

Effects of Ionic Strength, Background Electrolytes, Heavy Metals, and Redox-Active Species on the Reduction of Hexavalent Chromium by *Ecklonia* Biomass

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Abstract The biomass of the brown seaweed, *Ecklonia*, was used to remove Cr(VI) from wastewater. Previously, Cr(VI) was removed through its reduction to Cr(III) when brought into contact with the biomass. In this study, the effects of ionic strength, background electrolytes, and Cr(III), Ni(II), Zn(II), and Fe(III) on the Cr(VI) reduction were examined. An increased ionic strength inhibited the Cr(VI) reduction. The presence of other heavy metals, such as Cr(III), Ni(II), or Zn(II), only slightly affected the Cr(VI) reduction, while Fe(III) enhanced the reduction. Although the above various parameters could affect the reduction rate of Cr(VI) by *Ecklonia* biomass, these effects were relatively smaller than those of pH and temperature. In addition, the previously derived rate equation was found to be applicable over a range of ionic strengths and with different background electrolytes. In conclusion, *Ecklonia* biomass may be a good candidate as a biosorbent for the removal of Cr(VI) from wastewaters containing various other impurities, and scale-up to a practical process may be accomplished using the previously derived rate equation.

Key words: Biosorption, hexavalent chromium, reduction, *Ecklonia*, detoxification

Environmental pollution due to developments in technology is one of the most significant problems of this century. Chromium has been used in electroplating, leather tanning, metal finishing, and chromate preparation industries. Normally, industrial wastewaters contain both trivalent chromium [Cr(III)] and hexavalent chromium [Cr(VI)]. It is of interest to note that these two forms of chromium exhibit very different toxicities and mobilities. Cr(III) is relatively

insoluble at pHs above 5 in aqueous systems and exhibits little or no toxicity [2]. In contrast, Cr(VI) usually occurs as highly soluble and toxic chromate anions (HCrO_4^- or $\text{Cr}_2\text{O}_7^{2-}$), which are suspected carcinogens and mutagens [4]. Potable waters containing more than 0.05 mg/l of Cr(VI) are considered toxic [3]. Therefore, aqueous Cr(VI) pollution represents an important environmental issue.

The existing treatment process for chromate-containing wastewaters involves a chemical reduction process using chemical reductants, such as FeSO_4 , Na_2SO_3 , NaHSO_3 , and $\text{Na}_2\text{S}_2\text{O}_5$. However, this process has started to become undesirable as it uses expensive and toxic chemical reductants, and is limited to streams containing only low concentration of Cr(VI) due to an operational cost. Furthermore, this process produces secondary wastes, such as chemical sludge [12]. Thus, industry has begun to seek alternative ways of treating chromate wastewaters. The ion-exchange process may be used for the treatment of chromate wastewaters [17]. However, it seems uneconomical due to the expensive price of ion-exchange resin. As an alternative for dealing with chromate wastewater problems, some researchers have proposed a detoxification process using living cells, such as *Bacillus* sp. [4], *Pseudomonas putida* [9], and *Anabaena variabilis* [11]. However, there are also some problems related with these materials, such as cell death due to high toxicity of Cr(VI), expensive operation price, and separation of the liquid treated. In this respect, it seems to be very meaningful that the biomass of *Ecklonia*, an abundant and cheap brown seaweed, is able to completely detoxify Cr(VI) [13, 14].

In our previous studies, the removal of Cr(VI) by biomass of the brown seaweed *Ecklonia* could be explained through the complete reduction of Cr(VI) into Cr(III) [13, 14]. The converted Cr(III) appeared in the solution phase and was partly bound to the biomass. The electrons needed for the Cr(VI) reduction were supplied from the organic

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components of the biomass, resulting in oxidation of the biomass. Since protons were consumed during the Cr(VI) reduction, the reduction rate of Cr(VI) increased with a decrease of pH in the solution. However, Cr(VI) was completely removed even at pH 5, when enough protons were supplied. A series of laboratory experiments were conducted to examine the variability in the Cr(VI) reduction rate with regard to pH, temperature, and Cr(VI) and biomass concentrations. The Cr(VI) reduction rate increased with a decrease of the pH, and with increases of temperature, and Cr(VI) and biomass concentrations. Finally, despite the heterogeneity of the biomass, a simple rate equation could be developed in regards to the mechanism of Cr(VI) removal [14].

