

Equilibrium, kinetic and thermodynamic studies on biosorption of Pb(II) and Cd(II) from aqueous solution by fungus (*Trametes versicolor*) biomass

Munagapati Venkata Subbaiah, Gutha Yuvaraja, Yarramuthi Vijaya, Abburi Krishnaiah*

Biopolymers and Thermophysical Laboratories, Department of Chemistry, Sri Venkateswara University, Tirupati 517 502, A.P., India

ARTICLE INFO

Article history:

Received 13 December 2010
Received in revised form 23 March 2011
Accepted 5 April 2011
Available online 13 May 2011

Keywords:

Biosorption
Trametes versicolor
Kinetics
Isotherm
Thermodynamics

ABSTRACT

The biosorption characteristics of Pb(II) and Cd(II) ions from aqueous solution using the fungus (*Trametes versicolor*) biomass were investigated as a function of pH, biomass dosage, contact time, initial metal ion concentration and temperature. Langmuir and Freundlich models were applied to describe the biosorption of the metal ions by fungus (*T. versicolor*) biomass. Langmuir model fitted the equilibrium data better than the Freundlich isotherm. The monolayer biosorption capacity of *T. versicolor* biomass for Pb(II) and Cd(II) ions was found to be 208.3 mg g⁻¹ and 166.6 mg g⁻¹, respectively. The calculated thermodynamic parameters (ΔG° , ΔH° and ΔS°) showed that the biosorption of both metal ions was feasible, spontaneous and endothermic at 303–323 K. Experimental data were also used to study biosorption kinetics using pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models. The results showed that the biosorption processes of both metal ions followed well pseudo-second-order kinetics.

© 2011 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

1. Introduction

Heavy metal pollution has become one of the most serious environmental problems today. Unlike organic pollutants, heavy metals are non-biodegradable and so the removal of them is extremely important in terms of health of living specimens.

Lead poisoning in human causes severe damage to kidney, nervous system, reproductive system, liver and brain [1]. Different industrial processes, such as battery manufacturing, printing and pigment, metal plating and finishing, ammunition, soldering material, ceramic and glass industries, iron and steel manufacturing units are major sources of lead contamination in waste water [2,30]. Cadmium is also a dangerous pollutant that is released into aquatic medium from metal plating, metallurgical alloying, mining, ceramics and other industrial operations [3,4]. Cadmium toxicity may be observed by a variety of syndromes and effects including renal dysfunction, hypertension, hepatic injury, lung damage and teratogenic effects [3,4].

The most widely used methods for removing heavy metals from wastewaters include ion-exchange, chemical precipitation, reverse osmosis, evaporation, membrane filtration, adsorption and biological treatment [5]. Most of these methods suffer from some drawbacks, such as high capital and operational cost, the disposal of the residual metal sludge, and un-suitable for small scale industries [6]. Biosorption plays an important role in the elimination of metal ions from aqueous solutions in water

pollution control [7,8]. The main advantages of this technique are the reusability of biomaterial, low operating cost, improved selectivity for specific metals of interest, removal of heavy metals from effluent irrespective of toxicity, short operation time, and no production of secondary compounds which might be toxic [9].

Fungal cell walls mainly consisting of polysaccharides, proteins and lipids with many functional groups that are responsible for the binding of metals [10–12]. Several fungal biosorbents such as *Penicillium* [13], *Trametes versicolor* [31], *Lentinus sajor-caju* [14], *Rhizopus arrhizus* [32], *Rhizopus oryzae* and *Aspergillus oryzae* [15], and *Aspergillus niger* and *Mucor rouxii* [16] have been used for the removal of heavy metal from aqueous solution. *T. versicolor* is a basidiomycete fungus and has many functional groups responsible for the biosorption of heavy metals. The biosorbent material has proved to be both economic and eco friendly as it is available abundantly regeneration with potential for and high surface area to volume ratio. It provides a cost effective solution for industrial and natural water management. The new material was chosen as biosorbent in this study as it is natural, easily available, and thus a low-cost biomass for dissolved metal ions.

The present work is focused on the potential use of *T. versicolor* biomass for removal of Pb(II) and Cd(II) ions from aqueous solution. Experimental parameters affecting the biosorption process such as pH, contact time, biomass dosage, initial metal ion concentration and temperature were studied. The biosorption kinetic data were analysed in terms of pseudo-first-order, pseudo-second-order and intraparticle diffusion models. In addition thermodynamic parameters such as ΔG° , ΔH° and ΔS° for biosorption process was evaluated.

* Corresponding author. Tel.: +91 9393621986.

E-mail address: abburikrishnaiah@gmail.com (A. Krishnaiah).

2. Materials and methods

2.1. Biomass preparation

The fungus (*T. versicolor*) was used as biosorbent for the biosorption of Pb(II) and Cd(II) ions. Samples of the biomass were collected from the Tirumala Tirupati Hills, Andhra Pradesh, India. Samples were washed several times using deionized water to remove extraneous and salts. They were then dried in an oven at 70 °C for 24 h. The dried biomass was chopped, sieved and the particles with an average size of 0.5 mm were used for biosorption experiments.

2.2. Reagents and equipments

All chemical used in this work, were of analytical reagent grade and were used without further purification. Double deionized water (Milli-Q Millipore 18.2 MΩ cm⁻¹ conductivity) was used for all dilutions. A pH meter (Digisun D1-7007, India) was employed for measuring pH values in the aqueous phase. A flame atomic absorption spectrophotometer (Shimadzu AA-6300, Japan) with deuterium background corrector was used. All measurements were carried out in an air/acetylene flame. A 10 cm long slot burner head, a lamp and an air-acetylene flame were used. The operating parameters for working elements were set as recommended by the manufacturer. Surface area, pore volume and pore diameter of the *T. versicolor* biomass were determined on the basis of the Brunauer, Emmett, Teller (BET) method (Micromeritics ASAP-2010, USA). Fourier transform infrared (FTIR) spectra of dried unloaded biomass and Pb(II) and Cd(II) loaded biomass prepared as KBr discs were recorded at 400–4000 cm⁻¹ wavenumber range using a FTIR (Thermonicolet-200 series, Germany) spectrometer.

