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Reliable evidences that the removal mechanism of hexavalent chromium by natural biomaterials is adsorption-coupled reduction

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Abstract

For the last few decades, over 200 papers have been published in the Cr(VI) biosorption research field. Most early studies have claimed that Cr(VI) was removed from aqueous phase through an anionic adsorption, but this approach has been lost old original position. It has been newly explained that these findings were misinterpreted due to errors in measuring the concentrations of different chromium species in the aqueous phase, insufficient contact time required for equilibrium and the lack of information about the oxidation state of the chromium bound to biomaterials. Although 'adsorption-coupled reduction' is now widely accepted as the mechanism of Cr(VI) biosorption by natural biomaterials, a number of researchers still believe that Cr(VI) is removed by anionic adsorption onto the biomaterials. Therefore, the objective of this study was to show reliable evidences that the removal mechanism of Cr(VI) by natural biomaterials is 'adsorption-coupled reduction'. Sixteen natural biomaterials were used to study the Cr(VI) biosorption. Not only Cr(VI) but also total Cr in the aqueous phase were analyzed. X-ray photoelectron spectroscope was also used to verify the oxidation state of the chromium bound to the biomaterials. Finally, the removal behavior of Cr(VI) by each biomaterial was described by a kinetic model based on a redox reaction.

Keywords: Biosorption; Mechanism; Hexavalent chromium; Adsorption-coupled reduction

1. Introduction

Chromate is used or generated by a number of industrial processes including electroplating, tanning, cooling with water, pulp producing, and ore and petroleum refining (Barnhart, 1997). Chromate, Cr(VI), is known to be toxic to both plants and animals, as a strong oxidizing agent and potential carcinogen (Costa and Klein, 2006). The discharge of Cr(VI) to surface water is regulated to below 0.05 mg l^{-1} by the US EPA (Baral and Engelken, 2002). The existing chemical and electrochemical treatment processes for lowering Cr(VI) concentration generally involve the aqueous reduction of Cr(VI) to Cr(III) and the subsequent adjustment of the solution pH to near-neutral conditions to precipitate the Cr(III) ions produced (Eary and Rai, 1988). However, these methods have been considered undesirable due to the use of expensive chemicals, poor removal efficiency for meeting regulatory standards, and the production of large amounts of chemical sludge (Cabatingan et al., 2001).

Various biomaterials can retain relatively high quantities of metal ions by passive sorption and/or complexation, i.e., this is commonly known as biosorption (Veglio and Beolchini, 1997; Bailey et al., 1999). Since a report on the use of sawdust by Srivastava et al. (1986), many researchers have tested various biomaterials such as nonliving bacteria, microalgae, fungi, seaweed, agricultural byproduct and

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industrial bio-waste as an adsorbent for Cr(VI) removal (Mohan and Pittman, 2006). As far as our knowledge concerns, for the last few decades, over 200 papers on Cr(VI) biosorption have been published in various international journals. Most early studies have claimed that Cr(VI) was removed from the aqueous phase through an adsorption mechanism, whereby anionic Cr(VI) ion species bind to the positively charged groups of biomaterials. It has been recently explained that these findings were misinterpreted due to errors in measuring the concentrations of different chromium species in aqueous phase, insufficient contact time required for equilibrium and the lack of information about the oxidation state of the chromium bound to biomaterials (Mohan and Pittman, 2006).

Recently, it has been reported that Cr(VI) was completely reduced to Cr(III) in aqueous and solid phases by nonliving biomaterials of fungi and seaweed if enough contact time and protons were given (Park et al., 2004, 2005c). When Cr(VI) comes in contact with biomaterials, especially in an acidic solution, the Cr(VI) can be easily or spontaneously 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 phase with 1,5-diphenylcarbazide method and atomic absorption spectrophotometer (AAS) or inductively coupled plasma-atomic emission spectrometer (ICP-AES), and to verify the oxidation state of the chromium bound to biomaterials with X-ray absorption spectroscope (XAS) or X-ray photoelectron spectroscope (XPS) (Park et al., 2006). Regardless of whether or not researchers have recognized and/or confirmed the occurrence of Cr(VI) reduction to Cr(III) by the biomaterial tested, most of them have accepted 'adsorption-coupled reduction' as the mechanism of Cr(VI) biosorption (Barrera et al., 2006; Chen et al., 2006; Malkoc et al., 2006; Sankararamakrishnan et al., 2006; Verma et al., 2006; Garg et al., 2007; Malkoc and Nuhoglu, 2007). However, a number of researchers still believe that 'anionic adsorption' is the removal mechanism of Cr(VI) in their systems (Agarwal et al., 2006; Baral et al., 2006; Deepa et al., 2006; Sarin and Pant, 2006; Kiran et al., 2007; Ziagova et al., 2007).

