Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1048304

57 (2016) 12156–12167
June

Taylor & Francis
Taylor & Francis Group

Optimization of biosorption of Zn(II) ions from aqueous solutions with low-cost biomass *Trametes versicolor* and the evaluation of kinetic and thermodynamic parameters

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Received 18 March 2014; Accepted 29 April 2015

ABSTRACT

The optimum biosorption conditions for removing Zn(II) ions from aqueous solutions by naturally powdered *Trametes versicolor* were successfully evaluated through a multi-step response surface methodology. The conducted experiments were based on a central composite design. The most influential factors on the biosorption process were initial pH (5–6.7), temperature (18–30°C), and initial Zn(II) concentration (30–70 mg L^{-1}). Based on the statistical analysis, the optimum conditions for Zn(II) biosorption were found to be 5.74, 24.57°C, and 60.95 mg L^{-1} for initial pH, temperature and Zn(II) concentration, respectively. Under these optimum conditions, the maximum amount of biosorbed Zn(II) ions was 43.87 mg Zn(II) per g dry cells. The proposed quadratic model fits very well to the experimental data. Furthermore, a Dubinin–Radushkevich isotherm model described the biosorption of Zn(II) ions on the biosorbent better than the common isotherm models, while kinetic studies showed that Zn(II) biosorption matched pseudo-second-order kinetics. Moreover, thermodynamic parameters, such as the changes in free energy, enthalpy, and entropy, were also calculated for the biosorption of Zn(II) ions onto *T. versicolor*. It was concluded that naturally powdered *T. versicolor* is a suitable biosorbent for the removal of Zn(II) ions from aqueous solutions.

Keywords: Biosorption; Heavy metals; Response surface methodology; Wastewater treatment; *Trametes versicolor*

1. Introduction

In recent decades, due in part to rapid technological progress, toxic metal contamination has become a serious environmental pollution problem [1,2]. Heavy metals are neither biodegradable nor utilized in the environments they contaminate. They are generally discharged from industries including mining, ore processing, smelting, and metal plating [3,4]. In order to remove heavy metal ions from contaminated environments, several techniques such as ion exchange [5], flotation [6], adsorption [7], reverse osmosis, electrochemical treatments [1], hyper filtration [8], membrane separation, evaporation, coagulation, precipitation, oxidation, and biosorption processes [9–13] have been widely used in the literature. Zinc, considered one of

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the most hazardous metals [14,15], is generally discharged from acid mine drainage, galvanizing plants, natural ores, and municipal wastewater treatment plants [14]. Its removal has significant importance since it is a highly toxic and non-biodegradable metal and accumulates in the human body via the food chain [16].

In recent years, great attention has been paid to the use of biosorbents such as yeast, bacteria, and fungi because of their efficiency, selectivity for metal ions, availability, and ease of use without hazardous sludge byproducts [17]. Such distinctive properties make biosorption a good alternative to existing methods. In the biosorption process, several anionic ligands including carboxyl, phosphoryl, carbonyl, and sulfhydryl present in biomass play an important role in physicochemical interactions with metal ions [18]. The efficiency of the biosorption process depends on some factors that vary from the type of metal ion studied to the type of biosorbent material used [19].

Therefore, the objective of this study was to evaluate the use of powdered *Trametes versicolor* fungi as biosorbent to treat wastewater contaminated solely with Zn(II) ions. The scope of the study covers the exploration of the influence of operating parameters such as initial pH, temperature, and initial metal ion concentration on treatment effectiveness. Zn(II) was selected as the model contaminant because it is a common industrial pollutant and has been observed to exert negative effects at concentrations less than 5 mg L^{-1} [15]. The influences of the operating parameters were studied by response surface methodology (RSM). It is a powerful optimization method recently used for other optimization processes [9,20–22].

2. Materials and methods

2.1. Biosorbent preparation

T. versicolor fungi ((L.:Fr.) Pil. = *Coriolus versicolor* (L.:Fr.) Quél) was collected from Rize province, a city in the Black Sea Region of Turkey. It is a natural fungus and non-isolated. The gathered biomass was treated before use as a biosorbent. It was washed with distilled water several times to remove impurities, dried in a drying-oven at 60°C for 24 h and subsequently ground with a mill. Afterward, the biomass was sieved to select particles smaller than 180 μm (80 mesh), which were stored in a desiccator until use without further pretreatment. The biosorbent properties, like specific surface area, pore volume, and pore radius, were determined by [9] the Brunauer–Emmett–Teller method with a Quantachrome 3.12 apparatus.

2.2. Zinc(II) solutions

A stock solution of Zn(II) (1,000 mg L^{-1}) was prepared by dissolving $Zn(NO_3)_2.6H_2O$ in 250 ml of distilled water. Necessary dilutions were made from the stock solution to prepare solutions in the range of desired concentrations. The initial pH of each solution was adjusted to the required value with 0.1 M HNO_3 and 0.1 M NaOH solutions before mixing the biosorbent suspension.

