MATERIALS AND INTERFACES

Chromium Biosorption by Thermally Treated Biomass of the Brown Seaweed, *Ecklonia* sp.

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Biomass of the brown seaweed *Ecklonia* removed both cationic Cr(III) and anionic Cr(VI). The Cr(III) was removed through an ion-exchange mechanism; the Cr(VI) was removed through a redox reaction with the biomass. Among the various pretreatments for developing an efficient biomass, thermal treatment was used in this study. After thermal treatment, the biomass characteristics were investigated using SEM, BET, FTIR, potentiometric titration, and solution analysis. The Cr(III)/Cr(VI) removal performance of the biomass was also examined. The thermal treatment altered the physical and chemical properties of the biomass. The carboxyl groups present in the biomass were decreased to 76% by thermal treatment, but the intraparticular mass transfer resistance increased. These effects of thermal treatment on the biomass reduced the adsorption rate and efficiency of Cr(III) but made the biomass stronger as a Cr(VI) reductant, resulting in an increase in the Cr(VI) reduction rate and the Cr(VI) reducing capacity of the biomass. Therefore, the thermal treatment has to be selectively adopted according to Cr(III) and Cr(VI) concentrations, since it simultaneously reduces and enhances the Cr(III) and Cr(VI) removals, respectively.

Introduction

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 and exhibits little or no toxicity.[1] In contrast, Cr(VI) usually occurs as highly soluble and highly toxic chromate anions, which are suspected carcinogens and mutagens.[2] Potable waters containing more than 0.05 mg/L Cr(VI) are considered toxic;[3] therefore, aqueous Cr(VI) pollution represents an important environmental issue.

The existing chemical treatment processes for lowering Cr(VI) concentrations generally involve the aqueous reduction of Cr(VI) to Cr(III) using various chemical reductants, such as $FeSO_4$ or Na_2SO_3, and the subsequent adjustment of the solution pH to near-neutral conditions to precipitate the Cr(III) ions produced.[4] However, this process has started to become undesirable due to the use of expensive and toxic chemical reductants, so now, due to the operational cost, it tends to be limited to streams containing high concentration of Cr(VI). Furthermore, this process produces significant amounts of secondary wastes, such as chemical sludge.[5] Thus, industry has begun to seek alternative ways of treating Cr(VI)-containing wastewater. An ion-exchange process may be used for the treatment of wastewater;[6] however, this seems uneconomic due to the high cost of ion-exchange resins. As an alternative for dealing with Cr(VI) wastewater problems, some researchers have proposed a detoxification process using living cells.[7,8] However, there are also problems, such as cell death due to the high toxicity of Cr(VI), high operation costs, and the separation of the treated liquid. Bearing these factors in mind, it may be very meaningful that the *Ecklonia* biomass, an abundant and inexpensive brown seaweed, is able to efficiently remove both Cr(III) and Cr(VI).[9,10]

Cr(III), that is, Cr^{3+} and $CrOH^{2+}$, can bind to various functional groups of the seaweed biomass through an ion-exchange mechanism.[5,9] The main functional group of the protonated *Ecklonia* biomass is known to be a carboxyl group, with a pK_H of 4.6 ± 0.1.[9] Thus, the removal rate and equilibrium uptake of Cr(III) increase with increasing solution pH, which is the general pattern in cationic metal biosorption.[11] Cr(VI), that is, $HCrO_4^-$ and $Cr_2O_7^{2-}$, can be reduced to Cr(III) by being brought into contact with the *Ecklonia* biomass due to their reduction potentials (above +1.3 V), and the converted Cr(III) appears in the aqueous phase or is partly bound to the biomass.[10] Since protons are consumed during Cr(VI) reduction, the Cr(VI) removal rate decreases with increasing solution pH. However, Cr(VI) can be completely removed from aqueous solution, even at pH 5, if sufficient contact time is given. One gram of

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Ecklonia biomass can take up 34.1 mg of Cr(III) in equilibrium at pH 4 and reduce 233 mg of Cr(VI) to Cr(III) at pH 2.[9,10]

To enhance the removal efficiency of metal ions by the biomass, various pretreatments can be used, such as chemical and physical treatments.[11] Of these, thermal treatment may be a very simple and inexpensive method to develop an efficient biomass.

In this study, the *Ecklonia* biomass was thermally treated to enhance the Cr(III)/Cr(VI) removal efficiency. After thermal treatment under various conditions, the physical and chemical properties of the biomass were investigated using scanning electron microscopy (SEM), the BET (Brunauer, Emmett, and Teller) technique, Fourier transform infrared spectroscopy (FTIR), potentiometric titration, and solution analysis. The Cr(III)/Cr(VI) removal performance of the biomass was also examined according to degree of thermal treatment.

