Multi-Metal Biosorption Equilibria of Cr(VI), Cu(II), Cd(II), and Fe(III) Ions

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ABSTRACT

Four-component biosorption equilibria of Cr(VI), Cu(II), Cd(II), and Fe(III) ions were studied using Rhizopus arrhizus. As the multicomponent Langmuir model was able to predict the two ternary subsystems of these metal ions satisfactorily, it was further applied in describing the behavior of the quaternary metal systems. To present a summary of the effect of one metal on the uptake of the other, three-dimensional (3-D) sorption isotherm surfaces were constructed. The apparent equilibrium constant, the biosorption efficiency and the relative coverage of the four metals were in the order Fe≥Cr>Cd>Cu. © 2002 SDU. All rights reserved.

Keywords: Four-metal biosorption; Chromium(VI); Copper(II); Cadmium(II); Iron(III); Rhizopus arrhizus; Multicomponent Langmuir model

1. INTRODUCTION

Due to the increasing value of some metals, as well as due to a greater awareness of the ecological effects of toxic metals released into the environment, a number of studies of metal accumulation have been launched. Multi-metal systems are often encountered in industrial operations. Conventional methods for removing metals include chemical precipitation, chemical oxidation or reduction, ion exchange, electrochemical treatment, and membrane technologies. However, these processes may be ineffective or extremely expensive, especially when the metals are in solutions containing in the order of 1 to 100mg/l of dissolved metals. Four widely used metals that often appear together in metal-bearing industrial effluents are Cr(VI), Cu(II), Cd(II), and Fe(III). These ions are frequently encountered in a mixture in industrial waste waters during specific metal treatment operations, metal plating and finishing, iron and steel manufacturing, production of automobile parts, paint manufacturing, and ink formulation. In plating rinse, Cr(VI), Cu(II), Cd(II), and Fe(III) concentrations can approach 73-2310, 20-120, 0.1-3330, and 2-23000mg/l, respectively. Waste waters from paint and ink formulation, production of automobile parts, and iron and steel manufacturing industries contain concentrations ranging over 150 (average) mg/l Cr(VI), 0-100mg/l Cu(II), 134 (average) mg/l Fe(III), and 0-0.81mg/l Cd(II); 11.5-30mg/l Cr(VI), 24-33mg/l Cu(II), 1.5-31mg/l Fe(III), and 14-22mg/l Cd(II); 0.06-121mg/l Cr(VI), 25-96800mg/l Fe(III), and 0-80mg/l Cd(II), respectively (Patterson, 1975).

Alternative metal removal and/or recovery methods are being considered which are based on metal-sequestering properties of certain natural materials of biological origin. Certain types of microorganisms can retain relatively high quantities of metal ions by passive sorption mechanisms such as precipitation, physical adsorption, ion exchange, and complexation (Solari et al., 1996; Delgado et al., 1998; Sag, 2001). This is commonly known as biosorption. The active mode of metal accumulation by living cells is usually designated as bioaccumulation.

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This process is dependent on the metabolic activity of the cell, which in turn can be significantly affected by the presence of the metal ions (Muter et al., 2001; Donmez and Aksu, 2001; Rai et al., 2002). Biosorption is caused by a number of different physicochemical mechanisms, depending on a number of external environmental factors as well as on the type of a metal, its ionic form in the solution, and on the type of a particular active binding site responsible for sequestering the metal (Sag and Kutsal, 2001). When several components are present, interference and competition phenomena for adsorption sites occur. While the number of experiments required increases almost exponentially with the number of metallic species present in the solution, the prediction of biosorption equilibria becomes more complicated by the presence of several sorbed ions, requiring the use of multicomponent isotherm equations (Puranik and Paknikar, 1999; Ho and McKay, 2000; Pagnanelli et al., 2001).

The objectives of the present work are: 1) to present experimental equilibrium data for the quaternary system containing Cr(VI), Cu(II), Cd(II), and Fe(III); 2) to test if the multicomponent Langmuir model could represent biosorption equilibrium data of the four-metal system; 3) to verify the predictions of the four-metal system biosorption behavior based on the information derived from the two three-metal subsystems; 4) to provide quantitative details of selective biosorption, such as the extent of selectivity in terms of the relative metal i biosorption R_i (%), the individual biosorption efficiency Y_i (%), the total biosorption efficiency Y_t (%), or the relative surface coverage, θ_i (%), of each coadsorbate during selective biosorption.

