Biotechnol. Prog. **1995,** *11,* 39–44

Evaluation of the Cd, Cu, and Zn Biosorption in Two-Metal Systems Using an Algal Biosorbent

R. P. de Carvalho,[†] K.-H. Chong, and B. Volesky[*]

Department of Chemical Engineering, McGill University, 3480 University Street, Montreal, Quebec, Canada H3A 2A7

The equilibrium sorption capacity of the formaldehyde-cross-linked brown seaweed *Ascophyllum nodosum* biomass was studied using two-metal systems comprising either (Cu + Zn), (Cu + Cd), or (Zn + Cd). Three-dimensional sorption isotherm surfaces were used in the evaluation of sorption performance, replacing simple isotherm curves. While each of the metals tested can inhibit the sorption of the others, at low total residual metal concentrations the total metal sorption uptake increases. At higher total metal concentrations, the total metal sorption uptake either remains constant, or there may be a slight decrease compared to single-metal uptakes. This is an indication of a mutual interference in the sorption uptake of the two metals tested in each system.

Introduction

Biosorption processes have been proposed (Brierley, 1990; Gadd, 1990; Volesky, 1990a,b) as an efficient and potentially cost-effective way of removing toxic heavy metals from industrial effluents with metal concentrations in the range 1–100 mg/L. A new biosorbent material derived from seaweed has been examined for this purpose (Holan et al., 1993). However, most of the studies presented on this subject have been based on the sorption of one-metal solutions (Crist et al., 1991; Holan et al., 1993). Even when the influence of a second metal is examined, the results have usually been presented in a simplistic manner (Garnham et al., 1992; Kuyucak and Volesky, 1989) that does not allow the real performance assessment of the sorption system or the comparison of the different sets of results. While there are different possible ways of expressing the effect of additional sorbate species on the sorption process (Volesky and Holan, 1994), it is necessary to emphasize that citing the initial concentrations of sorbates when an equilibrium system is studied basically is not appropriate.

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

Materials and Methods

The biosorbent used was formaldehyde-cross-linked *Ascophyllum nodosum* seaweed biomass (FCAN). The preparation of the biosorbent has been described elsewhere (Holan et al., 1993). Chemicals used were of analytical grade from Fisher Scientific. Metal solutions were prepared from Cu(II), Cd, and Zn nitrates dissolved in distilled water. The pH adjustment to 4.5 of 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 constant at pH 4.5. Due to the unknown effects of buffer compounds on biosorption, buffering was not used. Metal solutions contained either (Cu + Zn), (Cu + Cd), or (Cd + Zn) in the concentration range 0–200 mg/L of each of the metals. Batch equilibrium sorption experiments were carried out using standard batch methodology described elsewhere (Volesky, 1990b; de Carvalho et al., 1994; Holan et al., 1993). The final (residual) metal concentrations C_f[M1] and C_f[M2] in the test solutions were determined by the AAS (Thermo Jarrel Ash Model Smith-Hieftje 11 or Perkin-Elmer 3100), leading to the respective calculated values for biosorbent metal uptakes q[M1] and q[M2] for the first metal [M1] and for the second metal [M2] in each sorption system using the general definition (Volesky, 1990b):

$$q[\text{mmol/g}] = V(C_i - C_f)/W$$

where C_i is the initial metal concentration in solution of volume V and W is the 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.

A linear interpolation of the resulting batch sorption data points obtained was necessary since the final metal concentrations for the data evaluation cannot be easily controlled in equilibrium sorption experiments. For fixed values of the second metal final concentration, C_f[M2], the uptake values for the first metal, q[M1], were taken as a function of the corresponding final concentration, C_f[M1]. Since some precipitation of a metal-bearing complex occurred in the solution due to alginates that leached into the solution from the biosorbent material used (de Carvalho et al., 1994), a correction had to be introduced in the calculation of metal uptake to account for the metal precipitated. The latter phenomenon demonstrated itself by an anomalous abrupt, but relatively constant, increase (shoulder) on the sorption isotherm curves (de Carvalho et al., 1994). The corrections were done for all of the sorption isotherms, q[M1] vs C_f[M1], for a selected different constant C_f[M2] of the other metal by considering only the smooth shape of the isotherm curves obtained when this fixed amount of

---

[*] Author to whom correspondence should be addressed.

[†] On leave from Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brazil.

