

Sorption of cadmium and other heavy metals by pine bark

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Abstract

Pine bark sorbs cadmium ions from aqueous solutions. A decrease in the bark concentration with a constant cadmium concentration, or an increase in the cadmium concentration with a constant bark concentration, increased cadmium loading per unit weight of the adsorbent. An increase in the initial pH exhibited the same effect. The maximum cadmium uptake was obtained using very fine particles of pine bark. The isotherms presented in this work fit the Freundlich isotherm model reasonably well. A high concentration of soft and hard ions strongly depressed the uptake of cadmium by pine bark. Bark can be used for the sorption of the following metals from aqueous solutions with the indicated order of capacity (mass basis): $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+}$. Generally, the same order of capacity was observed in a mixture containing these metal ions. Bark was found to respond better for sorption of metal ions when preloaded with another metal ion. © 1997 Elsevier Science B.V.

Keywords: Pine bark; Sorption; Desorption; Cadmium; Copper; Nickel; Lead; Soft ions

1. Introduction

Heavy metals are very harmful to humans, animals and plants. Federal and local agencies have therefore established certain limits on the quantities of heavy metals being discharged into the environment. Cadmium, which was predominantly used in this study,

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is one of these metals. It is an irritant to the respiratory tract, and prolonged exposure to this pollutant can cause anosmia and a yellow stain that gradually appears on the necks of the teeth. Acute toxicity is almost always caused by inhalation of cadmium fumes or dust which are produced by heating this metal [1]. However, cadmium also has practical applications; e.g., it is highly corrosion resistant and is used as a protective coating for iron, steel and copper. The industrial uses of cadmium are widespread and increasing in electroplating, paint pigments, plastics, silver–cadmium batteries [2], smelting [3], cadmium–nickel batteries, stabilizers, phosphate fertilizer, mining, and alloy industries [4]. The global annual production of cadmium is around 20000 tons. Discharge of cadmium into natural waters is derived partly from the electroplating industry which accounts for about 50% of the annual cadmium consumption in the US. [2].

Removal of cadmium before it is discharged into the environment can be accomplished by a number of processes such as chemical precipitation, cementation, solvent extraction, reverse osmosis and ion exchange. These processes are, sometimes, neither effective nor selective and some of them are very expensive [5]. Adsorption is another process for the removal of heavy metals which is quite selective and effective, and is able to remove very low levels of heavy metals from solution. Ion exchange resins and activated carbon are very well known materials that are used for this purpose. Relatively recently, some agricultural and forestry products and wastes have been recognized as new adsorbents. In general, the cost of these biomaterials is negligible compared with the cost of activated carbon and ion-exchange resins that is in the range of approximately \$2.0–\$4.0 per kilogram. Ferro-Garcia et al. [6] produced activated carbons from almond shells, olive stones and peach stones by heating them in CO_2 at 850°C and used them for adsorption of Zn^{2+} , Cd^{2+} and Cu^{2+} . Some Indian tree barks (*Accacia arbica*, *Pterocarpus marsupium*, *Terminalia tomentosa* and *Tectona grandis*) treated with formaldehyde and sulfuric acid were used for the removal of Zn^{2+} , Cd^{2+} , Pb^{2+} and Cu^{2+} [7]. Similarly, Singh et al. [8] treated powder derived from tea leaves with formaldehyde and sulfuric acid and used it for the removal of Pb^{2+} from aqueous solutions. Other agricultural materials such as raw rice husk, crushed coconut shell [9], rice hulls and rice bran [10], peat moss [11], apricot seed shell, walnut shell, peanut shell, orange skin and Irish peat [12] have been used without any treatment for adsorption of some of the following metals: Cd^{2+} , Co^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} and Cr^{3+} .

Sorption of heavy metals by these materials might be attributed to their protein, carbohydrates and phenolic compounds [13] which have metal-binding functional groups such as carboxyl, hydroxyl, sulfate, phosphate and amino groups [14]. Salim et al. [15] claimed that the loss of metal ions from their solutions in the presence of agricultural materials may be due to the adsorption on surface and pores, and to complexation by these materials.

The objective of this work was to study the possibility of the utilization of pine bark, pine cones and pine needles for the sorption of cadmium and other metals from single- or multi-metal solutions. The effects of bark and metal concentrations, pH, particle size of sorbent, and concentration of soft and hard ions on the removal of cadmium from its aqueous solutions were considered. The recovery of this metal from bark was also tested.

2. Experimental methods

2.1. Sorbents

Pine bark, cones and needles from the Ottawa region were washed several times with deionized water and left to dry at room temperature. Each kind of dry material was separately disintegrated in a blender and stored for further use.

2.2. Sorption tests

A batch process was carried out by transferring 10 ml of a Cd^{2+} solution into a plastic tube. The solution was prepared by solubilizing a desired amount of $\text{CdSO}_4 \cdot 7\text{H}_2\text{O}$ in deionized water and adjusting the pH to 5 (unless otherwise stated) with 0.1 M NaOH.

A certain amount of adsorbent was added to the above solution and the system was agitated on a rotary shaker (Fisher Roto-Rack Model 340) for 24 h. The adsorbent from the samples was separated by vacuum filtration through 0.45 μm cellulose filter paper (Millipore Corp.), and the filtrate was analyzed for the metal under consideration using an atomic absorption spectrophotometer (Varian AA-1475 series). Metal solutions without sorbent were agitated in the tubes and then filtered to determine metal precipitation or its adsorption to the tube walls. The concentration before and after filtration was the same. This is in agreement with reported data by Huang et al. [16] for the range of Cd^{2+} concentrations and the pH values covered in this study.

Each test was carried out in duplicate, and the average results are presented in this work. The results of a duplicate test were discarded if they differed by more than 7%.

