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 Sa, Yeşm , Ataçolu, Işil and Kutsal, Tüln(1999) 'Simultaneous Biosorption of Chromium(VI) and Copper(II) on *Rhizopus Arrhizus* in Packed Column Reactor: Application of the Competitive Freundlich Mode', Separation Science and Technology, 34: 16, 3155 — 3171

To link to this Article: DOI: 10.1081/SS-100100828

URL: http://dx.doi.org/10.1081/SS-100100828

SEPARATION SCIENCE AND TECHNOLOGY, **34**(16), pp. 3155–3171, 1999

Simultaneous Biosorption of Chromium(VI) and Copper(II) on *Rhizopus arrhizus* in Packed Column Reactor: Application of the Competitive Freundlich Model

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ABSTRACT

The simultaneous biosorption of Cr(VI) and Cu(II) on free *Rhizopus arrhizus* in a packed column operated in the continuous mode was investigated and compared to the single metal ion situation. The breakthrough curves were measured as a function of feed flow rate, feed pH, and different combinations of metal ion concentrations in the feed solutions. Column competitive biosorption data were evaluated in terms of the maximum (equilibrium) capacity of the column, the amount of metal loading on the *R. arrhizus* surface, the adsorption yield, and the total adsorption yield. In the single-ion situation the adsorption isotherms were developed for optimum conditions, and it was seen that the adsorption equilibrium data fit the noncompetitive Freundlich model. For the multicomponent adsorption equilibrium the competitive adsorption isotherms were also developed. The competitive Freundlich model for binary metal mixtures represented most the column adsorption equilibrium data of Cr(VI) and Cu(II) on *R. arrhizus* satisfactorily.

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Key Words. Waste water; Free microorganism; Simultaneous biosorption; Chromium(VI); Copper(II); Packed column; The competitive Freundlich model

INTRODUCTION

The presence of toxic heavy metals and radionuclides over the permissible levels in the environment is a severe public health problem. Hexavalent chromium is one of the toxic heavy metals which are common pollutants of the environment. In humans, chromate causes irritation and corrosion of the skin and respiratory tract, and it is believed to be responsible for lung carcinoma (1). Besides chromium, copper is also a common and serious environmental pollutant. Cr(VI) and Cu(II) ions are frequently encountered together in industrial wastewaters, e.g., from mining, metal cleaning, plating, electroplating, metal processing, manufacture of automobile parts, dyeing, and petroleum industries. In metal cleaning, plating, and metal processing industries, Cr and Cu concentrations can approach 100,000–270,000 $mg{\cdot}L^{-1}$ Cr(VI) and 100–120 $mg{\cdot}L^{-1}$ Cu(II). Wastewaters from the manufacture of automobile parts contain Cr and Cu concentrations ranging over 30–700 $mg{\cdot}L^{-1}$ and 24–33 $mg{\cdot}1^{-1}$, respectively (2).

The search for new technologies involving the removal of toxic metals, actinide elements (such as uranium and thorium), and other radionuclides from wastewaters has directed attention to biosorption based on the metal-binding capacities of various biological materials. Biosorption mechanisms vary, and in some cases they are still not very well understood (3, 4). Metabolism-dependent biosorption may take place only with viable cells. Living organisms are usually difficult to use in traditional equipment. Processing complications caused by using living microorganisms can be avoided by using dead biomass (5). Moreover, some methods of killing cells may actually improve the biosorption properties of the biomass. Better killing methods, such as immersion in formaldehyde, would crosslink the cells, thereby simultaneously immobilizing them (6). Since the removal of metal ions by biomass is similar to that of ion exchange, the most convenient configuration for continuous operation is that of a packed column.

Fungal biosorption has been studied more extensively because of the availability of large amounts of waste fungal biomass from fermentation industries and the amenability of the microorganisms to genetic and morphological manipulation (7, 8). The fungus *Rhizopus arrhizus* is able to take up metal ions from solutions and grows at high carbon concentrations. Food industrial wastes with a high carbohydrate content could be used in liquid or solid fermentation processes to produce fungal biomass for use in such biosorption systems (9–11). For industrial application, a freely suspended fungal biomass has several disadvantages which include low density and mechanical strength, which may make biomass/effluent separation difficult (7, 8). Immobilized or pelleted biomass can overcome such problems. Several kinds of immobilization treatment have been applied to *R. arrhizus*, including entrapment within polymeric matrices and attachment to inert surfaces or support particles such as semirigid reticulated polyester foam biomass support particles (8, 9, 12). Despite the advantages listed, biosorbent immobilization may constitute an additional and significant economic cost which may prevent its use under certain conditions. Treatment of a highly acidic effluent, such as that studied here, may lead to complications with organic and polymeric matrices. The major limitation of immobilization is that immobilization of cells may cause extra diffusional limitations as compared to free cultures. Diffusional limitations lead to a more dispersed breakthrough curve, with a decrease in column utilization for a given breakthrough concentration (13, 14). In this study a surface-attached *R. arrhizus* was grown at a very low stirring rate, and free-dead cells were used in a packed column. To use surface-attached *R. arrhizus* in a column-type reactor without immobilization, it can be obtained in an appropriate diameter based on the method used to grow, kill, and homogenize the cells.

One of the difficulties in describing the adsorption of metal ions from waste streams 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. The complex overlapping breakthrough curves for multicomponent mixtures where dispersive and nonequilibrium effects are important cannot be described easily. Although several complex mathematical models have been proposed, there is a definite lack of experimental breakthrough curves that can be used to test these models for multicomponent systems involving more than one species (15). Several isotherms have been proposed to describe competitive adsorption equilibrium for such systems. 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 (16).

The Freundlich expression is an empirical equation based on sorption on a heterogeneous surface. The Freundlich equation for single-component systems is commonly presented as (17, 18):

$$q_{\mathrm{eq}} = a^0 C_{\mathrm{eq}}^{\mathrm{b}^0} \tag{1}$$

and the equation may be linearized by taking logarithms:

$$\ln q_{\mathrm{eq}} = b^0 \ln C_{\mathrm{eq}} + \ln a^0 \tag{2}$$

Therefore a plot of $\ln q_{\mathrm{eq}}$ versus $\ln C_{\mathrm{eq}}$ enables the constant a^0 and exponent b^0 to be determined.

One of models related to the individual isotherm parameters and to correction factors is an empirical extension of the Freundlich model restricted to binary mixtures (19):

$$q_{1,\mathrm{eq}} = \frac{a_1^0 C_{1,\mathrm{eq}}^{b_1^0 + b_{11}}}{C_{1,\mathrm{eq}}^{b_{11}} + a_{12} C_{2,\mathrm{eq}}^{b_{12}}} \tag{3a}$$

$$q_{2,\mathrm{eq}} = \frac{a_2^0 C_{2,\mathrm{eq}}^{b_2^0 + b_{22}}}{C_{2,\mathrm{eq}}^{b_{22}} + a_{21} C_{1,\mathrm{eq}}^{b_{21}}} \tag{3b}$$

where the a_i^0 and b_i^0 are derived from the corresponding individual Freundlich isotherm equations. The six other parameters are the competition coefficients.

