Langmuir	Q_m	14.852	15.888	14.674	18.591
	K_L	0.074	0.044	0.059	0.028
	R_L	0.064	0.101	0.078	0.152
	R^2	0.980	0.992	0.987	0.975
Freundlich	K_f	1.621	2.029	2.782	1.747
	n	0.057	0.158	0.160	1.595
	R^2	0.929	0.963	0.949	0.993
D-R	Q_d	0.058×10^{-1}	0.007×10^{-1}	0.011×10^{-1}	0.008×10^{-1}
	E	7.551	11.337	9.990	10.030
	R^2	0.950	0.982	0.981	0.998

C: jatropha rind; E: endosperm; E + T: endosperm + peel; AC: activated coal; Q_m (mg g^{-1}): maximum capacity of adsorption; K_L or b (L mg^{-1}): constant related to the interactivity forces adsorbent/adsorbed; R_L: Langmuir´s constant; R^2: coefficient of determination; K_f (L mg^{-1}): related to adsorption capacity; n: related to the solid´s heterogeneity; Q_d (mol g^{-1}): maximum capacity of adsorption; E (kj mol^{-1}): mean sorption energy.

maximum adsorption capacities than all the materials compared, or rather, they are excellent materials for Cr^{3+} removal in the solution.

3.4.3 Characterization of the adsorbent´s functional groups after the adsorption process

The characterization of functional groups in the biosorbents´ structure after the adsorption process of metals under analysis by IR spectrometry (Fig. 7) shows that, in the case of the two metals, the three biosorbents did not have any significant change in their functional groups. Or rather, the biosorbents maintained their original features with the participation of the functional groups mentioned in 3.1 in the metals adsorption process.

3.5 Desorption

Results of the desorption of the metals by biosorbents and by activated coal (Table 9) demonstrated that desorption rates were low (C = 59.29; E = 56.99; E + T = 56.76 and AC = 44.02%) for Cu^{2+}. The above results may be related to the chemical adsorption with high energy between Cu^{2+} ions and the adsorbent´s active sites [54].

Desorption rates for Zn^{2+} were rather better (Table 9) by biosorbent from jatropha rind (E), with better results (C = 65.71; E = 82.09; E + T = 71.08 and AC = 42.22%). In fact, the material recovers the metal for use in sorption/de-sorption systems and for the recovery of the metal after the adsorption process. The same considerations for Cu^{2+} are valid in the case of biosorbents C and E+T.

As a general rule, a high desorption rate is a good characteristic for the adsorbent, it becomes possible to reuse the material in sorption/desorption processes as well as low costs in large scale remediation processes for removing heavy metals. But can be a problem in acidic environments because the metal can move on to the solution again, not allowing the effective removal.

4 Conclusions

The best conditions of the adsorption process between biosorbents and Cu^{2+} and Zn^{2+} ions are the solution´s pH at 5.0; 8.0 g L^{-1} of biosorbent in the solution and 60 min contact time.

Adsorption kinetics of the two metals indicated that adsorption of the active sites of the biosorbents occur chemically, with the best adjustment of the pseudo-first order model. In the case of the three biosorbents, since Langmuir´s mathematical model had the best adjustment in the study of isotherms, it indicated the prevalence of chemo-sorption by monolayers. The three biosorbents had a desorption rate that allowed the recovery after the adsorption process, with possible use in sorption/desorption flows.

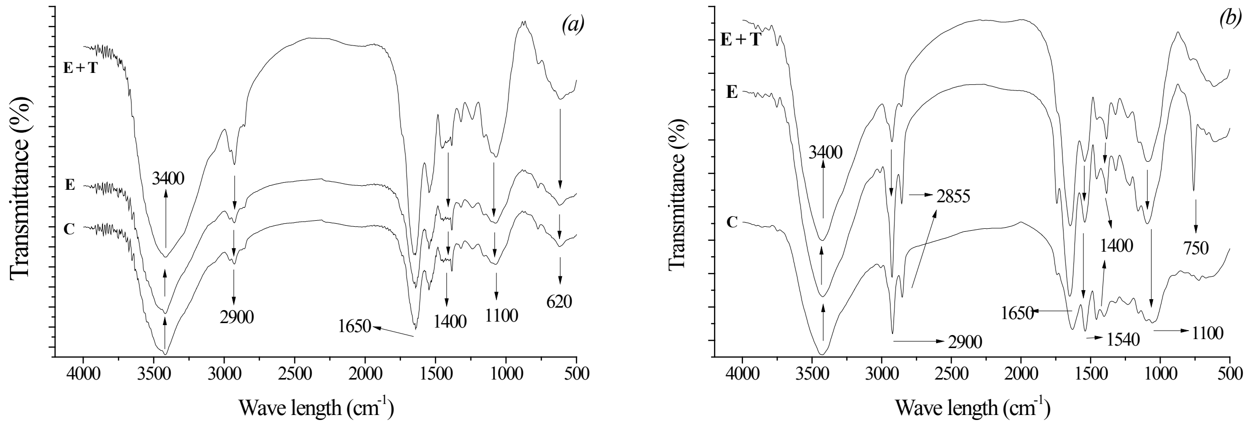

Figure 7: IR spectra of the biosorbents jatropha rind (C), endosperm (E) and endosperm + peel (E + T) after the adsorption process with Cu^{2+} (a) and Zn^{2+} (b).

Table 9: Mean percentages of Cu^{2+} and Zn^{2+} adsorption and de-sorption by biosorbents jatropha rind (C), endosperm (E), endosperm + peel (E+T) and for activated coal (AC).

Cu^{2+} **Adsorbent**	**Adsorption (%)**	**Desorption (%)**
C	59.49	59.29
E	76.54	56.99
E + T	79.07	56.76
CA	92.44	44.02
Zn^{2+}		
Adsorbent	Adsorption (%)	Desorption (%)
C	75.91	65.71
E	74.81	82.09
E + T	79.01	71.08
CA	86.14	45.22

C: jatropha rind; E: endosperm; E + T: endosperm + peel; AC: activated coal.

Results show that the three biosorbents obtained from jatropha biomass are capable of removing Cu^{2+} and Zn^{2+} from water solutions and may be used as alternative for adsorbents usually used in remediation systems of water resources contaminated by the two metals.

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