2.3. Desorption tests

Batch contact desorption experiments were performed by transferring 10 ml of 0.01 M HCl (unless otherwise specified) to a metal-laden bark having a specified metal uptake. The samples were agitated on a rotary shaker till equilibrium. The solutions were then separated by vacuum filtration through 0.45 μm cellulose filter paper (Millipore Corp.) and the filtrate was analyzed for the metal under consideration, as previously described. The amount of metal desorbed is reported as the ratio of the total metal released from the laden bark to that of the metal uptaken during its sorption.

3. Results and discussion

3.1. Sorption by pine constituents

When pine bark, cones and needles were tested for their ability to adsorb Cd^{2+} ions from aqueous solution, using sorbent and initial Cd^{2+} concentrations of 9.2 mg ml^{-1} and 100 ppm, respectively, it was noted that the sorption performance of these materials

Table 1

Sorption of cadmium by different parts of pine. Initial cadmium concentration: 100 ppm; sorbent concentration: 9.2 mg ml⁻¹; pH 5

Sorbent	Cd ²⁺ uptake (μg mg ⁻¹)	Amount removal (%)
pine bark	9.2 ± 0.52	84.7
pine cones	7.5 ± 0.47	69.0
pine needles	7.1 ± 0.41	65.3

(Table 1) was comparable to that of other biomaterials when the tests were carried out under similar conditions; *Accacia* bark [7], Irish peat [12] and tea leaves [17] removed about 91% of Cd²⁺, 88% of Cd²⁺ and 65% of Cd²⁺ from the solution, respectively. Since Cd²⁺ uptake by pine bark is higher than that by cones and needles (Table 1), bark was used in the further tests in this study for the sorption of this metal ion.

3.2. Dynamics of Cd²⁺ uptake

The dynamics of the Cd²⁺ uptake was studied in batch experiments by employing a bark suspension of 9.2 mg ml⁻¹ and an initial Cd²⁺ concentration of 1000 ppm. Samples were taken at various periods of time and analyzed for their Cd²⁺ concentration. The results (Fig. 1) show three stages of the uptake. In the beginning, a rapid initial increase in the rate of uptake is noted. This is due to a rapid attachment of Cd²⁺ ions to

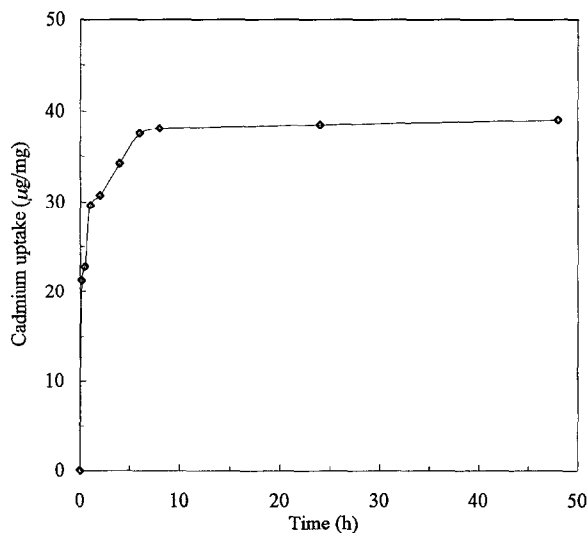


Fig. 1. Dynamics of cadmium uptake by pine bark. Initial Cd²⁺ concentration: 1000 ppm; bark concentration: 9.2 mg ml⁻¹; initial pH 5.2.

the surface of the bark by physical sorption. A slower rate of the uptake followed, indicating the existence of an intrapore diffusion mechanism. Intrapore diffusion does not appear to be the rate-controlling step because the curve obtained (not shown) by plotting the uptake rate vs the square root of the time does not pass through the origin [18]. Metal ions are attracted to negatively charged sites at the surface of the cells. A number of anionic ligands participate in binding the metal ions: phosphoryl, carboxyl, sulfhydryl and hydroxyl groups. The metal binding at the surface of the bark could be attributed to complexation with these groups or ion exchange with the hydrogen ions, since the tests showed a decrease in the pH of the solution after cadmium sorption. Similar dynamics curves were also obtained for the sorption of Hg^{2+} by *Hardwickia binata* bark [19] and for the uptake of Cd^{2+} by beech leaves [20]. Although sorption equilibrium was attained after 6 h (Fig. 1), all subsequent experiments with this sorbent were carried out for 24 h.

3.3. Effect of bark and cadmium concentrations

To investigate the effects of the Cd^{2+} and bark concentrations on the uptake of this metal, the process was carried out with initial Cd^{2+} concentrations between 20 and 1000 ppm and various bark concentrations. At equilibrium (24 h contact time), the Cd^{2+} concentration in each system was measured and isotherms, displayed in Fig. 2, were taken as a function of bark concentration. It can be noted that the Cd^{2+} uptake per unit weight of the sorbent increased with a decrease in the bark concentration, while the total

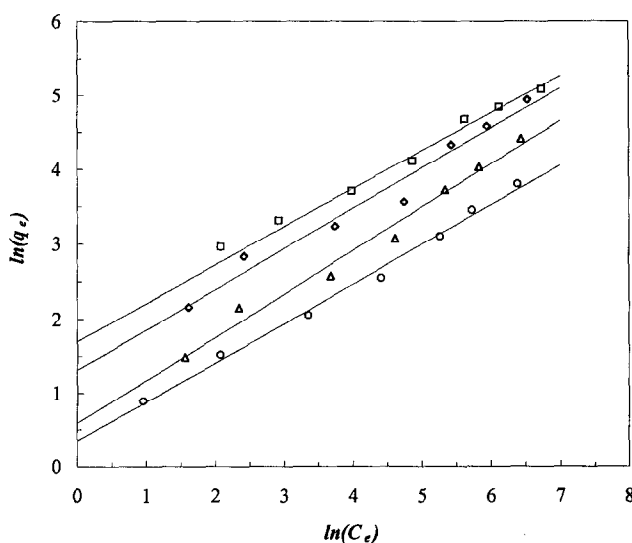


Fig. 2. Relationship between equilibrium cadmium concentration and its uptake at various bark concentrations at pH 5.0. Symbols are experimental and solid lines are predicted data using the Freundlich isotherm model. Bark concentration (mg ml^{-1}): (\square) 1.15, (\diamond) 2.3, (Δ) 4.6, (\circ) 9.2.