Materials and Methods

Preparation of the Biomass. The brown seaweed, *Ecklonia* sp., was collected along the seashore of Pohang, South Korea. After swelling and rinsing with deionized distilled water, the sun-dried biomass 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 and thereafter dried at room temperature for 3 days. The resulting dried biomass was designated as the control biomass in this article. Then the control biomass was again dried at 60 or 100 °C in an oven for 24 or 240 h. The control and thermally treated biomass were later stored in a desiccator and used for the following experiments.

Batch Experiments. The biosorption of chromium was examined in batch experiments. The test solutions containing Cr(III) or Cr(VI) were prepared by dissolving exact quantities of analytical grade $CrCl_3 \cdot 6H_2O$ (Sigma) or $K_2Cr_2O_7$ (Kanto) in deionized distilled water. For time-course experiments, each trial was performed by bringing into contact 1 g of biomass with 200 mL of test solution containing 100 mg/L of Cr(III) or Cr(VI) in a 500-mL Erlenmeyer flask. For equilibrium experiments, each trial was performed by bringing into contact 0.5 g of biomass with 100 mL of test solution containing ~25 to 500 mg/L of Cr(III) in a 250-mL Erlenmeyer flask. Before and after the biomass addition, the pH of each test solution was adjusted and maintained to the required value with concentrated H_2SO_4 or NaOH solutions. The flasks were agitated on a shaker at 200 rpm and room temperature (~20 to 25 °C). All experiments were performed without addition of any buffer solution to avoid the addition of any external electrolytes that may influence the biosorption process.

For the time-course experiments with both Cr(III) and Cr(VI), samples were intermittently removed from the flasks to analyze the Cr(III) and Cr(VI) concentrations. The total volume of withdrawn samples never exceeded 2% of the working volume. For the equilibrium experiments with Cr(III), the required contact time to reach sorption equilibrium was 12 h, as determined in the time-course experiments. After the sorption system reached the equilibrium state, the samples were taken from the flasks for analysis of the Cr(III) concentration. The Langmuir model was used to evaluate the maximum Cr(III) uptake of each biomass. Because the Cr(VI) was completely removed from the aqueous phase under an excess dosage of the biomass (5 g/L), the Cr(VI) reducing capacity of the biomass was determined as the amount of Cr(VI) removed by unit gram of biomass when the biomass concentration is limiting; i.e., ~0.02 to 0.06 g of each biomass was placed in contact with 100 mL of test solution containing 200 mg/L of Cr(VI) at pH 2 for 120 h. The Cr(III)/Cr(VI) experiments were reproducible to within, at most, a 5% error.

Characterization of the Biomass. The BET (Brunauer, Emmett, and Teller) technique, which measures the quantity of gas molecules needed to saturate a solid surface under equilibrium conditions, was used to analyze the surface area of the control and thermally treated biomasses.[12] Here, a known quantity of the sample was evacuated and then saturated with liquid nitrogen. The quantity of gas required for saturation of each sample was taken as a measure for the determination of the pore volume and surface area.

Scanning electron microscopy was used to detect physical structure changes in the biomass before and after the thermal treatment. Mounted samples were carbon-coated and analyzed with a cold field emission scanning electron microscope (model S-4200, Hitachi Co.).

Potentiometric titrations were carried out using 5 g/L of the biomass. Tens of 125-mL flasks were used for the titration experiments. First, the weighted biomass and 50 mL of deionized distilled water (CO_2-free) were put into each flask. Here, CO_2-free water was obtained by stripping deionized distilled water with nitrogen gas for 2 h with vigorous mixing. Different volumes of 1 M NaOH or 0.5 M H_2SO_4 were added to each flask containing the biomass suspension and agitated using a shaker (200 rpm) at room temperature for 12 h. Thereafter, the equilibrium pH was measured using a pH electrode (Mettler-Toledo). During the titration experiments, the CO_2-free condition was always maintained to avoid the influence of inorganic carbon on the solution pH.

Infrared spectra of the control and thermally treated biomasses were obtained using Fourier transform infrared spectrometry (FTIR 1600, Perkin-Elmer). For the FTIR study, 30 mg of finely ground biomass was encapsulated in 300 mg of KBr (Sigma) to prepare a translucent sample disk.

The solution containing soluble organic compounds was obtained by bringing into contact 0.5 g of each biomass with 100 mL of deionized distilled water (CO_2-free) for 24 h and filtering the slurry with a Whatmann GF/C (0.45-μm) filter to eliminate the biomass particles. The resulting solution was analyzed using a total organic carbon (TOC)/inorganic carbon (IC) analyzer (Shimadzu TOC 5000A), ion chromatography (Dionex DX 120), and a pH meter. The chromaticity (yellowish) of the solution was presented as the optical density at 400 nm using a spectrometer (Spectronic 21, Milton Roy Co.).