2.3. Batch biosorption studies

Biosorption experiments were carried out at the desired pH value, contact time and biomass dosage level using the necessary biomass in a 125 mL stoppered conical flask containing 100 mL of test solution. Initial solutions with different concentration of Pb(II) and Cd(II) were prepared by proper dilution from stock 1000 mg L⁻¹ Pb(II) and Cd(II) standards. Necessary amount of the biomass was then added and contents in the flask were shaken for the desired contact time in an electrically thermostatic reciprocating shaker at 120 rpm. The experiments were repeated at 303, 313 and 323 K. The time required for reaching the equilibrium conditions was estimated by drawing samples at regular intervals of time till equilibrium was reached. The contents of the flask were filtered through filter paper and the filtrate was analyzed for metal concentration using flame AAS. The amount adsorbed per unit mass of adsorbent at equilibrium was obtained using the equation:

$$q = \frac{(C_i - C_e)V}{M} \quad (1)$$

where q (mg g⁻¹) was the adsorption capacity at equilibrium, C_i and C_e are respectively initial and equilibrium concentration (mg L⁻¹) of Pb(II) and Cd(II), M (g) is the adsorbent dosage, and V (L) is the volume of the solution.

3. Results and discussion

3.1. Biosorbent characterization

3.1.1. Fourier transform infrared spectroscopy

The FTIR spectra of dried unloaded biomass, Pb(II) and Cd(II) loaded biomass were recorded to obtain information on the nature of possible interactions between the functional groups of *T.*

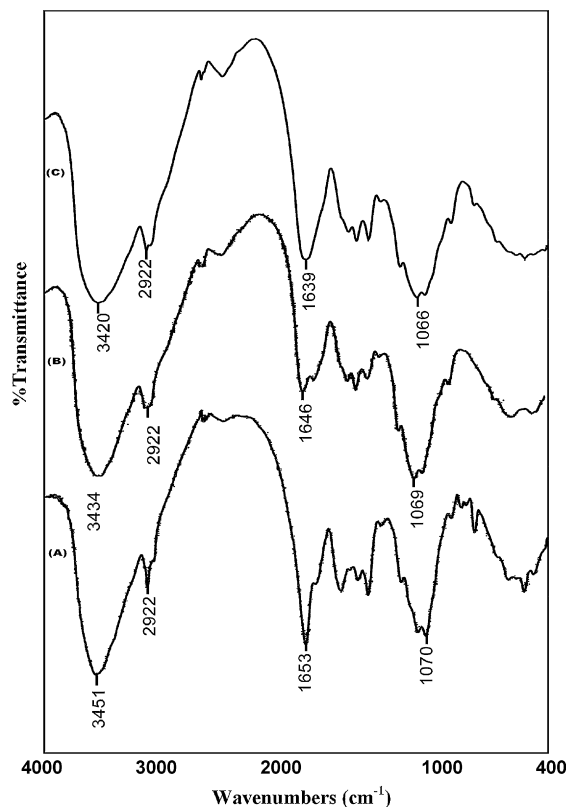


Fig. 1. FT-IR spectrum of (A) unloaded (B) Pb(II)-loaded and (C) Cd(II)-loaded *T. versicolor* biomass.

versicolor biomass and the metal ions and are presented in Fig. 1. The broad and strong bands at 3420–3451 cm⁻¹ were due to bounded hydroxyl group (–OH). The peaks at 1639–1653 cm⁻¹ were attributed to stretching vibration of carboxyl group (–C=O). The bands observed at 1066–1070 cm⁻¹ were assigned to CO stretching of alcohols and carboxylic acids. The peaks observed at 2922 cm⁻¹ can be assigned to the C–H group. The stretching vibration of OH group was shifted from 3451 cm⁻¹ to 3434 in case of Pb(II) loaded biomass and to 3420 cm⁻¹ in case of Cd(II) loaded biomass. These results revealed that chemical interactions between the metal ions and the hydroxyl groups occurred on the biomass surface. The carboxyl peak was observed at 1646 and 1639 cm⁻¹ for Pb(II) and Cd(II) loaded biomass samples, respectively. The peak at 1070 cm⁻¹ is shifted to 1066 cm⁻¹ corresponds to the C–O groups in the biomass. The results indicated that the functional groups mentioned (hydroxyl, carboxyl,) were mainly involved in the biosorption of Pb(II) and Cd(II) onto *T. versicolor* biomass. In addition, no frequency change was observed in the C–H group of the biomass after biosorption of metal ions. This suggested that this group did not participate in the biosorption of metal ions.

3.1.2. Surface area analysis

Surface area, pore volume and pore diameter are the key factors in determining whether the material is suitable for removal of metal ions from aqueous solutions. In addition the nature of the adsorbent–adsorbate and adsorbate–adsorbate interactions must also be taken into consideration. It is understood that the pore volume contributes to the accommodation of metal ion on the adsorbent. Surface area, pore volume and pore diameter of the *T. versicolor* biomass were determined on the basis of the BET method. The isotherm plots were used to calculate the specific surface area (N₂/BET method) and average pore diameter of *T. versicolor* biomass, while micro pore volume was calculated from

Table 1
Characteristics of *T. versicolor* biomass.

Surface area	
Single point surface area ($\text{m}^2 \text{g}^{-1}$)	3.102
BET surface area ($\text{m}^2 \text{g}^{-1}$)	2.95
Pore volume	
Single point adsorption total pore volume of pores ($\text{cm}^3 \text{g}^{-1}$)	0.0061
Pore size	
Adsorption average pore diameter (\AA)	47.48

the volume of nitrogen adsorbed at P/P_0 0.9966. The surface properties of *T. versicolor* biomass are summarized in Table 1.