In this study the single- and multicomponent biosorption of Cr(VI) and Cu(II) on free *R. arrhizus* in a packed column operating in the continuous mode is investigated as a function of flow rate, pH of inlet metal ion solutions, different combinations of metal ion concentrations, and ratios of metals. The mono- and multicomponent biosorption phenomena of Cr(VI) and Cu(II) ions in the packed column are characterized by the noncompetitive and competitive Freundlich models developed for optimum biosorption conditions for each metal ion.

EXPERIMENTAL

Microorganism and Preparation of the Microorganism for Biosorption

The culture used in this study was the surface-attached filamentous fungus *Rhizopus arrhizus* (US Department of Agriculture culture collection strain NRRL 2286). Batch experiments were conducted with 100 mL cultures, gently agitated at 50 rev·min^{-1} and at a temperature of 30°C. At the deceleration phase of the growth, agitation was stopped. The growth medium contained malt extract (17.0 g·L^{-1}) and soya peptone (5.4 g·L^{-1}). The pH was adjusted to 5.4–5.6 with H_2SO_4.

After the growth period the surface-attached *R. arrhizus* was washed twice with distilled water, inactivated using 1% formaldehyde, and then dried in a sterilizer at 60°C for 24 hours. For the column studies, dried cells (5 g) were suspended in 100 mL of distilled water and homogenized for 10 minutes in a homogenizer (Janke and Kunkel, IKA-Labortechnik, Ultra-Turrax T 25) at 8000 rev·min^{-1}. The homogenized cells were centrifuged at 5000 rev·min^{-1} for 20 minutes and then filled in the column. The diameter of thermally killed *R. arrhizus* pellets in the biosorption medium was determined to be in the 150–200 μm size range as the result of wet measurement.

Preparation of Biosorption Media Containing Single and Dual Metal Ions and Biosorption Studies

Cu(II) and Cr(VI) solutions were prepared by diluting 1.0 $g \cdot L^{-1}$ stock solutions of copper(II) and chromium(VI) obtained by dissolving anhydrous $CuSO_4$ or $K_2Cr_2O_7$ in distilled water, respectively. The range of concentrations of the prepared metal solutions varied between 25 and 250 $mg \cdot L^{-1}$

For the determination of adsorption characteristics of the dominant metal in binary metal mixtures, the initial concentrations of the dominant metal were varied between 100 and 250 $mg \cdot L^{-1}$ while the competing metal ion concentrations in each biosorption medium were held constant over the 100–250 $mg \cdot L^{-1}$ range. The pH of inlet metal ion solutions was adjusted to the required value with 1 $mol \cdot L^{-1}$ H_2SO_4.

Identical packed columns, 2.5 cm in diameter and 10 cm in height, were used in the adsorption studies. Packed bed experiments were carried out at 25°C. Solutions were fed to the bottom of the column (upflow) by a Masterflex L/S drive (Cole-Parmer Model H-07521-00) and an easy-load pump head (H-07518-00). The effluent samples were taken at 5 minute intervals at the beginning of column operation and at 25–30 minute intervals after reaching equilibrium. Experiments were terminated when the fungus bed was saturated by both metal ions.

Analysis of Cr(VI) and Cu(II) Ions

The Cr(VI) content in the column outflow was determined spectrophotometrically at 540 nm using diphenyl carbazide as the complexing agent. The presence of Cu(II) ions in the medium did not interfere with this analysis (20, 21).

The concentration of unadsorbed Cu(II) ions in the sample supernatant was determined using an atomic absorption spectrophotometer (ATI-UNICAM 929) with an air–acetylene flame. ATI-UNICAM copper hollow cathode lamps were used.

RESULTS

The optimum initial pH for the single and simultaneous biosorption of Cr(VI) and Cu(II) ions on *R. arrhizus* was determined to be 2.0 and 4.0, respectively, in batch-stirred reactors (22). For the determination of the effect of pH on the simultaneous biosorption of Cr(VI) and Cu(II) ions from binary metal mixtures, column studies were carried out at pH 2.0 and 4.0. The single-component biosorption of Cr(VI) and Cu(II) ions on *R. arrhizus* was investigated as a function of flow rate and inlet metal ion concentration. The breakthrough curves for the competitive biosorption of Cr(VI) and Cu(II) were measured as a function of different combinations of metal ion concentrations in the feed solutions. The results are given in terms of the maximum (equilibrium) capacity of the column, $C_{i,\mathrm{ads}}$ (mg), the amount of metal loading on the *R. arrhizus* surface, $q_{i,\mathrm{eq}}$ ($\mathrm{mg \cdot g^{-1}}$), and the adsorption yield (adsorbed metal percentage), % Y_i. The maximum (equilibrium) capacity of the column for a given feed concentration is equal to the area behind the breakthrough curve. The amount of metal that remains in the effluent, $C_{i,\mathrm{eq}}$, is the area under this curve (13). The amount of metal loading on the *R. arrhizus* surface is calculated from the weight of metal adsorbed per unit dry weight of *R. arrhizus* in the column (that is, the ratio of the maximum capacity of the column to the amount of microorganism filled in the column). The adsorption yield is the ratio of the maximum capacity of the column to the amount of metal loading into the column, W_i (mg).

To investigate the effect of flow rate on the single-component biosorption of Cr(VI) and Cu(II) ions by *R. arrhizus*, the inlet metal concentration in the feed was held constant as 150 $\mathrm{mg \cdot L^{-1}}$ while the flow rate was changed from 1.2 to 3.8 $\mathrm{mL \cdot min^{-1}}$. The retention time of metal ions through the column changed from 13.1 to 4.1 minutes. Much sharper breakthrough curves and maximum adsorption yields for single Cr(VI) and Cu(II) biosorption on *R. arrhizus* were obtained at a flow rate of 1.2 $\mathrm{mL \cdot min^{-1}}$ (Table 1). Thus, a longer contact time between metal solution and *R. arrhizus* led to a greater amount of metal sorbed. The flow rate was held constant at 1.2 $\mathrm{mL \cdot min^{-1}}$ in all simultaneous biosorption experiments.

