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Application of a by-product of *Lentinus edodes* to the bioremediation of chromate contaminated water

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Abstract

The agricultural by-product of *Lentinus edodes* was used as a novel biosorbent for bioremediation of chromate contaminated waste water in the simulated experimental conditions. The contact time, particle size, biosorbent dosage and optimum pH range were investigated to optimize the sorption condition. The biosorption by the biomass was strongly affected by pH. At pH 1.0–2.5, all hexavalent chromium was diminished, either removed by the biosorbent or reduced to less toxic trivalent chromium even in very high concentration of 1000 mg/L. The adsorbed hexavalent chromium and reduced trivalent chromium were both linearly dependent on the initial chromium concentration. Most uptake of Cr occurred at pH around 4. The maximum uptake of chromium was 21.5 mg/g when simulated with Langmuir model, which showed the potential biosorption capacity of this biomaterial. The change of oxidation–reduction potential (ORP) during biosorption process revealed strong reduction ability of this biosorbent. Comparing analysis from Fourier transform infrared spectrums indicated that nitrogen oxide and carboxyl groups were increased after biosorption. The energy-dispersive X-ray microanalyzer revealed the mechanism of cation exchange during biosorption.

Keywords: Bioremediation; Waste water; Chromium; Agricultural by-product

1. Introduction

Soluble hexavalent chromium among heavy metals are extremely toxic and exhibit carcinogenic effects on biological systems due to their strong oxidizing nature among heavy metals [1]. The industrial waste water from electroplating, pigment, metal cleaning, leather processing and mining is the main source causing water pollution. Many strategies are investigated to remove chromium from solutions such as chemical reduction, electrochemical treatment, ion exchange, etc. [2–4]. But obvious disadvantages, such as high energy requirements, incomplete metal removal, high quantity of toxic waste sludge and inhibit the application of the conventional strategies [4].

Bioremediation is an alternative method that has emerged in recent years to treat the waste water instead of the traditional processes. Plants, hydrophytes or microorganisms attract more attention of researchers to exploit the new field to protect the finite resources. The applications of microorganisms, such as bacteria [1,5–7], fungi [2,8], algae [9,10], dead microbial biomass [11] and other biomaterials [4,12,13], are the hot topics in this research realm. The prominent advantages are the selectivity of heavy metal from solutions and the high removing efficiency in low metal concentration [14]. But time consuming process and growing cost of appropriate biomass are the main drawbacks of the biosorption with living biomass. So research interest has turned to the dead biomass which is abundant at low cost.

The removal of heavy metals by plant tissues or by biomass by-products from agricultural, industrial or pharmaceutical industry has been proved with high efficiency and very low cost [3,15]. Cone biomass of *Thuja orientalis* can efficiently adsorb copper(II) from aqueous solutions [16]. Cone biomass of *Pinus sylvestris* has biosorption ability for chromium(VI) [4]. The rice milling by-product—rice husks, can be also used to treat the heavy metal containing solutions including Cd(II), Pb(II), Al(III), Cu(II) and Zn(II) [17]. These biomaterials are

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of little commercial value and tested good as substitutes for the expensive chemical drugs and live biomass.

These dead biomaterials usually are of low content of heavy metals and large quantity of adsorption sites [17,18,11]. Functional groups for ion exchange such as hydroxyl, carboxyl and phosphate groups are often found from Fourier transform infrared spectrum [17–19]. N-ligand of glucose or chitin in cell wall is of strong complex ability to form coordinated metal complex.

A kind of agricultural biomass by-product—*Lentinus edodes*, is proved to be very efficient to remove Pb(II), Cd(II) and Cr(III) from simulated waste water under experimental condition [19]. This kind of biomaterial is obtained in large quantities from the biggest solid-state-fermentation industry in the world [20]. About five times of the solid residue is brought about compared with the production of fungi. Not only much space is occupied but also some useful materials are wasted. Plentiful of functional groups in chitin, cellulose and mycelium are efficient to complex heavy metal ions [21].

The aim of this study was to investigate the biosorption potential of chromium(VI) and to characterize the biosorbent of the by-product biomass of *L. edodes*. The adsorption capacity of the biosorbent was evaluated by studying the equilibrium adsorption isotherms of Cr(VI) in batch experiment mode. The effect of factors, such as particle size, dose of biosorbent, pH, oxidation–reduction potential and initial concentration, was examined. Fourier transform infrared spectrum and the energy-dispersive X-ray microanalyzer were employed to understand the biosorption mechanism.

