Acta Scientiarum

http://www.uem.br/acta
ISSN printed: 1806-2563
ISSN on-line: 1807-8664
Doi: 10.4025/actascitechnol.v37i3.26809

Removal of Cu (II) and Zn (II) from water with natural adsorbents from cassava agroindustry residues

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ABSTRACT. Current study employs solid residues from the processing industry of the cassava (*Manihot esculenta* Crantz) (bark, bagasse and bark + bagasse) as natural adsorbents for the removal of metal ions Cu(II) and Zn(II) from contaminated water. The first stage comprised surface morphological characterization (SEM), determination of functional groups (IR), point of zero charge and the composition of naturally existent minerals in the biomass. Further, tests were carried out to evaluate the sorption process by kinetic, equilibrium and thermodynamic studies. The adsorbents showed a surface with favorable adsorption characteristics, with adsorption sites possibly derived from lignin, cellulose and hemicellulose. The dynamic equilibrium time for adsorption was 60 min. Results followed pseudo-second-order, Langmuir and Dubinin-Radushkevich models, suggesting a chemisorption monolayer. The thermodynamic parameters suggested that the biosorption process of Cu and Zn was endothermic, spontaneous or independent according to conditions. Results showed that the studied materials were potential biosorbents in the decontamination of water contaminated by Cu(II) and Zn(II). Thus, the above practice complements the final stages of the cassava production chain of cassava, with a new disposal of solid residues from the cassava agroindustry activity.

Keywords: Solid residue, biosorbent, decontamination, adsorption, water contamination, toxic metals.

Remoção de Cu(II) e Zn(II) de águas com adsorventes naturais de resíduos da agroindústria da mandioca

RESUMO. Este estudo propõe a utilização de resíduos sólidos da indústria de processamento de raízes de mandioca (*Manihot esculenta* Crantz) (cascas, bagaço e casca mistura + bagaço) como adsorventes naturais para a remoção de íons metálicos Cu (II) e Zn (II) de águas contaminadas. Em uma primeira fase foi realizada a caracterização morfológica superficial (MEV), determinação dos grupos funcionais (IR), ponto de carga zero e a composição de minerais naturalmente existentes na biomassa. Após esta etapa, foram realizados testes para avaliar o processo de sorção mediante estudos cinéticos, de equilíbrio e termodinâmica. Os adsorventes apresentam superfície com características de adsorção favoráveis, com sítios ativos possivelmente derivados da lignina, celulose e hemicelulose. O tempo de equilíbrio dinâmico do processo é de 60 min. Os resultados seguem aos modelos de pseudo-segunda ordem, Langmuir, Dubinin-Radushkevich, sugerindo quimissorção em monocamada. Os parâmetros termodinâmicos sugerem que o processo de biossorção de Cu e Zn é endotérmico, podendo ser espontâneo dependendo das condições. Concluiu-se que os materiais estudados são potenciais biosorventes para a descontaminação de águas contaminados por Cu (II) e Zn (II). Assim, esta prática complementa os estágios finais da cadeia produtiva da mandioca, dando um novo destino para resíduos sólidos de atividade mandioca agroindústria.

Palavras-chave: resíduo sólido, biossorvente, descontaminação, adsorção, contaminação de águas, metais tóxicos.

Introduction

Cassava root processing industries generate solid wastes, commonly called bark (bark + inner bark) and bagasse (roughage, bran), generally disposed of in animal feed and / or as biofertilizers (EMBRAPA, 2005).

Since approximately 3 to 5% of root wastes correspond to the cassava bark (EMBRAPA, 2005), it may be estimated that Brazil produces approximately 1 million tons per year of bark. Eleven million tons per year are produced worldwide, besides the even greater amount of cassava bagasse, root processing residues and starch production.

Due to the fact that cassava crops are extant in many countries, its increasingly high production in the coming years (EMBRAPA, 2005) will generate even greater amounts of solid residues proportionally to the expansion of cultivation. Research is thus required for new types of disposals and uses for the residues. A possible solution may be the use of cassava residues as alternative biosorbents in contaminated waters.

Alternative materials such as agro-industrial residues have been evaluated due to their high availability and accessibility, efficiency and competitiveness with regard to ion exchange resins and activated carbon (VALDMAN et al., 2001).

Different plant residues have been used as biosorbents in contaminated water, such as modified sugar cane bagasse or *in natura* for the removal of Pb and Cu (DOS SANTOS et al., 2010; 2011); banana and orange peels in the removal of Cu, Co, Ni, Zn, and Pb (ANNADURAI et al., 2002); mussel shells in the biosorption of Hg (PEÑA-RODRÍGUEZ et al., 2010); rice bran in the biosorption of Cd, Cu, Pb and Zn (MONTANHER et al., 2005); and water hyacinth dry biomass in removal of Cd, Pb, Cr, Cu, Zn and Ni (GONÇALVES Jr. et al., 2009).

Owing to the characteristics and advantages attributed to the biosorption process, assays on new adsorbent materials which are technically and economically feasible become crucial (DOS SANTOS et al., 2010).

Water pollution by heavy metals, particularly Cu in excess, may be toxic to humans, since the later metal has an affinity with SH groups of several proteins and enzymes associated with such diseases as epilepsy, melanoma and rheumatoid arthritis. Further, Cu may also lodge in the brain, liver and stomach, manifesting such symptoms as gastric ulcer, liver necrosis and kidney disease and also the loss of palatability (LIMA et al., 2006; ALMEIDA NETO et al., 2014).