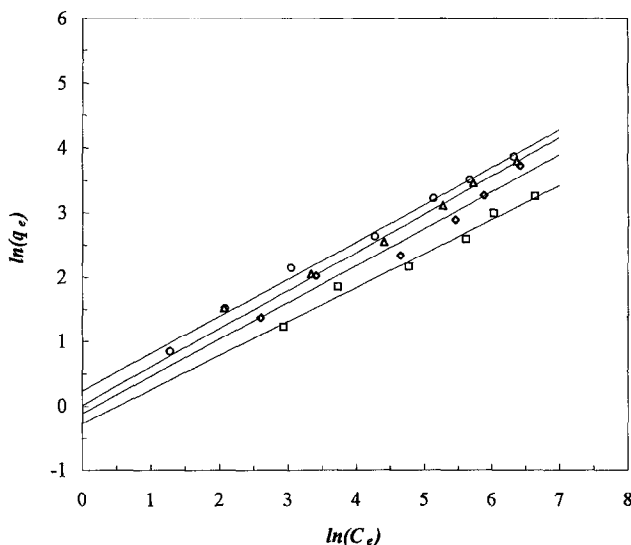


Fig. 3. Relationship between equilibrium cadmium concentration and its uptake at various pH values and a bark concentration of 9.2 mg ml^{-1} . Symbols are experimental and solid lines are predicted data using the Freundlich isotherm model. pH: (\square) 4.0, (\diamond) 4.5, (Δ) 5.0, (\circ) 5.5.

amount of the metal removed increased with an increase in the sorbent concentration. Such a trend was also reported for the removal of Pb^{2+} , Cd^{2+} and Zn^{2+} by waste tea leaves [17], and for Cd^{2+} uptake by beech leaves [20]. The results in Fig. 2 and those in Figs. 3 and 4 also indicate that the increase in the Cd^{2+} uptake was associated with an increase in its concentration. This can be explained by a progressive increase in electrostatic interactions, relative to covalent interactions, of the sites that have lower affinity for Cd^{2+} with an increase of its initial concentrations [21].

The following linearized form of the Freundlich isotherm model can represent all these experimental equilibrium results except those in Fig. 4, which show some deviation from the linearity:

$$\ln q_e = \ln k + \frac{1}{n} \ln C_e, \quad (1)$$

where q_e ($\mu\text{g mg}^{-1}$) is the amount of the sorbed Cd^{2+} ions at the final equilibrium concentration C_e ($\mu\text{g ml}^{-1}$), k is a Freundlich constant related to the sorption capacity, and $1/n$ is related to the sorption intensity which is defined as

$$\frac{1}{n} = \frac{RTq_m}{\sigma_0 - \sigma_1}, \quad (2)$$

where q_m ($\mu\text{g mg}^{-1}$) is the monolayer capacity of the sorbent for the solute, σ_0 (kcal g^{-1}) and σ_1 (kcal g^{-1}) are the free energies of the surface covered with pure solvent and with a monolayer of solute, respectively. Although this model is used to describe the adsorption process, its fitting to the experimental data does not necessarily

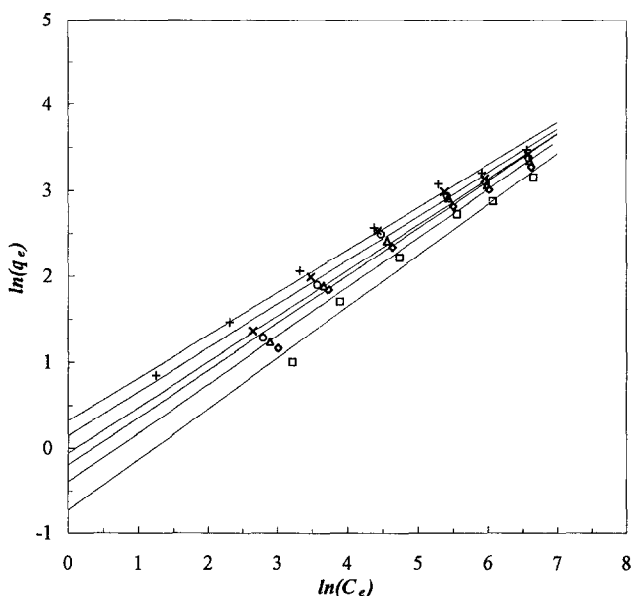


Fig. 4. Relationship between equilibrium cadmium concentration and its uptake by pine bark of various particle sizes. Bark concentration: 9.2 mg ml^{-1} ; pH 5.0; particle size (mm): (+) < 0.075 , (x) $0.075\text{--}0.14$, (O) $0.14\text{--}0.212$, (Δ) $0.212\text{--}0.425$, (\diamond) $0.425\text{--}0.71$, (\square) > 0.71 .

imply that only a 'pure' adsorption phenomenon has taken place [2]. A linear plot of $\ln q_e$ vs $\ln C_e$ at different sorbent concentrations (Fig. 2) suggests the formation of a monolayer coverage of the outer surface of the bark by Cd^{2+} ions. The values of k and $1/n$ for various bark concentrations were evaluated from the intercepts and the slopes of the plots, respectively (Table 2). The slopes of all the plots ($1/n$) indicate that the intensity of sorption was virtually the same regardless of the sorbent concentration, while the sorbent capacity (k values) increased as the sorbent concentration decreased.

3.4. Effect of pH

Many researchers have demonstrated that the binding of heavy metal ions on biomaterials is pH dependent. Kumar and Dara [7] obtained an optimum pH of 9 for the

Table 2
Freundlich constants^a at various bark concentrations at pH 5

Bark concentration (mg ml^{-1})	k	$1/n$
1.15	5.49	0.51
2.30	3.73	0.54
4.60	1.81	0.58
9.20	1.42	0.52

^aValues obtained from the data displayed in Fig. 2.