2. MATERIALS AND METHODS

2.1. Microorganism, preparation of biosorption media containing quaternary metal ions and biosorption studies

The culture used in this study was the filamentous fungus *Rhizopus arrhizus* (US Department of Agriculture culture collection strain no. NRRL 2286). *R. arrhizus* which belongs to a large class of phycomycetes is known for its strong metal-sorbent properties which are common to the whole genus. *R. arrhizus* possesses high chitin/chitosan content in the cell wall. For that reason, studies on the interaction between heavy metal ions in single and multi-metal combinations and *R. arrhizus* cells, a well-established biosorbent, are of great interest in environmental biotechnology. *R. arrhizus* was grown aerobically in batch culture at 30°C in complex medium and was prepared for biosorption as described previously (Sag and Kutsal, 1996a).

Cu(II), Cr(VI), and Cd(II) solutions were prepared by diluting 0.02M stock solutions of copper(II) and chromium(VI) and 0.01M stock solution of cadmium(II), obtained by dissolving anhydrous CuSO_4, K_2Cr_2O_7 or CdSO_4.8H_2O in distilled water, respectively. The stock solution of ferric iron (0.02M) from ferrous ammonium sulphate was prepared as described in the literature (Snell and Snell, 1961).

To determine multicomponent adsorption isotherms, the initial concentrations of Cd(II) ions were varied between 443 and 2905µmol/l while the Cu(II), Cr(VI) and Fe(III) ion concentrations in each metal mixture were held constant over the 407-2411, 433-2741 and 484-2847µmol/l ranges, respectively. The chosen initial metal ion concentration range for Cr(VI)-Cu(II)-Fe(III) and Cd(II) ions corresponds to 25-150 and 50-325mg/l, respectively, on the basis of weight. The dry cell weight in each sample was constant at 1.0g/l. Before the solutions were mixed with the fungal suspension, pH was adjusted to 2.5 by adding 1.0M of H_2SO_4. The fungal suspension (20ml) was mixed with 180ml of the desired metal solution in an Erlenmeyer flask. The flasks were agitated on a shaker at 25°C for 48h. Agitation rate was 150rpm. Standard batch biosorption equilibrium methodology applied has been described elsewhere (Sag and Kutsal, 1996b).

2.2. Measurement of heavy metal ions

The concentration of unadsorbed Cr(VI), Fe(III) and Cu(II) ions in the biosorption medium was determined spectrophotometrically. The coloured complexes of Cr(VI) ions with diphenyl
carbazide, Fe(III) ions with sodium salicylate and Cu(II) ions with sodium diethyl dithiocarbamate were read at 540, 530 and 460nm, respectively. No interference of Cr(VI), Fe(III), Cu(II) and Cd(II) ions on the analysis methods of the other metal ions was observed (Snell and Snell, 1961). The concentration of unadsorbed Cd(II) ions in the sample supernatant was determined using an atomic absorption spectrophotometer (ATI-UNICAM 929) with an air-acetylene flame. PHOTRON Cd(II) hollow cathode lamp was used. Cd(II) was measured at 228.8nm.

3. RESULTS AND DISCUSSION

3.1. Competitive biosorption equilibria of Cr(VI), Cu(II), Cd(II), and Fe(III) ions in quaternary systems

As the multicomponent Langmuir model was able to predict the binary (Sag and Kutsal, 1996b) and ternary biosorption equilibria of Cr(VI), Fe(III), Cu(II), and Cd(II) satisfactorily (Sag et al., 2001; Sag et al., 2002), it was further applied in describing the behavior of the quaternary metal systems. The major assumption of the multicomponent Langmuir model is that the surface sites are uniform, so that the adsorbates (Cr(VI), Cu(II), Cd(II), and Fe(III)) compete for the same surface sites. The multicomponent Langmuir model can be described as follows (Bellot and Condoret, 1993; Chong and Volesky, 1996):

\[ q_{i,eq} = \frac{q_{\text{max}} K_i C_{i,eq}}{1 + K_i C_{i,eq} + K_j C_{j,eq} + K_k C_{k,eq} + K_l C_{l,eq}} \]  

(1)

where the maximal capacity \( q_{\text{max}} \) is universal so that all four metals obey the fundamental hypothesis of the Langmuir model. The model given by Eq. (1) actually consists of four equations, one to compute the uptake of the first metal and other three for the uptakes of the second, the third metal, and the fourth metal, respectively. The denominators of the four equations are identical. \( q_{\text{max}} \), and the other four parameters, \( K_{Cr} \), \( K_{Cu} \), \( K_{Cd} \), and \( K_{Fe} \) associated with the Langmuir model were estimated by utilizing MS EXCEL 97 numerical analysis program. The optimal parameters were evaluated by minimizing the mean square of residuals. The optimal parameters estimated for the multicomponent Langmuir model are listed in Table 1.

