



Lead(II) adsorption by peach palm waste

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ABSTRACT

The aim of the present study was to investigate the efficiency of chemical treatments for peach palm sheaths, targeting the treatment of Pb(II) contaminated aqueous effluents. The modification was done with sodium hydroxide and citric acid to introduce carboxyl groups. Pb(II) adsorption was evaluated in function of pH, contact time, metal concentration, desorption ability and thermodynamic factors. An infrared adsorption peak was observed at 1740 cm⁻¹ due to the presence of carboxyl groups. The required time for the system to reach equilibrium was about 150 min, and the Pb(II) adsorption followed a pseudo-second-order kinetic model. The Langmuir model showed the best fit for the adsorption data. The maximum adsorption capacity and minimum desorption rate values of 65.32 mg g⁻¹ and 74.72%, respectively were obtained for the NaOH-modified peach palm sheath. After using the chemical treatment, the adsorbent properties improved and the system became more spontaneous, as confirmed by low Gibbs energy values.

Keywords: *Bactris gasipaes*; Adsorption; Biomaterials; Biosorption; Metals; Waste

1. Introduction

Lead is considered to be one of the major environmental pollutants discharged mainly in effluents from industries (e.g., foundries, battery, paper and cellulose manufacturing) [1,2]. Besides having a high polluting potential, residues containing these metals can reach groundwater, reservoirs or rivers, which are water sources for the population [3], and contaminate

human beings and other living organisms in the local environment.

Due to their toxicity and cumulateness in the organism, these metals may cause several types of diseases, such as allergic dermatitis and ulcers, possibly affecting the human immune system [4]. Considering this fact and also the high contamination effects on the environment, the CONAMA (Brazilian National Council for the Environment) Resolution no. 357/2005 regulates the maximum concentration level of these toxic metals in the environment; for Pb(II) it was established

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at 0.5 mg L⁻¹, the same value was set by the EPA (US Environmental Protection Agency) [5].

Thus, the metal removal from water and effluents has become extremely important to protect public health and the environment [6,7].

Therefore, since there is a demand for balanced, sustainable and alternative wastewater treatment technologies, the use of biomass as a biosorbent material has been pointed out to remove toxic metals by adsorption [8].

These technologies should present low operational cost and high pollutant removal efficiency. Besides, materials from renewable sources could be utilized. Hence, residues from agricultural activities have raised great interest over the past years [9].

Among the studies on toxic metal removal from wastewater by biomass, some noteworthy ones are: the use of tea leaves [10], *Aspergillus flavus* [11], *Rhizopus arrhizus* [12], beet pulp [13], rice hulls [14], bean shells [15], *Pinus sylvestris* sawdust [16], to name but a few. Apart from them, palm residues seem promising materials for this kind of study, since palm harvesting generates about 54–82 tons of green mass (residue) per acre [17]. This biomass shows great capacity to retain metal ions through adsorption, which increases significantly in the case of chemical modifications [18]. Therefore, the aim of the present study was to investigate the efficiency of chemical treatments for peach palm sheaths in order to estimate their better adsorption capacity – ability to retain toxic metals, particularly Pb(II) from wastewater.

2. Experimental

2.1. Reagents

Deionized water (Milli-Q Plus) was used for all procedures. Pb(II) solutions were prepared utilizing Pb(NO₃)₂ (Vetec, 98 %). To perform chemical modifications of the biomass and pH adjustments, the following reagents were used according to the protocol: NaOH (F. Maia, 97%), HCl (F. Maia, 37%), citric acid (F. Maia, 99.5%) and KCl (F. Maia, 99.5%).

2.2. Equipment

A Fourier transform infrared spectrophotometer (FTIR-8300, Shimadzu, Japan) at 4 cm⁻¹ resolution was used to characterize possible alterations in the residue chemical structures. The peach palm biomass surface images were obtained using a scanning electron microscope (SEM, Quanta 200, FEI, Japan) at 30 kV in order to verify superficial changes in the residues. A flame atomic absorption spectrophotometer (GBC 932PLUS, Australia) was used to determine the Pb(II) amount.

2.3. Residue modification

Peach palm sheaths were obtained at a private estate located in Umuarama-Paraná, Brazil. They were washed, ground and later dried in an air ventilation oven at 60 °C to withdraw moisture from them. Then, the materials were sieved through a 42-mesh Bertel sieve to standardize and obtain homogeneous granulometry to carry out two modifications (A). The modification with NaOH aims to remove residual impurities and also promote the extraction of lignin present in this material, thereby increasing the porosity of the adsorbent. Adding citric acid causes an esterification reaction in the residue, possibly increasing the amount of binding sites with the metal ion.

2.3.1. Modification with NaOH (B)

To perform the modification with NaOH, 20 mL of 0.1 mol L⁻¹ NaOH solution was added to the dried ground sheath. The mixture was agitated for 120 min, and the supernatant was discarded and sent to a specialized company to be treated. After that, the residue was washed several times with ultrapure water (Milli-Q) until reaching pH 7 and dried in an oven at 55 °C for 24 h.

2.3.2. Modification with NaOH and citric acid (C)

After treated with NaOH, the peach palm sheath residue was modified with citric acid (C₆H₈O₇), according to the procedure recommended by Rodrigues [19]. The peach palm sheath residue was immersed in a 1.2 mol L⁻¹ citric acid solution (proportion: 8.3 mL of solution/1 g of sample), agitated for 30 min, and then the supernatant was discarded. The residue was washed several times with ultrapure water (Milli-Q) until reaching pH 7 and dried in an oven at 55 °C for 24 h.

