SORPTION OF COBALT AND ZINC FROM SINGLE AND BINARY METAL SOLUTIONS BY *Evernia prunastri*

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Non-living lichen *Evernia prunastri* was studied as biosorbent material for zinc and cobalt removal from single and binary metal solutions. Sorption equilibrium of Zn^{2+} and Co^{2+} ions was reached within 1 hour. Both cobalt and zinc biosorption was not pH dependent within the range pH 4-6 and negligible at pH 2. The experimental results were fitted to the Langmuir, Freundlich, Redlich-Peterson and Langmuir-Freundlich adsorption isotherms to obtain the characteristic parameters of each model. The Langmuir, Redlich-Peterson and Langmuir-Freundlich isotherms were found to well represent the measured sorption data. According to the evaluation using the Langmuir equation, the maximum sorption capacities of metal ions onto lichen biomass were 112 μmol/g Zn and 97.2 μmol/g Co from single metal solutions. *E. prunastri* exhibited preferential uptake of zinc from equimolar binary Zn^{2+} - Co^{2+} mixtures within the range 50 – 4000 μM. Even thought mutual interference was seen in all Co-Zn binary systems. To evaluate the two-metal sorption system, simple curves had to be replaced by three-dimensional sorption surface. These results can be used to elucidate the behavior of lichens as bioindicators of cobalt and zinc pollution in water and terrestrial ecosystems.

Key words: zinc, cobalt, *Evernia prunastri*, sorption, equilibrium, isotherms

1. Introduction

Sorption processes represent one of the possible mechanisms of interaction of toxic metals in contaminated aquatic systems. Bioremoval of single species of metal ions is affected by several factors such as the specific surface properties of biosorbent, temperature, pH, initial metal ion concentration and biomass concentration. When several metals are present, many other parameters affect the sorption process.

Simple sorption isotherms are usually constructed as a result of studying equilibrium batch sorption behavior of different biosorbent materials. These curves enable quantitative evaluation of biosorption performance of these materials for only one metal (HAMMAINI *et al*., 2003; AKSU and DŐNMEZ, 2006)

When more than one metal at a time is present in a sorption system, evaluation, interpretation, and representation of biosorption results become much more complicated.

The aim of this study was to investigate the ability of the lichen *E. prunastri* growing in Slovak territory to sorb Co^{2+} and Zn^{2+} from single and binary metal solutions. Co-Zn system was chosen as representative of bivalent metals found in industrial effluents. A range of equilibrium adsorption isotherms were obtained to quantitatively describe cobalt and zinc uptake.

2. Materials and methods

2.1 Biomass

Biomass of fruticose lichen *E. prunastri* were taken from the spruces (*Picea abis*) grown in the forest of High Tatras, Slovak Republic. The lichen was washed twice in deionized water and oven-dried at 45°C for 72 h. Cut thallus sections of diameter 3-4 mm were used in experiments.

2.2 Sorption studies

Sorption experiments were carried out in 10 ml solutions ranged from 50 to 4000 µM of Zn^{2+}, Co^{2+} and Zn^{2+}-Co^{2+}, spiked with ^{65}Zn or ^{60}Co. The pH value was adjusted to 4.0. Biomass (50 mg, d.w.) was added, and the content in flasks was agitated on a reciprocal shaker (120 rpm) for 4 h at 20°C. At the end of the experiments radioactivity of both lichen and liquid samples was measured. All experiments were carried out four times. If not otherwise stated, presented data are arithmetic mean values. To calculate the $Q_{\max}$ values and the corresponding parameters of adsorption isotherms (Tab. 1) non-linear regression analysis was performed by the NLREG® software (Statistical analysis program, version 6.3 created by P.H. Sherrod) and ORIGIN 7.0 Professional (OriginLab Corporation, Northampton, USA). The 3-D sorption surfaces were obtained by plotting the experimental Zn and Co equilibrium concentrations C_{eq} on the X and Y axes, against the Co, Zn and total metal uptake Q_{eq} on the Z axis. The STATISTICA 7.0 (StatSoft, Inc., Tulsa, USA) and NLREG® software were used for this purpose.

Table 1. Adsorption isotherm models used in this work.