The objective of this study was to show reliable evidences that the removal mechanism of Cr(VI) by natural biomaterials is 'adsorption-coupled reduction'. Pine needle, pine bark, pine cone, oak leaf, sawdust, walnut shell, peanut shell, rice straw, rice husk, banana skin, orange peel, green tea waste, fungal biomass of *Rhizopus*, and seaweed biomasses of *Ecklonia*, *Sargassum* and *Enteromorpha* were used to study the Cr(VI) biosorption by biomaterials. To analyze both Cr(VI) and total Cr in aqueous phase, colorimetric method combined with excess potassium permanganate was used. XPS was also used to verify the oxidation state of the chromium bound to the biomaterials. Finally, the removal behavior of Cr(VI) by the biomaterials in the aqueous phase was described by a kinetic model based on a redox reaction.

2. Materials and methods

2.1. Preparation of biomaterials

Natural biomaterials used in this study were pine needle, pine bark, pine cone, oak leaf, sawdust, walnut shell, peanut shell, rice straw, rice husk, banana skin, orange peel, green tea waste, fungal biomass of *Rhizopus*, and seaweed biomasses of *Ecklonia*, *Sargassum* and *Enteromorpha*. Each biomaterial was cut or crushed into ≈0.1–0.3 cm sized pieces, washed with deionized-distilled water several times, and dried in an oven at 60 °C for 24 h. The resulting dried biomaterials were stored in a desiccator and used for batch experiments.

2.2. Batch experiments for Cr(VI) removal

Cr(VI)-removal behavior of sixteen biomaterials 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. Each trial was performed by mixing 0.2 g of each biomaterial with 40 ml of a Cr(VI) solution in a 50 ml conical tube. Initial Cr(VI) concentration was 200 mg l^{-1} and initial solution pH was 2.0. The tubes were horizontally agitated on a shaker (Vision Co.) at 200 rpm under room temperature. The sample 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 4% of the working volume. It was confirmed from three independent replicates that the Cr(VI) removal experiments were reproducible within at most 5% error.

2.3. Chromium analysis

A colorimetric method (Clesceri et al., 1998) 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 spectrophotometrically analyzed at 540 nm (GENESYS 5, Spectronic Ins.). 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 difference between the total Cr and Cr(VI) concentrations.

2.4. X-ray photoelectron spectroscopy (XPS) analysis

XPS was employed to verify the oxidation state of the chromium bound to the biomaterials. Prior to mounting for XPS, the biomaterials were washed with deionized-distilled water several times, and then freeze-dried in a vacuum freeze dryer (Bondiro, ILSHIN Lab Co.). The resulting biomaterials were transported to the spectrometer

in a portable, gas-tight chamber. $CrCl_3 \times 6H_2O$ (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 sized spot was analyzed on all surfaces, using an Mg Kα ($h\lambda = 1253.6$ eV) X-ray source, at 100 W and pass energy of 0.1 eV, with 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 C1s peak of the aliphatic carbons; 284.6 eV.

3. Results and discussion

3.1. Occurrence of the Cr(VI) reduction to Cr(III)

To examine the Cr(VI) biosorption characteristics of sixteen biomaterials, the time-dependent concentrations of Cr(VI) were measured in a batch system (Fig. 1). In all of the biomaterials studied, Cr(VI) concentration was found to sharply decreased and was finally below the lower limit of detection for analytical method employed. The removal rate of Cr(VI) depended on the types of biomaterials; the order was pine needle, pine bark > pine cone, banana skin, green tea waste > oak leaf > *Rhizopus*, *Ecklonia* > *Sargassum*, walnut shell, rice straw, peanut shell > sawdust, *Enteromorpha*, orange peel > rice husk. Pine needle completely removed Cr(VI) in 5 h, while *Ecklonia* and rice husk needed 126 h and 1270 h for the complete removal of Cr(VI), respectively.

