

CHARACTERIZATION AND USE OF *IN NATURA* AND CALCINED RICE HUSKS FOR BIOSORPTION OF HEAVY METALS IONS FROM AQUEOUS EFFLUENTS

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Abstract - Heavy metal removal by adsorption using rice husks as a bioadsorbent was evaluated as an alternative for wastewater treatment. Batch equilibrium experiments and kinetic sorption studies were performed using monocomponent solutions of Ni(II), Cd(II), Zn(II), Pb(II) and Cu(II) in surface samples of *in natura* (RH) and calcined rice husks (RHA). RHA showed higher potential for removing lead and copper. Experimental data for adsorption isotherms of lead and copper were adjusted by Langmuir, Freundlich and Dubinin-Radushkevich (D-R) models, being better represented by the Langmuir model. The calcination of RH increased its surface area, improving its adsorption properties. From a morphological analysis obtained by SEM and diffraction patterns (XRD), a longitudinal fibrous and amorphous structure was observed for RH. TGA results indicated a total mass loss of around 60% for RH and 24.5% for RHA.

Keywords: Rice husks; Heavy metals; Biosorption.

INTRODUCTION

Industrial and domestic effluents, as well as indiscriminate application of pesticides/herbicides to crop fields have contributed to the deterioration of environmental quality. Among these pollutants, heavy metals represent a special group because they are not chemically or biologically degraded in a natural manner.

Nowadays, with the aim of reducing waste residue generation in industrial and agricultural processes and improving reuse of these in the production process, companies are investing more

in research in order to transform them into commercially interesting by-products.

Rice is one of the most commonly grown and consumed grains in the world. It is considered to be the most economically important product in many developing countries, being a staple food for billions of people. World production for the 2008 crop was 661.3 million tons (Fao, 2010). Brazil ranks 10th in the production of this cereal.

During the processing of rice, the most voluminous by-product is husks, which represent about 20% of rice weight. Rice husk (RH) is a fibrous material, composed mainly of cellulose,

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lignin and inorganic and organic compounds. Rice husk ash (RHA) is a light material, bulky, porous and amounts to about 20% of the burnt husk.

Several technological alternatives have been associated in the literature with the use of RH and RHA: production of silica and silicon carbide, using the ashes like filler in polymers, in concrete, production of silicates, zeolite synthesis (Chumee *et al.*, 2009) and use as an adsorbent of heavy metals in synthetic wastewater (Srivastava *et al.*, 2006; Naiya *et al.*, 2009; Krishnani *et al.*, 2008; Tarley and Arruda, 2004; Ye *et al.*, 2010; Bhatnagar and Sillanpaa, 2010; Ahmaruzzaman, 2010).

The use of RH for the sorption of metals in aqueous solution has been recently discussed due to its low cost, abundance, easy availability and possibility of reuse (Vieira *et al.*, 2011; Kumar *et al.*, 2010; Giraldo and Moreno-Piraján, 2008). Studies on metal removal using different adsorbents, such as clays (Vieira *et al.*, 2010 a, b; Jiang *et al.*, 2009), zeolites, sugarcane bagasse and other materials (Bhatnagar and Sillanpaa, 2010; Ahmaruzzaman, 2010; Gupta and Ali, 2004; Farooq *et al.*, 2010; Garg *et al.*, 2008; Kalderis *et al.*, 2008; Sud *et al.*, 2008) have been reported in the literature.

In this context, this work characterizes the *in natura* (RH) and calcined rice husks (RHA) from northern Brazil, as well as evaluates the potential of this material as a bioadsorbent for the removal of heavy metals (Ni, Cu, Cd, Zn and Pb) through chemical affinity tests and investigations of the removal of adsorbed metals. Batch equilibrium experiments and kinetic sorption studies were performed using solutions of the metals that presented better chemical affinity.

MATERIALS AND METHODS

Oryza sativa L. rice husks from Boa Vista – RR, Amazon region, Brazil, were used as bioadsorbent. The rice husks were ground in a food processor and calcined at 500 °C in a muffle oven for 1 hour. This temperature was defined based on thermogravimetric analysis results.

Characterization

The physical–chemical characterization of RH and RHA was performed by Scanning Electron Microscopy (SEM) coupled to energy-dispersive X-ray spectroscopy (EDX) (Oxford, model 7060). This analysis also allows the overall chemical composition of a solid to be identified and qualified.

The surface area and volume of the pores were obtained by N₂ physisorption at 77 K. These analyses were performed with a Micromeritics Gemini III 2375 Surface Area Analyzer using the BET method.

X-ray diffraction powder patterns for the identification of particular peaks and to confirm the maintenance of its properties after calcination were obtained with samples in powder form (< 0.074 mm), copper K α radiation, voltage 40 kV, 40 mA current, step size of 0.02°, step time of 1s and 2 θ range of 3–50°. The FTIR studies were carried out using a Bomem-MB102 spectrometer (ABB-Bomem). The spectra were acquired in the range of 4000 to 400 cm⁻¹ at a resolution of 4 cm⁻¹.

Thermal analyses (TG, DTG and DSC) were carried out on a Shimadzu TGA-50 in a N₂ atmosphere (50 mL/min) at a heating rate of 10 °C/min. The samples were put in platinum pans and scanned from room temperature to 1000 °C. Helium pycnometry analysis was performed using an Accupyc 1330 equipment (Micromeritics) at 31 °C and an equilibration rate of 0.005 psig/min. The moisture content of *in natura* rice husks was obtained by gravimetric analysis (105 °C, 24 h.) in an oven with air circulation (TECNAL, model TE – 394/1). These analyses were performed to find out the physicochemical properties, aiming specifically at the application of rice husks for the removal of heavy metals.

pH_{ZPC}

The pH_{ZPC} corresponds to the zero-point charge pH of solid elements in suspension and was obtained using the potentiometric titration method (Davranche *et al.*, 2003). The titration was carried out with 0.5 M CH₃COOH and 0.5 M NH₄OH.

For each point of the titration, the charge density (Q [Coulomb/cm²]) was calculated according to the equation:

$$Q = \frac{C_a - C_b + [\text{OH}^-] - [\text{H}^+]}{A \cdot C_m} \cdot F \quad (1)$$

where C_a and C_b are the corrected concentrations (mol/L) of acid and base, respectively, and C_m is the solid concentration in suspension (g/L).

The charge density was calculated from the Q values divided by the BET areas of each material and multiplying this value by Faraday's constant. According to CODATA (2008), the best value for this constant is 96,485.3399 Coulomb/mol. The

pH_{ZPC} value of the solid is the pH where the curve crosses the x axis (load density = 0).

