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Adsorption mechanism of cadmium on juniper bark and wood ☆

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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

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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