Removal of heavy metal ions from solutions by coniferous barks

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Summary The abilities of 15 coniferous barks for removing toxic heavy metal ions were investigated. The barks considerably varied in the adsorption ability to each metal ion. Of the barks tested, high adsorption ability for heavy metal ions was found in *Picea abies* (Norway spruce). Equilibrium experiments using *P. jezoensis* (Yezo spruce) bark showed that the adsorption of Cd^{2+} was greatly affected by the pH of solution and the initial Cd^{2+} concentration in solution. The adsorption of Cd^{2+} by *P. jezoensis* bark followed Freundlich isotherm in the concentration range 10–330 mg Cd^{2+}/L. The continuous column experiments using *P. jezoensis* bark indicated that the packing had retained 10.1–14.2 mg Cd^{2+}/g adsorbent until the column broke through.

Introduction

In recent years, the removal of toxic heavy metal ions from waste water has been desired for prevention of possible hazards in our environment. Heavy metal ions can be removed from water by several methods, including basic precipitation, ion exchange, and so on. Basic precipitation is currently the most inexpensive method, but it introduces undesirable waste sludge in large quantities. Ion exchange is efficient in removing heavy metal ions from solution, but synthetic ion exchange resins are still expensive for this object.

It has been reported that certain lignocellulosic wastes such as nut wastes (Friedman *et al.* 1972; Waiss *et al.* 1973; Randall *et al.* 1975, 1978; Henderson *et al.* 1977), tree leaves (Kimura *et al.* 1986; Aoyama *et al.* 1991; Watanabe and Kishi 1991; Saito *et al.* 1992), barks (Masri *et al.* 1974; Randall *et al.* 1974; Henderson *et al.* 1977; Fujii *et al.* 1988; Aoyama *et al.* 1993) and barley straw (Larsenand and Schierup 1981) effectively adsorb heavy metal ions from aqueous solutions, indicating the potential utility of these materials to remove heavy metal ions from industrial effluents. Among these, barks are especially promising because of being available in large quantities from local sawmills.

In this paper, the adsorption abilities of coniferous barks for common toxic heavy metal ions were examined. The factors affecting removal of heavy metal ion from solution are also investigated using *Picea jezoensis* (Yezo spruce) bark.

Materials and methods

Materials
The barks of *Abies sachalinensis* (Japanese fir) and *Picea glehnii* (Saghalin spruce) were collected from Asahikawa district forest. The other bark samples were obtained from the experimental forest of Hokkaido Forestry Research Institute, Bibai. Each fresh bark was air-dried and ground in a Wiley mill to pass through a 1 mm screen. A fraction of the ground bark (42–80 mesh) was washed thoroughly with deionized water, dried overnight at 45 °C and used for adsorption experiments. Activated carbons were obtained from Wako Pure Chemical Industries, Ltd.

Extraction
Ground *P. jezoensis* bark (42–80 mesh) was extracted with cold-water, hot-water, 1% NaOH aqueous solution and ethanol-benzene (1 : 2, v/v) mixture, separately, using the Japanese Industrial Standard methods (JIS P8004-1959, JIS P8005-1959, JIS P8006-1959, JIS P8010-1961). The extracted residues were subsequently air-dried.

Equilibrium experiments
The abilities of coniferous barks to adsorb heavy metal ions were determined in batchwise conditions using 1 mM solutions of $Cd(NO_3)_2$, $Cu(NO_3)_2$ and $Zn(NO_3)_2$, separately. The pH of each solution was adjusted to the desired value with dilute HNO_3 or dilute NaOH solution. The test solution (100 mL) was added to the adsorbent (0.5 g), and the suspension was shaken at 30 °C for 24 h. The adsorbent was then filtered off and residual heavy metal ions in the filtrate were determined by the atomic absorption spectrometry with a Hitachi Z-6000 instrument. The amount of heavy metal ion captured by the adsorbent was calculated from the difference between the initial and final concentrations of the metal ion in solution. Experiments were duplicated and the results averaged.