Determination of Cation Exchange Capacity (CEC)

The Cation Exchange Capacity (CEC) of RH and RHA was performed in triplicate and was obtained from the Na^+ concentration in NH_4OH exchange solutions, determined by Atomic Absorption (Perkin Elmer®) and expressed in meq/100g of solid according to the following equation:

$$CEC = \frac{C_{Na^+} \cdot V}{10 \cdot m \cdot f} \quad (2)$$

where C_{Na^+} is the Na^+ concentration measured by atomic adsorption (mg/L), V is the volume of ammonium acetate 3M (mL), m is the sample mass (g) and f is the conversion factor of sodium to equivalents.

Experimental Procedure

Metal speciation diagrams were obtained by using the programs Hydra and Medusa (Puigdomenech, 2004) for the metals evaluated in preliminary tests of affinity; batch equilibrium experiments and kinetic sorption studies were performed using monocomponent solutions of Ni(II), Cd(II), Zn(II), Pb(II) and Cu(II) in surface samples of *in natura* and calcined rice husks. RHA showed higher potential for removing lead and copper.

Chemical Speciation and Affinity Tests

Chemical speciation diagrams of Ni, Cu, Cd, Zn and Pb based on pH were simulated using the applications Hydra and Medusa (Puigdomenech, 2004) in order to identify the different species in aqueous medium and determine the metal solution pH at which the cations of these metals do not precipitate. Speciation was obtained for various concentrations of ionic chemical species and considering the stoichiometric ratios of the salts of the metals used.

Preliminary assays of affinity (metal-adsorbent) were performed with 1 g of RH and RHA, both with a particle size of 0.855 mm, in a batch thermostatic system (24 °C) under continuous stirring at 225 rpm for 12 hours and in contact with 100 mL of metal solution in 250-mL Erlenmeyer flasks.

The initial metal concentrations were determined by metal speciation: 50 mg/L (0.76 mM) for Zn and

100 mg/L for Cu (1.57 mM), Cd (0.89 mM), Ni (1.70 mM) and Pb (0.48 mM). The pH of the solutions was adjusted using 0.2 M HNO_3 or 0.25 M NH_4OH . All the chemicals used were of Analytical grade. Table 1 presents the pH ranges obtained from metallic speciation.

Table 1: pH range for chemical precipitation of Ni, Cu, Cd, Zn and Pb.

Metal	Concentration in mg/L (mM)	pH range
Zn	50 (0.76)	5.0 – 8.5
Cu	100 (1.57)	5.2 – 6.5
Cd	100 (0.89)	8.2 – 9.5
Ni	100 (1.70)	6.5 – 8.0
Pb	100 (0.48)	5.5 – 7.0

Kinetic Adsorption

Kinetic adsorption assays were performed in batch for Pb and Cu ions on RHA, which presented higher removal in preliminary assays of metal-adsorbate affinity. The adsorption kinetics study of Pb and Cu was carried out under the following conditions:

At specific time intervals, solution aliquots were removed and centrifuged. The supernatant liquid was diluted and its concentration was determined by atomic absorption spectrometry (Perkin Elmer AA Analyst 100). The concentrations of metal ion in the solid phase (q) at each instant of time were obtained by Equation (3):

$$q(t) = \frac{V}{m}(C_0 - C(t)) \quad (3)$$

where C_0 is the initial concentration of metal ion in fluid phase [mmol/L], $C(t)$ [mmol/L] is the concentration of metal ion in solution at time t [min], V [mL] is the solution volume and m is the mass of RHA [g].

Removal percentage (%Rem) was calculated by Equation (4):

$$\% \text{ Rem} = \left(\frac{C_0 - C_e}{C_0} \right) \cdot 100 \quad (4)$$

where C_e is the metal ion concentration in solution at equilibrium.

The pH of the solutions was defined based on the chemical speciation (4.5 for Pb and 4.0 for Cu) to ensure that only the adsorption process will occur and was adjusted using 0.2 M HNO_3 or 0.25 M

NH₄OH when necessary to maintain the set pH values.

All experiments were carried out in duplicate and the maximum deviation was found to be less than 3 %.

Equilibrium Study

Adsorption isotherms of Cu and Pb on RHA were obtained at room temperature. The equilibrium study was conducted only for adsorption of Pb and Cu ions on RHA, according to the fraction of metal removed and the results of removal percentage obtained in metal-adsorbate affinity assays.

The experiments were performed in batch using 250-mL Erlenmeyer flasks, in which 1 g of calcined rice husks was added to 100 mL of metal solution at different concentrations. The mixture was agitated in a shaker at controlled temperature and the desired speed (225 rpm) for predetermined time intervals (600 min. for Cu and 1000 min. for Pb). The experimental time intervals were based on the results of kinetic assays. The supernatant was separated by centrifugation at 5000 rpm for 10 min. The residual concentration was determined as previously presented. The pH was kept constant at 4.5 for Pb and 4.0 for Cu.

Isotherm data were correlated by the Langmuir (Eq. (5)), Freundlich (Eq. (6)) and Dubinin-Radushkevich (D-R) (Eq. (7)) isotherm models, at initial concentrations ranging from 5 to 800 ppm for Pb and from 5 to 400 ppm for Cu:

Langmuir Isotherm

$$q_{\text{eq}} = \frac{q_m \cdot b \cdot C_{\text{eq}}}{1 + b \cdot C_{\text{eq}}} \quad (5)$$

in which C_{eq} [mmol/L] and q_{eq} [mmol/g] are, respectively, the concentrations of metal ions in the liquid and solid phase; b [L/g] and q_m [mmol/g] are the Langmuir coefficients that represent the adsorbate-adsorbent equilibrium constant and the maximum adsorbed capacity for a monolayer, respectively.

Freundlich Isotherm

$$q_{\text{eq}} = (K_f \cdot C_{\text{eq}})^n \quad (6)$$

in which K_f and n are Freundlich coefficients. Freundlich isotherms describe the heterogeneous surface energies by multilayer sorption.

Dubinin-Radushkevich Isotherm (D-R)

The Dubinin-Radushkevich isotherm (D-R) (Eq. (7)) is commonly used to describe monocomponent solution sorption. The D-R isotherm is more general than the Langmuir isotherm because it rejects the assumption of a homogeneous surface and constant potential adsorption (Kilisioglu and Bilgin, 2003):

$$\ln(q_{\text{eq}}) = \ln(q_m) - \beta \cdot \varepsilon^2 \quad (7)$$

in which β is a constant related to the free energy of sorption (E) in mol²/J², and ε is the Polanyi potential, given by Equation (8):

$$\varepsilon = RT \cdot \ln\left(1 + \frac{1}{C}\right) \quad (8)$$

where R is the universal ideal gas constant [J/mol.K] and T is the temperature [K].

The sorption free energy E [J/mol] can be calculated using Equation (9) (Akar *et al.*, 2009; Sljivic *et al.*, 2009; Dubey and Gupta, 2005; Ho *et al.*, 2002).

$$E = \frac{1}{\sqrt{2\beta}} \quad (9)$$

RESULTS AND DISCUSSION

Characterization

X-Ray Diffraction (XRD)

The X-ray diffraction patterns of RH and RHA are presented in Figure 1. RHA presented lower crystallinity than RH, although important changes in the diffractogram were not observed after calcinations.