The general applicability of an empirically derived rate equation remains questionable, primarily because the experimental conditions under which it would be derived are not likely to be encountered at many natural sites. For example, no background electrolytes were used in the experiments to develop the rate equation and there were no other metal ions present. However, mono- and divalent cations, heavy metals, and various anions exist in actual chromate wastewaters. Thus, these ions may affect the Cr(VI) reduction by binding to any functional groups of the biomass or changing the reduction potential of the system.

In this study, a series of laboratory experiments were conducted in which the Cr(VI) reduction by *Ecklonia* biomass was examined under various conditions, where the independent variables were different from those of our previous studies [13, 14]. The effects of ionic strength and background electrolytes on the Cr(VI) reduction were examined. The effects of Cr(III), Ni(II), Zn(II), and Fe(III) were also examined. Additionally, the validity in the rate equation derived in our previous studies was examined.

MATERIALS AND METHODS

Preparation of the Biomass

The brown seaweed *Ecklonia* sp. was collected along the seashore of Pohang, South Korea [20]. After swelling and rinsing the sun-dried biomaterial with deionized-distilled water, it was cut into approximately 0.5-cm sizes. The cut biomaterial was treated with 1 M H₂SO₄ solution for a day, replacing the natural mix of ionic species with protons and sulfates. The acid-treated biomaterial was washed several times with deionized-distilled water, and then dried at 80°C in an oven for 24 h. The resulting dried biomass was later stored in a desiccator.

Kinetic Studies

The reduction rate of Cr(VI) by the *Ecklonia* biomass was determined by measuring the time-dependent concentration of Cr(VI) in a batch system. The test solutions containing

Cr(VI) and various ions were prepared by dissolving the exact quantities of analytical grade K₂Cr₂O₇ (Kanto) and various other chemicals in deionized-distilled water. For kinetic experiments, each trial was carried out by mixing 1 g of biomass with 200 ml of test solution in a 500-ml Erlenmeyer flask. Before and after the biomass addition, the pH of the solution was adjusted to and maintained at 2.0, using 0.5 M H₂SO₄ and/or 1 M NaOH solution. The flasks were agitated on a shaker at 200 rpm and room temperature (20–25°C). Samples were intermittently taken from the supernatant solution of the flasks in order to analyze the Cr(VI) concentration. The total volume of samples withdrawn did not exceed 2% of the working volume. All experiments were performed in duplicate.

Several sets of rate experiments were conducted to examine the changes of the Cr(VI) reduction rate according to various solution parameters. A control experiment was conducted with Cr(VI) and biomass concentrations of 100 mg/l and 5 g/l, respectively, at pH 2. The effects of both monovalent (Li⁺, Na⁺, K⁺) and divalent (Mg²⁺, Ca²⁺) cations were studied by varying the background electrolytes. The concentrations of Cr(VI) and each cation were 100 mg/l and 0.1 M, respectively. The common anion was chloride. The effects of anions (Cl⁻, NO₃⁻, CO₃²⁻, SO₄²⁻, and HPO₄²⁻) were also studied by varying the background electrolytes. The concentrations of Cr(VI) and each anion were 100 mg/l and 0.1 M, respectively. The common cation was sodium ion. The reduction rate of Cr(VI) as a function of ionic strength was evaluated in the range of 0.01–1.0 M NaCl. The reduction rate of Cr(VI) was also evaluated with 500 mg/l of Cr(III), Ni(II), Zn(II), or Fe(III), which are frequently found in actual chromate wastewaters.

Analytical Methods

Colorimetric methods were used to measure the Cr(VI) and Fe(II) concentrations in the liquid [6]. The red-violet colored complex, formed by the reaction of 1,5-diphenylcarbazide with Cr(VI) in acidic solution, was spectrophotometrically analyzed at 540 nm (Spectronic 21, Milton Roy Co.). The red-orange colored complex, formed from the reaction of 1,10-phenanthroline with Fe(II) in acidic solution, was spectrophotometrically analyzed at 510 nm.

