

# Removal of Trivalent and Hexavalent Chromium by Seaweed Biosorbent

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Protonated or Ca-form *Sargassum* seaweed biomass bound up to 40 mg/g of Cr(III) by ion exchange at pH 4. An ion-exchange model assuming that the only species taken up by the biomass was Cr(OH)<sup>2+</sup> successfully fitted the experimental biosorption data for Cr(III). The maximum uptake of Cr(VI) by protonated *Sargassum* biomass at pH 2 was explained by simultaneous anion exchange and Cr(VI) to Cr(III) reduction. At pH <2.0, the reduction of Cr(VI) to Cr(III) dominated the equilibrium behavior of the batch systems, which was explained by the dependence of the reduction potential of HCrO<sub>4</sub><sup>-</sup> ions on the pH. At pH >2.0, the removal of Cr(VI) was linked to the depletion of protons in equilibrium batch systems via an anion-exchange reaction. The optimum pH for Cr(VI) removal by sorption lies in the region where the two mechanisms overlap, which for *Sargassum* biomass is in the vicinity of pH 2. The existence of the optimum pH for the removal of Cr(VI) may be explained by taking into account (a) the desorption of Cr(III) from biomass at low pH and (b) the effect of pH on the reduction potential of Cr(VI) in aqueous solutions. Seventy percent of Cr(VI) bound to the seaweed at pH 2 can be desorbed with 0.2 M H<sub>2</sub>SO<sub>4</sub> via reduction to Cr(III).

## Introduction

Hexavalent and trivalent chromium is often present in wastewater from electroplating and metal-finishing plants. Since chromium, along with most of the heavy metals, is considered toxic, discharge limits for both Cr(III) and Cr(VI) have been instituted by most industrialized countries.

The conventional treatment of spent plating and anodizing baths which are rich in chromium consists of four steps, including (1) the reduction of Cr(VI) to Cr(III), (2) the precipitation of Cr(III) as Cr(OH)<sub>3</sub> at high pH, (3) the settling of the insoluble metal hydroxide, and finally (4) the disposal of the dewatered sludge. The major shortcomings of the conventional treatment include costly safe disposal of toxic sludge, high cost of chemicals used for Cr(VI) reduction, and incomplete reduction of Cr(VI). Wastewater containing relatively low concentrations of Cr(VI) is usually treated with ion-exchange resins which offer the advantage of the recovery of chromic acid but at a high cost brought about mainly by the high cost of the resins.

Recently, in response to these shortcomings, the chromium sequestering capabilities of inexpensive biomasses, including peat moss (1), maize cob, sawdust, beet pulp, sugar cane bagasse (2), pine bark (3), waste fertilizer slurry (4), the

shrimp chitin (5), the dead cells of bacteria (6), and fungi (7, 8), have been studied. Some of the biomass types have been reported to bind more than 100 mg of Cr/gram of sorbent (2). The sorption of Cr by *Sargassum* seaweed biomass has never been studied. However, *Sargassum* is known to be a very good biosorbent for other heavy metals including Cu, Cd, and Zn (9, 10).

Although most of the treatment processes removing Cr from wastewater have to ensure successful removal of both Cr(III) and Cr(VI), hitherto, all investigations of biosorption of chromium have studied the removal of only a single chromium form. Moreover, the biomasses which were tested for uptakes of Cr(III) were different from the ones tested for binding with Cr(VI). Consequently, the characteristics of binding of these two forms of chromium have never been compared or related to each other.

The objective of this article is to provide a unified approach to the removal of chromium whereby the potential of employing *Sargassum* biomass at different stages of the conventional wastewater treatment is evaluated, based on sorption data obtained for both trivalent and hexavalent chromium.

## Materials and Methods

**Biosorbent Preparation.** *Sargassum* seaweed biomass was collected beach-dried on the Gulf Coast of Florida in August. H-biomass was prepared in the laboratory by first washing the seaweed with 0.2 M H<sub>2</sub>SO<sub>4</sub> and then rinsing it with distilled water. Ca-biomass was prepared by washing the H-biomass with 0.25 g/L solution of Ca(OH)<sub>2</sub>. The pH of the spent wash solution was 12. Finally, both the H-biomass and the Ca-biomass were dried in the oven overnight at 50 °C.

**Equilibrium Sorption Experiments.** Solutions of Cr(III) and Cr(VI) in distilled water were prepared using CrK(SO<sub>4</sub>)<sub>2</sub> and CrO<sub>3</sub>, respectively. Approximately 200 mg of dried protonated or Ca-biomass was combined with 50 mL of metal solutions in 200 mL Erlenmeyer flasks. This batch sorption system was gently mixed on a shaker, and left to equilibrate for 6 h. Uptakes of chromium were determined from the difference of metal concentrations in the initial and final solutions. The pH of the solutions before and during the sorption experiments was adjusted with NaOH, H<sub>2</sub>SO<sub>4</sub>, and/or Ca(OH)<sub>2</sub>.

**Analysis of Chromium.** The total concentration of chromium, i.e., Cr(VI) + Cr(III), in the liquid samples was determined by atomic absorption spectroscopy (Perkin-Elmer 3100). Hexavalent chromium was analyzed by measuring absorbance of the purple complex of Cr(VI) with 1,5-diphenylcarbohydrazide at 540 nm by UV spectrophotometer (11). The concentration of trivalent chromium was determined as the difference between total chromium and hexavalent chromium concentrations, respectively.

