J Wood Sci (1999) 45:266–270

NOTE

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Adsorption by coniferous leaves of chromium ions from effluent

Received: April 7, 1998 / Accepted: October 27, 1998

Abstract The chromium adsorption ability of leaves from 34 conifer species were examined. Among them, deciduous conifer species, such as *Larix*, *Ginkgo*, *Metasequia*, and *Taxodium*, showed high ability to adsorb chromium ions. Factors affecting chromium adsorption were studied using larch (*Larix leptolepis*) leaves to determine the optimum adsorption conditions. The factors included solution pH, contact time, temperature, and the initial concentration of chromium ions. Maximum adsorption for Cr^{3+} was observed at pH 5, and maximum Cr^{6+} adsorption occurred at pH 3. The amount of Cr^{6+} adsorbed on the adsorbent increased rapidly during the first 4h, then gradually increased, and finally reached equilibrium in 16h. The adsorption rate of Cr^{3+} was somewhat slower than that of Cr^{6+}. The adsorption isotherm for Cr^{6+} adsorption was composed of two straight lines, suggesting that the adsorbent could not practically reduce the concentration of Cr^{6+} in solution below 1.6mgCr/l. Column experiments using larch leaf packing suggested that the practical operation could be controlled by monitoring the effluent pH.

Key words Heavy metal ion · Chromium ion · Adsorption · Coniferous leaves · *Larix leptolepis*

Introduction

Chromium is often found in industrial wastewaters, the largest chromium pollution sources being metal finishing, electroplating, leather tanning, and textile industries. Of the various methods proposed to remove chromium, (1) reduction and precipitation and (2) ion exchange are most commonly used. The former method is reliable but requires large settling tanks for the precipitation of voluminous chromium hydroxides and subsequent sludge treatment. Ion exchange has the advantage of recovering hexavalent chromium, but it is more expensive and sophisticated. The removal of chromium ions by activated carbon has been developed into promising alternatives.[1–4]

It has also been reported that certain agricultural wastes,[5–7] tree barks,[7–15] and tree leaves[16–18] effectively adsorb heavy metal ions from aqueous systems. Their active sites for heavy metal binding are believed to be sulfhydryl and amino groups and *o*-quinone and vicinal phenolic hydroxyl groups.

Tree leaves are inexpensive and available in great quantity. They contain various components such as polyphenolics, plant pigments, and protein, which would provide active sites for heavy metal binding. This study was performed to determine the efficiency of coniferous leaves for removing chromium pollutants in waste copper-chromium-arsenic (CCA) solution. The factors affecting removal of chromium ions also were examined using Japanese larch (*Larix leptolepis*) leaves.

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Materials and methods

Materials

Coniferous leaves were collected from the Experimental Forest, Chungbuk National University, Cheongju, Korea; Tohma District Forest, Asahikawa, Japan; Hokkaido Forest Research Institute, Bibai, Japan; and the Institute of Wood Technology, Akita Prefectural College of Agriculture, Noshiro, Japan. The ground leaves (42–80 mesh) and activated carbon (Wako Pure Chemical Industries, Osaka, Japan) were washed thoroughly with deionized water and dried overnight in an oven for the experiment.

Batchwise adsorption for screening

The chromium solution was potassium dichromate or chromium nitrate with 10 mg Cr/l. The potassium dichromate solution was adjusted to pH 3 with diluted HNO_3 and NaOH solutions, whereas the chromium nitrate solution was adjusted to pH 5. The test solution (50 ml) was added to the adsorbent (0.1 g), and the suspension was shaken at 30°C for 24 h. The residual chromium ions in the filtrate were determined by atomic absorption spectrometry with a Hitachi Z-6000. Experiments were duplicated and the results averaged.

Equilibrium experiments

Chromium was supplied as potassium dichromate, a commercial copper-chromium-arsenic formulation (CCA type C), or chromium nitrate. The solutions were adjusted to the desired pH. The amounts of chromium, copper, and arsenic adsorbed on the adsorbent were determined with the same method as for chromium in the screening experiments.

Column experiments

Ground larch leaves were soaked in water and degassed under vacuum for 1 h. The resulting slurry was poured into a plastic column (i.d. 13 × 100 mm). After the adsorbent had settled and the liquids run down to the top of the bed, the bed was fed 800 ml potassium dichromate solution, or CCA solution, which was adjusted to a chromium concentration of 25 mg/l and pH 3. The amounts of chromium, copper, and arsenic in the effluents were determined with the same method as for chromium in the screening experiments.