2. Materials and methods

2.1. Biosorbent preparation

The by-product biomass of *L. edodes* was kindly presented by the Hunan Academy of Agricultural Sciences, Hunan Province in China. The biomass was oven-dried at 80 °C for 24 h after preliminary crumbing by hand. Then powder biomass, with different particle sizes, was obtained by using a sample mill (Foss Tecator, Sweden) through copper sieves. The ground biomaterial was water washed, redried and stored in polyethylene bottles in vacuum dryer and used as biosorbent in the following experiments.

2.2. Preparation of the dichromate containing solution

A stock solution containing 1000 mg/L chromium was prepared by dissolving potassium dichromate with deionised distilled water. Other different concentrations of chromium solutions were obtained by suitable dilution from the stock solution. The deionised distilled water was used throughout the experiment from a hyperfiltration pure water system (Labconco, Water Pro Plus, USA).

Final concentration of Cr(VI) was determined by a spectrophotometer at a wavelength of 540 nm using the complexing agent of 1,5-diphenylcarbazide in acid medium. The total Cr was determined with the flame atomic absorption spectrometry (FAAS) (AA700, Perkin-Elmer, USA). The reduced Cr(III) was calculated by the difference between the total Cr and Cr(VI) in the solution after filtration.

2.3. Contact time

To determine the contact time required for the adsorption equilibrium experiments, the adsorption dynamics was examined first. The initial concentration of chromium was 100 mg/L, and 20 g/L dose of biosorbent was added to the flask containing 200 mL of chromium solution. Then the flask was agitated on the incubator at 25 °C. Samples were intermittently removed from the flask in order to analyze the chromium remaining in solution. The total volume of samples withdrawn did not exceed 2% of the initial volume (200 mL) for each sampling. All experiments were done in triplicate throughout the study.

2.4. Particle size

Different particle sizes of biosorbent, 2 mm, 1 mm and 450 μm, were used to examine the effect of the granularity to the biosorption. One hundred milligrams per liter chromium solution was added to the biomaterial at the dosage of 20 g/L in an incubator at 25 °C for 24 h. Then the concentration of chromium in the filtered solution was determined.

2.5. Dosage of the biomaterial

To evaluate the optimum dosage of the biomaterial, different mass of the biomaterial were used to adsorb chromium in solution. Biomaterials with weight of 0.125 g, 0.250 g, 0.500 g and 0.75 g were added to 25 mL 100 mg/L chromium, respectively, after enough contacting for 24 h (determined by previous experiment). The filtrate was used to measure the content of Cr(VI) and total Cr with the method mentioned above. pH had not been adjusted.

2.6. Effect of pH and oxidation–reduction potential

One hundred milligrams per liter chromium solution and 20 g/L biomass dosage were utilized in the experiments. Different volumes of acid (0.5 mol/L H_2SO_4) or alkali (1 mol/L NaOH) were added to adjust the pH of the mixture and agitated in the same method as before. In the scheduled interval, the pH and the oxidation–reduction potential (ORP) of the solutions were examined with a pH electrode (E-201-C) and an ORP electrode (ORP-412, mV). The final concentration of Cr(VI) and total Cr were examined with the same methods.

2.7. Initial concentration of chromium

A series of Cr(VI) solution ranging from 20 mg/L, 50 mg/L, 100 mg/L, 200 mg/L, 400 mg/L, 600 mg/L and 1000 mg/L were prepared to determine the equilibrium isotherms following the addition of the biosorbent. The acid or alkali was added to maintain the best adsorption pH condition as determined above. The mixtures were agitated in the same incubator at 25 °C for 24 h.

After that, the concentrations of Cr(VI) and total Cr in the filtration solution were analyzed with the methods mentioned above.

2.8. Characterization of the biomaterial

To obtain the mechanism insights into the biosorption of chromium by the biomaterial, the biomass before or after sorption of chromium was characterized using Fourier transform infrared analysis (FT-IR) and energy-dispersive X-ray microanalyzer.

