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BIOSORPTION OF LEAD AND CADMIUM ONTO HAZELNUTS SHELLS IN A FIXED-BED COLUMN

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In the last years increasing number of experimental research and practical applications concern the used of vegetal structures as sorbents for the separation of selected species from primary extracts or for the removal of water pollutants. This study aimed to investigate experimentally and theoretically, by mathematical modelling, the influence of bed height on the dynamics of Pb(II) and Cd(II) removal from water, in a continuous fixed bed adsorption column. The obtained breakthrough curves were fitted to Thomas model and BDTS model, to determine how the parameters of these models depend on the height of the fixed bed. The models and the identified parameters can be used to determine the minimum bed height required to achieve solute concentration reduction from the value corresponding to the breakthrough to the value of saturation.

Keywords: biosorption, heavy metals, fix-bed column, breakthrough curves, process modeling

1. Introduction

Conventional or biological-driven technologies are now available for the removal of heavy metal ions from drinking water supplies and/or industrial wastewater [1,2]. Many of them are considered as practical and feasible at industrial scale, each having both advantages and disadvantages. When selecting the best applicable technology, plant simplicity and cost effectiveness are considered as key factors, however the treatment efficiency is always depending on contaminants type and level, water/wastewater quantity, and environmental quality standards [3,4].

Biosorption, as a method that uses the adsorption mechanism, has become widely studied for heavy metals removal from aqueous solutions. Using material of biological origin as sorbent, biosorption proves to be *simple* in design and operation, *economical*, especially when agro-industrial residues are utilized,

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environmentally friendly with minimal production of secondary wastes, and *highly effective* at low contaminant concentration [5–7].

This research is following previous investigations on lead, Pb(II) and cadmium, Cd(II) biosorption onto grinded hazelnut shells (HS). These investigations concerned metal ions adsorption conducted in classic, batch systems [8]. The influence of process factors (aqueous solution pH, initial metal ion concentration, solid-liquid ratio, and adsorbent particle diameter) was carefully analyzed and the optimum conditions for Pb(II) and Cd(II) biosorption were determined. The transition from batch to continuous fixed-bed column operation was considered as a necessary step to industrial practice since, it is well known, industrial treatment systems are generally characterized by large volumes of water in continuous flow [9,10]. Furthermore, the continuous fixed-bed column operation eliminates the necessity of sorbent particles separation after adsorption, and allows a more precise control of the pollutant concentration in the treated effluent (very low outlet concentrations until the breakthrough point can be achieved for continuous adsorbers) [11].

Thus, prior obtained results provided us valuable scientific background to allow fixed-bed adsorption process design and development. This investigation is presenting single Pb(II) and Cd(II) adsorption onto HS particles, in a laboratory fixed-bed column, packed with HS. The main objectives were experimental investigation to develop the characteristic breakthrough curves (BC) and modeling of the BC with two well established models: BDST (bed-depth-service-time) formulated by Hutchins and the Thomas model [12].

2. Materials and methods

a. Materials

Stock solutions containing 1000 mg/L Pb(II) and 1000 mg/L Cd(II) respectively, were prepared by dissolving lead nitrate ($Pb(NO_3)_2$), and cadmium acetate dihydrate ($Cd(CH_3COO)_2 \cdot 2H_2O$) in distilled water. Working solutions, of specified concentration, were prepared by dilution of the stock solutions with distilled water as well. The solutions' pH was adjusted with 0.1 N NaOH or 0.1N HCl and measured with a digital pH-meter. All used reagents, supplied by Merck KGaA, Germany, were analytical grade.

Shells of hazelnuts were purchased and prepared as described in our previous paper [8].

b. Fixed-bed column biosorption experiments

The experimental setup illustrated in Fig. 1 was used for fixed-bed adsorption studies. The column used has a 2 cm internal diameter and a vertical length of 15 cm and was operated in down-flow. Gravel layers were placed on the bottom and the top of the fixed bed to prevent solid particles loss.