The Simultaneous Biosorption of Cr(VI) and Cu(II) Ions at pH 2.0 from Binary Metal Mixtures by *R. arrhizus* and Application of the Competitive Freundlich Model

To obtain selectivity for Cr(VI) ions, the pH of the biosorption media was adjusted to 2.0, the optimum value for the biosorption of Cr(VI) ions. When a

TABLE 1
For the Single-Component Biosorption of Cr(VI) and Cu(II) Ions on *R. arrhizus*, the Amount of Metal Loading into the Column (*W*) the Amount of Metal Loading on the *R. arrhizus* Surface (q_{eq}) and the Adsorption Yield Obtained at Different Flow Rates (*Y*)

Flow rate ($\mathrm{mL \cdot min^{-1}}$)	*W* (mg)	q_{eq} ($\mathrm{mg \cdot g^{-1}}$)	*Y* (%)
	Chromium(VI)		
1.2	743.80	85.90	57.7
3.8	1769.30	70.50	19.9
	Copper(II)		
1.2	334.02	32.28	48.3
3.8	801.50	31.50	19.7

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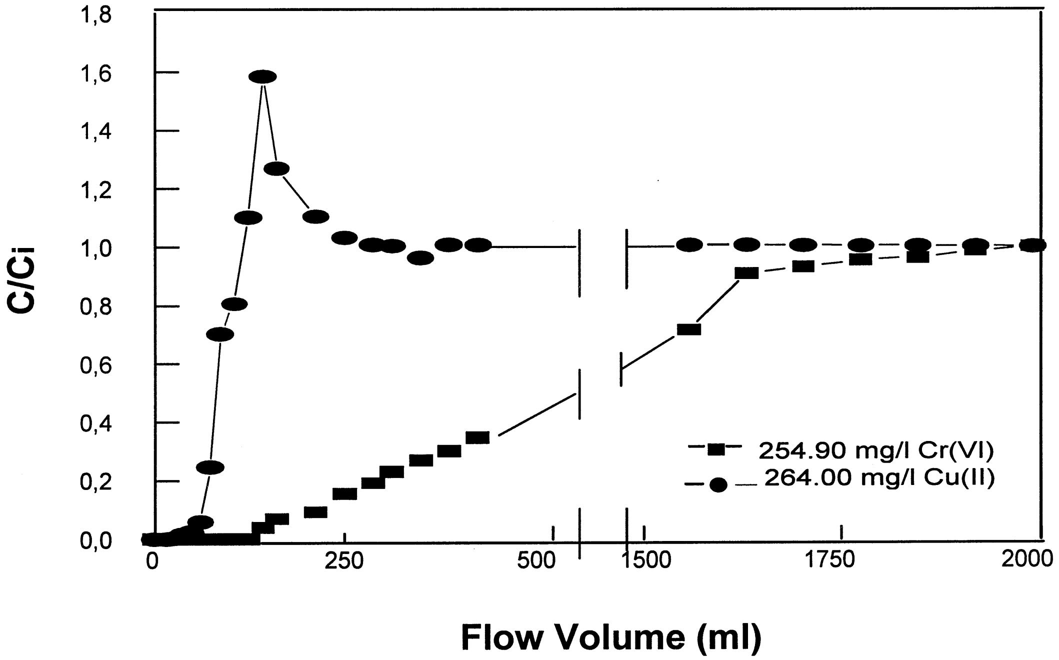

FIG. 1 The breakthrough curves for the simultaneous biosorption of Cr(VI) and Cu(II) ions on *R. arrhizus* at an equal inlet metal ion concentration of 250 mg·L^{-1} and at pH 2.0 ($T = 25$°C, $W_{R.\ arrhizus} = 5.0$ g, flow rate = 1.2 mL·min^{-1}).

binary metal mixture containing Cr(VI) and Cu(II) ions at a fixed concentration of 250 mg·L^{-1} was pumped through the column of *R. arrhizus*, the metal ions were adsorbed until the biomass was saturated with metal ions (Fig. 1). In all the breakthrough curves the normalized concentration, defined as the measured concentration divided by the inlet concentration, is plotted against volumes of synthetic aqueous solutions treated. Breakthrough occurs when that metal appears in the effluent. Cu(II) binds rapidly but not strongly. Cr(VI) binds slowly but binds almost irreversibly. Cu(II) binds first, then is pushed off by Cr(VI). When the *R. arrhizus*' capacity is approached, Cr(VI) with a higher affinity appears to displace Cu(II) with lower affinity. The adsorption and displacement of metal ions is the reason for the outlet concentrations sometimes rising to values greater than 1. The copper concentration reaches a maximum value in the effluent when chromium breaks through.

For determination of the adsorption characteristics of Cr(VI) ions in binary metal mixtures, the initial concentrations of Cr(VI) ions were varied between 100 and 250 mg·L^{-1} while the Cu(II) ion concentration in each metal mixture was held constant at 100, 150, or 250 mg·L^{-1}. In Figs. 2 and 3 the breakthrough curves of Cr(VI) ions obtained at the fixed Cr(VI) ion concentrations of 100 and 250 mg·L^{-1}, but with increasing Cu(II) ion concentrations in the 0 to 250 mg·L^{-1} range, are given. The general position of the breakthrough

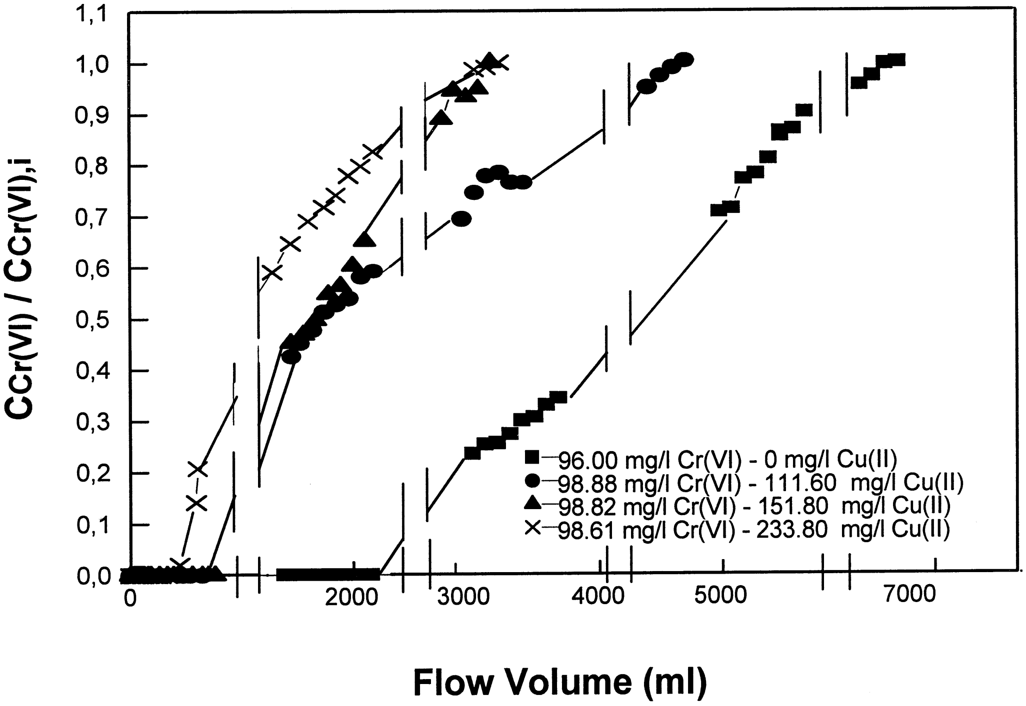

FIG. 2 The breakthrough curves of Cr(VI) obtained at the fixed Cr(VI) ion concentration of 100 mg·L^{-1} but with increasing Cu(II) ion concentrations in the 0–250 mg·L^{-1} range at pH 2.0 (T = 25°C, $W_{R.\ arrhizus}$ = 5.0 g, flow rate = 1.2 mL·min^{-1}).

