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A response surface approach for optimization of Pb(II) biosorption conditions from aqueous environment with *Polyporus squamosus* fungi as a new biosorbent and kinetic, equilibrium and thermodynamic studies

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ABSTRACT

We report optimization with response surface methodology (RSM) for Pb(II) biosorption conditions from aqueous solutions with powdered natural *Polyporus squamosus* biosorbent. Brunauer, Emmett and Teller and Fourier transform infrared analyses were performed primarily to determine and investigate the biosorbent surface properties. Central composite design (CCD) in RSM was used to optimize the most important biosorption parameters of pH, initial Pb(II) concentration (C_o, mg L^{-1}), contact time (min) and temperature (°C). With the quadratic model equation obtained from CCD, the optimum values were determined as C_o 74.55 mg L^{-1}, pH 5.75, temperature 20°C and contact time 112.6 min. In these conditions, the optimum adsorbed amount of Pb(II) was 13.65 mg Pb(II) per gram of biosorbent and biosorption yield was 89.4%. It was determined that the biosorption kinetic data fitted the pseudo-second-order kinetic equation and biosorption equilibrium data agreed well with the Freundlich isotherm model. Additionally, the thermodynamic parameters showed that biosorption was exothermic. Finally, by performing competitive biosorption from artificial wastewater containing multiple metals, the variation in Pb(II) biosorption capacity of *P. squamosus* in the presence of different metal ions was investigated.

Keywords: Biosorption; Central composite design; Lead; *Polyporus squamosus*; Response surface methodology

1. Introduction

Developments occurring in industry together with rising living standards of people have led to destruction of resources, and pollution of air, water and soil. One of the major problems that places human health at risk is heavy metal pollution in water. The sources of heavy metal release into the aqueous environment are industries such as oil and gas, plastic, mining, pharmaceutical, lead smelting, battery manufacturing, electroplating and other metallurgical processing, along with agricultural runoff, chemical spills and municipal wastewater [1].

Lead (Pb) is the most common toxic metal released into aqueous media because of its widespread use in industry such as in batteries, printing, coloring matter, fuels, photographic materials and explosives [2]. The World Health Organization (WHO) and Environmental Protection Agency (EPA) standards for lead in drinking water are 50 and 10 μg L^{-1}, respectively. At the same time the EPA standard for Pb in wastewater is 500 μg L^{-1} [3]. Thus, it is important to remove Pb(II) ions from industrial waste to protect the environment and living organisms.

Traditional techniques for removing heavy metals such as Pb from industrial effluents are chemical oxidation, sedimentation and sludge separation, ion exchange, reverse osmosis, separation, centrifugation and vaporization [4]. In dilute liquids these methods are costly and ineffective [5]. For this reason, it is essential to find new biomaterials or technologies to remove heavy metal ions from aqueous environments. Biosorption is an encouraging way to use industrial

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effluents, primarily because of its high efficiency, high metal-binding capacity, low cost and environmentally friendly [6]. Therefore, integrated technology, called biosorption, based on the binding ability of various biological materials is a possible preferred option because of its high yield, and the ease of obtaining and simple accessibility to biosorbent materials [7]. From this perspective, a number of biomaterial agrarian wastes, biopolymers, plant wastes and several other modified biomaterials have been extensively employed for heavy metal ion removal from aqueous environments [8].

Conventional methods can be used to recognize biosorption mechanisms, but when these methods are used, it is necessary to keep some parameters constant while changing others, such as metal concentration, pH, temperature or contact time. Using classical methods causes extra chemical consumption of all parameters involved in the adsorption, taking surplus time and labor. There are many statistical programs used to solve this issue. Among these statistical programs, response surface methodology (RSM) is one of the most frequently used statistical programs in literature reviews [4,9]. RSM has many advantages, such as the need for less labor and less time and thus is more economic. This method can be used in many fields as well as in heavy metal biosorption. RSM is a method that utilizes mathematical and statistical methods to analyze the effects of many independent variables. It is impossible to observe the effect of many parameters at the same time because we can change only one parameter at a time in conventional methods. These traditional methods have the disadvantage of determining the optimum points with extra time requirements and extra experiments which may increase the error rate [10,11], whereas RSM can examine the interaction of more than one variable at the same time. In addition, it has advantages such as higher percentage yield, reduced process variability, better recognition of nominal and target performance and minimum cost [12].

The present investigation first aims to test the potential of biomass of *Polyporus squamosus* for the biosorption of Pb(II) from aqueous solutions and to optimize parameters affecting the biosorption for maximum removal via a 24 full factorial central composite design (CCD) in RSM with software Design-Expert 7. We think that the present work is original and will contribute to related literature because the *P. squamosus* biological material collected from Hakkari, Turkey, is used for Pb(II) removal from aqueous environments for the first time. RSM, a mathematical and statistical method used to optimize the biosorption conditions, offers many advantages in terms of cost and time. It supplies more experimental data, tables and diagrams with very few experiments.

2. Experimental section

2.1. Biosorbent preparation

Natural *P. squamosus* fungi ((Huds.) Fr.) were collected from the Yüksekova area in Eastern Turkey. *P. squamosus* fungi were washed with pure water several times to remove dirt, then dried at 60°C in a drying oven for 24 h before use as biosorbent. After drying, the fungus was ground with a grinder. After the biomass was brought to dimensions of 125 μm and smaller (≤125 μm) with a 120 mesh sieve, it was stored with the aid of a desiccator to be used later without further processing.

2.2. Preparation of metal stock solution

Pb(II) stock solution was prepared using $Pb(NO_3)_2$ (purity ≥ 99, Sigma-Aldrich, Germany) in distilled water. Dilution was performed for the desired solutions from the prepared stock solution. To adjust the pH values of the adsorption solutions, the desired pH was reached by adding volumes of 0.10 M HNO_3 and NaOH before adding the biosorbent into the solution.

