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Application of Brazilian sawdust samples for chromium removal from tannery wastewater

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Abstract Brazilian sawdust samples (*Caryocar* spp.; *Manilkara* spp.; and *Tabebuia* spp.) have been used for Cr(VI) adsorption from water. The series of adsorption isotherms were adjusted to modified Langmuir equation. Thermodynamic data of interactions were studied by the calorimetric titration of Cr(VI) in aqueous solution. All liquid/solid interface adsorptions were entalpically and entropically driven. These sawdust samples were also used to remove chromium from tannery wastewater. The application of *Caryocar* spp.; *Manilkara* spp.; and *Tabebuia* spp. reduced the amount of chromium from 2.11 ± 0.18 mg L^{-1} to 1.15 ± 0.10; 0.29 ± 0.02 and 0.26 ± 0.02 mg L^{-1}, respectively.

Keywords Calorimetry · Chromium · Sawdust · Tannery

Introduction

Development of environmentally friendly processes to decrease waste and toxic effluents has been increasing by population and governmental authorities pressure on the chemical industry [1]. One of the major contributions that can be carried out from a chemical point of view is the application of new materials to degrade/remove waste from water [2–7]. However, metal ions are not degradable; thus, series of approaches can be applied to remove metal ion from waters [7]. These methods are based on chemical precipitation, cementation, exchange resins, membrane filtration and new modified adsorbents [8–11]. Alternative low-cost adsorbents such as chitosan, clays or certain waste products from industrial operations such as fly ash, coal, and oxides have been used in order to replace the costly ones in recent years [12–16].

Many byproducts of furniture industries and civil construction as sawdust have little or no economic value, and which have been disposed in large amounts during the years. In this direction, sawdust could be used as an adsorbent in order to clean water from inorganic contaminants [17–20].

Many metal ions presents risks to health, among these contaminants, chromium must be highlighted due to its toxicity. Chromium has been introduced into natural waters by many industrial processes such as: electroplating, paint manufacturing, metal processing, steel production, agricultural runoff, and mainly by tanning [21–23]. Chromium occurs in aquatic environment as trivalent Cr(III) and hexavalent Cr(VI) states. However, Cr(VI) presents significantly higher levels toxicity than in other oxidation states [24]. This toxicity valency state is present in water in the form of chromate (CrO_4^-), and mainly in dichromate ($Cr_2O_7^-$) form. In this way, the Cr(VI) removal from water is extremely important to protect the environment and mankind.

Taking into account the meaning of Cr(VI) ions toxicity in natural waters, the purpose of the present work is the application of Brazilian sawdusts to remove Cr(VI) from aqueous solution and the thermodynamic approach of the interaction between Cr(VI) and sawdust.

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Experimental

Chemicals

Brazilian sawdust samples of Pequiá (*Caryocar* spp.), Maçaranduba (*Manilkara* spp.) and Ipê (*Tabebuia* spp.) were obtained from Rancho da Cabocla Sawmill Ltd in Brazilian Santarém city. Sawdust adsorbents were grained and sieved by a range of sieves and according to ASTM Method D4749, only the particles smaller than 2.5 mm were used [25].

Potassium dichromate (Vetec), HCl (Vetec), NaOH (Vetec) were used without purification.

It was usually observed that waste liquors from beam house and tan house find their way into a common drain in tanneries. Thus, the mixing of these two streams forms was used as tannery effluent, which was collected into the glass bottles, and wastewater samples were stored in the refrigerator at 4 °C.

Metal ion removal

The adsorption process was followed batchwise in aqueous solution of $K_2Cr_2O_7$ with controlled pH = 5 at 298 ± 1 K. For this process, a series of samples of about 25.0 mg of sawdust were suspended in 50.0 mL of aqueous $K_2Cr_2O_7$ solutions of different concentrations, varying from zero to 5.0 mmol L^{-1}. The best pH value was determined by following 50 mg of sawdust suspended in 50 mL of aqueous $K_2Cr_2O_7$ solutions with pH varying from 1 to 12 controlled by Clark/Lubs buffers. 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 in the aqueous sample before and after treatment with sawdust. All experiments were carried out in triplicate.

