Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Aksu, Zümrye , Açikel, Ünsal and Kutsal, Tüln(1999) 'Investigation of Simultaneous Biosorption of Copper(II) and Chromium(VI) on Dried *Chlorella Vulgaris* from Binary Metal Mixtures: Application of Multicomponent Adsorption Isotherms', Separation Science and Technology, 34: 3, 501 — 524

To link to this Article: DOI: 10.1081/SS-100100663

URL: http://dx.doi.org/10.1081/SS-100100663

SEPARATION SCIENCE AND TECHNOLOGY, **34**(3), pp. 501–524, 1999

Investigation of Simultaneous Biosorption of Copper(II) and Chromium(VI) on Dried *Chlorella vulgaris* from Binary Metal Mixtures: Application of Multicomponent Adsorption Isotherms

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ABSTRACT

Although the biosorption of single metal ions to various kinds of microorganisms has been extensively studied and the adsorption isotherms have been developed for only the single metal ion situation, very little attention has been given to the bioremoval and expression of adsorption isotherms of multimetal ions systems. In this study the simultaneous biosorption of copper(II) and chromium(VI) to *Chlorella vulgaris* from a binary metal mixture was studied and compared with the single metal ion situation in a batch stirred system. The effects of pH and single- and dual-metal ion concentrations on the equilibrium uptakes were investigated. In previous studies the optimum biosorption pH had been determined as 4.0 for copper(II) and as 2.0 for chromium(VI). Multimetal ion biosorption studies were performed at these two pH values. It was observed that the equilibrium uptakes of copper(II) or chromium(VI) ions were changed due to the biosorption pH and the presence of other metal ions. Adsorption isotherms were developed for both single- and dual-metal ion systems at these two pH values, and expressed by the mono- and multicomponent Langmuir and Freundlich adsorption models. Model parameters were estimated by nonlinear regression. It was seen that the adsorption equilibrium data fitted very well to the competitive Freundlich model in the concentration ranges studied.

Key Words. Simultaneous biosorption: Binary mixture of copper(II) and chromium(VI); *Chlorella vulgaris*; Mono- and multicomponent adsorption isotherms

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INTRODUCTION

The removal of toxic heavy-metal contaminants from industrial wastewaters is one of the most important environmental issues to be solved today. The search for new and innovative treatment technologies has focused attention on the effect of heavy-metal toxicity on the uptake by microorganisms. Using microorganisms as biosorbents for heavy metals offers a potential alternative to existing methods for the detoxification and recovery of toxic or valuable metals from industrial wastewaters. Many yeasts, algae, bacteria, and various aquatic flora are known to be capable of concentrating metal species from dilute aqueous solutions and accumulating them within the structure of the microorganism (1–14). The adsorptivity of heavy-metal ions to the body is a very beneficial property of most algae. The biosorption of metal ions by the algal biomass arises from the coordination of the ions to different functional groups on the algal cell (1–3, 7–14). The kinetics of metal uptake, thought to be physical adsorption at the cell surface, is very rapid and occurs in a short time after the microorganism comes into contact with the metal. The mechanisms associated with metal sorption by microorganisms are complex, dependent on the metal ion and the biological system, and include extracellular and intracellular metal binding. Thermally killed microorganisms display a binding capacity for metal ions to the same or greater extent than that measured for living cells. The retention of heavy-metal cations by dead microbial cells is also termed “biosorption” (1–3).

While much research has been carried out on the uptake of single species of metal ions, little attention seems to have been given to the study of multimetal ion systems. Despite the fact that single toxic metallic species rarely exist in natural and wastewaters, and the presence of a multiplicity of metals often gives rise to interactive effects, insufficient attention seems to have been paid to this problem. Examination of the effects of divalent cations in various combinations is more representative of the actual environmental problems faced by organisms than are single metal studies. This recognition results from the realization that environmental loadings of cations from anthropogenic sources rarely involve single cation contributions, and if they do, the introduced cation will interact with a host of chemicals native to the receiving system. Thus, organisms potentially impacted by these toxicants face a multiple rather than a single toxicant insult.

Bioremoval of single species of heavy-metal ions using microorganisms is affected by several factors. These factors include the specific surface properties of the microorganism and the physicochemical parameters of the solution such as temperature, pH, initial metal ion concentration, and biomass concentration. Many other parameters affect the capacity of microorganisms to bind more than one metal ion simultaneously. The combined effects of two or more metal ions to microorganisms also depend on the number of metals competing for binding sites, metal combination, levels of metal ion concentration, order of metal addition, residence time, and test criterion, i.e., cell growth, dissolved oxygen, metal uptake, etc. (for living cells). Even though optimum adsorption conditions of heavy-metal ions to microorganism is known, there is a need to understand how combinations of metal ions affect the ecological processes of the biomass and the ability of biomass to accumulate heavy-metal ion combinations from the surrounding. In general, a mixture of heavy metals can produce three possible types of behavior: synergism, antagonism, and noninteraction (12–15).

At the first stage of biosorption, a rapid equilibrium is established between adsorbed metal ions on the cell and unadsorbed metal ions in solution. This equilibrium can be represented by adsorption isotherms. Both the noncompetitive Langmuir and Freundlich isotherm models have been shown to be suitable for describing the short-term and monocomponent adsorption of heavy-metal ions by algal cells. The well-known expression of the monocomponent Langmuir model is given by

$$q_{\mathrm{eq}} = \frac{Q^0 b C_{\mathrm{eq}}}{1 + b C_{\mathrm{eq}}} \tag{1}$$

where q_{eq} is the amount of metal bound to per gram of dried biomass at equilibrium, C_{eq} is the residual (equilibrium) metal concentration left in solution after binding, Q^0 is the maximum amount of metal ion per unit weight of adsorbent to form a complete monolayer on the surface bound at high C_{eq}, and b is a constant related to the affinity of the binding sites. Q^0 and b can be determined from a $1/q_{\mathrm{eq}}$ versus $1/C_{\mathrm{eq}}$ plot. The model, which is based on assumptions of surface adsorption, showed a good fit where passive biosorption prevailed.

The Freundlich expression is an empirical equation based on sorption on a heterogeneous surface suggesting (as expected) that binding sites are not equivalent and/or independent. The monocomponent Freundlich equation is given by

$$q_{\mathrm{eq}} = K_{\mathrm{F}} C_{\mathrm{eq}}^{1/n} \tag{2}$$

where K_{F} and n are the monocomponent Freundlich constants characteristic of the system. Equation (2) can be linearized in logarithmic form and Freundlich constants can be determined. Both models were developed for single-layer metal adsorption. However, the Freundlich model physically provides a more realistic description of metal adsorption by organic matter because it accounts for different binding sites. But, in most cases, both equations fit the data set reasonably well for experimental data over moderate ranges of concentration (1–6, 13–20).