In Figure 1, two peaks can be observed for RH and RHA: one between 15 and 35° 2 θ , which indicates the presence of amorphous silica, and another between 40 and 50° 2 θ , which corresponds to carbon (Krishnarao *et al.*, 2001). This peak was also observed by Krishnarao *et al.* (2001) and its intensity increased when the sample was suddenly heated. The authors proposed a treatment of RH with different concentrations of hydrochloric acid in order to obtain RHA with a high percentage of silica. The treated and untreated RH were in an amorphous state and retained the amorphous structure after calcination.

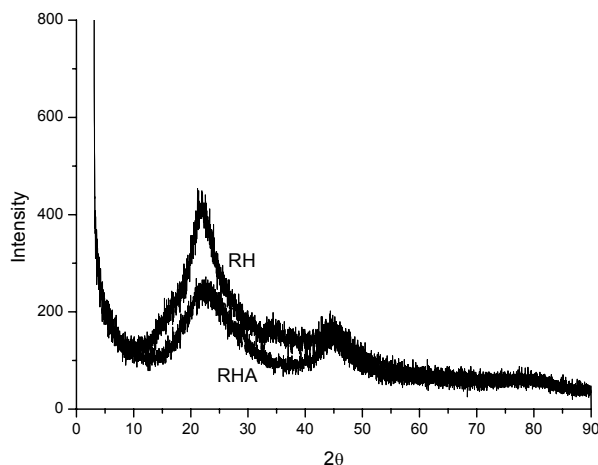


Figure 1: Diffractogram of RH and RHA.

Considering the angles that correspond to the silica and carbon peaks and applying Bragg's law ($n\lambda=2d \sin \theta$) with λ of 1.542 Å, d values are obtained, which represents the basal interlayer distances. RH and RHA samples presented the silica peak, at incidence angles (2θ) of 21.75 and 22.09, or values of basal interlayer distances of 4.08 and 4.02 Å, respectively. The carbon peak at incidence angles (2θ) between 44.25 and 44.30 corresponded to basal interlayer distances of 2.05 and 2.04 Å, respectively.

Fourier Transform Infrared Spectroscopy

The FT-IR spectra for RH and RHA samples are shown in Figure 2. From the FTIR spectra, there are bands in the OH stretching region at 3440 (for RH) and 3427 cm^{-1} (for RHA). This stretch is due to the silanol group (SiOH) and to the water adsorbed on the surface (Tarley and Arruda, 2004; Nakbanpote *et al.*, 2007; Tarley *et al.*, 2004). The presence of methyl groups is observed between 2915 and 2847 cm^{-1} for RH and between 2920 and 2855 cm^{-1} for RHA due to the presence of lignin (Tarley *et al.*, 2004). Between 1725 and 1635 cm^{-1} a stretch of aldehydes and ketones is observed for the RH sample, whereas in the RHA sample spectrum it occurs at 1610 cm^{-1} . The stretching of aromatic rings is observed at 1515 cm^{-1} for RH samples and at 1425 cm^{-1} for RHA samples (Tarley and Arruda, 2004). In both samples the presence of Si-O-Si groups is observed at 1100 cm^{-1} (Nakbanpote *et al.*, 2007; Tarley *et al.*, 2004). The bands between 800 and 468 cm^{-1} for RH and between 800 and 459 cm^{-1} for RHA suggest the presence of Si-H bonds (Srivastava *et al.*, 2006; Nakbanpote *et al.*, 2007).

The FTIR spectra did not show any significant changes between RH and RHA samples, i.e., calcination practically did not change the structure of rice husks.

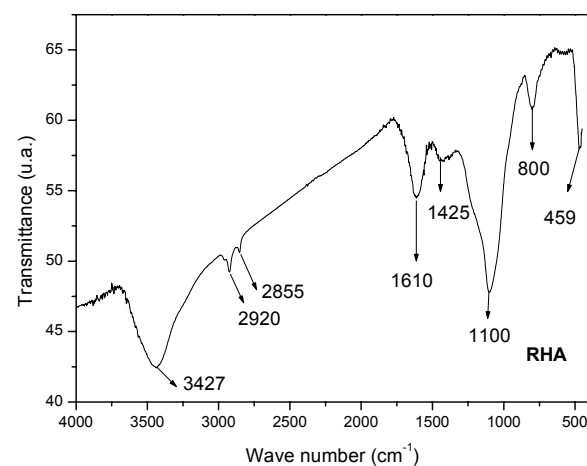
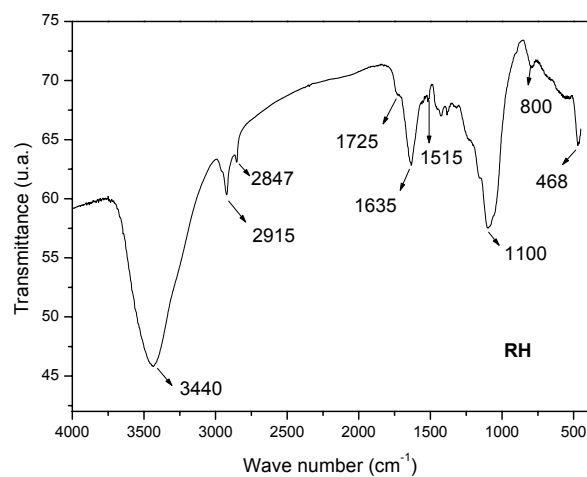


Figure 2: FTIR spectra of RH and RHA.

Thermogravimetric Analysis (TG, DTG and DSC)

The thermogravimetric analysis results for RH and RHA are presented in Figure 3(a) and 3(b). For RH (Figure 3(a)), there is a loss of initial mass of about 6%, equivalent to water and volatile material losses from the sample and a total mass loss of about 60%, of which 54% corresponds to the second loss, i.e., the beginning of ash formation by volatilization of organic compounds.

The burning of organic material (hemicellulose and most of the cellulose) begins at approximately 280 °C and extends up to 350 °C. Between 350 and 600 °C the decomposition of lignin occurs. From the moment that the percentage of mass reaches the

second level, all of the organic part of the bark has been burned, leaving mainly inorganic compounds, e.g., silicon oxide, which is more stable at high temperatures. Tarley and Arruda (2004) observed the decomposition of hemicellulose and cellulose between 250 and 360 °C and the decomposition of lignin between 360 and 525 °C. The calcination temperature was defined as 500 °C, according to the TG curve of RH, since the entire rice husk had been burnt. The rice husks were calcined in a muffle furnace for 1 hour.

For RHA (Figure 3(b)), there is an initial mass loss of approximately 2.5% between 25 and 150 °C. The total mass loss is around 24.5%, with a clear reduction in the mass loss of RHA compared to RH.

