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Preparation and evaluation of kinetics and thermodynamics studies of lead adsorption onto chemically modified banana peels

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ABSTRACT

The use of alternative materials for environmental decontamination has been intensively studied. In this study, the capacity of banana peels treated with sodium hydroxide (NaOH), hydrochloric acid (HCl), and phosphoric acid (H_3PO_4) to adsorb Pb (II) was evaluated. The physical and chemical changes on the banana peels after chemical treatment were evaluated by infrared spectroscopy and scanning electron microscopy. Batch adsorption experiments were carried out as a function of pH, time, metal concentration, and temperature; desorption tests were also performed. Pb (II) concentrations were determined by flame atomic absorption spectrometry. An increase in the adsorption capacity of the modified and natural peels was observed in the pH range of 3–5, and pH 5 was adopted for further experiments. The adsorption system reached equilibrium in 300 min, and its kinetics followed the pseudo-second-order equation. From adsorption isotherms, it was observed considerable enhance on adsorption capacity of banana peels, especially with treated with NaOH. Besides, the negative Gibbs free energy variation values showed that the Pb (II) adsorption was spontaneous. Moreover, the improvement in the Pb (II) desorption for the modified peels was observed, indicating that the proposed material can be reutilized.

Keywords: Adsorption; Banana peels; Lead (II)

1. Introduction

In recent years, the society has been increasingly concerned about environmental protection, and the pollution of superficial waters appears to be one of the greatest problems facing the modern world [1]. The industrialization in many regions has increased the discharge of industrial wastes, especially those containing heavy metal. Metal ion contamination of drinking water and wastewater, especially with lead, cadmium, copper, nickel, and zinc, is a serious problem [2].

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Some metals are considered essential to the development of plants or animals; however, the limits of tolerance to these microelements, in general, are very low [3]. Lead is a very toxic element and the chronic exposure, even at low levels, is associated with several health effects [4]. It is very well known that heavy metal contamination most commonly arises from untreated effluent discharges into rivers and lakes. Considering this fact, the US Environmental Protection Agency (US EPA) and Brazilian National Council for the Environment (CONAMA, Resolution No. 357/2005) have established quality standards for water bodies and effluent discharges. Thus, the maximum contaminant level for lead allowed by the US EPA and CONAMA is 0.015 and 0.010 mg L^{-1}, respectively [5,6]. Conventional methods of treatment of effluents containing heavy metals such as precipitation, oxidation or reduction, filtration, ion exchange, electrochemical treatment, among others, are often restricted by technical impracticability and/ or economic [7]. A considerable increase in industrial wastes containing heavy metals discharged into rivers and seas has caused serious environmental problems associated with the need for stricter laws and motivated studies in this area. Thereupon, it is very important to elaborate and apply alternative low-cost and more efficient methods for treating water and effluents. The heavy metal removal using biomass as adsorbent could be an example of such methods, since tropical countries like Brazil have abundant biomass resources [8,9].

The use of various agroindustrial materials as potential adsorbents for the removal of metal ions from wastewater is reported in the literature: sunflower stem, rice bran [10], walnut shell [11], pine bark [12], wood bark [13], sugarcane bagasse [14,15], orange subproducts [16–25].

Due to its abundance and low cost, banana peel could be utilized as an inexpensive and simple alternative to the above-mentioned biosorbents for removing toxic metals like lead in order to reduce urban environmental problems as well as metal-contaminated industrial effluent treatment expenses. Banana is one of the most consumed fruits in the world, but its bark does not have a noble application. For this reason, the banana peels were tested as adsorbents of metal ions toxic industries. This biomass that has polymeric groups such as cellulose, hemicellulose, pectin lignin and proteins as active centers for the adsorption of metal ions [26].

Besides these, other chemical groups such as carboxylic acid, phosphate, and hydroxyl are also present in the shells, playing an important role in the removal of metal ions [27]. Fig. 1 lists the major interactions between the metal ion and the chemical groups present in the banana peel; (a) carboxyl, (b) hydroxyl, (c) phosphate groups.