The values of calculated parameters are also shown in Table 2 together with those obtained from the four single- and two ternary systems. The value of the apparent equilibrium constant \( K \) determined for a metal differed for each system. Likewise, \( q_{\text{max}} \) values for each respective system were not identical. The biomass had the highest saturation capacity \( q_{\text{max}} \) for Cr(VI) in the single-metal system, followed by Fe(III)>Cd(II)>Cu(II).

Table 1

<table>
<thead>
<tr>
<th>( q_{\text{max}} ) (µmol/g)</th>
<th>( K_i ) (l/µmol)</th>
<th>RPE(^a) (%)</th>
<th>MSR(^b)</th>
<th>( E_i )(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1030</td>
<td>0.000150</td>
<td>5.3</td>
<td>15</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>0.000118</td>
<td>10.7</td>
<td>33</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>0.000513</td>
<td>4.6</td>
<td>116</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>0.000541</td>
<td>5.2</td>
<td>265</td>
<td>0.06</td>
</tr>
<tr>
<td>Average=6.4</td>
<td>Average=107</td>
<td>Average= 0.10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Relative percentage error

\[
(RPE)\% = \frac{\sum |(q_{i,eq})_{predicted} - (q_{i,eq})_{experimental}|}{N} \times 100
\]  

(2)

where \( N \) is the number of experimental data.

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Mean square of residuals (MSR)\[MSR = \frac{\sum (q_{i,exp} - q_{i,pre})^2}{N}\] (3)

Objective function\[E_i = \sum_{j=1}^{N} \left( \frac{q_{i,exp} - q_{i,pre}}{q_{i,exp}} \right)^2\] (4)

The Langmuir coefficient $K$ is the ratio of the adsorption rate constant to the desorption rate constant. A large value of $K$ implies strong binding and is related to the affinity of the biosorbent for the metal. The magnitude of those constants essentially followed a trend of $\text{Cd(II)} > \text{Cr(VI)} > \text{Fe(III)} > \text{Cu(II)}$ in the single-metal systems. Table 2 also indicates that in the three-component systems of $\text{Cr(VI)}$, $\text{Fe(III)}$ and $\text{Cu(II)}$ ions the magnitude of those constants was in the same order $\text{Cr(VI)} > \text{Fe(III)} > \text{Cu(II)}$. The magnitude of the multicomponent Langmuir constant decreased in order of $\text{Cu(II)} > \text{Cr(VI)} > \text{Cd(II)}$ in the ternary mixtures of $\text{Cu(II)}$, $\text{Cr(VI)}$, and $\text{Cd(II)}$ ions. As the values of $K$ for $\text{Fe(III)}$ and $\text{Cr(VI)}$ ions are very close to each other, these values indicate a decidedly better biomass affinity for, and stronger biosorption of, $\text{Fe(III)}$ and $\text{Cr(VI)}$ ions versus $\text{Cd(II)}$ and $\text{Cu(II)}$ ions in the four-component systems. The relative percentage errors (RPE), the variance (MSR) between the experimental values and the predicted values using the multicomponent Langmuir model, and the values of the objective functions ($E_i$) for each component are also given in Table 1. The predicted and experimental metal uptakes are quite consistent over a large range of the residual concentrations of the four metals. The best fit to the multicomponent Langmuir model was obtained for $\text{Cr(VI)}$ ions while the predictions for the $\text{Cu(II)}$ uptake are the least accurate. As the amounts of $\text{Cd(II)}$ and $\text{Cu(II)}$ adsorbed per unit weight of microorganism at equilibrium were low, the relative percentage errors between the experimental and predicted values for $\text{Cd(II)}$ and $\text{Cu(II)}$ increased, whereas the mean of sum of squared residuals decreased. The multicomponent Langmuir model generally showed better fits to the data from quaternary systems than single and ternary systems. This phenomena can be explained as a higher degree of freedom for the quaternary systems.

### Table 2
Comparison of kinetic parameters of four single, two ternary subsystems and one quaternary system adsorption isotherms estimated from multicomponent Langmuir model

<table>
<thead>
<tr>
<th>i (metal ion)</th>
<th>$q_{\text{max}}$ (µmol/g)</th>
<th>$K_i$ (l/µmol)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>177</td>
<td>$K_{Cd}=0.0035$</td>
<td>(Sag et al., 2002)</td>
</tr>
<tr>
<td>Cr</td>
<td>504</td>
<td>$K_{Cr}=0.0029$</td>
<td>(Sag et al., 2002)</td>
</tr>
<tr>
<td>Fe</td>
<td>358</td>
<td>$K_{Fe}=0.0017$</td>
<td>(Sag et al., 2001)</td>
</tr>
<tr>
<td>Cu</td>
<td>149</td>
<td>$K_{Cu}=0.0013$</td>
<td>(Sag et al., 2002)</td>
</tr>
<tr>
<td>Cr-Fe-Cu</td>
<td>689</td>
<td>$K_{Cr}=0.0014$</td>
<td>(Sag et al., 2001)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$K_{Fe}=0.0009$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$K_{Cu}=0.0002$</td>
<td></td>
</tr>
<tr>
<td>Cu-Cr-Cd</td>
<td>928</td>
<td>$K_{Cr}=0.000999$</td>
<td>(Sag et al., 2002)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$K_{Cd}=0.000935$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$K_{Cu}=0.000359$</td>
<td></td>
</tr>
<tr>
<td>Fe-Cr-Cd-Cu</td>
<td>1030</td>
<td>$K_{Fe}=0.000541$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$K_{Cr}=0.000513$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$K_{Cd}=0.000150$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$K_{Cu}=0.000118$</td>
<td></td>
</tr>
</tbody>
</table>

