Biosorption of Binary Mixtures of Copper and Cobalt by *Penicillium brevicompactum*

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This work reports on a study of the biosorption of copper and cobalt, both singly and in combination (in equimolar concentrations), by the resting cells of *Penicillium brevicompactum*. Equilibrium batch sorption studies were carried out at 30 °C and pH 5.0 for a contact time of 1 hour to guarantee that equilibrium was reached. The equilibrium data were analyzed using the Langmuir and Freundlich isotherms. The adsorption of binary mixtures of heavy metal solutions on the fungal biomass was found to be of competitive type where the adsorption capacity for any single metal decreased in the presence of the other. The cobalt ions showed a higher affinity for *Penicillium brevicompactum* than the copper ions.

Key words: Heavy Metals, Competitive Sorption, *Penicillium brevicompactum*

Introduction

Increased industrialization and human activities have impacted on the environment through disposal waste containing heavy metals. Physicochemical methods for removing metals such as chemical precipitation, electrochemical treatment, ion exchange, and membrane technologies may be expensive and sometimes ineffective depending on heavy metal ion concentrations (Banerjee, 2002). Biological processes such as biosorption (bioaccumulation) using a microbial biomass have been proposed as alternative methods for removing and recovering heavy metals from industrial effluents with metal concentrations up to 100 mg/L.

Although microbial-heavy metal interactions have long been investigated, the approach taken by most researchers has been to consider a single metal ion in a biological system (Kargi and Cikla, 2006; Vijayaraghavan *et al.,* 2004; Gabriel *et al.,* 2001). Such a situation rarely occurs in nature, and a study on the combined effect of two or more metals in the system would be more realistic and more important, but only a few works on the adsorption of a mixture of heavy metals were found in literature (Apiratikul *et al.,* 2004; Kaewsarn, 2000; Chong and Volesky, 1995). Our previous work (Tsekova *et al.,* 2005) illustrated the possibility of using *Penicillium brevicompactum* biomass for the biosorption of copper and cobalt ions in an aqueous solution for a single solute system. Moreover the interaction between both heavy metals could not be predicted based on single metal studies, and has not yet been investigated. The purpose of this work is therefore to investigate the competitive sorption of *Penicillium brevicompactum* in aqueous binary mixtures of copper(II) and cobalt(II) ions and to describe the two-metal biosorption equilibrium.

Materials and Methods

Microorganisms, culture medium and growth conditions

The fungus used in this study, *Penicillium brevicompactum*, is deposited at the Collection of the Institute of Microbiology at the Bulgarian Academy of Sciences. Spores of a 6- to 7-day-old culture incubated on potato-glucose agar slants at 30 °C were used for inoculation (concentration of spore suspension 10^6/mL).

Cultivation of *Penicillium brevicompactum* was carried out in 500 ml Erlenmeyer flasks with 100 ml growth medium on a rotary shaker at 30 °C. After 24 h cultivation the mycelium was centrifuged (3000 × *g*, 15 min), washed with bidistilled water and used as a biosorbent.

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Heavy metal uptake

Classically, biosorption experiments were carried out in batches as follows: 1 g wet biosorbent was added to 100 ml metal ions solution containing 0.5–4 mM of $CoCl_2 \cdot 6H_2O$ or $CuSO_4 \cdot 5H_2O$ in bidistilled water (pH 5) in Erlenmeyer flasks, which were then agitated at 220 rpm on a rotary shaker for 1 h at 30 °C. In a second set of experiments, for the uptake of heavy metals, the biosorbent was suspended in 100 ml of mixed solution (pH 5) containing equal concentrations of $CoCl_2 \cdot 6H_2O$ and $CuSO_4 \cdot 5H_2O$. The suspension was shaken for 1 h at 30 °C. Then the content of the flasks was separated by filtration using a Whatman No. 1 filter paper. The concentration of the metal ions in the filtrates was determined using an atomic absorption spectrophotometer with an air/acetylene flame (model 2380; Perkin Elmer, Überlingen, Germany).

