Description of Two-Metal Biosorption Equilibria by Langmuir-Type Models

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A biosorbent prepared from *Ascophyllum nodosum* seaweed biomass, FCAN2, was examined for its sorption capacity. Equilibrium batch sorption studies were performed using two-metal systems containing either (Cu + Zn), (Cu + Cd), or (Zn + Cd). In the evaluation of the two-metal sorption system performance, simple isotherm curves had to be replaced by three-dimensional sorption isotherm surfaces. In order to describe the isotherm surfaces mathematically, three Langmuir-type models were evaluated. The apparent one-parameter Langmuir constant **(b)** was used to quantify FCAN2 "affinity" for one metal in the presence of another one. The uptake of Zn decreased drastically when Cu or Cd were present. The uptake of Cd was much more sensitive to the presence of Cu than to that of Zn. The presence of Cd and Zn alter the "affinity" of FCAN2 for Cu the least at high Cu equilibrium concentrations. The mathematical model of the two-metal sorption system enabled quantitative estimation of one-metal (bio)sorption inhibition due to the influence of a second metal. © 1995 John Wiley & Sons, Inc.
Key words: biosorption • cadmium • copper • zinc • two-metal systems • *Ascophyllum nodosum*

INTRODUCTION

The term "biosorption" is used to describe metabolism-independent binding of heavy metals and/or radionuclides to nonliving biomass. The discovery and development of biosorption phenomena provide a basis for a whole new technology aimed at removal of heavy metallic species from dilute solutions in the range of 1 to 100 mg/L. Recovery of some of these metals is a possibility.

The degree of removal of heavy metals from wastewater by biosorption depends on the multimetal competitive interactions in solution with the sorbent material. However, almost all biosorption studies reported so far have been based on one-metal solutions.[8,10,19] Even when the influence of a second metal is examined,[9,14,17,21] the results cannot be extrapolated and no predictive conclusions can be drawn.

Moreover, in those two-metal equilibrium batch sorption studies, the effect of the second metal is usually reported based on its starting initial concentration. This is fundamentally inappropriate because the biosorbent is really exposed to the initial concentrations for only a very brief period of time. At equilibrium steady state, which is the predominant state of sorption systems examined, the sorbent material is not exposed to the initial concentration but to the final (equilibrium) concentrations of metal ions. This is why the final (equilibrium) concentrations have to be known when equilibrium conditions are dealt with or compared.

To design a cost-effective sorption system, the biosorption capacity of a metal in the presence of other metals has to be quantified. It is inherently more difficult to systematically study the sorption system at equilibrium since there is no control over the resulting equilibrium metal concentrations. Recent attempts[5] to examine two-metal biosorption systems resulted in three-dimensional plots of sorption isotherm surfaces using true equilibrium concentrations of solute metals. However, the surfaces have not been smoothed and show irregularities which may or may not truly reflect the behavior of the two-metal sorption system. Moreover, the sorption performance of the "virgin" biosorbent studied then was affected by the alginate leached from it[4] making it difficult to extrapolate the sorption uptake values over the range of the biosorption studies conducted.

This work illustrates a quantitative approach to studying the sorption capacity of a well-stabilized FCAN biosorbent, prepared from the biomass of brown marine alga *Ascophyllum nodosum*, in conjunction with solutions containing always two of the three metals of interest: Cd, Cu, and Zn. This is considered a first step in studying multimetal biosorption systems which would more closely represent composition of industrial effluents.

The choice of metals has been made with regard to their industrial use and potential pollution impact. Cadmium, being highly toxic, represents a great potential hazard to humans and the environment particularly since its use is rapidly increasing. Copper is not acutely toxic to humans but its extensive uses and increasing levels in the environment are causes for concern. Zinc is used very extensively by many industries, mainly in galvanizing and in manufacturing brass and other alloys. Zinc is toxic for humans at levels of 100 to 500 mg/day.[16]

MATERIALS AND METHODS

The biosorbent FCAN2 used was prepared from *Ascophyllum nodosum* seaweed biomass by crushing and sizing it, crosslinking with formaldehyde,[13] and washing it with dis-

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tilled water (3 h).[4] This preconditioning standardized the biosorbent and eliminated subsequent release of its component materials potentially causing some precipitation of the dissolved metal[4] which tends to interfere with sorption studies. A. nodosum seaweed was selected for its extraordinary ability to sequester Cu, Cd, Zn, and other metallic cations from solution.[5,7,11,13] Chemicals used were of analytical grade from Fisher Scientific, USA. The metal solutions were prepared from Cd, Cu(II), and Zn nitrates dissolved in distilled water. Batch equilibrium sorption experiments were carried out using standard batch methodology described elsewhere.[5,13,22] Metal solutions contained combinations of either (Cu + Zn), (Cu + Cd), or (Cd + Zn) in the concentration range of 0 to 350 mg/L of each one of the metals. Adjustment of pH to 4.5 in small equilibrium sorption batches was done every hour by adding small amounts of diluted HNO_3 or NH_4OH as required. By the end of the third hour of contact, the pH remained relatively constant at pH 4.5 (±0.2). Due to the unknown effects of buffer compounds on biosorption, buffering was not used.

The final (residual) metal concentration $C_f[M_1]$ and $C_f[M_2]$ in the test solutions were determined by AAS (Thermo Jarrel Ash Model Smith-Hieftje 11), leading to the respective calculated values for biosorbent metal uptakes $q[M_1]$ and $q[M_2]$ for the first metal $[M_1]$ and for the second metal $[M_2]$ in each biosorption system using the general definition[22]:

$$q(mmol/g) = V (C_i - C_f)/m$$

where C_i is the initial metal concentration in solution of volume V, and m is the dry mass of biosorbent. Appropriate controls and blanks were examined throughout the sorption experiments to check the glassware sorption of metals and other potential side effects. The seaweed and particularly FCAN derived from it contained no detectable amounts of Cu, Cd, or Zn that could influence the sorption results.

