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ORIGINAL ARTICLE

Linear and nonlinear regression analysis for heavy metals removal using *Agaricus bisporus* macrofungus

Boldizsar Nagy [a], Carmen Mânzatu [a], Andrada Măicăneanu [a], Cerasella Indolean [a], Barbu-Tudoran Lucian [b], Cornelia Majdik [a,*]

[a] *Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University, 11 Arany Janos st., Cluj-Napoca, Romania*
[b] *Electronic Microscopy Centre, Babes-Bolyai University, RO-400028 Cluj-Napoca, Romania*

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Abstract In the present study the biosorption characteristics of Cd (II) and Zn (II) ions from monocomponent aqueous solutions by *Agaricus bisporus* macrofungus were investigated. The initial metal ion concentrations, contact time, initial pH and temperature were parameters that influence the biosorption. Maximum removal efficiencies up to 76.10% and 70.09% (318 K) for Cd (II) and Zn (II), respectively and adsorption capacities up to 3.49 and 2.39 mg/g for Cd (II) and Zn (II), respectively at the highest concentration, were calculated. The experimental data were analyzed using pseudo-first- and pseudo-second-order kinetic models, various isotherm models in linear and nonlinear (CMA-ES optimization algorithm) regression and thermodynamic parameters were calculated. The results showed that the biosorption process of both studied metal ions, followed pseudo second-order kinetics, while equilibrium is best described by Sips isotherm. The changes in morphological structure after heavy metal-biomass interactions were evaluated by SEM analysis. Our results confirmed that macrofungus *A. bisporus* could be used as a cost effective, efficient biosorbent for the removal of Cd (II) and Zn (II) from aqueous synthetic solutions.

1. Introduction

Heavy metals pollution represents a serious problem to ecological systems including aquatic system, microorganisms and also to human health. They are not biodegradable and they have a tendency to accumulate in biological system (vegetables, aquatic inhabitants), which are enriched by human beings through food chain (Martins et al., 2004). Heavy metals can be introduced into ecosystems through industrial effluents and wastes, agricultural fungicides, domestic garbage dumps and mining activities (Merian, 1991). Some heavy metals (e.g. Zn) are essential to living organisms, others (e.g. Cd) have no apparent biological function (Xu et al., 2011). To remove or to reduce the toxicity of heavy metals, several methods were used including chemical precipitation (Brooks, 1991), ion-exchange (Tiravanti et al., 1997), activated carbon adsorption (Hu et al., 2003) and membrane filtration (Molinari et al., 2004). However these conventional methods have also many

* Corresponding author. Tel.: +40 264 593833x5761; fax: +40 264 590818.
E-mail address: majdik@chem.ubbcluj.ro (C. Majdik).

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disadvantages: are less effective, very expensive, high reagent cost and energy needs. An alternative method is represented by the biosorption process which attracted major interest from scientist. The main advantages of this technique can be ordered as follows: low operating cost, no production of secondary compounds, short operation time, environmental friendly etc. Biosorption involves a combination of active and passive transport mechanisms. The first stage, usually referred to as passive uptake, is an initial rapid and reversible accumulation step. The second stage, usually referred to as active uptake, is a slower intracellular bioaccumulation, often irreversible and related to metabolic activity (Sağ and Kutsal, 1995; Tsezos and Volensky, 1981; Ting et al., 1989; Wilde and Benemann, 1993). The heavy metals biosorption by different biological materials was previously reported, on biomasses such as fungi (Anayurt et al., 2009), wood sawdust (Semerjan, 2010), algae (Kumar et al., 2006), egg shells (Jai et al., 2007) or yeast (Tonk et al., 2011) shows a good removal capacity of toxic metal ions from wastewater. Studies have shown that macrofungus was represented as a good potential material for remediation of wastewaters containing toxic metal ions.

Agaricus bisporus macrofungus commonly known as button mushroom is an edible basidiomycete and is the most commonly and widely consumed mushroom in the world. Therefore, large amounts of by-products (stem, shell) obtained from mushrooms before consumption are available and could be used for heavy metals removal from aqueous solutions. The moisture content is between 89% and 92.3% on fresh weight and the dry based contents are formed from carbohydrate, crude protein, crude fiber, crude ash and crude fat (Tsai et al., 2007). The main components of the fungal cell wall are polysaccharides (80–90% of the dry mass) (Akar et al., 2009). Chitin is also a characteristic component of the basidomycetes (Vetter, 2007).

Cd (II) alongside with Hg (II) and Pb (II) are the heavy metals exhibit the greatest potential hazard to human health and various ecosystems. Zn (II) is relevant because it is a necessary trace element for fungal growth, but can be toxic at high concentrations (Melgar et al., 2007). Therefore the aim of this work was to investigate the biosorption potential of *A. bisporus*, a cheap and easily available biomass, for the removal of Cd (II) and Zn (II) ions from monocomponent aqueous solutions. The effect of initial metal ion concentrations, contact time, initial pH and temperature were investigated. Scanning electron microscopy analysis was employed to evaluate the consequence in *A. bisporus* structure after heavy metals loading. The Langmuir and Freundlich isotherm models were used to describe equilibrium isotherms. The experimental data were analyzed using pseudo-first- and pseudo-second-order kinetic models, various isotherm models in linear and nonlinear (Covariance Matrix Adaptation Evolution Strategy optimization algorithm) regression and thermodynamic parameters were calculated.

2. Materials and methods

2.1. Biosorbent

Fruit bodies of *A. bisporus* were purchased from a local commercial company from Nuşfalău, Sălaj County, Romania. A special substrate for cultivation is produced from nitrogen-amended cereal straw which is subjected to an aerobic solid-state fermentation or composting, that replaces easily available carbon and nitrogen compounds with humic-rich complexes. This highly selective medium is then pasteurized and inoculated with *A. bisporus* mycelium. The macrofungus was used as an adsorbent for the biosorption of Cd (II) and Zn (II) ions, in batch conditions. Before use, the macrofungus was washed several times with distilled water to remove dirt and impurities and then was dried in an oven at 70 °C for 24 h. The obtained biomass was then grinded and sieved through a 0.4–1.2 mm mesh size sieve and used for further experiments.

