Optimization of process parameters for heavy metals biosorption onto mustard waste biomass

Lăcrămioara (Negrilă) Nemeş, Laura Bulgariu*

Abstract: Mustard waste biomass was tested as a biosorbent for the removal of Pb(II), Zn(II) and Cd(II) from aqueous solution. This strategy may be a sustainable option for the utilization of such wastes. The influence of the most important operating parameters of the biosorption process was analyzed in batch experiments, and optimal conditions were found to include initial solution pH 5.5, 5.0 g biosorbent/L, 2 hours of contact time and high temperature. Kinetics analyses show that the maximum of biosorption was quickly reached and could be described by a pseudo-second order kinetic model. The equilibrium data were well fitted by the Langmuir model, and the highest values of maximum biosorption capacity were obtained with Pb(II), followed by Zn(II) and Cd(II). The thermodynamic parameters of the biosorption process (ΔG, ΔH and ΔS) were also evaluated from isotherms. The results of this study suggest that mustard waste biomass can be used for the removal of heavy metals from aqueous media.

Keywords: heavy metals, mustard waste biomass, biosorption, kinetics, isotherm, thermodynamic

1 Introduction

The substitution of petroleum-derived fuels, which are increasingly scarce and are important contributors to global warming, with renewable biodiesel is a goal for many researchers [1]. For this reason, many recent studies have focused on finding new technologically efficient and economically viable sources of feedstock for biodiesel production.

White mustard (Sinapis alba) is a common plant, which is mainly cultivated due to its importance in food industry, and recently it has been shown to have nematocidal properties that reduce soil-borne pathogens [2]. In addition, due to its relative high oil content and its adaptation to diverse climatic conditions [3], white mustard was also tested as alternative feedstock for biodiesel production. Although biodiesel production from biomass is included in the category of “clean technology” [4], the problem of waste biomass following the extraction stage requires urgent attention, because its storage has a severe negative impact on the environment. Because of these factors, the alternate use of waste from mustard biomass conversion as a low-cost biosorbent for the removal of heavy metal ions from aqueous media can be an adequate alternative for its valorisation, and this use would comply with the principles of sustainable development [5].

Technological applications of heavy metals, such as lead, zinc and cadmium, in many industrial processes (electroplating, and the production of pigments, paper pulp, and textiles, etc.), have produced wastewaters that are one of the main sources of environmental pollution with such contaminants [6, 7]. Pollution with heavy metals is an important issue with serious ecological and human health consequences, mainly because the heavy metals cannot be destroyed or degraded, have a toxic effect on most life forms, and also tend to accumulate in the environment [8]. Therefore, it is necessary to find some effective methods for removal of heavy metals from industrial wastewaters, in order to reduce their discharge into environment.

Biosorption processes are considered effective and low-cost techniques for the removal of various heavy metals from aqueous media, due to their important advantages (inexpensive removal of heavy metals, an almost complete recovery of the retained heavy metals from depleted biosorbents, the minimization of resulting sludge, the ease of operation and the high efficiency, etc.) [9, 10]. Numerous biomasses, such as fungi, yeasts, etc.
algae, peat and different agricultural wastes, have been tested as biosorbents for the removal of heavy metals in various experimental conditions [11-15], mainly because such biomasses have on their surface diverse functional groups, are available in large quantities and require only few steps of preparation [16-18]. In the case of biomass resulting from the production of biodiesel from mustard, all these advantages are maintained. In addition, several previous studies [13, 19, 20] have shown that the use of such waste biomasses significantly decreases secondary pollution that increase the oxygen demand of aqueous effluents when it appears during the biosorption process.

In this study, mustard waste biomass obtained from white mustard seeds after extraction of oil was used as an alternative low-cost biosorbent for the removal of the heavy metal ions Pb(II), Zn(II) and Cd(II) from aqueous solutions. The biosorptive performances of this waste biomass in the heavy metals biosorption processes was examined in batch experiments as a function of the most important operating parameters (initial solution pH, biosorbent dose, contact time, initial heavy metals concentration and temperature), in order to establish the optimal conditions. The experimental results were modelled using pseudo-first order, pseudo-second order and intra-particle diffusion kinetic models and Langmuir, Freundlich and Dubinin-Radushkevich isotherm models in order to highlight the most important characteristics of the biosorption mechanism. The thermodynamic parameters of biosorption process were also calculated for each heavy metal.

2 Experimental

2.1. Biosorbent preparation

The seeds of white mustard (Sinapis alba), which are commercially available, were crushed and used for oil extraction in a Soxhlet extractor (solvent: n-hexane, 24 hours). Mustard waste biomass obtained after the extraction step was washed several times with distilled water, dried in air at 60 °C for 10 hours, ground with mortar and pestle, and then sieved, until the grain-size of particles was lower than 1.0-1.5 mm. The obtained material was stored in desiccators and was used as a biosorbent, without any pre-treatment. In order to characterize the obtained biosorbent, the surface area was determined by using a BET analyzer (Monosorb model, N₂ as adsorbate). The chemical composition of the mustard biomass, before and after oil extraction, was analyzed with an energy dispersive X-ray spectrometer (Bruker EDX spectrometer). The samples used for EDX analysis were coated with a thin carbon film to prevent the measurements from being influenced by a charging effect. The FT-IR spectra of mustard biomass, before and after oil extraction, were recorded with a Bio-Rad FT-IR spectrometer, within 400 – 4000 cm⁻¹ spectral domain with a 4 cm⁻¹ resolution and 32 scans by KBr pellet technique and the obtained spectra were fitted by ACD/Spec Manager software.

2.2. Reagents

All chemical reagents used in this study were of analytical grade and were used without purifications. In all experiments distilled water, obtained in a commercial distillation system, was used for the preparation and dilution of the solutions. The heavy metal ions stock solutions (10⁻² mol M; M(II): Pb(II), Zn(II) and Cd(II), respectively) were prepared from metal nitrate salts (purchased from Aldrich). The stock solutions were then used to obtain the working solutions through dilution with distilled water. Fresh dilutions were prepared and used for each experiment. 10⁻¹ mol/L HNO₃ or NaOH solutions were used to adjust the initial pH of working solutions.