In spite of its essentiality, Zn present in high concentrations may cause harmful effects on the human body, such as nausea, vomiting, diarrhea, skin irritation, anemia and infertility, affecting the respiratory system (nose to lungs), gastrointestinal tract (digestive) and blood (blood formation) (SEOLATTO et al., 2009; ATSDR, 2015).

There are some researches reporting the use of cassava solid wastes for the removal of metal ions from water: the adsorption of Cd(II), Cu(II) and Zn(II) by cassava tuber bark waste (HORSFALL Jr. et al., 2006); cassava mesocarp treated with dye for Cu(II) and Zn(II) removal (AGIRI; AKARANTA 2009); activated carbon of cassava peels for Cu(II) adsorption (MORENO-PIRAJÁN; GIRALDO 2010) and others. All the above researches report on the use of cassava bark alone (there is no mention of cassava bagasse) or the resultant adsorbent is modified by some physical/chemical process which increases the cost of the treatment and fails to be an attractive technology in undeveloped countries.

Current research employs natural organic adsorbents derived from the cassava agro-industrial residues for the removal of Cu(II) and Zn(II) from water, and assesses the kinetic, equilibrium and adsorption thermodynamic assays.

Material and methods

Acquirement and characterization of adsorbents

The bark´s raw material, bagasse and bark + cassava bagasse were obtained directly from an agroindustry. They were dried, milled and standardized in particle size (14 to 60 mesh), resulting in biosorbents based on bark, bagasse and bark + bagasse mixture.

The biosorbents were characterized by their point of zero charge (pHPZC) (MIMURA et al., 2010), scanning electron microscopy (SEM), infrared spectrum (IR) and mineral composition (AOAC 2005; WELZ; SPERLING, 1999) to determine the concentrations of their constituent metals.

The pH correspondent to the point of zero charge (pH_{PZC}) of the adsorbent was determined. It refers to the pH rate when the resultant of surface charges of the adsorbent is null. Further, 50 mg of adsorbents and 50 mL of aqueous solution of KCl (Vetec 99%) 0.5 mol L^{-1} in pHi (pH initial) rates varying from 2.0 to 9.0 (adjusted with HCl 0.1 mol L^{-1} and NaOH 0.1 mol L^{-1}) were added. After stirring for 24 hours (200 rpm) at 25°C, pHf (pH final) rates were obtained, providing a graph of pHi versus Δ pH, with the point of null variation being pH corresponding to pH_{PZC} (MIMURA et al., 2010).

The characterization of the infrared spectrum was performed to evaluate the possible functional groups causing the binding with Cu(II) and Zn(II), by a spectrometer Shimadzu Infrared Spectrophotometer FTIR - 8300 Fourier Transform, in the region between 400 to 4000 cm^{-1}, with resolution 4 cm^{-1}. The spectrum was obtained using KBr tablets.

The surface was also evaluated morphologically by scanning electron microscopy (SEM), with a FEI Quanta 200 microscope at a voltage of 30 kV. The samples were placed in a double-sided tape attached to a carbon sample holder and then metallized with gold at a thickness of about 30 nm by a sputter coater Baltec Scutter SCD 050.

The biosorbents´ chemical characterization was performed by nitroperchloric digestion of the adsorbent materials (AOAC, 2005) and the concentrations of the metals potassium (K), calcium

(Ca), magnesium (Mg), copper (Cu), iron (Fe), manganese (Mn), zinc (Zn), cadmium (Cd), lead (Pb) and chromium (Cr) were determined by flame atomic absorption spectrometry (FAAS) (WELZ; SPERLING, 1999), model GBC 932 AA, with deuterium lamp for correction.

Kinetic, equilibrium and thermodynamics adsorption studies

For the adsorption assays, the mono-elementary solutions fortified with metal ions Cu^{2+} and Zn^{2+} were prepared from the copper nitrate salts [$Cu(NO_3)_2$ P.A. ≥ 99% Sigma-Aldrich], and zinc nitrate [$Zn(NO_3)_2$ P.A. ≥ 99% Sigma-Aldrich].

Adsorption kinetics were evaluated by measuring the amount of metal ion adsorbed through contact time between adsorbent and adsorbate (5, 10, 20, 40, 60, 80, 100, 120, 140, 160 and 180 minutes), whereas in the case of equilibrium assays the removal of metals was evaluated in solution according to the initial concentration of the metal ions (5, 10, 20, 40, 60, 80, 100, 120, 140 and 160 mg L^{-1}).

Thermodynamic parameters inherent to Cu(II) and Zn(II) adsorption process were measured by varying the temperature during the sorption process (15, 25, 35, 45, 55 and 65°C).

The following constant conditions were employed in all the studies evaluated: 400 mg of adsorbent matter (bark, bagasse and bark + bagasse) and Cu(II) and Zn(II) solutions at pH 5.5. These conditions had been defined in previous studies (SCHWANTES et al., 2013). It should also be noted that 125 mL Erlenmeyer flasks in a Dubnoff thermostatically system with constant stirring at 200rpm were used in the adsorption studies.

After the sorption process in the Dubnoff system was performed, the samples were filtered and aliquots removed for the determination of concentrations of metals by FAAS (WELZ; SPERLING, 1999).

Rates for the equilibrium concentration were used to calculate the adsorbed amount at equilibrium (Equation 1).

$$Q_{eq} = \frac{\left(C_0 - C_{eq}\right)}{m} . V \tag{1}$$

where Q_{eq} is the number of ions adsorbed per gram of adsorbent (mg g^{-1}); m is the material of the adsorbent used (g); C_0 represents the initial concentration of ion (mg L^{-1}); C_{eq} is the ion concentration in solution at equilibrium (mg L^{-1}); V is the volume of solution used (L).