8756-7938/95/3011-0039$09.00/0

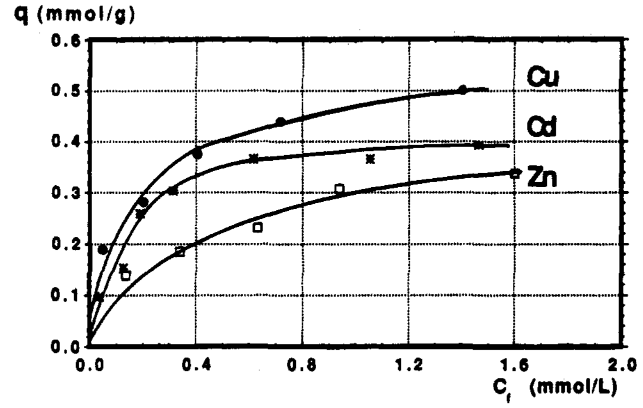

Figure 1. One-metal sorption isotherms for FCAN biosorbent and Cu (●), Cd (*), and Zn (□). Equilibrium contact at pH 4.5 and 22–25 °C.

additional fictitious uptake due to external alginate precipitation of metal was subtracted from q[M1]. For all practical purposes, this eliminated the isotherm shoulder caused by the external alginate–metal precipitation.

Results and Discussion

As a basis for the line of investigation considered, conventional one-metal sorption isotherms were determined experimentally for the FCAN biosorbent examined in this study. These isotherms, also derived for pH 4.5 at room temperature, are presented in Figure 1. Depending on the metal ion under consideration, an optimum pH exists for its biosorptive sequestering. The maximum cadmium uptake by *A. nodosum* biomass was at pH 4.5 (Holan et al., 1993), which was used in this study. Molar concentration units were used that are useful for eventual stoichiometric comparison of the sorption capacity for each of the three metals.

Two-metal sorption systems were examined that always contained two of the three metals of interest: Cd, Cu, and Zn. Following the classical sorption isotherm concept, the final (residual) concentrations of metals (C_f) were always used in the evaluation of results, considering that it is always what the sorbent ultimately "sees" in the aqueous system when the equilibrium becomes established between the solute bound to the sorbent and that left in the solution. Correspondingly, the effect of the secondary metal presence on the uptake of the primary one can be expressed as seen in Figure 2a–c.

The horizontal axes in Figure 2a–c always represent the concentration of the secondary metal (mmol/L). The vertical axes reflect how the primary metal uptake was affected (% q). The affected uptake of the primary metal q[M1] is compared with the original value when there was no secondary metal added (C_f[M2] = 0). However, it is important to select a certain uptake, corresponding to a selected final concentration value, C_f[M1], for which this effect is expressed. These points (isoconcentration lines) were selected arbitrarily so as to fall within the range of the relevant sorption isotherms for single metals, as seen in Figure 1.

Figure 2a–c depicts the effect of the secondary metal on the primary metal uptake of Cu, Zn, and Cd, respectively. Figure 2a shows the effect of Zn on Cu sorption and, vice versa, the effect of Cu on Zn sorption, which is much more pronounced. In both cases, the effect of the secondary metal on the sorption of the primary one is lesser in the higher final concentration region, as indicated by both upper curves resulting when comparing uptakes at 1.0 mmol/L for the final concentration of the