2.3. Batch biosorption experiments

The batch technique was used to investigate the biosorption of Pb(II) on *P. squamosus* fungi. All experiments were performed in 250 mL Erlenmeyer flasks containing 100 mL of Pb(II) solution on a temperature-controlled magnetic stirrer water bath. Samples taken after the desired contact period were filtered with Whatman filter paper to remove the biosorbent. For each solution, concentration of initial Pb(II) and unbiosorbed Pb(II) in residual solution after biosorption was determined using an atomic absorption spectrometer (AAS; Model THERMO Solar AA Series spectrometer, USA). The amount of biosorption was calculated according to the following equation:

$$q_e = \frac{(C_i - C_e) \bullet V}{W} \tag{1}$$

where q_e is the amount of biosorbed Pb(II) on the biosorbent at equilibrium (mg g^{-1}), C_i and C_e are the initial and equilibrium concentration of Pb(II) in solution (mg L^{-1}), V is the media volume (L) and W is the amount of biosorbent used in the biosorption mixture which is fixed at 0.5 g L^{-1}.

The paper and glass materials used for filtration were washed several times with 0.1 M HNO_3. The amount of Pb(II) in the solution during the filtration process was calculated using AAS. This value was less than 0.0001 mg L^{-1}, so it was not considered in the measurements.

3. Results and discussion

3.1. Characterization of biosorbent

3.1.1. BET analysis

The specific pore volume, pore radius and surface area were determined by using the Brunauer, Emmett and Teller (BET) method with Quantachrome 3.12 device. The specific pore radius, pore volume and surface area for the *P. squamosus* biomass were found to be 21.499 Å, 0.002 cm^3 g^{-1} and 1.08 m^2 g^{-1}, respectively.

3.1.2. Infrared spectroscopy study

Functional groups on biological material were confirmed using Fourier transform infrared (FTIR) analysis. FTIR analysis provides information about possible mechanism(s) involved in metal ion removal [13]. Ionizable groups such as amino, carboxyl, amide and hydroxyl on *P. squamosus* were determined by FTIR analysis. Considering Fig. 1, the broad absorption band in the spectrum of *P. squamosus* at

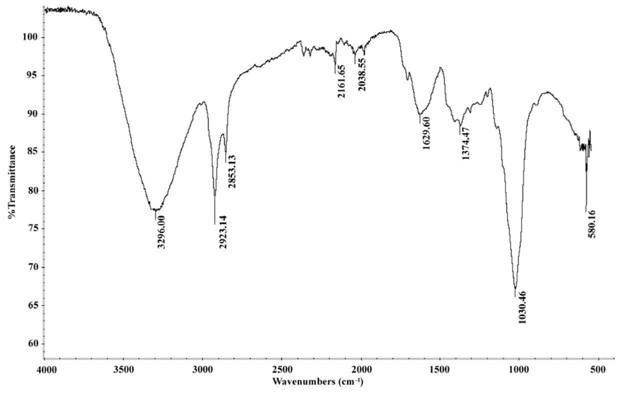

Fig. 1. FTIR spectra for *P. squamosus*.

3,200–3,600 cm^{-1} corresponds to NH tension vibration. The signal range at 2,850–3,000 cm^{-1} shows the OH bond stretching vibrations. The other basic characteristic peaks of *P. squamosus* are located at 2,923–2,853 cm^{-1} (C–H stretch), 1,630 cm^{-1} (–C=O stretch), 1,374 cm^{-1} (–C–N stretch and N–H bend) and 1,030 cm^{-1} (S=O stretch). These functional groups, especially hydroxyl, play an important role in biosorption of Pb(II).

3.2. Optimization of biosorption process using CCD approach

For the optimization of the Pb(II) biosorption conditions, the experimental intervals for initial Pb(II) concentration (C_o, X_1), pH (X_2), temperature (X_3) and contact time (X_4) were determined based on anterior experiments and a broad review of the literature and are shown in Table 1. The relationship between the parameters and response (biosorbed Pb(II) amount) were determined using CCD in Design Expert Software (version 7.0.0). The parameters presented in Table 1 are coded with three levels as –1, 0 and +1, respectively. The number of experiments to be done for four variables were 30 (=$2^k + 2k + 6$), where k is the number of studied independent variables that affect the response. Thirty experiments were conducted with six replicates at the center points (Table 2).

In CCD stage, the responses obtained in the optimization experiments may be related to the variables selected in connection with mathematical models. A quadratic model is given in Eq. (2):

$$\hat{y}_n = \beta_0 + \sum_{i=1}^{4} \beta_i x_i + \sum_{i=1}^{4} \beta_{ii} x_i^2 + \sum_{i=1}^{4} \sum_{j=i+1}^{4} \beta_{ij} x_i x_j \tag{2}$$

where $\hat{y}_n$ is the response predicted by the model, β_0 is the constant, β_i is the linear, β_{ii} is the quadratic and β_{ij} (i and j = 1–4) is the secondary order interaction factors, x_i and x_j symbolize the independent variables. Analysis of variance, which is called ANOVA, was obtained by Design Expert Software (version 7.0.0). The statistical value of the coefficient was confirmed with F test [14].

Table 1
Experimental independent variables

Parameters	Parameter code	Level and range (coded)		
		–1	0	1
Initial Pb(II) concentration (C_o), mg L^{-1}	X_1	10	55	100
pH	X_2	2	4.5	7
Temperature, °C	X_3	20	35	50
Contact time, min	X_4	10	80	150

3.3. Statistical analysis

In this study, it was seen that the correlation between the four independent variables and the response are consistent with the quadratic model. The quadratic regression model for Pb(II) biosorption obtained from CCD in terms of uncoded and coded factors is presented in Eqs. (3) and (4):

$$\begin{aligned}
&\text{Biosorbed Pb(II) amount (mgg}^{-1}\text{)(uncoded)} = -9.47717 \\
&+ 0.16169[C_o] + 4.73502[\text{pH}] - 6.25039\text{E}-03[\text{Temperature}] \\
&+ 4.13221\text{E}-03[\text{Contact Time}] + 0.018707[C_o][\text{pH}] \\
&- 8.73333\text{E}-04[C_o]\,[\text{Temperature}] + 1.70000\text{E} \\
&-04[C_o]\,[\text{Contact Time}] - 0.027187[\text{pH}]\,[\text{Temperature}] \\
&+ 4.44571\text{E}-03[\text{pH}]\,[\text{Contact Time}] - 3.81429\text{E} \\
&-04[\text{Temperature}]\,[\text{pH}]\,[\text{Contact Time}] - 1.55926\text{E} \\
&-03[C_o]^2 - 0.44440[\text{pH}]^2 + 2.27774\text{E}-003[\text{Temperature}]^2 \\
&-\ 9.1328\text{E}-05[\text{Contact Time}]^2
\end{aligned} \tag{3}$$

