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Cadmium Removal by *Juniperus monosperma*: the Role of Calcium Oxalate Monohydrate Structure in Bark

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Abstract−This study suggests that calcium oxalate monohydrate over *Juniperus monosperma* bark is an ion-exchangeable site for cadmium adsorption on the basis of its cadmium adsorption behavior and surface characterization. Cadmium adsorption behavior showed that juniper bark had a higher cadmium adsorption capacity (84.6 μmol Cd g^{-1} at pH 5) than juniper wood (32.0 μmol Cd g^{-1} at pH 5), and that the base-treatment improved the cadmium adsorption capacity of only juniper wood. This difference between juniper bark and wood might have originated from different cadmium binding sites. In calcium displacement, the cadmium uptake onto juniper bark was identical to the amount of calcium ions displaced, which indicated that calcium played an important role in cadmium adsorption onto juniper bark. X-ray diffraction (XRD) results gave evidence that only juniper bark contained the structure of calcium oxalate monohydrate. Furthermore, cadmium adsorption decreased the intensity of the characteristic XRD peaks for calcium oxalate monohydrate. In diffuse reflectance infrared Fourier transform (DRIFT) spectra, existence of oxalate on juniper bark was proven again and interpretation on IR band of carbonyl groups matched significantly the cadmium adsorption behavior.

Key words: Calcium Oxalate Monohydrates, *Juniperus monosperma* Bark, Cadmium Adsorption

INTRODUCTION

Juniperus monosperma, a forest material, has been applied to heavy metal removal processes as an adsorbent [Min et al., 2004; Shin et al., 2004; Shin and Rowell, 2005]. Like other biosorbents such as peat moss [Crist et al., 1992, 1996], algae [Davis et al., 2003a], and sugar beet pulp [Reddad et al., 2002], the adsorption capacity of juniper for cadmium (Cd) removal from water was ascribed to functional groups (carboxylic and sulfonic acid groups) for cation-exchange on a juniper surface. Hence, such chemical treatments as base treatment and sulfonation have been used to introduce more heavy metal binding sites onto juniper and, eventually, to improve heavy metal adsorption capacity [Min et al., 2004; Shin and Rowell, 2005].

Mechanisms of heavy metal sorption and the surface structure for the binding sites have been well described and fully understood for certain adsorbents. For example, brown algae containing carboxylic and sulfonic acid groups as key functional groups for heavy metal binding and mechanisms for the heavy metal removal process have been explained with ion-exchange and surface complexation models [Davis et al., 2003a]. In heavy metal uptake experiments, changes in solution pH as well as a release of light ions resulted from an ion-exchange of heavy metals [Schiewer and Volesky, 1995; Crist et al., 1996]. The surface complexation mechanism was closely related to the molecular structure of the binding sites. In this mechanism, heavy metal binding was regarded as the complexation of heavy metals to a multidentate ligand. The egg-box model described steric arrangements of a heavy metal coordinated to alginic acid sites; the orientation of the oxygen atoms with respect to COO^- was preferable to guluronic acid than mannuronic acid [Davis et al., 2003b]. Thus, to the extent of molecular structure, the interaction between the heavy metal binding sites and the functional groups over brown algae has been well understood.

Recent reports on *Juniperus monosperma* adsorbents have revealed that heavy metal sequestration depended on functional groups generated by chemical modifications [Min et al., 2004; Shin and Rowell, 2005]. However, unlike brown algae biosorbent, a detailed understanding the molecular structure of binding sites on adsorbents, which helps cadmium adsorption behavior, has not been suggested. In the present study, we demonstrated that calcium oxalate monohydrate (COM) is an binding structure on *Juniperus monosperma* bark for cadmium adsorption. The cadmium adsorption behavior is explained on the basis of the structure of the ion-exchangeable site.

