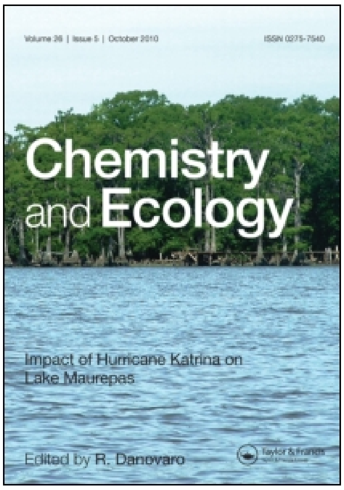

Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

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M. Pipíška[a]; M. Horník[a]; L. Vrtoch[a]; J. Augustín[a]; J. Lesný[a]
[a] Department of Biotechnology, University of SS. Cyril and Methodius, Trnava, Slovak Republic

To cite this Article Pipíška, M. , Horník, M. , Vrtoch, L. , Augustín, J. and Lesný, J.(2008) 'Biosorption of Zn and Co ions by *Evernia prunastri* from single and binary metal solutions', Chemistry and Ecology, 24: 3, 181 — 190
To link to this Article: DOI: 10.1080/02757540802069498
URL: http://dx.doi.org/10.1080/02757540802069498

Chemistry and Ecology
Vol. 24, No. 3, June 2008, 181–190

Biosorption of Zn and Co ions by *Evernia prunastri* from single and binary metal solutions

M. Pipíška*, M. Horník, L. Vrtoch, J. Augustín and J. Lesný

Department of Biotechnology, University of SS. Cyril and Methodius, Trnava, Slovak Republic

(*Received 31 October 2007; final version received 18 February 2008*)

Dried biomass of lichen *Evernia prunastri* was studied as biosorbent for zinc and cobalt removal from single and binary $ZnCl_2$ and $CoCl_2$ solutions. The solution pH significantly influenced both cobalt and zinc biosorption. Maximum uptake was reached at pH 4–6 and negligible biosorption was observed at pH 2. The experimental data were fitted to the adsorption isotherms. The Langmuir, Redlich-Peterson and Langmuir-Freundlich isotherms were found to represent the measured sorption data well. The maximum sorption capacities onto lichen biomass from single metal solutions calculated by Langmuir equation were 112 μmol g^{-1} for Zn and 97 μmol g^{-1} for Co. To evaluate the Zn-Co sorption system, simple curves were replaced by three-dimensional sorption isotherm surfaces. Binary Langmuir type equations were used to fit the experimental data. Results revealed that *E. prunastri* exhibited preferential uptake of zinc from equimolar binary $Zn^{2+} - Co^{2+}$ mixtures.

Keywords: sorption; *Evernia prunastri*; zinc; cobalt; isotherms

1. Introduction

The water resources of the world are being polluted through various anthropogenic activities such as metal mining and metal processing activities. As a result, removal of these contaminants from industrial effluents has become an important priority that is reflected in a tightening and enforcement of environmental regulations. Cobalt is anthropogenically released during ore mining and processing especially in nickel, copper, silver, lead and iron as well as in waste incineration and sewage sludge. Cobalt-60 ($\tau = 5.27$ y) is also present in low-level radioactive wastes and received considerable attention because it has a high energy γ-emission. When wastes were disposed *via* shallow land burial, in many instances, cobalt has migrated in the subsurface more rapidly than expected [1]. Zinc, although it is essential element, can be harmful at concentrations above certain limits. Additionally, zinc, besides metals such as Cu, Ni, Pb and Cr is commonly found in storm water run-off and landfill leachate [2].

Biosorption processes represent one of the possible interactions of toxic metals with biota 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 and

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*Corresponding author. Email: pipiskam@ucm.sk

ISSN 0275-7540 print/ISSN 1029-0370 online

DOI: 10.1080/02757540802069498
http://www.informaworld.com

biomass concentrations. Biosorption of metals is not based on only one mechanism. It consists of several ones that quantitatively and qualitatively differ according to the type of biomass. Metal sequestration may involve complex mechanisms, mainly ion exchange, chelation, adsorption by physical forces and ion entrapment in inter- and intrafibrilar capillaries and spaces of the structural polysaccharide cell wall network [3,4].