Table 1 shows the final solution pHs and removal efficiencies of total Cr when Cr(VI) was completely removed from the aqueous phase. In all cases, the solution pH increased from 2.00 to 2.17–2.50. Removal efficiency of total Cr by each biomaterial was not related with the removal rate of Cr(VI); pine bark showed the best removal efficiency of total Cr, but *Enteromorpha* showed the poorest one. The existence of total Cr in the aqueous phase implies the occurrence of Cr(VI) reduction to Cr(III) when brought into contact with the biomaterials.

Sharmar and Forster (1994a,b) reported that biomaterials such as leaf mould, sugar cane bagasse, sawdust, sugar beet pulp and maize cob removed Cr(VI) from aqueous solution through 'anionic adsorption' and 'partial reduction into Cr(III) below pH 3'. To the best of our knowledge, those were the first reports finding the occurrence of non-enzymatic reduction of Cr(VI) to Cr(III) by biomaterials under acidic conditions. However, since Sharmar and Forster (1994a,b) did not test the oxidation state of the chromium bound to the biomaterials, they believed, from limited information, that it was a hexavalent form.

3.2. Oxidation state of the chromium bound to the biomaterials

To characterize the main mechanism of Cr(VI) removal, it is very important to verify the oxidation state of the chromium bound to the biomaterial; if this state is only trivalent, it can be concluded that Cr(VI) was completely reduced to Cr(III) by the biomaterial. However, if both trivalent and hexavalent forms of chromium exist on the surface of biomaterial, it can be concluded that both Cr(VI) adsorption and Cr(VI) reduction contributed to the

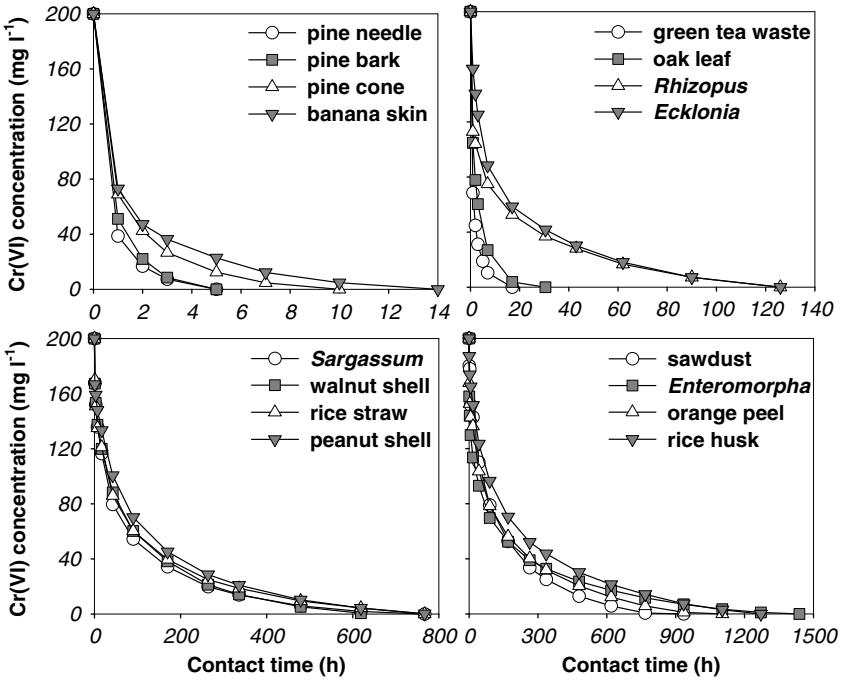

Fig. 1. Removal of Cr(VI) from aqueous solution by various biomaterials (Conditions: 200 mg l^{-1} initial Cr(VI) concentration, 5 g l^{-1} biomaterial concentration, initial pH 2.0). Regardless of the types of biomaterials, Cr(VI) was completely removed from aqueous phase when enough contact time was given.