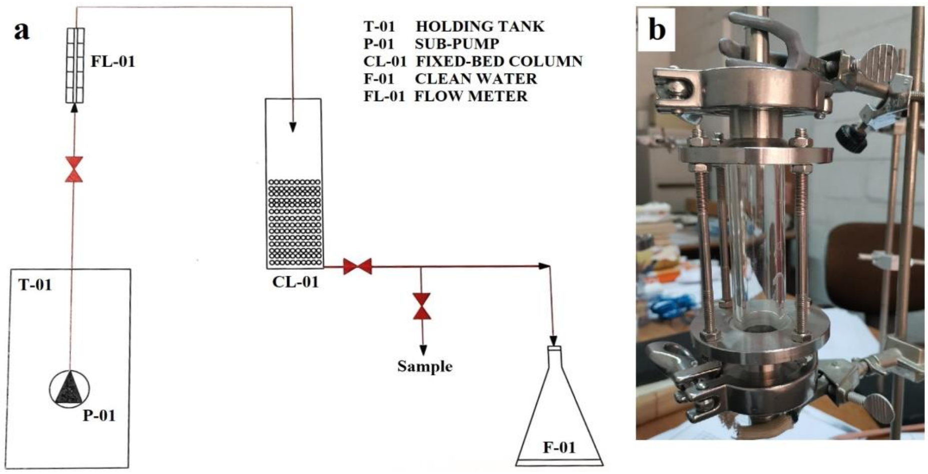


Fig. 1. Schematic diagram of the experimental setup (a), and the image of the used column (b)

The selection of operational conditions followed the objectives of this study and was based on literature survey and previous observations on Pb(II) and Cd(II) removal using HS [8]. Thus, the continuous sorption of Pb(II) and Cd(II) was performed considering the following operational parameters:

- Column was packed with grinded and sieved HS, with respective bed height of 10, 7.5 and 5 cm; in all experiments the fraction with the diameter between 0.75 and 1.00 mm was used. These dimensions were considered small enough to provide large adsorption surface, and a sufficient column-to-particle diameter to minimize wall effect [12]. In the same time the particles dimensions are considered appropriate to avoid blockage in the column, a common phenomenon occurring when particulate biomass is used [9].
- Inlet aqueous solution pH was adjusted to 5 when Pb(II) was the only contaminant, and 6 for Cd(II) solution [13–15].
- Temperature was maintained at 25 ºC (ambient temperature).
- Influent flow rate of the aqueous solution was fixed to 84 mL/min, corresponding to 0.0045 m/s, as fictive velocity for fixed bed flow.
- Inlet ion metal concentration was 50 mg/L for each experimental breakthrough curve elevation.

The metal ion concentration was measured at regular intervals (15 minutes) for the column outlet flow. Taken samples were analyzed with an Agilent ICP Triple Quad (ICP-QQQ), equipped with an octopole collision-reaction cell positioned between two quadrupole mass filters and autosampler. The samples were diluted using nitric acid 65% Suprapur supplied by Merck Millipore. The instrument was operated in single-quad mode.

c. Calculations and biosorption kinetic modelling

For each experiment the biosorption behavior of Pb(II) and Cd(II) onto HS was characterized by means of breakthrough curve. The curves were expressed as C_τ/C_0 in time, under different operation conditions, where C_τ is the effluent metal ion concentration (mg/L), and C_0 is the metal ion concentration in the column influent (mg/L)[16].The breakthrough time, τ_b was considered when effluent metal ion concentration was about 5 % of the influent concentration, and the exhaustion time, τ_e when the effluent concentration was 95 % of the influent concentration [9].