3.2. Effect of pH

The pH has been identified as one of the most important parameters on metal sorption. It is directly related with competition ability of hydrogen ions to active sites on the biosorbent surface [17]. The biosorption mechanisms are related to physicochemical interactions of the species in solution and the biosorptive sites of sorbent [18,19]. The effect of pH on the biosorption of Pb(II) and Cd(II) ions onto *T. versicolor* biomass was studied in the pH values in the range 2.0–7.0 and the results were presented in Fig. 2. At high acidic pH, the overall surface charge on the cells became positive and metal cations and protons compete for binding sites on cell wall, which results in lower uptake of metal [20]. When the pH of solution increased, biosorbent surface becomes less positive due to the deprotonation of the functional groups of the biomass and thus available for the metal ions. Especially, carboxyl, amine and hydroxyl groups are important functional groups involved in biosorption of metal ions. Decrease in biosorption at higher pH ($\text{pH} > 5.0$) is not only related the formation of soluble hydroxylated complexes of the metal ions (lead ions in the form of $\text{Pb}(\text{OH})_2$, and cadmium ions in form of $\text{Cd}(\text{OH})_2$) [19] but also to the ionized nature of the cell wall surface of the biomass under the studied pH [21]. Several researchers have investigated the effect of pH on biosorption of heavy metals by using different kinds of fungal biomass and reported that maximum biosorption occurred in the pH range 5.0–7.0 [22,23].

3.3. Effect of biomass dosage

The biomass dosage is an important parameter because this determines the capacity of a biosorbent for a given initial

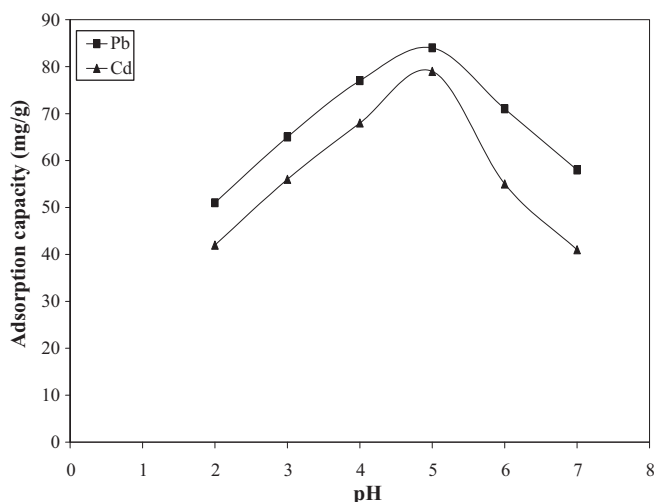


Fig. 2. Effect of pH on the biosorption of Pb(II) and Cd(II) onto *T. versicolor* biomass.

concentration. The biosorption efficiency for Pb(II) and Cd(II) ions as a function of biomass dosage was investigated. The percentage of the metal biosorption steeply increases with the biomass loading up to 0.6 g. This result can be explained by the fact that the biosorption sites remain unsaturated during the biosorption reaction whereas the number of sites available for biosorption site increases by increasing the biosorbent dose. Moreover, the maximum biosorption, 96% for Pb(II) and 92% for Cd(II), of the metal ions was attained at biomass dosage, 0.6 g (figure not shown). However, the biosorption capacity becomes nearly constant above this dosage. Therefore, the optimum biomass dosage was taken as 0.6 g for further experiments.

3.4. Effect of contact time

The rate of biosorption is important for designing batch adsorption experiments. Therefore, the effect of contact time on the biosorption of Pb(II) and Cd(II) was investigated. The biosorption capacity of Pb(II) and Cd(II) increased considerably until the contact time reached 210 min. Further increase in contact time did not enhance the extent of biosorption and hence 210 min was chosen as contact time selected for further experiments.

3.5. Biosorption kinetics study

The Lagergren's pseudo-first-order, pseudo-second-order, and intraparticle diffusion model were used to study the biosorption kinetics of Pb(II) and Cd(II) ions onto *T. versicolor* biomass. Using the experimental data at various initial concentrations 50–200 mg L^{-1} .

The linear form of the pseudo-first-order rate equation [24] is given as

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (2)$$

where q_t and q_e (mg g^{-1}) are the amounts of the metal ions sorbed at equilibrium time (mg g^{-1}) and t (min), respectively, and K_1 is the first-order rate constant (min^{-1}).

Experimental data were also analysed by the pseudo-second-order kinetic model which is given in the following form [25]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where K_2 ($\text{mg g}^{-1} \text{min}^{-1}$) is the second-order rate constant, q_t (mg g^{-1}) is the amount of biosorption time t (min) and q_e is the amount of biosorption equilibrium (mg g^{-1}).

The intraparticle diffusion equation is expressed as [26],

$$q_t = K_{id} t^{0.5} + C \quad (4)$$

where q_t (mg g^{-1}) is the amount adsorbed at time t (min), K_{id} ($\text{mg g}^{-1} \text{min}^{-0.5}$) is the rate constant of intraparticle diffusion. C is the value of intercept which gives an idea about the boundary layer thickness, i.e. the larger intercept; the greater is the boundary effect. If the intra-particle diffusion is the sole rate determining step, the plots of q_t versus $t^{0.5}$ should be linear passing through the origin. The plots in the figure are multi linear with three distinct regions. The initial curved region corresponds to the external surface uptake, the second stage relates the gradual uptake reflecting intraparticle diffusion as the rate limiting step and final plateau region indicates equilibrium uptake. Based on the results it may be concluded the intraparticle diffusion is not only the rate determining factor.

The values of rate constants and correlation coefficients for each model are shown in Table 2. The correlation coefficients R^2 , show that the adsorption process follows pseudo-second-order model. In addition, the sum of squared errors (SSE) were calculated to

Table 2Pseudo-first-order, pseudo-second-order and Intraparticle diffusion models for the biosorption of Pb(II) and Cd(II) onto *T. versicolor* biomass.