The infrared spectrums of the biosorbent and chromium-loaded biomass were obtained by a Fourier transform infrared spectrometer (WQF-410). The spectral range varied from 4000 cm^{-1} to 400 cm^{-1}. Some biomass ($\leq$450 μm) was encapsulated in KBr in order to prepare the translucent sample disks.

The energy distribution spectrums before and after adsorption were obtained using the energy-dispersive X-ray analysis (EDAX) with gold coated sample. Twenty kilovolts accelerated voltage, 52 spot size and 11 mm work distance were employed to observe the change in adsorption phenomenon after treatment.

3. Results and discussion

3.1. Kinetics of the biosorption

The biosorption observed in different time intervals is shown in Fig. 1. Unlike other biosorbents, the biomass by-product of *L. edodes* was a special biomaterial when used for chromium(VI) remediation. Trivalent chromium is much less toxic than hexavalent chromium [11]. In addition to some amount of chromium that had been adsorbed on the biomaterial, the amount of the Cr(III) produced by reduction was about 0.7–1.0 mg/g from the beginning. Twenty-four hours were enough for Cr(VI) reduction and for the adsorption of chromium. Hence, other experiments for the adsorption next were done with the duration of 24 h.

3.2. Particle size on the biosorption

Particle size is an important factor that affects the heavy metal biosorption from water. Because the particle with size of 450 μm was relatively easier to prepare than much finer particles, three sizes of biosorbent, 2 mm, 1 mm and 450 μm, were used in 100 mg/L Cr(VI) for adsorption in an incubator for 24 h (Table 1). With the finer biosorbent, the Cr(III) reduced decreased while the uptake of Cr was doubled. Total removal of Cr(VI) achieved was the highest at 450 μm among these three sizes. So 450 μm was chosen for the next experiments.

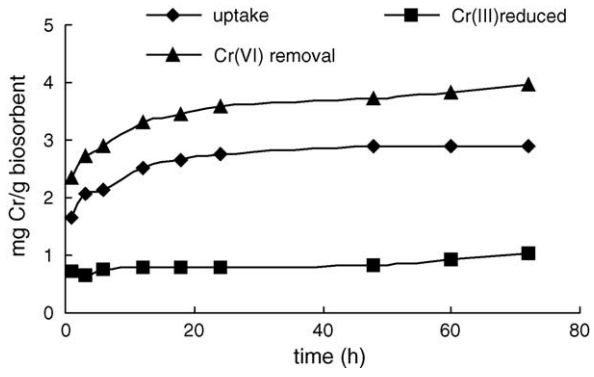

Fig. 1. Effect of time on biosorption (volume = 200 mL, initial concentration = 100 mg/L, biomass dosage = 20 g/L, pH 4.4 and temperature = 25 °C).

Table 1
Effect of particle sizes on biosorption (100 mg/L Cr(VI), 20 g/L dosage, 25 °C)

Particle size	Uptake (mg/g)	Cr(III) reduced (mg)	Cr(VI) removal (mg)
2 mm	1.30	0.76	2.06
1 mm	2.40	0.46	2.86
450 μm	2.90	0.29	3.19

3.3. Dosage of the biomaterial

In order to determine the optimal dosage of the biosorption, different quantities of the biomaterial were used varying from 5 g/L, 10 g/L, 20 g/L and 30 g/L. Based on Table 2, the uptake of chromium increased with the increase of the dosage of biomaterial. But in contrast with the uptake of chromium, the chromium reduced was not changed much with different biosorbent dosages. The removal of chromium, sum of uptake and reduced, was increasing. But the uptake of chromium was not in proportion with the increase of the dosage between 20 g/L and 30 g/L. 3.7 mg/g Cr removal increased if increasing the dosage from 5 g/L to 10 g/L. But there was no significant difference of Cr removal (2.0 mg/g) between the dosages increasing from 10 g/L to 20 g/L and from 20 g/L to 30 g/L. From the economic point of view, in the next experiments, 20 g/L biosorbent was used to get the removal of chromium.

3.4. Effect of pH on the biosorption

pH is a very important parameter that affects the biosorption efficiency [17]. The removal of Cr(VI) from solution was highly dependent on the pH of the solution, which also affected the uptake ability [4]. In this paper, experiments were carried out to study the uptake and reduction of chromium at varied pH in the chromium containing solution (100 mg/L), to optimize the pH condition for the maximum removal.