Calorimetric analysis

The adsorption of Cr(VI) by Brazilian sawdust samples was followed calorimetrically by titration using an solution calorimeter Parr 6755. 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 $K_2Cr_2O_7$ 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 [26, 27]. 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 ($\Delta_{sol}Q$) [26, 27].

Treatment of tannery wastewater with sawdust samples

The metal content in tannery wastewater was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) using a Varian Liberty RL Series II spectrometer. The metal removal from tannery wastewater was followed batchwise with pH = 4.6 (pH of tannery effluent) at 25 °C. During the treatment of wastewater with sawdust samples, 100 mL of tannery 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 tannery effluent before and after sawdust treatments were quantified by ICP-OES Varian Liberty RL Series II spectrometer.

Results and discussion

The capacity of these materials to remove Cr(VI) from water was followed by sorption isotherms. Under equilibrium conditions, the exchange processes occurred at the solid/liquid interface and could be characterized through the number of moles adsorbed (N_f) per gram of solid material. This value was calculated from the initial number of moles of cation (n_i) and those at the equilibrium (n_S) condition for a given mass (m) of the adsorbent in grams [26–29], by applying the Eq. 1:

$$N_f = \frac{n_i - n_S}{m} \quad (1)$$

The effect of pH values on Cr(VI) adsorption by the sawdust samples was followed through the data obtained, as shown in Fig. 1. Thus, the retention ability with changes

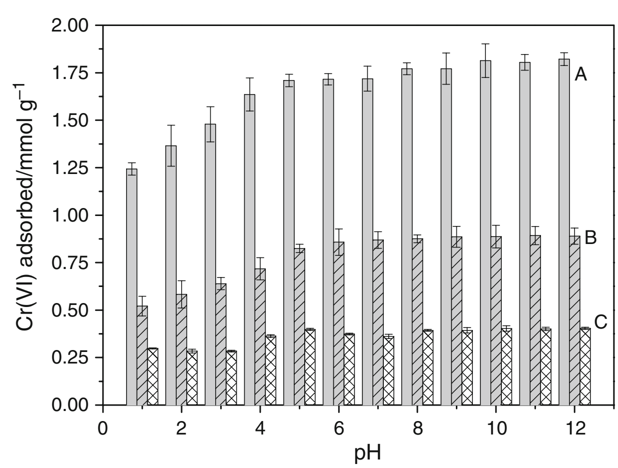

Fig. 1 Effect of pH on the adsorption of Cr(VI) by *Caryocar* spp. (A), *Manilkara* spp. (B) and *Tabebuia* spp. (C)

in pH presented the lowest value at pH 1.0 for all sawdust samples. Above this pH value, the adsorption increased up to pH 7.0, maintaining constant from this pH value for all sawdust samples. This figure showed that *Tabebuia* spp. adsorbed much more Cr(VI) ions than *Manilkara* spp., and this last one adsorbed more chromium ions than *Caryocar* spp. in any pH values.

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 Figs. 2, 3, 4. For the series of isotherms, the data reveal that the adsorption process conforms to the Langmuir model (Eq. 2) [3, 26–29].

$$\frac{C_S}{N_f} = \frac{C_S}{N_S} + \frac{1}{N_S K} \quad (2)$$

where C_S is the concentration of solution at equilibrium (mol L^{-1}), N_f and N_S are the concentration of Cr(VI) adsorbed and the maximum amount of Cr(VI) adsorbed per gram of material (mol g^{-1}), respectively, which depend on the number of available adsorption sites, and K is the equilibrium constant. All these adsorption studies were based on the linearized form of the adsorption isotherm derived from a plot of C_S/N_f as a function of C_S, as showed in Figs. 2, 3, 4. From this linearization the maximum retention capacity (N_S) for each cation–sawdust interaction can be obtained. 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 and from these data N_S were obtained. From these values, the Cr(VI) adsorption followed sequence *Tabebuia* spp. > *Manilkara* spp. > *Caryocar* spp. and the Free Gibbs energies for all interactions, ΔG, were calculated by Eq. 3, which showed that the adsorption of Cr(VI) by all sawdust samples were spontaneous processes as listed in Table 1.