## Results and Discussion

**Removal of Trivalent Chromium. Effect of pH.** The effect of pH on the removal of Cr(III) was examined. Figure 1 shows the sorption isotherms obtained for Cr(III) on H-biomass at equilibrium pHs of 4, 2, and 1. As can be seen from this figure, the equilibrium uptakes of Cr(III) at pH 4 were greater than the uptakes at pH 2 throughout the entire range of final concentrations of Cr(III) from 0 to 650 mg/L. The pH had a tendency to drop during the equilibration, hence NaOH was used to adjust the pH. Negligible uptakes of Cr(III) were obtained at pH 1. Similar trends in sorption data have previously been reported for Cu, Cd, and Zn, sorbing onto

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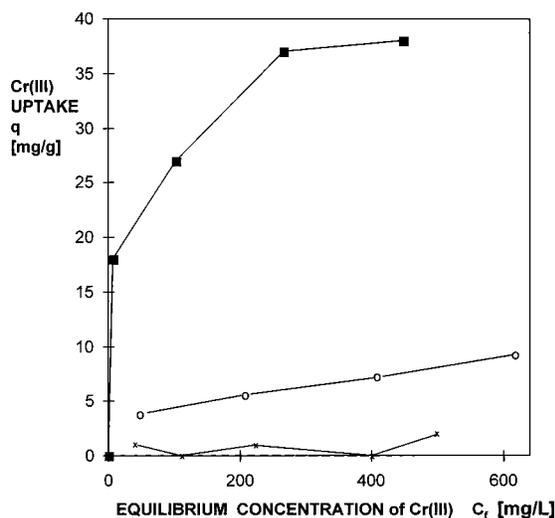
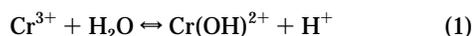


FIGURE 1. Effect of pH on the sorption of Cr(III) by *Sargassum* H-biomass. Cr(III) sorption isotherms at (■) pH 4; (○) pH 2; (×) pH 1.

algal biomass (12, 13). Moreover, it has been established that heavy metal cations bind to algae by ion exchange whereby weakly and strongly acidic functional groups in the biomass take up cations of heavy metals from solutions in exchange for protons and/or cations of light metals such as Na, Mg, and Ca (14, 15). Therefore, it may be assumed that (1) the pH was dropping during sorption as a result of ion exchange between protons and Cr(III), and (2) low uptakes of Cr(III) by *Sargassum* at low pH were caused by an increased ability of protons to compete with Cr(III) for the binding sites in the biomass. A decrease in Cr(III) uptake at low pH was also observed when ground bark (3) and fungal biomass (7) biosorption was examined, respectively. However, in these studies the effect of pH was not explained and there was no discussion of the sorption mechanism which led to fitting four different Langmuir isotherms to the latter experimental data, one for each pH value. Alves et al. (3) concluded that ion exchange played an important role in the sorption of Cr(III) by pine bark based on the pH changes observed during equilibration of the bark with metal solutions. However, there was no discussion of the pH changes and no account was made of the pH changes caused by complexation and hydrolysis of Cr(III) in water.

**Effect of Cr(III) Speciation.** It is well-known that  $\text{Cr}^{3+}$  cations in water can undergo hydrolysis and/or complexation reactions, the extent of which depend primarily on the total Cr(III) concentration, on the pH, and on the type of anions present in solutions. The simple hydrolysis of  $\text{Cr}^{3+}$  can be written as follows:



As can be seen, this reaction generates divalent cations  $\text{Cr}(\text{OH})^{2+}$  and protons which contribute to the increased acidity of Cr(III) solutions. It is the involvement of protons in reaction 1 that may lead to incorrect interpretations of the pH changes in the system. For example, if  $\text{Cr}^{3+}$  is being taken up by the biomass, reaction 1 proceeds to the left, leading to the depletion of protons and hence a rise in pH. In contrast, if  $\text{Cr}(\text{OH})^{2+}$  sorbs onto the biomass, reaction 1 naturally proceeds to the right and the solution becomes more acidic. However, the pH of a solution may also change due to the release and/or uptake of protons by the biomass. The value of the equilibrium constant of reaction 1 has been reported by Hunt (16) to be  $K_h = 10^{-3.82}$  yielding a  $\text{p}K_h$  of 3.82. This means that, at pH 3.8, approximately 50% of the overall

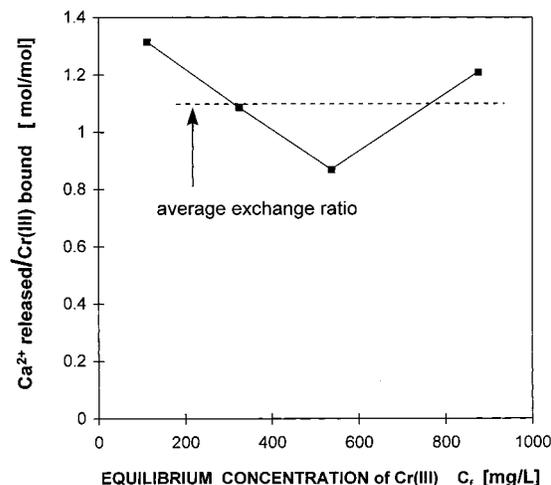


FIGURE 2.  $\text{Ca}^{2+} \rightleftharpoons \text{Cr}(\text{III})$  cation exchange. Ratio of  $\text{Ca}^{2+}$  released and Cr(III) sorbed by Ca-biomass, pH between 3.3 and 3.8. (■) Experimental data; (- -) ratio of Ca/Cr averaged over the datapoints.

