

STUDY OF BIOMASS OF REYNOUTRIA JAPONICA AS A NOVEL BIOSORBENT FOR REMOVAL OF METALS FROM AQUEOUS SOLUTIONS

TESTOVÁNÍ BIOMASY REYNOUTRIA JAPONICA JAKO NOVÉHO BIOSORBENTU PRO ODSTRAŇOVÁNÍ KOVŮ Z VODNÝCH ROZTOKŮ

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Abstract

In the present study, the sorption capacity of plant biomass has been studied; more precisely the ability of biomass of roots, stems and leaves of an invasive plant *Reynoutria japonica* to bind up Zn^{2+} ions from aqueous solutions. The results of this biosorption study revealed that the rate and extent of uptake were affected by pH level, contact time and initial metal concentration. The equilibrium sorption data for the metal system at pH 6.0 was described by the Langmuir isotherms model. The sorption equilibrium, when expressed by the Langmuir and Freundlich equations, indicated that the process was in compliance with the Langmuir isotherm, which showed the best match. The maximum uptake of metal ions was obtained at pH 6.0. The highest sorption capacity for Zn^{2+} , $q_{max} = 17$ mg/g, was achieved using the biomass from leaves. Removal of Zn^{2+} with 1g/l biosorbent from leaves was almost 77%, when zinc present in low concentrations, whereas it was lower at higher concentrations. With higher biomass doses the removal efficiency of Zn^{2+} was high even at high initial concentrations of the metal.

Abstrakt

V této studii byly studována sorpční kapacita rostlinné biomasy, konkrétně schopnost biomasy kořenů, stonků a listů invazivní rostliny křídlatky (*Reynoutria japonica*) vázat z vodného roztoku ionty Zn^{2+} . Výsledky této biosorpční studie ukazují, že rychlost a rozsah tohoto vázání byly ovlivněny hodnotou pH, dobou trvání adsorpce a počáteční koncentrací kovu. Sorpční rovnováha, vyjádřená pomocí Langmuirovy a Freundlichovy rovnice, naznačuje, že proces probíhal v souladu s Langmuirovou izotermou. Maximální vázání iontů kovu bylo zjištěno při pH 6.0. Pro Zn^{2+} bylo nejvyšší sorpční kapacity $q_{max} = 17$ mg/g dosaženo při užití biomasy listů. Odstraňování Zn^{2+} pomocí biomasy listů v dávce 1 g/l dosáhlo při nízkých koncentracích zinku téměř 77% účinnosti, při vyšších koncentracích byla účinnost nižší. Ve vyšších koncentracích biomasy byla účinnost odstraňování Zn^{2+} vysoká i při vyšších počátečních koncentracích iontů kovu.

Key words: *Reynoutria japonica*, biosorption, zinc, isotherms

1 INTRODUCTION

Heavy metal pollution of water has today become one of the most serious problems. Pollution of the environment by toxic metals arises as a result of many human activities like mining, metallurgy, electroplating, leather tanning, metal finishing, textile industry, and paper industry [1]. Heavy metals are discharged or transported into the atmosphere and aquatic and terrestrial environments mainly as solutes or particulates and may reach high concentrations, especially near the site of entry [2]. Heavy metals have several characteristics that increase their harmful nature: high toxicity, ability to accumulate in living organisms, and long time of staying in ecosystems [3]. Effects of these metals on ecosystems are of a large economic and public-health significance. By far the greatest demand for metal sequestration comes from the need of immobilizing the metals “mobilized” by and partially lost as a result of human technological activities [4].

As the Ostrava region is known for high density of mines and metallurgical plants, the issue of heavy metals pollution is of the highest interest.

Conventional methods for removing metals include chemical precipitation, chemical oxidation or reduction, ion exchange, filtration, membrane technologies and evaporation recovery, electrochemical treatments, adsorption on activated carbon etc. [5]. However, chemical precipitation and electrochemical treatments are ineffective, especially when concentration of metal ions in aqueous solution is within 1-100 mg/l, and also produce large quantity of sludge difficult to treat [6]. Ion exchange, membrane technologies and activated carbon adsorption processes are extremely expensive, when treating large amount of water and wastewater containing heavy metals in low concentrations, hence they cannot be used at large scale [7]. Another major disadvantage of conventional treatment technologies is the production of toxic chemical sludge, and its disposal/treatment becomes a costly affair and definitely not eco-friendly. Therefore, the removal of toxic heavy metals to environmentally safe level in a cost effective and environment friendly manner assumes a great importance [8].