$$\begin{aligned}
&\text{Biosorbed Pb(II) amount (mg g}^{-1}\text{)(coded)} = +9.27 \\
&+ 2.58[X_1] + 2.92[X_2] - 0.72\,[X_3] + 0.39[X_4] + 2.10[X_1X_2] \\
&- 0.59[X_1X_3] + 0.54[X_1X_4] - 1.02[X_2X_3] + 0.78[X_2X_4] \\
&- 0.40[X_3X_4] - 3.16[X_1]^2 - 2.78[X_2]^2 + 0.51[X_3]^2 - 0.45[X_4]^2
\end{aligned} \tag{4}$$

where X_1 (initial Pb(II) concentration), X_2 (pH), X_3 (temperature) and X_4 (contact time) were the coded values of the tested variables.

The significance of the quadratic model was demonstrated using ANOVA, given in Table 3. The value of F (>0.0001) obtained from the ANOVA table shows that the second quadratic model is significant. The high value of R^2 (93%) shows that 93% of the variability in the response is explained by the model.

The normal percentage probability vs. residuals obtained by the model is given in Fig. 2(a). We can observe that the points on the plot obtained are not very dispersed, indicating that data transformation is not required. Therefore, the conclusion is that the prediction of the experimental data obtained from the quadratic model is sufficient.

It is generally necessary to check whether the results obtained resemble the actual system. If the model is not in accordance with reality, it will provide misleading information for the optimization and investigation of the predicted response in the model. The residuals are very important in evaluating model competency. It is observed in Fig. 2(b) that the residuals

Table 2
Experimental response for CCD of Pb(II) ion removal

Run	Initial concentration (C_o), mg L^{-1} (X_1)	pH (X_2)	Temperature (°C; X_3)	Contact time (min; X_4)	Biosorbed Pb(II) amount (mg g^{-1})
1	55	4.5	35	150	8.28
2	55	4.5	20	80	10.47
3	55	4.5	35	80	9.44
4	100	2	20	150	0.01
5	55	4.5	35	80	9.55
6	10	4.5	35	80	1.81
7	100	2	20	10	0.01
8	10	2	50	10	0.08
9	10	2	20	10	0.87
10	100	7	20	150	18.01
11	10	2	20	150	0.12
12	10	7	50	150	1.84
13	55	7	35	80	9.63
14	55	4.5	35	10	8.65
15	10	7	50	10	1.79
16	55	4.5	35	80	9.74
17	100	4.5	35	80	9.7
18	55	2	35	80	2.64
19	10	7	20	150	1.78
20	55	4.5	35	80	9.8
21	10	2	50	150	0.092
22	100	7	20	10	10.46
23	10	7	20	10	1.71
24	55	4.5	35	80	9.86
25	55	4.5	50	80	8.38
26	100	2	50	10	2.71
27	55	4.5	35	80	9.4
28	100	7	50	150	8.5
29	100	2	50	150	0.89
30	100	7	50	10	6.28

are randomly distributed in the range of ±2.5. According to this, it can be concluded that the experimental data comply with the predicted ones evaluated from Eq. (3) [15].

3.4. Effects of process variables on biosorption capacity

Initial concentration and pH play a significant part in heavy metal biosorption as the combination of both impacts has a significant effect on Pb(II) biosorption. As seen in Fig. 3(a), the results showed that as the pH value of the solution increased from 2.0 to 4.5, the Pb(II) biosorption capacity increased. The maximum Pb(II) biosorption onto *P. squamosus* was observed at pH of approximately 5.75.

The negative charge amount on the biosorbent surface rises due to deprotonation of the metal binding area with increasing pH. The increase in Pb(II) biosorption with increasing pH can be clarified on the foundation of reduced competition among protons and Pb(II) ions for the same functional groups. In addition, the decreasing positive charge on the biosorbent surface results in a higher electrostatic pull among the Pb(II) and functional groups on the biosorbent surface. Similar results were reported by Kubilay et al. [16]. Depending on the –OH ions on the surface of biosorbents, a biosorption mechanism for high and low pH can be explained by Eqs. (5)–(7), respectively [17].

Table 3
ANOVA for Pb(II) biosorption using CCD

Source	Sum of squares	df	Mean square	*F* value	Prob > *F* (*p* value)	
Model	610.8627	14	43.63305	15.80668	<0.0001	Significance
X_1 Initial concentration (C_o)	120.0114	1	120.01136	43.4758	<0.0001	
X_2 pH	153.5803	1	153.58034	55.63663	<0.0001	
X_3 Temperature (°C)	9.213494	1	9.2134936	3.337717	0.0877	
X_4 Contact time (min)	2.692747	1	2.6927469	0.975485	0.3390	
X_1X_2	70.86272	1	70.862724	25.67102	0.0001	
X_1X_3	5.560164	1	5.560164	2.014247	0.1763	
X_1X_4	4.588164	1	4.588164	1.662127	0.2168	
X_2X_3	16.63008	1	16.630084	6.024481	0.0268	
X_2X_4	9.684544	1	9.684544	3.508362	0.0807	
X_3X_4	2.566404	1	2.566404	0.929716	0.3502	
X_1^2	25.83101	1	25.831005	9.357644	0.0080	
X_2^2	19.98771	1	19.987711	7.240829	0.0168	
X_3^2	0.680495	1	0.6804952	0.246519	0.6267	
X_4^2	0.518866	1	0.5188661	0.187967	0.6708	

$R^2 = 0.93$.