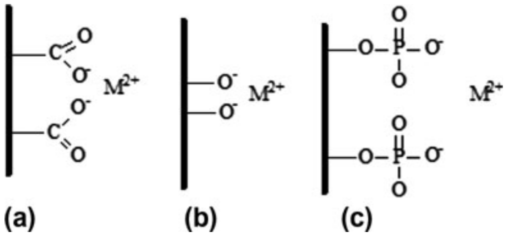


Fig. 1. Interactions between the metal ion (M^{2+}) and the chemical groups present in the banana peel; (a) carboxyl, (b) hydroxyl and (c) phosphate groups.

The objective of this study is to evaluate the efficiency of some chemical treatments of banana peels for improving their adsorption capacity and to test their Pb (II) (lead) adsorption capacity as a function of pH, time, concentration, and temperature in order to select a material that could be used in treating lead-contaminated wastewater effluents.

2. Experimental

2.1. Reagents

All chemicals used in this study were of analytical grade. 1,000 mg L^{-1} Pb (II) stock solutions were prepared from $Pb(NO_3)_2$ (Vetec, 99%), and required dilutions were done with deionized water obtained from a Millipore Milli-Q purification system (Bedford, MA, USA), 0.1 mol L^{-1} sodium hydroxide (NaOH) (F. Maia, 97%), hydrochloric acid (HCl) (F. Maia, 37%) and phosphoric acid (H_3PO_4) were used for chemical modifications of banana peels.

2.2. Equipment

Infrared spectra (FTIR) were recorded over the range of 4,000–400 cm^{-1} using a BOMEM MB-102 Fourier transform infrared spectrometer. Banana peel samples were macerated with KBr crystals (1 mg sample: 100 mg KBr) and placed on a disc pastillator.

Pb (II) was quantified using a GBC 932plus flame atomic absorption spectrometer (FAAS) equipped with a deuterium lamp for background correction and a hollow-cathode lamp as radiation source.

2.3. Adsorbent preparation and chemical modifications

Banana peels obtained from the market in Umuarama (Parana State, Brazil) were used as biomass in adsorption–desorption experiments. They were ground and sieved through a 100 mesh Bertel sieve, to obtain a more homogeneous particle size. Afterwards, 20 mL of 0.1 mol L^{-1} NaOH, HCl, and H_3PO_4 solutions were added separately to three flasks each containing 1 g of the banana peel powder. The mixtures were agitated for 2 h, and the supernatants were discarded. Then, the modified materials were washed with deionized water repeatedly and dried at 55 °C (NaOH-modified banana peel—BP-Na) or at 70 °C for 4 h (HCl and H_3PO_4-modified banana peels—BP-Cl and BP-P, respectively) [7].

2.4. Adsorption experiments

Batch adsorption tests were carried out with Pb $(NO_3)_2$ (Vetec, 99%) for the modified (BP-Na, BP-Cl, and BP-P) and natural (or non-modified, BP-NM) banana peel material without washing or pretreatment in order to study the pH, time, Pb (II) concentration, and temperature effects.

2.4.1. pH Effect

About 50 mL of 50 mg L^{-1} Pb (II) solutions at pH ranging from 2 to 7 was agitated with 0.5 g of the peel samples on an orbital shaker for 24 h. The Pb (II) adsorbed amount q_{eq} (mg g^{-1}) was calculated according to Eq. (1) given below.

$$q_{eq} = \frac{(C_o - C_{eq}) \times V}{M} \tag{1}$$

in which, C_0 and C_{eq} are the initial and equilibrium Pb (II) concentrations in the solutions (mg L^{-1}), respectively, V is the solution volume (L), and M is the sample mass (g).

2.4.2. Time effect

About 50 mL of 700 mg L^{-1} Pb (II) solutions was agitated with 0.5 g of the peel samples on an orbital shaker. Nine 500 μL aliquots were taken at time intervals ranging from 15 to 500 min, and Milli-Q water was added to each aliquot in order to reach a volume of 50 mL. Then, all the solutions were analyzed with a FAAS to determine Pb (II) concentrations and corrections to the material quantity were made for each aliquot. Finally, the obtained data were used to calculate the Pb (II) adsorbed amount q_{eq} according to Eq. (1).

2.4.3. Pb (II) concentration effect (adsorption isotherms)

About 50 mL of 100–1,000 mg L^{-1} Pb (II) solutions was individually agitated with 0.5 g of the peel samples on an orbital agitator for 12 h; the solution pH was adjusted with 0.1 mol L^{-1} NaOH or HCl and fixed at pH 5.0. Then, the mixtures were filtered, and the solutions were analyzed by FAAS in order to determine the initial and final Pb (II) concentrations. Finally, the obtained data were used to estimate the Pb (II) adsorbed amount q_{eq} by constructing a q_{eq} versus C_{eq} plot.