Chromium Analysis. A colorimetric method, as described in the Standard Methods, was used to measure the concentrations of the different Cr species.[13] The pink complex, formed from 1,5-diphenylcarbazide and Cr(VI) in acidic solution, was able to be spectrophotometrically analyzed at 540 nm. To estimate the total Cr, the Cr(III) was first converted to Cr(VI) at high temperature (~130 to 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

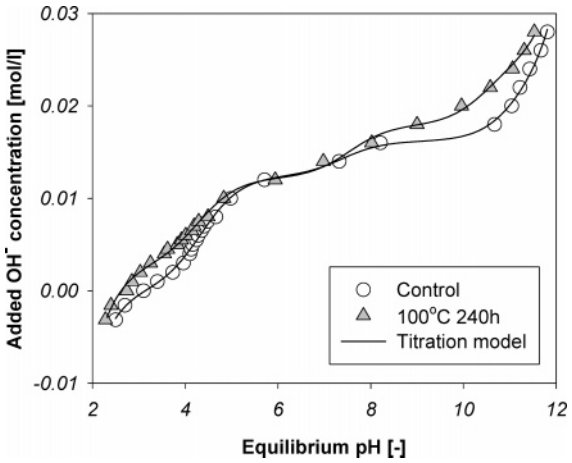

Figure 1. Potentiometric titration of the control and 100 °C thermally treated biomass. The lines are produced by the titration model (eq 5).

Cr(VI) concentrations. The detection limit of this method was 0.03 mg/L.

Results and Discussion

Physical Structure Change of the Biomass by Thermal Treatment. To examine the effect of thermal treatment on the physical structure of the biomass, the surface area of the biomass before and after thermal treatment was quantitatively measured using the BET technique. However, it was difficult to get reliable data, since the surface area determined using the BET technique was very small (below 0.08 m^2/g). In general, the surface area of activated carbon is >1000 m^2/g, since the thermal or chemical activation of raw materials, such as coconut shell and charcoal, produce many micropores that result in an increase in their surface areas.[12] Thus, the microstructures of the control and thermally treated biomasses were visually observed through SEM images, but there was insignificant differences in their microstructures (data not shown). These results imply that the thermal treatment hardly affected the microstructure of the biomass under the conditions used in this study. In addition, there was no micropore in the biomass, which is the reason for its small surface area. It is well-known that brown seaweed biomass has a gel-like structure because the outer layer of its cell wall is an amorphous embedding matrix.[11]

Meanwhile, it was observed that the control biomass was rigid and fully swollen with water, but the thermally treated biomass was very fragile and only slightly swollen. Fournel et al. reported that partially irreversible shrinking occurred during the drying step of chitosan bead, resulting in an increased intraparticular mass transfer resistance that plays a significant role in the adsorption of metal ions onto adsorbent.[14]

Chemical Structure Change of the Biomass by Thermal Treatment. The biomass titration curve displays distinct characteristics, depending on the types and amounts of functional groups present in the biomass. The titration results of the control and thermally treated biomasses are shown in Figure 1. In the case of the control biomass, an inflection point can obviously be seen between pH 3.5 and 4.5, indicating the existence of a functional group with a pK_H value between 3.5 and 4.5. The buffer capacity extends over a much larger region than this; therefore, other functional groups must be present. However, their identities could not be definitely confirmed from the inflection points of the titration curves, their quantities probably being much smaller than that of the main functional group.

To quantitatively evaluate the properties of the functional groups, the functional sites on the biomass can be considered. With respect to a certain group (B_jH), its reaction with a proton and its related equilibrium constant (K_j) may be defined as follows:

$$B_jH \leftrightarrow B_j^- + H^+ K_j = \frac{[B_j^-][H^+]}{[B_jH]} \quad (1)$$

The total concentration ($[B_j]_T$) of the functional groups is equal to the sum of the protonated and ionized configurations. The protonated group can be expressed using eq 1, as $[B_jH] = [B_j^-][H^+]/K_j$. Therefore,

$$[B_j]_T = [B_jH] + [B_j^-] = [B_j^-](1 + [H^+]/K_j) \quad (2)$$

Consequently, the concentration of the ionized group can be expressed as a function of the total concentration of the site and of the proton concentration.

$$[B_j^-] = \frac{[B_j]_T}{1 + [H^+]/K_j} \quad (3)$$

In the titration experiments, the electroneutrality condition must be satisfied. Therefore,

$$[Na]_{added} + [H^+] = \sum_{j=1}^{N} [B_j^-] + [OH^-] \quad (4)$$

where $\sum_{j=1}^{N}[B_j^-]$ represents the sum of the concentrations of all types ($1 \sim N$th type) of ionized groups, and $[Na]_{added}$ is identical to the concentration of added hydroxide ions. Combining eqs 3 and 4 yields

$$[Na]_{added} = \sum_{j=1}^{N} \frac{c_j X}{1 + [H^+]/K_j} + \frac{K_W}{[H^+]} - [H^+] \quad (5)$$

where c_j and X represent the quantity of the specific functional groups per unit mass of biomass (mmol/g) and the biomass concentration, respectively. In this work, the change in the working volume due to the addition of NaOH was compensated for during the data processing.

