PELLETIZED PONDEROSA PINE BARK FOR ADSORPTION OF TOXIC HEAVY METALS FROM WATER

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Bark flour from ponderosa pine (*Pinus ponderosa*) was consolidated into pellets using citric acid as cross-linking agent. The pellets were evaluated for removal of toxic heavy metals from synthetic aqueous solutions. When soaked in water, pellets did not leach tannins, and they showed high adsorption capacity for Cu(II), Zn(II), Cd(II), and Ni(II) under both equilibrium and dynamic adsorption conditions. The experimental data for Cd(II) and Zn(II) showed a better fit to the Langmuir than to the Freundlich isotherm. The Cu(II) data best fit the Freundlich isotherm, and the Ni(II) data fitted both Freundlich and Langmuir isotherms equally. According to the Freundlich constant K_F, adsorption capacity of pelletized bark for the metal ions in aqueous solution, pH 5.1 ± 0.2, followed the order Cd(II) > Cu(II) > Zn(II) >> Ni(II); according to the Langmuir constant *b*, adsorption affinity followed the order Cd(II) >> Cu(II) ≈ Zn(II) >> Ni(II). Although data from dynamic column adsorption experiments did not show a good fit to the Thomas kinetic adsorption model, estimates of sorption affinity series of the metal ions on pelletized bark derived from this model were not consistent with the series derived from the Langmuir or Freundlich isotherms and followed the order Cu(II) > Zn(II) ≈ Cd(II) > Ni(II). According to the Thomas kinetic model, the theoretical maximum amounts of metal that can be sorbed on the pelletized bark in a column at influent concentration of ≈10 mg/L and flow rate = 5 mL/min were estimated to be 57, 53, 50, and 27 mg/g for copper, zinc, cadmium, and nickel, respectively. This study demonstrated the potential for converting low-cost bark residues to value-added sorbents using starting materials and chemicals derived from renewable resources. These sorbents can be applied in the removal of toxic heavy metals from waste streams with heavy metal ion concentrations of up to 100 mg/L in the case of Cu(II).

Keywords: Bark, Sorbent, Adsorption, Metals, Pine, Nickel, Cadmium

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INTRODUCTION

Large amounts of bark residues are generated annually by primary timber processing mills worldwide. In the United States alone, an estimated 2.2 million metric tons of bark residues were generated in 2002 (McKeever and Falk 2004). In Canada, approximately 1,200 tons of residual bark was generated daily by Quebec mills (Frigon et al. 2003). Bark residues are therefore one of the most abundant renewable resources that are available for conversion into high-value, environmentally sustainable biomaterials, including low-cost sorbents for treatment of water streams contaminated with persistent organic pollutants (Brás et al. 1999, 2004; Ratola et al. 2003), toxic oily wastes (Haussard et al. 2003) and reactive dyes (Morais et al. 1999). Several investigators have also shown that bark from various species adsorbs toxic heavy metals from water to different extents (Randall 1977; Deshkar et al. 1990; Reddy et al. 1997; Seki et al. 1997; Gaballah and Kilbertus 1998; Villaescusa et al. 2000; Aoyama and Tsuda 2001; Martin-Dupont et al. 2002, 2004, 2006; Sekar et al. 2004).

In a review of potentially low-cost sorbents for heavy metals, Bailey et al, (1999) concluded that inexpensive, effective, readily available materials such as bark can be used in place of activated carbon or ion exchange resins for removal of heavy metals from solution, although cost comparisons of sorbents are difficult to make due to the scarcity of consistent cost information.

Concentrations of heavy metals in polluted streams vary, depending upon the type of heavy metal, source of pollution, stream location, and time of day. For example Van Hassel et al., (1980) found that heavy metal concentrations in stream water samples collected at three sites adjacent to highways were 2-6 μg/L for Pb; 8-43 μg/L for Zn; 1-7μg/L for Ni; and 0.1-1.1 μg/L for Cd. In a study on the assessment of heavy metal pollution at two South African harbors, Fatoki and Mathabatha, (2001) found that at one of the harbors, heavy metal concentrations in sea water receiving industrial discharges and urban stormwater runoff ranged from 0.2-72 mg/L for Cd; 0.6-42.6 mg/L for Cu; 0.6-16.3 mg/L for Pb; and 0.5-27.6 mg/L for Zn.

