Biosorption of Cr(VI) from aqueous solutions by nonliving green algae *Cladophora albida*

Liping Deng, Yang Zhang, Jie Qin, Xinting Wang, Xiaobin Zhu

**Abstract**

Biosorption of Cr(VI) from aqueous solutions by nonliving green algae *Cladophora albida* was investigated in batch experiments. The influence of pH, algal dosage, initial Cr(VI) concentration, temperature and co-existing anions on removal efficiencies of *C. albida* was studied. Cr(VI) removal process was influenced significantly by the variation of pH, and the optimum pH was chosen at a range of 1.0–3.0. The optimum algal dosage 2 g/L was used in the experiment. The removal rate of Cr(VI) was relatively rapid in the first 60 min, but then the rate decreased gradually. Removal mechanism was studied by analyzing Cr(VI) and total Cr in the solution. Biosorption and bioreduction were involved in the Cr(VI) removal. Biosorption of Cr(VI) was the first step, followed by Cr(VI) bioreduction and Cr(III) biosorption on the algal biomass. Actual industrial wastewater was used to evaluate the practicability of the biomass *C. albida*. From a practical viewpoint, the abundant and economic biomass *C. albida* could be used for removal of Cr(VI) from wastewater by the reduction of toxic Cr(VI) to less toxic Cr(III).

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**1. Introduction**

Chromium is widely used in electroplating, chromate manufacturing, alloy reparation industries, metal cleaning and processing, leather tanning and wood preservation (Barnhart, 1997). Chromium is present in these industrial effluents primarily as trivalent and hexavalent. Trivalent chromium is relatively less toxic and less mobile (Anderson, 1997), while hexavalent chromium is toxic, carcinogenic, and mutagenic to animals as well as humans (Costa, 2003). Chronic exposure to Cr(VI) causes cancer in digestive tract and lungs, and may cause epigastric pain, nausea, vomiting, severe diarrhea, and hemorrhage (Mohanty et al., 2005). Therefore, the removal of Cr(VI) from industrial wastewaters has been a research topic of great interest.

Various methods used for removal of Cr(VI) ions include chemical reduction and precipitation, reverse osmosis, ion exchange and adsorption on activated carbon or similar material. But all these methods suffer from severe constraints, such as incomplete metal removal, high reagent or energy requirements, generation of toxic sludge or other waste products that require safe disposal. Some of the treatment methods involve high operating and maintenance cost. The high cost of the chemical reagents and the problems of secondary pollution also make the above physico-chemical methods rather limited in application. There is, therefore, a need for some alternative technique, which is efficient and cost-effective.

Biosorption utilizes the ability of certain materials to accumulate heavy metal from aqueous solutions by either metabolically mediated or physico-chemical pathways of uptake (Fourrest and Roux, 1992). Biosorption has distinct advantages over conventional methods of treatments: the process does not produce chemical sludge; it is more efficient, easy to operate (Volesky, 1990). A major advantage of biosorption is that it can be used in situ, and with proper design that may not need any industrial process operations and can be integrated with many systems in the most eco-friendly manner (Tewaria et al., 2005). Various types of biomass, including bacteria (Bueno et al., 2008; Chang et al., 1997; Iyer et al., 2005; Zhou et al., 2007; Trivedi and Patel, 2007), yeast (Volesky et al., 1993; Seki et al., 2005; Göksungur et al., 2005), fungi (Dursun et al., 2003; Pal et al., 2006; Tunali et al., 2005, 2006), and algae (Yu et al., 1999; Lodeiro et al., 2005; Hansen et al., 2006) have been evaluated with the aim of identifying highly efficient metal removal biosorbent. Among them, marine algae available in large quantities in many regions are promising biological resources. Many studies found that alga had a high biosorption capacity for Cr(VI) (Gupta et al., 2001; Mohanty et al., 2006). Some researchers found that Cr(VI) removal from aqueous solutions was achieved partly through reduction (Kratochvil et al., 1998; Park et al., 2004, 2005; Yang and Chen, 2008; Shen et al., 2007).
Recently, green algae are attractive as they are ubiquitous in natural environment, have large surface area to volume ratio and high binding affinity to pollutants (Chong et al., 2000). Cladophora albida, a green filamentous macro-alga, is widely distributed in eutrophic wastewater, lagoon and inter-tidal zone in many parts of the world. In shrimp breeding ponds, C. albida, may flourish wildly to form “green blankets” which soon make the pond anoxic. About 40,000 tons of Cladophora sp. has to be dumped by manpower every year in brine pans, Jiangsu Province in China. The cost of C. albida is much cheaper than other brown seaweed such as Sargassum and Laminaria. Therefore the utilization of C. albida as an efficient and cost-effective biosorbent is of much interest and promise. Özer et al. (1994, 2004) studied the adsorption isotherms of Cu(II), Pb(II) and Cr(VI) on Cladophora crispate. Aksu and Kutsal (1998) determined adsorption kinetic parameters of Cu(II) on Cladophora sp. in a packed bed column reactor. To our best knowledge, there is no report on utilization of green algae C. albida for Cr(VI) removal.