2.4. Points of zero charge – PZC

PZC is defined as the pH at which the biomass surface has a neutral charge. In this study, the methodology chosen to determine the PZC was the one described by Guillarduci [20]. This procedure consisted of mixing 0.5 g of the biomass with 50 mL of an aqueous solution at different initial pH values (1, 2, 3, 4, 5, 6, 8, 9, 10, 11 and 12), adjusted using HCl and NaOH solutions. Besides, the solution ionic strength varied by adding three KCl concentrations (0.01, 0.1 and 0.5 mol L⁻¹) which resulted in three PZC values for each biomass sample. After *reaching equilibrium* (24 h), the final pH was measured, allowing constructing a final pH vs. initial pH plot based on these data, and the PZC pH, related to the final pH constant value, was determined. All analyses were carried out in triplicate.

2.5. Pb(II) adsorption experiments

2.5.1. Adsorption as a Function of pH

The Pb(II) adsorption assays were performed in 250 mL Erlenmeyer flasks by mixing the metal solution in a heterogeneous medium of materials. 0.5 g of natural (A) and modified (B) materials (C) were separately added to 50.00 mL of the studied Pb(II) solution at an initial concentration of 100 mg L⁻¹. The pH of the mixture ranged from 2 to 6, and it was adjusted with 0.1–1 mol L⁻¹ NaOH and HCl solutions. After that, the mixture was agitated in a shaker for 24 h and filtered through folded paper filter in a funnel. The metal concentration was evaluated by flame atomic absorption spectrometry, and the adsorbed metal content was determined according to the mass conservation principle expressed as follows:

$$q_{\text{eq}} = \frac{(C_0 - C_{\text{eq}})V}{M} \quad (1)$$

where C_0 and C_{eq} are the metal initial and equilibrium concentrations, respectively, in the solution (mg L⁻¹); V is the solution volume (L); M is the residue sample mass (g).

2.5.2. Adsorption as a function of time

In order to observe the metal adsorption as a function of time, 0.5 g of biosorbent material was mixed with the Pb(II) solution at 100 mg L⁻¹ initial concentration and pH 5. The agitation speed was 300 rpm, and the agitation time ranged from 15 to 1440 min. In total, 10 measurements were performed. From the obtained data, the amount of adsorbed Pb(II) per gram of sample (q_{eq}) was calculated.

2.5.3. Adsorption isotherms

Solutions with different Pb(II) concentrations (100–1000 mg L⁻¹) were used to obtain isotherms. For the adsorption, 50 mL of Pb(II) solutions were mixed individually with 0.5 g of each peach palm sheath sample (A, B and C) and agitated in an orbital shaker for 4 h. The solution pH was adjusted by NaOH or HCl and kept constant at 5.0. Then, the mixtures were filtered, and the solutions were analyzed by flame atomic absorption spectrometry in order to determine the initial and final metal concentrations. From the obtained data, the amount of adsorbed Pb(II) per gram of sample q_{eq} was calculated.

2.5.4. Adsorption as a function of temperature

Thermodynamic parameters were obtained from an analysis of the Pb(II) adsorption as a function of temperature. To carry out these experiments, 0.5 g of

residue samples A, B and C and 50 mL of the Pb(II) solution (700 mg L⁻¹) were mixed. The pH was fixed at 5.0, the agitation time was 8 h, and the following temperatures were established: 10, 20, 30, 40 and 60 °C. After that, the thermodynamic parameters –enthalpy (ΔH), Gibbs free energy (ΔG) and entropy (ΔS) – were calculated: according to the procedure described by Gök and Chakravarty [21,22].

2.5.5. Desorption

Pb(II) desorption rates were also evaluated. The desorption experiments were preceded by Pb(II) adsorption tests. 100 mg L⁻¹ Pb(II) solution and 0.5 g of residues A, B and C were mixed at pH 5 and agitated for 8 h. After the adsorption assays, the residue was washed with Milli-Q water to remove any metal excess from the surface, and then the material was dried in an oven at 50 °C for 24 h. Next, the residues were immersed in 25 mL of 0.1 mol L⁻¹ HCl solution for 24 h to remove the adsorbed metal, and finally, the Pb(II) concentration and desorption rate were determined.

3. Results and discussion

3.1. Adsorbent characterization

Initially, the analysis of modified and unmodified adsorbent samples was carried out with and without modification using infrared spectrometry, which provides information on cellulose, hemicellulose and lignin functional groups that may be present in the adsorbent structure and cause changes in it. Fig. 1 shows the spectra for residues A, B and C.

The strong wide band at 3402 cm⁻¹ is attributed to the O–H stretch vibration. The peak at 2518 cm⁻¹ refers to

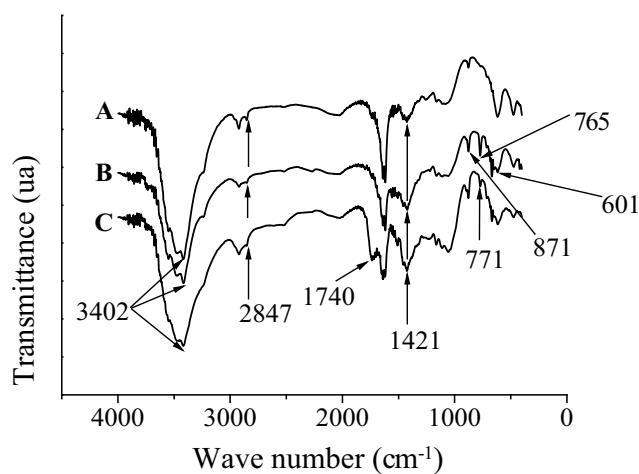


Fig. 1. Infrared spectra of peach palm sheath residues (A), (B) and (C).

the C–H stretch vibration. The wavenumber for the carbonyl group adsorption in compounds containing ester and carboxyl groups is approximately 1740 cm^{-1} [23].