For these reasons, alternative technologies that are practical, efficient and cost effective at low metal concentrations are being investigated. Under certain conditions, biotechnology may be an effective alternative for the removal and recovery of metals. In recent years, applying biotechnology in controlling and removing metal pollution has been paid much attention and gradually becomes a hot topic in the field of metal pollution control due to its potential application [9]. Biosorption and bioaccumulation belong to the group of biotechnological methods suitable for the heavy metal removal from wastewater. Biosorption has been emerging as the most prominent alternative technology for this purpose. The removal process is rapid, it lasts only few minutes and takes place under normal pressure and normal temperature conditions [10].

Biosorption has been defined as the ability of certain biomolecules (or types of biomass) to bind and concentrate selected ions or other molecules from aqueous solutions. As opposed to a much more complex phenomenon of bioaccumulation, which is based on active metabolic transport, biosorption by dead biomass (or by some molecules and/or their active groups) is passive and based mainly on the “affinity” between the (bio-)sorbent and sorbate [11]. Comparison of the features of biosorption and bioaccumulation is shown in Tab. 1.

Biosorption method, as it has been perceived thus far, could be considered for its economic edge as a possible alternative technique for metal recovery. The advantages of biosorption are the low operational costs, minimization of volume of chemical and/or biological sludge to be disposed, high

efficiency in detoxifying very dilute effluents, no nutrient requirements, regeneration of biosorbent and possibility of metal recovery [12].

The economic advantage of biosorption is in using biomass of raw materials, which are either abundant or wastes from other industrial operations. The unique capabilities of certain types of biomass to concentrate and immobilize particularly heavy metals can be more or less selective [13].

Tab. 1 Comparison of the features of biosorption and bioaccumulation

Features	Biosorption	Bioaccumulation
Costs	Usually low. Most biosorbents used were industrial, agricultural and other type of waste biomass. Costs involves mainly transportation and other simple processing charges.	Usually high. The process involves living cells and; hence, cell maintenance is cost prone.
pH	The solution pH strongly influences the uptake capacity of biomass. However, the process can be operated under a wide range of pH conditions.	In addition to uptake, the living cells themselves are strongly affected under extreme pH conditions.
Temperature	Since the biomass is inactive, temperature does not influence the process. In fact, several investigators reported uptake enhancement with temperature rise.	Temperature severely affects the process.
Maintenance/storage	Easy to store and use.	External metabolic energy is needed for maintenance of the culture.
Selectivity	Poor. However, selectivity can be improved by modification/processing of biomass.	Better than biosorption
Versatility	Reasonably good. The binding sites can accommodate a variety of ions	Not very flexible. Prone to be affected by high metal/salt conditions.
Degree of uptake	Very high. Some biomasses are reported to accommodate an amount of toxicants nearly as high as their own dry weight.	Because living cells are sensitive to high toxicant concentrations, uptake is usually low.
Rate of uptake	Usually rapid. Most biosorption mechanisms are rapid.	Usually slower than biosorption, since intracellular accumulation is time consuming.
Toxicant affinity	High under favourable conditions.	Depends on the toxicity of the pollutant.
Regeneration and reuse	High possibility of biosorbent regeneration, with possible reuse over a number of cycles.	Since most toxicants are intracellularly accumulated, chances are very limited.
Toxicant recovery	With proper selection of elutant, toxicant recovery is possible. In many instances, acidic or alkaline solutions proved to be an efficient medium to recover toxicants.	Even if possible, the biomass cannot be utilized for next cycle.

Biosorbents for the removal of metals/dyes belong mainly to the following categories: bacteria, fungi, algae, industrial wastes, agricultural wastes, and other polysaccharide materials. In general, all types of biomaterials have shown good biosorption capacities towards all types of metal

ions [14]. Abundant natural materials, particularly of cellulosic nature, have been suggested as potential biosorbents for heavy metals. Considering the number of candidate biomass types and the number of metals of interest, all multiplied by the number of experimental or process parameters, the task of prospecting for new and potentially feasible metal biosorbents has a very wide scope [15].

The mechanism of biosorption of heavy metals by biomass is still not clear. Most researchers (process engineers, chemical engineers, biologists and environmental engineers) have concentrated on the optimal conditions for developing large scale applications for heavy metal uptake from industrial waste water using living or nonliving biomass.

In this study, we have chosen a novel biosorbent - roots, stems and leaves of a plant species *Reynoutria japonica*. This plant species is an invasive ubiquitous plant investigated currently as a possible energetic plant. It is also known that the species of this genus are able to accumulate heavy metals from soil [16], [17].