The sorption phenomenon at different pH varying from 1 to 14 is shown in Fig. 2. The uptake of Cr increased from 1.60 mg/g at pH 1.09 to 3.28 mg/g at pH 4.03. Most uptake of Cr occurred at the pH around 4. Then a distinct decrease of uptake occurred when pH > 4. During the biosorption process, some Cr(VI) was reduced. With the increase in acidity, a continuous increase of

Table 2
Influence of dosage on biosorption (100 mg/L Cr(VI), 20 g/L dosage, 25 °C)

Dosage of biosorbent (g)	Cr uptake (mg/g)	Cr(III) reduced (mg/g)
0.125	0.48	0.40
0.250	0.93	0.42
0.500	1.41	0.44
0.750	1.79	0.57

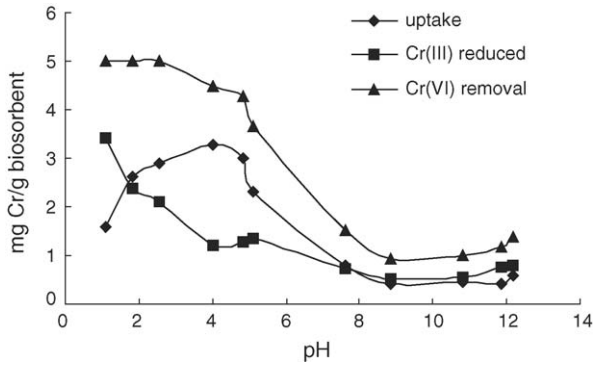

Fig. 2. Effect of pH on biosorption (initial concentration = 100 mg/L, biomass dosage = 20 g/L and temperature = 25 °C).

Cr(III) was observed from 0.8 mg/g at pH 12.2 to 3.4 mg/g at pH 1.09. Cr(VI) removal, that is the total of Cr uptake and Cr(III) produced by reduction, reached the maximum value of 5.0 mg/g, 100% removal of Cr(VI) in the range of 1.09–2.54. The removal efficiency decreased as the pH increased above this range. Similar results were observed by Aravindhan et al. [9] and Ucun et al. [4].

3.5. Effect of ORP

In contrast with other biosorbents, the biomaterial is different on the biosorption behavior because the biomaterial not only adsorbed the chromium from solution but also reduced some high valence chromium to low valence chromium. To get more information to understand the biosorption behavior, the oxidation–reduction potential was examined in two acid ranges on the dynamic sorption duration, in a series of initial Cr(VI) concentration from 20 mg/L to 1000 mg/L.

The ORP values were changed among 334 mV and 710 mV from the graph which showed some oxidation–reduction reaction occurred in the solution, by the addition of the biosorbent. The reduction ability of the biosorbent indicated the reduction of the hexavalent chromium to trivalent chromium in the solution [22]. The ORP potentials were changed during the process of sorption, while most dropped in the first 4 h and less change occurred in later intervals (Fig. 3). This explained the phenomenon shown in Fig. 1 that less Cr(III) was reduced after 4 h at initial concentration of 100 mg/L. There was stronger oxidation ability in high heavy metal containing solutions than in low concentration solutions. The reduction speeds were slower in stronger acid conditions than in less acid conditions. Higher ORP value in acid condition of pH < 2 indicated more Cr(VI) be reduced to Cr(III) than in pH > 4, which was the result of Fig. 2.

3.6. Adsorption isotherm

To study the adsorption isotherm by the biomaterial, a series of different concentrations of Cr(VI) were used to observe the biosorption rule in two acid conditions (pH < 2 and around 4).

In strong acid condition of pH < 2, the sorption characterization was different from other biosorption with the biosorbents such as chitin [23], cone biomass [16] and white-rot fungi [24].