The peak at 1421 cm^{-1} can be attributed to the C=O stretch [24]. The peaks observed at $871\text{--}771\text{ cm}^{-1}$ confirm the presence of aromatic rings and C–H ethyl groups [25]. It can be pointed out that for the sample modified with NaOH, the emergence of a peak at 765 at 601 cm^{-1} refers to the flexion outside the O–H stretch of the aromatic ring, indicating that this modification has caused the appearance of new aromatic sites containing O–H bonds in their structure that may interact with the metal ions in the solution.

Thus, the existence of hydroxyl, carbonyl and carboxyl groups in the peach palm sheath residues can be verified. An alteration in peak intensity at 1740 cm^{-1} was observed for the modified material, indicating an increase in the carboxyl group amount. These data corroborate the study performed by Rodrigues [19] in which the appearance of carboxyl groups was demonstrated for the metal adsorption on NaOH- and citric-acid-treated Paraju sawdust. These groups are important because they become negative depending on pH variation, and contribute to greater interactions with the metal ions [26].

3.2. Morphological characterization

The images of the peach palm sheath residue surfaces are presented in Fig. 2. They were obtained by scanning electron microscopy (SEM) and magnified 6000 times. When analyzing the obtained SEM images, it can be observed that all the samples have similar morphological characteristics, evidencing a fibrous and irregular nature as well as formation of fiber layers overlapping tubes, channels and cracks, which allow adsorption areas. When comparing Fig. 2(A) and (B), the latter presents a larger surface area. This flat surface favors the adsorption on the walls of tubes and cracks as it

increases the apparent surface area. Even after the reaction with citric acid, the porosity profile of the material can be observed as demonstrated in Fig. 2(C).

Mercerization can cause the breaking down of surface tension and cellulose defibrillation, as observed in Fig. 2(B) and (C), increasing the available surface area of contact with the liquid matrix. Moreover, it facilitates access to the hydroxyl groups present in cellulose chains [27]. This morphology promotes adherence of the metal ions present in the aqueous solutions to various sections of the biosorbent irregular surface.

3.3. Point of zero charge (PZC) determination

PZC describes the condition when the electrical charge density on a surface is zero, and it was determined herein for the biomass in order to check the pH at which the biosorbent surface charge changes from predominantly positive to negative. In the present study, PZC was evaluated based on the methodology proposed by Guillarduci [20]. The adsorption capacity of the sheath samples is related to their ion exchange capacity, chelation and physical adsorption [28]. According to Aksu [29], in general, these mechanisms involve surface groups which are able to capture and retain metal species in an aqueous medium where they can be modified by pH variation affecting the adsorption process. Therefore, through PZC determination, a preliminary study of the peach palm sheath acid–base behavior in the aqueous medium was carried out. The results are shown in Fig. 3 for 0.5 mol L^{-1} KCl only, because the values obtained for the other concentrations are almost the same, indicating that the ionic strength did not change PZC.

PZC pH values were found to be 8.55 for residue B, 2.75 for residue C and 4.42 for residue A, thus, characterizing the surface buffering effect for which the PZC of the peach palm sheath was considered. For the solutions at pH lower than the PZC, the residue would

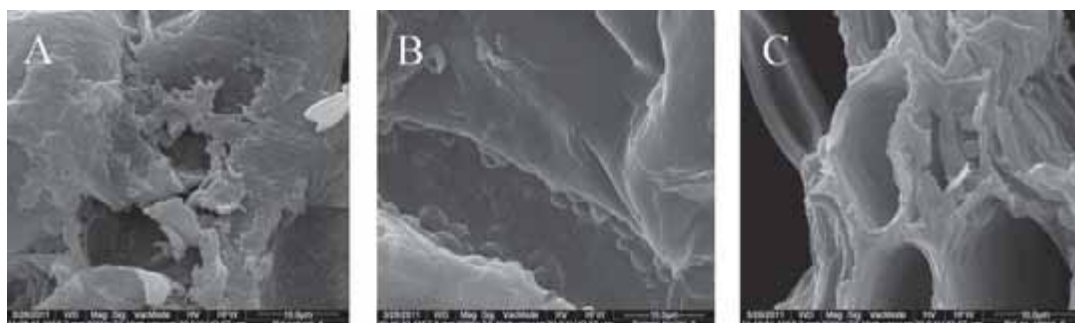


Fig. 2. Micrographs of peach palm sheath residues (A), (B) and (C).

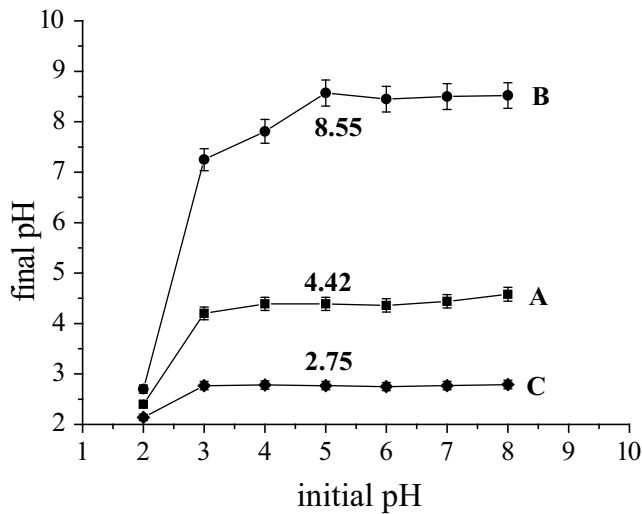


Fig. 3. Point of zero charge (PZC) characterization of peach palm sheath residues (A), (B) and (C). KCl concentration: 0.5 mol L⁻¹.

present predominantly a positive surface charge, and at pH higher than the PZC, the liquid surface charge would be negative.