The removal percentage of the metal was calculated with Equation 2:

$$\%R = 100 - \left(\frac{C_{eq}}{C_0} . 100\right) \tag{2}$$

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

The results obtained in the above tests were linearized according to mathematical models of pseudo-first-order, pseudo-second-order, Elovich, intraparticle diffusion, Langmuir, Freundlich, Dubinin-Radushkevich and determination of thermodynamic parameters ΔG, ΔH and ΔS (Equations 3 and 4), following Schimmel et al. (2010) and Feng et al. (2011).

$$\Delta G = -RT . \ln K_d \tag{3}$$

$$\ln\left(K_d\right) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{4}$$

R is the universal constant of gases (8.314 J mol^{-1} K^{-1}); T is the temperature in Kelvin (K); K_d is the coefficient of thermodynamic distribution, obtained by Q_{eq}/C_{eq}.

All evaluations of current adsorption experiment were performed in triplicate.

Results and discussion

According to Mimura et al. (2010), pH_{PZC} may be defined as the pH of the surface of the solid with neutral charge. In solutions with pH below pH_{PZC}, in adsorbent´s surface with predominate positive charges and in solutions with pH above pH_{PZC}, the surface liquid charge is negative and provides a better condition for the adsorption of cations.

Results for pH_{PZC} (Figure 1) show that the equivalence point of positive and negative charges for the adsorbents is 6.00 for bark, 6.17 for bagasse and 6.24 for bark + bagasse. Consequently, the adsorption of cations, in this case Cu(II) and Zn(II), are favored by pH rates above pH_{PZC} [5] (TAGLIAFERRO et al., 2011).

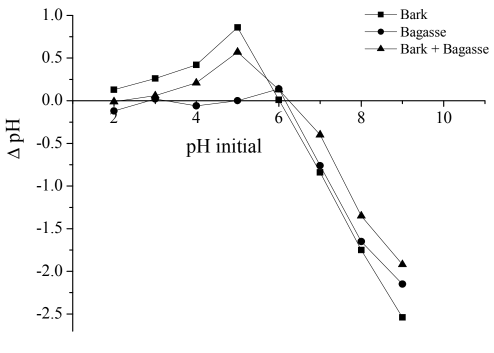

Figure 1. Point of zero charge in KCl 0.5 mol L^{-1} for bark, bagasse and bark + bagasse.

Figures 2, 3 and 4 illustrate the adsorbent micrographs at a magnification of 20,000 times.

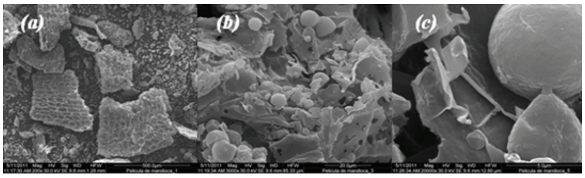

Figure 2. Scanning electron microscopy image of the adsorbent cassava root bark magnified (a) 200; (b) 3,000; (c) 20,000 x.

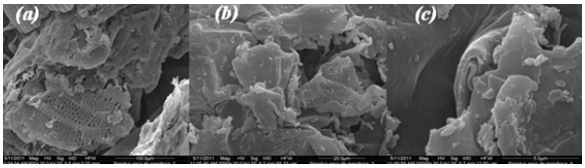

Figure 3. Scanning electron microscopy image of adsorbent cassava root bagasse adsorbent magnified (a) 200; (b) 3,000; (c) 20,000 x.

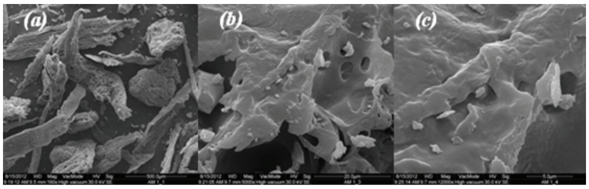

Figure 4. Scanning electron microscopy image of adsorbent cassava bark + root bagasse magnified (a) 160; (b) 5,000; (c) 12,000 x.

As Figures 2, 3 and 4 show, the adsorbent surface has a fibrous and porous appearance with an irregular and heterogeneous structure. The gaps indicate that the material´s characteristics suggest that the adsorbent possesses favorable conditions for the removal of ions in the solution.

The characterization by infrared (IR) contributes towards the understanding of the metal ion behavior or adsorption mechanism on a solid surface and provides information on the functional groups in the adsorbent´s structure (WAN NGAH; HANAFIAH, 2008), whereas biosorption is the result of electrostatic interaction and complex formation between the metal ions and the functional groups in the biomass (DOS SANTOS et al., 2011). Bands 3440, 2920, 1730, 1650, 1420 and 1030 cm^{-1} were employed for the adsorbent materials under analysis (Figure 5).

Figure 5 shows a broad and strong band at 3440-3330 cm^{-1} which may be attributed to the stretching vibration of the O-H bond. This band features the stretching vibration of hydroxyl groups in carbohydrates, fatty acids, proteins, lignin units, cellulose and absorbed water (FENG et al., 2011; HAN et al., 2010; STUART, 2004). Moreover, the band at 2920 cm^{-1} is attributed to a stretching vibration of C-H bond of the alkane groups (BARBOSA, 2007).

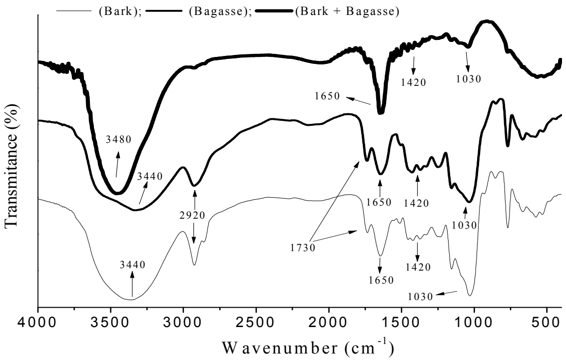

Figure 5. Infrared spectra for the bark, bagasse and bark + bagasse.