Simple sorption isotherms are usually constructed as a result of studying equilibrium batch sorption behaviour of different biosorbent materials. These curves enable quantitative evaluation of biosorption performance of these materials for only one metal [5,6]. Despite this, the majority of biosorption studies have focused on single metal solution. However, 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. With two metals in the solution, instead of two-dimensional biosorption isotherm curves the system evaluation results in a series of three-dimensional sorption isotherm surfaces [7–10]. Sánchez *et al.* [11] pointed out that this approach is very useful particularly because it permits a complete control over the values of the final concentrations of both metals present in the system.

Within this context, the objective of our study was firstly to quantify the ability of the lichen *E. prunastri* biomass to sorb Co^{2+} and Zn^{2+} ions from single and binary solutions. The second objective was to compare cobalt and zinc uptake in single metal systems using a range of equilibrium adsorption isotherms. Finally, binary Langmuir type models were chosen for obtaining quantitative data describing mutual competitive effect of Co^{2+} and Zn^{2+} ions in binary system. The choice of metals was made with regard to their industrial use and potential pollution impact. The lichen used in our study can persist in natural environment for decades of years and represents suitable biological model for biosorption study both in laboratory and field experiments.

2. Materials and methods

2.1. *Biomass*

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

2.2. *Sorption studies*

Sorption experiments were carried out in 10 ml solutions ranging from 50 to 4000 μM of Zn^{2+}, Co^{2+} and $Zn^{2+}- Co^{2+}$, spiked with ^{65}Zn or ^{60}Co and adjusted to pH 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 biomass and liquid phase 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 (Table 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 3D 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 for single metal systems 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	$Q_{eq} = KC_{eq}^{(1/n)}$	(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

2.3. *Effects of pH*

Lichen biomass was shaken in Co^{2+} and Zn^{2+} solutions of desired pH spiked with ^{65}Zn a ^{60}Co for 4 h on a reciprocal shaker at 120 rpm and 20°C. In order to eliminate interference of buffer components on biosorption, the non-buffered solutions in deionised water were adjusted to the desired pH values by adding 0.5 M HCl or 0.1 M NaOH throughout the entire study. This approach was also successfully used by other authors [12] and in our previous paper [13].

2.4. *Speciation modelling*

Prediction of the speciation of Co and Zn in the aqueous systems as a function of total salt concentration and solution pH was performed using the VisualMINTEQ (version 2.52) program. This speciation model allows the calculation of the composition of solutions for specified conditions.

2.5. *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. Standardised $^{60}CoCl_2$ 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) were obtained from the Czech Institute of Metrology, Prague (Czech Republic).

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 solutions at pH 4 occur practically as free cations (>99.4 % Co^{2+}, >97.6% Zn^{2+}) in concentration range studied. Data sets were calculated considering the carbonate system naturally in equilibrium with atmospheric CO_2 ($pCO_2 = 10^{-3.5}$ atm).

The time-course studies on the biosorption of cobalt and zinc ions were performed by contacting $CoCl_2$ and $ZnCl_2$ solutions with lichen biomass at pH 4.0 and 20°C. Biosorption of Co^{2+} and Zn^{2+} ions by *E. prunastri* is a rapid process. Maximum metal uptake, approx. 90% at biomass concentration 5.0 g l^{-1} and $C_0 = 0.1$ mmol l^{-1} $ZnCl_2$ or $CoCl_2$ were reached within 2 h. After this time there was no considerable increase during the next 22 h. Similar adsorption kinetics of Cd^{2+}, Zn^{2+}, Pb^{2+} and Cu^{2+} by lichen *E. prunastri* was observed by Antonelli *et al.* [14], where equilibrium was reached within a few minutes. The mechanism of short-term cation uptake by lichens is generally regarded as an abiotic process governed by surface complexation of cations with exposed functional groups on the lichen surface, or by the precipitation of solid phases on the cell walls [13]. It is known that the thallus surface contains ionogenic groups such as carboxyl, phenolic and alcoholic hydroxyl, and phosphate that generate a negative net charge [15]. Ulouzlu *et al.* [16] using FT-IR analysis confirmed that carboxyl and hydroxyl groups participate in Pb^{2+} and Cr^{3+} biosorption by lichen *Parmelina tiliaceae*. Valuable results can be found in the study by Ohnuki *et al.* [17]. By using μ-PIXE (particle induced X-ray emission) analysis they observed that cobalt concentration in foliose lichen *Parmotrema tinctorum* decreased in the order lower surface > upper surface, medullary layer > algal layer.