Table 3
Freundlich constants^a at various pH values and at 9.2 mg ml⁻¹ bark concentration

pH	<i>k</i>	1/ <i>n</i>
4.0	0.76	0.53
4.5	0.89	0.57
5.0	1.02	0.59
5.5	1.27	0.57

^aValues obtained from the data displayed in Fig. 3.

Cd²⁺ uptake by *Accacia* bark. They reported that tannins in the bark acted as weak acid ion exchangers in which two hydrogen ions were replaced by each divalent ion. The uptake of Cd²⁺ by waste tea leaves was almost negligible at pH values inferior to 4, while a significant increase was noted at higher pH values, with a maximum at pH 7 [17]. This was also attributed to the acidic cell wall functional groups of the leaves, and the optimum pH would likely fall under weakly acidic conditions. The authors suggested that, at low pH, the complex formed via interaction between metal ions and acidic functional groups would be expected to be destabilized since the values of conditional stability constants decreased with pH and, therefore, the metal ions desorbed into the solution. The authors also suggested the complexation of H⁺ for surface active sites, leading to a minimum or negligible metal ion uptake at low pH. Singh et al. [8] concluded, on the basis of their results of an increase in the Pb²⁺ sorption by chemically treated tea leaves at higher pH values (pH 6), that the exchange between H⁺ and metal ion is enhanced with pH increase. In this work, the effect of pH on the adsorption of Cd²⁺ was studied in systems with an initial Cd²⁺ concentration in the range 20–1000 ppm. At equilibrium, the isotherms were obtained as a function of pH. A significant increase in the Cd²⁺ uptake per unit weight of bark was noticed as the pH increased from 4 to 5.5 (Fig. 3). This can also be attributed to the tannin content of the bark, as suggested by researchers for other adsorbents. The constants *k* of the Freundlich-type isotherm model applied to these data (Table 3) showed that the sorption capacity of this biosorbent increased with the pH values of the aqueous metal solutions.

3.5. Effect of particle size of the bark

To investigate the effect of particle size on the sorption process, bark was screened through sieves and the following size distribution fractions were obtained: one smaller than 0.075 mm, four fractions with sizes between 0.075 and 0.71 mm, and one fraction with a particle size bigger than 0.71 mm. Each of these fractions was exposed to a series of Cd²⁺ solutions in the concentration range 20–1000 ppm. At equilibrium, the isotherms were obtained as a function of particle size (Fig. 4). The results indicated that the particle size influenced the sorption process, because of an increase of the surface area per unit weight of the sorbent with a decrease of its particle size. The linear Freundlich isotherm model was fitted to the experimental data (Fig. 4); the Freundlich constants for each particle size are shown in Table 4. Although the model shows some deviation, it represents the experimental data better than other equilibrium models (not

Table 4
Freundlich constants^a at different particle sizes at pH 5 and 9.2 mg ml⁻¹ bark concentration

Particle size (mm)	<i>k</i>	1/ <i>n</i>
< 0.075	1.38	0.49
0.075–0.140	1.16	0.51
0.140–0.212	0.94	0.53
0.212–0.425	0.82	0.55
0.425–0.71	0.67	0.57
> 0.710	0.48	0.59

^a Values obtained from the data displayed in Fig. 4.

shown here), such as the Langmuir model. A slight decrease in the 1/*n* values with the decrease of the particle size indicated a decrease of the sorption intensity. Jha et al. [22] also obtained an increase in the isotherm curves with a decrease in the particle size for the sorption of Cd²⁺ by chitosan but, in their case, the sorption intensity increased with a decrease in the particle size.

According to McKay and collaborators [23], the adsorption of Cd²⁺ on pine bark can be considered favorable because the 1/*n* values obtained in this work (Tables 2–4) are between 0.1 and 1.

3.6. Reutilization of the bark without regeneration

Bark was tested for its ability to be reutilized without regeneration. The tests were performed using an initial Cd²⁺ concentration of 100 ppm in a 9.2 mg ml⁻¹ bark suspension. Sorption was carried out for 24 h and then the bark was separated and transferred to another 100 ppm Cd²⁺ solution. The process was repeated five times. Each time the bark was able to adsorb some Cd²⁺. The largest amount of Cd²⁺ was removed from the solution with fresh bark. With each of its subsequent reutilizations the bark performance decreased (Fig. 5). Considering the uptake curve (Fig. 5) and the fact that bark can be loaded with about 40 μg of Cd²⁺ per mg of bark (Fig. 1), it can be concluded that the sorbent can be used even more than five times without regeneration. These results suggest that already used bark could be applied to fresh metal solutions, whereas used metal solutions that still contain residual metal ions could be treated with a fresh bark.

3.7. Desorption

The bark that contained on average 34 μg mg⁻¹ of Cd²⁺ was treated with HCl of various molarities to desorb the metal. Higher molarity of HCl was more efficient in the release of Cd²⁺ ions (Fig. 6). However, a complete desorption of Cd²⁺ ions could not be obtained even with 500 mM HCl, this might be due to Cd²⁺ ions becoming entrapped in the intrapores and therefore difficult to release.