$$\Delta G = -RT \ln K \quad (3)$$

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

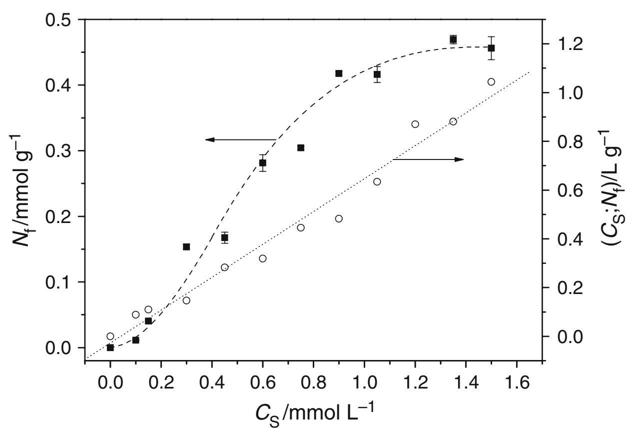

Fig. 2 Adsorption isotherm of aqueous $K_2Cr_2O_7$ solution for *Caryocar* spp. sawdust at 298 ± 1 K (*filled square*), and the linearized form of the adsorption isotherm (*open circle*)

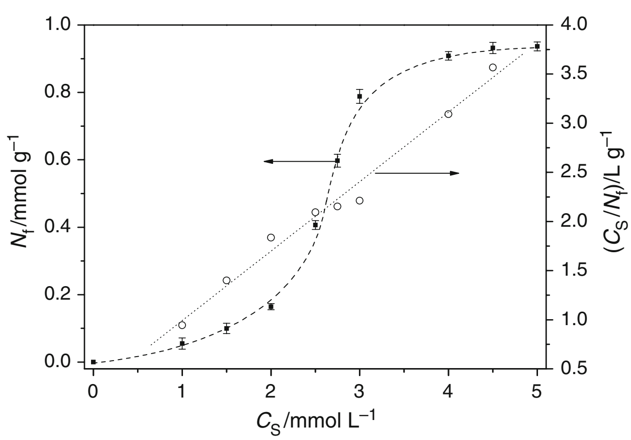

Fig. 3 Adsorption isotherm of aqueous $K_2Cr_2O_7$ solution for *Manilkara* spp. sawdust at 298 ± 1 K (*filled square*), and the linearized form of the adsorption isotherm (*open circle*)

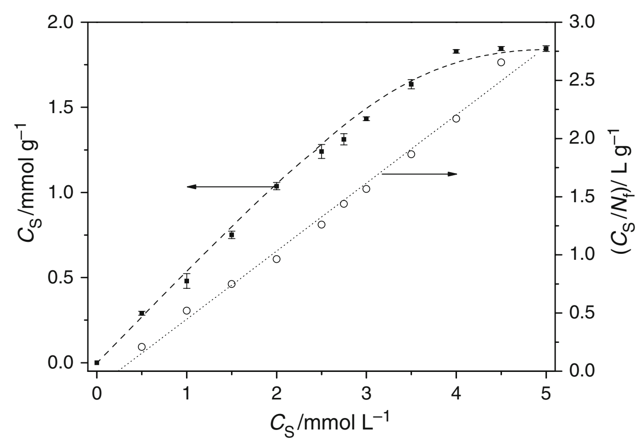

Fig. 4 Adsorption isotherm of aqueous $K_2Cr_2O_7$ solution for *Tabebuia* spp. sawdust at 298 ± 1 K (*filled square*), and the linearized form of the adsorption isotherm (*open circle*)

