

# Assessment of Interference in Biosorption of a Heavy Metal

M. M. Figueira,<sup>1,2</sup> B. Volesky,<sup>1</sup> V. S. T. Ciminelli<sup>2</sup>

<sup>1</sup>Department of Chemical Engineering, McGill University, Montreal, Quebec H3A 2A7, Canada; telephone: 514-398-4494; fax: 514-398-6678; e-mail: boya@chemeng.lan.mcgill.ca

<sup>2</sup>Department of Metallurgical Engineering, Universidade Federal de Minas Gerais, Belo Horizonte, Brazil

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**Abstract:** Nonliving biomass of *Sargassum*, a brown marine alga, is capable of binding more than 10% of its dry weight in toxic cadmium ions. Although ubiquitous iron interferes with Cd uptake, only approximately 4.5% of it is sequestered (biomass dry weight). Biosorption of both metals at pH 4.5 could be described by Langmuir-type isotherms with  $b$ , the affinity-related coefficient (Cd:  $b = 0.015$ ; Fe:  $b = 0.027$ ). The interference of Fe with Cd uptake, and vice versa, was assessed by deriving three-dimensional equilibrium two-metal sorption isotherm surfaces, smoothed and "cut" to reveal the inhibition effect of Fe on biosorption of Cd: at the equilibrium concentration  $C_f[\text{Cd}] = 1.5 \text{ mM}$ , the presence of Fe at 1.5 mM equilibrium concentration suppressed the Cd uptake to only 76% of the original value. For 50% Cd uptake reduction, a very high equilibrium Fe presence of 4.5 mM was required. The Cd presence affected the uptake of Fe very strongly. To obtain equal values of uptake for each metal in the biosorbent, the ratio of equilibrium concentrations of 0.42 Cd to 1 Fe is necessary in the liquid phase. © 1997 John Wiley & Sons, Inc. *Biotechnol Bioeng* 54: 344–350, 1997.

**Keywords:** biosorption; brown algae; cadmium; iron; metal uptake; *Sargassum*

## INTRODUCTION

Biosorption of heavy metals by various biological materials has been studied extensively in the last decade (Volesky, 1990a) due to its potential particularly in wastewater treatment. Different dead biomass types, such as fungi, bacteria, and algae have been screened for their capability of adsorbing heavy metals from solutions (Volesky and Holan, 1995). Considerable work carried out with seaweeds, especially from the genus *Sargassum*, have shown their capacity to bind gold selectively at low pH (Kuyucak and Volesky, 1989a, 1989b) and also cadmium, copper, nickel, lead, and zinc cations up to 20% of the biosorbent dry weight (Leusch et al., 1995).

The presence of a large number of metals in industrial metal-bearing solutions makes it necessary to investigate their effect on the final metal uptake by individual biosor-

bent materials. Considering the number of metals and different biosorbent materials of interest, in the absence of a convenient methodology, experimental testing of these effects requires tedious laboratory work. Although iron is not considered a major environmental problem, its ubiquitous presence in solutions makes it an obvious investigation target because of its effect on the biosorbent uptake of many other metals of interest. Among them, cadmium is of primary interest for its well-recognized acute toxicity and increasing discharge into the environment.

Simple sorption isotherm curves are usually constructed as a result of studying equilibrium batch sorption behavior of different biosorbent materials. These curves enable quantitative evaluation of (bio)sorption performance of these materials for only one metal at a time (Volesky, 1990b). However, when more than one metal is present in the sorption system, the evaluation, interpretation, and representation of biosorption results become much more complicated. With two metals in the solution, instead of a two-dimensional biosorption isotherm curve, the sorption system evaluation results in a series of three-dimensional sorption isotherm surfaces (de Carvalho et al., 1995; Volesky and Holan, 1995). This novel approach is very useful particularly because there is no control over the values of the final, equilibrium, residual concentration of the sorbate as it results from standard (isotherm) sorption experiments in which the residual liquid is analyzed for the equilibrium concentration of the sorbate ( $C_f$ ). Random experimental findings of both  $C_f$  values when two-sorbate systems are studied require such an approach. This approach was also taken in the study of cadmium biosorption by *Ascophyllum nodosum* biomass in a two-metal system, which revealed the competitive and inhibitive behavior of the metals present (Chong and Volesky, 1995; de Carvalho et al., 1995). At the same time, to facilitate such a study, mathematical models to represent the experimental data and sorption surfaces had to be proposed and examined for their suitability (Chong and Volesky, 1995).