RESULTS AND DISCUSSION

As a basis for the line of investigation considered, conventional one-metal sorption isotherms were experimentally determined for the biosorbent examined in this study. These isotherms, derived at the same pH (pH 4.5) and at room temperature, are presented in Figure 1. Depending on the metal ion under consideration, an optimum pH exists for its biosorptive sequestering. The respective maximum cadmium[18] and zinc uptakes by formaldehyde crosslinked A. nodosum biomass were at pH 4.5, which was used in this study also to avoid complications due to Cu-hydroxide precipitating at higher pH. The pH level in the sorption system was maintained constant by addition of either HNO_3 or NH_4OH. While hydrogen ions may play an important role in the multicomponent adsorption, only the three heavy metals of interest were followed in this work. Molar concentration units were used which are useful for eventual stoichiometric comparison of the sorption capacity for each of the three metals.
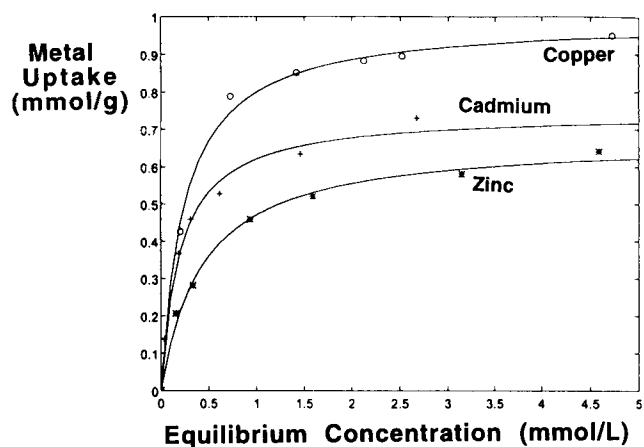
Figure 1. Biosorption isotherms for FCAN 2 and Cu (o), Cd (+), and Zn (*) at pH 4.5 and 22° to 25°C.

Biosorption of metals by FCAN can be approximated[12,13] by a Langmuir-type adsorption isotherm model:

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

where q_{max} is the maximum sorbate (metal) uptake and b is the Langmuir constant, a ratio of the adsorption rate constant to the desorption rate constant, which is related to the energy of adsorption through the Arrhenius equation. The apparent dissociation constant for the sorption system (K) is the ratio of the desorption rate constant to the adsorption rate constant and it is the inverse of the Langmuir constant b.

Experimental C_f and q data were used to evaluate the constants, q_{max} and b, according to the least square fitting method. The curves in Figure 1 were generated from Langmuir model equations with the appropriate constants as summarized in Table I.

The most appropriate and correct way of representing the biosorption equilibrium of a two-metal system is to construct a three-dimensional (3-D) sorption isotherm plot whereby the metal uptake is plotted as a function of the final equilibrium concentrations of the two metals. The metal uptake in this case can be either the uptake of one of the metals or the total uptake of both metals. Figures 2a and 2b are examples the copper uptake and the total metal uptake, respectively, for the (Cu + Cd) solution system.

The computer program, MATLAB (Version 4.0), a high-performance interactive software package for scientific and engineering numeric computation, is capable of plotting a 3-D diagram based on randomly generated experimental data. It can either simply connect the experimental data

Table I. Biosorption parameters for single-metal uptake.

Metal	q_{max} [mmol/g]	b	K
Cu	0.99	4.10	0.24
Cd	0.75	4.98	0.20
Zn	0.68	2.27	0.44

Interpolated Surfaces of Cu-Cd System

(a)

(b)

"Slicing" through the surface in Figure a

(c)
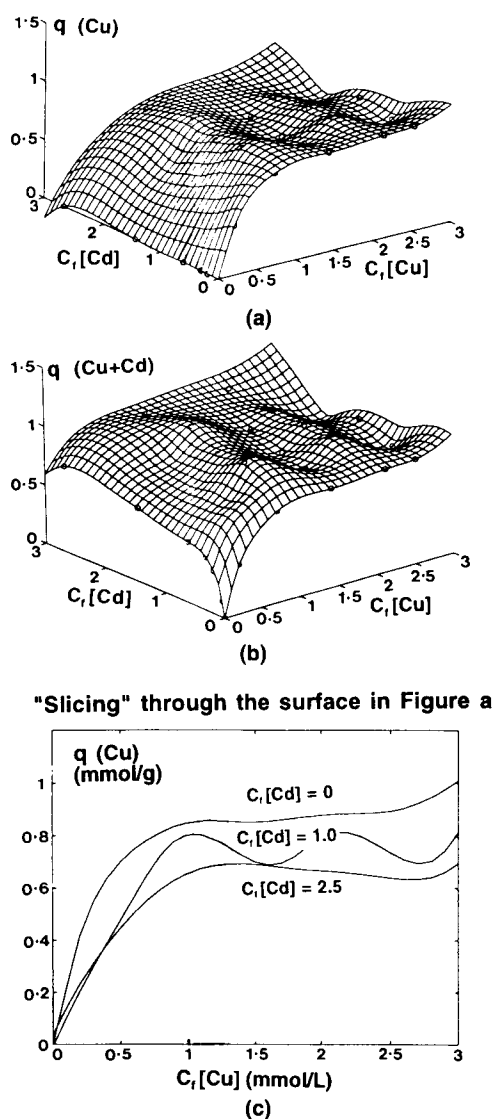
Figure 2. Interpolated sorption isotherm surfaces for FCAN2 and the two-metal system comprised of Cu–Cd. Equilibrium contact at pH 4.5 and 22° to 25°C. (a) Cu uptake is plotted as a function of the final equilibrium concentrations of Cu and Cd. (b) The total uptake of Cu and Cd is plotted as a function of the final equilibrium concentrations of Cu and Cd.

Figure 2. (continued) (c) "Slicing" through the surface in Figure 2(a) by "iso-concentration" (x–z)-planes representing C_f(Cd) of 0, 1.0, and 2.5 mmol/L, respectively.

points by a 3-D mesh through interpolation (Figs. 2a and 2b) or it can fit a smooth surface to the data. The latter approach, which is more desirable, requires the MATLAB user to input an appropriate equation representing the surface.

