Available online at www.sciencedirect.com

ScienceDirect

Bioresource Technology 98 (2007) 588–594

BIORESOURCE TECHNOLOGY

Adsorption mechanism of cadmium on juniper bark and wood ☆

Eun Woo Shin [a], K.G. Karthikeyan [b,*], Mandla A. Tshabalala [c]

[a] *School of Chemical Engineering and Bioengineering, University of Ulsan, San 29, Mugeo-dong, Nam-gu, Ulsan 680-749, South Korea*
[b] *Department of Biological Systems Engineering, University of Wisconsin – Madison, 460 Henry Mall, Madison, WI 53706, USA*
[c] *US Department of Agriculture, Forest Service, Forest Products Laboratory, One Gifford Pinchot Drive, Madison, WI 53705, USA*

Received 2 March 2005; received in revised form 9 January 2006; accepted 5 February 2006
Available online 30 March 2006

Abstract

In this study the capacity of sorbents prepared from juniper wood (JW) and bark (JB) to adsorb cadmium (Cd) from aqueous solutions at different pH values was compared. Adsorption behavior was characterized through adsorption kinetics, adsorption isotherms, and adsorption edge experiments. Results from kinetics and isotherm experiments showed that JB (76.3–91.6 μmol Cd g^{-1} substrate) had 3–4 times higher adsorption capacity for Cd than JW (24.8–28.3 μmol Cd g^{-1}). In addition to higher capacity, JB exhibited a higher strength of adsorption (45.3 versus 9.1 L $mmol^{-1}$) and faster uptake kinetics (0.0119 versus 0.0083 g μmol^{-1} min^{-1}) compared to JW. For both these adsorbents, increasing Cd adsorption with increasing solution pH in the range of 2–6 suggests that surface carboxyl groups (RCOOH) might be involved in interaction with Cd. Diffuse reflectance infrared Fourier transform (DRIFT) spectra showed that the surface concentration of carboxyl groups was higher on JB compared to JW. The ratio of Ca released to Cd adsorbed was 1.04 and 0.78 for JB and JW, respectively, indicating that Ca–Cd ion-exchange was the primary mechanism involved. The higher Ca content in JB (15 times more) and the surface RCOOH concentration (2.5 times more) can be attributed to the observed differences in Cd adsorption behavior between the two lignocellulosic adsorbents.

Keywords: Bark; Wood; Lignocellulosic sorbents; Cadmium; Calcium; Adsorption; Ion-exchange

1. Introduction

Cadmium (Cd) is one of the heavy metals considered to be toxic to humans and aquatic life. Over the last two decades there has been a sharp rise in the global use of Cd for batteries and a steady decline in its use for other applications, such as pigments, polyvinyl chloride stabilizers, and plating. This trend in the use of Cd products and compounds has inspired a number of international agreements to manage and control the release of Cd to the environment and limit human and environmental exposure (COWI, 2003). Chronic exposure to Cd can cause kidney damage in mammals and humans (Wase and Forster, 1997; Gaballah and Kibertus, 1998; Romero-Gonzalez et al., 2001). One of the major sources of surface water contamination by heavy metals, such as Cd, is urban and agricultural stormwater runoff. There is a great need for new and cost-effective processes for preventing excess concentrations of toxins from accumulating in streams, ponds, and lakes.

Various processes, including chemical precipitation and reverse osmosis, have been developed for removing heavy metal such as Cd from wastewater (Gaballah and Kibertus, 1998). However, when applied to non-point sources of Cd contamination such as stormwater runoff, these processes

---

☆ The Forest Products Laboratory is maintained in cooperation with the University of Wisconsin. This article was written and prepared by US Government employees on official time, and it is therefore in the public domain and not subject to copyright. The use of trade or firm names in this publication is for reader information and does not imply endorsement by the US Department of Agriculture of any product or service.

* Corresponding author. Tel.: +1 608 262 9367; fax: +1 608 262 1228.
E-mail address: kkarthikeyan@wisc.edu (K.G. Karthikeyan).

0960-8524/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biortech.2006.02.024

can be expensive to implement. Consequently, interest is growing in the use of sorbents made from low-cost renewable materials, such as solid wood waste or bark.

Several natural adsorbents, including algal biomass (Matheickal et al., 1999; Yang and Volesky, 1999; Figueira et al., 2000; Romero-Gonzalez et al., 2001; Davis et al., 2003), peat moss (Crist et al., 1996, 1999), bark (Randall et al., 1974; Seki et al., 1997; Gaballah and Kibertus, 1998; Al-Asheh et al., 2000), and sugar beet pulp (Reddad et al., 2002), have been investigated for their ability to sequester Cd from water. Adsorption of Cd from aqueous solutions can take place via two mechanisms, ion exchange and complexation. In the ion-exchange mechanism, Cd binds to anionic sites by displacing protons from acidic groups or existing alkali or alkali earth metals (e.g., sodium (Na) or calcium (Ca)) from anionic sites at high pH (Crist et al., 1996, 1999; Romero-Gonzalez et al., 2001). This mechanism explains the release of light metal ions during heavy metal uptake experiments. In the complexation mechanism, Cd sequestration is viewed as the coordination of Cd to surface functional groups. Cadmium adsorption is considered a complex formation where Cd is designated as the central atom and surrounding groups as the ligand(s) (Davis et al., 2003). However, in both cases, the extent of Cd adsorption from aqueous solutions is strongly influenced by the chemistry and surface morphology of the sorbent. For example, Gaballah and Kibertus (1998) suggested that uptake of copper (Cu) by wood takes place by several mechanisms: reaction between Cu^{II} species and surface carboxyl groups (RCOOH); hydrogen bonding of hydrated $Cu(H_2O)_6^{2+}$ ions with cellulose; and formation of complexes with surface hydroxyl groups of lignin.