Results and discussion

The ability of coniferous leaves to adsorb chromium ions was determined in batchwise conditions using chromium nitrate or potassium dichromate aqueous solution containing 10 mg Cr/l. The amounts of chromium ions adsorbed by the adsorbents are listed in Table 1. The coniferous leaves varied considerably in terms of their adsorption ability to chromium ions. Of 34 conifer species tested, a relatively high adsorption ability for Cr^{6+} was found in the deciduous species, such as *Ginkgo*, *Larix*, *Metasequia*, and *Taxodium* spp. The adsorption abilities of these leaves for Cr^{6+} (4.72–5.12 mg Cr/g adsorbent) compare favorably with that of commercial activated carbon (4.19 mg Cr/g), which is commonly used in wastewater treatment. Coniferous leaves generally showed higher affinity for Cr^{3+} in weak acidic solution than activated carbon. In particular, deciduous conifer species, *Cephalotaxus* spp., and the juniper (*Juniperus*) family effectively adsorbed Cr^{3+} from dilute chromium nitrate solution.

Table 1. Adsorption of chromium ions by coniferous leaves and commercial activated carbon

Adsorbent	Cr^{6+} Adsorption[a]		Cr^{3+} Adsorption[b]	
	mg/g	%	mg/g	%
Ginkgo biloba	4.94	92.8	5.06	92.8
Taxus cuspidata	3.75	69.4	4.09	78.0
Cephlotaxus harringtonia var. *nana*	3.59	70.6	4.87	90.8
C. koreana	2.49	45.8	5.09	93.4
Abies holophylla	2.87	54.2	3.16	61.4
A. sachalinensis	3.24	61.4	2.56	47.6
Picea abies	2.82	54.6	2.48	45.2
P. glehnii	2.84	52.8	2.21	42.6
P. jezoensis	3.31	63.8	2.65	50.2
Larix dahurica var. *japonica*	4.72	87.2	3.36	63.6
L. leptolepis	5.12	96.6	3.92	71.4
Pinus bungeana	3.99	75.4	3.42	65.0
P. densiflora	4.24	84.8	3.74	71.2
P. koraiensis	4.64	87.4	3.84	72.2
P. parviflora	4.83	89.0	3.07	58.2
P. parviflora var. *pentaphylla*	4.59	85.2	3.31	63.2
P. rigida	4.46	80.6	3.59	66.6
P. strobus	4.81	89.0	4.27	77.4
P. thunbergii	3.99	77.0	2.63	52.2
Cryptomeria japonica	4.15	77.6	4.18	82.4
Metasequoia glyptostroboides	4.78	90.2	5.27	95.0
Taxodium distichim	5.05	91.8	5.22	93.6
Thuja occidentalis	3.05	58.8	3.90	73.2
T. orientalis	3.86	71.2	4.20	77.0
Thujopsis dolabrata var. *hondae*	4.34	83.2	4.22	77.2
Chamaecyparis obtusa	4.24	82.8	4.59	86.2
C. pisifera	4.33	80.2	4.12	77.8
Juniperus chinensis	3.10	56.8	4.69	87.6
J. chinensis var. *globosa*	3.50	67.2	4.42	84.2
J. chinensis var. *horizontalis*	2.74	51.4	4.43	84.6
J. chinensis var. *kaizuka*	3.14	58.0	4.52	84.6
J. chinensis var. *sargentii*	3.92	73.0	4.65	84.6
J. rigida	2.84	53.2	3.73	71.4
J. virginiana	3.42	66.2	4.92	89/2
Commercial activated carbon	4.19	85.5	1.86	40.4

[a]The adsorbent (0.1 g) was shaken with 50 ml potassium dichromate solution (pH 3) containing 10 mg Cr/ml at 30°C for 24 h
[b]The adsorbent (0.1 g) was shaken with 50 ml chromium dichromate solution (pH 5) containing 10 mg Cr/ml at 30°C for 24 h

To determine optimum adsorption conditions, factors affecting chromium adsorption were studied using larch (*L. leptolepis*) leaves. As shown in Fig. 1, maximum adsorption was obtained at pH 3 for Cr^{6+}, whereas that of Cr^{3+} was recorded at pH 5.4. The initial pH of the Cr^{3+} solution varied from 2 to 5, as Cr^{3+} forms hydroxides to yield insoluble precipitates above pH 5.5. Although the amount of Cr^{3+} adsorbed by the adsorbent increased continuously with increasing pH, that of Cr^{6+} declined rapidly with a further increase in the pH of the solution.