Bark flour is effective for removal of toxic heavy metal ions from water because of its high content of polyhydroxy polyphenolic groups that are capable of chelating heavy metal ions (Gaballah, I., and Kilbertus, G., 1998). In addition, bark contains carboxylic groups, which can bind metals by ion-exchange mechanisms (Sakai, K., 2001). However, because bark also contains significant quantities of water-soluble extractives, including soluble tannins, which can be detrimental to aquatic life, the bark needs to be treated before it is used as a sorbent material for removal of contaminants from water. To avoid release of soluble tannins from the bark into the water, Haussard et al. (2003) treated the bark with microorganisms or with copper or chromium solution and Vázquez et al. (2002) used acidified formaldehyde. Earlier studies by Chow (1972) had indicated that water soluble phenolic substances in bark can be condensed into water-insoluble polymers by high-temperature heating. The objective of our study was to investigate whether or to what extent bark powder consolidated into pellets, using citric acid as cross linking agent and subjected to high-temperature heat treatment absorbs toxic heavy metals from water, under both static and dynamic flow conditions, without contributing to high chemical oxygen demand (COD) .

MATERIALS AND METHODS

Air-dried ponderosa pine (*Pinus ponderosa*) bark, obtained from a mill in St. Regis, Montana, U.S.A., was hammer milled into flour that passed through a 20-mesh screen. The flour was consolidated into pellets as described below.

Anhydrous citric acid was purchased from GFS Chemicals (Ohio, U.S.A.) and carboxymethylcellulose (CMC) was purchased from Hercules (Wisconsin, U.S.A.). Standard solutions of Cu (II), Ni (II), Zn (II), and Cd (II) were purchased from Fischer

Scientific (New Jersey, U.S.A.) and diluted with deionized water to the appropriate concentration, as needed. Metal concentration in solution was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Preparation of Pelletized Bark

Bark flour was mixed with CMC, citric acid, and deionized (DI) water in the proportions shown in Table 1. The ingredients were mixed thoroughly to form a stiff paste. CMC was used as a rheology modifier for pellet extrusion (Kulicke, W-M., et al., 1996). Citric acid was used as crosslinking agent to enhance the wet strength or water-soak properties and dimensional stability of the pellets (Caulfield, 1994). The stiff paste was extruded into cylindrical pellets, which were conditioned for 1 h at 180°C in a forced-draft furnace. The pelletized bark is shown in Figure 1. Type I pellets were selected for further studies because these pellets showed optimal wet strength and hydraulic conductivity in preliminary column experiments, and could be regenerated several times without measurable loss of weight and sorption capacity.

Characteristics of Pelletized Bark

A random sample of 10 pellets was taken for measurement of pellet size and breaking weight. Pellet size was measured by means of an electronic digital caliper, and breaking weight was measured on an Instron testing machine. Breaking weight is defined as the maximum compression load on the pellet just prior to failure.

The liquid-accessible pore volume of the pellets was measured according to the method described by DesMarais et al., (1993). For that purpose, 1.0-g samples of the pellets, weighed accurately to four decimal places, were immersed in DI water at 26.5 ± 0.2°C for 8 h. At the end of this period, the pellets were removed from the water, dabbed lightly with a piece of absorbent tissue paper to remove excess water from the surface, and weighed. Liquid-accessible pore volume V_{acc} was calculated as

$$V_{\mathrm{acc}} = (W_{\mathrm{wet}} - W_{\mathrm{dry}})d_{\mathrm{water}} \tag{1}$$

where W_{wet} is weight (g) of the sample after saturation with DI water, W_{dry} is initial weight of the sample at 30% RH, 27 ± 1°C, and d_{water} is density (g/cm^3) of DI water at 26.5°C. Characteristics of the pelletized bark are summarized in Table 2.

Leaching characteristics of the pelletized bark were determined by comparing the chemical oxygen demand and UV–visible spectrum of 40 mL DI water before and after equilibration at room temperature (25±1°C) for 2 h with 1 g pelletized bark. COD of DI water before and after equilibration were 0.55 ± 0.47 and 6.2 ± 3.0 mg/L, respectively.

Table 1. Weight of pellet ingredients

Type of pellet	Weight of ingredient (g)			
	Bark	CMC	Citric acid	DI water
I	200	0.5	40	140
II	200	0.14	20	74
III	200	10	10	200

Fig. 1. Pelletized bark (Type I).

Because the DI water before and after equilibration with the bark pellets did not show the UV–visible absorbance band with λ_{max} = 280 nm, which is characteristic of tannins, it can be concluded that no tannin leached from the bark pellets. The slight increase in COD may have been from soluble carbohydrates leaching from the pellets.