Recently, Min et al. (2004) reported on the use of juniper fiber for removing Cd from aqueous solution. The juniper fiber consisted of a mixture of wood and bark. They observed that base treatment of the juniper fiber increased Cd adsorption capacity and that adsorption of Cd was greater for bark compared to wood. However, there was no explanation as to why bark performed better than wood. These researchers focused on improving the sorption capacity by base hydrolysis of surface carboxylate functional groups (RCOOR′).

In the current study, we prepared separate sorbents from juniper wood and bark and investigated their adsorption behavior towards Cd in aqueous solutions of different pH values. An attempt was made to correlate adsorption behavior with the surface chemistry of each type of adsorbent. Adsorption behavior was characterized through Cd adsorption kinetics, adsorption isotherms, and adsorption edge experiments. Calcium and Na displacement were monitored simultaneously during adsorption experiments. Surface chemical composition of the adsorbents was characterized by diffuse reflectance infrared Fourier transform spectrometry (DRIFT). Elemental analysis of wood and bark was performed by inductively coupled plasma atomic emission spectroscopy (ICP–AES).

2. Experimental

2.1. Materials and characterization

Juniper (*Juniperus monosperma*) logs were randomly collected from New Mexico and shredded into small chips at the USDA Forest Products Laboratory (FPL) in Madison, WI. Bark was separated from wood chips, and each material was then ground to pass through a 3-mm screen using a Wiley mill. Juniper wood and bark will be denoted as JW and JB, respectively. Carbohydrate composition of JB and JW was determined using the experimental methods specified in Davis (1998).

Elemental analysis for Cd, Ca, and Na was conducted by ICP–AES (ULTIMA, Jobin Yvon Inc., Edison, NJ) at the USDA FPL. DRIFT spectra were acquired using a Mattson Galaxy 5020 (Mattson Instruments, Madison, WI) equipped with a Harrick Scientific (Ossining, NY) diffuse reflectance accessory. Each infrared (IR) spectrum is the average of 4000 scans between 400 and 4000 cm^{-1} (resolution = 4 cm^{-1}). Prior to analysis, samples were finely ground using a Wiley mill and sieved with a 0.18-mm screen. For comparison, each spectrum was baseline corrected at 400, 840, 2000, and 4000 cm^{-1} and normalized against the 1320-cm^{-1} band associated with the C–H bending mode (Yang et al., 1996). Zeta potential of the adsorbents was measured with a ZETASIZER 3000HS (ATA Scientific Ltd., Lucas Heights, Australia); 25-mg of sample was suspended in 40 mL of deionized water and solution pH was adjusted to be between 2 and 10 using either 0.1 M KOH or 0.1 M HNO_3. After pH adjustment, the suspensions were equilibrated in a shaker for 4 h and the zeta potential was measured.

2.2. Adsorption tests

All adsorption tests, namely, isotherms, kinetics, and pH-edge, were performed as batch experiments in duplicates. Isotherms are typically generated either with a fixed sorbent (JB or JW) mass and varying initial Cd concentrations (C_0) or with varying sorbent mass and a fixed C_0 level. The latter approach was used in this study. At least seven different samples weighing between 0.041 and 0.814 g (JB: 0.041, 0.099, 0.158, 0.238, 0.325, 0.420, 0.561, and 0.737 g; JW: 0.057, 0.107, 0.270, 0.361, 0.487, 0.611, and 0.814 g) were placed in 40-mL plastic tubes with 35 mL of Cd cation solution ($C_0 = 0.26$ mmol L^{-1}). The initial Cd solution was prepared by serial dilution of standard 1000 mg L^{-1} reference solution (Fisher Scientific, Pittsburgh, PA). Initial pH of the solution was adjusted to pH 5.6 ± 0.1. The sealed bottles were placed in a shaker for 4 h at 298 K. The suspension pH was not adjusted during the experiments and the final pH for sorption isotherms for JW and JB were 4.8 ± 0.1 and 5.3 ± 0.1, respectively. After equilibration, the supernatant was filtered through a 0.45 μm pore size MF-Millipore mixed cellulose ester (Millipore, Billerica, MA) membrane filter and then analyzed for dissolved Cd concentration by ICP–AES. The final concentration (C_e) differed with varying amounts of adsorbent in solution. The uptake capacity (q_e, amount of Cd adsorbed at equilibrium in μmol g^{-1}) was calculated by mass balance between C_0 and C_e.