Metal ion	Initial metal ion concentration (mg L ⁻¹)	Pseudo-first-order			Pseudo-second-order			Weber and Morris		
		K ₁ (min ⁻¹)	R ²	SSE	K ₂ (mg g ⁻¹ min ⁻¹)	R ²	SSE	K _{id} (mg g ⁻¹ min ^{-0.5})	R ²	SSE
Pb(II)	50	0.014	0.991	0.999	0.0003	0.991	0.009	1.440	0.985	0.935
	100	0.011	0.991	0.999	0.0003	0.996	0.005	2.327	0.992	0.944
	150	0.009	0.996	0.999	0.0003	0.992	0.008	3.932	0.985	0.939
	200	0.015	0.980	0.999	0.0004	0.997	0.004	4.022	0.988	0.949
Cd(II)	50	0.009	0.954	0.999	0.0007	0.996	0.004	0.815	0.983	0.953
	100	0.011	0.998	0.999	0.0007	0.998	0.003	1.370	0.981	0.957
	150	0.011	0.999	0.999	0.0006	0.999	0.003	1.915	0.988	0.961
	200	0.009	0.999	0.999	0.0007	0.999	0.007	1.981	0.981	0.969

predict the best fit kinetic model. Lower values of SSE indicated better fit to sorption data and can give an indication of the sorption mechanism.

$$SSE = \sum \frac{(q_{t,e} - q_{t,m})^2}{q_{t,e}^2} \mu_x \quad (5)$$

where $q_{t,e}$ and $q_{t,m}$ are the experimental biosorption capacities of metal ions (mg g⁻¹) at time t and the corresponding values that are obtained from the kinetic models. SSE values of reaction-based and diffusion based kinetic models were computed and summarized in Table 2. It is assumed that the model which gives the lowest SSE values is the best model for this system and then the mechanism of sorption can be explained based on that model. It is observed from Table 2 that pseudo-second-order model gives a better fit than the other two models (pseudo-first-order and intraparticle diffusion models).

3.6. Biosorption isotherms models

The equilibrium adsorption data were analyzed in terms of Langmuir and Freundlich adsorption isotherm models.

The Langmuir model can be written in linear form [27].

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \quad (6)$$

where q_e is the equilibrium metal ion concentration on the sorbent (mg g⁻¹), C_e is the equilibrium metal ion concentration in the solution (mg L⁻¹), q_m is the monolayer biosorption capacity of the adsorbent (mg g⁻¹), and K_L is the Langmuir sorption constant (L mg⁻¹) related to the free energy of biosorption. The plots of $1/C_e$ versus $1/q_e$ (Fig. 3) were used for three temperatures to calculate these constants (Table 3) at all the temperatures. The linearized forms of the isotherms at all temperatures are found to be linear over the whole concentration range studied, and the correlation coefficients are extremely high, as shown in Table 3. These values of the correlation coefficients strongly support the fact that the Pb(II) and Cd(II)-fungal biomass biosorption data closely follow the Langmuir model. The high degree of correlation for the linearized Langmuir relationship suggests a single surface reaction with constant activation energy is the predominant sorption step and possibly the predominant rate-controlling step. A comparison of adsorption capacity (q_m ; mg g⁻¹) of this biosorbent with those of different biosorbents reported in the literature is given in Table 4.

The Freundlich model assumes a heterogeneous sorption surface. The Freundlich model [28] is

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (7)$$

where K_f is a constant relating the biosorption capacity and $1/n$ is an empirical parameter relating the biosorption intensity, which

varies with the heterogeneity of the material. The plots of $\log C_e$ versus $\log q_e$ (Fig. 4) are used to calculate the values of K_f and $1/n$ and given in Table 3. However, the values of correlation coefficients in indicate the data are not well correlated to Freundlich compared to the Langmuir correlation coefficients.

3.7. χ^2 analysis

To identify the suitable isotherm for biosorption of Pb(II) and Cd(II) ions onto *T. versicolor* biomass, the χ^2 analysis is carried out.

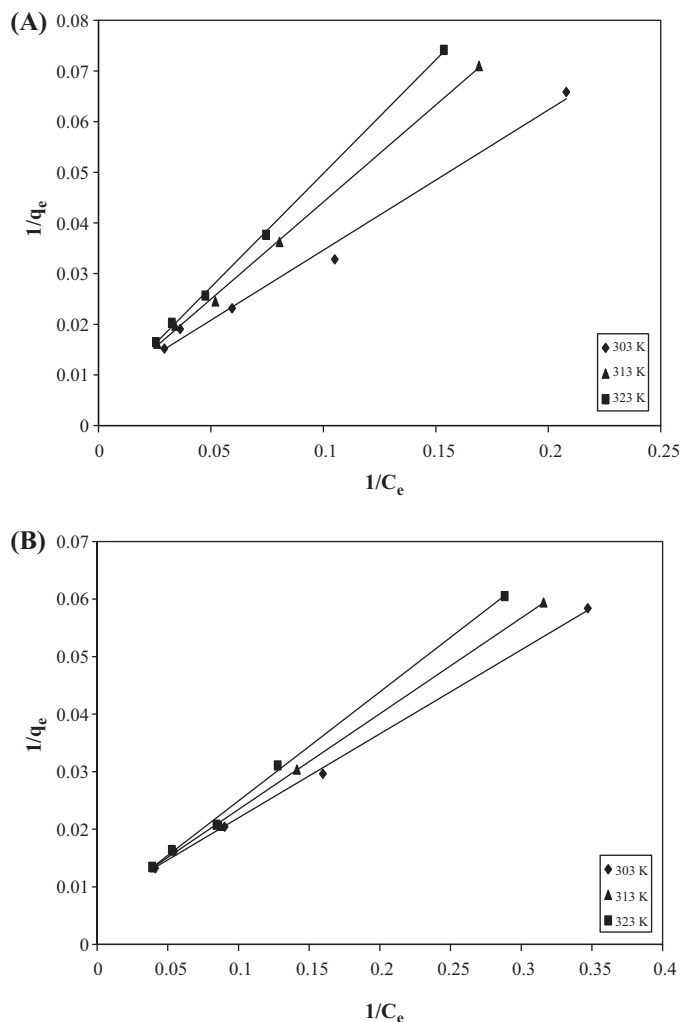


Fig. 3. Langmuir isotherm plots for the biosorption of (A) Pb(II) and (B) Cd(II) onto *T. versicolor* biomass at different temperatures.