Data Analysis

At constant pH, the rate equation of the Cr(VI) reduction by *Ecklonia* biomass is suggested to be first-order dependent with respect to both Cr(VI) and organic compounds capable of reducing Cr(VI) [14]. Thus, a rate equation of the Cr(VI) reduction by *Ecklonia* biomass is as follows:

$$\frac{d[\text{Cr(VI)}]}{dt} = -k[\text{OCs}][\text{Cr(VI)}] \quad [\text{mmol/l}\cdot\text{h}] \quad (1)$$

where OCs represents the organic compounds capable of reducing Cr(VI), with *k* being the rate coefficient.

However, the reduction rate of Cr(VI) will decrease with time due to depletion of the Cr(VI) and reduced reactivity of the organic compounds as they become oxidized. Thus, the oxidation of the organic compounds for reducing Cr(VI) must be considered.

For a given time, the concentration of organic compounds to reduce Cr(VI) is:

$$[\text{OCs}] = [\text{OCs}]_0 (1 - X_{\text{oxi}}) \quad [\text{mmol/l}] \quad (2)$$

where X_{oxi} presents the fraction of organic compounds oxidized, which can be calculated as follows when considering equivalent reactions between the OCs and the Cr(VI):

$$X_{\text{oxi}} = \frac{\Delta[\text{OCs}]}{[\text{OCs}]_0} = \frac{\Delta[\text{Cr(VI)}]}{[\text{OCs}]_0} = \frac{[\text{Cr(VI)}]_0 - [\text{Cr(VI)}]}{[\text{OCs}]_0} \quad [-] \quad (3)$$

The initial concentration of the OCs can be evaluated as follows:

$$[\text{OCs}]_0 = C_{\text{oc}}^* [\text{B}] \quad [\text{mmol/l}] \quad (4)$$

where B presents whole biomass and C_{oc}^* the amount of OCs per unit gram of biomass. One gram of the *Ecklonia* biomass dried at 80°C in an oven for 24 h could reduce 4.49 (± 0.12) mmol of Cr(VI) at pH 2, i.e., C_{oc}^* is 4.49 (± 0.12) mmol/g [13].

Combining Eqs. (1), (2), (3), and (4) gives:

$$\frac{d[\text{Cr(VI)}]}{dt} = -k[\text{Cr(VI)}](C_{\text{oc}}^* [\text{B}] - [\text{Cr(VI)}]_0 + [\text{Cr(VI)}]) \quad [\text{mmol/l}\cdot\text{h}] \quad (5)$$

and rearranging Eq. (5) gives:

$$\left(\frac{1}{[\text{Cr(VI)}]} - \frac{1}{C_{\text{oc}}^* [\text{B}] - [\text{Cr(VI)}]_0 + [\text{Cr(VI)}]} \right) d[\text{Cr(VI)}] = -k(C_{\text{oc}}^* [\text{B}] - [\text{Cr(VI)}]_0) dt \quad (6)$$

Finally, integration of Eq. (6) yields an equation in the following general form:

$$y = mt \quad (7)$$

where

$$m = k(C_{\text{oc}}^* [\text{B}] - [\text{Cr(VI)}]_0) \quad (8)$$

and

$$y = \ln \left(\frac{[\text{Cr(VI)}]_0 (C_{\text{oc}}^* [\text{B}] - [\text{Cr(VI)}]_0 + [\text{Cr(VI)}])}{C_{\text{oc}}^* [\text{B}] [\text{Cr(VI)}]} \right) \quad (9)$$

Thus, at constant pH, a plot of y versus time t should yield a straight line with slope m and the overall rate coefficient can then be calculated from Eq. (8). The numerical errors in the rate coefficients calculated from the integrated equation will be smaller than the numerical errors associated with

the approximation of the derivative. Consequently, all the experiments were analyzed using this integrated form.

RESULTS AND DISCUSSION

All the experiments described herein were conducted with excess biomass relative to the Cr(VI) concentration. The reaction was characterized by a nonlinear loss of Cr(VI) with time. The reaction was initially rapid, and then became slower as the fraction of oxidized biomass became greater. The reaction rates of the experiments were calculated using Eqs. (7)–(9).

