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Applicability of the Pinus bark (*Pinus elliottii*) for the adsorption of toxic heavy metals from aqueous solutions

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ABSTRACT. Current research evaluates the efficaciousness of pine (*Pinus elliottii*) bark as adsorbent of the toxic heavy metals cadmium (Cd), lead (Pb) and chromium (Cr) from aqueous solutions, at two pH conditions: 5.0 and 7.0. Approximately 500 mg of adsorbent material and 50 mL of solution contaminated by Cd, Pb and Cr at different concentrations prepared from standard solutions of each metal were added in 125 mL Erlenmeyer flasks. Flasks were stirred during 3h at 200 rpm at 25ºC. Further, 10 mL aliquots were then retrieved and concentration of metal Cd, Pb and Cr determined by AAS. Adsorption isotherms for each metal were consequently obtained and linearized according to Langmuir and Freundlich's mathematical models. Results show that the Pinus bark was efficacious in the removal of toxic heavy metals Cd, Pb and Cr from contaminated solutions and that the bark's adsorption capacity depended on pH solution.

Keywords: adsorption, cadmium, lead, chromium.

Aplicabilidade da casca de pinus (*Pinus elliottii*) para adsorção de metais pesados tóxicos de soluções aquosas

RESUMO. Este trabalho objetivou avaliar a eficácia do uso da casca de Pinus (*Pinus elliottii*) como adsorvente dos metais pesados tóxicos cádmio (Cd), chumbo (Pb) e cromo (Cr) de soluções aquosas em duas condições de pH: 5,0 e 7,0. Para tanto, em erlenmeyers de 125 mL, foram adicionados cerca de 500 mg do material adsorvente e 50 mL de solução contaminada pelos metais Cd, Pb e Cr em diferentes concentrações preparadas a partir de soluções padrão de cada metal. Os erlenmeyers foram agitados durante 3h, a 200 rpm e temperatura de 25ºC. Após a agitação, foram retiradas alíquotas de 10 mL de cada solução e então determinou-se a concentração dos metais (Cd, Cr e Pb) por EAA. A partir dos resultados, foram obtidas as isotermas de adsorção de cada metal, as quais foram linearizadas conforme os modelos matemáticos de Langmuir e Freundlich. A casca de Pinus comprovou ser eficiente na remoção dos metais pesados tóxicos Cd, Pb e Cr provenientes de soluções contaminadas, sendo a capacidade de adsorção da casca dependente do pH da solução.

Palavras-chave: adsorção, cádmio, chumbo, cromo.

Introduction

In the wake of contamination forms of the environment caused by industrial and agricultural activities, water contamination by heavy metals is a major concern to researchers and government departments involved in controlling water pollution. Water, one of the most important vital factors already a scarce commodity on the planet, is being contaminated with the discharge of industrial and urban wastes and other products resulting from several human activities (OLIVEIRA et al., 2001).

According to Duffus (2002), the term 'heavy metal', frequently used with pollution and toxicity, is applied to elements with specific mass greater than 5.0 g cm^{-3} or with atomic number higher than 20 (GONÇALVES JUNIOR et al., 2000). Chromium (Cr) is an essential element since it is used in biological metabolism. However, it also causes cancer in its hexavalent form, whereas lead (Pb) and cadmium (Cd) are not essential and they are toxic even at trace levels (TÜZEN, 2003).

Certain conventional treatment methods of effluents containing toxic heavy metals (precipitation, ion exchange, electro-chemical treatment, flocculation, ozonization and filtering) are generally limited in their effects since they are technically and economically non-viable.

Their application is difficult, especially when these techniques are used to remove dissolved metals in large volumes of water. Nevertheless, they produce solid residues which should be maintained and stored, constituting another important issue (FERREIRA et al., 2007; KANITZ JÚNIOR et al., 2009; SOUSA et al., 2007). Adsorption becomes an alternative treatment, highly efficient for the removal of toxic metals where, during the process, a certain element or substance is accumulated in the interface of a solid surface and the adjacent solution (KANITZ JÚNIOR et al., 2009; SOUSA et al., 2007).

The adsorption process is quantitatively evaluated by adsorption isotherms which express the relationship between the amount of metal adsorbed per mass unit of bio-sorbent and the concentration of metal in an equilibrium solution at constant temperature (SALEHIZADEH; SHOJAOSADATI, 2003).

Convex isotherms are highly favorable since great quantities adsorbed may be obtained from low concentrations of the solute. Isotherms' limit case is irreversible and the amount adsorbed does not depend on concentration (McCABE et al., 2005).

Figure 1 shows the most common forms of isotherms.