Table 3Langmuir and Freundlich isotherm constants and correlation coefficients for the biosorption of Pb(II) and Cd(II) onto *T. versicolor* biomass.

Metal ion	Temp. (K)	Langmuir				Freundlich				
		q_m (mg g ⁻¹)	K_L (L mg ⁻¹)	R^2	χ^2	K_f (mg g ⁻¹)	1/n	n	R^2	χ^2
Pb(II)	303	142.9	5.01	0.990	41.6	5.52	0.705	1.35	0.973	659.4
	313	172.4	6.03	0.998	71.1	3.66	0.787	1.78	0.990	922.2
	323	208.3	8.21	0.999	104.4	2.94	0.832	2.13	0.995	1138.0
Cd(II)	303	135.1	2.43	0.998	26.2	8.96	0.678	1.05	0.986	495.9
	313	147.1	2.71	0.999	35.6	7.83	0.713	1.12	0.988	571.4
	323	166.6	3.57	0.998	51.1	6.72	0.756	1.21	0.989	680.3

The mathematical equation for χ^2 analysis is written as,

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \quad (8)$$

where $q_{e,m}$ is the equilibrium capacity obtained from the model (mg g⁻¹) and q_e is the experimental equilibrium capacity (mg g⁻¹). The χ^2 values are presented in Table 3. If the experimental are predicted one data from the model are similar, χ^2 will be a small number, while if they differ; χ^2 will be a bigger number. The χ^2 values of both the isotherms included in Table 3 indicates that the χ^2 values are smaller for Langmuir model compared to Freundlich model and thus conforming the applicability of Langmuir model for the biosorption of Pb(II) and Cd(II) onto *T. versicolor*.

3.8. Biosorption thermodynamics

Thermodynamically, in an isolated system, energy cannot be gained or lost; the entropy change is the driving force. In the practice of environmental engineering, both energy and entropy factors ought to be considered in order to determine the processes that occur spontaneously. The thermodynamic parameters including the Gibbs free energy change of adsorption (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) for the biosorption of Pb(II) and Cd(II)

Table 4Comparison of biosorption capacity (mg g⁻¹) of *T. versicolor* biomass with other biosorbents for Pb(II) and Cd(II).

Biosorbent	Pb(II)	Cd(II)	Reference
<i>Streptomyces longwoodensis</i>	100.0	–	Friis and Myers-Keith [33]
<i>Rhizopus arrhizus</i>	15.5	–	Sag et al. [34]
<i>Phellinus badius</i>	170.0	–	Matheickal and Yu [35]
<i>C. vulgaris</i>	–	67.00	Aksu [36]
<i>Phanerochaete chrysosporium</i>	69.8	23.0	Say et al. [37]
<i>Mucor rouxii</i>	–	20.31	Yan and Viraraghavan [38]
<i>Sargassum</i> sp.	–	120.0	Cruz et al. [39]
<i>Phanerochaete chrysosporium</i>	–	15.2	Li et al. [40]
<i>Pantoea</i> sp.	–	52.00	Ozdemir et al. [41]
<i>Gracillaria</i> sp.	–	33.7	Sheng et al. [42]
<i>Spirulina</i> sp.	–	159.0	Chojnacka et al. [43]
<i>Aspergillus flavus</i>	13.5	–	Akar and Tunali [44]
<i>A. niger</i>	32.60	–	Arzu [45]
<i>Caulerpa lentillifera</i>	28.7	4.7	Pavasant et al. [46]
<i>Pinus sylvestris</i>	22.2	19.1	Rakhshae et al. [47]
<i>C. aphidicola</i>	36.91	–	Tunali et al. [48]
<i>P. putida</i>	180.41	–	Uslu and Tanyol [49]
Cystine-modified biomass	45.9	11.6	Yu et al. [50]
<i>Penicillium simplicissimum</i>	87.72	61.35	Fan et al. [51]
<i>Oedogonium</i> sp.	–	88.2	Gupta and Rastogi [52]
<i>H. splendens</i>	–	32.5	Sari et al. [53]
<i>Ulva lactuca</i>	34.7	29.2	Sari and Tuzen [54]
<i>A. rubescens</i>	38.4	27.3	Sari and Tuzen [55]
<i>L. scrobiculatus</i>	56.2	53.1	Anayurt et al. [56]
<i>Calophyllum inophyllum</i>	34.51	–	Lawal et al. [57]
<i>Trametes versicolor</i>	208.3	166.6	Present study

ions onto *T. versicolor* biomass were calculated using the following equations:

$$\Delta G^\circ = -RT \ln K_L \quad (9)$$

where R is the universal gas constant (8.314×10^{-3} kJ mol⁻¹ K⁻¹), T is a absolute temperature (K) and K_L is the Langmuir constant.

The enthalpy (ΔH°) and entropy (ΔS°) values were estimated from the following equations:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (10)$$

