Potential of Biosorption for the Recovery of Chromate in Industrial Wastewaters

ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · MAY 2001

Impact Factor: 2.59 · DOI: 10.1021/ie0008575

5 AUTHORS, INCLUDING:

Luis Cabatingan
University of San Carlos (Philippines)
2 PUBLICATIONS **105** CITATIONS
SEE PROFILE

Luuk A M van der Wielen
Delft University of Technology
218 PUBLICATIONS **2,834** CITATIONS
SEE PROFILE

Potential of Biosorption for the Recovery of Chromate in Industrial Wastewaters

Luis K. Cabatingan, Ramelito C. Agapay,[†] Johannes L. L. Rakels,[‡] Marcel Ottens, and Luuk A. M. van der Wielen*

Kluyver Laboratory for Biotechnology, Delft University of Technology, Julianalaan 67, 2628 BC Delft, The Netherlands

A biosorbent's low chemical stability against oxidative attack and its poor regenerability are problems that limit the applicability of biosorption in addressing the problem of recovering chromate in industrial wastewater. To provide a sufficient premise for such an argument, original equilibrium and kinetic data on the biosorption of chromate by the biomass of the brown seaweed *Sargassum siliquosum* are presented and benchmarked with other related reports. It is established that the optimal condition for chromate biosorption is around pH 2. It is shown that electrochemical reduction of some of the chromate in the solution occurs in parallel with biosorption. Aside from the solution pH, the other factors shown to influence the equilibrium and the kinetics of both biosorption and reduction are the amount of biomass and the total chromate concentration. The chromate bound by the seaweed is found to be difficult to desorb using H_2SO_4 without first reducing the hexavalent chromate into a trivalent chromium. These findings are shown to be common among other reported studies using different biosorbents. In conclusion, it is argued that biosorption is not a highly viable option for the recovery of chromate in industrial wastewaters.

Introduction

Owing to the growing stringency of environmental regulations, the disadvantages of a conventional chemical reduction-and-precipitation method[1] for detoxifying chromate-contaminated industrial wastewater have become more recognized. The method is becoming undesirable for reasons that (1) it uses expensive chemical reductants, (2) it cannot sufficiently remove chromate from wastewater to meet regulatory standards, (3) it generates large volumes of toxic sludge which requires a special storage facility, and (4) it does not allow complete recovery of chromium in the desired hexavalent oxidation state.

Chromic acid is used in the plating and anodizing operations in the surface finishing industry. Chromate eventually finds its way to a company's waste treatment system through the dumping of the spent plating baths, contaminated rinsewaters, and fume scrubber blowdown. Both the spent plating bath and contaminated rinsewaters are acidic; however, they generally differ in the amount of chromate contained. The former is apparently very concentrated[2] (ranging from 45 to 470 g of Cr(VI)/L), while the latter can be relatively dilute and can be further classified as high strength, typical strength, or dilute wastewaters with typical Cr(VI) levels of 500, 100, and 20 ppm, respectively.[1]

One alternative for dealing with the chromate wastewater problem is to remove chromate through sorption-based processes wherein activated carbon, synthetic resins, or the so-called biosorbents derived from dead biomass of organisms can be employed. The solid-bound metal can then be recovered as a concentrate through the use of an appropriate desorbent and then subsequently recycled to the plating bath. Sorption-based chromate recovery processes using commercial ion-exchange resins are operational in the electroplating industries.[3,4]

There are reports on the sorption of chromate ions using various sorts of cheap biomaterials including sawdust,[5,6] peat moss,[7] biomass of freshwater fern,[8] and dead biomass of many species of bacteria, fungi, and marine algae.[9,10] These reports generally claim the good potential of these biosorbents—claims that are based exclusively on the observed high chromate uptake capacity as determined from simple equilibrium experiments. The biosorbents' low cost is thought to be the main advantage over the use of synthetic resins and activated carbon adsorbents. However, despite this speculated economic advantage, the question on the practicability of biosorption in solving the problem regarding chromate-containing wastewaters is raised. A high equilibrium sorption capacity alone does not guarantee a stable and an efficient process for chromate removal and/or recovery. Among others, the stability of the sorbent against oxidation by chromate, the elution efficiency of bound chromate, and the regenerability of chromate-loaded sorbent are equally relevant considerations.

This paper presents equilibrium and kinetic data on chromate biosorption by the seaweed *Sargassum siliquosum*. Using our original data and related ones from published literature, we further identify the inherent characteristics and trends in chromate biosorption, regardless of the type of biosorbent employed. The impacts of the known equilibrium and kinetic charac-

* To whom correspondence should be addressed. E-mail: L.A.M.vanderWielen@tnw.tudelft.nl. Tel: +31 15 278 2361. Fax: +31 15 278 2355.

[†] Present address: Department of Chemical Engineering, University of San Carlos, Cebu City 6000, Philippines.

[‡] Present address: Center for International Cooperation and Appropriate Technology, Delft University of Technology, 2600 GA Delft, The Netherlands.

10.1021/ie0008575 CCC: $20.00
Published on Web 04/14/2001

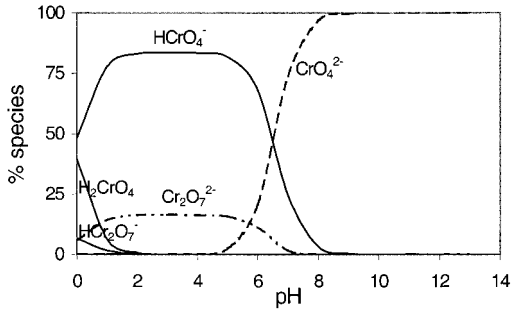

Figure 1. Calculated equilibrium distribution of Cr(VI) species in an aqueous medium with a total Cr(VI) concentration of 7.69 $\times$ 10^{-3} M and at a temperature of 25 °C.

teristics of chromate biosorption on the design of a chromate recovery process are speculated and discussed.