Equation 5 contains two parameters per functional group: the equilibrium constant (K_j) and the amount of the functional group per unit mass (c_j). To examine the number of functional groups, the titration model (eq 5) was simultaneously fitted to the titration data obtained. A nonlinear regression was performed by means of the Marquardt−Levenberg algorithm.[15]

As a result, one or two functional groups were insufficient to describe the titration results (data not shown). Meanwhile, the three- and four-site models were able to describe the entire titration curves of the control and thermally treated biomasses, respectively (Figure 1). The estimated parameters are summarized in Table 1. The negative logarithm of the equilibrium constant for proton binding to the first group was estimated to be 2.0 ± 0.3 and appeared to be a sulfonate group. Fourest and Volesky also detected a strong acidic functional group, sulfonate group, in the dry biomass of the brown seaweed *Sargassum*.[16] The second group was established as the most abundant and believed to

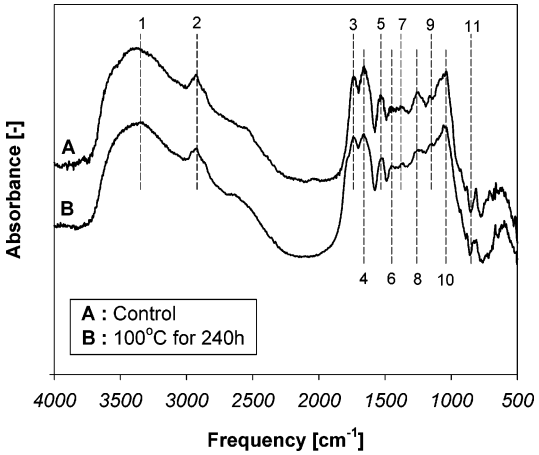

Figure 2. FTIR spectra of the control and 100 °C thermally treated biomass.

Table 1. Dissociation Constants (pK_H) and Contents (c) of the Functional Groups Present in the Biomass

functional group	control		100 °C for 240h	
	pK_H	c (mmol/g)	pK_H	c (mmol/g)
1st (sulfonate)			2.0 (±0.3)	0.5 (±0.1)
2nd (carboxyl)	4.3 (±0.0)	2.5 (±0.1)	4.3 (±0.1)	1.9 (±0.1)
3rd (?)	7.4 (±0.2)	0.8 (±0.1)	7.5 (±0.2)	1.1 (±0.1)
4th (hydroxyl)	11.1 (±0.1)	1.4 (±0.1)	10.5 (±0.1)	1.4 (±0.1)
R^2	0.99		0.99	

Table 2. Functional Groups of the Seaweed Biomass and the Corresponding Infrared Absorption Frequencies

IR band	frequency (cm^{-1})	assignment
1	3350	bonded hydroxyl group, −NH stretching[a]
2	2920	C−H stretching[a]
3	1740	C═O stretching of COOH[b]
4	1660	C═O chelate stretching,[b] amide I band[c]
5	1530	amide II band[c]
6	1450	symmetric bending of CH_3 of the acetyl moiety[a]
7	1380	amide or sulfamide bond[d]
8	1260	C−O stretching of COOH[c]
9	1150	−CN stretching[a]
10	1040	−CN stretching[a]
11	850	S═O bond[b]

[a] See ref 20. [b] See ref 16. [c] See ref 21. [d] See ref 22.

be the carboxyl group. A similar result was obtained for the biomass of the brown seaweed *Sargassum*, whereby its carboxyl group was shown to have a pK_H value of 4.5.[17] The last functional group seemed to be a hydroxyl (or phenolic) group that generally shows pK_H values between 9.5 and 10.5 depending on the structure of main chains.[18] The third group (pK_H = 7.4 ± 0.2) could not be identified, not even approximately, because there are many kinds of functional groups (i.e., phosphoryl, amino, and imidazole groups) within biological polymers that have pK_H values around 7.4.[18] Finally, these results indicate that the control biomass had at least three types of functional groups, with the carboxyl group being the most abundant (2.5 ± 0.1 mmol/g). The thermal treatment strongly affected the distribution of functional groups presented in the biomass: the content of carboxylic groups decreased to 76%, while that of the sulfonate groups increased (0.5 ± 0.1 mmol/g). Generally, it is well-known that the carboxyl group, which is the main functional group of alginate located on the surface of the seaweed biomass, is a key component for adsorption of cationic metal ions, such as Cd(II), Pb(II), and Cr(III).[9,16,17,19]

To confirm the types of functional groups, an FTIR study was carried out. As shown in Figure 2, the FTIR spectrum of the biomass displays a number of absorption peaks, indicating the complex nature of the biomass. The functional groups of the seaweed biomass and corresponding infrared absorption frequencies are summarized in Table 2. A significant shift in the absorption peaks can be seen when comparing the FTIR spectra of the control and thermally treated biomasses. The peaks around 1740 cm^{-1} (C═O stretching), 1660 cm^{-1} (C═O chelate stretching), and 1260 cm^{-1} (C−O stretching) were slightly reduced by thermal treatment, but the absorption peak around 850 cm^{-1} (S═O bond) was slightly increased. These results support that thermal treatment changed the chemical structure of the biomass, decreasing the carboxyl group and forming a sulfonate group.

