Chemical Engineering Journal 160 (2010) 549–555

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Thermodynamic aspects of the Pb adsorption using Brazilian sawdust samples: Removal of metal ions from battery industry wastewater

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ARTICLE INFO

Article history:
Received 16 October 2009
Received in revised form 25 March 2010
Accepted 26 March 2010

Keywords:
Lead
Wastewater
Calorimetry
Sawdust

ABSTRACT

Brazilian sawdust samples (*Caryocar* spp.; *Manilkara* spp.; and *Tabebuia* spp.) have been used for Pb(II) ions adsorption from water at 25 °C. The series of adsorption isotherms were adjusted to a modified Langmuir equation from data obtained by suspending the sawdust with $Pb(NO_3)_2$ solutions, which gave the maximum number of moles adsorbed as 89.10 ± 8.28; 145.04 ± 12.43 and 95.31 ± 8.28 mg g^{-1} for *Caryocar* spp.; *Manilkara* spp.; and *Tabebuia* spp., respectively. Thermodynamic data of interactions were studied by the calorimetric titration of Pb(II) in aqueous solution. Gibbs free energies were negative for all systems and the adsorption interactions presented the following exothermic enthalpic values: −1.99 ± 0.11; −3.20 ± 0.21 and −2.27 ± 0.11 kJ mol^{-1} for *Caryocar* spp.; *Manilkara* spp.; and *Tabebuia* spp., respectively. All liquid/solid interface adsorptions were entalpically and entropically driven. These sawdust samples were applied to remove Pb(II) from wastewater of a battery industry of Brasilia, DF, Brazil, which presented a Pb(II) concentration of 2.66 mg L^{-1}. The Pb(II) concentration in this wastewater was reduced to 2.49; 0.45 and 0.47 mg L^{-1} by application of *Caryocar* spp.; *Manilkara* spp.; and *Tabebuia* spp., respectively.

1. Introduction

The exponential growth of industrial activities and the increase of the use of many chemicals in industries have increased the pollution in the environment, mainly, in aquatic ecosystem [1–3]. The contamination of natural waters with toxic metals has become one of the major concerns of environmental researchers in recent years due to water importance to environment and mankind [4–6]. Thus, the presence of inorganic contaminants such as arsenic, cadmium, chromium, lead and mercury represents a big problem to the environment because they are not biodegradable and cause many diseases and disorders by accumulation in living organisms [7–9]. Among these toxic metal ions, lead must be highlighted, due to the Pb(II) is very toxic, causing many health problems to human such as: renal disturbances, hepatitis, encephalopathy, anaemia, lung inefficiency, bone lesions, hypertension, as well as, cancer [7,8,10].

Industries of pigments, mining, lead smelters, glass, and mainly, batteries have generated high levels of lead in waters [11,12]. In this way, the treatments used to remove toxic metals from industrial effluents based on exchange resins, chemical precipitation, electroflotation are expensive [7,8,13]. Thus, the application of low-cost materials, as byproducts of furniture industries, to remove contaminants from water is one way to develop a low expensive treatment of hazardous wastes [6,14–16].

In order to evaluate the interaction energy between contaminant and adsorbent, calorimetric studies have been extensively applied [17–20]. In 1784, Lavoisier and Laplace developed an ice calorimeter in order to determine the calorific capacity of materials, heat of reaction, of metabolic heat by applying the formula for the latent heat of melting water obtained by this ice calorimeter, once there were not accurate thermometers, thermistors or thermopiles to determine small energetic changes [21,22]. Since the development of technology of calorimeters, small energy values have been determined, and nowadays, it is possible to identify and quantify many phenomena of the distinct processes in colloidal systems in solid/liquid interfaces such as: energy distribution of the surface, adhesion energy, enthalpy of dilution, aggregation/micellization

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doi:10.1016/j.cej.2010.03.066

enthalpy, as well as, interaction between contaminant adsorbate molecules and the adsorbent [23]. Indeed, the calorimetric data is an important tool to understand the nature of the interactions between contaminant-adsorbent.