2.2. Morphological study

Scanning electron microscopy (SEM) images for *A. bisporus* biomass were obtained with a JEOL (USA) JSM 5510 LV apparatus. Prior to analyze, biosorbent samples were mounted on a stainless stab with a double stick tape. Then they were coated with a thin layer of gold under vacuum to improve electron conductivity and image quality.

2.3. Heavy metal solution preparation

The stock solution, 1 g/L of Cd (II) and Zn (II) was prepared by dissolving $Cd(NO_3)_2 \cdot 4H_2O$ and $ZnSO_4 \cdot 7H_2O$ in distilled water. The required concentrations were obtained by diluting the stock solution to the desired concentrations, in 50–245 mg/L range. HCl (0.1 M) and NaOH (0.1 M) volumetric solutions were used to adjust the solution pH. All chemicals used were of analytical grade.

2.4. Biosorption experiments

In order to optimize the experimental conditions and to collect data for the modelling study, batch experiments were performed, contacting 4 g of *A. bisporus* macrofungus at 400 rpm (magnetic stirring) with 100 mL aqueous solution of Cd (II) and Zn (II) ions at different initial concentrations (50–245 mg/L), at 298 K for 240 min to reach equilibrium. In order to determine the exact concentration of cadmium and zinc ions and establish the evolution of the removal process, samples of 100 μL were collected at different time intervals up to 240 min (contact time experiments showed that this time is sufficient for attaining the equilibrium).

At the end of the predetermined time, the suspension was filtered (0.45 μm cellulose syringe filters) and the remaining concentration of metal in the aqueous phase was determined using an Atomic Absorption Spectrometer (SensAA Dual GBS Scientific Equipment, Australia). In order to evaluate the amount of cadmium and zinc ions retained per unit mass of macrofungus, the adsorption capacity was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

Removal efficiency, E (%), was calculated as a ratio between Cd (II) or Zn (II) biosorbed at time t (mg/L) and the initial metal ion's concentration (mg/L):

$$E = \frac{C_0 - C_t}{C_0} \cdot 100 \quad (2)$$

In order to study the effect of pH on metal uptake by *A. bisporus* the initial pH solution was varied in pH range of 2.5–9.5 for Cd (II) and Zn (II) ions. pH value was adjusted using 0.1 M HCl and 0.1 M NaOH solutions at the beginning of the experiment. pH values were measured using an Consort C863 pH meter. In order to establish the thermodynamic parameters, 298, 308 and 318 K temperatures were used to conduct biosorption experiments.

Experimental data were used to determine the equilibrium time, equilibrium concentrations, amounts adsorbed at equilibrium, optimum initial pH, and temperature influence over the biosorption process. Also the experimental data were used to establish isotherm (linear and nonlinear regression), kinetics models and to calculate thermodynamic parameters. All the experiments were repeated three times, the values presented were calculated using averaged concentration values.

3. Results and discussions

3.1. SEM analysis

In order to examine the morphological structure of biomass, SEM micrographs of *A. bisporus* were taken before and after Cd (II) and Zn (II) biosorption and presented in Fig. 1. SEM micrograph of unloaded biosorbent indicates a smooth regular spherical structure of the macrofungus surface, Fig. 1a. After metal loading, some deformation and appearance of cavities onto the macrofungus surface were observed, (Fig. 1b and c). The spherical form remains unmodified after metal loading.

3.2. The effect of contact time and initial heavy metal concentrations

In order to establish the equilibrium time for Cd (II) and Zn (II) biosorption onto *A. bisporus* biomass, contact time influence over the process evolution was investigated until equilibrium was reached. As shown in Fig. 2 the removal efficiency increases rapidly (in the first 80 min) due to the abundant availability of active binding site of the biosorbent and gradually decreases (up to 240 min) with the occupancy of these sites. In the case of Zn (II) removal, the same tendency was observed. Further increase in contact time did not enhance the biosorption, therefore the contact time was selected 240 min for further experiments (equilibrium).

The effect of initial Cd (II) and Zn (II) ion's concentration on the adsorption capacity was also studied. Initial heavy metal concentration influence over the adsorption capacities obtained for each metal is presented in Fig. 3. Equilibrium adsorption capacities for Cd (II) increase from 1.00 mg/g biomass for the initial of 50 mg/L to 3.49 mg/g biomass for the initial of 235 mg/L. In case of Zn (II) adsorption capacities increase from 0.89 mg/g for the initial of 60 mg/L to 2.39 mg/g for the initial 245 mg/L. Further increase of the initial metal ion concentration does not lead to an increase in the adsorption capacity. These results sug-

