DRAGANA-LINDA
MITIĆ-STOJANOVIĆ[1]
DANIJELA BOJIĆ[2]
JELENA MITROVIĆ[2]
TATJANA ANDJELKOVIĆ[2]
MILJANA RADOVIĆ[2]
ALEKSANDAR LJ. BOJIĆ[2]

[1]Public waterworks enterprise
"VODOVOD", Vranje, Serbia
[2]Department of Chemistry, Faculty
of Science and Mathematics,
University of Niš, Serbia

SCIENTIFIC PAPER

EQUILIBRIUM AND KINETIC STUDIES OF Pb(II), Cd(II) AND Zn(II) SORPTION BY *Lagenaria vulgaris* SHELL*

The sorption of lead, cadmium and zinc ions from aqueous solution by Lagenaria vulgaris shell biosorbent (LVB) in batch system was investigated. The effect of relevant parameters such as contact time, biosorbent dosage and initial metal ions concentration was evaluated. The Pb(II), Cd(II) and Zn(II) sorption equilibrium (when 98% of initial metal ions were sorbed) was attained within 15, 20 and 25 min, respectively. The pseudo-first, pseudo-second order, Chrastil's and intra-particle diffusion models were used to describe the kinetic data. The experimental data fitted the pseudo-second order kinetic model and intra-particle diffusion model. Removal efficiency of lead(II), cadmium(II) and zinc(II) ions rapidly increased with increasing biosorbent dose from 0.5 to 8.0 g dm^{-3}. Optimal biosorbent dose was set to 4.0 g dm^{-3}. An increase in the initial metal concentration increases the sorption capacity. The sorption data of investigated metal ions are fitted to Langmuir, Freundlich and Temkin isotherm models. The Langmuir model best fitted the equilibrium data ($r^2 > 0.99$). Maximal sorption capacities of LVB for Pb(II), Cd(II) and Zn(II) at 25.0±0.5 °C were 0.130, 0.103 and 0.098 mmol g^{-1}, respectively. The desorption experiments showed that the LVB could be reused for six cycles with a minimum loss of the initial sorption capacity.

Keywords: sorption; Lagenaria vulgaris; heavy metals; kinetics; isotherms.

Contamination of the aquatic environment by heavy metals is a worldwide environmental problem. Many industries, such as metal finishing, automotive, aeronautical, non-ferrous metals and steel, generate large quantities of wastewater containing various concentrations of heavy metals. They are not biodegradable, and accumulate in living organisms causing diseases, disorders and other toxic effects [1,2]. Consequently, industries are required to reduce the contents of heavy metals in their effluents to acceptable levels.

Various treatment procedures, such as chemical precipitation and coagulation/flotation, ion exchange, oxidation/reduction, osmosis and reverse osmosis, electrodialysis and electrolytic technologies are available for the removal of heavy metal contaminants in effluents and industrial wastewaters [3-6]. However, these processes may have various disadvantages. Technoeconomic considerations sometimes limit their wide scale application. Some of these technologies are most suitable when the concentrations of heavy metal ions are relatively high. They are either ineffective or expensive when heavy metals are present in wastewater in low concentrations [7].

Among the physicochemical treatment processes, biosorption is an alternative technology and represents a highly effective, cheap and easy method. Application of activated carbon has been found to be an effective process for metal ions removal, but it is too expensive. Consequently numerous low cost alternatives have been studied, including agricultural wastes, sawdust, rice husk, orange wastes, seaweed,

Correspondence: A.Lj. Bojić, Department of Chemistry, Faculty of Science and Mathematics, University of Niš, Višegradska 33, Serbia.
E-mail: bojica@pmf.ni.ac.rs

peanut skins and breweries' waste biomass, among other biosorbent materials [8-13]. Many of these materials are mainly composed of lignin and cellulose, containing different functional groups. Predominant surface oxygen functional groups of lignocellulosis materials are: carboxyl, lactone, carbonyl and hydroxyl (aliphatic and aromatic), which are known to strongly bind metal cations in aqueous solution [6,8].

Lagenaria vulgaris (Cucurbitaceae), popularly known as bottle gourd, is a climbing, hardy plant used as a common vegetable in many countries [14]. This plant is found growing mainly on alluvial sandy soil and red loam, on flat areas and moderate slopes in higher-lying areas, and needs light and warmth [15]. The outer shell of the plant is hard with lignocellulosis structure, covering the spongy white pith characterized by its bitter taste. The plant finds its medicinal value in traditional medicine in the treatment of jaundice, diabetes, ulcer, piles, colitis, insanity, hypertension, congestive cardiac failure, and skin diseases. The fruit pulp is used as an emetic, sedative, purgetive, cooling, diuretic, antibilious and pectoral agent. Also, extracts of the plant have shown antibiotic activity [16,17].

The present study deals with lead, cadmium and zinc ions removal from aqueous solution by *Lagenaria vulgaris* shell as a potential biosorbent. This plant has remained almost unexplored as a biosorbent of metal ions from water. Experiments were performed under different conditions in order to optimize the efficiency of the sorption process. Equilibrium isotherms, kinetics and diffusion models were examined for a better understanding of the sorption process.

EXPERIMENTAL

Biosorbent preparation

Lagenaria vulgaris (wild type) shell was used as a biosorbent in this study. The plant was collected in the southeast area of Serbia, from different places at altitudes ranging from 400 to 700 m, where it was grown without cultivation(irrigation and fertilization). Harvested fruits have been emptied, crushed into 2 to 3 cm pieces, washed with deionized water and ground in a laboratory blender mill (Waring, Germany).The purification and activation of biomass was done as follows: the biomass was treated with 0.3 M HNO₃ for 24 h to remove all metal ions bio-accumulated in the plant during its growth. After the acid washing, the biomass was rinsed with deionized water and neutralized using a 0.1 M NaOH solution. Further, it was washed thoroughly to remove all other soluble materials until the pH of the washed water become neutral. The biomaterial obtained was oven dried to remove

its water and fractionized by sieving (Endecotts, England). The fraction, ranging from 1.00 to 1.25 mm, was selected for use in the sorption experiments. The structural and chemical composition of LVB was given in previous study [18].

Boehm's titrations

Oxygen acidic functional groups in LVB were determined by potentiometric titration based on Boehm's method [19,20]. This method is based on titration of functional groups with different acidity constants using base solutions of increasing strength (NaHCO₃, Na₂CO₃ and NaOH). Solutions of bases were freshly prepared and stored in nitrogen atmosphere. LVB samples were protonated with 0.01 M HCl stirring in period of 2 h. After that, samples were washed and dried at 40 °C to remove excess acid. Titrations were carried out in an enclosed glass cell at 25.0±0.5 °C, using precise digital burette Solarus (Hirschman, USA). Exactly weighed 0.5000 g of protonated LVB was suspended in 100 cm³ of a 0.1 M NaNO₃ solution to maintain constant ionic strength during the titration. One hour before and during the titration, nitrogen gas was bubbled through the solution to avoid dissolution of carbon dioxide. A control experiment was carried out in the same conditions without biosorbent.

Reagents and solutions

All chemicals used were of reagent grade and used without further purification. HNO₃, NaOH, and Pb, Cd and Zn in granular form, were purchased from Merck (Germany). H₂O₂ was purchased from Carlo Erba (Italy). Deionized water was used for all experiments.