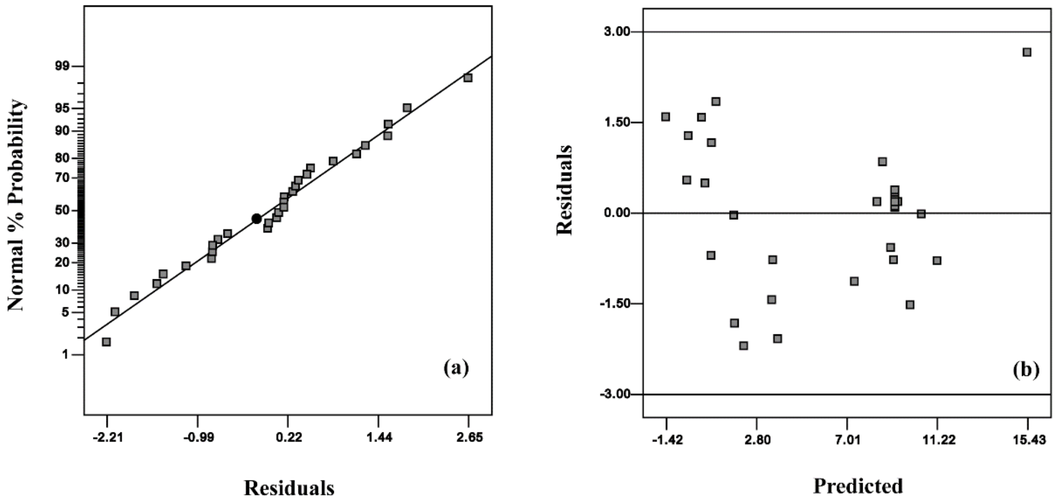

Fig. 2. (a) Validation of the prediction of Pb(II) biosorption residuals vs. normal percentage probability. (b) Residuals vs. predicted values.

$$\text{Surface–OH} + \text{OH}^- \leftrightarrow \text{Surface–O}^- + \text{H}_2\text{O} \quad (5)$$

$$\text{Surface–O}^- + \text{M}^{2+} \leftrightarrow \text{Surface–O–M}^{2+} \quad (6)$$

$$\text{Surface–OH} + \text{H}^+ \rightarrow \text{Surface–OH}_2^+ \quad (7)$$

To interpret the effect of pH on biosorption, it is essential to identify the pH of the point of zero charge (pH_{PZC}) of the biosorbent. Biosorption of cations is favored at pH > pH_{PZC}, whereas the biosorption of anions is favored at pH < pH_{PZC}. pH_{PZC} of *P. squamosus* was defined by the solid supplement method [18]. In this method, pH_{PZC} of *P. squamosus* was found to be 4.8 (Fig. 4). When pH value of the solution increases, it is likely that high biosorption yield is obtained because of the fact that at pH above the pH_{PZC} 4.8, the *P. squamosus* surface is generally negatively charged due to the deprotonation of surface sites.

The initial concentration is one of the parameters whose effect is important in order to understand the biosorption of metal ions. Pb(II) biosorption was implemented at different initial Pb(II) ion concentrations ranging from 10 to 100 mg L^{-1}. The results given in Fig. 3(a) show that Pb(II) biosorption increased with rising initial Pb(II) concentration. The biosorption capacity of *P. squamosus* rapidly increased with

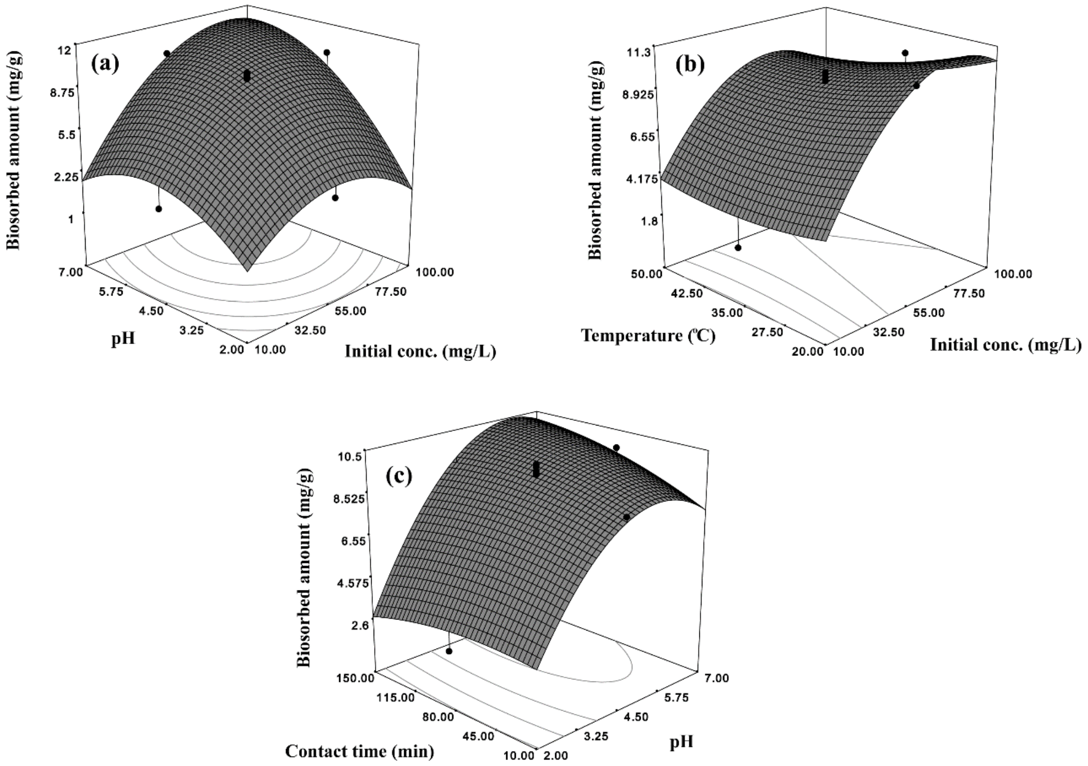

Fig. 3. Simultaneous effects of (a) C_o and pH on Pb(II) biosorption at fixed temperature of 35°C and contact time of 80 min. (b) C_o and temperature on Pb(II) biosorption at fixed pH of 4.5 and contact time of 80 min. (c) Contact time and pH on Pb(II) biosorption at fixed C_o of 55 mg L^{-1} and temperature of 35°C.