One of the difficulties in describing the adsorption of metal ions from wastestreams is that wastewaters contain not one but many metal ions. When several components are present, interference and competition phenomena for adsorption sites occur and lead to a more complex mathematical formulation of the equilibrium. Therefore, competitive isotherms attempt to express relationships between the adsorbed quantity of one component and the concentrations of all other components, either in solution or already adsorbed. Several isotherms have been proposed to describe equilibrium and competitive adsorption for such a system. These isotherms range from simple models related to the individual isotherm parameters only, to more complex models related to the individual isotherm parameters, and to correction factors (1, 14, 15, 19–24). One of them is a modified Langmuir model based on the same hypotheses as for the single-component Langmuir model with information other than that from experimental competitive adsorption data. Bellot et al. (20) defined in the modified Langmuir model an interaction term η which is a characteristic of each species and depends on the concentrations of the other components. The modified Langmuir isotherm is written as

$$q_{\mathrm{eq}_i} = \frac{Q_i^0 \mathrm{b}_i \, (C_{\mathrm{eq}_i}/\eta_i)}{1 + \sum_{j=1}^{N} b_j \, (C_{\mathrm{eq}_j}/\eta_j)} \tag{3}$$

For binary mixtures, Eqs. (4) and (5) can be rewritten for the first and the second component, respectively and these two equations can be solved simultaneously to obtain the multicomponent Langmuir adsorption constants of the first and the second metal ions, respectively, by means of a computer using the Excel program.

$$q_{\mathrm{eq}1} = \frac{Q_1^0 b_1 \dfrac{C_{\mathrm{eq}1}}{\eta_1}}{1 + b_1 \dfrac{C_{\mathrm{eq}1}}{\eta_1} + b_2 \dfrac{C_{\mathrm{eq}2}}{\eta_2}} \tag{4}$$

$$q_{\mathrm{eq}2} = \frac{Q_2^0 b_2 \dfrac{C_{\mathrm{eq}2}}{\eta_2}}{1 + b_1 \dfrac{C_{\mathrm{eq}2}}{\eta_1} + b_2 \dfrac{C_{\mathrm{eq}2}}{\eta_2}} \tag{5}$$

where b_1, b_2 = individual Langmuir adsorption constants of the first and the second metal ions related to the affinity of the binding sites, respectively

C_{eq1}, C_{eq2} = the unadsorbed concentrations of the first and the second metal ions, respectively, at equilibrium (mg/L)
q_{eq1}, q_{eq2} = the adsorbed quantities of the first and the second metal ions per gram of dried alga at equilibrium, respectively (mg/g)
Q_1^0, Q_2^0 = individual Langmuir adsorption constants of the first and the second metal ions give the maximum amounts bound at high C_{eq}'s, respectively
η_1, η_2 = multicomponent Langmuir adsorption constants of the first and the second metal ions, respectively, for two-component systems

Fritz and Schluender (21) and McKay and Duri (22) considered another approach and proposed an empirical extension of the Freundlich model restricted to binary mixtures, where the coefficients relating to isotherms could be determined from monocomponent isotherm data except for the biosorption competition coefficients, which had to be determined experimentally. The Freundlich models for the first and the second components restricted to binary mixtures are given by

$$q_{\mathrm{eq1}} = \frac{K_{\mathrm{F1}} C_{\mathrm{eq1}}^{n_1 + x_1}}{C_{\mathrm{eq1}}^{x1} + y_1 C_{\mathrm{eq2}}^{z1}} \tag{6}$$

$$q_{\mathrm{eq2}} = \frac{K_{\mathrm{F2}} C_{\mathrm{eq1}}^{n_2 + x_2}}{C_{\mathrm{eq2}}^{x_2} + y_2 C_{\mathrm{eq1}}^{z_2}} \tag{7}$$

where K_{F1}, K_{F2}, and n_1, n_2 are derived from the corresponding individual Freundlich isotherm equations, and the six other parameters (x_1, y_1, z_1 and x_2, y_2, z_2 are the multicomponent Freundlich adsorption constants of the first and the second metal ions, respectively, for a binary system) are the competition coefficients for two-metal ion species.

In this study a process of simultaneous biosorption of chromium(VI) and copper(II), which are frequently encountered together in industrial wastewaters, such as those from plants producing machine parts and chemicals, contain up to 6–300 ppm copper(II), 0–555 ppm chromium(VI), to *Chlorella vulgaris*, a green alga, was investigated and compared to single metal ion situation.

EXPERIMENTAL

Microorganism and Growth Conditions

Chlorella vulgaris, an unicellular green alga, obtained from Sammlung von Algen Kulturen Pflanzen Physiologisches Institut, University of Göthingen, Germany, was used in this study. It was grown at 25°C in agitated and aerated liquid media in fermentors containing (in g/L): glucose, 5.0; yeast extract, 1.0; peptone, 1.0; triptone, 1.0; $FeSO_4$, 0.01; and $MgSO_4$, 0.05. The pH of the feed media of *C. vulgaris* was adjusted to 6.8 with 1 M $H_2S\ O_4$.

Chemicals

Test solutions containing single chromium(VI) or copper(II) ions were prepared by diluting 1.0 g/L of stock solutions of metal ions to the desired concentrations. The stock solution of each metal ion was obtained by dissolving the exact quantity of potassium dichromate for chromium(VI) and anhydrous copper sulfate for copper(II) in 1 L of double-distilled water. The ranges of concentrations of both metal ions prepared from stock solutions varied between 25.0 and 250.0 mg/L.

Test solutions containing desired combinations of chromium(VI) and copper(II) were prepared by diluting 1.0 g/L of stock solutions of metal ions and mixing. Before mixing the alga solution, the pH of each test solution was adjusted to the required value with 1 M $H_2S\ O_4$.

Preparation of Microorganisms for Biosorption

In the stationary phase of growth, *C. vulgaris* cells are centrifuged at 5000 rpm for 5 minutes, washed twice with distilled water, and then dried at 60°C for 24 hours. For the biosorption studies, 1.0 g of dried biomass was suspended in 100 mL of double-distilled water and homogenized in a homogenizer (Janke and Kunkel, IKA-Labortechnick, Ultra Turrax T25) at 8000 rpm for 20 minutes and then stored in a refrigerator.

Biosorption Studies

The factors affecting the adsorption rate and equilibrium were examined in Erlenmeyer flasks. For Erlenmeyer flask studies, 10 mL of the microorganism solution was mixed with 90 mL of the metal ion or metal ions mixture-bearing solution at the desired level of each metal ion or both metal ions at the beginning of the adsorption. The flasks were agitated on a shaker at constant temperature for 24 hours, which was more than ample time for adsorption equilibrium. Samples of 3 mL were taken before mixing the alga solution and the metal ion or metal ions mixture-bearing solution at 5-minute intervals at the beginning of adsorption and at 25–30 minute intervals after reaching equilibrium, centrifuged at 5000 rpm for 3 minutes, and then the supernatant liquid was used to analyze for each metal ion. The biosorption experiments were repeated two times.

The studies were performed at 25°C to be representative of environmentally relevant conditions.

Analysis of Chromium(VI) and Copper(II)

The concentration of unadsorbed chromium(VI) and copper(II) in the adsorption medium was determined in a Unicam 929 atomic absorption spectrophotometer with a detection limit of 0.04 ppm at a wavelength of 324.8 nm for copper(II) and with a detection limit of 0.05 ppm at a wavelength of 357.9 nm for chromium(VI).

RESULTS

In this study the simultaneous biosorption of copper(II) and chromium(VI) to *C. vulgaris* from a binary metal mixture was studied and compared with the single metal ion situation in a batch-stirred system. The metal binding capacity of *C. vulgaris* was shown as a function of pH and of single- and dual-metal ion concentrations. The mono- and multicomponent sorption phenomena were expressed by the monocomponent (noncompetitive) and multicomponent (competitive) Langmuir and Freundlich adsorption models, adsorption isotherms were developed for both single- and dual-metal ion systems at two pH values, and model parameters were determined by the means of a computer.

The equilibrium results were given as the units of each adsorbed metal ion quantity per gram of dried biomass (q_{eq}; mg/g) and each unadsorbed metal ion concentration in the mixture (C_{eq}; mg/L) at equilibrium. The adsorption yield (%Ad) was defined as the ratio of the adsorbed quantity of metal ion per gram of dried biomass at equilibrium to the initial metal ion concentration for single metal biosorption. Individual and total adsorption yields (%Ad_i and %Ad_{Tot}) in the simultaneous removal from the mixture of metal ions were also defined as the ratios of individual and total adsorbed quantities of metal ions per gram of dried biomass at equilibrium to individual and total initial metal ion concentrations, respectively.