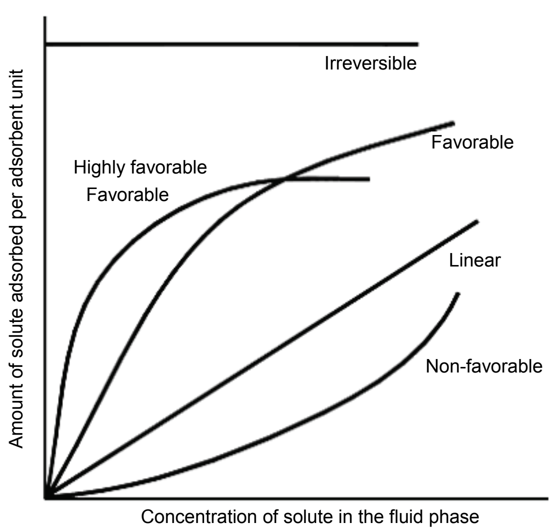

Figure 1. Types of isotherms.
Source: Adapted from McCabe et al. (2005).

Although the literature reports several models of convex isotherms to adjust adsorption data in a water solution (McCABE et al., 2005), isotherms proposed by Langmuir and Freundlich are extensively used.

Langmuir's adsorption isotherm is amply used to describe the behavior of an adsorbed product in equilibrium for the most diverse systems (LIU, 2006). The model was proposed by Langmuir in 1918 and was the first isotherm to show monolayer formation on the adsorbent and to consider the adsorbent's surface as homogeneous and with identical energy sites (GONÇALVES JUNIOR et al., 2010).

Freundlich's model described adsorption in multilayers (KALAVATHY et al., 2005) and, due to the isotherm's convex form, was considered favorable. Since it is empirical, it complies with data for many physical adsorption systems, especially in liquids (GEANKOPLIS, 2003).

Adsorption techniques use several adsorbing materials for the removal of organic (activated carbon, biomass etc.) or inorganic (zeolites, clays etc.) metal residues, either natural or synthetic (AKLIL et al., 2004). Alternative materials, such as sub-products and wastes of industrial processes, have been evaluated by their great availability, accessibility, efficiency and high competitiveness with regard to resins of ion exchange and activated carbon (VALDMAN et al., 2001). In fact, they may be employed as adsorbents that enhance the selective and reversible retention of metallic cations in industrial effluents.

Sub-products and wastes from agricultural and forest industries, such as the Pinus bark, are low cost materials due to simple processing and great abundance in nature. The material contains several organic compounds, such as lignin, cellulose and hemicellulose, which contain polyphenolic groups that may be useful for bonding ions of heavy metals (AKSU et al., 1999).

Current research evaluates the efficiency of using the Pinus bark (*Pinus elliottii*) as adsorbent of toxic heavy metals Cd, Pb and Cr from contaminated water and the dependence of the adsorption processes with regard to pH of the solution.

Material and methods

Experiment was conducted in the Laboratory of Environmental and Instrumental Chemistry of Unioeste, campus Marechal Cândido Rondon, Paraná State, Brazil.

Pinus elliottii whose bark was collected in the municipality of Marechal Cândido Rondon, Paraná State, Brazil, was the species chosen. Bark samples were retrieved from three different sites of the tree, namely, base, middle and top, so that the tree trunk could be entirely represented.

The material was then dried in a buffer (Marconi MA 035) at 103 ± 2°C during 48h, homogenized and triturated in a Wiley-type knife mill (Marconi

MA 048), for an average 0.2 mm granulometry. The material was sieved in a 60 mesh sieve and the particles that passed through were selected. A portion of the adsorbent material was retrieved prior to the start of the experiment so that the concentrations of toxic heavy metals Cd, Pb and Cr could be determined. Nitroperchloric digestion (AOAC, 2005) and metal determination by atomic absorption spectroscopy (GBC 932 AA), flame system (EAA/flame), were undertaken (WELZ; SPERLING, 1999).

The adsorption experiment was conducted in two pH conditions, namely 5.0 and 7.0, and the solutions with the metals under analysis were adjusted and tamponated with HCl or NaOH solutions standardized by a 0.100 mol L^{-1} concentration. Standard solutions of 100 mg L^{-1} of Cd, Cr and Pb with certified standards of 1000 mg L^{-1} for each metal were separately prepared in 1000 mL volumetric flasks.

