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How to study Cr(VI) biosorption: Use of fermentation waste for detoxifying Cr(VI) in aqueous solution

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Abstract

For the last few decades, many researchers have tested various biomaterials as biosorbent for Cr(VI) removal from aqueous solution. Unfortunately, however, they have misunderstood the Cr(VI) biosorption by biomaterials; they have used common kinetic and/or equilibrium models based on 'anionic adsorption' mechanism in order to evaluate the Cr(VI) removal from aqueous solution. In this study, a new efficient biomass, the fermentation waste of *Corynebacterium glutamicum*, capable of detoxifying Cr(VI) was used as a model biomass to study the Cr(VI) biosorption by biomaterials. To analyze both Cr(VI) and total Cr in aqueous solution, colorimetric method combined with excess potassium permanganate was used. X-ray photoelectron spectroscope was also used to ascertain the oxidation state of chromium bound on the biomass. These analytical methods showed that the removal mechanism of Cr(VI) by the fermentation waste was a reduction reaction of Cr(VI) to Cr(III). Thus, kinetic and equilibrium models based on the 'reduction' mechanism were used to describe Cr(VI) and total Cr behaviors in aqueous solution.

Keywords: Hexavalent chromium; *Corynebacterium glutamicum*; Biosorption; Reduction; Detoxification; Modeling

1. Introduction

Chromium and its compounds are widely used in industry, with the most usual and important sources coming from the electroplating, tanning, water cooling, pulp producing, and petroleum refining processes [1]. The effluents from these industries contain both Cr(VI) and Cr(III) in concentrations ranging from tens to hundreds of milligram per liters. Cr(VI) is known to be toxic to both plants and animals, as a strong oxidizing agent and potential carcinogen [2]. In contrast, Cr(III) is generally only toxic to plants in very high concentrations and is less toxic or nontoxic to animal [3]. Because of these differences, the discharge of Cr(VI) to surface water is regulated to below 0.05 mg/L by the U.S. EPA, while total Cr, including Cr(III), Cr(VI), and its other forms, is regulated to below 2 mg/L [4].

Various biomaterials can retain relatively high quantities of metal ions by passive sorption and/or complexation, i.e., this is commonly known as biosorption [5–8]. Since a report on the use of sawdust by Srivastava et al. [9], many researchers have tested various biomaterials such as nonliving bacteria, microalgae, fungi, seaweed, agricultural byproduct and industrial bio-waste as an adsorbent for Cr(VI) [10]. Over the last few decades, to the best of our knowledge, over 200 papers on Cr(VI) biosorption have been published in international journals. However, it has been recently reported that the biosorption mechanism of Cr(VI) by biomaterials is not 'anionic adsorption' but 'adsorption-coupled reduction' [11–18]. When Cr(VI) comes in contact with biomaterials, especially in an acidic solution, the Cr(VI) can easily or spontaneously be reduced to the Cr(III), because Cr(VI) has high redox potential value (above +1.3 V at standard condition). Therefore, it is very important to check the abiotic reduction of Cr(VI) by tested biomaterials: researchers have to analyze both Cr(VI) and total Cr in aqueous solution with 1,5-diphenylcarbazide method and atomic absorption spectrophotometer (AAS) or inductively coupled plasma-atomic emission spectrometer (ICP-AES), and to ascertain the oxidation state of chromium bound on the tested biomaterials with X-ray absorption spectroscope (XAS) or X-ray photoelectron spectroscope (XPS) [18]. Unfortunately, however, the oxidation states of chromium in aqueous solution and on biomaterials

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were not examined even in most recently accepted papers [19–25]. Authors of these papers still use common kinetic and/or equilibrium models based on 'anionic adsorption' mechanism in order to evaluate the Cr(VI) removal from aqueous solution.

The objectives of this work were to show how to study Cr(VI) biosorption and to introduce a new efficient biomaterial capable of detoxifying Cr(VI) from aqueous solution. We conducted batch experiments for Cr(VI) biosorption by the fermentation waste of *Corynebacterium glutamicum* at various pHs, biomass and initial Cr(VI) concentrations. Amino acid production industries have been plagued with a huge amount of biological solid waste, which is mainly composed of the biomass of *C. glutamicum* [26,27]. Oxidation states of chromium in aqueous solution and on the biomass were examined by a colorimetric method and XPS analysis. Kinetic and equilibrium models based on the 'reduction' mechanism were used to describe Cr(VI) and total Cr behaviors in aqueous solution.

