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Mechanism of electron transfer in the bioadsorption of hexavalent chromium within *Leersia hexandra Swartz* granules by X-ray photoelectron spectroscopy

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ABSTRACT

Leersia hexandra Swartz biogranules were used to adsorb Cr(VI) from aqueous solutions. Batch biosorption experiments showed that the Cr(VI) concentration sharply decreases in the first 15 min. The main functional groups that may be involved in chromium sorption were determined using Fourier transform infrared spectroscopy. The use of X-ray photoelectron spectroscopy confirmed the reduction of Cr(VI) to Cr(III) through *L. hexandra Sw*. Results indicate that Cr(III) is the dominant species on the surface of the biogranules and that the redox reaction can be accomplished within 40 min. The mechanism of electron transfer during Cr(VI) reduction to Cr(III) was investigated. Protonation of the oxygen-containing groups produces electrostatic-sorption power over Cr(VI). The nitrogen-containing groups serve as the electron-donor groups in the process of reduction–sorption. Moreover, after the complete reduction of Cr(VI), the pH of the suspension significantly increases.

1. Introduction

In recent years, environmental pollution caused by chromium has become a significant concern because of its use in a wide variety of applications, such as in electroplating, leather tanning, metal finishing, chromate preparation, and textile industries. Phytoremediation or the use of hyperaccumulator plants to clean up environmental contaminants has been used to solve heavy metal pollution. It has attracted increasing attention for its cost-effectiveness and environmentally friendly aspect, especially when it is used for cleaning low concentrations of heavy metal [1]. To date, numerous reports have been made on the removal of chromium ions from aqueous solutions using different organisms as adsorbents. These organisms include walnut hull [2], *Eichhornia crassipes* [3,4], *Cladonia rangiformis*(L.) [5], *Aspergillus niger* [6], *Ceramium virgatum* [7], and *Sargassum* sp. [8], among others.

Various reports have focused on the removal and reduction of heavy metals using several plant species. Extensive research has explored the biomass biosorption capability and the equilibrium thermodynamic and kinetic model of chromium adsorption [9–11]. The main purpose was to obtain useful information on the mechanism of heavy metal adsorption.

At present, the mechanism for chromium biosorption is usually based on the reduction of Cr(VI). To prove heavy metal reduction by the biomaterial, heavy metal species on the surface of the biomass are analyzed using several analytical techniques, such as X-ray photoelectron spectroscopy (XPS) [12], extended X-ray absorption fine structure (EXAFS) spectroscopy, and X-ray absorption near edge structure (XANES) spectroscopy [13–15]. According to Park et al. [16–18], the direct and indirect reduction mechanism of chromium-binding groups on the biomaterial during Cr(VI) biosorption and the valence variations of Cr(VI) can be clearly analyzed by determining the dominant heavy metal species on the surface of the material. Park et al. suggested that anionic Cr(VI) first bind with positively charged groups on the biomaterial surface. Subsequently, adjacent electron-donor groups reduce Cr(VI) to Cr(III). Finally, Cr(III) is released into the aqueous phase because of the electronic repulsion between the positively charged groups and Cr(III) or the complexation of the reduced Cr(III) with adjacent groups. However, scarcely any research has delved into the dynamic trend and direction of electron transfer between the characteristic functional group elements and metal ions.

Leersia hexandra Swartz is a newly discovered chromium hyperaccumulator. Our previous reports centered on its hyperaccumulation capability [19] and the removal of Cr(VI) and Cr(III) using abiotic biomass [20]. Batch experiments have been performed to investigate the biosorption process kinetics and equilibrium isotherm models of Cr(VI) and Cr(III) biosorption. Batch experiments were also conducted on the chemical interaction between functional groups on the surface of *L. hexandra Sw.* biomass and

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chromium in order to better understand the binding behavior of different species of chromium ions on the biomass surface.

However, reports involving the redox reaction between Cr(VI) and biomass, in particular, comprehensive information on valence variations of Cr(VI) on the surface of *L. hexandra Sw*. biogranules and the electron transfer mechanism involved, has not been found. Thus, obtaining information on the dynamic trend and direction of electron transfer between the characteristic elements of functional groups on the biomaterial and chromium ions is important.