2.3. Batch biosorption studies

Batch adsorption experiments were conducted at a fixed agitation speed of 600 rpm and biosorbent dosage of 1 g L^{-1} for 80 min to achieve equilibrium. The variation of the medium factors, pH, temperature (°C), and initial zinc ion concentration (C_0), were designed by RSM. All experiments were carried out in Erlenmeyer flasks containing 50 mL Zn(II) solution in a temperature-controlled water bath with a magnetic stirrer. The concentration of unbiosorbed Zn(II) in the final solutions, which was separated by filtration to remove the biosorbent, was measured using a flame atomic absorption spectrophotometer (THERMO Solar AA Series spectrometer, USA). Its response was periodically checked by standard metal solutions. The amount of biosorbed metal ions (Q_e) per gram of the biosorbent was calculated as follows:

$$Q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where Q_e is the amount of metal ions biosorbed on the biosorbent at equilibrium (mg g biosorbent^{-1}), C_0 is the initial metal ion concentration in solution (mg L^{-1}), C_e is the final metal ion concentration in solution (mg L^{-1}), V is the volume of the solution (L), and W is the amount of the biosorbent used in the adsorption media (g).

After filtration, filter paper and glass were washed with 0.1 M HNO3 several times. The amount of Zn(II) in the washing solution was determined with AAS and found to be lower than the detection limit of the AAS, which is 0.0001 mg L^{-1}. This loss of zinc was therefore ignored in the measurements.

2.4. Experimental design and optimization with central composite design

In order to explore the effect of different variables on the response in the region of investigation, a central composite design (CCD) with three variables at three levels was performed. Initial solution pH, temperature (℃), and initial metal ion concentration (C_0) were evaluated as the most effective independent variables and their levels were determined according to the literature [9,23]. Fourteen experiments were augmented with six replications at the center values (zero level) to evaluate the pure error, while the biosorbed Zn(II) amount (mg g^{-1}) in the batch experiment was taken as the response [24]. The range and the levels of the variables studied during the investigation are given in Table 1. The behavior of the system could be easily explained using the following second-order polynomial model:

$$\hat{y}_n = \beta_0 + \sum_{i=1}^{3} \beta_i x_i + \sum_{i=1}^{3} \beta_{ii} x_i^2 + \sum_{i=1}^{3} \sum_{j=i+1}^{3} \beta_{ij} x_i x_j \qquad (2)$$

where $\hat{y}_n$ is the response, β_0 is the constant coefficient, x_i (i = 1–3) are non-coded variables, and β_i is the linear, β_{ii} is the quadratic, and β_{ij} is (i and j = 1–3) the second-order interaction coefficients. The residuals, ε_n, for each experiment were computed as the difference between y_n and $\hat{y}_n$, which are the residuals of the nth experiment, the observed response and the predicted response, respectively.

The variance analysis (ANOVA) data were computed by Design-Expert 6.0 (trial version) in order to obtain the interaction between the process variables and the response. The quality of the fit of the polynomial model was expressed by the coefficient of determination (R^2) and the statistical significance was checked by the F-test using the same program. The optimum numerical values for studied parameters were determined by matrix notation previously applied in the literature [9,24].

3. Results and discussion

3.1. CCD

To determine the optimum value and understand the effect of one parameter in biosorption studies using traditional methods, the experimenter has to perform many experiments by keeping other parameters constant at their optimum values. If considered for each parameter in our study, many experiments must be carried out. However, in our study, only 20 experiments were performed using CCD in RSM.

A set of CCD involving the factors of initial solution pH, temperature, and initial Zn(II) concentration previously determined through Plackett–Burman design was conducted to locate the optimum [9] in order to evaluate the best operating conditions for Zn (II) biosorption by *T. versicolor* fungi. Panel A in Table 2 displays the conditions used with real units, while panel B shows the levels in terms of coded factors utilized in the software Design Expert 6.0 (trial version). The last column of Table 2 shows the data (responses) resulting from the investigation of the effects of the three factors.

The observed data were then processed through the program and a mathematical model was derived to represent the biosorption process. The model equation of coded values from quadratic model fitting of the experimental results is presented in Eq. (3).

$$\begin{aligned}\text{Biosorbed Zn } (\text{mgg}^{-1}) = {} & +41.71 - 0.37X_1 + 0.14X_2 \\ & + 7.47X_3 - 3.35{X_1}^2 - 3.24{X_2}^2 \\ & - 6.71{X_3}^2 - 0.54X_1X_2 \\ & - 0.91X_1X_3 + 0.43X_2X_3\end{aligned} \qquad (3)$$