Various soluble organic compounds may be released from the biomass and react with cationic Cr(III) ion or anionic Cr(VI) ion, affecting their removal efficiencies. Meanwhile, the characterization of the solution obtained by swelling the biomass with water may give indirect information about the chemical properties of it. As can be seen from Table 3, the equilibrium pH of the solution obtained from the control biomass was 3.04, whereas that from the thermally treated biomass was below 2.7. Particularly, the amount of soluble organic compounds in the solution significantly increased from 54.3 to 453.1 mg/L due to thermal treatment, resulting in the increase in the absorbance at 400 nm, which was used as an indirect indicator of the chromaticity of the yellowish solution, in this study. The change in the inorganic carbon concentration due to thermal treatment was negligible. Meanwhile, the data obtained from the ion chromatography show that the amount of soluble organic compounds containing sulfate and phosphate groups was increased in the solution by thermal treatment (Table 3). Therefore, it can be concluded that the chemical properties of some organic compounds in the biomass were changed by thermal treatment and more easily released into solution, resulting in the decrease of the solution pH due to the sulfate and phosphate groups contained within the biomass.

Effect of Thermal Treatment on Cr(III) Removal. The dynamics of Cr(III) removal were studied to determine the contact time required to reach equilibrium (Figure 3). The removal rate of Cr(III) by the biomass was initially fast, with the equilibrium state reached after 6 h of contact time. At a constant pH, the rate and efficiency of Cr(III) removal decreased with increasing degree of thermal treatment. The 100 °C thermally treated biomass showed ~50% of the removal efficiency of the control biomass. The removal rate and efficiency of Cr(III) was increased with increasing solution pH. It is well-known that the solution pH affects the protonation of various functional groups that exist on biomass surfaces, and an increase in the solution pH makes functional groups more available to cationic metal ions, resulting in their increased removal rate and efficiency.[9,17,19]

Figure 4 shows the equilibrium isotherms of Cr(III) for the control and thermally treated biomasses at pHs 2.5 and 3.5. The Cr(III) uptake increased with increasing equilibrium concentration and eventually reached a certain saturated value, depending on the degree of thermal treatment and the solution pH. Although empirical models, such as the Langmuir equation, cannot provide any mechanistic understanding of the sorption phenomena, they may be conveniently used to

Table 3. Characteristics of the Solution Containing Organic Compounds Leached from the Biomass[a]

drying condition	control	60 °C for 24 h	100 °C for 24 h	100 °C for 240 h
pH	3.04 (±0.02)	2.69 (±0.01)	2.65 (±0.00)	2.66 (±0.01)
TOC (mg/L)	54.3 (±1.8)	280.2 (±8.3)	451.1 (±7.8)	453.1 (±9.4)
IC (mg/L)	0.12 (±0.02)	0.14 (±0.01)	0.19 (±0.01)	0.13 (±0.01)
OD_{400}	0.032 (±0.002)	0.076 (±0.028)	0.339 (±0.017)	0.524 (±0.018)
sulfate (mg/L)	57.7 (±0.9)	84.2 (±1.7)	84.4 (±2.5)	84.3 (±1.8)
phosphate (mg/L)		2.8 (±0.2)	10.0 (±0.6)	10.5 (±0.8)

[a] The chromaticity (yellowish) of the solution was presented as the optical density at 400 nm.