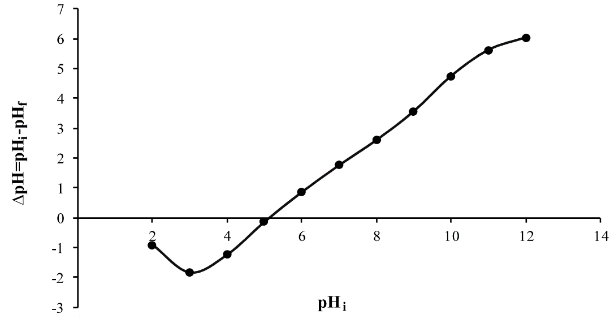

Fig. 4. Point of zero charge of *P. squamosus*.

rising C_o from 10 to 75 mg L^{-1} while change was not recorded with higher initial Pb(II) ion concentrations and a maximum level was roughly reached at about 75 mg L^{-1}. If the metal ion concentration is low, the surface area of the solution is high compared with the total metal ions and therefore all metal ions are more likely to interact with the biosorbent and can be removed from the solution. With increases in Pb(II) ion concentration, a rise in the amount of biosorbed metal ions is due to enhancement of the driving force of the metal ions towards the active sites on the biosorbent [19,20]. Therefore, it could be concluded that the surface active sites of the biosorbent reached saturation level for Pb(II) ions. This stage is the progressive biosorption phase and the rate of increase of biosorption capability became progressively slower with increasing C_o and eventually the metal uptake achieves equilibrium.

The effect of temperature on the Pb(II) biosorption capacity of *P. squamosus* was investigated in the temperature range of 20°C–50°C. As seen in Fig. 3(b), maximum Pb(II) uptake by *P. squamosus* was obtained at 20°C. The systematic temperature increase from 20°C to 50°C yielded a negative response of metal uptake at each concentration studied. Based on this fact, one may say that Pb(II) biosorption by *P. squamosus* is an exothermic process. The decrease in removal efficiency with increasing temperature may be due to the thermal sensitivity of the surface of *P. squamosus* which leads to physical degeneration of the biosorbent surface. In addition, the increasing temperature causes a decrease in biosorption due to the impoverishment of biosorptive forces among the active sites of the biosorbent and biosorbate species [9].

Fig. 3(c) shows the simultaneous effects of contact time and pH on biosorption capacity of *P. squamosus*. Contact time is an important parameter to understand biosorption kinetics. The experimental data indicate that the biosorption capacity of *P. squamosus* increased with increasing contact time. The biosorption reached equilibrium state between 110 and 115 min. Maximum Pb(II) biosorption occurred at 112 min. Initially, the biosorption rate is higher than the desorption rate. But, with increasing contact time the biosorption rate is equal to desorption rate and biosorption reached equilibrium.

3.5. Determination of optimum biosorption conditions

RSM can be used for the approximation of both experimental and numerical responses. The response corresponding to

Table 4
Comparison between *P. squamosus* and other adsorbents and biosorbents in the literature

Adsorbent/biosorbent	Pb(II) adsorption/ biosorption amount	References
China clay	0.289	[21]
Wollastonite	0.217	[21]
Pistacia vera L.	27.1	[22]
Biochar clay	44.7	[23]
γ-Alumina	65.67	[24]
Aspergillus terreus	247.2	[25]
Cauler palentillifera (green algae)	28.7	[26]
Rice husk	8.60	[14]
Hydrilla verticillata	104.2	[27]
Sargassum ilicifolium	195	[28]
Aeromonas hydrophila	163.3	[12]
Immobilized cells of *Pycnoporus sanguineus*	200	[29]
Parmelina tiliaceae	75.8	[30]
Pumice	7.59	[4]
P. squamosus	13.65	This work

each combination of all parameters can be obtained from the established functional relationship through numerical analysis. In this study, the numeric optimization program in CCD was used to identify the optimal values for studied parameters. The level of each parameter was selected as "in range". At these levels, the solutions with maximum response (biosorbed Pb(II) amount) were investigated. A solution resulting in maximum response was found. In this solution, the optimum values were determined as C_o 74.55 mg L^{-1}, pH 5.75, temperature 20°C and contact time 112.6 min, and these values were confirmed by obtained data. Under these optimum terms, the maximum amount of biosorbed Pb(II) was found to be 13.65 mg Pb(II) per gram of biosorbent and biosorption yield was calculated to be 89.4%.

The comparison between the biological material we used and some materials used in the literature is shown in Table 4. *P. squamosus* is a plentiful and cheap biosorbent in nature. It can be said that *P. squamosus* is a natural biosorbent with higher sorption capability than some other native biosorbents. In addition, *P. squamosus* waste does not contaminate the environment after biosorption. Because of these properties, it has the potential to remove heavy metals from environments.

3.6. Regeneration and reuse of fungal biomass

The effective use of biosorbent for heavy metal removal from aqueous environments depends not only on the biosorption capacity of the fungus but also on their regeneration and reusability. Regeneration and reuse of the biosorbent is of great importance in detecting its potential for commercial applications [31]. Regeneration is usually carried out by using different eluting agents (base or acids) with various desorption mechanisms to release the adsorbed heavy metal ions into the solution. The desorption of biosorbed Pb(II) ions was studied with the method of highest biosorption capacity, that is, under optimum conditions [32]. In this study, 0.1 M HCl solution was used as a desorption agent. More than 90% of the biosorbed Pb(II) ions were desorbed. The reusability of the biosorbent was examined with six serial biosorption–desorption cycles using the same preparation. As shown in Fig. 5, the biosorption yield of biomass for Pb(II) did not change significantly after six cycles. These results show that the *P. squamosus* biomass has important potential to be reused in Pb(II) biosorption studies without any significant loss in the total biosorption capacity.

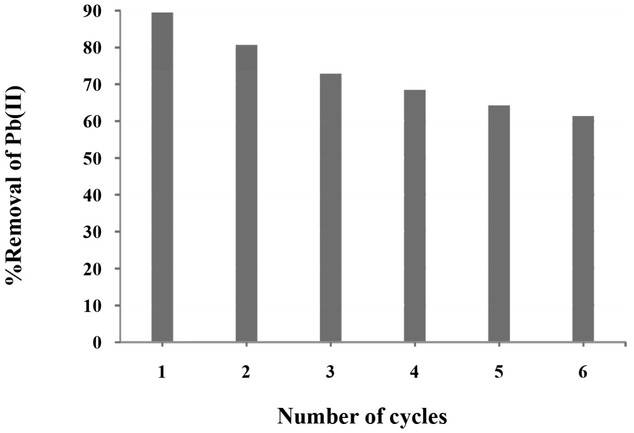

Fig. 5. Adsorption–desorption studies of *P. squamosus* over six cycles.