The ANOVA results of the quadratic model presented in Table 3 indicate that the predicted model describes the response surface of the biosorption of Zn(II) in the interval of investigation. In addition, the F-value of the quadratic model implies the significance of the model. The fit of the model was checked by the coefficient of determination R^2, which was calculated to be 0.98, indicating that 98% of the variability in the response could be explained by the model. This indicated an agreement between experimentally observed data and predicted values from the model and implies that the mathematical model is reliable for Zn(II) ion biosorption from aqueous media. The value under

Table 1
Experimental ranges and levels of the independent variables studied in CCD

Independent variables	Coded and uncoded values				
	− α (−1.68)	−1	0	+1	+ α (+1.68)
pH (X_1)	4.42	5.00	5.85	6.70	7.28
Temperature (T) (X_2)	13.91	18	24.00	30	34.09
Initial conc. (C_0, mg L^{-1}) (X_3)	16.36	30.00	50.00	70.00	83.64

Table 2
Corresponding results and experimental design based on CCD for Zn(II) biosorption

	Panel A			Panel B			
Run	X_1 (pH)	X_2 (T)	X_3 (C_0)	X_1	X_2	X_3	Biosorbed Zn(II), (mg $g_{biosorbent}^{-1}$)
1	5.85	24	83.64	0.00	0.00	+1.68	37.95
2	6.70	18	30	+1.00	−1.00	−1.00	20.72
3	6.70	18	70	+1.00	−1.00	+1.00	33.20
4	5.00	30	70	−1.00	+1.00	+1.00	37.90
5	5.85	24	50	0.00	0.00	0.00	41.74
6	4.42	24	50	−1.68	0.00	0.00	33.55
7	5.00	30	30	−1.00	+1.00	−1.00	20.06
8	5.00	18	70	−1.00	−1.00	+1.00	33.91
9	5.85	24	16.36	0.00	0.00	−1.68	10.22
10	7.28	24	50	+1.68	0.00	0.00	33.63
11	5.85	24	50	0.00	0.00	0.00	41.42
12	5.85	34.09	50	0.00	+1.68	0.00	33.63
13	6.70	30	70	+1.00	+1.00	+1.00	32.38
14	5.00	18	30	−1.00	−1.00	−1.00	20.46
15	5.85	24	50	0.00	0.00	0.00	42.89
16	5.85	13.90	50	0.00	−1.68	0.00	34.19
17	5.85	24	50	0.00	0.00	0.00	39.78
18	6.70	30	30	+1.00	+1.00	−1.00	20.83
19	5.85	24	50	0.00	0.00	0.00	42.00
20	5.85	24	50	0.00	0.00	0.00	41.95

Table 3
ANOVA results of the quadratic model for CCD

Source	Sum of squares	Degrees of freedom	*F*-value	*P*-value	
Model (quadr.)	1,608.23	9	49.83	<0.0001	Significant
X_1	1.88	1	0.52	0.4858	
X_2	0.28	1	0.08	0.7875	
X_3	761.16	1	212.25	<0.0001	
X_1^2	162.09	1	45.20	<0.0001	
X_2^2	151.34	1	42.20	<0.0001	
X_3^2	649.68	1	181.16	<0.0001	
X_1X_2	2.31	1	0.64	0.4408	
X_1X_3	6.59	1	1.84	0.2051	
X_2X_3	1.50	1	0.42	0.5328	

$R^2 = 0.9782$.
Standard deviation = 1.89.

0.0001 for "Prob > *F*" also indicated that the model terms were significant. Furthermore, the calculated lack of fit *p* value (0.04) and the determination of coefficient (R^2, 0.98) indicated how well the predicted quadratic model fits the experimentally monitored biosorption data. Fig. 1 presents the experimentally monitored Zn(II) biosorption data collected from the runs conducted in Table 2 vs. those computed from the empirical model (Eq. (3)).

The combined effects of initial pH and temperature on Zn(II) biosorption capacity of *T. versicolor* at the fixed initial Zn(II) concentration of 50 mg L^{-1} are illustrated in Fig. 2. As can be seen, Zn(II) biosorption capacity significantly increased when the pH of the initial solution increased from 4.42 to 5.8, then decreased as pH increased further. The results showed that the maximum removal of Zn(II) ions was achieved at pH 5.75. The biosorption under these

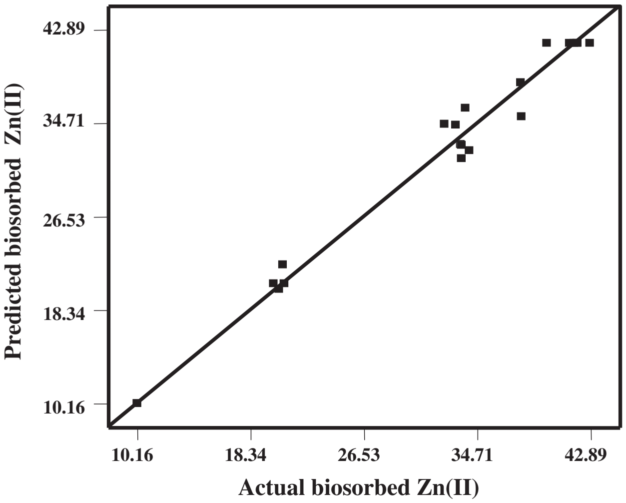

Fig. 1. The observed Zn(II) uptake vs. predicted Zn(II) uptake capacity of the biosorbent.

conditions was thus about 44 mg g^{-1} dry biosorbent. Similar results have been previously reported for Zn(II) biosorption [14,25].