To obtain two-dimensional (2-D) sorption isotherm curves for one metal at constant final concentration(s) of the other metal, the 3-D sorption isotherm surface can be "cut" by the constant second-metal concentration plane. Figure 2c represents the outcome of "cutting" through the surface in Figure 2a by "isoconcentration" (x–z)-planes representing C_f(Cd) values of 0, 1.0, and 2.5 mmol/L, respectively.

As shown in Figures 2a and b, creating an interpolated surface through the data has its disadvantages. There are lumps and irregularities on the surfaces possibly due to experimental errors associated with those data points in space. At times (Fig. 2a), the surface might even enter beyond the positive axis, thus creating a "negative" uptake. Not having a surface represented by an equation, the (isoconcentration) curves derived from the "cuts" of the 3-D plot have to be smoothed, possibly by using the Langmuir model as described earlier. A major disadvantage of this approach is, however, that there are no real experimental data which are represented by the "cut" curve (such as shown in Fig. 2c) which reflects only the intrapolated surface points. The resulting "wavy" curve may not represent the actual sorption phenomenon and there may be pitfalls in attempts to interpret it. Fitting of the surface to the experimental data points available throughout the 3-D domain results in a more accurate representation of the system behavior and it is superior to the earlier more simplistic attempts. The smoothed surface can be fitted by the most suitable known equation which, in turn, allows further convenient processing of experimental results. Moreover, the use of equations is preferable since the accuracy of mesh surfaces depends on the number of experimental data points available for interpolation.

To propose the most suitable equation to represent the sorption data in a 3-D space, three models were investigated. The first model produced an equation with three parameters, while the second and the third model had four and five parameters, respectively. These parameters, related to each of the two-metal systems studied, were evaluated by minimizing the sum of squared residuals (residual refers to the difference between experimental metal uptake and that predicted from the model). Again, the MATLAB 4.0 program was used for this purpose. The following are descriptions of each of the models together with the equations resulting from the models as well as parameters of the equations representing each two-metal system studied. Notation:

[B] = concentration (number) of unoccupied binding sites.
[B_o] = total concentration (number) of binding sites.
M_1 = metal 1; M_2 = metal 2.

Model 1

When equilibrium is established:

$$B + M_1 \rightleftharpoons B - M_1 \qquad K_1 = k_{-1}/k_1$$
$$B + M_2 \rightleftharpoons B - M_2 \qquad K_2 = k_{-2}/k_2$$
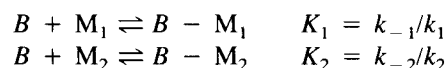
Assume:

$$d[B - M_1]/dt = 0, \quad d[B - M_2]/dt = 0$$

(The sorption system is in equilibrium: there are no net changes of [$B - M_1$] and [$B - M_2$] with respect to time).

$$[B_o] = [B] + [B - M_1] + [B - M_2]$$

Result:

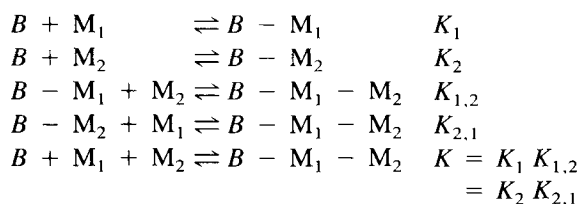$$[B - M_1] = \frac{[B_o][M_1]}{K_1 + [M_1] + (K_1/K_2)[M_2]}$$

We define $[B - M_1]$ as the number of binding sites occupied by M_1 per gram of biosorbent, and $[B_o]$ as the total number of binding sites per gram of biosorbent. Then, by multiplying both sides by a value having the units of "mmol M_1 per number of binding sites," we obtain:

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

Metal system	K_1 (mmol/L)	K_2 (mmol/L)	q_{max} (mmol/g)
Zn–Cd	Zn: 0.44	Cd: 0.15	0.67
Cu–Cd	Cu: 0.16	Cd: 0.53	0.98
Cu–Zn	Cu: 0.22	Zn: 1.11	0.92

Model 2

When equilibrium is established:

$$
\begin{aligned}
B + M_1 &\rightleftharpoons B - M_1 & K_1 \\
B + M_2 &\rightleftharpoons B - M_2 & K_2 \\
B - M_1 + M_2 &\rightleftharpoons B - M_1 - M_2 & K_{1,2} \\
B - M_2 + M_1 &\rightleftharpoons B - M_1 - M_2 & K_{2,1} \\
B + M_1 + M_2 &\rightleftharpoons B - M_1 - M_2 & K = K_1 K_{1,2} \\
& & = K_2 K_{2,1}
\end{aligned}
$$

Assume:

$$d[B - M_1]/dt = 0,$$
$$d[B - M_2]/dt = 0,$$
$$d[B - M_1 - M_2]/dt = 0$$

and

$$[B_o] = [B] + [B - M_1] + [B - M_2] + [B - M_1 - M_2]$$

(The sorption system is in equilibrium: there are no net changes of $[B - M_1]$, $[B - M_2]$ and $[B - M_1 - M_2]$ with respect to time.)

Result:

$$[B - M_1] =$$
$$\frac{[B_o][M_1]\{1 + (K_1/K)[M_2]\}}{K_1 + [M_1] + (K_1/K_2)[M_2] + 2(K_1/K)[M_1][M_2]}$$

By similar procedures as above for Model 1, we obtain:

$$q(M_1) =$$
$$\frac{q_{max} C_f[M_1]\{1 + (K_1/K)C_f[M_2]\}}{K_1 + C_f[M_1] + (K_1/K_2)C_f[M_2] + 2(K_1/K)C_f[M_1]C_f[M_2]}$$

Metal system	K_1 (mmol/L)	K_2 (mmol/L)	$K_{1,2}$ (mmol/L)	$K_{2,1}$ (mmol/L)	K (mmol/L)^2	q_{max} (mmol/g)
Zn–Cd	Zn: 0.45	Cd: 0.15	16.18	48.85	7.24	0.67
Cu–Cd	Cu: 0.15	Cd: 0.58	34.02	8.98	5.20	0.99
Cu–Zn	Cu: 0.22	Zn: 1.21	46.53	8.47	10.27	0.93