2. Experimental

2.1. Preparation of the biomass

The fermentation waste of *C. glutamicum* was obtained in a dried powder form from a lysine fermentation industry (BASF-Korea, Korea). The raw biomass was washed with deionized-distilled water several times, and then dried in an oven at 80 °C for 24 h. The resulting dried *C. glutamicum* biomass was stored in a desiccator and used for the following batch experiments.

2.2. Batch experiments for Cr(VI) biosorption

The removal of Cr(VI) by the fermentation waste of *C. glutamicum* was examined by measuring the time-dependent concentrations of Cr(VI) and total Cr in a batch system. The test solutions were prepared by dissolving the exact quantities of the analytical grade $K_2Cr_2O_7$ (Kanto) in deionized-distilled water. Batch experiments were conducted in 250 mL Erlenmeyer flasks with a working volume of 100 mL. The following set of factors was chosen as the standard conditions: 10 g/L of biomass, 50 mg/L of initial Cr(VI) concentration at pH 2 and room temperature (25 ± 2 °C). To determine the effects of Cr(VI) removal of pH variation, pH values of 1–4 were used; of initial Cr(VI) concentration variation, concentrations of 25, 50, 75 and 100 mg/L were used; and of biomass concentration variation, biomass concentrations of 5, 10, 15 and 20 g/L were used. The flasks were agitated on a shaker at 200 rpm. Except for the pH-shift experiment, the solution pH was maintained at the desired value using 0.5 M H_2SO_4 or 1 M NaOH solutions. The solution was intermittently sampled and centrifuged at 3000 rpm for 5 min, after which the Cr(VI) and total Cr concentrations of the supernatant were analyzed. The total volume of withdrawn samples never exceeded 3% of the working volume. It was confirmed from three independent replicates that the Cr(VI) biosorption experiments were reproducible within at most 5%.

2.3. Chromium analysis

A colorimetric method, as described in the standard methods [28], was used to measure the concentrations of the different chromium species. The pink colored complex, formed from 1,5-diphenylcarbazide and Cr(VI) in acidic solution, was able to be spectrophotometrically analyzed at 540 nm (GENESYS TM 5, Spectronic Inc.). To measure total Cr concentration, the Cr(III) was first converted to Cr(VI) at high temperature (130–140 °C) by the addition of excess potassium permanganate prior to the 1,5-diphenylcarbazide reaction. The Cr(III) concentration was then calculated from the difference between the total Cr and Cr(VI) concentrations.

2.4. X-ray photoelectron spectroscopy (XPS) analysis

XPS was employed to ascertain the oxidation state of the chromium bound on the biomass. The Cr-laden biomass was obtained through contact with 200 mg/L of Cr(VI) at pH 2 for 24 h, while the Cr(III)-laden biomass was obtained through contact with 200 mg/L of Cr(III) at pH 4 for 24 h. Prior to mounting for XPS, the biomasses were washed with deionized-distilled water several times, and then freeze-dried in a vacuum freeze dryer (Bondiro, ILSHIN Lab Co.). The resulting biomasses were transported to the spectrometer in a portable, gas-tight chamber. $CrCl_3 \cdot 6H_2O$ (Sigma) and $K_2Cr_2O_7$ (Kanto) were used as Cr(III) and Cr(VI) reference compounds, respectively. Spectra were collected on a VG Scientific model ESCALAB 220iXL. A consistent 2 mm spot size was analyzed on all surfaces using a Mg Kα ($h\lambda = 1253.6$ eV) X-ray source at 100 W and pass energy of 0.1 eV for 10 high-resolution scans. The system was operated at a base pressure of 2×10^{-8} mbar. The calibration of the binding energy of the spectra was performed with the C 1s peak of the aliphatic carbons, which is at 284.6 eV.

3. Results and discussion

3.1. Mechanism of Cr(VI) biosorption in aqueous solution

To examine the Cr(VI) removal characteristic of the fermentation waste of *C. glutamicum*, the Cr concentrations and pH profiles were investigated, with no pH adjustment (Fig. 1). The Cr(VI) concentration sharply decreased, and was completely removed in the aqueous solution. Meantime, the Cr(III), which was not initially present, appeared in the aqueous solution, and increased in proportion to the Cr(VI) depletion. These results indicated that some of the Cr(VI) was reduced to Cr(III) when brought into contact with the dead biomass of *C. glutamicum*. The solution pH increased abruptly from 2.00, and finally equalized to 2.10 after 4 h of contact time. The increase of the solution pH was likely to be related to the removal of Cr(VI); i.e., about 2.1 mols of protons were consumed for the removal of 1 mol of Cr(VI) (data not shown). Thus, it could be expected that the Cr(VI) removal rate increased as the solution pH decreased.