$$\ln K_L = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (11)$$

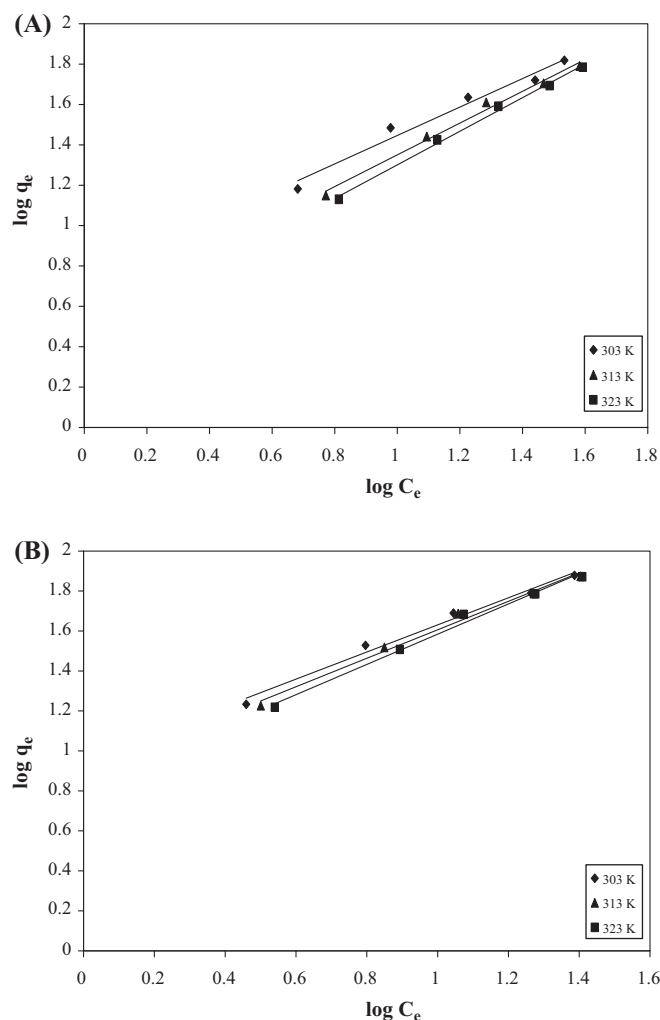


Fig. 4. Freundlich isotherm plots for the biosorption of (A) Pb(II) and (B) Cd(II) onto *T. versicolor* biomass at different temperatures.

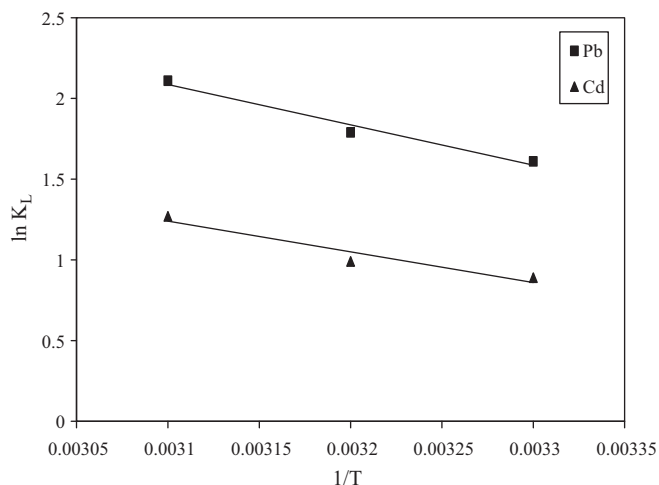


Fig. 5. Plot of $\ln K_L$ versus $1/T$ for biosorption of Pb(II) and Cd(II) onto *T. versicolor* biomass.

Table 5

Values of thermodynamic parameters for the biosorption of Pb(II) and Cd(II) ions onto *T. versicolor* biomass.

Metal ion	Temperature (K)	ΔG° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K)	ΔH° (kJ mol ⁻¹)
Pb(II)	303	-4.058	81.8	20.8
	313	-4.676		
	323	-5.654		
Cd(II)	303	-2.236	59.3	15.6
	313	-2.594		
	323	-3.417		

The values of ΔG° were calculated from Eq. (9). The values of ΔH° and ΔS° can be calculated from the slope and the intercept of the plot of $\ln K_L$ versus $1/T$, respectively (Fig. 5). The negative values of ΔG° imply that the biosorption of Pb(II) and Cd(II) ions onto *T. versicolor* biomass was spontaneous. The magnitude of ΔG° also increased with increase in the temperature indicating that the biosorption was more favorable at higher temperatures. The positive values of ΔH° indicate the endothermic nature of the biosorption of Pb(II) and Cd(II) ions onto *T. versicolor* biomass in the temperature range of 303–323 K. One plausible explanation of endothermicity of the enthalpy of adsorption is the well-known fact that ions like Pb(II) and Cd(II) are well solvated in water. In order that these ions get adsorbed, they are to some extent denuded of their hydration sheath. This dehydration process of ions requires energy. The investigators assume that this energy of dehydration exceeds the exothermicity of the ions attaching to the surface. The implicit assumption is that after adsorption, the environment of the metal ions is less aqueous than it was in the solution state. The removal of water from ions is essentially an endothermic process exceeds that of the enthalpy of adsorption to considerable extent [29]. The positive values of ΔS° suggested an increase in randomness at the solid/liquid interface during the biosorption of Pb(II) and Cd(II) ions onto *T. versicolor* biomass. The values of ΔG° , ΔH° and ΔS° for the biosorption of Pb(II) and Cd(II) ions onto *T. versicolor* biomass are given in Table 5.

4. Conclusion

This study is focused on the biosorption of Pb(II) and Cd(II) onto *T. versicolor* biomass from aqueous solution. The effect operating parameters, such as pH of solution, biomass dosage, contact time, initial metal ion concentration and temperature, on the uptake of Pb(II) and Cd(II). Biosorption equilibrium data were better

described by the Langmuir isotherm model than the Freundlich model. The maximum monolayer biosorption capacity of *T. versicolor* biomass was found to be 208.3 mg g⁻¹ for Pb(II) and 166.6 mg g⁻¹ for Cd(II), respectively. The thermodynamic parameters indicated the feasibility, endothermic and spontaneous nature of the biosorption process. Equilibrium data showed that the biosorption of Pb(II) and Cd(II) ions onto *T. versicolor* biomass followed well the pseudo-second-order kinetic model. Based on all results, it can be concluded that the *T. versicolor* is an effective and alternative biomass for the removal of Pb(II) and Cd(II) ions from wastewaters in terms of high biosorption capacity, available in natural and abundant with low cost.