Table 1
Final solution pHs and removal efficiencies of total Cr at equilibrium state[a]

	Pine needle	Pine bark	Pine cone	Banana skin	Green tea waste	Oak leaf	*Rhizopus*	*Ecklonia*
Final solution pH (–)	2.21	2.17	2.17	2.37	2.26	2.29	2.32	2.50
Removal efficiency of total Cr (%)[b]	38.0	85.0	71.8	25.5	64.8	48.7	27.2	77.2
	Sargassum	Walnut shell	Rice straw	Peanut shell	Sawdust	*Enteromorpha*	Orange peel	Rice husk
Final solution pH (–)	2.46	2.21	2.24	2.19	2.24	2.37	2.27	2.21
Removal efficiency of total Cr (%)[b]	64.1	24.6	26.3	41.0	19.9	15.8	49.9	25.2

[a] Cr(VI) was completely reduced to Cr(III) at equilibrium state.
[b] Standard deviations were below 3%.

removal of Cr(VI) from aqueous solution. To verify the oxidation state of the chromium bound to the biomaterials studied, XPS was employed in this study (Fig. 2). High-resolution XPS spectra collected from the Cr2p core region of sixteen biomaterials indicated that there were significant contributions of the chromium bound to the biomaterials. Significant bands of standard Cr(III) compound, $CrCl_3 \times 6H_2O$, appeared at binding energies of 577.0–579.0 and 586.5–588.0 eV; the former corresponds to $Cr2p_{3/2}$ orbital, the latter to $Cr2p_{1/2}$ orbital. Meanwhile,

