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Kinetic Analysis and Mathematical Modeling of Cr(VI) Removal in a Differential Reactor Packed with *Ecklonia* Biomass

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Abstract To set up a kinetic model that can provide a theoretical basis for developing a new mathematical model of the Cr(VI) biosorption column using brown seaweed *Ecklonia* biomass, a differential reactor system was used in this study. Based on the fact that the removal process followed a redox reaction between Cr(VI) and the biomass, with no dispersion effect in the differential reactor, a new mathematical model was proposed to describe the removal of Cr(VI) from a liquid stream passing through the differential reactor. The reduction model of Cr(VI) by the differential reactor was zero order with respect to influent Cr(III) concentration, and first order with respect to both the biomass and influent Cr(VI) concentrations. The developed model described well the dynamics of Cr(VI) in the effluent. In conclusion, the developed model may be used for the design and performance prediction of the biosorption column process for Cr(VI) detoxification.

Key words: Biosorption, hexavalent chromium, reduction, *Ecklonia*, differential reactor

Chromium is a redox-active element with oxidation states from −2 to +6, but only the +3 and +6 states are prevalent in the aqueous phase. The two environmentally stable oxidation states, Cr(III) and Cr(VI), exhibit very different toxicities and mobilities. Cr(III) is relatively insoluble in aqueous systems (above pH 5) and exhibits little or no toxicity [1]. In contrast, Cr(VI) usually occurs as highly soluble and highly toxic chromate anions ($HCrO_4^-$ or $Cr_2O_7^{2-}$), which are suspected carcinogens and mutagens [5, 9]. Potable waters containing more than 0.05 mg/l of Cr(VI) are considered toxic [2]; therefore, aqueous Cr(VI) pollution represents an important environmental issue.

Recently, an efficient method for removing Cr(VI) from aqueous solution has been proposed by Park *et al.* [12–17]. When Cr(VI) containing wastewater was placed in contact with the brown seaweed *Ecklonia* biomass, the toxic Cr(VI) was completely reduced to less toxic or nontoxic Cr(III). The converted Cr(III) appeared in the aqueous phase and was partially bound to the biomass. An X-ray photoelectron spectroscopy study revealed that the chromium bound on the biomass was in a trivalent state only [15]. During the Cr(VI) reduction, some of the organic carbons of the biomass were completely oxidized into inorganic carbons (HCO_3^- and CO_3^{2-}). The removal rate of Cr(VI) increased with decreasing solution pH, as the protons were consumed during Cr(VI) reduction. However, Cr(VI) could be completely removed from the aqueous phase, even at pH 5, if sufficient contact time is given. Since the reduction reaction of Cr(VI) to Cr(III) was endothermic, the removal rate of Cr(VI) increased with increasing temperature. These results were also obtained in the case of dead fungal biomasses such as *Aspergillus niger*, *Rhizopus oryzae*, *Saccharomyces cerevisiae*, and *Penicillium chrysogenum* [14, 17]. Effects of various parameters such as background electrolyte, ionic strength, other heavy metals, and redox-active species on the Cr(VI) removal were examined on the basis of "redox reaction" [13]. In particular, a new batch kinetic model fitted well with the experimental data obtained from a batch system under various conditions [12], which also supports that the Cr(VI) removal mechanism is a "redox reaction." It is meaningful to note that 223 g of *Ecklonia* biomass is required for the reduction of 1 mol of Cr(VI), whereas 834 g of $FeSO_4 \cdot 7H_2O$, which is a common Cr(VI)

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reductant, is required for the same reduction [15]. Based on these results, it was proposed that the abundant and inexpensive *Ecklonia* biomass can be used for the conversion of toxic Cr(VI) into the less or nontoxic Cr(III).