3.7. Biosorption kinetics of Pb(II) ions on P. squamosus

Biosorption kinetics is one of the major characteristics which represent the efficiency of the biosorbent. It helps in determining potential applications of the biosorbent. The kinetics of the biosorption process is one of the most important steps in wastewater treatment because it gives information on the rate of biosorbate removal. Pseudo-first-order and pseudo-second-order kinetic models and Weber–Morris intraparticle diffusion model were used to understand the biosorption mechanism (given in Eqs. (8)–(10), respectively).

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{8}$$

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

$$q_t = k_i t^{1/2} + C \tag{10}$$

where q_t and q_e (mg g^{-1}) are the amounts of the metal ions biosorbed at t (min) and equilibrium, respectively, and k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the rate constants of the pseudo-first-order and pseudo-second-order model, respectively. k_i is the intraparticle diffusion rate constant (mg g^{-1} min$^{-1/2}$) and C is the fixed value that accounts for the thickness of the film layer where the greater the value of C the greater the film layer impact. The obtained results are given in Fig. 6 and Table 5. According to this data, kinetic data abide by the pseudo-second-order kinetic model in accordance with the high R^2 value. For the Weber–Morris model, the plot of q_t vs. $t^{1/2}$ must be linear if intraparticle diffusion is involved in the biosorption process and if this line passes through the origin then intraparticle diffusion is the only rate-controlling step. If the resulting graph does not pass through the origin, this means some degree of border film layer control and this result shows that the intraparticle diffusion is not the only rate-limiting step, but other kinetic models may also control the rate of biosorption, all of which may be operating at the same time. As well as the boundary film layer controls the biosorption process if the line goes through linearity. Additionally, if there are too many linear lines in the plot, the biosorption process is controlled by a combination of diffusion types [33]. According to Fig. 6(c), the plot reveals linear characteristics. However, the linear plot did not pass through the origin. This result shows that the step controlling the biosorption rate is not the intraparticle diffusion step alone. The Pb(II) biosorption mechanism can be explained as a mixture of intraparticle and border film diffusion.

3.8. Biosorption isotherm models

In a biosorption system, biosorption proceeds until the remaining biosorbate is in dynamic equilibrium with the biosorbent surface. Biosorption isotherms provide some information on how a biosorption system proceeds, and indicate how the biosorbate interacts with the biosorbent surface [34]. In this study, the most well-known biosorption isotherm equations, including Langmuir [35], Freundlich [36] and Dubinin–Radushkevich (D–R) [37], were tested to understand the nature of the biosorption mechanism and the equilibrium terms.

The Langmuir model, if quantitatively defined, is the creation of a monolayer of adsorbate on the adsorbent surface which involves limitations of the same sites. Additionally, the desorption of the adsorbed species does not occur and the adsorption energy at the surface is assumed to be homogeneous. Considering all this information, Langmuir equality is shown in Eq. (11):

$$\frac{1}{Q_e} = \frac{1}{q_{\max} K_L C_e} + \frac{1}{q_{\max}} \tag{11}$$

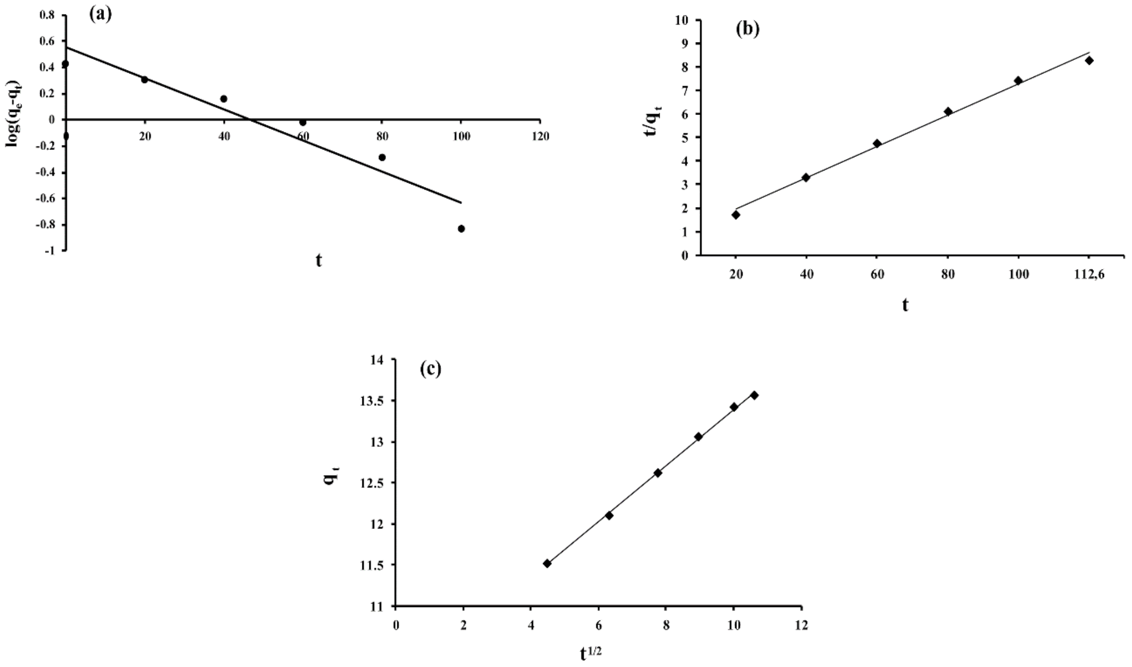

Fig. 6. (a) Pseudo-first-order, (b) pseudo-second-order and (c) Weber–Morris intraparticle diffusion kinetic models for Pb(II) biosorption onto *P. squamosus*.