Using these breakthrough curves, the following characteristic parameters were obtained [17,18]:

- Treated effluent volume, V_t (mL), calculated with equation (1), where Q represents effluent flow rate (mL/min), and τ_{total} is total time of the continuous adsorption (min).

$$V_t = Q \cdot \tau_{total} \tag{1}$$

- Total amount of adsorbed contaminant, q_{total} (mg), calculated with equation (2) [9]:

$$q_{total} = \frac{Q \cdot A}{1000} = \frac{Q}{1000} \cdot \int_{\tau_0}^{\tau_{total}} C \, d\tau = \frac{Q}{1000} \cdot \int_{\tau_0}^{\tau_{total}} (C_0 - C_\tau) \, d\tau \tag{2}$$

Here C is the difference between outlet and inlet column concentration (mg/L), A is the surface under the breakthrough curve (mg min/L).

- The amount of adsorbate spent in the column, w_{total} (mg) is given by:

$$w_{total} = \frac{C_0 \cdot Q \cdot \tau_{total}}{1000} \tag{3}$$

- The removal percent, R (%) calculated as the ratio between the amount of adsorbed metal and the amount of adsorbate spent in the column:

$$R = \frac{q_{total}}{w_{total}} \cdot 100 \tag{4}$$

- The quantity of contaminant absorbed at equilibrium, q_e(mg/g) can be calculated using eq. (5), where m (g) is the adsorbent amount:

$$q_e = \frac{q_{total}}{m} \tag{5}$$

Modelling of biosorption in fixed-bed column is a complex process, as the result of multiple factors that need to be considered at the same time: sorption kinetics, mass transfer, axial dispersion, and particle internal diffusion resistance [19]. However, in the literature there are presented some simple semi-empirical mathematical models that can be used to evaluate fixed-bed column dynamic properties. More precisely these models estimate column kinetic characteristics and equilibrium constants analyzing breakthrough performance [10,18].

For the modelling of the breakthrough curves the following models with their characterizing equations were employed:

i. ***Thomas model***, formulated by H.C. Thomas [12,20], can be used to determine, for specific operating parameters, the adsorption rate constant and maximum solid phase concentration of solute on the adsorbent from a breakthrough curve. It is based on Langmuir adsorption isotherm and the second order species sorption kinetics [18]. The linearized form of the model is expressed as follows:

$$ln\left(\frac{C_0}{C_\tau}-1\right)=\frac{k_{Th}\cdot q_0\cdot m}{Q}-\frac{k_{Th}\cdot C_0\cdot V_{eff}\cdot 10^{-3}}{Q} \quad (6)$$

Here k_{Th} is Thomas constant rate (mL/min/mg), q_0 is the solute maximum concentration at the surface of the adsorbent (mg/g), Q is the volumetric flow rate (mL/min) and V_{eff} is the volume of the effluent (mL). Values of k_{Th} and q_0 are determined from the intercept and slope of the linear plot of $ln\left(\frac{C_0}{C_\tau}-1\right)$ against $\frac{V_{eff}}{Q}$.

ii. ***BDTS (bed-depth-service-time)***, developed by R.A. Hutchins [12], assumes that the adsorption rate is only controlled by the surface reaction between sorbent and adsorbate (the resistances because of internal particle diffusion and external film are neglected) [16]. This model is expressed by eq. (7), where h is the bed height (cm), u is the linear flow velocity (cm/min), and τ is the service time to breakthrough (min).

$$C_0\cdot\tau=\frac{N_0\cdot h}{u}-\frac{1}{K}ln\left(\frac{C_0}{C_\tau}-1\right) \quad (7)$$

The model parameters N_0, the sorption capacity (mg/L), and K, the adsorption rate constant (L/mg/min) are determined from the intercept and slope of the linear plot of experimental data $C_0\cdot\tau$ against $ln\left(\frac{C_0}{C_\tau}-1\right)$ [21].

3. Results and discussion

a. Influence of fixed-bed height on biosorption performance

Monocomponent biosorption of Pb(II) and Cd(II) species was carried out to evaluate the performance of HS as biosorbent in a packed bed column. Since adsorption occurring in a fixed-bed column is especially depending on adsorbent quantity [19], the main investigated parameter in this study was the bed height. Thus, for a higher bed, a larger amount of adsorbent is used, and consequently more binding sites are available for the biosorption. Furthermore, higher bed depths allow a longer adsorbate-adsorbent contact period, minimizing the influence of axial dispersion [22].