2.4.4. Temperature effect

About 50 mL of 700 mg L^{-1} Pb (II) solutions was mixed with 0.5 g of the peel samples and agitated at five different temperatures (10, 20, 30, 40, and 60 °C) under the conditions (pH and time) determined in the previous experiments. Afterward, variations of the thermodynamic parameters—Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS)—were evaluated.

2.5. Desorption experiments

Desorption experiments were carried out in order to investigate the reutilization possibility for the present adsorbent. The banana peel samples used in the adsorption assays were filtered and washed with deionized water to remove non-adsorbed Pb (II) species. Then, they were transferred to flasks and agitated with 50 mL of 0.1 mol L^{-1} HCl solution for 12 h. Further, the samples were filtered again and analyzed according to the method proposed by Radojevic and Bashkin [28].The Pb (II) content in the liquid phase was measured by FAAS.

3. Results and discussion

3.1. Adsorbent characterization

In order to confirm the banana peel chemical modification arisen from NaOH, HCl, and H_3PO_4, FTIR spectroscopy was used to elucidate some functional groups (present in the non-modified (natural) and modified biomass samples) probably involved in the Pb (II) adsorption process (Fig. 2). Comparing the IR spectra obtained for the natural and modified peel samples, it was possible to identify structural alterations due to the modification reactions. The peaks observed at 3,400, 2,920, 1,737, 1,629, 1,525, 1,450, 1,027, and 536 cm^{-1} are presented in Fig. 2.

The wide and strong band at 3,400 cm^{-1} is attributed to the O–H stretching vibrations, the peak at 2,920 cm^{-1} is ascribed to the C–H stretching vibrations, whereas the peaks at 1,737 and 1,629 cm^{-1} can be related to the C–O stretching vibrations. According to the literature data, the adsorption of the carbonyl

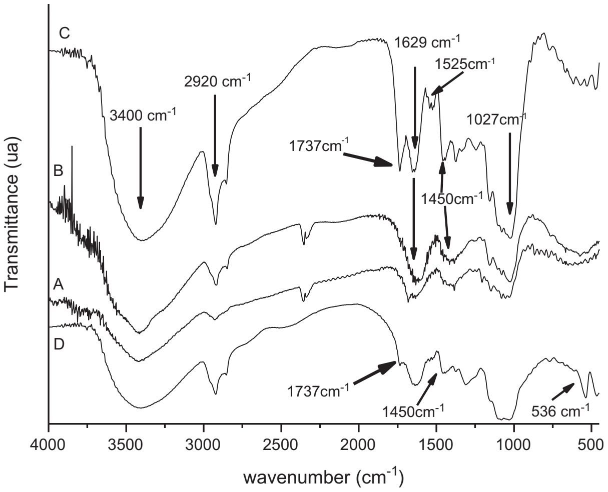


Fig. 2. IR spectra for the banana peel samples: (A) non-modified peel, (B) NaOH-modified peel, (C) HCl-modified peel, and (D) H_3PO_4-modified peel.

groups present in esters and carboxylic acids takes place at approximately 1,730 cm^{-1} [29]. For the carboxylate anions, axial deformities can be observed at 1,550 cm^{-1}, whereas for the C–O–H bonds, angular deformities can be seen in the region of 1,450 cm^{-1}. The peaks at 536 and 1,027 cm^{-1} are attributed to the phosphate groups and polysaccharides, respectively. Thus, it can be concluded that the hydroxyl, carbonyl, phosphate, and carboxyl groups were present in the studied biomass.

For the modified samples, there was an alteration in the peak intensity at 1,737 cm^{-1}. The most intense alteration was observed for the HCl-modified banana peel (Fig. 2(C)), indicating the strong presence of the carboxylate anions (peaks at 1,629, 1,525, and 1,450 cm^{-1}). For the NaOH-modified peel, these anions are confirmed by the increase in the peak intensity at 1,525 and 1,450 cm^{-1} (Fig. 2(B)). The peak at 536 cm^{-1} justifies the modification with the phosphate anions (Fig. 2(D)).