Solution Chemistry of Cr(VI). A good knowledge of the solution chemistry of hexavalent chromium [or Cr(VI)] is necessary in understanding the chromate biosorption phenomenon. Cr(VI) exists in different ionic forms and as a neutral acid in the aqueous environment. In this work, we will refer to the total chromate species as Cr(VI) or chromate, while each individual species will be represented by its chemical formula. The distribution of the species is dependent on the total chromate concentration and the pH of the solution. The following equations represent the equilibria governing that distribution in aqueous solution.[11]

reaction K (25 °C), mol/L

$$H_2CrO_4 \leftrightarrow H^+ + HCrO_4^-$$

$$K_1 = \frac{[HCrO_4^-][H^+]}{[H_2CrO_4]} = 1.21 \quad (1)$$

$$HCrO_4^- \leftrightarrow H^+ + CrO_4^{2-}$$

$$K_2 = \frac{[CrO_4^{2-}][H^+]}{[HCrO_4^-]} = 3 \times 10^{-7} \quad (2)$$

$$2HCrO_4^- \leftrightarrow Cr_2O_7^{2-} + H_2O$$

$$K_3 = \frac{[Cr_2O_7^{2-}]}{[HCrO_4^-]^2} = 35.5 \quad (3)$$

$$HCr_2O_7^- \leftrightarrow H^+ + Cr_2O_7^{2-}$$

$$K_4 = \frac{[Cr_2O_7^{2-}][H^+]}{[HCr_2O_7^-]} = 0.85 \quad (4)$$

Through species balance calculations using eqs 1−4, a species distribution diagram is drawn for a total Cr(VI) concentration of 7.69 $\times$ 10^{-3} M, a value that is representative for a high strength chrome-plating rinsewater.[1] The diagram is shown in Figure 1. It is observed that, at pH < 6.5, only $HCrO_4^-$ and $Cr_2O_7^{2-}$ anions are predominantly present and their concentrations appear independent of pH in the pH 2−5 range. Beyond neutral pH conditions chromate is mainly present as the CrO_4^{2-} anion. Though not shown, it is also observed that, as the total Cr(VI) concentration is made higher than the value used in the present calculation, the fraction of $Cr_2O_7^{2-}$ in the acidic pH range correspondingly increases.

It is equally important to note that chromate compounds are strong oxidizing agents; thus, Cr(VI) has the tendency to be reduced to Cr(III). The standard potentials of several half-reactions of the Cr(VI) system are given below.[11]

system	E^0,V	
$Cr_2O_7^{2-} + 14H^+ + 6e \leftrightarrow 2Cr^{3+} + 7H_2O$	+1.33	(5)
$CrO_4^{2-} + 8H^+ + 3e \leftrightarrow Cr^{3+} + 4H_2O$	+1.48	(6)
$H_2CrO_4 + 6H^+ + 3e \leftrightarrow Cr^{3+} + 4H_2O$	+1.33	(7)
$HCr_2O_4^- + 7H^+ + 3e \leftrightarrow Cr^{3+} + 4H_2O$	+1.35	(8)

The reduction of Cr(VI) to the more stable Cr(III) involves a three-electron change which has only a low probability of occurring in a single step. The formation of chromium in intermediate oxidation states such as Cr(V) and Cr(IV) is implied in practically every oxidation reaction.[11,12] The oxidation power of Cr(VI) is influenced by the structure of the reagent, the nature of the reaction medium, and its pH. Alkaline CrO_4^{2-} has a reduced oxidizing power, while strong acids enhance the oxidizing power of Cr(VI).[11]

Materials and Methods

Biosorbent. Biomass of the brown seaweed *S. siliquosum* was collected in the coastal waters of Cebu Island, Philippines. Entire seaweeds were pulled by hand at the basal portion and were immediately cleaned of attached shells, stones, and sand by rinsing with freshwater. After the seaweed was allowed to dry under direct sunlight, it was milled using a Wiley Mill, and the resulting particles were screened using ASTM standard sieves (nos. 18, 20, 40, and 45). Particles retained on a no. 40 sieve (420−840 μm size) were used in the experiments in their protonated form. Protonation was done by soaking the dried biomass portions in 0.1 M HCl (10 g of biomass/L of a HCl solution proportion) and by subsequent thorough rinsing using ultrapure water (Milli-Q Ultrapure Water Systems, Millipore Corp.). Drying was done overnight in an oven set at 60 °C. The biomass was later stored in a desiccator.

Batch Equilibrium Experiments. Each biosorption trial was done by contacting 150 mg of protonated biomass with 50 mL of a chromate solution of known Cr(VI) concentration in a 250-mL Erlenmeyer flask. A shaker moving at 100 rpm was used to agitate the flask in a 30 °C ambient condition. After 6 h of agitation, the biomass was allowed to settle and the supernatant solution was filtered and analyzed for Cr(VI) and total chromium (Cr_{tot}) contents.

To generate points for the equilibrium biosorption isotherms, sets of trials were done wherein the initial solution pH (pH_i) values were set uniform while the initial chromate concentrations were varied from 40 to 1000 mg/L Cr(VI). Other sets of trials were also done to countercheck the effect of pH on the chromate sorption. In this case, the initial chromate concentration was set at 400 mg/L Cr(VI) while the pH_i values ranged from 0.5 to 12.0. The chromate solutions used were prepared from analytical-grade $K_2Cr_2O_7$ (Fluka Chemika), and the pH_i values were set using either HCl or NaOH solutions.