Further, 500 mg of adsorbent material and 50 mL of solution with metals Cd, Pb and Cr at concentrations 10.0, 20.0, 30.0, 40.0, 50.0, 60.0, 70.0, 80.0 and 90.0 mg L^{-1}, prepared from a standard solution of 100 mg L^{-1} of each toxic heavy metal were placed in previously washed and dried 125 mL Erlenmeyer flasks. The flasks were stirred for 3 hours at 200 rpm, at 25ºC. Samples were then filtered and a 10 mL aliquot of each solution was removed to determine the metals under analysis in FAAS, using curves with certified standards for all metals (WELZ; SPERLING, 1999).

Adsorbed amount of each metal was determined by Equation 1:

$$q = \frac{(C_0 - C_{eq})}{m} V \qquad (1)$$

where:

q is the amount of adsorbed metal (mg g^{-1}); m is the mass of used adsorbent material (g); C_0 is the solution's initial concentration (mg L^{-1}); C_{eq} is the concentration of the metal in the solution (mg L^{-1}) and V is the volume (L).

Removal percentage (%R) was calculated by Equation 2:

$$\%R = 100 - \left(\frac{C_{eq}}{C_0} 100\right) \qquad (2)$$

where:

$\%R$ is the percentage of metal removal from the solution by the Pinus bark (%); C_{eq} is the concentration of metal in equilibrium in the solution (mg L^{-1}); C_0 is the solution's initial concentration (mg L^{-1}).

Adsorption isotherms for each metal (Cd, Pb and Cr) were obtained in the two pH conditions, 5.0 and 7.0, by determining the rate of adsorbed metal.

Langmuir's (Equation 3) and Freundlich's (Equation 4) mathematical model for the linearization of adsorption isotherms of toxic heavy metals studied on the Pinus bark:

$$\frac{C_{eq}}{q} = \frac{1}{q_m b} + \frac{C_{eq}}{q_m} \qquad (3)$$

where:

C_{eq} is the concentration in equilibrium (mg L^{-1}); q is the adsorbed amount in equilibrium per mass unit of adsorbent (mg g^{-1}); q_m is the maximum adsorption capacity (mg g^{-1}) and b is the parameter of Langmuir's isotherm related to the forces of the adsorbent-adsorbed interaction.

$$\log q = \log K_f + \left(\frac{1}{n}\right) \log C_{eq} \qquad (4)$$

where:

C_{eq} is the concentration in equilibrium (mg L^{-1}); q is the adsorbed quantity in equilibrium per mass unit of adsorbent (mg g^{-1}) and K_f and n are Freundlich's two parameters; K_f is related to the adsorption capacity and n is related to the heterogeneity of the solid. Greatness of exponent "n" indicates favorability: rates of "n" between 1 and 10 indicate favorable adsorption, according to Nassar et al. (1985 apud NAMASIVAYAN et al., 2001).

Results and discussion

No Cd and Pb concentrations were detected when the concentration of toxic heavy metals present in the adsorbent material prior to the experiment was determined, but rates of 2.00 μg g^{-1} Cr were found.

Rates of amounts of metal adsorbed (q) and removal percentage (%R) of each metal in the solution may be calculated from the results of the final concentration of the metal in equilibrium in the solution (C_{eq}). Table 1 shows rates of adsorbent mass used (m); initial concentration of metal in the solution (C_0); concentration of metal in equilibrium in the solution (C_{eq}); quantity of adsorbed metal (q); and removal percentage (%R) of Cd in the solution by the Pinus bark in pH 5.0.

Table 1. Studies on adsorption of Cd in pH 5.0.

	m (g)	C_0 (mg L^{-1})	Ceq (mg L^{-1})	q (mg g^{-1})	%R (%)
1	0.5093	10.00	0.23	0.96	97.70
2	0.5127	20.00	1.13	1.84	94.35
3	0.5220	30.00	1.97	2.59	93.43
4	0.5197	40.00	4.08	4.46	89.80
5	0.5160	50.00	5.55	4.92	88.90
6	0.5148	60.00	6.41	5.29	89.32
7	0.5247	70.00	6.88	6.01	90.17
8	0.5102	80.00	8.10	6.40	89.88
9	0.5178	90.00	8.67	6.46	90.37

Temperature 25ºC; contact and stirring period 3h; stirring speed 200 rpm.

Mean removal percentage of Cd from the solution in pH 5.0 reached 91.55%, with a trend towards a decrease in removal efficiency as from solutions with higher than 10.0 mg L^{-1} concentration.

Figure 2 shows adsorption isotherm of Cd in pH 5.0. According to Figure 1, the behavior of adsorption curve is favorable.