Model 3

The following equation is based on the multicomponent sorption isotherm model[3,15]:

$$q[M_1] = \frac{(q_{max}/K_1)C_f[M_1]}{1 + (1/K_1)C_f[M_1]^{K_3} + (1/K_2)C_f[M_2]^{K_4}}$$

Metal system	K_1 (mmol/L)	K_2 (mmol/L)	K_3 (dimensionless)	K_4	q_{max} (mmol/g)
Zn–Cd	Zn: 0.30	Cd: 0.10	0.95	0.87	0.62
Cu–Cd	Cu: 0.15	Cd: 0.51	0.98	1.14	0.98
Cu–Zn	Cu: 0.19	Zn: 0.91	0.97	1.13	0.91

Relatively little model development has been done for equilibrium binary or multimetal biosorption system. Model 1 presented here resembles that used for describing a competitive inhibition in enzyme kinetics studies.[1] The result of this model is a binary Langmuir-type equation which has been used in multicomponent biosorption for equilibrium isotherms.[20] For the Zn–Cd system, higher values of the K parameter for Zn than for Cd imply that the biosorbent has a higher affinity for Cd than for Zn. Higher values of K are associated with a higher ratio of the desorption rate constant to the adsorption rate constant. While true quantitative judgment cannot be done, using a similar argument it can also be concluded that the biosorbent has a higher affinity for Cu than Cd. Note that this could also be concluded from one-metal sorption isotherms.

The second model resembles that describing an uncompetitive inhibition in enzyme kinetics studies.[1] Similar to the first model, a Langmuir-type equation resulted but there are extra terms in the numerator and the denominator. It can be seen that the values of $K_{1,2}$ and $K_{2,1}$ are generally severalfold higher than those of K_1 and K_2. This implies that the formation of the B–M_1–M_2 complex is not as favorable when compared to the B–M_1 and B–M_2 complexes. Like in Model 1, the K values indicate the preference of the biosorbent according to the order Cu > Cd > Zn.

The third equation, derived from the multicomponent isotherm model, is similar to the first equation except that there is a new parameter incorporated as an exponent to each of the residual concentrations in the denominator. The values of K_1 and K_2 parameters obtained from this model also lead to similar conclusions as those drawn from Models 1 and 2. K_3 values are quite close to unity, while K_4 values deviate from unity by about ±13%. It can be concluded that Model 3 is very similar to Model 1.

The values of K for the Cd–Zn system, derived from Model 1 and Model 2 are quite similar to those obtained from corresponding one-metal systems (Table I). However, this is not the case for Cu–Zn and Cu–Cd systems. There is a possibility of predicting the two-metal biosorption equilibria from one-metal sorption isotherms depending on the type of metals studied. The presence of Cu decreases the affinity of FCAN2 for the other two metals as indicated by the higher K values. For example, the value of K for Cd increased from 0.20 for the one-metal system to 0.53

(Model 1) and 0.58 (Model 2). Similarly, K for Zn increased from 0.44 to 1.11 (Model 1) and 1.21 (Model 2).

Table II and Table III show the percentage of calculated data which deviated 10% (or less) from the experimental metal uptakes and the sum of the squared residuals (SSR) which resulted from applying the three models, respectively. The three models fit the Cu–Zn sorption system better than the other two-metal systems examined. Generally, Table II shows that the models can better predict the metal uptake for the system whereby Cu is favored. For example, in the Cu–Zn system, all three models predicted well almost 95% of the experimental Cu data as compared with only about 60% of the Zn data. However, when the biosorbent has a high affinity for both metals, as in the case of the Cu–Cd system, the experimental data of this system deviate the most from the model predictions (the SSR for the Cu–Cd system are the highest). Deviations from the Langmuir-like model in biosorption studies, especially at low residual concentration, have been reported.[2,6] However, in this study, the calculated data which deviated more than 10% are not concentrated in the more sensitive region of low final concentrations.

The largest and the smallest variances are associated with Model 1 and Model 3. In general, the selection criterion for the best model is usually based on the minimum variance. However, because the three models represent the data in a very similar manner, the choice of the best model is reduced to looking for the one with the lowest number of parameters. Because Model 1 has only three parameters, it can be judged as a model which is simpler and it will be further applied in describing the behavior of the three two-metal systems.

Equations from Model 1 can be represented by 3-D (bio)-

Table II. Percentage of calculated data which deviated (0% to 10%) from the experimental data.

	Model 1 [%]	Model 2 [%]	Model 3 [%]
Cd	76	73.7	79.0
	(32.4)	(29.6)	(33.7)
Zn	50.0	50.0	47.0
	(63.3)	(57.7)	(56.2)
Cd + Zn	79.0	81.5	86.8
	(20.9)	(21.6)	(21.4)
Cu	60.5	60.5	65.8
	(31.0)	(28.7)	(30.9)
Cd	50.0	55.0	50.0
	(73.4)	(51.8)	(69.3)
Cu + Cd	57.9	57.9	63.2
	(43.9)	(51.8)	(31.1)
Cu	94.6	94.6	94.6
	(11.9)	(10.7)	(19.8)
Zn	52.6	65.8	63.1
	(51.0)	(39.5)	(44.7)
Cu + Zn	86.8	86.8	97.4
	(31.7)	(39.5)	(10.6)

The maximum percentage deviations of calculated data from experimental data are indicated in parentheses.