The obtained breakthrough curves at different bed height are presented in Fig. 2. As can be seen as the bed height increased, the breakthrough occurred slower and the exhaustion time was delayed, for both metals. For instance in the case of Pb(II) the breakthrough time and the exhaustion time varied from 75 min and 210 min respectively for 0.05 m bed height to 110 and 250 min approximately when the bed height increased to 0.1 m (see Table 1). A stronger influence can be noticed for Cd(II), when the breakthrough time and the exhaustion time varied from 45 min and 175 min respectively for 0.05 m bed height, to 105 and 245 min approximately when the bed height increased to 0.1 m. The results were expected, as reported by other researchers [17]. Increasing the bed height the slope of the penetration curve decreased remained very similar, especially for Pb(II) (Fig. 2a), and the **S** shape profile, characteristic to ideal systems[18], can be observed in all cases.

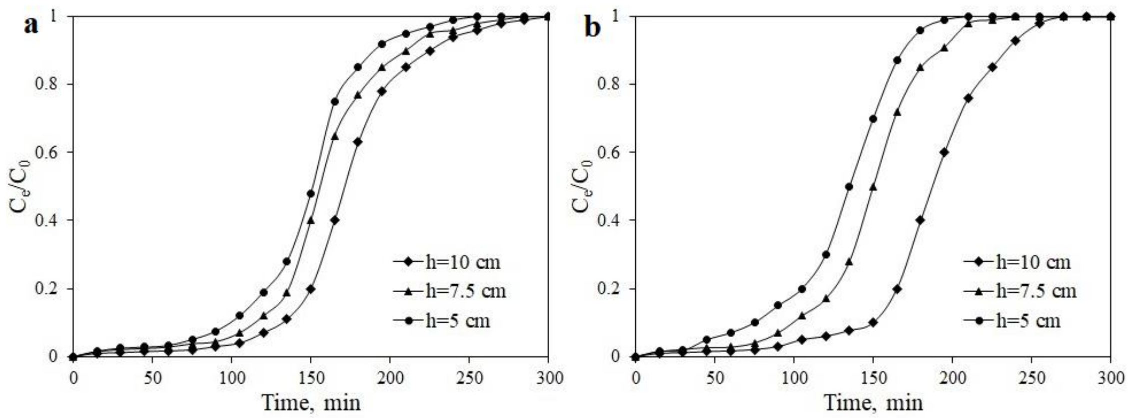


Fig. 2. Breakthrough curves obtained at different bed height for: (a) Pb(II) and (b) Cd(II)

Using the experimental data and the equations (1-4), biosorption characterizing parameters were calculated. The results, presented in Table 1, correlated with the above observations show that:

- Increase in bed height extended the breakthrough time, τ_b and saturation time, τ_e in case of both metals, since higher amount of HS determines larger biosorption area and more available binding sites [23]. On the other hand, output time of the breakthrough curve, $\tau_e - \tau_b$, is about the same for sorption on HS for Pb (II) and Cd (II) as well, disregarding different fixed bed height. This indicates that for each species, the breakthrough curves can be almost identical, but with translation after τ_b. Following this observation, we can expect that the parameters of the considered models will exhibit low dependency or non-dependency on the fixed bed height.
- Decrease in breakthrough curve slope as a result of a wider mass transfer zone, associated with bed height increase, determines larger treated effluent volume, V_t, higher amount of adsorbed contaminant, q_{total}, and a higher removal percent, R.