EXPERIMENTAL

1. Materials

Juniper logs were randomly collected from New Mexico, U.S.A. and shredded into small chips at the USDA Forest Products Laboratory (FPL) in Madison, Wisconsin, U.S.A. Juniper bark was separated from the chips and then ground to pass through a 3-mm screen using a Wiley mill. Juniper wood was also separately collected and then ground. The untreated juniper bark and wood were denoted UJB and UJW, respectively. For comparison, base-treated juniper bark (BJB) and wood (BJW) were prepared in this study. A 250-mL aliquot of 0.5 M NaOH solution was added to a 1 L-beaker containing 10 g of juniper powder. The samples were treated with a base-solution by stirring for 24 h. The solutions were decanted and the samples were continuously washed with deionized water until

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the pH of the wash water reached less than 8. The base-treated samples were dried in air at ambient temperature for 3 days.

2. Adsorption Test and Calcium Displacement

Adsorption kinetic experiments were carried out in 1-L solutions with 1.0 g of solid sample and 0.178 mmol L^{-1} of initial cadmium concentration. The experiments were conducted at two different pH conditions (pH 5.0±0.1 and pH 3.2±0.1) and the solution pH was kept constant during the experiment 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. Previous experiments showed that the 2-h kinetic time was enough to reach equilibrium. Cadmium concentration in the filtrate was determined by inductively coupled plasma - atomic emission spectroscopy (ICP-AES; ULTIMA, Jobin Yvon Inc.).

During the experiment, calcium concentrations of each solution sample were measured by an ICP-AES to calculate the amount of calcium ions displaced with cadmium ions. The amount of calcium ions displaced was calculated by subtracting the amount of calcium ions dissolved from the amount of calcium ions released. The calcium dissolved was the total calcium ions released from the adsorbents in the absence of cadmium ions in water. To measure the amounts of calcium ions dissolved, the same kinetic experiments were conducted at the same pH conditions after the adsorbents were put in deionized water that contained no cadmium ions. The calcium ions released represented the total calcium ions released from the adsorbents in the cadmium adsorption experiments. This value assumed the calcium dissolved plus the calcium displaced.

The pseudo-second-order equation was employed to determine the cadmium adsorption capacity (q_e) and the amounts of calcium ions by data fitting from the kinetic experiments [Ho and McKay, 1999]. This model assumed that adsorption followed the Langmuir equation and showed high correlation coefficients for data fitting. The kinetic rate equations can be written as follows:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \qquad (1)$$

where q_t, and q_e are the amounts of cadmium adsorbed at time t, and at equilibrium (μmol g^{-1}), respectively, and k is the equilibrium rate constant of the second order adsorption (g μmol^{-1} min^{-1}). The equation can be integrated and then rearranged to be applied to linear regressions. q_e was determined by calculating the values acquired from this linear regression.

3. Characterizations

An elemental analysis for cadmium, calcium, and sodium was conducted by ICP-AES (ULTIMA, Jobin Yvon Inc., Edison, NJ). DRIFT spectra were acquired by using a Mattson Galaxy 5020 (Mattson Instruments, Madison, WI) equipped with a Harrick Scientific (Ossining, NY) diffuse reflectance accessory. Each infrared (IR) spectrum was the average of 4,000 scans between 400 and 4,000 cm^{-1} (resolution=4 cm^{-1}). Prior to analysis, samples were finely ground with a Wiley mill and sieved with a 0.18-mm screen. Each spectrum was baseline corrected at 400, 840, 2,000, and 4,000 cm^{-1} and normalized against the 1,320 cm^{-1} band associated with the C-H bending mode [Yang et al., 1996].

An X-ray diffraction (XRD) analysis was performed to characterize the adsorbents. In addition to the prepared adsorbents (UJB, UJW, and BJB), Cd-adsorbed adsorbents were employed in this analysis for comparison. The adsorbents spent in kinetic experiments were used as Cd-adsorbed adsorbents. All XRD patterns were collected with a Scintag PAD V X-ray diffractometer equipped with CuKα radiation (40 kV, 35 mA) of wavelength 0.154 nm. All XRD patterns were obtained from 10° to 50° with a scan speed of 1.5° min^{-1}.

