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Characterization of Cr(VI) binding and reduction to Cr(III) by the agricultural byproducts of *Avena monida* (Oat) biomass

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Abstract

Chromium contamination of the environment has become an important issue due to the potential health threat it poses. Conventional technologies to clean up heavy metal ions from contaminated waters have been utilized, but these technologies are not cost-effective. However, the use of agricultural waste byproducts for the removal of Cr(VI) from contaminated waters may be a new cost-effective alternative. Oat byproducts from the Juarez Valley in Mexico were studied for the ability to bind Cr(VI) under different temperature and time conditions. The metal binding ability of oat byproducts was calculated from experimental data collected at temperatures of 8, 26, and 54°C, and time exposures of 1, 6, 24, 48, and 72 h at each temperature. These results showed that the binding of Cr(VI) to oat biomass increased as time and temperature increased. The bound chromium was recovered from the oat biomass by treatment with 0.2 M HCl. Through the use of X-ray absorption spectroscopy, the reduction of Cr(VI) to Cr(III) was determined to occur by the oat byproducts. These results indicate that the use of agricultural waste byproducts could be a better alternative for the removal and subsequent reduction of Cr(VI) to Cr(III) from contaminated waters.

Keywords: Chromium(VI); Bioreduction; Oat; Agricultural byproducts; XANES; EXAFS

1. Introduction

Throughout the last century, heavy metal contamination of the aqueous environment has gained much attention due to the significant potential health impact on the public. Due to the fact that chromium is one of the most toxic metals that have been released into

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the environment, it has become a serious health concern. Chromium is commonly used in industrial applications, such as: tanning processes, electroplating, pigmentation, catalyst for corrosion inhibitors, and wood preservatives [1]. While hexavalent and trivalent species of chromium are prevalent in industrial waste solutions, the hexavalent form of chromium has been considered more hazardous to the public health due to its mutagenic and carcinogenic properties [2]. The Agency for Toxic Substances and Diseases Registry (ATSDR) classifies Cr(VI) as the top 16th hazardous substance. Due to the severe toxicity of Cr(VI), the US EPA has set the maximum contaminate level (MCL) for Cr(VI) in domestic water supplies to be 0.05 ppm [3].

Many methods have been used for the recovery of Cr(VI) from aqueous solutions, including: ion-exchange resins, filtration, and activated charcoal [4–7]. However, these methods are costly and can themselves produce other waste problems. Therefore, there is a need to develop new cost-effective methods that are more environmentally friendly. Biological systems such as seaweed, freshwater macrophytes, algae and fungi, and other various plant materials have been studied for their chromium binding abilities [8–14]. Singh et al. found that sawdust had the ability to adsorb Cr(VI) ions from an aqueous solution [10]. In addition, Lytle et al. found that wetland plants have the ability to reduce toxic Cr(VI) to the more stable Cr(III) species [15]. However, few studies have been performed with agricultural products on the removal of Cr(VI) from contaminated solutions. Therefore, byproducts of *Avena monida* (oat) cultivation may hold potential for the removal of chromium from waste solutions in a cost-effective manner.

Oat (*A. monida*) is a common crop in the Juarez Valley in Mexico. The agricultural byproducts of oat cultivation were identified as a potential source of biomaterial for the adsorption of Cr(VI) from waste solutions. The byproducts of the oat plant (which are considered waste and are usually burned) typically consist of the stem and leaf portions after the oat grain is harvested. Therefore, the byproducts of oat cultivation are readily available and inexpensive. Since oat agricultural byproducts are of little use and are abundant throughout this region, they may be a good source of biomaterial for the accumulation and recovery of heavy metals from industrial waters.

The objective of this work was to characterize the binding of Cr(VI) and subsequent reduction of Cr(VI) to Cr(III) by the oat byproducts. Batch laboratory temperature and time dependence experiments were performed at pH 2.0 to assess the optimal time and temperature on the binding of Cr(VI) to the oat biomass. The amount of Cr(VI) bound to the biomass was determined using flame atomic absorption spectroscopy. Also, the bioreduction of Cr(VI) to Cr(III) by the oat byproducts was confirmed using X-ray absorption near-edge structure (XANES). In addition, the coordination environment of the Cr ions bound to the oat biomass was studied using extended X-ray absorption fine structure (EXAFS) to discern which functional group(s) may be binding, and subsequently, reducing the Cr(VI) to Cr(III).