The objective of the present work was to evaluate the biosorption behavior of a two-metal system involving cadmium, iron, and a generally better biosorbent material of *Sargassum* seaweed.

Correspondence to: B. Volesky

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### Biomass Preparation and Chemicals

Particles (0.5 to 0.84 mm) of disintegrated raw biomass of *Sargassum fluitans*, originally collected and sun dried in Florida (Naples), were washed twice in 1.0N HCl solution and distilled water for the release of common ions present in seawater. Biomass was dried at 60°C overnight and then used in the experiments.

Analytical grades of HCl, H<sub>2</sub>SO<sub>4</sub>, NaOH (Anachemia, Montreal), CdSO<sub>4</sub> · 8H<sub>2</sub>O, and FeSO<sub>4</sub> · 7H<sub>2</sub>O (BDH, Toronto, ON) were used for all the experiments. Atomic absorption standards (1000 mg/L) for all metals were purchased from Fisher Scientific (Montreal).

### Sorption Isotherm Curves

Biomass particles (0.1 g) were contacted with 50 mL of metal-bearing solutions of initial concentrations varying from 0.1 to 10 mM of Cd<sup>2+</sup> or Fe<sup>2+</sup> as sulfate salts. The contents of 125-mL Erlenmeyer flasks were adjusted to pH 4.5 and, because the suspension pH tended to decrease, it was corrected (1 M NaOH) to that value every hour over the 3-h experimental contact period when shaking took place at 3.3 Hz at room temperature.

The final (equilibrium) metal concentrations,  $C_f$  [M<sub>1</sub>] and  $C_f$  [M<sub>2</sub>], in the supernatant were determined by AAS (Thermo Jarrel Ash Model Smith Hieftje II), leading to the respective calculated values for biosorbent metal uptakes  $q$  [M<sub>1</sub>] and  $q$  [M<sub>2</sub>] for the first metal [M<sub>1</sub>] and for the second metal [M<sub>2</sub>] in each biosorption system using the general definition:

$$q \text{ (mM/g)} = V (C_i - C_f) / S$$

where  $C_i$  and  $C_f$  are the initial and final (equilibrium) metal concentrations in the solution, respectively,  $V$  is the solution volume, and  $S$  is the mass of the biosorbent used.

Appropriate controls and blanks were examined throughout the sorption experiments to check the glassware sorption of metals and other potential side effects.

### Three-Dimensional Sorption Isotherm Surfaces

The procedure for the equilibrium batch sorption experiments was the same as just described. The biomass was contacted with solutions containing Cd and Fe at concentrations varying from 0.1 to 10 mM. The three-dimensional (3-D) sorption surfaces were obtained by plotting the experimentally determined final (equilibrium) metal concentrations of both metals on the  $x$  and  $y$  coordinates, respectively, against the Cd, Fe, or total metal uptakes, respectively, on the  $z$ -coordinate. The computer program MATLAB (version 4.0) was used for this purpose.

*Sargassum* biomass has been identified as a potent biosorbent of heavy metals, which it sequesters best in the slightly acidic pH range, with pH 4.5 being the optimum for Cd biosorption (Chong and Volesky, 1995; Volesky and Prasetyo, 1994). Cadmium, known for its toxicity, is often accompanied by iron in industrial effluents and solutions. The effect of iron on the biosorption of cadmium is of interest. The concentrations of metals selected for this study represent a low to medium range of those often found in typical industrial metal-bearing effluents either raw or pretreated. The sorption performance of *Sargassum* biomass was evaluated by determining the (bio)sorption isotherms for the material with Cd and Fe, respectively, before examining it in solutions containing both metals together. As the mechanism of metal uptake by the *Sargassum* biomass was confirmed to be based on ion exchange (Fourest and Volesky, 1996; Schiewer et al., 1995), the single-metal sorption behavior of the material was particularly well approximated by a simple Langmuir-type isotherm model:

$$q = (b C_f q_{\max}) / (1 + C_f)$$

This equation allows easy expression of the maximum metal uptake ( $q_{\max}$ ) and the Langmuir coefficient,  $b$ , a ratio of the adsorption rate constant to the desorption constant, reciprocally related to the affinity of the sorbent material for the metal. Experimental  $C_f$  and  $q$  data were used to evaluate the constants,  $q_{\max}$  and  $b$ , according to the least-squares fitting method. Correspondingly, the values obtained for Cd were  $q_{\max} = 1.041$  mmol/g (standard deviation  $\sigma = 0.54\%$ ), with  $b = 0.015$  ( $\sigma = 0.16\%$ ); for Fe, the maximum uptake was calculated as  $q_{\max} = 0.99$  mmol/g ( $\sigma = 0.30\%$ ) and  $b = 0.027$  ( $\sigma = 0.045\%$ ). These values indicate a decidedly better biomass affinity for, and higher sorption of, Cd ions versus Fe ions.

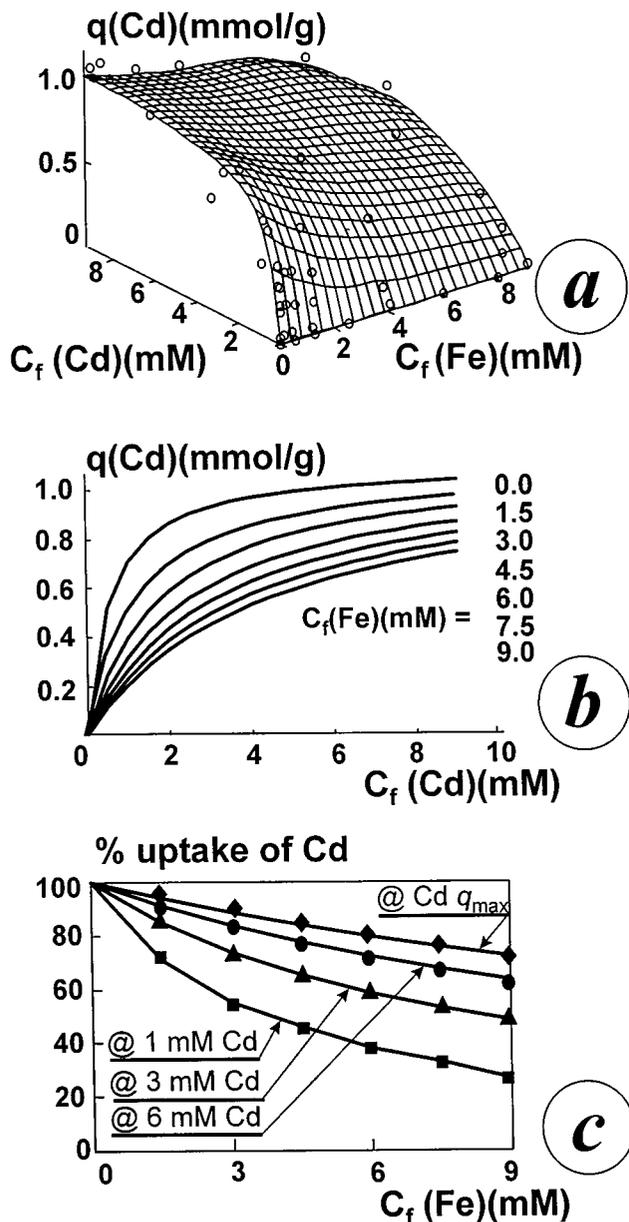
The correct and most illustrative way of representing the biosorption equilibrium of a two-metal system is to construct a 3-D sorption isotherm plot whereby the metal uptake is plotted as a function of the final equilibrium concentrations of the two metals. The computer program MATLAB 4.0 is capable of plotting a 3-D diagram based on randomly generated experimental data, fitting a smooth surface to the data according to the appropriate input equation, which represents the surface. The equation used was that adopted by Chong and Volesky (1995) for expressing the metal uptake by *Ascophyllum nodosum* seaweed biomass in the study of biosorption:

$$q (M_1) = \frac{(q_{\max}/K_1) C_f [M_1]}{1 + (1/K_1) C_f [M_1] + (1/K_2) C_f [M_2]}$$