After the complete Cr(VI) removal, the final Cr(III) concentration in the aqueous solution remained at 16.0 mg/L, indicating that the biomass adsorbed 34.0 mg/L of total Cr. To characterize

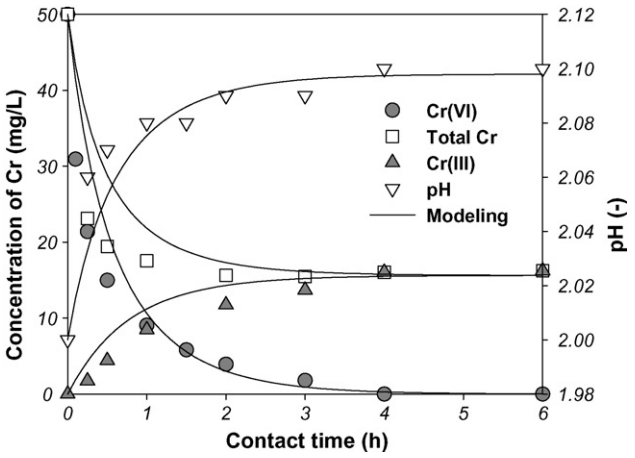

Fig. 1. Dynamics of Cr(VI) removal by the fermentation waste of *C. glutamicum* during pH-shifting experiments. Conditions: 50 mg/L initial Cr(VI) concentration, 10 g/L biomass concentration, initial pH 2.0.

the main mechanism of Cr(VI) removal, it is important to investigate the oxidation state of the chromium bound on the biomass; if this state is only trivalent, it can be concluded that Cr(VI) was completely reduced to Cr(III) by the biomass. However, if both trivalent and hexavalent forms of chromium exist on the biomass, it can be concluded that both Cr(VI) adsorption and Cr(VI) reduction contributed to the removal of Cr(VI) from aqueous solution. To ascertain the oxidation state of the chromium bound on the biomass, XPS was employed. Low-resolution XPS spectra of the Cr-unloaded biomass indicated that other than C, N and O, no significant contributions were present from other elements associated with biomass surfaces (data not shown). High-resolution spectra collected from the Cr 2p core region indicated that indeed there was no Cr associated with the biomass surface (Fig. 2). However, high-resolution spectra of both the Cr(III)-laden biomass and the Cr-laden biomass indicated that there were significant contributions of the Cr bound on the biomass. Significant bands appeared at binding energies of 577.0–578.0 and 586.5–588.0 eV; the former corresponds to Cr $2p_{3/2}$ orbitals, the latter to Cr $2p_{1/2}$ orbitals. The Cr $2p_{3/2}$ orbitals are assigned at 577.2 eV ($CrCl_3$) and 576.2–576.5 eV (Cr_2O_3) for Cr(III) compounds, while Cr(VI) forms are characterized by higher binding energies such as 578.1 eV (CrO_3) or 579.2 eV ($K_2Cr_2O_7$) [29]. Interestingly, the spectra of the Cr-laden biomass was identical with that of the Cr(III)-laden biomass. These results reached that the chromium bound on the biomass was only trivalent form. Therefore, it can be concluded that the Cr(VI) was removed from aqueous solution by reduction mechanism.

3.2. Effects of various parameters on Cr(VI) biosorption

Using the fermentation waste of *C. glutamicum*, the effects of pH, biomass concentration and initial Cr(VI) concentration on the Cr(VI) biosorption were investigated by batch experiments. Fig. 3 shows the time-dependent Cr(VI) concentration at various solution pHs. As expected from result of the pH-shift experiment, the removal rate of Cr(VI) was strongly pH dependent; the removal rate of Cr(VI) decreased with an increase in solution pH. In all of pH ranges studied, however, Cr(VI) was completely removed in aqueous solution at the end. The contact time required for the complete removal of Cr(VI) varied from 1.5 to 44 h depending on the solution pH. These results were due to the depletion of the protons participating in the reduction reaction of Cr(VI) by the biomass. The concentration of Cr(VI) versus time was also examined at various initial Cr(VI) concentrations in the range of 25–100 mg/L (Fig. 4). The removal rate of Cr(VI) increased with an increase in initial Cr(VI) concentration. For the 25 mg/L of initial Cr(VI) concentration, Cr(VI) was completely removed in 2 h, while the complete removal of 100 mg/L of Cr(VI) required 10 h of contact time. Fig. 5 shows the time-dependent concentration of Cr(VI) at various biomass concentrations in the range of 5–20 g/L. The removal