Standard metal ions stock solutions, in concentration of 1000 mg dm⁻³, were prepared by the dissolving pure metals: Pb, Cd, and Zn in HNO₃ (1:3). All standard solutions were stored in a refrigerator at 4 °C. Working metal ions solutions were prepared, just before use, by the appropriate dilution of the stock solutions. Dilute HNO₃ and NaOH solutions, concentrations 0.1 and 0.01 M, were used for the adjustment of solutions pH.

Sorption experiments

The sorption of Pb(II), Cd(II) and Zn(II) ions on *Lagenaria vulgaris* biosorbent was studied by batch technique. The contact time and biomass amount were predicted with respect to preliminary experiments. 250 cm³ of single metal ions solutions of desired concentration was contacted with 1.0 g of previously prepared biosorbent in Erlenmeyer flasks, stirred at 250 rpm, at room temperature 25.0±0.5 °C, maintained using a temperature-controlled water

bath. The initial pH of solutions was adjusted to value 5.0, using a precise pH meter (SensIon 3, Hach, USA), without buffering. This pH value corresponds to the optimal sorption of investigated metals determined in the study by Mitic-Stojanovic *et al.* [18]. At the beginning of the treatment, the metal ions solution was stirred for 5 min in order to ensure that it was well mixed, and the defined dose of LVB was added. Aliquots of solutions (5.0 cm³) were withdrawn at desired time intervals and the biosolids were removed immediately by filtration through a 0.45 μm regenerated cellulose membrane filter (Agilent Technologies, Germany). Samples were preserved with 0.10 cm³ of concentrated HNO₃, and were analyzed for residual metal ions concentrations using flame atomic absorption spectrophotometry, FAAS (Model AAnalyst 300, Perkin Elmer, USA).

Kinetic experiments were performed with initial metals ions concentration 0.05 mmol dm⁻³, by taking samples in the defined intervals up to 120 min, with all other parameters constant. The sorbed amount of metal ions was calculated from differences of initial and residual metal ion concentration, given by:

$$q_t = \frac{(c_i - c_t)V}{m_{LVB}} \qquad (1)$$

where q_t is the mass of metal ion sorbed (mmol g⁻¹) at time t; c_i and c_t are the initial metal ion concentration and concentration at appropriate time t (mmol dm⁻³), respectively; V is the volume of metal ions solution (dm³) and m_{LVB} is the weight of sorbent (1.0 g).

The effect of the initial metal ions concentration on the sorption of investigated metals on LVB was examined by varying concentrations from 0.20 to 4.00 mmol dm⁻³. In order to evaluate the sorption capacity of LVB, the experimental data were fitted to the Langmuir, Freundlich and Temkin isotherm models, which are commonly used in describing sorption.

Control experiments were carried out in the absence of biosorbent in order to find out whether there is any adsorption on the Erlenmeyer flasks walls. In all experiments, solution samples were taken in triplicate for the measurements of the metal ion concentrations. Statistical analysis, calculation of the data and linear least square fitting was performed using OriginPro 8.0 software (OriginLab Corporation, USA).

Regeneration of LVB

The reusability of biosorbent is directly related to the application potential of sorption technology. After sorption experiments with 4.00 mmol dm⁻³ of metal ions solutions and 4.0 g dm⁻³ of biosorbent, LVB was separated from water phase and gently washed with demineralzed water. The metal loaded LVB was treated

with 100 cm³ 0.1 M HNO₃ as the desorbing agent, in Erlenmeyer flasks, stirred at 250 rpm, in the period of 60 min, at 25.0±0.5 °C. 10 cm³ of aliquot was collected for metal ions analysis. After sampling, the biosorbent was separated from the water phase and washed with deionized water. LVB biomass was reconditioned (deprotonated) by being treated with 0.1 M NaOH solution. Further, it was washed thoroughly until the pH of the washed water become neutral. The metal-desorbed LVB was used as the regenerated sorbent in five repeated sorption-desorption cycles to determine the reusability potential of the adsorbent.

RESULTS AND DISCUSSION

Sorption kinetics

The sorption kinetics were investigated for better understanding of the dynamics of metal ions sorption onto LVB, which allows estimations of the amount sorbed with the contact time and provides information about the sorption mechanism. This information is essential for the scale-up to a larger system [21].

The effect of contact time was studied with initial metal ions concentration of 0.50 mmol dm⁻³, treated with 4.0 g dm⁻³ of LVB at initial pH 5.0 and 25.0±0.5 °C. Samples were withdrawn at contact times ranging from 0.5 up to 120 min, to determine the residual concentration of metal ions. The results are shown in Figure 1. Obviously, the uptake of metal ions, as a function of contact time, was found to occur in two phases. The first phase involved rapid metal ions uptake during the first 10, 15 and 18 min, for Pb(II), Cd(II) and Zn(II) ions, respectively, of sorbent-sorbate contact, which was followed by a slower phase of metal ions removal until the equilibrium was reached. The rapid uptake of metal ions during the first period of contact accounted for more than 90% of the total sorption at equilibrium. The time required for attaining equilibrium for investigated metal ions was about 40 min. The two-phase metal ions uptake in sorption process, where the first phase is rapid and the second slower, is characteristic of numerous biosorbents [22-24]. The rapid phase occurs probably due to the plenty of active sites on the biosorbent, whereas with the gradual occupancy of these sites, sorption becomes less efficient during the slower phase. For practical reasons contact times of 15, 20 and 25 min for Pb(II), Cd(II) and Zn(II), respectively, were selected as the optima for all further studies. These contact times were very close to reaching sorption equilibrium, and they correspond to 98% of total metal ions sorption onto LVB.

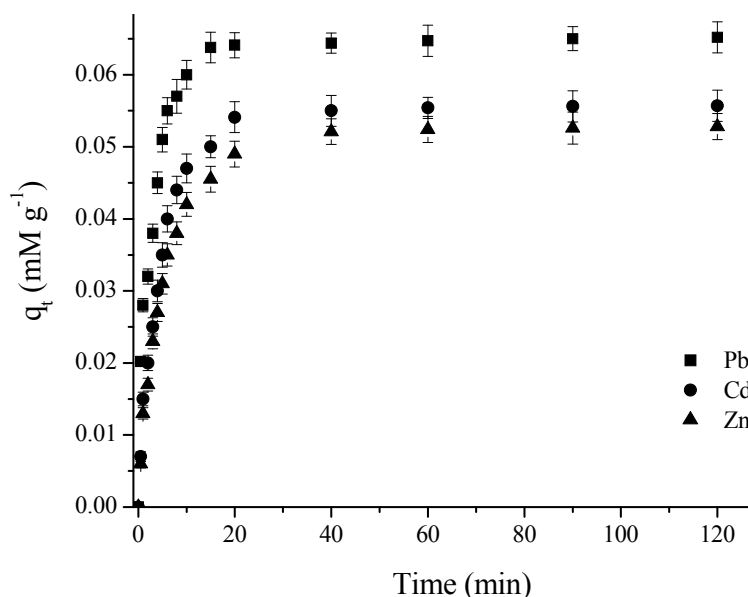Sorption kinetics may be controlled by several independent processes such as transport from the

Figure 1. The effect of contact time on Pb(II), Cd(II) and Zn(II) sorption onto LVB. $c_{Me(II)}$ = 0.50 mmol dm^{-3}, pH 5.0, c_{LVB} = 4.0 g dm^{-3}, t = 25.0±0.5 °C (error bars represent ± SD).

bulk to the surface, intra-particle diffusion and chemical binding reactions of the sorbate. In this study, experimental data obtained were fitted by four reaction/diffusion kinetic models: pseudo-first order, pseudo-second order, Chrastil's diffusion model and intra-particle diffusion.

