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Consideration of the methods for evaluating the Cr(VI)-removing capacity of biomaterial

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Abstract–Over the last few decades, many researchers have tested various biomaterials for the removal of toxic Cr(VI) from aquatic systems. It is now widely accepted that the mechanism of Cr(VI) biosorption is not 'anionic adsorption' but 'adsorption-coupled reduction'. Unfortunately, however, many researchers have still used common equilibrium isotherm models, such as Langmuir and Freundlich ones, based on 'anionic adsorption' mechanism in order to evaluate the Cr(VI)-removing capacity of biomaterial tested. In this study, a fermentation waste of *Corynebacterium glutamicum*, capable of removing Cr(VI) efficiently, was used as a model biomaterial to show why equilibrium isotherm models cannot be used to evaluate the Cr(VI)-removing capacity of biomaterial. Meanwhile, some alternative methods considering the mechanism of Cr(VI) biosorption were suggested; the maximum Cr(VI)-removing capacity of the biomaterial could be evaluated by a Cr(VI)-biosorption experiment under biomaterial-limited condition as well as by a simplified kinetic model based on the reduction mechanism of Cr(VI).

Key words: Biosorption, Hexavalent Chromium, Reduction, Langmuir, Freundlich

INTRODUCTION

Chromium is a redox active element, with oxidation states from –2 to +6, but only the +3 and +6 states are prevalent in aquatic systems. The two environmentally stable oxidation states, Cr(III) and Cr(VI), exhibit very different toxicities and mobilities. Cr(III) is relatively insoluble in the aquatic systems, and exhibits little or no toxicity [1]. In contrast, Cr(VI) usually occurs as a highly soluble and toxic chromate anion, and is a suspected carcinogen and mutagen [2]. Because of these remarkable differences, the treatment of Cr(VI)-bearing wastewaters has been widely studied and various technologies have been developed [3-5]. Among these, biosorption has been considered as one of the most efficient and environmentally-friendly technologies to remove heavy metals from aquatic systems [3,6].

Since a report on the use of sawdust by Srivastava et al. [7], many biomaterials such as nonliving bacteria, algae and fungi, agricultural byproducts and industrial bio-wastes have been examined to remove Cr(VI) from aquatic systems [3]. Although some outstanding types of biomaterials have already been identified and discussed in detail throughout international journals [8,9], extensive screening of additional biomaterials is taking place in both academic research laboratories and in some industrial research establishments [10-20]. For a long time, many early studies claimed that Cr(VI) was removed from aqueous phase through an adsorption mechanism, whereby anionic Cr(VI) ion species bind to positively-charged groups of biomaterials. However, this approach has lost its old original position [3,21,22].

Recently, 'adsorption-coupled reduction' has been proposed as the removal mechanism of Cr(VI) by biomaterials [21-25], and is now widely accepted [15-20]. When Cr(VI) comes in contact with biomaterial, especially in acidic solution system, the Cr(VI) can be easily or spontaneously reduced to Cr(III), because Cr(VI) has high redox potential value (above +1.3 V at standard condition). Regardless of whether or not researchers have recognized and/or confirmed the occurrence of Cr(VI) reduction by the biomaterial tested, they have used Langmuir and/or Freundlich equation(s) as equilibrium isotherm model to quantitatively evaluate the Cr(VI)-removing capacity of it (Table 1). Langmuir and Freundlich models are known to be derived from the basic assumption that the adsorption reaction between adsorbate and adsorbent reaches the thermal equilibrium state [26,27]. Therefore, we would like to insist that these isotherm models cannot be applied to the Cr(VI) biosorption research since its mechanism is not 'anionic adsorption' but 'adsorption-coupled reduction.'

In this study, we examined the Cr(VI) biosorption by a model biomaterial, the fermentation waste of *Corynebacterium glutamicum*, whose Cr(VI)-removal mechanism was recently confirmed as 'adsorption-coupled reduction' [25]. This biomass has also been known to be efficient in removing other metals [28] and dyes [29] from aqueous solutions. Removal behaviors of Cr(VI) and total Cr by the biomaterial were examined in various initial Cr(VI) concentrations at pH 2. Langmuir and Freundlich models were used to fit the isotherm curves of each chromium species, obtained at different contact times. In the end, alternative methods were employed to evaluate the Cr(VI)-removing capacity of the biomaterial.