In process applications, the most effective apparatus for continuous operation is a packed-bed column, much like that used for ion exchange. A continuous packed-bed reactor has a number of process engineering advantages, including high-yield operations and relatively easy scale-up from a laboratory scale procedure. Because of these advantages, many researchers have used a column packed with various biomasses capable of removing heavy metals [6–8, 10, 11, 19, 21, 22]. Many mathematical models have also been used to study packed-bed systems, and their dynamic behavior has been well described [6, 7, 10, 19]. All these models have originated mainly from research on activated carbon sorption and ion-exchange or chromatography applications. However, in the case of Cr(VI) biosorption in a packed-bed reactor, a few studies have been reported, but no theoretical model has been proposed to treat the experimental breakthrough data [11, 21, 22]. Since the removal mechanism of Cr(VI) by biomass is different to that of cationic heavy metals, such as Pb(II) and Cd(II), all mathematical models reported to date do not describe the dynamic behavior of Cr(VI) biosorption in a packed-bed reactor.

Unfortunately, the mathematical modeling of Cr(VI) biosorption in a packed-bed reactor was very difficult, since the removal mechanism of Cr(VI) by the *Ecklonia* biomass is very complex. A redox reaction occurs between Cr(VI) and the biomass and the binding of total Cr [reduced Cr(III)] to the biomass occurs during the redox reaction. In addition, the solution pH varies inside of the column depending on how much redox reaction and adsorption take place. Of all things, the dispersion effect of the packed-bed reactor makes the mathematical model more complex and less predictable for experimental data. It has been well proven that a differential reactor system is good for studying a basic kinetic study in a packed-bed reactor system, since distribution of pHs and chromium species inside of the differential reactor can be negligible [18]. It can be therefore assumed that the differential reactor has a constant reaction rate throughout the reactor volume. Accordingly, a differential reactor system may be used to set up a kinetic model that can provide a theoretical basis for developing a mathematical model of Cr(VI) biosorption in a packed-bed reactor.

In this study, a differential reactor packed with *Ecklonia* biomass was used to examine the effects of some operational parameters such as biomass concentration, influent pH, and influent Cr(III) and Cr(VI) concentrations on the Cr(VI) removal. Based on the Cr(VI) biosorption mechanism, a new mathematic model for differential reactor system was developed, and compared with experimental data.

MATERIALS AND METHODS

Preparation of the Biomass

The brown seaweed, *Ecklonia* sp., was collected along the seashore of Pohang, Korea [20]. After swelling and rinsing the sun-dried biomaterial with deionized-distilled water, it was cut into approximately 0.5-cm-sized pieces. The cut biomaterial was treated with a 1 M H_2SO_4 solution for 24 h, which replaced the natural mix of ionic species with protons and sulfates. The acid-treated biomaterial was washed with deionized-distilled water several times; thereafter, it was dried at 80°C in an oven for 24 h. The resulting dried biomass was later stored in a desiccator and used for differential reactor experiments.

Reagents

The Cr(VI) solution (25–200 mg/l) was prepared by dissolving analytical grade $K_2Cr_2O_7$ (Kanto) in deionized-distilled water, followed by pH adjustment to the desired values using 98% H_2SO_4 solution. All experiments were performed without the addition of any buffer solution to avoid the addition of any external electrolyte, which may influence the biosorption process. Potassium permanganate solution was prepared by dissolving 2.0 g $KMnO_4$ in 50 ml deionized-distilled water. Diphenylcarbazide solution was prepared by dissolving 250 mg 1,5-diphenylcarbazide in 50 ml HPLC-grade acetone, which was stored in a brown bottle.

Differential Reactor System

A differential reactor system was designed to operate under a short contact time with less influence on dispersion. The reactor consisted of a 2.0-cm-long glass column, with a 5.0-cm internal diameter (Fig. 1). The reactor column was densely packed with the biomass and operated in an upflow mode at room temperature (20–25°C). The flow rate was regulated with a variable speed pump by a Masterflex L/S digital drive, with an error below 0.5%. To minimize the effects of bubbles at the inlet and outlet