Between 400 and 800 °C there is a greater mass loss, around 22%, due to loss of constitutive water, volatile materials and carbon combustion. Tarley and Arruda (2004) observed the highest mass loss (20.5%) between 300 and 600 °C.

The DSC curves of RH and RHA samples shown in Figure 3(c) exhibit heat absorption due to loss of volatile materials and water of constitution at 77 °C for RH and at 96 °C for RHA. Two enthalpy changes were observed for RH at 300 and 319 °C, corresponding to heat absorption due to the loss of organic material from the sample. Comparing both DSC curves obtained, the RH curve presented a reduction in the endothermic band at 77 °C, sharper than in the RHA curve.

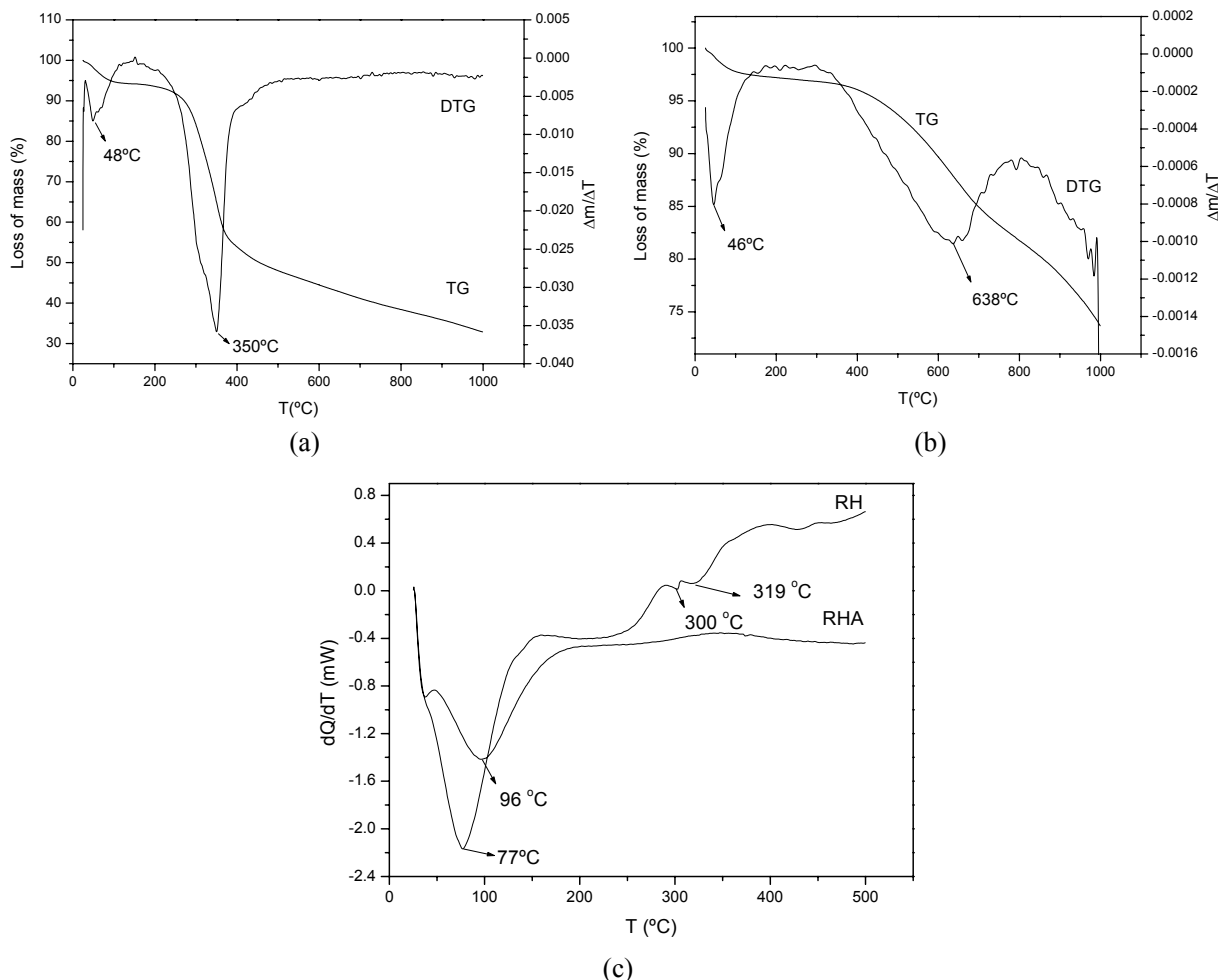


Figure 3: (a) TG and DTG curves of RH and (b) RHA; (c) DSC curves of RH and RHA.

Scanning Electron Microscopy (SEM)

The morphological analysis of RH and RHA particles by Scanning Electron Microscopy provided the micrographs shown in Figure 4. In the micrographs presented in Figure 4 (a), (b) and (c), it is possible to observe the fibrous and longitudinal structure of rice husks. Additionally, it is possible to see the difference between the roughness of the particle outer film (Figure 4(a)), the area with the largest percentage of silica, and the smooth appearance of the inner film, the area with the highest content of cellulose and lignin, the main organic compounds of RH.

According to Tarley and Arruda (2004), the material (adsorbent) morphology may facilitate the

adsorption of metals in different parts of this material. Therefore, based on morphology, as well as the fact that the highest concentration of silica is present in the outer film of RH, this material presents a morphological profile with the potential to retain metal ions.

In the micrographs presented in Figure 4 (d), (e) and (f), it is possible to observe an external morphology similar to that of *in natura* rice husks, Figure 4(d), besides ripples in the outer film (Figure 4(e)). Amick (1982) reported that the elongated and contorted shape, like a corncob, is caused by the burning process (Figure 4(d)). Figure 4(f) shows in more detail the outer film, with a thick cuticle of silicified cells, and the porous inner film of one of the RHA particles.