As shown in Fig. 2, the amount of Cr^{6+} adsorbed on the adsorbent increased rapidly during the first few hours (81% retention at 4 h), reaching equilibrium (92% retention) at 16 h. The amount of Cr^{3+} adsorbed on the adsorbent

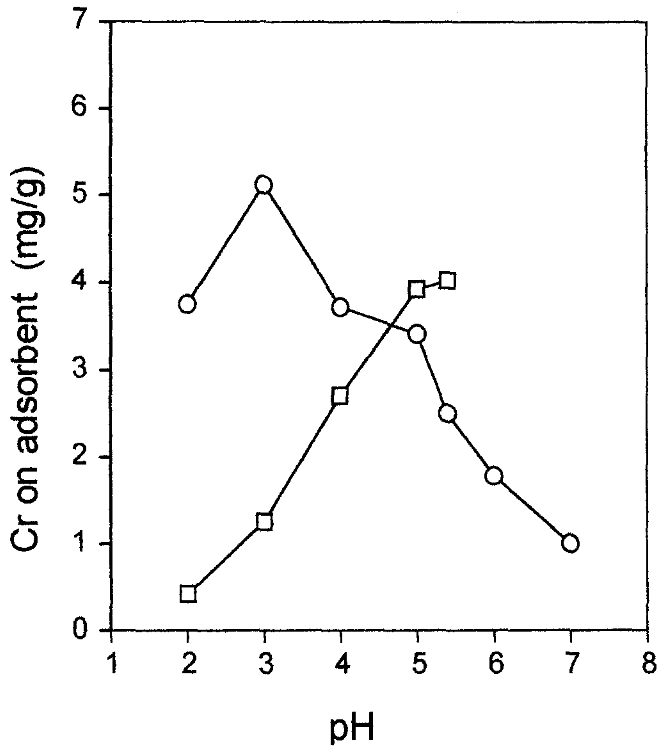

Fig. 1. Effect of pH on Cr adsorption by larch leaves. *Circles*, Cr^{6+}; *squares*, Cr^{3+}

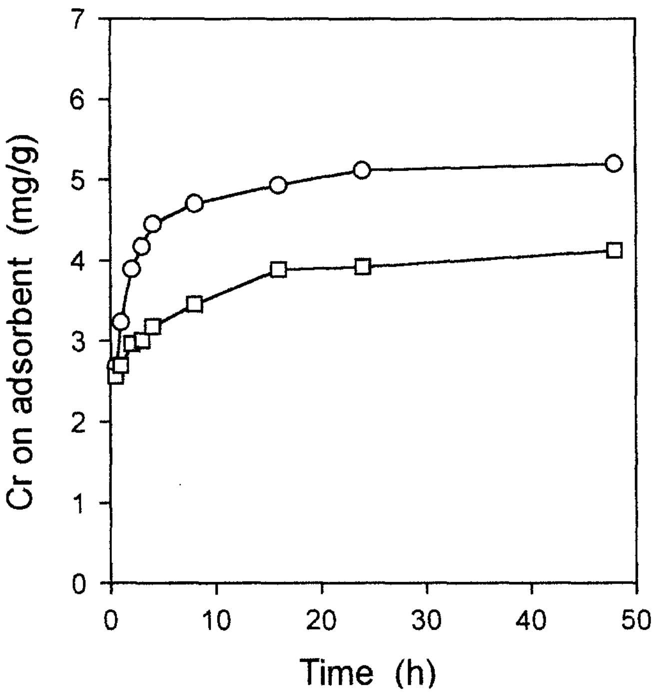

Fig. 2. Time course of Cr adsorption by larch leaves. *Circles*, Cr^{6+} (pH 3); *squares*, Cr^{3+} (pH 5)