2 MATERIAL AND METHODS

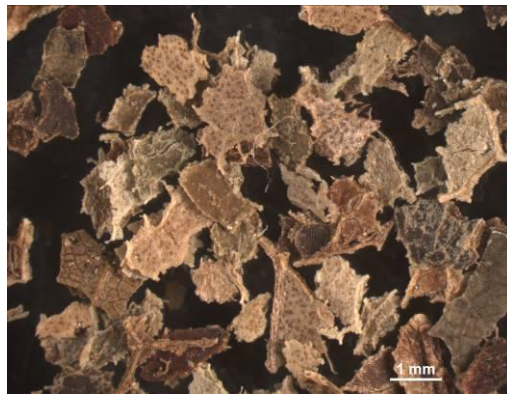
2.1 Preparation of biosorbents

All the samples of *Reynoutria japonica* used were collected from the same non-urban area in foothills of Lysá hora Mountain, in the area of Moravskoslezské Beskydy. This sampling area does not have any prior history of contamination by heavy metals. Roots, stems and leaves of this plant were air-dried at room temperature. The dried samples were ground and screened using a sieve shaker; uniform particle size fraction of 1-2 mm was obtained (Fig. 1). 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 [7]. The particles of roots, stems and leaves were twice washed with 0.01 M HCl (10 g/l litre), then with an extensive volume of de-ionized water, in order to remove soil or debris, and finally washed with distilled water. The biomass samples were then oven-dried at 90 °C for one day.

a



c



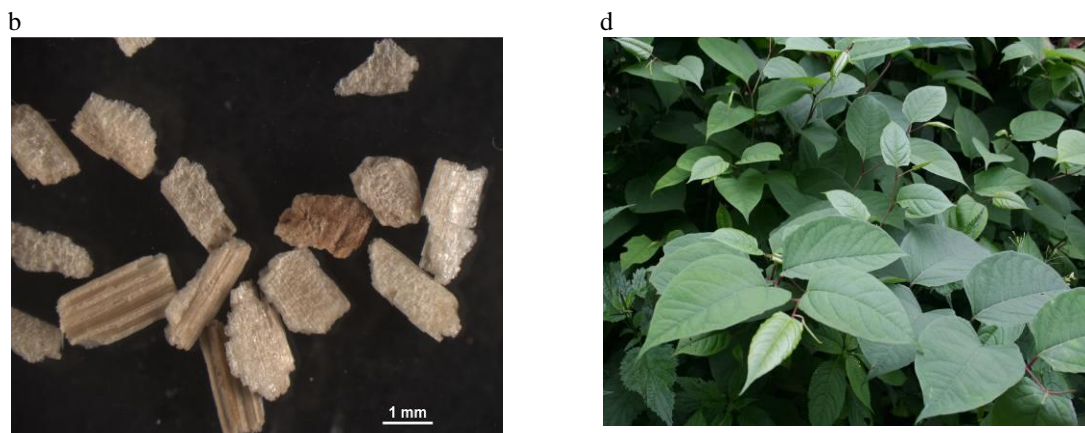


Fig. 1 Biomass particles: a roots, b stems, c leaves; d *Reynoutria japonica*

2.2 Chemicals

Zinc ions Zn^{2+} ($ZnSO_4 \cdot 7 H_2O$) were used in this study. The test solutions containing single ions were prepared by diluting a proper amount of 1g/l stock solution of the above mentioned metal ions to obtain desired concentrations. All chemicals used were of an analytical reagent grade and were used without further purification.

2.3. Procedures of experiments

2.3.1 Time course

The time course of Zn^{2+} uptake by *Reynoutria japonica* was investigated. Two samples of 5 g of sorbent biomass were each suspended in 500 ml of a heavy metal solution. The flasks were placed for 6 hours on a shaker at 120 rpm, at the room temperature of 25 °C. pH of solutions tended to drop during the equilibration and therefore it was, during the sorption experiments, adjusted with 0.1 M solution of NaOH or 0.1 M H_2SO_4 . The temperature and pH were measured by a microcomputer meter. Samples were taken from the solution at intended intervals and were filtered through a filter paper. Heavy metal concentrations in the resulting supernatant were measured by the Atomic Absorption Spectrometry (AAS) Unicam 969. All samples were tripled, with the averages presented as the results.