Pseudo-first order model

The pseudo-first order kinetic model describes the rate of sorption, which is proportional to the number of unoccupied binding sites of sorbent. It can be expressed based on Lagergren equation [25]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (2)$$

where q_e and q_t (mmol g^{-1}) are the amounts of metal ions sorbed at equilibrium and at given time, t, respectively, k_1 (min^{-1}) is the pseudo-first order kinetic rate constant. Integrating Eq. (2) and rearranging obtained equation, pseudo-first order kinetics can be expressed by a linear equation:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (3)$$

The overall rate constant, k_1 in min^{-1}, was calculated from the slope by plotting $\ln(q_e-q_t)$ *versus* t, and q_e was determined from the intercept of the obtained line (Figure 2). The results are summarized in Table 1. The correlation coefficients obtained using the pseudo-first rate model has low values, for all investigated metals ($R^2 \leq 0.8$). Also, the calculated q_e values of first-order did not give reasonable values and they are too low compared to experimental results. Also, the values of calculated q_e have the opposite, unexpected, order: Pb < Cd < Zn (Table 1) in comparison with experimental ones. It is obvious that the kinetics of Pb(II), Cd(II) and Zn(II) ions sorption onto LVB does not match the pseudo-first order model, possibly because of the limitations of the boundary layer controlling the sorption process. The obtained results are in accordance with the studies of Witek-Krowiak *et al.* [23] and Iftiqhar *et al.* [24] who also found very poor agreement with the pseudo-first order model, using similar biosorbents.

Pseudo-second order model

Bearing in mind that the pseudo-first order model may fit sorption kinetic only when it occurs rapidly, Ho and McKay [26] developed the pseudo-second order model, which may describe the entire sorption period and can be applied to most biosorbents. The pseudo-second order model implies that the rate of sorption sites covering is proportional to the square of the number of unoccupied sites and occupied sites are proportional to the fraction of the metal ion sorbed.

The pseudo-second order kinetic can be expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (4)$$

Integration and rearrangement gives the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (5)$$

In this equation the relationship between t/q_t and t is linear, with a slope of $1/q_e$ and intercept $1/(k_2 q_e^2)$
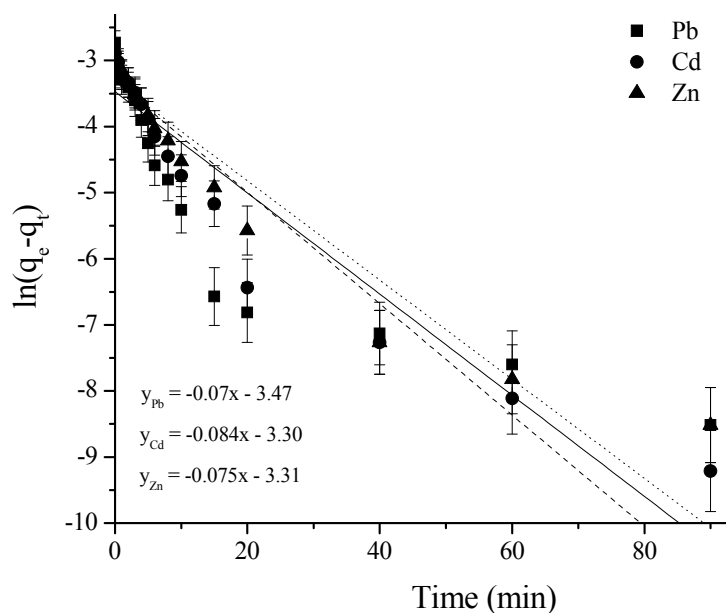
Figure 2. Pseudo-first order sorption kinetics of Pb(II), Cd(II) and Zn(II) onto LVB (error bars represent ± SD).

(Figure 3). Results of Pb(II), Cd(II) and Zn(II) sorption onto LVB fitted by the pseudo-second order model are shown in Table 1.

Results show that for all three studied metals the pseudo-second order model fits the experimental data very well (Table 1). As can be seen in Table 1, the corelation coefficients for the linear plots of t/q_t against t for the pseudo-second-order equation are very high ($R^2 = 0.999$) for contact times of 120 min. Coefficients are much better than for the first order

kinetic (Table 1). Theoretical q_e values predicted from the second-order model were very close to the experimental data, with differences up to 0.4% (Table 1). These observations indicate that sorption of Pb(II), Cd(II) and Zn(II) on LVB followed the second-order reaction, suggesting that the process of metal cations binding is probably controlled by a chemical reaction. The pseudo-second-order model has already been successfully applied to the description of heavy metals ions sorption by different biosorbents. In studies

Table 1. Pseudo-first order, pseudo-second order, Chrastil's diffusion and intra-particle diffusion kinetic parameters for sorption of Pb(II), Cd(II) and Zn(II) ions onto LVB

| Parameter		Pb(II)	Cd(II)	Zn(II)
($q_{e\,exp} \pm SD$) / mmol g^{-1}		0.065±0.002	0.055±0.003	0.052±0.002
Pseudo-first order	($q_e \pm SD$) / mmol g^{-1}	0.031±0.001	0.036±0.001	0.038±0.002
	k_1 / min^{-1}	0.076	0.084	0.075
	R^2	0.722	0.812	0.798
Pseudo-second order	($q_e \pm SD$) / mmol g^{-1}	0.066±0.002	0.057±0.002	0.053±0.002
	k_2 / g mmol^{-1} min^{-1}	12.78	6.91	6.21
	R^2	0.999	0.999	0.999
Chrastil's diffusion	q_e / mmol g^{-1}	0.066	0.056	0.053
	k_C	0.044	0.041	0.033
	n	0.513	0.776	0.720
	R^2	0.991	0.997	0.997
Intra-particle diffusion	($q_e \pm SD$) / mmol g^{-1}	0.064±0.002	0.054±0.0018	0.052±0.002
	k_{I1}	0.022	0.016	0.014
	R^2	0.979	0.983	0.984
	k_{I2}	0.0069	0.0059	0.0055
	R^2	0.954	0.916	0.950
	k_{I3}	0.00019	0.00023	0.00024
	R^2	0.978	0.872	0.849
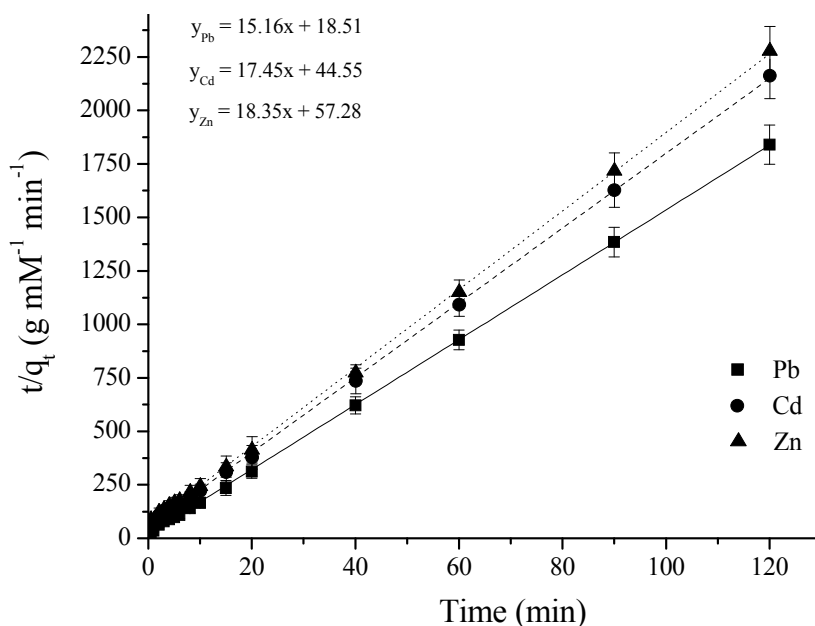
Figure 3. Pseudo-second order sorption kinetics of Pb(II), Cd(II) and Zn(II) onto LVB (error bars represent ±SD).