Column experiments
Ground bark of *P. jezoensis* was soaked into water for 1 h and the resulting slurry poured into a glass column (15 × 250 mm) fitted with a porous plug and a stopcock. After the adsorbent had settled, a wad of glass wool was placed on the top of the bed, and the liquid level run down to the top of the bed. The bed was fed with 1000 mL of 1 mM $Cd(NO_3)_2$ solution which was adjusted to pH 5 with dilute nitric acid. Flow of the test solution through the column was controlled by the stopcock at the bottom of the column. The amount of Cd^{2+} in the column effluent was determined in the same manner described for the determination of heavy metal ions in the equilibrium experiments.

Results and discussion
The abilities of coniferous barks to adsorb heavy metal ions were determined in batchwise conditions using 1 mM solutions of $Cd(NO_3)_2$, $Cu(NO_3)_2$ and $Zn(NO_3)_2$, separately. The bark adsorbents were equilibrated by shaking with the solutions at 30 °C for 24 h, and the decrease in the concentration of metal ion was determined by the flame atomic absorption spectrometry. For comparison, commercial activated carbons (powder and granular) were also examined.

The amounts of heavy metal ions adsorbed by coniferous barks are summarized in Table 1. It is apparent that barks considerably varied in the adsorption

Table 1. Adsorption of Cd^{2+}, Cu^{2+}, and Zn^{2+} by various coniferous barks and commercial activated carbons

Species	Cd^{2+}		Cu^{2+}		Zn^{2+}	
	%	mg/g	%	mg/g	%	mg/g
Taxus cuspidata Sieb. et Zucc.	59.4	14.4	55.3	7.6	55.0	7.9
Abies sachalinensis Masters	28.1	6.7	31.5	4.4	26.0	3.6
Picea jezoensis Carr.	51.0	12.2	50.3	7.1	50.2	7.1
P. glehnii Masters	50.2	12.1	54.5	7.6	50.0	7.0
P. abies Karst.	63.1	15.8	68.9	9.6	56.8	8.2
Larix leptolepis Gordon	38.4	9.1	35.8	5.0	33.3	4.7
L. gmelinii var. *japonica* Pilg.	40.4	9.8	45.9	6.4	35.5	5.0
Pinus densiflora Sieb. et Zucc.	40.5	9.7	33.3	4.7	32.7	4.6
P. thunbergii Parlat.	29.7	7.2	44.8	6.3	35.2	5.0
P. strobus Linn.	38.3	9.4	41.6	5.8	26.9	3.9
Sciadopitys verticillata Sieb. et Zucc.	44.0	10.7	53.9	7.5	44.1	6.3
Cryptomeria japonica D. Don	49.8	12.1	46.7	6.5	46.9	6.6
Thujopsis dolabrata var. *hondae* Makino	57.5	13.9	40.7	5.6	42.6	5.9
Chamaecyparis obtusa Sieb. et Zucc.	47.8	11.6	34.4	4.8	41.1	5.8
C. pisifera Sieb. et Zucc.	47.3	11.6	36.3	5.0	43.5	6.1
Activated carbon (granular)	33.7	7.3	50.6	6.5	44.9	5.7
Activated carbon (powder)	30.2	7.1	45.5	5.8	18.9	2.5

ability to the metal ions. Of the conifer species tested, high adsorption ability for Cd^{2+} was found in *Taxus cuspidata* (Japanese yew), *Picea abies* (Norway spruce) and *Thujopsis dorabrata* var. *hondae* (common name: Hinokiasunaro), which captured 13 mg of Cd^{2+} and over per gram adsorbent. *P. abies* bark also removed Cu^{2+} and Zn^{2+} effectively. In addition, the adsorption abilities of some barks (*T. cuspidata, P. jezoensis and P. abies*) to Ag^+, Co^{2+}, Mn^{2+} and Ni^{2+} are listed in Table 2. These barks showed only slight affinity to Ag^+, but *T. cuspidata* and *P. abies* were efficient in capturing Co^{2+}, Mn^{2+} and Ni^{2+} from aqueous solutions. In general, the adsorption abilities of the barks for heavy metal ions compare