In this context, the adsorption of Pb(II) by Brazilian sawdust samples (*Caryocar* spp.; *Manilkara* spp.; and *Tabebuia* spp.) was followed. An understanding of the thermochemical characteristics of the adsorption interaction was developed by the determination of the calorimetric adsorption data at the solid/liquid interface, and these low-cost materials were applied to remove Pb(II) ions from battery industry wastewater.

2. Experimental

2.1. Chemicals

Brazilian sawdust samples of Piquiá (*Caryocar* spp.), Maçaranduba (*Manilkara* spp.) and Ipê (*Tabebuia* spp.) were obtained from Rancho da Cabocla Sawmill Ltda in Brazilian Santarém city. Sawdust adsorbents were grained and sieved by a range of sieves and only the particles smaller than 2.5 mm were used, as according to ASTM Method D4749 [17].

$Pb(NO_3)_2$, HCl, H_2SO_4, NaOH, benzene, ethanol, chloroform from Vetec and Folin-Denis reagent, vanillin from Aldrich were used without purification.

The water streams were collected in a battery industry effluent located in Distrito Federal, Brazil. Wastewater samples were collected into glass bottles, and the samples were stored in a refrigerator at 4 °C.

2.2. Characterization of sawdust samples

2.2.1. Extracts for lignin determination

33 g of sawdust samples were sequentially extracted in a soxhlet apparatus with benzene, benzene:ethanol (2:1), chloroform, and water. The isolated extracts were dried in an oven at 70 °C for 12 h and the residual air-dried wood powder. This powder was separated in order to determine the lignin content [18,19].

2.2.2. Extracts for total phenol, proanthocyanidin and tanin determinations

50 g of sawdust samples were submitted to an extraction with methanol:water (80:20) in a beaker at room temperature with stirring for 24 h. The mixture was filtered and the methanol was evaporated under reduced pressure at 40 °C. The remaining aqueous extract was divided in four fractions, freeze-dried for its conservation and separated in order to determine the total phenols, proanthocyanidins and tannins contents [18,19].

2.2.3. Proanthocyanidin contents

Proanthocyanidin determination was carried out by the vanillin method [18,19]. 1 mL of the aqueous extract was mixed with 2 mL of a freshly prepared vanillin solution (1 g/100 mL of 70% H_2SO_4) and maintained at 20 °C for 15 min. The absorption was measured at 500 nm. Calibration was performed with catechin aqueous solutions (2–40 $\mu g\,mL^{-1}$).

2.2.4. Lignin content

Lignin content of sawdust samples was determined as according to Björkmann technique. 100 g of dried sawdust samples were extracted in a soxhlet apparatus with ketone–water (9:1) and the organic solvent was evaporated under reduced pressure at 70 °C. After that, the aqueous mixture was acidified with diluted HCl until pH 2 was reached. The precipitated lignin was filtered and washed with a small amount of water. The lignin was dried at 70 °C for 12 h [18,19].

2.2.5. Total phenol contents

The total phenol content was determined by the Folin-Ciocalteu method. 2.5 mL of Folin-Ciocalteu reagent and 2 mL of aqueous solution of sodium carbonate (75 $g\,L^{-1}$) were added to 0.5 mL of the aqueous extract, and the mixture was kept at 50 °C for 5 min. After cooling, absorbance was measured at 760 nm. Aqueous solution of gallic acid (2–40 μg) was used as standard [18,19].

2.2.6. Tannin content

0.25 mL of aqueous extract was solubilized in 100 mL of aqueous solution with 5 mL Folin-Ciocalteau reagent, and 10 mL of aqueous solution of Na_2CO_3 7.5%. The tannin contends was determined using a UV–vis spectrophotomer at 760 nm [18,19].

2.2.7. Surface area

Nitrogen adsorption–desorption data were taken from an instrument Quantachrome NOVA 2200 gas sorption analyzer at 77 K. Surface area was calculated by the Brunauer–Emmett–Teller (BET) method, and pore size distribution was derived from the adsorption branches by using the Barrett–Joyner–Halenda (BJH) method.