Table 5
The kinetic constants for Pb(II) biosorption onto *P. squamosus* (C_o 74.50 mg L^{-1}, biosorbent dosage 5 g L^{-1}, pH 5.75, stirring speed = 750 rpm and temperature 20°C)

T (K)	$q_{e,\text{exp.}}$	Pseudo-first-order model			Pseudo-second-order model			Weber–Morris model		
		q_e	k_1	R^2	q_e	k_2	R^2	k_i	C	R^2
293.15	13.65	3.577	0.027	0.915	13.2	0.16	0.992	0.34	9.9	0.998

where C_e is the equilibrium metal ion concentration in solution (mg L^{-1}), Q_e (mg g^{-1}) is the biosorbed metal ion amount at equilibrium, $q_{\max}$ (mg g^{-1}) and K_L (L mg^{-1}) are constants representing the maximum monolayer biosorption capacity and the Langmuir equilibrium constant, respectively. The most important feature of the Langmuir isotherm can be expressed in terms of the dimensionless stable separation factor (R_L) given in Eq. (12). It is a measure of a favorable biosorption process which is expected to be between 0 and 1 for suitable processes. The R_L value computed from Eq. (12) is 0.324 indicating that *P. squamosus* is a suitable biosorbent for Pb(II) biosorption.

$$R_L = \frac{1}{1 + K_L C_o} \tag{12}$$

The Freundlich isotherm is an experimental correlation between the concentration of a solute on the surface of an adsorbent to the concentration of the solute in the liquid with which it is in contact. The linear form of the Freundlich isotherm is given by Eq. (13):

$$\ln Q_e = \ln K_f + \frac{1}{n}\ln C_e \tag{13}$$

where K_f (L g^{-1}) is a constant indicating biosorption capacity and $1/n$ is an empirical parameter related to the biosorption intensity.

The Dubinin–Radushkevich (D–R) model is useful for determining whether biosorption is due to a physical or chemical process. The D–R model is more general compared with the Langmuir equation. The test results are more successful in high and intermediate resolution concentrations of porous and non-porous solids. It is defined in linear form in Eq. (14):

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \tag{14}$$

where q_e (mg g^{-1}) is the biosorbed metal ion amount at equilibrium, q_m (mg g^{-1}) is the maximum biosorption capacity, β is the activity factor concerning mean biosorption energy (mg^2 J^{-2}) and ε is the Polanyi potential which is equal to:

$$\varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right) \tag{15}$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature in Kelvin and β gives an estimate of the mean adsorption free energy E (kJ mol^{-1}) which can be calculated using the equation. A low value obtained for E (4.08 kJ mol^{-1}) indicates that Pb(II) biosorption is a physical process [38].

$$E = \frac{1}{\sqrt{-2\beta}} \tag{16}$$

The isotherm parameters and their correlation coefficients R^2 acquired from Fig. 7 for the mentioned isotherm models are presented for comparison in Table 6. Finally, the Freundlich isotherm is more suitable because the R^2 values of this isotherm are larger than the values of other isotherms. Also, the calculated value of n (>1) in the Freundlich equation indicates it is favorable biosorption [39].

3.9. Thermodynamic parameters for Pb(II) biosorption

The thermodynamics parameters including free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) are important to evaluate the spontaneousness and the heat change of the biosorption processes. These parameters for Pb(II) biosorption can be calculated using the Van't Hoff equation (Eq. (20)). This equation can be obtained as follows:

$$K_C = \frac{C_A}{C_S} \tag{17}$$

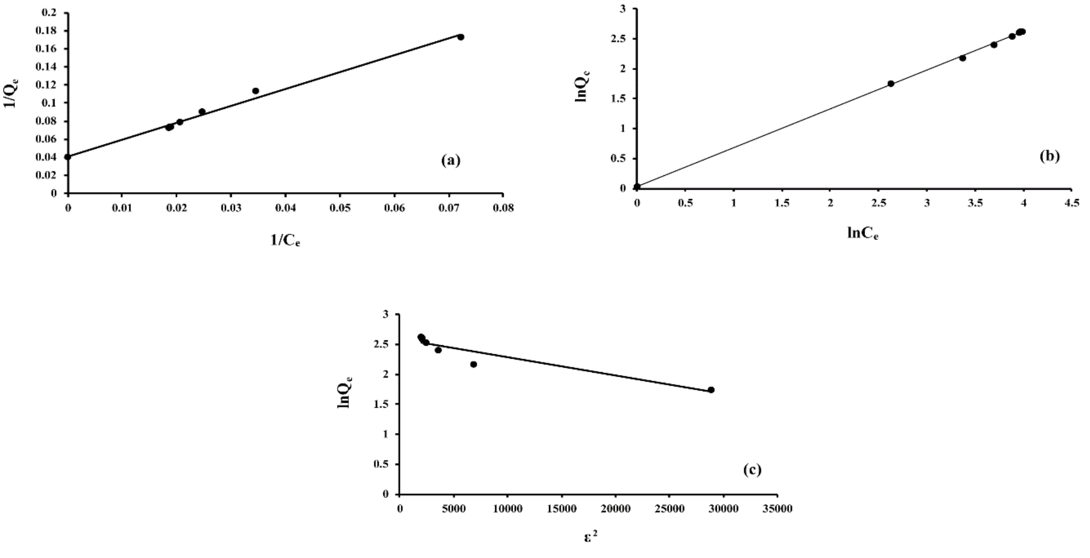

Fig. 7. (a) Langmuir isotherm, (b) Freundlich isotherm and (c) D–R isotherm for Pb(II) biosorption onto *P. squamosus*.