The morphologies of adsorbents are displayed in Fig. 3. It can be seen that the morphology, represented by irregular flakes of BP-P (Fig. 3(D)) and BP-NM (Fig. 3(A)), is very similar, indicating that the chemical modification with H_3PO_4 does not alter the morphological structure of adsorbent. On the other hand, using NaOH (Fig. 3(B)) or HCl (Fig. 3(C)) as chemical modifier agents, it can be seen some imperfections on the adsorbent surface in the form of lamellar pore channel as regard BP-NM, probably due to hydrolyses of carbohydrates and fibers of banana peels. This finding shows that chemical modification with NaOH or HCl promotes adequate morphological profile to banana peels to adsorb metal ions.

The material modified with NaOH (Fig. 3(B)) showed a morphology rougher compared with in nature material and other modifications. This can also contribute to increased efficiency of the sorption process. This same behavior was observed in the modification of rice husk with NaOH [21].

3.2. *pH Effect*

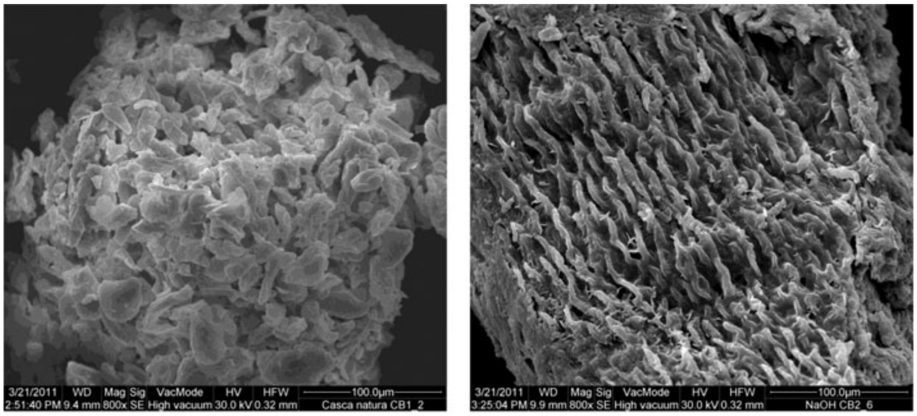
The available literature data show that pH is one of the most important variables in the process of heavy metal removal by biomass. According to Swaminathan et al. [30], the removal of metal ions from aqueous solutions through adsorption depends on the solution pH, since it affects superficial adsorbent loading, ionization level, and adsorbate species.

Liu et al. [31] also reports that H^+ ions compete with metal ions for the adsorption sites at pH below 7.0, and because of the greater presence of the H^+ ions, the adsorbent surface tends to become less negatively charged, thus reducing the attraction of the positively charged metal species like Pb (II). The pH effect on the Pb (II) adsorption capacity was studied herein, and the pH values were varied from 3 to 7, as shown in Fig. 4. As seen in this Fig. 4, a slight decrease on Pb (II) adsorption was observed for the pH interval of 3.0–5.0, probably by the formation of $Pb(OH)^+$ which makes the analyte adsorption less effective [32]. At pH 7.0, the increase in the lead retention possibly is attributed to the precipitation of Pb $(OH)_2$. In strong acidic media, the H^+ ions competed with the Pb (II) ions for the hydroxyl and carbonyl groups, and the Pb (II) adsorption was lower, as observed at pH 2.0. Thus, in order to avoid drastic sample pH changes by inserting acid solution in aqueous sample, bearing in mind the treatment of natural water or effluent samples, the pH 5.0 was chosen for further experiments.