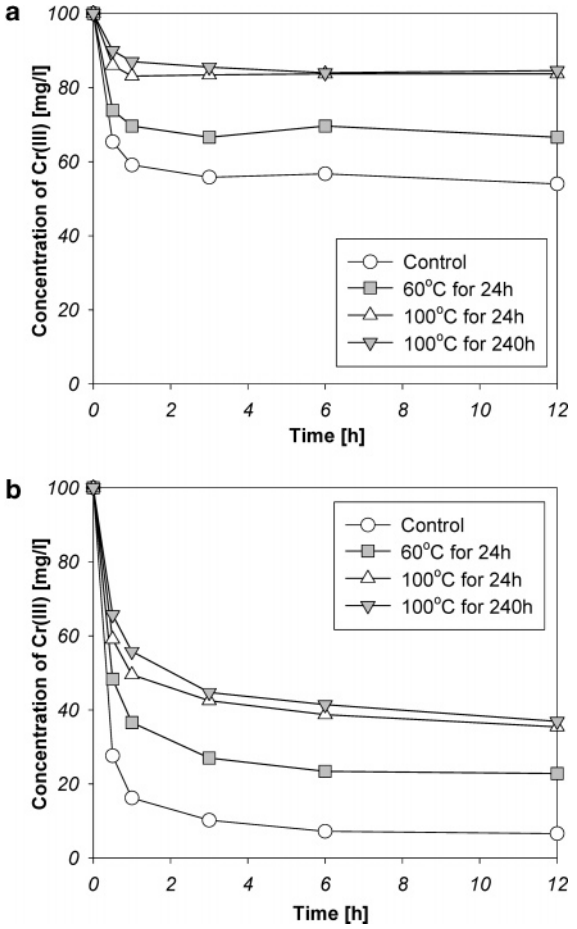

Figure 3. Dynamics of the Cr(III) removal by the biomass at solution pHs 2.5 (a) and 3.5 (b). The biomass and initial Cr(III) concentrations were 5 g/L and 100 mg/L, respectively.

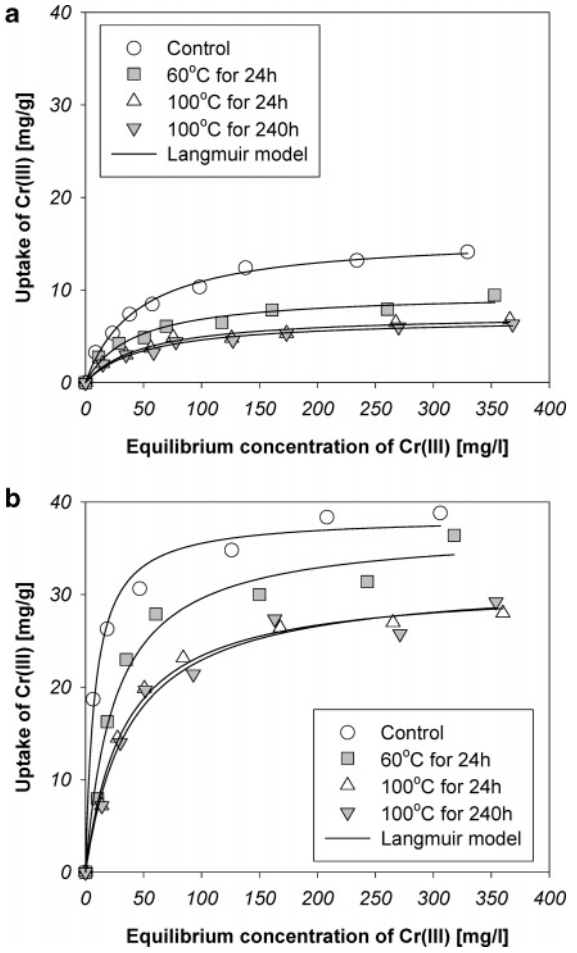

Figure 4. Adsorption isotherms of Cr(III) onto the biomass at pHs 2.5 (a) and 3.5 (b) in the equilibrium state. The biomass concentration and contact time were 5 g/L and 12 h, respectively.

estimate the maximum uptake of Cr(III) from experimental data,

$$q_{eq} = \frac{q_{max} b C_{eq}}{1 + b C_{eq}} \quad (6)$$

where, q_{eq} is the amount of metal bound to per gram of dried biomass at equilibrium (mg/g), C_{eq} is the residual (equilibrium) metal concentration left in solution after binding (mg/L), q_{max} is the maximum amount of metal ion per unit mass of adsorbent to form a complete monolayer on the surface bound at high C_{eq}, and b is a constant related to the affinity of the binding sites (L/mg). The Langmuir parameters were estimated using a nonlinear regression method and are summarized in Table 4. The magnitude of the correction factor was above 0.97. As expected, both the maximum uptake (q_{max}) and affinity (b) increased with increasing equilibrium pH but decreased with increasing degree of thermal treatment.

Table 4. Langmuir Model Regression Constants of the Biomass

drying condition	pH	q_{max} (mg/g)	b (l/mg)	R^2
control	2.5	15.87	0.022	0.993
	3.5	38.40	0.124	0.989
60 °C for 24 h	2.5	9.68	0.024	0.971
	3.5	37.04	0.040	0.977
100 °C for 24 h	2.5	7.42	0.020	0.976
	3.5	31.11	0.029	0.990
100 °C for 240 h	2.5	7.00	0.019	0.979
	3.5	31.64	0.026	0.983

On the basis of the results on the physical properties of the biomass, thermal treatment did not affect its surface area, but it might make the biomass become more resistant to the intraparticular mass transfer of Cr(III) ions. The studies on the chemical properties of the biomass revealed that several functional groups were affected by thermal treatment; i.e., 0.6 mmol/g of carboxyl groups disappeared, but 0.5 mmol/g of sulfonate groups were formed. As shown in Table 1, although the total amount of functional groups with pK_H