Effect of Background Electrolytes

The dependence of the reduction rate on the background electrolytes was examined using three monovalent (Li^+ , Na^+ , K^+) and two divalent (Mg^{2+} , Ca^{2+}) cations. The concentration of each cation was 0.1 M, and the common anion was chloride. Figure 1 shows the time courses in the change of [Cr(VI)]. There was almost no difference in the reduction rate of Cr(VI) with regard to the change of cations, with the exception of Ca^{2+} . To accurately evaluate the effect of cations on the Cr(VI) reduction, the reduction rates of Cr(VI) were calculated; values of y vs. time were plotted for various background electrolytes (Fig. 2). Straight plots of y vs. time guaranteed the validity of our approach. The slope of the straight line was related with reduction rate; the lower the slope, the slower the rate of reduction. The reduction rate could be calculated from the slopes and Eq. (8) (Table 1). The high magnitude of correction reaffirmed that the removal of Cr(VI) by *Ecklonia* biomass followed an oxidation/reduction reaction. The reduction rate of the

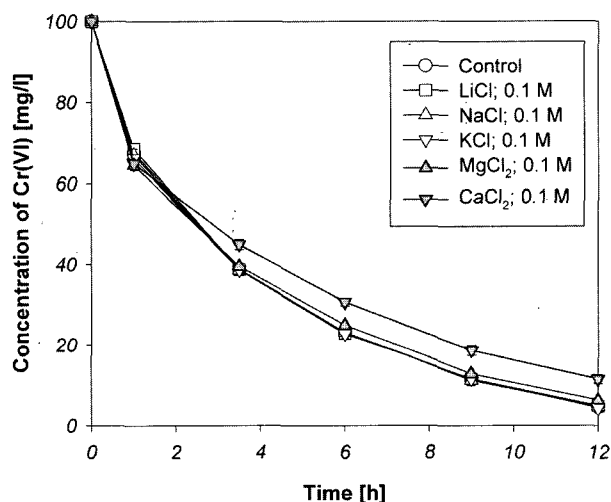


Fig. 1. The effects of various cations on the Cr(VI) reduction by *Ecklonia* biomass at pH 2.

A control experiment was conducted without background electrolytes. The experiment was performed at a biomass concentration of 5 g/l.

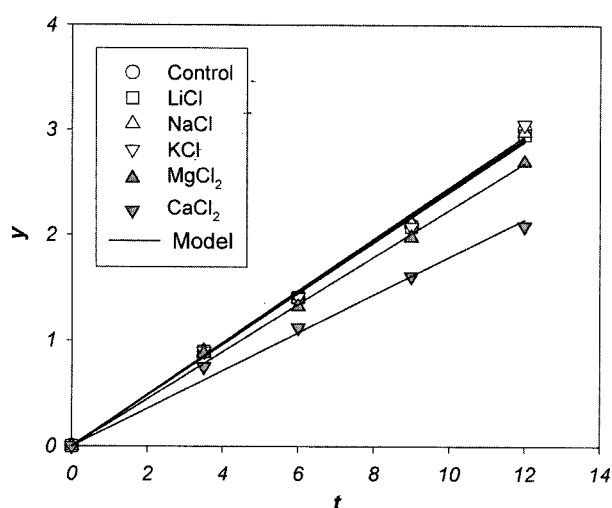


Fig. 2. Plots of y versus time t with various background electrolytes containing different cations. The k values obtained from the slope of the line and the correction factors are listed in Table 1.

control experiment was 0.0118 l/mmol·h. For monovalent cations, there was only a 0.0002 unit difference between the maximum and minimum values of the reduction rates. This implies that the presence of monovalent cations barely affected the reduction of Cr(VI). However, divalent cations caused a decrease of the reduction rate of Cr(VI). In particular, Ca^{2+} significantly reduced the reduction rate of Cr(VI) (about

Table 1. k Values evaluated from experiments under various conditions.