References

- [1] Naiyaa TK, Bhattacharya AK, Mandal S, Das SK. The sorption of lead(II) ions on rice husk ash. *J Hazard Mater* 2009;163:1254.
- [2] Jamali MK, Kazi TG, Arain MB, Afridi HI, Jalbani N, Menon AR. Heavy metal contents of vegetables grown in soil, irrigated with mixtures of wastewater and sewage sludge in Pakistan, using ultrasonic assisted pseudo-digestion. *J Agron Crop Sci* 2007;193(3):218.
- [3] Kazi TG, Jalbani N, Kazi N, Jamali MK, Arain MB, Afridi HI, et al. Evaluation of toxic metals in blood and urine samples of chronic renal failure patients, before and after dialysis. *Ren Fail* 2008;30:737.
- [4] Kazi TG, Menon AR, Afridi HI, Jamali MK, Arain MB, Jalbani N, et al. Determination of cadmium in whole blood and scalp hair samples of Pakistani male lung cancer patients by electro thermal atomic absorption spectrometer. *Sci Total Environ* 2008;389:270.
- [5] Xiangliang P, Jianlong W, Daoyong Z. Biosorption of Pb(II) and Cr(III) from aqueous solution by lichen (*Parmelina tiliaceae*) biomass. *Process Biochem* 2005;40:2799.
- [6] Kobya M, Demirbas E, Senturk E, Ince M. Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone. *Bioresour Technol* 2005;96:1518.
- [7] Veglio F, Beolchini F. Removal of metals by biosorption: a review. *Hydrometallurgy* 1997;44:301.
- [8] Ferraz AI, Tavares T, Teixeira JA. Cr(III) removal and recovery from *Saccharomyces cerevisiae*. *Chem Eng J* 2004;105:11.
- [9] Mungasavalli DP, Viraraghavan T, Chunglin Y. Biosorption of chromium from aqueous solutions by pretreated *Aspergillus niger*: batch and column studies. *Colloids Surf A Physicochem Eng Aspects* 2007;301:214.
- [10] Akhtar N, Sastry KS, Mohan PM. Mechanism of metal ion biosorption by fungal biomass. *Biometals* 1996;9:21.
- [11] Kapoor A, Viraraghavan T. Heavy metal biosorption sites in *Aspergillus niger*. *Bioresour Technol* 1997;61:221.
- [12] Veglio F, Beolchini F, Gasbarro A. Biosorption of toxic metals: an equilibrium study using free cells of *Arthrobacter* sp.. *Process Biochem* 1997;32:99.
- [13] Galun M, Keller P, Malki D, Feldstein H, Galun E, Siegel S. Recovery of uranium(VI) from solution using precultured *Penicillium* biomass. *Water Air Soil Pollut* 1983;20:221.
- [14] Bayramoglu G, Denizli A, Bektas S, Arica MY. Entrapment of *Lentinus sajor-caju* into ca-alginate gel beads for removal of Cd(II) ions from aqueous solution: preparation and biosorption kinetics analysis. *Microchem J* 2002;72:63.
- [15] Huang C, Huang CP. Application of *Aspergillus oryzae* and *Rhizopus oryzae* for Cu(II) removal. *Water Res* 1996;30:1985.
- [16] Mullen MD, Wolf DC, Beheridge TJ, Bailey GW. Sorption of heavy metals by the soil fungi *Aspergillus niger* and *Mucor rouxii*. *Soil Biol Biochem* 1992;24:129.
- [17] Lodeiro P, Barriada JL, Herrero R, Sastre de Vicente ME. The marine macroalga *Cystoseira baccata* as biosorbent for cadmium(II) and lead(II) removal: kinetic and equilibrium studies. *Environ Pollut* 2006;142:264.
- [18] Aksu Z, Gonen F, Demircan Z. Biosorption of chromium(VI) ions by Mow-ital B₃OH resin immobilized activated sludge in a packed bed: comparison with granular activated carbon. *Process Biochem* 2002;38:175.
- [19] Amini M, Younesi H, Bahramifar N, Lorestani AAZ, Ghobani F, Daneshi A, et al. Application of response surface methodology for optimization of lead biosorption in an aqueous solution *Aspergillus niger*. *J Hazard Mater* 2008;154:694.
- [20] Iqbal M, Edyvean R. Biosorption of lead, copper and zinc ions on loofa sponge immobilized biomass of *Phanerochaete chrysosporium*. *Miner Eng* 2004;17:217.
- [21] Yan G, Viraraghavan T. Heavy metal removal in a biosorption column by immobilized *M. rouxii* biomass. *Bioresour Technol* 2001;78:243.
- [22] Akar T, Tunali S. Biosorption performance of *Botrytis cinerea* fungal by products for removal of Cd(II) and Cu(II) ions from aqueous solutions. *Miner Eng* 2005;18:1099.
- [23] Akar T, Tunali S, Kiran I. *Botrytis cinerea* as a new fungal biosorbent for removal of Pb(II) from aqueous solutions. *Biochem Eng J* 2005;25:227.
- [24] Lagergren S. Zur Theorie Der Sogenannten Adsorption Geloster Stoffe. *Kunigliga Svenska Vetenskapsakademiens. Handlingar Band 1898*;24:1.
- [25] Ho YS, McKay G. Pseudo-second order model for sorption processes. *Process Biochem* 1999;34:451.
- [26] Weber WJ, Morris JC. Kinetics of adsorption on carbon from solution. *J Sanitary Eng Div Am Soc Civil Eng* 1963;89:31.