Table 1. Cadmium uptake and calcium displacement of each adsorbent

Samples	pH	$Q_{Ca,D}$[a]	$Q_{Ca,R}$[b]	$Q_{Ca,DP}$[c]	Q_{Cd}[d]	$Q_{Ca,DP}/Q_{Cd}$
UJB	5.0	86.6	168.4	81.8	84.6	0.967
	3.2	283.9	311.7	27.8	30.8	0.903
UJW	5.0	25.5	48.9	23.4	32.0	0.731
	3.2	53.4	56.5	3.1	9.07	0.342
BJB	5.0	22.5	125.1	102.6	88.6	1.15
BJW	5.0	6.56	33.5	26.9	76.2	0.353

[a] Amount of calcium ions dissolved at equilibrium (μmol g^{-1}).

[b] Amount of calcium ions released at equilibrium (μmol g^{-1}).

[c] Amount of calcium ions displaced at equilibrium. This was calculated by subtracting $Q_{Ca,D}$ from $Q_{Ca,R}$ (μmol g^{-1}).

[d] Amount of cadmium adsorbed at equilibrium (μmol g^{-1}).

RESULTS AND DISCUSSION

1. Cadmium Adsorption Behavior and Calcium Displacement

Table 1 shows the cadmium uptake and the calcium displacement of each adsorbent. The metal amounts at equilibrium in Table 1 were acquired by fitting the kinetic data to the pseudo-second-order equation. The fitting results showed high correlation coefficients of >0.998. In cadmium uptake, lowering pH of the solutions decreased the adsorption capacity of UJB as well as of UJW, which accorded with previous reports [Romero-Gonzalez et al., 2001; Yun et al., 2001; Shin and Rowell, 2005]. As cadmium ions competed with many more protons at lower pH conditions, it was natural that the cadmium uptake was reduced. The juniper bark (UJB) had higher adsorption capacities for cadmium (84.6 and 30.8 μmol Cd g^{-1}) under both pH conditions than did the juniper wood (UJW: 32.0 and 9.07 μmol Cd g^{-1}). Additionally, the base-treatment on the juniper bark had little effect on cadmium capacity (BJB: 88.6 μmol Cd g^{-1}), whereas the base-treatment increased cadmium uptake on the juniper wood adsorbent to 76.2 μmol Cd g^{-1} (BJW). In a previous report [Min et al., 2004], the cadmium adsorption capacity of juniper fiber that consisted of juniper wood and bark was improved by the base-treatment. This result in the previous study was due to changes in the surface structure of juniper wood not juniper bark, as proven in this study. The distinct effects of the base-treatment on juniper wood and bark as well as differences in the adsorption capacity between juniper bark and wood might indicate a difference in the chemical structures responsible for cadmium adsorption over both the adsorbents.

The calcium displacement behavior of UJB and UJW was also not similar. In Table 1, the ratios of $Q_{Ca,DP}/Q_{Cd}$, representing the molar ratios of calcium ions displaced to cadmium uptake, were at least above 0.9 for juniper bark (UJB and BJB), while those of juniper wood (UJW and BJW) were 0.731, 0.342 and 0.353, respectively

(Table 1). This indicated that in juniper bark, over 90% of cadmium uptake was displaced with calcium ions whereas, on average, 50% of the cadmium uptake was achieved by ion-exchange with calcium ions over juniper wood. Accordingly, calcium played an important role in cadmium adsorption onto the juniper bark.