2.3. Biosorption experiments

The biosorption experiments were performed for each heavy metal ion by batch technique by mixing the given quantity of biosorbent with 25 mL of aqueous solution with known heavy metal ion concentration, in 150 mL conical flasks. The flakes were intermittently stirred for an adequate period of time, depending on the purpose of the experiment. The influence of initial solution pH was studied at room temperature (20 °C), using heavy metal ions solutions with an initial concentration of 0.41 mmol/L M(II), and pH values varying between 1.0 and 6.5. This pH interval was chosen so that all studied heavy metals would remain in the solution as the free M²⁺ ions and to significantly reduce the impact of some possible secondary processes to the biosorption. The effect of biosorbent dose on heavy metal biosorption was also examined at room temperature (20 °C) by mixing biomass samples ranging between 4.0 and 40 g/L with 25 mL of heavy metal solution (0.41 mmol M(II)/L) at pH 5.5. In the kinetic experiments, the same quantity of mustard waste biomass (0.125 g) was mixed with 25 mL of aqueous solution containing 0.41 or 0.85 mmol M(II)/L at various time intervals between 5 and 180 min. The influence of initial heavy metal concentration on
the biosorption efficiency was investigated within 0.20 – 2.85 mmol/L concentration range and three different temperatures (5, 20 and 55 °C) for 2 hours contact time. After biosorption, the two phases were separated through filtration and the heavy metals in the filtrate were analysed spectrophotometrically (Digital Spectrophotometer S 104 D, 1 cm glass cell) [21], using prepared calibration graphs.

In desorption experiments, three different samples of 1.5 g mustard waste biomass were treated with 300 mL of each heavy metal solution at 0.41 mmol M(II)/L; M(II): Pb(II), Zn(II) and Cd(II), respectively) at 20 °C, under optimal conditions established previously (initial solution pH of 5.5; 5.0 g biosorbent/L). After a 24 hour contact time, the biosorbent was separated by filtration, washed with double distilled water several times to remove the excess of heavy metals from surface and subsequently dried. The biosorbent samples loaded with heavy metals (1.0 g) were treated with 15 mL of 10^{-1} mol/L HCl solution and intermittently stirred for 2 hours. After filtration, the concentration of heavy metals was determined. This procedure was repeated for each heavy metal ion in three biosorption/desorption cycles, using the same sample of biosorbent.

**2.4 Data evaluation**

The biosorption process of heavy metal ions onto mustard waste biomass was evaluated using the following parameters, which were calculated from experimental results:

(a) amount of heavy metals retained on mass unit of mustard waste biomass (q, mmol/g):

\[
q = \frac{(c_0 - c) \cdot (V / 1000)}{m}
\]  

(b) percent of heavy metals removed (R, %):

\[
R \% = \frac{(c_0 - c)}{c_0} \cdot 100
\]

where: \(c_0\) is the initial concentration of heavy metal ions in the solution (mmol/L), \(c\) is the equilibrium concentration of heavy metal ions in the solution (mmol/L), \(V\) is volume of solution (mL), and \(m\) is the mass of the mustard waste biomass (g).

All the data are the mean values of three replicate measurements, and the standard deviation calculated in each case was lower than ± 1.0%.

For the kinetic modelling, three kinetics models have been used to fit the experimental data. The mathematical equations of the linear forms for the pseudo-first order and pseudo-second order kinetics models may be expressed as [22, 23]:

- pseudo-first order model:

\[
\ln(q_e - q_t) = \ln q_e - k_1 \cdot t
\]  

- pseudo-second order model:

\[
\frac{t}{q_t} = \frac{1}{q_e^2 \cdot k_2} + \frac{t}{q_e}
\]

where: \(q_e\) and \(q_t\) are the amounts of heavy metal ions retained per mass unit of mustard waste biomass, at equilibrium and at time \(t\), (mmol/g); \(k_1\) and \(k_2\) are the rate constants of pseudo-first kinetics model (1/min) and of pseudo-second order kinetics model (g/mmol min), respectively.

The straight lines in the graphical representation of \(ln (q_e - q_t)\) vs. \(t\) for the pseudo-first order kinetics model, and \(t/q_t\) vs. \(t\) for the pseudo-second order kinetics model highlight the applicability of these models in the describing of biosorption kinetics and will allow the calculation of characteristic kinetics parameters (\(k_1, k_2\) and \(q_e\)) from the slopes and intercepts of the linear plots.

The intra-particle diffusion model was considered to estimate the role of the diffusion process in the biosorption of Pb(II), Zn(II) and Cd(II) ions onto mustard waste biomass. The mathematical expression of this model is given by the equation [24, 25]:

\[
q_t = k_{diff} \cdot t^{1/2} + c
\]

where: \(k_{diff}\) is the intra-particle diffusion rate constant (mmol/g min^{1/2}) and \(c\) is the concentration of heavy metal ions in aqueous solution, at equilibrium (mmol/L).

Theoretical principles of this model have shown that if the intra-particle diffusion had a major contribution to the biosorption process, the plots \(q_t\) vs. \(t^{1/2}\) would lead to straight lines. Furthermore, if the obtained straight lines pass through the origin, the intra-particle diffusion is the only rate limiting step; if not, the biosorption mechanism may involve other kinds of elementary processes [24, 25].

The experimental equilibrium data were modelled using three isotherm models, namely Langmuir, Freundlich and Dubinin-Radushkevich.

According to the Langmuir isotherm model, the biosorption process occurs at specific homogeneous sites on the biosorbent surface, until a complete monolayer is formed.
This model is used to estimate the maximum biosorption capacity \( q_{\text{max}} \) (mmol/g) that corresponds to the biosorbent surface saturation, and its linear form is [26, 27]:

\[
\frac{c}{q} = \frac{1}{q_{\text{max}} \cdot K_L} + \frac{c}{q_{\text{max}}} \tag{6}
\]

where: \( q \) is the amount of heavy metal retained on mass unit of mustard waste biomass at equilibrium (mmol/g), \( q_{\text{max}} \) is the maximum biosorption capacity required for compete monolayer coverage of biosorbent surface (mmol/g) and \( K_L \) is the Langmuir constant (L/mmol).

The essential characteristics of the Langmuir isotherm model can be expressed by a dimensionless separation factor \( (R_L) \) [28], which is defined by:

\[
R_L = \frac{1}{1 + K_L \cdot c_0} \tag{7}
\]

where: \( c_0 \) is the highest initial heavy metal concentration (mmol/L) and \( K_L \) is the Langmuir constant (L/mmol).

Unlike the Langmuir model, the Freundlich isotherm model can be used to describe the biosorption on a heterogeneous surface or a surface supporting different sites and is not therefore restricted to the formation of monolayer. This model is used to estimate the intensity of the biosorption process and its linear form is expressed by the equation [27, 28]:

\[
\ln q = \ln K_F + \frac{1}{n} \ln c \tag{8}
\]

where: \( K_F \) is the Freundlich constant, and \( 1/n \) is the heterogeneity factor.