Adsorption kinetic experiments were performed in 1-L solutions with 1.0 g of sample at pH 5.0 ± 0.1. Initial Cd concentration of the solution was 0.17 mmol L^{-1} and solution pH was maintained by using 0.1 M HNO_3 and 0.1 M KOH. The suspension was stirred by a magnetic bar and supernatant was collected at various time intervals during the 2-h experiment. The sampling times for the experiment with JB were 0, 4, 8, 12, 17, and 31 min while those with JW were 0, 3, 8, 14, 22, and 29 min. The slight difference in the sampling times was observed not to affect the overall results from the kinetics experiment. Cadmium concentration in the filtrate was determined by ICP–AES.

Data from the kinetics experiment were fitted to the pseudo second order rate equation (Ho and McKay, 2000) to determine Cd sorption capacity (q_e) and rate constant (k). This model assumes that adsorption follows the Langmuir equation. The kinetic rate equations can be written as follows:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k(q_e - q_t)^2 \qquad (1)\leftarrow$$

where q_t, and q_e are the amounts of Cd adsorbed at time t, and at equilibrium (μmol g^{-1}), respectively, and k is the equilibrium rate constant for second order sorption (g μmol^{-1} min^{-1}). By integrating Eq. (1) for the boundary conditions ($t = 0$ to $t = t$; $q_t = 0$ to $q_t = q_t$) the following linearized form can be obtained:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \qquad (2)\leftarrow$$

A plot of t versus t/q_t was used to determine values of k and q_e.

Adsorption edge (pH effect) experiments were conducted in 40-mL sample tubes containing 30 mg of JB or JW and 30 mL of 0.17 mmol L^{-1} Cd solution at different pH values. The sample tubes were placed in a shaker for 4 h; pH and final Cd concentration in the filtrate were determined after equilibration.

2.3. Data analysis and representation

The ability of linearized form of pseudo second-order kinetic model (Eq. (2)) and the Langmuir equation (Eq. (3)) to describe the experimental data (adsorption kinetics and adsorptions isotherms, respectively) was analyzed using Microsoft® Excel 2002 software. The corresponding sorption constants and coefficient of determination (r^2) were determined from the fit of the above model equations to the experimental data. All sorption tests were performed in duplicates and error bars in Figs. 1–4 and 6 correspond to ±1 standard deviation values.

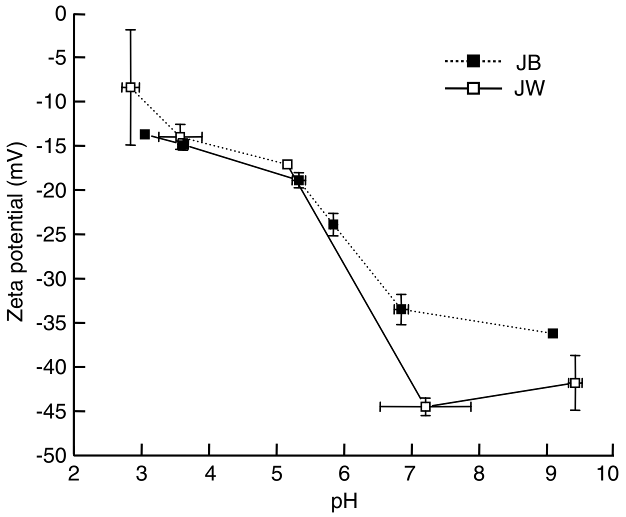

Fig. 1. Surface charge characteristics of juniper bark (JB) and juniper wood (JW). Error bars (±1 standard deviation from duplicate measurements) if not shown are within the symbols.

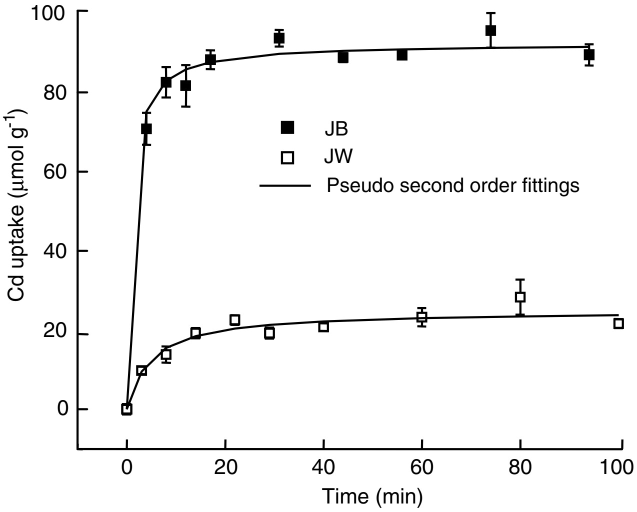

Fig. 2. Cadmium adsorption kinetics for juniper bark (JB) and juniper wood (JW) (initial Cd concentration = 0.17 mmol L^{-1}; pH = 5.0 ± 0.1). Error bars (±1 standard deviation from duplicate measurements) if not shown are within the symbols.