The objective of this work is to characterize the binding of Cr(VI) to *L. hexandra Sw.* biogranules and its subsequent reduction to Cr(III). The electron transfer in the process of reduction and the adsorption and the sorption sites involved in metal accumulation are investigated. The ability of the granules to adsorb Cr(VI) and the mechanism governing the reduction of Cr(VI) to Cr(III) are investigated as well. The reduction of Cr(VI) on *L. hexandra Sw.* biogranules is determined using Fourier transform infrared (FT-IR) spectroscopy, and X-ray photoelectron spectroscopy (XPS).

2. Materials and methods

2.1. Materials

The samples of *L. hexandra Sw*. were collected from Guilin Botanical Garden, which is located south of Guilin. The *L. hexandra Sw*. plant was washed thoroughly using distilled water to remove soil or debris. The plant sample was oven-dried at 65 °C for 2 days. The dried sample was then ground using a blender and was made to pass through a sieve to obtain uniform particle size (0.3–0.6 mm).

The stock solutions of Cr(VI) were prepared by dissolving 0.2830 g $K_2Cr_2O_7$ in distilled water, and the Cr(III) stock solutions were obtained by dissolving 0.3848 g $Cr(NO_3)_3{\cdot}9(H_2O)$ in distilled water. Working solutions were obtained by the dilution of stock solutions as required. The pH of the solutions was adjusted to a desired value with 0.1 M HCl or 0.1 M NaOH before they were mixed with the biosorbent. All chemicals used were of analytical-reagent grade.

2.2. XPS and FT-IR analysis

The chromium-loaded biomaterials were obtained by immersion in 50 mL, 1000 mg/L of Cr(VI) or Cr(III) solutions at various adsorption times of 3, 20, and 60 min, respectively. The different loaded biogranule samples were oven-dried at 65 °C for 3 days.

A Kratos XSAM800 X-ray photoelectron spectrometer with an MgKα incident X-ray beam was used to record the XPS spectra of chromium ions bound on the *L. hexandra Sw*. biogranule surface. The X-ray source was operated at 100 W, and spectra were recorded at 12.5 kV. Calibration of the binding energy of the spectra was performed with the C 1s peak of the aliphatic carbons (284.6 eV) as reference. Analysis of the adsorbed chromium oxidation state was conducted by comparing the experimental spectra with those of the standard Cr(III) and Cr(VI).

To provide a preliminary and qualitative analysis of the main functional groups that could participate in the biosorption of metal chromium ions, the solid phase was analyzed by FT-IR spectroscopy (Nicolet Nexus 470 FT-IR spectrometer). Samples (10 mg) were mixed with (300 mg) KBr and pelletized. FT-IR spectroscopy was performed at a resolution of 1 cm^{-1} from 4000 to 450 cm^{-1}.

2.3. Batch sorption experiments

Biosorption studies were performed using procedures similar to those used in previous research [20]. Briefly, 250 mg of dry biogranules was washed twice with 0.01 M HCl by centrifugation to remove any debris or soluble biomolecules that might cause interference. Then, the biomass was cleaned with deionized water thrice before the batch biosorption experiment. The biomass was then resuspended in 50 mL deionized water with a final biomass concentration of 5 mg mL^{-1}. The Cr(VI) solution (100 mg L^{-1}) was mixed with the biomass suspension (5 mg mL^{-1}) at pH 2.0 ± 0.1. Samples were taken at different time intervals and centrifuged immediately to remove the biomass. Supernatants were then transferred, and tubes were cleaned by decantation to analyze Cr(VI) and total chromium ion concentrations.

To examine the change in initial pH, 5 mg/mL of *L. hexandra Sw.* biogranules was immersed in Cr(VI) solution, with concentrations varying from 10 to 100 mg/L. The initial pH and final solution pH were measured with a pH meter. Each experiment was repeated thrice for statistical analysis. The pH was not controlled during the batch experiment. All experiments were conducted at room temperature (25 ± 1 °C).