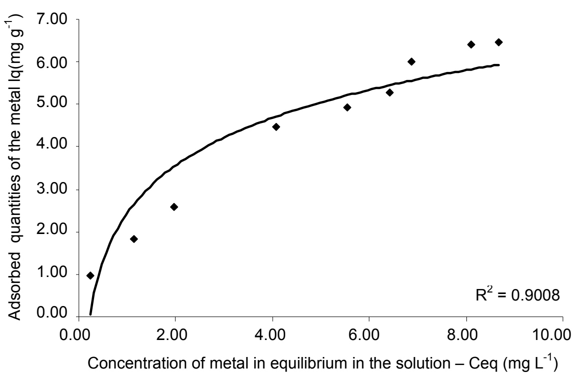

Figure 2. Adsorption isotherm for Cd in pH 5.0.

Table 2 shows rates for the adsorption of Cd by the Pinus bark in pH 7.0.

Table 2 shows that mean rate of removal of Cd from the solution is 93.41%, with a decreasing trend in removal efficiency of Cd from solutions with over 30.00 mg L^{-1} concentrations.

Table 2. Studies on adsorption of Cd in pH 7.0.

	m (g)	C_0 (mg L^{-1})	C_{eq} (mg L^{-1})	q (mg g^{-1})	%R (%)
1	0.5248	10.00	0.40	0.91	96.00
2	0.5367	20.00	0.66	1.80	96.70
3	0.5106	30.00	1.46	2.79	95.13
4	0.5133	40.00	2.82	3.62	92.95
5	0.5223	50.00	3.98	4.41	92.04
6	0.5477	60.00	4.67	5.05	92.22
7	0.5202	70.00	6.09	6.11	91.30
8	0.5166	80.00	6.40	6.38	92.00
9	0.5158	90.00	6.92	6.86	92.31

Temperature 25ºC; contact and stirring time 3h; stirring speed 200 rpm.

Proportion between active adsorption sites and quantity of ions is high in low initial concentrations of the metal in the solution. When initial ion concentration increases, the active sites on the surface of the adsorbent are quickly saturated and thus removal efficiency decreases with the increase in the initial concentration of ions (CHANDRA et al., 2003).

Figure 3 shows adsorption isotherm for Cd in pH 7.0. Curve behavior is also favorable.

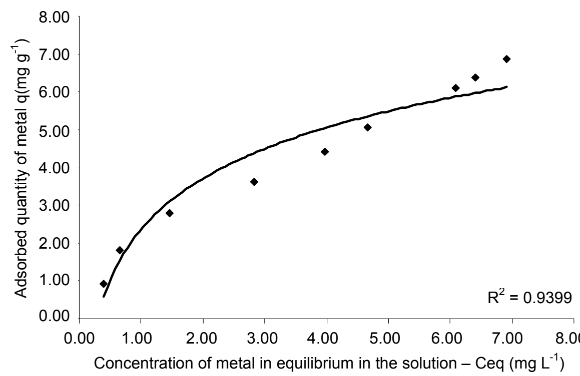

Figure 3. Adsorption of isotherm for Cd in pH 7.0.

pH influences the solubility of metals and the ionization of functional groups at the surface. Its influence lies in the competition between ions of the metal and H^+ ions in the solution through the active sites of the biomass surface. Further, dependence of ion capture by the adsorbent due to pH may be explained by the association and dissociation of certain functional groups, such as carboxyls. According to Chubar et al. (2003), most carboxyl groups are not dissociated in low pH levels and do not blend with ions of metals in the solution, although they may participate in complex reactions. When pH rate increases, most functional groups (carboxyls) have negative charges and may attract positive charged ions.

Table 3 shows adsorption rates of Pb by the Pinus bark in pH 5.0.

Table 3. Studies on adsorption of Pb in pH 5.0.

	m (g)	C_0 (mg L^{-1})	C_{eq} (mg L^{-1})	q (mg g^{-1})	%R (%)
1	0.5115	10.00	0.00	0.98	100.00
2	0.5112	20.00	0.00	1.96	100.00
3	0.5123	30.00	0.28	2.90	99.07
4	0.5338	40.00	0.58	3.69	98.55
5	0.5198	50.00	1.06	4.71	97.88
6	0.5105	60.00	1.08	5.77	98.20
7	0.5198	70.00	1.19	6.62	98.30
8	0.5244	80.00	1.60	7.48	98.00
9	0.5090	90.00	2.26	8.62	97.49

Temperature 25ºC; contact and stirring period 3h; stirring speed 200 rpm.

Table 3 shows that mean %R of Pb by the Pinus bark is 98.61%, with a decreasing trend in Pb removal percentage from the solution in proportion to the increase of concentration of the solution.

Figure 4 demonstrates the adsorption isotherm for Pb in pH 5.0. Curve behavior indicates favorability with regard to Pb adsorption in the pollution at pH above.