Cr(III) content of the system will be in the  $\text{Cr}(\text{OH})^{2+}$  form. When compared to other trivalent cations,  $\text{Cr}^{3+}$  cations appear to be more susceptible to hydrolysis via reaction 1 than  $\text{Al}^{3+}$  cations whose  $\text{p}K_h$  is 5.09, but less susceptible than  $\text{Fe}^{3+}$  cations which have a  $\text{p}K_h$  value of 2.17.

In addition to hydrolysis,  $\text{Cr}^{3+}$  can undergo complexation reactions with anions. The constants of complexation reactions have been measured and subsequently included in the thermodynamic databases of software packages such as MINEQL 17, which are used for calculating chemical equilibria in aqueous solutions. Therefore, MINEQL was used to examine the existence of various ionic species of trivalent chromium in solutions of  $\text{CrKSO}_4$ , with  $\text{CrKSO}_4$  concentrations ranging 2–20 mM and pH 2–4. According to the program, the following species may exist in water under the condition stated above:  $\text{Cr}^{3+}$ ,  $\text{Cr}(\text{OH})^{2+}$ ,  $\text{CrSO}_4^+$ ,  $\text{Cr}_2\text{-(OH)}_2(\text{SO}_4)]^{2+}$ ,  $\text{CrOHSO}_4$ , and  $\text{Cr}_2(\text{OH})_2(\text{SO}_4)_2$ .

**Ion Exchange in Cr(III) Biosorption.** To be able to model the sorption of Cr(III) by *Sargassum* biomass, one or several reactions between Cr(III) and the biomass have to be assumed. Thus far, the discussion of the experimental results and of the Cr(III) speciation have revealed that (1) Cr(III) is likely to sorb onto the seaweed by an ion-exchange mechanism and (2) it may be very difficult to determine the stoichiometry of the exchange from pH changes occurring in the system since protons participate in several reactions at the same time. Therefore, the mechanism of Cr(III) removal was investigated using Ca-biomass, in experiments without pH adjustment, by measuring the uptake of Cr(III) and the release of  $\text{Ca}^{2+}$ , respectively. Figure 2 summarizes the ion exchange observed between  $\text{Ca}^{2+}$  and Cr(III). According to this figure, the uptake of 1 mol of Cr(III) by the biomass is accompanied by a release of, on average, 1.1 mol of  $\text{Ca}^{2+}$ ; thus, yielding the Cr(III):Ca exchange ratio of 1.1. The pH of the solution decreased slightly during the sorption experiment yielding the final pH of the metal solutions in the interval of pH from 3.3 to 3.8, depending on the metal concentration. The 1.1:1 stoichiometry implies that over 90% of the Cr(III) sorbed onto the biomass as divalent cations, i.e., probably as  $\text{Cr}(\text{OH})^{2+}$ . The remaining less than 10% of Cr(III) was probably taken up by the biomass in the form of  $\text{Cr}^{3+}$  cations. Consequently, if the uptake of  $\text{Cr}^{3+}$  is assumed negligible, the following reaction may be used to describe the sorption of Cr(III) by *Sargassum* (12):



where B symbolizes a free binding site in the biomass. In

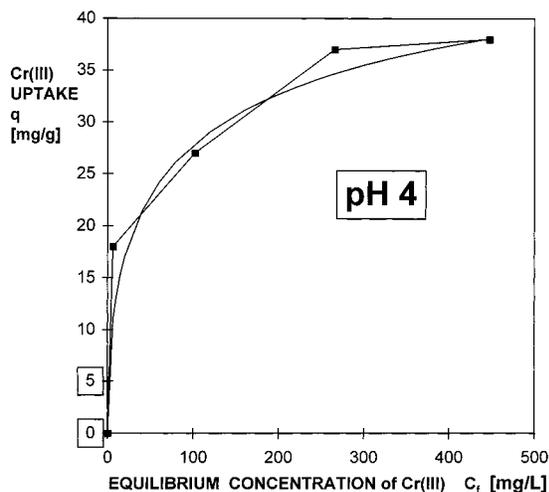


FIGURE 3. Model and experimental sorption isotherm of Cr(III) on H-biomass at pH 4. (■) Experiment; (—) model ( $K_H = 4262$ ;  $K_{Cr(OH)^{2+}} = 2500$  L/mequiv).