2.4. Chromium analysis

The concentration of Cr(VI) in the supernatant liquid was analyzed at 540 nm using a UV/Vis spectrophotometer (Model Cecil, CE2021) after forming a complex with 1,5-diphenycarbazide in acidic solution. The total concentration of chromium was determined through flame absorption atomic spectrometry (FAAS). The differences between the total chromium and Cr(VI) yielded the concentrations of Cr(III).

3. Results and discussion

3.1. Characterization of surface functional groups on biogranules

Fig. 1 presents the XPS wide-scan of freshly prepared *L. hexandra Sw*. biogranules under different pH conditions. The photoelectron peaks reveal that the surface of *L. hexandra Sw.* biogranules consists mainly of carbon (287.25 eV, C 1s), oxygen (535 eV, O 1s), and small amounts of nitrogen (399.5 eV, N 1s). A detailed XPS survey on the N 1s and O 1s regions is presented in Fig. 2a and b. The chemical forms of the different elements can be determined according to its binding energies. The single peak and binding energies suggest that N and O mainly exist in the form of –NH– [21] and –OH [22].

FT-IR spectroscopy was used to investigate the major functional groups involved in the Cr(VI) reduction process. The major peaks observed in virgin *L. hexandra Sw.* are as follows: The region between 1800 and 3500 cm^{-1} contains two major absorption bands located at approximately 3416 cm^{-1} (N–H stretching vibration) and 2920 cm^{-1} (C–H stretching of $–CH_2$ groups). The stretching vibration of the C–O and C–N (amide I) bonds of the protein is at 1654 cm^{-1}. The region between 1550 and 1000 cm^{-1} is the fingerprint region, which contains the C–O bending vibration (1374 cm^{-1}) and C–OH stretching vibration (1060 cm^{-1}). The absorption peak at 1518 cm^{-1} can be attributed to the amide I band of the protein peptide bonds [23]. The band at 1738 cm^{-1} is attributed to the stretching vibration of the ketone C=O.

The spectrum corresponding to the *L. hexandra Sw.* loaded with Cr(VI) exhibits an apparent shift in the band absorption peak 1518 cm^{-1} and a few changes in the other bands. These results indicate that the amide groups specifically play a major role in Cr(VI) binding, whereas carboxyl and hydroxyl groups play a minor role in Cr(VI) chemical binding, as illustrated by the slight changes in the peak wave number (1738, 1160, and 1060 cm^{-1}) and shape. The results provide sufficient evidence of the chemical interaction between chromium and nitrogen-containing (NC) functional groups on the surface of *L. hexandra Sw.* biogranules. Moreover,

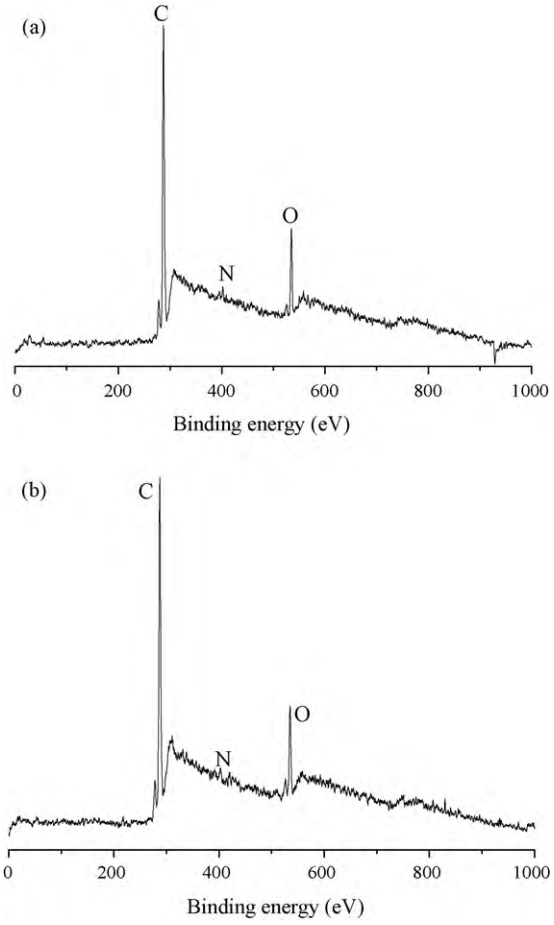

Fig. 1. XPS wide-scan survey of atiosic *L. hexandra Sw.* biogranules at pH = 2.0 (a) and pH = 5.0 (b).