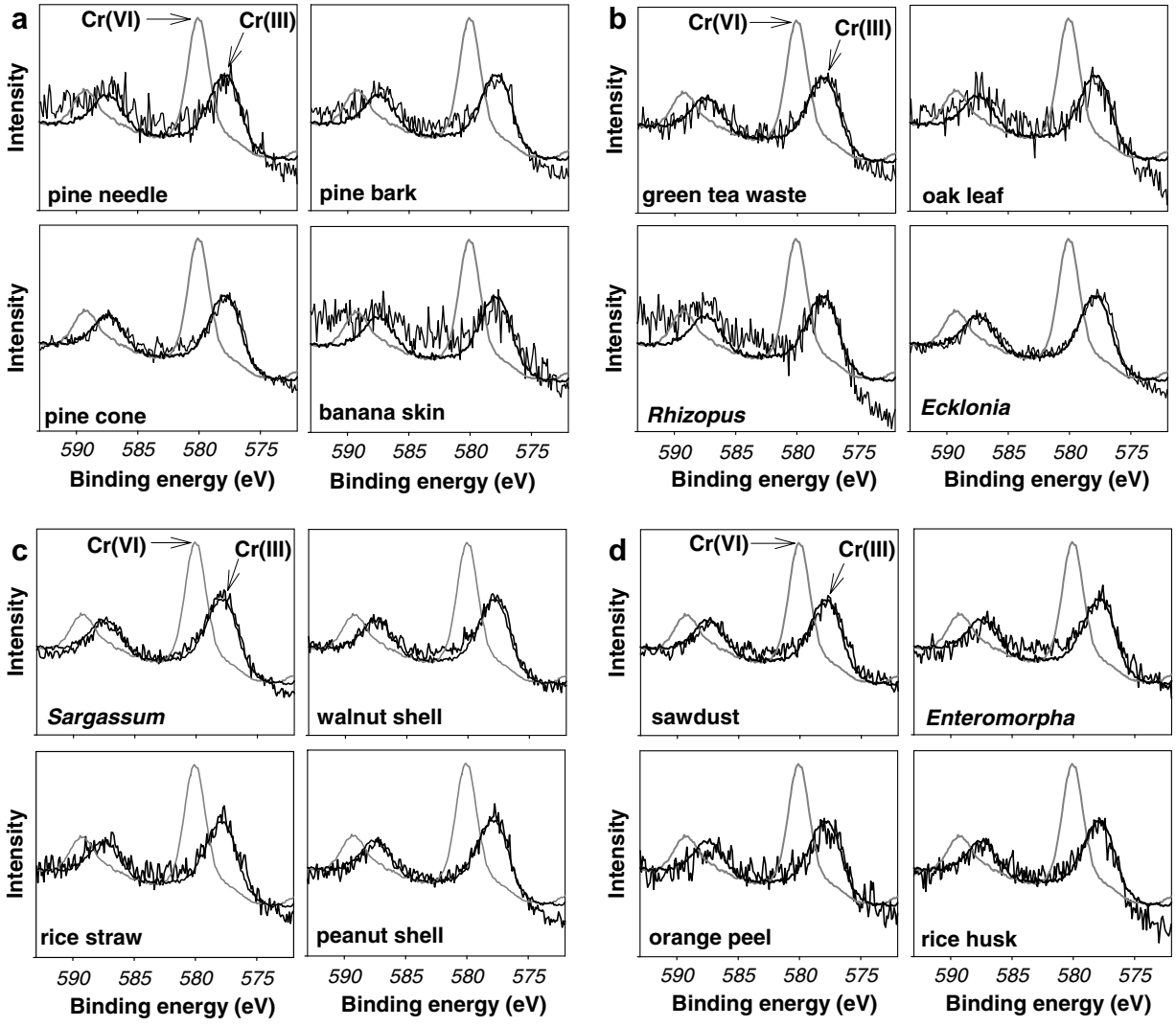

Fig. 2. High-resolution spectra collected from the Cr2p core region of various biomaterials bound with chromium. The spectra of the Cr-laden biomaterials were well matched with that of standard Cr(III) compound. This result implies that the chromium bound to the surface of sixteen biomaterials were mostly or totally in trivalent form.

those of standard Cr(VI) compound, $K_2Cr_2O_7$, appeared at binding energies of 579.0–581.0 and 588.5–590.0 eV, respectively. Namely, Cr(VI) was characterized by higher binding energies than Cr(III) since hexavalent form draws electron more strongly than trivalent form. Surprisingly, the spectra of the Cr-laden biomaterials were well matched with that of Cr(III). These results imply that the chromium bound to the surface of sixteen biomaterials were mostly or totally in trivalent form. Regardless of the types of biomaterials, therefore, it can be concluded that the reduction reaction of Cr(VI) to Cr(III) also occurred on its surface.

There have been several reports on the chromium species bound to other biomaterials. Dupont and Guillon (2003) studied the removal mechanism of Cr(VI) by a lignocellulosic substrate extracted from wheat bran, and they reported that the adsorption reaction consumed a large amount of protons, which is consistent with the reduction of Cr(VI) to Cr(III); the oxidation of lignin moieties occurred concurrently to the Cr(VI) reduction and led to the formation of hydroxyl and carboxyl functions. XPS results of Deng and Ting (2005) indicated that redox reaction occurred on the surface of polyethylenimine-modified fungal biomaterial, and whether the converted Cr(III) ions were released to solution or adsorbed on the biomaterial depended on the solution pH. Desorption study of Cr(VI) on coir pith and XANES analysis suggested that most of the chromium bound on the coir pith was in Cr(III) form and the reduced Cr(III) might be bound with C=O groups and O–CH_3 groups of the coir pith. (Suksabye et al., 2007). Sawalha et al. (2007) also observed that some of the Cr(VI) bound to saltbush biomass (*Atriplex canescens*) was reduced to Cr(III). Liu et al. (2006) reported that the reduction rate of Cr(VI) by wine processing waste sludge, containing considerable quantities of activated sludge, was so high that the reduced form of Cr(III) could be observed on the sludge after 1.5 min by XANES analysis. These studies reach the same conclusion as this study, that is, the chromium bound to the natural biomaterials was mostly or totally in Cr(III) form.

3.3. Kinetic modeling of Cr(VI) biosorption

Previously, a kinetic model could well describe the Cr(VI) behavior in aqueous phase when brought into contact with fungal or seaweed biomaterial (Park et al., 2005b, 2007). The kinetic model could be developed from a concept based on the redox reaction between Cr(VI) and biomaterial.

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

When pH is constant, the rate equation of Cr(VI) reduction is represented as follows:

$$\frac{\mathrm{d[Cr(VI)]}}{\mathrm{d}t} = -k[\mathrm{OC}][\mathrm{Cr(VI)}] \quad (2)$$

where OC represents the equivalent organic compound capable of reducing Cr(VI), [mM], and k presents its rate