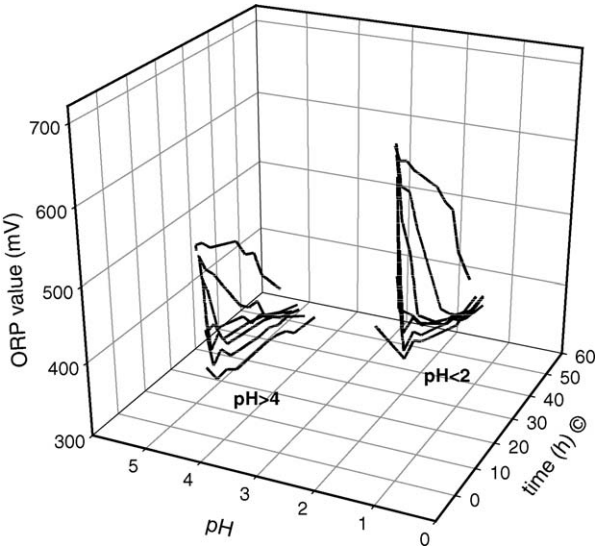

Fig. 3. ORP change with different initial Cr(VI) concentrations at different pH condition in sorption duration (initial concentration of Cr(VI) in turn from front to back: 20 mg/L, 50 mg/L, 100 mg/L, 200 mg/L, 400 mg/L, 600 mg/L and 1000 mg/L; biomass dosage = 20 g/L; temperature = 25 °C).

Cr(VI) removal by the biomaterial was linearly dependent on the initial metal concentration in strong acid condition (Fig. 4). The uptake of Cr and Cr(III) reduced by the biosorbent all increased with the initial Cr(VI) concentration. Even in the solution with very high Cr(VI) concentration of 1000 mg/L, the removal ratio of hexavalent chromium, the sum of uptake and Cr(III) reduced, was 100% as shown in Fig. 4. No Cr(VI) could be detected in the acid solutions. About 57–69% Cr(VI) was reduced to Cr(III). Other 31–43% Cr, unclearly Cr(VI) or Cr(III), was sorbed on the biosorbent.

From the results of pH effect on the biosorption (Fig. 2), less residue of Cr at pH around 4 was observed in the solution. For more uptake of chromium, the adsorption isotherm at pH 3.9–4.4 was also studied in different initial concentrations of Cr(VI) (Fig. 5). The adsorption behavior was obviously different from that at pH < 2. The increase of pH resulted in 8.2–133.2% more of uptake of chromium. At pH around 4, the uptake of chromium

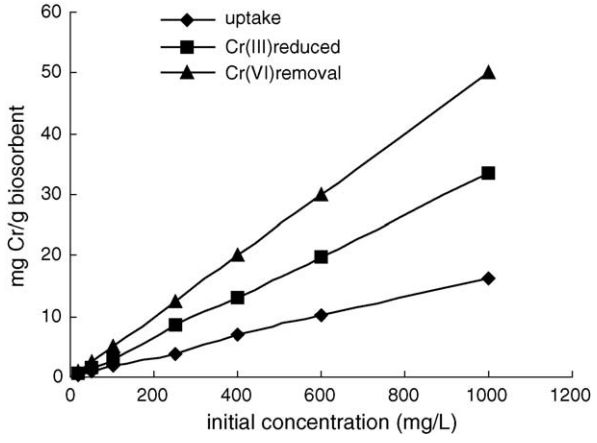

Fig. 4. Effect of the initial concentration of Cr(VI) on biosorption (pH 1.0–2.5, biosorbent dosage = 20 g/L and temperature = 25 °C).

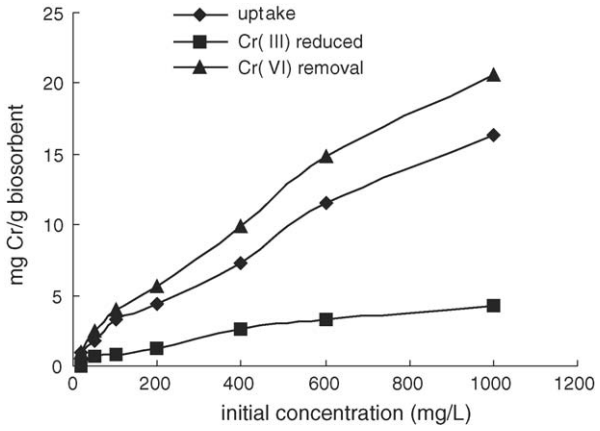

Fig. 5. Effect of the initial concentration of Cr(VI) on biosorption (pH 3.9–4.4, biosorbent dosage = 20 g/L and temperature = 25 °C).