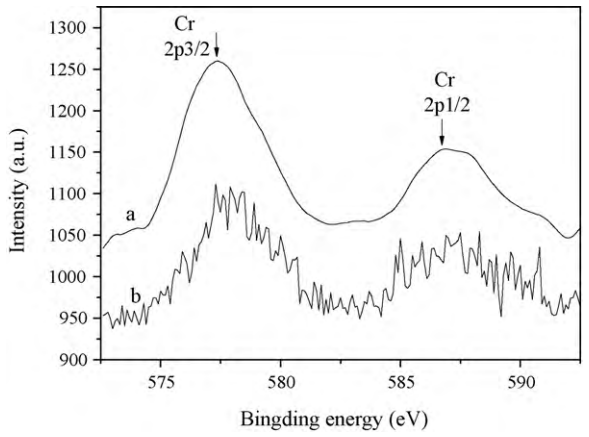

Fig. 3. Cr 2p XPS spectra of atiosic biogranules loaded with 1,000 mg/L Cr(VI) at pH 2.0 (a) and 1,000 mg/L Cr(III) at pH = 5 (b).

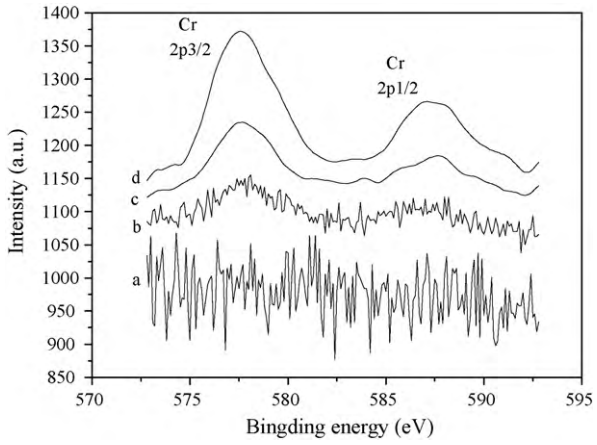

Fig. 4. XPS spectra of *L. hexandra Sw.* biogranules loaded with 0 mg/L Cr(VI) (a) and 1,000 mg/L Cr(VI) under an immersion time of 3 min (b), 20 min (c), and 60 min (d) at pH = 2.0.

oxygen-containing (OC) functional groups of biogranules are evidently not involved in the chemical adsorption of Cr(VI).

3.2. Reduction–adsorption of Cr(VI) in situ

To determine the change in the oxidation state of the chromium that is bound to the granules during biosorption, chromium sorbed onto atiosic *L. hexandra Sw.* biogranules after being sufficiently immersed in 1000 mg/L Cr(VI) and Cr(III) solutions was analyzed by XPS. The spectra of chromium loaded on *L. hexandra Sw.* and the Cr(VI) and Cr(III) standard spectra are shown in Fig. 3a and b, respectively.

The XPS spectrum presented in Fig. 3a displays two Cr 2p peaks. The Cr 2p3/2 and Cr 2p1/2 peaks in the spectrum of the biomass loaded with Cr(VI) are located at 576.8 ± 0.1 and 586.7 ± 0.1 eV. The values are close to the binding energy of the references in Cr(III). Therefore, Cr(III) is present on the surface of *L. hexandra Sw.* biogranules when it was immersed in Cr(VI). This implies that the adsorption process involved the reductive transformation of Cr(VI) into Cr(III) on the contact surface.

