

Scientific paper

# Biosorption of Cadmium, Cobalt and Zinc by Moss *Rhytidiadelphus squarrosus* in the Single and Binary Component Systems

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## Abstract

Biomass of moss *Rhytidiadelphus squarrosus* was studied as a potential biosorbent for cadmium, cobalt and zinc removal from single and binary solutions. It was shown that solution pH significantly influenced Cd, Co and Zn biosorption. Maximum uptake was reached at pH 5.0–6.0 and negligible biosorption was observed at pH 2.0. Experimental equilibrium biosorption data for cadmium, cobalt and zinc were analysed by the Langmuir and Freundlich isotherm models. The Langmuir isotherm was found to well represent the measured sorption data in single metal systems. The maximum sorption capacities  $Q_{max}$  onto moss biomass were 186  $\mu\text{mol/g}$  for Zn, 173  $\mu\text{mol/g}$  for Cd and 123  $\mu\text{mol/g}$  for Co. Results revealed that the presence of Cd more significantly decreased the sorption of Co in binary Cd-Co mixtures than vice versa. In Cd-Zn binary system, both cadmium and zinc were sorbed with equal efficiency. The competitive Langmuir equations were used to fit the experimental data from the Zn-Cd and Cd-Co binary systems and simple two-dimensional isotherm curves were replaced by three-dimensional sorption isotherm surfaces.

**Keywords:** Metals, biosorption, competitive biosorption, *Rhytidiadelphus squarrosus*, isotherms

## 1. Introduction

The removal of toxic metals from industrial wastewaters and aquatic environment is an important environmental issue to be solved today. Biosorption processes represent one of the possible interactions of toxic metals with biological systems in contaminated environment. 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 biomass concentrations.<sup>1,2</sup> Biosorption of metals is not based on only one mechanism. It consists of several mechanisms that quantitatively and qualitatively differ according to the type of biomass. Metal sequestration may involve the complex mechanisms, mainly ion exchange, chelation, adsorption by physical forces and ion entrapment in inter- and intrafibrillar capillaries and spaces of the structural polysaccharide cell wall network.<sup>3,4</sup>

While much research has been carried out on the uptake of single metal species, little attention seems to have

been given to the study of multi-metal systems. Since industrial effluents can contain several metals, it is necessary to study the simultaneous sorption of two or more metal ions and also to quantify the mutual effect of one metal on the other. Therefore to ensure the applicability of biosorption technology, more works are still needed for the sorption of a mixture of metals at various operating conditions.<sup>5</sup>

To optimize the design of the sorption system (either single or multi-component) it is important to establish the most appropriate correlation for the equilibrium isotherms. Various simple isotherm models suitable for description of single component system are not suitable for prediction of ion equilibrium in multi-component system.<sup>6</sup> They are unable to describe the sorption behavior of primary metal ion as a function of the concentration of both metal ions in the binary metal solution. For this purpose multi-component isotherm equations have been used. Recent reports on the sorption of multi-metal systems include that of Srivastava et al<sup>7</sup> who studied the

simultaneous sorption of  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  by rice husk ash using multi-component Langmuir and Freundlich adsorption isotherms. They found that the extended Freundlich model could be used to describe the sorption equilibrium in binary system. Romera et al.<sup>8</sup> used binary Langmuir type equations to describe the sorption of  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  in binary, ternary and multi-metallic systems by brown alga *Fucus spiralis*. Papageorgiou et al.<sup>9</sup> found that the extended predictive Langmuir isotherm accurately predicted the experimental data from  $\text{Cu}^{2+}$ - $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ - $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ - $\text{Cd}^{2+}$  binary systems. The extended Sips, Sheindorf-Rebuhn-Sheintuch (SRS) and Redlich – Peterson multi-component models as well as Ideal Adsorbed Solution Theory (IAST) were also employed to evaluate multi-component data.<sup>9–12</sup> In general, although the binary sorption could be described using various isotherm models, the extended competitive Langmuir model was more commonly used than the others.<sup>8,13,14</sup> In the case of multi-component systems, evaluation and interpretation in 2-D geometry is rather complicated. In such cases, 3-D biosorption isotherm surfaces are more appropriate and correct way of representing the sorption equilibrium of two metal systems.<sup>15</sup> This approach was successfully used by Ma and Tobin<sup>16</sup>, Hammami et al.<sup>17</sup> and Fraile et al.<sup>18</sup>

Within this context, the objective of our study was firstly to quantify the ability of the moss *R. squarrosus* to sorb  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  ions from single and binary solutions using radiometric analysis. The second objective was to compare the affinity of biosorbent for the above mentioned ions in binary metal systems Cd-Co and Cd-Zn. Finally, binary competitive Langmuir equations were chosen for describing mutual competitive effect of  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  ions in binary systems and three-dimensional sorption isotherm surfaces for each binary system were generated. The choice of metals was made with regard to their industrial use and potential pollution impact.

## 2. Experimental

### 2.1. Biosorbent Preparation

Biomass of moss *R. squarrosus* was collected in June 2008 from the forests of High Tatras Mountains, Slovak Republic. The biomass was washed twice in deionised water, oven-dried for 72 h at a maximum of 45 °C to avoid the degradation of binding sites. After drying, the biomass was milled and sieved. The 300 – 600  $\mu\text{m}$  particle size was used in biosorption experiments.

### 2.2. Batch Experiments for Single-metal Systems

Batch biosorption experiments in single-metal systems were carried out in solutions ranged from 100 to 4000  $\mu\text{M}$  of  $\text{CdCl}_2$ ,  $\text{CoCl}_2$  or  $\text{ZnCl}_2$  in deionised water, spiked with  $^{109}\text{CdCl}_2$ ,  $^{65}\text{ZnCl}_2$  or  $^{60}\text{CoCl}_2$  and adjusted to

pH 4.0 and 6.0. Biomass (2.5 g/L, d.w.) was added to 8 ml of solution, and the content in Erlenmeyer flasks was agitated on a reciprocal shaker (Multi-shaker PSU 20, Biosan) at 120 rpm for 4 h at 20 °C. Contact time 4 h was sufficient to reach equilibrium which was shown in preliminary experiments. At the end of each experiment biomass was filtered out, washed twice with deionised water and radioactivity of both moss biomass and liquid phase was measured. This approach was also successfully used in research published in our previous papers.<sup>19,20</sup> The metal uptake was calculated as

$$Q = \frac{V(C_0 - C_{eq})}{m} \quad (1)$$

where  $Q$  is the uptake ( $\mu\text{mol/g}$ ),  $C_0$  and  $C_{eq}$  are the initial and the final metal concentrations in solution ( $\mu\text{mol/L}$ ) and  $m$  is the amount of dried biosorbent (given in grams).