addition to the metal-binding reaction 2, a mathematical expression for the sorption isotherm of a divalent cation sorbing onto *Sargassum* in the presence of protons is also available (12, 18, 19). For the specific case of  $Cr(OH)^{2+}$ , this expression can be written as

$$q_{Cr(OH)^{2+}} = \frac{0.5M_{WCr}C_t(K_{Cr(OH)^{2+}}C_{iCr})^{1/2}}{1 + K_H C_{iH} + (K_{Cr(OH)^{2+}}C_{iCr})^{1/2}} \quad (3)$$

where  $q_{Cr(OH)^{2+}}$  stands for the equilibrium uptake of Cr(III), and  $C_{iH}$  and  $C_{iCr}$  represent the final concentrations of  $H^+$  and Cr(III) in the solution, respectively. Equation 3 can be used to predict the sorption of Cr(III) onto *Sargassum*, provided that (1) the values of the constants  $K_H$ ,  $C_t$ , and  $K_{Cr(OH)^{2+}}$  are known, and (2) most of the Cr(III) is sorbed as  $Cr(OH)^{2+}$ . The values of the constants  $K_H = 4624$  and  $C_t = 2.3$  have previously been determined by Kratochvil (14) for the same *Sargassum* biomass. The value of the constant  $K_{Cr(OH)^{2+}} = 2500$  was determined by fitting eq 3 to the experimental data presented in Figure 1. In addition, the program MINEQL was used to calculate the range of pH in which  $Cr(OH)^{2+}$  exists in the solution and the pH at which  $Cr^{3+}$  ions start precipitating. According to this program, no more  $Cr(OH)^{2+}$  cations exist in solutions at pH  $< 2.5$ , and  $Cr^{3+}$  starts precipitating as  $Cr(OH)_3$  at pH  $> 5$ . These facts set the limits for the effective removal of Cr(III) by *Sargassum* as well as for the applicability of the eq 3 to the pH range of pH 2.5–5. Figure 3 compares the experimental and model sorption isotherms for Cr(III) at pH 4.

**Removal of Hexavalent Chromium.** In the second part of this work, the removal of hexavalent chromium by *Sargassum* biomass was investigated.

**Effect of pH.** First, the equilibrium uptakes of chromium by *Sargassum* from solutions containing dissolved hexavalent chromium were measured at pH = 1, 2, and 4, and the resulting sorption isotherms were plotted in Figure 4. As can be seen from this figure, the uptakes of Cr at pH 2 were higher than the corresponding uptakes at pH 1 and 4 over the entire range of the equilibrium concentration of total chromium in the solution. A similar behavior, whereby lowering of the equilibrium pH from neutral to acidic initially yielded an increase in the Cr uptake but when at pH values below pH 2 the Cr uptake decreased, has been reported by Sharma and Forster for a variety of biomasses including peat moss (1), sawdust, sugar cane bagasse, beet pulp, and maize cob (2). Furthermore, the existence of an optimum pH, at which the removal of Cr was maximized, has also been

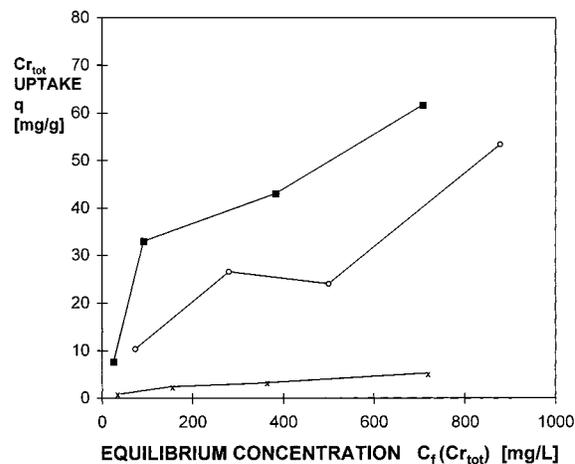


FIGURE 4. Effect of pH on the sorption uptake of chromium from solutions originally containing only Cr(VI); uptake of chromium at pH 1, 2, and 4. (x) pH 4; (■) pH 2; (○) pH 1.

TABLE 1. Removal of Cr(VI) by *Sargassum* Biomass

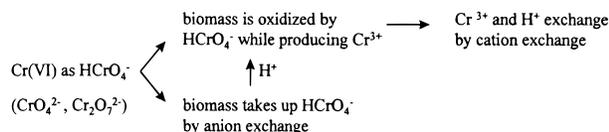
initial conditions			equilibrium conditions (after 6 h)				
$C_i$ [Cr(VI)] (mg/L)	$C_i$ [Cr(III)] (mg/L)	pH <sub>i</sub>	$C_f$ [Cr(VI)] (mg/L)	$C_f$ [Cr(III)] (mg/L)	pH <sub>f</sub>	$q(Cr_{tot})$ (mg/g)	Cr(VI):Cr(III) (—)
101	0	2	16	41	2.1	9	0.4
200	0	2	86	49	2.2	15	1.8
343	0	2	233	7	2.4	25	33.3
648	0	2	484	1	2.6	38	484
1022	0	2	773		2.6	60	
blank	0	6.5	0	0	3.8	0	

observed by Huang and Wu (20) who studied the sorption of hexavalent chromium on activated carbon. Although Sharma and Forster have discussed some of the factors underlying the complexity of interactions between Cr(VI) and solid biomaterials (1, 2), a complete explanation of the existence of the optimum pH for removing Cr by biosorption has never been given. Furthermore, the presentation of the biosorption data for Cr(VI) by these authors was rather equivocal due to the fact that under certain conditions hexavalent chromium was found to be reduced to Cr(III).