of Liang *et al.* [22], Areco and Afonso [27] and Iqbal *et al.* [28], the correlation coefficients (R^2) for the linear plots of t/q_t against t for the pseudo-second order equation were observed to be close to 1. The mentioned authors suggest that the chemical reaction seems significant in the rate-controlling step and the pseudo-second order reaction kinetics provide the best correlation of the experimental data, whereas the pseudo-first order model proposed fits the experimental data well for an initial period of the first reaction step only.

Chrastil's model

Chrastil's model describes sorption in diffusion-limited systems and can be expressed by the following equation [29,30]:

$$q_t = q_e[1 - \exp(-k_C A_0 t)]^n \tag{6}$$

where q_t and q_e are as in the previous equations, k_C is a rate constant (dm^3 g^{-1} min^{-1}), A_0 is the concentration of biosorbent (g dm^{-3}) and n is a heterogeneous structural diffusion resistance constant ($0 < n < 1$). The rate constant k_C depended on diffusion coefficients and sorption capacity of the sorbent, but it is independent of biosorbent concentration, A_0. Constant n characterizes the overall heterogeneous diffusion structure of the sorbent. When diffusion resistance is small n is equal to 1 and the reaction is of the first order kinetics. In systems strongly limited by diffusion resistance, n is smaller (0.5-0.6). The constant n is independent of the metal ions concentration, sorbent concentration, A_0, q_e and temperature.

Plots of q_e against t for investigated metals are shown in Figure 4. Parameters q_e, k_C and n were determined by non-linear fitting of experimental data using OriginPro 8.0 software (OriginLab Corporation, USA).

Values of parameters are given in Table 1. The analysis of the results shows that the correlation coefficients obtained for Chrastil's diffusion kinetic model for all investigated metals were very high ($R^2 > 0.99$). Values of parameter n are 0.513, 0.776 and 0.720 for Pb(II), Cd(II) and Zn(II), respectively, which indicate that the sorption process on LVB is significantly limited by diffusion, where diffusion resistance is slightly higher in the case of Pb(II) ions, compared with Cd(II) and Zn(II). Lopez-Mesas *et al.* [31] investigated the kinetics of Pb(II) and Cd(II) sorption by cork waste biomass using Chrastil's diffusion model. They found similar values for parameter n (0.51-0.87) as in this study and pointed out that the sorption process was controlled by diffusion, too.

Intra-particle diffusion model

Results obtained by the application of Chrastil's diffusion model indicate that the sorption process was under the significant influence of diffusion control. The intra-particle diffusion model can be expressed by the following equation:

$$q_t = k_{id} t^{0.5} \tag{7}$$

where k_{id} is the intra-particle diffusion rate constant (mmol g^{-1} min$^{0.5}$) and q_t is the amount of sorbed metals ions at time t (mmol g^{-1}). Plots of q_t *vs.* $t^{0.5}$ for investigated metals are shown in Figure 5.
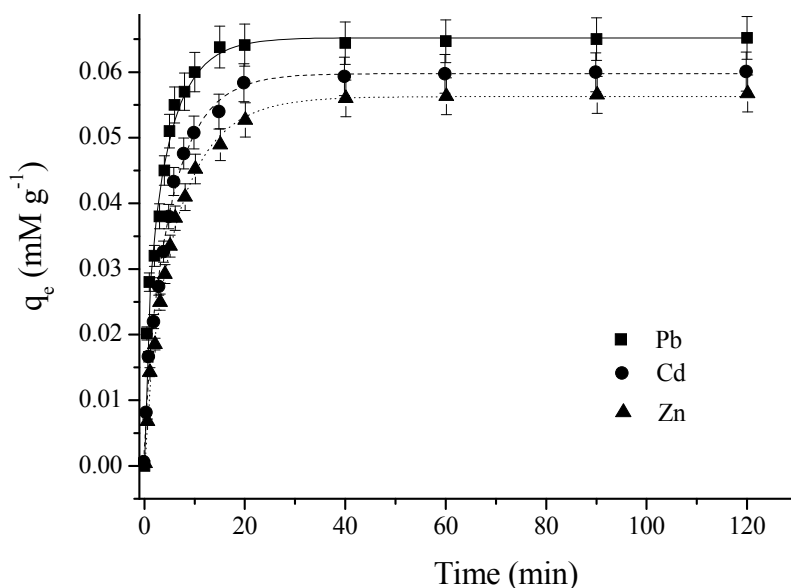
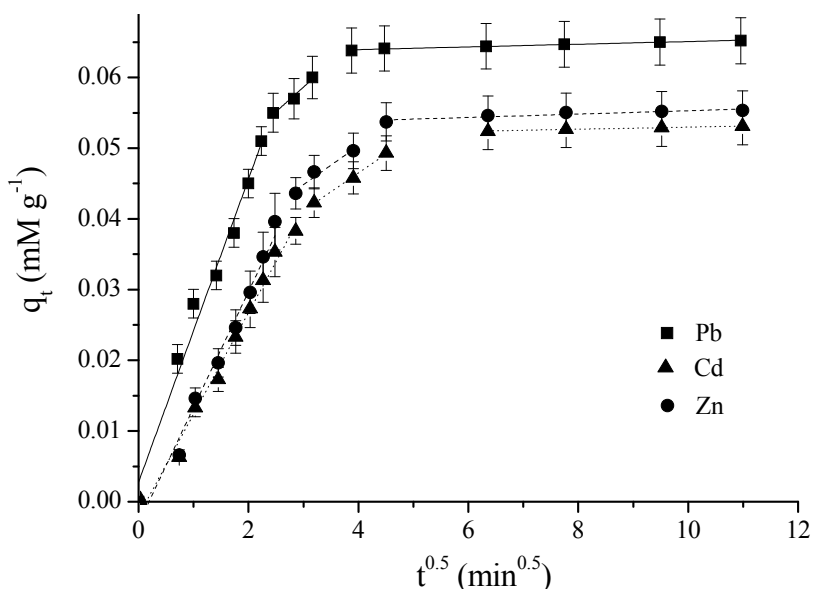*Figure 4. Chrastil's diffusion sorption kinetics of Pb(II), Cd(II) and Zn(II) onto LVB (error bars represent ±SD).*

Figure 5. Intra-particle diffusion sorption kinetics of Pb(II), Cd(II) and Zn(II) onto LVB (error bars represent ±SD).