Moreover, the released or dissolved calcium ion amounts ($Q_{Ca,R}$ and $Q_{Ca,D}$)of juniper bark (UJB: 86.6-311.7 μmol g^{-1}) were much higher than those of juniper wood (UJW: 25.5-56.5 μmol g^{-1}). Even after base-washing, the values of BJB (22.5-125.1 μmol g^{-1}) were higher than those of BJW (6.56-33.5 μmol g^{-1}). These results were attributed to more calcium content in juniper bark. In the results of ICP-AES, the calcium content in UJB was 945 μmol g^{-1}, fifteen times more than that in UJW (61.7 μmol g^{-1}), which also implied that the role of calcium ions in juniper bark was important for the cadmium uptake.

2. X-Ray Diffraction

XRD patterns of UJB and UJW are shown in Fig. 1. The pattern of UJB looked superimposed on the pattern of UJW with several sharp peaks, which implied that UJB contained a unique chemical structure showing the sharp peaks at 2θ=15.0, 24.5, 30.2, 36.1, and 38.3. Though the pattern seemed too complicated to discover the chemical structure of the sharp peaks, most of the peaks could be assigned to one structure, calcium oxalate monohydrate [Kontoyannis et al., 1997; Yu et al., 2002; Quyang et al., 2004]. On the basis of the literature, the peak at 2θ=30.2 was chosen as a main peak for calcium oxalate monohydrate while the characteristic peak for the juniper structure was exhibited at 2θ=22.7.

The XRD patterns of the juniper bark before and after cadmium uptake are shown in Fig. 2. After cadmium adsorption, the characteristic peaks of calcium oxalate monohydrate decreased. The heights of the main calcium oxalate monohydrate peak (2θ=30.2) and juniper peak (2θ=22.7) were measured to calculate the ratios of the heights (H_{COM}/H_{bark}) that are proportional to the amount of calcium oxalate monohydrate in the juniper bark. Table 2 presents these results calculated. In the case of UJB, H_{COM}/H_{bark} was reduced from 0.814 to 0.573 after cadmium adsorption. For BJB, 0.670 of the ratio went to 0.457 after cadmium uptake. The decrease in these ratios clearly indicated disappearance of the structure of calcium oxalate monohydrate. We suggest that this reduction of calcium oxalate monohydrate after cadmium adsorption is due to the ion-exchange of calcium in calcium oxalate monohydrate with cadmium ions.

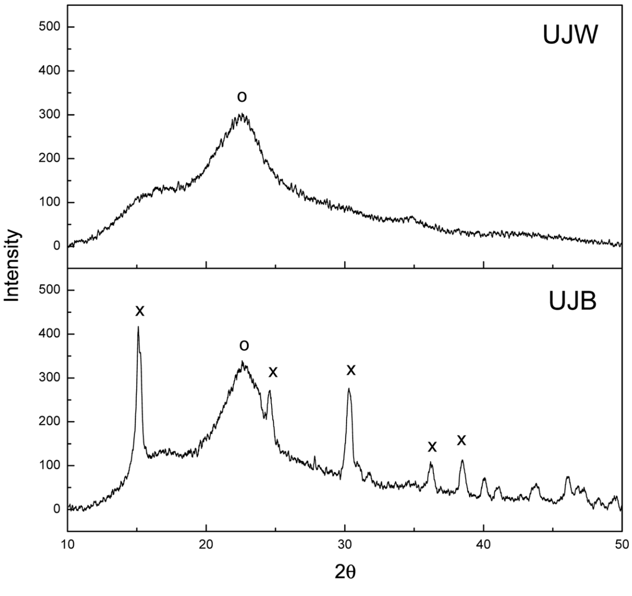

Fig. 1. X-ray diffraction (XRD) patterns of UJW and UJB. x and o marks represent the characteristic peaks for calcium oxalate monohydrate and juniper, respectively.