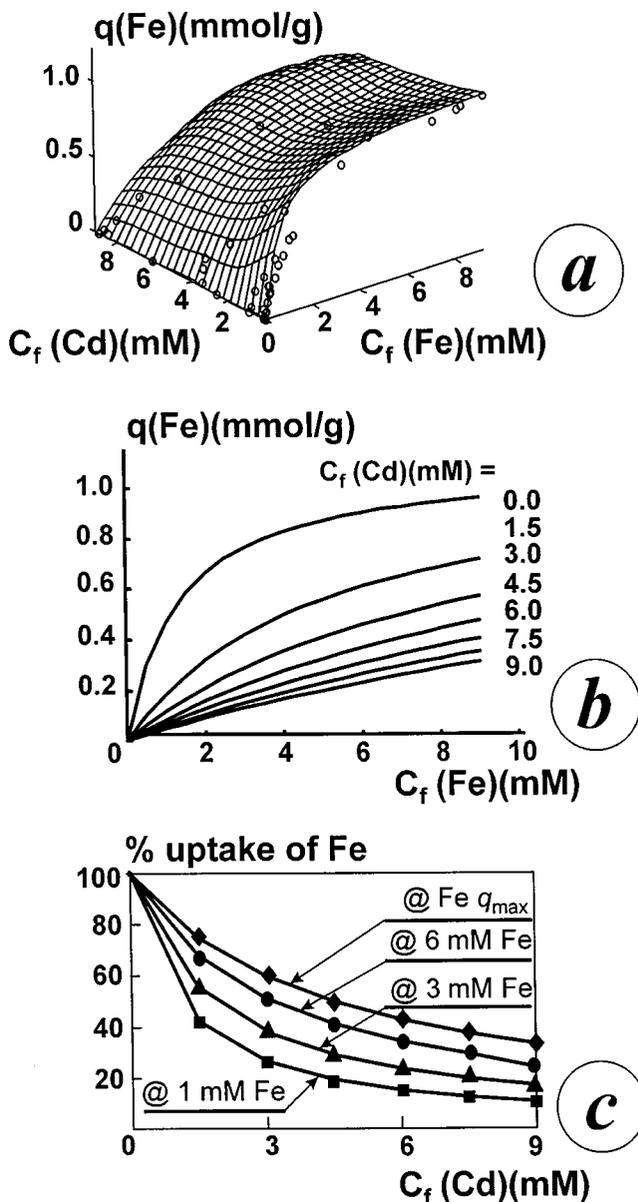
This relationship may resemble that used for describing competitive inhibition in enzyme kinetics studies. The result is a binary Langmuir-type equation, which created the sorption isotherm surfaces seen in Figures 1a, 2a, and 3a, smoothed and fitted to randomly generated experimental

biosorption data. The quality of fit was reasonably good as shown in Table I.

In Figures 1a, 2a, and 3a, the two (equilibrium) metal concentrations are plotted against the Cd, Fe, and total metal uptakes, respectively. When both Fe and Cd ions were present in the solution together (two-metal experiments), some reduction of the Cd uptake could be observed with increasing Fe concentrations. It should be pointed out that the two one-metal biosorption isotherms for Cd and Fe are, respectively, seen on the sides of these 3-D plots in the corresponding one-metal vertical planes. They are both seen in

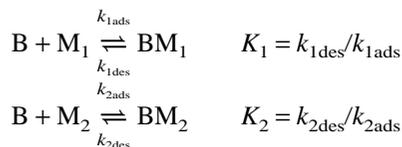


**Figure 1.** (a) A three-dimensional sorption surface for the Cd–Fe–*Sargassum* biosorption system: cadmium uptake at pH 4.5. (b) The effect of Fe on equilibrium uptake of Cd by *Sargassum* biomass at pH 4.5. (c) Summary of the effect of Fe presence on the Cd uptake by *Sargassum* biomass at pH 4.5. Equilibrium Cd concentrations arbitrarily selected: (■) [Cd] = 1 mM; (▲) [Cd] = 3 mM; (●) [Cd] = 6 mM; (◆) [Cd] for  $q_{\text{max}}$ .