EXPERIMENTAL

1. Preparation of the Biomaterial

The fermentation waste of *C. glutamicum* was obtained in a dried powder form from a lysine fermentation industry (BASF-Korea,

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Table 1. Proposed mechanisms of the Cr(VI) removal by various biomaterials and its Cr(VI)-removal capacity

Ref.	Biomaterials	Analytical methods	Proposed mechanism of the Cr(VI) removal	Condition for equilibrium experiment[d]	Model used for evaluating Cr(VI)-removal capacity and its value
[10]	Adsorbent driven from coir pith	Cr(VI)	Adsorption[a]	pH 2 <4 h	Langmuir: q_m=76.92 mg/g
[11]	Pistachio hull	Cr(VI)	Adsorption[a]	pH 2 6 h	Langmuir: q_m=116.3 mg/g
[12]	Microbial biomass (*Yarrowia lipolytica*)	Cr(VI)	Adsorption[a]	pH 1 2 h	Langmuir: q_m=150.18 mg/g Freundlich: K_F=0.1503 mg/g
[13]	Sawdust	Cr(VI)	Adsorption[a]	pH 1 17.5 h	Langmuir: q_m=41.52 mg/g
[14]	Alligator weed	Cr(VI)	Adsorption[a]	pH 1 8 h	Langmuir: q_m=82.57 mg/g
[15]	Seaweed biomass (*Hydrilla verticillata*)	Cr(VI)	Adsorption-coupled reduction[b]	Initial pH 1.8 6 h	Langmuir: q_m=20.41 mg/g
[16]	Lichen biomass (*Cladonia rangiformis*)	Cr(VI)	Adsorption-coupled reduction[b]	pH 5.11 2 h	Freundlich: K_F=71.78 mg/g
[17]	Palm flower	Cr(VI) Total Cr	Adsorption-coupled reduction[c]	Initial pH 4.5 3 h	Langmuir: q_m=7.137 mg/g
[18]	Grape waste	Cr(VI) Total Cr	Adsorption-coupled reduction[c]	pH 4 25 h	Langmuir: q_m=99.3 mg/g
[19]	Banana peel	Cr(VI) Total Cr	Adsorption-coupled reduction[c]	pH 2 1 h	Langmuir: q_m=96.2 mg/g
[20]	Wheat bran	Cr(VI) Total Cr	Adsorption-coupled reduction[c]	pH 2 3 h	Langmuir: q_m=282.54 mg/g

[a]Researchers analyzed only Cr(VI) in aqueous phase and claimed that the Cr(VI) was removed through 'anionic adsorption' mechanism in their study
[b]Researchers analyzed only Cr(VI) in aqueous phase but accepted 'adsorption-coupled reduction' as the removal mechanism of Cr(VI) by citing several references supporting it
[c]Researchers confirmed the occurrence of the Cr(VI) reduction to Cr(III) through Cr(VI) and total Cr analyses and reported that 'adsorption-coupled reduction' was also the removal mechanism of Cr(VI) by the biomaterial used in their study
[d]Batch experiments were conducted at room temperature

Korea) [25]. The dried powder was washed with deionized-distilled water several times without any pre-treatments like acid or alkaline washing, and then dried in an oven at 80 °C for 24 h [25]. The resulting dried biomaterial of *C. glutamicum* was stored in a desiccator and used for the batch experiments.

2. Batch Experiments for Cr(VI) Biosorption

The removal of Cr(VI) by the fermentation waste was examined by measuring the time-dependent concentrations of Cr(VI) and total Cr in a batch system. A standard solution of Cr(VI) was prepared by dissolving 2.828 g of analytical grade $K_2Cr_2O_7$ (Kanto) in a 1 L of deionized-distilled water. Batch experiments were conducted in 500 mL Erlenmeyer flasks with a working volume of 200 mL. 1 g of the dried biomaterial was brought into contact with Cr(VI) in the concentrations of 50, 100, 150, 200, 250 and 300 mg/L at pH 2. The flasks were agitated on a shaker at 200 rpm and 25 °C until Cr(VI) was completely removed in aqueous phase. The contact time required for the complete removal of Cr(VI) was in the range of 12 to 240 h, depending on initial Cr(VI) concentration. Thus, 6, 24, 84 and 240 hours were chosen as the contact times at which each isotherm curve was gained for isotherm modeling work. During batch experiments, the solution pH was maintained at pH 2 using 0.5 M H_2SO_4. Each batch experiment was run until all Cr(VI) was completely removed from aqueous solution.