The analyses of the residual solutions for Cr(VI) and Cr_{tot} contents were done colorimetrically following a standard procedure.[13] The Cr_{tot} contents were analyzed

in order to check whether electrochemical reduction of Cr(VI) to Cr(III) occurred during biosorption. The concentration of Cr(III) was estimated as the difference between the Cr_{tot} and Cr(VI) concentration values for a given sample. The total chromium uptake ($q_{Cr_{tot}}$) was computed through the mass balance:[14]

$$q_{Cr_{tot}} = (C_i - C_f)V/m$$

(mg of Cr_{tot}/g of dry biomass) (9)

C_i and C_f are the initial and final total chromium concentrations, respectively, V is the solution volume, and m is the mass of biomass used.

Kinetic Experiments. A 2-L-capacity jacketed fermentation vessel equipped with a stirrer was used in the batch biosorption kinetic experiments. In each trial, 2 L of a chromate solution was contacted with a known amount of biomass in the vessel. A set of trials made use of a solution with an initial concentration of 400 mg/L Cr(VI), and the biomass concentrations were varied, resulting in proportions of 2.0, 3.0, and 9.0 g of biomass/L of a chromate solution. A separate trial was also conducted in which the initial chromate concentration was set at 50 mg/L Cr(VI) and the biomass concentration was 3.0 g of biomass/L of a chromate solution. For all trials, the pH of the solution was initially adjusted to pH 2.0 using HCl and the jacket temperature was maintained at 30 °C. The pH was monitored on-line, while 5-mL samples were collected at various times for off-line analyses of Cr(VI) and Cr_{tot}. Analyses for the Cr(VI) content were done colorimetrically as described above. In the determination of the Cr_{tot} content, the samples were diluted 1:10 with 1 M HNO_3 and analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES). The instrument used was Perkin-Elmer Plasma 2000 with two analytical lines (205.552 and 206.149 nm wavelengths). The applied power was 1 kW, and the flow rates set for the nebulizer, auxiliary gas, and plasma were 1.0, 1.0, and 15 L/min, respectively. Calibration ranges of 0−40 mg of Cr/L were used, consistently yielding correlation coefficients better than 99.99% for both wavelengths. The difference in determined concentrations between two wavelengths was found to vary 97−101%; thus, the averages of both values were reported. Recalibration was done after every nine samples. For each sample, triplicate readings were performed.

Desorption Experiments. Protonated biomasses (150-g portions) were first loaded with chromium in Erlenmeyer flasks each containing 50 mL of 400 mg/L Cr(VI) solutions at pH 2.0. After equilibration, the supernatant solutions were decanted and the chromium-loaded biomass left in the Erlenmeyer flasks were dried overnight in an oven at 70 °C. Desorption tests were carried out by adding 50 mL of desorbent to the flasks containing the dried loaded biomass. The flasks were agitated in a water-bath shaker for a controlled period ranging from 2 to 48 h. Desorption tests were carried out using 0.2 M H_2SO_4 at three different temperatures, specifically, 22, 30, and 43 °C. At the end of the set shaking time, the solutions were analyzed for Cr(VI) and Cr_{tot} contents using the standard colorimetric method described earlier. The amount of chromium desorbed was calculated through mass balance.

Results and Discussion

Chromate Biosorption Equilibrium. In the presentation of the equilibrium data for chromate biosorption, it is important to recognize that the equilibrium solution can contain both Cr(VI) and Cr(III) even when the original solution contained only Cr(VI). The possible presence of Cr(III) is due to the electrochemical reduction of Cr(VI) via an overall route represented by any of eqs 5−8. Part of Cr(III) can be taken up by the biomass together with Cr(VI). We actually did countercheck biosorption tests using solutions containing only Cr(III) at pH 2.0. At equilibrium, the uptake turned out to be 7.81 mg of Cr(III)/L while the liquid concentration was 377 mg of Cr(III)/L. Because Cr(III) is present in solution as cations, it is suggested that its uptake by protonated *S. siliquosum* is by ion exchange with the protons in the biomass.[9] The protons come from the weak carboxylic acids whose apparent pK_a is approximately 4.8 as determined by potentiometric titration.[14]

It is easy to determine the concentrations of both Cr(VI) and Cr(III) in solution, but determining them in the biosorbent is difficult, and it could be more complicated because the biosorbed Cr(VI) may be subject to ongoing oxidation. For this reason, the isotherms are drawn based on Cr_{tot} disappearance from solution.

The isotherms are shown in Figure 2. Each set of isotherm data was obtained from batch equilibrium trials using different initial chromate concentrations but the same pH_i values. Because either an increase or decrease from the pH_i value takes place upon reaching equilibrium (see Figure 4), each isotherm drawn is thus associated with a particular equilibrium pH (pH_{eq}) range.

As is illustrated by the plots in Figure 2, the pH obviously influences the amount of Cr_{tot} sorbed by the biomass. Lower pH appears to favor the biosorption of the chromium metal. This trend is counterchecked by the sets of batch sorption trials conducted using solutions with the same initial chromate concentration (400 mg/L Cr(VI)) but individually set at different pH_i values. The results are shown in Figure 3 and, in addition to confirming the results in Figure 2, they indicate that

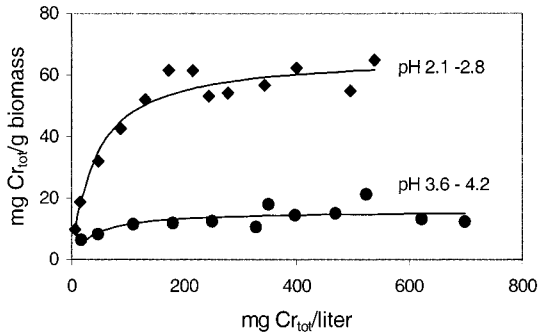

Figure 2. Equilibrium partitioning of the total chromium between the liquid and the *S. siliquosum* biosorbent phases as a function of pH (points, experimental data; lines, Langmuir model).