Uptake of metal ions was calculated from a metal mass balance yielding (Volesky, 1990): $q = V (C_i - C_f)/\text{m M}$, where q is the heavy metal ions uptake (mmol/g dry biomass), V is the sample volume (L), C_i and C_f are the initial and residual metal concentrations (mg/L), respectively, m is the amount of dry biomass (g) and M is the molecular mass of the metal. Control samples with no added biomass were used as blanks.

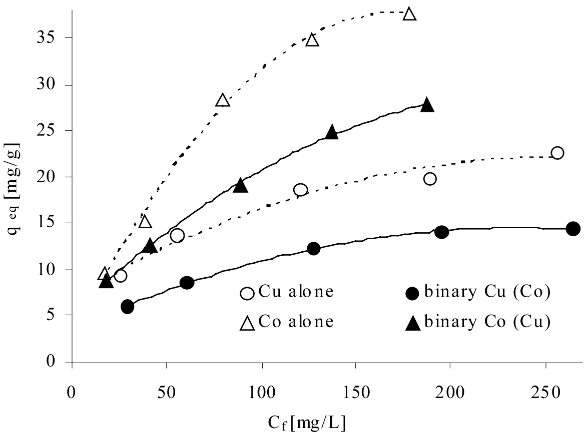

Fig. 1. Copper and cobalt biosorption by *Penicillium brevicompactum.* Initial pH value and biomass concentration in solutions were 5.0 and 1 g/L as dry weight. q_{eq}, equilibrium metal uptake; C_f, residual metal concentration at equilibrium.

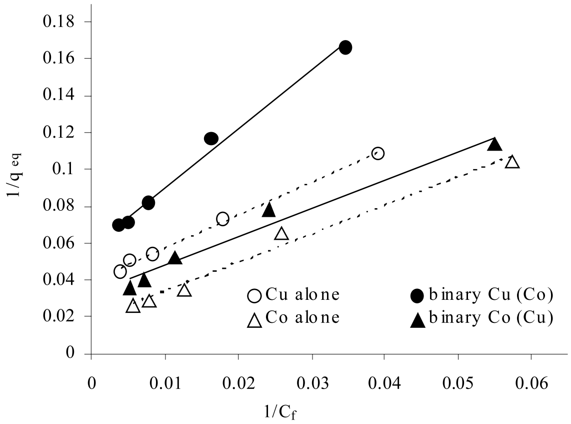

Fig. 2. Langmuir plots of heavy metals adsorption by resting cells of *Penicillium brevicompactum* derived from data shown in Fig. 1.

Results and Discussion

The effect of metal concentration on Cu(II) and Co(II) biosorption by *Penicillium brevicompactum* in a single-metal as well as in binary-metal system is given in Fig. 1. A linear relationship was not observed for any of the cases investigated, but the heavy metal uptake capacities of fungal biomass were directly proportional to the initial metal concentrations. It can be observed from Fig. 1, that there was direct competition for the binding sites between Cu(II) and Co(II) ions in the binary metal system. Co(II) uptake overtook the uptake of Cu(II) at all tested concentrations.

Two different biosorption models were used to correlate the equilibrium data for heavy metals by *Penicillium brevicompactum* (Kargi and Cikla, 2006; Apiratikul *et al.*, 2004). Biosorption equilibrium isotherms showing the relationship between equilibrium uptake q_{eq} vs. residual metal concentration C_f were mathematically expressed by linearized Langmuir and Freundlich models. The values of $1/q_{eq}$ were plotted against the values of $1/C_f$ yielding straight line relationships for each of Cu(II) and Co(II) as individual metal ions and also as binary mixtures (Fig. 2). Similarly the values of log q_{eq} were plotted against the values of log C_f, also giving straight lines for all tested conditions (Fig. 3). The values of q_{max} (maximum biosorption capacity, mg/g) and K_s (saturation constant, mg/L) as derived from the Langmuir isotherms and the Freundlich constants K (capacity constant, mg/g) and n (affinity constant) were obtained from the linear equations of both models.