In this work, biosorption features of C. albida were investigated as a function of pH, algal dosage, initial Cr(VI) concentration, temperature, and co-existing ions. The kinetics was obtained from batch experiments. The removal mechanism was discussed by analyzing the concentration of Cr(VI) and total Cr in the solution. Finally, actual industrial wastewater was used to evaluate the practicality of the biomass C. albida.

2. Materials and methods

2.1. Preparation of biomass

C. albida were sampled along the seaside of Qingdao, China. Before use, they were washed several times with distilled water to remove dirt and dried in an oven at 60 °C for 24 h. The length of the biosorbent was cut between 4 and 5 mm.

2.2. Chromium solution

Stock chromium solution (100 mM) was prepared by dissolving an accurate quantity of K$_2$Cr$_2$O$_7$ (GR) in deionized distilled water. Chromium solutions of different concentrations were obtained by diluting the stock solution.

2.3. General uptake procedure

The experiments were conducted in 250 mL flasks containing 50 mL Cr(VI) solution and 0.1 g biomass with varying pH from 0.5 to 12. The pH value was adjusted to required value using 0.5 M H$_2$SO$_4$ or 1.0 M NaOH hourly throughout the experiment. Effect of initial Cr(VI) concentration from 20 to 154 mg/L was studied. The mixtures were shaken on a rotary shaker (agitation rate, 200 rpm) for 24 h. The biosorbent was filtered through an acid-cleaned 0.45 μm Millipore filter. The concentration of Cr(VI) was analyzed spectrophotometrically at 540 nm complexing with 1,5-diphenylcarbazide using an UV/Vis spectrophotometer (Model 1601, Shimadzu, Japan). To determine total Cr concentration, Cr(III) was first converted to Cr(VI) at high temperature by the addition of excess potassium permanganate prior to using the 1,5-diphenylcarbazide method. Each experiment was repeated three times. All chemicals used in this study were of analytical-reagent grade.

2.4. Effect of anions on biosorption

The effect of anions was studied using 2 g/L biosorbent and 50 mg/L Cr(VI) solution containing respective anions (NO$_3^-$, Cl$^-$, SO$_4^{2-}$) at pH 2. Blank samples without anions were used as control.

2.5. Kinetic experiments

Kinetic experiments were performed in continuously stirred beakers containing 500 mL Cr(VI) solution (50 mg/L) and 1.0 g biosorbent at various pH at 25 °C. Samples of 3 mL solution were withdrawn at scheduled time intervals and analyzed for residual Cr(VI) concentration.