2.3. Adsorption studies

The adsorption process was followed batchwise in an aqueous solution of $Pb(NO_3)_2$ with controlled pH 5 at 298 ± 1 K for 12 h. For this process, a series of samples containing about 25.0 mg of sawdust were suspended in 50.0 mL of aqueous $Pb(NO_3)_2$ solutions of different concentrations, varying from zero to 5.0 $mmol\,L^{-1}$. The best pH value was determined by using 50.0 mg of sawdust suspended in 50.0 mL of different aqueous $Pb(NO_3)_2$ solutions, which pH values varied from 1 to 6 and they were controlled by Clark/Lubs buffers [20]. The time required to reach the adsorption equilibria was determined by suspension of 25.0 mg of sawdusts in 50.0 mL of aqueous $Pb(NO_3)_2$ 5.0 $mmol\,L^{-1}$. At appropriate time intervals, the supernatant from each flask was collected and Pb(II) concentration was determined.

The effect of pH was determined by using 50.0 mg of sawdust suspended in 50.0 mL of different aqueous $Pb(NO_3)_2$ solutions, which pH values varied from 1 to 6 and they were controlled by Clark/Lubs buffers [20].

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The amount of metal ion adsorbed was determined from the difference in metal ion concentration measured by atomic adsorption spectrometry using a Buck model A-200 instrument (Buck Scientific, East Norwalk, CT, USA) in the aqueous sample before and after treatment with sawdust. All experiments were carried out in triplicate.

2.4. Calorimetric analysis

The adsorption of Pb(II) ions by Brazilian sawdust samples was followed calorimetrically by titration using an Adiabatic Solution Calorimeter Parr 6755 (Parr Instrument Company, Moline, IL, USA). In a typical experiment, 0.50 g of the material was suspended in 50.0 mL of water, equilibrated at 298.15 ± 0.02 K (thermostatically controlled), and titrated with aqueous solution of $Pb(NO_3)_2$

0.50 mol L^{-1}. The metal solution was added in increments of 0.05 mL, via a syringe coupled to the calorimetric vessel, up to saturation of the active surface sites of the material. Following each addition, the constant heat flux ($\Delta_{tit}Q$) was recorded at the end of the operation, and the mixture allowed to re-equilibrate. A similar procedure was used to monitor the heat flux due to metal dilution ($\Delta_{dil}Q$) in the absence of sawdust and also the heat flux of solvation of the suspended sawdust ($\Delta_{sol}Q$) [21].

2.5. Treatment of battery wastewater with Brazilian sawdust samples

The metal contents in battery industry effluent were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) using a Varian Liberty RL Series II spectrometer (Varian, Palo Alto, CA, USA). Metal removal from battery industry wastewater was followed batchwise with pH 4.2 (pH of battery industry effluent) at 25 °C. During the treatment of wastewater with sawdust samples, 100 mL of battery industry wastewater was mechanically stirred with 5 g of the sawdust samples during 24 h at 25 °C. The solutions were decanted, and a clear solution was collected and analyzed. The metal amounts of battery industry effluent before and after sawdust treatments were quantified by ICP-OES. This treatment was repeated once in order to decrease of Pb(II) levels as according to Brazilian standard limits.

3. Results and discussion

The knowledge about the chemical and physical properties of Brazilian sawdust samples is necessary in order to understand their adsorptive behavior. These data are listed in Table 1.

The chemical results of Brazilian sawdust samples showed that the wood adsorbent components (protoanthocianidins, total phenols and tannins) presented the following sequence: *Manilkara* spp. > *Tabebuia* spp. > *Caryocar* spp.

Detailed adsorptive and thermochemical studies were followed in order to understand the ability of these sawdust samples to remove Pb(II) from water. Thus, the numbers of moles of Pb(II) adsorbed per gram of each adsorbent (Nf) were obtained from the Eq. (1) [22,23]

$$N_f = \frac{n_i - n_s}{m} \tag{1}$$

where n_i is the initial number of moles of Pb(II) added to the system, n_S is the number of moles at equilibrium after adsorption, and m is the mass (g) of sawdust adsorbents.

The effect of pH values on Pb(II) adsorption by the sawdust samples was followed by the data obtained, as shown in Fig. 1. This graph shows that the retention ability with changes in pH values presented the lowest value at pH 1.0 for all sawdust samples. Above this pH value, the adsorption increased up to pH 5.0 maintaining constant up to pH 6.0 for all sawdust samples. This figure showed that *Tabebuia* spp. and *Manilkara* spp. adsorbed Pb(II) in a similar amount, which adsorbed more lead than *Caryocar* spp. in any range of pH values.