### 2.3. Batch Experiments for Binary-metal Systems

Batch biosorption experiments in binary-metal systems were carried out in series of solutions (Cd-Zn or Cd-Co) containing each metal in concentrations varying from 100 to 4000  $\mu\text{M}$  in various molar ratios 2:1, 1:1, 1:2 spiked with  $^{109}\text{CdCl}_2$ ,  $^{60}\text{CoCl}_2$  or  $^{65}\text{ZnCl}_2$  and adjusted to pH 6.0 with 0.1 M NaOH. Metal solutions were prepared by dissolving  $\text{CdCl}_2$ ,  $\text{CoCl}_2$  and  $\text{ZnCl}_2$  in deionised water to the desired initial concentrations. Biomass (2.5 g/L, d.w.) was added, and the content in Erlenmeyer flasks was agitated on a reciprocal shaker (120 rpm) for 4 h at 20 °C. At the end of each experiment biomass was filtered out, washed twice with deionised water and radioactivity of both moss biomass and liquid phase was measured. All experiments were performed in duplicate. If not otherwise stated, presented data are arithmetic mean values.

### 2.4. Effects of pH

The moss biomass sample was shaken in  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$  or  $\text{Zn}^{2+}$  solutions of desired pH spiked with  $^{109}\text{CdCl}_2$ ,  $^{65}\text{ZnCl}_2$  and  $^{60}\text{CoCl}_2$  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.

### 2.5. Speciation Modeling

Prediction of the Cd, Co and Zn speciation in the aqueous systems as a function of total salt concentration and solution pH was performed using the Visual Minteq version 2.53.<sup>21</sup> The programme has an extensive thermodynamic database for the calculation of metal speciation, solubility and equilibrium.

## 2. 6. Radiometric Analysis

For radiometric determination of  $^{109}\text{Cd}$ ,  $^{60}\text{Co}$  and  $^{65}\text{Zn}$  in liquid samples and biomass, gamma spectrometric scintillation detector 54BP54/2-X and 76BP76/3 with well type crystal NaI(Tl) (Scionix, Netherlands) and data processing software Scintivision32 (Ortec, USA) were used. Standardized  $^{109}\text{CdCl}_2$  (3.857 MBq/mL,  $\text{CdCl}_2$  50 mg/L in 3 g/L HCl),  $^{60}\text{CoCl}_2$  (5.181 MBq/mL,  $\text{CoCl}_2$  20 mg/L in 3 g/L HCl) and  $^{65}\text{ZnCl}_2$  (0.8767 MBq/mL,  $\text{ZnCl}_2$  50 mg/L in 3 g/L HCl) solutions were obtained from the Czech Institute of Metrology (Prague, Czech Republic).

## 2. 7. Data Analysis

To calculate the maximum sorption capacities  $Q_{max}$  values and the corresponding parameters of adsorption isotherms non-linear regression analysis was performed by the ORIGIN 7.0 Professional (OriginLab Corporation, Northampton, USA). The 3-D sorption surfaces for each binary system were obtained by plotting the experimental metal equilibrium concentrations  $C_{eq}$  on the X and Y axes, against the metal uptake  $Q_{eq}$  on the Z axis. The TableCurve 3D 4.0 (Systat Software, Inc., Chicago, USA) software was used for this purpose. The corrected Akaike's information criterion (AICc), residual sum of squares (RSS), coefficients of determination between theoretical and experimental values ( $R^2$ ) and root mean squared errors (RMSE), were used to assess the goodness-of-fit.

## 3. Results and Discussion

### 3. 1. Metal Uptake

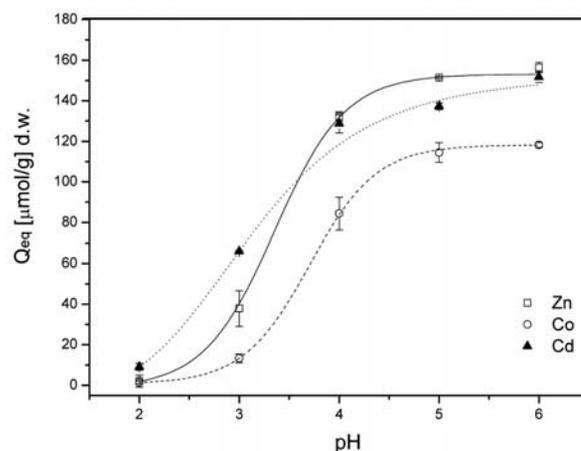
Metals speciation in solution is important in biosorption processes since the metal uptake depends on the solution pH. According to the Visual Minteq speciation results (data not shown), cobalt and zinc in the single and binary systems Co-Cd and Zn-Cd at pH 6.0 occur practically as free cations (>99.4 %  $\text{Co}^{2+}$ , >97.8%  $\text{Zn}^{2+}$ ) in the concentration range studied. Cadmium in single and Co-Cd or Zn-Cd binary systems occurs as free divalent cation  $\text{Cd}^{2+}$  and  $\text{CdCl}^+$  cation. At pH 6.0, free  $\text{Cd}^{2+}$  form ranged between 98% and 55.4% of the total cadmium within concentration range 100–4000  $\mu\text{M}$ , while  $\text{CdCl}^+$  increased from 3% to 43%.  $\text{CdCl}_2$  (aq) form represent max. 1.9% in concentration range studied. The speciation of cadmium is very similar in both Cd-Co and Cd-Zn binary systems. Data sets were calculated considering the carbonate system naturally in equilibrium with atmospheric  $\text{CO}_2$  ( $p\text{-CO}_2 = 38.5 \text{ Pa}$ ).