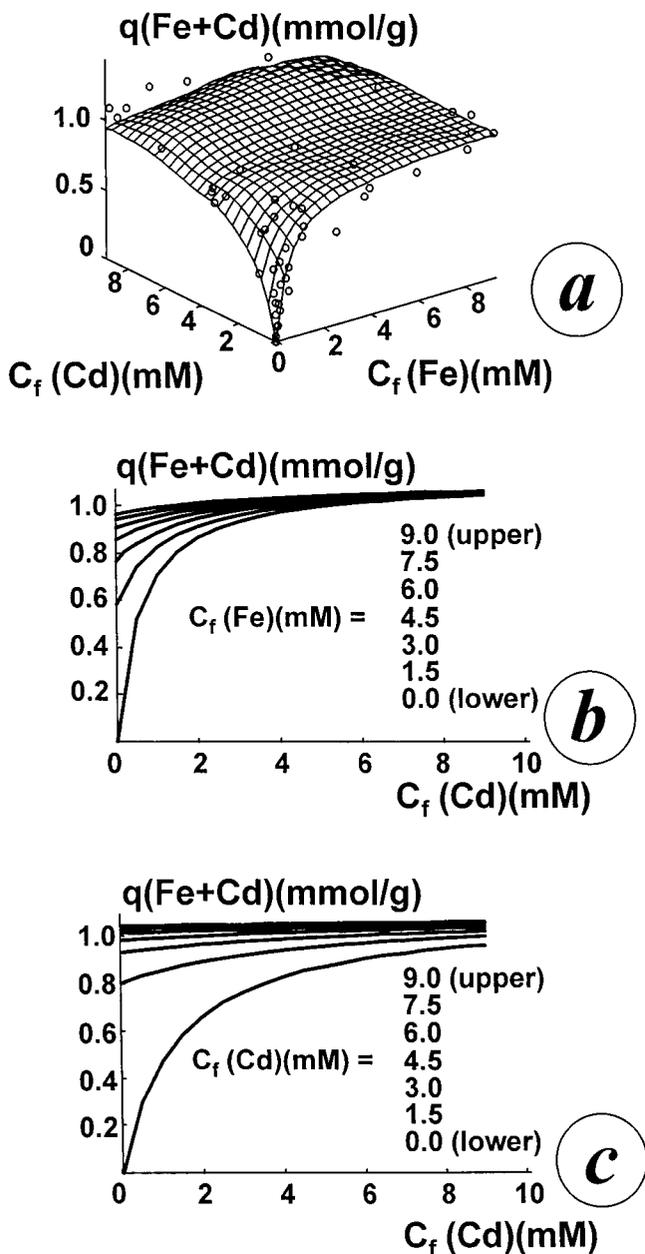


**Figure 2.** (a) A three-dimensional sorption surface for the Cd–Fe–*Sargassum* biosorption system: iron uptake at pH 4.5. (b) The effect of Cd on the equilibrium uptake of Fe by *Sargassum* biomass at pH 4.5. (c) The summary of the effect of Cd presence on the Fe uptake by *Sargassum* biomass at pH 4.5. Equilibrium Fe concentrations arbitrarily selected: (■) [Fe] = 1 mM; (▲) [Fe] = 3 mM; (●) [Fe] = 6 mM; (◆) [Fe] for  $q_{\text{max}}$ .

the side one-metal end-planes in Figure 3a, showing the total metal uptake by *Sargassum* biomass on a 3-D sorption surface. In general, when biosorption equilibrium is established in a two-metal system the following relationships hold:



where B stands for the biosorbent, BM for each biosorbent–



**Figure 3.** (a) A three-dimensional sorption surface for the Cd–Fe–*Sargassum* biosorption system: total metal uptake at pH 4.5. (b) The effect of Fe on equilibrium total metal uptake by *Sargassum* biomass at pH 4.5. (c) The effect of Cd on equilibrium total metal uptake by *Sargassum* biomass at pH 4.5.

metal complex, and  $M$  for the respective metal ions.  $k_{\text{ads}}$  and  $k_{\text{des}}$  are the adsorption and desorption rate constants, respectively.