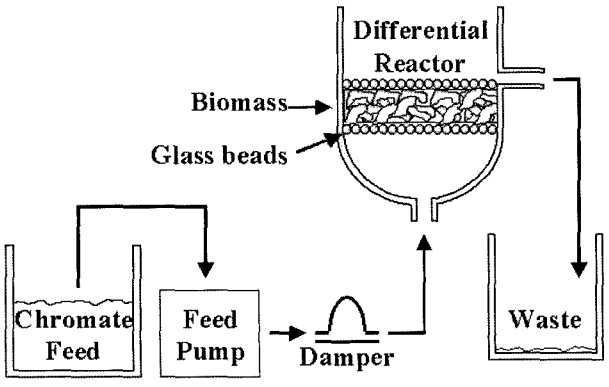

Fig. 1. Schematic diagram of a differential reactor system.

regions of a packed column, a supporter made of glass beads was installed inside the column. A damper was also used to minimize the pulse effect due to the mechanical movement of the pump head.

Reactor Startup

To determine the time required for stabilization of the differential reactor, it was continuously operated for 120 h, with a pH 2.0 solution containing 100 mg/l of Cr(VI). The column was densely packed with 5.50 g of the biomass. The flow rate of the influent was set at 10 ml/min; *i.e.*, the contact time was lower than 4 min. During the reactor operation, effluents were sampled to analyze the Cr(VI) and total Cr concentrations.

Real wastewaters generally contain tens to hundreds of mg/l of Cr(VI) and at below pH 4, thus the following parameters were chosen as the standard conditions: 0 mg/l of influent Cr(III) concentration, 100 mg/l of influent Cr(VI) concentration, 5.50 g of packed biomass, and influent solution pH at 2.0. To study the effect of Cr(III) on Cr(VI) removal in the differential reactor, the influent Cr(III) concentrations of 0, 50, 100, and 200 mg/l were used. To study the effect of Cr(VI), the influent Cr(VI) concentrations of 25, 50, 100, 150, and 200 mg/l were used. To study the effect of biomass, 2.75, 4.12, 5.50, 6.87, and 8.25 g of biomasses were employed. In the experiments carried out to study the effect of influent solution pH, pH values of 1.1, 1.5, 2.0, 2.5, and 3.0 were used. After each reactor operation, the column was washed and repacked with fresh biomass. Before the test, the differential reactor was stabilized by the flow of a pH 2.0 solution containing 100 mg/l of Cr(VI) through the reactor for 12 h. Thereafter, each influent was fed into the reactor, and the effluents were sampled every 15 min. In all experiments, the flow rate of the influent was set at 10 ml/min.

Chromium Analysis

A colorimetric method, as described in the standard methods [4], 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 (Spectronic 21, Milton Roy Co.). To estimate the 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 differences between the total Cr and Cr(VI) concentrations. The detection limit of this method was 0.03 mg/l.

Cr(VI) Speciation

Aqueous Cr(VI) exists as five species in aqueous system: H_2CrO_4, $HCrO_4^-$, CrO_4^{2-}, $Cr_2O_7^{2-}$, and $HCr_2O_7^-$ [3]. The distribution of these species is both solution pH and total Cr(VI) concentration dependent. In the pH range 2–4, most Cr(VI) exist as $HCrO_4^-$ and $Cr_2O_7^{2-}$, the ratio of which increases as the concentration of total chromium increases. Their standard reduction potentials are very similar:

$$HCrO_4^- + 7H^+ + 3e^- \leftrightarrow Cr^{3+} + 4H_2O \quad E^0 = +1.35\ V \quad (1)$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \leftrightarrow 2Cr^{3+} + 7H_2O \quad E^0 = +1.33\ V \quad (2)$$

In this study, to simplify a model equation, the Cr(VI) speciation was not considered, and was written in terms of [Cr(VI)].

Chemistry of Biomass

In our previous study, the heterogeneity of the *Ecklonia* biomass made it difficult to precisely characterize the nature of Cr(VI)-reducing sites [15, 16]. It was merely assumed that a variety of biological molecules, including polysaccharides, glycoproteins, glycolipids, and nucleic acids, of the *Ecklonia* biomass may reduce Cr(VI) to Cr(III). Furthermore, both the particles of the biomass and the soluble organic compounds released from the biomass could reduce Cr(VI), but the latter was minor. Thus, to develop an empirical rate equation for Cr(VI) reduction, the biomass must be replaced by organic compounds capable of reducing Cr(VI). In our previous study, 1 g of *Ecklonia* biomass could reduce 4.49 (±0.12) mmol of Cr(VI) at pH 2 [15]. Here, 1 mol of equivalent organic compounds was defined as the amount of organic carbon able to reduce 1 mol of Cr(VI) or to provide 3 mol of electrons [12]. Therefore, the initial concentration of equivalent organic compounds could be related to the biomass concentration, as follows:

$$[OCs]_0 = C^*_{OC}[B] \qquad [mmol/l] \quad (3)$$

where B is the biomass, OCs represents the equivalent organic compounds capable of reducing Cr(VI), and C^*_{OC} indicates the content of equivalent organic compounds per unit gram of biomass; *i.e.*, C^*_{OC} is 4.49 (±0.12) mmol/g.

This approach was successfully used to develop a kinetic equation of Cr(VI) reduction in a batch system [12].

RESULTS AND DISCUSSION

Determination of Quasi-Steady State Condition

To determine the time for stabilizing the differential reactor system, it was continuously operated for 118 h, with the solution containing 100 mg/l of Cr(VI) at pH 2.0. Fig. 2A shows the dynamics of the Cr(VI) and total Cr concentrations in the effluent of the reactor. The Cr(VI) concentration in the effluent was 74 mg/l at 1 h, and abruptly increased to 85 mg/l in 9 h, and then gently increased to 94 mg/l in 118 h. The former abrupt increase in the Cr(VI) concentration might be related to soluble organic

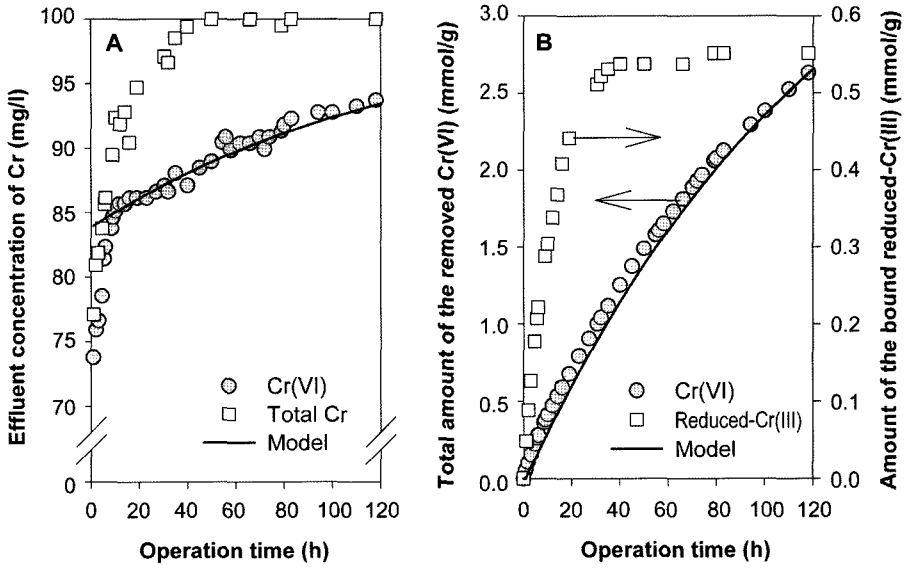

Fig. 2. Dynamics of (**A**) Cr(VI) and total Cr concentrations in the effluent, and (**B**) total amounts of the removed Cr(VI) and the bound reduced-Cr(III) in the differential reactor packed with the *Ecklonia* biomass.
Conditions: 140 g/l biomass concentration; 100 mg/l influent Cr(VI) concentration; influent solution pH 2.0; 10 ml/min flow rate. The lines represent the effluent Cr(VI) concentration and the total amount of the removed Cr(VI), as predicted by Eq. (13).