The time-course studies of the biosorption of cadmium, cobalt and zinc ions from single systems showed that sorption of metal ions by moss *R. squarrosus* is a rapid process. Similar kinetic behaviours were observed for

all experiments (data not shown) and equilibrium was reached within one hour. The mechanism of short-term metal cations uptake by moss is generally regarded as an abiotic process<sup>22</sup> governed by surface complexation of cations with exposed functional groups (such as carboxyl-, sulfhydryl- and amino- group) on the moss surface, coordination and chelation of metals, ion exchange, adsorption or by the precipitation of solid phases on the cell walls. Sari et al<sup>23</sup> using FTIR analysis confirmed that carboxyl and hydroxyl groups participate in  $\text{Pd}^{2+}$  biosorption by moss *Racomitrium lanuginosum*. It was reported in another study that the same functional groups of terrestrial moss *Pleurozium schreberi* was responsible for metal-binding capacity.<sup>24</sup> Due to the complexity of biomaterials, it is probable that at least some of the above-mentioned mechanisms are acting simultaneously, to varying degrees, depending on the biosorbent and the solution chemistry. The same conclusions were also postulated by Sheng et al.<sup>25</sup>

### 3. 2. Effect of Initial pH on Metal Sorption

To establish the effect of pH on the  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$  or  $\text{Zn}^{2+}$  sorption onto *R. squarrosus* biomass from single metal systems, batch equilibrium studies at different pH values were carried out, and the results are shown in Fig. 1. Analysis of the experimental data shows that maximum biosorption of  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$  occurred at pH of 5.0 and 6.0 after 4 h incubation. Observed lower biosorption at pH 3.0 and negligible at pH 2.0 can be explained by protonation of active sites, resulting in competition between  $\text{H}^+$  and  $\text{Cd}^{2+}$ ,  $\text{H}^+$  and  $\text{Co}^{2+}$  or  $\text{H}^+$  and  $\text{Zn}^{2+}$  for occupancy of the binding sites.<sup>26</sup> The pH value can change the state of the binding sites, which are usually acidic. Their protonation and consequently their availability can chan-



**Figure 1.** Effect of initial pH on  $\text{Cd}^{2+}$  (1000  $\mu\text{mol/L}$   $\text{CdCl}_2$ , 90 kBq/L  $^{109}\text{CdCl}_2$ ),  $\text{Co}^{2+}$  (1000  $\mu\text{mol/L}$   $\text{CoCl}_2$ , 75 kBq/L  $^{60}\text{CoCl}_2$ ) and  $\text{Zn}^{2+}$  (1000  $\mu\text{mol/L}$   $\text{ZnCl}_2$ , 63 kBq/L  $^{65}\text{ZnCl}_2$ ) biosorption by moss *R. squarrosus* (2.5 g/L; d.w.) after 4 h incubation at 20 °C. Error bars represent standard deviation (SD) of the mean (n = 3).

ge dramatically if the pH varied by 1 or 2 units.<sup>27</sup> Our recent research showed similar effects of pH on Co<sup>2+</sup> and Zn<sup>2+</sup> sorption by lichen *Evernia prunastri*.<sup>20</sup> Also Martins et al<sup>28</sup> observed maximum biosorption of Cd<sup>2+</sup> and Zn<sup>2+</sup> at pH 5.0 and 6.0 using aquatic moss *Fontinalis antipyretica*.

At higher pH values (pH > 8.0) cobalt exists mainly as [Co(OH)]<sup>+</sup> form and therefore it becomes difficult to distinguish between sorption and precipitation. Similarly, insoluble cadmium and zinc species occurred at pH > 9.0. It is reasonable to suppose that the dependence of metal uptake on pH is related to both the surface functional groups on the biomass cell walls and the metal speciation in solution. Moreover, extreme pH values can damage the structure of biosorbent and therefore decrease metal uptake.<sup>29</sup>

### 3. 3 Equilibrium Modeling in Single Systems

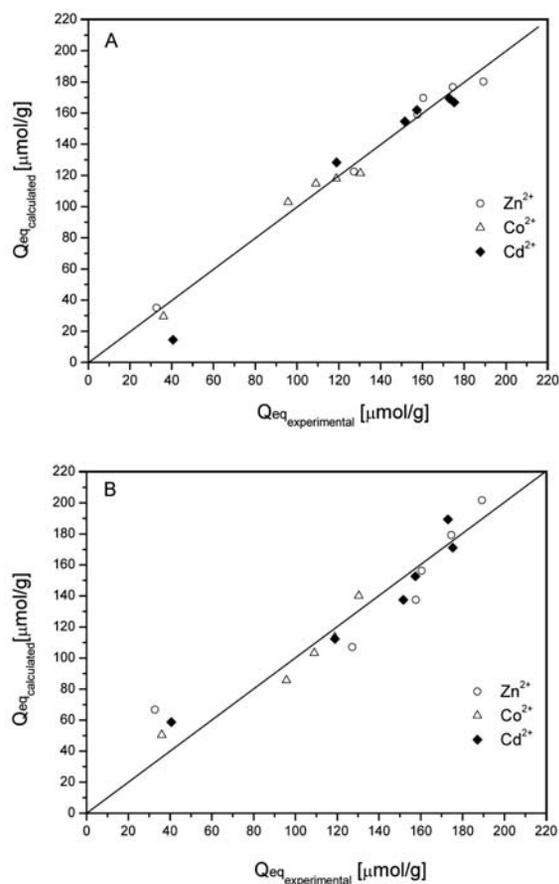
Analysis of equilibrium data on a specific mathematical equation is of significance for comparing different sorbents under different experimental conditions. The two well known adsorption isotherm models Langmuir (2) and Freundlich (3) were applied for the analysis of the experimental data in single sorption systems.

$$Q_{eq} = \frac{bQ_{max}C_{eq}}{1 + bC_{eq}} \quad (2)$$

$$Q_{eq} = KC_{eq}^{(1/n)} \quad (3)$$

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. The Langmuir and Freundlich isotherm were fitted to the equilibrium data for Cd<sup>2+</sup>, Co<sup>2+</sup> and Zn<sup>2+</sup> biosorption on moss *R. squarrosus*. Parameters of the models determined from the experimental data using non-linear regression are reported in Table 1.