Table 2. Adsorption of Ag^+, Co^{2+}, Mn^{2+} and Ni^{2+} by coniferous barks and commercial activated carbons

Species	Ag^+		Co^{2+}		Mn^{2+}		Ni^{2+}	
	%	mg/g	%	mg/g	%	mg/g	%	mg/g
Taxus cuspidata Sieb. et Zucc.	22.5	5.6	47.3	6.2	47.2	5.6	47.7	6.1
Picea jezoensis Carr.	20.4	5.0	28.6	3.7	34.6	4.1	31.5	4.2
P. abies Karst.	23.1	5.7	44.5	5.4	42.8	5.3	53.7	7.7
Activated carbon (granular)	–	–	33.4	3.8	28.6	3.1	27.2	3.2
Activated carbon (powder)	–	–	22.4	2.8	11.7	1.3	21.3	2.6

Table 3. Adsorption of Cd^{2+}, Cu^{2+}, and Zn^{2+} by *Picea jezoensis* bark extracted with various solvents

Extraction	Extractives	Cd^{2+}		Cu^{2+}		Zn^{2+}	
	%	%	mg/g	%	mg/g	%	mg/g
Untreated	–	50.0	12.5	54.7	7.4	54.7	7.4
Cold-water	19.4	51.0	12.2	51.3	7.1	50.1	7.1
Hot-water	29.4	49.7	12.4	55.2	7.4	47.3	6.9
Ethanol-benzene (1 : 2, v/v)	9.8	54.6	13.8	56.9	7.7	51.2	7.6
1% NaOH aq. solution	48.7	18.3	4.5	8.8	1.2	15.1	2.2

favorably with those of commercial activated carbons, which are commonly used in waste water treatment.

Ground *P. jezoensis* bark (42–80 mesh) was extracted with hot water, 1% NaOH aqueous solution and ethanol-benzene (1 : 2, v/v) mixture to examine the effects of pre-extraction on heavy metal adsorption on the bark substrates. As shown in Table 3, the amounts of heavy metal ions adsorbed by the bark extracted with dilute alkaline solution markedly decreased. There are no significant differences in the adsorption ability for heavy metals between untreated bark and the bark treated with other solvents. Leaching of soluble organic matter from the bark inhibits its use in waste water treatment (Randall *et al.* 1974). Simple hot-water extraction of ground bark could reduce the undesirable problem.

To search for the appropriate conditions for the removal of heavy metal ion from solution, the factors affecting Cd^{2+} adsorption by bark were studied using *P. jezoensis* bark.

Figure 1 shows the effect of solution pH on the adsorption of Cd^{2+} by the adsorbent. Since Cd^{2+} forms hydroxide to yield insoluble precipitate above pH 8, the initial pH of the solution varied from 2 to 7. Maximum adsorption was obtained in the pH range from 4 to 7, and little adsorption occurred at pH 2.
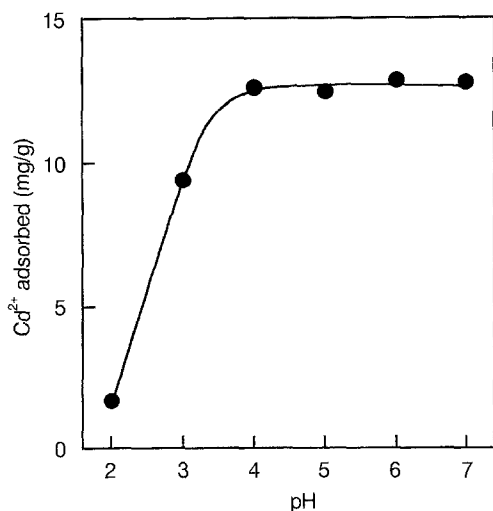