Biosorption of heavy metal ions onto the surface of a micro-organism is affected by the initial solution pH [26]. Metal ion uptake is generally suppressed by increasing the H$^+$ concentration, although exceptions may exist [27]. As stated in the literature [9], the pH dependence of metal uptake is due to the solubility of the metals and the ionization state of the various functional groups (e.g. carboxylate, phosphate, and amino groups) on the fungal cell walls. At relatively high pH values, these negatively charged functional groups allow the cell wall components to be potential binding sites for cations [28]. However, at low pH values, the overall surface charge on the active sites becomes positive and metal cations and protons compete for binding sites on the cell wall, which results in lower uptake of metals [29,30]. Stated another way, negative charge density on the cell surface increases with increasing pH due to deprotonation of the metal binding sites and the metal ions then compete more effectively for available binding sites. This causes an increase in biosorption [19,30].

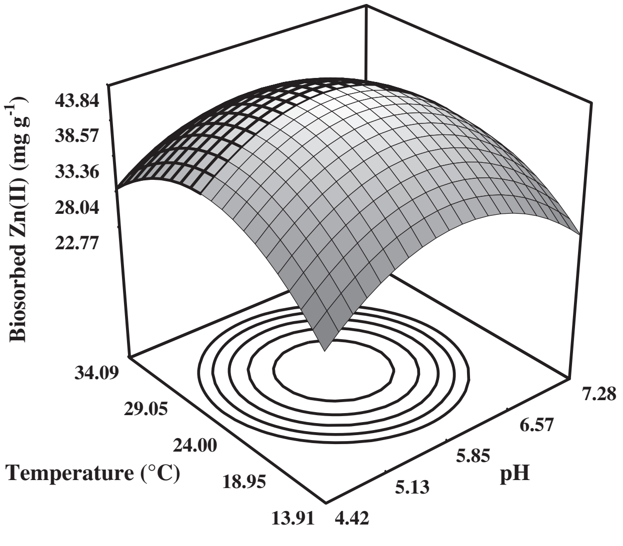

Fig. 2. Simultaneous effects of initial solution pH and temperature on Zn(II) removal at a fixed initial Zn(II) ion concentration of 50 mg L^{-1}.

Increasing solution temperature resulted in a decrease in the biosorption of Zn(II), indicating that the biosorption of Zn(II) ions onto *T. versicolor* is exothermic in nature. It has been previously reported that metal ion sorption was exothermic in nature [31], which was verified in our study. The increase in temperature causes a decrease in adsorption due to the weakening of adsorptive forces between the active sites of the adsorbents and adsorbate species [32]. In addition, the decrease in sorption capacity at higher temperatures could be attributed to the destruction of active binding sites in the biomass [33]. The Zn(II) ions biosorbed earlier on the biosorbent surface tend to desorb from the surface with increasing temperature. This may be due to a tendency for the Zn(II) ions to escape from the solid phase to the bulk phase with an increase in the solution temperature. This effect suggests that an explanation of the adsorption mechanism associated with the removal of Zn(II) ions onto the biosorbent involves a physical process in this situation, in which adsorption arises from the electrostatic interaction. This is usually associated with low adsorption heat [34]. Finally, it could be concluded that initial solution pH and temperature were the most important environmental parameters influencing the biosorption of key heavy metal ions.

At a fixed solution temperature of 24°C, a 3D figure (Fig. 3) was generated to evaluate the joint effects of initial solution pH and initial Zn(II) ion concentration on the biosorption capacity of *T. versicolor*. As is apparent, the biosorption capacity of *T. versicolor* increased with increasing initial Zn(II) concentration up to 60 mg L^{-1}, while no change was recorded with higher initial Zn(II) concentrations. Therefore, it could be concluded that the biosorbent surface had reached its saturation level for Zn(II) ions.