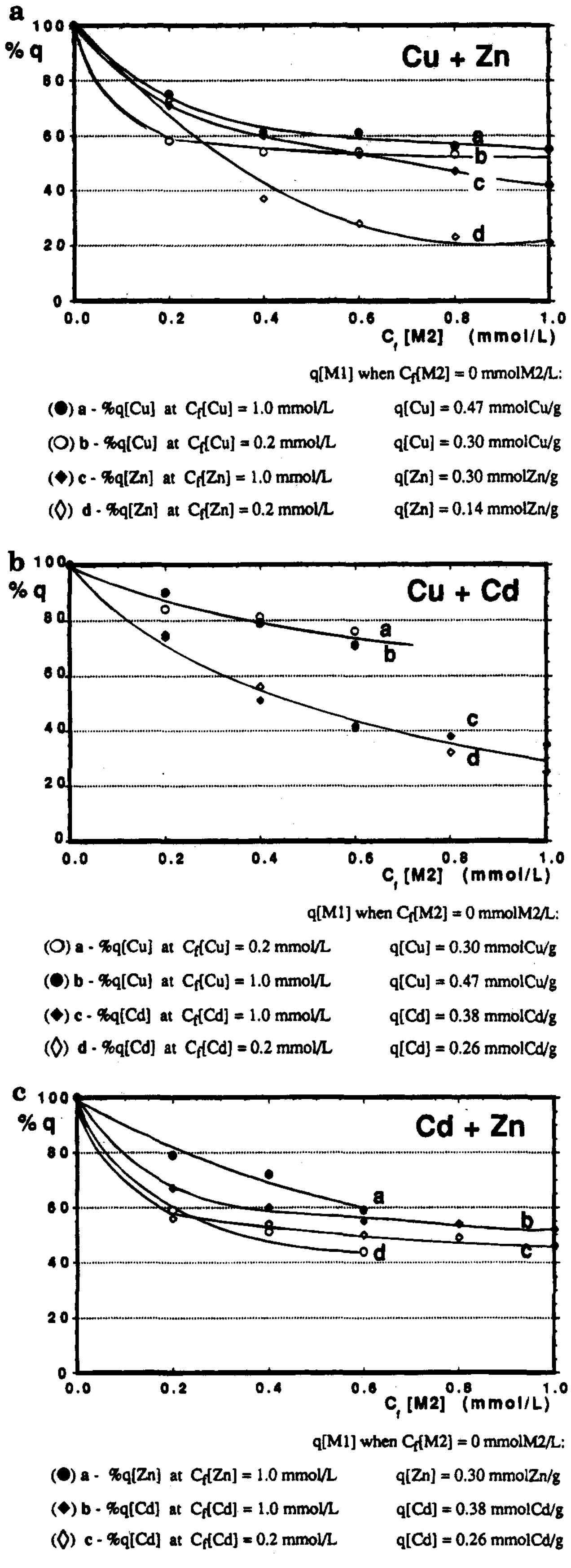

Figure 2. Effects of another metal on the metal uptake by FCAN biosorbent from a solution system containing a mixture of two of the three metals: Cd, Cu, or Zn. Equilibrium contact at pH 4.5 and 22–25 °C. (a) Two-metal system containing (Cu + Zn) in solution. (b) Two-metal system containing (Cu + Cd) in solution. (c) Two-metal system containing (Zn + Cd) in solution.

primary metal. Similar types of effects are seen in Figure 2c for the sorption systems containing Zn–Cd mixtures. The general conclusion from these results is that the presence of a secondary metal in the sorption system always lowers the sorption capacity for the primary one, an apparent case of sorption competition. However, this does not necessarily mean that the total amount of metal sequestered by the biosorbent is not increased upon exposure to the solution containing two metals.

While the two-metal sorption evaluation approach reflected in Figure 2 always focuses on the sorption uptake of one (primary) metal as it is affected by the presence of the other (secondary) metal, another evaluation can be made by looking at the total metal uptake for both metals together, $q[\Sigma] = q[\mathrm{M1}] + q[\mathrm{M2}]$, plotted on the vertical axis. On the horizontal axis, there can be the final concentration of one or the other metal. In fact, when this approach is expressed in its full complexity, it leads to a three-dimensional plot of a sorption surface instead of a two-dimensional sorption isotherm curve. Then there are two horizontal axes, one for each of the two final metal concentrations. Three such sorption surfaces are depicted, one for each of the three two-metal systems studied, in Figure 3a–c. This figure shows the total metal uptake, $q[\Sigma]$, for each system as a transparent surface, while the uptake of one of the metals is shown as a shadowed surface. The uptake of the other metal is represented by the difference between the two surfaces. However, it is not plotted separately in this work.

The total metal uptake can be broken down into its composite parts for each of the two metals sequestered from the two-metal solution used. The results of this approach are shown, respectively, in the a and b parts of Figures 4–6 for each of the two-metal combinations examined. These sets of diagrams actually represent sections through the corresponding three-dimensional sorption surfaces by planes at constant final concentrations of one metal or the other. As such, they represent isoconcentration sections of the sorption surfaces. In this case, one metal final concentration becomes a parameter of the two-dimensional sorption plot, while the other metal final concentration remains the independent variable on the horizontal axis, as usual.

Figures 4a, 5a, and 6a show the total metal uptake broken down into both individual metal uptakes, $q[\mathrm{M1}]$ and $q[\mathrm{M2}]$, at several selected fixed values of $C_f[\mathrm{M2}]$, with the $C_f[\mathrm{M1}]$ variable. This is done for the three two-metal systems studied. Conversely, in Figures 4b, 5b, and 6b, the selected isoconcentration $C_f[\mathrm{M1}]$ sections are seen with the $C_f[\mathrm{M2}]$ variable. Since it is more revealing to compare the results for the same two-metal sorption system, they are grouped accordingly.

Together, all of these different plots of experimental results offer some insight into the sorption behavior of the two-metal systems studied. The resulting three-dimensional graphs were composed by superimposing individual metal three-dimensional plots produced using the Delta Graph software on a Macintosh computer. The software, however, is not capable of surface fitting and providing the cuts of the surfaces. This had to be done by interpolation and calculation of the data points corresponding to the surface sections. Out of the total of nine surfaces that could be plotted for all of the two-metal systems, only the key six are presented in Figure 3. However, the data for surface cuts presented in Figures 4–6 were derived from all nine surfaces. While the three-dimensional isotherm surfaces in Figure 3a–c represent the summary of the two-metal equilibrium sorption results, the selected cuts through the three-dimensional diagrams presented in Figures 4–6 better reveal the quantitative trends observed in the two-metal sorption systems.