2.6. Actual industrial wastewater sorption experiments

The actual industrial wastewater was sampled from Jiaozhou Fuyong wastewater treatment plant in Qingdao. The initial pH was 2.35 and the biomass was 2 g/L. The mixtures were shaken for 24 h at the initial pH. Then pH value was adjusted to 5.0 using 1.0 M NaOH, and the mixtures were shaken for 24 h again. The heavy metal ions were detected before and after contact with the biomass.

3. Results and discussion

3.1. Effect of pH

The pH of aqueous solution is an important environmental factor influencing not only site dissociation, but also the solution chemistry of the heavy metals: hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, precipitation are strongly influenced by pH and, on the other hand, strongly influence speciation and biosorption availability of the heavy metals (Esposito et al., 2002). In this study, Cr(VI) removal process was influenced significantly by variation of pH and the results were shown in Fig. 1. At pH 0.5, the removal percentage was 95%. As pH increased, the removal percentage decreased gradually. At a pH range of 4.0–7.0, the removal of Cr(VI) was found to be relatively constant, while there was a small peak at pH 8.0. The removal percentage decreased gradually when pH > 8.0.

Generally, industrial wastewaters contain Cr(VI) at a concentration ranging from tens to hundreds of mg/L, and these waters are very acidic (pH < 3) (Baral and Engelken, 2002). At lower pH, the removal percentage was higher. However, this requires relatively large amounts of acid, which can lead to secondary waste and increase the cost. The optimum pH was chosen at a range of 1.0–3.0. So the actual wastewater could be treated directly to remove Cr(VI) at its original pH without additional acid. The small peak at pH 8.0 will be useful for neutral or alkaliescent solution.

The pH dependence of Cr(VI) removal can largely relate with type and ionic state of these functional groups and also the metal...
chemistry in solution (Matheickal and Yu, 1999). Chromium exhibits different types of pH dependent equilibriums in aqueous solutions (Rollinson, 1973). As pH is shifted, the equilibrium will also shift; at lower pH (pH < 2.0) values, Cr$_3$O$_2$$^{10}$ and Cr$_4$O$_2$$^{13}$ species are formed; at a pH range of 2–6, HCrO$_4$ and Cr$_2$O$_2$$^{7}$ ions are in equilibrium. When pH > 8.0, CrO$_4$$^{2–}$ is the predominant species in the solution (Rollinson, 1973; Bai and Abraham, 2001; Mor et al., 2006). At lower pH, the negatively charged chromium species bind through electrostatic attraction to positively charged functional groups on the surface of biomass cell wall because more functional groups carrying positive charges would be exposed. As pH increased, the overall surface charge on cell walls became negative and biosorption decreased. On the other hand, the reduction process of hexavalent to trivalent chromium requires a large amount of proton (Barrera et al., 2006).

3.2. Effect of algal dosage

The experiment was conducted with 50 mg/L test solution of Cr(VI), 24 h contact time, pH 2.0 and algal dosage was varied from 0.2 to 10 g/L in 50 mL metal solution at 25 $^\circ$C. The removal percentage of Cr(VI) as a function of adsorbent dosage was shown in Fig. 2. It was apparent that the removal percentage of Cr(VI) increased rapidly with increasing algal biomass due to the greater availability of the biosorbents. Specific removal capacity is a measure of the amount of Cr(VI) bound by unit weight of sorbent, as shown in Fig. 3. The competition of the ions for the available sites caused decrease in the specific removal capacity with increment in adsorbent dosage. The optimum algal dosage 2 g/L was used in the experiment.