curve along the volume axis depends on the capacity of the column with respect to the feed concentration. This is set by the equilibrium. By comparing the breakthrough curves in Figs. 2 and 3, it is seen that decreasing the feed concentration increases the volume of the feed that can be processed and shifts the breakthrough curve to the right. As the concentration of Cr(VI) ions increases in the feed, the breakthrough curves become steeper. At lower inlet concentrations of Cr(VI) and Cu(II) ions, the breakthrough curves disperse, breakthrough occurs very late, and the surface of *R. arrhizus* is saturated with Cr(VI) after a very long time. Much sharper breakthrough curves but lower adsorption capacities for Cr(VI) ions are obtained at higher concentrations of Cu(II) ions.

In Fig. 4 the breakthrough curves of Cu(II) ions obtained at the fixed Cu(II) ion concentration of 250 mg·L^{-1}, but with increasing Cr(VI) ion concentrations in the 0 to 250 mg·L^{-1} range are given. There appeared to be a significant inhibition in the uptake of Cu(II) in the presence of increasing concentrations of Cr(VI) at constant Cu(II) ion concentrations. Previously bound Cu(II) ions were eluted from the column by Cr(VI) ions, giving a negative accumulation for the period when the two metals were present in excess.

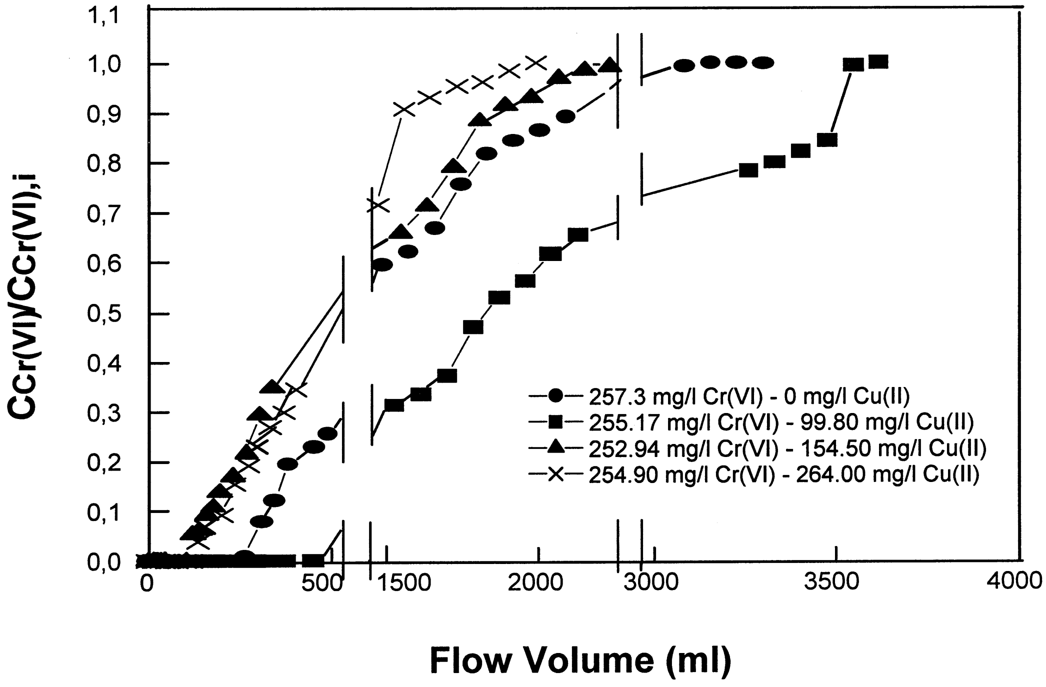

FIG. 3 The breakthrough curves of Cr(VI) obtained at the fixed Cr(VI) ion concentration of 250 mg·L^{-1} but with increasing Cu(II) ion concentrations in the 0–250 mg·L^{-1} range at pH 2.0 (T = 25°C, $W_{R.\ arrhizus}$ = 5.0 g, flow rate = 1.2 mL·min^{-1}).

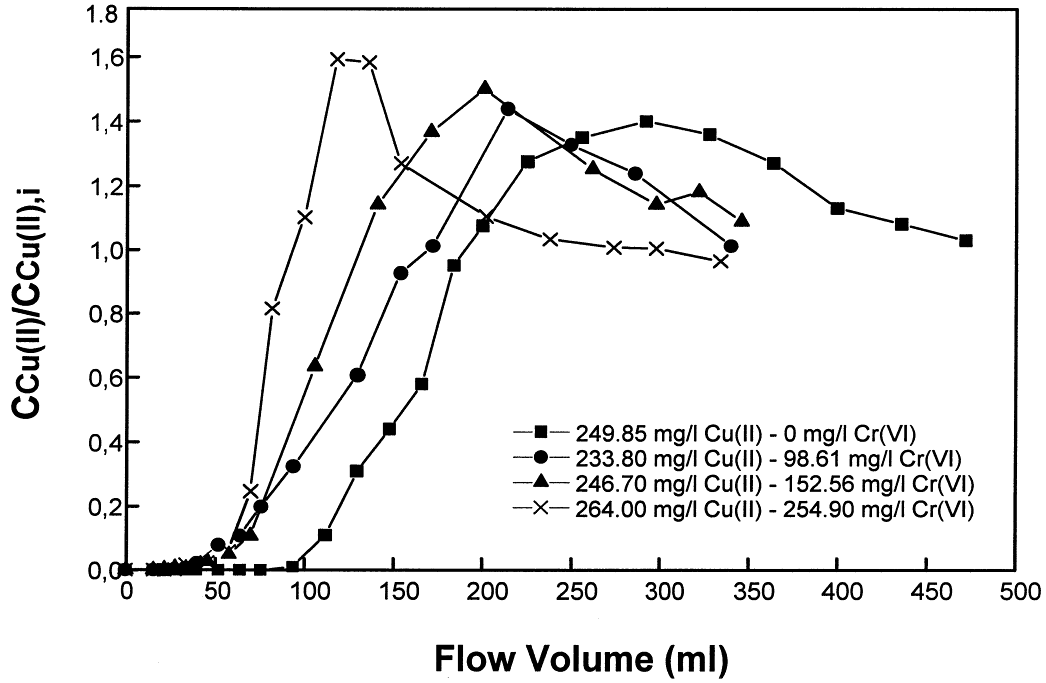

FIG. 4 The breakthrough curves of Cu(II) obtained at the fixed Cu(II) ion concentration of 250 mg·L^{-1} but with increasing Cr(VI) ion concentrations in the 0–250 mg·L^{-1} range at pH 2.0 (T = 25°C, $W_{R.\ arrhizus}$ = 5.0 g, flow rate = 1.2 mL·min^{-1}).