Fig. 2 shows the plots of Nf versus time for the adsorption of Pb(II) from aqueous solutions by using *Tabebuia* spp., *Manilkara* spp., and *Caryocar* spp. This figure clearly shows that the time necessary to reach the adsorption equilibra for all samples was about 70 min.

Profiles of the obtained adsorption isotherms represented by the number of moles adsorbed (N_f), versus the number of moles at equilibrium per volume of solution (C_S), are shown in Fig. 3. For the series of isotherms, the data reveal that the adsorption process is

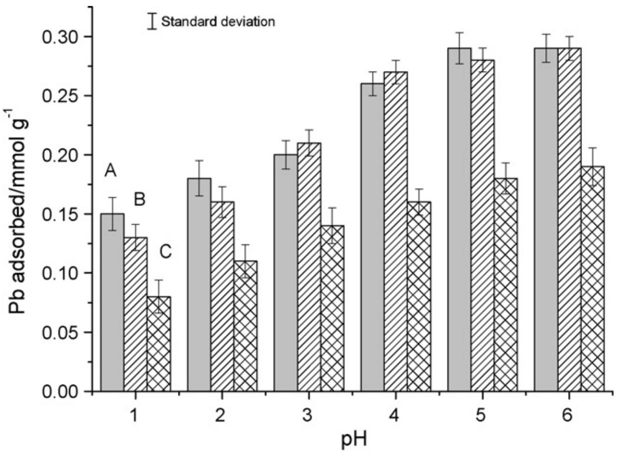

Fig. 1. Effect of pH on the adsorption of Pb(II) by *Tabebuia* spp. (A), *Manilkara* spp. (B) and *Caryocar* spp. (C).

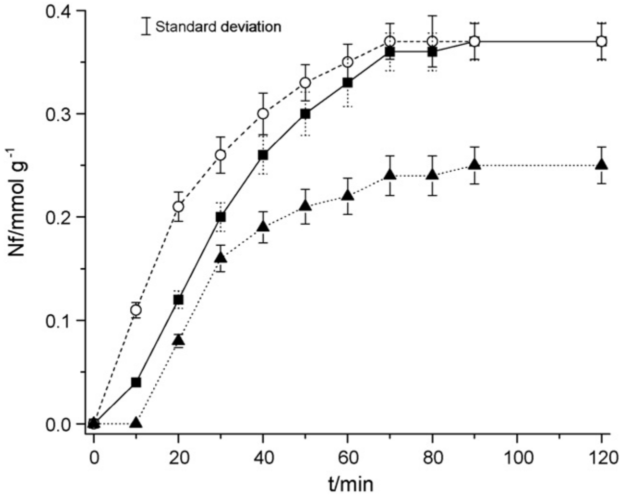

Fig. 2. Pb(II) adsorption on *Tabebuia* spp. (■), *Manilkara* spp. (○) and *Caryocar* spp. saw dust samples (▲) as a function of time.

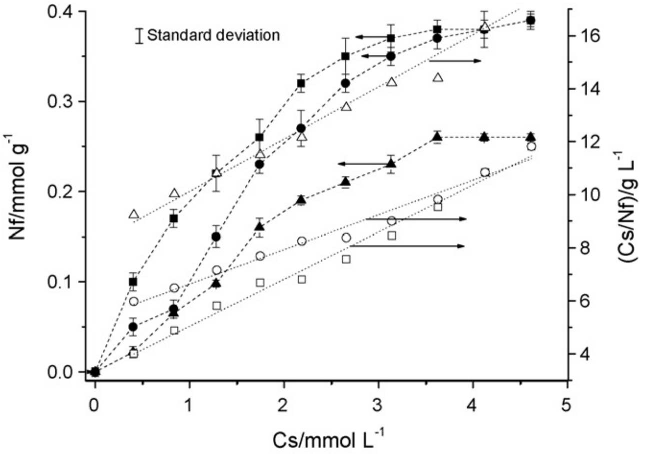

Fig. 3. Adsorption isotherm of aqueous $Pb(NO_3)_2$ solution for *Tabebuia* spp. (■), *Manilkara* spp. (●) and *Caryocar* spp. sawdusts (▲) at 298 ± 1 K, and the linearized form of the adsorption isotherms (□), (○) and (△), respectively.

