

STUDY OF BIOSORPTION OF Zn(II) IONS FROM AQUEOUS SOLUTIONS BY ACTIVATED MIXED BIOMASS OF KNOTWEED *REYNOUTRIA JAPONICA*

Iva MELČÁKOVÁ¹, Daniela PLACHÁ¹, Jana NOVÁKOVÁ¹, Tomáš RUŽOVIČ¹ & Peter ANDRÁŠ^{2,3}

¹VŠB -Technical University of Ostrava, 17.listopadu 15/2172, 708 33 Ostrava-Poruba, Czech Republic
iva.melcakova@vsb.cz, daniela.placha@vsb.cz, jana.novakova@vsb.cz, tomas.ruzovic@vsb.cz

²Faculty of Natural Sciences, Matej Bel University, Tajovského 40, 974 01 Banská Bystrica; Slovakia
peter.andras@umb.sk

³Geological Institute, Slovak Academy of Sciences, Ľumbierska, 1, 974 01 Banská Bystrica, Slovakia
andras@savbb.sk

Abstract: The ability of mixed biomass (stems and leaves) of an invasive plant *Reynoutria japonica* to bind up Zn(II) ions has been studied. For modelling of kinetic data, pseudo-second-order model was used. The sorption equilibrium data were described by the Langmuir and Freundlich models; the processes were in concordance with obtained Langmuir and Freundlich isotherms. Both linear and non-linear models were suitable for data modelling. Maximal sorption capacity for Zn(II) was 8.97 mg/g (PAB 0.5). The sorption mechanism explained as ion exchange was described using EDS analyses. The binding groups of leaves and stems of *R. japonica* biomass were analyzed using FTIR method. For desorption of Zn(II) from *R. japonica* mixed biomass, 0.2M H₂SO₄ was successfully used.

Keywords: *Reynoutria japonica*, PAB 0.5, PAB 2.5, biosorption, Zn(II), isotherms, FTIR, EDS analysis

1. INTRODUCTION

The presence of metal ions in natural or industrial wastewater and their potential impact has been a subject of research in environmental science for a long time (Hasan et al., 2008). Nowadays, with the exponentially increasing population, need for controlling metal emission into the environment is even more pronounced. Controlling metal discharges and removing toxic metals from aqueous solutions has become a challenge for the 21st century (Volesky, 2001). Environmental engineers and scientists are faced with the challenging task to develop appropriate low cost technologies for effluent treatment (Ahluwalia & Goyal, 2007).

A new cost-effective technology that can find its largest application in the removal of metal from contaminated industrial effluents is biosorption. The concept of biosorption includes concentrating sorbent metal from the solution onto the dead biomass. The process is simple in operation and very similar to conventional adsorption or ion-exchange, except that

sorbent of biological origin is employed (Chojnacka, 2010). A vast array of biological materials, especially bacteria, algae, yeast and fungi, have received increasing attention for metal removal and recovery due their good performance, low cost and large quantities available (Wang & Chen, 2009).

Similarly in our laboratory, we are interested in development and employment of low cost biosorbents as well - for instance biosorbent of knotweed *Reynoutria japonica* - for the treatment of aqueous solutions containing metal ions.

In the Czech Republic, the genus *Reynoutria* we have used comprises four species. The most widely distributed representative of the genus, *Reynoutria japonica* var. *japonica*, was first recorded in 1883 by A. Weidmann in cultivation in Southern Bohemia. The first record outside cultivation was from Northern Bohemia in 1902. Up to year 2000, it has been recorded in 1335 localities, most frequently in riparian and man-made habitats (Mandák et al., 2004). Mass spread of knotweed brings many negative impacts.

In addition to obvious negative effects on natural communities, knotweed also damage flood provisions, penetrate through roads and sidewalks, or make contested areas inaccessible. The plant is nevertheless energetically very profitable. Calorific value of its dry matter is greater than 17 MJ/kg and autumn crop yield can reach 30 to 40 t/ha (Patočka, 2005).

In the present study, the sorption capacity of knotweed biomass has been studied; more precisely the ability of biomass of mixture of stems and leaves of *R. japonica* to bind up Zn(II) ions from aqueous solutions. Spent biosorbent was regenerated to find out the adsorption potential on reuse. Various equilibrium models and a kinetic model were applied to describe the biosorption process of this biomass. FTIR analyses were also used in this study to look for potential binding sites and possible functional groups of *R. japonica* biomass, and EDS analysis was used for identifying weight percentages of elements before and after biosorption by leaves and stems biomass.

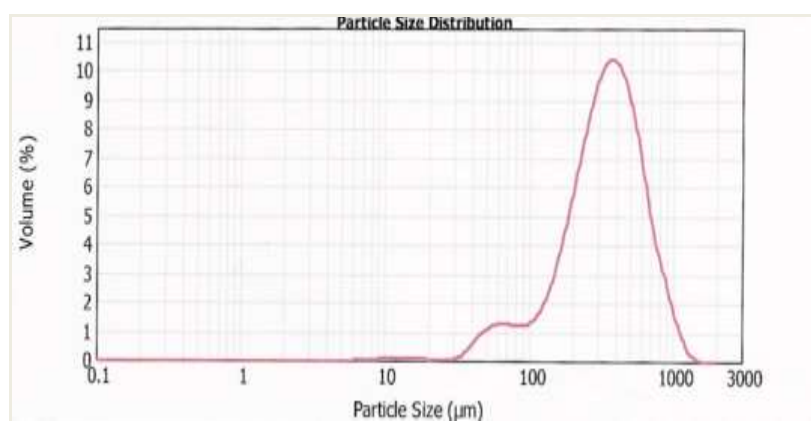


Figure 1. Distribution of particles of activated leaves.

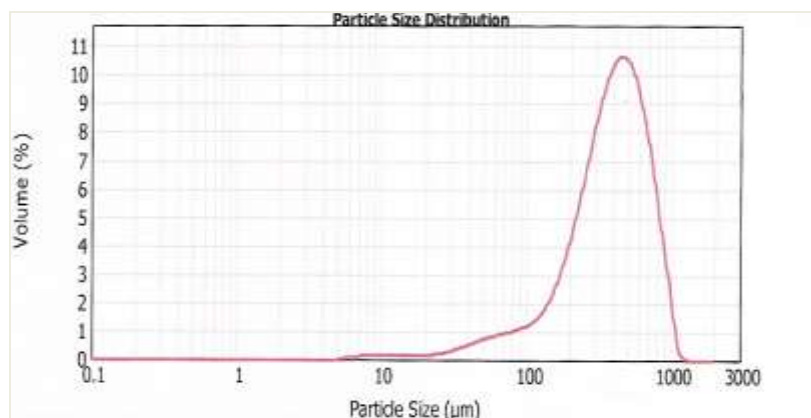


Figure 2. Distribution of particles of activated stems.