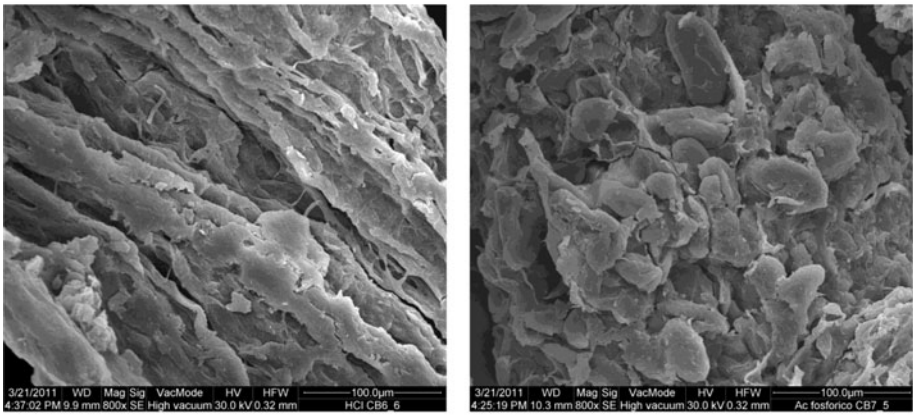
3.3. *Time effect*

The study of adsorption kinetics appears to be important, since it demonstrates the influence of the contact time on the contaminant Pb (II) amount adsorbed on the biomass (banana peels) and allows to adequately calculate effluent treatment system parameters by evaluating the speed at which this contaminant is removed from the solution.

Fig. 5 illustrates the Pb (II) adsorption kinetics for the banana peel samples: BP-NM, BP-Na, BP-Cl, and BP-P. It was observed that the greater Pb (II) adsorption was for BP-Na followed by BP-Cl. Thus, it was preliminarily noticed that the chemical modifications



(A) Non-modified banana peel (B) NaOH-modified banana peel



(C) HCl-modified banana peel (D) H_3PO_4-modified banana peel

Fig. 3. Micrographs of banana peel samples at 800× magnification; Non-modified banana peel (A); NaOH-modified banana peel (B); HCl-modified banana peel (C); and H_3PO_4-modified banana peel (D).

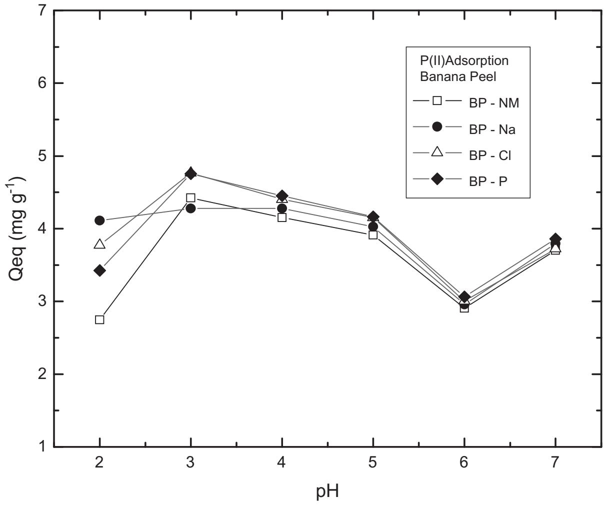


Fig. 4. Pb (II) adsorption on the banana peels at different pH and initial concentration of 50 mg L^{-1}. BP-NM (non-modified peel), BP-Na (NaOH-modified peel), BP-Cl (HCl-modified peel), and BP-P (peel H_3PO_4-modified peel).

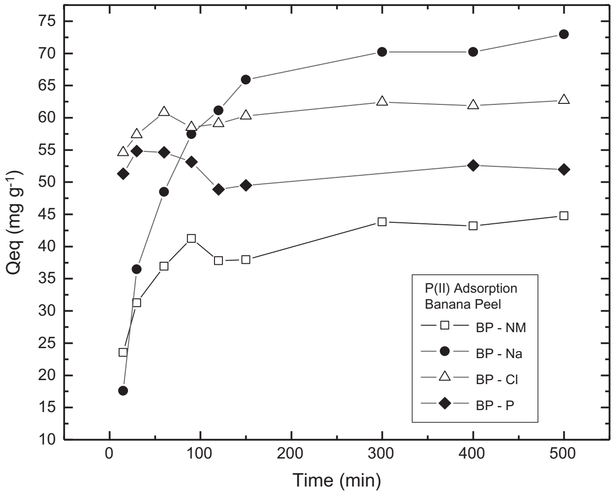


Fig. 5. Pb (II) adsorption kinetics for the banana peel samples: BP-NM (non-modified peel), BP-Na (NaOH-modified peel), BP-Cl (HCl-modified peel), and BP-P (H_3PO_4-modified peel).

improved the adsorption properties of the present biomass.