The solution was intermittently sampled and centrifuged at 500 g 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 2% of the working volume. It was confirmed from three independent replicates that the Cr(VI) biosorption experiments were reproducible within 5% error.

3. Chromium Analysis

A colorimetric method, as described in the standard methods [30], 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 analyzed at 540 nm with a spectrophotometer (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 [23,24]. The Cr(III) concentration was then calculated from the difference between the total Cr and Cr(VI) concentrations.

RESULTS AND DISCUSSION

1. Mechanism of Cr(VI) Biosorption by the Fermentation Waste in Aqueous Solution

To examine the characteristics of Cr(VI) biosorption by the fer-

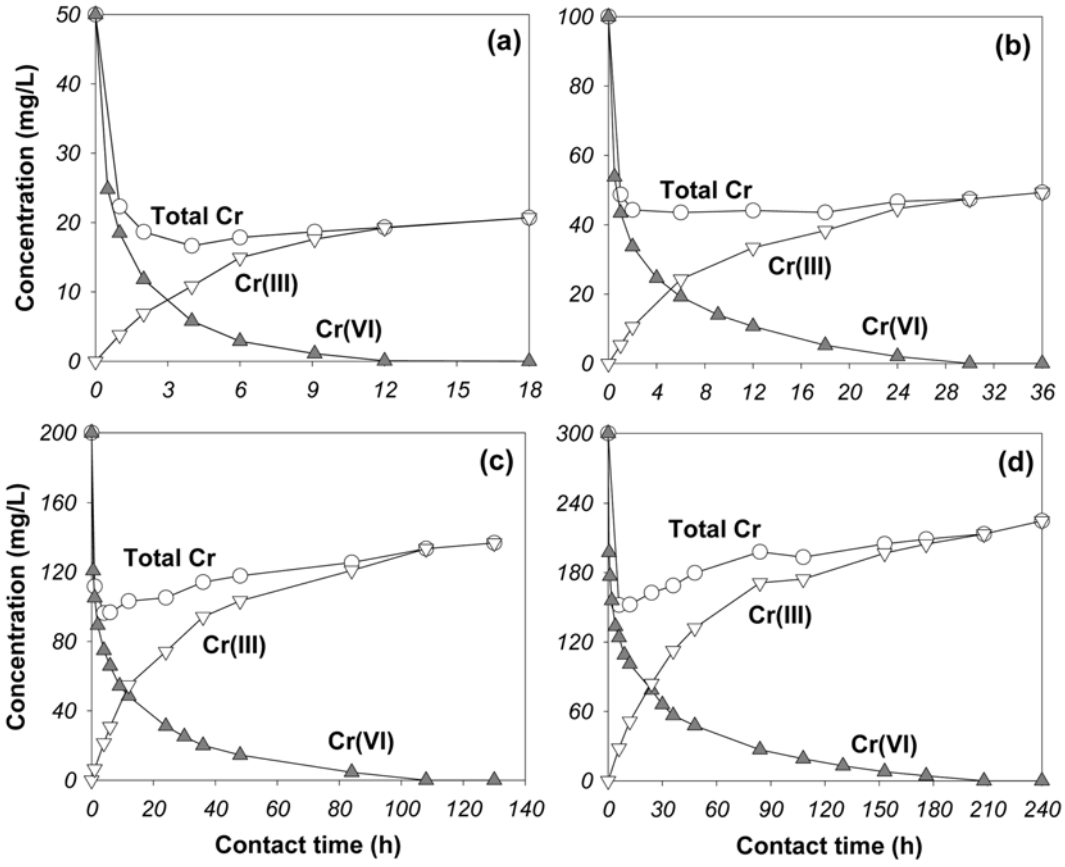

Fig. 1. Cr concentrations profiles during the Cr(VI) biosorption by the fermentation waste at pH 2. Initial Cr(VI) concentrations were (a) 50, (b) 100, (c) 200 and (d) 300 mg/L, respectively.