The maximal total capacity, $q_{\text{max}}$, resulting from the four single, two ternary, and one quaternary systems was 504µmol/g (for $\text{Cr(VI)}$ alone), 689µmol/g ($\text{Cr(VI)}$- $\text{Fe(III)}$- $\text{Cu(II)}$), 928µmol/g ($\text{Cu(II)}$-$\text{Cr(VI)}$-$\text{Cd(II)}$), and 1030µmol/g ($\text{Fe(III)}$-$\text{Cr(VI)}$-$\text{Cd(II)}$-$\text{Cu(II)}$), respectively. The sum of the maximal total capacities of $\text{Cr(VI)}$, $\text{Cu(II)}$, $\text{Cd(II)}$, and $\text{Fe(III)}$ ions (1188µmol/g) resulting from single systems was slightly greater than the maximal total capacity resulting from quaternary systems. It may imply that there exists a variety of binding sites on the biomass that are partially specific for individual metal species. When number of metals competing for binding sites was increased, the maximal total capacity increased, the active
surface sites of the biomass was used more effectively. On the other hand, the saturation capacity for Cr(VI) alone was essentially equivalent to the half of the maximal capacities obtained from four-metal systems. For that reason, the adsorption sites of Cu(II), Cd(II) and Fe(III) were likely to be partially overlapped, and the competition phenomena for the same sorption sites occurred. The information provided from maximal capacities, \( q_{\text{max}} \), seems to violate basic assumptions of the Langmuir model which propose that the entire adsorbent surface is homogeneous, the affinity of each binding site for the adsorbate molecules is uniform, and the adsorbent has identical maximum capacity for each adsorbate present. Actually, the competitive biosorption system of Cr(VI), Cu(II), Cd(II), and Fe(III) is nonideal because the equilibrium constants of the ternary and quaternary systems differ. In other words, the K values for the quaternary system can not be predicted from those of the two corresponding ternary systems. Nevertheless, some behavior of the quaternary system, postulated from the information from the two ternary subsystems, appears to be consistent with that predicted from the four-component Langmuir model.

From the information on the two ternary systems, some predictions can be made as to possible behavior of the quaternary Cr(VI), Cu(II), Cd(II), and Fe(III) system.

i. At approximately equal initial concentrations of each metal ion, the percent metal uptake by \( K. arrhizus \) in a four-metal system will be: Fe(III) 38% to 14%; Cr(VI) 35% to 18%; Cd(II) 18% to 8%; and Cu(II) 11% to 4%.

ii. At approximately equal initial metal ion concentrations, the adsorbed chromium(VI) ion quantity per unit weight of dried biomass would be 1.1 to 1.4 times higher than that of Fe(III); 2.0 to 2.6 times higher than that of Cd(II); 3.2 to 6.8 times higher than that of Cu(II) (Sag et al., 2001; Sag et al., 2002). Similar types of predictions can be made from the multicomponent Langmuir model whereby its parameters had been evaluated from the experimental data of the four-component system.

i. For the same equal initial metal ion concentrations, the predicted percent metal uptakes are Fe(III) 27% to 19%; Cr(VI) 26% to 18%; Cd(II) 11% to 6%; and Cu(II) 9% to 5%.

ii. For the same equal initial metal ion concentrations, the adsorbed chromium(VI) ion quantity per unit weight of dried biomass would have to be 0.9 to 1.0 times higher than that of Fe(III); 3.2 to 2.7 times higher than that of Cd(II); 3.5 to 4.1 times higher than that of Cu(II).

These results obtained from the multicomponent Langmuir model generally fell within the predicted ranges postulated from the results of the two ternary subsystems.