2. Methodology

2.1. Oat collection

Oat samples were collected from fields in the Juarez Valley in Mexico during the months of May and June when the crop is typically harvested. The plant samples (which included

the stems, leaves, and hulls) were removed from the soil after harvest and then washed to remove any soil debris. The biomass sample was oven-dried at 95°C for one week. The dried sample was then ground using a blender and sieved to pass through a 100-mesh sieve to obtain uniform particle size.

2.2. pH profile for Cr(III) and Cr(VI) ion binding

Batch laboratory techniques similar to those previously reported by Gardea-Torresdey et al. were utilized to determine the optimal binding pH of the biomass [4]. A 250 mg sample of the biomass was washed twice with 0.01 M HCl using a centrifuge to remove any soluble materials or metal ions that may be present on the biomass. The biomass was then resuspended in 50 ml of 0.01 M HCl with a final biomass concentration of 5 mg/ml and the pH was adjusted to 2. Two milliliter of the biomass suspension (10 mg) was placed into three clean test tubes. The tubes were then centrifuged at approximately 3000 rpm for 5 min and the supernatants were removed and placed into three clean test tubes. Separate solutions of 0.1 mM chromium(III) or chromium(VI) were prepared from the corresponding salts: $Cr(NO_3)_3$ and $K_2Cr_2O_7$ and adjusted to pH 2.0. A 2 ml aliquot of the chromium solution (either Cr(III) or Cr(VI)) was added to the respective pH biomass pellets, and to the respective separated supernatant solutions. The tubes were then rocked for 1 h and centrifuged. This was repeated for each of the following pHs: 3.0, 4.0, 5.0, and 6.0. The final pH of the supernatants were recorded and analyzed for chromium content using flame atomic absorption spectroscopy. Each experiment was performed in triplicate for quality control and statistical purposes.

2.3. Time dependency for Cr(III) and Cr(VI) ion binding

The time dependence experiments were performed in a similar fashion to that previously reported by Gardea-Torresdey et al. [4]. In summary, a sample consisting of 250 mg of biomass was washed to remove any metal ions or soluble materials and then resuspended in 50 ml of de-ionized (DI) water with a final biomass concentration of 5 mg/ml. The biomass suspension was then adjusted to the appropriate optimal binding pH for the metal ion being studied; pH 2 for Cr(VI) and pH 5 was chosen for Cr(III) to reduce possible precipitation of the metal. Two milliliter of the biomass suspension was placed into each of 21 clean test tubes, three tubes for each of the following reaction times: 5, 10, 15, 30, 60, 90 and 120 min. The test tubes were centrifuged and the supernatants were discarded. Two milliliter of 0.3 mM metal solution (Cr(VI) at pH 2 or Cr(III) at pH 5) was added to the 21 tubes containing biomass pellets. In addition, separate controls were maintained for each time period. The tubes (containing approximately 10 mg of biomass and 2 ml of 0.3 mM metal solution) and controls were equilibrated using a rocker for their respective time interval and then centrifuged at 3,000 rpm for 5 min. The same procedure was used for both metals being studied at their optimal binding pH (Cr(VI) at pH 2 or Cr(III) at pH 5). The supernatants for all of the pellets were transferred to clean test tubes and the final pH was recorded. Analysis for chromium content in the supernatants and controls were performed by flame atomic absorption spectroscopy.

2.4. Temperature and time dependence studies for Cr(VI) binding

In order to better understand how temperature may affect the binding and possible reduction of Cr(VI), the biomass was exposed to Cr(VI) solutions at the temperatures of 8, 26, and 54°C, following similar batch laboratory procedures previously described by Gardea-Torresdey et al. [16,17]. In addition, it would be necessary to determine how time of exposure at each temperature affects the binding and possible reduction of Cr(VI) by the biomass. Therefore, the temperature experiments were performed for different time exposures of 1, 6, 24, 28, and 72 h. Each experiment was also performed in triplicate for statistical purposes, thus generating a total of 45 samples. Control solutions were also maintained for each temperature and time exposure. Each of the 45 samples used in this experiment consisted of 300 mg of oat biomass which were washed twice with diluted 0.01 M HCl followed by one additional washing with DI water to remove any soluble molecules that could interfere with the metal ions studied. The samples were then centrifuged at 3000 rpm for 5 min and the washings were subsequently discarded. In addition, a 1000 ppm Cr(VI) solution was prepared from $K_2Cr_2O_7$ and adjusted to pH 2.0. Prior to each experiment, all of the biomass pellets and Cr(VI) solutions were separately maintained at the following temperatures for 20 min: 8° in a refrigerator, 26° on the lab bench, and 54°C in an oven. After the temperatures of the biomass and Cr(VI) solutions had equalized, the biomass was resuspended in 10 ml of Cr(VI) solution to make a 30 mg/ml suspension mixture of biomass and Cr(VI) in solution. The biomass/Cr(VI) mixtures were then equilibrated by rocking at their respective temperature and time. Also, controls of Cr(VI) solution and biomass alone were reacted in the same manner. When the reaction time was complete, the samples were centrifuged, and their supernatants were collected and saved for analysis by flame atomic absorption spectroscopy.