2 MATERIAL AND METHODS

2.1. Preparation of biosorbent

All the samples of *R. japonica* used were collected from the same non-urban area in foothills of Lysá hora, in the area of Moravskoslezské Beskydy mountains. This sampling area does not have any prior history of contamination by heavy metals. Stems and leaves of this plant were air-dried at room temperature, after that dried for 24 hours at temperature of 90°C and ground with Fritsch Pulverisette 19 device. Dried samples were screened using a sieve

shaker (Fritsch Analysette 3 Spartan); uniform particle size fraction 0.01-2 mm (with maximum in the range between 0.25-0.55mm for leaves and 0.3-0.65mm for stems) was obtained - see figures 1 and 2.

Ion exchange resins manufactured for the same purpose generally feature particle sizes between 0.7 and 1.5 mm, and biosorbents granule size usually ranges between 0.5 to 2 mm (Naja et al., 2007).

Particles of stems and leaves were washed twice by de-ionized water and 0.01M HCl (20 g/L) for 90 minutes to remove soil or debris, and finally washed with de-ionized water again. The biomass samples were then oven-dried at 90°C for one day. For possible future industrial use of this biosorbent, weight of stems and leaves at different height classes of *R. japonica* plants was experimentally verified, and weight ratio of stems and leaves characterizing plants of a certain height was calculated. For sorption of zinc, pilot stem and leaf mixture in a 0.5 ratio (corresponding to plant height of about 130 cm) was subsequently used. This biosorbent mixture is in this text called PAB 0.5. The second pilot mixture of stem and leaf had a ratio of 2.5 (corresponding to plant height of about 300 cm); in text called PAB 2.5.

2.2. Chemicals

Zinc ions Zn(II) ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) were used in this study. Test solutions containing single ion were prepared by diluting proper amount of 1g/l stock solution of above mentioned metal ion to obtain desired concentrations. All chemicals used were of analytical reagent grade and were used without further purification.

2.3. Determination of adsorption isotherm

We have designed this experiment based on previous studies (Melčáková & Horvatová, 2010). In the present experiment, adsorption isotherms of a mixture of stems and leaves for zinc were determined. 10 g samples of dry PAB 0.5 and PAB 2.5 were suspended in 100 ml samples of various concentrations (10-200 mg/L) of Zn(II) solutions. pH 6 of solutions before and during equilibration was adjusted with 0.1M H₂SO₄ and 0.1M NaOH. Batch experiments were performed at 25°C. After 60 minutes of incubation, zinc samples were filtered in order to remove the biomass, and metal concentration in supernatant was measured with AAS (AAS Varian AA280FS). The quality of sorbent material was judged based on how much sorbate it can attract and retain in an „immobilized“ form. For this purpose, it is customary to determine the metal uptake (q) by the biosorbent as the amount of sorbate bound by unit of solid phase. The equation (1) is

$$q = \frac{V(C_i - C_f)}{S} \quad (1)$$

where V is the volume of metal-bearing solution contacted with the sorbent [L], C_i is initial concentration of metal in solution [mg/L], C_f is residual concentration of metal in solution [mg/L], and S is the amount of added biosorbent [g].

2.4. Langmuir and Freundlich Isotherms

In the design of biological sorption wastewater treatment plant, it is very important to propose simple mathematical models that would enable to describe kinetics and statics of the process on theoretical basis (Chojnacka, 2010). The process of zinc sorption on the biosorbent was described by the Langmuir and Freundlich adsorption models.

The Langmuir model is based on reaction hypotheses. The solid is assumed to have a limited adsorption capacity q_{max} . All the adsorption sites are (a) assumed to be identical, (b) each site retains one molecule of the given compound and (c) all sites are energetically and sterically independent of the adsorbed quantity (Limousin et al., 2007). Langmuir isotherm is described by equation (2)

$$q = \frac{q_{max} b C_f}{1 + b C_f} \quad (2)$$

where q is experimental metal uptake [mg/g], q_{max} is the maximal metal uptake [mg/g], b is a constant related to the affinity of the binding sites [L/mg], and C_f is residual concentration of metal in the solution [mg/L].

q_{max} and b can be determined from the linear plot of C_f/q vs C_f for Langmuir 1, $1/q$ vs $1/C_f$ for Langmuir 2,

q/C_f vs q for Langmuir 3 or q vs q/C_f for Langmuir 4 (Witek-Krowiak et al., 2011).

The Freundlich isotherm defines adsorption to heterogeneous surfaces, i.e. surfaces possessing adsorption sites with varying affinities. Freundlich isotherm equation is equation (3)

$$q = k C_f^{\frac{1}{n}} \quad (3)$$

where q is experimental metal uptake [mg/g], C_f is residual concentration of metal in the solution [mg/L], k is affinity parameter [L/g], and n is dimensionless heterogeneity parameter (Gadd, 2009).

The equation can be linearized in the following logarithmic form and Freundlich constants can be determined from equation 4 (Ho et al., 2005)

$$\log q = \frac{1}{n} \log C_f + \log k \quad (4)$$

2.5. Kinetic model

The chemical kinetics describes reaction pathways, along with time to reach the equilibrium. Sorption kinetics show large dependence on the physical and/or chemical characteristics of sorbent material, which also influence the sorption mechanism (Hasan et al., 2008). In this study the process kinetics was described by the pseudo-second-order model. Pseudo-second-order model can be shown as equation (5)

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (5)$$

where k_2 is the pseudo-second-order rate constant [g/(mg min)], q_e is the amount of metal ion sorbed at equilibrium [mg/g], and q_t is amount of metal ion on the surface of the biosorbent at any time t [mg/g]. The linear form is equation (6)

$$\frac{t}{q_t} = \frac{1}{k_2 (q_e)^2} + \frac{t}{q_e} \quad (6)$$

A plot of (t/q_t) vs t should generate a straight line with intercept of $1/k_2 q_e^2$ and slope $1/q_e$. Value of q_e can be calculated and compared with data from experiment (Farooq et al., 2010).