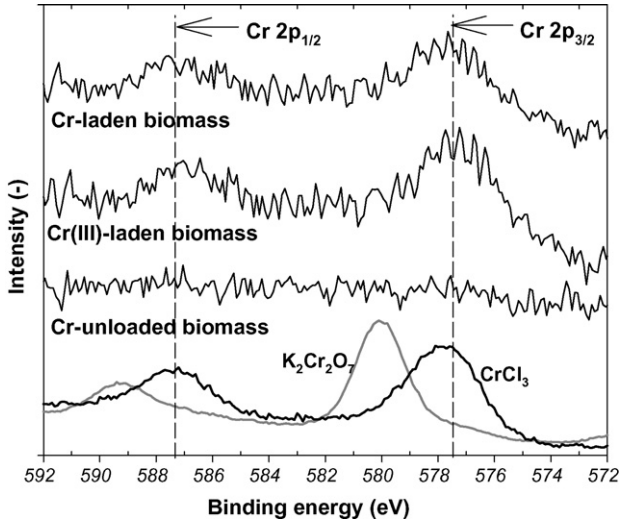

Fig. 2. High-resolution spectra collected from the Cr 2p core region; the Cr-laden biomass was obtained after Cr(VI) biosorption at pH 2.0, whereas the Cr(III)-laden biomass after Cr(III) biosorption at pH 4.0.

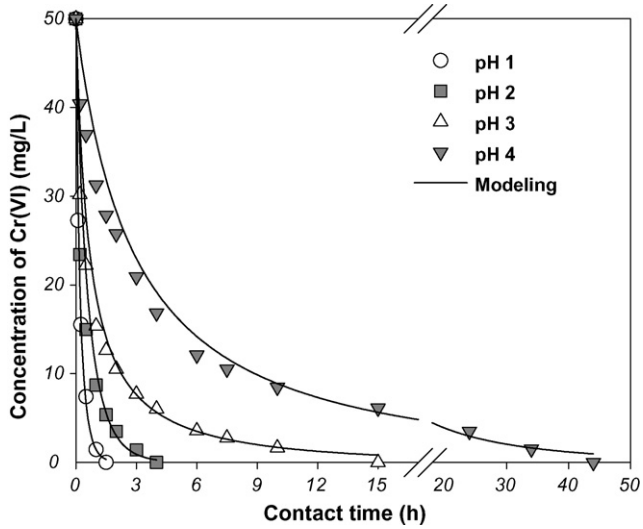

Fig. 3. Time courses of Cr(VI) removal at various pHs by the fermentation waste of *C. glutamicum*. Conditions: 50 mg/L initial Cr(VI) concentration, 10 g/L biomass concentration.

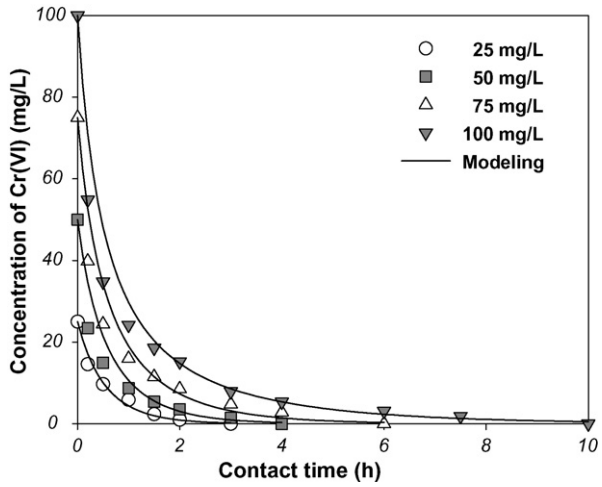

Fig. 4. Time courses of Cr(VI) removal at various initial Cr(VI) concentrations by the fermentation waste of *C. glutamicum*. Conditions: 10 g/L biomass concentration, pH 2.0.