Table III. Residual sum of squares.[a]

System	Degree of freedom	Sum of square residuals	Mean square
Zn–Cd			
Model 1	35	1027.4	29.3
Model 2	34	1020.3	30.0
Model 3	33	858.6	26.0
Cu–Cd			
Model 1	35	2341.9	66.9
Model 2	34	2246.1	66.0
Model 3	33	2081.3	63.0
Cu–Zn			
Model 1	34	400.0	11.7
Model 2	33	347.6	10.5
Model 3	32	271.5	8.5

[a]Residual = difference between experimental metal uptake in milligrams per liter and that from model prediction.

sorption isotherm surfaces as presented in Figure 3. While these 3-D isotherm surfaces represent the summary of the two-metal equilibrium results, the selected cuts through the 3-D diagrams presented in Figure 4 better reveal the quantitative trends observed in the two-metal sorption systems. Moreover, the effect of the secondary metal presence on the uptake of the primary metal (Fig. 5) can be derived from Figure 4. The curves resulting from the cuts of the 3-D diagrams conform well to the Langmuir model. The Langmuir parameter, **b**, the ratio of the adsorption rate constant to the desorption rate constant, is an indication of the "apparent affinity" of the biosorbent toward a metal. The Langmuir **b** value differs for each of the selected cuts of the 3-D sorption isotherm surfaces. It is useful to plot these **b** values as a function of the equilibrium concentration of a cocation (Fig. 6).

Cu–Cd System

For a given $C_f[Cd]$, as $C_f[Cu]$ increased, the uptake of Cu also increased (see Fig. 4a). However, this increase became gradually smaller at higher Cu concentrations, possibly due to the "saturation" of sites within the biosorbent. The total uptake of metals increased with increasing C_f of one metal when the C_f of the other metal was held constant. For the case when $C_f[Cu] = 2.5$ mmol/L (last segment of Fig. 4a), increasing $C_f[Cd]$ did not alter much the total uptake, whereby it remained quite constant at 0.93 mmol/g, as it gradually approached the limit of q_{max}. Note that Figure 4 is produced from Model 1 whereby the parameter $q_{max} = 0.98$ mmol/g.

In general, application of Model 1 indicated that the presence of one metal in the sorption system always lowers the sorption capacity for the other metal, an apparent case of sorption competition. Compared with single-metal sorption, the total amount of metal sequestered by the biosorbent was always higher when the material was exposed to two-metal solutions except for the case mentioned above.

At low final concentrations of cadmium and copper (0.5
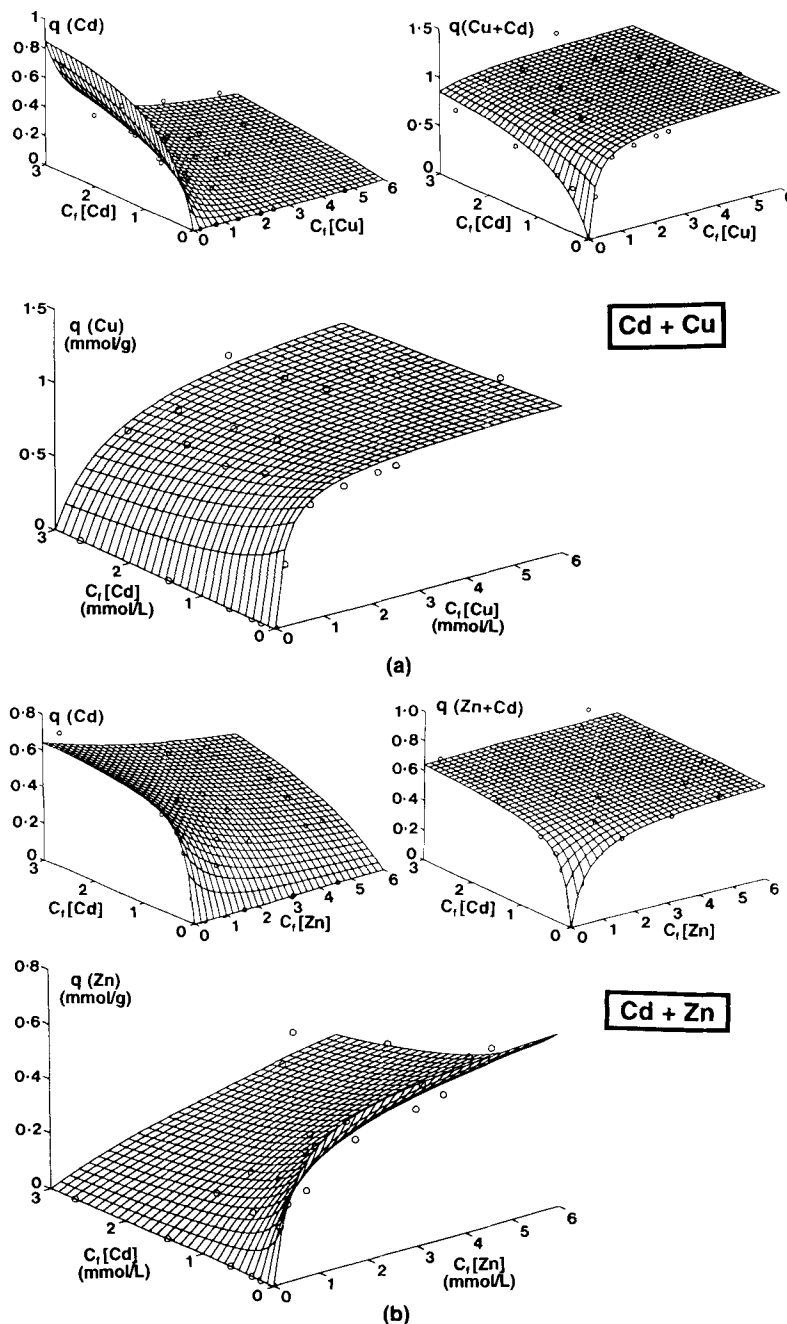
Figure 3. Two-metal sorption isotherm surfaces for FCAN2 biosorbent. The total and individual metal uptakes are plotted as a function of the final equilibrium concentrations of the two metals. All three possible plots for each two-metal system are presented. Equilibrium contact at pH 4.5 and 22° to 25°C. (a) Two-metal system containing (Cd + Cu) in solution. (b) Two-metal system containing (Cu + Zn) in solution. (c) Two-metal system containing (Cd + Zn) in solution.

mmol/L of each), FCAN2 demonstrated a preference for sorbing Cu over Cd, whereby, of the total metal uptake of 0.79 mmol/g, 77% was contributed by the uptake of copper. At high concentrations (2.5 mmol/L of each metal), the total metal uptake increased to 0.94 mmol/g, but again 77% was due to copper uptake. For the case in which each metal would comprise approximately 50% of the total metal uptake, the residual concentration of cadmium would have to be three or four times greater than that of copper. An example of this case is when C_f[Cu] = 0.5, while C_f[Cd] = 1.5 or 2 mmol/L. At high concentrations of copper (2.5 mmol/L), although the inhibition of Cu sorption was being

compensated by the Cd uptake, the total uptake remained relatively constant.