compounds in the effluent. It was observed that a large amount of soluble organic compounds was released from the biomass during its swelling with the chromate solution (data not shown). Soluble organic compounds can more rapidly reduce Cr(VI) to Cr(III) than the equal amount of solid biomass [15]. Thus, it can be assumed that the release of soluble organic compounds at initial operational time enhanced the removal performance of Cr(VI) by the differential reactor. However, after the release of soluble organic compounds from the biomass was blunted, the Cr(VI) concentration in the effluent stabilized. The latter gentle increase in the Cr(VI) concentration might be due to the loss of available organic compounds capable of reducing Cr(VI). As the redox reaction between Cr(VI) and biomass proceeds, the biomass loses Cr(VI)-reducing capacity [15]. Nevertheless, it is very meaningful to note that the variance of the effluent Cr(VI) after stabilization of the differential reactor was below 1 mg/l within 10 h. Therefore, it can be postulated that the differential reactor system attained a quasi-steady-state in 12 h, and the removal performance of Cr(VI) was constant within at least 5 h.

Meanwhile, the total Cr concentration in the effluent was higher than that of the Cr(VI), reflecting the reduction of Cr(VI) into Cr(III) (Fig. 2A). The difference of total chromium between the influent and the effluent indicates that a portion of total chromium was adsorbed to the biomass packed inside the reactor. An XPS analysis of chromium-laden biomass showed that the chromium bound on the biomass was the trivalent form [15]. Thus, it can be concluded that the Cr(VI) was removed through the reduction into Cr(III), and a portion of the reduced Cr(III) was adsorbed to the biomass; *i.e.*, the amount of Cr(VI) in the influent is the sum of the amounts of Cr(VI) in the effluent, Cr(III) in the effluent, and Cr(III) retained on the surface of the biomass. As the operation of the reactor proceeded, the total Cr concentration in the effluent increased, reaching a maximum equal to that in the influent. This indicates that the biomass was saturated with the reduced Cr(III) in 40 h. Fig. 2B shows the total amount of the reduced-Cr(III) bound on the biomass. One g of the biomass could bind 0.55 mmol of the reduced-Cr(III) at pH 2. Meanwhile, the total amount of the removed Cr(VI) increased with increasing operation time, and was 2.7 mmol/g at 118 h. In a batch system, 1 g of *Ecklonia* biomass can reduce 4.49 (±0.12) mmol of Cr(VI) at pH 2 [15]. Thus, it can be noted that about 60% of the Cr(VI)-reducing capacity of the biomass inside the reactor was deactivated in 118 h.

Based on the above results, the operating conditions of the differential reactor were determined to be as follows. Before the test, the reactor was stabilized by the flow of a solution containing 100 mg/l of Cr(VI) at pH 2 through the column for 12 h. Thereafter, the designed influent was fed into the reactor at a flow rate of 10 ml/min, and all tests were performed within 5 h.

Effects of Various Parameters

Fig. 3A shows the effect of Cr(III), the final product of a redox reaction between Cr(VI) and the biomass, on the Cr(VI) reduction in the differential reactor. The Cr(III) concentration in the influent was increased from 0 to 200 mg/l. It was observed that the presence of Cr(III) did not affect the removal behavior of Cr(VI) by the biomass.