The most critical parameter in the treatment of multimetal ion systems by alga is the pH of the adsorption medium because previous investigations concerning single-metal ion situation had shown that the optimum adsorption pH depended on the physicochemical properties of metal ions and alga in aqueous solutions. The uptake of chromium(VI) and copper(II) by the biomass was also a function of pH. From previous investigations it was known that the removal of a single species of copper(II) ions from an aqueous solution was more efficient with increasing pH. The adsorption rate of copper(II) ions was greatest when the solution pH was adjusted to 4.0. At pHs higher than 5.0, copper(II) ions precipitated because of the concentration of OH^- ions in the biosorption medium, and adsorption studies could not be performed. Chromium(VI) was more effectively adsorbed by the biomass than copper(II) at very low pH. The optimum adsorption pH was determined as 2.0 for chromium(VI). The different pH binding profiles for heavy-metal ions could be due to the nature of the chemical interactions of each metal ion with the microbial cells and are related to the isoelectric point of the cells. Heavy-metal ions have a strong affinity for proteins of the cell wall. At pHs above the isoelectric point, there is a net negative charge on the cells, and the ionic state of ligands such as carboxyl, phosphate, and amino groups will be such as to promote reaction with the metal cations. As the pH is lowered, however, the overall surface charge on the cells will become positive, which will inhibit the approach of positively charged metal cations. Metal ions in anionic form in the aqua solution, such as chromium(VI) as CrO_4^{-2}, will interact with the cells in this case (1, 3).

To determine the monocomponent (noncompetitive) isotherms, the initial metal ion concentrations were varied while the dry cell weight in each sample was kept constant for each metal ion. The monocomponent Langmuir and Freundlich adsorption isotherms for chromium(VI) and copper(II) ions obtained at pH 2.0 and pH 4.0 are shown in Figs. 1 and 2. The monocomponent adsorption constants for each metal ion obtained by evaluating the isotherms are also listed in Table 1. The magnitude of K_F and n, the monocomponent Freundlich constants, showed a selective uptake for chromium(VI) at pH 2.0 and for copper(II) at pH 4.0 from wastewater, with a higher adsorptive capacity of algal biomass. The magnitude of Q^0 and b, the monocomponent Langmuir

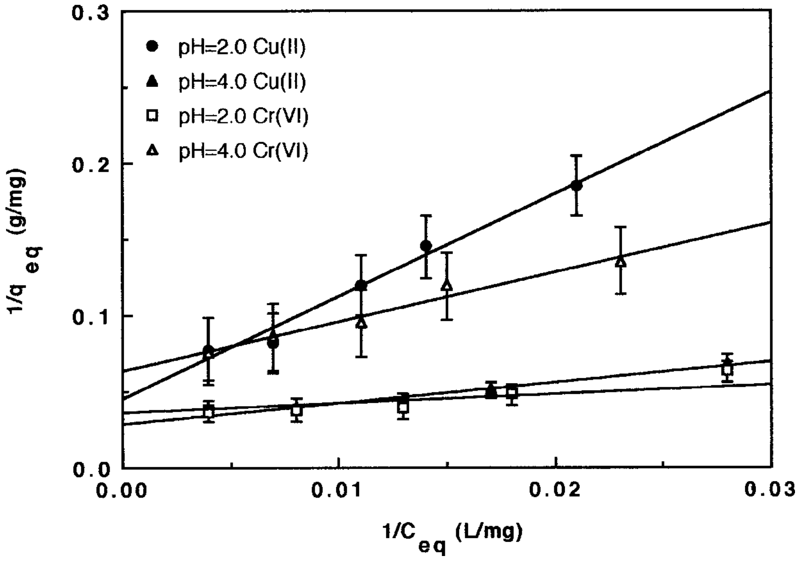


FIG. 1 The monocomponent (noncompetitive) Langmuir adsorption isotherms for chromium(VI) and copper(II) at pH 2.0 and at pH 4.0 in the single metal ion situation (T = 25°C; alga concentration = 1.0 g/L).

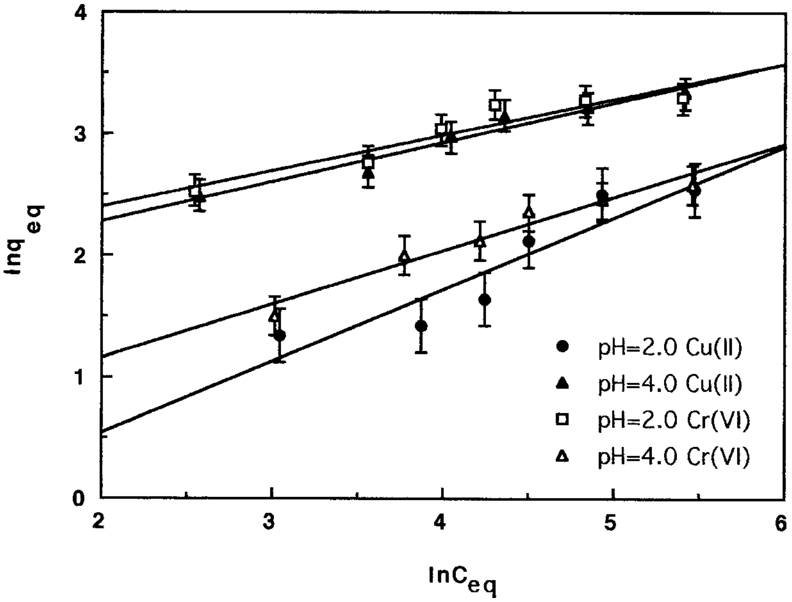


FIG. 2 The monocomponent (noncompetitive) Freundlich adsorption isotherms of chromium(VI) and copper(II) ions obtained at pH 2.0 and at pH 4.0 in the single metal ion situation ($T = 25°C$; alga concentration = 1.0 g/L).

TABLE 1
Comparison of the Individual Langmuir and Freundlich Adsorption Constants Obtained from Monocomponent Langmuir and Freundlich Adsorption Isotherms for Chromium(VI) and Copper(II) at pH 2.0 and at pH 4.0 ($T = 25°C$; alga concentration = 1.0 g/L)

The Monocomponent Langmuir Model				
	pH 2.0		pH 4.0	
Metal ion	Q^0	b	Q^0	b
Copper(II)	16.17	0.007	34.86	0.021
Chromium(VI)	27.77	0.052	15.77	0.011
The Monocomponent Freundlich Model				
	pH 2.0		pH 4.0	
Metal ion	K_F	n	K_F	n
Copper(II)	0.52	1.69	5.17	3.12
Chromium(VI)	6.04	3.33	1.31	2.27

constants, indicated that the amount of chromium(VI) or copper(II) ions per unit weight of adsorbent required to form a complete monolayer on the surface was higher for chromium(VI) at pH 2.0 and for copper(II) at pH 4.0, and the affinity for the binding of copper(II) ions was higher than that of chromium(VI) at pH 4.0. A large value of *b* also implied strong bonding of copper(II) ions to the algae at pH 4.0 and chromium(VI) ions at pH 2.0.

The equilibrium uptakes and adsorption yields obtained for the single-metal ion situation at pH 2.0 and at pH 4.0 are presented in Table 2. As seen from Table 2, increasing the metal ion concentration generally caused an increase in the equilibrium uptake and a decrease in the metal adsorption yield for each metal ion at both pH values. The adsorption of copper(II) ions at pH 2.0 and the adsorption of chromium(VI) ions at pH 4.0 appeared to be significantly low. It was obvious that the microorganism used a significant part of its capacity for chromium(VI) adsorption at pH 2.0 and for copper(II) adsorption at pH 4.0.