Overall, preference of the FCAN2 material for sorbing Cu over Cd is apparent over the entire concentration range studied.

Cu–Zn System

As C_f of one of the metals increased, both the total metal uptake and the uptake of that metal increased when the C_f of the other metal was held constant (see Fig. 4b). The exception was clearly seen when C_f[Cu] = 2.5 mmol/L (last
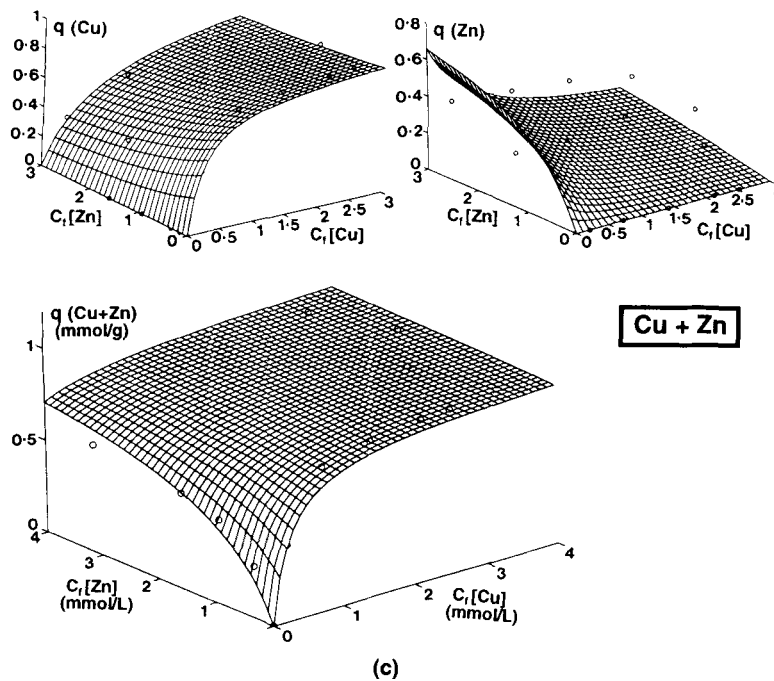
Figure 3. (Continued).

segment of Fig. 4b), whereby increasing $C_f[Zn]$ only augmented the total metal uptake by a minute amount (q_{total} increased from 0.84 to 0.85 mmol/g for the range of $C_f[Zn]$ from 0 to 2.5 mmol/L), since the total metal concentrations at these conditions were high enough to load the biosorbent near its limiting uptake capacity. Since Model 1 predicted the q_{max} of this system to be 0.92 mmol/g, the biosorbent still had some reserve metal uptake ability, however, only when subjected to higher total metal concentrations.

When the residual concentrations of copper and zinc were the same (e.g., 0.5 mmol/L each or 2.5 mmol/L each), about 83% of the total metal uptake was due to copper uptake. At $C_f[Cu] = 0.5$ and $C_f[Zn] = 2.5$ mmol/L, the uptake of each metal was 0.38 mmol/g. Thus, the equilibrium concentration of zinc would have to be five times greater than that of copper to obtain the same proportion of uptake for each metal. Similar to the case of the Cu–Cd system, at high concentrations of copper (2.5 mmol/L), the inhibition of Cu sorption was being compensated by the Zn uptake with the total uptake remaining relatively constant.

In general, the biosorbent exhibited a net preference for the Cu ion over Zn. However, when comparing (Cu–Cd) and (Cu–Zn) systems, the uptake of Cu is more susceptible to interference from Cd than from Zn.

Cd–Zn System

The total q_{max} of this system is the lowest among the three systems examined (see Fig. 4c). Again, the same phenomena are being described by Model 1: each metal inhibits the sorption of the other and, at low total residual metal concentrations, the total metal sorption uptake increased. At higher total metal concentrations, the total metal sorption

uptake remained relatively constant. At $C_f[Cd] = 2.5$ mmol/L (last segment of Fig. 4c), Zn must have been progressively replacing Cd on the same sorption sites since the total metal uptake remained unchanged.

Cadmium uptake accounted for 75% of the total metal uptake when the final concentrations of both metals were similar. The residual concentration of zinc would have to be three times that of cadmium to produce the same amount of uptake of each metal. For example, at $C_f[Cd] = 0.5$ and $C_f[Zn] = 1.5$ mmol/L, each individual metal uptake would account for 50% of the total metal uptake. At higher residual concentrations of Cd (2.5 mmol/L), the metal uptakes of Cd and Zn remained relatively constant with respect to the case when there was an absence of zinc.

A definite preference of the FCAN2 biosorbent for sorbing Cd over Zn could be observed over the equilibrium concentration range examined.

The metal preference exhibited by FCAN2 can be exemplified by Figures 5 and 6. For the following discussion, two concentrations have been arbitrarily chosen to represent "low" (0.5 mmol/L) and "high" (2.5 mmol/L) residual concentrations, respectively.

Figure 5a demonstrates that, at both low and high residual concentrations of zinc, its uptake would become less than 80% of the initial value when the concentration of Cu or Cd exceeded 0.3 mmol/L. The apparent "affinity" exhibited by FCAN2 for Zn decreased drastically when Cu or Cd were present: Langmuir **b** values decreased from 2.3 to below 0.6 when the equilibrium concentration of cocations exceeded 0.5 mmol/L (Figure 6a).