Maximal Zn(II) removal by *T. versicolor* was observed at 60 mg L^{-1}. In comparison, another study [14] determined that the optimum conditions for Zn(II) biosorption by *Botrytis cinerea* were approximately pH 5 and 100 mg L^{-1} of initial Zn(II). The

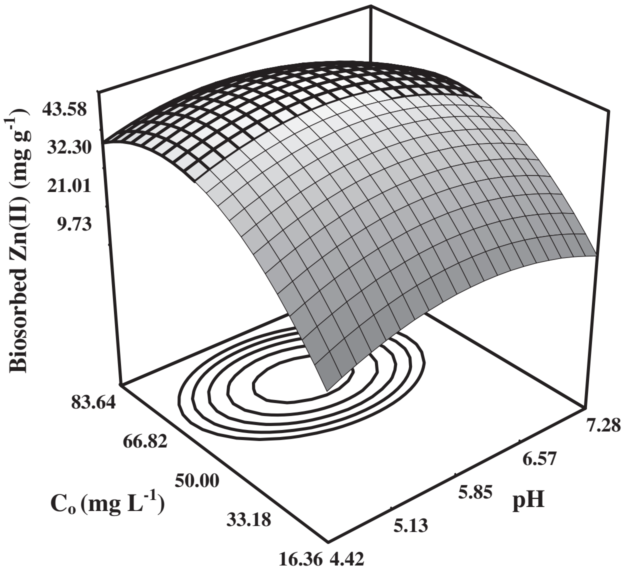

Fig. 3. Simultaneous effects of initial solution pH and initial Zn(II) ion concentration at a fixed temperature of 24℃.

initial concentration provides a significant driving force to overcome mass-transfer resistance of Zn(II) ions between the aqueous and solid phases; hence, a higher initial concentration of Zn(II) ions may increase the adsorption capacity [35]. The joint effects of temperature and initial Zn(II) ion concentration on Zn(II) removal capacity for *T. versicolor* at a fixed pH of 5.85 are presented in Fig. 4. Furthermore, the biosorption capacity of *T. versicolor* increased with increasing initial Zn(II) concentration up to 60 mg L^{-1}, while no change was recorded above this initial Zn(II) concentration. As illustrated in Fig. 4, the decrease in adsorption with the rise in temperature showed that Zn(II) biosorption was exothermic in nature.

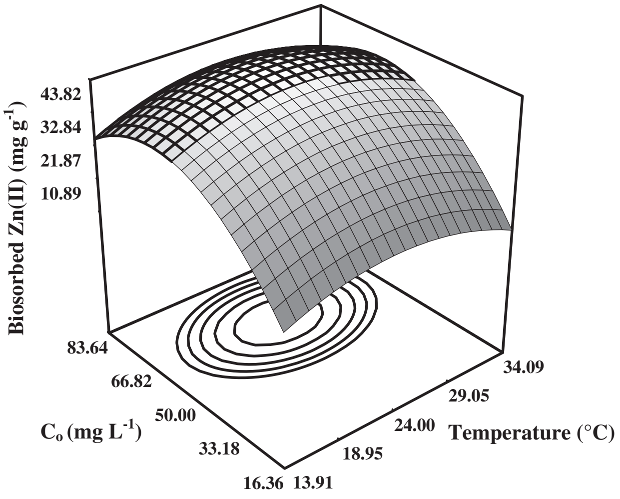

Fig. 4. Simultaneous effects of solution temperature and initial Zn(II) ion concentration at a fixed pH of 5.85.

3.2. Evaluation of the best solution conditions

In order to compute the numerical magnitudes of the investigated factors, a matrix notation previously used in the literature was applied [9,24]. Based on the solution matrixes (data not shown), optimum values of initial solution pH, temperature, and initial Zn(II) ion concentration to maximize the biosorption of Zn (II) ion were 5.74, 24.57℃, and 60.95 mg L^{-1}, respectively. Under the evaluated optimum experimental conditions, maximal Zn(II) ion biosorption was discovered to be 43.87 mg $g^{-1}$and the corresponding removal efficiency of Zn(II) was 72%. Table 4 contains a comparison between the adsorption capacity of *T. versicolor* and other adsorbents in the literature in terms of the capacity of the biosorbent.

Finally, an artificial wastewater modeling, a typical coating industry discharge, was prepared for the investigation of the biosorbent sorption capacity. A multi-component artificial wastewater containing 100 mg L^{-1} Zn(II), 50 mg L^{-1} Cu(II), 50 mg L^{-1} Cr(III), 100 mg L^{-1} Ni(II), and 50 mg L^{-1} Cd(II) was prepared and several experiments were carried out at the optimum pH and solution temperature given above. The treatment times were held constant at 100 min and all metal ion removals were observed to reach their maximum values after 75 min. As can been seen in Fig. 5, the average Zn(II) ion removal was 5.5 mg g^{-1}, while 7, 5, 5, and 3 mg g^{-1} were recorded for Ni(II), Cr(III),

Table 4
Comparison between *T. versicolor* and other adsorbents discussed in the literature