Isotherm	**Equation**	**Equation No.**	**Adjustable parameters**
Langmuir	$Q_{eq} = \frac{bQ_{\max}C_{eq}}{1+bC_{eq}}$	1	Q_{max}, b
Freundlich	$Q_{eq} = K\ C_{eq}^{(1/n)}$	2	b, n
Redlich – Peterson	$Q_{eq} = \frac{AC_{eq}}{1+B(C_{eq})^{g}}$	3	A, B, g
Langmuir – Freundlich	$Q_{eq} = \frac{Q_{\max}(bC_{eq})^{1/n}}{1+(bC_{eq})^{1/n}}$	4	Q_{max}, b, n
Binary Langmuir	$Q_{eq1} = \frac{b_1Q_{\max}C_{eq1}}{1+b_1C_{eq1}+b_2C_{eq2}}$	5	Q_{max}, b_1,b_2

2.3 Speciation modeling

Prediction of the speciation of Co and Zn in the aqueous systems was performed using the VisualMINTEQ (version 2.52) program. This speciation model allows the calculation of the composition of solutions for specified conditions.

2.4 Radiometric analysis

For radiometric determination of ^{60}Co and ^{65}Zn in liquid samples and lichen biomass, gamma spectrometric scintillation detector 54BP54/2-X with well type crystal NaI(Tl) (Scionix, Netherlands) and data processing software Scintivision32 (Ortec, USA) were used. Standardized $^{60}CoCl_2$ solution (5.181 MBq.ml^{-1}, $CoCl_2$ 20 mg.l^{-1} in 3 g.l^{-1} HCl) and $^{65}ZnCl_2$ (0.8767 MBq.ml^{-1}, $ZnCl_2$ 50 mg.l^{-1} in 3 g.l^{-1} HCl) obtained from Alldeco Inc., Slovakia were used in all experiments.

3. Results and discussion

3.1 Metal uptake

Metals speciation in solution is important in sorption studies since the metal uptake depends on the solution pH. As can be calculated by VisualMINTEQ speciation program, cobalt and zinc in the single and binary solutions at pH 4 occur practically as free cations (>99,5 % Co^{2+}, >98 % Zn^{2+}) (data not shown). The time-course studies on the biosorption of cobalt and zinc ions were performed by contacting Co and Zn solutions with lichen biomass at pH 4.0 and 20 °C. Biosorption of Co^{2+} and Zn^{2+} ions by *E. prunastri* shown in Fig. 1 is a rapid process. Maximum uptakes (approximately 90%) were reached within 1 hour and practically did not change during the next 24 hours.

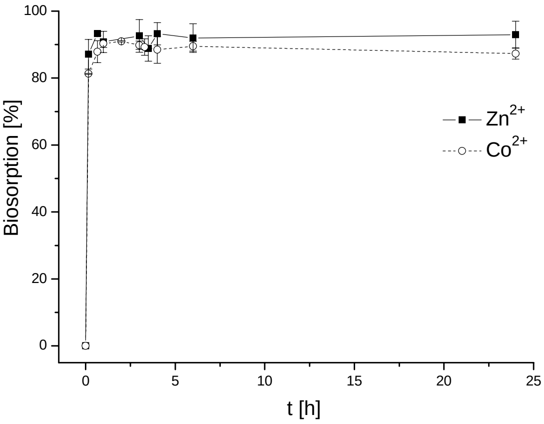

Fig. 1. Biosorption kinetics of Co^{2+} (100 µmol/L, $^{60}CoCl_2$ 89 kBq/L) and Zn^{2+} (100 µmol/L, $^{65}ZnCl_2$ 70 kBq/L) by *E. prunastri* (5 g /L, d.w.) from single metal solutions at 20°C. Initial pH 4.0; pH 4.2 after 24 hours. Error bars represent standard deviation of the mean (n = 4).

Similar adsorption kinetics of Cd^{2+}, Zn^{2+}, Pb^{2+} and Cu^{2+} by lichen *E. prunastri* was observed by ANTONELLI *et al.*, (1998), where equilibrium was reached within a few minutes. The above mentioned results indicate that biosorption of the aforementioned cations was not dependent on metabolic activity. The biosorption process can be attributed to interactions of cations with anionic functional groups on the thallus surface. The thallus surface was supposed to contain ionogenic groups that generate a negative net charge (GARTY, 2001).

3.2 Sorption equilibrium in single metal solution

Analysis of equilibrium data on a specific mathematical equation is of significance for comparing different sorbents under different experimental conditions. Four well known adsorption isotherm models: Langmuir, Freundlich, Redlich-Peterson and Langmuir-Freundlich (see equations in Table 1) were applied for the analysis of the experimental data. These models use parameters that reflect the nature of the sorbent and can be used to compare biosorption performance. Q_{max} represents the maximum sorption capacity, b is a constant related to the energy of adsorption. k and $1/n$ values are the Freundlich constants referring to adsorption capacity and intensity of adsorption, respectively. A, B and g ($0<g<1$) are the Redlich –Peterson constants.