The effect of immersion time on the reduction of Cr(VI) was also investigated. As illustrated in Fig. 4, the peak for the Cr 2p3/2

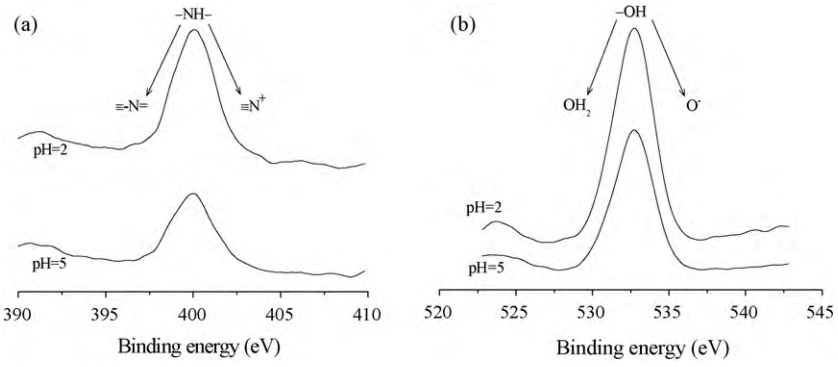

Fig. 2. Typical XPS spectra of N (a) and O (b) of virgin *L. hexandra Sw.* soaked in solutions with different pH levels.

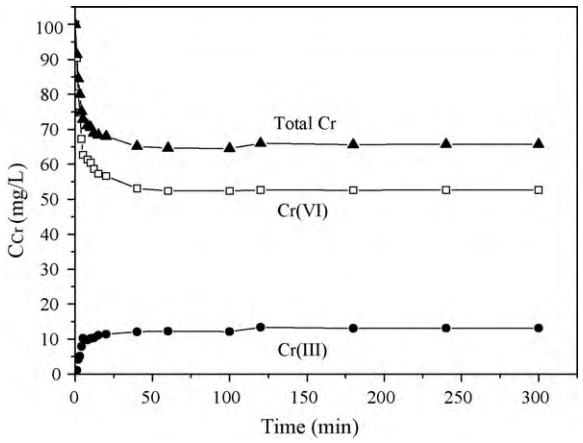

Fig. 5. Concentration change of Cr(VI) and Cr(III) in supernatant liquid after 100 mg/L Cr(VI) adsorption by 5 mg/mL of biogranule at pH = 2.0.

orbital increases with increasing immersion time because more chromium is bound to the biogranules. The results imply that the redox reaction occurring on the biogranule surface may be extremely fast. Thus, Cr(VI) may be reduced to Cr(III) within 60 min. Several authors have reported that *Ocimum americanum* [24], grape stalks and yohimbe bark [25], *Avena monida* (oats) [13], *A. niger* [26], *Chlorella miniata* [27], and *Cladophora albida* [28] also possess the capacity to reduce Cr(VI) to Cr(III) at acidic pH.

The chromium concentration profiles in the supernatant liquid were investigated to examine the Cr(VI)-reductive characteristics of *L. hexandra Sw*. The Cr(VI) concentration decreases sharply within the first 15 min (Fig. 5). Moreover, Cr(III) appears in the supernatant liquid after the biogranules were immersed in Cr(VI) solutions. The presence of Cr(III) in the solution indicates that *L. hexandra Sw.* biogranules possess the ability to reduce Cr(VI) to Cr(III) under the present experimental conditions. Fig. 5 shows the reduction trend toward equilibrium within 40 min.

3.3. Mechanism of reduction–adsorption

Protonation of the functional groups of biogranules at low pH is easy, especially for OC functional groups [29]. The abundant groups on the surface of *L. hexandra Sw*. are easily protonated, and hydroxyl ions are released into the solution, which raise the equilibrium pH. This is similar to earlier observations of other authors on the increase of the pH value of the solution after Cr(VI) sorption on other biomaterials, such as *yohimbe* bark [25], *hazelnut* shell [30], *eucalyptus* bark [31], and biogas residual slurry [32]. The process of

Table 1
Variation of solution pH after Cr(VI) adsorption on *L. hexandra Sw* biogranules.