Adsorbent	Zn(II) biosorption (mg g^{-1})	References
Kaolin	80.07	[36]
Active carbon	31.11	[37]
Bentonite	52.91	[38]
Streptoverticillium cinnamoneum	21.30	[39]
Rhizopus arrhizus	13.50	[40]
Azolla filiculoides	45.20	[41]
Sargassum sp.	24.35	[42]
Botrytis cinerea	12.98	[14]
Pseudomonas putida CZ1	27.40	[35]
Mucor rouxii	53.85	[43]
Penicillium simplicissimum	25.54	[25]
Natural *T. versicolor*	43.87	This study

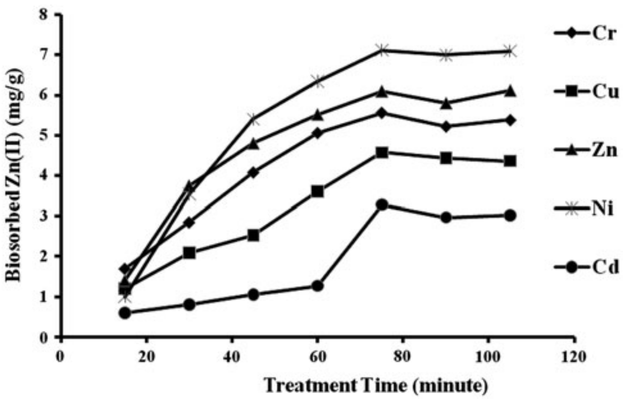

Fig. 5. Biosorbed amounts from multi-metal systems at optimum conditions.

Cu(II), and Cd(II), respectively. It was therefore concluded that the biosorbent could not only be used for Zn(II) ion removal, but also be easily used for other metal ions as well.

3.3. Adsorption isotherms

Most common adsorption isotherm equations, including Langmuir, Freundlich, and Dubinin–Radushkevich (D–R), were tested to understand the nature of the adsorption mechanism and the equilibrium conditions [44–46]. The Langmuir isotherm model assumes a monolayer sorption, which takes place at specific homogeneous sites within the biosorbent. The linearized Langmuir isotherm equation is then represented by Eq. (4) [47].

$$\frac{C_e}{Q_e} = \frac{1}{q_{\max} K_L} + \frac{1}{q_{\max}} C_e \qquad (4)$$

where Q_e (mg g^{-1}) and C_e (mg L^{-1}) are the amount of biosorbed Zn(II) per unit mass of biosorbent and the Zn (II) concentration at equilibrium, respectively. In addition, the Langmuir constant, $q_{\max}$ (mmol g^{-1}), is the maximum amount of Zn(II) per unit mass of biosorbent to form a complete monolayer on the biosorbent surface, while K_L is a Langmuir constant related to the affinity of the binding sites (L mmol^{-1}). Both $q_{\max}$ and K_L were evaluated from the plot of C_e/Q_e vs. C_e. The essential characteristic of the Langmuir isotherm is a dimensionless constant separation factor (R_L), which is a measure of a favorable biosorption process (Eq. (5)). The computed value of 0.108 for R_L, which is expected to be between 0 and 1 for favorable processes, indicates that Zn(II) biosorption is feasible [48]. Li et al. [49] reported that R_L values for Zn(II) biosorption on live and dead *Streptomyces ciscaucasicus* were 0.22 and 0.10, respectively.

$$R_L = \frac{1}{1 + K_L C_0} \qquad (5)$$

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The linearized form of the Freundlich equation can be expressed as follows [50]:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (6)$$

where K_F (L g^{-1}) and n are the Freundlich isotherm constants. The plot of lnQ_e vs. lnC_e was completed to calculate K_F and n from the intercept and the slope, respectively.

On the other hand, the D–R isotherm is more general than the Langmuir isotherm since it does not assume a homogeneous surface or constant biosorption potential. It was applied to determine the nature of biosorption of Zn(II) ions. The linearized form of the D–R isotherm is given by the following equation [51]:

$$\ln Q_e = \ln q_D - B_D \left[RT \ln\left(1 + \frac{1}{C_e}\right) \right]^2 \qquad (7)$$

where β_D is a constant related to the mean free energy of biosorption (mmol^2 J^{-2}) and q_D is the theoretical saturation capacity (mmol g^{-1}). D–R constants were calculated by plotting lnQ_e vs. $[RT \ln(1+1/C_e)]^2$.

The mean free energy E (kJ mol^{-1}) was computed as 4.77 kJ mol^{-1} from Eq. (8) to determine whether the biosorption was occurring chemically or physically [52,53]. The lower mean free energy (<8 kJ mol^{-1}) revealed that the biosorption was taking place through a physical process [54,55].

$$E = \frac{1}{\sqrt{2B_D}} \qquad (8)$$

Table 5 lists the corresponding computed parameters for the isotherm equations given above for the biosorption of Zn(II) ions onto *T. versicolor*. Biosorption capacity obtained from experimental studies was accurately predicted with Langmuir and D–R isotherm equations.