Table 2. Characteristics of Pelletized Bark—Type I

Parameter	**Value**
Shape	Cylindrical
Length, mm	11.60 ± 2.11
Diameter, mm	3.28 ± 0.16
Breaking weight, kg/pellet	6.15 ± 2.0
Shipping weight, g/L	310
Liquid-accessible pore volume, cm^3/g	0.8–1.0

Equilibrium Adsorption Experiments

Equilibrium adsorption experiments were performed in triplicate by adding 0.5-g aliquots of pelletized bark to labeled 125-mL polyethylene bottles. 20-mL aliquots of Cu(II), Zn(II), Ni(II), or Cd(II) solutions of various initial concentrations (C_0 = 0.1, 0.5, 1.0, 2.0, 5.0, 10, 50, 100, 200, 500 mg/L), pH 5.1 ± 0.02, were equilibrated at 25 ± 1°C with the pelletized bark by shaking the capped bottles for 24 h on a horizontal shaker at 150 rpm. Preliminary experiments had indicated that equilibrium could be reached within 2 h. At the end of this period, equilibrium concentration C_e of the metal ion in the supernatant liquid was determined by ICP-AES (USEPA Method 6010B, 1996).

Adsorption Kinetics Experiments

Adsorption kinetics experiments were performed in 1-L solutions with 1.0 g samples of the pelletized bark. The initial metal ion concentration in solution was 10 mg/L, and initial pH was 2, 4, or 6. The initial pH of the solution was adjusted by adding 0.1 M HNO_3 or KOH as needed. The suspension was stirred using a magnetic bar, and 1-mL aliquots of the supernatant liquid were withdrawn for metal concentration determination by ICP-AES at various time intervals during the 2-h experiment.

Dynamic Adsorption Experiments

Dynamic adsorption experiments were conducted in a glass column, 25 mm in diameter and 400 mm in length. The column was packed with 40 g pelletized bark to a bed height of 300 mm. Five column volumes of DI water were pumped through the column before each metal ion solution of a given initial concentration was pumped through the column at a flow rate of 5 mL/min. The initial metal ion concentration of the solutions was C_{infl} = 1, 10, 25, 50, 70, 100, 250 mg/L. The column effluent was collected in test tubes by means of a fraction collector, and the effluent metal ion concentration C_{effl} was determined by ICP-AES.

RESULTS AND DISCUSSION

Adsorption Isotherms

The amount of metal ions adsorbed at equilibrium, q_e (mg/g), was calculated as

$$q_e = (C_0 - C_e)V/W \tag{2}$$

where C_0 and C_e are concentrations (mg/L) of metal ions in the initial and equilibrium solutions, respectively, V is volume (L) of the initial solution taken for equilibration, and W (g) is the weight of the pellets taken for equilibration.

Experimental results obtained for adsorption of metal ions at equilibrium were analyzed by both the Freundlich and Langmuir adsorption isotherms. The Freundlich isotherm is described by

$$q_e = K_F C_e^{1/n} \tag{3}$$

where K_F is a constant related to the adsorption capacity and n is an empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the adsorbent. Adsorption is favorable for values $0.1 < 1/n < 1$ (Namasivayam and Yamuna 1992; Raji and Anirudhan 1998). The Langmuir isotherm is described by

$$q_e = q_{\max}\, bC_e/(1 + bC_e) \tag{4}$$

where $q_{\max}$ is the maximum amount of adsorbate per unit weight of adsorbent and b is a parameter related to the free energy of adsorption of a monolayer of the adsorbate. It reflects the adsorption intensity and characterizes the affinity of the adsorbent for the adsorbate.

Fig. 2 shows Freundlich and Langmuir adsorption isotherms for Cu(II), Zn(II), Ni(II), and Cd(II) ions on pelletized bark. Isotherm parameters for adsorption of each of the metal ions on pelletized bark are summarized in Table 3. As shown by the values of the root mean squared errors of the nonlinear least squares fit (RMSE), the experimental data for Cd(II) and Zn(II) showed a better fit to the Langmuir than to the Freundlich isotherm. The Cu(II) data best fit the Freundlich isotherm, and the Ni(II) data fitted both Freundlich and Langmuir isotherms equally. According to the Freundlich constant K_F, adsorption capacity of pelletized bark for the metal ions in aqueous solution, pH 5.1 ± 0.2, followed the order Cd(II) > Cu(II) > Zn(II) >> Ni(II); according the Langmuir constant *b*, adsorption affinity followed the order Cd(II) >> Cu(II) ≈ Zn(II) >> Ni(II).

Table 3. Freundlich and Langmuir isotherm parameters for metal ion adsorption on pelletized bark, pH 5.1 ± 0.2

Ion	Freundlich isotherm				Langmuir isotherm			
	K_F	$1/n$	R	RMSE	q_{max} (mg/g)	b	R	RMSE
Cu(II)	84.6	0.79	0.9993	102	24.1	0.0016	0.9982	171
Zn(II)	73.7	0.80	0.9960	238	20.6	0.0018	0.9971	200
Ni(II)	19.8	0.88	0.9964	117	20.6	0.0006	0.9964	120
Cd(II)	203	0.54	0.9947	200	6.8	0.0069	0.9998	41

R is correlation coefficient.
RMSE is root mean squared error of nonlinear least squares fit.