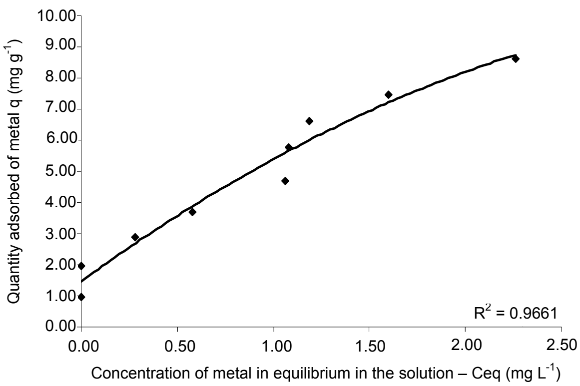

Figure 4. Adsorption isotherm for Pb in pH 5.0.

Table 4 also shows Pb adsorption rates in pH 7.0.

Table 4. Studies on Pb absorption in pH 7.0.

	m (g)	C_0 (mg L^{-1})	C_{eq} (mg L^{-1})	q (mg g^{-1})	%R
1	0.5074	10.00	0.02	0.98	99.80
2	0.5193	20.00	0.01	1.92	99.95
3	0.5283	30.00	0.12	2.83	99.60
4	0.5596	40.00	0.41	3.54	98.98
5	0.5070	50.00	0.49	4.88	99.02
6	0.5112	60.00	0.66	5.80	98.90
7	0.5095	70.00	1.26	6.75	98.20
8	0.5164	80.00	1.95	7.56	97.56
9	0.5219	90.00	2.29	8.40	97.46

Temperature 25°C; contact and stirring duration 3h; stirring speed 200 rpm.

A slight decreasing trend in Pb removal percentage may be observed in proportion to increase in pH and that practically no decrease of %R occurred in proportion to the initial concentration of Pb in the solution. Mean %R of Pinus bark was 98.83%.

Figure 5 shows adsorption isotherm for Pb in pH 7.0, with an extremely favorable behavior. High quantities may be adsorbed by small concentrations in the solution.

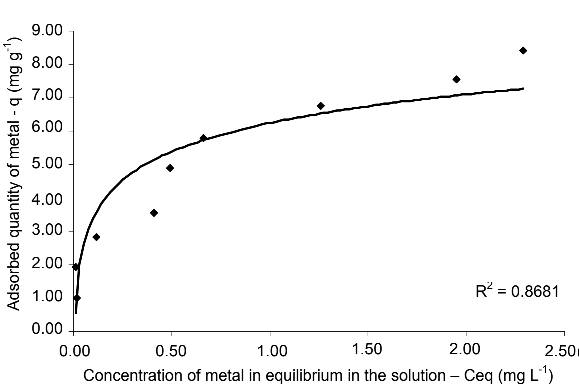

Figure 5. Isotherm of adsorption for Pb in pH 7.0.

In the case of %R, Pb adsorption was more effective in pH 7.0 in the initial concentration of the solution lower than 70.00 mg L^{-1}. However, as from this rate Pb adsorption by the Pinus bark was the same in the initial concentration in both pH conditions (5.0 and 7.0).

Table 5 provides data for the studies on Cr adsorption by the Pinus bark in pH 5.0.

Table 5. Studies on Cr adsorption in pH 5.0.

	m (g)	C_0 (mg L^{-1})	C_{eq} (mg L^{-1})	q (mg g^{-1})	%R
1	0.5097	10.00	1.27	0.40	87.30
2	0.5504	20.00	2.63	2.24	86.85
3	0.5096	30.00	3.25	3.20	89.17
4	0.5171	40.00	4.45	4.62	88.88
5	0.5061	50.00	4.64	5.03	90.72
6	0.5067	60.00	5.13	5.41	91.45
7	0.5101	70.00	5.31	6.37	92.41
8	0.5106	80.00	5.93	7.26	92.59
9	0.5136	90.00	6.43	7.69	92.86

Temperature 25°C; contact and stirring duration 3h; stirring speed 200 rpm.

Table 5 shows that mean percentage of Cr removal is 90.25%. Increase in Cr initial concentrations in the solution triggered an increase in Cr removal percentage by the Pinus bark. This event may be due to an increase in ions in the solution when in contact with adsorption sites of the adsorbent.

Figure 6 shows Cr adsorption curve by the Pinus bark in pH 5.0. Curve behavior indicates favorableness.