3.3. Effect of initial Cr(VI) concentration

The effect of initial Cr(VI) concentration was investigated by varying initial Cr(VI) concentration, ranging from 20–154 mg/L at various pH and temperatures. The results showed that the removal efficiency of C. albida increased with the increasing initial Cr(VI) concentration at the same pH and temperature (Figs. 4 and 5). When the initial Cr(VI) concentration increased from 20 to 154 mg/L at 25 $^\circ$C, the removal efficiency increased from 10.2 to 47.1 mg/g at pH 0.5, from 10.2 to 38.2 mg/g at pH 1, from 8.3 to 25.4 mg/g at pH 2, and from 1.4 to 11.8 mg/g at pH 8. As the initial Cr(VI) concentration increased from 20 to 154 mg/L at pH 2, Cr(VI) removal efficiency increased from 8.3 to 25.4 mg/g at 25 $^\circ$C, from 9.9 to 32.1 mg/g at 35 $^\circ$C, and from 10.7 to 41.7 mg/g at 45 $^\circ$C. At the same initial concentration of Cr(VI), the removal of Cr(VI) increased with the increasing temperature and decreasing pH. The increase of Cr(VI) removal with the initial Cr(VI) concentration is due to higher availability of Cr(VI) ions in the solution. The initial Cr(VI) concentration in the solution provides an important driving
force to overcome mass transfer resistance of metal ions between the aqueous and solid phases (Dönmez and Aksu, 2002).

3.4. Effect of anions on biosorption

Industrial wastewater often contains other ions such as nitrate, chloride, and sulphate which may interfere with the uptake of Cr(VI) by biomass. Effect of anions on removal of Cr(VI) was studied and the results were shown in Fig. 6. It was evident that the effect of nitrate, chloride, and sulphate on adsorption of Cr(VI) was very small. The presence of nitrate, chloride, and sulphate at 10 mmol/L caused removal percentage to drop by 1.96%, 6.63%, and 4.25%, respectively. Effect of anions on adsorption is due to the competition with Cr(VI) for the binding sites.

3.5. Kinetics of biosorption

Fig. 7 depicted Cr(VI) removal percentage vs. t profiles at different pH at 25 °C, with the initial Cr(VI) concentration of 50 mg/L. The removal rate of Cr(VI) was relatively rapid in the first
60 min, but then the rate decreased gradually. This could be explained on the basis of the biosorption mechanism. Further discussion is provided in Section 3.4. The removal rate of Cr(VI) at lower pH was faster than at higher pH. This result coincided with the effect of pH.

3.6. Removal mechanism

Until now, many studies have claimed that Cr(VI) was removed from the aqueous solution through anionic adsorption mechanism (Bayramo˘glu et al., 2005; Khezami and Capart, 2005). Recently, it has been proved that, when Cr(VI) comes in contact with organic substances or reducing agents, especially in an acidic medium, the Cr(VI) is easily or spontaneously reduced to the Cr(III), because Cr(VI) has high redox potential value (above +1.3 V at standard condition) (Park et al., 2004, 2005; Nakajima and Baba, 2004; Lytle et al., 1998). Park et al. (2004, 2005) clarified that the Cr(VI) was completely reduced to Cr(III) by contact with brown seaweed Ecklonia biomass, and the biosorption mechanism included direct and indirect reduction. Yang and Chen (2008) reported that the removal of Cr(VI) by Sargassum sp. was a complicated process, in which reduction, surface complex formation and ion exchange were involved.

In the present study, the decrease of total Cr and Cr(VI) in the solution at pH 2.0 were determined as shown in Fig. 8. In the first 60 min, the decrease of total Cr was equal to the decrease of Cr(VI), and there was no Cr(III) in the solution. From 60 to 90 min, the concentrations of total Cr and Cr(VI) increased and there was a little Cr(III) existing. After 90 min, the decrease of total Cr was less than the decrease of Cr(VI), and Cr(III) in the solution increased gradually. So the biosorption process included three steps as depicted in Fig. 9: (1) the binding of anionic Cr(VI) ions with the positively charged groups present on the biomass surface; (2) the reduction of Cr(VI) to Cr(III) by adjacent electron-donor groups; (3) the release of the Cr(III) ions into the aqueous phase due to electronic repulsion between the positively charged groups and the Cr(III) ions, or the formation of complexes of the Cr(III) with adjacent groups capable of Cr-binding. This statement was consistent with that of Park et al. (2004, 2005, 2006).