In an attempt to gain an insight into the role of  $H^+$  in the binding of Cr(VI) and to investigate whether *Sargassum* reduces Cr(VI) in the same pH range as other biomasses, a set of experiments was carried out at the initial pH 2 and without pH adjustment. Table 1 summarizes the initial and final compositions of the liquid as well as the uptake of Cr by the biosorbent. As can be seen from Table 1, the uptake of chromium increased with increasing equilibrium pH of the sorption system. This implies that the binding of Cr by *Sargassum* may be responsible for the depletion of protons in the system. The data in Table 1 indicate that the lower the equilibrium pH of the mixture, the lower the concentration ratio of trivalent to hexavalent chromium in the liquid. This suggests that Cr(VI) reduction to Cr(III) was favored at lower pH values. Similar trends in equilibrium sorption data were observed by Sharma and Forster (1, 2). However, these authors tried to link the percentage removals of Cr(VI) and total chromium, respectively, to the final concentration of the total Cr in the system, which made the interpretation of their experimental data very difficult. The focus of our work was on the character of interactions between hexavalent chromium and the seaweed biomass.

**Mechanism of Cr(VI) Removal by *Sargassum*.** To explain both the existence of the optimum pH for the removal of Cr by sorption as observed in Figure 4 and the trends in

experimental data in Table 1 discussed above, the following combined ion exchange-redox reaction mechanism for the sorption of Cr(VI) by the biomass is proposed:



redox reactions: biomass:  $\text{C(org)} \rightarrow \text{CO}_2$  and/or  
 $\text{C(org)} \rightarrow \text{C(org oxidized)}$  (4)

chromium:  $\text{HCrO}_4^- + 7\text{H}^+ + 3\text{e} \rightarrow \text{Cr}^{3+} + 4\text{H}_2\text{O}$  (5)

cation exchange:  $(\text{Cr-B}_3) + 3\text{H}^+ \rightleftharpoons 3(\text{B-H}) + \text{Cr}^{3+}$  (6)

anion exchange:  $\text{B}' + \text{HCrO}_4^- + \text{H}^+ \rightleftharpoons \text{B}'\cdot\text{H}_2\text{CrO}_4$  (7)

It should be mentioned that while all the reactions in the scheme above are written for  $\text{HCrO}_4^-$  ions, the mechanism can easily be extended to include the other Cr(VI) species which are likely to be present in the system, such as  $\text{Cr}_2\text{O}_7^{2-}$ , and/or  $\text{CrO}_4^{2-}$ . The reaction scheme suggests that  $\text{HCrO}_4^-$  ions can simultaneously sorb onto biomass by ion exchange according to reaction 7 and oxidize the biomass according to reaction 4. Furthermore, as the scheme above indicates, the ion exchange and the redox reactions may proceed either sequentially and/or in parallel. To elucidate the role of pH in the biosorption of hexavalent chromium, the effect of pH on the equilibria of the individual reactions 5 and 7 is discussed in the following two paragraphs.

Reaction 5 describes the biomass as an anion exchanger removing Cr(VI) from aqueous solutions by the "acid adsorption" mechanism which has previously been established as one of the mechanisms of ion exchange on weak anion-exchange resins (21). One type of weakly basic group in the biomass may be phenolic groups of polyphenolic compounds, such as polyphloroglucinols which are known to be present in brown seaweed (22). The most important feature of the acid adsorption mechanism is that, in order for the uptake of chromium to occur, the liquid has to contain enough protons to effectively push the equilibrium of reaction 7 to the right. Consequently, the equilibrium uptake of hexavalent chromium by *Sargassum* is expected to increase with decreasing pH or decrease with increasing pH.

From the thermodynamic point of view, the redox reactions 4 and 5 may proceed in the direction as they are written only if the reduction potential of  $\text{HCrO}_4^-$  ions is greater than the reduction potential of the biomass, i.e., when  $E(\text{CrO}_4^{2-}/\text{Cr}^{3+}) > E(\text{B-red, B-ox})$ . While the value of  $E(\text{B-red, B-ox})$  is generally unknown, the value of  $E(\text{HCrO}_4^-/\text{Cr}^{3+})$  at 25 °C can be calculated from the Nernst equation which can be written for the reaction 5 as follows:

$$\begin{aligned}
 E(\text{HCrO}_4^-/\text{Cr}^{3+}) &= E^\circ + \Delta E_{\text{HCrO}_4^-/\text{Cr}^{3+}} + \Delta E_{\text{pH}} = \\
 E^\circ(\text{HCrO}_4^-/\text{Cr}^{3+}) &+ \frac{0.059}{3} \log \frac{C(\text{HCrO}_4^-)}{C(\text{Cr}^{3+})} - 7 \times \frac{0.059}{3} \text{pH}
 \end{aligned} \quad (8)$$

Assuming isothermal conditions, eq 8 shows that the value of the reduction potential  $E(\text{HCrO}_4^-/\text{Cr}^{3+})$  can be obtained as a sum of three terms including  $E^\circ$ ,  $\Delta E_{\text{HCrO}_4^-/\text{Cr}^{3+}}$ , and  $\Delta E_{\text{pH}}$  which reflect respective contributions of the standard reduction potential  $E^\circ(\text{HCrO}_4^-/\text{Cr}^{3+})$ , the ratio of hexavalent to trivalent chromium, and the pH. The higher the ratio  $C(\text{HCrO}_4^-)/C(\text{Cr}^{3+})$  and the lower the pH, the greater the value