3.4. Biosorption kinetics and activation energy

The most common adsorption kinetics models, which are the Lagergren pseudo-first- and second-order

Table 5
Biosorption isotherm constants for Zn(II) biosorption

Langmuir		Freundlich		D–R	
$q_{\max}$ (mmol g^{-1})	0.709	n	1.825	q_D (mmol g^{-1})	0.717
B (L $mmol^{-1}$)	8.87	K_f (L g^{-1})	0.925	B_D ($mmol^2$ J^{-2})	0.022
R_L	0.108			E (kJ mol^{-1})	4.77
R^2	0.944		0.847		0.955

models, in the literature were tested to determine the best kinetics model of Zn(II) biosorption on *T. versicolor* [25,45]. The linearized Lagergren pseudo-second-order model, which is given in Eq. (9), showed the best fit with experimental observations [56,57].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \tag{9}$$

where q_t and q_e are the biosorbed amount of Zn(II) at time t and equilibrium (mg g^{-1}), respectively and k_2 is the pseudo-second-order rate constant. A series of runs were carried out at three different temperatures in order to calculate k_2 values and activation energy. The kinetic constant, k_2, was calculated from the plot of t/q_t vs. time t at different temperatures (Fig. 6(a)). The q_e calculated from pseudo-second-order is 47.39 mg g^{-1} for 293 K. It is compatible with experimental results. Bhatti et al. [58] reported that removal of Zn(II) ions from aqueous solution using *Moringa oleifera* Lam. (horseradish tree) biomass was better described by a second-order rate equation and Fan et al. [25] stated that the biosorption of Zn(II) on *Penicillium simplicissimum* fits a pseudo-second-order model rather than a pseudo-first-order model.

The activation energy for biosorption of Zn(II) on *T. versicolor* was determined according to the Arrhenius equation:

$$\ln k_2 = \ln A - \frac{E_a}{RT} \tag{10}$$

where A is the constant called the frequency factor, R is the ideal gas constant (J mol^{-1} K^{-1}), and T is the solution temperature (K). The activation energy (E_a) was thus calculated to be 18.90 kJ mol^{-1} from the slope of the $\ln k_2$ vs. $1/T$ plot (data not shown). This result also supported the idea that Zn(II) biosorption was a physical adsorption process. Lower activation energies (5–40 kJ mol^{-1}) are characteristics of physisorption, while higher activation energies (40–800 kJ mol^{-1}) suggest chemisorption [59].

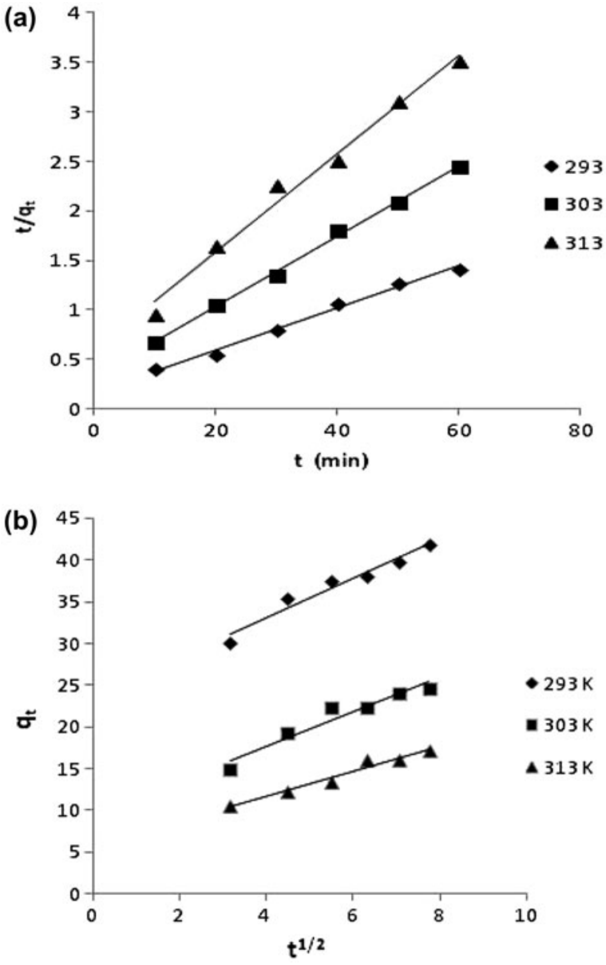

Fig. 6. (a) Pseudo-second-order kinetic plots for biosorption of Zn(II) on *T. versicolor* and (b) Weber–Morris intraparticle plots for biosorption of Zn(II) on *T. versicolor*.

3.4.1. The intraparticle diffusion model (Weber–Morris model)

The adsorption process may happen in several steps. The overall adsorption process may be controlled either by intraparticle (pore) diffusion or boundary layer (film) diffusion or a combination. The equation developed by Weber and Morris [60] using the intraparticle diffusion model is shown by Eq. (11).