Table 6
Isotherm model parameters and correlation coefficients for Pb(II) biosorption by *P. squamosus*

Langmuir isotherm	Freundlich isotherm	Dubinin–Radushkevich isotherm
$q_{\max}$ (mg g^{-1}) 24.51	n 1.545	q_m (mg g^{-1}) 13.45
K_L (L mg^{-1}) 0.028	K_f 1.025	B_D (mg^2 J^{-2}) 0.003
R_L 0.324	R^2 0.9995	E (kJ mol^{-1}) 4.08
R^2 0.9901		R^2 0.8833

$$\Delta G^\circ = -RT\ln K_C \tag{18}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{19}$$

$$\ln K_C = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{20}$$

where K_C is the equilibrium constant, C_A (mg L^{-1}) and C_S (mg L^{-1}) are the biosorbed and unbiosorbed Pb(II) concentration at equilibrium, respectively, T (K) is temperature and R is the gas constant (8.314 J mol^{-1} K^{-1}). The thermodynamic parameters were obtained from the gradient and intercept point of the graph of lnK_C vs. 1/T (Fig. 8), and information obtained from the graph is given in Table 7. While the negative ΔG° value shows that the nature of the biosorption is thermodynamically possible and spontaneous, the increase in ΔG° values with increasing temperature shows an increase in feasibility and spontaneity of biosorption at lower temperatures. The ΔG° for physical adsorption is usually between –20 and 0 kJ mol^{-1}; however, chemical adsorption has a range of –80 to 400 kJ mol^{-1} [40]. The ΔG° values for the 20°C–50°C temperature range are calculated as between –1.71 and –5.27 kJ mol^{-1}, these values indicate that the biosorption is physical biosorption. The negative value of ΔH° demonstrated that Pb(II) biosorption has an exothermic nature. A negative value of ΔS° implies reduced irregularity at the liquid or solid interface during the biosorption process causing the biosorbate ions or molecules to escape from the solid phase to the liquid phase [41].

3.10. Competitive effect on biosorption

One of the major objectives of this study was to demonstrate the effect of other heavy metal ions on Pb(II) biosorption capacity. For this reason, an artificial wastewater sample that is similar to real industrial wastewater was prepared to analyze Pb(II) biosorption capability in the presence of different metal ions for industrial applications. With the consideration that wastewater from industries contains multiple heavy metals, such as the case of coating industry residuals, we prepared the artificial wastewater with multiple metals containing 75 mg L^{-1} Pb(II), 75 mg L^{-1} Zn(II), 75 mg L^{-1} Cd(II), 75 mg L^{-1} Cu(II) and 75 mg L^{-1} Mn(II) metal ions and the required number of experiments were carried out under optimum conditions [42]. As seen in Fig. 9, the medium Pb(II) removal yield was 72.55%, while it was 34.72%, 8.48%, 16.89% and 6.65% for Cu(II), Cd(II), Zn(II) and Mn(II), respectively. *P. squamosus* is a beneficial and potential biosorbent for wastewater containing Pb(II) and for wastewater contaminated by Pb(II) and other heavy metal ions.

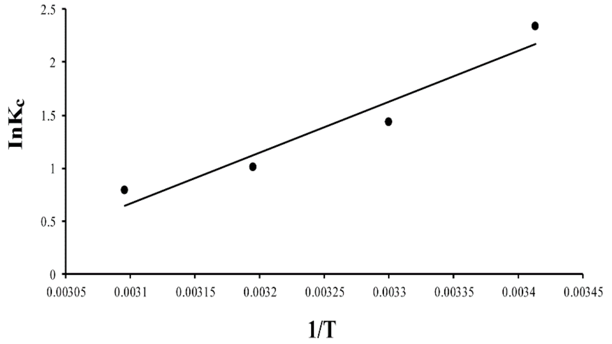

Fig. 8. Plot of lnK_C vs. 1/T for the prediction of thermodynamic parameters of Pb(II) biosorption on *P. squamosus*.

Table 7
Thermodynamic parameters for Pb(II) biosorption on *P. squamosus*

T (K)	lnK_C	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
293	2.33	–5.27	–40.06	–118.72
303	1.43	–4.09		
313	1.003	–2.90		
323	0.79	–1.71		

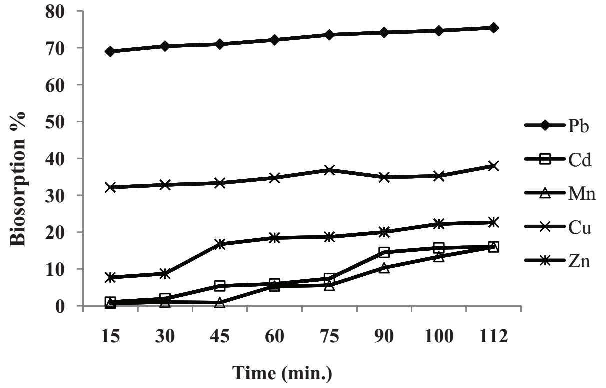

Fig. 9. Biosorption yields for each metal ion during multimetal biosorption.

Finally, it can be concluded that this study is original in terms of the biosorbent used and optimization method for Pb(II) biosorption. Studies of heavy metal biosorption by biosorbents such as fungi materials are limited. In addition, *P. squamosus* biological material is a native material that does not produce toxic hazardous waste and is found abundantly in nature. Therefore, it is possible to use in different areas. Also, the studied metal ion Pb(II) is a highly toxic metal and its removal from waste and drinking water has become increasingly important.

In our study, *P. squamosus*, a biosorbent collected in the east of Turkey, was primarily used for Pb(II) removal from aqueous environments in the literature. In this respect, this study provides a significant addition to the literature because it is a new biosorbent–biosorbate compound. In addition, our research group has worked to modify the *P. squamosus* surface with different chemical agents and to synthesize composites with some polymeric materials. In the future, obtained data will be submitted for publication in scientific journals.

4. Conclusion

The conditions of Pb(II) biosorption on *P. squamosus* were optimized using CCD in RSM. RSM is an important method in the optimization of experimental conditions. With a quadratic model obtained from CCD, the optimum biosorption conditions were determined as initial Pb(II) concentration 74.55 mg L^{-1}, initial pH 5.75, temperature 20°C and contact time 112.6 min. At these optimum conditions, the optimum biosorbed Pb(II) amount and biosorption yield were found to be 13.65 mg Pb(II) per gram of biosorbent and 89.4%, respectively. The biosorption equilibrium and kinetic data fitted very well with both Freundlich and Langmuir isotherms and a second-order kinetic model, respectively. Thermodynamic studies demonstrated that the biosorption process was exothermic and spontaneous. Also, *P. squamosus* was observed to have high biosorption capacity for Pb(II) ions from wastewater in the presence of different metal ions under competitive biosorption. As a result, we can say that *P. squamosus* is a suitable, natural biosorbent with abundant availability and low cost for the removal of Pb(II) from wastewaters.

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