In multicomponent systems, it is useful to present a summary of the effect of one metal on the uptake of the other. This can be done in three-dimensional (3-D) sorption isotherm surfaces. To evaluate quantitatively this interference, experimental 3-D sorption isotherm plots need to be mathematically represented. In this stage, mathematical models to represent the experimental data and sorption surfaces have to be proposed and tested for their suitability (Volesky and Holan, 1995; Figueira et al., 1997; Sag et al., 2001). A 3-D diagram based on randomly generated experimental data is plotted and the data are fitted a smooth surface according to the appropriate input equation, which represents the surface. The input equation is the quaternary Langmuir-type equation, which created the biosorption isotherm surfaces seen in Figures 1-3, and smoothed and fitted to experimental biosorption data. As there is a preferential biosorbent selectivity for Cr(VI) and Fe(III) over Cd(II) and Cu(II), firstly empirically selected initial concentrations of Cd(II) and Cu(II) were chosen as parameters, and were held constant over the 443-2905, and 407-241 µmol/l ranges, respectively. Three different biosorption-isotherm surface plots are given in Figure 1: a) for the uptake of Cr(VI), yielding the effect of Fe(III) on Cr(VI); b) for the uptake of Fe(III), yielding the effect of Cr(VI) on Fe(III); and c) for the total uptake (Cr(VI)+Fe(III)). In the range of low equilibrium Cr(VI) concentrations (460-930µmol/l) the Cr(VI) uptake was more severely affected by the presence of Fe(III) (Figure 1 a)). The effect of Fe(III) was less pronounced at higher Cr(VI) concentrations. The uptake of Fe(III) ions also decreased with increasing equilibrium Cr(VI) concentrations (Figure 1 b)). However, the inhibition effect of Cr(VI) ions on Fe(III) ions decreased with increasing equilibrium Fe(III) concentrations. Figure 1 c) depicts total metal uptake behavior as a function of the two-metal equilibrium concentrations (Cr(VI) and Fe(III)) with the other metal equilibrium concentrations.
(Cd(II) and Cu(II)) as a parameter. The two main planes (x-z and y-z) show the single-metal biosorption isotherms for Cr(VI) and Fe(III), respectively.

Figure 1. Three-dimensional biosorption isotherm surfaces created by using multicomponent Langmuir model for the Cr(VI)+Cu(II)+Cd(II)+Fe(III) systems with \( C_{Cu(II)}^{eq} \) and \( C_{Cd(II)}^{eq} \) as a parameter. The initial concentrations of Cd(II) and Cu(II) were held constant over the 443-2905, and 407-2411 \( \mu \text{mol/l} \) ranges, respectively. (a) The effect of Fe(III) on equilibrium uptake of Cr(VI); (b) the effect of Cr(VI) on equilibrium uptake of Fe(III); (c) the effect of Cr(VI) and Fe(III) on equilibrium total Cr(VI)+Fe(III) uptake.
The lowest isotherm curves in Figure 1 c) represent simple one-metal biosorption isotherms for Cr(VI) and Fe(III), respectively. Although one type of the metal ion present interfered with the uptake of another one in the system, the overall total metal uptake was not lowered, even increased.

In Figure 2 (a-c), unadsorbed Cr(VI) and Cd(II) ion concentrations in solution at equilibrium are plotted against the Cr(VI), Cd(II), and total metal uptake, respectively. The initial concentrations of Fe(III) and Cu(II) ions were held constant over the 484-2847 and 407-2411µmol/l ranges, respectively. As also seen from Figure 2, a similar biosorption pattern was observed in the case of Cr(VI) and Cd(II) ions when empirically selected initial concentrations of Fe(III) and Cu(II) ions were chosen as parameters. However, the equilibrium uptake of Cr(VI) ions was less affected by the presence of Cd(II) ions than Fe(III) ions. There is a marked difference between the shape of the two isotherm surfaces for the Cr(VI)+Cd(II) and Cd(II)+Cr(VI) systems as illustrated in Figure 2 (a),b). Since the uptake of Cr(VI) ions was less affected with increasing concentrations of Cd(II) ions, the Cr(VI)+Cd(II) biosorption surface was curved convexly upward. The Cd(II) uptake was more severely affected by the presence of Cr(VI), and the Cd(II)+Cr(VI) biosorption surface was curved concavely downward. The summary of the Cu(II) interference in the Cr(VI) uptake is presented in Figure 3 a), when the initial concentrations of Fe(III) and Cd(II) ions were held constant over the 484-2847 and 443-2905µmol/l ranges, respectively. The effect of different levels of Cr(VI) on the uptake of Cu(II) is demonstrated in Figure 3 b), showing how the uptake of Cu(II) decreased in the presence of Cr(VI). A significant reduction in the Cu(II) uptake was observed at relatively low Cu(II) and high Cr(VI) ion concentrations. Figures 1-3 c) shows that, with high levels of overall metal concentration present in the solution, the biosorbent approximates the saturation level demonstrated by a wide plateau of the surface.
Figure 2. Three-dimensional biosorption isotherm surfaces created by using multicomponent Langmuir model for the Cr(VI)+Cu(II)+Cd(II)+Fe(III) systems with \( C_{\text{Fe(III)}},eq \) and \( C_{\text{Cu(II)}},eq \) as a parameter. The initial concentrations of Fe(III) and Cu(II) ions were held constant over the 484-2847 and 407-2411 \( \mu \text{mol/l} \) ranges, respectively. (a) The effect of Cd(II) on equilibrium uptake of Cr(VI); (b) the effect of Cr(VI) on equilibrium uptake of Cd(II); (c) the effect of Cr(VI) and Cd(II) on equilibrium total Cr(VI)+Cd(II) uptake.
Figure 3. Three-dimensional biosorption isotherm surfaces created by using multicomponent Langmuir model for the Cr(VI)+Cu(II)+Cd(II)+Fe(III) systems with $C_{\text{Fe(III),eq}}$ and $C_{\text{Cd(II),eq}}$ as a parameter. The initial concentrations of Fe(III) and Cd(II) ions were held constant over the 484-2847 and 443-2905µmol/l ranges, respectively. (a) The effect of Cu(II) on equilibrium uptake of Cr(VI); (b) the effect of Cr(VI) on equilibrium uptake of Cu(II); (c) the effect of Cr(VI) and Cu(II) on equilibrium total Cr(VI)+Cu(II) uptake