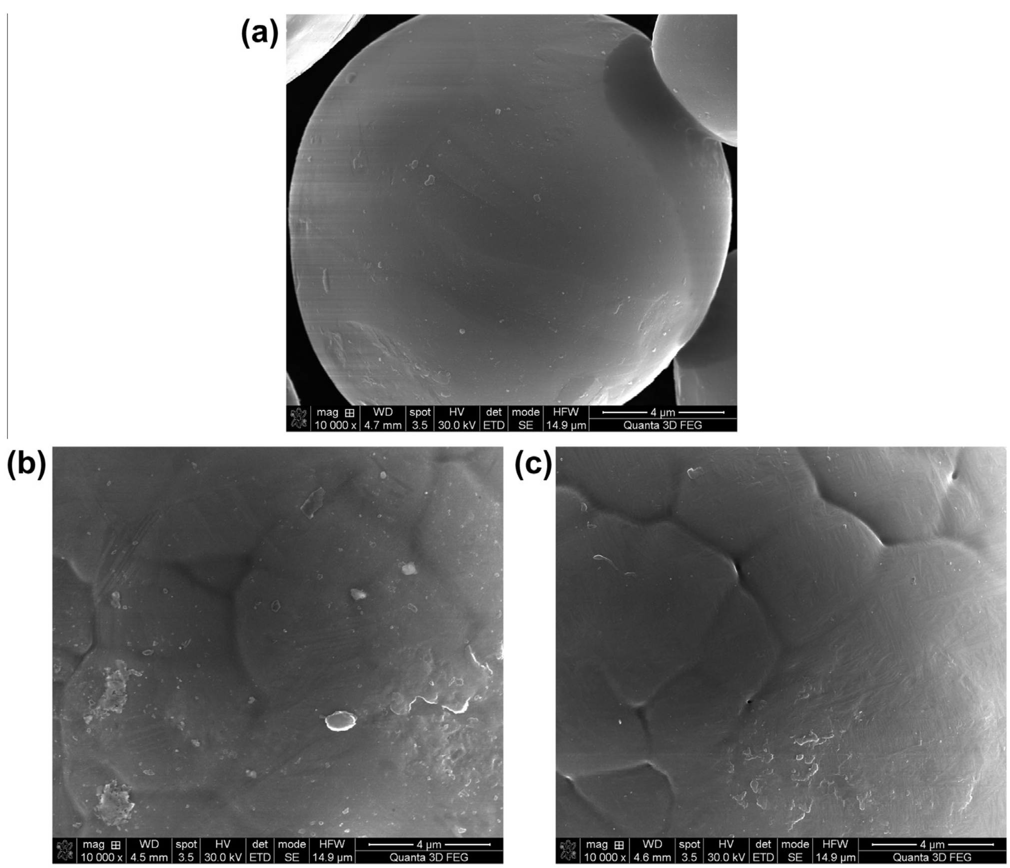

Figure 1 SEM images of the *Agaricus bisporus* macrofungus (a) unloaded, (b) Cd (II) loaded and (c) Zn (II) loaded.

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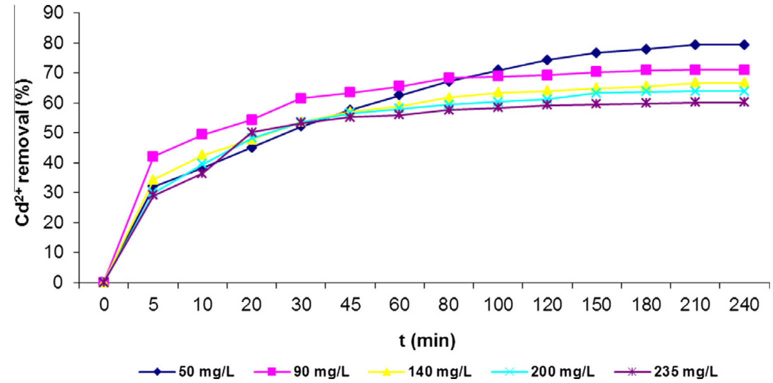

Figure 2 Effect of contact time over the removal efficiency for *A. bisporus* biomass on Cd (II) biosorption; *Ci* = 50–235 mg/L, 4 g biomass, 0.4 < d < 1.2 mm, 298 K, 5.6 pH, 400 rpm.

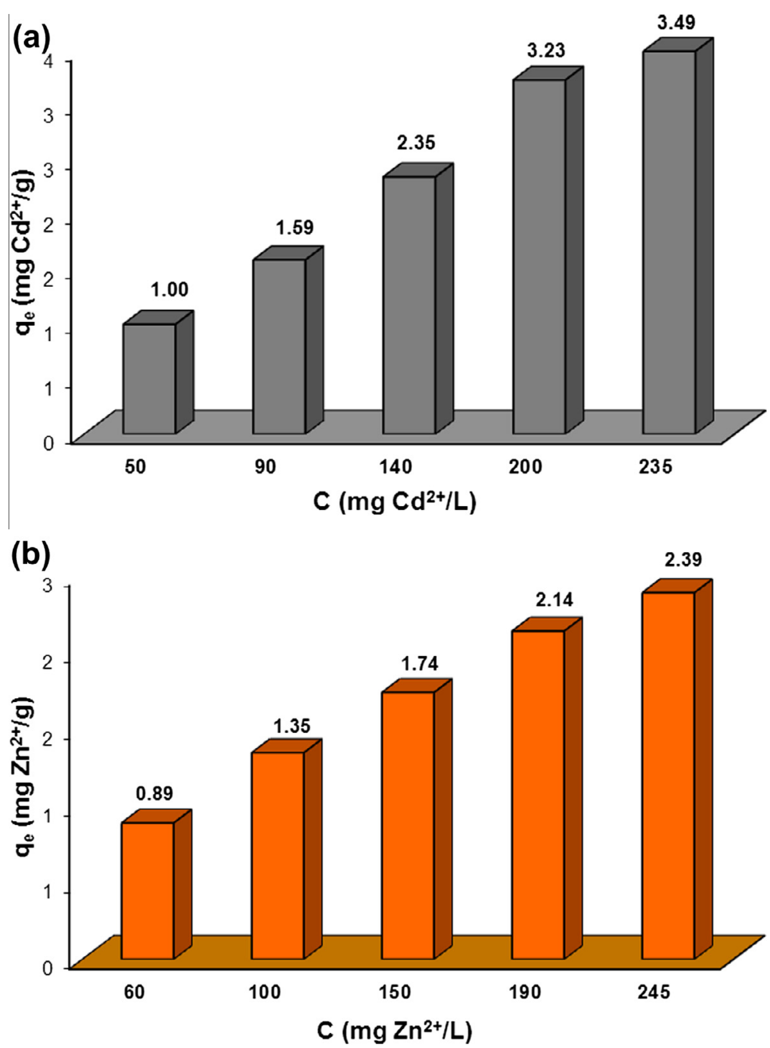

Figure 3 Influence of the initial (a) Cd (II) and (b) Zn (II) concentration over the adsorption capacity onto the *A. bisporus* biomass; Ci = 50–245 mg/L, 4 g biomass, 0.4 < d < 1.2 mm , 298 K, 5.6 (Cd)/5.3 (Zn) pH, 400 rpm.

gest that the adsorption capacity increases with the increase of concentration up to a limit. This fact indicates that if the metal ion concentration in solution increases, the difference in concentration between bulk solution and surface also increases, intensifying the mass transfer processes. Accordingly a higher quantity will be adsorbed, proving that *A. bisporus* biomass has a high adsorption capacity for metal ions.