2.3.2 Determination of adsorption isotherms

In the present experiment we have determined the adsorption isotherms for zinc. Amounts of 0.1 g of dry acid-pre-treated plant biomass (all three types: roots, stems and leaves) and, in additional experiment, 1 g of leaves biomass were suspended in 100 ml samples of various concentrations (10-100 mg/l) of Zn^{2+} solutions. pH of solutions before and during equilibration was adjusted with 0.1 M solutions of H_2SO_4 and 0.1 M solutions of NaOH. After 60 minutes of incubation, the zinc samples were filtered, in order to remove the biomass, and metal concentration in supernatant was measured with AAS. The quality of the sorbent material is judged according to 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 a unit of solid phase [4].

$$q = V(C_i - C_f) / S \quad (1)$$

where:

V – the volume of metal-bearing solution contacted with the sorbent some [l],

C_i – initial and residual concentrations of metal in the solution [mg/l],

C_f – residual concentrations of metal in the solution [mg/l],

S – the amount of the added biosorbent [g].

3 RESULTS AND DISCUSSION

3.1 Time-course of sorption

Time-course profiles of sorption of Zn^{2+} by *Reynoutria japonica* biomass at the concentration of 10 mg/l are illustrated in Fig. 2. The sorption rate for zinc was distinctly divided into two stages: fast initial sorption stage was followed by a much slower sorption stage. At pH 6 the metal concentration dropped rapidly during the first 10 minutes. Biosorption equilibrium was achieved in 60 minutes; after that a further biosorption was negligible. These results are in accordance with other biosorption studies using various groups of microorganisms and plants, where fast initial rates of metal binding, followed by slower onset of equilibria have been reported [18]. In the sample with the biomass concentration of 1 g/l the fastest adsorption of Zn^{2+} was on leaves biomass, followed by stems and then by roots. After initial steep decrease of zinc concentration, some mild increase was observed (Fig. 3). This phenomenon was previously described in bioaccumulation of copper by alive cells of *Chlorella kessleri*, when copper caused the destruction of algae cell walls. However, in biosorption experiments with dead biomass observation like this is exceptional [19].

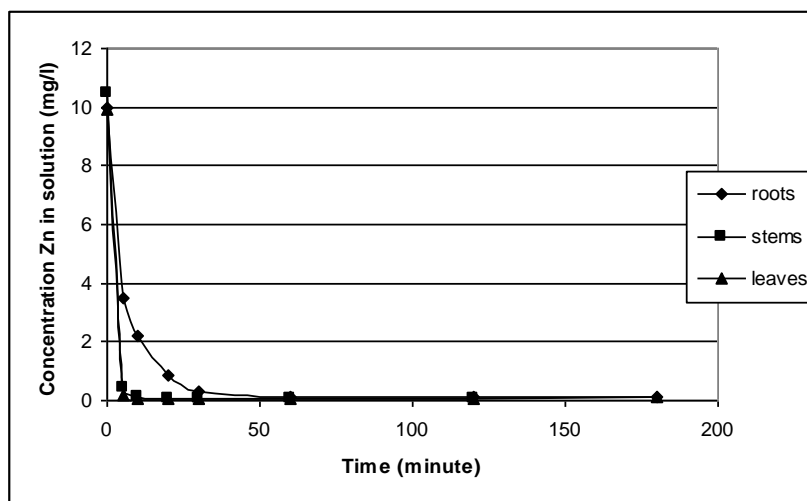


Fig. 2 Time course of metal sorption of divalent zinc by roots, stems and leaves of *Reynoutria japonica* (biomass dosage 10g/l, initial metal concentration 10 mg/l, pH 6.0, room temperature 25 °C).

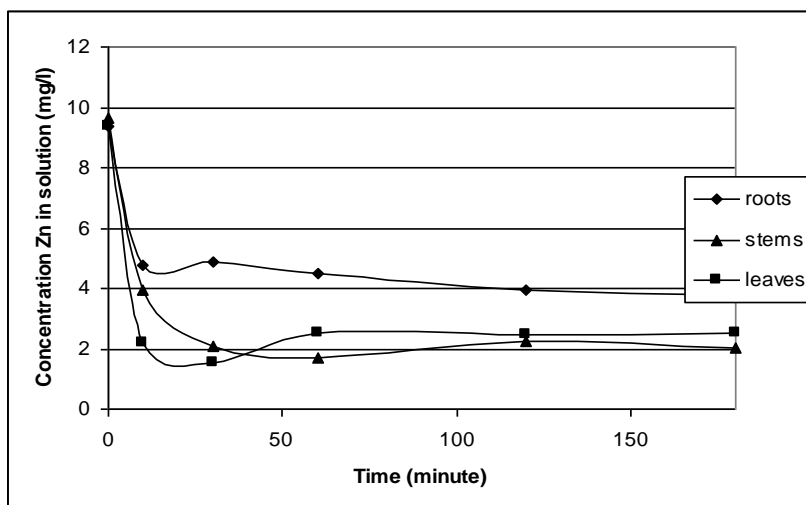


Fig. 3 Time course of metal sorption of divalent zinc by roots, stems and leaves of *Reynoutria japonica* (biomass dosage 1g/l, initial metal concentration 10 mg/l, pH 6.0, room temperature 25 °C).