These quaternary-metal data indicate that *R. arrhizus* is unsaturated even in the system containing high concentrations of two-metals of interest (Cr(VI)- Fe(III)), the overall maximum metal uptake approached a value of 628µmol/g (Figure 1 a)). The unsaturated biosorbent demonstrates itself in the low concentration region of the plots by sharply lower metal uptake by the biosorbent, as indicated in Figure 3 c).

In Figure 4 the percentage deviations between the experimental and predicted values using the multi-component Langmuir model for Cd(II), Cr(VI), Cu(II) and Fe(III) ions in four-metal systems are presented. The variation between predicted and experimental values is also listed in Table 1 and the maximum average value of the percentage deviation is not more than 10% for the multi-component Langmuir model.

3.2. Quantitative analysis of selective biosorption of Cr(VI), Cu(II), Cd(II) and Fe(III) ions in four-metal systems

The selectivity of *R. arrhizus* for Cr(VI), Cu(II), Cd(II) and Fe(III) in the quaternary mixtures was evaluated in terms of relative metal i biosorption $R_i$ (%), individual biosorption efficiency $Y_i$ (%), total biosorption efficiency ($Y_t$ %), and relative coverage $\theta_i$ (%), whose definitions are as follows:

Relative metal i biosorption (Chang and Chen, 1998):

$$R_i = \frac{\text{metal i biosorption capacity with the coexistence of metal j and k}}{\text{metal i biosorption capacity without the coexistence of metal j and k}} \times 100\%$$

If $R_i$ % > 100, biosorption is promoted by the presence of other metal ions, $R_i$ % = 100, net interaction effect is not observable, and $R_i$ % < 100, biosorption is suppressed by the presence of other metal ions.
Relative percentage error vs. initial concentration of Cd(II) (μmol l⁻¹) a)

Relative percentage error vs. initial concentration of Cr(VI) (μmol l⁻¹) b)

Relative percentage error vs. initial concentration of Cu(II) (μmol l⁻¹) c)
Figure 4. Percentage deviation of the multi-component Langmuir model for Cd(II), Cr(VI), Cu(II) and Fe(III) ions, respectively in four-metal systems.

Individual biosorption efficiency (Sag and Kutsal, 1996a)
\[
Y_i = \frac{\text{concentration of metal } i \text{ biosorbed}}{\text{initial concentration of metal } i} \times 100\% \tag{6}
\]

Total biosorption efficiency (Sag et al., 2002)
\[
Y_t = \frac{\text{total concentration of metal ions biosorbed}}{\text{total initial metal ion concentration}} \times 100\% \tag{7}
\]

Relative coverage (Chang and Chen, 1998)
\[
\theta_i = \frac{\text{moles of metal } i \text{ biosorbed}}{\text{moles of all three metals biosorbed}} \times 100\% \tag{8}
\]

The values of \(Y_i\)% and \(\theta_i\)% are indications of the relative biosorption preference and distribution of each metal of interest on the biosorbent.