It was observed that the pH was above 7.0 only for residue B which could be explained by the possible presence of residual sodium hydroxide in the palm fibers, although the material was washed until the water had pH of approximately 7.0.

3.4. pH effect

pH has a direct effect on metal ion adsorption, resulting in the competition between metal and H⁺ ions for active sites. Its dependence on adsorption of metal species by biomass can also be justified by association–dissociation of certain functional groups, such as carboxyl groups [30]. At low pH values, the carboxyl groups are not dissociated and cannot be linked to the metal ions in the solution, although they may participate in chelation reactions [31]. This behavior is evident in Fig. 4 which represents the results of Pb(II) adsorption as a function of pH values. Thus, there was an increase in the adsorption capacity when increasing the pH, and the maximum values were obtained at around pH 5.0 for residue B (71.14 mg g⁻¹) and residue C (64.20 mg g⁻¹), and at pH 6.0 only for residue A (31.63 mg g⁻¹).

Therefore, pH 5.0 was fixed for the other experiments, since the formation of some Pb(II) precipitates was observed at pH 6.0. However, this pH value (5.0) was below the PZC for residue B (8.55); this indicates that the biomass surface would be predominantly positive, contradicting the presented values, because a metal ion has positive charge, and the ion would not be

attracted by the adsorbent as this surface is also positively charged [32]. Nevertheless, in the modification (B) of the residue, apart from increasing the adsorbent porosity, the higher adsorption capacity may be related to the increasing number of hydroxyl groups which possibly chelate the metal ion.

3.5. Adsorption time effect

The effect of contact time in Pb(II) adsorption by the palm sheath is shown in Fig. 5. It was verified that the Pb(II) adsorbed amount increased during the first 150 min of contact, and the adsorption stability occurred within 150–500 min. After this time, the biosorption process reached equilibrium and did not present a significant variation of the Pb (II) adsorbed amount when increasing the contact time.

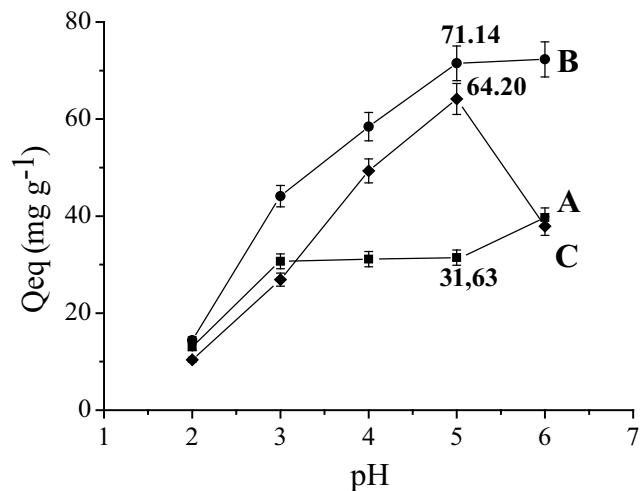


Fig. 4. pH effect on Pb(II) adsorption by peach palm sheath residues (A), (B) and (C).

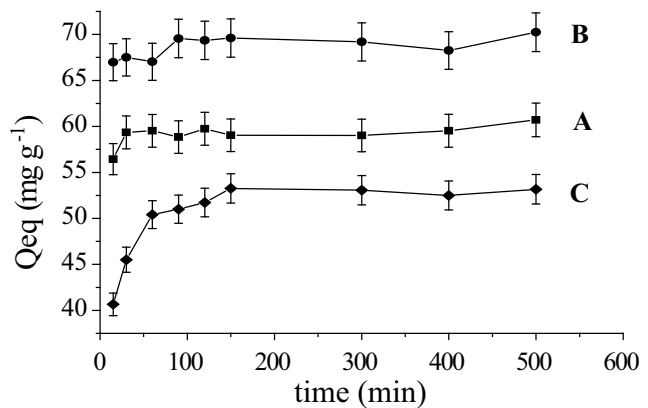


Fig. 5. Pb(II) adsorption kinetics for peach palm sheath residues (A), (B) and (C).

The highest Pb(II) adsorbed amount was 69.59 mg g⁻¹ for residue B, 59.04 mg g⁻¹ for residue A and 53.14 mg g⁻¹ for C, as seen in Fig. 5. It was determined that the Pb(II) adsorption was greater on residue B than on the other adsorbents, corroborating the data obtained from the experiments on Pb(II) adsorption as a function of pH. This result is mainly a consequence of increases in the number of hydroxyl groups (Fig. 1) as well as in the material surface porosity (Fig. 2).