Table 4. Pseudo-first- and second-order kinetic parameters for Cu(II) sorption

pH	Pseudo-first order				Pseudo-second order			
	q_e (mg/g)	k_1 (min^{-1})	R	RMSE	q_e (mg/g)	k_2 (g/mg/min)	R	RMSE
2	0.728 ± 0.021	0.0641 ± 0.000	0.9835	0.0496	0.786 ± 0.022	0.114 ± 0.003	0.9592	0.0788
4	0.669 ± 0.030	0.0882 ± 0.004	0.9955	0.0250	0.731 ± 0.027	0.170 ± 0.008	0.9770	0.0558
6	0.524 ± 0.004	0.0532 ± 0.006	0.9948	0.0200	0.567 ± 0.002	0.128 ± 0.017	0.9872	0.0313

Table 5. Pseudo-first- and second-order kinetic parameters for Zn(II) sorption

pH	Pseudo-first order				Pseudo-second order			
	q_e (mg/g)	k_1 (min^{-1})	R	RMSE	q_e (mg/g)	k_2 (g/mg/ min)	R	RMSE
2	0.646 ± 0.011	0.0348 ± 0.000	0.9910	0.0319	0.696 ± 0.013	0.0645 ± 0.000	0.9884	0.0366
4	0.406 ± 0.015	0.0514 ± 0.000	0.9676	0.0403	0.437 ± 0.016	0.158 ± 0.006	0.9316	0.0580
6	0.438 ± 0.030	0.0502 ± 0.001	0.9960	0.0150	0.473 ± 0.034	0.146 ± 0.019	0.9834	0.0296