Table 2
Kinetic model parameters for Cr(VI) removal in aqueous phase

	Pine needle	Pine bark	Pine cone	Banana skin	Green tea waste	Oak leaf	*Rhizopus*	*Ecklonia*
k ($\mu M^{-1} h^{-1}$)	557 (±70)	244 (±69)	218 (±41)	275 (±52)	323 (±42)	103 (±17)	34.9 (±6.8)	16.0 (±3.6)
C^*_{OC} (mmol g^{-1})	1.00 (±0.05)	1.43 (±0.24)	1.11 (±0.09)	0.88 (±0.05)	0.86 (±0.03)	1.09 (±0.07)	0.81 (±0.04)	1.06 (±0.10)
R^2	0.999	0.998	0.995	0.988	0.994	0.997	0.979	0.989
	Sargassum	Walnut shell	Rice straw	Peanut shell	Sawdust	*Enteromorpha*	Orange peel	Rice husk
k ($\mu M^{-1} h^{-1}$)	4.3 (±0.6)	3.1 (±0.6)	4.3 (±0.6)	2.2 (±0.4)	1.8 (±0.4)	2.6 (±0.4)	1.8 (±0.4)	1.3 (±0.2)
C^*_{OC} (mmol g^{-1})	0.96 (±0.05)	1.09 (±0.10)	0.90 (±0.04)	1.16 (±0.11)	1.23 (±0.12)	0.90 (±0.04)	1.10 (±0.11)	1.13 (±0.10)
R^2	0.993	0.990	0.992	0.992	0.993	0.985	0.986	0.990

coefficient. For a given time, the concentration of OC is as follows:

$$[\mathrm{OC}] = [\mathrm{OC}]_0(1 - X_{\mathrm{oxi}}) \tag{3}$$

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):

$$X_{\mathrm{oxi}} = \frac{\Delta[\mathrm{Cr(VI)}]}{[\mathrm{OC}]_0} = \frac{[\mathrm{Cr(VI)}]_0 - [\mathrm{Cr(VI)}]}{[\mathrm{OC}]_0} \tag{4}$$

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

$$[\mathrm{OC}]_0 = C^*_{\mathrm{OC}}[B] \tag{5}$$

where B is the biomaterial, and C^*_{OC} indicates the content of equivalent organic compound per unit gram of biomaterial, mmol g^{-1}.

Combining Eqs. (2)–(5) gives

$$\frac{\mathrm{d}[\mathrm{Cr(VI)}]}{\mathrm{d}t} = -k[\mathrm{Cr(VI)}]\left([\mathrm{Cr(VI)}] + C^*_{\mathrm{OC}}[B] - [\mathrm{Cr(VI)}]_0\right) \tag{6}$$

and rearranges Eq. (6)

$$\left(\frac{1}{[\mathrm{Cr(VI)}]} - \frac{1}{[\mathrm{Cr(VI)}] + C^*_{\mathrm{OC}}[B] - [\mathrm{Cr(VI)}]_0}\right)\mathrm{d}[\mathrm{Cr(VI)}] = -k(C^*_{\mathrm{OC}}[B] - [\mathrm{Cr(VI)}]_0)\mathrm{d}t \tag{7}$$

Finally, the integration of Eq. (7) yields a model equation in the general form, as follows:

$$[\mathrm{Cr(VI)}] = \frac{C^*_{\mathrm{OC}}[B][\mathrm{Cr(VI)}]_0 - [\mathrm{Cr(VI)}]_0^2}{C^*_{\mathrm{OC}}[B]\exp\left(k(C^*_{\mathrm{OC}}[B] - [\mathrm{Cr(VI)}]_0)t\right) - [\mathrm{Cr(VI)}]_0} \tag{8}$$

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

With the aid of SigmaPlot V 6.00, a weighted least-squares linear regression using experimental data obtained in this study gave constant values of k and C^*_{OC} as shown in Table 2. The values were used to describe the Cr(VI) behavior in the aqueous solution when brought into contact with various biomaterials (Fig. 3). Although this model initially overestimated the Cr(VI) concentrations, the correlation coefficient value above 0.98 means that the Cr(VI) removal behavior was well fitted by the simplified reduction equation.

3.4. Proposed mechanism of Cr(VI) biosorption

Analyses of different chromium species in aqueous and solid phases showed that the main mechanism of Cr(VI) removal by various biomaterials was the reduction reaction of Cr(VI) to Cr(III). Regardless of the types of biomaterials, the kinetic model based on the redox reaction between Cr(VI) and biomaterial described well the Cr(VI) removal behavior in the aqueous phase. Therefore, a mechanism proposed for the Cr(VI) removal by biomaterial of *Ecklonia* (Park et al., 2005a) can be accepted as that by various biomaterials. Cr(VI) can be removed from an aqueous system by natural biomaterials through both direct and indirect reduction mechanisms (Fig. 4). 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, and the reduced Cr(III) forms complexes with biomaterials or remains in the aqueous phase. Mechanism II (indirect reduction mechanism) 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. Amino and carboxyl groups may take part in reaction (i) of mechanism II (Park et al., 2005a, Sawalha et al., 2007). 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. 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 (solution pH, temperature and