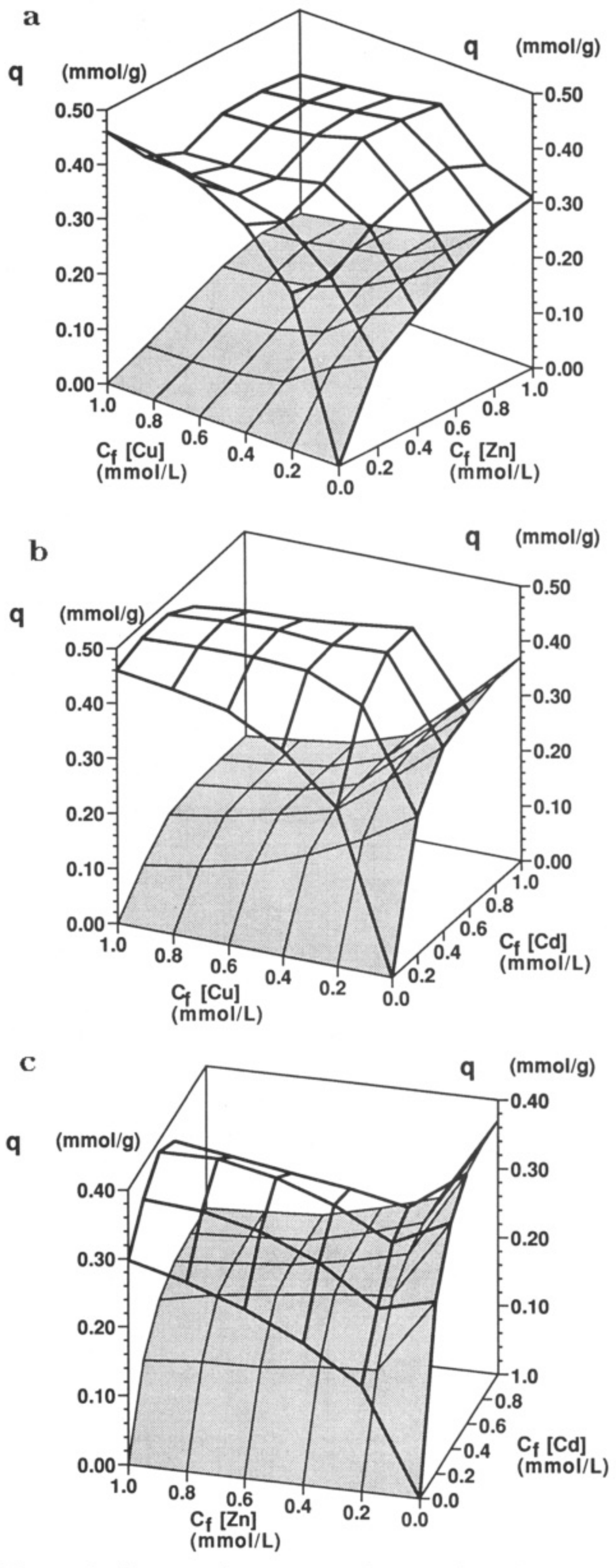

Figure 3. Two-metal sorption isotherm surfaces for FCAN biosorbent. The total and individual metal uptakes are plotted in three-dimensionally against two final concentrations of Cd, Cu, and Zn, respectively. Equilibrium contact at pH 4.5 and 22–25 °C. (a) Two-metal system containing (Cu + Zn) in solution (the Zn uptake is shaded). (b) Two-metal system containing (Cu + Cd) in solution (the Cd uptake is shaded). (c) Two-metal system containing (Zn + Cd) in solution (the Cd uptake is shaded).