According to Horn et al. (2011), bands included in 1730 indicate the presence of starch, or, according to Pastore et al. (2004), they may be attributed to the carbonyl groups of ketone and aldehyde functions in lignin and holocellulose.

The bands located between 1420 and 1650 cm^{-1} may be attributed to the stretching vibration of C-O bond from amide and carboxylic groups (HAN et al., 2010). The bands observed at 1030 cm^{-1} may be attributed to C-O stretching, suggesting the presence of lignin too (PASCOAL NETO et al., 1995), which, according to Guo et al. (2008), has compounds similar to carboxyl groups that provide adsorption sites.

According to Pehlivan et al. (2009), vegetal biomass primarily comprises cellulose, hemicellulose and lignin.

Thus, according to Sharma et al. (2006) and Pehlivan (2009), the adsorption of metals by plant residues, natural materials and agro-industrial residues may be attributed to some functional groups such as lignin, alcohols, carboxylic groups, carbohydrates and proteins, which adsorb metal ions.

Since Pb concentrations were also detected in adsorbent materials (Table 1), this fact indicated heavy metal concentration in the soil where the cassava plants were grown.

Pb in biosorbents may have been retrieved from plants grown in soil contaminated with the heavy metal. Pb may migrate from the adsorbent biomass to the solution and contaminate the remaining solution. However, tests performed in current research have shown that Pb was strongly adsorbed by the biomass since no traces of lead concentration were detected. Gonçalves Jr. et al. (2011) evaluated the residual effect of fertilizers on wheat by using fertilizers from unknown origin and registered soil contamination by Pb through the fertilizers and consequent absorption of Pb by wheat plants. Similarly, it may be theorized that when grown in contaminated soils, cassava plants also absorb metals (such as Pb) in its tissues, and in the case of toxic heavy metals, they tend to accumulate them in the roots.

Table 2 shows the rates for Cu(II) and Zn(II) adsorption kinetics for the adsorbents under analysis.

Table 1. Metal levels in adsorbent materials as bark, bagasse and bark + bagasse.

Biosorbent	K	Ca	Mg	Cu	Fe	Mn	Zn	Cd	Pb	Cr
	---------g kg^{-1}---------			----------------------------mg kg^{-1}------------------------------						
Bark	24.10	35.03	6.83	14.33	35.67	123.33	32.00	<0.005	11.00	<0.01
Bagasse	5.77	23.23	4.58	5.67	24.50	27.67	18.67	<0.005	14.67	<0.01
Bark + Bagasse	7.77	22.58	5.12	6.00	26.00	34.00	17.00	<0.005	3.33	<0.01

LOQ (limit of quantification): K = 0.01; Ca = 0.005; Mg = 0.005; Cu = 0.005; Fe = 0.01; Mn = 0.01; Zn = 0.001; Cd = 0.005; Pb = 0.01; Cr = 0.01.

Table 2. Kinetic parameters obtained in the adsorption of Cu(II) and Zn(II) on bark, bagasse and bark + bagasse

Adsorbents	Bark	Bagasse	Bark + Bagasse	Bark	Bagasse	Bark + Bagasse
Pseudo-first-order	------Cu------			------Zn------		
K_1 (min.$^{-1}$)	0.0090	0.0050	-0.0046	0.0041	-0.0148	0.0167
Q_{eq} (cal.) (mg g^{-1})	0.4059	0.5837	1.0117	0.4370	1.0261	0.0755
R^2	0.96	0.24	0.61	1.00	0.99	0.99
Pseudo-second-order						
K_2 (g mg^{-1} min.$^{-1}$)	-0.1202	1.3395	0.3472	0.7348	-0.1042	-0.0290
Q_{eq} (cal.) (mg g^{-1})	5.2963	7.5233	7.5053	7.1633	7.1644	7.3649
R^2	1.00	1.00	1.00	1.00	0.99	0.99
Elovich						
A (mg g^{-1} h^{-1})	8.9174	7.3211	7.2982	7.8024	5.9065	13.8118
B (g mg^{-1})	-0.3350	0.2079	-0.4015	-0.1702	0.3926	-1.2370
R^2	0.64	0.68	0.80	0.90	0.83	0.71

K_1: first-order rate constant; Q_{eq}: amount of adsorbate retained per gram of adsorbent at equilibrium; K_2: pseudo-second-order rate constant; A: constant indicating the chemisorption initial speed; B: number of suitable sites for the adsorption related to the surface covering extension and to the chemisorption activation energy; R^2: coefficient of determination.

Although the pseudo-first-order model showed a good adjustment to the experimental results for the adsorbent bark in the removal of Cu(II) and Zn(II) from water (Table 2), rates of Q_{eq} estimated by this model were underestimated and fell far short of the rates obtained experimentally (Q_{eq} experimentally obtained: Cu = 7.22 mg g^{-1}; Zn = 5.69 mg g^{-1}).

Table 2 still shows that the model of pseudo-second-order has better adjustment (R^2) and estimates satisfactorily the Q_{eq} rates, very close to the experimental ones (Table 3). Thus, the model suggests the occurrence of chemisorption for Cu (II) and Zn (II).

As Table 2 demonstrates, the rates by the Elovich model are unsatisfactory for understanding the sorption phenomenon observed. The model is not useful for the experimental data obtained in current study.