Table 1 The maximum number of moles adsorbed, N_S, equilibrium constants, K, and the thermodynamic data, ΔH, ΔG and ΔS, for Cr(VI) 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}	0.68 ± 0.05	1.22 ± 0.16	3.23 ± 0.26
N_S/mg g^{-1}	35.39 ± 2.61	63.67 ± 8.35	168.57 ± 13.57
K	1.045 ± 0.033	1.074 ± 0.28	1.18 ± 0.29
ΔG/kJ mol^{-1}	−0.11 ± 0.01	−0.17 ± 0.01	−1.37 ± 0.07
ΔH/kJ mol^{-1}	−3.62 ± 0.22	−4.17 ± 0.23	−3.85 ± 0.25
ΔS/J $mol^{-1}K^{-1}$	12 ± 1	13 ± 1	8 ± 1

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 [30, 31], adsorption studies in different temperatures [32–35] and calorimetric titration [36–38]. In this direction, a suspension of the sawdust samples were calorimetrically titrated with Cr(VI), in order to obtain more information about the cation–sawdust interactions.

Three separated titration experiments were carried out in order to determine the component parts: (a) the heat evolved by the sawdust titrated with Cr(VI) (Q_{tit}), (b) the heat of solvation of the solid sawdust samples (Q_{sol}) and (c) the heat of dilution of Cr(VI) solution (Q_{dil}). The net heat of interaction between sawdust and Cr(VI) (Q_{ads}) (d) is given by the Eq. 4.

$$\Sigma Q_{ads} = \Sigma Q_{tit} + \Sigma Q_{sol} - \Sigma Q_{dil} \quad (4)$$

Since the heats of solvation of the aqueous suspended sawdust samples were zero, the equation was reduced to Eq. 5.

$$\Sigma Q_{ads} = \Sigma Q_{tit} - \Sigma Q_{dil} \quad (5)$$

The corresponding Q values were collected for all interactions between Cr(VI) and the sawdust samples. The net heat outputs for these interactions in the solid/liquid interface were obtained and illustrated in Fig. 5. This figure showed that the interaction between Cr(VI) and sawdust samples presented an exothermic behavior because all Q_{ads} for all interactions were negative.

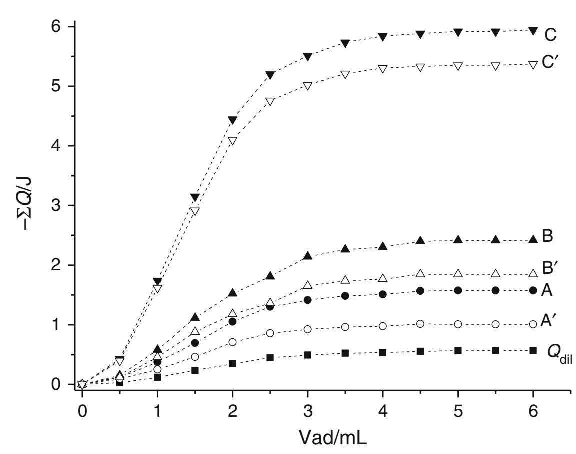

Fig. 5 Calorimetric titration of a suspension of 0.50 g of *Caryocar* spp. (A), *Manilkara* spp. (B) and *Tabebuia* spp. (C) sawdust samples in 50.0 mL of water with 0.50 mol L^{-1} $K_2Cr_2O_7$ solution at 298.15 ± 0.02 K. The experimental points in the curves represent the sum of the heat output, $\Sigma_r Q$ 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)

Using the net resultant heat output from the reaction, adjusted to a modified Langmuir equation, the integral enthalpies involved in the formation of a monolayer per unit mass of adsorbate, $\Delta_{mono}H$, was calculated through the Eq. 6.

$$\frac{X}{\Sigma\Delta_R H} = \frac{1}{b-1}\Delta_{mono}H + \frac{X}{\Sigma\Delta_{mono}H} \quad (6)$$

In this equation, X is the total mol fraction of Cr(VI) in solution after adsorption, and X values were 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 $\Delta_R H$ 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. 7.

$$\Sigma\Delta_R H = \frac{\Sigma Q_{ads}}{N_S} \quad (7)$$

Thus, enthalpic values for these interactions were plotted in Figs. 6, 7, 8. Using the angular coefficient values from the $X/\Delta_R H$ versus X plot, $\Delta_{mono}H$ values for all interactions could be determined, and the entropy of interactions were calculated by using Eq. 8.