- While the removal percent, R in the case of Pb(II) increase is almost neglectable for different bed heights, in the case of Cd(II) the influence is significant. Table 1 presents higher removal rates for Cd(II), which could be surprising, but, if we correlate the removal rates with lower volumes of treated water, and lower quantities of contaminant absorbed at equilibrium, obtained for Cd(II) then, overall the results indicate that Pb(II) caption on adsorbent is more facile. As previously reported, the affinity of Pb(II) is explained by its higher electronegativity constant and larger ionic radius comparing to Cd(II) [24].

Table 1.

Experimental data obtained for Pb(II) and Cd(II) at different bed height ($C_0 = 50$ mg/L, $Q = 85$ mL/min, $pH = 5$ for Pb(II) and $pH = 6$ for Cd(II), $t = 25$°C)

Metal ion	h (cm)	τ_b (min)	τ_e (min)	τ_{total} (min)	V_t (L)	q_{total} (mg)	q_e (mg/g)	w_{total} (mg)	R (%)
Pb(II)	5	75	210	270	22.7	617.0	43.7	1134	54.4
	7.5	95	225	285	23.9	661.5	31.2	1197	55.3
	10	110	250	300	25.2	727.4	25.7	1260	57.7
Cd(II)	5	45	175	210	17.6	540.3	38.2	882	61.3
	7.5	80	205	240	20.2	616.1	29.1	1008	61.1
	10	105	245	270	22.7	780.4	27.6	1134	68.8

The experimental removal rates are in accordance with numerous data reported by the literature [17,25,26]. Our obtained quantity of contaminant absorbed at equilibrium is lower than reported for *Vetiveria zizanioides* biochar [26], higher than for iron modified bamboo, bagasse and tyre biochar [27], and comparable to other obtained values for biosorbents [17].

b. Kinetic modelling of continuous biosorption

For an advanced study of the experimentally obtained breakthrough curves, Thomas and BDTS models were used in their linear form.

Model equations and determined kinetic parameters obtained using Thomas model are presented in Fig. 3 and Table 2. The values of the correlation coefficient, R^2>0.93 indicate that Thomas model, a plug flow behaviour based model [28], is suitable to describe the biosorption kinetics in both cases, but the model fitted better Pb(II) column behavior than Cd(II) column. As it can be seen in Table 2, the increase in bed height results in slowly decrease of the Thomas rate constant value, k_{Th}. The same observation could be extended to saturation adsorption capacity, q_0. But in this case, we appreciate that the effect of axial dispersion (which changes the concentration field along the bed height) and radial dispersion (which makes the liquid flow preferentially along the bed wall), increase with the bed height, and contribute to q_0 reduction. In fact, the axial and radial dispersion, always occurring at the granular start flow, reduces the mass transfer intensity [16] for the transferable component and in other words modifies the parameters of the Thomas model, not necessarily the one that expresses saturation q_0.

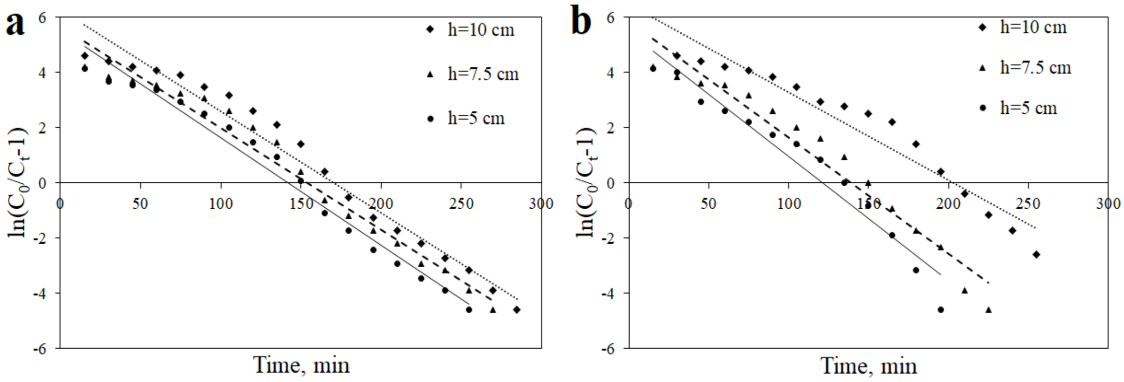


Fig. 3. Thomas model plots for the biosorption at different bed height of: (a) Pb(II) and (b) Cd(II); experimental data and linear trendlines (······· h=10 cm, ----- h=7.5 cm and —— h=5 cm)