3.2. *Effect of pH*

To establish the effect of pH on the sorption of Co^{2+} and Zn^{2+} from single metal systems onto *E. prunastri* biomass, batch equilibrium studies at different pH values were carried out, and the results are shown in Figure 1. It can be seen that maximum biosorption of both Co^{2+} and Zn^{2+} occurred at pH of 4–6 after incubation for 4 h. Observed slightly lower biosorption at pH 3 and negligible at pH 2 can be explained by protonation of active sites, resulting in competition between H^+ and Co^{2+} or Zn^{2+} ions for occupancy of the binding sites [18]. Ohnuki *et al.* [17] also observed that cobalt sorption by foliose lichen *Parmotrema tinctorum* was the highest at pH 3–5. The strong pH dependence of uranium uptake by the lichen *Peltigera membranacea* was shown by Haas *et al.* [19]. Maximum U uptake occurred at an initial fluid pH of 4–5, and precipitously decreased at more acidic and more basic conditions. The dependence of metal uptake on pH is related to both the surface functional groups on the biomass cell walls and to the metal speciation chemistry in solution. The pH value can change the state of the active-binding sites, which are usually acidic. Their protonation and consequently their availability can change dramatically if the pH varied by 1 or 2 units [20].

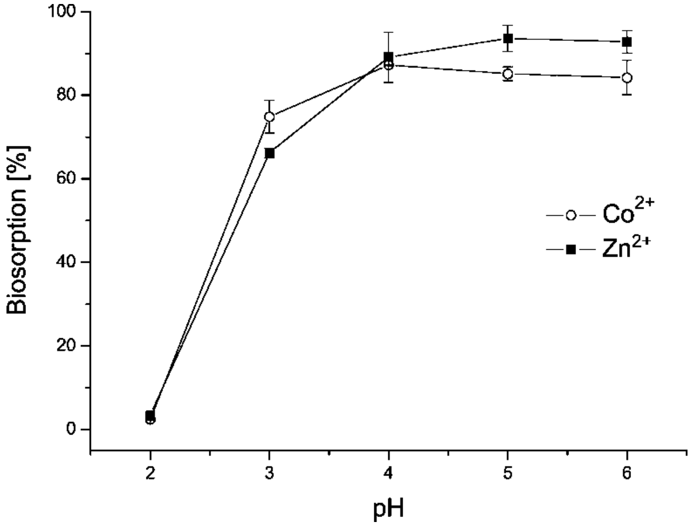

Figure 1. Effect of pH on the biosorption of Zn^{2+} (100 μmol l^{-1} $ZnCl_2$, $^{65}ZnCl_2$ 70 kBq l^{-1}) and Co^{2+} ions (100 μmol l^{-1} $CoCl_2$, $^{60}CoCl_2$ 89 kBq l^{-1}) by *E. prunastri* (5 g l^{-1}, d.w.) from single metal solutions after 4 h interaction at 20°C. Error bars represent standard deviation (SD) of the mean ($n = 4$).

3.3. *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 upon complete saturation of the sorbent, 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. Simplicity and easy interpretability are some of the important reasons for the extensive use of these models. Moreover, linear regression has been frequently used to evaluate the model parameters. However, transformations of nonlinear equations to linear forms usually result in parameter estimation error and distort the fit [21]. For that reason, nonlinear methods for parameters estimation were used in our work.

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 h. Figure 2(A) and 2(B) show the experimental data fitted to the isotherm models for Co^{2+} and Zn^{2+} 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 [22,23]. 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 the process well and quantitatively. However, we draw attention to some published papers stressing that the application of adsorption models is not able to explain the biosorption mechanisms of complex biological systems [8,24].

Estimates of maximum sorption capacities Q_{max} for Co sorption obtained from Langmuir and Langmuir-Freundlich isotherms were 97 and 107 μmol g^{-1} d.w., respectively (Table 2). The Q_{max} 112 μmol g^{-1} d.w. (Langmuir isotherm) and 127 μmol g^{-1} d.w. (Langmuir-Freundlich isotherm) for Zn sorption were obtained. This indicates higher affinity of *E. prunastri* for Zn than Co sorption from single metal solutions. Moreover, this is consistent with the idea that difference in sorption capacity under similar environmental conditions could be attributed to different ionic characteristics of metal ions [7,25]. Chen and Wang [26] demonstrated that metal uptake capacities of divalent cations by *Saccharomyces cerevisiae* increased with increase of atomic number, covalent index and atomic weight in the order $Ni^{2+} < Sr^{2+} < \mathbf{Co}^{2+} < Cd^{2+} < \mathbf{Zn}^{2+} < Cu^{2+} < Pb^{2+}$.