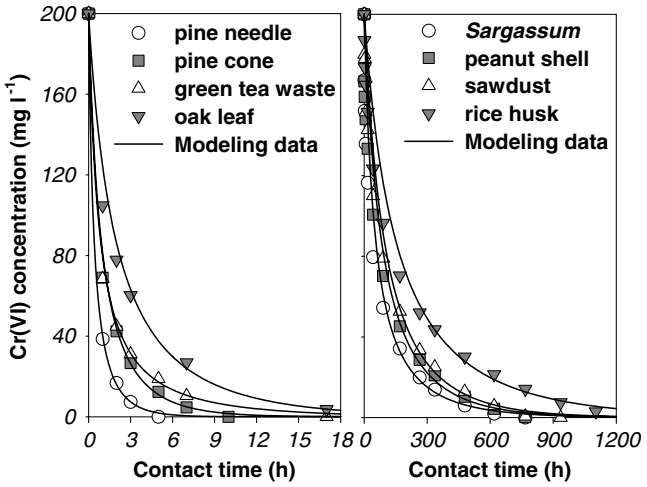

Fig. 3. Comparison of experimental data with simulation result using Eq. (8) (Conditions: 200 mg l^{-1} initial Cr(VI) concentration, 5 g l^{-1} biomaterial concentration, initial pH 2.0.). The Cr(VI) removal behavior was well fitted by the simplified reduction equation in a form of $-\mathrm{d}[\mathrm{Cr(VI)}]/\mathrm{d}t = k[\mathrm{Cr(VI)}][\mathrm{OC}]$.

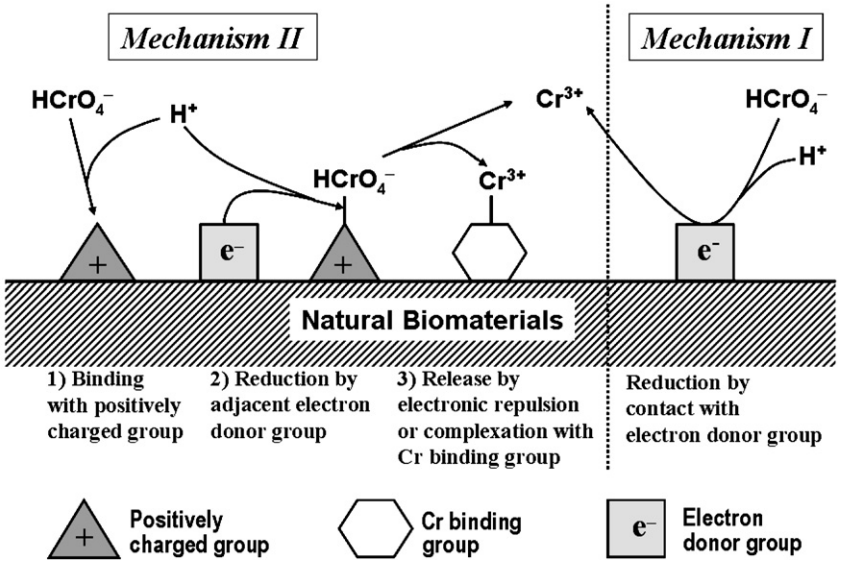

Fig. 4. Proposed mechanism of the Cr(VI) biosorption by natural biomaterials (Park et al., 2005a). Cr(VI) is removed from an aqueous system by natural biomaterials through both direct and indirect reduction mechanisms.

species on the biomaterial, as well as the biomaterial and Cr(VI) concentrations, etc.).

4. Conclusions

Regardless of the types of biomaterials, Cr(VI) was completely removed from aqueous phase and the chromium bound to its surface was in trivalent form. Simplified reduction equation in a form of $-d[Cr(VI)]/dt = k[Cr(VI)][OC]$ was used as a kinetic model for the Cr(VI) biosorption by biomaterials and successfully predicted the time-dependent concentration of Cr(VI) in the aqueous phase. In conclusion, the main mechanism of Cr(VI) removal by natural biomaterials is 'adsorption-coupled reduction'.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2007.06.007.

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