2.6. Desorption

For desorption, used biosorbent was first dried at temperature of 25°C for 48 hours, and then it was regenerated in 250 ml Erlenmeyer flasks with 50 ml working volume of 0.2 M/L H₂SO₄. Mixture was stirred at 330 rpm using magnetic stirrer in order to avoid biosorbent floating on water surface or sedimenting on the bottom. At room temperature (approximately 25°C), desorption lasted 60 minutes. After desorption, zinc samples were filtered (filter KA-01) in order to remove the biomass, and metal concentration in supernatant was

measured with AAS (AAS Varian AA280FS).

The eluted metal per gram of biomass (q_{des}) from the concentration of metal desorbed (C_{des}) in the solution was calculated by equation (7) (Javaid et al., 2011)

$$q_{des} = \frac{C_{des}V}{W} \quad (7)$$

where V is the volume of the solution [L] and W is weight of a biosorbent [g].

Percentage desorption was acquired by comparing metal desorbed (q_D) to metal adsorbed (q_A) on biomass. Desorption percentage ratio $D\%$ was calculated by equation (8)

$$D\% = \frac{q_D}{q_A} 100 \quad (8)$$

2.7. FTIR Spectroscopy

The presence of functional groups in the cell walls of the plant parts was identified by FTIR (in range of 400-4000 cm^{-1}) using IR spectrometer FTIR 2000 PerkinElmer.

2.8. Electron - Dispersive Spectroscopy (EDS)

Using a scanning electron microscope (JEOL JSM-6409 analytical SEM) and its EDS analysis, weight percentage of elements concentrations in stems and leaves of *R. japonica* before and after biosorption were obtained.

3. RESULTS AND DISCUSSION

The present study describes the efficiency of mixed biomass of *R. japonica* for removal of Zn(II) from aqueous solutions.

3.1. Adsorption isotherm and isotherm models

To create models of biosorption processes for PAB 0.5 and PAB 2.5 (initial Zn(II) concentration 10-200 mg/l), Langmuir (1-4) and Freundlich models in both linear and non-linear forms were used. Equilibrium isotherms are calculated in order to determine the capacity of the biosorbent for metal ions. During the biosorption, rapid equilibrium is established between adsorbed metal ions on the biomass (q) and unadsorbed metal ions in solution (C_f) (Volesky, 2003).

Langmuir sorption model served for estimation of maximum metal uptake values (q_{max}) when they could not be found in experiments, and for finding affinity constant b (representing affinity of a sorbent for given sorbate).

Although q_{max} is dependent on experimental conditions, e.g. solution pH, it is a good measure for comparing different sorbents for the same metal

(Murphy et al., 2008). It is necessary to point out that two opposite descriptions of constant b can be found in the literature. For example, Kratochvil & Volesky (1998), Norton et al., (2004), Singh et al., (2007) or Wang & Chen (2009) say that good biosorbent has high q_{max} and low b ; on the other hand, Davis et al., (2003) or Romera et al., (2007) state that good biosorbent has high value of both q_{max} and b . This contradiction is probably due to confusion of two different constants in different literature sources: K and b . Similarly to b , K also represents affinity of sorbate to binding places of sorbant, but it is deduced from equation 9

$$q = \frac{q_{max} C_f}{K + C_f} \quad (9) \text{ where } K=1/b$$

From the equation it is clear that b is directly correlated to q , and both b and q increase at the same time. Thus, in general, for good biosorbents both high q_{max} and high b are desirable.

The value of correlation coefficient R^2 and constants of the Langmuir models are shown in table 1.

Table 1. Langmuir and Freundlich constants and correlation coefficient for biosorption of Zn(II) on PAB 0.5 and PAB 2.5, pH 6, room temperature 25 °C – linear form.

Langmuir 1			
	q_{max} [mg/g]	b [L/mg]	R^2
PAB 0.5	9.65	0.1789	0.9972
PAB 2.5	9.52	0.2142	0.9964
Langmuir 2			
	q_{max} [mg/g]	b [L/mg]	R^2
PAB 0.5	11.14	0.1663	0.861
PAB 2.5	8.66	0.4245	0.9332
Freudlich			
	k [L/g]	n	R^2
PAB 0.5	1.95	2.5569	0.840
PAB 2.5	2.14	2.7397	0.875

From table 1 and figure 3 it is evident that linear form of the Langmuir isotherm model 1 is well fitted for zinc sorption. R^2 values are very high, and, in the case of PAB 2.5, reach 0.9964.

Langmuir models 3 and 4 had low correlation coefficient values and hence they are not suitable for this purpose. From table 1 it is also evident that Langmuir models 1 and 2 show different values of parameters.

Yet, in both linear form models, constant b was higher in the case of biosorbent PAB 2.5. Its value reached 0.4245 L/mg (model 2), which gives evidence about high affinity of this sorbent for Zn(II) ions in low final metal concentrations. In addition, correlation coefficient was in this case very high as well (0.9332). The feasibility of Langmuir isotherm can be expressed by equilibrium parameter R_L defined as:

$$R_L = \frac{1}{1 + bC_0} \quad (10)$$

b being the Langmuir constant and C_o the initial concentration of metal [mg/L]. The parameter R_L indicates the shape of the isotherm and nature of the biosorption process (Li et al., 2010). In this study, the equilibrium parameter was found to be in the range $0 < R_L < 1$ as shown in table 2. This indicated the fact that biosorption was very favorable and adsorbent employed exhibited good potential for future use.

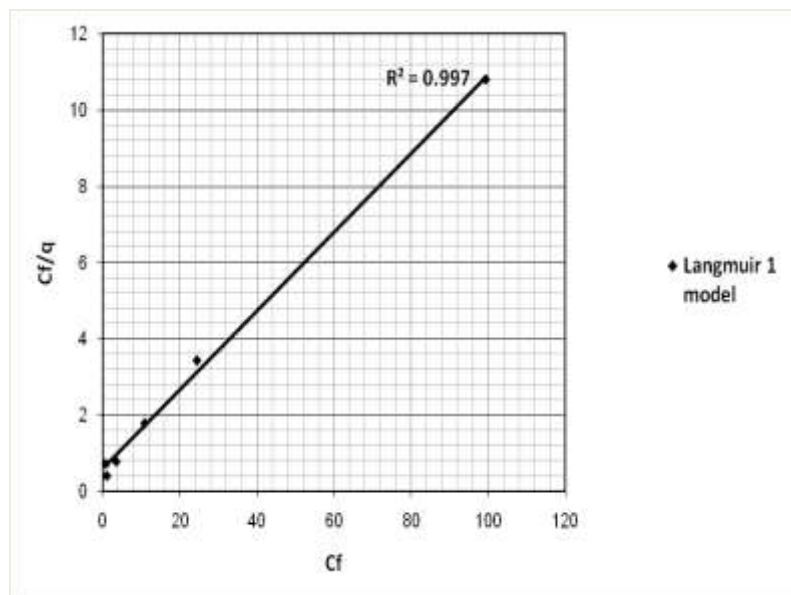


Figure 3. Fitting of linear function Langmuir 1 model to the experimental results for PAB 0.5, initial metal concentration 10-200 mg/L, biomass concentration 10g/L, pH 6, room temperature 25 °C.