mentation waste of *C. glutamicum*, the concentrations of Cr(VI), Cr(III) and total Cr were investigated at various initial concentrations of Cr(VI) (Fig. 1). Regardless of initial Cr(VI) concentration, the concentration of Cr(VI) was found to decrease sharply, and was removed completely from the aqueous phase. Meanwhile, the Cr(III), which was not present initially, appeared in the aqueous phase and increased proportionately to the Cr(VI) depletion (Fig. 1). As a result, the concentration of total Cr abruptly decreased to its minimum value and then gradually increased to its final value, the same as the final concentration of Cr(III) in aqueous phase. These results indicate that some of the Cr(VI) was reduced to Cr(III) when brought into contact with the biomaterial. As shown in Fig. 1, the removal rate of Cr(VI) increased as its initial concentration was increased. For a Cr(VI) concentration of 50 mg/L, Cr(VI) was completely removed in the solution in 12 h, whereas the complete removal of 300 mg/L of Cr(VI) required 208 h of contact time.

To characterize the Cr(VI) biosorption, it is very important to investigate the oxidation state of the Cr bound onto biomaterial [22]. Previous study using the X-ray photoelectron spectroscopy (XPS) analysis showed that the Cr bound on the fermentation waste was only trivalent form [25]. Therefore, it was concluded that the Cr(VI) was removed from the aqueous solution by its reduction reaction to Cr(III) [25].

Recently, a new mechanism has been proposed for the biosorption of Cr(VI) onto nonliving biomaterial [21-25]. Cr(VI) can be reduced to Cr(III) in an aqueous system by nonliving biomaterial

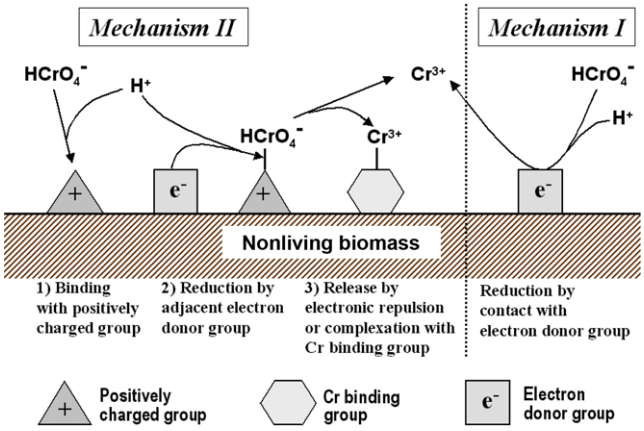

Fig. 2. Proposed mechanism for the biosorption of Cr(VI) by nonliving biomaterial [21,22].

through both direct and indirect reduction mechanisms (Fig. 2). In mechanism I (direct reduction mechanism), Cr(VI) is directly reduced to Cr(III) in the aqueous phase by contact with the electron-donor groups of the biomaterial, i.e., organic groups having lower reduction potential value than that of Cr(VI), with the reduced Cr(III) remaining in the aqueous phase [21-25]. Mechanism II (indirect reduction mechanism), however, consists of three steps: i) the binding of anionic Cr(VI) to the positively-charged groups present on

the biomaterial surface, ii) the reduction of Cr(VI) to Cr(III) by adjacent electron-donor groups, and iii) the release of the reduced Cr(III) into the aqueous phase due to electronic repulsion between the positively-charged groups and the Cr(III), or the complexation of the reduced Cr(III) with adjacent groups [21-25]. As the pH of the aqueous phase is lowered, a large number of hydrogen ions can easily coordinate with the amino and carboxyl groups present on the biomaterial surface. Thus, a low pH makes the biomaterial surface more positive. The more positive the surface charge of the biomaterial, the faster the rate of Cr(VI) removal from the aqueous phase, since the binding of anionic Cr(VI) ion species with the positively-charged groups is enhanced. A low pH also accelerates the redox reactions in both mechanisms I and II, since the protons take part in this reaction [21-25]. Meanwhile, if there are a small number of electron-donor groups in the biomaterial or protons in the aqueous phase, the chromium bound onto the biomaterial surface may remain in the hexavalent state. Therefore, a portion of mechanisms I and II depends on the biosorption system (pH, temperature, biomaterial species, Cr(VI) concentration, etc.) [21-25]. Regardless of whether or not researchers have recognized and/or confirmed the occurrence of Cr(VI) reduction by the biomaterial tested, most of them have accepted this mechanism in terms of 'adsorption-coupled reduction' [15-20].