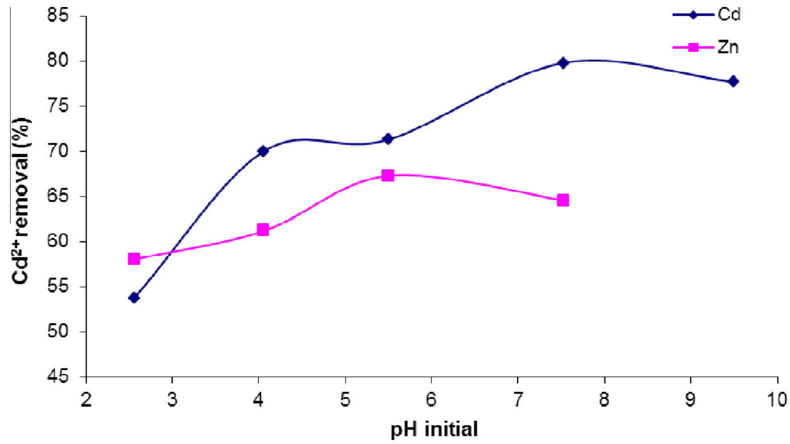

Figure 4 The effect of initial pH values on removal efficiency for Cd (II) and Zn (II) biosorption using *A. bisporus* biomass, C_i = 50 mg/L, 4 g biomass, 0.4 < d < 1.2 mm, 298 K, 400 rpm.

3.3. The effect of initial pH

The pH is one of the most important factors that affect the uptake of heavy metal ions from aqueous solution. This parameter is directly related to competition ability of hydrogen ions with metal ions to active sites on the biosorbent surface (Tsai et al., 2007). The role of initial hydrogen ion concentration on the biosorption of Cd (II) and Zn (II) ions onto *A. bisporus* was studied within 2.5–9.5 pH range. Measuring pH values at the beginning and at the end of the biosorption process, we observed for both metals that irrespective of the initial pH value (acid or basic), equilibrium pH value increases (from the initial acid) and decreases (from the initial basic) toward neutral (slightly acidic). Modifying the initial pH values of the metal solutions, it was observed that the biosorbent resets the solution pH from the initial value to 6.3 in all cases (after around 80 min) and this value is maintained to the end of experiments. In case of Zn (II) a steep increase observed after pH 7 is due to the starting of the precipitation process. Minimum removal efficiencies 53.75% and 58.02% at pH 2.50 were calculated, while the maximum removal efficiencies were 79.82% at pH 7.5 and 67.30% at pH 5.5 for Cd (II) and Zn (II), respectively (Fig. 4). These studies concluded that the competition of hydrogen ions on the biomass surfaces is not metal specific. As the pH is lowered, the overall surface charge on the cell wall will become positive, which inhibits the approach of positively charged metal cations. With the increase of solution pH, biosorbent surface is more negatively charged and the functional groups of the biomass were more deprotonated and thus available for metal ions (Lodeiro et al., 2006).

3.4. The effect of temperature

The effects of temperature on biosorption of Cd (II) and Zn (II) ions onto *A. bisporus* were conducted at 25, 35 and 45 °C. Results presented in Fig. 5 showed that the adsorption of Cd (II) and Zn (II) increases significantly with the increase in temperature from 298 (70.27%) to 318 K (76.11%) and 298 K (61.35%) to 318 K (70.09%), respectively, indicating that the biosorption process is endothermic. The increase in the adsorption capacity with temperature may be attributed to either change in pore size of the adsorbent improving intra-particle diffusion within the pores or enhancement in the chemical affinity of metal cations to the surface of the adsorbent. This leads to increased disorder at the biosorbent surface and intensification of chemical interactions that take place during the biosorption process which have as a result an increase in adsorption capacity (Meena et al., 2008). Higher temperatures were not considered due to the fact that preliminary studies showed that after 50 °C desorption process begins.

3.5. Biosorption kinetics

In order to examine the controlling mechanism of Cd (II) and Zn (II) ions on biosorption process such as chemical reaction onto cultivated *A. bisporus* biomass, pseudo-first- (Lagergren) (Lagergren, 1898) and pseudo-second-order (Ho) (Ho and McKay, 1999; Ho, 2006) were used to test the experimental data (Table 1). Linear regression analysis (coefficient of determination, R^2) was used to analyze the linear forms of kinetic models. Kinetic constants were determined using slope and intercept values of the linear plots.

Table 2 presented pseudo-first-order and pseudo-second-order rate constants, calculated and experimental q_e values for Cd (II) and Zn (II) biosorption on *A. bisporus* macrofungus biomass using different initial concentrations. Correlation coefficients obtained when the pseudo-first-order kinetic model (Fig. 6a) was applied to metal ions biosorption, have very low values. Also, calculated adsorption capacities values show great differences by comparison with experimental values. Based on this remark it can be concluded that the biosorption process cannot be classified as pseudo-first-order. When pseudo-second-order kinetic model was applied for the considered adsorption process, Table 2 and Fig. 6b, coefficients of determination higher than 0.99, were obtained, in both cases (Cd (II) and Zn (II)). A comparison between calculated and experimental adsorption capacities showed a good agreement. Therefore it was concluded that Cd (II) and Zn (II) metal ion biosorption on *A. bisporus* biomass obeyed the pseudo-second-order kinetic model, suggesting that the considered process takes place as chemisorption.