As copper(II) and chromium(VI) had different pH optimums, the pH of the wastewater could provide selectivity for the removal of a desired heavy metal ion in a mixture of heavy metals and this situation was observed in the simultaneous removal of copper(II) and chromium(VI) at these two pH values. In the first stage of adsorption studies, the initial copper(II) concentration was changed from 25 to 250 mg/L while the initial chromium(VI) concentration was held constant at 25, 50, 100, or 150 mg/L. The nonlinearized adsorption isotherms of copper(II) ions in the absence of chromium(VI) ions and in the presence of increasing concentrations of chromium(VI) ions are shown in Figs. 3 and 4 at two pH values. As seen from the figures, the equilibrium copper(II) uptake increased by increasing the initial copper(II) concentration up to 250 mg/L at both pH values. A significant increase for copper(II) uptake was also observed at pH 4.0, as expected. But the presence and increasing of chromium(VI) concentration caused a lessening of adsorbed copper(II) quantities at equilibrium. The inhibitory effect of chromium(VI) ions on the equilibrium copper(II) uptakes was dominant at pH 2.0. Although copper(II) ions were preferentially adsorbed at pH 4.0, chromium(VI) ions were also adsorbed by the alga at this pH. This situation shows the partial competition between the copper(II) and chromium(VI) ions although the pH has a significant effect in selective biosorption. It is also obvious that not only one but different kinds of biosorption mechanisms are important in the simultaneous biosorption of metal ions to the green alga. At pH 2.0 and at 100 mg/L of initial copper(II) concentration, in the absence of chromium(VI) and in the presence of 100 mg/L of chromium(VI) concentration, adsorbed copper(II) quantities at equilibrium were found to be 8.3 g and 3.9 mg/g, respectively. At pH 4.0 and the aforesaid conditions, copper(II) uptakes at equilibrium were determined to be 23.2 and 17.1 mg/g, respectively. It was obvious that copper(II)

TABLE 2

Comparison of the Equilibrium Uptakes and Adsorption Yields Obtained at Different Metal Ion Concentrations at pH 2.0 and at pH 4.0 for Each Metal Ion for the Single-Metal Ion Situation

pH 2.0						pH 4.0					
Cu(II)			Cr(VI)			Cu(II)			Cr(VI)		
C_{0Cu} (mg/L)	q_{eqCu} (mg/g)	$\%Ad_{Cu}$	C_{0Cr} (mg/L)	q_{eqCr} (mg/g)	$\%Ad_{Cr}$	C_{0Cu} (mg/L)	q_{eqCu} (mg/g)	$\%Ad_{Cu}$	C_{0Cr} (mg/L)	q_{eqCr} (mg/g)	$\%Ad_{Cr}$
24.8	3.8	15.3	25.2	12.5	49.7	25.1	12.0	47.8	24.8	4.5	18.1
51.9	4.1	7.9	51.0	15.8	31.0	49.8	14.7	29.5	51.2	7.4	14.5
75.0	5.2	6.9	74.9	20.7	27.7	76.8	19.6	25.5	75.6	8.4	11.1
98.9	8.3	8.4	99.8	25.6	25.6	101.8	23.2	22.8	101.0	10.5	10.4
149.9	12.2	8.1	150.9	26.3	17.5	150.9	24.9	16.5	149.5	11.6	7.7
251.2	12.8	5.1	249.2	27.1	10.8	251.5	28.0	11.1	249.0	13.2	5.3

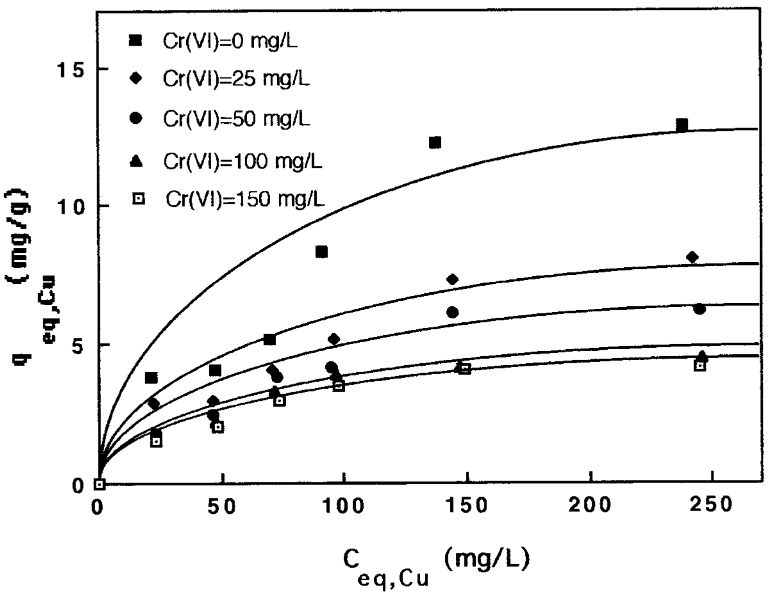


FIG. 3 Comparison of the nonlinearized adsorption isotherms for copper(II) adsorption to *C. vulgaris*, with the copper(II) present as the single metal ion and in the presence of increasing-concentrations of chromium(VI) ions at pH 2 (T = 25°C; alga concentration = 1.0 g/L).

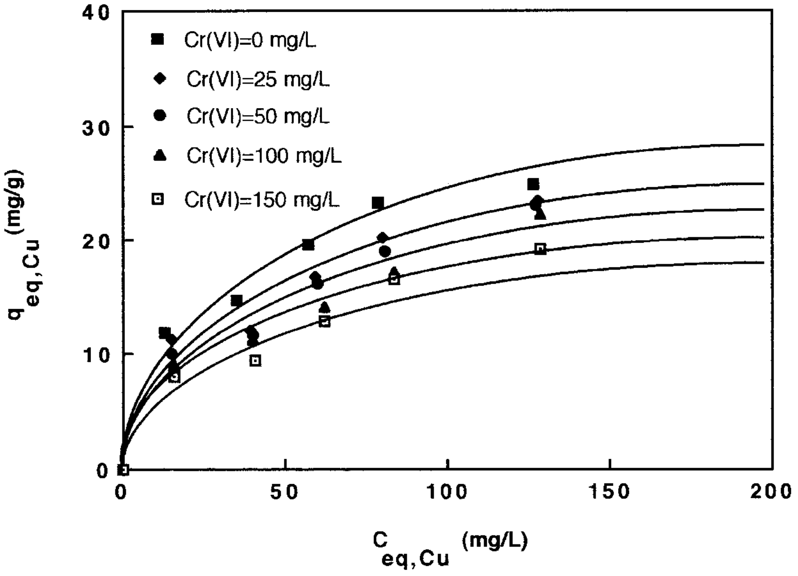


FIG. 4 Comparison of the nonlinearized adsorption isotherms for copper(II) adsorption to *C. vulgaris*, with the copper(II) present as the single metal ion and in the presence of increasing concentrations of chromium(VI) ions at pH 4. (T = 25°C; alga concentration = 1.0 g/L).

uptakes obtained at pH 4.0 were much more higher than those obtained at pH 2.0, and the presence of a second metal ion [chromium(VI)] reduced the uptake of copper(II) in both cases. The combined effects of metal ions seemed to be antagonistic.