TABLE 2
The Effect of Cr(VI) and Cu(II) Concentrations in the Feed on the Simultaneous Biosorption of Cr(VI) and Cu(II) by *R. arrhizus* at pH 2.0 in the Packed Column Reactor

$C_{\mathrm{Cr},i}$ (mg·L^{-1})	$C_{\mathrm{Cu},i}$ (mg·L^{-1})	W_{Cr} (mg)	W_{Cu} (mg)	$q_{\mathrm{Cr,eq}}$ (mg·g^{-1})	$q_{\mathrm{Cu,eq}}$ (mg·g^{-1})	$q_{\mathrm{t,eq}}$ (mg·g^{-1})	Y_{Cr} (%)	Y_{Cu} (%)	Y_{T} (%)
96.00	0	684.30	—	79.70	—	79.70	58.2	—	58.2
147.00	0	743.80	—	85.90	—	85.90	57.7	—	57.7
257.30	0	931.30	—	102.90	—	102.90	55.2	—	55.2
0	103.00	—	32.75	—	4.05	4.05	—	61.8	61.8
0	153.20	—	33.70	—	6.14	6.14	—	91.1	91.1
0	249.85	—	49.97	—	9.29	9.29	—	93.0	93.0
98.88	111.60	473.20	25.04	43.68	2.04	45.72	46.2	40.7	45.9
98.82	151.80	332.98	22.41	35.36	2.61	37.97	53.1	58.2	53.4
98.61	233.80	272.16	41.52	26.50	5.35	31.85	48.7	64.4	50.8
255.17	99.80	612.41	9.58	62.29	0.98	63.27	50.9	51.2	50.9
252.94	154.50	555.46	15.39	49.50	2.30	51.80	44.6	74.7	45.4
254.90	264.00	507.15	24.08	46.24	3.44	49.68	45.6	71.4	46.8

The breakthrough curves were evaluated. The combined effects of Cr(VI) and Cu(II) ions on *R. arrhizus* were evaluated in terms of the amount of metal loading into the column, the weight of metal adsorbed per unit dry weight of *R. arrhizus*, and the adsorption yield. A comparison of the effect of metal ion concentration in the feed on the amount of metal loading into the column, the weight of metal adsorbed per unit dry weight of *R. arrhizus*, the adsorption yield, and the total adsorption yield (i.e., the ratio of the total amount of metal adsorbed, $C_{\mathrm{T,ads}}$, to the total amount of metal loading into the column, W_{T}) with metal ions present as the single metal and in the presence of increasing concentrations of the second metal ion are presented in Table 2. At a constant concentration of Cr(VI) ions, the amount of Cr(VI) loading into the column and the weight of Cr(VI) adsorbed per unit dry weight of *R. arrhizus* decreased with increasing inlet Cu(II) ion concentrations. At a constant concentration of Cu(II) ions, the amount of Cr(VI) loading into the column and the weight of Cr(VI) adsorbed per unit dry weight of *R. arrhizus* increased with increasing inlet Cr(VI) ion concentrations. A similar adsorption pattern was also observed for the simultaneous biosorption of Cu(II) ions. The uptake of Cr(VI) ions by *R. arrhizus* as the single and dual species at pH 2.0 was considerably greater than that of Cu(II) ions. Although Cr(VI) ions were selectively adsorbed by *R. arrhizus*, the column was initially saturated with Cu(II) ions at all combinations of metal ion concentrations. Since the amount of metal loading into the column and the amount of metal adsorbed per unit dry weight of *R. arrhizus* decreased with increasing concentration of the other metal ion, the combined action of Cr(VI) and Cu(II) ions was found to be antagonistic.

The equilibrium biosorption data of Cr(VI) and Cu(II) ions from binary mixtures by *R. arrhizus* were analyzed using the competitive Freundlich model. The data in Table 2 indicate that the mutual interference of the two metals is very different. The chromium adsorption capacity of *R. arrhizus* at pH 2.0 was significantly higher than the copper adsorption capacity. In order to describe the adsorption isotherms mathematically, some well-known relationships were tested (16), but there was no satisfactory agreement with the measured data. Such competitive adsorption data can be well characterized by using the competitive Freundlich model (19). Competitive models related only to the individual isotherm parameters, such as the competitive Langmuir model and the competitive Redlich–Peterson model, failed for the data. Individual adsorption constants used alone cannot define exactly the multicomponent adsorption behavior of the metal mixtures. Multicomponent systems are characterized by additional features beyond those of single components. There are possible interaction effects between different species in solution, with potential interactions on the surface in particular depending on the adsorption mechanism. Competition between the different metal ion species for surface sites will occur and will depend on the ionic characteristics. For that reason, better accuracy may be achieved by using competitive isotherms related to the individual isotherm parameters and to correction factors such as in the competitive Freundlich model. In addition, the Freundlich model physically provides a more realistic description of metal adsorption by organic matter because it accounts for different binding sites.

The monocomponent adsorption constants and the competition coefficients for the competitive Freundlich model are given in Table 3. The individual Freundlich constants, a_i^0 and b_i^0, were determined from the intercept and slope of the linearized equilibrium equation, respectively. a_i^0 is an indication of the adsorption capacity of the adsorbent; b_i^0 indicates the effect of concentration on

TABLE 3
The Individual Freundlich Constants and Competition Coefficients for the Simultaneous Biosorption of Cr(VI) and Cu(II) Ions on *R. arrhizus* in the Packed Column Reactor at pH 2.0 and pH 4.0 [1 denotes Cr(VI) and 2 denotes Cu(II)]

pH 2.0	a_1^0	b_1^0	b_{11}	a_{12}	b_{12}
	38.4208	0.2001	0.8153	1.8032	0.7881
pH 2.0	a_2^0	b_2^0	b_{22}	a_{21}	b_{21}
	0.0492	1.2500	0.0003	0.0009	1.7163
pH 4.0	a_1^0	b_1^0	b_{11}	a_{12}	b_{12}
	5.2984	0.4361	0.8226	0.2009	1.0796
pH 4.0	a_2^0	b_2^0	b_{22}	a_{21}	b_{21}
	4.2589	0.4680	0.0009	0.0003	1.7748