	k (l/mmol·h)	Std. Error (l/mmol·h)	R^2
Control*	0.0118	0.0002	0.9957
NaCl; 0.01 M	0.0118	0.0002	0.9956
NaCl; 0.05 M	0.0117	0.0002	0.9964
NaCl; 0.1 M	0.0118	0.0002	0.9968
NaCl; 0.5 M	0.0084	0.0002	0.9939
NaCl; 1.0 M	0.0070	0.0002	0.9905
LiCl; 0.1 M	0.0117	0.0002	0.9968
KCl; 0.1 M	0.0119	0.0003	0.9968
MgCl ₂ ; 0.1 M	0.0109	0.0002	0.9976
CaCl ₂ ; 0.1 M	0.0087	0.0002	0.9918
NaNO ₃ ; 0.1 M	0.0109	0.0002	0.9940
Na ₂ CO ₃ ; 0.1 M	0.0103	0.0001	0.9976
Na ₂ SO ₄ ; 0.1 M	0.0093	0.0003	0.9897
Na ₂ HPO ₄ ; 0.1M	0.0094	0.0001	0.9971
Cr(III); 500 mg/l	0.0113	0.0002	0.9947
Ni(II); 500 mg/l	0.0114	0.0002	0.9970
Zn(II); 500 mg/l	0.0115	0.0002	0.9957
Fe(III); 25 mg/l	0.0167	0.0004	0.9969
Fe(III); 100 mg/l	0.0170	0.0006	0.9945
Fe(III); 500 mg/l	0.0076	0.0001	0.9968

*Control experiment was conducted at biomass and Cr(VI) concentrations of 5 g/l and 100 mg/l, respectively, at pH 2.

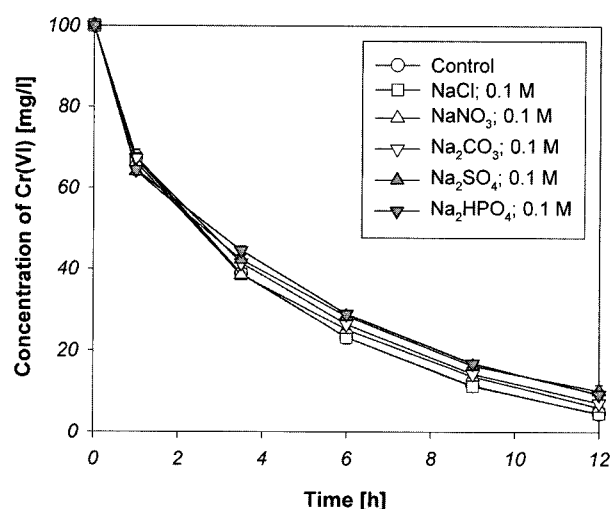


Fig. 3. The effects of various anions on the Cr(VI) reduction by *Ecklonia* biomass at pH 2.

A control experiment was conducted without background electrolytes. The experiment was performed at a biomass concentration of 5 g/l.

26%). Alkali-metals and alkaline-earth cations are known to be able to bind to negatively charged groups of the biomass, primarily by electrostatic interaction [5, 10, 18, 19]. However, mono- or divalent light metals might not bind to the biomass at pH 2, and therefore might not affect the Cr(VI) reduction to any significant extent. It is also reasonably safe to presume that the conformational change of the biomass might not occur with cationic concentration lower than those tested in our experiments. The decrease of the reduction rate by Ca^{2+} could be explained as follows: Ca^{2+} might form insoluble complexes with OH^- or SO_4^{2-} on the surface of the biomass, which might hinder the contact between the Cr(VI) and the biomass.

The effect of anions on the reduction rate of Cr(VI) was also examined using various background electrolytes (Cl^- , NO_3^- , CO_3^{2-} , SO_4^{2-} , and HPO_4^{2-}). The concentration of each anion was 0.1 M, with sodium ion as the common cation. Figure 3 shows the time courses of Cr(VI) change due to reduction. There was little difference in the reduction rates of Cr(VI) in relation to the different anions. The effects of anions on the Cr(VI) reduction were further evaluated by calculating the reduction rate (Fig. 4). The reduction rate constants varied by up to 21% according to the anion tested. For the redox reaction between Cr(VI) and the biomass, an intermediate of Cr(VI)-biomass might be formed. However, the high concentration of anions might competitively inhibit the formation of this Cr(VI)-biomass intermediate. This inhibition might be exaggerated by the increase of the electrostatic force of the anions. The order of the electrostatic force of anions tested in this experiments was $\text{Cl}^- < \text{NO}_3^- < \text{CO}_3^{2-}$, SO_4^{2-} , HPO_4^{2-} , while the order of reduction rate measured in the experiments was $\text{Cl}^- > \text{NO}_3^- > \text{CO}_3^{2-} > \text{SO}_4^{2-}$, HPO_4^{2-} .