- [27] Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum. *J Am Chem Soc* 1918;40:1361.
- [28] Freundlich H. Über die adsorption in losungen. *J Phys Chem* 1907;57:385.
- [29] Tahir SS, Rauf N. Thermodynamic studies of Ni(II) adsorption onto bentonite from aqueous solution. *J Chem Thermodyn* 2003;35:2003.
- [30] Ghaedi M, Asadpou E. Simultaneous preconcentration and determination of copper, nickel, cobalt, lead, and iron content using a surfactant-coated alumina. *Bull Chem Soc Jpn* 2006;79:432.
- [31] Jarosz-wilkolazka A, Malarczyk E, Pirszel J, Skowronski T, Leonowicz A. Uptake of cadmium ions in white-rot fungus *Trametes versicolor*: effect of Cd(II) ions on the Activity of Laccase. *Cell Biol Int* 2002;26:605.
- [32] Tsezos M, Velosky B. The mechanism of uranium biosorption by *Rhizopus arrhizus*. *Biotechnol Bioeng* 1982;29:385.
- [33] Friis N, Myers-Keith P. Biosorption of uranium and lead by *Streptomyces longwoodensis*. *Biotechnol Bioeng* 1986;28:21.
- [34] Sag Y, Ozer D, Kutsal T. A Comparative study of the biosorption of lead(II) ions to *Z. ramigera* and *R. arrhizus*. *Process Biochem* 1995;30:169.
- [35] Matheickal JT, Yu Q. Biosorption of lead(II) from aqueous solutions by *Phellinus badius*. *Miner Eng* 1997;10:947.
- [36] Aksu Z. Equilibrium and kinetic modeling of cadmium(II) biosorption by *C. Vulgaris* in a batch system: effect of temperature. *Sep Purif Technol* 2001;21:285.
- [37] Say R, Denizli A, Arica MY. Biosorption of cadmium(II), lead(II) and copper(II) with the filamentous fungus *Phanerochaete chrysosporium*. *Bioresour Technol* 2001;76:67.
- [38] Yan G, Viraraghavan T. Heavy metal removal from aqueous solution by fungus *Mucor rouxii*. *Water Res* 2003;37:4486.
- [39] Cruz CCV, Da Costa ACA, Henriques CAV, Luna AS. Kinetic modeling and equilibrium studies during cadmium biosorption by dead *Sargassum* sp. biomass. *Bioresour Technol* 2004;91:249.
- [40] Li Q, Wu S, Liu G, Liao X, Deng X, Sun D, et al. Simultaneous biosorption of cadmium(II) and lead(II) ions by pretreated biomass of *Phanerochaete chrysosporium*. *Sep Purif Technol* 2004;34:135.
- [41] Ozdemir G, Ceyhan N, Ozturk T, Akirmak F, Cosar T. Biosorption of chromium(VI), cadmium(II) and copper(II) by *Pantoea* sp. TEM18. *Chem Eng J* 2004;102:249.
- [42] Sheng PX, Ting YP, Chen JP, Hong L. Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms. *J Colloid Interface Sci* 2004;275:131.
- [43] Chojnacka K, Chojnacki A, Gorecka H. Biosorption of Cr⁺³, Cd⁺² and Cu⁺² ions by blue-green alga *Spirulina* sp.: kinetics, equilibrium and the mechanism of the process. *Chemosphere* 2005;59:75.
- [44] Akar T, Tunalı S. Biosorption characteristics of *Aspergillus flavus* biomass for removal of Pb(II) and Cu(II) ions from an aqueous solution. *Bioresour Technol* 2006;97:1780.
- [45] Arzu YD. A comparative study on determination of the equilibrium, kinetic and thermodynamic parameters of biosorption of copper(II) and lead(II) ions onto pretreated *Aspergillus niger*. *Biochem Eng J* 2006;28:187.
- [46] Pavasant P, Apiratikul R, Sungkhum V, Suthiparinyanont P, Wattanachira S, Marhaba TF. Biosorption of Cu(II), Cd(II), Pb(II) and Zn(II) using dried marine green macroalga *Caulerpa lentillifera*. *Bioresour Technol* 2006;97:2321.
- [47] Rakhshae R, Khosravi M, Ganji MT. Kinetic modeling and thermodynamic study to remove Pb(II), Cd(II), Ni(II) and Zn(II) from aqueous solution using dead and living *Azolla filiculoides*. *J Hazard Mater* 2006;134:120.
- [48] Tunalı S, Akar T, Ozcan AS, Koran I, Ozcan A. Equilibrium and kinetics of biosorption of lead(II) from aqueous solutions by *Cephalosporium aphidicola*. *Sep Purif Technol* 2006;47:105.
- [49] Uslu G, Tanyol M. Equilibrium and thermodynamic parameters of single and binary mixture biosorption of lead(II) and copper(II) ions *Pseudomonas putida*: effect of temperature. *J Hazard Mater* 2006;135B:87.
- [50] Yu J, Tong M, Sun X, Li B. Cystine-modified biomass for Cd(II) and Pb(II) biosorption. *J Hazard Mater* 2007;143:277.
- [51] Fan T, Liu Y, Feng B, Zeng G, Yang C, Zhou M, et al. Biosorption of cadmium(II) and lead(II) by *Penicillium simplicissimum*: Isotherms, kinetics and thermodynamics. *J Hazard Mater* 2008;160:655.
- [52] Gupta VK, Rastogi A. Equilibrium and kinetic modeling of cadmium(II) biosorption by nonliving algal biomass *Oedogonium* sp. from aqueous phase. *J Hazard Mater* 2008;153:759.
- [53] Sari A, Mendil D, Tuzen M, Soylak M. Biosorption of Cd(II) and Cr(III) from aqueous solution by moss (*Hylocomium splendens*) biomass: equilibrium, kinetic and thermodynamic studies. *Chem Eng J* 2008;144:1.
- [54] Sari A, Tuzen M. Biosorption of Pb(II) and Cd(II) from aqueous solution using green alga (*Ulva lactuca*) biomass. *J Hazard Mater* 2008;152:302.
- [55] Sari A, Tuzen M. Kinetic and equilibrium studies of biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (*Amanita rubescens*) biomass. *J Hazard Mater* 2009;164:1004.
- [56] Anayurt RA, Sari A, Tuzen M. Equilibrium, thermodynamic and kinetic studies on biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (*Lactarius scrobiculatus*) biomass. *Chem Eng J* 2009;151:255.
- [57] Lawal OS, Sanni AR, Ajayi IA, Rabi OO. Equilibrium, thermodynamic and kinetic studies for the biosorption of aqueous lead(II) ions onto the seed husk of *Calophyllum inophyllum*. *J Hazard Mater* 2010;177:829.