In a concentrated form, Thomas model parameters for Pb(II) and Cd(II) biosorption on HS sorbent could be expressed, as follows:

$$k_{Th\,Pb} = 0.75 \pm 0.02 \tag{8}$$

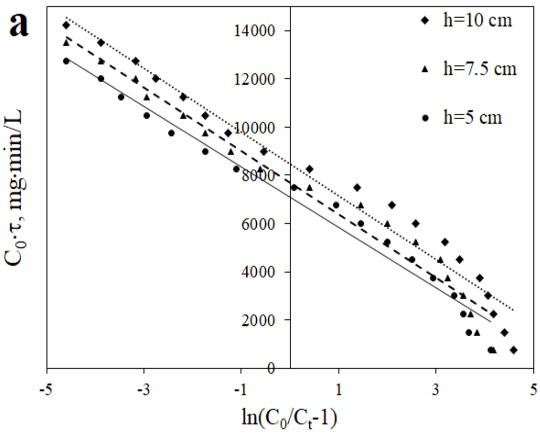
$$k_{Th\,Cd} = 0.722 + 0.082\,h - 0.0089\,h^2 \tag{9}$$

$$q_{0Pb} = 84.5 - 11.05\,h + 0.512h^2 \tag{10}$$

$$q_{0Cd} = 30.967 \pm 3.138 \tag{11}$$

For the modelling of column performance using BDST model, the variation of $C_0 \cdot \tau$ against $ln\left(\frac{C_0}{C_\tau} - 1\right)$ was plotted. The graphs are presented in Fig. 4, and the computed parameters, rate constant of adsorption and column adsorption capacity, corresponding to each studied bed height, are recorded in Table 2. The correlation coefficients ranging from 0.931 to 0.950 for Cd(II) biosorption and from 0.971 to 0.977 for Pb(II) biosorption, indicate a good agreement between experimental and model data.

It can be observed for both metal ions that the bed height increase determined a slow decrease of the adsorption rate constant, K. Since the adsorption rate constant can be defined as solute transfer rate from liquid phase to biosorbent, we can conclude, that increased mass transfer resistance negatively affects the adsorption process. The results confirm the conclusions of the Thomas model. The same trend can be noticed for column adsorption capacity, N_0. Increase in column bed height while its adsorption capacity is decreasing could indicate that surface interaction between the biosorbent and adsorbate it's not the controlling step of the adsorption process [23].



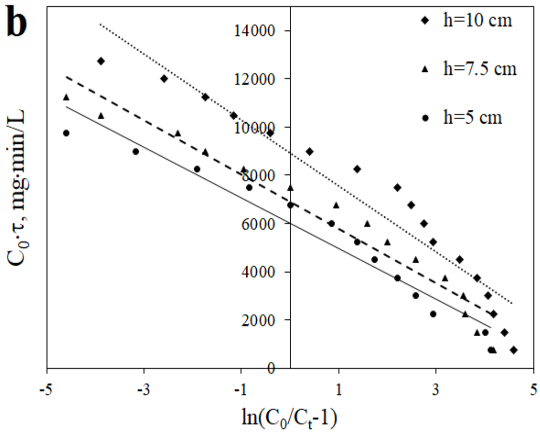


Fig. 4. BDST model plots for the biosorption at different bed height of: (a) Pb(II) and (b) Cd(II); experimental data (points) and linear trendlines (······· for h=10 cm, ----- for h=7.5 cm and —— for h=5 cm)