Tang et al. (2014) reported similar results with Loofah fibers for the removal of Cu(II) from contaminated solutions. According to their results, the model of pseudo-first-order also failed in the adsorption process, with K_1 (min.$^{-1}$) = 0.0076; Q_{eq} (mg g^{-1}) = 7.33; R^2 = 0.97, which were very unlike the visualized results.

However, Tang et al. (2014) state that the pseudo-second-order model explains with reliability the adsorption of Cu(II) by Loofah fibers and presents rates for K_2 (min.$^{-1}$) = 0.0034; Q_e (mg g^{-1}) = 10.82; R^2 = 0.999.

Similar results are shown by Paduraru et al. (2015) who removed Zn(II) from aqueous solutions with rapeseed waste. According to these authors, the pseudo-second-order kinetic model implies that the rate of sorption sites covering is proportional to the square of the number of unoccupied and occupied sites.

Following the results obtained, Paduraru et al. (2015) concluded that the sorption of Zn(II) ions on the tested rapeseed fitted better the pseudo-second-order kinetic model, with values of k_1 (g mg^{-1} min.$^{-1}$) = 0.0022 and R^2 = 0.997, for an initial Zn(II) concentration of 48 mg L^{-1}.

Table 3 shows the rates derived from the linearization of the intraparticle diffusion model.

The intraparticle diffusion model explains mathematically the movement of the polluting particle from the external environment to the interior of the adsorbent pore (GUPTA and BHATTACHARYYA, 2011). However, Table 3 reveals slightly significant adjustments (R^2) for the model, indicating that it fails to be satisfactory to explain the sorption phenomenon.

Table 4 presents the rates obtained from the linearization of adsorption equilibrium assays.

Table 4 shows that the Langmuir model satisfactorily explains the monolayer adsorption of Cu(II) and Zn(II) by the adsorbents Bark, Bagasse and Bark + Bagasse, with maximum adsorption capacity (Q_m) for Bagasse and Bark + Bagasse for the adsorption of Cu(II) and Zn(II).

The Langmuir model presented satisfactory R^2 for the removal of Cu(II) by adsorbents Bark and Bagasse and the removal of Zn(II) by adsorbent Bark + Bagasse. The occurrence of multilayer biosorption occurred in these cases.

Table 3. Kinetic parameters obtained in the study of adsorption of Cu(II) and Zn(II) on bark, bagasse and bark + bagasse by the intraparticle diffusion model and Q_{eq} experimental rates.

Parameters		Cu	Zn	Experimental Q_{eq} (Cu)	Experimental Q_{eq} (Zn)
Bark	C_i (mg g^{-1})	6.2875	7.5324	5.690	7.224
	K_{id} (g mg^{-1}min.$^{-1/2}$)	-0.0815	-0.0519		
	R^2	0.71	0.83		
Bagasse	C_i (mg g^{-1})	7.5750	6.2344	7.726	7.250
	K_{id} (g mg^{-1}min.$^{-1/2}$)	0.0700	0.1679		
	R^2	0.67	0.93		
Bark + Bagasse	C_i (mg g^{-1})	8.2173	10.6248	7.526	7.984
	K_{id} (g mg^{-1}min.$^{-1/2}$)	-0.0827	-0.2463		
	R^2	0.55	0.77		

K_{id}: intraparticle diffusion constant; C_i: suggests the thickness of the boundary layer effect; R^2: coefficient of determination.

Table 4. Parameters of the Langmuir, Freundlich and Dubinin-Radushkevich (D-R) mathematical models for the biosorption process of Cu(II) and Zn(II) on bark, bagasse and bark + bagasse.

Parameters		Bark	Bagasse	Bark + Bagasse	Bark	Bagasse	Bark + Bagasse
		Cu			Zn		
Langmuir	Q_m	3.608	8.112	10.007	5.965	8.228	7.481
	K_L	0.415	0.188	0.129	0.170	0.120	0.048
	R_L	0.012	0.026	0.037	0.029	0.040	0.094
	R^2	0.97	0.98	0.98	0.97	0.98	1.00
Freundlich	K_f	0.1754	0.9587	1.4333	1.1416	1.2707	2.0858
	n	1.2107	2.0533	2.2840	2.6950	2.2530	2.8954
	R_2	0.86	0.96	0.98	0.90	0.93	0.96
D-R	Q_d	0.0008	0.0008	0.0008	0.0003	0.0004	0.0003
	E	8.9300	10.0301	10.6843	11.3961	11.1249	13.2686
	R^2	0.98	0.97	0.98	0.97	0.98	0.99

Q_m (mg g^{-1}):): maximum adsorption capacity; K_L or b (L mg^{-1}): constant related to the adsorbent / adsorbate interaction strength; R_L: Langmuir constant; R^2: coefficient of determination; K_f (L mg^{-1}): related to the adsorption capacity; n: related to the heterogeneity of the solid; Q_d (mol g^{-1}): maximum adsorption capacity; E (kj mol^{-1}): sorption average energy.

As mentioned above, the concomitant occurrence of adsorption of metal ions in mono- and multilayers may occur in the biosorption process, since the biosorbent materials are very heterogeneous and may present more or less energetic, active sites.

Gonçalves Jr. et al. (2012) evaluated the Pinus bark as a natural adsorbent and reported that the Freundlich model fitted best for Cd and Cr adsorption, whereas Langmuir and Freundlich models fitted best for Pb, indicating mono- and multilayer adsorption of the metal.

Since Table 4 also shows rates of E (sorption average energy) greater than 8 kj mol^{-1}, the occurrence of chemical adsorption between adsorbate / adsorbent was again suggested (WAN NGAH et al., 2008).