The Dubinin-Radushkevich isotherm model is useful to estimate the nature of interactions between heavy metal ions from aqueous solution and the surface functional groups of biomass during the biosorption process. The mathematical expression of this model is [29]:

\[
\ln q = \ln q_{\text{max}}^{D-R} - \beta \cdot c^2 \tag{9}
\]

where: \( q_{\text{max}}^{D-R} \) is the maximum amount of heavy metals retained per mass unit of biosorbent (mmol/g), \( \beta \) is a constant related to the biosorption energy (mol²/kJ) and \( c \) is the equilibrium concentration of heavy metals in solution (mol/L).

The most important parameter of the Dubinin-Radushkevich isotherm model is the mean biosorption energy \( E \) (kJ/mol), which gives information about the biosorption mechanism, and which is calculated according to the equation:

\[
E = \frac{1}{\sqrt{2 \beta}} \tag{10}
\]

Thus, the values of \( E \) between 8 – 16 kJ/mol indicate that the biosorption mechanism involves chemical interactions, while a \( E \) value lower than 8kJ/mol shows that the main interactions which occur during of biosorption process are of a physical nature [29].

The thermodynamic parameters: changes of free energy \( (\Delta G) \), enthalpy \( (\Delta H) \) and entropy \( (\Delta S) \) were evaluated from the temperature dependence of Langmuir constant \( (K_L) \), for each studied heavy metal ion, using the following equations:

\[
\Delta G = -RT \cdot \ln K_L \tag{11}
\]

\[
\frac{d \ln K_L}{d(1/T)} = \frac{\Delta H}{R} \tag{12}
\]

\[
\Delta S = \frac{\Delta H - \Delta G}{T} \tag{13}
\]

where: \( R \) is the gas constant (J/mol K) and \( T \) is the absolute temperature (K).

### 3 Results and discussion

#### 3.1 Characterization of biosorbent

The mustard waste biomass used as biosorbent in these experiments was obtained from crushed white mustard seeds by using an extraction procedure similar to those applied in biodiesel production (organic solvent: n-hexane, extraction time of 24 hours). 38.45% (w/w) of oil was extracted through this procedure; therefore, mustard biomass can be considered a suitable feedstock for this purpose [30, 31].

The values of BET surface area and elemental analysis, before and after extraction step, (Table 1) show that during the extraction stage the disruption of cell walls occurs (since the BET surface area increases from 0.61 to 1.14 m²/g), and only certain components from the biomass composition are removed through extraction (since the contents of C, O, S and P slightly decrease after the solvent extraction stage).

The FT-IR spectrum of mustard biomass before extraction (Fig. 1 – spectrum a) presents some characteristic bands of functional groups of proteins, lipids and polysaccharides. The broad band from 3402 cm⁻¹
can be attributed to the overlapping of O–H and N–H stretching vibrations. The weak band at 3008 cm\(^{-1}\) corresponds to =C–H stretching vibration in cis CH=CH bonds [32], and indicates the presence of the unsaturated fatty acids from mustard biomass. The absorption bands from 2924 and 2854 cm\(^{-1}\) can be assigned to asymmetric and symmetric C–H stretching vibrations of methyl and methylene groups, respectively. The absorption band at 1745 cm\(^{-1}\) is attributed to C=O stretching vibrations of the ester groups and is characteristic of lipids [33]. The intense peaks at 1656 cm\(^{-1}\) and 1544 cm\(^{-1}\) correspond to the C=O stretching of primary and secondary amides from proteins [34]. The peaks at 1242, 1103 and 1056 cm\(^{-1}\) can be attributed to P=O asymmetric and symmetric stretching vibrations from phosphate functional groups, while the peaks between 1200 and 900 cm\(^{-1}\) may be attributed to the C–OH and C–O–C groups from polysaccharides.

After the extraction stage, in the FT-IR spectrum of mustard waste biomass (Fig. 1–spectrum b), the absorption bands at 3008 cm\(^{-1}\), 2924 cm\(^{-1}\), 2854 cm\(^{-1}\) and 1745 cm\(^{-1}\), which are characteristic of lipids, either disappear or decrease in intensity. Therefore, during of extraction step only such compounds are removed, while most of proteins and polysaccharides remain in the biomass composition and their functional groups will represent the potential binding sites for heavy metal ions from aqueous solution.

### 3.2 Effect of initial solution pH

The effect of the initial solution pH on the biosorption efficiency of Pb(II), Zn(II) and Cd(II) ions onto mustard waste biomass was studied in the pH interval between 1.0 and 6.5 (Fig. 2), at a constant heavy metal ions concentration (0.41 mmol M(II)/L), contact time (24 h) and temperature of 20 °C.

The dependencies illustrated in Fig. 2 show that the removal percentages increase when the initial solution pH increases from 1.0 to 5.5, after which a slow decrease can be observed for the biosorption of all studied heavy metal ions. This trend may be attributed to the easy biosorption of heavy metal ions on dissociated functional groups of mustard waste biomass. In acidic media (pH = 1.0), where most functional groups from biosorbent surface are un-dissociated, the values of removal percentages are low (28.22% for Pb(II), 24.87% for Zn(II) and 17.89% for Cd(II)). The increase of pH correlates with an increase of heavy metal ion removal efficiency until a pH of 5.5. After that point, the biosorption efficiency slowly decreases with increasing pH, an effect that is more evident in

| Characteristics | Before extraction | After extraction |
|-----------------|------------------|-----------------|
| BET surface area (m\(^2\)/g) | 0.61 | 1.14 |
| C (wt%) | 50.44 | 45.78 |
| O (wt%) | 41.25 | 40.33 |
| S (wt%) | 2.32 | 0.99 |
| P (wt%) | 1.18 | 0.72 |
| Ca (wt%) | 1.53 | 0.98 |
| Mg (wt%) | 0.59 | 0.28 |

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**Table 1:** Some characteristics of mustard biomass before and after oil extraction.

**Figure 1:** FT-IR spectra of mustard biomass before (a) and after oil extraction (b).

**Figure 2:** Effect of initial solution pH on the biosorption of heavy metals onto mustard waste biomass (biosorbent dose = 5 g/L; \(c_0 = 0.41 \text{ mmol M(II)/L}\); contact time = 24 hours; \(t = 20 \degree C\).
The case of Cd(II) ions than in case of Pb(II) and Zn(II) ions, respectively. The decrease of biosorption efficiency under these conditions may be a consequence of some secondary processes that can change the speciation of metal ions in aqueous solutions, thereby affecting their availability to interact with functional groups from the biosorbent surface.

The data shown in figure 2 suggest that an initial solution pH of 5.5 is optimal, and this condition was used in further experiments. This value is in agreement with the experimental results of other studies in the literature [19, 35, 36], which also report a pH between 5.0 and 6.0 as being the optimum value for the biosorption of considered heavy metal ions onto various biomasses.