3.2 Effect of pH

One of the most important parameters in biosorption processes is the pH value of solution. It is commonly agreed that the sorption of metal cations (Cd^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Ni^{2+} , Mn^{2+} , Al^{3+} , Co^{2+} , Cr^{3+} , Fe^{3+}) increases with increasing pH [7]. Solution pH affects cell wall metal binding sites and the metal ion chemistry in water [20]. pH could affect the protonation of functional groups in the biomass [21]. Since the solubility of many metal complexes in solution decreases with increasing pH, the sorption increases with increasing pH [22]. The effect of initial pH on biosorption is shown in Fig. 4. The experiment showed an increase of sorption with pH values growing from 4 to 6; at pH 7 decrease of sorption occurred in all three types of biomass. The results were, however, to a certain extent, different in the case of stems biomass, where sorption of Zn^{2+} was rather low at pH 5. These results are in accordance with the fact, that at low pH protons (H^+) would compete for active sites on the cells and thus restrict the interaction of metal ions and the biomass. Similar results for Zn^{2+} were obtained with the biomass (also roots, stems and leaves) of creosote bush *Larrea tridentata* [23]. Schneider et al. [24], and Miretzky et al. [25] suggested that heavy metals adsorb onto the dead biomass of many macrophyta through two mechanisms: specific ion exchange between heavy metal ions and protons, and simple surface precipitation, although it is not possible to differentiate between them based solely on the sorption data. As mentioned above, pH had a tendency to drop during the sorption of metal ion onto biomass; NaOH was therefore used for adjustments. Kratochvil et al. [26] confirmed that pH is dropping during sorption as a results of ion exchange between a proton and a metal ion. This pH decrease in our experiments hence suggests that the binding mechanism of zinc onto *Reynoutria japonica* biomass may be an ion-exchange type process as well.

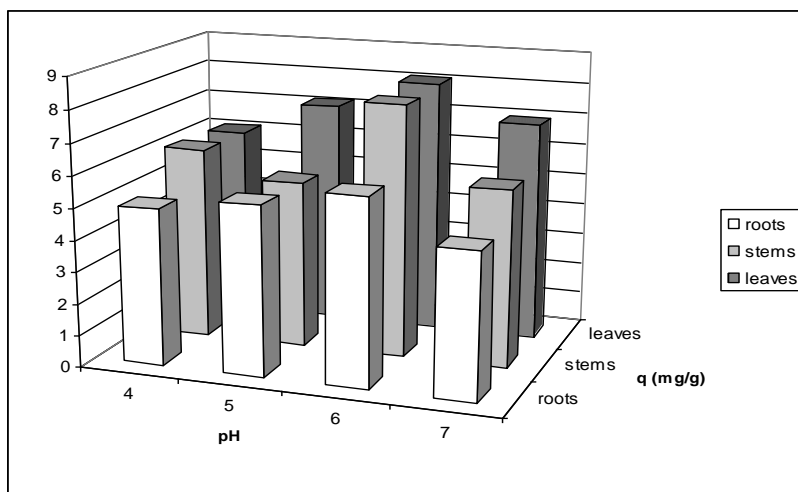


Fig. 4. Effect of pH on the sorption of Zn^{2+} by *Reynoutria japonica* (biomass dosage 1 g/l, pH 4.0-7.0, initial Zn^{2+} concentration 10 mg/l, room temperature 25 °C).

3.3 Biomass concentration

Yet another important factor affecting biosorption is the biomass concentration. As the leaves biomass demonstrated high affinity to zinc, it seemed to be the most suitable biosorbent for testing the effect of two different concentrations of sorbent to various concentrations of zinc solution. Increase in biomass concentrations from 1 g/l to 10 g/l decreased the loading capacity q in all initial concentrations of Zn^{2+} in solution (Fig. 5). As opposed to the zinc uptake capacity, the Zn^{2+} removal efficiency increased. In our experiment the removal efficiency in the sample with the biomass content of 10 g/l and with the initial Zn^{2+} concentration of 10 mg/l reached 99.4% - see Fig. 6. This was attributed to the increase in concentration of biosorbent, resulting in the increase of adsorption surface area.