3.6. Biosorption isotherm models

In the present study, two parameters of isotherm models, Langmuir and Freundlich were used for linear regression

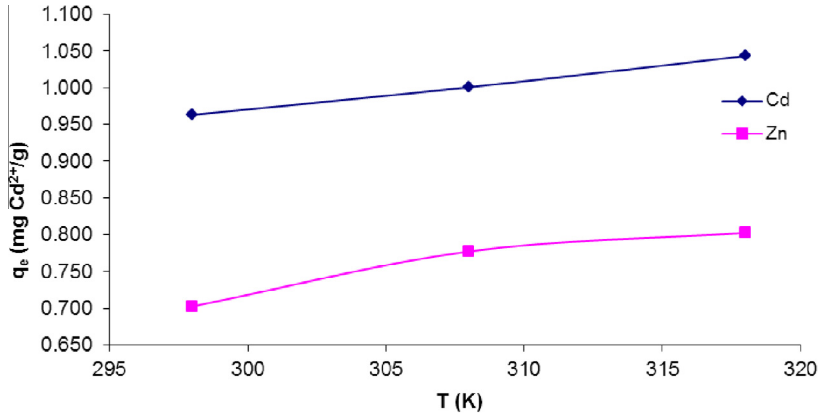

Figure 5 Temperature influence over the removal efficiency of Cd (II) and Zn (II) biosorption using *A. bisporus* biomass; C_i = 50 mg/L, 4 g biomass, 0.4 < d < 1.2 mm, 5.6 (Cd)/5.3 (Zn) pH, 400 rpm.

Table 1 Kinetic model equations used to investigate Cd (II) and Zn (II) biosorption onto *A. bisporus* macrofungus biomass.

Kinetic model	Nonlinear form	Linear form
Pseudo-first-order	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	$\ln(q_e - q_t) = \ln q_e - k_1 t$
Pseudo-second-order	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$

analysis to describe (coefficient of determination, R^2) the equilibrium of Cd (II) and Zn (II) adsorbed onto *A. bisporus* biomass, Table 3. These two isotherm models are the most widely used isotherms for the biosorption of a solute from a liquid solution. The Freundlich isotherm model assumes a heterogeneous adsorption surface and active sites with different energies (Freundlich, 1947). The Langmuir model assumes that a monomolecular layer is formed when biosorption takes place without any interaction between the adsorbed molecules (Langmuir, 1906). Based on similar literature data the metal ion uptake differences in adsorption capacity are influenced by the individual properties of the biosorbent, such as the biomass structure, functional groups and surface area (Sari and Tuzen, 2009; Ertugay and Bayhan, 2010).

The linear plots of the two considered isotherms for Cd (II) biosorption are showed in Fig. 7. Biosorption equilibrium constants obtained from Langmuir and Freundlich isotherms are presented in Table 3. The adsorption isotherm studies clearly indicates that the adsorptive behavior of metal ions satisfies not only the Langmuir assumptions but also the Freundlich assumptions Therefore, high values of correlation coefficients of determination, were found to be highest for Freundlich model, (0.9946) and (0.997) for Langmuir model for Cd (II) and Zn (II) biosorption, respectively. This indicates that the biosorption of the Cd (II) onto *A. bisporus* biomass fitted well for the Freundlich model, while on other hand, Zn (II) biosorption was best described by the Langmuir isotherm. The monolayer saturation capacity, q_{max} was calculated to be 4.31 and 3.51 mg/g, for Cd (II) and Zn (II) ions, respectively.

Nonlinear regression is a more general method that can be used to estimate models' parameters, and it can be applied even if the isotherm model cannot be linearized. For linearized regression, the major problem is the linearization step: modifying the original equation can violate the theories

Table 2 Pseudo-first-order and pseudo-second-order rate constants, calculated and experimental q_e values for Cd (II) and Zn (II) biosorption onto *A. bisporus* macrofungus biomass using different initial concentrations; C_i = 50–245 mg/L, 4 g biomass, 0.4 < d < 1.2 mm, 298 K, pH 5.2 (Cd), 5.6 (Zn), 400 rpm.

C (mg/L)	q_e (exp) (mg/g)	Pseudo-first-order			Pseudo-second-order		
		k_1 (1/min)	q_e (calc) (mg/g)	R^2	k_2 (g/mg min)	q_e (calc) (mg/g)	R^2
Cd (II)							
50	1.00	2.13×10^{-2}	0.88	0.9966	3.08×10^{-2}	1.14	0.9954
90	1.59	2.68×10^{-2}	0.72	0.9582	10.50×10^{-2}	1.63	0.9999
140	2.35	2.00×10^{-2}	1.12	0.9349	4.85×10^{-2}	2.42	0.9997
200	3.23	2.62×10^{-2}	1.89	0.9536	3.58×10^{-2}	3.34	0.9995
235	3.49	2.64×10^{-2}	1.46	0.9376	5.09×10^{-2}	3.58	0.9999
Zn (II)							
60	0.89	2.37×10^{-2}	0.49	0.9616	12.42×10^{-2}	0.92	0.9996
100	1.35	1.63×10^{-2}	0.72	0.8967	6.09×10^{-2}	1.39	0.997
150	1.74	1.35×10^{-2}	0.78	0.7610	6.01×10^{-2}	2.09	0.9966
190	2.14	1.57×10^{-2}	1.09	0.9297	4.00×10^{-2}	2.21	0.9975
245	2.39	2.42×10^{-2}	0.89	0.9111	8.53×10^{-2}	2.44	1.0000