2.5. Recovery of adsorbed metal ions

The pellets used for the time and temperature studies with the bound metal were washed five times with 10 ml distilled water followed by centrifugation to remove any excess of Cr(VI) in the surface of the pellets. Next, the pellets were exposed to 10 ml of 0.2 M HCl and rocked for 10 min. The samples were then centrifuged and the supernatants were collected for analysis and diluted as necessary to remain within the linear calibration range. Metal analysis was performed by flame atomic absorption spectroscopy.

2.6. Chromium analyses

The concentration of chromium in all of the experiments performed was determined by using a 3110 Perkin-Elmer Flame Atomic Absorption Spectrometer (FAAS) with background subtraction. The parameters required for chromium analysis were obtained from the Perkin-Elmer manual and are as follows: wavelength at 359.4 nm, current of 25 mA, slit of 0.7 nm, and air to fuel ratio of 2:2. To gain a better sensitivity, an impact bead was used. The instrument was calibrated with known standards to obtain a correlation coefficient of 0.99 or greater, and the response was periodically checked using known standards to validate its accuracy. Each sample analysis was performed in triplicate, and the mean value and standard deviation were recorded. The supernatant and controls were diluted to

remain within the calibration linear range. The amount of the metal adsorbed by the oat biomass was calculated from the difference between the Cr(VI) concentration of the control solutions and the final concentration in the respective supernatant solutions.

2.7. X-ray absorption spectroscopy

Samples from the time and temperature studies were retained for further analysis by X-ray absorption spectroscopy (XAS). Due to the limited availability of beam time, the samples with the highest uptake (72 h at 54°C) were chosen for this study. In addition, a weak cation exchange resin sample (Diaion® WT01S) containing carboxylic groups was analyzed by XAS for comparison. The resin was reacted with a 1000 ppm Cr(III) solution at pH 5.0 for approximately 1 h followed by rinsing with DI water three times to remove any unbound chromium.

X-ray absorption spectra were collected for the Cr K-edge (5989 eV) at beam-line 7-3 at the Stanford Synchrotron Radiation Laboratory (SSRL). Standard operating conditions were 3 GeV and 50–100 mA beam current. A Si (1 1 1) double crystal monochromator with an entrance slit of 1 mm was utilized for all the measurements. The monochromator was de-tuned approximately to 50% to reduce interference from higher order harmonics. All samples and model compounds were measured as solids and packed into 1 mm path-length aluminum holders with mylar tape windows. In addition, in order to reduce damping from the Debye–Waller factor, all samples were run at approximately 10 K by using a liquid helium cryostat. Fluorescence XAS data for the samples was collected with a Canberra 13-element germanium detector. On the other hand, transmission XAS data was collected for the $Cr(NO_3)_3{\cdot}9H_2O$ and $K_2Cr_2O_7$ model compounds using argon filled ion chambers. The model compounds were ground and diluted with X-ray transparent boron nitride prior to measurements. The calibration for all spectra was performed against the edge position of Cr(0) foil. Several scans (2–4) were averaged for each XANES and EXAFS spectra to improve the signal to noise level.

The analysis of the experimental EXAFS data was performed with the EXAFSPAK software package obtained from SSRL using standard methods [18,19]. In short, the background of the pre-edge region was removed by means of polynomial linear fit subtraction. This was followed by a spline removal of three segments and normalization of the data by means of a Victoreen polynomial. The EXAFS energy spectra were then converted to wavevector k space. The resulting scattering curve was weighted by k^3, to enhance damped scattering oscillations, before Fourier transformation to yield the radial structure function. The first shell contribution to the radial structure function was isolated by Fourier filtering (transforming back into k space) the first peak (R-window ∼1–2.2 Å). The total phase and amplitude shift functions were calculated with the ab initio, single-scattering code FEFF (v. 6.01) [20]. Nonlinear least square fits (shown in Figs. 5 and 6) were obtained to approximate the coordinating environment of the involved ligands on the biomass with the metal ion studied.