Plots for the intraparticle diffusion presented in Figure 5 show multi-linearity, indicating that three steps are operational in the sorption process of Pb(II), Cd(II) and Zn(II) ions. The first shape portion is the diffusion of metal ions through the solution to the external surface of the biosorbent or the boundary layer//film diffusion of the sorbate. The second shape describes gradual sorption, where intraparticle diffusion is rate-limiting and the third portion corresponds to the final equilibrium for which the intraparticle diffusion starts to slow down due to low metal ions concentrations left in the solution [32].

From the presented plot (Figure 5), it is possible to identify whether external transport or intraparticle diffusion control the rate of sorption. The plots were found to be linear at the initial period of sorption and do not pass through the origin, cutting the y-axis at 0.276, -0.165 and -0.183 for Pb(II), Cd(II) and Zn(II), respectively. However, relatively high correlation co-efficient sand corresponding calculated q_e values relatively close to experimental ones (Table 1), indicate that external mass transfer is relevant as the rate-limiting step at the beginning of the sorption process. After that, intra-particle diffusion slowed down and stabilized.

Presented reaction and diffusion based models would indicate that the rate of metal ions sorption is probably a complex mix of surface chemisorptions oc-

curring on the boundary layer of the LVB particle and intra-particle diffusion.

Functional groups analysis

Based on Boehm's method, the amount of acidic groups was calculated assuming that NaOH neutralizes carboxylic, phenolic and lactonic groups; Na_2CO_3 neutralizes carboxylic and lactonic groups, while $NaHCO_3$ neutralizes only carboxylic groups. The total content of acidic functional groups at LVB surface, determined by titration with NaOH as a reagent, was calculated to be 0.735 mmol g^{-1}. The content of carboxyl groups, as strongly acidic functional groups, was 0.275 mmol g^{-1}. The concentrations of lactones and phenols determined for LVB are 0.160 and 0.295 mmol g^{-1}, respectively. The large concentration of the acidic functional groups on LVB, especially carboxyl groups and phenols, is responsible for the relatively high sorption capacities of this biosorbent for Pb(II), Cd(II) and Zn(II) ions (Table 1) and adsorption mechanism probably based on ionic interaction [28,40].

The effect of biomass concentration

The effect of biosorbent concentration was carried out at 25.0±0.5 °C and pH 5.0 by varying the LVB concentration from 0.5 to 8.0 g dm^{-3}, at the initial concentration of investigated metals of 0.50 mmol dm^{-3}. The results in Figure 6 show that an increase in LVB concentration from 0.5 to 4.0 g dm^{-3} resulted in a rapid increase in the removal efficiency of Pb(II), Cd(II) and Zn(II) ions. A further increase of LVB concentration to 8.0 g dm^{-3} did not result in a sufficient

increase in the removal efficiency in the case of all three metals. The initial increase in the sorption capacity can be attributed to increased biosorbent surface area and the availability of more sorption sites. A negligible change of the removal efficiency at LVB dosage higher than 4.0 g dm^{-3} may be attributed to the presence of the excess of active centers for metal ions binding on LVB surface, with regard to the amount of metal ions at applied initial concentration. The biosorbent concentration of *Lagenaria vulgaris* shell for further sorption experiments was selected as 4.0 g dm^{-3}. These observations are in agreement with others reported in the literature for the sorption of metal ions by different biological materials [33,34].

The effect of initial metal ions concentration

Initial metal ions concentration provides an important driving force to overcome all mass transfer resistances of the metal ions between the aqueous and solid phase [34]. The effect of initial metal ions concentrations was investigated in the range from 0.20 up to 4.00 mmol dm^{-3}, at 25±0.5 °C and pH 5.0 and optimal time. The results are shown in Figure 7.

The results indicate that the absolute amount of sorbed metalsions an increased with increase in initial metal ions concentration in solution for all three investigated metals. The solutions containing a smaller concentration of Pb(II), Cd(II) and Zn(II) ions were able to attain equilibrium quickly probably because the metal ions adsorbed first on to unhindered sites. The more concentrated solution filled these sites initially, and then it took longer to fill the hindered sites
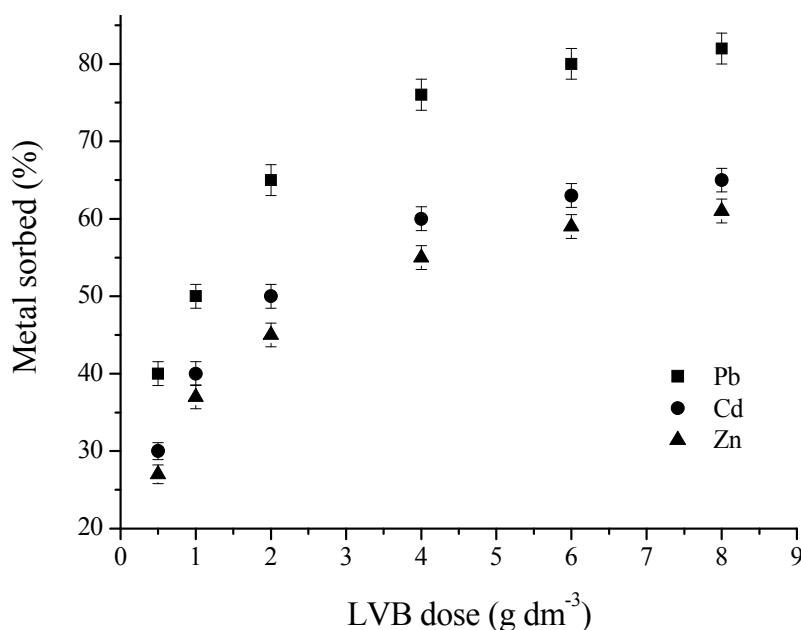

Figure 6. Effects of biosorbent concentration for Pb(II), Cd(II) and Zn(II) sorption onto LVB. pH 5.0, $c_{Me(II)}$ = 0.5 mmol dm^{-3}, t = 25.0±0.5 °C, contact time: 15 (Pb), 20 (Cd) and 25 (Zn) min (error bars represent ±SD).
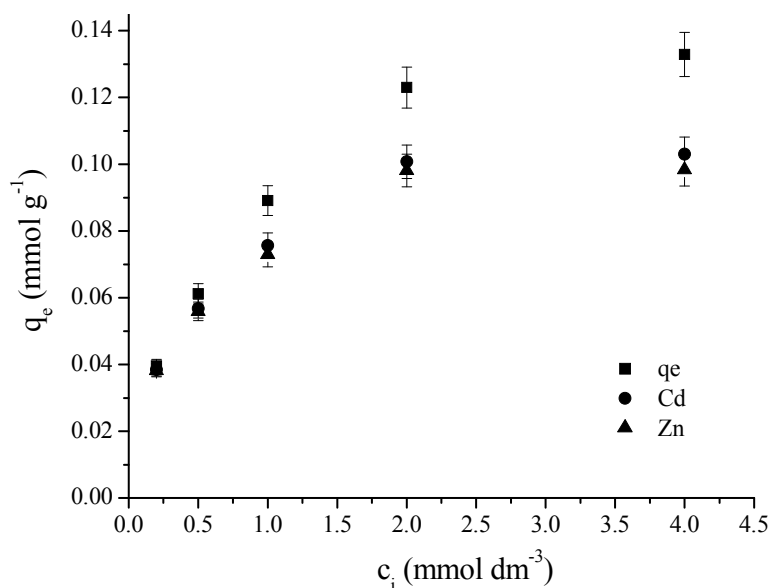
Figure 7. The effect of initial metal concentration on Pb(II), Cd(II) and Zn(II) sorption onto LVB. pH 5.0, c_{LVB} = 4.0 g dm^{-3}, t = 25.0±0.5 °C, contact time: 15 (Pb), 20 (Cd) and 25 (Zn) min (error bars represent ±SD).

with the remaining metal ions. This can be confirmed by the fact that the time needed for optimal sorption to be achieved increases with initial metal ions concentration for all investigated metals (Figure 8).