Desorption has also been studied by treating bark samples containing various initial Cd²⁺ concentrations with a 10 mM HCl solution. Desorption from the samples with 2.5

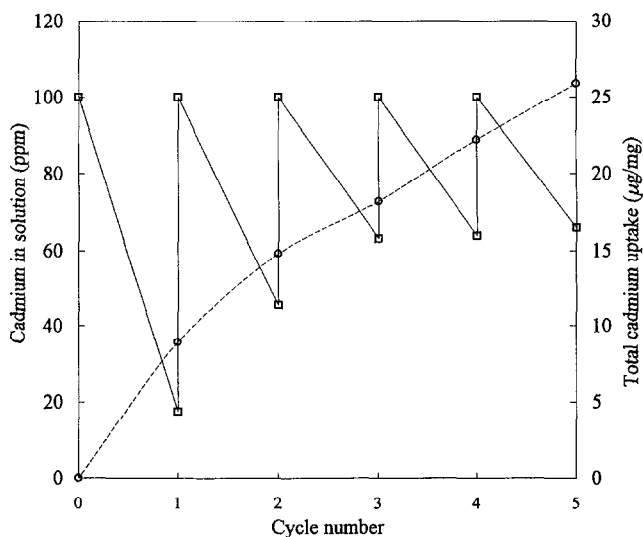


Fig. 5. Re-utilization of pine bark for Cd^{2+} sorption. Bark concentration: 9.2 mg ml^{-1} ; Cd^{2+} concentration: 100 ppm; pH 5. Solid line represents the amount of Cd^{2+} in solution and interrupted line represents the uptake curve.

and $6 \mu\text{g}$ of Cd^{2+} per mg of bark resulted in a 100% and about 97% release of Cd^{2+} ions from the bark, respectively (Fig. 7). The high level of desorption attained in these two cases could mean that surface adsorption was predominant in the case of low metal ion concentration in this sorbent. The desorption efficiency decreased to about 70% when the metal concentration was above $6 \mu\text{g}$ of Cd^{2+} per mg of bark.

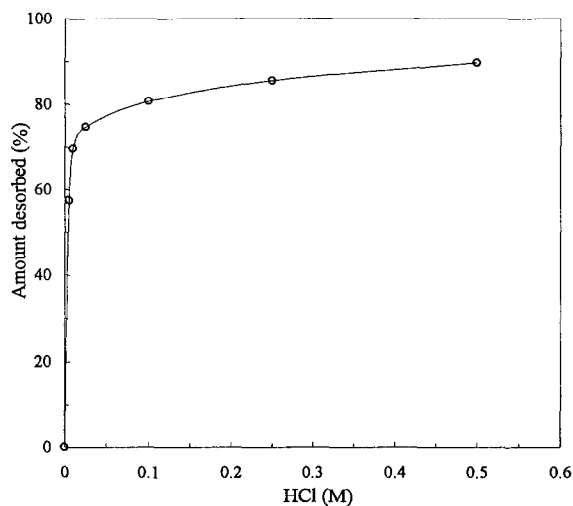


Fig. 6. Effect of HCl concentration on desorption of Cd^{2+} from bark. Amount of Cd^{2+} on bark: $34 \mu\text{g mg}^{-1}$. The volume of the desorbent and the bark concentration were 10 ml and 9.2 mg ml^{-1} respectively.

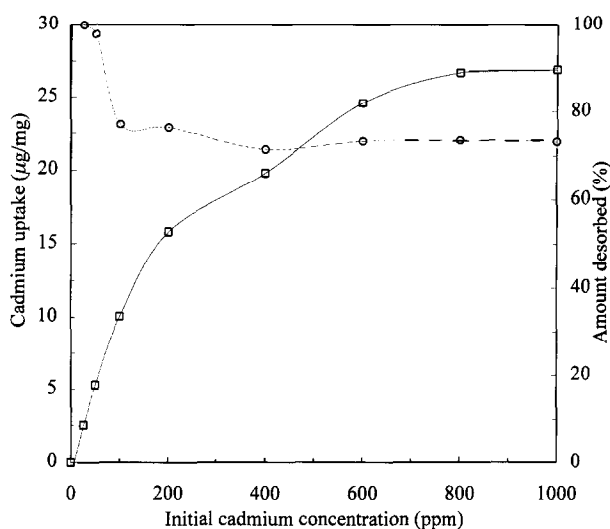


Fig. 7. Sorption/desorption of Cd^{2+} by/from pine bark using different initial Cd^{2+} concentrations and 0.01 M HCl as desorbent. Solid line: Cd^{2+} uptake vs its initial concentration. Interrupted line: percentage of Cd^{2+} desorbed from the bark.

3.8. Reuse of the bark after regeneration

In these tests, Cd^{2+} was desorbed from the bark, which was exposed to a concentration of 100 ppm of this metal, with a 10 mM HCl solution. The bark was separated by filtration, washed several times with deionized water until the pH of the filtrate corresponded to that of the water, and then reused for the Cd^{2+} sorption. This process was repeated five times. The results showed (Fig. 8) that with each subsequent reutilization of the bark the amount of the newly sorbed Cd^{2+} decreased, but the total amount of this metal, i.e. the sum of the newly sorbed and that retained after desorption, increased. It was logical that the amount of the newly sorbed Cd^{2+} decreased because some sorption sites were already occupied by previously sorbed ions of this metal which had resisted desorption treatment.

3.9. Effect of soft and hard ions

Soft and hard ions are among those complexing agents which interfere with the sorption of heavy metal ions by biomaterials. Norris and Kelly [24] reported that the initial rate of Cd^{2+} uptake by the cells of *Saccharomyces cerevisiae* was strongly depressed by Ca^{2+} ions when the initial concentrations of Cd^{2+} and Ca^{2+} in the solution were 22.5 and 8 ppm respectively. Muzzarelli and Tubertini [25] showed that K^+ , Na^+ and Mg^{2+} did not interfere with the removal by chitin of many metal ions from their solutions. The results of Jha et al. [22] indicated that, in the presence of 100 ppm of Ca^{2+} ions and 5 ppm of Cd^{2+} ions, the initial rate of Cd^{2+} removal by chitosan decreased. Our results showed (Fig. 9) that the presence of 100 ppm of Na^+ , K^+ , Mg^{2+}