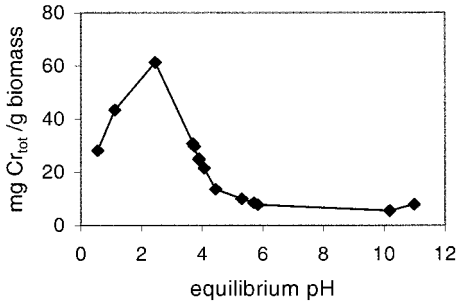

Figure 3. Cr_{tot} biosorption as a function of equilibrium pH.

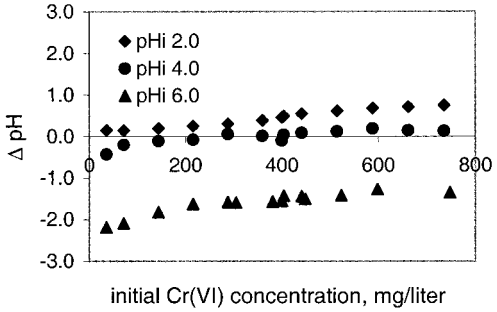

Figure 4. Change of pH of solutions during biosorption as a function of the initial pH and the initial Cr(VI) concentration.

pH 2.5 is an apparent optimum pH for maximum biosorption of Cr_{tot} by the *S. siliquosum* biomass. Kratochvil et al.[9] also reported chromate biosorption isotherms for *Sargassum sp.* biomass, and they made the same conclusion about the existence of this optimum pH based on three equilibrium isotherms obtained for pH 1, 2, and 4 conditions. Their conclusion is supported by this work.

The same trend of pH influence on chromate biosorption was observed in studies using peat moss, leaf mould, sugar beet pulp, bagasse and maize cob biosorbents,[7,15,16] *Azolla filiculoides*,[8] and sawdust.[5,6,15] From these reports, it can be concluded that chromate sorbs best at pH 2−3 conditions regardless of the biosorbent used. It is interesting to note that in the case of commercial anion-exchange resins, IRA-400 and Reillex HPQ, pH 3.0 was also reported to be the optimum pH for maximum chromate sorption.[17] The question as to why there exists an optimum pH is not addressed sufficiently in the chromate sorption literature and thus remains a subject for discussion.

Because pH is undoubtedly a major influencing variable, it might be useful in further discussions to recognize the trends of pH change during chromate biosorption. In the biosorption trials conducted, it was observed that the pH_{eq} values obtained differed depending on the pH_i and the initial chromate concentration. The results are shown in Figure 4. Defining $\Delta pH = pH_{eq} - pH_i$, a negative value would indicate a decrease in pH and thus an increase of proton concentration in the solution. Conversely, a positive value would mean consumption of protons in the solution. What can be observed in Figure 4 is that ΔpH values at pH_i 6.0 were negative (protons released into the solution) while those at pH_i 2.0 were positive (protons consumed from solution) over the whole range of initial chromate concentrations. However, solutions at pH_i 4.0 seem to be well buffered. Also, at a particular pH_i, an increased chromate concentration results in more positive values. Sharma and Forster[7,15,16] also reported similar changes in pH as a result of chromate uptake.

The isotherms in Figure 2 were found to comply well with the Langmuir equation. The Langmuir equation relates the equilibrium metal uptake Q (mg of metal/g of biosorbent) of the sorbent to the equilibrium metal concentration C_f (mg of metal/L) of the solution. It is expressed mathematically as

$$Q = Q_{max}\frac{kC_f}{1 + kC_f} \qquad (10)$$

where Q_{max}(mg/g) and k (L/mg) are parametric constants that respectively indicate the maximum metal uptake and the affinity of the metal to the biosorbent. Some of the reported Langmuir constants for chromate (bio)-sorption are presented in Table 1. The Q_{max} values we obtained are comparably close to those reported by Zhao and Duncan[8] in their work using *A. filiculoides* biosorbent. The k values, however, differ by an order of magnitude.

Because the chromate biosorption isotherms are pH-dependent, the Langmuir parameters are likewise functions of pH. The temperature is also another influencing variable, as suggested by Zhao and Duncan's report[8] that chromium uptake by *A. filiculoides* can be significantly improved by an increase in temperature (see Table 1).

Chromate Reduction during Biosorption. In the analyses of the residual solutions from biosorption trials, Cr_{tot} and Cr(VI) concentrations were found to be consistently noncoincident. The disparity is indicative of the formation of Cr(III). The Cr(III) could only come from the electrochemical reduction of Cr(VI) because only Cr(VI) was present in the solution prior to biosorption. By parity plots between equilibrium Cr_{tot} and Cr-(VI) concentrations (Figure 5), it is observed that solutions at pH_i 2.0 and 4.0 led to relatively wider disparity, i.e., more Cr(III) produced and thus more Cr-(VI) reduced. On the other hand, there was practically no disparity in the case where pH_i is 6.0. Another observation that can be made is that the respective slopes of the three different sets of points in Figure 5 appear to be constant. This means that the amount of Cr(III) produced has a linear dependence on the total chromium present in solution.

Other authors also report the incidence of Cr(VI) reduction during chromate biosorption.[7−9,15,16] They unanimously observed that lower pH led to more chromate reduced. Kratochvil et al.[9] demonstrated through calculations using the Nernst equation that the reduction potential of Cr(VI) increases with a decrease in pH. Other studies,[5,6,18] however, do not mention having counterchecked for reduction in their respective chromate biosorption experiments. In the case of chromate sorption by commercial anion-exchange resin IRA-900, Sengupta and Clifford[19] reported that sorption carried out in columns produced no Cr(III) in the aqueous phase. However, for lengthy column runs at acidic pH, some hexavalent chromium was reduced inside the ion-exchange resins, although the amount reduced did not exceed 2% of the total chromium in the resin.