(a) Cu–Zn System. Figure 1 indicates that, in molar

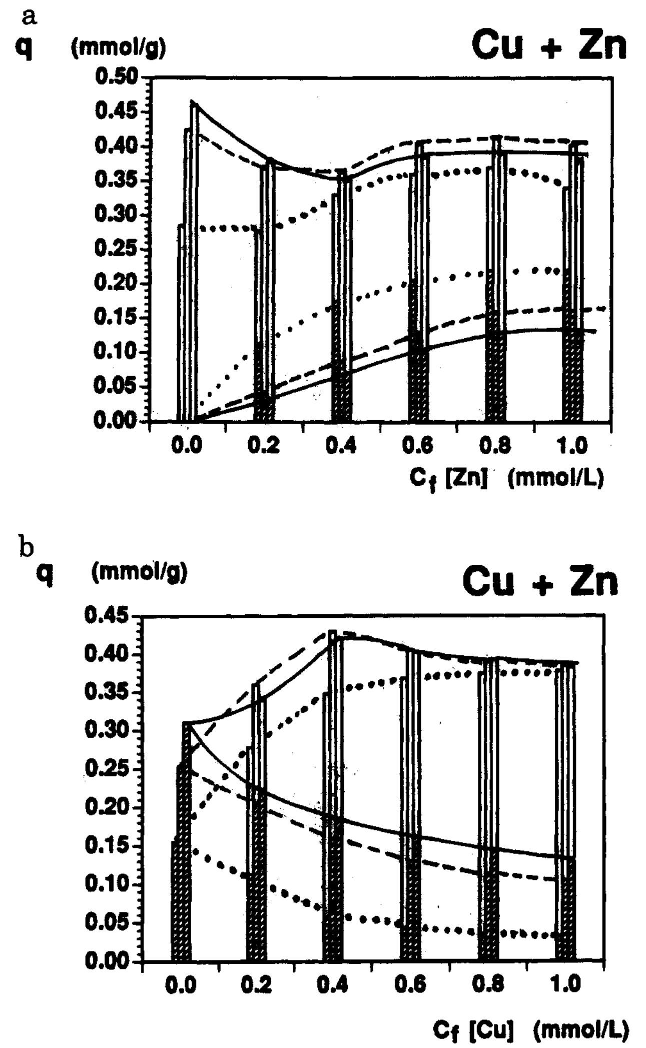

Figure 4. Isoconcentration cuts of the two-metal sorption isotherm surfaces for FCAN biosorbent. Sorption uptakes from the two-metal (Cu–Zn) solution vs the final concentration of one metal while the final concentration of the other metal is constant. Equilibrium contact at pH 4.5 and 22–25 °C. (a) Additive Cu (open) and Zn (hatched) metal uptakes as a function of the equilibrium Zn concentration. The Cu equilibrium concentration is the constant parameter: (dotted line) C_f[Cu] = 0.2 mmol of Cu/L; (dashed line) C_f[Cu] = 0.6 mmol of Cu/L; (solid line) C_f[Cu] = 1.0 mmol of Cu/L. (b) Additive Cu (open) and Zn (hatched) metal uptakes as a function of the equilibrium Cu concentration. The Zn equilibrium concentration is the constant parameter: (dotted line) C_f[Zn] = 0.2 mmol of Zn/L; (dashed line) C_f[Zn] = 0.6 mmol of Zn/L; (solid line) C_f[Zn] = 1.0 mmol of Zn/L.

quantities, almost twice as much Cu as Zn was sequestered by FCAN when only one metal was present in the solution. It can be expected that if the same functional binding sites on the biosorbent material are involved, Cu may be preferred and would be less susceptible to Zn interference. This was confirmed in the next experiment.