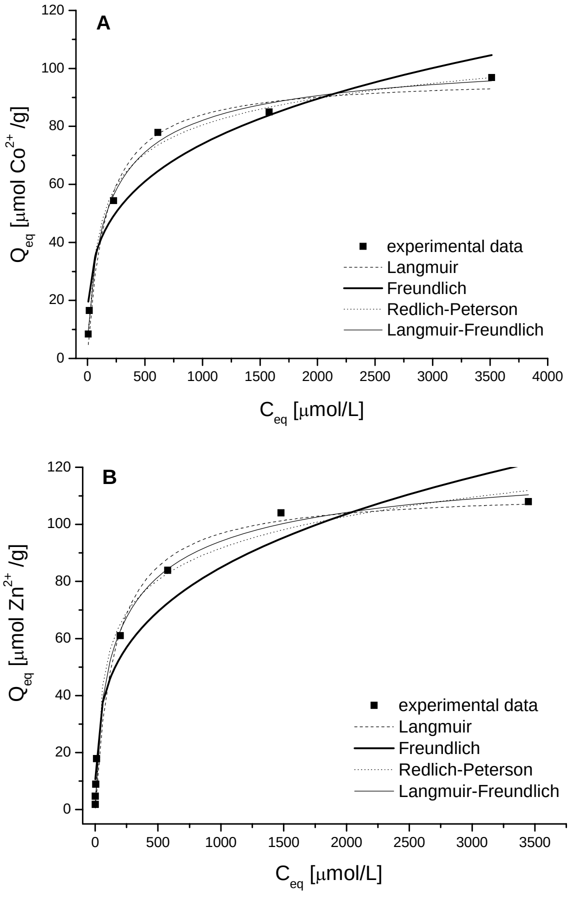

Fig. 2. Fit of the Langmuir, Freundlich, Redlich-Peterson and Langmuir-Freundlich isotherms of cobalt **(A)** and zinc **(B)** sorption by *E. prunastri* (5 g /L, d.w.) from single metal solutions at 20°C. Initial pH 4.0; pH 4.2 after 4 hours.

We found, that the sorption of Co^{2+} and Zn^{2+} ions by *E. prunastri* increased with the increasing concentration of $CoCl_2$ and $ZnCl_2$ in solutions (data not shown) and the equilibrium was reached within 2 hours. Fig. 2 shows the experimental data fitted to the isotherm models for Co (A) and Zn (B) sorption by *E. prunastri* at pH 4 from single metal solutions. The obtained adjustable parameters are shown in Table 2 with the corresponding coefficients of determination. The values of R^2 are generally regarded as a measure of the goodness of fit of experimental data on the isotherm models (Al-ASHEH *et al*., 2000). As can be seen from Table 2, higher coefficients of determination R^2 were obtained for Langmuir-Freundlich ($R^2 = 0.996$ for Co, 0.998 for Zn), Redlich-Peterson ($R^2 = 0.995$ for Co, 0.995 for Zn) and Langmuir ($R^2 = 0.986$ for Co, 0.987 for Zn) models compared to Freundlich isotherm ($R^2 = 0.934$ for Co, 0.952 for Zn). This shows that the Langmuir-Freundlich, Redlich-Peterson and Langmuir isotherms are better fitted to the experimental data of Co^{2+} and Zn^{2+} sorption by *E. prunastri* in the concentration range studied and describe process well and quantitatively. However we draw attention to some published papers stressing that the application of adsorption models are not able to explain the biosorption mechanisms of complex biological systems (DINIZ and VOLESKY, 2005; CORDERO *et al.* 2004).

Estimates of maximum sorption capacities Q_{max} for Co sorption obtained from Langmuir and Langmuir-Freundlich isotherms were 97.2 and 107 μmol/g d.w., respectively (Table 2). The Q_{max} 112 and 127 μmol/g d.w. for Zn sorption was obtained. This indicates higher affinity of *E. prunastri* for Zn than Co sorption from single metal solutions. The sorption capacity for cobalt and zinc by the lichen *E. prunastri* is of the same order of magnitude than that has been found using similar biosorbents such as aquatic mosses (MARTINS et al., 2004), fungi (PAL *et al*., 2006), foliose lichens (OHNUKI *et al*., 2003) and wood fibers (SAEED *et al*., 2005).