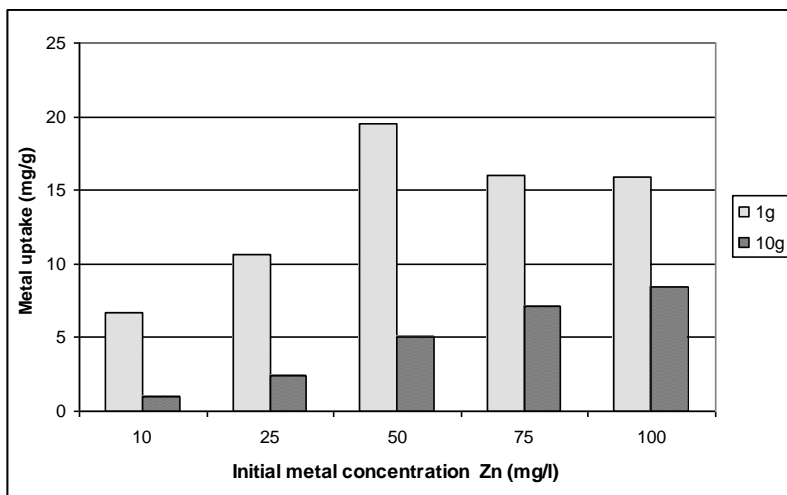


Fig. 5 Comparison of Zn^{2+} uptake (mg/g) in samples with 1 g/l and 10 g/l of *Reynoutria japonica* leaves biomass.

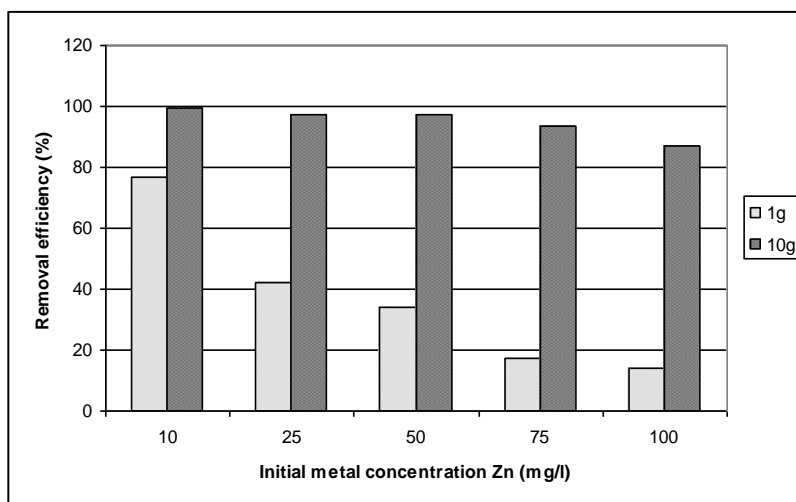


Fig. 6 Comparison of Zn^{2+} removal efficiency (%) in samples with 1 g/l and 10 g/l of *Reynoutria japonica* leaves biomass.

3.4 Sorption isotherms

3.4.1 Adsorption isotherm

Equilibrium isotherms are calculated, in order to determine the capacity of the biosorbent for metal ions. During the biosorption, a rapid equilibrium is established between adsorbed metal ions on the biomass (q) and unadsorbed metal ions in solution (C_f) [4].

In order to describe the sorption of Zn^{2+} by *Reynoutria japonica* at pH 6.0, experiments were carried out with zinc concentrations ranging from 10 to 100 mg/l. In the present study the experimentally observed uptake capacity was 19.48 mg/g of leaves of *Reynoutria japonica* in a residual concentration of 35 mg/l (1g of leaves biomass per 1l of sample). However, in both low and high concentrations, leaves showed the best results (Fig. 7). Due to these excellent results, we have tried to create the adsorption isotherm also for the leaves biomass concentration of 10 g/l. In this concentration, the isotherm exhibited an increasing trend and the highest sorption 8.4 mg/g was achieved with a residual concentration of 12.53 mg/l (Fig. 8).