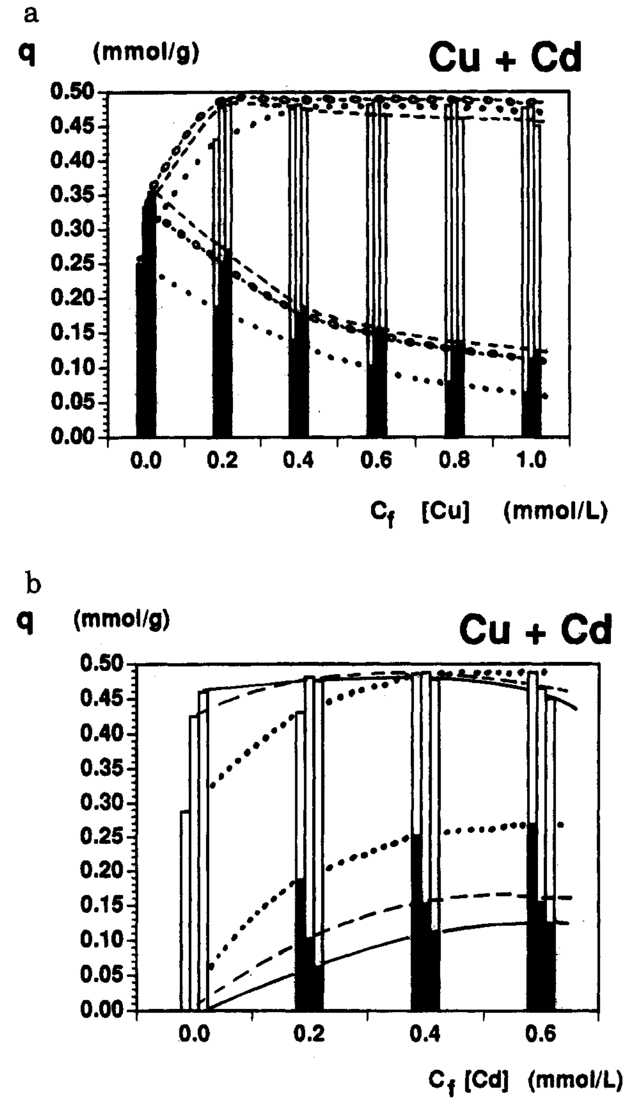

Figure 5. Isoconcentration cuts of the two-metal sorption isotherm surfaces for FCAN biosorbent. Sorption uptakes from the two-metal (Cu–Cd) solution vs the final concentration of one metal while the final concentration of the other metal is constant. Equilibrium contact at pH 4.5 and 22–25 °C. (a) Additive Cu (open) and Cd (solid) metal uptakes as a function of the equilibrium Cu concentration. The Cd equilibrium concentration is the constant parameter: (dotted line) C_f[Cd] = 0.2 mmol of Cd/L; (dashed line) C_f[Cd] = 0.6 mmol of Cd/L; (dot-dashed line) C_f[Cd] = 0.4 mmol of Cd/L. [Note: Groups of three bars correspond to second metal concentrations of C_f[Cd] = 0.2, 0.4, and 0.6 mmol of Cd/L, respectively, because the C_f[Cd] in Figure 2b does not reach 1 mmol of Cd/L.] (b) Additive Cu (open) and Cd (solid) metal uptakes as a function of the equilibrium Cd concentration. The Cu equilibrium concentration is the constant parameter: (dotted line) C_f[Cu] = 0.2 mmol of Cu/L; (dashed line) C_f[Cu] = 0.6 mmol of Cu/L; (solid line) C_f[Cu] = 1.0 mmol of Cu/L.

Figure 2 shows that if both of these metals were present in the solution, each inhibited the uptake of the other. Both metal uptakes became less than 80% of their respective initial values when the concentration of the other metal exceeded 0.15 mmol/L. However, the inhibition of Zn uptake was much stronger at its final concentration of 0.2 mmol/L (curve d), whereas the inhibition of Cu uptake showed very little sensitivity to the final Cu concentrations. Figure 4a implies that when the total concentration of metals in the solution was low (at C_f[Cu] = 0.2 mmol/L and C_f[Zn] = 0.2 mmol/L), the presence of Zn inhibited Cu uptake more strongly but the sorption of Zn did not replace that of Cu, as indicated by the lowered $q[\Sigma]$. Only at higher concentrations of C_f[Zn] > 0.6 mmol/L, did the sorption of Zn contribute to an increase in $q[\Sigma]$. However, the total metal uptake in the two-metal system exceeded the uptake of Cu in a single-metal system only for the lowest examined C_f[Cu] = 0.2 mmol/L. For example, q[Cu] = 0.28 mmol/g (first bar at C_f[Zn] = 0) and q[Cu+Zn] = 0.37 mmol/g for the (Cu+Zn) system (first bar at C_f[Zn] = 0.8 mmol/L). Figure 4b shows that with increasing C_f[Cu], the total metal uptake increases. In this case, Cu was progressively replacing Zn on the biosorbent to the point where the Zn contribution to the total metal uptake was diminishing, as also indicated by a slight decrease in $q[\Sigma]$ at C_f[Cu] > 0.4 mmol/L. In general, the biosorbent exhibited a net preference for the Cu ion over Zn.