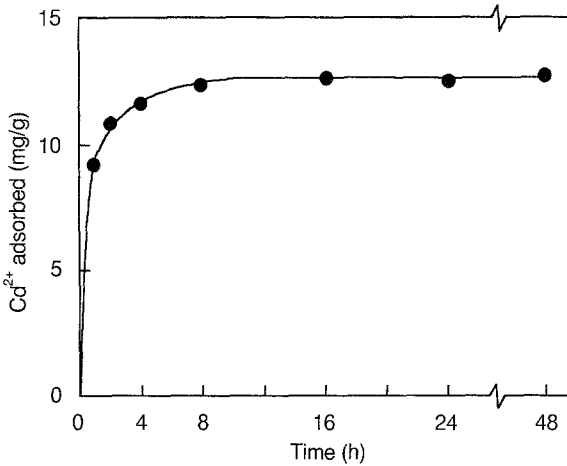**Fig. 1.** Effect of solution pH on Cd^{2+} adsorption by *Picea jezoensis* bark

Fig. 2. Time course of Cd^{2+} adsorption by P. jezoensis bark

As shown in Figure 2, the amounts of Cd^{2+} adsorbed by the adsorbent increased rapidly during the first 1 h, and then gradually increased and finally reached equilibrium in 8 h. Figure 3 shows that the amounts of Cd^{2+} adsorbed by the adsorbent increased with the increase of the initial concentration of Cd^{2+} in the solution, but the adsorbent was finally saturated by a constant amount of the ion. The capacity of P. jezoensis bark for Cd^{2+} was estimated to be about 24 mg/g. It is apparent from Figure 4 that the amounts of Cd^{2+} adsorbed by the adsorbent (mg/g) decreased with the increase of the amount of the adsorbent. On the other hand, the total amount of Cd^{2+} adsorbed by the adsorbent increased as the amounts of the adsorbent increased. Three grams of the adsorbent adsorbed Cd^{2+} almost quantitatively from 100 mL of 1 mM Cd(NO$_3$)$_2$ solution. These results indicate that the adsorption of heavy metal ion by bark depends largely upon the pH of solution and the initial concentration of heavy metal ion in the solution.

As shown in Fig. 5, a linear relationship exists between the saturated amount of Cd^{2+} adsorption and equilibrium Cd^{2+} concentration which were graphed logarithmically. The results turn out to be represented by isotherms according to Freudlich.
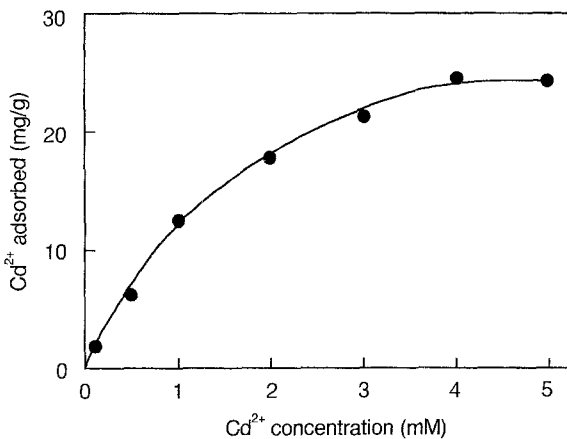

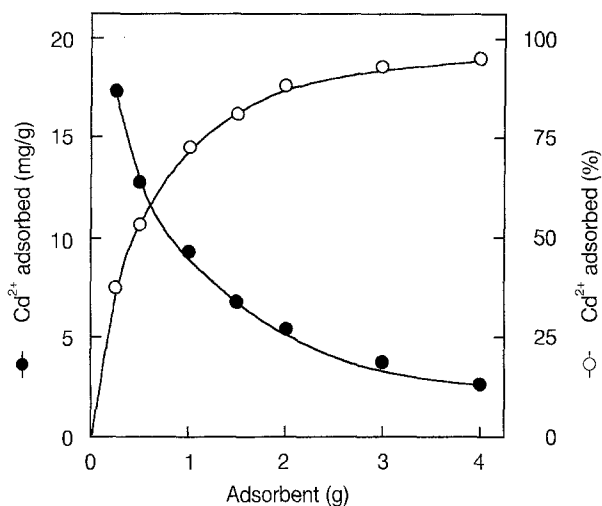Fig. 3. Effect of initial Cd^{2+} concentration on Cd^{2+} adsorption by P. jezoensis bark