### 3.3 Effect of biosorbent dose

The effect of biosorbent dose on the biosorption of Pb(II), Zn(II) and Cd(II) ions was tested by using different quantities of mustard waste biomass and maintaining constant all other experimental parameters. The obtained results are presented in Fig. 3.

The experimental results show that the removal percentages increase with the increasing of biosorbent dose for each heavy metal but that this variation is not significant. The increase of biosorbent dose from 4.0 to 40.0 g/L displayed a weak improvement of biosorption efficiency from 91.63 to 94.56% for Pb(II), from 80.19 to 96.15% for Zn(II), and from 68.71 to 76.48% for Cd(II) ions, respectively. The increase of the mustard waste biomass concentration over 40 g/L did not display an additional increase of the heavy metal biosorption efficiency, probably due to the saturation of the biosorbent surface [37]. Therefore, for economic considerations, the optimum biosorbent dose was selected as 5.0 g/L.

### 3.4 Effect of contact time and kinetics modelling

The influence of contact time on Pb(II), Zn(II) and Cd(II) ions biosorption onto mustard waste biomass, at room temperature (20 °C), constant biosorbent dose (5 g/L) and an initial solution pH of 5.5 is illustrated in Fig. 4. The initial concentrations of metal ions were 0.41 and 0.85 mmol M(II)/L, respectively.

The experimental data from Fig. 4 indicates that the biosorption efficiency of the considered heavy metal ions onto mustard waste biomass increases with contact time, and reaches a maximum after 30 min in case of Pb(II) and after 60 min in case of Zn(II) and Cd(II), for both values of initial heavy metal ion concentrations. In this time...
interval the most efficiently retained heavy metal ion was Pb(II) \((R > 90\%)\), followed by Cd(II) \((R > 76\%)\) and Zn(II) \((R > 74\%)\). The differences between \(q\) values obtained in these conditions and those obtained after 24 hours of contact time are lower than 4.7\% (Table 2).

In order to be sure that the biosorption process reached equilibrium, a contact time of 2 hours was considered sufficient and was used in all subsequent experiments for the biosorption of all studied heavy metal ions. The obtained experimental results were modelled using pseudo-first order, pseudo-second order and intra-particle diffusion kinetics models, in order to describe the mechanism that controls the biosorption of Pb(II), Zn(II) and Cd(II) ions onto mustard waste biomass. The kinetics parameters of the pseudo-first order and pseudo-second order models, together with the corresponding correlation coefficients \((R^2)\), for the biosorption of Pb(II), Zn(II) and Cd(II) onto mustard waste biomass, are summarized in Table 3, for both values of initial metal ions concentration.

In case of pseudo-first order model, the correlation coefficients are lower than 0.9766 (see Table 3) indicating that this model has a limited applicability in the interpretation of experimental results. Furthermore, the values of equilibrium biosorption capacities calculated from the pseudo-first order equation \((q_{e,\text{calc}}, \text{mmol/g})\), are very different from those obtained experimentally \((q_{e,\text{exp}}, \text{mmol/g})\) for all studied heavy metal ions. Therefore, the pseudo-first order kinetic model is not suitable to describe the kinetics of Pb(II), Zn(II) and Cd(II) biosorption onto mustard waste biomass.

The pseudo-second order kinetics model was also used to fit the experimental data, and high correlation coefficients \((R^2)\) were obtained in all cases (see Table 3). In the case of pseudo-second order kinetics model, the plots \(t/q_e\) vs. \(t\) gives straight lines along the entire contact time interval. This, together with the very good correlation between calculated and experimental values of \(q_e\) indicate that all of these biosorption systems predominantly follow the pseudo-second order kinetics model. The compatibility of experimental data with the pseudo-second order kinetic model shows that in the biosorption processes onto mustard waste biomass, the rate-limiting step is the chemical interaction (that can involve ion exchange and/or sharing of electrons) between heavy metal ions from aqueous solution and superficial functional groups of the biosorbent [22]. On the other hand, comparing the values of rate constants it can be said that the Pb(II) ions have the higher affinity for the functional groups of biosorbent, and its biosorption efficiency will be highest.

In case of the intra-particle diffusion model, the plots of \(q_e\) vs. \(t^{1/2}\) obtained for the biosorption of Pb(II), Zn(II) and Cd(II) ions onto mustard waste biomass (Fig. 5) do not pass through the origin, and the two obtained regions have been separately analyzed according with Eq. (5). The values of kinetics parameters \((k_{\text{diff}}\) and \(c\)), calculated from

\[
\Delta q = q^{2h} - q^{1h} = 0.0002 - 0.0013 = 0.0018 - 0.0019 = 0.0024 - 0.0038
\]

\(c_{01} = 0.41 \text{ mmol/L}; c_{02} = 0.85 \text{ mmol/L}\).

### Table 2: Comparative values of \(q\) (mmol/g) obtained after 24 h (time required to reach maximum biosorption) and after 2 hours (time required to reach equilibrium).

| Heavy metal | Pb(II) | Zn(II) | Cd(II) |
|-------------|--------|--------|--------|
| \(c_{01}\)  | 0.0756 | 0.1495 | 0.0611 |
| \(c_{02}\)  | 0.1268 | 0.0586 | 0.1233 |
| \(q^{2h}\)  | 0.0754 | 0.1508 | 0.0593 |
| \(q^{1h}\)  | 0.1249 | 0.0561 | 0.1159 |
| \(\Delta q\) | 0.0002 | 0.0013 | 0.0018 |
|            | 0.0019 | 0.0024 | 0.0038 |

\(c_{01} = 0.41 \text{ mmol/L}; c_{02} = 0.85 \text{ mmol/L}\).

### Table 3: Kinetic parameters for the biosorption of Pb(II), Zn(II) and Cd(II) onto mustard waste biomass.

| Kinetic parameter | Pb(II) | Zn(II) | Cd(II) |
|-------------------|--------|--------|--------|
| \(q_{e,\text{exp}}, \text{mmol/g}\) | 0.0772 | 0.1502 | 0.0591 |
| \(R^2\)          | 0.8015 | 0.8248 | 0.9689 |
| Pseudo-first order | \(q_{e,\text{calc}}, \text{mmol/g}\) | 0.0114 | 0.0393 | 0.0318 |
| \(k_1\) (1/min)  | 0.0168 | 0.0487 | 0.0311 |
| \(R^2\)          | 0.9997 | 0.9999 | 0.9993 |
| Pseudo-second order | \(q_{e,\text{calc}}, \text{mmol/g}\) | 0.0776 | 0.1524 | 0.0618 |
| \(k_2\) (g/mmol min) | 5.9666 | 3.2113 | 2.1301 |

\(c_{01} = 0.41 \text{ mmol/L}; c_{02} = 0.85 \text{ mmol/L}\).
the slopes and intercepts of each region for each heavy metal ions are summarized in Table 4.