The respective  $K$  values, reflecting the affinity between the biosorbent and the metals examined, obtained for the Fe–Cd system were 1.339 mM for Fe and 0.564 mM for Cd. The overall total metal uptake,  $q_{\text{max}} = 1.106$  mmol/g, was just slightly higher than the respective  $q_{\text{max}}$  values for these metals individually. A higher value of the  $K$  parameter for Fe than for Cd implies that the biosorbent has a higher affinity for Cd than for Fe. Higher values of  $K$  correspond

**Table I.** Two-metal biosorption: Model fit.

Equilibrium concentration range (mM)	Standard deviation (%)	
	Cd	Fe
0.0–9.3	1.96 ( $N = 51$ )	1.96 ( $N = 51$ )
0.0–0.5	2.07 ( $N = 27$ )	3.41 ( $N = 24$ )
0.5–8.3	2.40 ( $N = 36$ )	2.22 ( $N = 25$ )
8.3–9.3	4.31 ( $N = 07$ )	4.26 ( $N = 05$ )

to a higher ratio of desorption and adsorption rate constants. This aspect of affinity also reflects the selectivity of the biosorbent material for a metal.

Some selective uptake of metals by *Streptomyces* waste biomass was observed by Mattuschka and Straube (1993). Copper, silver, chromium, and lead were bound by biomass in large amounts from solutions with one metal as well as from mixed-metal solutions and this was postulated to be due to competition for biomass active sites, especially sulfhydryl groups. *Sargassum* biomass in particular demonstrated a very high specific affinity for gold at low pH (Kuyucak and Volesky, 1989b). The metal-binding capacity of *Penicillium* was observed to follow the series  $\text{Fe} > \text{Cu}$ ,  $\text{Zn}$ ,  $\text{Ni} > \text{Cd}$ ,  $\text{Pb} > \text{UO}_2$  (Galun et al., 1987), showing that Fe could present serious interference with biosorption of other metals.

To assess quantitatively this interference, experimental 3-D sorption isotherm plots need to be mathematically represented. The sorption model used for smoothing of the sorption isotherm surfaces makes it possible to eventually derive two-dimensional sorption isotherm curves from the complex 3-D image by cutting through it by a series of parallel “isoconcentration” planes for selected metal concentrations of one or the other metal, respectively (Chong and Volesky, 1995; Volesky and Holan, 1995).

The mathematical form of these isotherm equations is again based on the Langmuir-type adsorption of several metal ions competing for ion exchange or free sites in the biomass. The resulting set of sorption isotherm curves depicts either the effect of the second metal on the biosorption of the first one or vice versa in an easily understandable manner. Thus, these curves reflect correctly the actual equilibrium biosorption conditions as appropriate (de Carvalho et al., 1995; Volesky and Holan, 1995).

The effect of different levels of Fe on the biosorbent uptake of Cd is quantitatively much better demonstrated in Figure 1b, showing how the biosorption uptake of Cd decreases in the presence of Fe. The curves in Figure 1b represent series of Fe “isoconcentration cuts” of the Cd sorption surface in Figure 1a. For example, whereas in the one-metal Cd system the Cd uptake was 0.80 mM Cd/g of biomass at equilibrium  $C_f[\text{Cd}] = 1.5$  mM, when 1.5 mM Fe was present in the system (final equilibrium Fe concentration), the Cd uptake decreased to 0.61 mM/g or 76% of the original value. A significant reduction in the Cd uptake was observed only at relatively high Fe concentrations. To reach 50% Cd uptake reduction at the same Cd equilibrium con-

centration, a high equilibrium Fe presence of 4.5 mM was required.

Similarly and conversely, the effect of Cd on the biosorbent uptake of Fe is seen in Figure 2b showing the "iso-concentration cuts" of the Fe sorption uptake surface from Figure 2a. The interference of Cd with the Fe uptake was much more pronounced and was observed at much higher ratios of Fe:Cd concentrations. For instance, only 1.5 mM Cd caused a 55% reduction of the Fe uptake [ $q(\text{Fe}) = 0.26 \text{ mM/g}$ ] at the selected equilibrium,  $C_e(\text{Fe}) = 1.5 \text{ mM}$ .

Eventually, it is useful to present a summary of the effect of one metal on the uptake of the other. This is done in the third diagrams of the series (in Figs. 1c and 2c). Figure 1c summarizes the effect of Fe on the uptake of Cd in different selected concentration regions. In the range of low equilibrium Cd concentrations (1 mM and 3 mM, the two lower curves) the Cd uptake is more severely affected by the presence of Fe. The effect of Fe is less pronounced at higher Cd concentrations. For example, the  $q_{\text{max}}$  for Cd decreases only to 64% of its full value at 9.0 mM Fe (equilibrium) concentration present in the system. For the same Fe presence (9.0 mM), however, only 27% of the Cd full uptake is effected when the Cd content in the sorption system is much lower (1 mM).