In the second part of the biosorption studies, the uptake of chromium(VI) ions in the presence of increasing concentrations of copper(II) ions in the 25 to 250 mg/L range was investigated at both pH values. While the initial chromium(VI) concentration was changed from 25 to 150 mg/L, the initial copper(II) concentration was held constant between 25 and 250 mg/L for each experimental set. Figures 5 and 6 depict the variations of chromium(VI) uptakes at equilibrium with increasing initial copper(II) concentrations at pH 2.0 and pH 4.0. The figures show that chromium(VI) equilibrium uptakes increase with increasing initial chromium(VI) concentrations up to 150.0 mg/L at both pH values. But increases of both copper(II) concentration and pH also reduce the chromium(VI) quantities at equilibrium. At pH 2.0 and pH 4.0 in the absence of copper(II), equilibrium chromium(VI) uptakes were determined as 25.6 and 10.5 mg/g, respectively, at 100 mg/L initial chromium(VI) concentration. When initial copper(II) concentration was kept at 100 mg/L at the same initial chromium(VI) concentration, these values were reduced to 18.2 and 7.8 mg/g, respectively. It was also obvious that chromium(VI) uptakes obtained at pH 2.0 were much higher than those obtained at pH 4.0, and the presence of a second metal ion [copper(II)] also reduced the uptake of

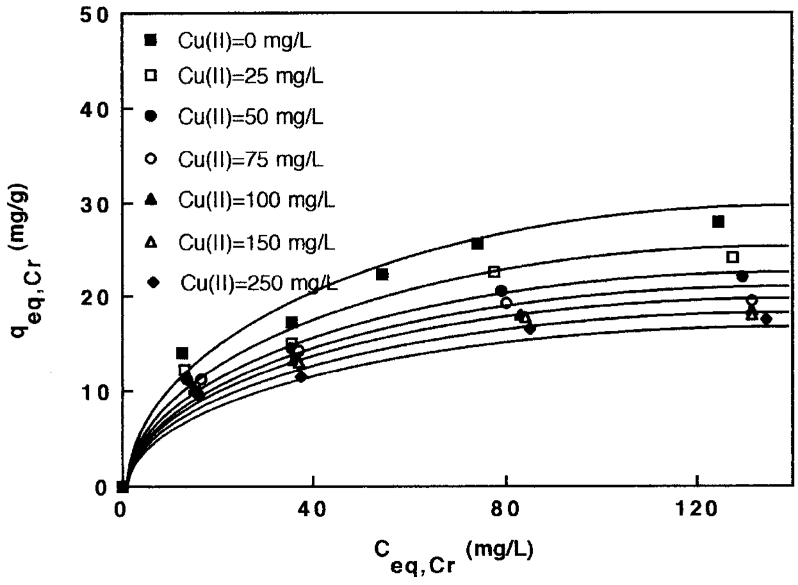


FIG. 5 Comparison of the nonlinearized adsorption isotherms for chromium(VI) adsorption to *C. vulgaris,* with the chromium(VI) present as the single metal ion and in the presence of increasing concentrations of copper(II) ions at pH 2.0 ($T = 25°C$; alga concentration = 1.0 g/L).

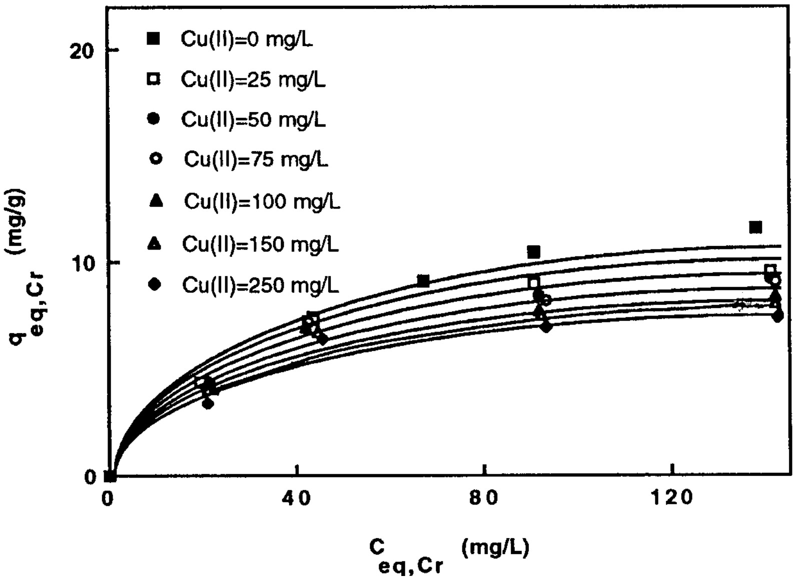


FIG. 6 Comparison of the nonlinearized adsorption isotherms for chromium(VI) adsorption to *C. vulgaris*, with the chromium(VI) present as the single metal ion and in the presence of increasing concentrations of copper(II) ions at pH 4.0. (T = 25°C; alga concentration = 1.0 g/L).

chromium(VI) in both cases. The presence of a second metal ion [copper(II)] also had a significant and but lessened effect on the uptake of chromium(VI) in this situation.

In addition to the equilibrium uptakes and unadsorbed metal ion concentrations, individual copper(II), individual chromium(VI), and total adsorption yields found at different copper(II) concentrations in the presence of increasing concentrations of chromium(VI) at pH 2.0 and pH 4.0 are also listed in Tables 3 and 4. It is seen from both tables that increasing in total metal ion concentration causes decreasing individual and total adsorption yields at these two pH values. The results also show that the equilibrium uptakes are reduced by chromium(VI) ions at both pH values, and the inhibitory effects of chromium(VI) ions on the copper(II) equilibrium uptakes increase with increasing initial chromium(VI) concentrations. The selectivity of the algae for chromium(VI) ions increases while the adsorption pH decreases and the chromium(VI) concentration in the binary mixture is increased. To decide whether those cation combinations are interacting in an antagonistic manner, the adsorption yields of single- and multi-ion systems were also compared. For instance, using Table 2, at pH 2.0 it was expected that the total adsorption yield would be equal to 17.1% for a total 198.7 mg/L heavy metal mixture made up of 98.9 mg/L copper(II) and 99.8 mg/L chromium(VI). But from Table 3 the experimental total adsorption yield was found to be 15.8% for a total 200 mg/L heavy metal mixture consisting of 100.0 mg/L copper(II) and

TABLE 3

Comparison of the Equilibrium Uptakes, Equilibrium Residual Metal Ion Concentrations, and Individual Copper(II), Individual Chromium(VI), and Total Adsorption Yields Found at Different Initial Copper(II) Concentrations at pH 2.0 in the Presence of Increasing Concentrations of Chromium(VI)

$C_{0\mathrm{Cu}}$ (mg/L)	$C_{0\mathrm{Cr}}$ (mg/L)	q_{eqCu} (mg/g)	C_{eqCu} (mg/L)	%$\mathrm{Ad}_{\mathrm{Cu}}$	q_{eqCr} (mg/g)	C_{eqCr} (mg/L)	%$\mathrm{Ad}_{\mathrm{Cr}}$	$C_{0\mathrm{Cu+Cr}}$ (mg/L)	$q_{\mathrm{eq(Cu+Cr)}}$ (mg/g)	%$\mathrm{Ad}_{\mathrm{Tot}}$
25.0	25.1	2.9	22.1	11.6	12.2	12.9	48.6	50.1	15.1	30.1
49.8	24.8	3.0	46.8	6.2	11.4	13.4	45.8	74.6	14.4	19.3
74.9	24.9	4.1	70.8	5.5	11.2	13.7	44.8	99.8	15.3	15.3
101.2	25.1	5.2	96.0	5.1	10.2	14.9	40.6	126.3	15.4	12.2
151.2	26.0	7.3	143.9	4.8	10.0	16.0	38.4	177.2	17.3	9.7
249.9	25.3	8.1	241.8	3.2	9.5	15.8	37.5	275.2	17.6	6.4
25.0	50.3	1.8	23.2	7.2	15.0	35.3	29.8	75.3	16.8	22.3
49.8	49.9	2.5	47.3	5.1	14.5	35.4	29.1	98.8	17.0	17.2
76.0	51.2	3.8	72.2	5.0	14.2	37.0	27.7	127.2	18.0	14.1
99.2	49.3	4.2	95.0	4.2	13.3	36.0	26.9	148.5	17.5	11.8
150.5	50.2	6.1	144.4	4.0	13.1	37.1	26.1	200.7	19.2	9.6
251.1	50.3	6.2	244.9	2.5	12.9	37.4	25.6	301.4	19.1	6.3
24.9	100.3	1.7	23.2	6.8	22.5	77.8	22.4	125.2	24.2	19.3
49.8	99.9	2.2	47.6	4.4	20.5	79.4	20.5	149.7	22.7	15.2
74.9	99.6	3.3	71.6	4.4	19.3	80.3	19.4	174.5	22.6	12.9
101.0	101.3	3.9	97.1	3.8	18.2	83.1	17.9	202.3	22.1	10.9
151.2	101.9	4.2	147.0	2.8	17.8	84.1	17.5	253.1	22.0	8.7
250.1	101.5	4.5	245.6	1.8	16.5	85.0	16.2	351.6	21.0	5.9
25.0	150.2	1.5	23.5	6.0	22.5	127.7	14.9	175.2	24.0	13.7
50.1	149.9	2.0	48.1	4.0	20.6	129.3	13.7	200.0	22.6	11.3
76.1	151.0	3.0	73.1	3.9	19.5	131.5	12.9	227.1	22.5	9.9
101.2	149.8	3.5	97.7	3.5	18.5	131.3	12.3	251.0	22.5	8.8
150.9	149.7	4.1	146.8	2.7	18.0	131.7	12.0	300.6	22.1	7.3
249.1	151.8	4.3	244.8	1.7	17.7	134.1	11.5	400.9	22.0	5.4