Table 1
Physical properties of Brazilian sawdust samples.

	Proanthocyanidin (μg/g)	Lignin (μg/g)	Total phenol (μg/g)	Tanin (μg/g)	Surface area (m^2/g)
Caryocar spp.	106.4	300.0	107.3	29.7	3.50
Manilkara spp.	328.2	550.0	332.4	98.2	1.27
Tabebuia ssp.	173.5	450.0	197.2	60.3	2.25

Table 2
The maximum number of moles adsorbed, Ns, equilibrium constants, K, and the thermodynamic data, ΔH, ΔG and ΔS, for Pb(II) adsorption on *Caryocar* spp.; *Manilkara* spp.; and *Tabebuia* spp. at 298.15 ± 0.02 K.

	Caryocar spp.	*Manilkara* spp.	*Tabebuia* spp.
N_S, mmol g^{-1}	0.43 ± 0.04	0.70 ± 0.06	0.56 ± 0.04
N_S, mg g^{-1}	89 ± 8	145 ± 12	95 ± 8
K	323 ± 29	371 ± 33	539 ± 32
ΔG, kJ mol^{-1}	−14.3 ± 1.3	−14.7 ± 1.3	−15.6 ± 0.9
ΔH, kJ mol^{-1}	−2.0 ± 0.1	−3.2 ± 0.2	−2.3 ± 0.1
ΔS, J mol^{-1} K^{-1}	41 ± 2	38 ± 2	45 ± 2

Table 3
Summary plant wastes as adsorbents for the removal of metal ions from aqueous solution.

Adsorbent	Ns (mg g^{-1})	Reference
Manilkara spp. sawdust	145 ± 12	This work
Tabebuia spp. sawdust	95 ± 8	This work
Caryocar spp. sawdust	89 ± 8	This work
Wheat bran	122.11	[7]
Banana stem	91.74	[11]
Walnut sawdust	2.24	[14]
Pinus sylvestrys sawdust	9.78	[15]
Peanut sawdust	29.14	[32]
Tea waste	48	[33]
Rice hust	120.48	[34]
Alfafa biomass	89.2	[35]
Sugarcane bagasse	196	[36]

according to the Langmuir model, as shown in Eq. (2) [24]

$$\frac{C_S}{N_f} = \frac{C_S}{N_S} + \frac{1}{N_S K} \tag{2}$$

where C_S is the concentration (mol L^{-1}) of the solution at equilibrium, N_S is the maximum amount of Pb(II) adsorbed per gram of adsorbent (mol g^{-1}), which depends on the number of adsorption sites, and K is the equilibrium constant (mol L^{-1}). All further data from Fig. 3 were derived from the linear form of the adsorption isotherm, i.e. from plots of C_S/N_f versus C_S, in which N_S and K are represented by the slope and intercept, respectively, as shown in Fig. 3.

Thus, through the application of the modified Langmuir equation, N_S values were calculated from the angular coefficient and K from the linear coefficient of the straight line. From these data, N_S values were obtained. According to the N_S values, the Pb(II) adsorption sequence was *Manilkara* spp. > *Tabebuia* spp. > *Caryocar* spp. These data corroborate with adsorbent extractives of sawdust, which presented the same sequence. The free Gibbs energies for all interactions, ΔG, were calculated by Eq. (3), which showed that the adsorption process of Pb(II) for all sawdust samples were spontaneous as listed in Table 2

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

where R is the universal gas constant and T is the temperature in Kelvin.

Thermodynamic effects accompanying adsorption of any compound onto the sawdust surface at a solid/liquid interface can be determined in different ways, such as theoretical treatment [25], adsorption studies at different temperatures [26], and calorimetric titration [27]. In this way, a suspension of the sawdust samples was calorimetrically titrated with Pb(II), in order to obtain more information about the cation–sawdust interactions.