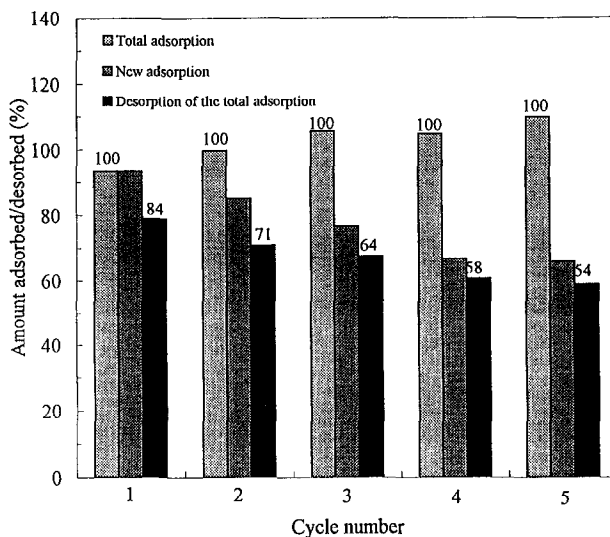


Fig. 8. Reuse of pine bark for sorption/desorption of Cd^{2+} . Initial Cd^{2+} concentration: 100 ppm; bark concentration: 9.2 mg ml^{-1} ; pH 5; 10 ml of 0.01 M HCl for desorption.

and Ca^{2+} , individually, in 100 ppm Cd^{2+} solution containing 9.2 mg ml^{-1} of bark, partially depressed the uptake of Cd^{2+} by this sorbent. Mg^{2+} and Ca^{2+} exhibited a stronger inhibition of Cd^{2+} adsorption than Na^+ and K^+ . This is in agreement with

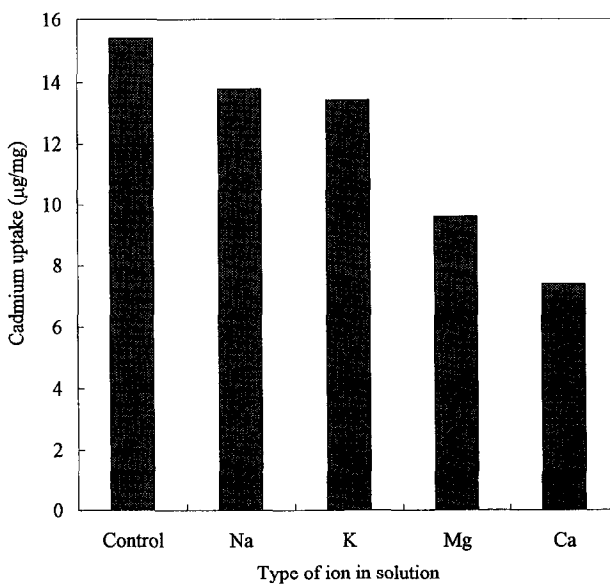


Fig. 9. Effect of soft and hard ions on Cd^{2+} uptake by pine bark. Initial Cd^{2+} and soft ions concentrations: 100 ppm of each; bark concentration: 9.2 mg ml^{-1} ; pH 5.0.

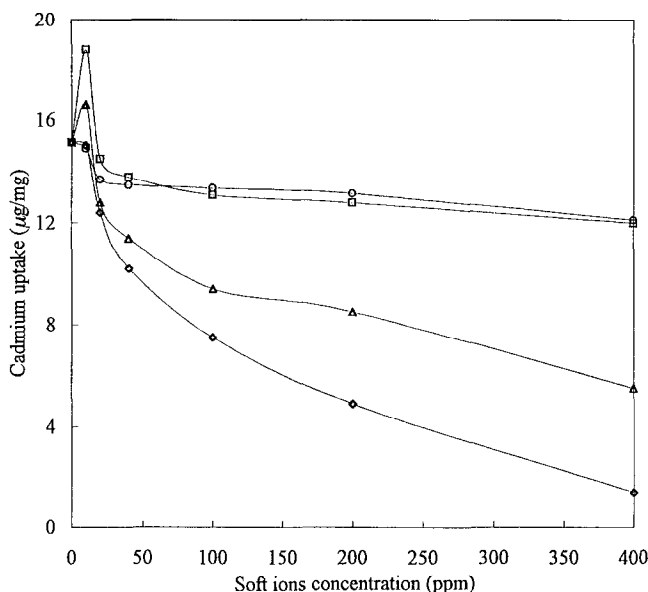


Fig. 10. Effect of soft and hard ions concentration on Cd^{2+} uptake. Initial Cd^{2+} concentration: 100 ppm; bark concentration: 9.2 mg ml^{-1} ; pH 5.0. Soft metal ions: (□) Na^+ , (○) K^+ , (△) Mg^{2+} , (◇) Ca^{2+} .

already published data for other sorbents which showed that the inhibition was stronger with higher valent ions than with lower ones.

The concentration of soft and hard ions plays an important role in this respect. It is noticed that lower concentrations (10 ppm) of Na^+ and Mg^{2+} resulted in an increase of Cd^{2+} uptake by bark (Fig. 10). With an increase in the concentration of these soft and hard ions of between 40 and 400 ppm, the effects of Mg^{2+} and Ca^{2+} were much more pronounced than those of K^+ and Na^+ . The latter is consistent with the results of Deshkar et al. [19], who reported a negative effect of soft and hard ions on the sorption of Hg^{2+} by *Hardwickia binata* bark when their concentrations were from 40 to 200 ppm. However, there are also data that showed an increase in Hg^{2+} sorption by activated carbon with an increase of Ca^{2+} concentration [26].

3.10. Single, binary, ternary and quaternary metal systems

Table 5 summarizes results of sorption of single metals from their various initial concentration solutions, using a bark suspension of 9.2 mg ml^{-1} at an initial pH value of 4. The following order of metal uptake per unit weight of bark was observed; $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+}$.