Thermodynamic data for interaction between Cr(VI) and sawdust samples are presented in Table 1.

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (8)$$

Adsorption and calorimetric data show that the interaction between Cr(VI) and Brazilian sawdust was spontaneous and these adsorption processes were enthalpically and entropically favored. These data show the high ability of these sawdust samples in removing Cr(VI) from water.

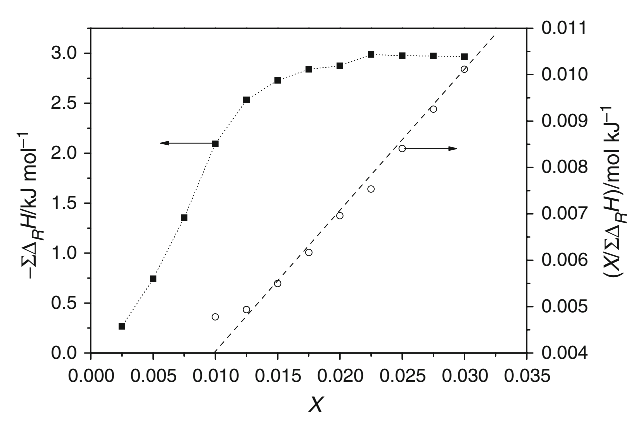

Fig. 6 Isotherm for the integral enthalpy of the adsorption of Cr(VI) adsorption onto the surface of *Caryocar* spp. sawdust obtained from calorimetric titration (*filled square*) and the linear form of this isotherm (*open circle*) at 298.15 K

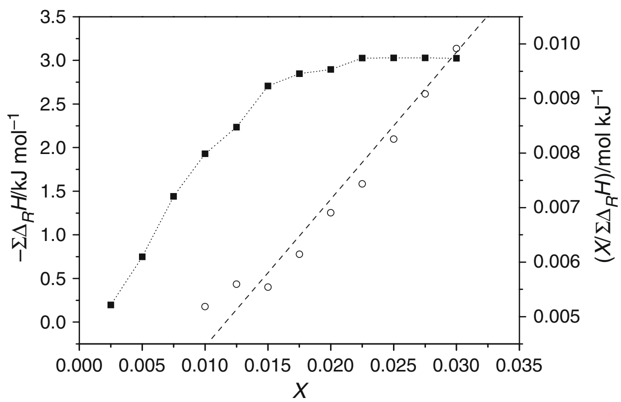

Fig. 7 Isotherm for the integral enthalpy of the adsorption of Cr(VI) adsorption onto the surface of *Manilkara* spp. sawdust obtained from calorimetric titration (*filled square*) and the linear form of this isotherm (*open circle*) at 298.15 K

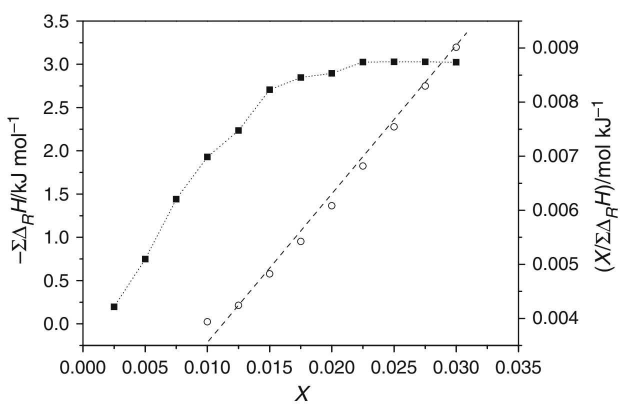

Fig. 8 Isotherm for the integral enthalpy of the adsorption of Cr(VI) adsorption onto the surface of *Tabebuia* spp. sawdust obtained from calorimetric titration (*filled square*) and the linear form of this isotherm (*open circle*) at 298.15 K

Thus, the application of these low-cost materials in environment samples must be followed.