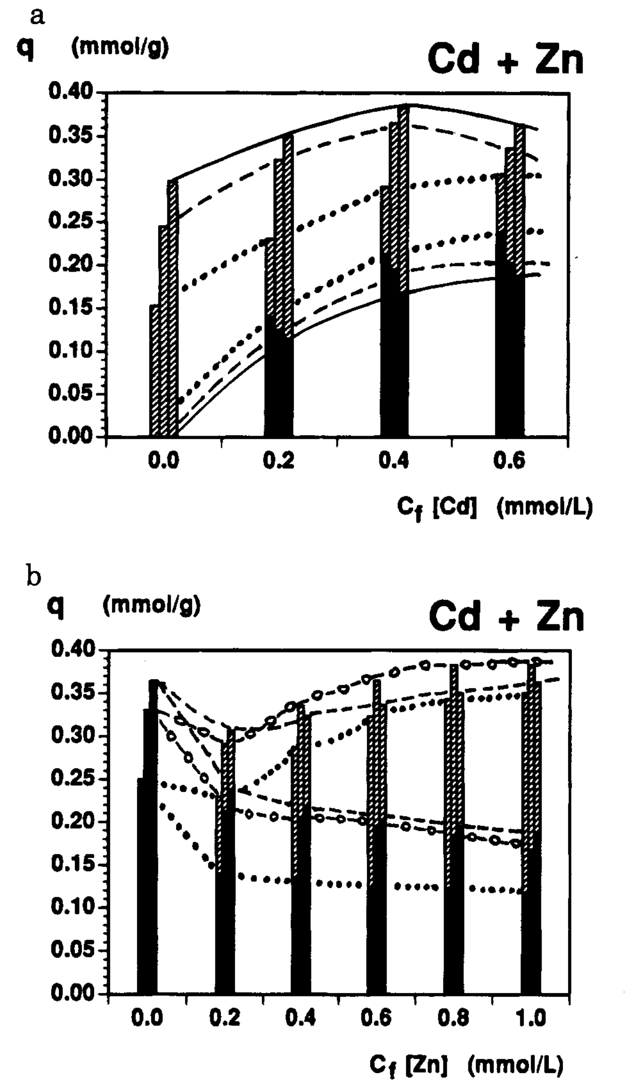

Figure 6. Isoconcentration cuts of the two-metal sorption isotherm surfaces for FCAN biosorbent. Sorption uptakes from the two-metal (Cd–Zn) solution vs the final concentration of one metal while the final concentration of the other metal is constant. Equilibrium contact at pH 4.5 and 22–25 °C. (a) Additive Cd (solid) and Zn (hatched) metal uptakes as a function of the equilibrium Cd concentration. The Zn equilibrium concentration is the constant parameter: (dotted line) C_f[Zn] = 0.2 mmol of Zn/L; (dashed line) C_f[Zn] = 0.6 mmol of Zn/L; (solid line) C_f[Zn] = 1.0 mmol of Zn/L. (b) Additive Cd (solid) and Zn (hatched) metal uptakes as a function of the equilibrium Zn concentration. The Cd equilibrium concentration is the constant parameter: (dotted line) C_f[Cd] = 0.2 mmol of Cd/L; (dashed line) C_f[Cd] = 0.6 mmol of Cd/L; (dot-dashed line) C_f[Cd] = 1.0 mmol of Cd/L.

The sorption preference for Cu over Zn has been reported for other sorbent materials, such as resins (Chandra and Rempel, 1993) or apple residues (Maranon and Sastre, 1992). When the experimental conditions could be compared, FCAN presented stronger preference effects than the other sorbents.

(b) Cu–Cd System. Figure 1 demonstrates that the single-metal sorption uptake capacity of biosorbent FCAN for Cu was higher than that for Cd. However, when both elements were present in the solution, Figure 2 shows that Cd was much more sensitive to Cu presence than the other way around. An approximately 20% decrease in Cd equilibrium uptake resulted at 0.15 mmol of Cu/L, whereby the same decrease in the Cu uptake did not occur until approximately 0.4 mmol/L residual Cd in the solution.

Figure 5a,b shows that at low total metal concentrations ($C_f[\Sigma] < 0.6$ mmol/L), the inhibition in the uptake of one metal was compensated by the uptake of the other one, increasing the value of $q[\Sigma]$. For $C_f[\Sigma] > 0.6$ mmol/L, the total uptake remained relatively constant, always higher or at least equal to the respective individual uptakes from one-metal solutions. The preference of the FCAN material for sorbing Cu over Cd is clear over the entire concentration range studied.

(c) Cd–Zn Systems. Figure 1 indicates that the single-metal sorption uptake capacity of biosorbent FCAN for Cd was higher than that for Zn. When both elements were present in solution, Figure 2 demonstrates that they both interfered with each other's sorption to a similar general extent. A decrease in excess of 20% could be noted in the equilibrium sorption of either Cd or Zn at a residual concentration of the other metal of 0.2 mmol/L. However, for the low concentration of C_f[Zn] = 0.2 mmol of Zn/L, Zn uptake was somewhat more sensitive to the presence of Cd than at the other extreme of higher C_f[Zn] = 1.0 mmol of Zn/L examined. The net decreases in the respective single-metal uptakes in the presence of the other metal were not reflected in the total metal uptake, which either increased (Figure 6a) or remained almost constant (Figure 6b) for this two-metal system. In the (Cd–Zn) two-metal sorption system examined, the inhibition in Zn sorption was compensated by the Cd uptake. A lowering of the total metal uptake could be noted between C_f[Zn] = 0 and 0.2 mmol of Zn/L, where Zn sorption apparently was not sufficient to compensate for the inhibition of Cd uptake, as was the case at higher Zn levels. In general, a slight preference for Cd sorption over Zn could be observed over the final equilibrium concentration range examined.

The sorption from cadmium–zinc solutions was reported in other sorbent materials as presenting the same trend that was observed for FCAN. The combined sorption of both metals on manganese oxide was lower in the two-metal system when compared to the uptake of individual metals from solutions containing only a single metal (Zasosky and Burau, 1988). The total uptake was reported to decrease for metal concentrations higher than those used in the present study. In studies of sorption by chitosan (Jha et al., 1988), the presence of Zn inhibited Cd uptake very strongly: only 40% of the original Cd uptake value (at C_f[Zn] = 0) remained at C_f[Zn] < 0.1 mmol/L.

The sorption preferences observed with the FCAN material and the results of the competition aspects observed will likely have repercussions in the continuous-flow dynamic sorption column system. A net FCAN sorption preference for Cu uptake over Cd or Zn in the relevant concentration range studied (0.1–1.5 mmol/L) indicates the possible potential of its use in a flow arrangement as a selective filter for enrichment of the given metallic species, provided that appropriate process control could be exercised. Other authors reported the use of a microbial biosorbent for the separation of Pd from Cu (Brierley and Vance, 1988) or resins for the separation of Cu from Zn (Akita and Takeuchi, 1990). In the latter case, Zn was sorbed more strongly than Cu, leaving the Cu ions in the residual solution. It is important to stress that all of the sorption experiments in the present work were done at pH 4.5. A change in the pH of the sorption system could significantly alter the sorption capacities and preferences in two-metal sorption systems (Brierley and Vance, 1988).