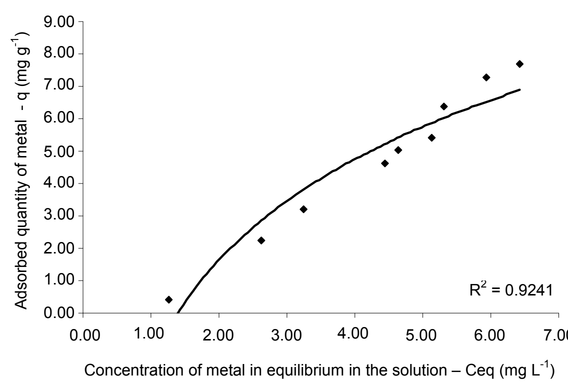

Figure 6. Adsorption isotherm for Cr in pH 5.0.

Table 6 shows Cr adsorption rates by the Pinus bark in pH 7.0.

Table 6. Studies on Cr adsorption in pH 7.0.

	m (g)	C_0 (mg L^{-1})	C_{eq} (mg L^{-1})	q (mg g^{-1})	%R
1	0.5113	10.00	1.36	0.45	86.40
2	0.5084	20.00	2.77	1.68	86.15
3	0.5160	30.00	3.30	2.59	89.00
4	0.5143	40.00	4.55	3.60	88.63
5	0.5115	50.00	5.21	4.38	89.58
6	0.5079	60.00	5.67	5.35	90.55
7	0.5263	70.00	6.13	6.07	91.24
8	0.5161	80.00	6.49	7.12	91.89
9	0.5216	90.00	6.94	7.96	92.29

Temperature 25°C; contact and stirring duration 3h; stirring speed 200 rpm.

Figure 7 shows Cr adsorption isotherm in pH 7.0. Adsorption curve shows favorable behavior.

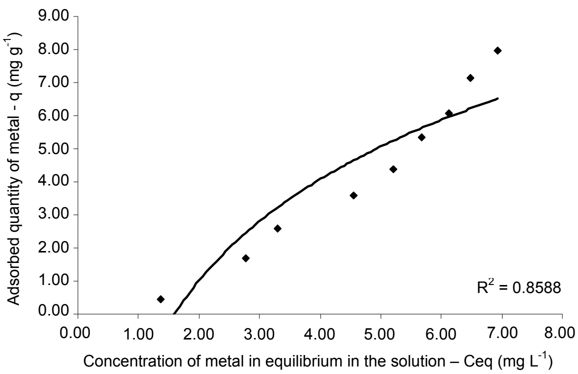

Figure 7. Adsorption isotherm for Cr in pH 7.0.

In the above pH condition, Cr removal from the solution is 89.52%. Removal percentage tends to increase in proportion to an increase in the concentration of the initial solution.

Cr removal capacity by the Pinus bark depends on the solution's pH in which pH 5.0 was the most efficacious, with mean %R 90.25%, when compared to that by pH 7.0, with mean %R 89.52%.

Decrease in adsorption capacity of the Pinus bark for Cr by a pH increase may be due to the decrease of solubility of the metal species (GABALLAH, 1994). Cr may react with cellulose, hemicellulose or lignin according to pH conditions and to the predominant species in the solution. Data in the literature show that Cr^{6+} is reduced to Cr^{3+}. Some authors report that only a part of Cr^{6+} is reduced, whereas others state that reduction is total. Oxidation of biomass is brought about by a reduction of the metal species. In fact, these interactions lead towards a decrease in C-OH and C-O-C bonds and an increase in C=O and COOH bonds (GABALLAH; KILBETUS, 1998).

Isotherm linearization of toxic heavy metals under analysis on the Pinus bark within pH concentrations 5.0 and 7.0 was undertaken both for Langmuir's (Figure 8) and for Freundlich's (Figure 9) mathematical models respectively by Equations 3 and 4.