Table 6 gives the sorption of heavy metals from binary, ternary and quaternary metal systems, in which each metal had an initial concentration of 100 ppm. Comparing these results with those displayed in Table 5, it can be noted that in most cases the sorption capacity for one ion was significantly affected by the presence of others. The effect of ionic interaction on the sorption process may be represented by the ratio of the sorption

Table 5
Sorption of metal ions at pH 4 using 9.2 mg ml⁻¹ bark concentration

Metal ion	Sorbate concentration (ppm)			
	100	200	300	400
	Metal uptake (μg mg ⁻¹)			
Cu ²⁺	6.4	8.0	11.4	15.6
Cd ²⁺	7.5	8.7	12.6	16.3
Ni ²⁺	3.4	6.8	9.6	12.4
Pb ²⁺	10.3	21.7	25.5	28.6

capacity for one metal in the presence of other metal ions, q_{mix} , to the sorption capacity for the same metal when it is alone in solution, q_0 [27], such that for

$$\frac{q_{\text{mix}}}{q_0} > 1 \text{ sorption is promoted by the presence of other metal ions;}$$

$$\frac{q_{\text{mix}}}{q_0} = 1 \text{ there is no observable net interaction effect;}$$

$$\frac{q_{\text{mix}}}{q_0} < 1 \text{ sorption is suppressed by the presence of other metal ions.}$$

From the ratios given in Table 6 for six binary systems, the various suppressers and promoters can be identified for each of the ions studied. These results are consistent with the results for ternary and quaternary systems. For example, in the Cu²⁺, Pb²⁺ and Cd²⁺ ternary system, lead ions suppressed the sorption of both Cu²⁺ and Cd²⁺. The same level of suppression can be identified in the binary systems of Cu²⁺/Pb²⁺ and Cd²⁺/Pb²⁺ (Table 6). It is also noted that Ni²⁺ sorption was strongly inhibited by Cu²⁺ in the ternary system and in quaternary systems containing both of these metals.

The relative affinity of the bark for different metal ions in a mixed metal ions system may also be described by the binary selectivity index K_{ij} between a pair of ions i and j that is often used to describe the selectivity of ion exchange resins; this is defined as

$$K_{ij} = \frac{y_i x_j}{y_j x_i} \quad (3)$$

where x is the equilibrium molar fraction of sorbate in solution and y is its equilibrium molar composition on bark. The K_{ij} values for various pairs of metal ions are given in Table 6, where the following affinity series may be established: Pb²⁺ > Cu²⁺ > Cd²⁺ > Ni²⁺.

3.11. Preloading of bark with other metal ions

To examine the response of the bark for sorption of a particular metal ion if it was previously loaded with another metal ion, the bark was preloaded, individually, with Cu²⁺, Ni²⁺ and Cd²⁺ and then, after separation from solution, transferred to another metal ion solution. Sorption was followed in the new solution until equilibrium, and the

Table 6

Sorption capacity of pine bark for metal ions from ion mixtures. Initial concentration of each ion: 100 ppm; bark concentration: 9.2 mg ml⁻¹; initial pH 4

System	q_{mix} ($\mu\text{g mg}^{-1}$)	q_0 ($\mu\text{g mg}^{-1}$)	x	y	K_{ij}	q_{mix} / q_0
(A) Cu ²⁺	7.1	6.4	0.53	0.73	(AB) 2.40	1.11
(B) Cd ²⁺	5.0	7.5	0.47	0.27		0.85
(A) Cu ²⁺	4.9	6.4	0.43	0.53	(AB) 1.49	0.76
(B) Ni ²⁺	3.8	3.4	0.57	0.47		1.11
(A) Cu ²⁺	4.5	6.4	0.88	0.64	(AB) 0.24	0.70
(B) Pb ²⁺	8.2	10.3	0.12	0.36		0.80
(A) Cd ²⁺	5.9	7.5	0.31	0.38	(AB) 1.36	1.00
(B) Ni ²⁺	5.0	3.4	0.69	0.62		1.47
(A) Cd ²⁺	3.9	7.5	0.93	0.42	(AB) 0.054	0.66
(B) Pb ²⁺	9.9	10.3	0.07	0.58		0.96
(A) Ni ²⁺	4.5	3.4	0.94	0.62	(AB) 0.104	1.32
(B) Pb ²⁺	9.4	10.3	0.06	0.38		0.91
(A) Cu ²⁺	6.5	6.4	0.22	0.66	(AB) 1.50	1.01
(B) Cd ²⁺	5.3	7.5	0.16	0.32	(BC) 62.0	0.98
(C) Ni ²⁺	0.14	3.4	0.62	0.02	(AC) 93.0	0.04
(A) Cu ²⁺	4.3	6.4	0.54	0.50	(AB) 2.05	0.67
(B) Cd ²⁺	2.6	7.5	0.40	0.18	(BC) 0.08	0.44
(C) Pb ²⁺	8.5	10.3	0.06	0.32	(AC) 0.17	0.82
(A) Cd ²⁺	3.1	7.5	0.33	0.21	(AB) 0.84	0.52
(B) Ni ²⁺	3.4	3.4	0.61	0.46	(BC) 0.14	1.00
(C) Pb ²⁺	8.6	10.3	0.06	0.33	(AC) 0.11	0.83
(A) Ni ²⁺	0.0	3.4	0.67	0.00	(AB) 0.00	0.00
(B) Cu ²⁺	5.8	6.4	0.28	0.70	(BC) 0.42	0.90
(C) Pb ²⁺	8.0	10.3	0.05	0.30	(AC) 0.00	0.77
(A) Cu ²⁺	4.0	6.4	0.29	0.43	(AB) 0.87	0.62
(B) Cd ²⁺	4.3	7.5	0.16	0.27	(BD) 0.22	0.73
(C) Ni ²⁺	0.0	3.4	0.51	0.00	(CD) 0.00	0.00
(D) Pb ²⁺	8.3	10.3	0.04	0.30	(AD) 0.20	0.80

q_{mix} = sorption of a metal ion in mixture; q_0 = sorption of a metal ion in single ion system; x = equilibrium molar fraction of sorbate in solution; y = equilibrium molar sorbate fraction on bark; K_{ij} = selectivity index (i refers to the first symbol in brackets and j refers to the second one).

uptake was measured. It was shown that, for example, the capacity of bark for Ni²⁺ was higher when it was preloaded with Cu²⁺ and Cd²⁺ ions than when it was not preloaded with these metals (Table 7). It was also observed that some preloaded Ni²⁺ and Cd²⁺ ions had been released from the bark during the second stage of sorption, while almost