Conclusions

For biosorption on FCAN at pH 4.5: (1) The sorption capacities for single metals decrease in the order Cu > Cd > Zn. (2) The inhibition dominance observed in two-metal sorption systems was Cu > Zn, Cu > Cd, Cd ~

Zn. (3) Due to this, FCAN exhibited a net preference for Cu sorption over Cd or Zn, indicating the possibility for its use in a flow-through arrangement as a metal-selective filter. (4) The presence of Zn tends to lower the total metal uptake in two-metal systems (with Cu or Cd). Its own uptake cannot compensate for the uptake inhibition of the other metal. (5) The FCAN sorption active sites for Cu and Cd show independence at low total metal concentrations (<0.6 mmol/L). Progressive sorption interference among the metals examined indicates a degree of overlap in the sorption site function at higher equilibrium total metal concentrations (>1 mmol/L).

Acknowledgment

R.P.d.C. was sponsored as a Visiting Researcher by the CNPq, Brazil. K.-H.C. was the recipient of an FCAR Quebec Scholarship. The assistance of Mr. E. Siliauskas with the AAS sample analyses, Mr. V. Mathur with laboratory experiments, and Mr. J. C. Ferreira with figure diagrams is gratefully acknowledged.

Literature Cited

Akita, S.; Takeuchi, H. Sorption and separation of metals from aqueous solution by a macromolecular resin containing tri-n-acetylamine. *J. Chem. Eng. Jpn.* **1990**, *23*, 439–443.

Brierley, J. A. Production and application of a *Bacillus*-based product for use in metals biosorption. In *Biosorption of Heavy Metals*; Volesky, B., Ed.; CRC Press, Inc.: Boca Raton, FL, 1990; pp 305–312.

Brierley, J. A.; Vance, D. B. Recovery of precious metals by microbial biomass. In *BioHydroMetallurgy: Proceedings of the International Symposium.* ; Norris, P. R., Kelly, D. P., Eds.; Sci. Technol. Letters: Kew, Surrey, U.K., 1988; pp 477–486.

Chandra, M.; Rempel, G. L. Polyethyleneimine adduct of poly-(vinyl benzaldehyde): a highly selective sorbent for iron(III). *React. Polym.* **1993**, *19*, 213–223.

Crist, R. H.; Martin, J. R.; Crist, D. R. Interaction of metals and protons with algae. Equilibrium constants and ionic mechanisms for heavy metal removal as sulfides and hydroxides. In *Mineral Bioprocessing*; Smith, R. W., Misra, M., Eds.; The Minerals, Metals and Materials Society: Washington, D.C., 1991; pp 275–287.

de Carvalho, R. P.; Chong, K.-H.; Volesky, B. Effects of leached alginate on metal biosorption. *Biotechnol. Lett.* **1994**, submitted for publication.

Gadd, G. M. Biosorption. *Chemistry Industry* **1990**, *1990*, 421–426.

Garnham, G. W.; Codd, G. A.; Gadd, G. M. Kinetics of uptake and intracellular location of cobalt, manganese and zinc in the estuarine green alga *Chlorella salina*. *Appl. Microbiol. Biotechnol.* **1992**, *37*, 270–276.

Holan, Z. R.; Volesky, B.; Prasetyo, I. Biosorption of cadmium by biomass of marine algae. *Biotechnol. Bioeng.* **1993**, *41*, 819–825.

Jha, I. N.; Iyengar, L.; Prabhakara Rao, A. V. S. Removal of cadmium using chitosan. *J. Environ. Eng.* **1988**, *114*, 962–974.

Kuyucak, N.; Volesky, B. Accumulation of gold by algal biosorbent. *Biorecovery* **1989**, *1*, 189–204.

Maranon, E.; Sastre, H. Behaviour of lignocellulosic apple residues in the sorption of trace metals in packed beds. *React. Polym.* **1992**, *18*, 173–176.

Volesky, B. Biosorption and biosorbents. In *Biosorption of Heavy Metals*; Volesky, B., Ed.; CRC Press, Inc.: Boca Raton, FL, 1990a; pp 3–6.

Volesky, B. Removal and recovery of heavy metals by biosorption. In *Biosorption of Heavy Metals*; Volesky, B., Ed.; CRC Press, Inc.: Boca Raton, FL, 1990b; pp 7–44.

Volesky, B.; Holan, Z. R. Biosorption of heavy metals. *Biotechnol. Prog.* **1994**, in press.

Zasosky, R. J.; Burau, R. G. Sorption and sorptive interaction of cadmium and zinc on hydrous manganese oxide. *Soil Sci. Soc. Am. J.* **1988**, *52*, 81–87.

Accepted September 9, 1994.®

® Abstract published in *Advance ACS Abstracts,* October 15, 1994.