2. Application of Langmuir and Freundlich Models to Cr(VI) Biosorption

In the field of biosorption research, the (bio)sorptive metal uptake has been quantitatively evaluated from experimental biosorption equilibrium isotherms similar to those used for the performance evaluation of activated carbons [6,31]. An adsorption isotherm relates the amount of solute adsorbed onto the adsorbent and the residual solute concentration at equilibrium condition at a given temperature. Among various isotherm models [6,31], there are two widely accepted and easily linearized adsorption isotherm models, which were proposed by Langmuir [26] and Freundlich [27], respectively. Needless to say, these two-parameter isotherm models have also been used to evaluate the Cr(VI)-biosorptive capacity of various biomaterials (Table 1).

A general form of the Langmuir model equation is

$$q = \frac{q_m b C_e}{1 + b C_e} \quad (1)$$

where q=uptake of species (mg/g); q_m=maximum uptake (mg/g); C_e=equilibrium (final) concentration in solution (mg/L); and b=constant related to energy of adsorption (L/mg).

A general form of the Freundlich model equation is

$$q = K_F C_e^{1/n} \quad (2)$$

where K_F gives a measure of the adsorbent capacity (mg/g), and n gives the intensity of adsorption (1<n).

Excepting Chand et al. [18], as shown in Table 1, all researchers conducted batch experiments within 24 h since they believed that the biosorption systems had reached equilibrium. Surprisingly, most of them used isotherm data obtained from batch experiments conducted within 6 h. Using these isotherm data, q_m in the range of 7.137 to 282.54 mg/g were obtained by Langmuir model, and K_F of 0.1503 to 71.78 mg/g by Freundlich model. The Cr(VI)-biosorptive capacity of biomaterials depended on their types [32].

To apply the Langmuir and Freundlich models to the Cr(VI) biosorption by the fermentation waste, isotherm data were obtained from batch experiments conducted at pH 2 and 25 °C. For each chromium species, i.e., Cr(VI), Cr(III) and total Cr, four isotherm curves

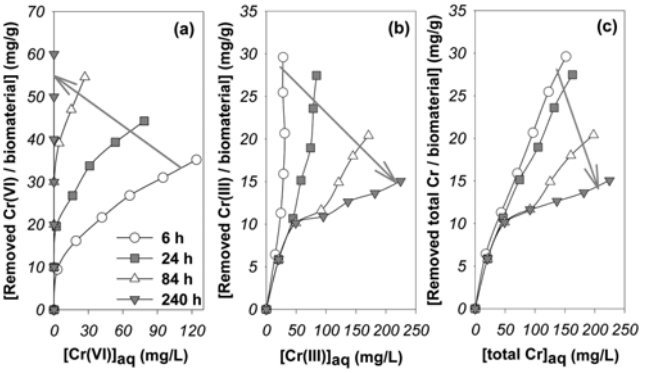

Fig. 3. Isotherm curves of (a) Cr(VI), (b) Cr(III), and (c) total Cr at different contact times.

Table 2. Isotherm parameters obtained by Langmuir and Freundlich models

		Langmuir model			Freundlich model		
		q_m (mg/g)	b (L/mg)	r^2	K_F (mg/g)	n	r^2
Cr(VI)	6 h	41.2	0.033	0.9513	5.29	2.57	0.9960
	24 h	400.6	0.033	0.8679	14.8	4.08	0.9272
	84 h	N.F.[a]	N.F.[a]	N.F.[a]	N.F.[a]	N.F.[a]	N.F.[a]
	240 h	N.F.[a]	N.F.[a]	N.F.[a]	N.F.[a]	N.F.[a]	N.F.[a]
Cr(III)	6 h	N.F.[a]	N.F.[a]	N.F.[a]	N.F.[a]	N.F.[a]	N.F.[a]
	24 h	N.F.[a]	N.F.[a]	N.F.[a]	N.F.[a]	N.F.[a]	N.F.[a]
	84 h	35.4	0.0069	0.9638	0.083	1.63	0.9804
	240 h	16.7	0.027	0.9923	2.52	3.03	0.9856
Total Cr	6 h	86.1	0.0034	0.9949	0.640	1.31	0.9986
	24 h	77.0	0.0033	0.9963	0.566	1.31	0.9990
	84 h	31.2	0.0083	0.9722	1.03	1.79	0.9887
	240 h	16.7	0.027	0.9923	2.52	3.03	0.9856