Long-term variation of Cr(VI) and Cr(III) in the solution was shown in Fig. 10. After 5 days, Cr(VI) was completely removed. Cr(III) in the solution accounted for 36% of initial total Cr. After 9 days, Cr(III) in the solution increased, which further indicated that Cr(VI) adsorbed on the biomass was reduced to Cr(III) and released to solution gradually. So the Cr(VI) can be completely removed as long as the contact time is sufficient. The mechanism of Cr(VI) removed by C. albida was not “anionic adsorption” but “adsorption coupled reduction” (Park et al., 2006).

3.7. Industrial wastewater sorption experiments

Actual industrial wastewater was used to evaluate the practicality of the biomass C. albida. The actual industrial wastewater was sampled from Jiaozhou Fuyong wastewater treatment plant in Qingdao. The initial pH was 2.35 and the initial concentration of Cr(VI) was 28.12 mg/L. The mixtures were shaken for 24 h at the initial pH 2.35. Then pH value was adjusted to 5.0 using 1.0 M NaOH, and the mixtures were shaken for 24 h to remove other heavy metal ions such as Cu(II), Pb(II) and Cd(II). The heavy metal ions were detected and the results were shown in Table 1. After the first time adsorption, the concentration of Cr(VI) was 0.021 mg/L, but total Cr did not decrease. That was because Cr(VI) was removed by reducing to Cr(III). After adsorption at pH 5, all the metal ions detected were below the wastewater discharge standard in China. From a practical viewpoint, the biomass C. albida was effective for removal of heavy metal ions from industrial wastewater.

### Table 1

Removal of heavy metal ions from industry wastewater by C. albida.

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Initial concentration (mg/L)</th>
<th>pH = 5 control (mg/L)</th>
<th>pH = 2.35 concentration (mg/L)</th>
<th>pH = 5 concentration (mg/L)</th>
<th>Wastewater discharge standard in China (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>28.03</td>
<td>28.03</td>
<td>28.03</td>
<td>28.12</td>
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</tr>
<tr>
<td>Pb</td>
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<td>3.69</td>
<td>3.58</td>
<td>3.62</td>
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</tr>
<tr>
<td>Cd</td>
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<td>0.88</td>
<td>0.75</td>
<td>0.87</td>
<td>0.1</td>
</tr>
<tr>
<td>Zn</td>
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<td>4.70</td>
<td>4.70</td>
<td>4.70</td>
<td>5.0</td>
</tr>
<tr>
<td>Cr(VI)</td>
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<td>28.12</td>
<td>28.12</td>
<td>28.12</td>
<td>5.0</td>
</tr>
<tr>
<td>Total Cr</td>
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<td>28.12</td>
<td>28.12</td>
<td>28.12</td>
<td>5.0</td>
</tr>
</tbody>
</table>

### 4. Conclusion

Biosorption properties of C. albida were studied as a function of pH, initial Cr(VI) concentration and temperature. The removal of Cr(VI) increased with the increasing temperature and decreasing pH at the same initial concentration of Cr(VI), and increased as the increasing initial concentration at the same pH and temperature. The removal rate of Cr(VI) was relatively rapid in the first 60 min, but then the rate decreased gradually. The mechanism of Cr(VI) removed by C. albida was is not “anionic adsorption” but “adsorption coupled reduction”. Cr(VI) adsorbed on the biomass is reduced to Cr(III) and released to solution gradually. Actual industrial wastewater was used to evaluate the practicality of C. albida. The results showed that C. albida was an effective and economical biosorbent material for removal of Cr(VI) from wastewater. However, further research is needed to establish the process with specific attention to the regeneration of the sorbent and the recovery of the sorbed metal. Therefore, future research will be oriented towards column studies.

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### References