3. Results and discussion

Fig. 1 shows the effect of pH on the percentage binding of Cr(III) and Cr(VI) to oat biomass. As seen from the figure, the binding of both Cr(VI) and Cr(III) is pH dependent.

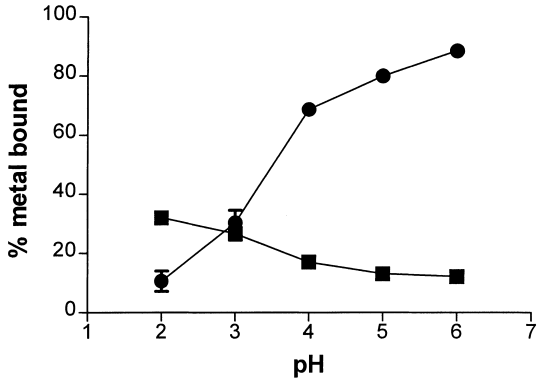

Fig. 1. pH profile for Cr(VI) (■) and Cr(III) (●) by oat biomass; 10 mg of oat biomass were reacted with 2 ml of 0.1 mM solution of Cr(VI) and Cr(III) separately at pH 2, 3, 4, 5, and 6 for 1 h. The pH was adjusted for the biomass and the metal separately before the reaction. Error bars indicate 95% confidence interval.

However, the amount of Cr(III) bound to oat biomass increases as the pH increases with a maximum of nearly 90% binding at pH 6, while the maximum binding of Cr(VI) to the oat biomass was nearly 32% at pH 2. This trend in pH dependency suggests that the binding of the metals to the biomass is through an ion exchange mechanism [21]. Several studies have been performed with other biomasses which have shown similar pH dependent binding as seen with the Cr(III) and may indicate that the metal ion binding may be occurring via functional groups such as carboxylic ligands found within the cell walls of the biomass [4,21]. The ionization constants for various carboxyl groups have been reported to be around 3–4 [22]. Therefore, at pHs higher than 4, the carboxyl group is deprotonated, making the uptake of Cr(III) cations possible by the cell walls of the biomass. In contrast, Cr(VI) behaves as an oxo-anion (CrO_4^{-2} or $Cr_2O_7^{-2}$) in aqueous solution with an overall charge of -2 and may not bind to a negatively charged functional group such as carboxylates because of the repulsion of charges [4,10]. Therefore, the binding of Cr(VI) at low pHs could be occurring either via positively charged ligands (e.g. amino groups) or through the reduction of Cr(VI) to Cr(III) subsequently resulting in the binding of Cr(III) to the biomass. Other researchers have shown that biomasses, such as *Bacillus* or humic substances have the ability to reduce Cr(VI)–Cr(III) either through enzymatic or iron cofactor processes [2,23].

In order to determine how the exposure time affects the amount of chromium binding by the oat biomass, time dependent experiments were performed. Fig. 2 demonstrates the percentage of chromium bound by the oat biomass for the various time exposures studied. While both Cr(VI) and Cr(III) bound rapidly to the oat biomass within a 5 min period, binding of Cr(III) increased as a function of time up to 120 min and Cr(VI) remained somewhat stable. The trend in binding of Cr(III) suggests that the binding may be through interactions with functional groups located on the surface of the oat cell tissue. However, the mechanism of Cr(VI) binding is different. This difference in binding could be due to the reduction of Cr(VI) to Cr(III), thus liberating the responsible ligand for Cr(VI).

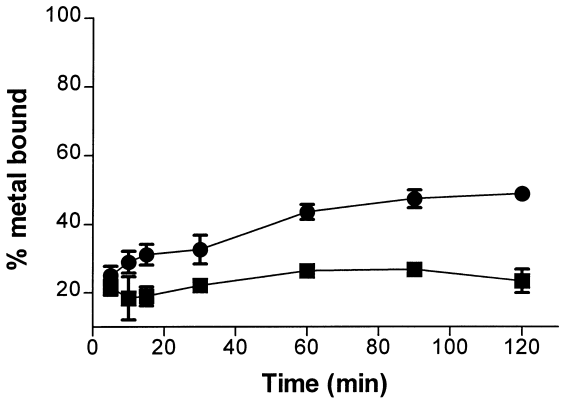

Fig. 2. Time dependency experiment for Cr(VI) (■) at pH 2, and Cr(III) (●) at pH 5 by oat biomass; 10 mg of oat biomass were reacted with 2 ml of 0.3 mM Cr(VI) and Cr(III), respectively, for intervals of 5, 10, 15, 30, 60, 90, and 120 min separately. Error bars indicate 95% confidence interval.