Considering the kinetic data, each adsorbent can be characterized by using pseudo-first-order and pseudo-second-order kinetic models. The pseudo-first-order kinetics follows the Lagergren model expressed by Eq. (2) [27–33].

$$\log(q_{\text{eq}} - q_t) = \log q_{\text{eq}} - \frac{K_1 t}{2.303} \quad (2)$$

where q_t is the metal adsorbed amount (mg g⁻¹) at time t ; K_1 is the pseudo-first-order constant (min⁻¹). q_{eq} and K_1 can be calculated using linear and angular coefficients of the $\log(q_{\text{eq}} - q_t)$ vs. t plot, respectively. It can be observed that the q_{eq} values obtained experimentally differ from those calculated with Eq. (2). Besides, the r^2 values are far from unity, suggesting that the adsorption did not follow the first-order equation. Therefore, the pseudo-second-order model (Eq. (3)) was applied to assess the Pb(II) adsorption kinetics for the peach palm sheath residues [34].

$$\frac{t}{q_t} = \frac{1}{K_2 q_{\text{eq}}^2} + \frac{t}{q_{\text{eq}}} \quad (3)$$

where K_2 is the pseudo-second-order constant (g mg⁻¹ min⁻¹) obtained from the linear coefficient of the t/q_t vs. t plot, since q_{eq} can be evaluated through the angular coefficient. The calculated and experimental q_{eq} , K_2 and r^2 values are shown in Table 1. They prove that better adjustments can be made using the pseudo-second-

order model (Eq. (3)), as the values obtained through it are close to those determined experimentally, and consequently, r^2 values close to unity, confirming that the speed control mechanism was based on a strong interaction between the adsorbent and adsorbate, thus, indicating the availability of more energetic adsorption sites [35].

In many cases, the pseudo-first order kinetic model is not an appropriate method. It is predominantly used at initial stages of adsorption processes in order to describe a reversible reaction at equilibrium between liquid and solid phases [36].

3.6. Adsorption isotherms

It was observed that the adsorption capacity and intensity values increased for residue B, showing that the characteristics of this adsorbent were improved after its treatment (Fig. 6). The NaOH/citric acid-modified sample (residue C) did not cause a significant increase

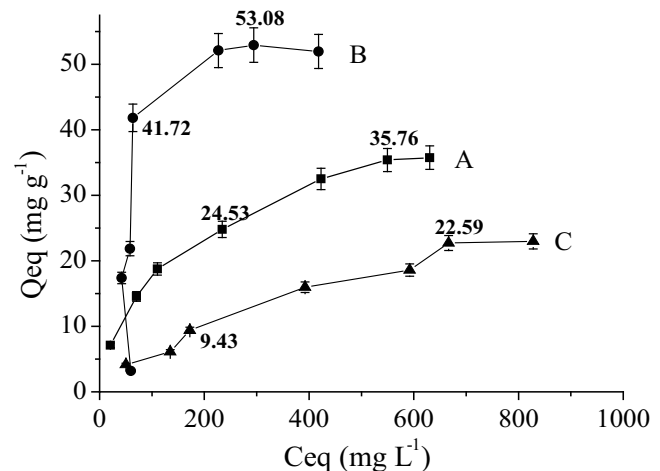


Fig. 6. Pb(II) adsorption isotherms for peach palm sheath residues A, B and C.

Table 1

Pb(II) adsorption pseudo-first-order and pseudo-second-order kinetic parameters for peach palm sheath residues

	$q_{\text{eq(Exp.)}}$	Pseudo-first-order			Pseudo-second-order		
		K_1 (10^{-3})	$q_{\text{eq(cal.)}}$	r^2	K_2 (10^{-3})	$q_{\text{eq(cal.)}}$	r^2
A	61.36	2.24	2.87	0.42	3.45	61.35	0.99
B	69.79	0.95	1.70	0.22	8.83	69.83	0.99
C	53.61	5.39	4.76	0.48	3.87	53.76	0.99

Obs.: A, B and C stand for the peach palm residues.

$q_{\text{eq(Exp.)}}$ and $q_{\text{eq(cal.)}}$ values are expressed in mg g⁻¹.

in Pb(II) adsorption, and the values obtained for this residue were lower than those determined for residue A. Although the presence of carboxyl groups was assumed, their insertion was not enough to cause better Pb(II) adsorption. The reverse was observed for residue B, where the metal sorption capacity increased probably due to two factors: (1) the availability of greater amount of hydroxyl groups; (2) the increase of material porosity, as previously discussed.

Pb(II) adsorption was adjusted to the Langmuir (Eq. (4)) and Freundlich (Eq. (5)) models.

$$\frac{C_{\text{eq}}}{q_{\text{eq}}} = \frac{1}{q_m b} + \frac{C_{\text{eq}}}{q_m} \quad (4)$$

where b is the adsorption intensity constant; q_m is the maximum adsorption capacity.

$$\log q_{\text{eq}} = \log K_f + \left(\frac{1}{n}\right) \log C_{\text{eq}} \quad (5)$$

where K_f is the adsorbate–adsorbent affinity parameter; n is the adsorbent surface heterogeneity factor. If $1 < n < 10$, then favorable adsorption takes place [37].

The Langmuir model assumes that there is no interaction between adsorbed molecules, but there is only interaction between them and the adsorbent; besides, it considers that adsorption occurs onto monolayers at homogeneous fluid–solid interfaces. The Freundlich model is based on the idea that metal ions are infinitely accumulated onto the adsorbent surface [38], and it suggests that the adsorption energy decreases logarithmically with the solute surface coverage, thus differently from Langmuir equation [39].

According to the values obtained from each model (Table 2), it can be seen that the Pb(II) adsorption behavior on the peach palm sheath residues is better described using the Langmuir model (near-unity r^2 values). Furthermore, for all the samples, the n values are greater than unity, indicating that Pb(II) adsorption was favorable.

Correlating the q_m values obtained for the residues of the present study with those determined by other studies on Pb(II) adsorption by various biosorbents, it can be observed that the highest Pb(II) adsorption capacity value (65.32 mg g⁻¹) belongs to residue B when compared to other adsorbents (Table 3), being around 1.7–8 times. This value was defined by the Langmuir isotherm – a model widely used to estimate the adsorption capacity (q_m) of several chemical elements and species, even at high concentrations [40].