The experimental and calculated  $Q_{eq}$  values for biosorption of Cd<sup>2+</sup>, Co<sup>2+</sup> and Zn<sup>2+</sup> ions by using the Langmuir and Freundlich isotherms are shown in scattered plots (Fig. 2). Since most of the data points are distributed around the line, this indicates that both Langmuir and Freundlich isotherms could represent the experimental sorption data well. The adequacy of the two models was also compared by using the corrected Akaike's informa-



**Figure 2.** Correlation between calculated and experimental sorption equilibrium capacities  $Q_{eq}$  using the Langmuir (A) and Freundlich (B) isotherm for biosorption of Co, Cd and Zn ions by *R. squarrosus* in single systems at pH 6.0 and 20 °C.

**Table 1.** Langmuir and Freundlich equilibrium parameters ( $\pm$  SD) for Zn<sup>2+</sup>, Co<sup>2+</sup> and Cd<sup>2+</sup> biosorption by moss *R. squarrosus* obtained by non-linear regression analysis.

Metal	pH	Langmuir			Freundlich		
		$Q_{max}$ [ $\mu\text{mol/g}$ ]	$b$ [L/ $\mu\text{mol}$ ]	$R^2$	$K$ [L/g]	$1/n$	$R^2$
Zn <sup>2+</sup>	4.0	156 $\pm$ 3	0.008 $\pm$ 0.001	0.992	27.3 $\pm$ 10.3	0.22 $\pm$ 0.05	0.876
	6.0	186 $\pm$ 5	0.009 $\pm$ 0.002	0.988	32.6 $\pm$ 13.5	0.22 $\pm$ 0.06	0.865
Co <sup>2+</sup>	4.0	109 $\pm$ 4	0.005 $\pm$ 0.001	0.977	14.8 $\pm$ 4.1	0.25 $\pm$ 0.04	0.949
	6.0	123 $\pm$ 6	0.018 $\pm$ 0.006	0.962	29.2 $\pm$ 8.2	0.20 $\pm$ 0.04	0.914
Cd <sup>2+</sup>	4.0	139 $\pm$ 4	0.018 $\pm$ 0.005	0.976	33.8 $\pm$ 10.2	0.19 $\pm$ 0.04	0.893
	6.0	173 $\pm$ 10	0.013 $\pm$ 0.007	0.932	40.6 $\pm$ 10.1	0.19 $\pm$ 0.03	0.933

**Table 2.** Comparison of corrected Akaike's information criterion (AIC<sub>c</sub>) and residual sum of squares (RSS) values of Langmuir and Freundlich isotherms for Co<sup>2+</sup>, Cd<sup>2+</sup> and Zn<sup>2+</sup> biosorption by *R. squarrosus*.

Metal	pH	Langmuir			Freundlich		
		RSS	AICc	Akaike's weight	RSS	AICc	Akaike's weight
Zn <sup>2+</sup>	4.0	<b>79.9</b>	<b>33.54</b>	<b>0.9998</b>	1290	50.23	2.38 × 10 <sup>-4</sup>
	6.0	<b>198</b>	<b>38.99</b>	<b>0.9992</b>	2165	53.33	7.68 × 10 <sup>-4</sup>
Co <sup>2+</sup>	4.0	<b>102</b>	<b>35.00</b>	<b>0.9185</b>	229	39.84	0.0815
	6.0	<b>205</b>	<b>48.58</b>	<b>0.8862</b>	467	52.68	0.1138
Cd <sup>2+</sup>	4.0	<b>189</b>	<b>38.70</b>	<b>0.9890</b>	846	47.69	0.0110
	6.0	890	47.99	0.4900	<b>879</b>	<b>47.91</b>	<b>0.5010</b>

tion criterion (AIC<sub>c</sub>) and residual sum of squares (RSS). AIC<sub>c</sub> is able to answer the question: which model is better for mathematical description of Co<sup>2+</sup>, Cd<sup>2+</sup> and Zn<sup>2+</sup> biosorption by *R. squarrosus* and is defined as following:

$$AIC_c = N \ln \left( \frac{SSE}{N} \right) + 2(p+1) + \frac{2(p+1)(p+2)}{N-p-2} \quad (4)$$

where  $N$  is the number of observations,  $p$  is the number of fitting parameters and SSE is the sum of the squared errors.<sup>30</sup> The isotherm model with the lower AIC<sub>c</sub> value is considered most likely to be correct. The Langmuir isotherm fits the data better than the Freundlich isotherm, as is demonstrated by the more homogeneous standard deviation of each observed parameter (Table 1) and by the lower AIC<sub>c</sub> values obtained, as well as the residual sum of squares (Table 2). Only negligible difference between AIC<sub>c</sub> values was observed in the case of Cd<sup>2+</sup> biosorption at pH 6.0 and therefore each model is equally likely to be correct. Moreover, Sari and Tuzen<sup>31</sup> showed that the sorption of Cd and Cr by moss *Hylocomium splendens* was best fitted with Langmuir isotherm. However, we draw attention to some published papers stressing that the appli-

cation of adsorption models is not able to explain the biosorption mechanisms of complex biological systems.<sup>32</sup>

The maximum sorption capacity  $Q_{max}$  obtained from Langmuir isotherm increased as the solution pH increased, which supports discussion on the effect of solution pH on Cd<sup>2+</sup>, Co<sup>2+</sup> and Zn<sup>2+</sup> sorption. The maximum uptake capacity  $Q_{max}$  at pH 4.0 and 6.0 in single systems followed the order Zn > Cd >> Co (Table 1). This indicates higher affinity of *R. squarrosus* for Zn<sup>2+</sup> than Cd<sup>2+</sup> and Co<sup>2+</sup> sorption from single metal solutions. Moreover, this is consistent with the idea that the difference in sorption capacity under similar environmental conditions could be attributed to different ionic characteristics of metal ions.<sup>33,34</sup> Chen and Wang<sup>35</sup> demonstrated that metal uptake capacities  $Q_{eq}$  of divalent cations by *Saccharomyces cerevisiae* were significantly influenced by atomic number, covalent index, electronegativity, ionic radius and atomic weight and increased in the order Ni<sup>2+</sup> < Sr<sup>2+</sup> < Co<sup>2+</sup> < Cd<sup>2+</sup> < Zn<sup>2+</sup> < Cu<sup>2+</sup> < Pb<sup>2+</sup>. Comparison of  $Q_{max}$  values obtained in our work with those of other authors indicates that sorption of cadmium, zinc and cobalt ions by moss *R. squarrosus* is comparable with sorption of these metals by other algae, fungi, lichens and mosses (Table 3).