The thermal effects of the adsorption of Pb(II) on sawdust surfaces were determined by a series of calorimetric experiments. The complete thermodynamic cycle can be summarized in Eq. (4)

$$H_2O + {Pb_{(sol)}}^{2+} \rightarrow {Pb_{(solA)}}^{2+} \quad (a)\, Q_{dil} \tag{4}$$

$$H_2O + Sawdust_{(solid)} \rightarrow Sawdust_{(aq)} \quad (b)\, Q_{sol}$$

$${Pb_{(sol)}}^{+} + Sawdust_{(aq)} \rightarrow [Pb^{2+}Sawdust]_{(sol)} \quad (c)\, Q_{tit}$$

$${Pb_{(sol)}}^{2+} + Sawdust_{(solid)} \rightarrow [Pb^{2+}Sawdust]_{(sol)} \quad (d)\, Q_{ads}$$

These separated titration experiments were carried out in order to determine the following component parts: (a) the heat of dilution of Pb(II) solution (Q_{dil}); (b) the heat of solvation of the solid sawdust samples (Q_{sol}) and (c) the heat evolved in the sawdust titrated with Pb(II) (Q_{tit}). The net heat of interaction between sawdust and Pb(II) (Q_{ads}) (d) is given by Eq. (5) [27,28]

$$\Sigma Q_{ads} = \Sigma Q_{tit} + \Sigma Q_{sol} - \Sigma Q_{dil} \tag{5}$$

Since the heats of solvation of the aqueous suspended sawdust samples were calculated, the equation was reduced to Eq. (6)

$$\Sigma Q_{ads} = \Sigma Q_{tit} - \Sigma Q_{dil} \tag{6}$$

The corresponding Q values were collected for all interactions between Pb(II) and the sawdust samples. These net heat outputs for these interactions in the solid/liquid interface were obtained and illustrated in Fig. 4. This figure showed that the interaction between Pb(II) ions and sawdust samples presented an exothermic behavior because all the Q_{ads} values for all interactions were negative.

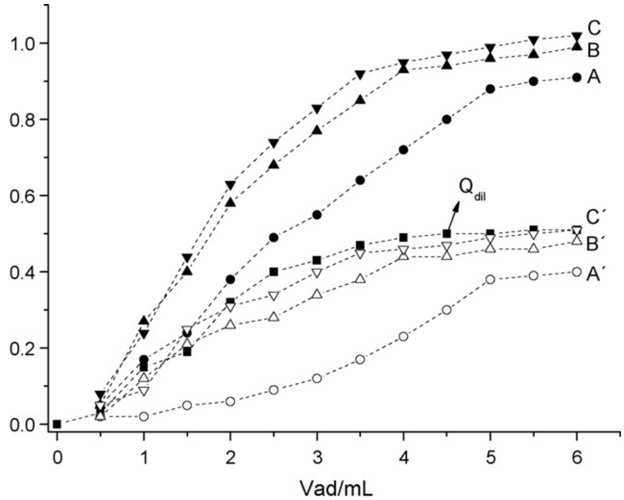

Fig. 4. Calorimetric titration of a suspension of 0.50 g of *Caryocar* spp. (A), *Manilkara* spp. (B) and *Tabebuia* spp. (C) sawdust samples in 50.0 mL of water with 0.50 mol L^{-1} $Pb(NO_3)_2$ *solution* at 298.15 ± 0.02 K. The experimental points in the curves represent the sum of the heat output, $\Sigma_r Q$ for *Caryocar* spp. (A′), *Manilkara* spp. (B′) and *Tabebuia* spp. (C′) by considering the respective titration and Cr(VI) dilution $\Sigma_{dil} Q$ values (Dil).