The reduction of Cr(VI) directly suggests that some of the components in the biomass are oxidized. It is possible knowing that components in *S. siliquosum* include the polyphenols, polysaccharides, low molecular weight carbohydrates, and proteins[20] whose standard oxidation potentials are generally lower than those of chromate species at acidic conditions.[21] Seaweeds may also contain trace amounts of metals such as Fe,[22,23] which can also be oxidized by chromate.

It might be argued that the reduction of Cr(VI) might be due to leached out components from the biomass and that it consequently occurs in the liquid phase. However, we made a check by first vigorously contacting a known amount of biomass with ultrapure water at pH 2.0, which is the pH condition that led to more Cr(VI) reduction in the batch experiments. After the big biomass particles are allowed to settle, the liquid which contained the leached components was decanted and

Table 1. Langmuir Constants for Chromate (Bio)sorption Isotherms

(bio)sorbent	conditions pH	conditions T (°C)	Q_{max} (mg/g)	$k \times 10^{-3}$ (L/mg)	r^2	ref
A. filiculoides (freshwater fern)	1.5	18	19.7	6.57	0.93	8
	2	18	70.6	3.04	0.99	
		25	72.0	2.64	0.98	
		32	120.2	0.97	0.96	
	4	18	20.5	6.66	0.94	
S. siliquosum (brown seaweed)	2.1−2.8	30	66.4	24.0	0.993	this work
	3.6−4.2	30	15.9	22.1	0.957	
leaf mould	1.5	25	27.6	11.23	0.993	16
	2.0	25	43.1	13.16	0.997	
	4.0	25	7.1	33.31	0.983	
Amberlite IRA-400[a] (anion-exchange resin)	3.0	20	98	0.001	NR	17
	5.7	20	87	0.0006	NR	

[a] The values shown for this sorbent were read off from a plot of Langmuir constants vs pH and converted to milligram units on a wet resin basis. Correlation coefficients were not reported (NR).

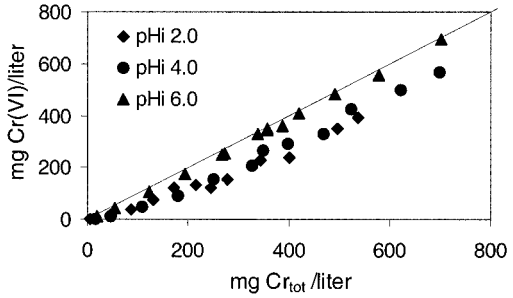

Figure 5. Parity plot of the Cr(VI) and total chromium concentration of the solutions after reaching biosorption equilibrium.

was immediately contacted with solutions of Cr(VI) for 6 h. No reduction of Cr(VI) was noted.

Kinetics of the Simultaneous Biosorption and Reduction of Chromate. The simultaneous biosorption and reduction of chromate by *S. siliquosum* biomass were monitored with respect to time in batch reactors. Shown in Figure 6a−d are the time-dependent changes of the Cr_{tot} and Cr(VI) concentrations. The decrease in the Cr(VI) concentration is due to both biosorption and reduction, while the change in the Cr_{tot} concentration is due to sorption only. The difference between the Cr_{tot} and Cr(VI) concentrations at any given time is equivalent to the Cr(III) concentration, which in turn indicates the amount of Cr(VI) reduced, if it is assumed that the biomass does not take up Cr(III) at pH 2.0 conditions.

A first inspection of the changes in the chromium concentration with time gives the impression that biosorption and reduction are parallel processes occurring at different rates. Zhao and Duncan[8] and Sharma and Forster[16] presented similar data plots. To quantitatively validate that biosorption and reduction processes are indeed parallel, the following simplified model is tested.

Sorption

$$Cr(VI)_L + B_S \overset{k_s}{\longleftrightarrow} B{-}Cr(VI)_S \qquad (11)$$

Reduction

$$Cr(VI)_L + B_S \xrightarrow{k_r} Cr(III)_L \qquad (12)$$

The subscripts S and L signify that the component is present in the solid or liquid phase, respectively. The model is based on the idea that a portion of the total Cr(VI) in solution sorbs to the available B sites on the biosorbent while another portion is reduced simultaneously on other B sites, thereby forming Cr(III). The Cr(III) formed is assumed not to sorb to the biosorbent. The two competing processes thus result in the consumption of Cr(VI) in the solution. The complete solution chemistry of Cr(VI) is not incorporated in the model because the particular conditions of pH and total chromate concentrations used in the kinetic experiments are such that the concentration of the predominant $HCrO_4^-$ practically equals that of the total Cr(VI). The reverse reaction for sorption is assumed to occur at a negligible rate, knowing the biosorbent's very high affinity for Cr(VI). Reduction is also taken to be irreversible because there is no possible component in the solution that can reoxidize Cr(III) back to Cr(VI).

For a constant-volume and constant-density batch sorption system, the component mass balances in the liquid phase are as follows.

$$dC_{Cr(VI)}/dt = -k_s C_B C_{Cr(VI)} - k_r C_B C_{Cr(VI)} \qquad (13)$$

$$dC_{Cr(III)}/dt = k_r C_B C_{Cr(VI)} \qquad (14)$$

$$dC_B/dt = -\frac{k_r}{\gamma} C_B C_{Cr(VI)} \qquad (15)$$

C_B is the B site density in mmol/L, while $C_{Cr(VI)}$ and $C_{Cr(III)}$ are the millimolar concentrations of the chromium species. The initial conditions ($t = 0$) are $C_{Cr(III),0} = 0$, $C_{Cr(VI),0} = 7.69$ or 0.96 mmol/L, and $C_{B,0} = C_{B0}$. C_{B0} is taken to be equal to our determined Q_{max} value (1.3 mmol of Cr/g of biomass at pH 2.0) multiplied by the biomass concentration (2−9 g/L). In eq 15, γ serves as a kind of efficiency factor for the oxidation of the B sites.