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TABLE 4

Comparison of Experimental and Predicted q_{i},eq Values for Competitive Cr(VI) and Cu(II) Biosorption by *R. arrhizus* at pH 2.0

		Experimental		Freundlich fit			
$C_{\mathrm{Cr},i}$ ($\mathrm{mg \cdot L^{-1}}$)	$C_{\mathrm{Cu},i}$ ($\mathrm{mg \cdot L^{-1}}$)	$q_{\mathrm{Cr,eq}}$ ($\mathrm{mg \cdot g^{-1}}$)	$q_{\mathrm{Cu,\ eq}}$ ($\mathrm{mg \cdot g^{-1}}$)	$q_{\mathrm{Cr,eq}}$ ($\mathrm{mg \cdot g^{-1}}$)	$q_{\mathrm{Cu,eq}}$ ($\mathrm{mg \cdot g^{-1}}$)	$\varepsilon_{\mathrm{Cr}}$ (%)	$\varepsilon_{\mathrm{Cu}}$ (%)
98.88	111.60	43.68	2.04	42.34	1.84	3.08	9.56
98.82	151.80	35.36	2.61	36.51	2.40	3.25	8.07
98.61	233.80	26.50	5.35	26.32	5.82	0.70	8.88
146.95	111.75	49.21	1.92	48.48	1.79	3.16	6.64
152.91	152.50	41.32	2.60	42.23	2.46	2.20	5.64
152.56	246.70	33.84	4.67	34.50	4.79	1.96	2.53
255.17	99.80	62.29	0.98	68.20	0.98	9.49	0.00
252.94	154.50	49.50	2.30	49.91	2.40	0.84	4.13
254.90	264.00	46.24	3.44	44.08	3.44	4.68	0.00

the adsorption capacity and represents the adsorption intensity. The six other parameters given by Eqs. (3a) and (3b) were estimated from the competitive adsorption data of Cr(VI) and Cu(II) ions by using the MS Excel 7.0 computer program. The average percentage errors (% $\varepsilon = [|(q_{i,\mathrm{eq}})_{\mathrm{predicted}} - (q_{i,\mathrm{eq}})_{\mathrm{experimental}}|/(q_{i,\mathrm{eq}})_{\mathrm{experimental}}] \times 100$) between the predicted and the experimental values of Cr(VI) and Cu(II) for the entire data set are 3.07 and 5.05%, respectively (Table 4). The correlation coefficients between the experimental and the predicted values using the competitive Freundlich model for each data set range between 0.9945 and 0.9995.

The Simultaneous Biosorption of Cr(VI) and Cu(II) Ions at pH 4.0 from Binary Metal Mixtures by *R. arrhizus* and Application of the Competitive Freundlich Model

To obtain selectivity for Cu(II) ions, the pH of the biosorption media was adjusted to 4.0, the optimum value for the biosorption of Cu(II) ions. At this pH value the maximum capacity of the column for the single-component biosorption of Cr(VI) and Cu(II) ions and the adsorption yields are about the same order of magnitude (Table 5). As also seen from the individual Freundlich constants, the adsorption capacity of the column for Cr(VI) ions, a_1^0, is slightly higher than that for Cu(II) ions, a_2^0. On the other hand, the adsorption intensity of the column for Cr(VI) and Cu(II) ions, b_1^0 and b_2^0, seems to be similar (Table 3).

When a binary metal mixture containing Cr(VI) and Cu(II) ions at an equal concentration of 100 $\mathrm{mg \cdot L^{-1}}$ at pH 4.0 was pumped through the column of *R. arrhizus*, the column saturated with Cr(VI) and Cu(II) ions at flow volumes of 2995 and 2880 mL, respectively (Fig. 5). In contrast to pH 2.0, the column ini-

TABLE 5
The Effect of Cr(VI) and Cu(II) Concentrations in the Feed on the Simultaneous Biosorption of Cr(VI) and Cu(II) by *R. arrhizus* at pH 4.0 in the Packed Column Reactor

$C_{Cr,i}$ (mg·L^{-1})	$C_{Cu,i}$ (mg·L^{-1})	W_{Cr} (mg)	W_{Cu} (mg)	$q_{Cr,eq}$ (mg·g^{-1})	$q_{Cu,eq}$ (mg·g^{-1})	$q_{t,eq}$ (mg·g^{-1})	Y_{Cr} (%)	Y_{Cu} (%)	Y_T (%)
95.25	0	331.49	—	29.50	—	29.50	44.5	—	44.5
149.30	0	477.09	—	38.67	—	38.67	40.5	—	40.5
243.39	0	514.62	—	44.31	—	44.31	43.1	—	43.1
0	97.25	—	296.54	—	27.07	27.07	—	45.6	45.6
0	146.50	—	334.02	—	32.28	32.28	—	48.3	48.3
0	252.00	—	816.48	—	47.91	47.91	—	29.3	29.3
97.25	98.95	291.29	284.98	19.91	20.45	40.36	34.2	35.9	35.0
99.13	151.95	193.66	282.45	16.33	25.35	41.68	42.2	44.9	43.8
96.08	243.80	175.02	394.37	14.33	30.09	44.42	40.9	38.2	39.0
255.32	98.45	520.85	146.85	35.04	10.37	45.41	33.6	35.3	34.0
258.80	141.60	492.24	218.18	32.34	11.71	44.05	32.9	26.8	31.0
263.80	282.60	319.73	305.21	22.48	15.91	38.39	35.2	26.1	30.7