Table 2. Fruendlich parameters* of Cr^{3+}

Temperature	30°C
pH	5.0
K	3.040
1/m	0.239

*$\log x/m = (1/n)\log c + \log k$, where x is the amount of adsorbate (mg); *m* is the amount of adsorbent (g); c is the equilibrium concentration (mg/l); and *k* and $1/n$ is a constant

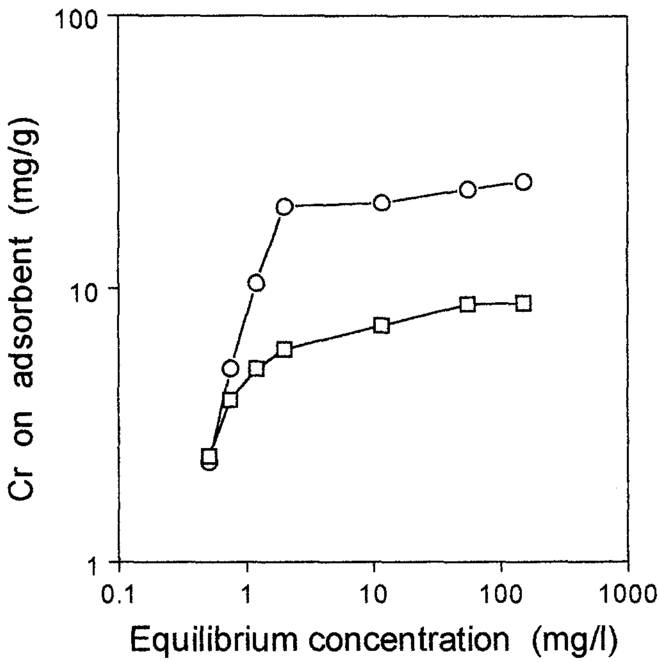

Fig. 3. Adsorption isotherm for Cr by larch leaves. *Circles*, Cr^{6+} (pH 3); *squares*, Cr^{3+} (pH 5)

increased rather gradually and reached equilibrium after 24 h.

The amount of Cr^{6+} adsorbed varied with the reaction temperature, which ranged from 10°C to 40°C. A 6%–10% increase in adsorption capacity was recognized at higher temperatures, indicating that parts of the Cr^{+6} complex in aqueous solution react with the surface complexes of the adsorbents. In regard to the adsorption isotherms for chromium ions, a linear relation exists between the saturated amount of chromium adsorbed and the equilibrium chromium concentration, which are recorded logarithmically in Fig. 3. The result is represented by an empirical isotherm[3] according to Freundlich (Table 2). As shown in Fig. 3, the adsorption isotherm for adsorption of Cr^{6+} was composed of two straight lines, suggesting that the adsorbent could not practically reduce the concentration of Cr^{6+} in solution below 1.6 mg Cr/l.

In actual operation, continuous adsorption on a packed bed is often more economically feasible than a batch process. In this study, potassium dichromate solution or a dilute CCA solution, which was adjusted to a chromium concentration of 25 mg Cr/l and to pH 3, was passed through a column packed with washed ground larch leaves at two flow rates: 30 ml/h [space velocity (SV) 5] and 60 ml/h (SV 10).

The high effluent pH values (around pH 5) during the initial stage of adsorption, as shown in Fig. 4, were probably

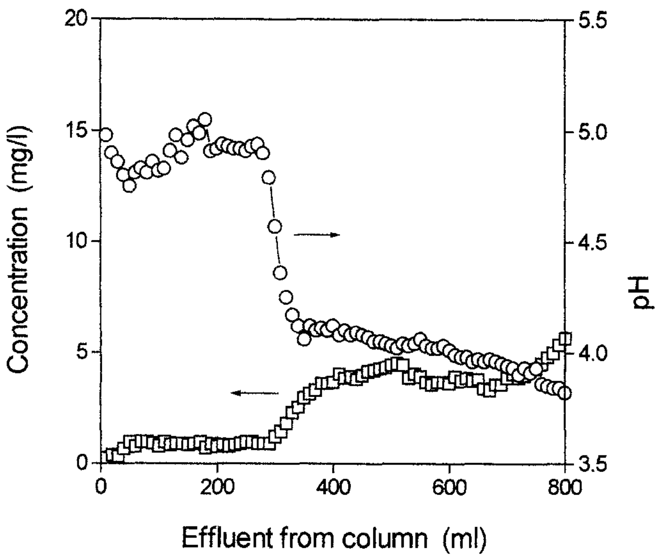

Fig. 4. Elution profile for potassium dichromate solution from a column packed with larch leaves. Initial concentration Cr 25 mg/l; flow rate 30 ml/h