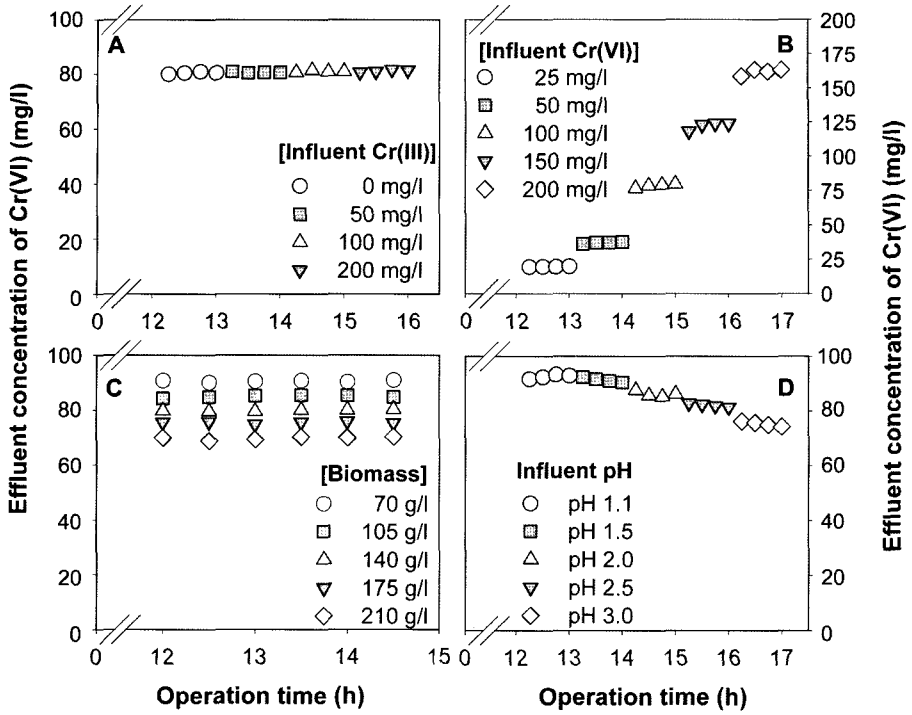

Fig. 3. The effluent concentration behaviors of Cr(VI) with regard to (**A**) the influent Cr(III) concentration, (**B**) the influent Cr(VI) concentration, (**C**) the biomass concentration, and (**D**) the influent solution pH.
Standard conditions: 0 mg/l influent Cr(III) concentration, 100 mg/l influent Cr(VI) concentration, 5.50 g packed biomass, and influent solution pH 2.0.

This result supports our previous result, where the reduction of Cr(VI) by *Ecklonia* biomass was an irreversible process under the conditions examined [15].

The concentration behavior of Cr(VI) versus operation time was examined with various influent Cr(VI) concentrations, in the range 50–200 mg/l (Fig. 3B). As the influent Cr(VI) concentration was increased, the effluent Cr(VI) concentration increased, and the difference between the influent and effluent Cr(VI) concentrations also increased. This means that the amount of the removed Cr(VI) increased with increasing influent Cr(VI) concentration.

Fig. 3C shows the Cr(VI) concentration behavior in the effluent at various biomass concentrations. For each operation of the reactor, the effluent Cr(VI) concentration stabilized in 12 h, and remained reasonably stable during the test. The difference between the influent and effluent Cr(VI) concentrations increased with increasing biomass concentration. This means that the amount of the removed Cr(VI) increased with increasing biomass concentration.

The effect of the influent pH on Cr(VI) reduction was also examined (Fig. 3D). As expected, the amount of the removed Cr(VI) increased with decreasing influent pH, as protons were consumed during the Cr(VI) reduction.

Mathematical Modeling of the Differential Reactor

The redox reaction between Cr(VI) and *Ecklonia* biomass can be represented as follows:

$$B+Cr(VI)+H^+ \xrightarrow{k} B(oxidized)+Cr(III) \quad (4)$$

Thus, a reduction model of Cr(VI) in a differential reactor system is a function of the biomass concentration, the influent pH, and Cr(III) and Cr(VI) concentrations.

$$R=f([B], [H^+]_0, [Cr(III)]_0, [Cr(VI)]_0, \ldots) \quad [mmol/h] \quad (5)$$

At quasi-steady-state, the reduction model can be represented as follows:

$$R=Q\Delta[Cr(VI)] \quad [mmol/h] \quad (6)$$

where Q represents the influent flow rate and Δ[Cr(VI)] the difference between the influent and effluent Cr(VI) concentrations. Thus, Eq. (6) could be used to calculate the reduction rate of Cr(VI) by the differential reactor (Fig. 4).