**Table 3.** Biosorption of Cd<sup>2+</sup>, Zn<sup>2+</sup> and Co<sup>2+</sup> ions using different biosorbents.

Biosorbent	$Q_{max}$ [μmol/g]			Reference
	Cd <sup>2+</sup>	Zn <sup>2+</sup>	Co <sup>2+</sup>	
<i>Chlorella minutissima</i> (marine green alga)	99	–	–	Roy et al 1993 <sup>36</sup>
<i>Fontinalis antipyretica</i> (aquatic moss)	249	225	–	Martins et al 2004 <sup>28</sup>
<i>Hylocomium splendens</i> (moss)	289	–	–	Sari et al 2008 <sup>37</sup>
<i>Bifurcaria bifurcate</i> (marine brown alga)	543	–	–	Lodeiro et al 2005 <sup>38</sup>
<i>Penicillium chrysogenum</i> (fungus)	191	199	–	Skowroński et al 2001 <sup>39</sup>
<i>Ulva fasciata</i> sp. (marine green alga)	–	207	–	Kumar et al 2007 <sup>40</sup>
<i>Hypogymnia physodes</i> (foliose lichen)	–	–	168	Pipíška et al 2007 <sup>19</sup>
<i>Parmotrema tinctorum</i> (foliose lichen)	–	–	375	Ohnuki et al 2003 <sup>41</sup>
<i>Oscillatoria angustissima</i> (blue-green alga)	–	–	260	Mohapatra and Gupta 2005 <sup>42</sup>
<i>Pilayella littoralis</i> (marine brown alga)	–	–	560	Carrilho and Gilbert 2000 <sup>43</sup>
<i>Sargassum wightii</i> (marine brown alga)	–	–	350	Vijayaraghavan et al 2005 <sup>44</sup>
<i>Rhytidadelphus squarrosus</i> (moss)	173	186	123	this study

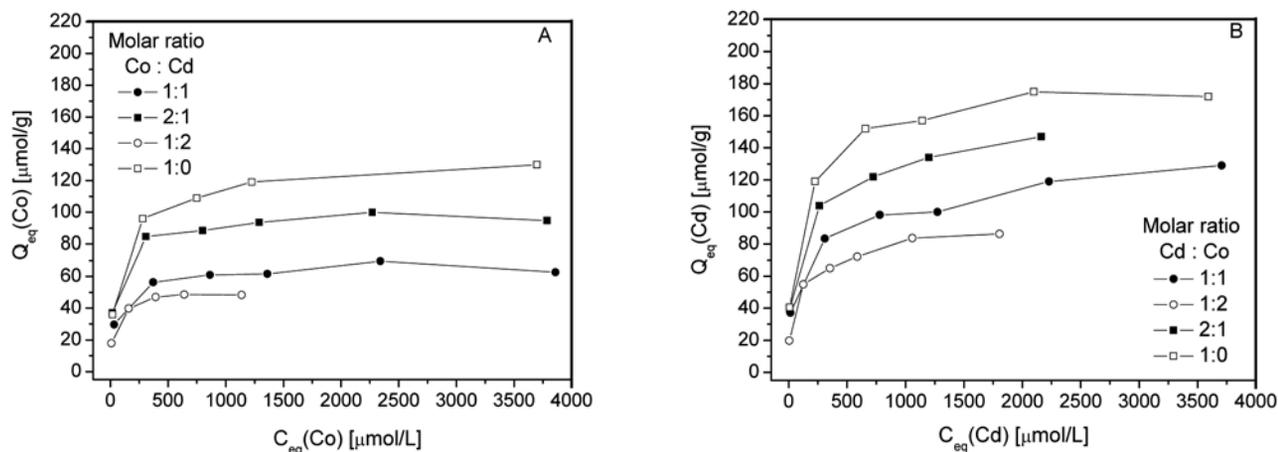
### 3. 2. Equilibrium Modeling in Binary Systems

Sorption in binary systems is complicated, because of the possible interactions among the metals. Experimental data describing sorption of metal ions by *R. squarrosus* from binary system Zn-Cd and Co-Cd at pH 6.0 are shown in Fig. 3 and Fig. 4. Sorption of metal ions increased with the increasing solution concentration until the saturation level was obtained. In all cases, the addition of co-ions caused the decrease of sorption of primary ion. The presence of  $\text{Cd}^{2+}$  in different molar  $[\text{Cd}]:[\text{Co}]$  ratios caused significant decrease in  $\text{Co}^{2+}$  sorption from 130 to 48  $\mu\text{mol/g}$  moss biomass (Fig. 3B). On the contrary the presence of cobalt caused less pronounced decrease in cadmium sorption from 172 to 87  $\mu\text{mol/g}$  (Fig. 3A). The competing effect of cadmium is proportional to  $\text{Cd}^{2+}$  concentration.

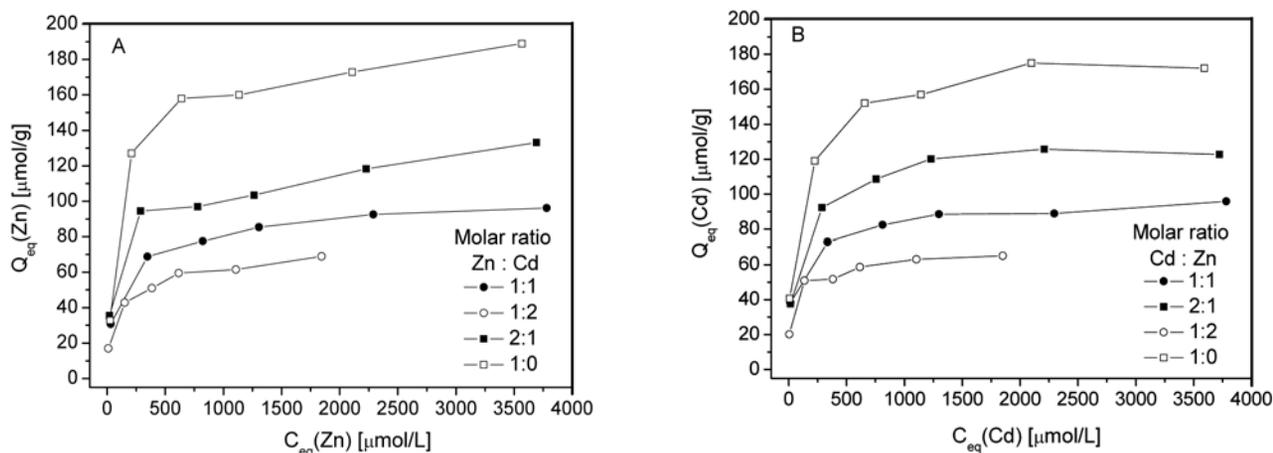
Sorption of Zn and Cd ions in binary Zn-Cd system is depicted in Fig. 4A, B. It is evident that both metals ha-