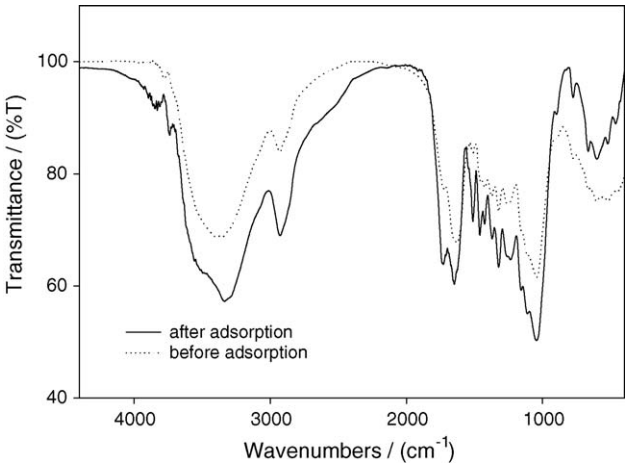

Fig. 6. Fourier transform infrared (FT-IR) spectrum of the biosorbent.

was 49.4–100% of more than Cr(III) reduced, which showed the uptake is more important than reduction of chromium at this condition.

Langmuir isotherm model is often used to simulate the sorption behavior to get the maximum sorption capacity. The model is usually shown as:

$$\frac{C_e}{Q} = \frac{1}{Q_m \cdot k} + \frac{C_e}{Q_m}$$

where Q_m is the maximum adsorption capacity of the sorbent (mg/g) and C_e is the equilibrium concentration in solution (mg/L). The maximum adsorption capacity of this biomass was 21.5 mg/g at pH around 4. The biomaterial was a potential biosorbent for chromium biosorption when compared with other biosorbents (Table 3) [9,10,25].

3.7. Biosorbent characterization

Some characterization of the biosorbent was examined to get more information about the biosorption mechanism of chromium in solution.

The FT-IR is an important tool to identify the functional groups in materials, which were capable of adsorbing metal ions. The spectrum, which displayed a number of adsorption peaks, was very similar to the rice milling by-products used by Tarley and Arruda [17] (Fig. 6). The broad absorption peak around 3348 cm^{-1} was indicative of the existence of bound hydroxyl group (3400–2500 cm^{-1}) [11,17]. The group was corresponding to the possible group of hydroxyl group, which has $pK_H = 10.45$ as expected from the titration model mentioned in Chen et al. [19]. The peak observed at 2929 cm^{-1} could be assigned to the CH_2 group bound by the stretching of the OH groups. The peaks at 1716 cm^{-1} and 1630 cm^{-1} were the characteristics of carbonyl group stretching from aldehydes and ketones. These groups could be conjugated or non-conjugated to aromatic rings (1716 cm^{-1} and 1630 cm^{-1}, respectively) [26]. The spectrum also displayed the absorption peak at 1508 cm^{-1} corresponding to nitrogen oxide in the fingerprint region. The carboxylic acid linked to the aromate was determined by the absorptions of 3348 cm^{-1}, 2929 cm^{-1} and 1423 cm^{-1}. The peak at 1371 cm^{-1} and 1647 cm^{-1} must be assigned to the $–NO_2$. The sulfur in the protein or amino acid also existed from the adsorption peaks of 1424 cm^{-1}, 1236 cm^{-1}, 1111 cm^{-1}, 1045 cm^{-1} and 899 cm^{-1}.

Some changes could be observed comparing the initial state of the biomass with that after adsorption in the spectrum. A significant shift could be found in contrast with the biosorbent before and after adsorption (Fig. 6). The peak around 1630 cm^{-1}, 1508 cm^{-1} and 1460 cm^{-1} was strengthened, indicating that the form of nitrogen oxide and carboxyl group were the results of the biomass participating in the reduction of Cr(VI), while the Cr(III) reduced by the biosorption was half more than that taken up by the biomass observed above.

The oxidation phenomenon was also found as sorbing of Cr(VI) by wheat bran [25]. Hexavalent chromium induced an oxidation of lignin component reaction involving carboxylate moieties after comparing with the IR spectra of untreated wheat bran and wheat bran contacted 24 h with acidic containing Cr(VI) solution. The research of adsorption mechanism of Cr(VI) onto the lignocellulosic substrate of wheat bran showed