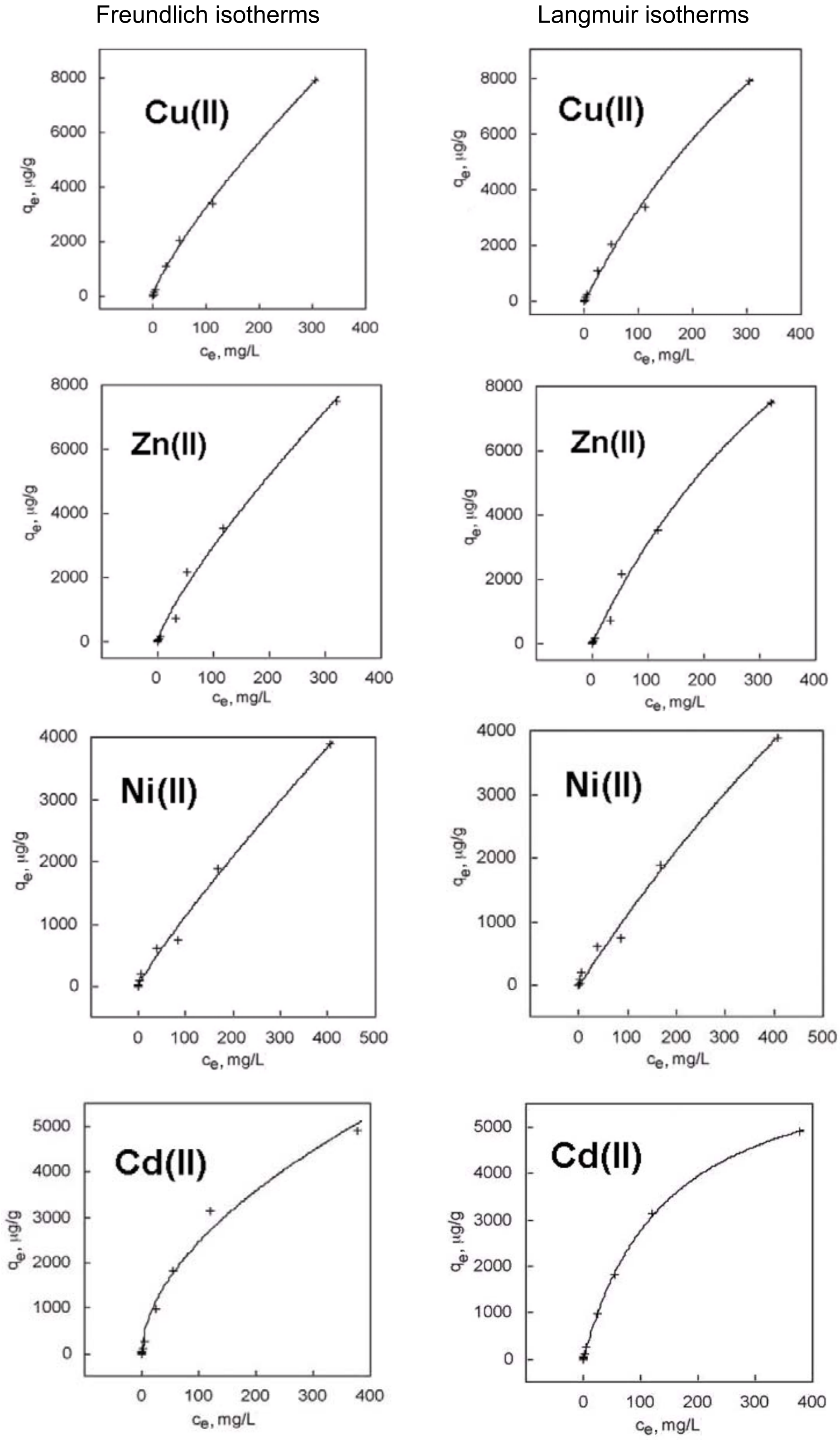

Fig. 2. Freundlich and Langmuir adsorption isotherms for Cu(II), Zn(II), Ni(II), and Cd(II) ions on pelletized bark. [Note: markers (+) represent experimental data points, and the lines (-----) represent the fitted isotherms]

Adsorption Kinetics

Experimental data were analyzed by both pseudo-first- and second-order kinetic models, as described in the following equations, respectively (Ho and McKay 1999):

$$q_t = q_e\,[1 - \exp(-k_1 t)] + \varepsilon \tag{5}$$

$$q_t = q_e - 1/[(1/q_e) + k_2 t] + \varepsilon \tag{6}$$

where k_1 is the rate constant of the pseudo-first-order model (1/min), k_2 is the rate constant of the pseudo-second-order model (g/mg/min), q_e is the amount of solute adsorbed at equilibrium (mg/g), q_t is the amount of solute adsorbed on the surface of the sorbent at any time t (mg/g), and ε denotes random error.

The kinetic parameters for metal ion sorption on pelletized bark determined by fitting the experimental data to both pseudo-first- and second-order kinetic models are summarized in Tables 4–7. As shown by the values of RMSE, sorption of metal ions on pelletized bark, except for Cd(II), best fit the pseudo-first-order kinetic model under all three pH conditions, 2, 4 and 6. Cd(II) deviated from this trend at pH 4, where it best fit the pseudo-second-order kinetic model.

Adsorption kinetics of a given metal ion on pelletized bark are determined by its characteristic solution chemistry and by the surface chemistry of the pelletized bark. Specifically, solution pH plays an important role in determining both the nature of metal ionic species available in aqueous solution and the nature and concentration of adsorption sites on the bark pellet. Bark pellets have a high content of polyhydroxyl polyphenolic groups that are capable of chelating heavy metal ions. In addition, bark pellets contain carboxylic groups that can bind metals by ion-exchange mechanisms (Vázquez et al., 2002; Martin-Dupont et al 2006). Availability of ion-exchange groups is strongly influenced by pH. Thus at low pH values, carboxylic groups should be predominantly non-ionized, and therefore unavailable for ion-exchange with a metal ion. However as pH increases, more and more carboxylic groups will be ionized and become available for ion-exchange with a metal ion. On the contrary, the distribution of hydrolysis species of metal ions as a function of pH is different for each metal ion. Thus, each metal ion will show its own characteristic adsorption kinetics depending on the distribution of its hydrolysis products at a given solution pH.

Cu(II) adsorption kinetics

The speciation diagram for Cu(II) indicates that in the pH range 2–4.9, Cu(II) ions in aqueous solution may exist in two forms: $Cu(aq)^{2+}$ and $Cu(NO_3)^{+}$. In the pH range 5.0–6.0 an additional two species may appear: $Cu(OH)^{+}$ and $Cu(OH)_{aq}$ (Vuceta and Morgan 1977). Thus, adsorption kinetics of Cu(II) ions will be limited by the rate of adsorption of the dominant species at a given solution pH. As shown in Table 4, q_e values for Cu(II) sorption predicted by both kinetic models decreased with increase in pH. However both pseudo-first-order (k_1) and pseudo-second-order (k_2) rate constants showed a maximum at pH 4. This suggests that the rate of Cu(II) sorption is determined by $Cu(aq)^{2+}$ ion concentration, and as this concentration decreases at pH greater than 4, the rate of Cu(II) sorption decreases accordingly because of formation of other Cu(II) species, such as