3. Results and discussion

3.1. Chemical composition and elemental analysis

The chemical composition of JB and JW is shown in Table 1 and is comparable to that previously reported by Min et al. (2004). Both JB and JW had similar lignin content, but different amounts of carbohydrate (39.9% and 51.1% of total weight for JB and JW, respectively). Since the Na content in both JB and JW (32.7 and 17.4 μmol g^{-1}, respectively) was much lower than the Ca content (945 and 61.6 μmol g^{-1}), it is likely that Ca might play a more significant role in Cd sorption from aqueous solution. These alkali and alkali earth metals are believed to constitute

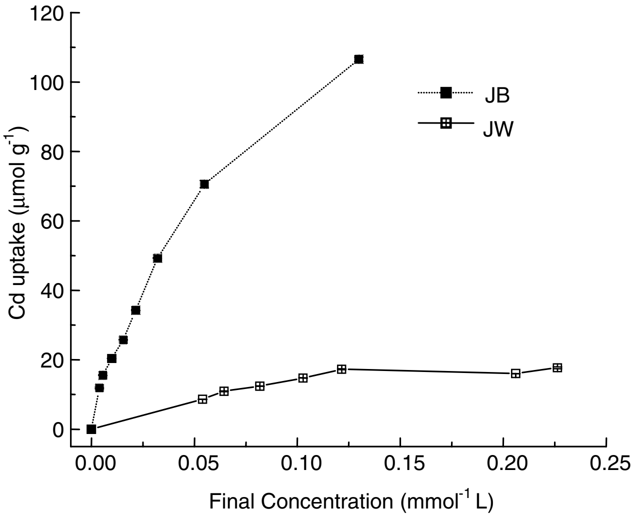

Fig. 3. Cadmium adsorption isotherms for juniper bark (JB) and juniper wood (JW) (initial Cd concentration = 0.26 mmol L^{-1}; final pH 5.3 ± 0.1 and 4.8 ± 0.1 for JB and JW, respectively). Error bars (±1 standard deviation from duplicate measurements) if not shown are within the symbols.

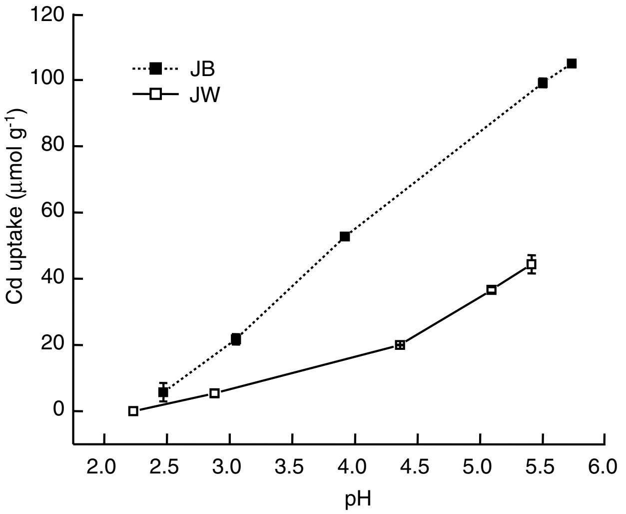

Fig. 4. Dependence of Cd uptake on juniper bark (JB) and juniper wood (JW) as a function of solution pH (initial Cd concentration = 0.17 mmol L^{-1}). Error bars (±1 standard deviation from duplicate measurements) if not shown are within the symbols.

the counter ions involved in the ion-exchange mechanism for Cd removal (Crist et al., 1996). It is important to note that the Ca content of JB was 15 times higher than that of JW, and JB showed a relatively greater tendency to adsorb Cd than JW.

3.2. Surface charge characterization

The zeta potential as a function of pH for both adsorbents is shown in Fig. 1. Both JB and JW were negatively charged throughout the entire pH range investigated (2.5–9.5). Therefore, the surface charge characteristics of JB and JW favor cation removal even under highly acidic conditions. The difference in zeta potential between JB and JW was negligible between pH 2.5 and 5.5.

Table 1
Chemical composition of juniper bark (JB) and juniper wood (JW)

Component	Chemical content (%)	
	JW	JB
Klason lignin	37.6 ± 0.49	35.3 ± 0.46
Glucan	33.3 ± 0.37	26.0 ± 0.29
Arabinan	1.23 ± 0.03	2.43 ± 0.06
Galatan	3.00 ± 0.06	2.03 ± 0.04
Rhamnan	0.30 ± 0.02	0.39 ± 0.02
Xylan	8.45 ± 0.08	4.70 ± 0.05
Mannan	4.84 ± 0.20	4.84 ± 0.20
Total carbohydrate	51.1	39.9
Total yield	88.8	75.7
Other	11.2	24.3

3.3. Batch adsorption experiments

3.3.1. Adsorption kinetics

Time-dependent (3–100 min) adsorption of Cd onto JB and JW is shown in Fig. 2, which also includes the fittings of the kinetic data by the pseudo second-order model (Eqs. (1) and (2)). This model described the data adequately ($r^2 > 0.96$; determined based on a fit of the experimental data to Eq. (2)) and the relevant kinetic parameters are included in Table 2. As expected, Cd adsorption on both JB and JW was rapid and an "apparent" equilibrium was reached within 30 min. The adsorption capacity at equilibrium (q_e) as determined using Eq. (2) was 91.6 and 24.8 μmol g^{-1} for JB and JW, respectively, indicating that JB has four times as much capacity for Cd than JW. These values are consistent with the adsorption capacities obtained from other experiments in this study (i.e., adsorption edge) and values reported elsewhere (Min et al., 2004). The rate constant (k) for JB is higher than that of JW (Table 2) indicating faster Cd uptake, in addition to higher removal levels, onto JB.