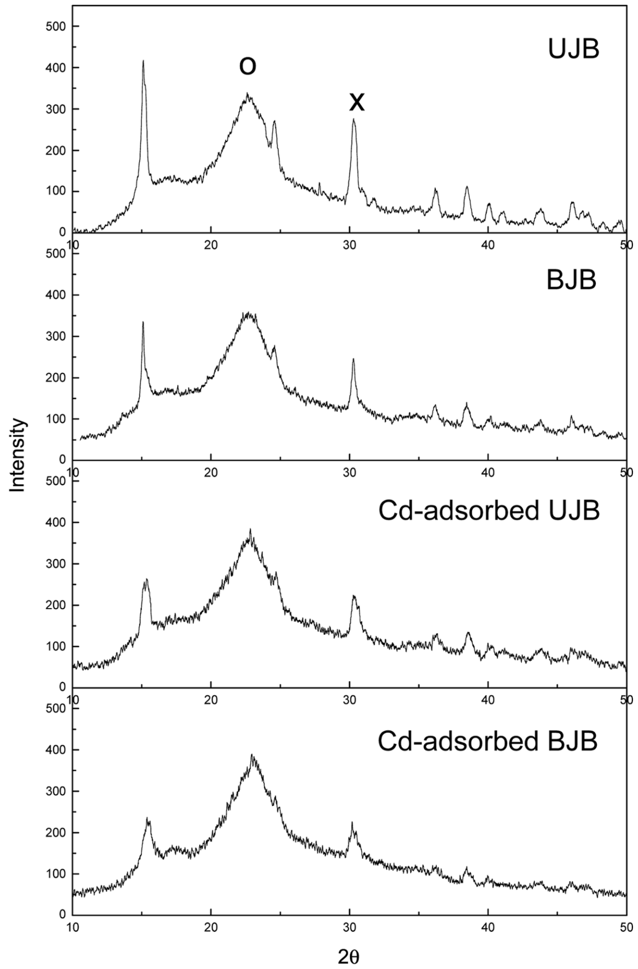

Fig. 2. XRD patterns of UJB, BJB, Cd-adsorbed UJB and Cd-adsorbed BJB. x and o marks represent the characteristic peaks for calcium oxalate monohydrate and juniper, respectively.

Table 2. Heights of the main XRD peaks of calcium oxalate monohydrate and juniper and ratios of the heights

Samples	$H_{COM}{}^{a}$	$H_{bark}{}^{b}$	H_{COM}/H_{bark}
UJB	276	339	0.814
BJB	201	300	0.670
Cd-adsorbed UJB	176	307	0.573
Cd-adsorbed BJB	150	328	0.457

[a] The height of the peak at 2θ=30.2

[b] The height of the peak at 2θ=22.7

The disappearance of calcium oxalate monohydrate could be ascribed to other factors. For example, the base-treatment could lessen calcium concentration in solids, which was supported by the XRD and the calcium displacement experiments - decreases in H_{COM}/H_{bark} and the amounts of calcium displaced after the base-treatment. Nonetheless, a decrease in the characteristic peak of calcium oxalate monohydrate during cadmium adsorption kinetics was caused mainly by the ion-exchange with cadmium ions. The base-treatment was likely to reduce more amounts of calcium oxalate monohydrate than cadmium adsorption because of a longer reaction time (24 h to 2 h). However, in Table 2, results showed the opposite that the reduction in H_{COM}/H_{bark} by the base treatment (0.144=0.814-0.670) was lower than that by cadmium uptake (0.241=0.814-0.573). In addition, even though the solubility (K_{sp}) of calcium oxalate monohydrate in water at 25 °C is very low at 2.0×10^{-9} mol^{2}L^{-2} [Nancollas and Gardner, 1974], the dissolution rate of calcium oxalate monohydrate was increased in the presence of aluminum and iron ions according to the report by Petrova et al. [2004]. Similarly, the presence of cadmium ions in solution should facilitate the dissolution of calcium oxalate monohydrate and then the interaction between oxalic groups and cadmium ions can remove the cadmium ions from solution. Table 1 exhibits clearly that cadmium ions in solution promoted the release of calcium from juniper bark. Consequently, cadmium adsorption reduced the XRD peak intensity of calcium oxalate monohydrate, indicating an ion-exchange between cadmium and calcium.