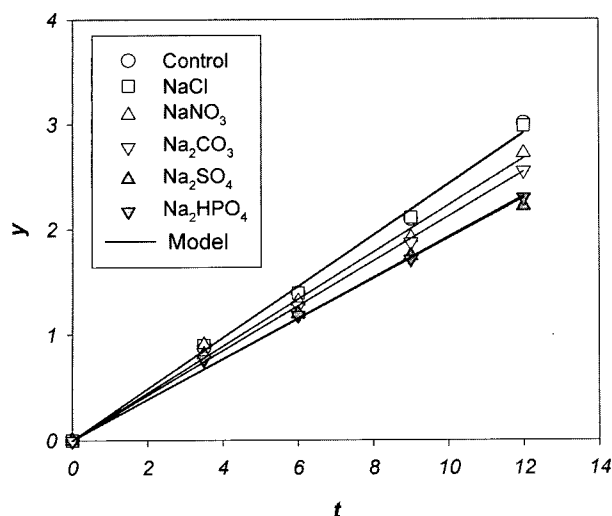


Fig. 4. Plots of y versus time t with various background electrolytes containing different anions.

The k values obtained from the slope of the line and the correction factors are listed in Table 1.

Effect of Ionic Strength

Changes in the ionic strength of the solution may cause conformational modification of the functional groups of the biomass [16]. It was suspected that these conformational changes would make the reactive functional groups either more or less accessible to the Cr(VI), thereby altering the reduction rate of Cr(VI). The Cr(VI) reduction by the biomass was studied in the ionic strength range of 0.01–1.0 M NaCl. The time courses of the [Cr(VI)] change

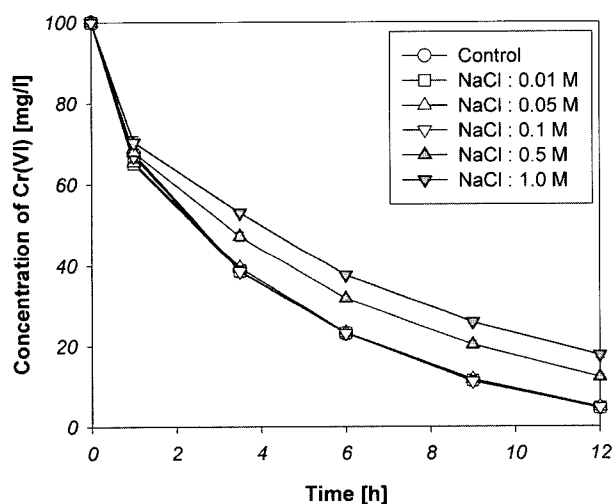


Fig. 5. The effects of ionic strength on the Cr(VI) reduction by *Ecklonia* biomass at pH 2.

A control experiment was conducted without background electrolytes. The experiment was performed at a biomass concentration of 5 g/l. The k values obtained from the plots of y versus time and the correction factors are listed in Table 1.

displayed no difference with ionic strengths below 0.1 M NaCl (Fig. 5). However, significant differences were observed above 0.5 M NaCl. The reduction rate at 0.5 and 1.0 M decreased to 29 and 41% of the control, respectively (Table 1). These results suggest that conformational changes in the functional groups of the biomass with ionic strength below 0.1 M NaCl did not affect the reduction rate of Cr(VI) to any significant extent. Although high solution ionic strengths may affect the Cr(VI) reduction by *Ecklonia* biomass, this may be ignored in actual process since the ionic strength of actual chromate wastewaters would be lower than 0.1 M NaCl. In a separate experiment, other factors, such as pH and temperature, were found to give much greater impacts than the ionic strength [13].