The effect of initial metal concentration may be explained by an increase in the number of the same metal ions competing for the constant available active sites in the biomass and the deficiency of binding sites for binding of metal ions at higher initial concentration levels. Also, because of the occupancy of surface binding sites metal ions need to diffuse inside biomass pores by intraparticle diffusion. However, the sorption capacity of LVB for Pb(II), Cd(II) and Zn(II)

ions increased with increasing initial metals ions concentration, becoming saturated at about 2.00 mmol dm^{-3} and reaching the maxima of 0.130, 0.103 and 0.098 mmol g^{-1}, respectively, at the initial concentration of 4.00 mmol dm^{-3}.

Sorption isotherms

Sorption isotherms are important criteria for optimizing the usage of sorbents because they describe the relationship between the mass of adsorbate per biosorbent mass as a function of its concentration in solution, and the nature of interaction between the adsorbate and sorbent [21]. There are numerous ex-
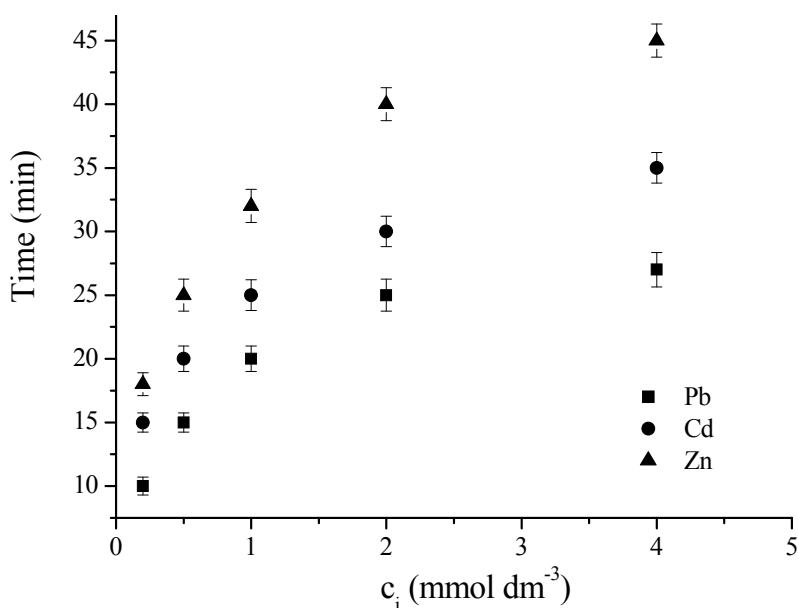

Figure 8. Optimal sorption time as a function of initial metal ions concentration (error bars represent ±SD).

pressions that describe sorption isotherms. Three well-known isotherms were chosen in this study to fit the experimental data of Pb(II), Cd(II) and Zn(II) sorption on LVB: Langmuir, Freundlich and Temkin model.

Langmuir adsorption isotherm

The Langmuir isotherm assumes a monolayer adsorption of adsorbate onto the surface comprised of a finite number of identical sites with homogenous adsorption energy, where there is no interaction between molecules sorbed on neighboring sites. No further adsorption can take place at that site and adsorption energy is constant not dependent on the degree of occupation of a sorbent's active centers [21,35-37].

The Langmuir sorption model can be expressed in linear form by the following equation:

$$\frac{c_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{c_e}{q_{max}} \qquad (8)$$

where q_e (mmol g^{-1}) is the mass of sorbed metals ions at equilibrium per unit mass of LVB; c_e (mmol dm^{-3}) is the equilibrium concentration of metal ions remaining in the solution (mmol dm^{-3}) and K_L (dm^3 mmol^{-1}) is Langmuir isotherm constant related to the free energy of the reaction. The parameters of adsorption of Pb(II), Cd(II) and Zn(II) ions onto LVB were obtained from Langmuir isotherm graph by plotting c_e/q_e against c_e. Values of q_{max} (mmol g^{-1}), theoretical monolayer saturation capacity of LVB, were calculated from the slope and the value of K_L from the intercept of the graph (Figure 9). Langmuir parameters and the correlation coefficients for three metals are given in Table 2.

Freundlich adsorption isotherm

The Freundlich isotherm assumes a heterogeneous surface with a nonuniform distribution of heat of adsorption over the surface. Thus, the Freundlich model describes the adsorption on an energetically heterogeneous surface on which the sorbed molecules are interactive. The linearized form of the Freundlich isotherm is given by the following equation:

$$\ln q_e = \ln K_F + b_F \ln c_e \qquad (9)$$

where q_e (mmol g^{-1}) is the equilibrium adsorption mass of metal ions per unit mass of LVB, c_e (mmol dm^{-3}) is the equilibrium concentration of metal ions remaining
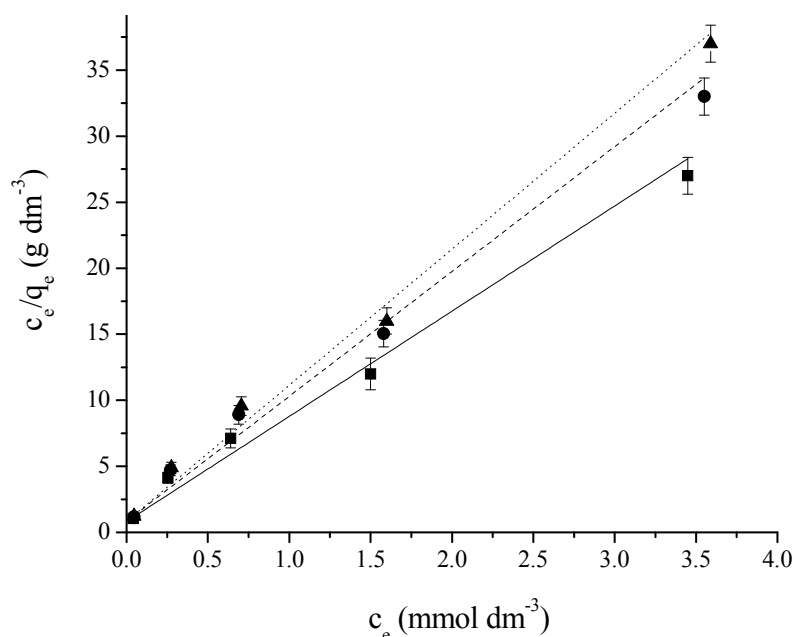

Figure 9. Langmuir adsoption isoterms for sorption of Pb(II), Cd(II) and Zn(II) by LVB, at 25.0±0.5 °C and pH 5.0 (error bars represent ±SD).