3.3.2. Adsorption isotherms

Adsorption isotherms for Cd onto JB and JW are shown in Fig. 3. Two well-known adsorption isotherm models, namely, the Freundlich and Langmuir equations, were applied to describe the batch experimental data. While both the models adequately predicted Cd sorption to JB, application of only the Langmuir equation yielded a better

Table 2
Kinetic parameters from fit of experimental data to the pseudosecond-order reaction model

Sample	Kinetic parameter		
	k (g μmol^{-1} min^{-1})	q_e (μmol g^{-1})	R^2
Juniper bark	0.0119	91.6	0.997
Juniper wood	0.0083	24.8	0.962

fit ($r^2 \geqslant 0.90$; determined based on a fit of the experimental data to Eq. (3)) for JW. The linearized Langmuir equation has the following form (Snoeyink, 1990):

$$\frac{1}{q_e} = \frac{1}{q_{\max} b C_e} + \frac{1}{q_{\max}} \qquad (3)\leftarrow$$

where, C_e is the equilibrium Cd concentration, mmol Cd L^{-1}; q_e is the amount of Cd sorbed, mmol Cd g^{-1}; $q_{\max}$ is the maximum Cd sorption capacity, mmol Cd g^{-1}; b is a constant, related to the strength of adsorption, L $mmol^{-1}$. A fit of the experimental data using the Langmuir equation yielded the following parameters: b values for JB and JW are 45.3 and 9.1 L $mmol^{-1}$ and $q_{\max}$ equals to 76.3 and 28.3 μmol g^{-1}, respectively. These sorption capacities are lower than those determined from the pseudo second-order kinetic model attributable to differences in solution conditions (sorbate-to-sorbent ratios and, consequently, solid-to-solution ratios; initial Cd concentration) between the adsorption isotherm and kinetics experiments.

3.3.3. Adsorption edge

Cadmium adsorption capacity of both adsorbents under different pH conditions is shown in Fig. 4. On the whole, adsorption capacity increased with solution pH because less H^+ were available to compete with Cd^{2+} for the adsorption sites. Adsorption capacity of JB and JW was almost zero around pH 2 but differed by more than a factor of three above pH 5, which indicates that Cd removal is controlled by the extent of functional group dissociation in these adsorbents. According to the literature (Fourest and Volesky, 1996; Davis et al., 2003), carboxylic group and sulfonic acid groups are identified as main adsorption sites on these types of adsorbents. The acidity constant (pK_a) of carboxylic groups, weak acidic sites, is between 3.5 and 5.5 (Fourest and Volesky, 1996; Yun et al., 2001). In contrast, the pK_a of sulfonic acid, a strong acidic site, is around 1.5 (Crist et al., 1992). However, the lack of adsorption capacity at pH around 2 for both JB and JW indicates that carboxylic acid is the major functional group responsible for Cd removal by these adsorbents. In other experiments (Shin and Rowell, 2005) while comparing sulfonated and untreated JW, a substantial difference was observed in Cd adsorption capacity between these adsorbents only below pH 4 attributable to the role played by sulfonic acid groups.

3.4. Displacement of Ca and Na during Cd adsorption

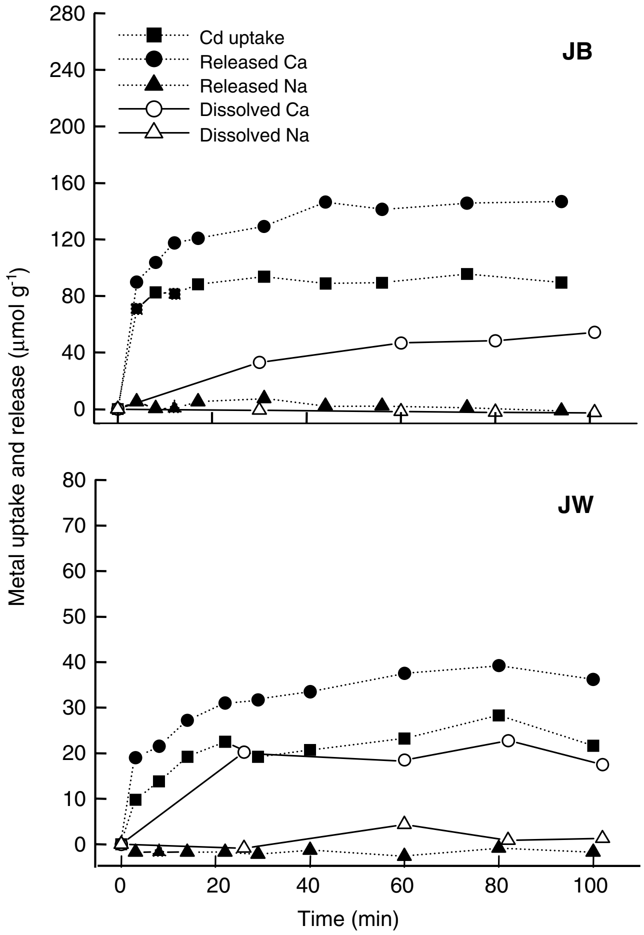

Fig. 5. Time dependence of Cd uptake and respective metal (calcium and sodium) release during Cd sorption on juniper bark (JB) and juniper wood (JW).