Table 3. Langmuir and Freundlich constants and correlation coefficients for biosorption of Zn(II) on PAB 0.5 and PAB 2.5, pH 6, room temperature 25°C – non-linear form.

Langmuir – non-linear form			
	q_{max} [mg/g]	b [L/mg]	R^2
PAB 0.5	8.97	0.2400	0.9928
PAB 2.5	7.32	0.5448	0.9802
Freundlich – non-linear form			
	k [L/g]	n	R^2
PAB 0.5	2.69	3.5723	0.9503
PAB 2.5	2.84	3.7544	0.9674

For comparison, maximum adsorption capacity q_{max} for zinc Zn(II) by palm tree leaves was 14.6 mg/g (pH 5.5 and temperature 25°C) (Al Rub et al., 2006). For *Caulerpa lentillifera*, uptake capacity of 2.66 mg/g was obtained (Pasavant et al., 2006). The use of biomass from *Myriophyllum spicatum* resulted in capacity of 6.8 mg/g (Lesage et al., 2007).

The value of a constant n (2.5569 for PAB 0.5 and 2.7397 for PAB 2.5) of the Freundlich model (Table 1) ranged between 1-10, suggesting relatively strong adsorption onto the biosorbent.

However, low correlation coefficient suggests that this model in the linear form was not the best one for describing sorption equilibrium. The non-linearized adsorption isotherms (q versus C_f) of Zn(II) on activated biosorbents with excellent fitting results are shown in

figures 4-5.

The value of correlation coefficient R^2 and constants of the Langmuir and Freundlich models (non-linear form) are shown in table 3.

Table 2. Parameter R_L

R_L	
PAB 0.5	PAB 2.5
0.3334	0.1605
0.1807	0.0717
0.1063	0.0359
0.0726	0.0247
0.0552	0.0183
0.0283	0.0096

The non-linear adsorption isotherms for Zn(II) for various sorbents show that the amount of metal adsorbed increases along with increase of its equilibrium concentration. Figure 4 also manifests higher effectiveness of PAB 2.5 biosorbent in low final metal concentrations. In agreement with this result, Li et al., (2010) points out that sometimes at low metal concentration a biosorbent with low q_{max} and high b could outperform a biosorbent with high q_{max} and low b .

The isotherm plots of experimental sorption data in the non-linearized Freundlich model did not show a distinct plateau; this type of curve is called by Limousin et al., (2007) „L-isotherm without strict plateau“, proposing that sorbent did not reach limits of its sorption capacity.

The applicability of both Langmuir and Freundlich isotherms to the sorption of zinc ions show that monolayer adsorption as well as heterogenous distribution of active sites on the surface of adsorbent exist under the experimental conditions employed (Ozdemir et al., 2009). The reason is that the mechanism of biosorption is rarely uniform. Usually it is a combination of physical and chemical sorptions (Chojnacka, 2006).

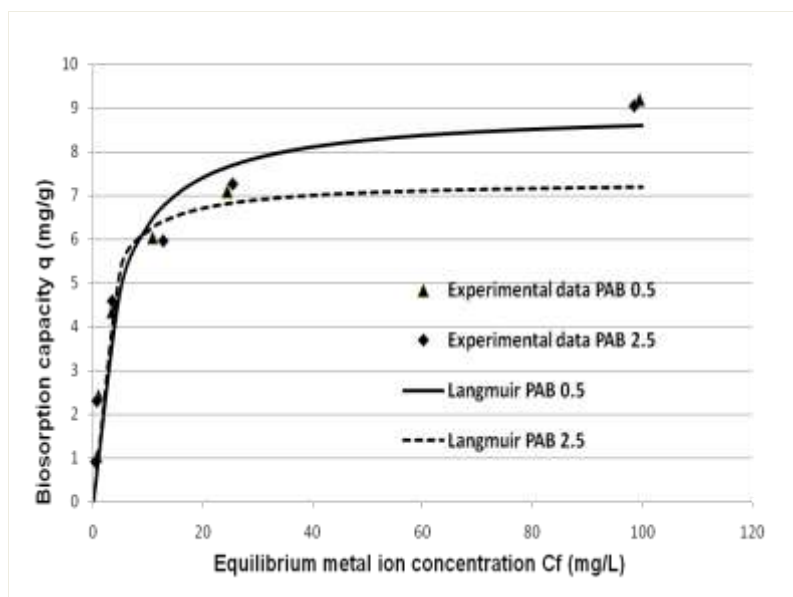


Figure 4. The non-linearized Langmuir fitting plots and experimental data of biosorption of Zn(II) onto PAB 0.5 and PAB 2.5, initial metal concentration 10-200 mg/L, biomass concentration 10g/L, pH 6, room temperature 25°C.

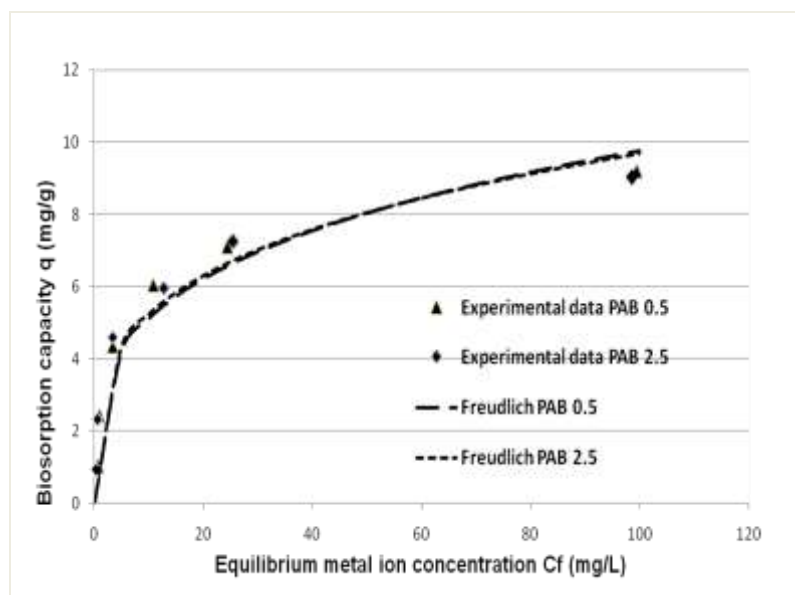


Figure 5. The non-linearized Freundlich fitting plots and experimental data of biosorption of Zn(II) onto PAB 0.5 and PAB 2.5, initial metal concentration 10-200 mg/L, biomass concentration 10g/L, pH 6, room temperature 25°C.