The total interactive effects of Cr(VI), Cu(II), Cd(II) and Fe(III) ions on the biosorption by \(R.\) arthizus were antagonistic (Table 3). The presence of these metal ions together strongly inhibited in particular the uptake of Fe(III) and Cd(II) ions, while the Cr(VI) biosorption maintained over 72% (average) of its single-component biosorption capacity. The degree of inhibition in the case of Cu(II) was also small in most instances so that the amount of bound Cu(II) was 65% (average) of its amount bound when added singly. The biosorption of Fe(III) decreased to 60% (average) of its original capacity. The Cr(VI), Cu(II) and Fe(III) ions exhibited significant inhibition effects on the biosorption of Cd(II) ions, and the Cd(II) biosorption capacity remained only 51% (average) of its original capacity. The relative metal \(i\) biosorption increased, when the metal \(i\) concentration or the ratio of the metal \(i\) concentration was increased with respect to the concentration of each metal ion or the total metal ion concentration.

An increase in the initial metal concentration led to a decrease in the biosorption efficiency of each metal. For all initial concentrations detected, the biosorption efficiency of the four metals was in the order \(Y_{Fe} > Y_{Cr} > Y_{Cd} > Y_{Cu}\). The individual biosorption efficiency of Cu(II) and Cd(II) ions was also lower than the total biosorption efficiency for all combinations of metal ion concentrations.

The selective biosorption in the quaternary system was also evaluated in terms of relative coverage of each metal. Fe(III) ions had the highest relative coverage (\(\theta_{Fe}\) %) of 32-55% over the range of the initial concentrations examined. The relative coverage of Cr(VI) (\(\theta_{Cr}\) %) was slightly lower with a value of 27-56. The relative coverage of Cd(II) (\(\theta_{Cd}\) %) was 8-24%, while the value of \(\theta_{Cu}\) % was the lowest (7-17%) among the four metals. However, the relative coverage of the four metals did not vary considerably at approximately equal molar concentrations of Cr(VI), Cu(II), Cd(II), and Fe(III) ions. \(\theta_{Fe}\) %, \(\theta_{Cr}\) %, \(\theta_{Cd}\) %, and \(\theta_{Cu}\) % showed a nearly constant ratio of 40: 37: 13: 10, respectively.
Table 3
Selective biosorption in quaternary mixtures: dependence of the relative metal biosorption, the individual and total biosorption efficiencies and the relative coverage of Cr(VI), Cu(II), Cd(II), and Fe(III) on initial concentrations of each metal