Table 6. Pseudo-first- and second-order kinetic parameters for Cd(II) sorption

pH	Pseudo-first order				Pseudo-second order			
	q_e (mg/g)	k_1 (min^{-1})	*R*	RMSE	q_e (mg/g)	k_2 (g/mg/min)	*R*	RMSE
2	0.463 ± 0.032	0.1158 ± 0.004	0.9926	0.0204	0.502 ± 0.036	0.356 ± 0.042	0.9740	0.0378
4	0.398 ± 0.029	0.0730 ± 0.030	0.9798	0.0333	0.458 ± 0.044	0.207 ± 0.117	0.9877	0.0240
6	0.414 ± 0.037	0.0816 ± 0.010	0.9928	0.0184	0.447 ± 0.040	0.272 ± 0.020	0.9798	0.0292

Table 7. Pseudo-first- and second-order kinetic parameters for Ni(II) sorption

pH	Pseudo-first order				Pseudo-second order			
	q_e (mg/g)	k_1 (min^{-1})	*R*	RMSE	q_e (mg/g)	k_2 (g/mg/min)	*R*	RMSE
2	0.434 ± 0.014	0.0765 ± 0.012	0.9938	0.0185	0.471 ± 0.016	0.235 ± 0.054	0.9786	0.0311
4	0.376 ± 0.004	0.0509 ± 0.003	0.9960	0.0127	0.408 ± 0.005	0.167 ± 0.008	0.9884	0.0206
6	0.257 ± 0.018	0.0791 ± 0.022	0.9813	0.0173	0.280 ± 0.018	0.408 ± 0.117	0.9708	0.0215

$Cu(OH)_{aq}$ in solution that are not adsorbed by ion-exchange reaction with H^+ ions on the bark pellets. Gaballah and Kilbertus, 1998 also reported a similar trend in pH dependence of Cu(II) adsorption on modified pine bark

Zn(II) adsorption kinetics

The speciation diagram for Zn(II) indicates that in the pH range 2–6.5, Zn(II) ions in aqueous solution exist only in one form, $Zn(aq)^{2+}$ (Zhang and Muhammed 2001). Thus, adsorption kinetics of Zn(II) ions should be independent of pH in the range 2–6. Indeed, as shown in Table 5, no relationship is apparent between solution pH values and q_e values or pseudo-first- and second-order rate constants (k_1 and k_2, respectively) for Zn(II) sorption on bark pellets. This suggests that interaction of Zn(II) in the pH range 2–4 is not by ion-exchange with H^+ ions on the bark pellets, but rather involves other mechanisms, such as surface complexation or hydrogen-bonding between the hydrated $Zn(aq)^{2+}$ ions and the bark polyhydroxyl-polyphenolic groups (Ravat et al., 2000; Reddy et al., 1997).

Cd(II) adsorption kinetics

Similar to Zn(II), at pH values below 7, Cd(II) exists in aqueous solution only as the $Cd(aq)^{2+}$ species (Leyva-Ramos et al. 1997). Accordingly, its adsorption kinetics on bark pellets should also be similar to that of Zn(II). As shown in Table 6 there was no correlation between solution pH and q_e values or the rate constants k_1 or k_2 for Cd(II) sorption on bark pellets. Thus, a reasonable conclusion is that in the pH range 2–6, adsorption mechanism of Cd(II) is by surface complexation with polyphenolic groups in the bark. This is consistent with observations made by Ravat et al., (2000) that sorption of

Cd(II), Zn(II) and Ni(II) on lignocellulosic substrates showed less dependence on pH than that of Cu(II).

Table 8. Some physical and chemical characteristics of metal ions[a]

Ion	Charge-size function, Z^2/r	Hydration enthalpy, ΔH_h (kJ/mol)	First hydrolysis constant, pK_{pq}
Cu^{2+}	5.48	–2,100	7.9
Zn^{2+}	5.33	–1,807	7.5
Ni^{2+}	5.71	–2,105	9.6
Cd^{2+}	4.21	–2,046	9.0

[a] Huheey 1972; Ahmed et al. 1998; Martin-Dupont et al. 2002.

Ni(II) adsorption kinetics

Although at pH values below 7 Ni(II) exists in aqueous solution only as the $Ni(aq)^{2+}$ species (Ji and Cooper 1996), its adsorption kinetics on bark appeared to be similar to Cu(II) adsorption kinetics because the q_e values showed a decrease with increase in pH from 2 to 6. However, unlike for Cu(II), rate constants k_1 and k_2 showed a minimum at pH 4 (Table 7), which is difficult to explain. However, above pH 4 the increase in the rate constant appears to be consistent with H^+ ion-exchange reaction mechanism.