3.2. Kinetic model

In recent years, the pseudo-second-order rate expression has been widely applied to the adsorption of pollutants from aqueous solutions. The pseudo-second-order rate expression was used to describe chemisorption involving valency forces through the sharing or exchange of electrons between the adsorbent and adsorbate as covalent forces, and ion exchange. The advantage of using this model is that there is no need to know the equilibrium capacity q_e from the experiments, as it can be calculated from the model. In addition, the initial adsorption rate can be obtained from the model as well (Ho,

2006). Straight line plot of t/q_t versus t , with correlation coefficient R equal to 1, showed the validity of pseudo-second-order model (Fig. 6).

Sorption equilibrium was reached within 10 minutes. It was found that contact time of 60 minutes was sufficient for accomplishment of the equilibrium stage. Kinetic parameters of linear pseudo-second-order equation for sorption of Zn(II) ions on *R. japonica* are provided in table 4. In this table, empty cells for PAB 2.5 reflect results without linear correlation.

Table 4 The pseudo-second-order model parameters and correlation coefficient.

	q_e [mg/g]	k_2 [g/(mg.min)]	R^2
PAB 0.5	0.993	34.52	1
PAB 2.5	-	-	-

The rate constant k_2 of the pseudo-second-order model is a complex function of the initial concentration of the solute. The value of constant k_2 is in comparison to different studied biosorbents quite high, proposing possible practical use of our sorbents. For example, k_2 of biomass of *Ceratophyllum demersum* in concentration of zinc 10 mg/L was 0.0147 (Keskinkan et al., 2004); palm tree leaves biomass sorption of Zn in concentration of 100 mg/L reached 0.0460 g/(mg min) (Al Rub et al., 2006), while ovulate cones of *Pinus sylvestris* 0.107 g/(mg min) (Ucun et al., 2009).

3.3. Desorption

It was found that 0.2M H_2SO_4 is appropriate desorption agent. Desorption of zinc from biomass was after 1 hour higher for sorbent PAB 0.5 than for PAB 2.5, irrespective final zinc concentrations (Fig. 7).

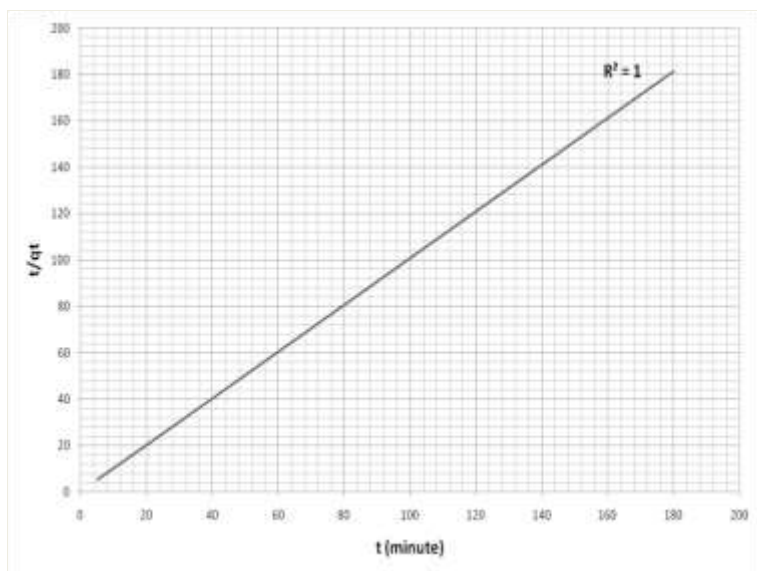


Figure 6. Kinetics of Zn(II) biosorption by PAB 0.5, initial metal concentration 10 mg/L, biomass concentration 10g/L, pH 6, room temperature 25°C.

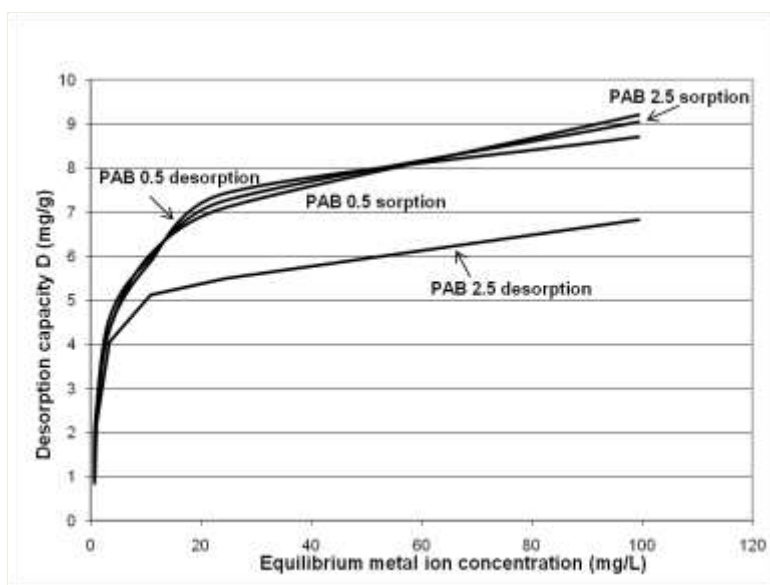


Figure 7. Desorption using 0.2 M H₂SO₄ of biosorbents PAB 0.5 and PAB 2.5, room temperature 25°C.

Desorption percentage ratio D was also higher for PAB 0.5, ranging from 81% in samples with initial concentration 10 mg/L to 97% in samples with initial concentration 50-200 mg/L.

3.4 FTIR Spectroscopy

Cell wall composition of dicotyledonous plants is usually as follows: 25-40% of cellulose, 15-25% of hemicellulose, 15-40% of pectin, 5-10% of proteins and minor amount of phenolic compounds (Taiz & Zeiger, 2006). Dry mass of knotweed *R. japonica* contains 18.9% of lignin, 20% of hemicellulose and 24% of cellulose (Sladký, 2009).