The kinetics of Ca and Na release during Cd adsorption on JB and JW are shown in Fig. 5. The release of Ca and Na from JB and JW can be divided into two types of ions: dissolved and ion-exchanged. Since the adsorbents were not washed, Ca and Na could be transferred to the aqueous phase by simple dissolution without ion-exchange with Cd. This form of Ca and Na is referred to as “dissolved” and the ions released in the presence of Cd are termed as “released” in Fig. 5. The amount of Ca exchanged with Cd (B, Table 3) was, therefore, calculated from the difference between the dissolved and released Ca fractions. Since Na was not released from the adsorbents under our experimental conditions, we believe that Na is not involved in ion-exchange interactions with Cd. In contrast, the amount of ion-exchanged Ca was almost identical to Cd uptake (*B* and *A* in Table 3, respectively) implying that Ca–Cd ion-exchange is an important mechanism responsible for Cd binding.

In Table 3, the ratio of ion-exchanged Ca to Cd uptake (*B*/*A*) represents the fraction of Ca displaced during Cd removal. For JB, *B*/*A* is almost equal to unity, which suggests that for every mole of Cd adsorbed, one mole of Ca

Table 3
Displacement of calcium during cadmium adsorption[a]

Sample	Cd uptake (*A*) (μmol g^{-1})	Ion-exchanged calcium (*B*) (μmol g^{-1})	*B*/*A*
Juniper bark	91.6	95.4	1.04
Juniper wood	24.8	19.5	0.78

[a] From adsorption kinetics experimental data.

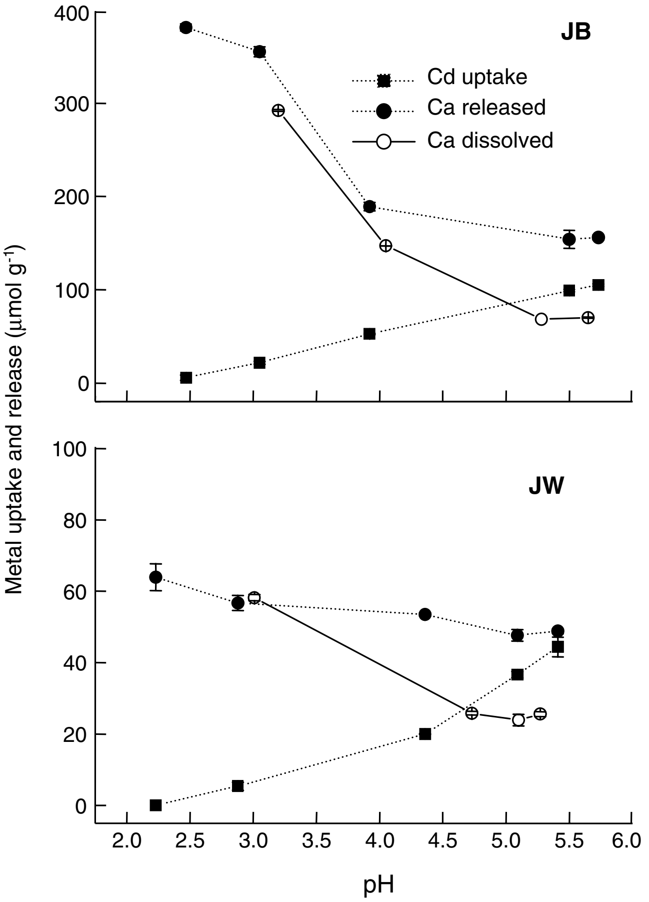

Fig. 6. pH dependence of Cd uptake, and dissolved and released Ca fractions (juniper bark (JB) and juniper wood (JW)). Error bars (±1 standard deviation from duplicate measurements) if not shown are within the symbols.

was released. In the case of JW, 78% of Cd removed can be attributed to ion-exchange reactions with Ca. Based on explanations provided in Reddad et al. (2002), the remaining fraction of adsorbed Cd could be interacting with JW through formation of complexes directly on the solid surface without any Ca displacement.

The effect of pH on Ca levels in solution in the presence (released Ca) and absence (dissolved Ca) of Cd provides additional evidence that Cd binding occurs primarily through the ion-exchange mechanism (Fig. 6). At low pH, protons occupy virtually all ion-exchange sites, resulting in high Ca release but low Cd adsorption. For JB and JW up to pH 4 and 3, respectively, the dissolved and released Ca levels are almost the same. As pH increased, Cd adsorption occurred concomitantly with Ca displacement resulting in substantially higher levels of released Ca than the dissolved Ca fraction.