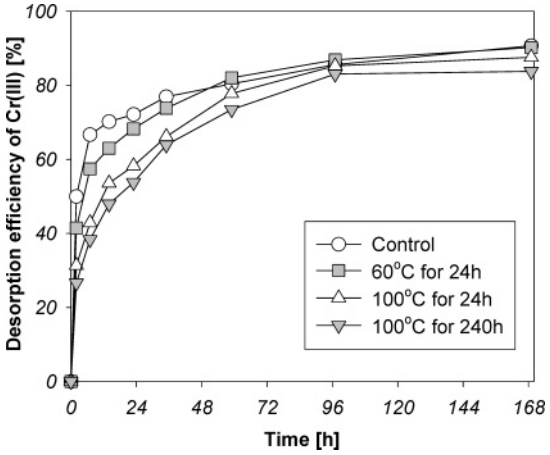

Figure 5. Dynamics of the Cr(III) desorption efficiency with 1 M H_2SO_4 solution.

values below 5, where Cr(III) adsorption occurs, remained relatively unchanged by thermal treatment, both the removal rate and efficiency of Cr(III) decreased. In addition, the Cr(III) did not bind to the thermally treated biomass at pH 2, where half the sulfonate groups might have an ionized configuration (data not shown). The ion chromatography data showed that soluble organic compounds containing a sulfonate group were released from the thermally treated biomass and could not participate in Cr(III) adsorption. Fourest and Volesky reported that sulfonate groups present in the seaweed biomass contribute, to a small extent, to heavy metal binding, particularly at low pH.[16] Therefore, it can be concluded that the carboxyl groups present in the biomass mainly participated in Cr(III) adsorption, and the decrease in the content of carboxyl groups by thermal treatment caused the decreases in the removal rate and efficiency of Cr(III) by the biomass. Meanwhile, soluble organic compounds released from the biomass might complex with the Cr(III) ion, resulting in a decrease of Cr(III) uptake by the solid biomass by competing for it.

To examine the desorption efficiency of the Cr(III) absorbed onto the control and thermally treated biomasses, desorption experiments were conducted with 1 M H_2SO_4 solution (Figure 5). In all cases, the desorption efficiency of Cr(III) was below 90%. In general, the desorption rate and efficiency of Cr(III) by acids were lower than those of divalent metal ions, such as Cd(II), Ni(II), Zn(II), and Pb(II).[5] The poor desorption rate and efficiency of Cr(III) by acids may be due to physical or chemical properties of Cr(III), but little information about this is available. Thus, there is a need for detailed study on Cr(III) desorption from biosorbents. As shown in Figure 5, the desorption rate of Cr(III) was strongly affected by the degree of thermal treatment, but the desorption efficiency was slightly affected. The desorption rate of Cr(III) adsorbed onto the control biomass was faster than the others, and the desorption rate of Cr(III) decreased with increasing degree of thermal treatment. This might have resulted from the increased intraparticular mass transfer resistance due to thermal treatment.

Effect of Thermal Treatment on the Cr(VI) Removal. The dynamics of Cr(VI) removal by the control and thermally treated biomasses were studied at pHs 2.5 and 3.5 (Figure 6). The behavior of Cr(VI) in the aqueous phase was monitored, and the concentration of total Cr was measured in equilibrium. The

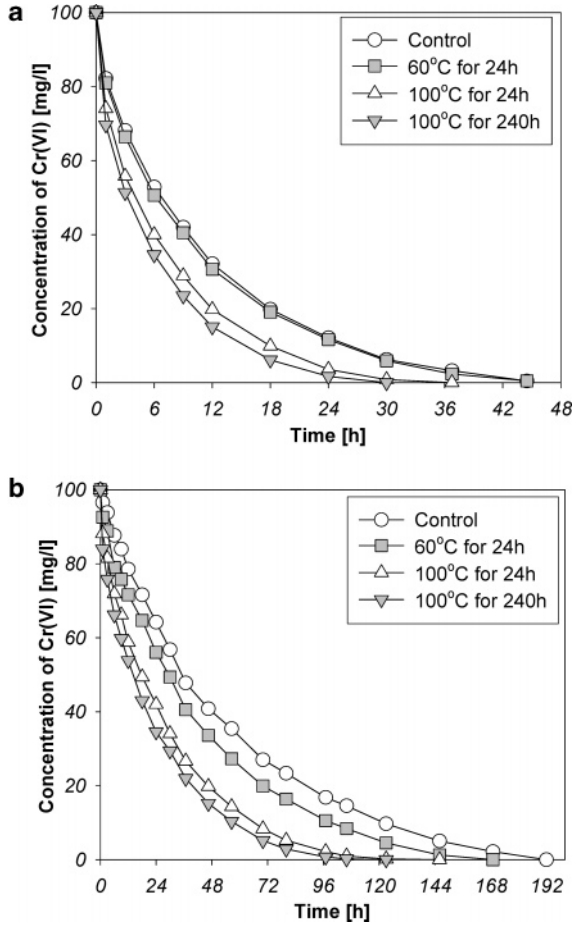

Figure 6. Dynamics of the Cr(VI) removal by the biomass at solution pHs 2.5 (a) and 3.5 (b). The biomass and the initial Cr(VI) concentrations were 5 g/L and 100 mg/L.