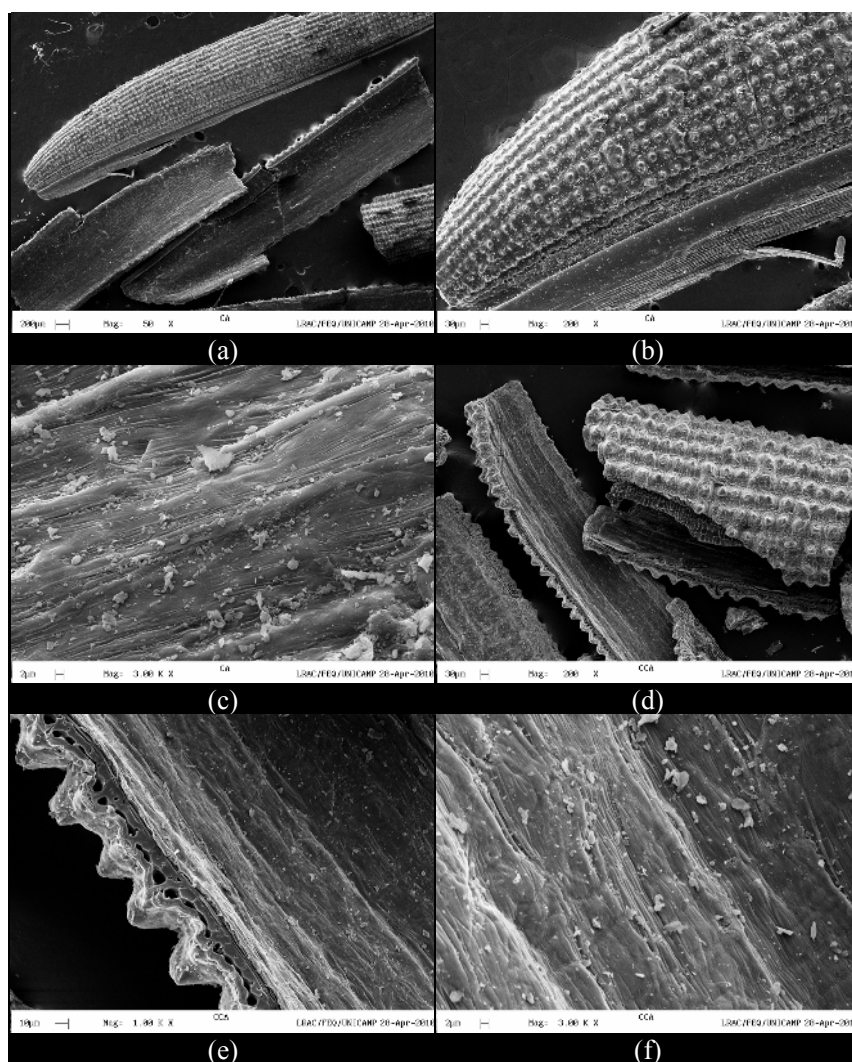


Figure 4: SEM micrographs of RH: (a) Inner and outer film (50x. mag.); (b) Morphological structure (200x. mag.); (c) and (d) (3000x. mag.); and RHA: (d) Inner and outer film (200x. mag.); (e) Morphological structure of the inner film of RHA (1000x. mag.) and (f) (3000x. mag.).

N₂ Physisorption (BET)

The results obtained by the BET method for the surface area of RH and RHA are shown in Table 2, with their respective N₂ adsorption and desorption isotherms (Figure 5(a)) and pore diameters based on the increment of intrusion presented in Figure 5(b). Table 2 shows that the calcination of RH results in an increase in surface area. This fact shows that RHA has a greater capacity to adsorb ions on its surface in relation to RH. A similar result was obtained by Nakata *et al.* (1989) for RHA calcined at 800 °C.

Real *et al.* (1996) developed a process to obtain pure silica from RH with high surface area. The authors conducted assays in baths with hydrochloric acid solution; ash with low surface area (< 1.0 m²/g) with the acid treatment resulted in a surface area of 260 m²/g, when calcined at 600 °C and of 211 m²/g,

when calcined at 800 °C. These surface area values may be due to the interaction of silica with impurities during the combustion process, particularly the K⁺ ion.

Table 2: Surface area of RH and RHA obtained by the BET equation.

Rice Husks	Surface Area (m ² /g)
<i>In natura</i>	1.4
Calcined at 500 °C	5.7

The isotherms obtained for RH and RHA belong to type II according to the classification of IUPAC for isotherms of physical sorption, i.e., they were characterized by hysteresis loops, as expected for mesoporous materials. Figure 5(a) (left) shows the desorption curve back to the origin under the adsorption curve.

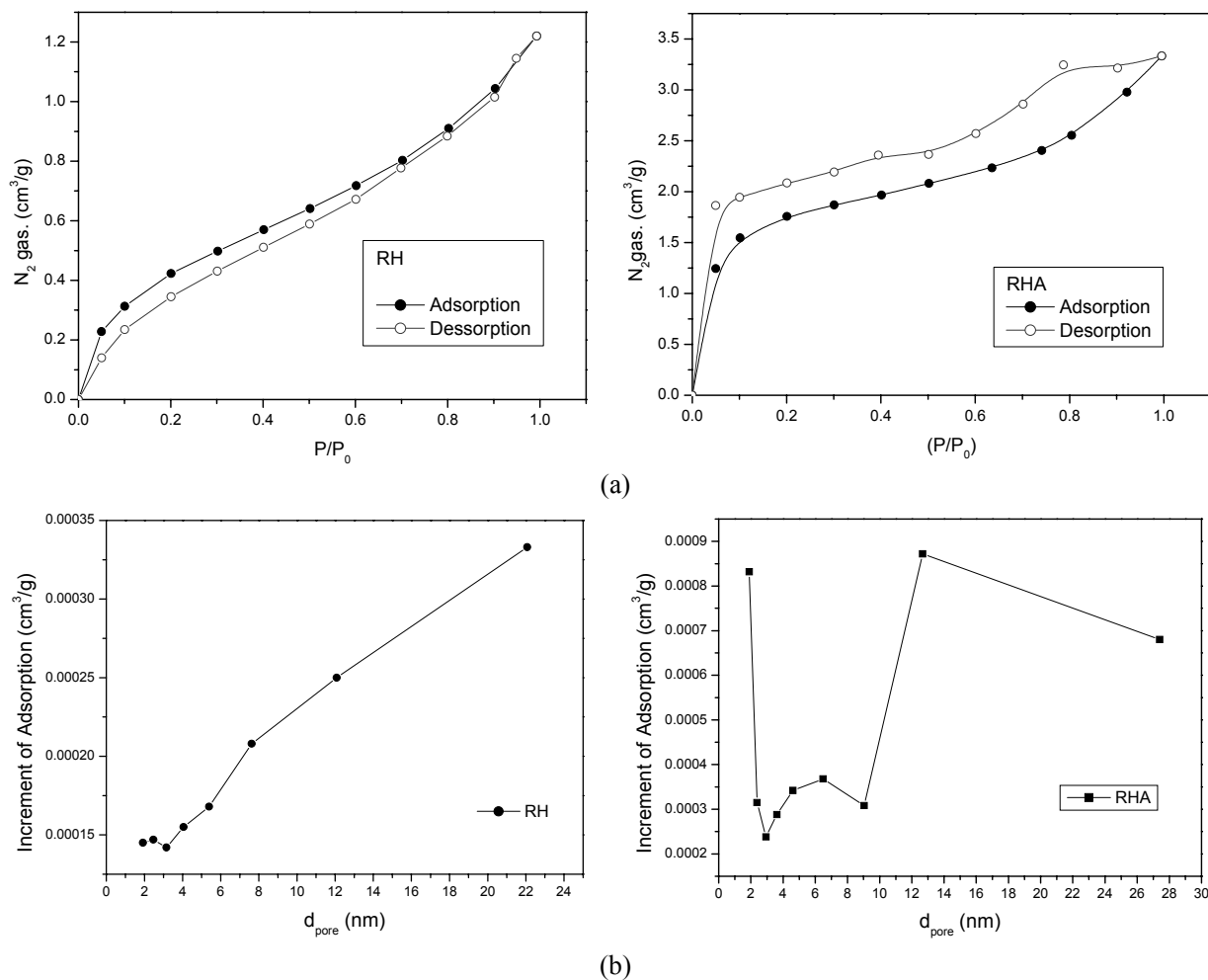


Figure 5: (a) Adsorption isotherms and N₂ desorption of RH and RHA; (b) Increase in adsorption *versus* pore diameter of RH ($d_p < 200$ mesh) and RHA ($d_p = 0.855$ mm).