3.4.2 Langmuir and Freudlich isotherms

The process of zinc sorption on the biosorbent was described by the Langmuir and Freudlich adsorption models, which are widely used to analyze the data for water and wastewater treatment applications. The Langmuir equation which is valid for monolayer sorption onto a surface with a finite number of identical sites is given by Eq. (2).

$$q = q_{max} bC_f / 1 + bC_f \quad (2)$$

where:

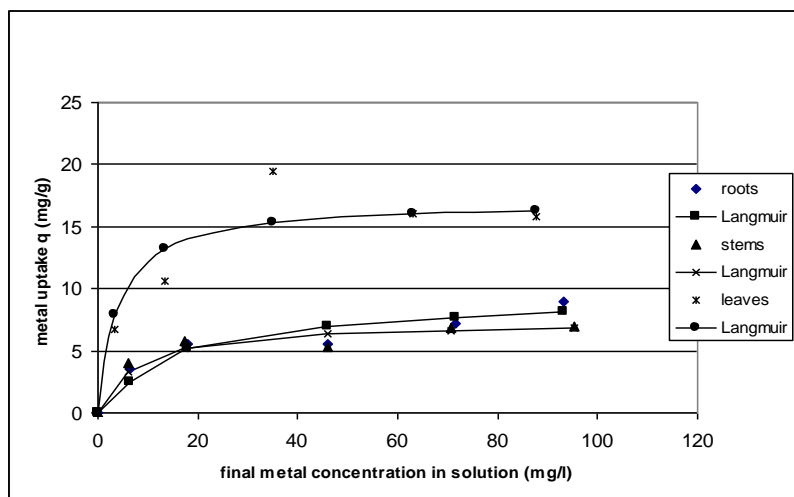
- q_{max} – maximal metal uptake [mg/g],
- b – constant related to the affinity of the binding sites [l/mg],
- q – experimental metal uptake [mg/g],
- C_f – residual concentration of metal in solution [mg/l].

q_{max} and b can be determined from the linear plot of C_f/q vs C_f for Langmuir 1 or $1/q$ vs $1/C_f$ for Langmuir 2 [27].

The Langmuir sorption model served to estimate the maximum metal uptake values when they could not be reached in the experiments. In general, for good biosorbents, high q_{max} and high b are desirable [28]. The Langmuir constants (q_{max} , b) and correlation coefficient R^2 for the zinc biosorption onto biomass of *Reynoutria japonica* are presented in Table 2. The results indicate the applicability of the Langmuir 1 model for biosorbents of *Reynoutria japonica*, and the metal examined.

Tab.2 Langmuir constants and correlation coefficient for biosorption of zinc on biomass.

		q_{max}	b	R^2	
Langmuir model 1 - adsorption constants					
Biosorbent 1,5 mm 1g/l					
Zn	Roots	7.36	0.05	0.9128	
	Stems	9.73	0.13	0.9779	
	Leaves	17.00	0.26	0.9807	
	Biosorbent 1,5 mm 10g/l				
	Leaves	9.14	0.85	0.9923	
	Langmuir model 2 - adsorption constants				
	Biosorbent 1,5 mm 1g/l				
	Roots	7.78	0.12	0.8984	
	Stems	6.82	0.25	0.857	
Leaves	17.57	0.18	0.9361		

**Fig. 7** Sorption isotherms for the sorption of Zn^{2+} onto roots, stems and leaves of *Reynoutria japonica* (biomass dose 1 g/l, contact time 60 minutes, pH 6.0, room temperature 25 °C).

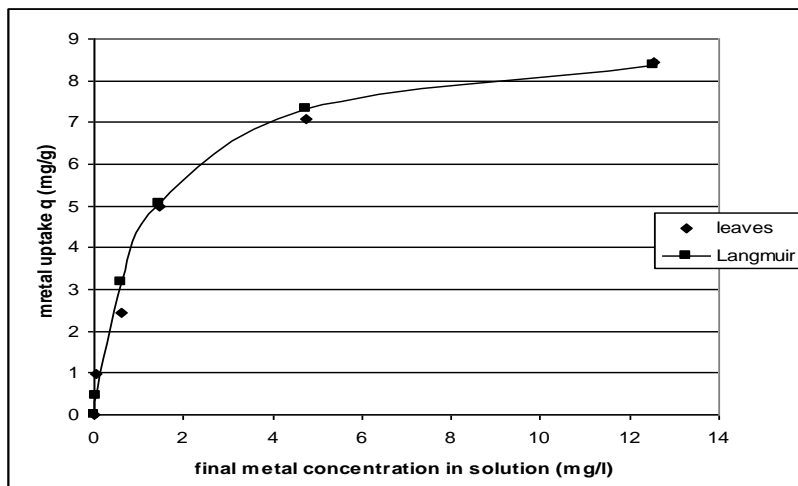


Fig. 8 Sorption isotherm for the sorption of Zn^{2+} onto leaves of *Reynoutria japonica* (biomass dose 10 g/l, contact time 60 minutes, pH 6.0, room temperature 25 °C).