| C_{Cd} (μmol/l) | C_{Cu} (μmol/l) | C_{Fe} (μmol/l) | C_{Cr} (μmol/l) | \%_Cd | \%_Cu | \%_Fe | \%_Cr | \%_Cd | \%_Cu | \%_Fe | \%_Cr | \%_Cd | \%_Cu | \%_Fe | \%_Cr | \%_Cd | \%_Cu | \%_Fe | \%_Cr | \%_Cd | \%_Cu | \%_Fe | \%_Cr |
|----------------|-----------------|-----------------|-----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 443            | 490             | 407             | 537             | 45.4  | 10.5  | 12.9  | 62.9  | 26.3  | 35.8  | 67.5  | 9.1   | 10.3  | 50.7  | 27.4  | 40.9  | 39.0  | 16.5  | 26.1  | 16.8  | 34.8  | 55.4  | 17.9  |
| 888            | 469             | 491             | 591             | 56.9  | 8.9   | 19.5  | 60.8  | 26.6  | 31.0  | 77.3  | 8.7   | 10.5  | 54.0  | 26.6  | 39.0  | 16.5  | 26.1  | 34.8  | 55.4  | 17.9  |
| 452            | 930             | 407             | 591             | 38.9  | 8.9   | 9.1   | 86.0  | 23.2  | 48.8  | 58.4  | 7.9   | 7.3   | 52.9  | 26.1  | 34.8  | 18.6  | 26.1  | 34.8  | 55.4  | 17.9  |
| 455            | 433             | 687             | 483             | 42.4  | 9.6   | 13.3  | 53.3  | 25.2  | 33.3  | 68.2  | 7.3   | 15.4  | 43.0  | 25.9  | 38.1  | 15.9  | 26.1  | 34.8  | 55.4  | 17.9  |
| 454            | 483             | 429             | 967             | 38.1  | 8.6   | 9.4   | 55.3  | 23.5  | 27.1  | 61.3  | 7.9   | 8.1   | 68.9  | 23.9  | 55.4  | 17.9  |
| 888            | 880             | 743             | 842             | 51.8  | 8.1   | 14.4  | 76.3  | 21.8  | 38.5  | 63.0  | 6.3   | 9.4   | 55.8  | 22.3  | 37.7  | 14.8  |
| 1766           | 858             | 886             | 838             | 7.9   | 7.0   | 23.8  | 65.7  | 19.2  | 32.0  | 64.4  | 5.4   | 9.2   | 53.7  | 21.5  | 35.0  | 11.9  |
| 889            | 1909            | 802             | 842             | 36.7  | 5.7   | 8.4   | 85.1  | 17.5  | 55.5  | 60.1  | 5.5   | 7.4   | 51.5  | 20.6  | 28.7  | 13.6  |
| 886            | 887             | 1627            | 842             | 44.6  | 6.9   | 12.3  | 68.2  | 19.3  | 34.3  | 75.5  | 5.2   | 16.8  | 54.4  | 21.7  | 36.6  | 11.8  |
| 880            | 969             | 827             | 1910            | 36.2  | 5.7   | 7.9   | 76.1  | 19.7  | 30.2  | 57.9  | 5.2   | 6.8   | 83.9  | 18.3  | 55.1  | 13.8  |
| 1360           | 1375            | 1167            | 1353            | 52.9  | 5.6   | 12.0  | 78.7  | 17.8  | 38.4  | 67.2  | 5.1   | 9.4   | 61.8  | 19.0  | 40.3  | 12.1  |
| 2905           | 1363            | 1184            | 1432            | 94.0  | 5.3   | 22.8  | 71.0  | 16.2  | 32.5  | 56.2  | 4.2   | 7.4   | 60.9  | 17.7  | 37.3  | 9.9   |
| 1347           | 2741            | 1184            | 1450            | 48.7  | 5.2   | 9.4   | 100.9 | 14.3  | 52.6  | 54.4  | 4.1   | 6.5   | 56.6  | 16.2  | 31.5  | 11.1  |
| 1390           | 1344            | 2410            | 1358            | 49.3  | 5.1   | 10.8  | 76.6  | 17.7  | 36.1  | 89.5  | 4.0   | 14.8  | 60.8  | 18.6  | 38.3  | 10.1  |
| 1344           | 1325            | 1184            | 2847            | 44.8  | 4.8   | 9.4   | 62.2  | 14.6  | 28.2  | 54.6  | 4.1   | 7.1   | 84.0  | 14.6  | 55.3  | 10.2  |
It is really complicated to find a common rule to identify how metal properties affect the selective biosorption. A general rule in heavy metal biosorption is that the higher charged the ions, the higher the affinity, and the metal ions tested followed this pattern. Another factor is the ionic radius itself, especially since a smaller ionic radius implies more molecules can sorb onto a fixed surface area of biosorbent. The metal ions tested also followed this trend. As metals with a higher reduction potential or electronegativity tend to exhibit a stronger ionic interaction with an electron-rich surface of biosorbents, an increase in the reduction potential and electronegativity leads to a higher biosorption preference by the biosorbent. As Cr(VI) has the highest reduction potential, Cr(VI) reflected this trend. Although Cu(II) has a higher reduction potential than Fe(III), it is sorbed the least. The sorption capacity of Cd(II) was smaller than Fe(III) due to its low electronegativity. On the other hand, Cu(II) ions are more electronegative than the other metal ions, but they are sorbed the least. However, the order of metal biosorption preference does not necessarily follow the general trends described above. Because the observed behavior may result from a combination of the physicochemical parameters of the solution, specific surface properties of the microorganism, and physical and chemical properties of metals. This inconsistency most likely originates from variations in composition and structure of the biosorbent surface and chemistry of metals by changing physicochemical parameters of the solution. pH of the biosorption medium plays a dominant role in the selectivity order of metal ions. The optimum biosorption pH of Cu(II) and Cd(II) ions is 4.0 (Sag et al., 2002), whereas Cr(VI) and Fe(III) ions are best adsorbed on the biomass at pH 2.5 (Sag et al., 2001). Since Fe(III) ions precipitats at pH values higher than 2.5, the simultaneous biosorption of Cr(VI)-Fe(III)-Cd(II)-Cu(II) were studied at pH=2.5. For that reason, the order of metal biosorption preference may have been determined directly by pH of the medium.

4. CONCLUSIONS

The following major conclusions can be made based on this study: 1) Although the information provided from maximal capacities seems to violate basic assumptions of the multicomponent Langmuir model, predictions of the behavior of Cr(VI), Cu(II), Cd(II), and Fe(III) quaternary metal system were in a reasonably good agreement with experimental results. 2) Application of the multicomponent Langmuir model to describe the four-metal system revealed its nonideal characteristics, whereby the value of apparent equilibrium constants for the particular metals differed for the quaternary and two ternary subsystems. However, some predictions of the quaternary system behavior from the model were consistent with conclusions postulated from the two possible ternary subsystems. 3) The competition of Cr(VI) and Fe(III) ions for the sorption sites was comparative, while the biosorption of Cd(II) and Cu(II) ions was overwhelmed by the competititon of Cr(VI) and Fe(III) ions.

REFERENCES


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