According to Rouquerol *et al.* (1999) this desorption is associated with significantly weaker interactions. From the isotherm curves (Figure 5(a), right), it is possible to observe that the position of the desorption isotherm of N_2 deviates even more from the position of the adsorption isotherm of RHA. This indicates that the calcination increases the surface area and also the phenomenon of hysteresis, which characterizes the irreversibility of the sorption process. According to IUPAC, the loop hystereses are classified as type H3, typical of slitlike mesopores formed by platelike particles or layers of globular agglomerates.

Pore sizes are classified in accordance with the classification adopted by IUPAC (1985). From Figure 5(b), the distribution of mesopore diameters obtained by the BJH method is within the range between approximately 2 and 22 nm for RH and between 2 and 28 nm for RHA.

Real and Bulk Densities

The real and bulk density values for RH and RHA are found in Table 3. Based on the results, calcination reduces the values of real and bulk densities of RHA compared to RH. The dehydration suffered by RH during calcination causes a mass loss per unit volume. The values of bulk density obtained in this study are in the range of values found in the literature (Srivastava *et al.*, 2006; Naiya *et al.*, 2009).

Table 3: Real and Bulk densities of RH and RHA.

Sample	Real Density (g/cm^3)	Bulk Density (g/cm^3)
RH	3.6540 ± 0.1006	0.2749 ± 0.0008
RHA	1.4717 ± 0.0023	0.1737 ± 0.0021

Moisture Content

The value obtained for the moisture content of RH samples was $7.1210 \pm 0.1244\%$, close to the

values found in the literature (3.0% of residual moisture) (Della *et al.*, 2001).

Determination of pH_{ZPC}

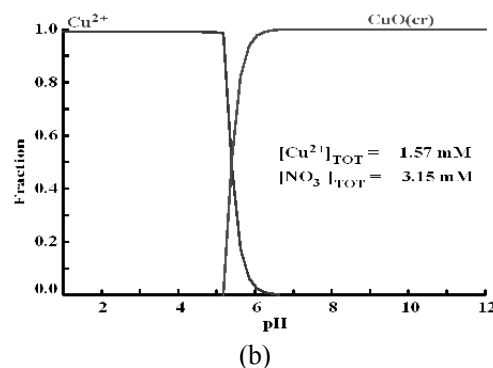
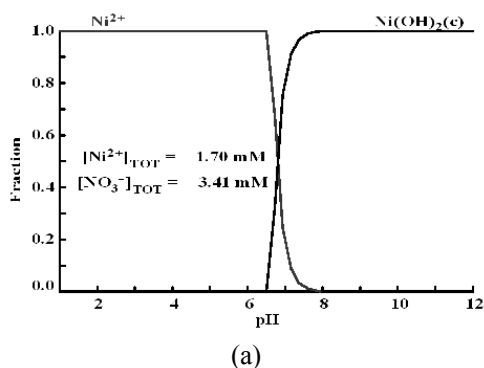
The values of pH_{ZPC} obtained for RH and RHA are, respectively, 6.45 and 7.45. Thus, with the aim of ensuring that the surface of rice husks presented zero or negative charge, being more favorable for the adsorption of metal ions with positive charge, the pH of the adsorbate solution should be kept above the values 6.45 and 7.45 for RH and RHA, respectively. However, the adsorption tests were conducted at pH 4.5 due to metal speciation, indicating that the adsorption in this case did not occur due to electrical forces, but due to Van der Waals forces.

Determination of Cation Exchange Capacity (CEC)

The results of CEC for RH and RHA were respectively: 30.724 ± 2.46 meq/100g and 57.391 ± 4.26 meq/100g. Calcined rice husks have approximately twice the cation exchange capacity compared to RH, being more favorable for use as adsorbent in heavy metal removal.

Chemical Speciation

The speciation diagrams in Figure 6 present the distribution of metal species for Ni, Cu, Cd, Zn and Pb as a function of pH in aqueous solution. The diagrams show the concentrations in which the metal species are in the +2 oxidation states without the presence of other chemical species: 1.70 mM for Ni, 1.57 mM for Cu, 0.89 mM for Cd, 0.76 mM for Zn and 0.48 mM for Pb. These chemical species are constant and there is no formation of other ionic species until the pH is approximately equal to 6.0, 5.0, 7.5; 4.5 and 5.0, respectively.



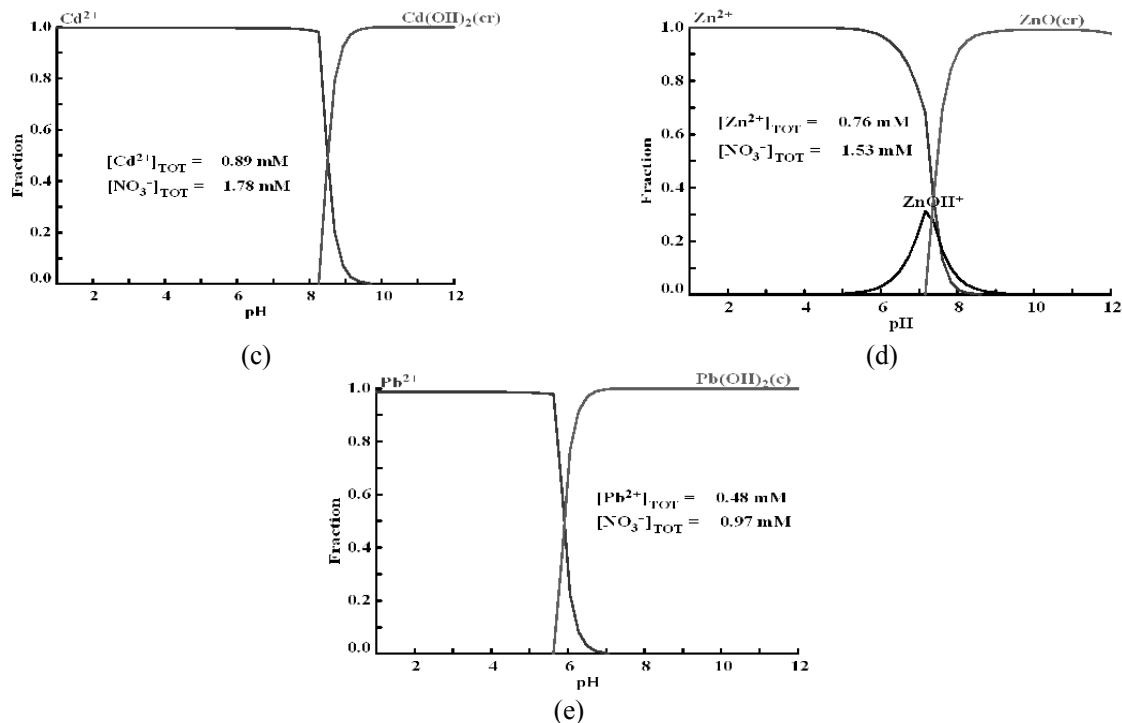


Figure 6: Metallic speciation curves of (a) Ni; (b) Cu; (c) Cd; (d) Zn and (e) Pb.