It should be noted that just because the straight lines illustrated in Fig. 5 have deviated from the origin, the intra-particle diffusion is not the rate-limiting step, but it does control the studied biosorption processes to some extent. The first region (Region 1) can be attributed to the mass transfer effect, which occurs in boundary layer diffusion, whilst the Region 2 corresponds to the intra-particle diffusion [25]. Also, the fact that the first region has a higher slope in comparison to the second region, for all studied heavy metal ions, indicates that the binding sites of mustard waste biomass are at the surface, and are easily accessible to heavy metal ions [24].

All of these observation are in agreement with the experimental results presented in Fig. 4, which indicates that the biosorption of Pb(II), Zn(II) and Cd(II) ions from aqueous solution onto mustard waste biomass occurs through two consecutive stages. During the first stage, which is a fast one, the biosorption processes take place at the surface and are probably determined by the chemical interactions that bind the heavy metal ions on the biomass surface. The second stage, which occurs more slowly, involves the diffusion of heavy metal ions inside of biosorbent structure.

3.4 Influence of initial heavy metal concentrations and temperature

The effect of initial heavy metal concentrations on the biosorption performances of mustard waste biomass, at three distinct temperature values (5, 20 and 55 °C), under optimum experimental conditions (5 g biosorbent/L; initial solution pH of 5.5 and 2 hours of contact time) is illustrated in Fig. 6.

It can be seen from Fig. 6 that the biosorption capacity of mustard waste biomass increases with the increase of initial heavy metal concentration, in all cases. For example, at 20 °C the increase of initial heavy metals concentration within the studied range (0.20 to 2.85 mmol/L) has determined an increase of biosorption capacity of mustard waste biomass from 0.04 to 0.34 mmol/g.

![Figure 5](image_url): Intra-particle diffusion kinetics for biosorption of Pb(II), Zn(II) and Cd(II) onto mustard waste biomass at 20 °C.

| Kinetics parameter | Pb(II) | Zn(II) | Cd(II) |
|--------------------|--------|--------|--------|
| $c_{01}$ (mmol/L)  | 0.0532 | 0.0191 | 0.0037 |
| $k_{diff1}$ (mmol/g min$^{1/2}$) | 0.0037 | 0.0052 | 0.0007 |
| $R^2$              | 0.9862 | 0.9540 | 0.9998 |
| $c_{02}$ (mmol/L)  | 0.0841 | 0.0207 | 0.0007 |
| $k_{diff2}$ (mmol/g min$^{1/2}$) | 0.0115 | 0.0107 | 0.0006 |
| $R^2$              | 0.9771 | 0.9998 | 0.9963 |
| $c_{01}$ (mmol/L)  | 0.0191 | 0.0207 | 0.0332 |
| $k_{diff2}$ (mmol/g min$^{1/2}$) | 0.0007 | 0.0009 | 0.0207 |
| $R^2$              | 0.9998 | 0.9963 | 0.9879 |

$c_{01} = 0.41$ mmol/L; $c_{02} = 0.85$ mmol/L.
for Pb(II), from 0.03 to 0.24 mmol/g for Zn(II) and from 0.03 to 0.21 mmol/g for Cd(II), respectively. These significant increases of the \( q \) values are expected because high initial heavy metal concentrations correlate with a higher probability of collisions between heavy metal ions and superficial functional groups of the biosorbent [38]. Furthermore, a differentiation in the biosorption efficiency as a function of the nature of heavy metals can be observed only at higher metal ion concentrations, where the number of available biosorption sites is significantly reduced, and the yield of uptake processes depends on the affinity of heavy metal ions for superficial functional groups of the biosorbent. In the case of the heavy metals analyzed here, biosorption onto mustard waste biomass followed the sequence: Pb(II) > Zn(II) > Cd(II).

It can be also observed from Fig. 6 that the biosorption efficiency of these heavy metals onto mustard waste biomass is favoured at increased temperatures. The increase of temperature from 5 to 55 °C correlated with the increase of biosorption capacity of mustard waste biomass over entire studied initial concentration domain from 0.27 to 0.47 mmol/g for Pb(II), from 0.17 to 0.30 mmol/g for Zn(II) and from 0.14 to 0.28 mmol/g for Cd(II), indicating the endothermic nature of the biosorption process. A possible explanation for this behaviour is that the temperature provides the necessary energy for breaking down certain chemical barriers that could not have been otherwise broken, thus facilitating the interactions between the heavy metal ions and the superficial functional groups of the biosorbent [39].

### 3.5 Biosorption isotherms and their modelling

In this study, three isotherm models (Langmuir, Freundlich and Dubinin-Radushkevich) were used for the modelling of isotherms obtained in cases of biosorption of Pb(II), Zn(II) and Cd(II) ions onto mustard waste biomass, at three different temperatures. The isotherm parameters have been calculated from linearized plots corresponding to each isotherm model, and the obtained values are summarized in Table 5.

The correlation coefficients higher than 0.9922 indicate in all cases the higher applicability of the Langmuir isotherm model in describing the biosorption process of Pb(II), Zn(II) and Cd(II) ions onto mustard waste biomass, at all studied temperatures, in comparison with the Freundlich isotherm model. Therefore, it can be noted that the biosorption process occurs until a heavy metal ion monolayer is formed on the surface of the mustard waste biomass. In addition, the maximum biosorption capacity (\( q_{\text{max}}, \text{mmol/g} \)) follows the order: Pb(II) > Zn(II) > Cd(II), and this is in agreement with previous observations, which argued that Pb(II) ions have a higher affinity for the functional groups of mustard waste biomass and can be retained in higher amounts. Moreover, the high values of the Langmuir constant (\( K_L \)), which are related to the biosorption energy, suggest that strong interactions occur
between heavy metal ions and superficial functional groups of the biosorbent [40] and that the biosorption processes are favourable, since the values of $R_L$ factor are in the range of $0 - 1$ in all cases. As also shown in Table 5, the values of the Langmuir model parameters ($q_{\text{max}}$ and $K_L$) increase with the increase of temperature, thereby confirming the endothermic character of the biosorption process. Even if the Freundlich isotherm model is not adequate to describe the studied biosorption processes ($R^2 = 0.8804 - 0.9955$), the obtained values of $1/n$ constant confirm these observations.