Temperature may play an important role in the reduction of Cr(VI) to Cr(III). Therefore, batch Cr(VI) binding experiments were performed at pH 2.0 to determine the temperature dependency of Cr(VI) binding and subsequent reduction by oat biomass. Fig. 3 shows the effects of temperature on the percentage of chromium bound by the oat biomass as a function of time. These results indicate that oat biomass is able to adsorb greater amounts of Cr(VI) as the temperature was increased from 8 to 54°C temperature range. In addition, with increased time exposure, greater amounts of Cr(VI) were adsorbed. However, equilibrium was not achieved within the 72 h of exposure time, indicating that the process is not only temperature dependent, but also time dependent. This phenomenon could indicate that the oat biomass could be catalyzing the reduction of Cr(VI) to Cr(III).

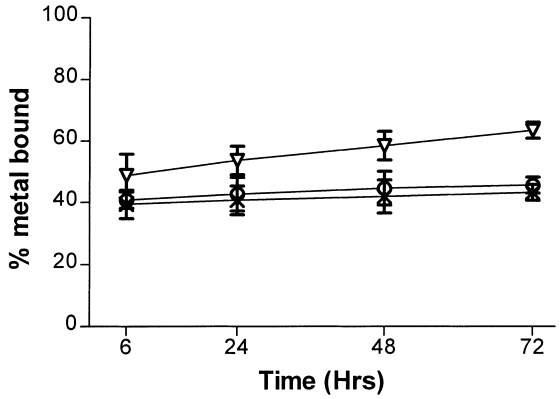

Fig. 3. Temperature dependency for 1000 ppm Cr(VI) at 8°C (×), 26°C (○), and 54°C (▽); 300 mg of oat biomass per 10 ml of Cr(VI) were reacted in triplicates at 6, 24, 48, and 72 h at pH 2. Error bars indicate 95% confidence interval.

As demonstrated by the pH profile seen in Fig. 1, the binding of Cr(III) by oat biomass was reduced at lower pHs. Therefore, if the bound Cr(VI) had been reduced to Cr(III), it should be desorbed by reducing the pH. In this experiment, the biomass from the temperature dependent studies were first washed with DI water, and then exposed to 0.2 M HCl. The supernatants from these reactions were then analyzed for chromium content by atomic absorption spectroscopy(data not shown). We noted that strippings (supernatant from reaction with 0.2 M HCl) from the biomass had turned purple, indicating the formation of Cr(III). Although the reduction of Cr(VI) to Cr(III) may occur in highly acidic solutions, the biomass free Cr(VI) control had shown no color change, indicating that the oat biomass had some how accelerated or catalyzed this reduction. The intensity of the color formation increased with temperature and time exposures, giving the deepest purple color for the supernatant of the biomass reacted at 54°C for the 72 h period. The purple color formation, which is characteristic of Cr(III), may also support the reduction of Cr(VI) to Cr(III) by the oat biomass, as seen by other researchers with *Spirulina* and humic biomasses [23,24].

Since the apparent binding and reduction of Cr(VI) by the biomass increased with temperature and time, an endothermic process could be responsible for such a mechanism. In order to better understand this process, Van't Hoff's equation $(\ln(K_2/K_1) = (\Delta H^0(T_2 - T_1))/RT_2T_1$, where $R = 8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}$) was utilized to calculate the apparent enthalpies for the binding of Cr(VI) to oat biomass at pH 2.0. When calculating the enthalpies (ΔH^0), the K_2 and K_1 were replaced by the distribution ratio values, D, which is the ratio of the metal ion absorbed by the biomass versus the metal ions in solution at equilibrium [23,24]. This was necessary since the equilibrium constants cannot be used due to the complexity of the biomass cell walls where more than one unknown group may be binding Cr(VI) to the biomass. Thus, the values calculated are not true thermodynamic equilibrium constants, but will help us to gain further insight into the binding process of Cr(VI) by the oat biomass. The values for the estimated enthalpies of Cr(VI) binding by oat biomass are shown in Table 1. As seen in Table 1, the calculated ΔH^0 are all positive and increase with temperature and time. Small positive enthalpies typically are characteristic of metal ions coordination with carboxyl groups, whereas coordination with amino and sulfhydryl