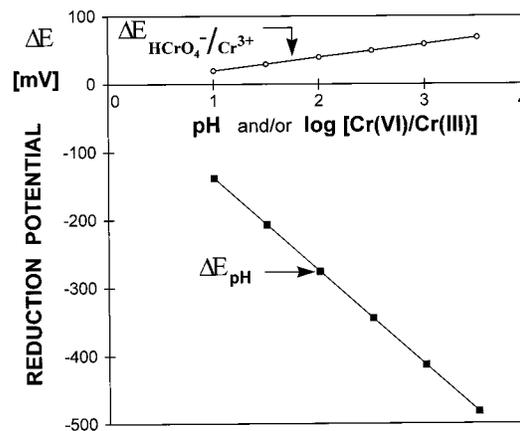


FIGURE 5. Effects of pH and Cr(VI)/Cr(III) ratio on the reduction potential of chromate ions calculated from eq 8. (○)  $\Delta E_{\text{pH}}$ ; (■)  $\Delta E_{\text{HCrO}_4^-/\text{Cr}^{3+}}$ .

of the potential  $E(\text{HCrO}_4^-/\text{Cr}^{3+})$ , and hence the stronger the ability of  $\text{HCrO}_4^-$  to oxidize the biomass.

To assess the respective impacts of chromium speciation and pH on the redox behavior of the system, the changes of  $E(\text{HCrO}_4^-/\text{Cr}^{3+})$  caused by variations in pH and in the ratio of  $C(\text{HCrO}_4^-)/C(\text{Cr}^{3+})$  were calculated from eq 8 and plotted in Figure 5. As can be seen from this figure, an increase of the ratio  $C(\text{HCrO}_4^-)/C(\text{Cr}^{3+})$  by 2 orders of magnitude produces a positive  $\Delta E_{\text{HCrO}_4^-/\text{Cr}^{3+}}$  of +39 mV while the change of the same magnitude in pH yields a negative  $\Delta E_{\text{pH}}$  of -275 mV. This means that pH has a much stronger effect on the reduction potential of chromate than the ratio of hexavalent to trivalent chromium. In fact, an increase of pH causes the value of  $E(\text{HCrO}_4^-/\text{Cr}^{3+})$  to drop dramatically, thereby weakening the oxidizing power of  $\text{HCrO}_4^-$  ions with respect to the biomass. Consequently, a critical value of pH, designated as  $\text{pH}_C$ , may be defined for any given biomass, so that at  $\text{pH} = \text{pH}_C$ , the reduction potential of  $\text{HCrO}_4^-$  ions and the biomass, respectively, are equal, i.e.,  $E(\text{HCrO}_4^-/\text{Cr}^{3+}) = E(\text{B-red, B-ox})$ . It follows from the discussion above that at pH lower than  $\text{pH}_C$ ,  $E(\text{HCrO}_4^-/\text{Cr}^{3+}) > E(\text{B-red, B-ox})$ , and hence  $\text{HCrO}_4^-$  ions oxidize the biomass, while at pH greater than  $\text{pH}_C$ ,  $E(\text{HCrO}_4^-/\text{Cr}^{3+}) < E(\text{B-red, B-ox})$ , and all of the chromium stays in the hexavalent form.

**Explanation of the Optimum pH Existence.** At a relatively high pH, there are not enough protons to shift the equilibrium of the reaction 7 sufficiently to the right. Consequently, only a small uptake of  $\text{HCrO}_4^-$  was seen at pH 4 in Figure 4. As the equilibrium pH decreased to pH 2, the uptake of  $\text{HCrO}_4^-$  by anion exchange increased. However, as soon as the equilibrium pH was lowered below the value of  $\text{pH}_C$ ,  $\text{HCrO}_4^-$  ions started oxidizing the biomass while producing  $\text{Cr}^{3+}$  ions. These  $\text{Cr}^{3+}$  ions then competed for the binding sites in the biomass with protons via cation exchange reaction (6). Therefore, a further decrease of pH caused not only the value of  $E(\text{HCrO}_4^-/\text{Cr}^{3+})$  to increase according to eq 8, thus facilitating the biomass oxidation, but also a fast desorption of  $\text{Cr}^{3+}$  from the biomass leading to low uptakes of chromium as seen at pH 1 in Figure 2. Consequently, the uptake of Cr from solutions containing Cr(VI) by biomass is maximized at a value of pH which is low enough for the equilibrium of the anion-exchange reaction 7 to be shifted to the right, but still high enough to be in the vicinity of  $\text{pH}_C$  so that the reduction of  $\text{HCrO}_4^-$  to  $\text{Cr}^{3+}$  does not dominate the system. On the basis of the data in Table 1, it may be concluded that  $\text{pH}_C$  for *Sargassum* biomass is approximately equal to 2.5.