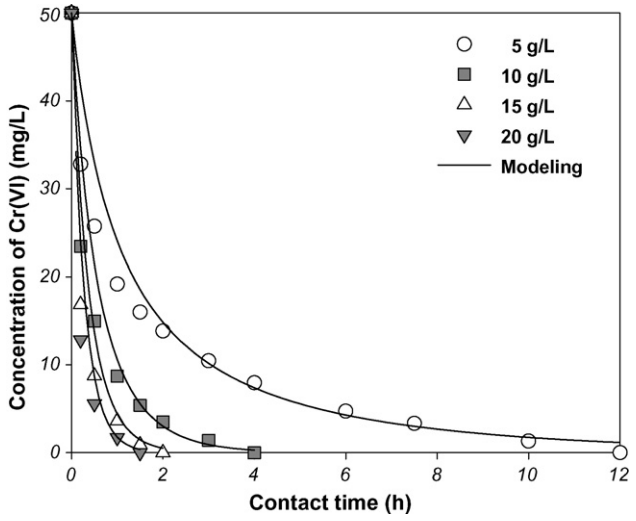

Fig. 5. Time courses of Cr(VI) removal at various biomass concentrations by the fermentation waste of *C. glutamicum*. Conditions: 50 mg/L initial Cr(VI) concentration, pH 2.0.

rate of Cr(VI) increased with an increase in biomass concentration, while the contact time required for the complete removal of Cr(VI) decreased with increasing biomass concentration (i.e., from 12 to 1.5 h).

In short, the removal rate of Cr(VI) increased with a decrease in pH or with increases in Cr(VI) and biomass concentrations. From a practical view point, although Cr(VI) can be completely removed from the aqueous solution in the end, there exists an optimum condition due to the limitations of operational time, cost, and space. Among various other parameters, the pH may be a major operational parameter because the pH can easily be controlled by using industrial sulfuric acid or waste-acid. Generally, wastewaters contain Cr(VI) at a concentration ranging from tenths to hundreds of milligram per liters, and these wastewaters are acidic (i.e., below pH 4) [4].

Table 1 shows the removal efficiencies of total Cr at equilibrium state, where Cr(VI) was completely reduced to Cr(III). As the biomass concentration increased, the removal efficiency of total Cr increased. An increase in initial Cr(VI) concentration reduced the removal efficiency of total Cr, but enhanced total amount of the removed total Cr. As the solution pH decreased, the removal efficiency of total Cr decreased because reduced Cr(III) was easily desorbed from the biomass at a lower pH.

3.3. Modeling of Cr(VI) biosorption

Although we already suggested a new kinetic model based on 'reduction' mechanism of Cr(VI) by brown seaweed, *Ecklonia* sp., biomass [17] and dead fungal biomass of *Rhizopus oryzae* [15], many researchers in this field have still used common kinetic and/or equilibrium models based on 'anionic adsorption' mechanism in order to evaluate the Cr(VI) removal from aqueous solution by tested biomaterials [19–25]. Thus, one of the aims of this work was to show how to do modeling of the Cr(VI) biosorption.

A rate equation for Cr(VI) removal by the biomass can be developed from a concept based on the redox reaction [15,17]:

$$B + \mathrm{Cr(VI)} \xrightarrow{k} B(\mathrm{oxidized}) + \mathrm{Cr(III)} \quad (1)$$

Since some part of the biomass may be related with the reduction of Cr(VI), it is reasonable to replace the term 'biomass' with

Table 1
Equilibrium concentration and removal efficiency of total Cr in aqueous solution at equilibrium state[a]

Biomass concentration (g/L)	Cr(VI) concentration (g/L)	Solution pH	Contact time required for equilibrium (h)	Total Cr concentration (mg/L)	Removal efficiency of total Cr (%)
5	50	2.0	12	20.2	60
10	50	2.0	4.0	16.2	68
15	50	2.0	2.0	12.3	75
20	50	2.0	1.5	9.84	80
10	25	2.0	2.0	6.15	75
10	75	2.0	6.0	28.1	63
10	100	2.0	10	45.9	54
10	50	1.0	1.5	32.2	36
10	50	3.0	15	6.43	87
10	50	4.0	44	2.34	95

[a] Where, total Cr was only trivalent form since Cr(VI) was completely reduced to Cr(III).

the concept of 'organic compounds capable of reducing Cr(VI)'. However, there has been no information about the organic compounds capable of reducing Cr(VI) due to the heterogeneity of the biomass. Thus, to describe the biomass, it is assumed that there exists one kind of organic compound capable of reducing Cr(VI). And so, a redox reaction between the Cr(VI) and the biomass is as follows:

$$\mathrm{OC} + \mathrm{Cr(VI)} \xrightarrow{k} \mathrm{OC(oxidized)} + \mathrm{Cr(III)} \quad (2)$$