TABLE 4

Comparison of the Equilibrium Uptakes, Equilibrium Residual Metal Ion Concentrations, and Individual Copper (II), Individual Chromium (VI), and Total Adsorption Yields Found at Different Initial Copper (II) Concentrations at pH 4.0 in the Presence of Increasing Concentrations of Chromium (VI)

C_{0Cu} (mg/L)	C_{0Cr} (mg/L)	q_{eqCu} (mg/g)	C_{eqCu} (mg/L)	$\%Ad_{Cu}$	q_{eqCr} (mg/g)	C_{eqCr} (mg/L)	$\%Ad_{Cr}$	C_{0Cu+Cr} (mg/L)	$q_{eq(Cu+Cr)}$ (mg/g)	$\%Ad_{Tot}$
25.0	24.1	10.0	15.0	40.1	4.5	19.6	18.7	49.1	14.5	29.6
50.1	26.0	11.1	39.0	21.9	4.3	21.7	16.5	76.1	14.3	20.1
74.9	25.1	15.5	59.4	20.7	4.2	20.9	16.7	100.0	19.7	19.7
100.0	26.0	20.2	79.8	20.2	4.1	21.9	15.8	126.0	24.3	19.3
151.2	24.9	23.5	127.7	15.5	4.1	20.8	16.4	176.1	27.6	15.7
250.0	24.8	25.5	224.5	17.0	4.0	20.8	16.1	274.9	29.3	10.7
25.1	51.1	10.0	15.1	39.8	7.3	36.0	14.3	76.2	17.3	22.7
50.2	49.9	10.5	39.7	20.9	7.2	42.7	14.4	100.1	17.7	17.7
74.9	49.9	15.0	59.9	20.0	7.2	42.7	14.4	124.8	22.2	17.7
99.9	49.2	19.0	80.9	19.0	7.0	42.2	14.2	149.1	26.0	17.4
150.2	51.3	23.0	127.2	15.3	6.8	44.5	13.2	201.5	29.8	14.4
249.9	52.0	24.0	225.9	9.6	6.5	45.5	12.5	301.9	30.5	10.1
24.9	99.8	9.0	15.9	36.1	9.0	90.8	9.0	124.7	18.0	14.4
49.9	100.1	10.0	39.9	20.0	8.5	91.6	8.5	150.0	18.5	12.3
76.0	101.2	14.2	61.8	18.7	8.2	93.0	8.1	177.2	22.4	12.6
100.5	99.7	17.1	83.4	17.0	7.8	91.9	7.8	200.2	24.9	12.4
151.2	99.6	22.2	129.0	14.7	7.5	92.1	7.5	250.7	29.7	11.8
249.9	100.5	22.5	227.4	9.0	7.0	93.5	7.0	350.4	29.5	8.4
25.0	150.3	9.0	16.0	36.0	9.5	140.8	6.3	175.3	18.5	10.5
50.0	149.9	9.5	40.5	19.0	9.2	140.7	6.1	199.9	18.7	9.3
76.0	151.0	14.0	62.0	14.0	9.1	141.9	6.0	227.0	23.1	10.2
150.2	149.9	21.5	128.7	14.3	8.1	141.8	5.4	300.1	29.3	9.8
250.0	150.2	21.0	229.0	8.8	8.0	142.2	5.3	400.2	29.0	7.2

100.0 mg/L chromium(VI) at the same pH. As a result, the effect of the mixture was found to be less than that of the individual effects of the constituents in the mixture, so the interaction between copper(II) and chromium(VI) can be assumed to be antagonistic. The active sites on the algal cell can be more effectively used owing to the competitive adsorption of metal ions from binary mixtures. The most logical reason for the antagonistic action can be explained as being the competition for adsorption sites on the algae cells in the case of copper(II) and chromium(VI) for both pH values.

The simultaneous biosorption phenomena of chromium(VI) and copper(II) to *C. vulgaris* were expressed by the multicomponent Langmuir and Freundlich adsorption models. The multicomponent Langmuir and Freundlich adsorption constants for each metal ion evaluated from the multicomponent Langmuir and Freundlich adsorption models at pH 2.0 and pH 4.0 are given in Table 5. Using the monocomponent and multicomponent Langmuir and Freundlich adsorption constants for each metal ion given in Tables 1 and 5, respectively, q_{eq} values were predicted from the related competitive Langmuir and Freundlich adsorption formulas. For simultaneous biosorption of copper(II) and chromium(VI) to *C. vulgaris*, comparisons of the experimental and predicted q_{eq} values obtained at pH 2.0 and pH 4.0 are given in Figs. 7–10. As seen from Figs. 7 and 8, the magnitudes of deviations found in the competitive Langmuir adsorption model are much higher than those of the competitive Freundlich adsorption model. It is also observed from Figs. 9 and 10 that

TABLE 5
Comparison of the Multicomponent Langmuir and Freundlich Adsorption Constants for Each Metal Ion Evaluated from the Competitive Langmuir and Freundlich Adsorption Models at pH 2.0. and at pH 4.0. for Simultaneous Biosorption of Copper(II) and Chromium(VI) to *C. vulgaris*

The Multicomponent Langmuir Model						
	pH 2.0			pH 4.0		
	η_1	η_2		η_1		η_2
	0.386	0.921		0.513		0.946
The Multicomponent Freundlich Model						
	pH 2.0			pH 4.0		
Metal ion	x_i	y_i	z_i	x_i	y_i	z_i
Copper(II)	0.051	0.097	0.563	0.188	0.242	0.198
Chromium(VI)	0.166	0.007	0.831	−1.495	0.000	0.513