On the other hand, the Dubinin-Radushkevich model matched relatively well with the experimental data obtained for the biosorption of Pb(II), Zn(II) and Cd(II) ions onto mustard waste biomass, since the values of the correlation coefficients ($R^2$) are higher than 0.9379 in all cases. The higher value of the $Q_{\text{max}}^{D-R}$ parameter in comparison with those obtained experimentally shows that mustard waste biomass has a wrinkled structure and that the intra-particle diffusion process controls the heavy metal ion biosorption only up to a certain degree. In addition, the values of mean biosorption energy calculated from this model were between 9.12 and 15.26kJ/mol. This indicates that the biosorption of Pb(II), Zn(II) and Cd(II) ions onto mustard waste biomass mainly involves chemical interactions, probably ion-exchange type, between heavy metal ions from aqueous solution and functional groups on the biosorbent surface. The increase of the biosorption energy with the increase of temperature is another argument that supports the endothermic nature of these biosorption processes.

### 3.6 Biosorption thermodynamics

The values of thermodynamic parameters, calculated according with eqs (11-13) for the biosorption of Pb(II), Zn(II) and Cd(II) onto mustard waste biomass, are summarized in Table 6.

The values of free energy changes ($\Delta G$) were negative for all studied heavy metal ions and indicate that their biosorption onto mustard waste biomass is a spontaneous and energetically favourable process. The positive values of $\Delta H$ is in agreement with the hypothesis that the biosorption of Pb(II), Zn(II) and Cd(II) onto mustard waste biomass is an endothermic process. In addition, the positive values of $\Delta S$ suggest that at the solid/liquid interface an increase of randomness occurs after biosorption of Pb(II), Zn(II) and Cd(II) ions.

### 3.7 Desorption and reutilization of mustard waste biomass

Desorption studies give useful information about the possibilities of biosorbent regeneration after its exhaustion, and are necessary to increase the economical feasibility of the biosorption process. The desorption of
heavy metal ions from loaded mustard waste biomass (1 g) was examined using 15mL of HCl solution (10^{-1} mol/L). Under these conditions, the desorption percentages were 97.81% for Pb(II), 94.24% for Zn(II) and 89.67% for Cd(II). The biomass samples (washed several times with twice distilled water and dried) were reused in three biosorption/desorption cycles. The biosorptive performances of mustard waste biomass decreased with increasing of number of utilization cycles, but the loss in the biosorption capacity is low (5.4% for Pb(II), 5.9% for Zn(II) and 7.3% for Cd(II)). The quantitative recovery of heavy metal ions from loaded mustard waste biomass and its small losses of biosorption capacity after multiple uses, confirm the importance of ion-exchange? interactions in the biosorption mechanism, and support the potential applicability of this waste biomass in wastewater treatment systems.

### 3.8 Comparison of mustard waste biomass with other biosorbents

As with biomasses from all plants, the waste biomass from mustard seeds contains cellulose and lignin as its main constituents, as well as hemi-cellulose, lipids, proteins, polysaccharides, starch, water and other compounds that have various functional groups that can be involved in the uptake processes of heavy metal ions [30]. During the solvent extraction stage, only the lipids and some easy extractable compounds are removed from the mustard biomass, without affecting the composition of the cell walls. Therefore, most of initial components remain in the composition of mustard waste biomass, including their ionisable functional groups (such as carboxyl, amine, hydroxyl, etc.) that could represent potential binding sites for heavy metal ions from aqueous solutions. In order to highlight the practical applicability of mustard waste biomass in the heavy metal removal processes, the biosorption capacity of this biosorbent was compared with those of other biomasses reported in the literature (Table 7).

It can be observed that the maximum biosorption capacity of mustard waste biomass is comparable with the values obtained for other biosorbents that were tested under similar experimental conditions. Therefore, mustard waste biomass can be used as a potential biosorbent in removing heavy metals from aqueous media, and this could be also a suitable solution for the sustainable use of wastes obtained from biodiesel production.

### Table 6: Thermodynamic parameters for Pb(II), Zn(II) and Cd(II) biosorption onto mustard waste biomass.

| Heavy metal | t (°C) | ΔG (kJ/mol) | ΔH (kJ/mol) | ΔS (J/mol K) |
|-------------|--------|-------------|-------------|--------------|
| Pb(II)      | 5      | -21.9871    | 17.8901     | 14.7374      |
|             | 20     | -23.7063    | 19.8505     | 34.0658      |
|             | 55     | -29.0637    | 30.0575     | 47.6367      |
| Zn(II)      | 10     | -18.6857    | 16.8362     | 22.5667      |
|             | 20     | -19.0523    | 17.6334     | 22.5667      |
|             | 40     | -24.2381    |             | 22.5667      |
| Cd(II)      | 10     | -18.8241    |             | 14.3982      |
|             | 20     | -19.8446    |             | 17.1440      |
|             | 40     | -23.0946    |             | 25.2232      |

### Table 7: Comparative values of maximum biosorption capacities (q_{max} mmol/g) for three heavy metals on various biomasses, at room temperature (20 ± 3 °C).

| Biomass                        | Heavy metal | Pb(II) | Zn(II) | Cd(II) | Reference |
|--------------------------------|-------------|--------|--------|--------|-----------|
| Ulva lactuca (green algae)     | 0.1669      | -      | 0.2597 | [41]   |
| Green algae waste biomass     | 0.3206      | -      | 0.3079 | [19]   |
| Laminaria hyperborea (brown algae) | 0.1472   | 0.2937 | 0.4661 | [42]   |
| Sargassum sp. (seaweed)        | 0.6714      | 0.4558 | 0.5444 | [43]   |
| Caulerpa lentillifera          | 0.1399      | 0.0407 | 0.0417 | [44]   |
| non-living Pseudomonas strains| 0.2103      | 0.2819 | -      | [45]   |
| Geobacillus thermodenitrificans| 0.1751      | 0.3816 | 0.3176 | [7]    |
| Romanian peat                  | 0.2026      | -      | 0.1165 | [15]   |
| Lignin                         | 0.4320      | 0.2260 | 0.1720 | [46]   |
| Coconut shell                  | 0.2636      | 0.2613 | 0.1063 | [47]   |
| Mustard biomass                | 0.3105      | 0.2043 | 0.1656 | [3]    |
| Mustard waste biomass          | 0.3561      | 0.2836 | 0.2397 | This study|

### 4 Conclusions

In this study, it was shown that mustard waste biomass, obtained from white mustard seeds after oil extraction, can be successfully used as biosorbent for the removal of some heavy metals (Pb(II), Zn(II) and Cd(II) ions) from aqueous solution. The experiments were performed in batch systems, and the results demonstrate that the highest biosorption capacity of mustard waste biomass was attained at an initial solution pH of 5.5, 5 g of biosorbent/L,
2 hours of contact time and high temperature (55 °C). The pseudo-second order model was the most adequate in describing the kinetics of the biosorption process, and the Langmuir isotherm model best fitted the equilibrium data for all studied heavy metal ions. The maximum biosorption capacity, calculated from the Langmuir model, follows the order: Pb(II) > Zn(II) > Cd(II). The negative values of free energy changes (∆G) confirm that the biosorption of heavy metal ions onto mustard waste biomass is spontaneous and feasible, while the positive value of ∆H points to an endothermic nature of the biosorption process. The exhausted biosorbent can be easily regenerated with 10⁻¹mol/L HCl solution, and the retained heavy metal ions can be quantitatively recovered. Also, after regeneration the biosorbent samples can be reused in at least three biosorption/desorption cycles, with little affect on the biosorption capacity of the mustard waste biomass. The results presented in this study indicate that mustard waste biomass can be used as potentially low-cost biosorbent. Use of this biomass in the heavy metal removal process will be helpful for environmental protection, and it offers a possible way of valorising this waste. Both aspects are important in the conception of sustainable development strategies.