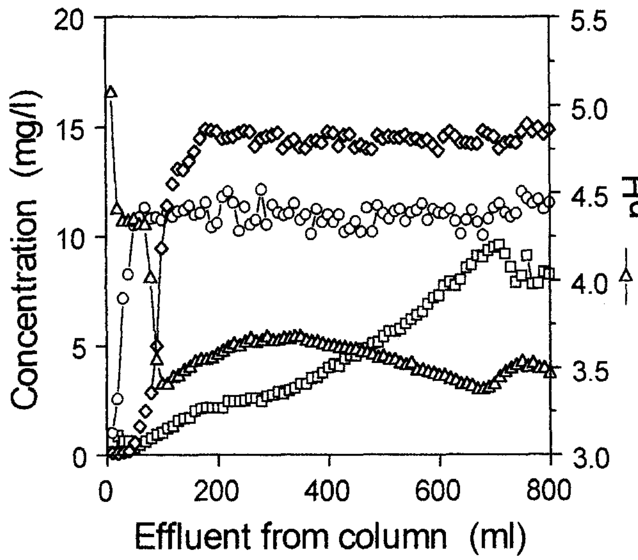

Fig. 5. Elution profile for commercial chromium-copper-arsenic (CCA) (Tanalith-C) solution from a column packed with larch leaves. Initial concentration Cr 25 mg/l, Cu 15 mg/l, As 12 mg/l; flow rate 30 ml/h. *Squares*, Cr; *circles*, As; *diamonds*, Cu

due to both the chemical reduction and physico-chemical adsorption of Cr^{6+}. At the 300-ml elution, a significant decrease in pH was observed. This pH decrease occurred concomitantly with lowered removal efficiency of Cr^{6+}. The actual run could therefore be easily controlled by monitoring the effluent pH. The slow flow rate (30 ml/h) resulted in better chromium removal than the fast one.

A commercial CCA-C formulation was used as a contaminated effluent in this study. As shown in Fig. 5, Cr^{6+} in CCA solution was effectively removed by larch leaves packing, compared to removal of cupric and arsenic ions. Furthermore, the elution profile of the CCA solution showed different adsorption behavior for Cr^{6+} than that of pure potassium dichromate solution. At the initial adsorption stage, the effluent pH increased more than 5 points. This pH increase might be due to the chemical reduction of Cr^{6+}. Although relatively good chromium removal was attained during the elution of the first 100 ml, a significant decrease in the effluent pH was observed. The decreased pH suggested that the column had begun to overload. In conclusion, deciduous conifer leaves are an excellent substrate for removing toxic hexavalent chromium ions from dilute aqueous solution. The informations obtained from the present study are the preliminary data required for further studying the physico-chemical adsorption of chromium on coniferous leaves and the chemical reduction of hexavalent chromium.

Conclusions

This study was performed to investigate the efficiency of coniferous leaves for removing chrome pollutants such as waste CCA solution. The factors affecting removal of chromium ions also were examined using Japanese larch (*Larix leptolepis*) leaves.

Among 34 conifer species, deciduous conifer species (e.g., *Larix*, *Ginkgo*, *Metasequia*, *Taxodium*) showed high ability to adsorb chromium ions. Maximum adsorption of Cr^{3+} was observed at pH 5, and maximum Cr^{6+} adsorption was obtained at pH 3. The amount of Cr^{6+} adsorbed on the adsorbent increased rapidly during the first 4 h, gradually increased, and finally reached equilibrium in 16 h. For Cr^{3+} the adsorption rate was somewhat slower. A linear relation was observed between the amount of Cr^{3+} adsorbed and the equilibrium concentration of Cr^{3+} in solution and was graphed logarithmically. On the other hand, the adsorption isotherm for Cr^{6+} adsorption was composed of two straight lines, suggesting that the adsorbent could not practically reduce the concentration of Cr^{6+} in solution below 1.6 mg Cr/l. Column experiments using larch leaf packing suggested that a practical operation could be controlled by monitoring the effluent pH. Deciduous conifer leaves are thus an excellent substrate for removing toxic hexavalent chromium ions from dilute aqueous solution.

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