Table 8 shows some physical and chemical characteristics of metal ions that may have a bearing on their respective rates of reaction with the ligands on the bark. As a first approximation, it can be argued that the ease with which each hydrated metal ion reacts with a ligand on the bark sorbent should be determined by how readily a molecule of water is displaced from its hydration shell. The hydration enthalpy ΔH_h corresponds to the energy required to displace H_2O molecules from cations, and therefore reflects how easily the cation reacts with a ligand located on the bark; the higher the hydration enthalpy, the more difficult for the cation to react with the ligand on the bark. For the cations under consideration in this study, hydration enthalpy follows the decreasing order: Ni(II) > Cu(II) > Cd(II) > Zn(II), which should translate to the following decreasing order of theoretical affinity of the cations for the bark ligand: Zn(II) > Cd(II) > Cu(II) > Ni(II). However this order of theoretical affinity is not in agreement with our experimental data. In the case of divalent cations, the first hydrolysis constant, pK_{pq} represents the extent to which the cation is converted to a monovalent species, $M(OH)^+$ by hydrolysis. For the cations under consideration in this study, the first hydrolysis constant follows the decreasing order: Zn(II) > Cu(II) > Cd(II) > Ni(II), which is in better agreement with our experimental data. This supports the hypothesis that in addition to the effect of pH on the speciation of each metal ion, pH effect on the degree of ionization of the carboxyl (R-COOH), hydroxyl (R-OH) and phenolic (φ-OH) ligands on the bark is equally important. Thus under a given set of solution conditions, such as pH and ionic strength, each metal ion species, depending on its respective physical and chemical characteristics, will react more readily with those ligands that are available under the given pH conditions.

Dynamic Adsorption Experiments

Breakthrough curves for Cu(II), Zn(II), Ni(II), and Cd(II) are shown in Figure 3. The breakthrough volume, defined as the volume of column effluent where the ratio of the effluent-to-influent concentration of a metal ion is equal to 0.5, was estimated from a logarithmic curve fit of the experimental data. The regression equations and the value of breakthrough volumes, calculated from these equations for each of the ions, are summarized in Table 9. Breakthrough volumes decreased in the order Cu(II) > Zn(II) > Cd(II) > Ni(II) at influent pH 5.1 ± 0.2.

To determine the amount of metal ion adsorbed per unit weight of pellets under flow through column conditions, the breakthrough data were fitted to the linearized form of Thomas equation (Kapoor and Viraraghavan 1998):

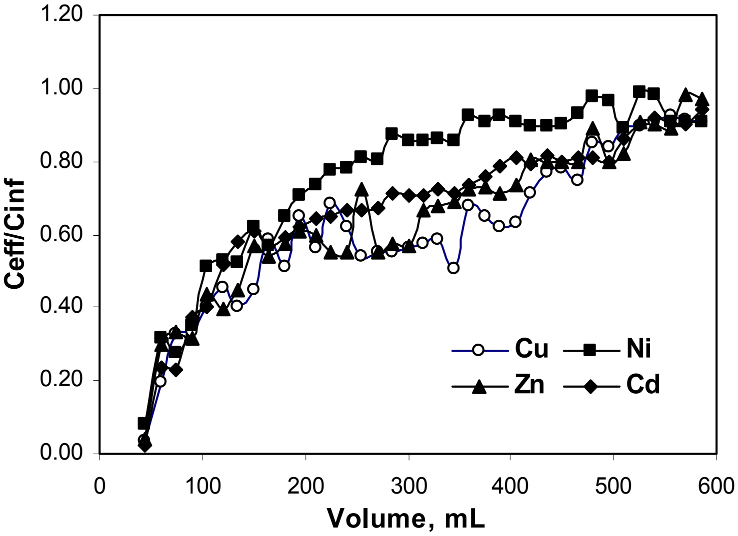

Fig. 3. Breakthrough curves for Cu(II), Zn(II), Ni(II), and Cd(II) at flow rate 5 mL/min, influent pH 5.1 ± 0.2, influent concentration ≈10.0 mg/L.

Table 9. Calculated breakthrough volumes of Cu(II), Zn(II), Ni(II), and Cd(II) on pelletized bark at flow rate 5 mL/min, influent pH 5.1 ± 0.2, and influent concentration ≈10.0 mg/L

Metal ion	Regression equation	R^2	Breakthrough volume, mL
Cu(II)	$y = 0.2857\text{Ln}(x) - 0.9758$	0.8628	175
Zn(II)	$y = 0.2948\text{Ln}(x) - 0.9949$	0.9198	159
Ni(II)	$y = 0.3208\text{Ln}(x) - 1.0263$	0.9542	116
Cd(II)	$y = 0.2952\text{Ln}(x) - 0.9702$	0.9419	146

$y = C_{\text{effl}}/C_{\text{infl}}$; x is volume of effluent (mL); R^2 is coefficient of determination.

$$\log(C_{\mathrm{inf}}/C_{\mathrm{eff}} - 1) = kq_0M/Q - kC_{\mathrm{inf}}V/Q \quad (7)$$

where C_{inf} and C_{eff} are solute concentrations (mg/L) in the influent and effluent, respectively, k is the Thomas rate constant (ml/min mg), q_0 is the maximum solid-phase concentration of solute (mg/g), M is the mass of adsorbent (g), V is the throughput volume (mL), and Q is the volumetric flow rate (mL/min).