**Further Support of the Proposed Mechanism.** To further support the above hypothesis concerning the mechanism of Cr(VI) removal, two experiments were conducted at a relatively high and at an extremely low equilibrium pH value,

TABLE 2. Removal of Cr(VI) by *Sargassum* Ca-Biomass at pH = 7, and by *Sargassum* H-Biomass in 0.2 M H<sub>2</sub>SO<sub>4</sub>

initial conditions			equilibrium conditions (after 6 h)				after 1 day
C <sub>i</sub> [Cr(VI)] (mg/L)	C <sub>i</sub> [Cr(III)] (mg/L)	pH <sub>i</sub>	C <sub>f</sub> [Cr(VI)] (mg/L)	C <sub>f</sub> [Cr(VI)] (mg/L)	pH <sub>f</sub>	q(Cr <sub>tot</sub> ) (mg/g)	C <sub>f</sub> [Cr(VI)] (mg/L)
220	0	7.2	210	0	7.0	4	210
400	0	7.2	380	0	7.1	8	380
720	0	7.2	680	0	7.1	10	680
252	0	0.2 M H <sub>2</sub> SO <sub>4</sub>	0.134	250		0.5	0
407	0	0.2 M H <sub>2</sub> SO <sub>4</sub>	0.828	385		5.5	0.1
773	0	0.2 M H <sub>2</sub> SO <sub>4</sub>	87	680		1.5	0.5

respectively. According to the proposed reaction scheme, at high pH, HCrO<sub>4</sub><sup>-</sup> should not be taken up by the biomass at all due to the low concentration of protons in the system. In contrast, at low pH, ΔE<sub>pH</sub> ≈ 0 and the value of E(HCrO<sub>4</sub><sup>-</sup>/Cr<sup>3+</sup>) is high. Thus, the redox reactions 4 and 5 are expected to dominate the equilibrium behavior of the system. The first experiment was performed with *Sargassum* biomass in the Ca-form at pH 7. The pH of the initial solution was adjusted prior to the sorption experiment by adding Ca(OH)<sub>2</sub> to the solution of H<sub>2</sub>CrO<sub>4</sub>. Table 2 reveals that the uptake of chromium at pH 7 was indeed negligible, complemented by no significant change in the pH of the system. Furthermore, no Cr(III) was detected in the liquid in equilibrium. The second experiment was carried out in 0.2 M H<sub>2</sub>SO<sub>4</sub>, and as can be seen from Table 2, almost all HCrO<sub>4</sub><sup>-</sup> ions present in the initial solution were reduced to Cr<sup>3+</sup> over the course of 6 h, and practically no Cr(VI) was left unreacted in the systems after 1 day.

The results obtained under the acidic conditions have two major implications for the potential use of biosorbents: (1) it is possible to desorb most of the chromium from biomass by mineral acids via reduction to Cr(III), and (2) biosorbents may be considered as a low-cost alternative to oxidizing agents such as SO<sub>2</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> used for the reduction of Cr(VI) to Cr(III) in the first step of the conventional treatment process. The latter suggestion is further favored by the fact that the spent plating baths are very acidic as they contain residual chromic acid.

A visual inspection of the biomass after the 24 h exposure to acid in the presence of Cr(VI) revealed that the seaweed lost, to a varying degree, its originally brown coloring. In fact, a gradient of brown color was observed in the samples, ranging from completely discolored and transparent biomass which had been exposed to the highest concentration of Cr(VI), to almost unchanged color of the biomass from the blank sample which contained only H<sub>2</sub>SO<sub>4</sub> and no Cr(VI). Therefore, it may be concluded that the loss of color was due to the oxidation and/or extraction of pigments by Cr(VI). The main pigments in brown algae are chlorophyll and fucoxanthin; the latter being an accessory pigment which lends the brown color to the seaweed (23).

On the basis of the present results, the following conclusions can be drawn. At pH > 2.5, Cr(III) sorbs onto *Sargassum* biomass by ion exchange in the form of Cr(OH)<sub>2</sub><sup>2+</sup> divalent cation. The uptake of Cr(III) by the seaweed can be modeled using Schiewer's ion-exchange model. The uptake of Cr(III) at pH < 2 is negligible. The interaction between Cr(VI) and the biomass includes (a) sorption, most likely by anion exchange and (b) reduction of Cr(VI) to Cr(III) at pH < 2.5. Under highly acidic conditions (0.2 M H<sub>2</sub>SO<sub>4</sub>), *Sargassum* biomass is capable of effectively reducing Cr(VI) to Cr(III). The optimum pH for Cr(VI) removal by sorption lies in the region where the two mechanisms overlap, which for *Sargassum* biomass is in the vicinity of pH 2.

**Desorption.** The possibility of desorbing chromium from biomass with mineral acids was examined by first sorbing

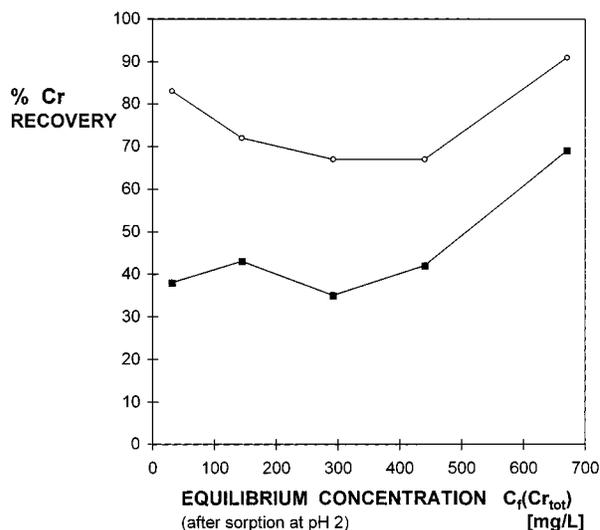


FIGURE 6. Percentage recovery of Cr from desorption experiments using 0.2 M H<sub>2</sub>SO<sub>4</sub> Chromium originally sorbed onto the biomass from Cr(VI) solutions at pH 2. (■) After 2 h; (○) after 24 h.