Among the mathematical models evaluated, the Langmuir and D-R models presented the best adjustments (R^2) and suggested the occurrence of chemisorption of Cu(II) and Zn(II) in monolayers.

The assessment of the Langmuir R_L rates (Table 4) showed that the conditions under which adsorption tests were developed indicated that the adsorptive process was favorable in all cases, since rates ranged between '0' and '1' (LIN; JUANG, 2009).

Table 5 shows the results obtained in the Cu(II) adsorption thermodynamic studies.

As may be observed in Table 5, the adsorption of Cu(II) was significantly influenced by temperature increase since increase in the temperature of the environment causes a significant increase in metal removal.

Positive rates of ΔH are a strong indication of an endothermic sorption system (WAN NGAH; FATINATHAN, 2010).

According to Crini and Badot (2008), the laws of thermodynamics indicate that in a constant temperature and pressure, the ΔG value is the main criterion for the indication of system spontaneity.

Moreover, negative ΔG rates indicate the spontaneous nature of the reaction, whereas positive ΔS rates demonstrate an increase in disorder and randomness of the solid/solution interface during the sorption process, as occurred in the biosorbents under analysis (WAN; NGAH HANAFIAH, 2008).

Thus, according to rates for ΔG (Table 5), the removal of Zn(II) by the adsorbents Bark and Bagasse has a non-spontaneous and endothermic nature, while the adsorption of this metal ion by the adsorbent Bark + Bagasse becomes spontaneous at temperatures above 35°C.

Figure 6 evidences the batch temperature increase system and the consequent increase or decrease of Zn(II) adsorption.

Table 6 shows the thermodynamic parameters obtained for the removal of Cu(II) by the natural adsorbents under analysis.

In an analogous manner to the above, the ΔG and ΔH rates shown in Table 6 indicate non-spontaneous and endothermic nature for the removal of Cu(II) by the adsorbent Bark, while spontaneity of the adsorption reaction was noted for Bagasse and Bark + Bagasse

Table 5. Q_{eq} rates and the thermodynamic parameters of adsorption of Zn(II) on biosorbents bark, bagasse and bark + bagasse, C_0 = 40 mg L^{-1}.

Adsorbents	TEMP °C	Thermodynamic Parameters				
		Q_{eq} (mg g^{-1})	ΔG (kJ mol^{-1})	ΔH (J mol^{-1})	ΔS (J mol^{-1})	R^2
Bark	15	4.369	3.527	4.803	4.431	0.99
	25	4.431	3.483			
	35	4.306	3.439			
	45	4.381	3.394			
	55	4.379	3.350			
	65	4.285	3.306			
Bagasse	15	5.05	1.881	8.258	22.144	0.98
	25	5.00	1.660			
	35	5.13	1.438			
	45	5.24	1.217			
	55	5.25	0.995			
	65	5.35	0.774			
Bark + Bagasse	15	5.60	0.402	7.621	25.067	0.99
	25	5.63	0.151			
	35	5.59	-0.100			
	45	5.71	-0.350			
	55	5.68	-0.601			
	65	5.66	-0.852			

Q_{eq}: amount of metal ion adsorbed per unit of adsorbent; *ΔG*: variation of Gibbs free energy; *ΔH*: enthalpy change; *ΔS*: entropy change; R^2: coefficient of determination

Table 6. Q_{eq} rates and thermodynamic parameters of adsorption of Cu(II) on biosorbents bark, bagasse and bark + bagasse, C_0 = 40 mg L^{-1}.

Adsorbents	TEMP °C	Thermodynamic Parameters				
		Q_{eq} (mg g^{-1})	ΔG (kJ mol^{-1})	ΔH (J mol^{-1})	ΔS (J mol^{-1})	R^2
Bark	15	4.936	2.902	4.934	7.056	1.00
	25	4.620	2.831			
	35	4.643	2.761			
	45	4.620	2.690			
	55	4.718	2.620			
	65	4.747	2.549			
Bagasse	15	5.77	-0.798	3.906	16.337	0.96
	25	5.79	-0.962			
	35	5.79	-1.125			
	45	5.78	-1.288			
	55	5.68	-1.452			
	65	5.73	-1.615			
Bark + Bagasse	15	5.76	-0.732	2.806	12.284	0.99
	25	5.76	-0.854			
	35	5.72	-0.977			
	45	5.75	-1.100			
	55	5.70	-1.223			
	65	5.77	-1.346			

Q_{eq}: amount of metal ion adsorbed per unit of adsorbent; *ΔG*: variation of Gibbs free energy; *ΔH*: enthalpy change; *ΔS*: entropy change; R^2: coefficient of determination.

Conclusion

SEM analysis showed a fibrous and porous material with irregular and heterogeneous structure, with many gaps, suggesting that the adsorbent had favorable conditions for the adsorption of ions. IR analysis indicated bands O-H, C-H and C-O, suggesting the presence of hydroxyl, alkane and carbonyl groups from carbohydrates, proteins, lignin, cellulose and hemicellulose, which indicated the possible active sites for Cu(II) and Zn(II) adsorption

Results obtained in current study demonstrated that the adsorption of Cu(II) and Zn(II) occurred in monolayers and had a chemical nature. Moreover, the above-mentioned natural adsorbents provided high removal rates for the metal ions studied.

Results show that the use of solid residues from cassava agroindustry proves to be potentially viable as biosorbents in the decontamination of water bodies polluted by metal ions.

Acknowledgments

The authors would like to thank the Brazilian Council for the Upgrading of Higher Education Personnel (CAPES) and to the Universidade Estadual do Oeste do Paraná for their support and funding.