Fig. 4. Effect of the amount of adsorbent (*P. jezoensis* bark) on Cd^{2+} adsorption

$$\log_{10} X = 0.73 \log_{10} C + 0.34 \tag{1}$$

This gives the Cd^{2+} adsorption, X (mg Cd^{2+}/g bark) for a given residual concentration, C (mg Cd^{2+}/L), within the range of C from 10 to 330.

A continuous adsorption on a packed bed is often more economically feasible than a batch process. In this study, 1000 mL of 1 mM $Cd(NO_3)_2$ solution was passed through a column packed with 6.3 g of washed *P. jezoensis* bark at different flow rates. The results are shown in Table 4.

In all runs, the steady state concentrations of Cd^{2+} in the effluents were less than 0.1 mg Cd^{2+}/L. Before the column broke through, the packing had retained 10.1–14.2 mg Cd^{2+}/g adsorbent. At steady state conditions, the effluent pH was almost constant at 4.0, although it was slightly higher than that of the feed solution. The pH-decrease might be due to the buffer action of the adsorbent. In a continuous process using a packed bed, the flow rate of feed solution is an important factor for practical operation. The flow rates used in this study varied
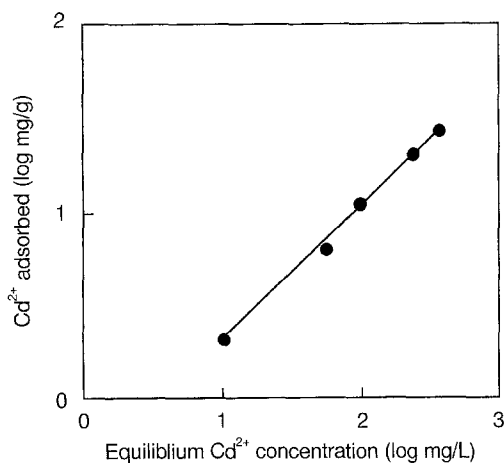

Fig. 5. Adsorption isotherm for adsorption of Cd^{2+} by *P. jezoensis* bark

Table 4. Removal of Cd^{2+} from $Cd(NO_3)_2$ solution by a packed bed

Feed concentration (mg Cd^{2+}/L)	112.1	112.1	112.1	112.1
Flow rate (ml/min)	5	20	33	50
(bed vol/h)	7.5	30	50	75
Total feed (mg Cd^{2+}/g)	22.4	22.4	22.4	22.4
Cd^{2+} adsorbed at steady state (mg Cd^{2+}/g)	13.5	11.2	10.1	9.0
Steady state Cd^{2+} concentration in effluent (mg Cd^{2+}/L)	<0.1	<0.1	<0.1	<0.1
pH effluent at steady state	4.0	4.0	4.0	4.0
Final effluent Cd^{2+} concentration (mg Cd^{2+}/L)	85.0	89.6	92.8	93.0
Total Cd^{2+} adsorbed (mg Cd^{2+}/g)	14.2	12.0	11.0	10.1

packing was 5.0g of *Picea jezoensis* bark

from 5 to 50 mL/min (7.5 to 75 bed vol/h). These values are greater than those used by Randall *et al.* (1974, 1976) and large enough for practical use.

Conclusions
Several coniferous barks effectively remove common heavy metal ions from aqueous solutions. Continuous column processes using *P. jezoensis* bark show that the packing markedly reduces Cd^{2+} concentration of the effluents and can retain 10.1–14.2 mg Cd^{2+}/g adsorbent. The coniferous bark, which is inexpensive and locally available, shows the potential utility to remove heavy metal ions from waste waters and could be applied to a pollution control system.

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