Effect of Other Heavy Metals

The Cr(VI) reduction by the biomass ultimately results in the formation of Cr(III), which may affect the Cr(VI) reduction by binding to the functional groups on the surface of the biomass. It is presumed that the binding of Cr(III) may make the biomass more resistant to oxidation by Cr(VI). In addition to Cr(III), other heavy metals coexisting in actual chromate wastewaters may also be bound to the surface of the biomass, resulting in a decrease of the reduction rate. The effects of other heavy metals on the Cr(VI) reduction were examined with 500 mg/l of Cr(III), Ni(II), or Zn(II). As seen in Fig. 6, there was almost no change in the time course of [Cr(VI)] with each solution. It is likely that the functional groups responsible for the Cr(VI) reduction may not be the same as those responsible for cationic heavy metal binding. Of course, other heavy

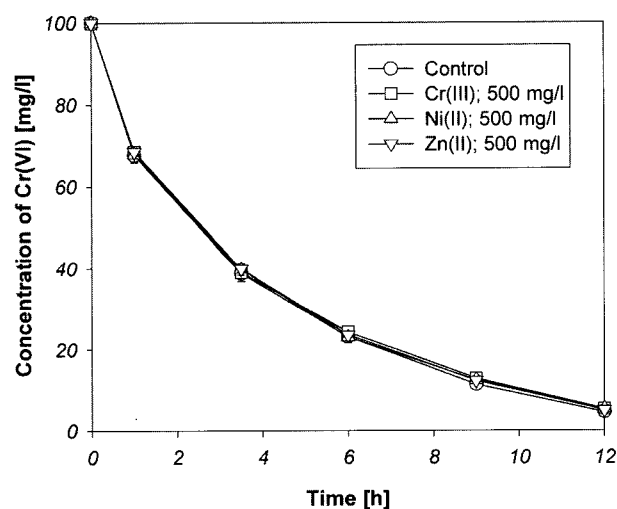


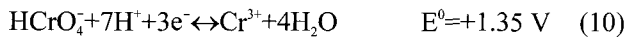
Fig. 6. The effect of heavy metals on the Cr(VI) reduction by *Ecklonia* biomass at pH 2.

A control experiment was conducted without background electrolytes. The experiment was performed at a biomass concentration of 5 g/l. The k values obtained from the plots of y versus time and the correction factors are listed in Table 1.

metals over 500 mg/l may affect the Cr(VI) reduction, but their effects may be insignificant, compared to those of other factors, such as pH and temperature. Therefore, the presence of other heavy metals may be ignored in the actual application of Cr(VI) detoxification.

Effect of Fe(III)

During the plating process operations, iron is frequently contained in the chromate wastewater [1, 15]. Iron can exist in the ferric and ferrous forms, and their molar ratio depends on pH of the solution and their concentrations. However, if Cr(VI) coexists in solution, Fe(II) is oxidized into Fe(III) due to the large difference in their reduction potentials ($\Delta E^0 = +0.58$ V at standard condition).



Thus, the presence of Fe(II) was of no concern in our system. However, Fe(III) may affect the Cr(VI) reduction by binding any functional groups of the biomass or forming complexes with Cr(VI) and/or organic compounds present in the solution. Therefore, a series of experiments were conducted to examine how the presence of Fe(III) in the Cr(VI)-biomass system affects the Cr(VI) reduction. As seen in Fig. 7, the presence of Fe(III) affected the Cr(VI) reduction. The reduction rate of Cr(VI) increased with 25 and 100 mg/l of Fe(III). However, the addition of 500 mg/l Fe(III) caused a 35% reduction of the reduction rate of Cr(VI) (Table 1). Figure 8 shows the time course of experiments conducted with the Fe(III)-biomass and Cr(VI)-Fe(III)-

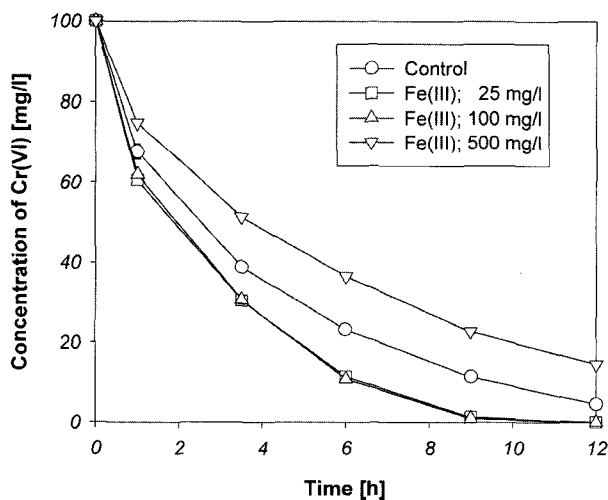


Fig. 7. The effects of Fe(III) on the Cr(VI) reduction by *Ecklonia* biomass at pH 2.