Metal-Adsorbate Affinity

Table 4 presents the results for Cu, Cd, Ni, Pb and Zn removal by RH and RHA. The highest removal percentages were obtained for lead and copper in RHA. Based on these results, kinetic and equilibrium assays were performed for copper and lead, which had high affinity for the calcined rice husks.

Table 4: Fraction of metal removed and removal percentage.

System	q (mg/g)*	% Removal*	System	q (mg/g)*	% Removal*
Cu/RHA	3.25	30.65	Cu/RH	2.376	22.41
Zn/RHA	1.1	19.10	Zn/RH	0.905	15.71
Cd/RHA	0.45	4.04	Cd/RH	1.975	17.74
Ni/RHA	0	0	Ni/RH	0	0
Pb/RHA	6.69	63.81	Pb/RH	6.41	61.14

* Mean value

The adsorption kinetics of lead and copper ions by RHA at the concentration of 100 mg/L (0.48 mM for Pb and 1.57 mM for Cu, according to the study of metal speciation) are shown in Figure 7. The equilibrium times for the removal of lead and copper were 1000 and 600 min., respectively. The maximum amount of lead adsorbed was 0.0530 mmol of metal/g of RHA. Feng *et al.* (2004) obtained similar results for the adsorption capacity of lead in activated rice husk

ashes (0.0609 mmol Pb/g). Krishnani *et al.* (2008) presented results for the maximum adsorbed amounts of Pb by *in natura* rice husks obtained by several authors: Wong *et al.* (2003) (0.521 mmol Pb/g), Tarley *et al.* (2004) (0.217 mmol Pb/g). According to Naiya *et al.* (2009), Chuah *et al.* (2005) found $q_{max} = 0.0531$ mmol/g for the removal of Pb ions by RH. The maximum amount of copper adsorbed was 0.05732 mmol Cu/g of RHA. Nakbanpote *et al.* (2007) found the following values of maximum copper adsorption capacity: 0.112 mmol of Cu/g of RH, 0.102 mmol of Cu/g of RHA calcined at 300 °C and 0.253 mmol of Cu/g of RHA calcined at 500 °C. The results obtained in the present work are in agreement with those already reported.

The rice husks from the northern region of Brazil have the ability to remove toxic species such as Pb and Cu from aqueous solutions and an adsorbent material can thus be developed from an agricultural residue to be used in water treatment or wastewater contaminated by the metals studied.

Several agricultural waste materials are reported in the literature as excellent adsorbents of Pb and Cu metal species. Table 5 presents a summary of work using a variety of agricultural waste materials employed in the removal of the above species. The extremely low cost and abundance of rice husks in Brazil justifies the potential application of this material as an alternative adsorbent.

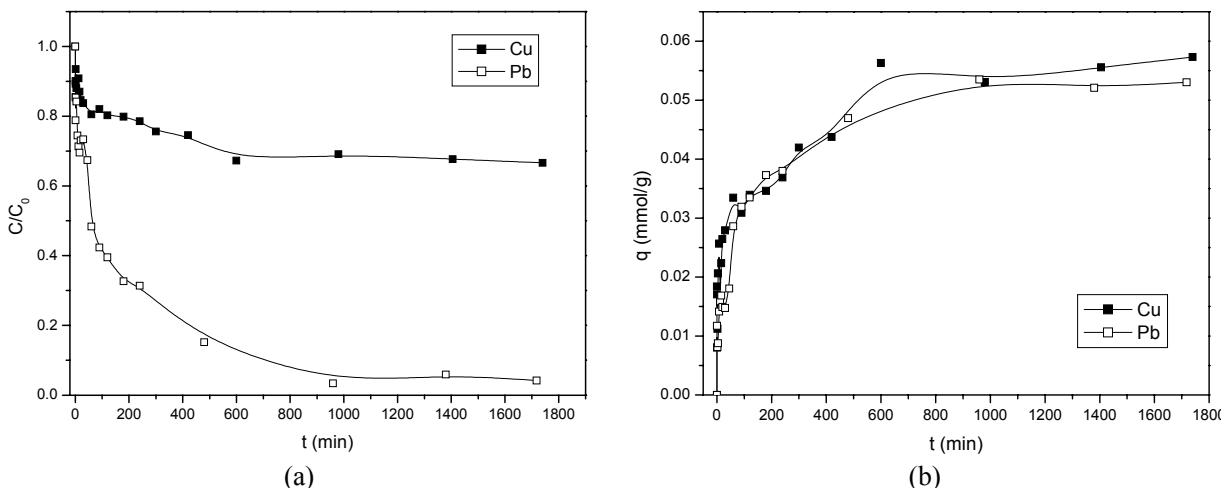


Figure 7: Kinetic curve for Pb and Cu on RHA: (a) dimensionless solution concentration as a function of adsorption time; (b) adsorbed amount at equilibrium.

Table 5: Agricultural waste materials used as alternative adsorbents for the removal of Lead and Copper ions.

Agricultural waste	Metal	Adsorption capacities (mg/g)	Reference
Coir pith waste	Pb	263	Kadirvelu and Namasivayam (2000)
Wheat bran	Pb	69-87	Bulut and Baysal (2006)
Tea waste	Cu/Pb	48-65	Amarasinghe and Williams (2007)
Coffee residue	Pb	63	Boudrahem <i>et al.</i> (2009)
Black gram husk	Pb, Cd, Zn, Cu, Ni	19.56-49.97	Saeed <i>et al.</i> (2005)
Mango peel	Cu	46.09	Iqbal <i>et al.</i> (2009)
Sugar beet pulp	Cu	28.5	Aksu and Isoglu (2005)
Almond shell	Pb	28.18, 8.08	Pehlivan <i>et al.</i> (2009a)
Barley straw	Cu/Pb	4.64, 23.2	Pehlivan <i>et al.</i> (2009b)
Peanut hull	Cu	21.25	Zhu <i>et al.</i> (2009)
Chestnut shell	Cu	12.56	Yao <i>et al.</i> (2010)
<i>Pinus pinaster</i> bark	Pb	3.33, 1.59	Vasconcelos and Beça (1993, 1994)
Grape bagasse	Pb	0.428	Farinella <i>et al.</i> (2004)
Peanut hull	Cu/Pb	0.21, 0.18	Oliveira <i>et al.</i> (2009)

Equilibrium Study

Figure 8 shows the adsorption isotherms for RHA adapted to the Langmuir and Freundlich models. The Langmuir and Freundlich models were adjusted to experimental data through the Gauss–Newton nonlinear estimation method (Statistic 7.0 for Windows® software). The regression coefficients for both adjustments and the Henry constants obtained by fitting linear isotherms only in the region of low concentrations (infinite dilution) are shown in Table 6.