Sorption capacities for cobalt and zinc by the lichen *E. prunastri* are of the same order of magnitude than those have been found using other biosorbents such as aquatic mosses [27], fungi [28], foliose lichens [13,17] and wood fibers [18].

3.4. *Sorption equilibrium in binary metal solution*

Since industrial effluents contain several metals, it is necessary to study the simultaneous sorption of two or more metals and also to quantify the interference of one metal with the sorption of the other. 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, 3D biosorption isotherm

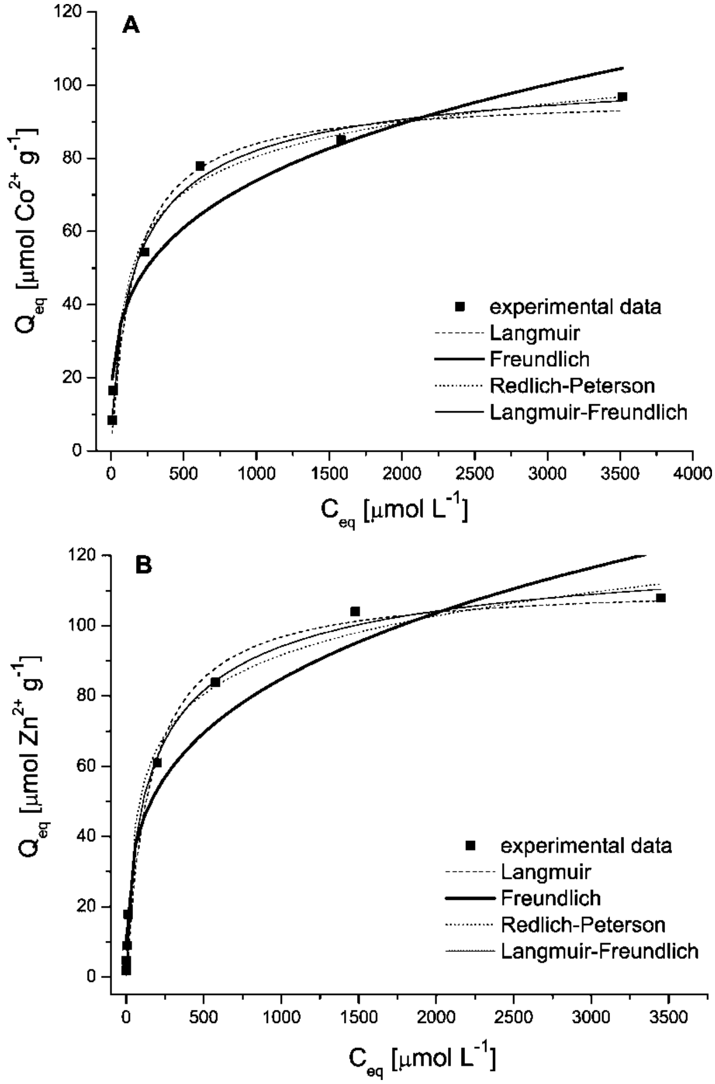

Figure 2. Fit of the Langmuir, Freundlich, Redlich-Peterson and Langmuir-Freundlich isotherms of cobalt (A) and zinc (B) sorption by *E. prunastri* (5 g l^{-1}, d.w.) from single metal solutions after 4 h interaction at 20°C. Initial pH 4.0.

surfaces are the most appropriate and correct way of representing the sorption equilibrium of two metal systems [9]. This approach was successfully used by Ma and Tobin [29], Hammaini *et al.* [5,30], Romera *et al.* [7], Fraile *et al.* [8] and Fiol *et al.* [10].

In our sorption experiments Co-Zn binary system were tested. Binary Langmuir type equations (Equations (5, 6, and 7) in Table 3) were used to fit the experimental data. Parameters obtained by the application of these models are presented in Table 3. Because Langmuir constant *b* is related to the energy of adsorption through the Arrhenius equation, the higher *b* represents the higher affinity of the sorbent for the sorbate. 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 (5). 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 5).