Table 2

Comparison of Langmuir and Freundlich isotherm parameters for Pb(II) adsorption by the peach palm sheath residues

	Langmuir			Freundlich		
	q_m (mg g ⁻¹)	b (L mg ⁻¹)	r^2	K_f (mg g ⁻¹)	n	r^2
A	43.31	7.29 ⁻²	0.990	1.88	2.13	0.984
B	65.32	1.20 ⁻²	0.942	4.44	2.30	0.667
C	36.06	1.99 ⁻³	0.975	0.47	1.70	0.970

Obs.: A, B and C stand for the peach palm sheath residues.

Table 3

Comparison of various biosorbents for Pb (II)

Adsorbents	q_m (mg g ⁻¹)	References
Peanut shell	39.40	[41]
Coconut shell	11.40	[42]
Sawdust	21.05	[43]
Nut peel	8.08	[44]
Sugarcane bagasse	30.70	[45]
B – NaOH ^a	65.32	Present study

^aNaOH-modified peach palm sheath (Residue B).

3.7. Thermodynamic parameters

The thermodynamic parameters: enthalpy (ΔH), entropy (ΔS) and Gibbs free energy (ΔG), which determine whether the adsorption process was spontaneous, exothermic or endothermic, were evaluated according to Eqs. (6) and (7). The obtained values are given in Table 4.

$$\Delta G = -RT \cdot \ln K_d \quad (6)$$

$$\ln K_d = (\Delta S / R) - (\Delta H / R) / T \quad (7)$$

where K_d is the adsorbate distribution coefficient (L g⁻¹) corresponding to the q_{eq} -to- C_{eq} ratio; T is the temperature (K); R is the universal gas constant (8.314 J (K. mol)⁻¹).

The linear coefficient, ΔH and ΔS values were estimated by plotting $\ln K_d$ versus $1/T$ and calculating the straight line slope. The ΔG variation values – a fundamental criterion for spontaneity of processes – were all negative, meaning that Pb(II) adsorption process occurred spontaneously at any given temperature [46–48].

For residue B (Table 4), a decrease in the ΔG value was observed, becoming more negative when compared to the other residues. Therefore, it was noticed that Pb(II) adsorption was more favorable for this type of modification. It was verified that the adsorption was more spontaneous for residue B which presented the highest q_m value, related to the increase in the system spontaneity when increasing the metal adsorption capacity, as shown in Table 2.

The positive ΔH values obtained for residues A and C show that this adsorption process was endothermic, and, only for residue B, it was exothermic. The ΔS values higher than zero, observed for residues A, B and C, demonstrate an increase in disorder at the solid–solution interface, indicating that entropy contributed to the adsorption reaction spontaneity for these samples.

3.8. Pb(II) desorption

The Pb(II) desorption experiments were performed using 0.10 mol L⁻¹ HCl solution. Under this condition, H⁺ ions are expected to substitute the cation adsorbed through the ion exchange mechanism.

The desorption results are presented in Table 5, demonstrating that over 70% of the adsorbed metal species was desorbed individually from all the tested materials, which means that Pb(II) adsorption by the peach palm

Table 4
Thermodynamic parameters obtained from Pb(II) adsorption results for peach palm sheath residues

	K_d^*	ΔG (kJ mol ⁻¹) ^a	ΔH (kJ mol ⁻¹)	ΔS (J K ⁻¹ mol ⁻¹)
A	4.77	-11.24	9.75	72.30
B	7.13	-16.78	-4.04	48.26
C	4.03	-9.49	9.53	64.97

Obs: A, B and C stand for the peach palm sheath residues.

^aValues calculated at 30 °C.

Table 5
Pb(II) adsorption-desorption values for peach palm sheath residues (Pb(II) initial concentration: 100 mg L⁻¹)

Material	Adsorbed concentration (mg L ⁻¹)	Desorbed concentration (mg L ⁻¹)	Desorption rate (%)
A	79.76	61.79	77.46
B	91.20	68.15	74.72
C	87.39	71.54	81.86

Obs: A, B and C stand for the peach palm sheath residues.

sheath residues was mainly reversible. Thus, after being used, this biomass can be dried and reutilized or possibly incorporated into concrete blocks, reinforcing them in order to prevent environmental pollution.

4. Conclusion

The chemical modifications of the peach palm sheath were verified by the alterations observed in the infrared spectra and the porosity increase determined via SEM. The Pb(II) adsorption capacity depended on pH, and the greater efficiency was obtained at pH 5.0. Residue B was more efficient in spite of presenting the PZC pH value higher than 5.0. The system reached the equilibrium after 150 min, and the residues followed the pseudo-second-order kinetic model. The maximum adsorption capacity value of 65.32 mg g⁻¹ was obtained for residue B using Langmuir equation. Considering the thermodynamic parameters, the Pb(II) adsorption process was determined as spontaneous, causing the increase in disorder. Better desorption values obtained for the residues indicate their reusability, especially for residue C, which presented Pb(II) desorption value of 81.86%. Therefore, peach palm residues showed good sorption capacity and may be utilized in the future to pre-treat Pb(II)-containing effluents.