[a]Could not be fitted by the model since r^2 was below 0.8 or n was out of the range of valid value (>1)

were gained at different contact times of 6 h, 24 h, 84 h and 240 h in this study (Fig. 3). Parameters of each model were calculated by a non-linear method (Sigma Plot V6.00) and represented in Table 2. Contact time significantly affected the determination coefficient of model, r^2. As the contact time was increased, model parameter confidences decreased in the case of Cr(VI) isotherm, but increased in the cases of Cr(III) and total Cr isotherms. The Freundlich model well fitted the Cr(VI) isotherm at the contact times of 6 h and 24 h than did the Langmuir model, and the adsorbent capacity, K_F, increased with increasing contact time. Meanwhile, the Langmuir model described the trends of Cr(III) and total Cr isotherms better than did the Freundlich model, and the maximum uptakes of Cr(III) and total Cr, q_m, decreased with the increase of contact time.

Note that the Cr(VI) was completely removed from the aqueous phase by the reduction reaction into Cr(III) when enough contact time had been given (Fig. 1); thus, it was theoretically nonsense to apply the isotherm models based on adsorption reaction in order to evaluate the maximum Cr(VI)-removing capacity of the biomaterial tested in this study. In all previous studies, however, it might have been possible to use the Langmuir and Freundlich models to evaluate the Cr(VI)-biosorptive capacity of biomaterial tested since enough contact time was not given for the Cr(VI)-biosorption system to reach real equilibrium (Table 1). Without doubt, any equilibrium isotherm model based on adsorption reaction cannot be applied to a redox reaction. However, the Langmuir or Freundlich model may be used to evaluate the total Cr adsorption capacity of biomaterial, if enough contact time is given to attain real equilibrium condition.

3. Methods to Evaluate Cr(VI)-biosorptive Capacity of Biomaterial

Considering the mechanism of Cr(VI) biosorption, new concepts on the Cr(VI)-biosorptive capacity of biomaterial can be suggested as follows [23,25]:

$$\text{Cr(VI)-removing capacity} = \frac{\text{amount of Cr(VI) removed}}{\text{amount of biomaterial added}} \quad \text{(mg/g)} \quad (3)$$

$$\text{total Cr-adsorbing capacity} = \frac{\text{amount of total Cr removed}}{\text{amount of biomaterial added}} \quad \text{(mg/g)} \quad (4)$$

The Cr(VI)-removing capacity of biomaterial represents the amount of Cr(VI) removed through adsorption and reduction by unit gram of it under a given condition. Meanwhile, the total Cr-adsorbing capacity represents the total amounts of Cr(VI) and Cr(III) adsorbed onto the biomaterial by unit gram of it. The maximum value of the latter can be easily evaluated by common equilibrium isotherm models such as Langmuir and Freundlich ones. In this study, the maximum total Cr-adsorbing capacity of the fermentation waste was 16.7 mg/g in terms of q_m or 2.52 mg/g in terms of K_F at pH 2 (Table 2).

Two methods could be used to obtain the maximum Cr(VI)-removing capacity of the biomaterial, in this study. The first method was to conduct the Cr(VI)-biosorption experiment under biomaterial-limited condition at acidic pH and 25 °C for a long time (20 days) [23]. It must be noted that enough contact time should be provided for the system to reach equilibrium where biomaterial would be nearly oxidized but some of the Cr(VI) remained in the aqueous phase. As shown in Table 3, 1 g of the fermentation waste removed

Table 3. The maximum Cr(VI)-removing capacity of the fermentation waste[a]

Biomaterial concentration (g/L)	1.025	1.075	1.160
Final Cr(VI) concentration (mg/L)	228.7	223.8	196.0
Cr(VI) removed/biomaterial (mg/g)	264.7	256.9	262.1
Averaged Cr(VI)-removing capacity (mg/g)	261.2 (±4.0)[b]		