ve very similar maximum sorption of 173  $\mu\text{mol/g}$  for Cd and 189  $\mu\text{mol/g}$  for Zn from single metal systems (calculated from Langmuir isotherm). Also, competition effects exhibited by each ion on the uptake of other ion were very similar. When Cd and Zn ions are present in equimolar ratio 1:1 maximum uptake was 95.8  $\mu\text{mol/g}$  for  $\text{Cd}^{2+}$  and 96.2  $\mu\text{mol/g}$  for  $\text{Zn}^{2+}$ . It can be pointed out that at the highest initial concentration of  $\text{Cd}^{2+}$ , a decrease of approx. 50% could be noted in the  $\text{Zn}^{2+}$  uptake and vice versa.

In the next steps the collected equilibrium data from the binary systems Cd-Zn and Co-Cd were analysed using binary isotherm models. Romera et al<sup>8</sup> pointed out that the most appropriate form to describe sorption equilibrium in binary systems is to adjust the experimental data to a mathematical model from which number of parameters can be obtained for quantitative interpretation of sorption equilibrium uptake. Since, practically in all cases the biosorption of cadmium, cobalt and zinc ions in single metal systems by *R. squarrosus* was well described by Lang-



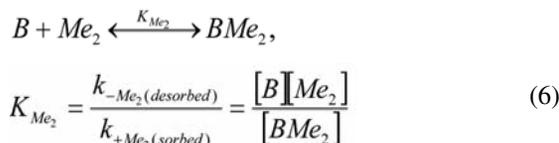
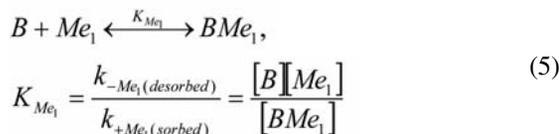
**Figure 3.** Isotherms of the cobalt (A) and cadmium (B) biosorption by *R. squarrosus* (2.5 g/L, d.w.) at 20 °C and pH 6.0 from binary system at different initial molar  $[\text{Co}]:[\text{Cd}]$  ratios.



**Figure 4.** Isotherms of the zinc (A) and cadmium (B) sorption from by *R. squarrosus* (2.5 g/L, d.w.) at 20 °C and pH 6.0 from binary system at different initial molar  $[\text{Zn}]:[\text{Cd}]$  ratios.

muir isotherm (Table 1), we used in our study the competitive Langmuir model developed under the concept of original Langmuir isotherm for single systems where one binding site was only available for one sorbate.<sup>45</sup>

When equilibrium is established:



where  $Me_1$  and  $Me_2$  are metal ions in solution,  $B$  represents the free binding site,  $K_{Me_1}$  and  $K_{Me_2}$  represent equilibrium constants for binding sites occupied with metals  $Me_1$  and  $Me_2$ , respectively. The final expression of competitive Langmuir model is as follows:

$$Q_{eq}[Me_1] = \frac{Q_{max Me_1} b_{Me_1} C_{eq}[Me_1]}{1 + b_{Me_1} C_{eq}[Me_1] + b_{Me_2} C_{eq}[Me_2]} \quad (7)$$

$$Q_{eq}[Me_2] = \frac{Q_{max Me_2} b_{Me_2} C_{eq}[Me_2]}{1 + b_{Me_1} C_{eq}[Me_1] + b_{Me_2} C_{eq}[Me_2]} \quad (8)$$

$$b_{Me_1} = \frac{1}{K_{Me_1}} \quad \text{and} \quad b_{Me_2} = \frac{1}{K_{Me_2}}$$

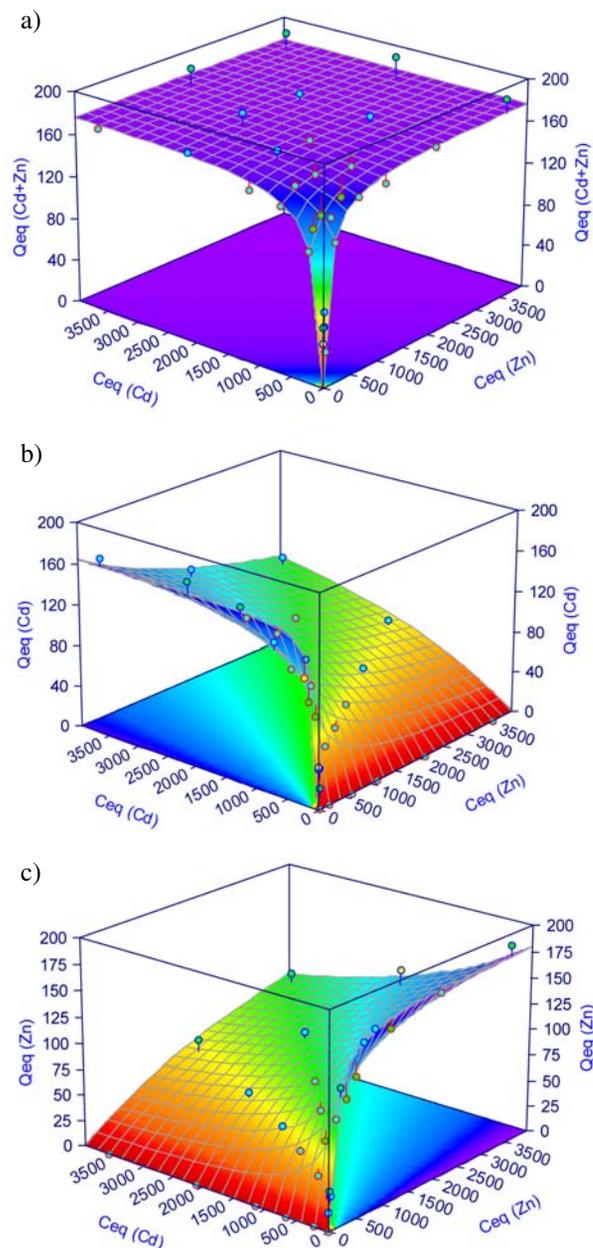
The total metal uptake in binary systems can be expressed as follows:

$$Q_{eq}[Me_1 + Me_2] = Q_{eq}[Me_1] + Q_{eq}[Me_2] =$$

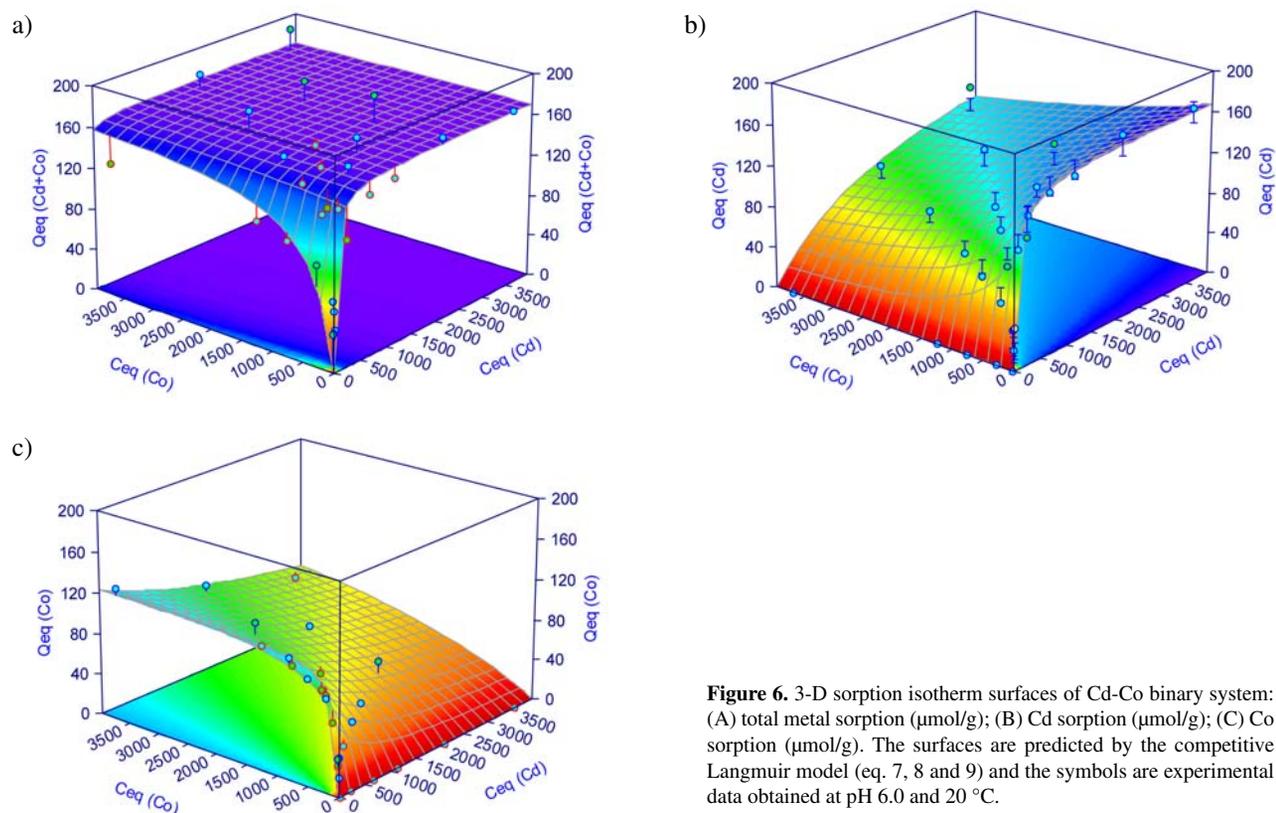
$$= Q_{max} \frac{b_{Me_1} C_{eq}[Me_1] + b_{Me_2} C_{eq}[Me_2]}{1 + b_{Me_1} C_{eq}[Me_1] + b_{Me_2} C_{eq}[Me_2]} \quad (9)$$

where  $Q_{eq}[Me_1]$  and  $Q_{eq}[Me_2]$  represent equilibrium sorption capacities of metals  $Me_1$  and  $Me_2$ ,  $Q_{eq}[Me_1 + Me_2]$  is the sum of uptakes of the two metals,  $C_{eq}[Me_1]$  and  $C_{eq}[Me_2]$  represent equilibrium concentration of metals remaining in solution and  $Q_{max}$  is the maximum sorption capacity for the binary component systems.  $b_{Me_1}$  and  $b_{Me_2}$  represent affinity constants of Langmuir model for the first and second metal ions.<sup>46</sup> The competitive Langmuir model equations can be represented by 3-D sorption isotherm surfaces. Binary Langmuir type equations (7, 8, and 9) were used to fit the experimental data and parameters obtained by the application of these models are presented in Table 4. Because Langmuir constant  $b_{Me_i}$  is related to the energy of adsorption through the Arrhenius equation,

the higher  $b_{Me_i}$  represents the higher affinity of the sorbent for the sorbate. The values of  $b_{Me_1}$  and  $b_{Me_2}$  in binary system Cd-Zn are 0.012 L/ $\mu\text{mol}$  for  $\text{Cd}^{2+}$  and 0.009 L/ $\mu\text{mol}$  for  $\text{Zn}^{2+}$ . The negligible difference between values indicates approximately equal affinity of *R. squarrosus* biomass to Cd and Zn ions. The total metal uptake  $Q_{eq}$  Cd + Zn ( $\mu\text{mol/g}$ ) as a function of equilibrium concentration  $C_{eq}$  ( $\mu\text{mol/L}$ ) of cadmium and zinc is presented in Figure 5A. Continuous surface represents total metal uptake as predicted by the equation (9). Experimental values of the



**Figure 5.** 3-D sorption isotherm surfaces of Cd-Zn binary system: (A) total metal sorption ( $\mu\text{mol/g}$ ); (B) Cd sorption ( $\mu\text{mol/g}$ ); (C) Zn sorption ( $\mu\text{mol/g}$ ). The surfaces are predicted by the competitive Langmuir model (eq. 7, 8 and 9) and the symbols are experimental data obtained at pH 6.0 and 20 °C.