Table 2. Adsorption isotherm models and corresponding parameters for Co and Zn sorption by *E. prunastri* from single metal solutions.

Model		Q_{max} [μmol/g]	**b** [L/μmol]	**K** [μmol/g] [L/μmol]$^{1/n}$	**1/n**	R^2
Langmuir	**Co**	97.2 ± 4.5	0.01± 0.001	-	-	0.986
	Zn	112 ± 5.2	0.01 ± 0.001	-	-	0.987
Freundlich	**Co**	-	-	11.0 ± 4.2	0.28 ± 0.05	0.934
	Zn	-	-	11.6 ± 3.6	0.29 ± 0.04	0.952
Langmuir -Freundlich	**Co**	107 ± 6.6	0.02 ± 0.005	-	0.73 ± 0.08	0.996
	Zn	127 ± 6.0	0.03 ± 0.005	-	0.60 ± 0.05	0.998
		A [L/μmol]	**B**	**g** [L/μmol]		
Redlich -Peterson	**Co**	1.22 ± 0.36	0.03 ± 0.01	0.89 ± 0.04	-	0.995
	Zn	2.25 ± 0.72	0.06 ± 0.03	0.86 ± 0.03	-	0.995

3.3 Sorption equilibrium in binary metal solution

Water systems contain the whole spectrum of cations and anions competing for adsorption sites of solid phase. Isotherms suitable for description of single component system are not suitable for prediction of ion equilibrium in multi-component system.

In the case of multi-component systems, evaluation and interpretation in 2D geometry is rather complicated. In such cases, 2D biosorption isotherms have to be replaced by 3D biosorption isotherm surfaces. This approach was successfully used by MA and TOBIN, (2003), HAMMAINI *et al.*, (2002, 2003) and FRAILE *et al.*, (2005).

In our sorption experiments Co-Zn binary system were tested. Binary Langmuir type equations (equations No. 6, 7, 8 in Table 3) were used to fit the experimental data. Parameters obtained by the application of these models are presented in Table 3. Total uptake *Q* (Co+Zn) as a function of equilibrium concentration C_{eq} of cobalt and zinc is presented in Figure 3. Continuous surface represents total metal uptake as predicted by the equation No. 6. Experimental values of total metal uptake are shown as individual data points. At high total metal concentrations in solution sorbent easily reaches the saturation level demonstrated by the plateau of the sorption surface (Figure 3).

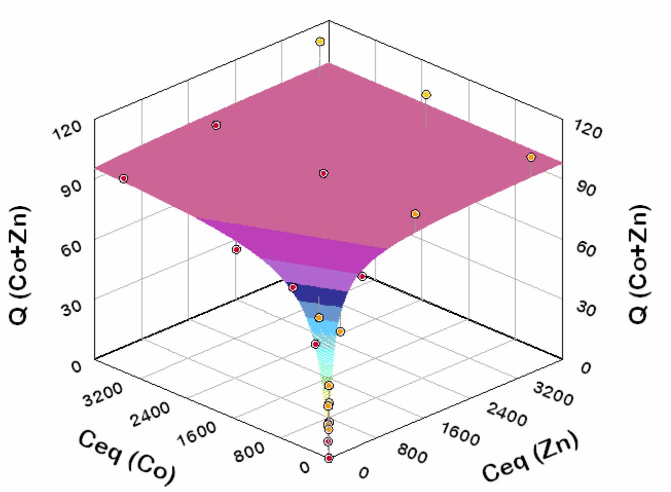

Fig. 3. Two-metal sorption isotherm surface corresponding to the equation No. 6 (Tab. 3). The uptake as a sum of Co + Zn (µmol/g, d.w.) is plotted as a function of the equilibrium concentration of Co and Zn (µmol/L) on X and Y axes.

Table 3. Langmuir parameters derived from binary Langmuir type equations for Zn-Co sorption from binary metal solutions by *E. prunastri*.