Table I summarizes the results of the isotherm constants for the models tested. As it is obvious

Table I. Langmuir and Freundlich model parameters for Cu(II) and Co(II) biosorption by resting cells of *Penicillium brevicompactum.*

Metal form	Langmuir parameters			Freundlich parameters		
	q_{max} [mg/g]	K_s [mg/L]	R^2	K [mg/g]	n	R^2
Cu alone	25.32	45.34	0.996	2.83	2.64	0.977
Co alone	54.64	84.41	0.985	1.64	1.60	0.980
Binary Cu (Co)	17.39	55.97	0.992	1.56	2.43	0.978
Binary Co (Cu)	30.96	48.21	0.970	1.98	1.97	0.997

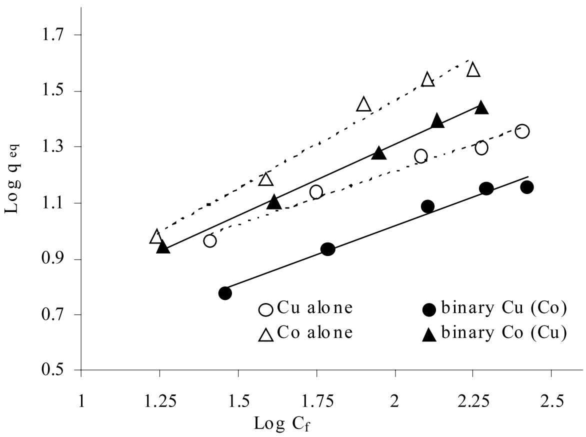

Fig. 3. Freundlich plots of heavy metals adsorption by resting cells of *Penicillium brevicompactum* derived from data shown in Fig. 1.

from Table I, the coefficients of determination (R^2) of both models were close to one indicating that both models adequately describe the experimental data with slightly better performance on the Langmuir model, indicating that the adsorption leads to apparent deposition of a single layer of solute molecules on the adsorbent.

In general, the application of the Langmuir model indicated that the presence of one metal ion in the sorption system always lowers the sorption capacity for the other metal, an apparent case of sorption competition. The total adsorption capacity for the binary mixture was found to be always higher than the adsorption for Cu(II) alone but was almost the same as the adsorption of Co(II) in a single-component system. This indicated that the binding sites for both heavy metals might be the same and the adsorption of Co(II) was more favorable than the one for Cu(II) for this fungus. There are no reported data on Cu(II) and Co(II) biosorption from a binary-metal system to compare our results with. Therefore, as compared to the literature studies on biosorption of Cu(II) as well as Co(II) in a single-metal system, the biosorption capacity of *Penicillium brevicompactum* obtained in this study showed the range of the literature values for both heavy metals (Vijayaraghavan *et al.,* 2004; Gabriel *et al.,* 2001; Churchill *et al.,* 1995). In his examination of the effect of other heavy metal ions on Cu(II) uptake by *Durvillaea potatorum* Kaewsarn (2000) reported that Cu(II) sorption was significantly affected by other heavy metals (Ag^{+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Fe^{2+}, Cd^{2+}, Pb^{2+}) because the binding sites on the biosorbent were limited. So these ions competed simultaneously for the sites. The amount of suppression for Cu(II) uptake depended on the affinity of these ions for binding sites and binding strength of the respective heavy metal ions to the biosorbent. However, the adsorption of mixtures of Cd and Cu, and Pb and Cu did not show a reduction in the total adsorption capacity as described by Apiratikul *et al.* (2004).

The results from this work indicated that there was a complex interaction between each metal species in the biosorbent. This finding is highly important for the design of adsorption systems for actual wastewater containing a mixture of Cu(II) and Co(II) as it provides the adsorption characteristic of the binary component mixture.

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