Table 7

Metal sorption using pine bark previously loaded with other metals. Initial metal concentration: 100 ppm; bark concentration: 9.2 mg ml^{-1} ; pH 4

Metal preloaded	Amount preloaded ($\mu\text{g mg}^{-1}$)	Metal used for second sorption	Amount of metal uptaken ($\mu\text{g mg}^{-1}$)	Amount of preloaded metal in solution (%)
Cu^{2+}	6.1	Ni^{2+}	5.4	0.0
	5.9	Cd^{2+}	7.0	1.1
Ni^{2+}	3.8	Cu^{2+}	6.6	84.4
	4.1	Cd^{2+}	7.8	31.3
Cd^{2+}	7.7	Cu^{2+}	6.5	29.5
	7.3	Ni^{2+}	6.2	28.1

no preloaded Cu^{2+} was released from the sorbent. This indicates a stronger binding of Cu^{2+} on the bark than that of Ni^{2+} and Cd^{2+} .

4. Conclusions

Pine bark is a better sorbent for Cd^{2+} ion than pine cones or needles. Decreasing bark concentration and increasing Cd^{2+} ions concentration resulted in an increase in cadmium uptake per unit weight of bark. An increase in pH significantly increased the cadmium uptake per unit weight of bark over the range of pH 4.0–5.5. The uptake of cadmium ions was enhanced with decreasing pine bark particle sizes. The Freundlich model fits the equilibrium data reasonably well, and the $1/n$ values obtained indicated favorable adsorption. Bark can be re-utilized several times for further adsorption processes without regeneration. The desorption of Cd^{2+} was more efficient with HCl of higher molarity than of lower molarity. A complete release of Cd^{2+} ions could not be achieved at higher concentrations of this metal on the bark. Reuse of the bark after regeneration resulted in a decrease of the absolute value of the newly adsorbed Cd^{2+} ions compared to the fresh bark, but the total uptake increased. Magnesium and calcium are more efficient in suppressing Cd^{2+} uptake than sodium and potassium, particularly at higher concentrations of these hard ions. Bark is also able to sorb the following metals in the indicated order (mass basis): $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+}$, from their aqueous solutions. The sorption capacity for Ni^{2+} ions of bark preloaded with Cu^{2+} or Cd^{2+} is higher than that of fresh bark.

References

- [1] Sittig, M., Handbook of Toxic and Hazardous Chemicals, Noyes Publications, Park Ridge, NJ, 1981, pp. 119–120, 185–186.
- [2] Volesky, B., Biosorption of Heavy Metals, CRC Press, Boca Raton FL, 1992, pp. 13–14, 24.
- [3] M.J. Buchauer, Environ. Sci. Technol. 7 (1973) 131.
- [4] K.S. Low, C.K. Lee, Bioresour. Technol. 38 (1991) 1.
- [5] Patterson, J.W. and Minear, R.M., in: Krenkel, P.A. (Ed.), Heavy Metals in the Aquatic Environment, An International Conference, Pergamon Press, 1975, pp. 261–272.

- [6] M.A.F. Ferro-Garcia, J.R. Utrilla, J.R. Gordillo, I.B. Toledo, *Carbon* 26 (1988) 363.
- [7] P. Kumar, S.S. Dara, *Indian J. Environ. Health* 22 (1980) 196.
- [8] D.K. Singh, D.P. Tiwari, D.N. Saksena, *Indian J. Environ. Health* 35 (1993) 169.
- [9] A.K. Bhattacharya, C. Venkobachar, *J. Environ. Eng.* 110 (1984) 110.
- [10] W.E. Marshall, E.T. Champagne, W.J. Evans, *J. Environ. Sci. Health A28* (1993) 1977.
- [11] T. Viraraghavan, M.M. Dronamaraju, *J. Environ. Sci. Health A28* (1993) 1261.
- [12] M. Azab, P.J. Paterson, *Wat. Sci. Tech.* 21 (1989) 1705.
- [13] M. Friedman, A.C. Waiss, *Environ. Sci. Tech.* 6 (1972) 457.
- [14] N. Kuyucak, B. Volesky, *Biotechnol. Lett.* 2 (1988) 137.
- [15] R. Salim, M.M. Al-Subu, S. Qashoa, *J. Environ. Sci. Health A29* (1994) 2087.
- [16] C. Huang, M. Asce, F.B. Ostovic, *J. Environ. Eng. Div.* 104 (1978) 863.
- [17] T.W. Tee, R.M. Khan, *Environ. Tech. Lett.* 9 (1988) 1223.
- [18] W.J. Weber, A.M. Asce, J.C. Morris, *J. Sanit. Eng. Div., Proc. Am. Soc. Civil Eng.* 89 (1963) 31.
- [19] A.M. Deshkar, S.S. Bokade, S.S. Dara, *Wat. Res.* 24 (1990) 1011.
- [20] R. Salim, M.M. Al-Subu, E. Sahrhage, *J. Environ. Sci. Health A27* (1992) 603.
- [21] P. Van Cutsem, M.M. Metdagh, P.G. Rouxhet, C. Gillet, *React. Polym.* 2 (1984) 31.
- [22] I.N. Jha, L. Iyengar, A.V.S. Parabhakara Rao, *J. Environ. Eng.* 114 (1989) 962.
- [23] G. McKay, H.S. Blair, G.R. Garden, *J. Appl. Polym. Sci.* 27 (1982) 3043.
- [24] P.R. Norris, D.P. Kelly, *J. Gen. Microbiol.* 99 (1977) 317.
- [25] R.A.A. Muzzarelli, O. Tubertini, *Talanta* 16 (1969) 1571.
- [26] L. Thiem, D. Badorek, J.T. O'Connor, *J. Am. Wat. Wks Ass.* 8 (1976) 447.
- [27] T.C. Tan, C.K. Chia, C.K. Teo, *Wat. Res.* 19 (1985) 157.