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^{-1}]	b [l μmol^{-1}]	K [l g^{-1}]	$1/n$	R^2
Langmuir	Co	97 ± 5	0.006 ± 0.001	–	–	0.986
	Zn	112 ± 5	0.007 ± 0.001	–	–	0.987
Freundlich	Co	–	–	11 ± 4	0.28 ± 0.05	0.934
	Zn	–	–	12 ± 4	0.29 ± 0.04	0.952
Langmuir-Freundlich	Co	107 ± 7	0.020 ± 0.005	–	0.73 ± 0.08	0.996
	Zn	127 ± 6	0.030 ± 0.005	–	0.60 ± 0.05	0.998
		A [l μmol^{-1}]	B	g [l μmol^{-1}]		
Redlich-Peterson	Co	1.2 ± 0.4	0.03 ± 0.01	0.89 ± 0.04	–	0.995
	Zn	2.3 ± 0.7	0.06 ± 0.03	0.86 ± 0.03	–	0.995

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^{-1}]	b_{Co} [l μmol^{-1}]	b_{Zn} [l μmol^{-1}]
$Q(Co+Zn) = \dfrac{Q_{max}(b_{Co}C_{eqCo} + b_{Zn}C_{eqZn})}{1 + b_{Co}C_{eqCo} + b_{Zn}C_{eqZn}}$	(5)	101 ± 3	0.005 ± 0.002	0.012 ± 0.004
$Q(Co) = \dfrac{b_{Co}Q_{max\,Co}C_{eqCo}}{1 + b_{Co}C_{eqCo} + b_{Zn}C_{eqZn}}$	(6)	93 ± 3	0.008 ± 0.002	0.013 ± 0.003
$Q(Zn) = \dfrac{b_{Zn}Q_{max\,Zn}C_{eqZn}}{1 + b_{Zn}C_{eqZn} + b_{Co}C_{eqCo}}$	(7)	115 ± 4	0.004 ± 0.001	0.006 ± 0.001

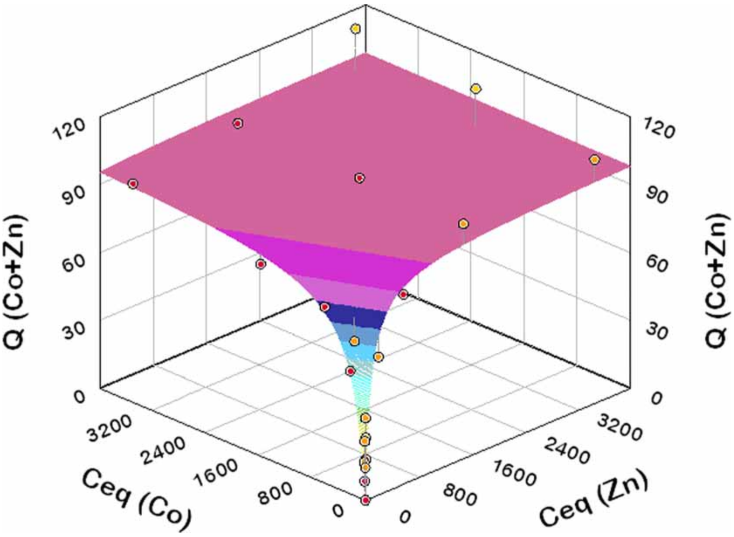

Figure 3. Two-metal sorption isotherm surface corresponding to the Equation (5) (Table 3). The uptake as a sum of Co + Zn (μmol g^{-1}, d.w.) is plotted as a function of the equilibrium concentration of Co and Zn (μmol l^{-1}) on X and Y axes.

When metals are present in equimolar concentrations within the range 500 – 4 000 μmol l^{-1}, the ratio of cobalt to zinc sorbed by biomass is constant with the value [Co]/[Zn] = 0.64. In all cases b_{Zn} was higher than b_{Co}, what indicates higher affinity of metal binding sites of *E. prunastri* for Zn^{2+} ions comparing with the affinity to Co^{2+} ions (Table 3).