Table 6
The thermodynamic parameters for Zn(II) biosorption onto *T. versicolor*

	Experimental				Calculated			
Temperature (°C)	K_c	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	K_c	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
20	2.35	−1.85	−67.65	−224.56	3.48	−2.77	−74.07	−243.35
30	0.68	0.39			0.86	−0.34		
40	0.39	2.64			0.49	2.10		

$$q_t = k_{id} t^{1/2} + C \tag{11}$$

where k_{id} is the intraparticle diffusion rate constant (mg (g min$^{1/2}$)$^{-1}$) and C is the constant that accounts for the thickness of the film layer where the larger the value of C the greater the film layer effect. If the plot of q_t vs. square root of time ($t^{1/2}$) gives a straight line that passes through the origin, then the adsorption process is controlled by intraparticle diffusion only. However, if the plot deviates from linearity, the film layer controls the sorption process. In addition, if the data shows multi-linear plots, then a combination of diffusion types influences the adsorption process [61].

According to Fig. 6(b), the curves plotted at different temperatures reveal linear characteristics. However, the linear plots at each temperature did not pass through the origin. These results indicate that intraparticle diffusion was not the only rate-controlling step. Mechanism of Zn(II) adsorption is explained as a mixture of the intraparticle diffusion and film diffusion. Similar results have been reported in the literature [62]. As shown in Fig. 6(b), the k_{id} values were also observed ranging from 1.49 to 2.35 mg (g min$^{1/2}$)$^{-1}$ with the changing temperature. At lower temperatures, the increase in k_{id} was due to the decrease in the intraparticle diffusion resistance. In addition, the value of C decreased with increasing temperature.

3.5. Thermodynamic parameters

To evaluate the temperature dependence of Zn(II) biosorption by *T. versicolor*, the changes in the thermodynamic parameters including free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) needed to be computed using the following equations:

$$K_C = \frac{C_A}{C_S} \tag{12}$$

$$\Delta G^\circ = -RT \ln K_C \tag{13}$$

$$\Delta G^\circ = \Delta H^\circ - T(\Delta S^\circ) \tag{14}$$

$$\ln K_C = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{15}$$

where K_C is the equilibrium constant, C_A (mg L^{-1}) is the amount of biosorbed Zn(II) at equilibrium, C_S (mg L^{-1}) is the equilibrium concentration of unbiosorbed Zn(II) in the solution, R is the gas constant (8.314 J mol^{-1} K^{-1}), and T (K) is the temperature. The thermodynamic parameters were then calculated from the slope and intercept of the ln K_C vs. $1/T$ plot (data not shown).

The thermodynamic parameters were evaluated for both experimentally obtained maximum biosorption ($q_{e,exp}$) and theoretical biosorption ($q_{e,cal}$), calculated from Eq. (9). As seen in Table 6, the negative value of ΔH° suggested that the biosorption was exothermic in nature [63]. The value of the entropy change, ΔS°, was also negative. This indicated that the metal ions had a more ordered behavior or greater affinity to the sorbent at the solid–solution interface during the biosorption process [33]. Moreover, the value of ΔG° increased with increasing temperature, which indicated that biosorption was better at lower temperatures [64].

4. Conclusions

The optimum biosorption conditions for Zn(II) ions from aqueous solutions were systematically studied by RSM. It was observed that the initial solution pH, temperature, and initial Zn(II) concentration were the most significant factors for Zn(II) biosorption. The optimum biosorption conditions, such as pH, temperature, and initial Zn(II) concentration, for removal of Zn(II) were evaluated as 5.74, 24.57°C, and 60.95 mg L^{-1}, respectively by utilization of CCD in RSM. Under these optimum conditions, the maximum amount of biosorbed Zn(II) ions and the maximum yield were computed to be 43.87 mg Zn(II) per g biosorbent and 72%, respectively. A multi-variable mathematical model was then developed to represent the Zn(II) biosorption. The prepared biosorbent was also utilized in a multi-component metal solution including Zn(II), Ni(II), Cr(III), Cu(II), and Cd(II) metal ions. Finally, well-known isotherm and kinetics models were used to calculate the corresponding coefficients, thermodynamic parameters, and activation energies. Langmuir and D–R isotherm equations provide the best fit to the biosorption equilibrium data. The kinetic data indicated that the biosorption process was controlled by pseudo-second-order equation. The negative value of ΔH° showed exothermic heat of biosorption. The value of ΔG° increased with increasing temperature. This result indicated that biosorption was better at lower temperatures. The biosorption kinetic data were analyzed using the Weber–Morris intraparticle diffusion model. It was found that the biosorption mechanism was a mixture of the intraparticle diffusion and film diffusion. Consequently, *T. versicolor*, a plentiful and inexpensive biological material, is a potential candidate material for the removal of heavy metal ions from industrial wastewaters.

Acknowledgment

This work was supported by the Yuzuncu Yil University Research Fund with Grant # 2006-FED-YTR.13.

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