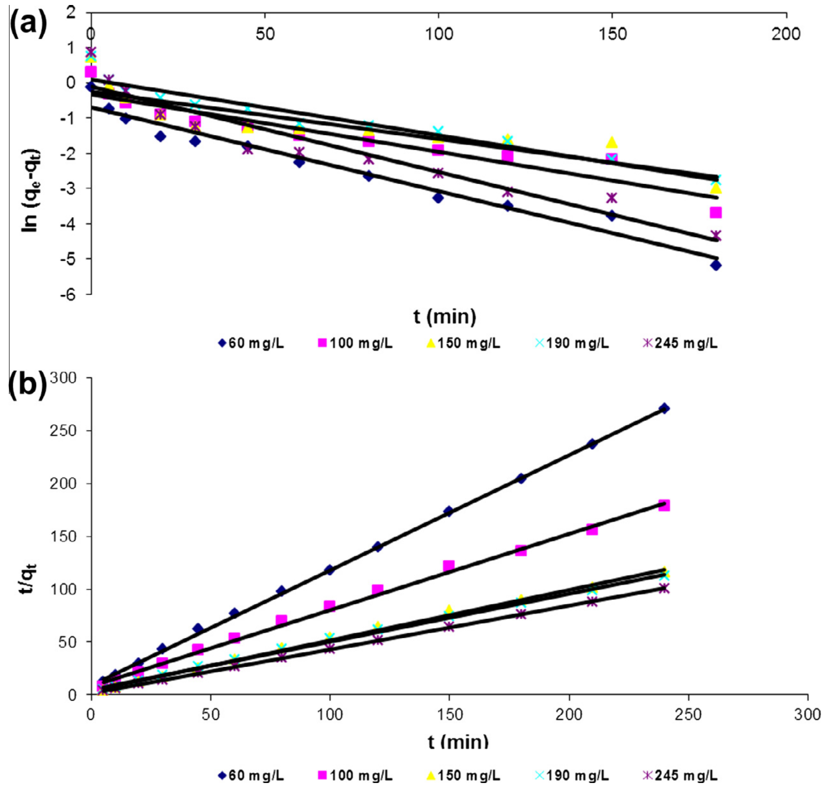

Figure 6 Plots of the pseudo-first-order (a) and pseudo-second-order (b) kinetic models for Zn (II) biosorption using *A. bisporus* biomass; C_i = 60-245 mg/L, 4 g biomass, 0.4 < d < 1.2 mm, 5.3 pH, 400 rpm.

Table 3 Langmuir and Freundlich coefficients calculated using linear regression analysis for Cd (II) and Zn (II) biosorption onto *A. bisporus* macrofungus biomass; C_i = 50–245 mg/L, 4 g biomass, 0.4 < d < 1.2 mm, 298 K, pH 5.2 (Cd), 5.6 (Zn), 400 rpm.

	Langmuir coefficients			Freundlich coefficients		
	K_L (L/mg)	q_{max} (mg/g)	R^2	n	K_F ($mg^{(1-1/n)}$ $L^{1/n}$/g)	R^2
Cd (II)	1.91	4.31	0.9721	1.70	0.25	0.9946
Zn (II)	5.92	3.51	0.9970	2.25	0.26	0.9801

existing behind the model so in fact the parameter estimation gives the best fitting parameters for the linear form of the model, not necessarily for the original nonlinear one. The mathematical reason for this is that the linear regression considers the standard deviations (so the differences between the measured and the calculated values) equally in each point. But, due to the linearization, the unity standard deviation in points of the linear form is not valid for the nonlinear form.

Therefore, comparing the two methods, nonlinear regression are the most feasible method that can be used to estimate isotherm model parameters. Moreover, it deals with the original equations so that the problem of violating the model theories does not exist anymore. The obtained model parameters calculated using nonlinear regression is more relevant that those obtained with linear regression. Nonlinear regression can be performed in different ways. In this case least square based mathematical optimization was applied by using a global optimization algorithm CMA-ES (Covariance Matrix Adaptation Evolution Strategy) (Hansen et al., 2003). The standard deviation function defined by the following equation, was chosen as objective function (Tvrdík et al., 2007):

$$S_D = \sqrt{\frac{1}{n} \cdot \sum_{i=1}^{n} (q_{\text{calc}(i)} - q_{\exp(i)})^2} \quad (3)$$

The decision variables of the objective function were the isotherm model parameters:

$$S_D(\text{par1}, \text{par2}, \text{par3}) \stackrel{!}{=} \min \quad (4)$$

For nonlinear regression analysis nine isotherm models (Table 4) were considered to describe the biosorption process. Standard deviation (S_D) and coefficients of determination (R^2) were calculated in order to compare the linear and nonlinear regression analysis results.

The results obtained for Cd (II) biosorption onto *A. bisporus* biomass, are presented in Table 5 (isotherm parameters, standard deviation and coefficient of determination).

Comparing the standard deviation values obtained for each of the considered isotherms, the fitting degree follows the sequence: Sips (best fit) > Freundlich = Toth = Redlich-Peterson = Radke-Prausnitz > Langmuir > Tempkin > Dubinin-Radushkevich (Fig. 8).

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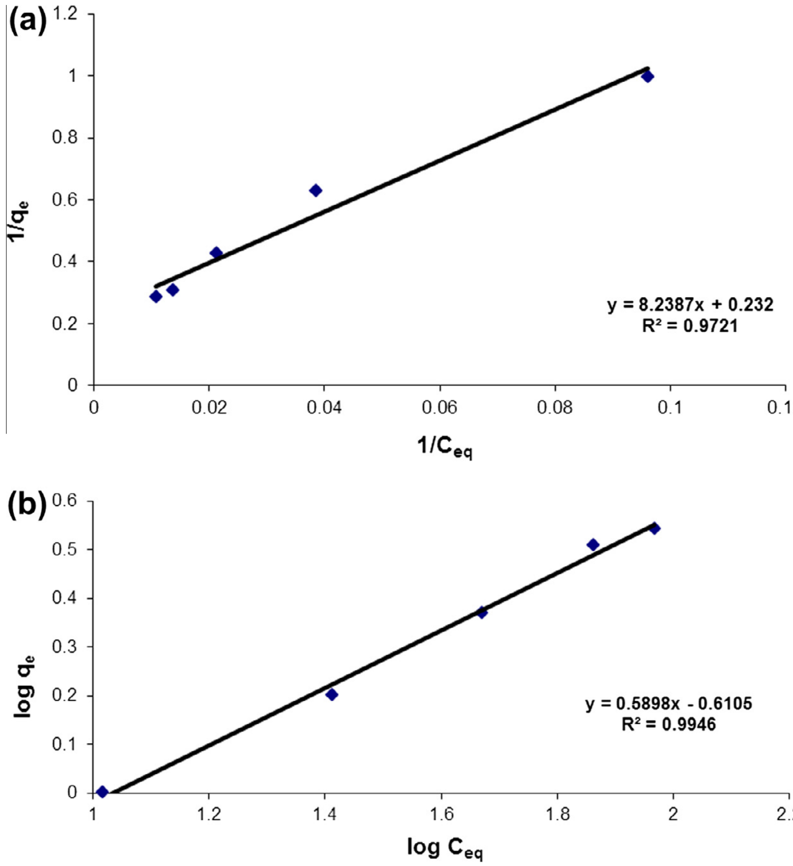