Table 1
Apparent ΔH values for Cr(VI) binding to oat biomass[a]

$R\times n$ time (h)	Temperature range (°C)	Apparent ΔH (kJ/mol)	95% C.I., +/−
6	8–26	2.20	0.60
	26–54	9.42	2.47
24	8–26	3.09	0.87
	26–54	12.95	2.73
48	8–26	4.24	0.98
	26–54	16.29	4.48
72	8–26	3.74	0.77
	26–54	21.34	4.44

[a] Apparent heats of formation for Cr(VI) binding oat biomass at different reaction times.

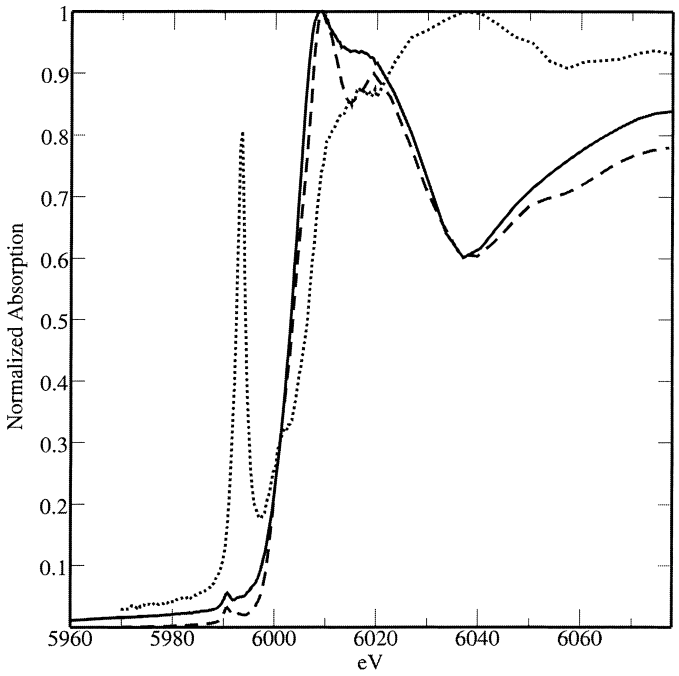

Fig. 4. XANES: $K_2Cr_2O_7$ (···); Oat + Cr(VI) (—); and $Cr(NO_3)_3$ (- - -).

groups results in large negative enthalpies. As seen in Table 1, the apparent enthalpies for Cr(VI) binding by the biomass increased with temperature and time exposure. However, the small positive enthalpies exhibited are characteristic of carboxylic functional groups, as indicated for Cr(III) binding in the pH profile experiment. This data further indicates that the biomass is catalyzing the reduction of Cr(VI) to Cr(III). Therefore, a possible answer could be that the Cr(VI) is bound and then reduced to Cr(III) by positive functional groups (such as amines) and subsequently adsorbed by available carboxyl groups.

In order to further examine the reduction of Cr(VI) to Cr(III) by the oat biomass, X-ray absorption spectroscopic studies were performed. X-ray Absorption Near-Edge Structure (XANES) is a technique used to determine oxidation state, coordination geometry, and the nature of the bond between the absorbing atom and its ligands [25]. The XANES spectra for the oat biomass reacted with Cr(VI), as well as for the Cr(VI) and Cr(III) model compounds, are depicted in Fig. 4. The pre-edge feature of the Cr(VI) model compound (∼5993 eV) is due to a bound state 1s to 3d transition, which is enhanced by its $3d^0$ electronic configuration [26]. This peak is not present in the Cr(III) XANES because octahedral $Cr(III)O_6$ has a center of symmetry and this transition is forbidden; Cr(VI) is tetrahedral, thus, the transition is allowed due to the Cr(3d) with O(2p) orbital mixing [26].