Cr(VI) (mg/L)	$pH_{intianl}$	pH_{final}	ΔpH
10	2.04	2.26	0.22
20	2.06	2.24	0.18
30	2.04	2.19	0.15
50	1.96	2.12	0.16
80	2.03	2.23	0.20
100	1.76	1.92	0.16

protonation yields the following formula (1):

$$C_xN_yO + 2H_2O \rightarrow C_xN_yOH_2^+ + 2OH^- \quad (1)$$

Cr(VI) ions in the acidic solution are possibly a different kind of anion species that is prone to adsorb on the protonated active sites of the biosorbent, primarily at low pH, as a result of electrostatic interaction. The progress can be expressed as the following equation:

$$C_xN_yOH_2^+ + HCrO_4^- \rightarrow C_xN_y(OH_2)(OCrO_3H) \quad (2)$$

Combining Eqs. (1) and (2), the following is obtained:

$$C_xN_yO + 2H_2O + HCrO_4^- \rightarrow C_xN_y(OH_2)(OCrO_3H) + 2OH^- \quad (3)$$

As illustrated in Table 1, the increase in the final solution pH suggests that protons are involved in Cr(VI) adsorption. This further verifies the theory on the protonation of OC functional groups. However, the valence of chromium anions remains unchanged in this electrostatic adsorption process.

Fig. 6 demonstrates that the peaks of O and N shift in the XPS spectra. A fundamental relation between XPS shifts and charge is available for oxygen in the following formula [33]:

$$Q = -4.372 + \frac{[385.023 - 8.976 \times (545.509 - E_B)]^{1/2}}{4.488}$$

where Q is the average oxygen charge (esu), and E_B is the experimental value of binding energy (eV). As illustrated in Fig. 6a, the binding energy of O 1s spectrum exhibits negligible change from 523.7 to 523.9 eV after Cr(VI) adsorption. The average oxygen charges at these two values are −1.307 and −1.292, respectively, indicating that the binding energy of the inner electron of O 1s has a slight variation. This suggests that OC functional groups can adsorb Cr(VI) but cannot supply the electron charge. Thus, the OC groups have no reducing capacity for Cr(VI). This is consistent with the previous conclusion.

The binding energy of the typical XPS spectra of N 1s exhibits a significant change from 400 to 401.3 eV after adsorption of Cr(VI) for 20 min. This suggests that the nitrogen electron binding energy of the inner layer of electrons increases. Nitrogen has an obvious tendency to lose electrons, making it positively charged. The neg-

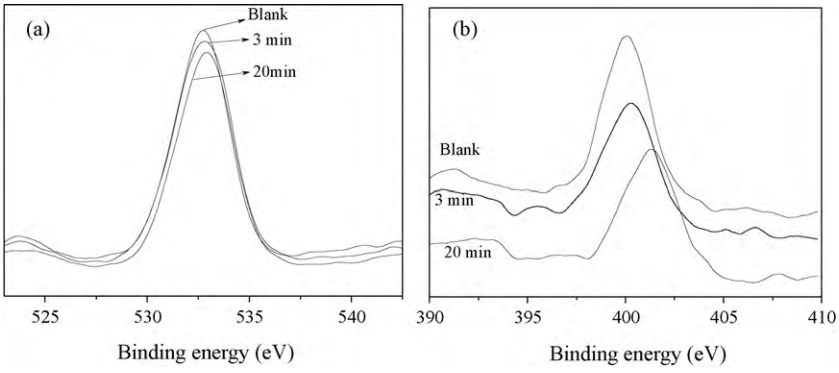

Fig. 6. XPS of O (a) and N (b) in *L. hexandra Sw.* biogranules.

ative charge on the surface of nitrogen moves from the inner layer of the biogranules to their outer shell. The nitrogen-containing electron-donor groups exhibit a loss of electrons in the process of Cr(VI) reduction.

4. Conclusion

Using XPS, the reduction of Cr(VI) to Cr(III) in situ was determined on *L. hexandra Sw.* Cr(III) was the dominant species on the surface of the biogranules. The protonation of OC groups in a low-acid environment produced electrostatic interactions that enabled Cr(VI) sorption. The increase in the solution pH was attributed to the release of hydroxide ions during the hydrolysis reaction. The NC-groups served as electron-donor groups in the process of reduction–sorption. This capacity for fast adsorption on surface functional groups contributed to the hyperaccumulation ability of *L. hexandra Sw.*

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