Figure 7 Langmuir (a) and Freundlich (b) plots in linear regression analysis for Cd (II) biosorption using *A. bisporus* biomass; C_i = 50-235 mg/L, 4 g biomass, 0.4 < d < 1.2 mm, 5.6 pH, 298 K, 400 rpm.

Table 4 Equilibrium model equations used to investigate Cd (II) and Zn (II) biosorption onto *A. bisporus* macrofungus biomass.

Isotherm	Nonlinear form	Linear form
Langmuir	$q_e = \frac{q_{\max} \cdot K_L \cdot C_e}{1+K_L \cdot C_e}$	$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} \cdot K_L} \cdot \frac{1}{C_e}$
Freundlich	$q_e = K_F \cdot C_e^{1/n}$	$\log q_e = \log K_F + \frac{1}{n} \cdot \log C_e$
Dubinin-Radushkevich	$q_e = q_s \cdot \exp(-k_{\mathrm{ad}} \cdot \varepsilon^2)$	$\ln q_e = \ln q_s - k_{\mathrm{ad}} \cdot \varepsilon^2$
Tempkin	$q_e = \frac{RT}{b_t} \ln A_t \cdot C_e$	$q_e = \frac{RT}{b_t} \ln A_t + (\frac{RT}{b_t}) \ln C_e$
Redlich-Peterson	$q_e = \frac{K_R \cdot C_e}{1+a_R \cdot C_e^g}$	$\ln(K_R \frac{C_e}{q_e} - 1) = g \ln C_e + \ln a_R$
Sips	$q_e = \frac{K_S \cdot C_e^{\beta_S}}{1+a_S \cdot C_e^{\beta_S}}$	$\beta_S \ln C_e = -\ln\left(\frac{K_S}{q_e}\right) + \ln a_S$
Toth	$q_e = \frac{K_t \cdot C_e}{(a_t+C_e)^{1/t}}$	$\ln\left(\frac{q_e}{K_t}\right) = \ln C_e - \frac{1}{t} \cdot \ln(a_t + C_e$
Khan	$q_e = \frac{q_S \cdot b_K \cdot C_e}{(1+b_K \cdot C_e)^{a_K}}$	-
Radke-Prausnitz	$q_e = \frac{a_{\mathrm{RP}} \cdot r_R \cdot C_e^{\beta_R}}{a_{\mathrm{RP}} + r_R \cdot C_e^{\beta_R - 1}}$	-

Comparing the coefficient of determination values obtained for each of the considered isotherms, the fitting degree follows a similar sequence: Sips (best fit) > Freundlich = Toth = Redlich-Peterson = Radke-Prausnitz = Khan > Langmuir > Tempkin > Dubinin-Radushkevich.

As values showed (lower S_D and highest R^2), Sips isotherm model fits better the biosorption process compared with the other isotherm models. This model is a combined form of Langmuir and Freundlich expressions (Foo and Hameed, 2010), therefore, the obtained result shows that the Cd (II) biosorption onto studied macrofungus biomass is a complex process, which cannot be described by basic isotherm models.

The linear regression method approximates that the scatter of points around the line follows a Gaussian distribution and the standard deviation at every value of C_e. In reality this behavior is impossible with equilibrium isotherm models. Nonlinear regression method avoids these types of errors making this technique the most appropriate to estimate the isotherm model parameters (Tvrdík et al., 2007).

3.7. Biosorption thermodynamics

In order to describe the thermodynamic behavior of metal ion biosorption, thermodynamic parameters were calculated using the following equations:

$$\ln K_D = \frac{-\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \quad (5)$$

and:

$$\Delta G^{\circ} = -RT \ln K_C \quad (6)$$

where: $\Delta H°$, $\Delta S°$, $\Delta G°$, and T are the enthalpy, entropy, Gibbs free energy, and absolute temperature, respectively, and R is the gas constant (8.3144 J/Kmol). Thermodynamic parameters can be determined using the equilibrium constant, K_d (q_e/C_e), which depends on temperature.

Experimental results were used to calculate the thermodynamic parameters and are presented in Fig. 9 and Table 6. The positive values of enthalpy (11.74 and 15.40 kJ/mol for Cd (II) and Zn (II) biosorption, respectively) suggested the endothermic nature of the biosorption and reflected the affinity of the biosorbent for Cd (II) and Zn (II) ions (Lin et al., 2008). Positive values of entropy (1.6×10^{-2} and 2.5×10^{-2} kJ/K mol for Cd (II) and Zn (II) biosorption, respectively) showed that

Table 5 Adsorption isotherm models and their coefficients calculated using nonlinear regression analysis for Cd (II) onto *A. bisporus* macrofungus biomass; C_i = 50–235 mg/L, 4 g biomass, 0.4 < d < 1.2 mm, 298 K, pH 5.2 (Cd), 5.6 (Zn), 400 rpm.