It is evident that the pre-edge peak characteristic of Cr(VI) is absent in the XANES of the oat biomass sample. On the other hand, the near-edge structure of the biomass is similar to the Cr(III) model compound. Thus, we may conclude that the oat biomass is reducing

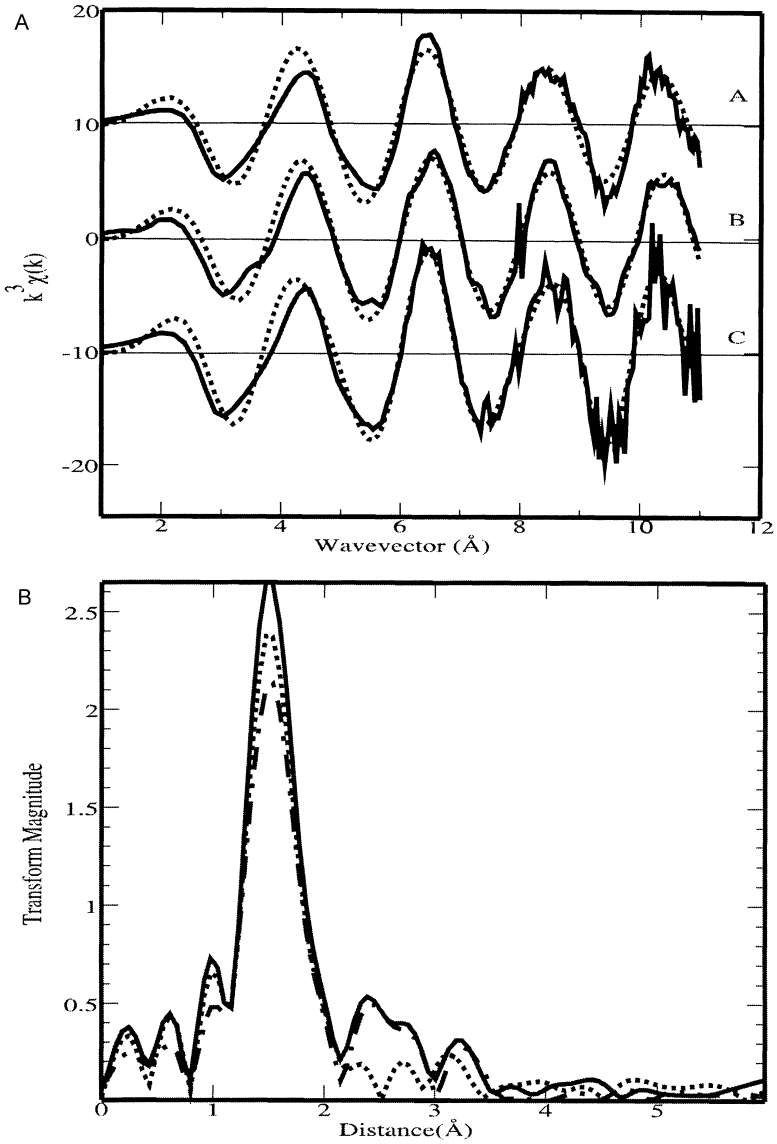

Fig. 5. (A) EXAFS: Resin + Cr(III): A, $Cr(NO_3)_3$: B, Oat + Cr: C; experiment (—); fitting (···). (B) Fourier Transform EXAFS (Radial Structure Function): Resin + Cr(III) (–·–·); Oat + Cr (—); and $Cr(NO_3)_3$ (···).

the much more toxic (VI) state of chromium to the less toxic (III) state. Further XANES combined with kinetic experiments are needed to determine the mechanism of this reaction.

Extended X-ray Absorption Fine Structure (EXAFS) is a tool that is becoming more and more popular in the determination of the coordination environment of metal ions in biological systems [14,27]. Fig. 5A and B show the k^3 weighted EXAFS spectra and the

corresponding Fourier Transform, respectively, for Cr(III)NO_3, oat biomass reacted with $K_2Cr_2O_7$, and a weak cation exchange resin loaded with Cr(III) ions. Since other biosorbents have indicated that Cr(III) coordination is via carboxylic groups, a weak cation exchange resin consisting of carboxyl groups was included in the EXAFS study for comparison with the oat biomass [14]. In addition, carboxylic groups have been found to be heavily involved in the biosorption of other metal ions of similar and different oxidation states [27]. From close comparison of the Fourier Transforms, we may see that the coordination environment of the resin is very close to that of the biomass. This indicates that the binding could be through similar ligands (most likely carboxyl groups).