The uptake of Cd was much more sensitive to the presence of Cu than to that of Zn. Langmuir **b** parameters for Cd decreased from 5.0 to below 1.0 in the presence of Cu while they did not reach below 1.0 when Zn was present at high concentrations (Fig. 6b). At high residual concentrations of
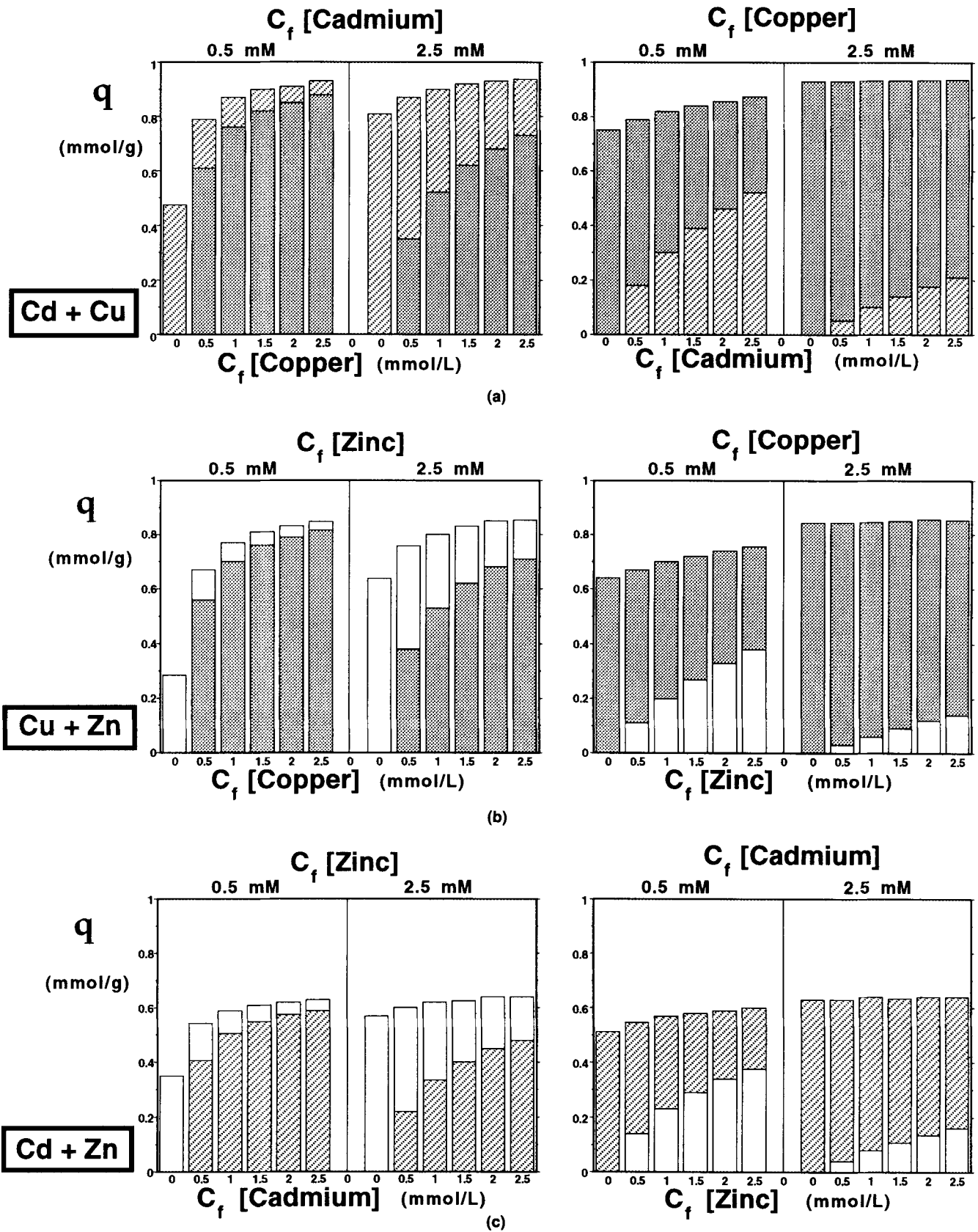
Figure 4. "Iso-concentration" cuts of the two-metal sorption isotherm surfaces for FCAN2 biosorbent: sorption uptakes from the two-metal solution vs. the equilibrium concentration of one metal, while the equilibrium concentration of the other metal is held as a constant parameter. (a) Additive Cd (▨) and Cu (■) metal uptakes as a function of the final Cu concentration and the final Cd concentration, respectively. (b) Additive Cu (■) and Zn (□) metal uptakes as a function of the final Cu concentration and the final Zn concentration, respectively. (c) Additive Cd (▨) and Zn (□) metal uptakes as a function of the final Cd concentration and the final Zn concentration, respectively.
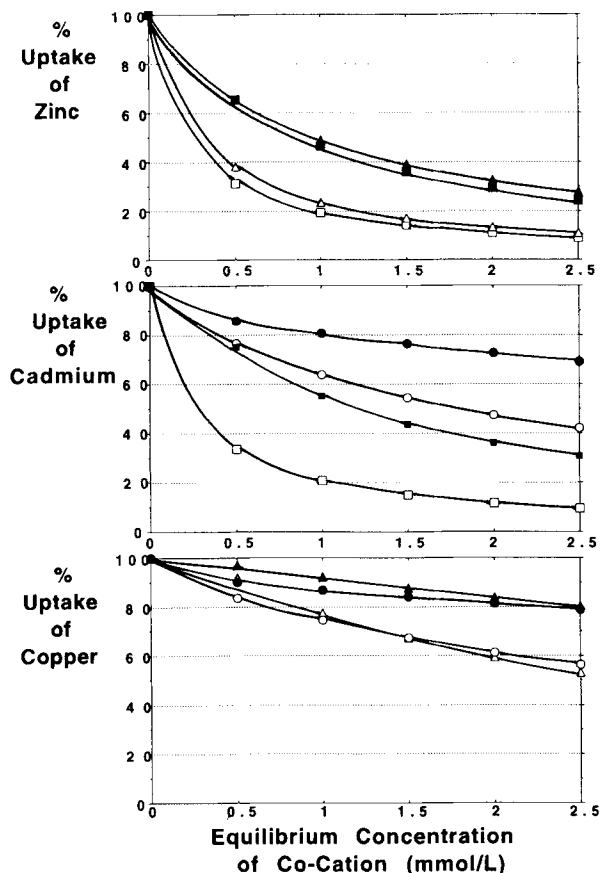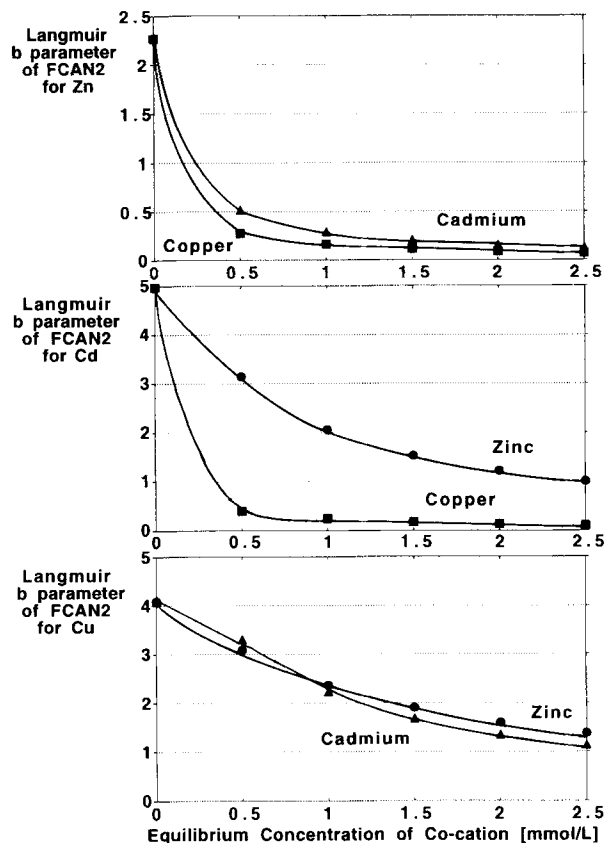
Figure 5. Effects of cocation (M_2) on the uptake of the primary metal (M_1) by FCAN2 biosorbent. Curves: (□) $C_f[M_1]$ = 0.5 mmol/L, M_2: copper; (■) $C_f[M_1]$ = 2.5 mmol/L, M_2: copper; (△) $C_f[M_1]$ = 0.5 mmol/L, M_2: cadmium; (▲) $C_f[M_1]$ = 2.5 mmol/L, M_2: cadmium; (○) $C_f[M_1]$ = 0.5 mmol/L, M_2: zinc; (●) $C_f[M_1]$ = 2.5 mmol/L, M_2: zinc.