Isotherm	Calculated parameters			S_D	R^2
Langmuir	q_{max} = 6.102	K_L = 0.015	–	0.1183	0.9844
Freundlich	K_F = 0.236	n = 1.666	–	0.0802	0.9928
Dubinin-Radushkevich	q_s = 3.509	$k_{ad} = 9.6 \times 10^{-5}$	–	0.4770	0.7458
Tempkin	b_T = 2072.1	A_T = 0.189	–	0.2019	0.9545
Redlich-Peterson	K_R = 216.96	a_R = 920.04	g = 0.400	0.0802	0.9928
Sips	K_s = 0.220	β = 0.633	a_S = 0.005	0.0798	0.9929
Toth	K_T = 0.236	a_T = 0	t = 2.502	0.0802	0.9928
Khan	q_s = 0.005	b_K = 679.54	a_K = 0.400	–	0.9928
Radke-Prausnitz	a_{RP} = 135.140	r_R = 0.236	β_r = 0.600	0.0802	0.9928

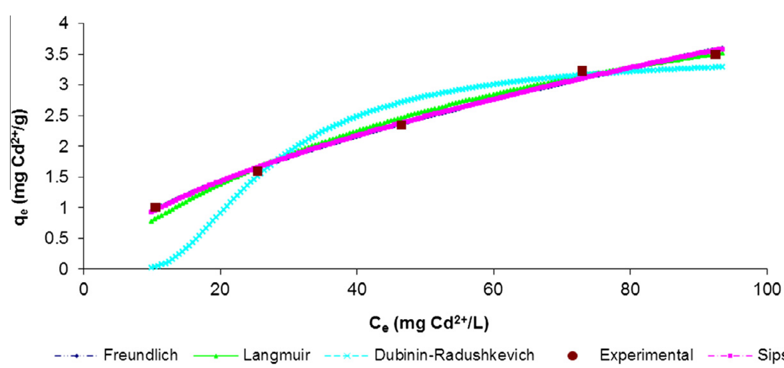

Figure 8 Representation of Freundlich, Langmuir, Dubinin-Radushkevich and Sips isotherm models for *A. bisporus* biomass in nonlinear regression analysis by comparison with experimental data, for Cd (II) biosorption; C_i = 50–235 mg/L, 4 g biomass, 0.4 < d < 1.2 mm, 5.6 pH, 298 K, 400 rpm.

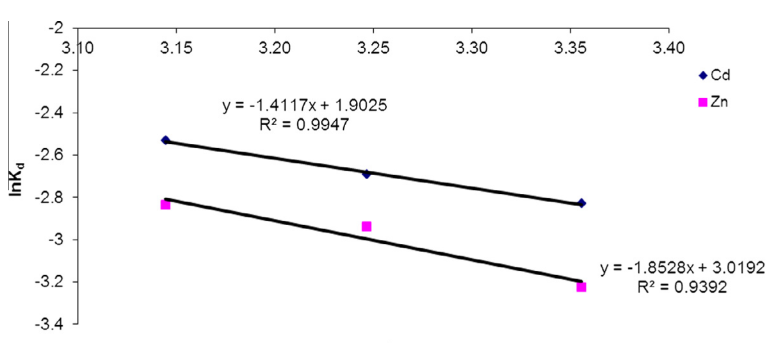

Figure 9 Plot of $\ln K_d$ versus $1/T$ for the estimation of the thermodynamic parameters for Cd (II) and Zn (II) biosorption using *A. bisporus* biomass.

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Table 6 Termodynamic parameters for the adsorption of Cd (II) and Zn (II) onto *A. bisporus* macrofungus biomass at various temperatures.

Metal	ΔS° (kJ/K × mol)	ΔH° (kJ/mol)	ΔG°, (kJ/mol)		
			298 K	308 K	318 K
Cd (II)	1.6×10^{-2}	11.74	6.97	6.81	6.65
Zn (II)	2.5×10^{-2}	15.40	7.95	7.70	7.45

randomness at the solute-solution interface increases with Cd (II) and Zn (II) retention in the biosorption process. Positive small values of free energy indicate a non-spontaneous process of the biosorption, which will be promoted by specific temperature conditions, leading to increased adsorption capacities (Schneider et al., 2007).

4. Conclusion

The ability of macrofungus (*A. bisporus*) to adsorb Cd (II) and Zn(II) ions from monocomponent aqueous solutions was investigated. The effects of initial metal ion concentrations, contact time, initial pH and temperature were considered. Maximum removal efficiencies up to around 80% and 70% were calculated for Cd (II) and Zn (II), respectively. The experiments using different initial pHs conclude that the concentration of protons plays an important role in the biosorption process. In 80 min the biosorbent resets the pH at 6.3 in each case. The biosorption rate of both metal ions is very fast in the first 80 min and the biosorption equilibrium was reached after 240 min. The experimental data were analyzed using pseudo-first- and pseudo-second-order kinetic models, various isotherm models in linear and nonlinear (CMA-ES optimization algorithm) regression and thermodynamic parameters were calculated. It was concluded that nonlinear regression analysis has better performances, with Sips model describing biosorption process the best. The results also showed that the biosorption process of both studied metal ions, followed pseudo second-order kinetics, suggesting that the process takes place as chemisorption. Two types of mechanisms, adsorption on the cell wall and an intracellular binding of the studied heavy metals were observed. The interactions between metal ions and functional groups on the cell wall surface of macrofungus cells were confirmed by SEM analysis. The calculated thermodynamic parameters show the feasibility, endothermic and spontaneous nature of the biosorption of Cd (II) and Zn (II) ions onto *A. bisporus* biomass.

Results showed that *A. bisporus* is an alternative biosorbent for treatment of wastewaters containing Cd (II) and Zn (II) ions. This study demonstrated the good removal efficiency of Cd (II) and Zn (II) from monocomponent aqueous solution as well as the high accumulation potential of toxic elements onto macrofungus which is the most widely consumed mushroom in the world.

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