As seen in Fig. 5, the system tended to reach equilibrium in about 300 min. Ferreira et al. [33] obtained the system equilibrium after a longer contact period, approximately 48 h, but they did not get a better result for the Pb (II) adsorption by *Saccharomyces cerevisiae*. According to dos Santos et al. [14], the system reached the equilibrium in about 500 min for all modified sugarcane bagasse samples. Therefore, the adsorption process using the banana peels was efficient, since it needed a little time to reach the equilibrium

In order to investigate the nature of kinetic adsorption mechanism, the pseudo-first-order and pseudo-second-order models were employed [34,35].

The pseudo-first-order kinetics follows the Lagergren model expressed by Eq. (2) [22,36–38].

$$\log(q_{\mathrm{eq}} - q_t) = \log q_{\mathrm{eq}} - \frac{K_1 x t}{2.303} \tag{2}$$

in which q_t is the metal adsorbed amount (mg g^{-1}) at time t (min.), and K_1 is the pseudo-first-order rate constant (min^{-1}); q_{eq} and K_1 can be determined through the linear and angular coefficients of the $\log(q_{\mathrm{eq}} - q_t)$ versus t plot, respectively. This equation is one of the models most commonly used for studies of sorption processes, and it considers that the adsorption speed depends proportionally on the number of available active sites [39].

Comparing the q_{eq} values obtained experimentally (exp.) and those calculated through Eq. (2), it can be observed that they are not so close to each other (Table 1). Besides, the r^2 values are far from unity, suggesting that the adsorption did not follow a pseudo-first-order reaction.

Thus, the pseudo-second-order model was applied, since it is based on the adsorption capacity at equilibrium and considers chemical adsorption involving valence forces through exchange and/or sharing of electrons between the adsorbent and adsorbate [40,41], as represented by Eq. (3) regarding the metal adsorption kinetics for various banana peels [22,36–38].

$$\frac{t}{q_t} = \frac{1}{K_2 q_{\mathrm{eq}}^2} + \frac{t}{q_{\mathrm{eq}}} \tag{3}$$

in which k_2 is the pseudo-second-order constant (g mg^{-1} min^{-1}) obtained from the straight line slope of the t/q_t versus t plot, and q_{eq} can be evaluated through the linear coefficient. The q_{eq}, k_2 and r^2 calculated values are given in Table 1.

Based on the data presented in Table 1, it can be verified that the q_{eq} (cal.) values calculated using the pseudo-second-order kinetic model are close to the experimental ones, and the r^2 values are near 1, thus confirming that the Pb (II) adsorption process followed pseudo-second-order kinetics.

3.4. Adsorption isotherms

After establishing the pH and equilibrium time (Sections 3.2 and 3.3), the Pb (II) solutions at pH 5.0 were put in contact with the banana peel samples for 300 min to determine the minimum amount of the adsorbent material required for the maximum Pb (II) removal. Fig. 6 shows the Pb (II) adsorption isotherms for the banana peel samples.

The isotherm constructed for BP-Na (Fig. 6) has a different format compared with the other materials. According to Giles et al. [42], this isotherm (type represents a rare case, when, at high adsorbate concentrations, adsorbate–adsorbate interactions are favorable, and they increase rapidly in comparison with adsorbate–adsorbent interactions.

The equilibrium data were adjusted to Langmuir and Freundlich models. The Langmuir adsorption model represented by Eq. (4) (in linear form) considers the formation of monolayers on a surface with a finite number of identical (homogeneous) adsorption sites [43]. Besides, it assumes that adsorption forces are similar to chemical reactions, and the only

Table 1
Pseudo-first-order and pseudo-second-order kinetic parameters of Pb(II) adsorption

Material	q_{eq} (exp.) (mg g^{-1})	Pseudo-first-order kinetics			Pseudo-second-order kinetics		
		K_1	q_{eq} (cal.) (mg g^{-1})	r^2	K_2	q_{eq} (cal.) (mg g^{-1})	r^2
BP-NM	44.77	1.16E−03	11.66	0.867	5.53E+03	45.75	0.999
BP-Na	72.97	1.78E−03	39.54	0.978	1.30E+04	78.19	0.999
BP-Cl	62.69	9.73E−04	6.19	0.991	3.10E+05	96.15	0.999
BP-P	54.82	2.01E−04	4.38	0.649	8.72E+05	85.47	0.999