Figure 6. Effects of co-cations on the Langmuir b value of FCAN2 biosorbent for the primary metal.

Cd, an approximately 20% decrease in the Cd equilibrium uptake resulted already at 0.5 mmol Cu/L at equilibrium, whereby the same decrease in the Cd uptake did not occur until approximately 1.2 mmol/L of residual Zn in the solution (Fig. 5b).

The presence of Cd and Zn alter the "apparent affinity" of FCAN2 for Cu as shown in Figure 6c. At low residual concentrations of Cu, a decrease in excess of 20% could be noted in the Cu sorption uptake at residual concentrations of the other metals of 1 mmol/L. At a high residual concentration of Cu, the same amount of decrease would only occur when the residual concentrations of the other metals exceeded 2.5 mmol/L (Fig. 5c).

The value of apparent dissociation constant K for a metal in one two-metal system is different from that in another two-metal system. Moreover, the maximum uptake capacity of FCAN2 biosorbent is different depending on which two metals are in solution (q_{max} values for each of the two-metal systems are not the same). This might indicate the possibility of at least some portion of different adsorption sites binding different metal ions. Future work should include performing experiments to investigate these phenomena, which are apparently related to the mechanisms of

metal biosorption. However, one has to realize the complexity of investigating the mechanisms of biosorption which could be any or a combination of these processes: complexation, coordination, chelation, ion exchange, physical adsorption, or inorganic microprecipitation of metals.

From the information on the three two-metal systems, some predictions can be made as to the possible behavior of a three-metal system. In a three-metal system comprised of Cu, Cd, and Zn, for the same equilibrium concentrations of each of the metals (regardless of "low" or "high" residual concentrations), the following would be the predicted range of percent metal uptake by FCAN2 biosorbent: copper, 55% to 71%; cadmium, 20% to 34%; and zinc, 8% to 14%. For the same amount of each metal to be sequestered by the biosorbent, a possible ratio of the residual concentrations

$$C_f[Zn] : C_f[Cd] : C_f[Cu] \text{ is } 5:3.5:1.$$

These predictions need to be verified in a next set of experimental 3-metal equilibrium (bio)sorption studies.

It would be of interest to examine if the Langmuir-like multicomponent isotherm models could represent the equilibria data of the three-metal system in a reasonable manner. Otherwise, other models would have to be sought to describe the three-metal (bio)sorption equilibria and to provide a desirable tool for predicting the respective metal uptakes.

Earlier work with the new FCAN biosorbent[5] did not employ models to describe the 3-D sorption isotherm surfaces and, consequently, the results of two-metal studies in that work could not be extrapolated and only qualitative comparison for the biosorption of two metals could be made (i.e., no predictive conclusions could be drawn). Further inaccuracies stemmed from the fact that the crude fresh FCAN biosorbent used leached alginate during the metal biosorption[4] and corrections were introduced in the calculation of metal uptakes to account for the metal precipitated outside in the solution. The results of that work used "Delta Graph" software to plot the 3-D sorption isotherm surfaces. Tedious and error-prone manual interpolations had to be performed prior to data input when using this system. FCAN2 used in the present experiments was preconditioned so that no release of its component materials or precipitation of metals occurred and "pure" sorption could be studied. The application of MATLAB 4.0 enabled the current work to produce results which can serve as a more reliable and accurate quantitative basis for judging the performance of the new biosorbent material. At the same time, a suitable methodology is outlined here which represents another step in standardizing the evaluation of biosorption performance.

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