The component balance equations were solved numerically, and the k_r, k_s, and γ values were determined by minimizing the sum of the squares of the difference between the experimental and predicted values of the Cr(VI) and Cr(III) concentrations. It can be seen in Figure 6 that the time curves predicted by the model agree very well with the experimental data. The results reveal that the sorption rate constants have higher values than the reduction rate constants.

Because the model used is based on the idea that both rates of sorption and reduction are dependent on the initial Cr(VI) and biomass concentrations, the trends regarding the rates should be associated with the ratio of the two concentrations. A plot of the rate constants k_r and k_s against the initial concentration ratio $C_{Cr(VI),0}/C_{B0}$ in Figure 7 shows that, with $C_{Cr(VI),0}/C_{B0}$ around 0.5,

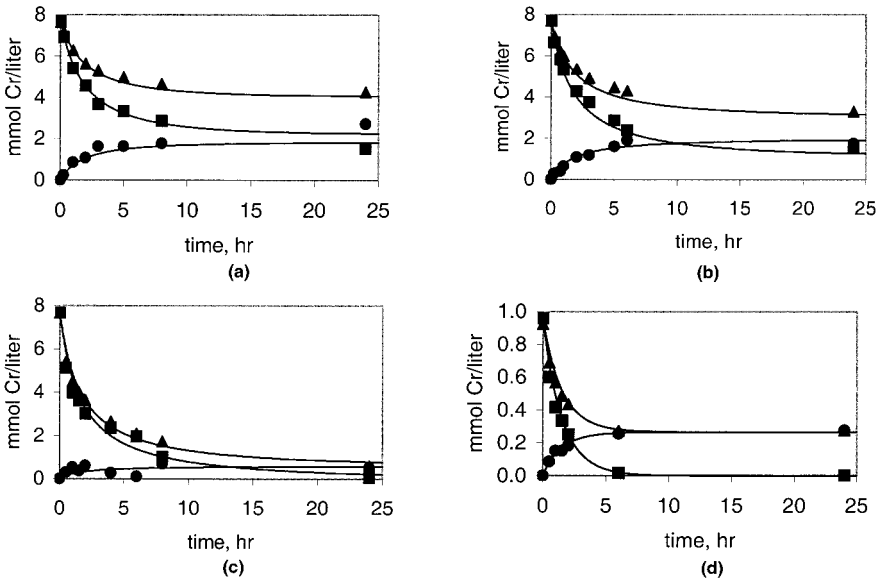

Figure 6. Progress of biosorption and reduction as a function of the biomass concentration, B, and the initial Cr concentration, C_i: (a) $B = 2.0$ g/L, $C_i = 400$ ppm; (b) $B = 3.0$ g/L, $C_i = 400$ ppm; (c) $B = 9.0$ g/L, $C_i = 400$ ppm; (d) $B = 3.0$ g/L, $C_i = 50$ ppm. Initial pH = 2.0 (▲, TCr; ■, Cr(VI); ●, Cr(III); lines are model curves).

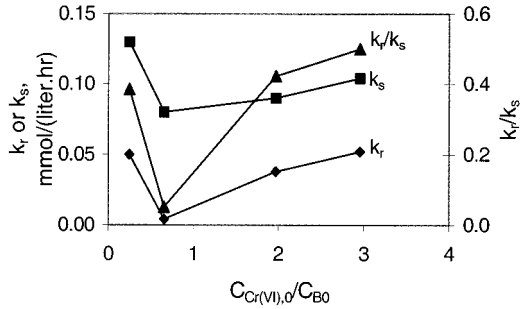

Figure 7. Rate constants for sorption and reduction as a function of the initial biomass to Cr(VI) concentration ratio.

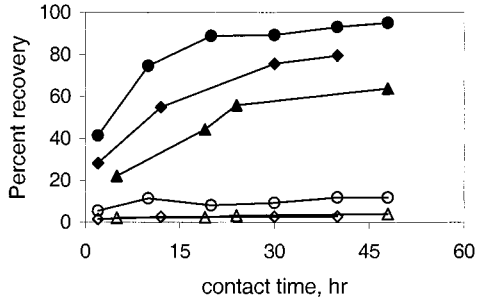

Figure 8. Percentage recovery of Cr_{tot} and Cr(VI) originally sorbed onto biomass from a solution containing 400 mg/L Cr(VI) at pH 2.0. The desorbent used was 0.2 M H_2SO_4, whose volume was equal to that of the chromate solution used during the loading step (solid symbols, Cr_{tot}; hollow symbols, Cr(VI); ● and ○, 45 °C; ◆ and ◇, 30 °C; ▲ and △, 22 °C).

both the sorption and reduction rate constants are minimum. From such a value, either decreasing the ratio (by using more biomass) or increasing it (by putting more Cr(VI)) will lead to faster rates. The important conclusion is that sorption and reduction are coupled in a parallel way; increasing the rate of one process will also increase the rate of the other. The only way to completely avoid Cr(VI) reduction is to have no sorption at all!

Desorption of Chromate. It is known that desorption of chromate from commercial anion-exchange resins such as IRA-400 is effectively done using a concentrated strong base such as 1 N NaOH.[17] However, the procedure is not advisable when working with *S. siliquosum* because concentrated NaOH leaches out various components and destroys the cellular structure of the seaweed.[9] In this study desorption trials were done using a 0.2 M solution of the common mineral acid H_2SO_4. In Figure 8 are the results which show the effect of the contact time and the temperature on the percentage recovery of chromium.