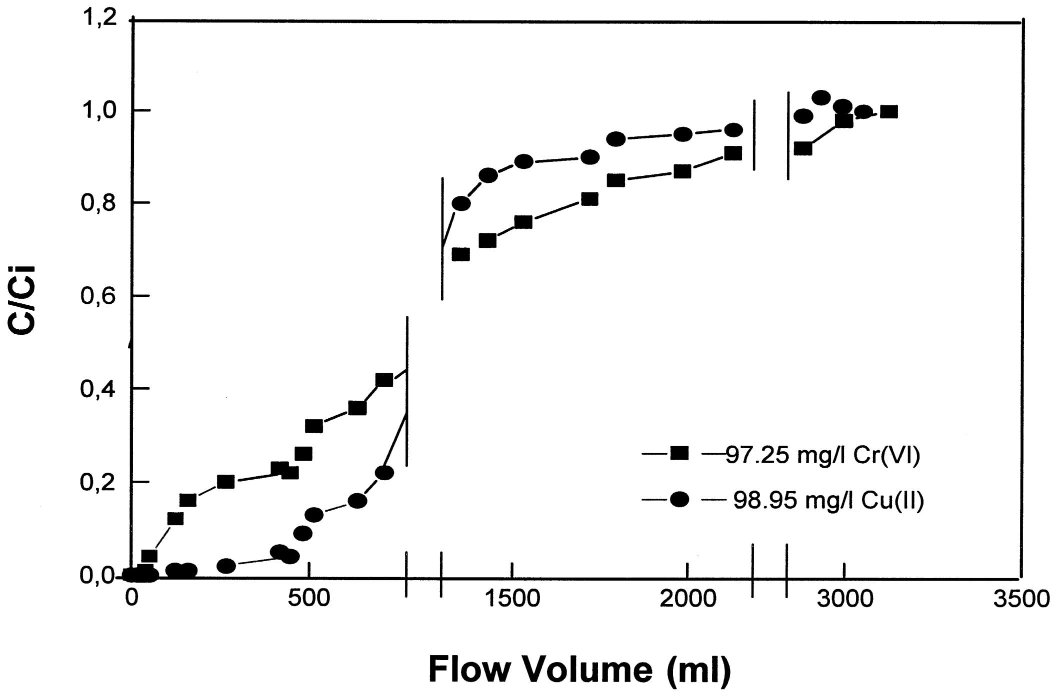

FIG. 5 The breakthrough curves for the simultaneous biosorption of Cr(VI) and Cu(II) ions on *R. arrhizus* at an equal inlet metal ion concentration of 100 mg·L^{-1} and at pH 4.0 (T = 25°C, $W_{R.\ arrhizus}$ = 5.0 g, flow rate = 1.2 mL·min^{-1}).

tially saturated with Cr(VI) ions at pH 4.0 and at lower concentrations of Cr(VI) ions and/or lower ratios of the Cr(VI) ion concentration to the Cu(II) ion concentration. No release of chromium(VI) ions was observed following saturation of the column with Cr(VI) ions. It is evident that Cr(VI) ions are adsorbed strongly and irreversibly.

In Fig. 6 the breakthrough curves of Cr(VI) ions obtained at a fixed Cr(VI) ion concentration of 250 mg·L^{-1}, but with increasing Cu(II) ion concentrations in the 0 to 250 mg·L^{-1} range, are given. In binary mixtures of Cr(VI) and Cu(II) ions, the amount of Cu(II) loading on the *R. arrhizus* surface at pH 4.0 increased substantially compared with pH 2.0, while the amount of Cr(VI) loading on the *R. arrhizus* surface decreased. However, the amount of Cr(VI) loading on the *R. arrhizus* surface was approximately equal or higher than that of Cu(II) loading on the *R. arrhizus* surface at higher Cr(VI) ion concentrations and/or higher ratios of the Cr(VI) ion concentration to the Cu(II) ion concentration in the binary mixtures. As also observed at pH 2.0, the elution of Cu(II) ions increased with increasing concentrations of both the metal ions (Fig. 7).

It was interesting to find that the total amount of metal loading into the column, W_T, and the total weight of metal adsorbed per unit dry weight of *R. arrhizus*, $q_{t,eq}$, are higher than what was obtained in biosorption media containing

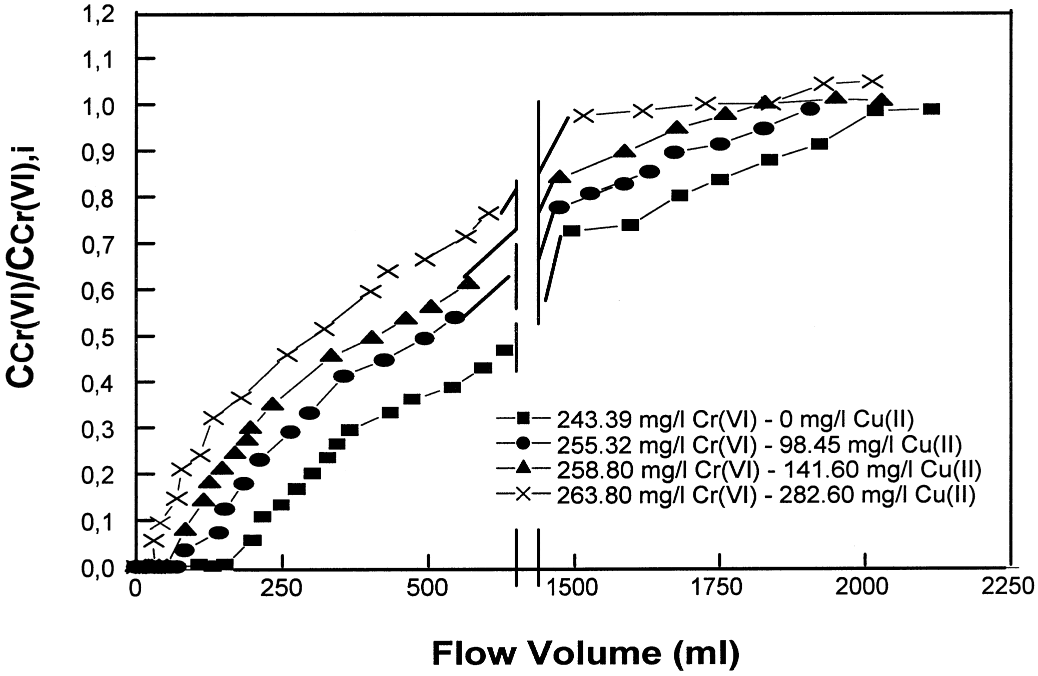

FIG. 6 The breakthrough curves of Cr(VI) obtained at the fixed Cr(VI) ion concentration of 250 mg·L^{-1} but with increasing Cu(II) ion concentrations in the 0–250 mg·L^{-1} range at pH 4.0 ($T = 25$°C, $W_{R.\ arrhizus} = 5.0$ g, flow rate = 1.2 mL·min^{-1}).

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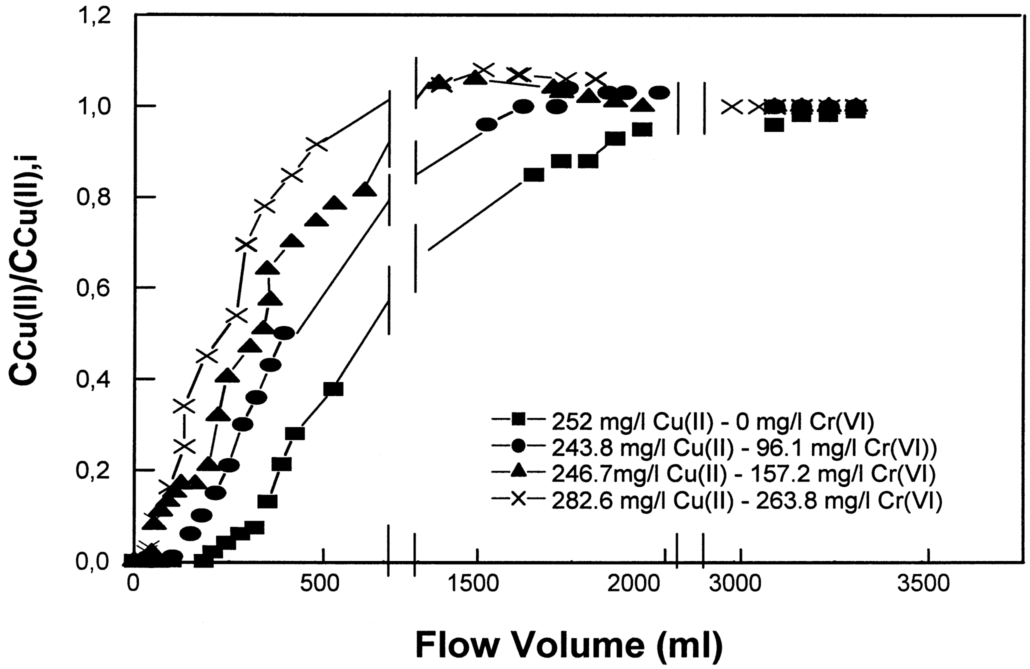