It was observed that the reduction rate of Cr(VI) was not affected by the presence of Cr(III) (Fig. 4A). Thus, the reduction model was zero order with respect to Cr(III). Figs. 4B and 4C show the effects of the biomass and influent Cr(VI) concentrations on the Cr(VI) reduction in the differential reactor. The reduction rate of Cr(VI) increased linearly as the biomass or influent Cr(VI) concentration increased. This implies that the reduction model was first order with respect to both the biomass and influent Cr(VI) concentrations. As expected, the reduction rate increased with increasing influent proton concentration. The relation between the reduction rate and proton concentration may be written as follows:

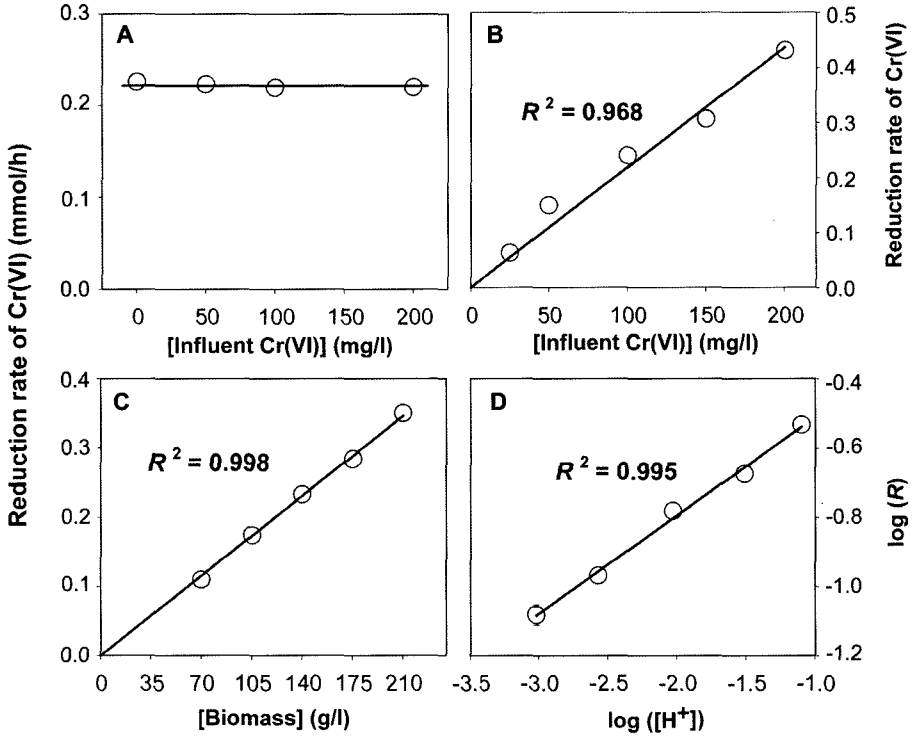

Fig. 4. Reduction rates of Cr(VI) in relation to (**A**) the influent Cr(III) concentration, (**B**) the influent Cr(VI) concentration, (**C**) the biomass concentration, and (**D**) the influent solution pH.
Curves were fitted by a weighted least-squares linear regression.

$$R=k'[H^+]^n \quad [\text{mmol/h}] \tag{7}$$

Fig. 4D shows the plot of log[R] versus log[H^+]. An n value of 0.284 (±0.012) was obtained using a weighted least-squares linear regression.

Finally, the reduction model of Cr(VI) in the differential reactor can be rewritten as follows:

$$R=Q\Delta[Cr(VI)]=k[B][Cr(VI)]_0[H^+]_0^n \quad [\text{mmol/h}] \tag{8}$$

Eq. (8) can be used to describe the Cr(VI) reduction by the differential reactor at steady state, where the reduction rate (R) is independent of operation time (t). However, as shown in Fig. 2A, as the operation time of the reactor increased, the effluent Cr(VI) concentration increased, owing to the loss of the Cr(VI)-reducing capacity of the biomass. Therefore, for developing a model capable of predicting long-term operation of the differential reactor, the term for the biomass in Eq. (8) must be replaced by the organic compounds capable of reducing Cr(VI); *i.e.*, OCs.

$$R'(t)=Q\Delta[Cr(VI)]=k''[OCs][Cr(VI)]_0[H+]_0^n \quad [\text{mmol/h}] \tag{9}$$