First, the temperature significantly affects the percentage recovery of Cr_{tot}. Increased temperature leads to an increase in the percentage recovery. This is a common phenomenon for adsorption but not for ion exchange.[24]

Second, it can be noted that the percentage recovery for Cr(VI) is only around 10%, even at 43 °C. The desorbent is thus able to recover chromium as Cr(III). The same was reported by Kratochvil et al.[9] This result shows that the bound Cr(VI) first has to be reduced to Cr(III) before it is desorbed from the biomass. This supports our idea that the reduction of Cr(VI) at highly acidic conditions is brought about by components in the biomass. This difficulty of recovering bound chromate in the Cr(VI) form was also demonstrated by Zhao and Duncan[25] in their attempts to desorb the chromate bound by formaldehyde-cross-linked *Saccharomyces cerevisiae* in a fixed-bed column. The use of 0.1 M NaOH only led to 5.2% Cr(VI) recovery and worse; leaching of biomass components was observed. Positive desorption results were, however, obtained by Raji and Anirudhan.[6] They reported up to 98.2% and 99.2% recoveries of Cr(VI) from polyacrylamide-grafted sawdust using 0.5 M NaCl and 0.2 M NaOH, respectively. The success was attributed to the fact that the polyacrylamide-grafted sawdust was pretreated with ethylenediamine and later on with HCl. The sawdust was thus functionalized with quaternary ammonium groups, thereby leading to a reversible ion-exchange mechanism for the chromate uptake, similar to the case with IRA-400.

Last, it is observed that relatively long contact times are necessary to obtain the maximum percentage recovery at a given temperature condition. These contact

times which are on the order of 24 h or longer compare to ca. 15 min that is required to completely strip IRA-400 resin (containing 218 mg of chromium/g of dry weight of resin) using 1 N NaOH at 20 °C.[17] Taking further the supposition that the bound chromate has to be reduced first to Cr(III) before it is desorbed, it would follow that the reduction is the slow limiting step. Incidentally, the reduction of Cr(VI) in the batch biosorption reactor experiments approached completion after 6 h or more.

Applicability of Biosorption in the Chrome-Plating Industry. Two apparent problems concerning chromate wastewaters in the chrome-plating industries are recognizable: purification of the chrome-plating bath and recovery of the chromate from the contaminated rinsewaters.

In order for the spent plating bath to be reused, the cationic contaminants [one or a combination of Fe(III), Cr(III), Ni(II), Cu(II), Zn(II), and Al(III) cations] need to be removed because they affect the plating efficiency and the quality of the plate. In this case, only the cations must be sorbed to the solid sorbent and chromate should remain in the highly concentrated solution. In the so-called reciprocating flow ion-exchange process[4] for plating bath purification, commercial cation-exchange resins are used and the chromic acid bath is first diluted to lower the oxidizing potential of the acid. Evidently, the basic requirements are that the sorbent must be able to selectively remove the cations and must, in addition, be highly resistant to oxidation by high concentrations of chromate. These requirements cannot be met using a biosorbent with weak acid groups for two reasons. On the one hand, the uptake of the chromate anions, not the cations, would be favored because the weak acid groups in the biosorbent believed to be responsible for cationic exchange[9] are fully associated considering the very acidic conditions of the bath. On the other hand, there would be more chromate loss because the high oxidation capacity of the bath brings about oxidation of the sorbent, and thus reduction of chromate to Cr(III).

The chromate-sorbing capacity of biosorbents may find potential application in recovering the chromate from the rinsewaters. In the case of rinsewaters, chromate concentrations are relatively dilute and there is the need to separate chromate anions from the metal cations. Ideally, chromate should be the only ion taken up by the sorbent and then subsequently eluted by an appropriate desorbent, thereby recovering the chromate as a concentrate that can be reused in the bath. Given this requirement, two advantages readily stand out for biosorbents. Because chrome-plating rinsewaters are acidic, it is an advantage that the maximum uptake for chromate by biosorbents is obtainable in the pH 2−3 range. Adjustment of the rinsewater pH will thus only require less volume of mineral acid/base solution. The biosorbents' high affinity for chromate is also an advantage especially in recovering chromate in dilute rinsewaters.

It is not favorable that the biosorbent is not resistant to oxidation because, in chromate recovery operation, it would mean a loss of reusable Cr(VI). More unfavorable is the fact that biosorbent-bound chromate cannot be easily recovered as chromate but only as Cr(III). As a consequence, a biosorbent-based recovery process cannot be made as part of a closed-loop chromate-plating process that requires recycling of chromate recoverable from the rinsewaters.

As shown by the kinetic experiments, relatively longer times are required for biosorption of chromate. Batch-wise rather than continuous operation may be a more expedient choice.

Conclusion

The biosorption equilibrium data reveal that while *Sargassum sp.* biomass sorbs chromate, some of the Cr(VI) is electrochemically reduced, thereby resulting in the appearance of Cr(III) in the equilibrium solution. The solution pH exerts a strong influence on the chromate biosorption, and the same trends are obtainable irrespective of which (bio)sorbent is used. Likewise, the electrochemical reduction of chromate is influenced by pH and chromate and biomass concentrations in the solution. The optimum pH for maximum chromium uptake lies within the pH 2.0−3.0 range; this is advantageous given the acidic nature of chromate-containing wastewaters. The influence of pH suggests that the solution chemistry of chromate and the biomass, both being pH-dependent themselves, provides the basic clues on the mechanism of the chromate sorption/reduction by biosorbents.