When pH is constant, it can be suggested that the rate equation of Cr(VI) reduction is a first-order equation with respect to both Cr(VI) concentration and concentration of organic compound capable of reducing Cr(VI). Thus, the rate equation of Cr(VI) reduction should be as follows:

$$\frac{\mathrm{d[Cr(VI)]}}{\mathrm{d}t} = -k[\mathrm{OC}][\mathrm{Cr(VI)}] \qquad (\mathrm{mM/h}) \quad (3)$$

where OC represents the equivalent organic compound capable of reducing Cr(VI) (mM), and k presents rate coefficient of it. However, the reduction rate of Cr(VI) will decrease with time due to the depletion of not only the Cr(VI) but also the OC. Thus, the oxidation of OC must be considered. For a given time, the concentration of OC is as follows:

$$[\mathrm{OC}] = [\mathrm{OC}]_0(1 - X_{\mathrm{oxi}}) \qquad (\mathrm{mM}) \quad (4)$$

where X_{oxi} presents the fraction of OC oxidized, and can be calculated as follows, when considering equivalent reaction between the OC and the Cr(VI):

$$X_{\mathrm{oxi}} = \frac{\Delta[\mathrm{Cr(VI)}]}{[\mathrm{OC}]_0} = \frac{[\mathrm{Cr(VI)}]_0 - [\mathrm{Cr(VI)}]}{[\mathrm{OC}]_0} \quad (5)$$

Also, the initial concentration of OC, $[\mathrm{OC}]_0$, can be evaluated as follows:

$$[\mathrm{OC}]_0 = C^*_{\mathrm{OC}}[B] \qquad (\mathrm{mM}) \quad (6)$$

where B is the biomass, and C^*_{OC} indicates the content of equivalent organic compound per unit gram of biomass (mmol/g).

Combining Eqs. (3)–(6) gives:

$$\frac{\mathrm{d[Cr(VI)]}}{\mathrm{d}t} = -k[\mathrm{Cr(VI)}]([\mathrm{Cr(VI)}] + C^*_{\mathrm{OC}}[B] - [\mathrm{Cr(VI)}]_0) \quad (\mathrm{mM/h}) \quad (7)$$

and rearranges Eq. (7):

$$\left(\frac{1}{[\mathrm{Cr(VI)}]} - \frac{1}{[\mathrm{Cr(VI)}] + C^*_{\mathrm{OC}}[B] - [\mathrm{Cr(VI)}]_0}\right) \mathrm{d[Cr(VI)]} = -k(C^*_{\mathrm{OC}}[B] - [\mathrm{Cr(VI)}]_0)\,\mathrm{d}t \quad (8)$$

Finally, the integration of Eq. (8) yields a model equation in the general form, as follows:

$$[\mathrm{Cr(VI)}] = \frac{C^*_{\mathrm{OC}}[B][\mathrm{Cr(VI)}]_0 - [\mathrm{Cr(VI)}]_0^2}{C^*_{\mathrm{OC}}[B]\exp(k(C^*_{\mathrm{OC}}[B] - [\mathrm{Cr(VI)}]_0)t) - [\mathrm{Cr(VI)}]_0} \quad (\mathrm{mM}) \quad (9)$$

where k and C^*_{OC} are model constant parameters and t is a variable.

This model could well predict the Cr(VI) dynamics in aqueous solution during Cr(VI) biosorption by the *Ecklonia* biomass [17] or the *Rhizopus* biomass [15], thus it was also used to describe the Cr(VI) removal by the fermentation waste of *C. glutamicum* (Figs. 1, 3–5). With the aid of SigmaPlot V 6.00, a weighted least-squares linear regression using seven independent experimental data obtained at pH 2 gave constant values of k and C^*_{OC} as 0.834 (±0.062) and 0.236 (±0.006), respectively. The values were used to describe the Cr(VI) behaviors in aqueous solution at various biomass and initial Cr(VI) concentrations (Figs. 1, 4 and 5). This model initially overestimated the Cr(VI) concentrations due to the assumption where one kind of organic compound participated in the reduction of Cr(VI) by the tested biomass. Nevertheless, the correlation coefficient value of 0.973 means that this model was reasonable in spite of the absence of a comprehensive understanding about the redox reaction between Cr(VI) and the fermentation waste containing various unknown organic compounds.