FTIR spectra of activated biomass of *R. japonica* stems prior and after Zn(II) sorption can be seen in graphs (Fig. 8 - 9). After Zn(II) adsorption by stems biomass, there was a band shift from 3335 to 3404

cm⁻¹, representing either changes in amount of surface water adsorbed, or binding onto O-H and N-H groups. Decrease of intensity of bands from 1738 and 1733 to 1735 cm⁻¹ can indicate creation of C=O binding in either esters, carboxylic acids, aldehydes or ketones. Intensive peak in area of 781cm⁻¹, possibly indicating binding between N-H groups and Zn(II), entirely disappeared.

After Zn(II) adsorption by leaves biomass, there was marked band shift from 1527 to 1516 cm⁻¹, representing N-H binding in amides. Band shift from 1061 to 1050 cm⁻¹ indicates binding to OH groups. Intensity of peak in 781 cm⁻¹, which wasn't found in stems biomass after sorption at all, conversely increased in the case of leaves. Decrease of band intensity in 1106 cm⁻¹ could reflect binding of Zn(II) to sulphur.

3.5. Electron Dispersive Spectroscopy

Schneider et al., (2001) reported that for sorption of heavy metals on dead macrophyte biomass two mechanisms are crucial: ion exchange and simple surface precipitation, which cannot be distinguished solely on the basis of sorption calculations. EDS analysis of the *R. japonica* plant shows that the surface of leaves and stems prior to sorption contain the following elements: C, O and Ca. Additional elements, S, P and K, occurred only in leaves (Table 5).

After sorption of Zn(II), peak of zinc was detected in stems while the peak of calcium after sorption significantly decreased (Fig. 10 - 11). Results were analogical for leaves. These results suggest that in the sorption of zinc on stems and leaves of *R. japonica*, ion exchange played an important role, specifically exchange of zinc ions for calcium ions.

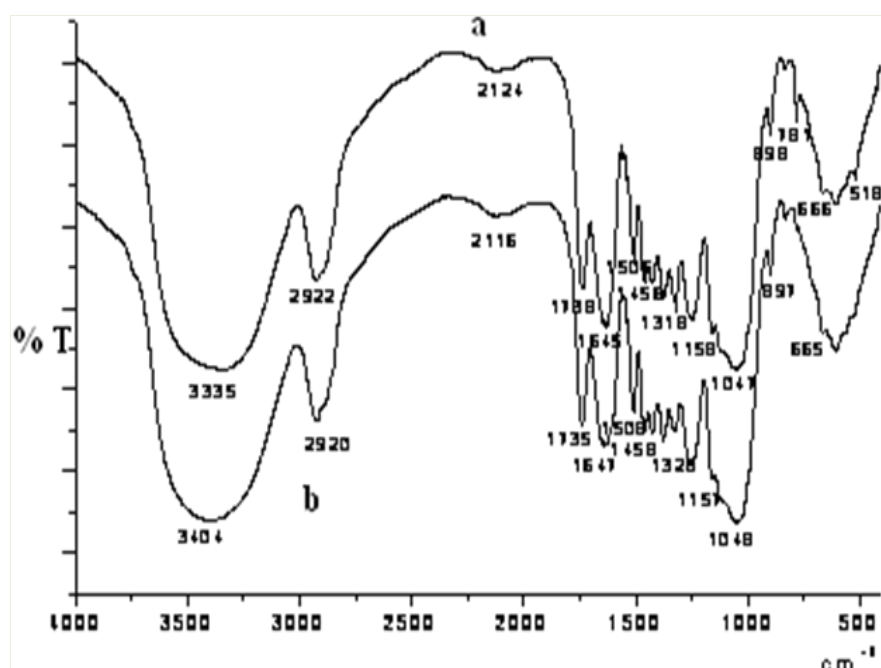


Figure 8. FTIR spectra of *R. japonica* stems prior to (a) and after (b) sorption of Zn (II).

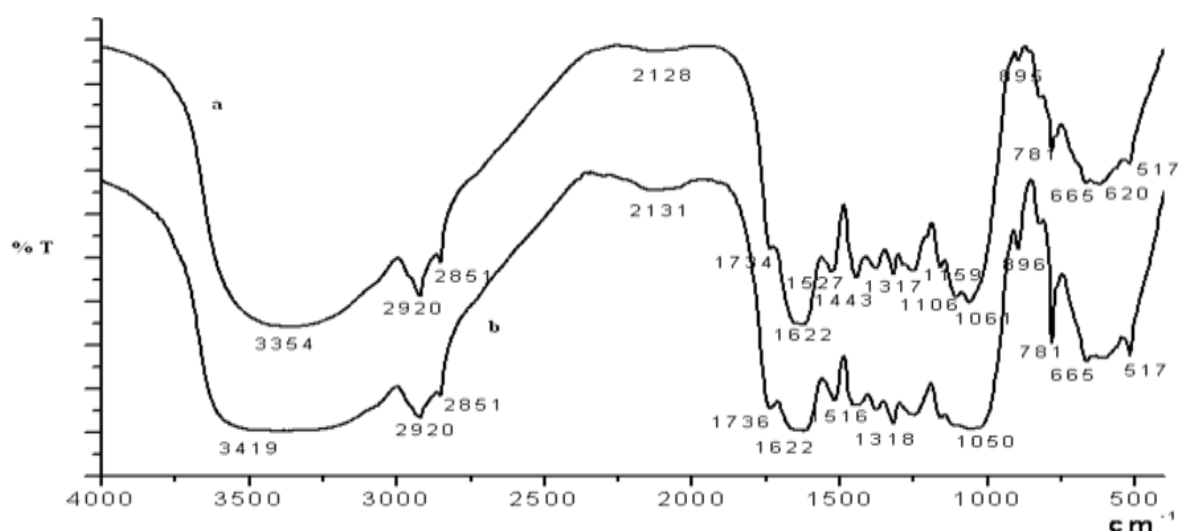


Figure 9. FTIR spectra of *R. japonica* leaves prior to (a) and after (b) sorption of Zn (II).

Table 5. The weight percentage of elements in leaves (1-3) and stems (4-6) of knotweed *R. japonica*.

	Weight %					
	C	O	P	S	K	Ca
1	56.88	42.36		0.14	0.12	0.50
2	55.68	43.59		0.18		0.30
3	57.94	41.43	0.10	0.14	0.09	0.29
4	49.39	50.35				0.25
5	49.89	49.65				0.47
6	49.64	49.84				0.52

Similarly, release of Ca and Mg ions as a result of

lead uptake by leaves of *Ficus religiosa* was observed by Qaiser et al., (2009).