Sorption and reduction of chromate are parallel processes. At pH 2.0, the rates of both processes are influenced by the amount of biomass and initial chromate concentration. Both rates can be increased by increasing either the biomass or the Cr(VI) concentration.

In chromate sorption by *Sargassum sp.*, or by any biosorbent for that matter, the flaws deemed to affect its applicability in chromate recovery processes lie especially in the difficulty of recovering the bound chromate as Cr(VI) and in avoiding Cr(VI) reduction from taking place. Perhaps, something can be profited in reformulating the biomass into a more oxidation-resistant sorbent and into one that allows easy desorption of bound chromate. This however, requires a thorough understanding of the complex biochemistry of the biosorbent.

Acknowledgment

The authors especially thank Pamela Habivovich for having patiently done the desorption experiments.

Literature Cited

(1) Patterson, J. W.; Gasca, E.; Wang, Y. Optimization for reduction/precipitation treatment of hexavalent chromium. *Water Sci. Technol.* **1994**, *29* (9), 275.

(2) Leatherdale, J.; Dejak, M. Ion exchange systems for chromic acid recovery from plating and anodizing operations. *SAE Tech. Paper Ser.* **1991**, *909* (20), 1.

(3) Dorfner, K. Ion Exchangers in Industry. In *Ion Exchangers: Properties and Applications*; Coers, A. F., Ed.; Ann Arbor Science: Newton, MA, 1972; pp 177−180.

(4) Pajunen, P. Hard chrome bath purification and recovery using ion exchange. *Metal Finish.* **1987**, Nov, 40.

(5) Ajmal, M.; Rao, R. A. K.; Siddiqui, B. A. Studies on removal and recovery of Cr(VI) from electroplating wastes. *Water Res.* **1996**, *30* (6), 1478.

(6) Raji, C.; Anihudran, T. S. Batch Cr(VI) removal by polyacrylamide-grafted sawdust: kinetics and thermodynamics. *Water Res.* **1998**, *32* (12), 3772.

(7) Sharma, D. C.; Forster, C. F. Removal of hexavalent chromium using Sphagnum moss peat. *Water Res.* **1993**, *22*, 1201.

(8) Zhao, M.; Duncan, J. R. Batch removal of sexivalent chromium by *Azolla filiculoides*. *Biotechnol. Appl. Biochem*. **1997**, *26*, 179.

(9) Kratochvil, D.; Pimentel, P.; Volesky, B. Removal of trivalent and hexavalent chromium by seaweed biosorbent. *Environ. Sci. Technol.* **1998**, *32*, 2693.

(10) Nourbakhsh, M.; Sag, Y.; Ozer, D.; Aksu, Z.; Kutsal, T.; Caglar, A. A comparative study of various biosorbents for removal of chromium(VI) ions from industrial waste waters. *Proc. Biochem.* **1994**, *29*, 1.

(11) Cainelli, G.; Cardillo, G. *Chromium oxidations in organic chemistry*; Springer-Verlag: Berlin, 1994; pp 1−7.

(12) Rao, C. P.; Kaiwar, S. P. Reduction of potassium chromate by D-fructose, D-galactose, D-mannose, D-glucose, and L-sorbose. *Carbohydr. Res.* **1993**, *244*, 15.

(13) Eaton, A. D.; Clesceri, L. S.; Greenberg, A. E. *Standard Methods for the Examination of Water and Wastewater*, 19th ed.; United Book Press: Baltimore, MD, 1995; pp 3.59−3.60.

(14) Schiewer, S.; Volesky, B. Modeling of Proton-Metal Ion Exchange in Biosorption. *Environ. Sci. Technol.* **1995**, *29*, 3049.

(15) Sharma, D. C.; Forster, C. F. A preliminary examination into the adsorption of hexavalent chromium using low-cost adsorbents. *Bioresour. Technol.* **1994**, *47*, 257.

(16) Sharma, D. C.; Forster, C. F. The treatment of chromium wastewaters using the sorptive potential of leaf mould. *Bioresour. Technol.* **1994**, *49*, 31.

(17) Chanda, M.; Rempel, G. L. Selective chromate recovery with quaternized poly(4-vinylpyridine). *React. Polym.* **1993**, *21*, 77.

(18) Aksu, Z.; Acikel, U.; Kutsal, T. Application of Multicomponent Adsorption Isotherms to Simultaneous Biosorption of Iron-(III) and Chromium(VI) on *C. vulgaris*. *J. Chem. Technol. Biotechnol.* **1997**, *70*, 368.

(19) Sengupta, A. K.; Clifford, D. Some Unique Characteristics of Chromate Ion Exchange. *React. Polym.* **1986**, *4*, 113.

(20) Siegel, B. Z.; Siegel, S. M. The chemical composition of algal cell walls. *CRC Crit. Rev. Microbiol.* **1973**, *3* (1), 1.

(21) Clark, W. M. *Oxidation−reduction potentials of organic systems*; Williams & Wilkins: Baltimore, MD, 1960; pp 356−518.

(22) Sivalingam, P. M. Biodeposited Trace Metals and Mineral Content Studies of Some Tropical Marine Algae. *Bot. Mar.* **1978**, *21*, 327.

(23) Agadi, V. V.; Bhosle, N. B.; Untawale, A. G. Metal Concentration in Some Seaweeds of Goa (India). *Bot. Mar.* **1978**, *21*, 247.

(24) Helfferich, F. *Ion Exchange*; McGraw-Hill: New York, 1962; p 166.

(25) Zhao, M.; Duncan, J. R. Column sorption of Cr(VI) from electroplating effluent using formaldehyde cross-linked *Saccharomyces cerevisiae*. *Biotechnol. Lett.* **1998**, *20* (6), 603.

Received for review October 2, 2000
Revised manuscript received January 24, 2001
Accepted January 26, 2001

IE0008575