For a given operation time, t, the concentration of the organic compounds capable of reducing Cr(VI) is

$$[OCs]=[OCs]_0(1-X_{oxi}) \quad [\text{mmol/l}] \tag{10}$$

where X_{oxi} represents the fraction of total organic compounds oxidized for any given operation time, t, and can be calculated as follows, considering an equivalent reaction between OCs and Cr(VI):

$$X_{oxi}=\frac{\text{Total amount of the oxidized organic compounds}}{\text{Initial amount of the organic compounds}};$$

$$\frac{\text{Total amount of the removed Cr(VI)}}{\text{Initial amount of the organic compounds}}$$

$$=\frac{\int_0^t(Q\Delta[Cr(VI)])dt}{V_{DR}[OCs]_0}=\frac{Q\int_0^t\Delta[Cr(VI)]dt}{V_{DR}C^*_{OC}[B]} \tag{11}$$

where V_{DR} represents the volume of the differential reactor.

Combining Eqs. (3), (9), and (10), and then rearranging gives

$$R'(t)=Q\Delta[Cr(VI)]=k''C^*_{OC}[B][Cr(VI)]_0[H^+]_0^n(1-X_{oxi}) \quad [\text{mmol/h}] \tag{12}$$

Fig. 5 shows the plot of R'(t) versus $(1-X_{oxi})$. It was observed that the plots were a straight line, with the exception of the data before 9 h. Thus, a k'' value of 5.78 (±0.06)×10^{-4} could be calculated from the slope obtained from the experimental data after 9 h.

Finally, a new model for Cr(VI) biosorption by the differential reactor can be developed, as follows:

$$R'(t)=Q([Cr(VI)]_0-[Cr(VI)](t))$$
$$=k''C^*_{OC}[B][Cr(VI)]_0[H^+]_0^n$$

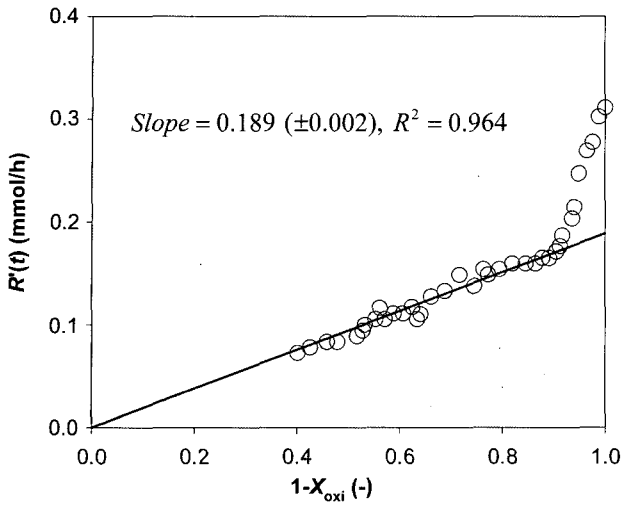

Fig. 5. The plot of R'(t) versus ($1-X_{oxi}$).
The curve was fitted by a weighted least-squares linear regression with experimental data obtained after 9 h.

$$\left(1-\frac{Q\int_0^t([Cr(VI)]_0-[Cr(VI)](t))dt}{V_{DR}C^*_{OC}[B]}\right) \quad (13)$$

where k''=5.78 (±0.06) $\times 10^{-4}$, C^*_{OC}= 4.49 (±0.12), and n= 0.284 (±0.012).

Since the integral term of this model contains an unknown time-dependent variable, [Cr(VI)](t), it could be only analytically solved using known parameters with the aid of the SigmaPlot 2000 (V 6.00) program. As shown in Figs. 2A and 2B, this model predicted well the experimental data after stabilization of the differential reactor; *i.e.*, 9 h.

In conclusion, the developed model may be used for the design and performance prediction of biosorption column processes for Cr(VI) detoxification.

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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)
Δ	Representative of difference
B	Representative of biomass
OCs	Representative of the organic compounds capable of reducing Cr(VI)
C^*_{OC}	Amount of OCs per unit gram of biomass (mmol/g)
R, R'(t)	Reduction rate of Cr(VI) of the differential reactor (mmol/h)
Q	Flow rate of influent solution (l/h)
V_{DR}	Volume of differential reactor (l)
X_{oxi}	Fraction of organic compounds oxidized for any given operation time, t (-)

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