Wastewaters of tanneries present an environmental problem due to their high level of chromium. The total chromium discharge limits in water and sewers in Brazil is 0.5 mg L^{-1} [39]. However, the tannery wastewater analyzed presented 2.11 mg L^{-1}, which is a value much higher than Brazilian limits.

The Table 2 shows that the treatment of wastewater by sawdust samples reduced the amount of chromium from 2.11 ± 0.18 mg L^{-1} to 1.15 ± 0.10; 0.29 ± 0.02 and 0.26 ± 0.02 mg L^{-1} for application of *Caryocar* spp., *Manilkara* spp. and *Tabebuia* spp., respectively. These facts suggest that the *Manilkara* spp. and *Tabebuia* spp. present high potential to remove this inorganic contaminant from wastewater. This table also shows that this treatment was efficient to remove other metal from wastewaters.

Table 2 Amount of inorganic elements in aquatic effluent of battery tannery before and after treatment with *Caryocar* spp., *Manilkara* spp. and *Tabebuia* spp. sawdusts

Element	Effluent (mg L^{-1})	*Caryocar* spp. (mg L^{-1})	*Manilkara* spp. (mg L^{-1})	*Tabebuia* spp. (mg L^{-1})
Ag	ND	ND	ND	ND
Al	2.78605	0.23	ND	ND
As	ND	ND	ND	ND
Au	ND	ND	ND	ND
B	2.78605	2.05183	1.95327	1.26242
Ba	ND	ND	ND	ND
Be	ND	ND	ND	ND
Bi	ND	ND	ND	ND
Ca	60.71	60.75	62.47	62.31
Cd	ND	ND	ND	ND
Co	ND	ND	ND	ND
Cr	2.11	1.15	0.29	0.26
Cu	ND	ND	ND	ND
Fe	0.77323	ND	ND	ND
Ga	ND	ND	ND	ND
Hg	ND	ND	ND	ND
La	ND	ND	ND	ND
Li	ND	ND	ND	ND
Mg	29.61	29.92	29.63	29.66
Mn	1.63467	1.6997	ND	0.37659
Mo	ND	ND	ND	ND
Na	3220.34	104.604	141.829	62.8545
Nb	ND	ND	ND	ND
Ni	ND	ND	ND	ND
Pb	ND	ND	ND	ND
Pd	ND	ND	ND	ND
Sb	ND	ND	ND	ND
Sc	ND	ND	ND	ND
Se	ND	ND	ND	ND
Si	ND	ND	ND	ND
Sn	ND	ND	ND	ND
Sr	2.2344	1.47534	0.82205	0.76433
Ta	ND	ND	ND	ND
Te	ND	ND	ND	ND
Ti	0.46211	0.40732	0.38667	0.40932
Tl	ND	ND	ND	ND
V	ND	ND	ND	ND
W	ND	ND	ND	ND
Y	ND	ND	ND	ND
Zn	5.1459	1.46836	ND	ND
Zr	ND	ND	ND	ND

Conclusions

Brazilian sawdust samples: Ipê (*Tabebuia* spp.), Maçaranduba (*Manilkara* spp.) and Pequiá (*Caryocar* spp.) presented an efficient ability of adsorbing Cr(VI) from water and wastewater. Adsorption data showed that 168.57 ± 13.57; 63.67 ± 8.35; and 35.39 ± 2.61 mg of Cr(VI) per gram of *Tabebuia* spp.; *Manilkara* spp.; and *Caryocar* spp. sawdust samples were adsorbed respectively. Thermodynamic data for adsorption processes showed that all interactions were spontaneous, exothermic and presented a disfavoured increasing of entropy, then all interactions were enthalpic and entropic driven. Tannery wastewater treatment showed that all sawdust samples are capable to remove chromium from wastewater. Treatments by using *Tabebuia* spp.; *Manilkara* spp. Brazilian sawdust samples showed high efficiency in removing chromium from tannery effluent, thus, these residual Brazilian sawdusts can be used to purify wastewater of this inorganic contaminant with thoroughness.

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