Table 3
Estimated parameters with Langmuir model by different biosorbents

Biosorbent	T (°C)	pH	Q_m (mg/g)	k (L/mg)	R^2	Reference
LCS from wheat bran	25	2.1	37.4	0.15	0.99	[25]
	25	3.1	9.9	0.31	0.97	
S. siliquosum (brown seaweed)	30	3.6–4.2	15.9	0.02	0.96	[10]
S. wightii (brown seaweed) (20 g/L dosage)	25	3.5–3.8	38.0	0.06	0.99	[9]
By-product of *Lentinus edodes*	25	3.9–4.4	21.5	0.15	0.96	This study

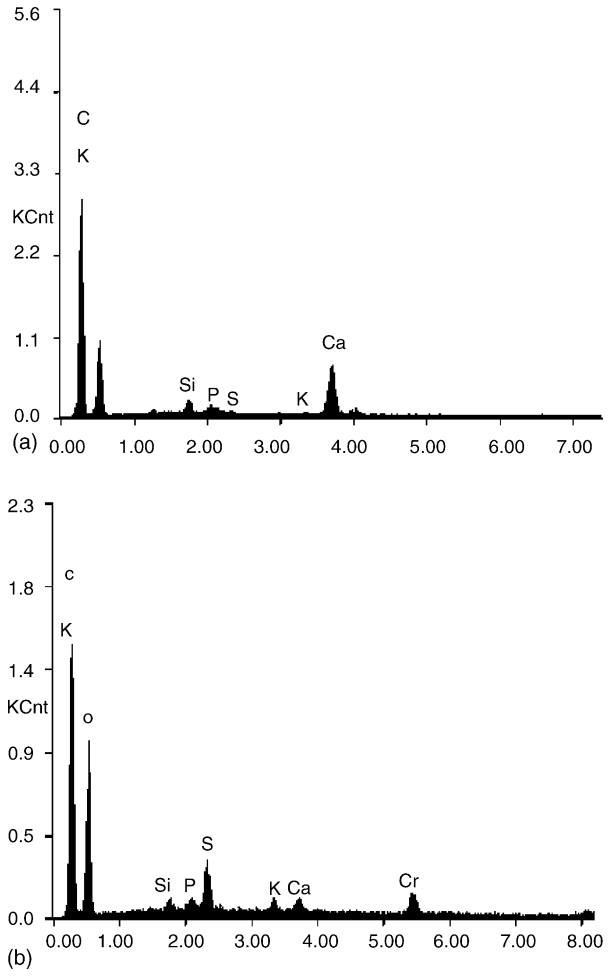

Fig. 7. EDAX spectrums of biosorbent before (a) and after (b) treated with chromium solution (chromium concentration = 1000 mg/L).

that the adsorption reaction consuming a large amount of protons goes along the reduction of Cr(VI) into Cr(III).

The energy-dispersive X-ray analysis spectrums of the biomaterial are shown in Fig. 7. The figure indicated that many elements existed in the biosorbent such as carbon, oxygen, calcium, silicon, phosphorus, potassium and sulfur. Carbon and oxygen were the main components of the by-product of brown-rot fungi.

Comparing the spectrum of the biosorbent treated with chromium with that of untreated biomass, there was an appearance of a chromium peak, a decrease peak of calcium and an increase peak of sulfur. The increase of sulfur may be due to the addition of dilute sulfuric acid to maintain the acid condition of the solution. Thus, there was a possibility that there must be a cation exchange mechanism in the biosorption process of chromium, which was also found in the brown seaweed *Sargassum wightii* by Aravindhan et al. [9].

4. Conclusions

The by-product of *L. edodes* was a very effective biosorbent for chromium remediation in solutions. The biosorbent could not only adsorb chromium from solution, but also reduce hexavalent chromium to trivalent chromium. In strong acid condition of pH < 2.5, nearly 100% of hexavalent chromium was disappeared, either uptake or reduced to Cr(III). About 57–69% Cr(VI) was reduced to Cr(III). Other 31–43% Cr, unclearly Cr(VI) or Cr(III), was absorbed on the biosorbent. The maximum uptake of Cr occurred at pH around 4. The increase of pH resulted in 8.2–133.2% more of uptake of chromium. There was some oxidation ability in acid condition as observed through the ORP, which resulted in the formation of less toxic trivalent chromium. The strengthened peaks of nitrogen oxide and carboxyl groups were attributed to the oxidation result during biosorption from the FT-IR spectrums. Cation exchange was another important mechanism as observed from the EDAX spectrums.

Acknowledgments

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