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References

- [1] S.S. Gupta and K.G. Bhattacharyya, Interaction of metal ions with clays: I. A case study with Pb (II). *Appl. Clay Sci.*, 30 (2005) 199–208.
- [2] S. Tunali, T. Akar, A.S. Ozcan, I. Koran and A. Ozcan, Equilibrium and kinetics of biosorption of lead (II) from aqueous solutions by *Cephalosporium aphidicola*. *Sep. Purif. Technol.*, 47 (2006) 105–112.
- [3] P.A. Kumar, M. Ray and S. Chakraborty, Hexavalent chromium removal from wastewater using aniline formaldehyde condensate coated silica gel. *J. Hazard. Mater.*, 14 (2007) 24–32.
- [4] J. Geier, W. Uter, H. Lessmann and P.J. Frosch, Patch testing with metalworking fluids from the patient's workplace. *Contact Dermatitis*, 51 (4) (2004) 172–179.
- [5] Brasil Conselho Nacional do Meio Ambiente (CONAMA). Secretaria do Meio Ambiente da presidência da república. Resolução nº 357 de 17 de março de 2005.
- [6] N. Unlu and M. Ersoz, Adsorption characteristics of heavy metal ions onto a low cost biopolymeric sorbent from aqueous solutions. *J. Hazard. Mater.*, 136 (2006) 272–280.
- [7] J. Li, Q. Lin, X. Zhang and Y. Yan, Kinetic parameters and mechanisms of the batch biosorption of Cr (VI) and Cr (III) onto *Leersia hexandra* Swartz biomass. *J. Colloid Interface Sci.*, 333 (2009) 71–77.