[a]Batch experiments were conducted at 25 °C until the Cr(VI) concentration did not nearly change (20 days). Initial Cr(VI) concentration was 500 mg/L, and initial solution pH was 1.5
[b]Standard deviation was given in parentheses

261.2 (±4.0) mg of Cr(VI) from aqueous phase under biomaterial-limited condition. Thus the maximum Cr(VI)-removing capacity of it could be determined to be 261.2 (±4.0) mg/g. While insufficient contact time may undervalue the maximum value, too acidic or high-temperature condition may overvalue it. The second method was to use a kinetic model, based on the 'reduction' mechanism of Cr(VI) [25]. An integrated form of this kinetic model is as follows:

$$[\text{Cr(VI)}] = \frac{C^*_{OC}[\text{B}][\text{Cr(VI)}]_0 - [\text{Cr(VI)}]_0^2}{C^*_{OC}[\text{B}]\exp(k(C^*_{OC}[\text{B}] - [\text{Cr(VI)}]_0)t) - [\text{Cr(VI)}]_0} \quad \text{(mM)} \quad (5)$$

where B, k, t and C^*_{OC} represent the biomaterial, rate coefficient, contact time and the content of equivalent organic compound per unit g of biomaterial, respectively [25]. The equivalent organic compound means the organic compounds capable of reducing Cr(VI). If this model well fits the dynamics of Cr(VI) concentration in the aqueous phase, the Cr(VI)-removing capacity of biomaterial can be obtained in terms of C^*_{OC} (mmol/g). As seen in Fig. 4, the kinetic model could predict the Cr(VI) concentrations under various initial Cr(VI) concentrations. With the aid of SigmaPlot 2000 (V 6.00) program, a weighted least-squares linear regression using six independent experimental data gave constant values of k and C^*_{OC} as 0.0352 (±0.0023) $mM^{-1}h^{-1}$ and 1.011 (±0.014) mmol/g, respectively. As a result, the Cr(VI)-removing capacity of the fermentative waste

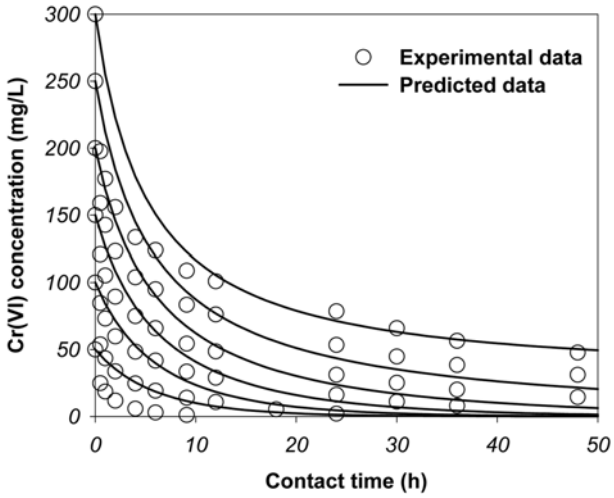

Fig. 4. Dynamics of Cr(VI) removal at various its initial concentrations. Predicted data (solid line) were obtained using Eq. (5).

could be determined at 52.5 (±0.7) mg/g by the kinetic model, but its value was much lower than that obtained by the Cr(VI)-biosorption experiment under biomaterial-limited condition. It was because the kinetic model was driven from the simple concept that Cr(VI) is removed by the redox reaction with one kind of organic compound present on biomaterial [25]. Therefore, there is a need to develop a new model considering complex mechanism of Cr(VI) biosorption, as shown in Fig. 2.

CONCLUSIONS

The fermentation waste of *C. glutamicum* effectively removed toxic Cr(VI) from acidic solution through adsorption-coupled reduction mechanism. To quantitatively evaluate the Cr(VI)-removing capacity of the biomaterial, Langmuir and Freundlich models were applied to the isotherm curves of various chromium species, but none of them could describe the isotherm curve of Cr(VI) at equilibrium since the models had been derived from a concept of adsorption reaction. In consideration of the Cr(VI) biosorption mechanism, therefore, alternative methods were developed in this study. In conclusion, the maximum Cr(VI)-removing capacity of the biomaterial could be evaluated by the Cr(VI)-biosorption experiment under biomaterial-limited condition as well as by the simplified kinetic model based on the reduction mechanism of Cr(VI).

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