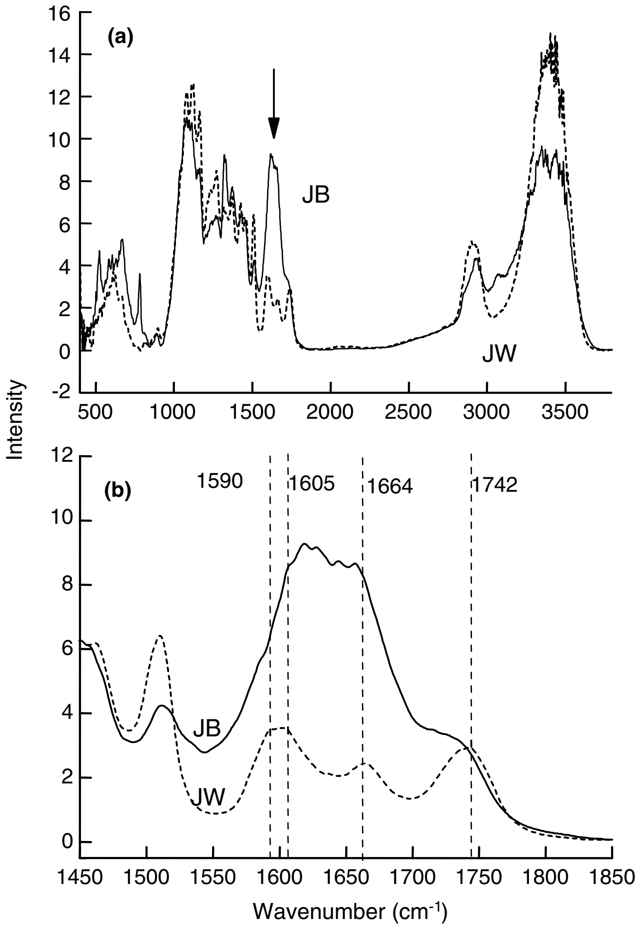

Fig. 7. DRIFT spectra of juniper bark (JB) and juniper wood (JW): (a) 400–3800 cm^{-1} spectra; and (b) 1450–1850 cm^{-1} spectra.

3.5. Spectroscopic analysis

DRIFT spectra were obtained to understand the difference in Cd adsorption between the two absorbents. The whole spectra of JB and JW are shown in Fig. 7a. Band

Table 4
IR band assignments

Position	Assignment	References
3000–3600	O–H stretching	Brown et al. (2001) and Romero-Gonzalez et al. (2001)
2930	C–H stretching	Brown et al. (2001) and Romero-Gonzalez et al. (2001)
1743	C=O stretching from ester	Pappas et al. (1999) and Shin and Rowell (2005)
1660	C=O stretching from ketone and aldehyde	Pappas et al. (1999) and Shin and Rowell (2005)
1630	Water	Pappas et al. (1999) and Shin and Rowell (2005)
1605	COO$^-$ stretching (asymmetric)	Pappas et al. (1999), Brown et al. (2001), Romero-Gonzalez et al. (2001) and Shin and Rowell (2005)
1590	Aromatic ring vibration	Pappas et al. (1999) and Shin and Rowell (2005)

assignments are presented in Table 4. The IR bands consisted of four regions: the broad hydrogen band (3200–3600 cm^{-1}), C–H stretching region (2800–3000 cm^{-1}), carbonyl group stretching region (1550–1750 cm^{-1}), and fingerprint bands (below 1550 cm^{-1}). The most remarkable difference between the two spectra is the intensity of the carbonyl group vibration in the 1600–1700 cm^{-1} range. The intensity of this band was much greater for JB compared to JW. As the spectra were already normalized, the relative difference in band intensity corresponds to the difference in the concentration of respective functional groups associated with the bands. The IR bands for carbonyl functional groups are shown in detail in Fig. 7b. There were three major bands in this region: carboxylate (COO^-) asymmetric stretching at 1605 cm^{-1}, carbonyl group from ketone and aldehyde at 1664 cm^{-1}, and carbonyl group from ester at 1742 cm^{-1}. Among these functional groups, the COO^- group has been implicated in the adsorption of heavy metals (Romero-Gonzalez et al., 2001; Min et al., 2004). The band height at 1605 cm^{-1} was 8.6 for JB and 3.4 for JW, indicating that JB contained more carboxylate functional groups than JW (Fig. 7b), resulting in a higher Cd adsorption capacity.

4. Conclusions

The Cd adsorption capacity of JB is about three to four times higher than that of JW at an initial Cd concentration of 0.17 mmol L^{-1} (pH 5). The dominant mechanism for Cd adsorption is ion-exchange with Ca. On bark, this was the only significant mechanism, whereas it may account for up to 80% of Cd adsorption on wood. DRIFT spectra showed that the surface concentration of carboxylate groups, adsorption sites for heavy metals, is higher in JB than JW, which can help explain the difference in the extent of Cd removal between these adsorbents. Surface charge characterization and Cd uptake data for bark and wood suggest that these materials can work as adsorbents for other cations such as zinc, lead, and mercury in neutral or acidic solutions.

Acknowledgements

The authors gratefully thank the USDA Forest Service, Forest Products Laboratory for financial support. Appreciation is also extended to Dan Foster and Jim Beecher of the Analytical Chemistry and Microscopy Laboratory at the Forest Products Laboratory.