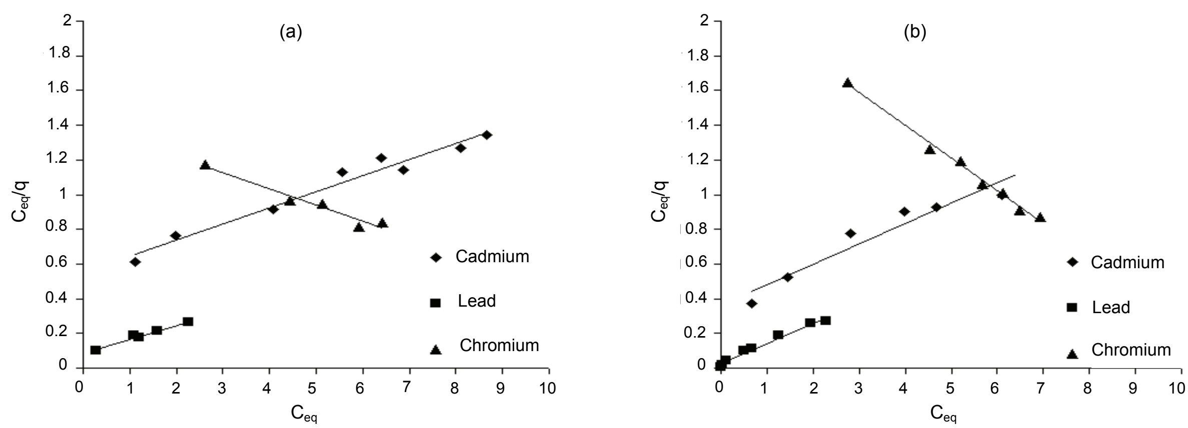

Figure 8. Linear adjustment of isotherm of toxic heavy metals on the Pinus bark in pH 5.0 (a) and pH 7.0 (b) according to Langmuir's model.

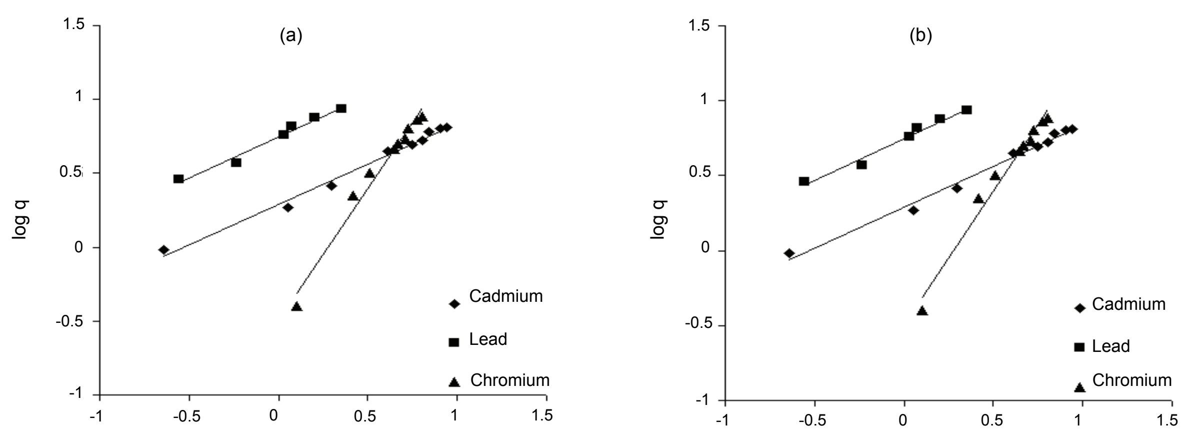

Figure 9. Linear adjustment of isotherms of toxic heavy metals on the Pinus bark in pH 5.0 (a) and pH 7.0 (b) according to Freundlich's model.

Tables 7 and 8 demonstrate the parameters and their respective coefficients of correlation for linear adjustment of adsorption data, according to Langmuir's and Freundlich's equations.

Table 7. Parameters of equilibrium isotherm models of Langmuir and Freundlich's model for the adsorption process of toxic heavy metals on the Pinus bark in pH 5.0.

Adsorbent/	Langmuir's constants			Freundlich's constants		
Metal	q_m (mg g^{-1})	b ou K_L (L mg^{-1})	R	K_f (mg g^{-1})	n	r
CP-Cd	10.834	0.166	0.984	1.953	1.820	0.993
CP-Pb	12.422	0.942	0.988	5.600	1.792	0.987
CP-Cr	-10.661	-0.066	-0.977	0.319	0.561	0.988

When Figures 8a and 9a and the correlation coefficient rates (Table 7) obtained for the experiment of metal adsorption by the Pinus bark in pH 5.0 are taken into account, it may be observed that Cd and Cr adsorption by the Pinus bark had a better adjustment by Freundlich's model. This fact indicates the multilayer adsorption of the metals on the adsorbent. In the case of Pb adsorption parameters by the bio-sorbent, the mathematical adjustments by Langmuir's and Freundlich's models were similar since the difference between the correlation coefficients was small, or rather, more than one type of adsorption site may exist interacting with this metal. In fact, both correlation coefficients were close to 1 and extremely close one to another.

When parameter rates in Table 7 obtained from the linearization of isotherms by Langmuir's and Freundlich's models are taken into account, the Pinus bark had the highest capacity of maximum adsorption (q_m) with regard to Pb, followed by Cd. Further, the same behavior occurred with the highest bonding energies (b or K_L), probably due to the interactions between the groupings in the Pinus bark and the chemical characteristics of these metals. On the other hand, Cr had low adsorption characteristics according to the parameters analyzed.