Table 5. Cr(VI) Reducing Capacity of the Biomass[a]

drying condition	Cr(VI) reducing capacity (mg/g)	error range (±mg/g)
control	100.3	2.2
60 °C for 24 h	121.6	1.2
100 °C for 24 h	156.9	0.8
100 °C for 240 h	181.6	1.9

[a] Initial pH, 2.0; Cr(VI) concentration, 200 mg/L; biomass concentration, ~0.2 to 0.6 g/L; contact time, 120 h.

concentration of Cr(VI) decreased with increasing contact time and, finally, completely disappeared from the aqueous phase. The contact time for the complete removal of Cr(VI) was affected by the solution pH and degree of thermal treatment. The control biomass completely removed Cr(VI) at pH 3.5 in 200 h, whereas that of the 100 °C thermally treated biomass required 30 h at pH 2.5. The removal rate of Cr(VI) decreased with increasing solution pH, since the redox reaction between Cr(VI) and the biomass consumed protons.[10] Meanwhile, thermal treatment increased the removal rate of Cr(VI), but Cr(VI) was completely removed in all cases (Figure 6). To quantify the Cr(VI) reducing capacity of the biomass according to the degree of thermal treatment, an experiment was conducted in which the biomass concentration was the limiting factor for Cr(VI) removal. As shown in Table 5, as the degree of thermal treatment increased, the Cr(VI) reducing capacity of the biomass increased, from 100.3 to 181.6 mg/g.

On the basis of studies on the physical/chemical properties of the biomass before and after thermal

Table 6. Removal Efficiency of Total Chromium by the Biomass at Various Equilibrium pHs[a]

drying condition	pH 2.5	pH 3.5
control	80.8	93.5
60 °C for 24 h	74.8	86.3
100 °C for 24 h	61.6	77.2
100 °C for 240 h	58.0	74.0

[a] The Cr(VI) was absent in the equilibrium state.

treatment, it can be assumed that thermal treatment might make the biomass stronger as a Cr(VI) reductant, resulting in enhanced Cr(VI) reduction. Furthermore, since the soluble organic compounds released from the biomass could also participate in Cr(VI) reduction,[10] the increase in the soluble organic compound concentration by thermal treatment might result in an increased Cr(VI) removal rate, despite the increased intraparticular mass transfer resistance. In addition, the thermal treatment diminished the content of moisture contained in the biomass, resulting in the increase of organic compounds per unit gram of biomass. This compactness of the biomass might enhance its Cr(VI) reducing capacity; however, there is still little information on the functional groups or organic compounds corresponding to the Cr(VI) reduction reaction.

Table 6 shows the removal efficiency of total Cr in the equilibrium state, in which Cr(VI) was absent in the aqueous phase before and after thermal treatment of the biomass. The thermal treatment decreased the removal efficiency of total Cr, from 80.8 to 58.0% and from 93.5 to 74% at pHs 2.5 and 3.5, respectively. In considering the Cr(III) removal mechanism by the biomass, thermal treatment might decrease the amount of functional groups responsible for binding of total Cr, resulting in a decrease in the total Cr removal efficiency in the equilibrium state.

Conclusions

The biomass of the brown seaweed *Ecklonia* removed both cationic Cr(III) and anionic Cr(VI): the Cr(III) was removed through an ion-exchange mechanism; the Cr(VI) was removed through a redox reaction with the biomass. The thermal treatment altered the physical and chemical properties of the biomass. The content of carboxyl groups present in the biomass was decreased to 76% by thermal treatment. In addition, thermal treatment increased the intraparticular mass transfer resistance. These effects of thermal treatment on the biomass reduced the adsorption rate and efficiency of Cr(III). Meanwhile, thermal treatment made the biomass stronger as a Cr(VI) reductant, resulting in an increased Cr(VI) reduction rate and Cr(VI) reducing capacity of the biomass.

Considering the effect of pH on Cr(III) and Cr(VI) removals, a two-stage biosorption process can be used for complete removal of both Cr(III) and Cr(VI). The first stage can remove Cr(VI) by means of reduction into Cr(III) at a low pH; the second stage can remove residual Cr(III) at a higher pH where the cationic Cr(III) is easily sorbed; thus, the treated water is virtually free of Cr(VI) and total Cr. In this process, the thermally treated biomass is proper to the former; the native biomass is proper to the latter. Therefore, thermal treatment has to be selectively adopted according to Cr(III) and Cr(VI) concentrations.

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