3. Diffuse Reflectance Infrared Fourier Transform Spectra

DRIFT spectra of *Juniper monosperma* were introduced in previous reports [Min et al., 2004; Shin and Rowell, 2005]. The characteristic IR bands of carboxylate (COO$^-$), which are known as a heavy metal binding site, and an oxalate, which is an interesting structure as a new binding site in this study, appeared around 1,550-1,800 cm^{-1} because those contain a carbonyl group. In addition, the IR bands in other regions were not useful for analyzing the functional groups according to previous studies [Min et al., 2004; Shin and Rowell, 2005]. Therefore, in this study, the IR bands of carbonyl groups were displayed and primarily interpreted. Fig. 3 and Fig. 4 show the IR bands of carbonyl groups for juniper wood and bark, respectively. In Fig. 3 and 4, the IR bands related to the carbonyl groups were exhibited at four positions: 1,605, 1,618, around 1,660, and around 1,744 cm^{-1}. The bands at 1,660 and 1,744 cm^{-1} were assigned to C=O stretching from the aldehyde/ketone and ester groups, correspondingly [Chatjigakis et al., 1998; Pappas et al., 1999; Brown et al., 2001; Min et al., 2004; Shin and Rowell, 2005]. These bands commonly appear over both juniper wood and bark although the positions of the bands were shifted a little. In contrast, UJB and BJB showed the band at 1,618 cm^{-1} which may be assigned to C=O stretching from the oxalate [Ouyang et al., 2004] while UJW and BJW the band was at 1,605 cm^{-1} which may be assigned to C=O stretching from carboxylate [Chatjigakis et al., 1998; Fransioso et al., 1998; Pappas et al., 1999; Zhang and Kamdem, 2000; Brown et al., 2001; Shin and Rowell, 2005]. This indicates once again that oxalate structure existed only on the juniper bark and not on the juniper wood.

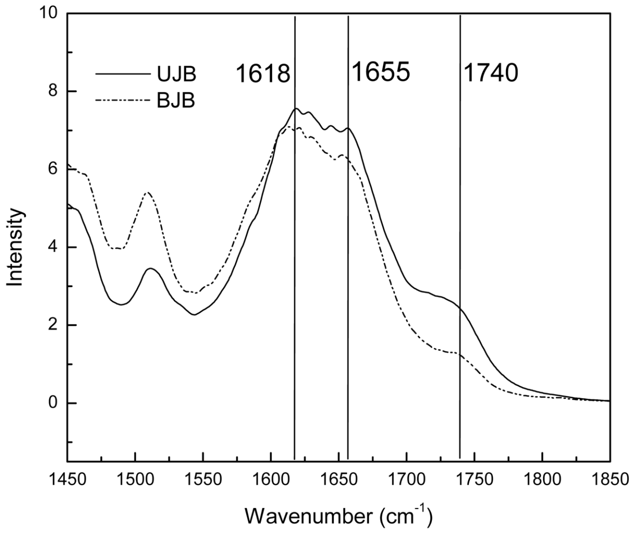

Fig. 3. IR bands of carbonyl groups for UJB and BJB.