4. CONCLUSIONS

Basic research in the field of Zn(II) biosorption by activated mixed biosorbents PAB 0.5 and PAB 2.5, prepared from stems and leaves of *R. japonica*, had the following results:

For zinc, maximal sorption capacity q_{max} and b was the highest for biosorbent PAB 0.5 mixture: q_{max} was 8.97 mg/g and b was 0.2400 (R^2 0.9928).

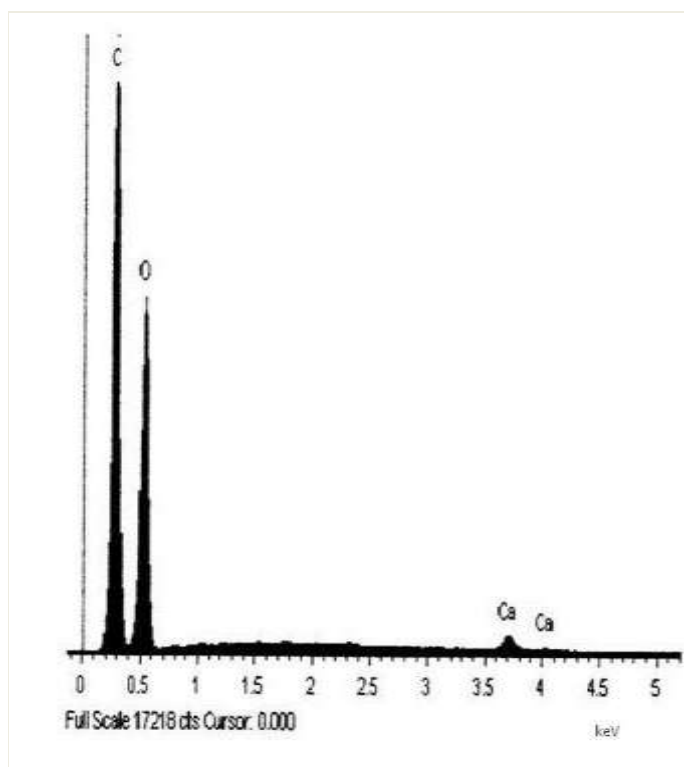


Figure 10. EDS spectrum prior to biosorption of Zn(II) on to stems of *R. japonica*.

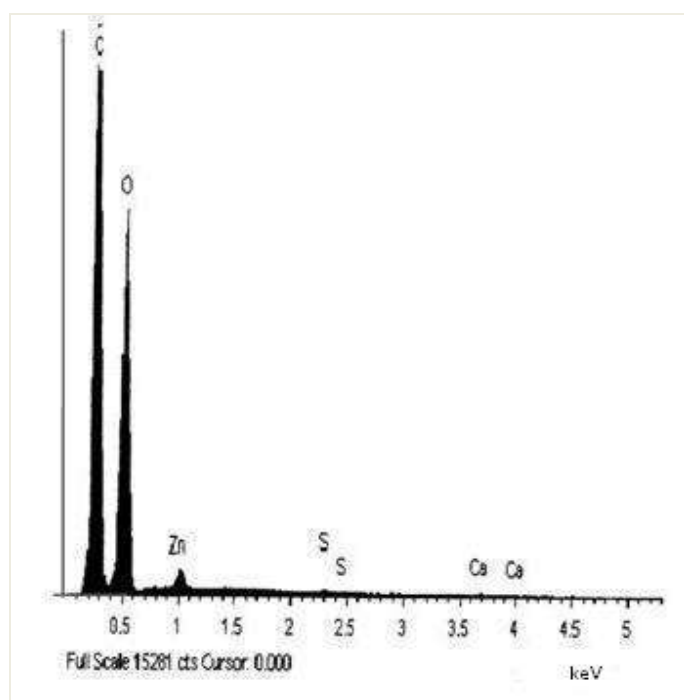


Figure 11. EDS spectrum prior after biosorption of Zn (II) on to stems of *R. japonica*.

Constants q_{max} , b and correlation coefficient R^2 were different depending on linear or non-linear regression model used; therefore it seems to be useful to use both models for biosorption data modeling. PAB 0.5 biosorbent was also characterized by very high value of k_2 (pseudo-second-order rate constant) - 34.52 g/(mg min).

EDS analysis confirmed the main mechanism of binding action: in both stems and leaves it was an ion exchange process between Zn(II) and Ca(II) at binding sites within the cell wall. This fact was confirmed also by extremely high desorption of Zn(II) from biosorbent back into solution (up to 97%). According to FTIR analysis, binding sites in stems and leaves slightly differ. For stems, esters, carboxylic acids, aldehydes or ketones as well as amine groups were found. For leaves, there are mostly amide, hydroxy and possibly also sulfonate groups. Based on all results it can be concluded that PAB 0.5 mixture of stems and leaves of *R. japonica* is very effective biosorbent for removing Zn(II) from aqueous solutions.

REFERENCES

- Ahluwalia, S.S. & Goyal, D., 2007. *Microbial and plant derived biomass for removal of heavy metals from wastewater*. Bioresource Technology, 98, 2243–2257.
- Al Rub, F.A.A., 2006. *Biosorption of zinc on palm tree leaves: equilibrium, kinetics and thermodynamics studies*. Separation Science and Technology, 4, 3499–3515.
- Chojnacka, K., 2006. *Biosorption of Cr(III) Ions by Wheat Straw and Grass: a Systematic Characterization of New Biosorbents*. Polish Journal of Environmental Studies, 15, 845–852.
- Chojnacka, K., 2010. *Biosorption and bioaccumulation – the prospects for practical applications*. Environment International, 36, 299–307.
- Davis, T.A., Volesky, B. & Mucci, A., 2003. *A review of the biochemistry of heavy metal biosorption by brown algae*. Water Research, 37, 4311–4330.
- Farooq, U., Kozinski, J.A., Khan, M.A. & Athar, M., 2010. *Biosorption of heavy metal ions using wheat based biosorbents – A review of the recent literature*. Bioresource