As seen in Fig. 3, the removal rate of Cr(VI) greatly depended on the acidity of the solution. The constant values of model parameters at various pHs could be also obtained using Eq. (9), and the correlation coefficients (R^2) were higher than 0.99, except at pH 2 (Table 2). Modeling using these values gave a close fit to the experiment data at various pHs (Fig. 3). However, there was a misrelation between model parameters and the solution pH, especially at pH 3 (Table 2). This might be due to small amount of experimental data used to calculate model parameters at pHs 1, 3 and 4 (note that constant values at pHs 1, 3 and 4 were obtained from one batch experiment, whereas those at pH 2 were obtained from seven batch experiments conducted under various biomass and initial Cr(VI) concentrations). Anyhow, there is a need for developing an upgraded model considering the pH effect on Cr(VI) biosorption.

As seen in Fig. 1, some of total Cr, i.e., the reduced Cr(III), could be bound to the biomass during Cr(VI) biosorption. The adsorption rate of the reduced Cr(III) might be faster than the reduction rate of Cr(VI) [17,30]. Thus, it might be assumed that the reduced Cr(III) remains an equilibrium state between the biomass and aqueous solution. In general, equilibrium isotherm of heavy metals follows Langmuir model, as follows:

$$q_{\mathrm{Cr(III)}} = \frac{q^{\max}_{\mathrm{Cr(III)}} b[\mathrm{Cr(III)}]}{1 + b[\mathrm{Cr(III)}]} \qquad (\mathrm{mmol/g}) \quad (10)$$

where $q_{\mathrm{Cr(III)}}$ is the amount of the reduced Cr(III) bound to per unit g of dried biomass, $q^{\max}_{\mathrm{Cr(III)}}$ the maximum amount of the reduced Cr(III) bound at high [Cr(III)] and b is a constant

Table 2
Values of modeling parameters at various pHs

pH	Rate coefficient; k ($\mathrm{mM^{-1}\,h^{-1}}$)	Equivalent organic compound per unit gram of biomass; C^*_{OC} (mmol/g)	R^2
1	2.272	0.236	0.997
2	0.834[a]	0.236[a]	0.973[a]
3	1.516	0.103	0.996
4	0.333	0.110	0.990

[a] It was obtained from seven independent batch experiments conducted at various biomass and initial Cr(VI) concentrations (Figs. 4 and 5).

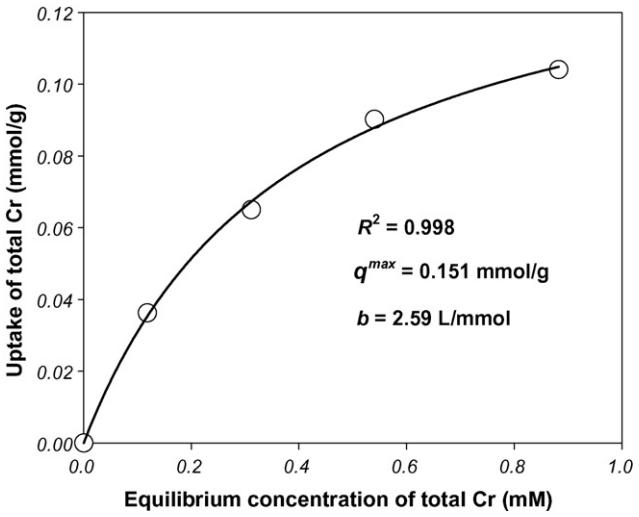

Fig. 6. Equilibrium isotherm of total Cr, i.e., the reduced Cr(III), at pH 2.0. Equilibrium data was obtained from Table 1. The curve was fitted by a weighted least-squares linear regression using Eq. (10).