As shown in Table 10, the experimental data did not show a good fit to the Thomas model regression equation. Consequently, q_0 values calculated according to this model should be treated as approximations of the actual values. The amount of metal ion adsorbed per unit weight of pellets decreased in the order Cu(II) > Zn(II) > Cd(II) > Ni(II). This affinity sequence is almost consistent with that obtained from adsorption isotherm experiments described above, with Zn(II) and Cd(II) in reversed positions.

Table 10. Thomas adsorption model parameters for dynamic adsorption of Cu(II), Zn(II), Ni(II), and Cd(II) on pelletized bark at flow rate 5 mL/min, influent pH 5.1 ± 0.2, and influent concentration ≈10.0 mg/L

Metal ion	Regression equation	R^2	k, mL min-1 mg-1	q_0, mg g^{-1}
Cu(II)	$y = -0.0138x + 0.6258$	0.7948	1.383	57
Zn(II)	$y = -0.0153x + 0.6319$	0.8015	1.483	53
Ni(II)	$y = -0.0169x + 0.4040$	0.7965	1.856	27
Cd(II)	$y = -0.0138x + 0.5204$	0.7659	1.314	50

$y = \log(C_{\mathrm{inf}}/C_{\mathrm{eff}} - 1)$; $x = V/Q$

Pellet Regeneration and Metal Recovery

Pellets were regenerated by gentle stirring in 0.5 M HNO_3 for 12 h. Figure 4 shows breakthrough curves for six influent concentrations of copper (1, 25, 50, 70, 100, 250 mg/L) passed successively through the column packed with virgin or regenerated pellets. There was practically no difference between the performance of the virgin and regenerated pellets, except at the high influent concentration (250 mg/L).

It is also important to note that recovery of the metals in dilute nitric acid has the effect of concentrating the metals in solution from which they could be recovered by suitable precipitation or electrochemical methods. The regenerated bark pellets could then be safely used as hog fuel in cogeneration plants.

CONCLUSIONS

Bark flour from ponderosa pine was consolidated into pellets, using citric acid as cross-linking agent. The pellets were subjected to high-temperature heat treatment.

1. The pellets did not leach tannins when soaked in water. In the pH range 2–6, the pellets showed different capacities for removal of heavy metal ions from synthetic metal ion solutions.
2. The equilibrium amount q_e of Cu(II) adsorbed per gram of sorbent increased from approximately 0.5 mg at pH 6 to 0.7 mg at pH 2, and for Zn(II), from approximately 0.4 mg to 0.7 mg.
3. For Cd(II) and Ni(II), no pH effect was apparent on the amounts adsorbed per gram of sorbent, which ranged from approximately 0.4 to 0.5 mg and 0.3 to 0.4 mg, respectively.
4. This study demonstrated the potential for converting low-cost bark residues to value-added sorbents using starting materials and chemicals derived from renewable resources. These sorbents can be applied in the removal of low-concentration toxic heavy metals from waste streams.

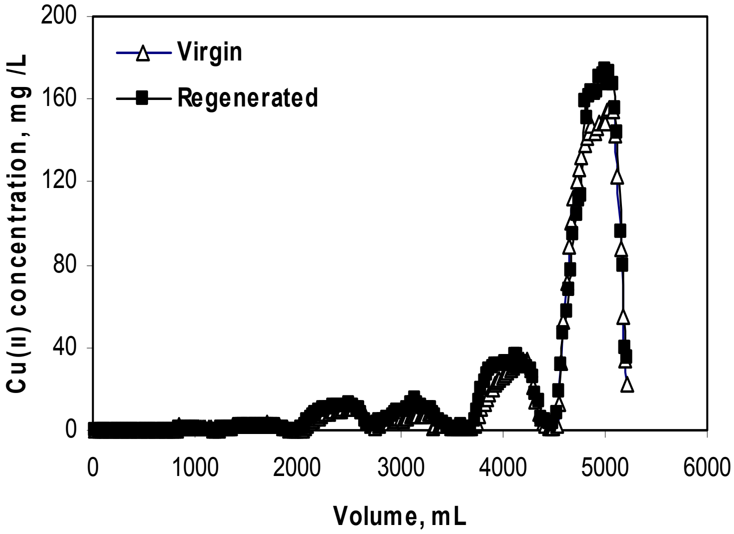

Fig. 4. Breakthrough curves for six influent concentrations (1, 25, 50, 70, 100, 250 mg/L) of Cu(II) passed successively through column packed with virgin and regenerated pellets.

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