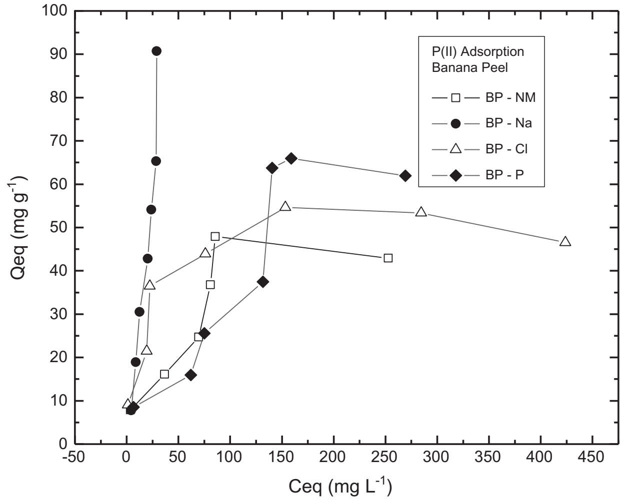


Fig. 6. Pb (II) adsorption isotherms for the banana peel samples: BS-NM (non-modified peel), BS-Na (NaOH-modified peel), BS-Cl (HCl-modified peel), and BS-P (H_3PO_4-modified peel).

interaction between the adsorbed species and the microporous adsorbent takes place.

$$\frac{C_{\mathrm{eq}}}{q_{\mathrm{eq}}} = \frac{1}{q_m^b} + \frac{C_{\mathrm{eq}}}{q_m} \tag{4}$$

in which b is the adsorption intensity (L mg^{-1}), and q_m is the maximum adsorption capacity (the maximum metal amount adsorbed when the material becomes saturated with the adsorbate) (mg g^{-1}).

For a favorable adsorption process, b values should lie between 0 and 1 ($0 < b < 1$); the cases of $b = 1$ and 0 represent a linear and irreversible process, respectively [44]. Thus, the values shown in Table 2 show the adsorption process is favorable by the values for b.

The Freundlich model proposes an empirical isotherm for a non-ideal system, assuming multilayer structures and predicting an exponential distribution of some adsorption sites with different energies. It does not consider the adsorbent material saturation, thus accepting the existence of incomplete superficial layers [45]. This isotherm model is expressed by Eq. (5) (in linear form).

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

in which K_f is the adsorbent–adsorbate affinity (L g^{-1}), and n is the heterogeneity factor quantitatively indicating the reactivity of energetic sites on the adsorbent surface [46].

Table 2 gives a small comparison of the Langmuir and Freundlich model parameters for the banana peel samples. As seen, the data can be well explained by both the Langmuir and Freundlich models.

The Langmuir adsorption model has been widely used to estimate the adsorption capacity (q_m) of some chemical elements and evaluate the constant related to the bonding energy (b) [46].

For the Freudlich model, when n values do not equal unity, the energetic site distribution tends to vary with the adsorption density [46], fact observed for residues BP-NM, BP-Cl and BP-P.

It can be verified that among the tested samples, the BP-Na peel was the one that showed the best result. It was observed that this kind of chemical treatment brought a considerable increase in the Pb (II) adsorption, with at least nine times greater than that for the non-modified peel (BP-NM). However, the value obtained by the Langmuir isotherm for BP-Na is overestimated, so, when observing Fig. 4 graph, which shows the experimental values, note that the maximum value is about 90 mg g^{-1}, or, approximately twice that for BP-NM. In lead adsorption assay using other adsorbents (Table 3), it was noticed that BS-Na was the one that presented the greatest adsorption capacity, indicating that this material can be a promising adsorbent for this metal.

3.5. Thermodynamic parameters

The thermodynamic parameters (Table 4) reflected the viability and spontaneity of the Pb (II) adsorption process. ΔH values were found by calculating the

Table 2
Langmuir and Freundlich model parameters for Pb (II) adsorption on the banana peel samples

Material	Langmuir constants			Freundlich constants		
	q_m (mg g^{-1})	b (L mg^{-1})	r^2	K_f (L g^{-1})	n	r^2
BP-NM	50.454	0.020	0.966	3.838	2.102	0.945
BP-Na	469.48	0.005	0.926	1.624	0.902	0.950
BP-Cl	49.776	0.148	0.994	8.302	2.822	0.988
BP-P	71.124	0.037	0.985	3.194	2.043	0.965

Table 3
Pb(II) adsorption capacity for some adsorbents reported in the literature