References

AGIRI, G. O.; AKARANTA, O. Adsorption of metal ions by dye treated cassava mesocarp. **Scientific Research and Essay**, v. 4, n. 5, p. 526-530, 2009.

ALMEIDA NETO, A. F.; VIEIRA, M. G. A.; DA SILVA, M. G. C. Insight of the removal of nickel and copper ions in fixed bed through acid activation and treatment with sodium of clay. **Brazilian Journal of Chemical Engineering**, v. 31, n. 4, p. 1047-1056, 2014.

ANNADURAI, G., JUANG, R. S., LEE, D. J. Adsorption of heavy metals from water using banana and orange peels. **Water Science and Technology**, v. 47, n. 1, p. 185-190, 2002.

AOAC-Association of Official Analytical Chemists. **Official methods of analysis of the Association Analytical Chemists**. Maryland: AOAC, 2005.

ATSDR-Agency for Toxic Substances and Disease Registry. **The Priority List of Hazardous Substances**. Available from: <http://www.atsdr.cdc.gov/SPL/index.html>. Access on: Apr. 7, 2015.

BARBOSA, L. C. A. **Espectroscopia no infravermelho na caracterização de compostos orgânicos**. Viçosa: UFV, 2007.

CRINI, G.; BADOT, P. M. Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature. **Progress in Polymer Science**, v. 33, n. 4, p. 399-447, 2008.

DOS SANTOS, V. C, G.; SOUZA, J. V. T. M.; TARLEY, C. R. T.; CAETANO, J.; DRAGUNSKI, D. C. Copper ions adsorption from aqueous medium using the biosorbent sugarcane bagasse *in natura* and chemically modified. **Water, Air and Soil Pollution**, v. 216, n. 1-4 p. 351-359, 2011.

DOS SANTOS, V. C. G.; SOUZA, J. V. T. M.; TARLEY, C. R. T.; CAETANO, J.; DRAGUNSKI, D. C. Assessment of chemically modified sugarcane bagasse for lead adsorption from aqueous medium. **Water Science e Technology**, v. 62, n. 2, p. 457-465, 2010.

EMBRAPA-Empresa Brasileira de Pesquisa Agropecuária. **Processamento e utilização da mandioca**. 21. ed. Cruz das Almas: Embrapa Mandioca e Fruticultura Tropical, 2005.

FENG, N.; GUO, X.; LIANG, S.; ZHU, Y.; LIU, J. Biosorption of heavy metals from aqueous solutions by chemically modified orange peel. **Journal of Hazardous Materials**, v. 185, n. 1, p. 49-54, 2011.

GONÇALVES JR., A. C.; STREY, L.; LINDINO, C. A.; NACKE, H.; SCHWANTES, D.; SEIDEL, E. P. Applicability of the Pinus bark (*Pinus elliottii*) for the adsorption of toxic heavy metals from aqueous solutions. **Acta Scientiarum. Technology**, v. 34, n. 1, p. 79-87, 2012.

GONÇALVES Jr., A. C.; NACKE, H.; SCHWANTES, D.; NAVA, I. A.; STREY, L. Phytoavailability of toxic heavy metals and productivity in wheat cultivated under residual effect of fertilization in soybean culture. **Water Air Soil Pollution**, v. 220, p. 205-211, 2011.

GONÇALVES Jr., A. C.*; SELZLEIN, C.; NACKE, H.* Uso de biomassa seca de aguapé (*Eichornia crassipes*) visando à remoção de metais pesados de soluções contaminadas. **Acta Scientiarum. Technology**, v. 31 n. 1, p. 103-108, 2009.

GUO, X.; ZHANG, S.; SHAN, X. Adsorption of metal ions on lignin. **Journal of Hazardous Materials**, v. 151, n. 1, p. 134-142, 2008.

GUPTA, S. S.; BHATTACHARYYA, K. G. Kinetics of adsorption of metal ions on inorganic materials: A review. **Advances in Colloid and Interface Science**, v. 162, n. 1-2, p. 39-58, 2011.

HAN, R.; ZHANG, L.; SONG, C.; ZHANG, M.; ZHU, H.; ZHANG, L. Characterization of modified wheat straw, kinetic and equilibrium study about copper ion and methylene blue adsorption in batch mode. **Carbohydrate Polymers**, v. 79, p. 1140-1149, 2010.

HORN, M. M.; MARTINS, V. C. A.; PLEPIS, A. M. G. Effects of starch gelatinization and oxidation on the rheological behavior of chitosan/starch blends. **Polymer international**, v. 60, n. 6, p. 920-923, 2011.

HORSFALL JR., M.; ABIA, A. A.; SPIFF, A. I. Kinetic studies on the adsorption of C(II), Cu(II) and Zn(II) ions from aqueous solutions by cassava (*Manihot sculenta* Cranz) tuber bark waste. **Bioresource Technology**, v. 97, n. 2, p. 283-291, 2006.

LIMA, A. J. B.; CARDOSO, M. G.; GUERREIRO, M. C.; PIMENTEL, F. A. Using activated carbon to remove copper from sugar cane spirit. **Química Nova**, v. 2, n. 29, p. 247-250, 2006.

LIN, S. H.; JUANG, R. S. Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents: A review. **Journal of Environmental Management**, v. 90, n. 3, p. 1336-1349, 2009.

MIMURA, A. M. S.; VIEIRA, T. V. A.; MARTELLI, P. B.; GORGULHO, H. F. Aplicação da casca de arroz na adsorção dos íons Cu^{+2}, Al^{+3}, Ni^{+2} e Zn^{+2}. **Química Nova**, v. 33, n. 6, p. 1279-1284, 2010.