A control experiment was conducted without background electrolytes. The experiment was performed at a biomass concentration of 5 g/l. The k values obtained from the plots of y versus time and the correction factors are listed in Table 1.

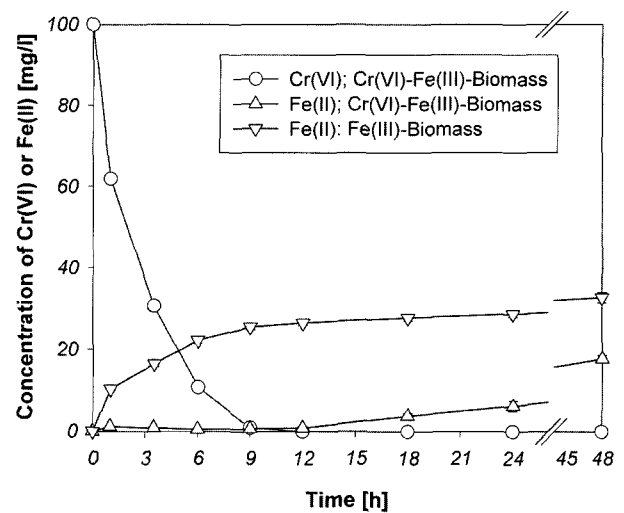


Fig. 8. Time courses of the Fe(III)-biomass and the Cr(VI)-Fe(III)-biomass systems.

The experiment was performed at biomass and Fe(III) concentrations of 5 g/l and 100 mg/l, respectively, at pH 2.

biomass systems. In the Fe(III)-biomass system, the Fe(II), which did not initially exist, appeared in the solution and increased to 33 mg/l. In the Cr(VI)-Fe(III)-biomass system, the Fe(II) concentration was insignificant during the Cr(VI) reduction; however, there was a slight increase in the Fe(II) concentration of the solution after the Cr(VI) had completely been reduced to Cr(III). These results imply that Fe(III) was reduced to Fe(II) by contact with the biomass; i.e., the reduction potential of the *Ecklonia* biomass might be lower than that of Fe(III) at pH 2.

A potential mechanism by which Fe(III) could enhance the Cr(VI) reduction is proposed. Since Fe(II) is oxidized to Fe(III) by Cr(VI) thermodynamically, the coexistence of Fe(II) and Cr(VI) is not possible under acidic conditions. However, Fe(III) can be reduced to Fe(II) by contact with the biomass in an acidic solution, such as pH 2. The reduced Fe(II) can immediately be reoxidized to Fe(III) by the Cr(VI) present in the solution, because a redox reaction between Cr(VI) and Fe(II) is very rapid under acidic conditions [7, 8]. Since the reduction mechanism of cationic Fe(III) may be different from that of anionic Cr(VI), their reduction reactions may be noncompetitive, and the reduction reaction of Fe(III) may not directly interfere with the Cr(VI) reduction by the biomass. Therefore, the redox reaction between Fe(III) and the biomass may be the rate-limiting step for the enhancement of the Cr(VI) reduction in the presence of Fe(III). However, at high pH or high Fe(III) concentration, where Fe(III) may form insoluble complexes with other ions or organic compounds in the solution, the enhancing effect of Fe(III) on the Cr(VI) reduction may be diminished due to the hindering effect of insoluble Fe(III)-complexes on contact of Cr(VI) with the biomass.

Acknowledgments

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NOMENCLATURE

- [] : Concentration of the bracketed species (mmol/l or g/l)
 []₀ : Initial concentration of the bracketed species (mmol/l or g/l)
 B : Representative of biomass
 OC : Representative of organic compound
 OCs : Representative of organic compounds reducing Cr(VI) in biomass
 k : Rate coefficient
 C_{OC}^{*} : Amount of OCs per unit gram of biomass (mmol/g)
 X_{oxi} : Fraction of organic compounds oxidized

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