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References

[1] Azmir J., Zaidul I.S.M., Rahman M.M., Sharif K.M., Mohamed A., Sahena F., Jahurul M.H.A., Ghafoor K., Norulaini N.A.N., Omar A.K.M., Techniques for extraction of bioactive compounds from plant materials: A review, J. Food. Eng., 2013, 117, 426-436. doi:10.1016/j.jfoodeng.2013.01.014

[2] Kurki A., Hill A., Morris M., Biodiesel: The sustainability dimensions. ATTRA—National Sustainable Agriculture Information Service, (2010) on line: www.attra.ncat.org

[3] Bulgariu L., Hilhor R., Bulgariu D., Gavrilcescu M., Sorptive removal of cadmium(II) ions from aqueous solution by mustard biomass, Environ. Eng. Manag. J., 2012, 11(8), 1969-1976.

[4] Leung D.Y.C., Wu X., Leung M.K.H., A review on biodiesel production using catalyzed transesterification, Appl. Energy, 2010, 87(4), 1083-1095.

[5] Naik S.N., Goud V.V., Rout P.K., Dalai A.K., Production of first and second generation biofuels: A comprehensive review, Renew. Sustain. Energy Rev., 2010, 14(2), 578-597. doi:10.1016/j.rser.2009.10.003.

[6] Han R., Li H.Y., Zhang J., Xiao H., Shi J., Biosorption of copper and lead ions by waste beer yeast, J. Hazard. Mater., 2006, 137, 1569-1576. doi:10.1016/j.jhazmat.2006.04.045.

[7] Abdel-Ghani N.T., El-Chaghaby G.A., Biosorption for metal ions removal from aqueous solutions: A review of recent studies, Int. J. Latest Res. Sci. Technol., 2014, 3(0), 24-42.

[8] Malin A., Metal bioremediation through growing cells, Environ. Int., 2004, 30, 267–278. doi:10.1016/j.envint.2003.08.001.

[9] Febrianto J., Kosasih A.N., Sunarso J., Ju Y.H. Indrawati N., Isumaji S., Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies, J. Hazard. Mater., 2009, 162, 616-645. doi:10.1016/j.jhazmat.2008.06.042.

[10] Montazer-Rahmati M.M., Rabbani P., Abdolali A., Keshkhar A.R., Kinetics and equilibrium studies on biosorption of cadmium, lead, and nickel ions from aqueous solutions by intact and chemically modified brown algae, J. Hazard. Mater., 2011, 185, 401-407. doi:10.1016/j.jhazmat.2010.09.047.

[11] Demirbas A., Heavy metal adsorption onto agro-based waste materials: A review, J. Hazard. Mater., 2008, 157, 220-229. doi:10.1016/j.jhazmat.2008.01.024.

[12] Meena A.K., Kadiivelu K., Mishraa G.K., Rajagopal C., Nagar P.N., Adsorption of Pb(II) and Cd(II) metal ions from aqueous solution by mustard husk, J. Hazard. Mater., 2008, 150, 619-625. doi:10.1016/j.jhazmat.2007.05.011.

[13] Lupea M., Bulgariu L., Macoveanu M., Biosorption of Cd(II) from aqueous solutions on marine algae biomass, Environ. Eng. Manag. J., 2012, 11(3), 607-615.

[14] Khan M.A., Nagbara M., Choong T.S.Y., Masood H., Chuan L.A., Biosorption and desorption of nickel on oil cake: Batch and column studies, Biore. Technol., 2012, 103, 35-42. doi:10.1016/j.biortech.2011.09.065.

[15] Bulgariu L., Balan C., Bulgariu D., Macoveanu M., Valorisation of romanian peat for the removal of some heavy metals from aqueous media, Desalination Water. Treat., 2014, 53(31-33), 5891-5899. doi:10.1080/19443994.2013.811105.

[16] Donmez G., Aksu Z., Ozturk A., Kutsal T., A comparative study on heavy metal biosorption characteristics of some algae, Process Biochem., 1999, 34, 885-892. doi:10.1016/S0032-9592(99)00005-9.

[17] Bulgariu L., Lupea M., Bulgariu D., Rusu C., Macoveanu M., Equilibrium study of Pb(II) and Cd(II) biosorption from aqueous solution on marine green algae biomass, Environ. Eng. Manag. J., 2013, 12(1), 183-190.

[18] Bulgariu L., Bulgariu D., Algae Waste Biomass: A New Class of Low-Cost Material with Potential Applications in Environmental Engineering, in Marine Algae Extracts, Wiley-VCH Verlag GmbH&Co., Weinheim, Germany, 2015.

[19] Bulgariu D., Bulgariu L., Equilibrium and kinetics studies of heavy metals ions biosorption on green algae waste biomass, Biore. Technol., 2012, 103, 489-493. doi:10.1016/j.biortech.2011.

[20] Xie Y., Li H., Wang X., Ng I.S., Lu Y., Jing K., Kinetic simulating of Cr(VI) removal by the waste Chlorella vulgaris biomass, J. Taiwan Inst. Chem. Eng., 2014, 45(4), 1773-1782. doi:10.1016/j.jtice.2014.02.016.

[21] Dean J.A., Handbook of Analytical Chemistry, Mc-Grow Hill Inc., New York, USA, 1995.
[22] Ho Y.S., McKay G., Pseudo-second-order model for sorption processes, Process Biochem., 1999, 34, 451-465. doi: 10.1016/S0032-9592(98)00112-5.

[23] Gerente C., Lee V.K.C., Lee P., McKay G., Application of chitosan for the removal of metals from wastewaters by adsorption-mechanisms and models review, Critical Rev. Environ. Sci. Technol., 2007, 37(1), 41-127. doi: 10.1080/106439080600729089.