The fitting for the first shell of the EXAFS data for the biomass sample is shown in Fig. 6. The corresponding results, along with the results of the fittings for the other samples, are given in Table 2. The *R* distance from the Fourier Transforms, which is around 2 Å, may correspond to either oxygen or nitrogen ligands, but because neighbors in the periodic table have similar phase shifts and scattering potential it is difficult to differentiate between them in the EXAFS data [28]. On the other hand, better fits were obtained with oxygen than with nitrogen ligands (data not shown). In addition, typical coordination bond lengths from Cr(III)–oxygen range from ∼1.90 to 1.98 Å, while Cr(III)–nitrogen range from ∼2.06 to 2.125 Å [29]. This further indicates that the ligand could be an oxygen atom rather than a nitrogen atom. Moreover, the similarity of the EXAFS from the weak cation-exchange resin

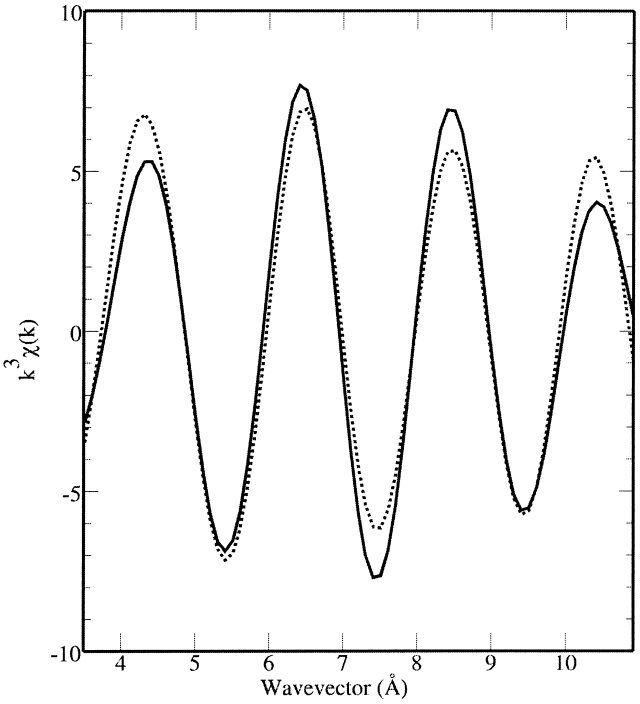

Fig. 6. Isolated first shell EXAFS: Oat biomass (—); fitting (···).

Table 2
EXAFS fitting results for Cr–Oat samples[a]

Compound	*N*	*R* (Å)	σ^2
Cr–Oat	5	1.98	0.003
Cr(III)–Resin	5	1.97	0.001
Cr(III)NO_3	6	1.97	0.002

[a] *N* refers to the coordination number of Cr in the sample. The interatomic distance (*R*) between the coordinating atom and the Cr was taken from first shell fits of the corresponding EXAFS data. The Debye–Waller factor is represented by σ^2.

to that of the biomass suggest oxygen ligation, and further supports the concept of Cr(VI) reduction to Cr(III) and subsequent binding by carboxylic groups.

4. Conclusion

We observed that the binding of both Cr(III) and Cr(VI) by the oat biomass are pH dependent processes, with a maximum binding of Cr(III) at pH 5.0, while Cr(VI) bound best at pH 2.0. These data indicate that the initial interaction of the different chromium species was through different ligands. The pH profile observed for Cr(III) suggested that binding is occurring through negatively charged ligands such as carboxylic groups with p*K*a values near three to four, while Cr(VI) may be binding by positively charged ligands such as amine groups. Stable binding was observed for Cr(VI) over a 120 min period while Cr(III) binding increased as time increased. Temperature and time dependent studies indicated an increased binding for Cr(VI) with increasing temperature and time exposure periods. However, desorption experiments from the Cr(VI) temperature study resulted in purple supernatants (indicative of Cr(III)), while biomass-free controls showed no color change. X-ray absorption studies further corroborated the reduction of Cr(VI) to Cr(III) by the oat biomass. Furthermore, EXAFS studies demonstrated that the reduced Cr(III) was bound to oxygen containing ligands (possibly carboxyl groups) similar to that of a weak cation-exchange resin. These results suggest that binding of Cr(VI) and subsequent reduction of Cr(VI) to Cr(III) is somehow catalyzed by the oat biomass. Therefore, byproducts of the cultivation of *A. monida* (oat) may have the advantage of converting Cr(VI) to the less toxic Cr(III), and could potentially be used for the removal of chromium from wastewaters through a cost-effective and environmentally friendly process.

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