FIG. 7 The breakthrough curves of Cu(II) obtained at the fixed Cu(II) ion concentration of 250 $mg \cdot L^{-1}$ but with increasing Cr(VI) ion concentrations in the 0–250 $mg \cdot L^{-1}$ range at pH 4.0 ($T = 25°C$, $W_{R.\ arrhizus} = 5.0$ g, flow rate = 1.2 $mL \cdot min^{-1}$).

Cr(VI) and Cu(II) ions alone at the same concentrations (Table 5). The greater the total metal loading, the more effective is the competitive metal uptake because of a strong driving force or a large difference in concentration between adsorbent surface and metal solution. It is also implied that there are a variety of binding sites on the biomass that are partially specific for Cr(VI) and Cu(II) at pH 4.0. For that reason, the total interactive effects of Cr(VI) and Cu(II) ions on the biosorption of Cr(VI) and Cu(II) ions by *R. arrhizus* can be considered to be synergistic at pH 4.0. Since a fixed cell biomass offers a finite number of surface binding sites, the maximum column capacity would be expected to show saturation kinetics. The total weight of metal adsorbed per unit dry weight of *R. arrhizus* reaches an approximately constant saturated capacity of 43.5 $mg \cdot g^{-1}$ (average value) at all combinations of metal ion concentrations. Thereafter, the inhibition effect caused by excess metal ion concentration begins in a binary metal mixture containing 263.80 $mg \cdot L^{-1}$ Cr(VI) and 282.60 $mg \cdot L^{-1}$ Cu(II).

The competitive Freundlich model was also used successfully to characterize the simultaneous biosorption of Cr(VI) and Cu(II) from two component systems at pH 4.0. The competition coefficients estimated from the competitive biosorption data of Cr(VI) and Cu(II) ions at pH 4.0 are also given in Table 3. The experimental values of the amount of metal loading on the *R. arrhizus* surface, $q_{i,\mathrm{eq}}$, and the predicted values using the competitive Freundlich

TABLE 6
Comparison of Experimental and Predicted $q_{i,\mathrm{eq}}$ Values for Competitive Cr(VI) and Cu(II) Biosorption by *R, arrhizus* at pH 4.0

		Experimental		Freundlich fit			
$C_{\mathrm{Cr},i}$ (mg·L^{-1})	$C_{\mathrm{Cu},i}$ (mg·L^{-1})	$q_{\mathrm{Cr,eq}}$ (mg·g^{-1})	$q_{\mathrm{Cu,\ eq}}$ (mg·g^{-1})	$q_{\mathrm{Cr,eq}}$ (mg·g^{-1})	$q_{\mathrm{Cu,eq}}$ (mg·g^{-1})	$\varepsilon_{\mathrm{Cr}}$ (%)	$\varepsilon_{\mathrm{Cu}}$ (%)
97.26	98.95	19.91	20.45	20.30	21.08	1.96	3.08
99.13	151.95	16.33	25.35	16.35	25.35	0.11	0.00
96.08	243.80	14.33	30.09	14.33	28.91	0.00	3.92
153.73	110.35	28.36	17.06	27.21	15.99	4.08	6.30
142.75	149.20	21.23	21.18	21.16	21.59	0.33	1.91
157.21	246.70	18.89	24.97	18.90	23.92	0.03	4.21
255.32	98.45	35.04	10.37	36.92	10.07	5.36	2.92
258.80	141.60	32.34	11.71	33.49	11.71	3.55	0.00
263.80	282.6	22.48	15.91	22.38	19.09	0.46	19.99

model for Cr(VI) and Cu(II) ions are shown in Table 6. The average percentage errors between the experimental values and the predicted values using the competitive Freundlich model for the entire data set of Cr(VI) and Cu(II) were 1.76 and 4.70%, respectively. The correlation coefficients between the predicted and the experimental values for the entire data set range between 0.9859 and 0.9995.

CONCLUSIONS

In this study the simultaneous biosorption of Cr(VI) and Cu(II) on *R. arrhizus* in a packed column reactor was investigated and compared with single-metal adsorption. The breakthrough curves for simultaneous column biosorption of Cr(VI) and Cu(II) from binary metal mixtures were measured. The feed aqueous pH and levels of metal concentration are the two important factors affecting the saturated capacity. The amount of biosorption is greater at higher concentrations of the dominant metal ion at a defined pH value, and at lower concentrations of the competing metal ion. The breakthrough curve is found to be gentler at lower concentrations of the competing metal ion and steeper at higher concentrations of the dominant metal ion. These both lead to a greater saturated capacity. The saturated capacity for Cr(VI) at all combinations of the metal concentrations in the *R. arrhizus* bed is greater than that for Cu(II) at pH 2.0. Since both metal ions are more effectively adsorbed to the biomass at pH 4.0, this situation can be thought of as a suitable representation of fully competitive adsorption. The selectivity of the fungus bed for Cu(II) ions at pH 4.0 increased when the Cu(II) ion concentration and/or the ratio of the Cu(II) ion concentration was increased with respect to the Cr(VI) ion concentration. The high affinity of *R. arrhizus* for Cr(VI) in a wide pH range may be due to chromium's higher ionic charge. Since required amounts of Cr(VI) and Cu(II) ions are removed simultaneously, wastewaters containing these metal ions should be treated with *R. arrhizus* at pH 4.0 rather than pH 2.0. The Freundlich model for single and binary systems satisfactorily represented the experimental column data of Cr(VI) and Cu(II) at both pH values. The individual Freundlich constants evaluated from the noncompetitive isotherms were used to compare the biosorptive capacities of the microorganisms for Cr(VI) and Cu(II) at a defined pH value, and the competition coefficients were estimated from the competitive adsorption data.

ACKNOWLEDGMENT

The authors thank TÜBİTAK, the Scientific and Technical Research Council of Turkey, for partial financial support of this study (Project 409).

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Received by editor September 25, 1998
Revision received March 1999

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