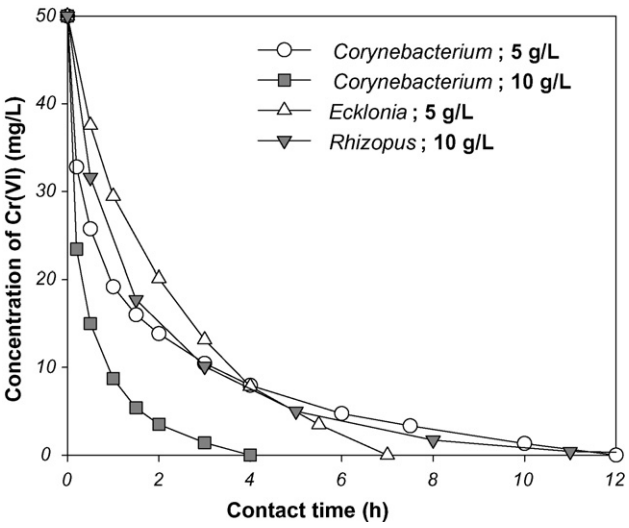

Fig. 7. Time courses of Cr(VI) removal by various biomasses. Conditions: 50 mg/L initial Cr(VI) concentration, pH 2.0.

related to the affinity of the binding sites. Clearly, the sum of chromium present in aqueous solution and on the biomass is always constant, as follows:

$$[\mathrm{Cr(VI)}]_0 = [\mathrm{Cr(VI)}] + [\mathrm{Cr(III)}] + q_{\mathrm{Cr(III)}}[B] \quad (\mathrm{mM}) \quad (11)$$

Combining Eqs. (10) and (11) gives:

$$[\mathrm{Cr(VI)}]_0 = [\mathrm{Cr(VI)}] + [\mathrm{Cr(III)}] + \frac{q^{\max}_{\mathrm{Cr(III)}} b[\mathrm{Cr(III)}][B]}{1 + b[\mathrm{Cr(III)}]} \quad (\mathrm{mM}) \quad (12)$$

Thus, for a certain time, the reduced Cr(III) present in aqueous solution can be calculated from Eqs. (9) and (12). Fig. 6 shows the equilibrium isotherm of total Cr, i.e., the reduced Cr(III), at pH 2. A weighted least-squares linear regression using Eq. (10) gave values of isotherm parameters: $q^{\max}_{\mathrm{Cr(III)}}$, 0.151 mmol/g and b, 2.59 L/mmol, and the values obtained were used to predict the reduced Cr(III) and the total Cr concentrations versus time (Fig. 1). Meanwhile, the pH profile during Cr(VI) biosorption could be predicted by using relation constant between consumed-proton and removed-Cr(VI) concentrations, i.e., 2.1 mol of proton consumption per mol of removed-Cr(VI) (Fig. 1).

Finally, kinetic and equilibrium models based on the 'reduction' mechanism could predict Cr(VI) and Cr(III) concentrations in the aqueous solution, and amount of total Cr bound on the biomass. To study the Cr(VI) biosorption by biomaterials, therefore, we recommend our models instead of common kinetic and/or equilibrium models based on 'anionic adsorption' mechanism.

3.4. Potentiality of the fermentation waste of C. glutamicum as a bioreductant for Cr(VI)

To examine the potentiality of the fermentation waste of *C. glutamicum* as a bioreductant for Cr(VI), this biomass was compared with two reported biomasses, i.e., brown seaweed *Ecklonia* biomass and fugal *Rhizopus* biomass; the former was screened among eight seaweed biomasses [12], whereas the latter from four fungal biomasses [17]. Removal rate of Cr(VI) by the fermentation waste was faster than that by the seaweed biomass or the fungal biomass (Fig. 7). Although this fermentation waste is potentially recyclable, until now most of it has been dumped at sea [26,27]. Therefore, the fermentation waste of *C. glutamicum* has a great potential as a bioreductant capable of detoxifying toxic Cr(VI) into less toxic or nontoxic Cr(III) in aqueous solution.

4. Conclusions

The fermentation waste of *C. glutamicum* effectively removed Cr(VI) in acidic aqueous solution than seaweed or fungal biomass. Colorimetric method and XPS study showed that the removal mechanism of Cr(VI) by the fermentation waste was a redox reaction. The removal rate of Cr(VI) in aqueous solution increased with a decrease in pH or with increases of Cr(VI) and biomass concentrations. A form of $-\mathrm{d[Cr(VI)]}/\mathrm{d}t = k[\mathrm{Cr(VI)}][\mathrm{OCs}]$ was used as kinetic model for Cr(VI) biosorption by the fermentation waste and successfully predicted the Cr(VI) concentrations under various biomass and Cr(VI) concentrations, especially at pH 2. The reduced Cr(III) behavior could be also predicted by combining the kinetic model with Langmuir model. These results strongly supported the proposed mechanism for Cr(VI) biosorption by the fermentation waste. In conclusion, this study would be helpful for researchers in this field to understand the Cr(VI) biosorption by biomaterials.

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