Cr(VI) onto *Sargassum* at pH 2 and then desorbing the heavy metal with 0.2 M H<sub>2</sub>SO<sub>4</sub>. The percentage of chromium recovery, represented by the ratio of the amount of Cr released per gram of the biosorbent during desorption and the equilibrium sorption uptake, was calculated for desorption experiments lasting 2 h and 1 day, respectively. Figure 6 displays the percentage of Cr recovery as a function of final concentration of Cr in solution after sorption. As can be seen, approximately 40 and 70% of Cr was recovered after 2 and 24 h, respectively. It should be mentioned that all of Cr desorbed from the seaweed was in the Cr(III) form. The fact that 100% recovery was not achieved may be due to the slow reduction of Cr(VI) bound by the biomass to Cr(III).

The difference in the percentage of Cr recovery at high and low metal concentrations may be due to the existence of multiple binding sites possessing different affinity toward Cr(VI) and exhibiting different kinetics of the redox reaction between these sites and Cr(VI). It is reasonable to assume that, at low concentrations of Cr<sub>tot</sub> in solution, Cr(VI) occupies binding sites with higher affinity toward Cr(VI). It follows that sites with lower affinity become occupied by Cr(VI) only at relatively high metal concentrations. Consequently, the results in Figure 6 may indicate that the rate of reduction of Cr(VI) atoms occupying the sites with high affinity for Cr(VI) is slower than the corresponding rate for low-affinity sites.

The effective desorption/regeneration of weak base anion-exchange resins is usually accomplished by washing the resins with concentrated solutions of strong bases such as NaOH. However, in the case of *Sargassum*, the use of concentrated NaOH leads to a massive leaching of a variety of compounds from the seaweed and to the destruction of the seaweed's

cellular structure. The use of lime would prevent this massive leaching; however, the concentration of  $\text{OH}^-$  in the solution would then be limited by the low solubility of  $\text{Ca}(\text{OH})_2$  in water.

**Potential Use of Biomass to Treat Chromium-Bearing Effluents.** In addition to being a good biosorbent for Cr(VI) at pH 2, *Sargassum* biomass is also capable of removing substantial quantities of Cr(III) from water at pH >3. The biosorbent can be regenerated using  $\text{H}_2\text{SO}_4$  and Cr(III) can be recovered in the form of Cr(III) concentrate. The removal of  $\text{Cr}^{3+}$  via sorption holds the promise to reduce the cost of the wastewater treatment by reducing the volume of the toxic sludge to be disposed of. Furthermore, the potential of using biomass as a cheap reducing agent for the reduction of Cr(VI) to Cr(III) should be recognized. In this case, the cost reduction lies in a full or a partial replacement of the conventional reducing agents such as  $\text{SO}_2$ ,  $\text{Na}_2\text{S}_2\text{O}_5$ , and  $\text{FeSO}_4$  with inexpensive and readily available seaweed biomass.

The results presented in this work are not complete to the point as to allow the design of a biosorption process to successfully and completely treat Cr-bearing effluents. Clearly, more development is required to establish the effect of biomass oxidation by Cr(VI) under acidic conditions on the cation-exchange capacity of the seaweed, to determine the capability of the biomass to sorb and/or reduce Cr(VI) in several consecutive cycles, and to establish the kinetics of Cr(VI) reduction.

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### Glossary

$C_f(\text{Cr}_{\text{tot}})$ , $C_f[\text{Cr}(\text{III})]$ , $C_f[\text{Cr}(\text{VI})]$	concentration of total, trivalent, and hexavalent chromium in liquid (mg/L)
$C_f[\text{Cr}(\text{III})]$	equilibrium concentration of Cr(III) in liquid (mequiv/L)
$E(\text{HCrO}_4^-/\text{Cr}^{3+})$	reduction potential of the $\text{HCrO}_4^-/\text{Cr}^{3+}$ couple calculated from Nernst eq 8 (mV)
$E^\circ(\text{HCrO}_4^-/\text{Cr}^{3+})$	standard reduction potential for reaction 5 (mV)
$K_H$ , $K_{\text{Cr}(\text{OH})^{2+}}$	binding constant of Schiewer's model (L/mequiv)
$q(\text{Cr}_{\text{tot}})$ , $q[\text{Cr}(\text{III})]$ , $q[\text{Cr}(\text{VI})]$	equilibrium uptake of total, trivalent, and hexavalent chromium by <i>Sargassum</i> biomass (mg/g)
$q_{\text{Cr}(\text{OH})^{2+}}$	equilibrium uptake of Cr(III) by <i>Sargassum</i> (mequiv/L)

Q

concentration of binding sites in biomass (mequiv/g)

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