The presence of Zn^{2+} caused a significant decrease in Co^{2+} sorption capacity even at lower concentrations of zinc, which can be seen from Figure 4. On the contrary, the presence of Co^{2+} caused only moderately decrease of Zn^{2+} sorption capacity (Figure 5). These results also confirm the fact that *E. prunastri* biomass exhibited higher affinity for Zn than for Co. Comparable higher

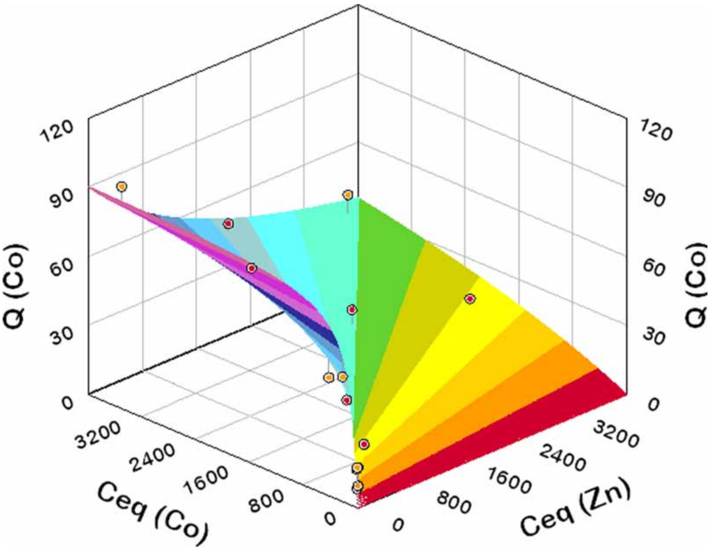

Figure 4. Two-metal sorption isotherm surface corresponding to Equation (6) (Table 3). The uptake of Co (μmol g^{-1}, d.w.) is plotted as a function of the equilibrium concentration of Co and Zn (μmol l^{-1}).

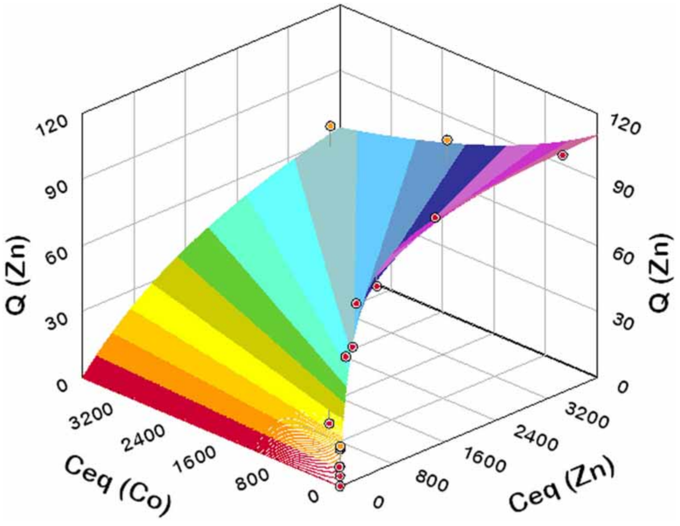

Figure 5. Two-metal sorption isotherm surface corresponding to Equation (7) (Table 3). The uptake of Zn (μmol g^{-1}, d.w.) is plotted as a function of the equilibrium concentration of Co and Zn (μmol l^{-1}).

affinity of *Chlorella vulgaris* for Zn sorption from Zn – Ni binary system was described by Fraile *et al.* [8] and Romera *et al.* [7].

4. Conclusions

Cobalt and zinc biosorption by lichen *E. prunastri* is a rapid, pH dependent process. Maximum uptake of both metals was found to occur at pH 4 to 6. Sorption capacities of *E. prunastri* for cobalt and zinc are of the same order of magnitude than those have been found using other biosorbents. According to the evaluation using the Langmuir equation, the maximum sorption capacities of metal ions onto lichen biomass from single metal solutions were 112 μmol g^{-1} Zn and 97 μmol g^{-1} Co.

Sorption of cobalt and zinc from binary metal solutions was described by binary Langmuir equations. Presented 3D sorption isotherms showed a good agreement with experimental data. *E. prunastri* exhibited higher affinity for Zn^{2+} than for Co^{2+} ions from both single and binary solutions. It can be concluded that competition effects of these metals are determined mainly by physico-chemical characteristics of metal ions. However, the overall sorption capacities are related not only to the characteristics of metals but will depend also on the type of biomass used.

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