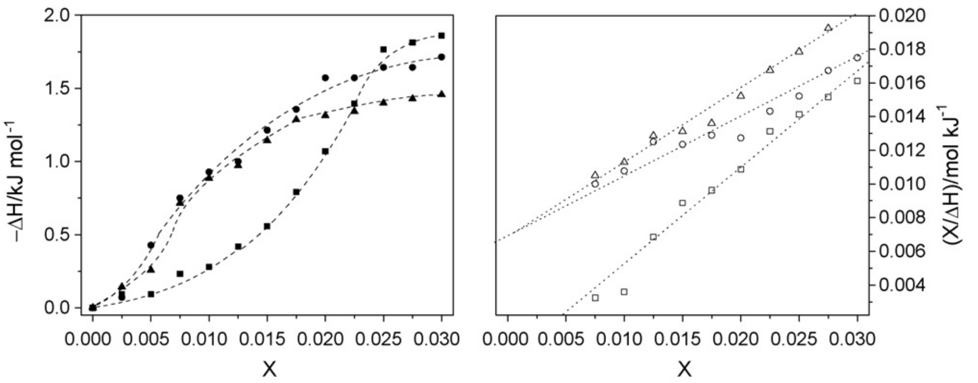

Fig. 5. Isotherm for the integral enthalpy of the adsorption of Pb(II) adsorption onto the surface of *Caryocar* spp. (■), *Manilkara* spp. (●) and *Tabebuia* spp. (▲) sawdusts obtained from calorimetric titration and the linear form of these isotherms (□), (○) and (△) at 298.15 K, respectively.

Using the resulting net heat output from the reaction, which was adjusted to a modified Langmuir equation, the integral enthalpies involved in the formation of a monolayer per unit mass of adsorbate $\Delta_{\text{mono}}H$, were calculated through Eq. (7) [29,30]

$$\frac{X}{\Sigma\Delta_{\text{R}}H} = \frac{1}{b-1}\Delta_{\text{mono}}H + \frac{X}{\Sigma\Delta_{\text{mono}}H} \tag{7}$$

In this equation, X is the total mol fraction of Pb(II) ions in solution after adsorption, and X values are obtained for each addition of titrant, using the modified Langmuir equation, whose behavior was shown to be a good adjustable model for such heterogeneous systems. b is a proportionality constant that also includes the equilibrium constant, and $\Delta_{\text{R}}H$ is the integral enthalpy of adsorption (kJ mol^{-1}) obtained from the net heat outputs of adsorption and the maximum retention capacity as presented in Eq. (8) [31]

$$\Sigma\Delta_{\text{R}}H = \frac{\Sigma Q_{\text{ads}}}{N_{\text{S}}} \tag{8}$$

Table 4

Amount of inorganic elements in aquatic effluent of battery industry before and after treatment with *Caryocar* spp., *Manilkara* spp. and *Tabebuia* spp. sawdust adsorbents.

Element	Effluent	*Caryocar* spp.	*Manilkara* spp.	*Tabebuia* spp.
Ag	0.03849	N.D.	N.D.	N.D.
Al	N.D.	N.D.	N.D.	N.D.
As	N.D.	N.D.	N.D.	N.D.
Au	N.D.	N.D.	N.D.	N.D.
B	0.12624	0.140134	0.133427	0.134456
Ba	N.D.	N.D.	N.D.	N.D.
Be	N.D.	N.D.	N.D.	N.D.
Bi	N.D.	N.D.	N.D.	N.D.
Ca	67.5	62.17	60.71	51, .88
Cd	N.D.	N.D.	N.D.	N.D.
Co	N.D.	N.D.	N.D.	N.D.
Cr	N.D.	N.D.	N.D.	N.D.
Cu	N.D.	N.D.	N.D.	N.D.
Fe	N.D.	N.D.	N.D.	0.17526
Ga	N.D.	N.D.	N.D.	N.D.
Hg	0.1146	0.102413	0.102599	0.095539
La	N.D.	N.D.	N.D.	N.D.
Li	N.D.	N.D.	N.D.	N.D.
Mg	29.924	29.918	29.904	29.86
Mn	0.02841	0.58163	0.56304	0.28791
Mo	N.D.	N.D.	N.D.	N.D.
Na	62.8545	79.4717	116.745	100.37
Nb	0.28913	0.27446	0.21403	0.24006
Ni	N.D.	N.D.	N.D.	N.D.
Pb	2.66446	T1: 2.58832; T2: 2.4911	T1: 1.17239; T2: 0.44773	T1: 1.24865; T2: 0.47325
Pd	N.D.	N.D.	N.D.	N.D.
Sb	N.D.	N.D.	N.D.	N.D.
Sc	N.D.	N.D.	N.D.	N.D.
Se	N.D.	0.22136	N.D.	N.D.
Si	N.D.	N.D.	N.D.	N.D.
Sn	N.D.	N.D.	N.D.	N.D.
Sr	0.217157	0.208286	0.2036667	0.197146
Ta	N.D.	N.D.	N.D.	N.D.
Te	N.D.	N.D.	N.D.	N.D.
Ti	0.66248	0.39801	0.38031	0.37576
Tl	N.D.	N.D.	N.D.	N.D.
V	N.D.	N.D.	N.D.	N.D.
W	0.39541	N.D.	N.D.	N.D.
Y	N.D.	N.D.	N.D.	N.D.
Zn	1.05586	1.05557	0.549	0.67455
Zr	N.D.	N.D.	N.D.	N.D.