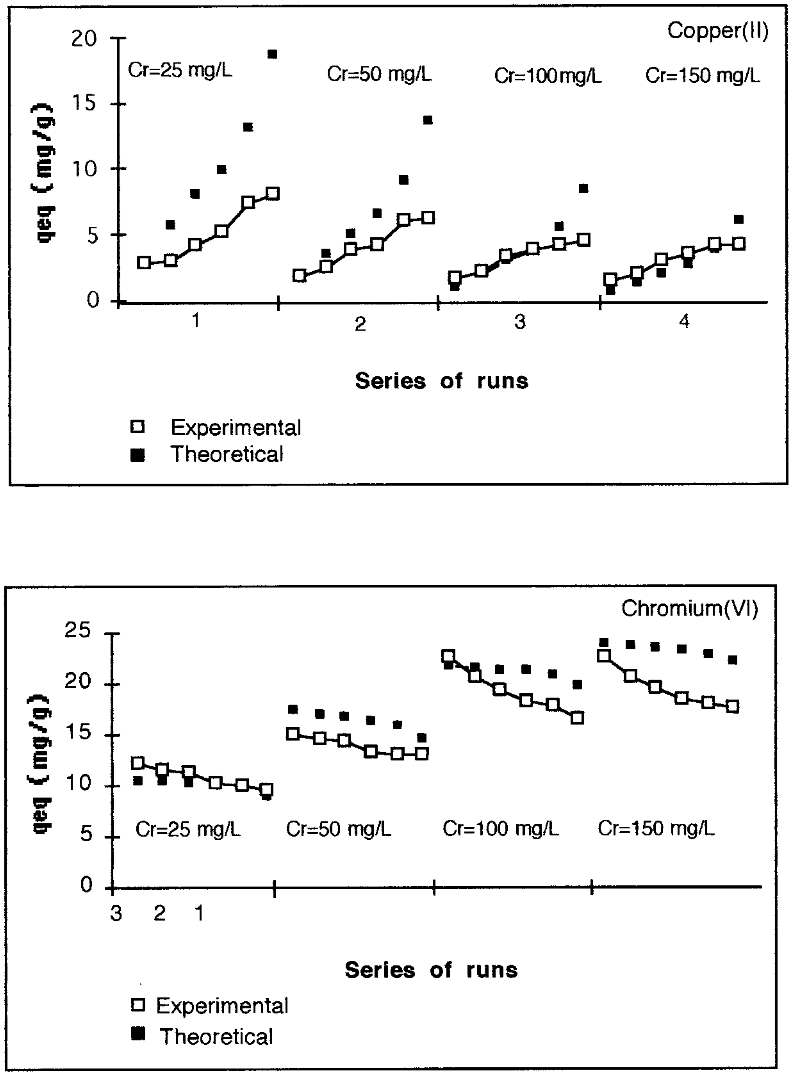


FIG. 7 Comparison of the experimental and theorotical q_{eq} values evaluated from the competitive Langmuir equation for copper(II) and chromium(VI) adsorption from binary mixtures of copper(II)–chromium(VI) at increasing copper(II) and at constant chromium(VI) concentration for each experimental set at pH 2.0.

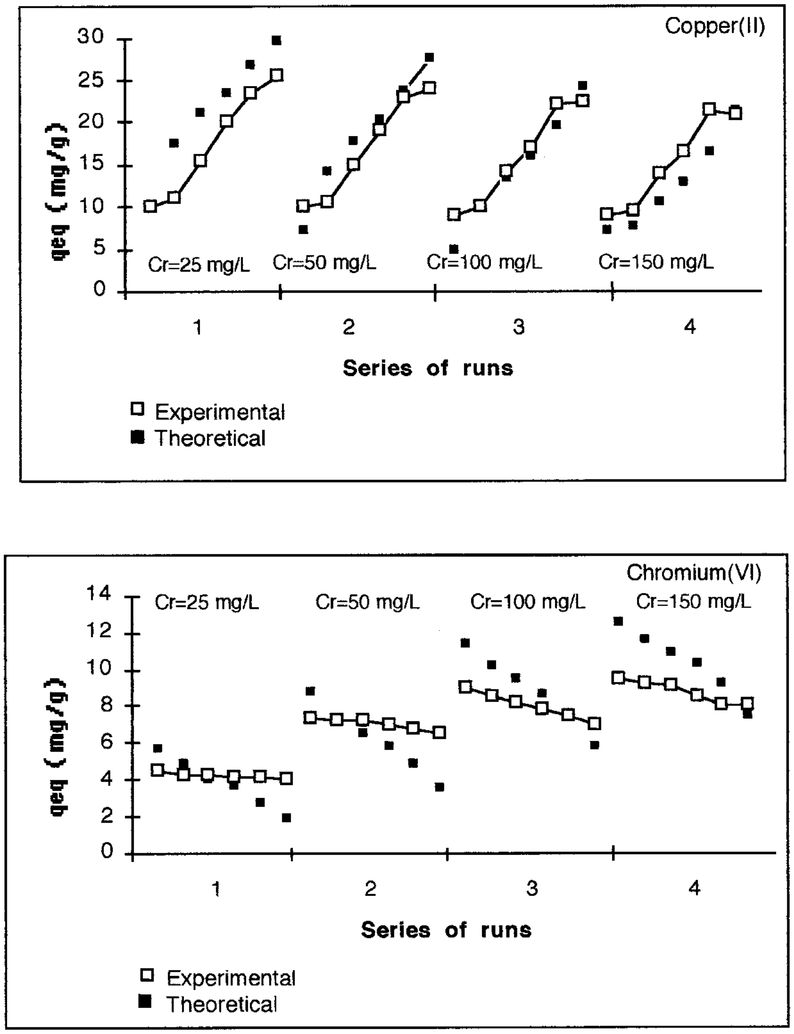
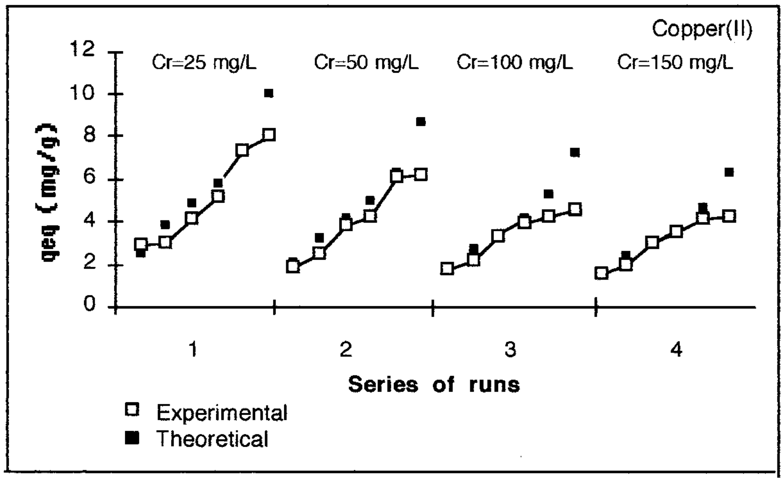


FIG. 8 Comparison of the experimental and theorotical q_{eq} values evaluated from the competitive Langmuir equation for copper(II) and chromium(VI) adsorption from binary mixtures of copper(II)–chromium(VI) at increasing copper(II) and at constant chromium(VI) concentration for each experimental set at pH 4.0.