**Figure 6.** 3-D sorption isotherm surfaces of Cd-Co binary system: (A) total metal sorption ( $\mu\text{mol/g}$ ); (B) Cd sorption ( $\mu\text{mol/g}$ ); (C) Co sorption ( $\mu\text{mol/g}$ ). The surfaces are predicted by the competitive Langmuir model (eq. 7, 8 and 9) and the symbols are experimental data obtained at pH 6.0 and 20 °C.

total metal uptake are shown as individual data points. At high total metal concentrations sorbent easily reaches the saturation level demonstrated by the plateau of the sorption surface (Figure 5A). The overall total metal ions uptake by *R. squarrosus* calculated from equation (9) is  $181 \pm 3 \mu\text{mol/g}$ . This value is very close to maximum sorption capacities ( $Q_{max}$ ) of Cd and Zn ions from single systems, which indicates that cadmium and zinc ions in binary Cd-Zn system compete for the same binding sites.<sup>47</sup> Figures 5B and 5C show sorption of Zn and Cd in the presence of co-ion. Continuous surfaces represent Zn and Cd uptake as predicted from equations (7, 8). The amount of cadmium or zinc ions sorbed decreased with increasing concentration of the co-ion. The high value of coefficient of determination ( $R^2$ ) and low root mean squared error (RMSE) shown in Table 4 suggested that the competitive Langmuir model well describes the experimental biosorp-

tion data. Similarly, Pérez-Marín et al<sup>47</sup> in the case of the Cd-Zn binary system observed that the removal of cadmium and zinc by orange wastes was moderately affected by the presence of another metal and the competitive Langmuir model adequately represented the experimental data for the Cd-Zn binary system.

The values of  $b_{Me1}$  and  $b_{Me2}$  in binary system Cd-Co are 0.032 L/ $\mu\text{mol}$  for  $\text{Cd}^{2+}$  and 0.003 L/ $\mu\text{mol}$  for  $\text{Co}^{2+}$  (Table 4). The significant difference between these values indicates higher affinity of *R. squarrosus* biomass to Cd ions in comparison with Co ions in multi-component system. The total metal uptake  $Q_{eq} \text{ Cd} + \text{Co}$  ( $\mu\text{mol/g}$ ) as a function of equilibrium concentration  $C_{eq}$  ( $\mu\text{mol/L}$ ) of cadmium and cobalt is presented in Figure 6A. Sorption surfaces (Fig. 6B, 6C) show sorption of  $\text{Co}^{2+}$  and  $\text{Cd}^{2+}$  in the presence of co-ion as predicted from equations (7, 8). Despite the fact that slightly lower value of  $R^2$  and slightly

**Table 4.** Equilibrium parameters for  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$  biosorption from the binary mixtures Cd-Zn and Cd-Co by moss *R. squarrosus* calculated from competitive Langmuir model by non-linear regression analysis.

Binary system	$Q_{max}$ [ $\mu\text{mol/g}$ ]	$b_{Me1}^*$ [L/ $\mu\text{mol}$ ]	$b_{Me2}^{**}$ [L/ $\mu\text{mol}$ ]	$R^2$	RMSE <sup>***</sup>
Cd-Zn	$181 \pm 3$	$0.012 \pm 0.002$	$0.009 \pm 0.002$	0.938	12.28
Cd-Co	$172 \pm 4$	$0.032 \pm 0.009$	$0.003 \pm 0.001$	0.901	16.13

\* Me1 – Cd in binary systems Cd-Zn and Cd-Co

\*\* Me2 – Zn in binary system Cd-Zn, Co in binary system Cd-Co

\*\*\* Root mean squared error (fit standard error)

higher value of RMSE were observed for Cd-Co than for Cd-Zn binary system, the competitive Langmuir model well describes the experimental biosorption data in Cd-Co binary system.

## 4. Conclusions

Investigation of the metal ions removal from aqueous solution by dried moss *R. squarrosus* showed that Cd<sup>2+</sup>, Co<sup>2+</sup> and Zn<sup>2+</sup> biosorption is a rapid, pH dependent process. Maximum uptake of metals was found to occur at pH 5.0 to 6.0. The experimental equilibrium data of the single-component systems for Cd<sup>2+</sup>, Co<sup>2+</sup> and Zn<sup>2+</sup> ions were well described by the Langmuir isotherm. The maximum sorption capacity  $Q_{max}$  increased up to pH 6.0 and followed the order Zn > Cd >> Co. The competitive Langmuir model well describes the experimental biosorption data in both Cd-Zn and Cd-Co binary systems. The presence of Cd more significantly decreased the sorption of Co in binary Cd-Co mixtures than vice versa. In Cd-Zn binary system both cadmium and zinc were sorbed with equal efficiency. It can be also 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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## 6. References

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## Povzetek

Raziskovali smo adsorpcijo Cd, Co in Zn iz vodnih raztopin na biomaso mahu *Rhytidiadelphus squarrosus* (biosorpcija). Izkazalo se je, da na biosorpcijo bistveno vpliva pH sistema: maksimalna je bila dosežena pri pH = 5.0–6.0, medtem ko je pri pH = 2.0 skoraj zanemarljiva. Izoterme smo opisali z Langmuirjevim modelom ter Freundlichov izotermo. Ugotovili smo, da Langmuirjev model dobro opiše biosorpcijo preiskovanih sistemov ter da je maksimalna sorpcijska kapaciteta za posamezne kovine različna 186  $\mu\text{mol/g}$  za Zn, 173  $\mu\text{mol/g}$  za Cd in 123  $\mu\text{mol/g}$  za Co. Prisotnost Cd bolj zmanjša sorpcijo Co iz binarne mešanice Cd–Co kot obratno. Iz mešanic Cd–Zn je učinkovitost sorpcije enaka za obe kovini. Za mešanice smo uporabili model kompetitivne Langmuirjeve izoterme.