Thus, enthalpic values for these interactions were plotted in Fig. 5. Using the angular coefficient values from the $X/\Delta_R H$ versus X plot, $\Delta_{\text{mono}}H$ values for all interactions can be determined, and the entropy of interactions were calculated by using Eq. (9). Thermodynamic data for interaction between Pb(II) and sawdust samples are presented in Table 2

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{9}$$

Entropic data of the interactions showed that these adsorptions were entropically favored as shown in Table 2. Indeed, the thermodynamic data for processes involving sawdust as adsorbent are a novelty, and these data are an elegant method to understand the interactions between contaminants and sawdust samples. For these sawdust samples and for both inorganic contaminants, the interactions were spontaneous, exothermic and presented an increase in entropy; then, all interactions were enthalpically and entropically driven. These data clearly showed that these sawdust samples can be applied to clean contaminated waters.

In order to compare this adsorption datum with the literature data, Table 3 is listed with Pb(II) adsorption results. This table shows that the results obtained in this work are good when compared with other various plant wastes used as adsorbents. *Manilkara* spp. sawdust in our paper adsorbed 145.04 mg of lead per gram of sawdust, whereas other plant wastes can reach the maximum of 122.11 mg/g.

Table 4 shows the concentration of metal ions that are present in the effluent of a battery industry, and their concentrations after treatments with Brazilian sawdust adsorbents. The main inorganic contaminant present in this effluent is lead, which concentration (2.66 mg L^{-1}) is much higher than Brazilian standard limits of total lead discharge in water and sewers, which is 0.5 mg L^{-1} [37]. Thus, the removal of this contaminant from this wastewater is extremely important in order to improve the quality of aqueous ecosystem of the Brazilian District City. The treatments of wastewater by Brazilian sawdust samples reduced the amount of lead from 2.66 mg L^{-1} to 2.59; 1.17 and 1.24 mg L^{-1} by the application of *Caryocar* spp., *Manilkara* spp. and *Tabebuia* spp., respectively. However, these amounts were still above the Brazilian limits. In order to remove this toxic inorganic contaminant from battery industry wastewater, this effluent was treated once more with fresh Brazilian sawdust adsorbents. After these treatments, the lead concentrations reached 2.49; 0.45 and 0.47 mg L^{-1} by the application of *Caryocar* spp., *Manilkara* spp. and *Tabebuia* spp., respectively (Table 2). These data suggest that the *Manilkara* spp. and *Tabebuia* spp. have high potential to remove lead from effluents, whereas the treatment with *Caryocar* spp. is not efficient. The application of sawdust to remove contaminants from real typical industry wastewaters is rarely reported in literature, which corroborates with the differential novelty of this study.

4. Conclusion

Adsorption data showed that 95.31 ± 8.28; 145.04 ± 12.43; and 89.10 ± 8.28 mg of Pb(II) per gram of *Tabebuia* spp.; *Manilkara* spp.; and *Caryocar* spp. sawdust materials were adsorbed respectively, which is in agreement with the amount adsorbent components of sawdust samples. Thermodynamic data for adsorption processes showed that all interactions were spontaneous, exothermic and presented an increasing in entropy; then, all interactions were enthalpically and entropically driven.

Brazilian sawdust samples: Ipê (*Tabebuia* spp.), Maçaranduba (*Manilkara* spp.) presented an efficient ability to adsorb Pb(II) from battery industry wastewater, whereas Pequiá (*Caryocar* spp.) did not show an efficient removal of Pb(II). Indeed, these residual Brazilian sawdust samples can be used to purify wastewater from this inorganic contaminant.

Acknowledgements

The authors thank FAPDF for financial support and FAPDF and CNPq for fellowships.

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