The summary of the Cd interference in the Fe uptake is presented in Figure 2c. Whereas Cd obviously interferes with the Fe uptake, upon quantitative analysis it can be easily seen that it does so much more than vice versa. The higher affinity of *Sargassum* biomass for Cd than for Fe is obvious and can be quantitatively evaluated from this series of diagrams. Similar competition was observed in the two-metal biosorption performance of another biosorbent based on the *Ascophyllum nodosum* seaweed examined earlier (de Carvalho et al., 1995). One type of the metal ion present interfered with the uptake of another one in the system, although the overall total metal uptake was not necessarily lowered.

The total metal uptake sorption surface is the product of adding the two individual metal uptake surfaces (Cd and Fe uptake). Figure 3a shows that, with high levels of overall metal concentration present in the solution, the biosorbent easily reaches the saturation level demonstrated by a wide plateau of the surface. It is worth noticing that, in this plot, the two main planes ( $x-z$  and  $y-z$ ) show the single-metal sorption isotherms for Cd and Fe, respectively. When the total metal uptake sorption surface is analyzed and viewed in two series of "isoconcentration cuts" by constant Cd and Fe concentration planes, respectively, data of Figures 3b and 3c were obtained. Figures 3a and 3b depict total metal uptake behavior as a function of the one-metal equilibrium concentration with the other metal equilibrium concentration as a parameter. These data reveal that, in the present study, when *Sargassum* biosorbent becomes saturated in the system containing high concentrations of both metals of interest (Cd and Fe), the overall maximum metal uptake at pH 4.5 approaches a value of 1.1 mM/g. It should be noted that the lowest isotherm curves in Figures 3b and 3c again

represent simple one-metal biosorption isotherms for Cd and Fe, respectively. More detailed examination again confirms the higher affinity of this biosorption system for Cd as quantitatively expressed previously. Naturally, the unsaturated biosorbent demonstrates itself in the low-concentration region of the plots by sharply lower metal uptake by the solid phase.

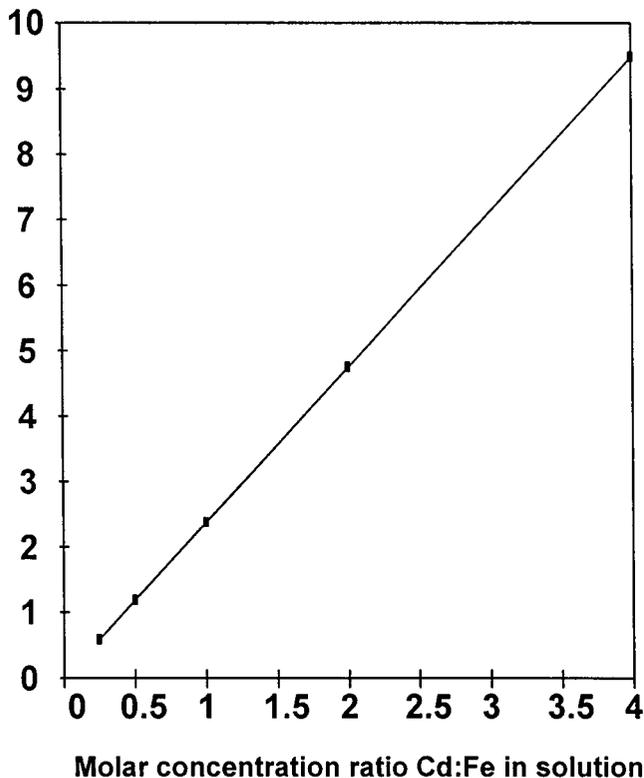
Analysis of the 3-D plots, which represent a very illustrative way of presenting a binary sorbate (metal) system, would not be possible without an appropriate mathematical model to incorporate all the randomly distributed sorption data points into a smooth surface. This approach also answers a question very important for the operation and overall optimization of the sorption system: Given the composition of the liquid phase, what would be the proportion of sorbate species in the solid sorbent phase? This is particularly relevant when the elution of the deposited species is considered and their proportion needs to be established in the desorption liquid for downstream processing. In the case of metals, this may be the metal recovery from the elutant. With the 3-D sorption surface and its model available, this aspect can be easily handled.