- Technology, 101, 5043–5053.
- Gadd, G.M.**, 2009. *Biosorption: critical review of scientific rationale, environmental importance and significance for pollution treatment*. Journal Chemical Technology and Biotechnology, 84, 13–25.
- Hasan, S.H., Singh, K.K., Prakash, O., Talat, M. & Ho, Y.S.**, 2008. *Removal of Cr(VI) from aqueous solution using agricultural waste maize bran*. Journal of Hazardous Materials, 152, 356–365.
- Ho, Y.-S.**, 2006. *Review of second-order models for adsorption systems*. Journal of Hazardous Materials, 136, 681–689.
- Ho, Y.-S., Chiu, W.-T. & Wang, Ch.-Ch.**, 2005. *Regression analysis for the sorption isotherms of basic dyes on sugarcane dust*. Bioresource Technology, 96, 1285–1291.
- Javaid, A., Bajwa, R., Shafique, U. & Anwar, J.**, 2011. *Removal of heavy metals by adsorption on Pleurotus ostreatus*. Biomass and bioenergy, 35, 1675–1682.
- Keskinkan, O., Goksu, M.Z.L., Basibuyuk, M. & Forster, C.F.**, 2004. *Heavy metal adsorption properties of a submerged aquatic plant (Ceratophyllum demersum)*. Bioresource Technology, 92, 197–200.
- Kratochvil, D. & Volesky, B.**, 1998. *Biosorption of Cu from ferruginous wastewater by algal biomass*. Water Research, 32, 2760–2768.
- Lesage, E., Mundia, C., Rousseau, D.P.L., Van de Moortel, A.M.K., Du Laing, G., Meers, E., Tack, F.M.G., De Pauw, N. & Verloo, M.G.**, 2007. *Sorption of Co, Cu, Ni and Zn from industrial effluents by the submerged aquatic macrophyte Myriophyllum spicatum L.* Ecological Engineering, 30, 320–325.
- Li, H., Lin, Y., Guan, W., Chang, J., Xu, L. Guo, J. & Wie, G.**, 2010. *Biosorption of Zn(II) by live and dead cells of Streptomyces ciscaucasicus strain CCNWHX 7214*. Journal of Hazardous Materials, 179, 151–159.
- Limousin, G., Gaudet, J.-P., Charlet, L., Szenknect, S., Barthès, V. & Krimissa, M.**, 2007. *Sorption isotherms: A review on physical bases, modelling and measurement*. Applied Geochemistry, 22, 249–275.
- Mandák, B., Pyšek, P. & Bímová, K.**, 2004. *History of the invasion and distribution of Reynoutria taxa in the Czech Republic: a hybrid spreading faster than its parents*. Preslia, 76, 15–64.
- Melčáková, I. & Horváthová, H.**, 2010. *Study of biomass of Reynoutria japonica as a novel biosorbent for removal of metals from aqueous solutions*. GeoScience Engineering, 1, 55–70.
- Murphy, V., Hughes, H. & McLoughlin, P.**, 2008. *Comparative study of chromium biosorption by red, green and brown seaweed biomass*. Chemosphere, 70, 1128–1134.
- Naja, G., Murphy, V. & Volesky, B.**, 2007. *Biosorption metals*. Wiley Encyclopedia of Industrial Biotechnology. 147. <http://biosorptionmngill.ca/publications/PDFs/ENCYwiley%2710.pdf>.
- Norton, L., Baskaran, K. & McKenzie, T.**, 2004. *Biosorption of zinc from aqueous solutions using biosolids*. Advances in Env. Research, 8, 629–635.
- Ozdemir, S., Kilinc, E., Poli, A., Nicolaus, B. & Guven, K.**, 2009. *Biosorption of Cd, Cu, Ni, Mn and Zn from aqueous solutions by thermophilic bacteria, Geobacillus toebii sub.sp. decanicus and Geobacillus thermoleovorans sub.sp. stromboliensis: Equilibrium, kinetic and thermodynamic studies*. Chemical Engineering Journal, 152, 195–206.
- Pasavant, P., Apiratikul, R., Sungkhum, V. Suthiparinyanont, P. Wattanachira, S. & Marhaba, T.F.**, 2006. *Biosorption of Cu²⁺, Cd²⁺, Pb²⁺, and Zn²⁺ using dried marine green macroalga Caulerpa lentillifera*. Bioresource Technology, 97, 2321–2329.
- Patočka, J.**, 2005. *Knotweed: Annoying Weed or Promising Raw Material? (Křídlatka: obtížný plevel, nebo perspektivní surovina? -In Czech)*. Vesmír, 84, 362.
- Qaiser, S., Saleemi, A.R. & Umar, M.**, 2009. *Biosorption of lead from aqueous solution by Ficus religiosa leaves: Batch and column study*. Journal of Hazardous Materials, 166, 998–1005.
- Romera, E., Gonzalez, F., Ballester, A., Blazquez, M.L. & Munoz, J.A.**, 2007. *Comparative study of biosorption of heavy metals using different types of algae*. Bioresource Technology, 98, 3344–3353.
- Schneider, I., Rubio, J. & Smith, R.**, 2001. *Biosorption of heavy metals onto plant biomass: exchange adsorption or surface precipitation*. International Journal of Mineral Processing, 62, 111–120.
- Singh, A., Dhananjay, K. & Gaur, J.P.**, 2007. *Cooper (II) and lead(II) sorption from aqueous solution by non-living Spirogyra neglecta*. Bioresource Technology, 98, 3622–3629.
- Sladký, V.** 2009. *Knotweed – Promising Energy Crop (Křídlatka - perspektivní energetická plodina - In Czech)*. [online]. 2009-13-10 [cit. 2011-03-13]. [www: http://stary.biom.cz/biom/6/sladky.html](http://stary.biom.cz/biom/6/sladky.html).
- Taiz, L. & Zeiger, E.**, 2006. *Plant Physiology*. 4th edition Sunderland: Sinauer Associates., ISBN 0-878-93856-7, 700 p. http://www.amazon.com/Plant-Physiology-LincolnTaiz/dp/0878938567/ref=sr_1_4?ie=UTF8&s=books&qid=1250151896&sr=8-4-#
- Ucun, H., Aksakal, O. & Yildiz, E.**, 2009. *Copper (II) and zinc(II) biosorption on Pinus sylvestris L*. Journal of Hazardous Materials, 161, 1040–1045.
- Volesky, B.**, 2001. *Detoxification of metal-bearing effluents: biosorption for the next century*. Hydrometallurgy, 59, 203–216.
- Volesky, B.**, 2003. *Sorption and biosorption*. St. Lambert Quebec: BV-Sorbex, ISBN 0-9732983-0-8, 326 p.
- Wang, J. & Chen, C.**, 2009. *Biosorbents for heavy metals removal and their future*. Biotechnology advances, 27, 195–226.
- Witek-Krowiak, A., Szafran, R.G. & Modelski, S.**, 2011. *Biosorption of heavy metals from aqueous solution onto peanut shell as low-coast biosorbent*. Desalination, 265, 126–134.

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