The empirical Freundlich equation based on sorption on a heterogeneous surface is given below by Eq. (3).

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

where:

- q – experimental metal uptake [mg/g],
- C_f – residual concentrations of metal in the solution [mg/l],
- k – maximum adsorption capacity [mg/g],
- n – constant related to the affinity of the binding sites or binding strength [l/mg].

The equation can be linearized in the following logarithmic form and Freundlich constants can be determined: $\ln q = \ln k + 1/n \ln C_f$ [29].

The plot of $\ln q$ versus $\ln C_f$ for the biosorption of Zn^{2+} onto dried biomass of *Reynoutria japonica* was employed to generate the intercept value of k and the slope of $1/n$ and is presented in Fig. 8.

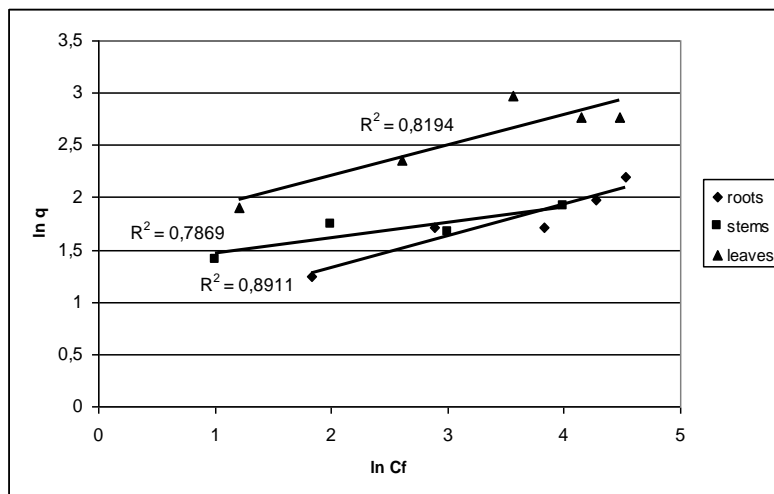


Fig. 9 Freundlich sorption isotherms for the sorption of Zn^{2+} onto leaves of *Reynoutria japonica* (biomass dosage 1g/l, contact time 60 minute, pH 6.0, room temperature 25 °C).

The sorption capacity parameter obtained from a batch experiment comes in useful for providing information about the effectiveness of the metal–biosorbent system.

It is evident from Tab.1 and Fig. 7-9 that the Langmuir isotherm model is well fitted for Zn^{2+} sorption which seems to suggest that the zinc sorption by dried biomass of *Reynoutria japonica* was more likely monolayer surface adsorption, instead of heterogeneous sorption. In the case of adsorption by leaves biomass this fact was also evidenced by the high R^2 values (>0.999). Leaves of *Reynoutria japonica* had a higher affinity for zinc at lower equilibrium concentrations, as indicated by the desirably steeper sorption isotherm in Fig. 7. The stronger affinity for metal is demonstrated by steeper isotherm slopes at low residual metal concentrations.

For comparison, the maximum adsorption capacity for waste tea leaves was found to be 11.77 mg/g [30] and for palm tree leaves maximum uptake capacity of 14.70 mg/g was obtained at 25.0°C [31]. The use of biomass of submersed aquatic plant *Ceratophyllum demersum* resulted in the capacity of 13.98 mg/g [32] and binding capacity of zinc by creosote bush biomass *Larrea tridentata* were 6.24 mg/g for roots, 5.05 mg/g for stems and 6.20 mg/g for leaves [23].

4 CONCLUSIONS

This work has tested the possibility of utilization of biomass of the *Reynoutria japonica* for biosorption of heavy metals.

Capacity experiments have demonstrated:

- Kinetics of zinc biosorption by inactive biomass was fast, and in the sample with a biomass concentration of 10 g/l most of the metal was adsorbed within 10 minutes. The maximum decrease of the zinc concentrations (that is removal efficiency) was in the sample of leaves biomass (99.4%). Biosorption equilibria were usually achieved in 60 minutes.
- pH had a strong effect on the zinc biosorption capacity. The capacity of zinc biosorption by biomass increased with the increase of pH values; optimal pH was detected to be 6.
- Maximal sorption capacity was obtained, when using the leaves biomass in 1 g/l concentration.

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