MONTANHER, S. F.; OLIVEIRA, E. A.; ROLLEMBERG, M. C. Removal of metal ions from aqueous solutions by sorption onto rice bran. **Journal of Hazardous Materials**, v. 117, n. 2-3, p. 207-211, 2005.

MORENO-PIRAJÁN, J. C.; GIRALDO, L. Adsorption of copper from aqueous solution by activated carbons obtained by pyrolisis of cassava peel. **Journal of Analytical and Applied Pyrolysis**, v. 87, n. 2, p. 188-193. 2010.

PADURARU, C.; TOFAN, L.; TEODOSIU, C.; BUNIA, I.; TUDORACHI, N.; TOMA, O. Biosorption of zinc(II) on rapeseed waste: Equilibrium studies and thermogravimetric investigations. **Process Safety and Environmental Protection**, v. 94, p. 18-28, 2015.

PASCOAL NETO, C.; ROCHA, J.; GIL, A.; CORDEIRO, N.; ESCULCAS, A. P.; ROCHA, S.; DELGADILLO, I.; DE JESUS, J. D.; CORREIA, A. J. 13C solid-state nuclear magnetic resonance and Fourier transform infrared studies of the thermal decomposition of cork. **Solid State Nuclear Magnetic Resonance**, v. 4, n. 3, p. 143-151, 1995.

PASTORE, T. C. M.; SANTOS, K. O.; RUBIM, J. C. A spectrocolorimetric study on the effect of ultraviolet irradiation of four tropical hardwoods. **Bioresource Technology**, v. 93, n. 1, p. 37-42, 2004.

PEHLIVAN, E.; ALTUN, T.; CETIN, S.; BHANGER, M. I. Lead sorption by waste biomass of hazelnut and almond shell. **Journal of Hazardous Materials**, v. 167, n. 1-3, p. 1203-1208, 2009.

PEÑA-RODRÍGUEZ, S.; FERNÁNDEZ-CALVIÑO, D.; NÓVOA-MUÑOZ, J. C.; ARIAS-ESTÉVEZ, M.; NÚÑEZ-DELGADO, A.; FERNÁNDEZ-SANJURJO, M. J.; ÁLVAREZ-RODRÍGUEZ, E. Kinetics of Hg (II) adsorption and desorption in calcined mussel shells. **Journal of Hazardous Materials**, v. 180, n. 1-3, p. 622-627. 2010.

SCHIMMEL, D.; FAGNANIL, K. C.; OLIVEIRA DOS SANTOS, J. B.; BARROS, M. A. S. D.; ANTONIO DA SILVA, E. Adsorption of turquoise blue QG reactive bye commercial activated carbon in batch reactor: kinetic and equilibrium studies. **Brazilian Journal of Chemical Engineering**, v. 27, n. 2, p. 289-298, 2010.

SCHWANTES, D.; GONÇALVES Jr., A. C.; STREY, L.; SCHWANTES, V.; NACKE, H. Kinetics, equilibrium and thermodynamics of the adsorption process of lead using cassava industry wastes. In: BÁRTOLO, H.; DUARTE, J. P. (Org.). **Green design, materials and manufacturing process**. Boca Raton: CRC Press Taylor and Francis Group, 2013. p. 417-422.

SEOLATTO, A. A.; CÂMARA, M. M.; TAVARES, C. R.; COSSICH, E. S.; DA SILVA, E. A. Remoção de níquel(II) de soluções aquosas pela biomassa *Sargassum filipendula* em múltiplos ciclos de sorção-dessorção. **Acta Scientiarum. Technology**, v. 31, n. 1, p. 57-64, 2009.

SHARMA, P.; KUMARI, P.; SRIVASTAVA, M. M.; SRIVASTAVA, S. Removal of cadmium from aqueous system by shelled *Moringa oleifera* Lam. seed powder. **Bioresource Technology**, v. 97, n. 2, p. 299-305, 2006.

STUART, B. H. **Infrared spectroscopy**: fundamentals and applications. Sidney, Australia: John Wiley and Sons, Inc., 2004.

TAGLIAFERRO, G. V.; PEREIRA, P. H. F.; RODRIGUES, L. A.; DA SILVA, M. L. C. P. Cadmium, lead and silver adsorption in hydrous niobium oxide prepared by homogeneous solution method. **Química Nova**, v. 34, n. 1, p. 101-105, 2011.

TANG, X.; ZHANG, Q.; LIU, Z.; PAN, K.; DONG, Y.; LI, Y. Removal of Cu(II) by loofah fibers as a natural and lo-cost adsorbent from aqueous solutions. **Journal of Molecular Liquids**, v. 199, p. 73-78, 2014.

VALDMAN, E.; ERIJMAN, L.; PESSOA, F. L. P.; LEITE, S. G. F. Continuous biosorption of Cu and Zn by immobilized waste biomass *Sargassum sp.* **Process Biochemistry**, v. 36, n. 8-9, p. 869-873, 2001.

WAN NGAH, W. S. W.; HANAFIAH, M. A. K. M. Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. **Bioresource. Technology**, v. 99, n. 10, p. 3935-3948, 2008.

WAN NGAH, W. S.; FATINATHAN, S. Adsorption characterization of Pb(II) and Cu(II) ions onto chitosan-tripolyphosphate beads: Kinetic, equilibrium and thermodynamic studies. **Journal of Environmental Management**, v. 91, n. 4, p. 958-969, 2010.

WELZ, B.; SPERLING, M. **Atomic absorption spectrometry**. 2nd ed. Weinheim: Wiley-VCH, 1999.

Received on February24, 2015.
Accepted on April 22, 2015.