The results are in agreement with previous studies on Pb(II) and Cd(II) biosorption [29]. In this model case, the discussion about the effect of axial and radial dispersion (by means of the height of the fixed layer) on its parameters maintain its validity. The bellow written equations (12-15) express the effect of fixed height on BDST model parameters.

$$K_{BDST\ Pb} = (7.67 \pm 0.29)\ 10^{-4} \quad (12)$$

$$K_{BDST\ Cd} = (8.39 + 0.58\ h - 0.069\ h^2)10^{-4} \quad (13)$$

$$N_{0Pb} = (7.63 - 1.02\ h + 0.046h^2)10^4 \quad (14)$$

$$N_{0Cd} = (6.75 - 0.98h + 0.054h^2)10^4 \quad (15)$$

Table 2.

Breakthrough curve model parameters

Metal ion	h (cm)	Thomas model			BDTS model		
		k_{Th} (mL/min/mg)	q_0 (mg/g)	R^2	K (L/mg/min)	N_0 (mg/L)	R^2
Pb(II)	5	0.778	42.1	0.977	$7.97 \cdot 10^{-4}$	$3.79 \cdot 10^4$	0.977
	7.5	0.738	30.5	0.972	$7.35 \cdot 10^{-4}$	$2.74 \cdot 10^4$	0.972
	10	0.734	25.3	0.971	$7.65 \cdot 10^{-4}$	$2.27 \cdot 10^4$	0.971
Cd(II)	5	0.902	35.9	0.950	$9.50 \cdot 10^{-4}$	$3.21 \cdot 10^4$	0.950
	7.5	0.844	27.5	0.950	$8.87 \cdot 10^{-4}$	$2.46 \cdot 10^4$	0.950
	10	0.634	30.2	0.934	$7.31 \cdot 10^{-4}$	$2.39 \cdot 10^4$	0.931

In practical cases of fixed-bed adsorption, the interest is to use a large amount of sorbent to have its replacement or its regeneration as rare possible. When a specific mass of sorbent is used in a column, then the ratio bed height/column diameter should be small. As shown in Table 3, where h/D had the values 2.5, 3.75, 5, the productivity is higher for a lower ratio value, despite of small reduction in process efficiency.

Table 3.

Effect of h/D ration on separation productivity and efficiency

No	h/D	Pb(II) removal		Cd(II) removal	
		Productivity ($L/L_{sorbent}$)	Efficiency (%)	Productivity ($L/L_{sorbent}$)	Efficiency (%)
1	2.5	353	54.4	280	61.3
2	3.75	252	55.3	214	61.1
3	5	205	57.7	180	67.8

The obtained results show that both used models, whose parameters have been identified, can be used in determining a minimum fixed bed height, allowing solute concentration reduction from 0.05 C_0 (τ_b) to 0.95 C_0 (τ_e). Adsorption practice shows that the working height of the fixed bed is about 10-15 times higher than this minimum height. Many adsorption systems work with h/D in the range 0.8-1.5, which means that column diameter is well above the minimum layer height.

4. Conclusions

This study showed the effectiveness of using hazelnut shells, as low cost and available biosorbent, for ion metals removal in continuous operating systems. The breakthrough curves were obtained, and column characterizing parameters were calculated. The results showed good removal efficiency, even for lower bed heights. The highest amount of adsorbed contaminant at equilibrium (bed capacity) was found to be 44 mg/g for Pb(II) and 38 mg/g for Cd(II), obtained for 50 mg/L inlet contaminant concentration and 5 cm bed height (equivalent of 13 grams of hazelnut shells). The values are acceptable for porous vegetal structures.

Column parameters, describing the dynamics of continuous biosorption, considered as essential for process design, were identified using Thomas and bed depth service time (BDST) model. The experimental data fitted well to both models, showing their suitable applicability. Furter experiments will be conducted to determine the influence of inlet ion metal concentration and of flow rate on sorption dynamics in single and competitive continuous systems.

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