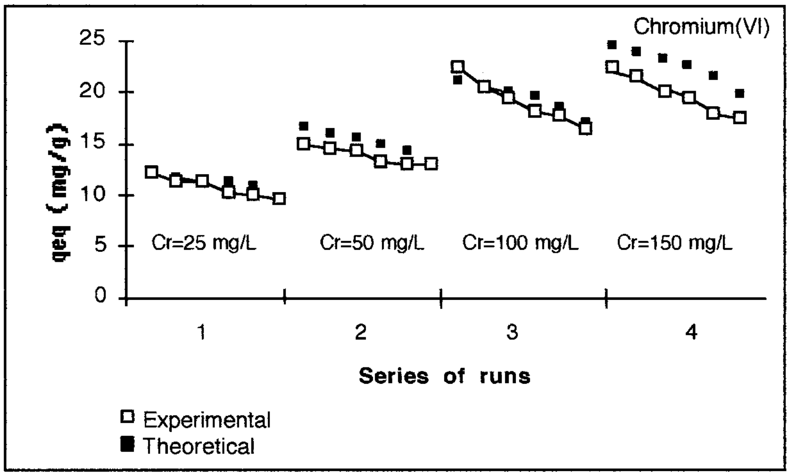
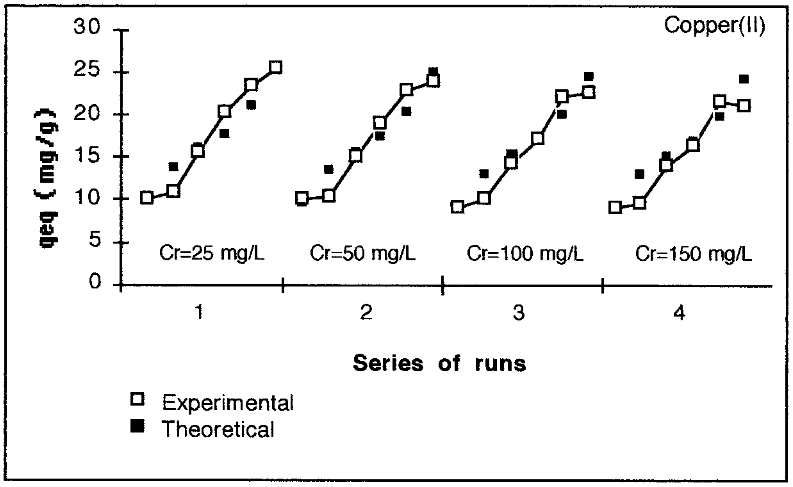


FIG. 9 Comparison of the experimental and theorotical q_{eq} values evaluated from the competitive Freundlich equation for copper(II) and chromium(VI) adsorption from binary mixtures of copper(II)–chromium(VI) at increasing copper(II) and at constant chromium(VI) concentration for each experimental set at pH 2.0.



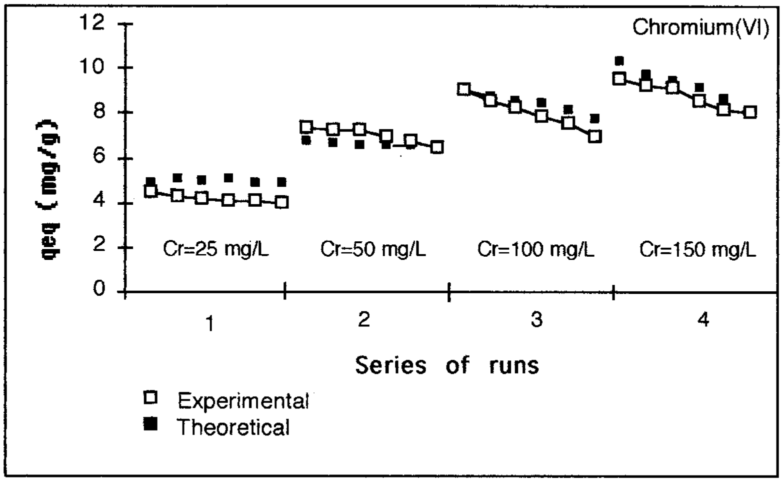


FIG. 10 Comparison of the experimental and theorotical q_{eq} values evaluated from the competitive Freundlich equation for copper(II) and chromium(VI) adsorption from binary mixtures of copper(II)–chromium(VI) at increasing copper(II) and at constant chromium(VI) concentration for each experimental set at pH 4.0.

the correlation between experimental and calculated results in the competitive Freundlich model for both metal ions and for both pH values are very good at the initial mixture concentrations studied except for very high initial metal ion concentrations. It is concluded that the competitive, multicomponent Freundlich model provides a more realistic description of the biosorption process.

CONCLUSION

In this study the ability of algae to bind copper(II) and chromium(VI) ions simultaneously from copper(II)–chromium(VI)-bearing solutions was investigated, and the results were compared with single metal ion adsorption. In mixtures of two or more heavy metal species in a solution, the synergistic or antagonistic interaction occurring between the metal ions may affect the individual metal uptake by the algae. Although *C. vulgaris* had a higher adsorption capacity for copper(II) and chromium(VI) in the single metal ion situation, the adsorption uptake of copper(II) and chromium(VI) in the binary mixture of metal ions was found to decrease due to the pH of wastewater and the levels of metal ion concentrations because of the antagonistic interaction between the metal ions. The most logical reason for this behavior is claimed to be the competition for different kinds of adsorption sites on the cells and/or the screening effect by the second metal ion at both pH values. It can be said that although the order of second metal ion addition affects the adsorption rate and uptake negatively, *C. vulgaris* offers a practical approach to the binary removal of copper(II) and chromium(VI) from wastewater due to the pH of wastewater and the levels of metal ion concentrations. Higher adsorption capacities for selective or the simultaneous removal of metal ions could be carried out in a batch reactor by adjusting the pH of wastewater and diluting wastewater to the lower levels of metal ion concentrations.

For the single metal ion situation, adsorption isotherms were developed at pH 2.0 and pH 4.0, and it was seen that the equilibrium data for two metal ions fit both the monocomponent Langmuir and Freundlich models. The individual Langmuir and Freundlich constants evaluated from the monocomponent isotherms were used to compare the biosorptive capacity of the algae for both metal ions and to find the multicomponent Langmuir and Freundlich constants in the competitive Langmuir and Freundlich models describing multicomponent adsorption equilibrium. It was seen that the adsorption equilibrium data fitted very well to the competitive Freundlich model in the concentration ranges studied except for very high total initial concentrations of both metal ions and pH values. The copper(II)–chromium(VI) multi-ion system can be defined with competitive Freundlich adsorption isotherms and used to model the adsorption of binary systems from aqueous solutions.

NOTATION

b	monocomponent (noncompetitive) Langmuir adsorption constant of a single metal ion related to the affinity of the binding sites
b_1, b_2	individual Langmuir adsorption constants of the first and the second metal ions related to the affinity of the binding sites, respectively
C_{eq}	the unadsorbed concentration of the single metal ion at equi librium (mg/L)
C_{eq1}, C_{eq2}	the unadsorbed concentrations of the first and the second metal ions, respectively, at equilibrium (mg/L)
C_0	initial metal ion concentration (mg/L)
K_F	monocomponent (noncompetitive) Freundlich adsorption constant of the single metal ion related to the adsorption capacity
K_{F1}, K_{F2}	individual Freundlich adsorption constants of the first and the second metal ions, respectively
n	monocomponent (noncompetitive) Freundlich adsorption constant of the single metal ion related to adsorption intensity
n_1, n_2	individual Freundlich adsorption constants of the first and the second metal ions, respectively
x_1, y_1, z_1	multicomponent (competitive) Freundlich adsorption constants of the first component (the first metal ion) for two-component systems
x_2, y_2, z_2	multicomponent (competitive) Freundlich adsorption constants of the second component (the second metal ion) for two-component systems
q_{eq}	the adsorbed quantity of the metal ion per gram of dried alga at equilibrium (mg/g)
q_{eq1}, q_{eq2}	the adsorbed quantities of the first and the second metal ions, respectively, per gram of dried alga at equilibrium (mg/g)
Q^0	monocomponent (noncompetitive) Langmuir adsorption constant of single metal ion shows the maximum amount of metal ion bound to the algae
Q_1^0, Q_2^0	individual Langmuir adsorption constants of the first and the second metal ions show the maximum amount of metal ion bound to the algae, respectively
η_1, η_2	multicomponent (competitive) Langmuir adsorption constants of the first and the second metal ions, respectively, for two-component systems

ACKNOWLEDGEMENT

We thank TÜBİTAK (the Scientific and Technical Research Council of Turkey), Project No. YDABÇAG 31, for the partial financial support of this study.

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Received by editor June 24, 1997
First revision received March 1998
Second revision received May 1998

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