According to Figure 8 and Table 6, the Langmuir model represented better the experimental data for the adsorption isotherms of both Pb and Cu ions. The Langmuir isotherm is specific for monolayer adsorption, which may have been the case in this study, while the Freundlich model is employed more

for adsorption at heterogeneous sites on solid surfaces, without a definite mechanism.

The D-R model was also used to describe the experimental data. Table 7 presents the parameters from the graph of $\ln(q_m)$ versus ϵ^2 for the adsorption processes of lead and copper ions by RHA. The values of q_m by the D-R method differ from the values found with the Langmuir model. The fit of the D-R model was more satisfying for copper.

Outlet concentrations of copper and lead in the fluid phase were below the limits established by National Environmental Council (CONAMA), an agency subordinated to the Ministry of the Environment, Water Resources and the Legal Amazon (MMA) in Brazil, which dictates 1.0 and 0.5 mg/L of Cu and Pb, respectively, as the maximum standard for effluent (CONAMA 430, 2011).

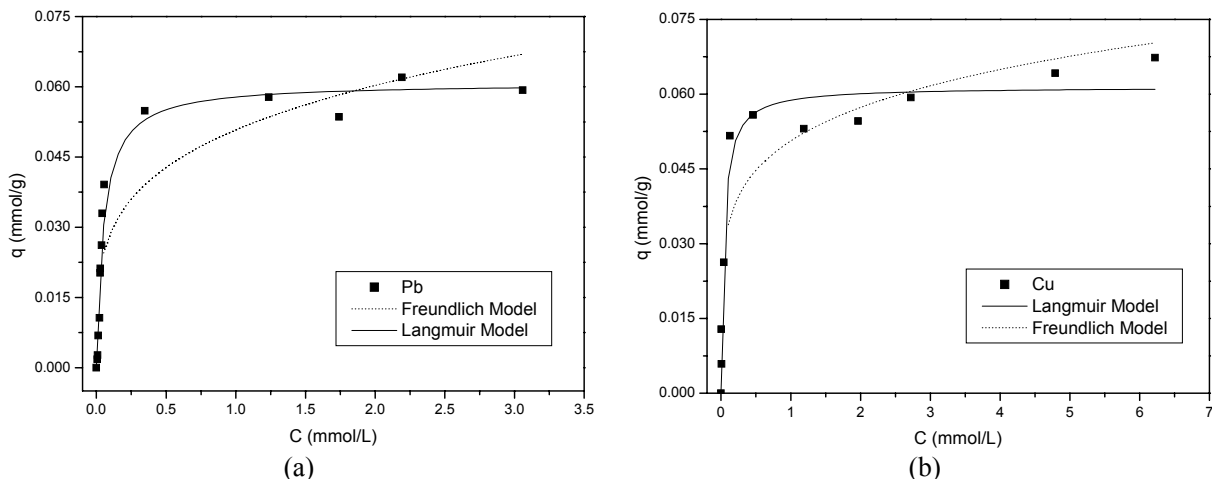


Figure 8: (a) Adsorption isotherms of Pb and (b) Cu on RHA adjusted to Langmuir and Freundlich models.

Table 6: Langmuir and Freundlich parameters for Pb and Cu ion adsorption on RHA.

System	Exp.	Langmuir			Freundlich			Henry*	
	q (mmol/g)	q _m (mmol/g)	b (L/g)	R ²	K _f	n	R ²	K (L/g)	R ²
Pb/RHA	0.0511	0.0608	19.374	0.9628	0.0508	0.2471	0.8202	0.7752	0.9753
Cu/RHA	0.0323	0.0614	22.286	0.9592	0.0506	0.1796	0.8295	0.3675	0.9378

* Data extracted from low concentration regions (linear) of the isotherms.

Table 7: Dubinin-Radushkevich (D-R) parameters for Pb and Cu ion adsorption on RHA.

System	q _m (mmol/g)	β (mol ² /kJ ²)	E (kJ/mol)	R ²
Pb/RHA	0.03373	1.17642*10 ⁻⁶	0.6519	0.70944
Cu/RHA	0.05446	3.71075*10 ⁻⁷	1.1608	0.93215

CONCLUSIONS

RHA and RH are predominantly mesoporous materials and the calcination of RH caused an increase in the surface area. RH and RHA presented amorphous, fibrous and longitudinal structures, elongated shapes, with the appearance of corncobs and ripples in the outer film. The -OH, Si-O-Si and Si-H groups on the RHA surface were important for metal adsorption.

The study of metal-adsorbent affinity conducted for Ni, Cu, Cd, Zn and Pb on RH and RHA indicated that RHA has a higher potential for removing lead and copper ions from effluents. The present study shows that RHA from northern Brazil (Amazon region) can be used as an adsorbent for the individual removal of Pb(II) and Cu(II) ions from aqueous effluents and the maximum sorptions for these ions on RHA were found to be 0.0530 and 0.0573 mmol of metal/g of RHA, respectively. Adsorption isotherms of lead and copper were better represented by the Langmuir model.

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NOMENCLATURE

A	specific surface area	cm ² /g
b	Langmuir constant	L/g
C ₀	initial concentration of metal ion in the fluid phase	mmol/L
C _a and C _b	acid and base concentration, respectively	mol/L
C _{eq}	concentration of metal ions in the fluid phase in equilibrium	mmol/g
C _m	solid content	g/L
C _{Na+}	Na ⁺ concentration	mg/L
C(t)	concentration of metal ion in solution at time t	mmol/L
f	conversion factor of sodium to equivalents	23 g/eq

E	sorption free energy	J/mol
F	Faraday constant	
K_f and n	Freundlich coefficients	
m	mass of adsorbent	g
q_{eq}	concentration of metal ions in the solid phase at equilibrium	mmol/g
q_m	maximum adsorbed capacity	mmol/g
$q(t)$	concentration of metal ion in the solid phase	mmol/g
R	ideal gas constant	J/molK
T	temperature	K
V	solution volume	mL
%Rem	removal percentage	
β	Dubinin-Radushkevich constant	
ϵ	Polanyi potential	

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