[24] Wu Y., Zhang S., Guo X., Huang H., Adsorption of chromium(III) on lignin, Biore. Technol., 2008, 99, 7709-7715. doi: 10.1016/j.biortech.2008.01.069.

[25] Cheung W.H., Szeto Y.S., McKay G., Intra-particle diffusion processes during acid dye adsorption onto chitosan, Biore. Technol., 2007, 98, 2897-2904. doi: 10.1016/j.biortech.2006.09.045.

[26] Chong K.H., Volesky B., Description of two-metal biosorption equilibria by Langmuir-type models, Biotechnol. Bioeng., 1995, 47(4), 451-460.

[27] Youssef N.S., Farouq R., Hazzaa R., Adsorption kinetics and isotherms for the removal of nickel ions from aqueous solutions by an ion-exchange resin: application of two and three parameter isotherm models, Desalination Water. Treat., 2016, (in press), doi: 10.1080/19443994.2015.1132474.

[28] Rangabashiyam S., Anu N., Nandagopal Girî M.S., Selvaraju N., Relation of isotherm models in biosorption of pollutants by agricultural byproducts, J. Environ. Chem. Eng., 2014, 2(1), 398-414. doi: 10.1016/j.jece.2014.01.014.

[29] Farooq U., Kozinski J.A., Khan M.A., Athat M., Biosorption of heavy metal ions using wheat based biosorbents – A review of the recent literature, Biore. Technol., 2010, 101, 5043-5053. doi: 10.1016/j.biortech.2010.02.030.

[30] Gupta V.K., Ali I., Utilisation of bagasse fly ash (a sugar industry waste) for the removal of copper and zinc from wastewater, Sep. Purif. Technol., 2000, 18(2), 131-140. doi: 10.1016/S1383-5866(99)00058-1.

[31] Arica M.Y., Bayramoglu G., Biosorption of Reactive Red-120 dye from aqueous solution by native and modified fungus biomass preparations of Lentinus sajor-caju, J. Hazard. Mater., 2007, 149, 499-507. doi: 10.1016/j.jhazmat.2007.04.021.

[32] Yeh K.L., Chang J.S., Effects of cultivation conditions and media composition on cell growth and lipid productivity of indigenous microalga Chlorella vulgaris ESP-31, Biore. Technol., 2012, 105, 120-127. doi: 10.1016/j.biortech.2011.10.103.

[33] Murdock J.N., Wetzel D.L., FT-IR microspectroscopy enhances biological and ecological analysis of algae, Appl. Spec. Rev., 2009, 44, 335-361. doi: 10.1080/0570492090297440.

[34] Pistorius A.M., DeGrip W.J., Egorova-Zachernyuk T.A., Monitoring of biomass composition from microbiological sources by means of FT-IR spectroscopy, Biotechnol. Bioeng., 2009, 103, 123-129. doi: 10.1002/bit.22220.

[35] Dabrowski A., Hubicki Z., Podkoscieleń P., Robens E., Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method, Chemosphere, 2004, 56, 91-106. doi: 10.1016/j.chemosphere.2004.03.006.

[36] Gautam R.K., Mudhoo A., Lofranco G., Chattopadhyaya M.C., Biomass-derived biosorbents for metal ions sequestration: Adsorbent modification and activation methods and adsorbent regeneration. J. Environ. Chem. Eng., 2014, 2(1), 239-259. doi: 10.1016/j.jece.2013.12.019.

[37] Tunali A.S., Arslan S., Alp T., Arslan D., Akar T., Biosorption potential of the waste biomaterial obtained from Cucumis melo for the removal of Pb \(^{2+}\) ions from aqueous media: Equilibrium, kinetic, thermodynamic and mechanism analysis. Chem. Eng. J., 2012, 185-186, 82-90. doi: 10.1016/j.cej.2012.01.032.

[38] Cruz C.C.V., da Costa A.C., Henriques C.A.O., Luna A.S., Kinetic modeling and equilibrium studies during cadmium biosorption by dead Sargassum sp. biomass, Biore. Technol., 2004, 91, 249-257. doi: 10.1016/S0960-8524(03)00194-9.

[39] Anayurt R.A., Sari A., Tuzen M., Equilibrium, thermodynamic and kinetic studies on biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (Lactarius scrobiculatus) biomass, Chem. Eng. J., 2009, 151(1-3), 255-261. doi: 10.1016/j.cej.2009.03.002.

[40] Bulgariu L., Bulgariu D., Macoveanu M., Adsorptive performances of alkaline treated peat for heavy metal removal, Sep. Sci. Technol., 2011, 46, 1023-1033. doi: 10.1080/01496395.2010.536192.

[41] Sari A., Tuzen M., Biosorption of Pb(II) and Cd(II) from aqueous solution using green alga (Ulva lactuca) biomass, J. Hazard. Mater., 2008, 152, 302-308. doi: 10.1016/j.jhazmat.2007.06.097.

[42] Freitas O.M.M., Martins R.J.E., Delerue-Matos C.M., Boaventura R.A.R., Removal of Cd(II), Zn(II) and Pb(II) from aqueous solution by brown marine macro algae: Kinetic modelling. J. Hazard. Mater., 2008, 153, 493-501. doi: 10.1016/j.jhazmat.2007.08.081.

[43] Sheng P.X., Ting Y.P., Chen P., Hong L., Sorption of lead, copper, cadmium, zinc and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms, J. Coll. Interface Sci., 2004, 275, 131-141. doi: 10.1016/j.jcis.2004.01.036.

[44] Pasavant P., Apiratikul R., Sukghum V., Suthiparinyanont P., Wattanachira S., Marhaba T.F., Biosorption of Cu\(^{2+}\), Cd\(^{2+}\), Pb\(^{2+}\) and Zn\(^{2+}\) using dried marine green macroalga Caulerpa lentillifera, Biore. Technol., 2006, 97, 2321-2329. doi: 10.1016/j.biortech.2005.10.032.

[45] Shaker M.A., Thermodynamic profile of some heavy metal ions adsorption onto biomaterial surfaces, Am. J. Appl. Sci., 2007, 4, 605-612. doi: 10.3844/ajassp.2007.605.612.

[46] Guo X., Zhan X., Shan X.Q., Adsorption of metal ions on lignin, J. Hazard. Mater., 2008, 151, 134-142. doi: 10.1016/j.jhazmat.2007.05.065.

[47] Abdolali A., Guo W.S., Ngo H.H., Chen S.S., Nguyen N.C., Tung K.L., Typical ligninicellulosic wastes and by-products for biosorption process in water and wastewater treatment: A critical review, Biore. Technol., 2014, 160, 57-66. doi: 10.1016/j.biortech.2013.12.037.