According to Sodré et al. (2001), parameter n in the linearization by Freundlich's model indicated the re-activity of the adsorbent's active sites. Further, n rates above 1 for Freundlich's isotherm were a strong indication of highly energetic sites, suggesting that they were the first to be occupied by the metals. Such behavior comprising high energetic interaction and high re-activity may be observed for values on the adsorption of the metals Cd and Pb by the Pinus bark, given in Table 7

In the case of rates of Freundlich's constants (K_f) for the adsorption capacities of metals on the Pinus bark, a more effective adsorption for Pb, followed by Cd, and very low K_f rate for Cr have been reported. Constant K_f has been associated with the interaction of the adsorbent with the metals' characteristics.

Table 8 shows the parameters obtained and their respective coefficients of correlation for the linear adjustment of adsorption data according to Langmuir's and Freundlich's equations for the adsorption experiment of toxic heavy metals by the Pinus bark in pH 7.0.

Rates of coefficients of correlation (Table 8) and adsorption data of metals Cd and Cr by the Pinus bark in pH 7.0 in Figures 8b and 9b show a better adjustment by Freundlich's model and may suggest multilayer adsorption of these metals on the adsorbent. In the case of Pb adsorption parameters by the bio-solvent, the mathematical adjustments by Langmuir's and Freundlich's models were similar since the difference between the two coefficients of correlation was small. This suggests the existence of more than one type of adsorption site interacting with this metal. In fact, both coefficients of correlation remained very close.

Table 8. Parameters of equilibrium isotherm models of the Langmuir's and Freundlich's model for the adsorption process of toxic heavy metals on the Pinus bark in pH 7.0.

Adsorbent/	Langmuir's constants			Freundlich's constants		
Metal	q_m (mg g^{-1})	b or K_L (L mg^{-1})	r	K_f (mg g^{-1})	N	r
CP-Cd	8.496	0.324	0.960	1.954	1.574	0.988
CP-Pb	8.628	4.390	0.989	6.103	1.272	0.986
CP-Cr	-5.305	-0.087	-0.995	0.284	0.585	0.996

According to parameter rates in Table 8, obtained by the linear adjustments of the isotherms and employing Langmuir's and Freundlich's model, the Pinus bark has the highest maximum adsorption capacity (q_m) for Pb, followed by Cd. The adsorbent shows a higher bonding energy (b or K_L) with regard to Pb for solutions in pH 7.0. However, when experiments in the two pH under analysis were compared (5.0 and 7.0), it was registered that in pH 5,0 this bio-sorbent has the highest maximum capacity for adsorption (q_m) for metals Pb and Cd, respectively. Since an inverse behavior may be obtained for bonding energies (b or K_L), higher bonding energies for Pb and Cd in pH 7.0 are demonstrated (Tables 7 and 8). On the other hand, Cr suggested characteristics with low adsorption between the Pinus bark and this metal, according to parameters in both pH conditions.

When rates of n are taken into account (Table 8), it was reported that Cd and Pb had higher rates than 1. This fact showed good reactivity of the energetic sites of the Pinus bark as adsorbent when compared to the metals' adsorption. A similar behavior was obtained in pH 5.0, albeit with higher rates

(Table 7). Cr showed low rates of n, which indicated low reactivity of the energetic sites according to parameters in the two pH conditions (Tables 7 and 8).

Rates of Freundlich's constants (K_f) for the adsorption capacities of Pb, Cd and Cr on the Pinus bark varied between 6.103; 1.954 and 0.284 (mg g^{-1}) respectively, with a higher adsorption for Pb. This fact may be associated with the metal's characteristics and its interaction mode with the adsorbent.

Conclusion

The analysis on the adsorption process in different pH demonstrated that in the treatment of natural water contaminated with the metals Cd, Pb and Cr, the use of Pinus bark as adsorbent in the removal and adsorption process is efficient within a pH range between 5.0 and 7.0. In current study, the best adsorption for Cd and Cr was obtained in pH 5.0; in the case of Pb, the most efficient adsorption was obtained in the two pH conditions analyzed.

Results from isotherm linearization and adsorption data of Cd and Cr by Pinus bark in the two pH conditions showed a better adjustment by Freundlich's model, whereas Pb adsorption data by the bio-solvent showed that mathematical adjustments were similar by Langmuir's and Freundlich's models.

Results by adsorption isotherms revealed that the bark of the Pinus tree (*Pinus elliottii*) is a very important adsorbent material, recommended for the removal of pollutants and for the treatment of water bodies contaminated with the toxic heavy metals Cd, Pb and Cr.

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