For any ratio of the (two) metals in the liquid phase, their ratio in the solid phase (and eventually in the elutant) can be determined by cutting the sorption surface in yet another way: using the vertical polar "isoratio" cutting planes. Closer examination of these cuts revealed that, for the given *Sargassum*-Cd-Fe biosorption system, there was no difference in these cuts for different total metal concentrations. The results could, therefore, be conveniently summarized by one relationship such as that seen in Figure 4. This relationship can be used for determining the ratio of the two metals on the sorbent when their concentration ratio in the liquid phase is known and vice versa. Needless to say, the equilibrium concentrations in the case of a flow-through sorption column apparatus usually deployed in the sorption process represent the feed to the column. Most of its sorbent material content will eventually be saturated under these conditions.

An example of using the plot in Figure 4 demonstrates that an equimolar equilibrium concentration of Cd and Fe (Cd:Fe = 1) would result in the molar uptake ratio of Cd:Fe = 2.37 (the slope of the straight-line relationship). Similarly, equal molar amounts of the two metals sequestered in the solid biosorbent (Cd:Fe uptakes = 1) would result when the equilibrium concentration ratio of Cd:Fe is 0.42. In fact, considering the  $K$  values obtained from the fitting of the experimental data, the ratio of equilibrium concentrations for which an equal uptake of each metal would result is 0.42 Cd:1 Fe in the liquid.

The presence of anions in actual waste streams may reduce the biosorptive capacity of the biomass. As a result, effects of the presence of both anions and competing cations should be included in process design considerations. For a complex waste stream the biosorptive equilibrium can be best described by the application of competitive adsorption models and chemical equilibrium models capable of simu-

### Molar concentration ratio Cd:Fe in biosorbent



**Figure 4.** The general relationship between the sorbate molar concentration ratio (Cd:Fe) and the ratio of the same sequestered species (molar uptakes) in the solid phase of the biosorbent (*Sargassum* biomass at pH 4.5).

lating equilibrium concentrations of metal species in multimetal-multiligand mixtures (Kapoor and Viraraghavan, 1995). The present equilibrium biosorption study demonstrates a practical methodological basis for evaluation of equilibrium sorption results, which would be difficult to handle otherwise. The equilibrium results are essential for further work with and the design of the sorption process perhaps best configured as the typical flow-through packed-bed column arrangement. The saturated sorbent region expanding gradually through the column represents its section where the sorption equilibrium has been established for the incoming concentration. The length (and thus volume) of the dynamic sorption region moving in the direction of the flow ahead of the saturated column section heavily depends, apart from other flow and mass transfer parameters, on the equilibrium sorption properties of the sorbent employed. Reflected eventually in the breakthrough curve, the shape and length of this "moving front" determines the degree of the sorption column utilization which in turn is the key to the economics of the process (Weber, 1972). Because of its inherent optimal sorption configuration aided by possible microprecipitation metal deposition on the biosorbent, it is expected that the biosorption column performance, when

optimized, might well exceed the sorption performance indicated by the equilibrium studies.

Ion exchange has been revealed as the predominant sequestering mechanism in algae-based (Crist et al., 1994) and particularly seaweed-based metal biosorption systems (Fourest and Volesky, 1996; Schiewer et al., 1995). However, there could also be other factors such as electrostatic attraction and some covalent bonding to specific groups in the biomass (Crist et al., 1994), depending on the metal involved. More sophisticated mathematical models have recently been proposed for the *Sargassum* biosorbent (Schiewer et al., 1995; Schiewer and Volesky, 1995, 1996), which are essential and perhaps even more suitable for the purpose demonstrated in this work. Their validity will be examined in further studies.

Two-metal biosorption studies are particularly important for assessing the degree of interference with a biosorption process of common metal ions such as, for example, iron or aluminum. Although this work has outlined a suitable methodology for the purpose, more specific data for other systems will be presented elsewhere. Two-metal biosorption studies can lead to assessing the behavior or more complex (ternary) systems (Chong and Volesky, 1996). Overall, reliable and well-interpreted equilibrium metal-uptake studies provide an essential basis for two lines of further investigation: elucidation of the metal biosorption mechanism(s), and optimization of dynamic flow-through (bio)sorption column application systems.

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