- [8] K.S. Smith, G.S. Plumlee and M.J. Logsdon, The environmental geochemistry of mineral deposits. *Soc. Econom. Geol., Rev. Econom. Geol.*, 7 (1999).
- [9] K. Kadirvelu and C. Namasivayam, Activated carbon from coconut coirpith as metal adsorbent: adsorption of Cd (II) from aqueous solution. *Environ. Res.*, 7 (2003) 471–478.
- [10] S.S. Ahluwalia and D. Goyal, Removal of heavy metals by waste tea leaves from aqueous solutions. *Eng. Life Sci.*, 5 (2005) 158–162.
- [11] T. Akar and S. Tunali, Biosorption characteristics of *Aspergillus flavus* biomass for removal of Pb (II) and Cu (II) ions from an aqueous solution. *Bioresour. Technol.*, 97 (2006) 1780–1787.
- [12] H. Salehizadeh and Shojaosadatisa, Removal of metal ions from aqueous solution by polysaccharide produced from *Bacillus firmus*. *Water Res.*, 37 (2003) 4231–4235.
- [13] V.M. Nurchi and I. Villaescusa, Agricultural biomasses as sorbents of some trace metals. *Coord. Chem. Rev.*, 252 (2008) 1178–1188.
- [14] C.R.T. Tarley, S.L.C. Ferreira and M.A.Z. Arruda, Use of modified rice husks as a natural solid adsorbent of trace metals: characterization and development of an on-line preconcentration system for cadmium and lead determination by FAAS. *Microchem. J.*, 77 (2004) 163–175.
- [15] A. Saeed, M. Iqbal and M.W. Akhtar, Removal and recovery of lead(II) from single and multimetal (Cd, Cu, Ni, Zn) solutions by crop milling waste (black gram husk). *J. Hazard. Mater.*, 117 (2005) 65–73.
- [16] V.C. Taty-costodes, H. Fauduet, C. Porte and A. Delacroix, Removal of Cd(II) and Pb(II) ions, from aqueous solutions, by adsorption onto sawdust of *Pinus sylvestris*. *J. Hazard. Mater.*, 105 (2003) 121–142.
- [17] S.E. Bailey, T.J. Olin, R.M. Bricka and D.D. Adrian, A review of potentially low-cost sorbents for heavy metals. *Water Research*, 33 11 (1999) 2469–2479.
- [18] F.A. Abulal-rub, M.H. El-Naas, I. Ashour and M. Al-Marzouqi, Biosorption of copper on *Chlorella vulgaris* from single binary and ternary metal aqueous solutions. *Process Biochem.*, 41(2006) 457–464.
- [19] R.F. Rodrigues, R.L. Trevenzoli, L.R.G. Santos, V.A. Leão and V.R. Botaro, Adsorção de metais pesados em serragem de madeira tratada com ácido cítrico. *Engenharia Sanitária e Ambiental*, 11 (2006) 21–26.
- [20] V.V.S. Guillarduci, J.P. Mesquita, P.B. Martelli, H.F. Gorgulho, Adsorção de fenol sobre carvão ativado em meio alcalino. *Quim. Nova*, 29 (6) (2006) 1226–1232.
- [21] Ö. Gök, A. Özcan, B. Erdem and A.S. Özcan, Prediction of the kinetics, equilibrium and thermodynamic parameters of adsorption of copper (II) ions onto 8-hydroxy quinoline immobilized bentonite. *Colloids Surfaces A: Physico chem. Eng. Asp.*, 317 (2008) 174–185.
- [22] S. Chakravarty, S. Pimple, H.T. Chaturvedi, S. Singh and K.K. Gupta, Removal of copper from aqueous solution using newspaper. *J. Hazard. Mater.*, 159 (2008) 396–403.
- [23] T. Yang and A.C. Lua, Characteristics of activated carbons prepared from pistachio-nut shells by physical activation. *J. Colloid Interface Sci.*, 267 (2003) 408.
- [24] R. Muhammad, N. Raziya, A.H. Muhammad, M.A. Tariq and Khalil-ur-Rehman, Pb (II) biosorption from hazardous aqueous streams using *Gossypium hirsutum* (Cotton) waste biomass. *J. Hazard. Mater.*, 161 (2009) 88–94.
- [25] M. Ramesh, R.M. Saravanakumar and P.S. Karutha, Benzyl amino purine and adenine sulphate induced multiple shoot and root induction from nodal explants of *Brahmi*, *Bacopa monnieri* (Linn.) Penn. *Nat. Prod. Radiance.*, 5 (2006) 44–51.
- [26] N.X. Feng and G.S. Liang, Adsorption study of copper (II) by chemically modified orange peel. *J. Hazard. Mater.*, 164 (2009) 1286–1292.
- [27] O.K. Júnior, L.V.A. Gurgel and L.F. Gil, Removal of Ca (II) and Mg (II) from aqueous single metal solutions by mercerized cellulose and mercerized sugarcane bagasse grafted with EDTA dianhydride (EDTAD). *Carbohydr. Polym. Sci. Direct.*, 79 (2010) 184.
- [28] S. Ilhan, A. Çabuk, C. Filik and F. Çaliskan, Effect of pretreatment on biosorption of heavy metals by fungal biomass. *J. Trakya Univ. Sci.*, 5 (2004) 11–17.
- [29] Z. Aksu, Application of biosorption for the removal of organic pollutants: a review. *Process Biochem.*, 40 (2005) 997–1026.
- [30] Y. Yalçincaya, L. Soysal, A. Denizli, M.Y. Arica, S. Bectas and O. Genç, Biosorption of cadmium from aquatic systems by carboxymethylcellulose and immobilized *Trametes versicolor*. *Hydrometallurgy*, 63 (2002) 21–40.
- [31] J.R. Evans, W.G. Davids, J.D. Macrae and A. Amirbahman, Kinetics of cadmium uptake by chitosan-based crab shells. *Water Res.*, 36 (13) (2002) 3219–3226.
- [32] N. Fiol, I. Villaescusa, M. Martinez, N. Miralles, J. Poch and J. Serarols, Sorption of Pb (II), Ni(II), Cu (II), and Cd (II) from aqueous solution by olive stone waste. *Sep. Purif. Technol.*, 50 (2006) 132.
- [33] B.F. Noeline, D.M. Manohar and T.S. Anirudhan, Kinetic and equilibrium modeling of lead (II) sorption from water and wastewater by polymerized banana stem in a batch reactor. *Sep. Purif. Technol.*, 45 (2005) 131–140.
- [34] M. Dogan, M. Alkan, A. Türilyılmaz and Y. Ozdemir, Kinetics and mechanism of removal of methylene blue by adsorption onto perlite. *J. Hazard. Mater.*, 109 (2004) 141–148.
- [35] V.A. Spinelli, M.C.M. Laranjeira, V.T. Fávere and I.Y. Kimura, Cinética e equilíbrio de adsorção dos oxianions Cr (VI), Mo (VI) e Se (VI) pelo sal de amônio quartenário de quitosana. *Revista Polímeros*, 15 (3) (2005) 218–223.
- [36] V.C. Srivastava, M.M. Swamy, I.D. Mall, B. Prasad and I.M. Mishra, Adsorptive removal of phenol by bagasse fly ash and activated carbon: equilibrium, kinetics and thermodynamics. *Colloids Surf.*, 272 (2006) 89–104.
- [37] M.A.K. Alcântara and O.A. Camargo, Isotermas de adsorção de Freundlich para cromo (III) em latossolos. *Sci. Agric.*, 58 (2001) 567–572.
- [38] U.K. Garg, M.P. Kaur, V.K. Garg and D. Sud, Removal of hexavalent chromium from aqueous solution by agricultural waste biomass. *J. Hazard. Mater.*, 140 (2007) 60–68.
- [39] B. Volesky, Detoxification of metal-bearing effluents: biosorption for the next century. *Hydrometallurgy*, 59 (2001) 203–216.
- [40] V.K. Gupta and I. Ali, Removal of lead and chromium from wastewater using bagasse fly ash – a sugar industry waste. *J. Colloid Interface Sci.*, 271 (2004) 321–328.
- [41] M. Kazemipour, M. Ansari, M. Tajrobehkar and H.R. Kermani, Removal of lead, cadmium, zinc and copper from industrial wastewater by carbon developed from walnut, hazelnut, almond, pistachio shell and apricot stone. *J. Hazard. Mater.*, 150 (2008) 322.
- [42] F.W. Sousa, Adsorção de metais tóxicos em efluentes aquosos usando pó da casca de coco verde tratado. *Fortaleza, UFCE, Pós Graduação em Engenharia Civil. Dissertação de mestrado*, 125 (2007).
- [43] S.S. Shukla, L.J. Yu, K.L. Dorris and A. Shukla, Removal of nickeç from aqueous solutions by sawdust. *J. Hazard. Mater.*, 121 (2005) 243.
- [44] E. Pehlivan, T. Altun, S. Cetin and M.I. Bhangar, Lead sorption by waste biomass of hazelnut and almond shell. *J. Hazard. Mater.*, 167 (2009) 1203–1208.
- [45] V.C.G. Dos Santos, J.V.T.M. De Souza, C.R.T. Tarley, J. Caetano and D.C. Dragunski, Assessment of chemically modified sugarcane bagasse for lead adsorption from aqueous medium. *Water Sci. Technol.*, 62 (2) (2009) 457–465.
- [46] F.F. Sodré, E. Lenzi and A.C. Costa, Applicability of adsorption models to the study of copper behaviour in clayey soils. *Quim. Nova.*, 24 (2001) 324–330.
- [47] Al-G. Nawash, A. Al-A. Mohammed, A. Al-A. Zaid, El-H. Tayel and Al-M. Idrees, Decontamination and adsorption modelling of aqueous Pb²⁺ and Co²⁺ ions using natural inorganic materials: tripoli (NT) and bentonite (NB). *Desal. Water Treat.*, 24 (2010) 336–343.
- [48] J.V.T.M. De Souza, K.M. Diniz, C.L. Massocatto, C.R.T. Tarley, J. Caetano and D.C. Dragunski, Removal of Pb (II) from aqueous solution with orange sub-products chemically modified as biosorbent. *Bioresources* 7 (2012) 2300–2318.