Table 2. Langmuir, Freundlich and Temkin isotherm parameters for sorption of Pb(II), Cd(II) and Zn(II) by LVB, at 25.0±0.5 °C and pH 5.0

Metal	$q_{exp}\pm SD$	Langmuir			Freundlich			Temkin		
		$q_{max}\pm SD$	K_L	R^2	K_F	b_F	R^2	B	k_T	R^2
Pb	0.130±0.005	0.139±0.003	8.85	0.991	0.045	0,423	0.754	0.0196	158.75	0.922
Cd	0.103±0.002	0.119±0.004	9.87	0.987	0.044	0,316	0.782	0.0146	275.66	0.914
Zn	0.098±0.003	0.108±0.002	11.10	0.992	0.047	0.260	0.694	0.0138	313.73	0.911

in the solution, K_F is the Freundlich constant proportional to the sorption capacity and b_F is the constant which corresponds to the intensity of adsorption. These constants are determined from a plot ln q_e *versus* ln c_e, as a slope and intercept, respectively (Figure 10). Values of Freundlich constants and R^2 are given in Table 2.

Temkin adsorption isotherm

The Temkin isotherm [38] assumes that the heat of adsorption of all the sorbed molecules in the layer on biosorbent decreases linearly with coverage due to sorbent-sorbate interactions, and that the adsorption is characterized by a uniform distribution of the binding energies, up to some maximum energy. This isotherm can be expressed in linear form as:

$$q_e = B \ln k_t + B \ln c_e \qquad (10)$$

where the constant $B = RT/b$ is related to the heat of adsorption, R is the universal gas constant (J mol^{-1} K^{-1}), T is the temperature (K), b is the variation of a adsorption energy (J mol^{-1}) and k_t is the equilibrium binding constant (dm^3 mmol^{-1}) corresponding to the maximum binding energy [21,39]. Constants B and k_t were determined for adsorption of Pb(II), Cd(II) and Zn(II) onto LVB from a plot q_e *versus* ln c_e as the slope and the intercept, respectively (Figure 11). Temkin isotherm parameters for investigated metals are listed in Table 2.

Discussion of isotherms

The values of linear correlation coefficients for three applied isotherm models in Table 2 suggest that the Langmuir isotherm, with R^2 higher of 0.99 best fitted the experimental data and provides a suitable model for describing the sorption equilibrium of Pb(II), Cd(II) and Zn(II) onto *Lagenaria vulgaris* biosorbent in the studied concentration range. In contrast, Freundlich and Temkin models have rather smaller values of correlation coefficients in the case of all three investigated metals. Also, it can be seen that values of experimental adsorption capacity (q_{exp}) of LVB for investigated metals and maximum capacity (q_{max}) calculated from Langmuir model are quite close, with a difference of about 5% (Table 2).

Many other studies, such as Dang *et al.* [6], Guangqun *et al.* [41] and Miretzky *et al.* [44], which deal with similar lignocellulosis biosorbents, show that Langmuir isotherm is in quite good agreement with experimental data. These studies indicate thatthe presence of oxygen functional groups on biosorbents surface (especially carboxylic and phenolic groups) is of crucial importance for the sorption of heavy metals because they have the ability to bind heavy metals by the donation of an oxygen electron pair to metal ions in solution. In accordance with Langmuir model, sorption follows the monolayer coverage of investigated metal ions on LVB surface and the interaction between two ions is negligible [42-45]. Langmuir isotherm model indicates a chemically equilibrated and saturated mechanism of sorption, which is characteristic of LVB. The maximum adsorption capacities of LVB are calculated to be: 0.139, 0.119 and 0.108 mmol g^{-1} for Pb(II), Cd(II) and Zn(II), respectively. It was hard to compare q_{max} with other studies due to differences in experimental conditions and models used to fit the
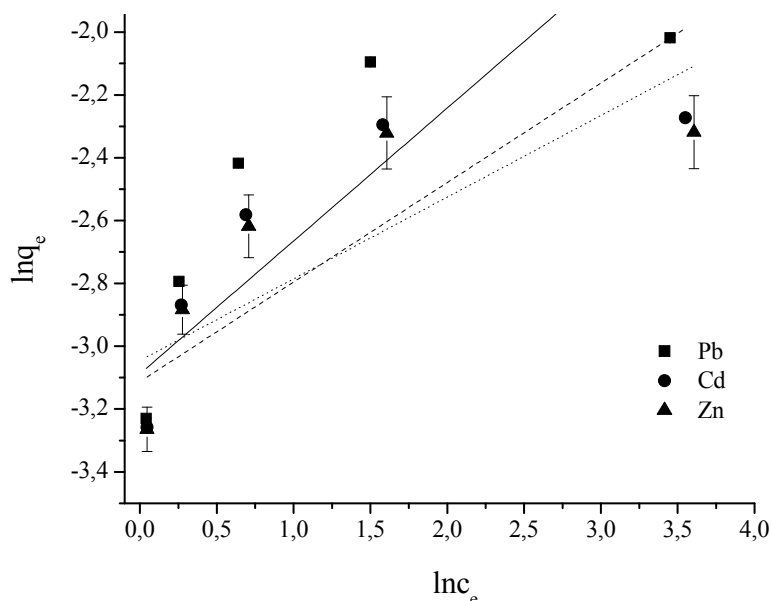

Figure 10. Freundlich adsoption isoterms for sorption of Pb(II), Cd(II) and Zn(II) by LVB, at 25.0±0.5 °C and pH 5.0
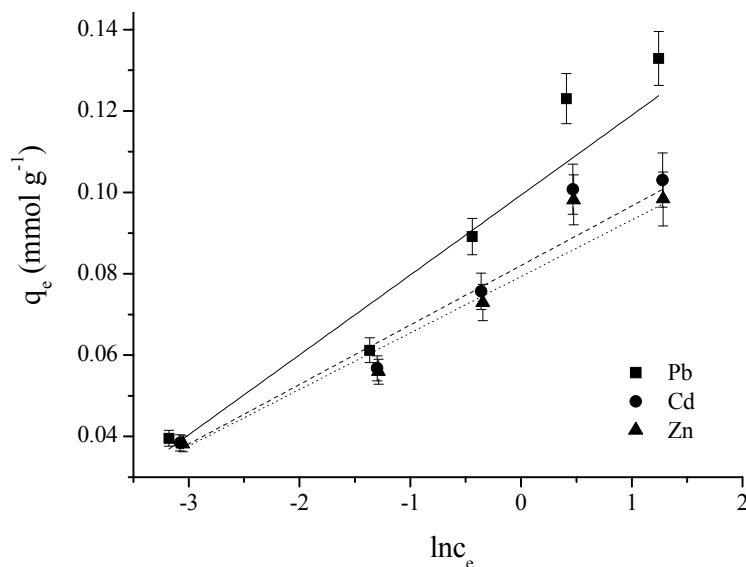(error bars represent ±SD).

Figure 11. Temkin adsoption isoterms for sorption of Pb(II), Cd(II) and Zn(II) by LVB, at 25.0±0.5 °C and pH 5.0 (error bars represent ±SD).

data in each study. However, obtained values for LVB are similar with many materials used as heavy metals biosorbents, as corncobs with q_{max} = 0.078 mmol Pb(II) [41], 0.065 mmol Pb(II) and 0.021 mmol Cd(II) per g of cork waste biomass [31], 0.273 mmol Zn(II) per g of activated sludge [47], 0.113 mmol Zn(II) per g of coniferous bark [48]. The Langmuir constants, K_L, related to the apparent energy of adsorption, are 8.85, 9.87 and 11.10 dm^3 mmol^{-1} for Pb(II), Cd(II) and Zn(II) ions, respectively, which indicates moderate affinity of LVB for investigated metals [21]. Relatively high concentration of oxygen functional groups on LVB surface which are responsible for metal binding, involving different mechanisms as ion exchange, chelation, complexation, etc. [42-45]. Based on presented results it can be concluded that LVB has an important potential for the removal of heavy metals from aqueous solutions.