References

Al-Asheh, S., Banat, F., Al-Omari, R., Duvnjak, Z., 2000. Predictions of binary sorption isotherms for the sorption of heavy metals by pine bark using single isotherm data. Chemosphere 41, 659–665.

Brown, P., Gill, S., Allen, S.J., 2001. Determination of optimal peat type to potentially capture copper and cadmium from solution. Water Environ. Res. 73, 351–362.

COWI, 2003. Cadmium Review. Nordic Council of Ministers. Report No. 1, Issue No. 4, 26p. Available from: <www.norden.org/miljoe/uk/NMR_Cadmium.pdf> (accessed 27.12.05).

Crist, R.H., Oberholser, K., McQarrity, J., Crist, D.R., Johnson, J.K., Brittsan, J.M., 1992. Interaction of metals and protons with algae. 3. Marine algae, with emphasis on lead and aluminum. Environ. Sci. Technol. 26, 496–502.

Crist, R.H., Martin, R.J., Joseph, C., 1996. Uptake of metals on peat moss: an ion-exchange process. Environ. Sci. Technol. 30, 2456–2461.

Crist, R.H., Martin, R.J., Crist, D.R., 1999. Interaction of metal ions with acid sites of biosorbents peat moss and vaucheria and model substances alginic and humic acids. Environ. Sci. Technol. 33, 2252–2256.

Davis, M.W., 1998. A rapid modified method for compositional carbohydrate analysis of lignocellulosics by HPAEC/PAD. J. Wood Chem. Technol. 18, 235–252.

Davis, T.A., Volesky, B., Mucci, A., 2003. A review of the biochemistry of heavy metal biosorption by brown algae. Water Res. 37, 4311–4330.

Figueira, M.M., Volesky, B., Ciminelli, V.S.T., Roddick, F.A., 2000. Biosorption of metals in brown seaweed biomass. Water Res. 34, 196–204.

Fourest, E., Volesky, B., 1996. Contribution of sulfonate groups and alginate to heavy metal biosorption by the dry bi interaction of metals and protons with algae. 3. Marine algae, with emphasis on lead and aluminum mass of *Sargassum fluitans*. Environ. Sci. Technol. 30, 277–282.

Gaballah, I., Kibertus, G., 1998. Recovery of heavy metal ions through decontamination of synthetic solutions and industrial effluents using modified barks. J. Geochem. Explor. 62, 241–286.

Ho, Y.S., McKay, G., 2000. The kinetics of sorption of divalent metal ions onto sphagnum peat moss. Water Res. 34, 735–742.

Matheickal, J.T., Yu, Q., Woodburn, G.V., 1999. Biosorption of cadmium(II) from aqueous solutions by pre-treated biomass of marine alga *Durvillaea potatorum*. Water Res. 33, 335–342.

Min, S.H., Han, J.S., Shin, E.W., Park, J.K., 2004. Improvement of cadmium ion removal by base treatment of juniper fiber. Water Res. 38, 1289–1295.

Pappas, C., Rodis, P., Tarantilis, P.A., Polissiou, M., 1999. Prediction of the pH in wood by diffuse reflectance infrared Fourier transform spectroscopy. Appl. Spectrosc. 53, 805–809.

Randall, J.M., Bermann, R.L., Garrett, V., Waiss, A.C.J., 1974. Use of bark to remove heavy metal ions from waste solutions. Forest Products J. 24, 80–84.

Reddad, Z., Gerente, C., Andres, Y., Cloirec, P., 2002. Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies. Environ. Sci. Technol. 36, 67–73.

Romero-Gonzalez, M.E., Williams, C.J., Gardiner, P.H.E., 2001. Study of the mechanisms of cadmium biosorption by dealginated seaweed waste. Environ. Sci. Technol. 35, 3025–3030.

Seki, K., Saito, N., Aoyama, M., 1997. Removal of heavy metal ions from solutions by coniferous barks. Wood Sci. Technol. 31, 441–447.

Shin, E.W., Rowell, R.M., 2005. Cadmium ion sorption onto lignocellulosic biosorbent modified by sulfonation: the origin of sorption capacity improvement. Chemosphere. 60, 1054–1061.

Snoeyink, V.L., 1990. Adsorption of organic compounds. In: Pontius, F.W. (Ed.), Water Quality and Treatment. McGraw-Hill Inc., New York, pp. 781–876.

Wase, J., Forster, C., 1997. Biosorbents for Metal Ions. Taylor & Francis Inc., Bristol, PA.

Yang, J., Volesky, B., 1999. Cadmium biosorption rate in protonated *Sargassum* biomass. Environ. Sci. Technol. 33, 751–757.

Yang, C.Q., Xu, Y., Wang, D., 1996. FT-IR spectroscopy study of the polycarboxylic acids used for paper wet strength improvement. Ind. Eng. Chem. Res. 35, 4037–4042.

Yun, Y.-S., Park, D., Park, J.M., Volesky, B., 2001. Biosorption of trivalent chromium on the brown seaweed biomass. Environ. Sci. Technol. 35, 4353–4358.