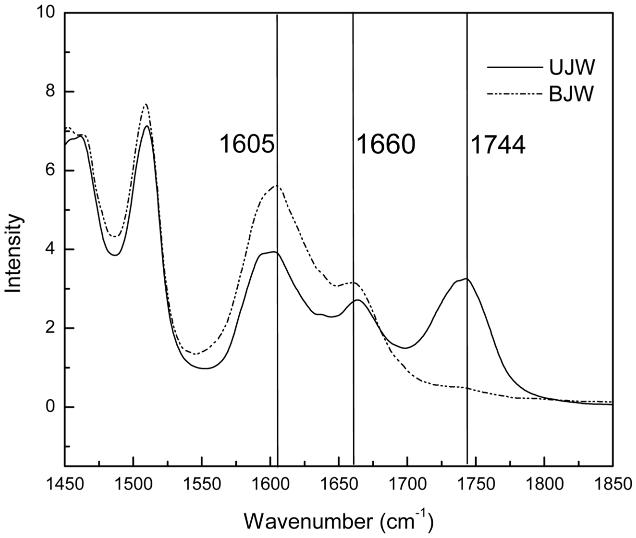

Fig. 4. IR bands of carbonyl groups for UJW and BJW.

In Fig. 3, the IR bands changed little after the base-treatment. The band of C=O stretching from ester (1,740 cm^{-1}) decreased a little, but the other bands were almost the same. On the contrary, the base-treatment affected the pattern of IR bands in Fig. 4. After the base-treatment, the band at 1,605 cm^{-1} increased while the band at 1,744 cm^{-1} disappeared. This phenomenon is well-known as 'saponification' where ester reacts with water under base conditions to produce a carboxylate group (COO$^-$). According to previous studies [Tiemann et al., 1999; Min et al., 2004], the intensity of the IR band of carboxylate was proportional to the heavy metal uptake, implying that carboxylate was a binding site for heavy metal removal. Therefore, this significantly explains that the cadmium adsorption capacity of the juniper wood was increased after the base-treatment and that little change in the cadmium adsorption capacity of the

Table 3. IR band assignments

Position (cm^{-1})	Assignment
1,744	C=O stretching from ester
1,660	C=O stretching from ketone and aldehyde
1,618	C=O stretching from oxalate
1,605	C=O stretching from carboxylate

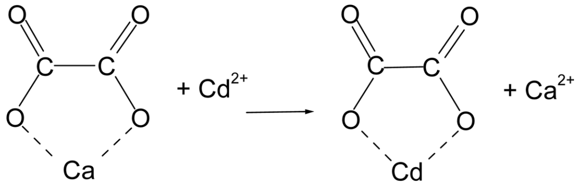

Fig. 5. A proposed mechanism for ion-exchange between calcium and cadmium.

juniper bark occurred after the base-treatment. The carbonyl groups accountable for the cadmium uptake, the carboxylate and the oxalate groups, were not changed on the juniper bark surface by the base-treatment, which is significantly consistent with the cadmium adsorption results in Table 1.

A mechanism for the ion-exchange of calcium oxalate with cadmium ions was proposed in Fig. 5. Around pH 5, cadmium existed mainly in the form of Cd^{2+} ions that can exchange calcium ions in calcium oxalate in competition with protons. As seen in Fig. 5, as a result of the ion-exchange, the cadmium ions were trapped in oxalate form and the calcium ions were released into the solution.

CONCLUSIONS

Based on the present study, the following can be concluded:

1. In cadmium adsorption, UJB showed about two to three times higher adsorption capacity than UJW at 0.178 mmol L^{-1} of initial cadmium concentration and at pH 3.2 and pH 5. As well, the base-treatment improved the cadmium adsorption capacity of UJW, and not that of UJB. From the results of the calcium displacement, ion-exchange with calcium was prevalent in cadmium adsorption on UJB. These results implied that the mechanism of cadmium adsorption onto UJB would be different than that of UJW.

2. XRD analysis proved that the calcium oxalate monohydrate structure existed only on UJB. The characteristic peaks for calcium oxalate monohydrate on UJB were reduced after cadmium adsorption, which indicated that calcium oxalate is closely related to cadmium uptake.

3. DRIFT spectra also gave evidence that UJB contained the oxalate structure, and that UJW did not. The change in IR bands of carbonyl groups by the base-treatment matched well the cadmium adsorption results.

4. Calcium oxalate monohydrate on UJB was ion-exchangeable structure for cadmium binding, which did not exist on UJW.

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