Desorption and reuse of LVB

In order to make the sorption process more economical and environmentally friendly through repeated use of the sorbent, the desorption and regeneration potential of LVB was investigated. The reusability of LVB can be simply evaluated by comparing the metal ions uptakes by the regenerated biomass with initial sample (Table 3).

The results in Table 3 show that more than 98% desorption recovery was obtained for all three investigated metals in six adsorption-desorption cycles, using diluted HNO$_3$ as desorbing agent, which indicates that sorption process is significantly based on the ion exchange mechanism. Also, the LVB retained good metal ions adsorption capacity even after six cycles. The total decrease in sorption capacity of LVB for Pb(II), Cu(II) and Zn(II) after six cycles was only 3.07, 2.91 and 4.08%, respectively, which shows that LVB has good potential for multiple using for heavy metals ions removal.

Also, considering that all metal ions (Ca^{2+} and Mg^{2+}) were removed from LVB during the preparation and activation of biomass, it is possible to carry out an efficient recovery of investigated metals from desorbing solution (0.1 M HNO$_3$). Desorbed metal ions can be separated from acid solution in pure form by electrolysis, or if recovery is not of concern metal ions

Table 3. Sorption and desorption quantities (mmol g^{-1}) of Pb(II), Cd(II) and Zn(II) by LVB

Cycle	Pb(II)		Cd(II)		Zn(II)	
	Adsorption	Desorption	Adsorption	Desorption	Adsorption	Desorption
1	0.130±0.03	0.127±0.02	0.103±0.01	0.101±0.02	0.098±0.01	0.096±0.01
2	0.129±0.02	0.126±0.02	0.102±0.02	0.100±0.01	0.097±0.01	0.095±0.01
3	0.128±0.02	0.125±0.03	0.101±0.01	0.099±0.02	0.097±0.02	0.095±0.01
4	0.127±0.01	0.124±0.02	0.101±0.02	0.099±0.02	0.096±0.02	0.094±0.01
5	0.127±0.02	0.124±0.01	0.100±0.01	0.098±0.02	0.095±0.01	0.093±0.01
6	0.126±0.02	0.123±0.02	0.100±0.01	0.098±0.01	0.094±0.01	0.093±0.01

can be separated by chemical precipitation. The obtained results are in accordance with previous studies [27,28,46].

CONCLUSION

The present study focused on the biosorptive removal of Pb(II), Cd(II) and Zn(II) ions from aqueous solution using the *Lagenaria vulgaris* shell as a low cost biosorbent. The operating parameters such as contact time, biomass concentration and initial metal ions concentration influence the uptake of investigated metal ions onto LVB. The kinetics of Pb(II), Cd(II) and Zn(II) ions sorption by LVB was extraordinarily fast, reaching 98% of the total sorption at equilibrium in the first 15, 20 and 25 min, respectively. Kinetics results were fitted by pseudo-first order and pseudo-second order reaction models, and Chrastil's and intra-particle diffusion models. The obtained results show that pseudo-second order kinetics was not the only rate-determining step and intra-particle diffusion was applicable to all the sorption data over the entire time range. Potentiometric functional groups analysis, based on Boehm's method, show relatively high concentration of oxygen acidic groups where the most abundant are carboxylic and phenolic groups which are responsible for the strong binding of Pb(II), Cd(II) and Zn(II) ions by LVB. Increase in the LVB concentration resulted in a rapid increase in the removal efficiency of Pb(II), Cd(II) and Zn(II) ions, as a result of increasing of biosorbent surface area and the availability of more sorption sites. Optimal LVB concentration was set to 4.0 g dm^{-3}. Equilibrium data were fitted to three isotherm models: Langmuir, Freundlich and Temkin. The biosorption capacity of Pb(II), Cd(II) and Zn(II) ions for LVB increased with increasing the initial concentration of metal ions with maximum theoretical sorption capacities 0.130, 0.103 and 0.098 mmol g^{-1}, respectively. The Langmuir sorption model has been shown to fit the experimental data well, with the correlation coefficient R^2 > 0.99, and very close values of theoretical and experimental maximum sorption capacity. Complete recovery of Pb(II), Cd(II) and Zn(II) ions from the metal loaded LVB, and the reusability of desorbed biosorbent in six repeated sorption–desorption cycles, showed that the material was an efficient sorbent. Complete desorption of the Pb(II), Cd(II) and Zn(II) ions also indicate that the sorption process involved ion exchange. It may be concluded from the reported observations that LVB has the potential to be used as an efficient and cost-effective sorbent for the removal and recovery of heavy metals from aqueous solution, as an alternative to more costly activated carbon.

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DRAGANA-LINDA
MITIĆ-STOJANOVIĆ[1]
DANIJELA BOJIĆ[2]
JELENA MITROVIĆ[2]
TATJANA ANDJELKOVIĆ[2]
MILJANA RADOVIĆ[2]
ALEKSANDAR LJ. BOJIĆ[2]

[1]JKP "VODOVOD", Vranje, Srbija
[2]Departman za hemiju, Prirodno-matematički fakultet, Univerzitet u Nišu, Srbija

NAUČNI RAD

RAVNOTEŽNA I KINETIČKA STUDIJA SORPCIJE Pb(II), Cd(II) I Zn(II) KOROM *Lagenaria vulgaris*

U ovom radu je proučavana sorpcija jona olova, kadmijuma i cinka iz vodenih rastvora korom Lagenaria vulgaris u stacionarnim uslovima. Ispitan je uticaj najvažnijih faktora kao što su: kontakno vreme, količina biosorbenta i inicijalna koncentracija metalni jona. Ravnoteža sorpcije Pb(II), Cd(II) i Zn(II) jona (uklanjanje 98% početne koncentracije jona) se postiže nakon 15, 20 i 25 min, redom. Kinetički modeli pseudo-prvog reda, pseudo-drugog reda, Krastilov model i model međučestične difuzije, su korišćeni za opisivanje eksperimentalnih rezultata. Model pseudo-drugog reda i model međučestične difuzije pokazuju najbolje slaganje sa eksperimentalnim rezultatima. Efikasnost uklanjanja olova(II), kadmijuma(II) i cinka(II) značajno raste sa povećanjem doze biosorbenta od 0,5 to 8,0 g dm^{-3}. Kao optimalna vrednost izabrana je doza od 4,0 g dm^{-3}. Sorpcioni kapacitet raste sa povećanjem inicijalne koncentracije. Ravnotežni rezultati su fitovani Langmuir-ovim, Freundlich-ovim i Temkin-ovim izotermskim modelima. Najbolje slaganje sa eksperimentalnim rezultatima (r^2 > 0.99) pokazuje Langmuir-ov model. Maksimalni sorpcioni kapaciteti LVB za Pb(II), Cd(II) i Zn(II) na 25,0±0,5 °C iznose 0,130, 0,103 i 0,098 mM g^{-1}, redom. Desorpciona ispitivanja pokazuju da se LVB može ponovo koristiti u šest ciklusa sa minimalnim smanjenjem inicijalnog sorpcionog kapaciteta.

Ključne reči: sorpcija, Lagenaria vulgaris, teški metali, kinetika, izoterme.