Adsorbent	Sorption capacity ($mg\,g^{-1}$)	Reference
Tea leaves	78.87	[29]
Pine bark	3.33	[20]
Bentonite clay	6.00	[20]
Apple residue	8.00	[20]
Non-modified (natural) *Luffa cylindrical*	9.20	[20]
Sugarcane bagasse	52.63	[14]
NaOH-modified banana peel	90.00	Present study

Table 4
Thermodynamic parameters for Pb(II) adsorption

Material	K_d	ΔG ($kJ\,mol^{-1}$)	ΔH ($kJ\,mol^{-1}$)	ΔS ($J^{-1}\,mol^{-1}$)
BP-NM	2.76E + 02	−14.16	11.11	36.80
BP-Na	9.09E + 02	−17.16	15.20	50.33
BP-Cl	6.38E + 01	−10.47	42.15	139.17
BP-P	2.09E + 02	−13.46	32.83	108.43

Table 5
Pb(II) adsorption–desorption values; initial concentration = 934 $mg\,L^{-1}$

Material	Adsorbed concentration ($mg\,L^{-1}$)	Desorbed concentration ($mg\,L^{-1}$)	Desorption rate (%)
BP-NM	609.7	376.2	61.70
BP-Na	688.7	486.5	70.64
BP-Cl	485.1	383.20	78.99
BP-P	637.7	238.60	37.42

straight line slope of the ln K_d versus $1/T$ plot based on the van´t Hoff equation, whereas ΔG and ΔS values were determined according to Eqs. (6) and (7).

$$\Delta G = -RT \ln K_d \tag{6}$$

$$\Delta G = \Delta H - T\Delta S \tag{7}$$

in which $K_d = q_{\mathrm{eq}}/C_{\mathrm{eq}}$ is the Pb (II) distribution coefficient ($L\,g^{-1}$), $R = 8.314$ is the universal gas constant ($J\,K^{-1}\,mol^{-1}$), T is the temperature (K).

As seen from Eqs. (6) and (7), the free energy variation (ΔG) is followed by the enthalpy and entropy simultaneous variations (ΔH and ΔS, respectively); thus, the relative behavior of the latter parameters defines the free energy value that determines the system spontaneity. Negative ΔG values indicate favorable interactions between the adsorbent and adsorbate, and the higher the modulus of these negative values, the more spontaneous the adsorption system [47]. Nevertheless, non-spontaneous processes characterized by positive ΔG values may be found in some adsorption systems where the adsorbate nature and adsorbent surface nature do not favor the retention of species [48,49].

For BP-Na, it was possible to verify a negative increase in the ΔG value when compared to BP-NM (Table 4). However, it can be seen that for the other samples, the ΔG values were also negative, demonstrating the energetically favorable Pb (II) adsorption process. The ΔH values were positive, confirming the endothermic nature of the process. Finally, the ΔS values were positive as well, showing an increase in the system disorder at the solid/liquid interface during the Pb (II) adsorption.

3.6. *Pb (II) desorption*

To study the Pb (II) desorption from the surface of each adsorbent, the peels were rinsed with 150 mL of Milli-Q water, dried in an oven at 50˚C for 24 h and then immersed in a 0.1 $mol\,L^{-1}$ HCl solution (50 mL) in order to remove Pb (II). Finally, the Pb (II) concentrations and desorption rates were determined [36]. The obtained results are presented in Table 5.

Based on the found desorption rate values, it can be verified that BP-Na also favored the Pb (II) desorption process. These values can be considered satisfactory for possible reutilization of this modified banana peel material as new adsorption phase.

4. Conclusion

It was verified that the treatment of the banana peels, especially with NaOH caused an increase in the Pb (II) adsorption capacity. The adsorption process followed the pseudo-second-order kinetic model. The Pb (II) adsorption data were successfully fitted to both the Langmuir and Freundlich models, thus indicating surface heterogeneity. However, the Freundlich model was very well fitted for the NaOH-modified banana peels, and thus, a saturation condition was not reached, but under range studied of Pb (II) concentration, the adsorption capacity was very high close to 90 $mg\,g^{-1}$. Additionally, the chemical modification with NaOH made the system more energetically favorable, which was confirmed by the highest negative ΔG value. In addition, it caused an improvement in the Pb (II) desorption, thus indicating that the proposed material can be reutilized.

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