Model	**Equation No.**	Q_{max} [µmol/g]	b_{Co} [L/µmol]	b_{Zn} [L/µmol]
$Q(Co+Zn)=\dfrac{Q_{\max}(b_{Co}C_{eqCo}+b_{Zn}C_{eqZn})}{1+b_{Co}C_{eqCo}+b_{Zn}C_{eqZn}}$	6	101 ± 3.4	0.005 ± 0.002	0.012 ± 0.004
$Q(Co)=\dfrac{b_{Co}Q_{\max}C_{eqCo}}{1+b_{Co}C_{eqCo}+b_{Zn}C_{eqZn}}$	7	93.1 ± 3.4	0.008 ± 0.002	0.013 ± 0.003
$Q(Zn)=\dfrac{b_{Zn}Q_{\max}C_{eqZn}}{1+b_{Zn}C_{eqZn}+b_{Co}C_{eqCo}}$	8	115 ± 4.4	0.004 ± 0.001	0.006 ± 0.001

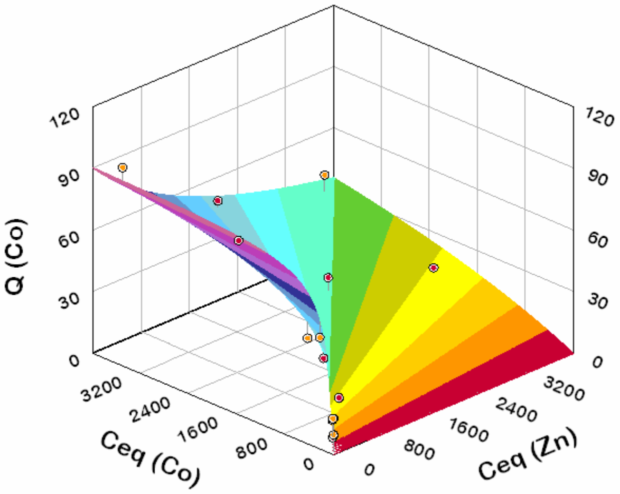

Fig. 4. Two-metal sorption isotherm surface corresponding to equation 7 (Tab. 3). The uptake of Co (μmol/g, d.w.)is plotted as a function of the equilibrium concentration of Co and Zn (μmol/L).

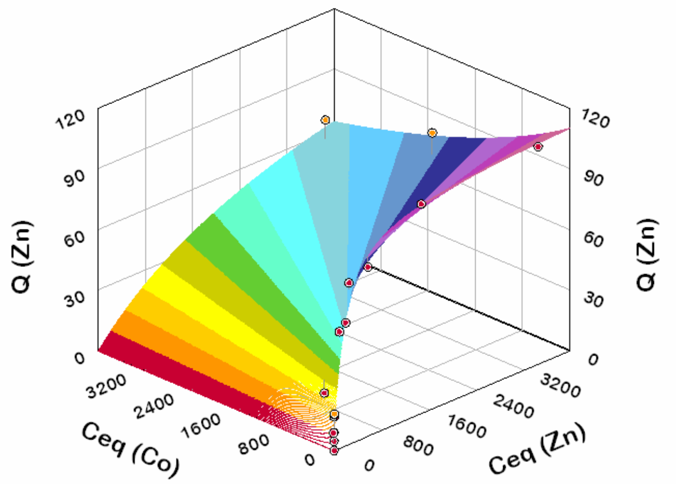

Fig. 5. Two-metal sorption isotherm surface corresponding to equation 8 (Tab. 3). The uptake of Zn (μmol/g, d.w.)is plotted as a function of the equilibrium concentration of Co and Zn (μmol/L).

When metals are present in equimolar concentrations within the range 500 – 4 000 μmol/L, the cobalt to zinc concentration ratio sorbed by biomass is constant with the value [Co]/[Zn] = 0.64. This indicates higher affinity of metal binding sites of *E. prunastri* for Zn^{2+} ions comparing with the affinity to Co^{2+} ions.

The presence of Zn caused a significant decrease in Co sorption capacity which can be seen from Fig. 4. On the contrary, the presence of Co caused only moderately decrease of Zn sorption capacity (Fig. 5). These results also confirm the fact that *E. prunastri* biomass exhibited higher affinity for Zn than for Co. Comparable higher affinity of *Chlorella vulgaris* for Zn sorption from Zn – Ni binary system was described by FRAILE *et al*., (2005).

4. Conclusions

The adsorption capacity of *E. prunastri* for cobalt and zinc is of the same order of magnitude than that has been found using similar biosorbents. According to the evaluation using the Langmuir equation, the maximum sorption capacities of metal ions onto lichen biomass were 112 µmol/g Zn and 97.2 µmol/g Co from single metal solutions.

Sorption of cobalt and zinc from binary solutions was investigated using binary Langmuir equations. *E. prunastri* exhibited higher affinity for Zn. Presented 3D-sorption isotherms showed good agreement with experimental data. It can be concluded that differences in competition effect of individual metals are determine mainly by physico-chemical properties of metal ions, and not in differences in chemical composition of microbial biomass. Chemical composition of biomass will determine the overall sorption capacity Q_{max}.

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