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Biosorption of cadmium(II), zinc(II) and lead(II) by *Penicillium simplicissimum*: Isotherms, kinetics and thermodynamics

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ABSTRACT

The isotherms, kinetics and thermodynamics of Cd(II), Zn(II) and Pb(II) biosorption by *Penicillium simplicissimum* were investigated in a batch system. The effects of pH, initial metal ions concentration, biomass dose, contact time, temperature and co-ions on the biosorption were studied. Adsorption data were well described by both the Redlich–Peterson and Langmuir model. Chemical ion-exchange was found to be an important process based on free energy value from Dubini–Radushkevich isotherm for all metal ions. The results of the kinetic studies of all metal ions at different temperature showed that the rate of adsorption followed the pseudo second-order kinetics well. The thermodynamics constants ΔG°, ΔH° and ΔS° of the adsorption process showed that biosorption of Cd(II), Zn(II) and Pb(II) ions on *Penicillium simplicissimum* were endothermic and spontaneous.

1. Introduction

Heavy metal pollution has become one of the most serious environmental problems today. Many industries including metal plating, mining, battery, pigment, dyestuff and chemical industries release heavy metals [1]. These heavy metals cause serious threat to environment, animals and human for their extreme toxicity. Cadmium, zinc and lead are potential hazardous if discharged in large quantity due to high toxicity, which is why they arouse special consideration.

Heavy metal ions are commonly removed by chemical precipitation, ion exchange, solvent extraction and chemical oxidation–reduction, but these methods are relatively expensive and ineffective especially when the concentration of heavy metal is in the range of 1–100 mg l^{-1} [2,3]. Biosorption, based on the interactions between living or non-living microorganisms and metallic ions in the system [4,5], offers the advantages such as low operating cost and high efficiency of removing low concentration heavy metal from wastewater [6]. Biosorption has received more attraction recently in the investigation of operating conditions and machines for scavenging heavy metal ions from industrial wastewater by microorganisms [7].

Many microbial species such as algae (e.g. *Sargassum natans*), bacteria (e.g. *Bacillus subtillis*) fungi (e.g. *Rhizopus arrhizus*), yeast (e.g. *Saccharomyces cerevisae*) and waste microbial biomass from fermentation and food industry were known to have high metal adsorbing capacities [8–10]. Among the main strains, fungi biomasses have a high percentage of cell wall material that shows excellent metal-binding properties. *Penicillium* such as *Penicillium notatum*, *Penicillium chysogenum* and *Penicillium austurianum* have already been studied as potential biomass for removal of heavy metals from aqueous solution [11,12]. However, much less is known about temperature dependence of biosorption kinetics and thermodynamics by *Penicillium simplicissimum* (*P. simplicissimum*).

The present study investigates the ability of *P. simplicissimum* in Cd(II), Zn(II) and Pb(II) removal. The biosorption process was studied through batch experiments with regard to the effects of pH, initial metal ions concentration, biomass dose, contact time, temperature and co-ions. In addition to this, the biosorption equilibrium was evaluated using the Langmuir, Freundlich, Redlich–Peterson and Dubini–Radushkevich isotherm. Kinetics and thermodynamics of the biosorption at various temperatures were also studied.

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2. Materials and methods

2.1. Microorganisms and growth conditions

P. simplicissimum used in this study was isolated from the soil of Yuelu Mountain (Hunan University, Changsha, Hunan, China), which was identified by Biolog Microatation System (Biolog Company, USA). The strain was maintained on potato-dextrose agar slants and stored at 4 °C.

The fungus was cultivated on a rotary shaker (120 rpm) at 28 °C for 72 h in 250 ml conical Erlenmeyer flask containing 100 ml of growth medium. The growth medium consisted of ($g\,l^{-1}$): dextrose, 20; peptone, 10; NaCl, 0.2; $CaCl_2$, 0.1; KCl, 0.1; K_2HPO_4, 0.5; $NaHCO_3$, 0.05; $MgSO_4$, 0.25; $FeSO_4{\cdot}7H_2O$, 0.005. The harvested biomass was washed with distilled water, dried at 60 °C for 24 h, and powdered in a mortar to pass through a 60-mesh sieve, then was stored in a desiccator and used for the following experiments.

2.2. Chemicals

Nitrate salts ($Cd(NO_3)_2{\cdot}4H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$ and $Pb(NO_3)_2$) of analytical grade were used to prepare 1000 mg l^{-1} stock metal ions solutions, which were diluted to make metal ions solutions for the adsorption. Before the microorganisms were mixed, the pH value of each test metal solution was adjusted to desirable value with 1 mol l^{-1} NaOH or 1 mol l^{-1} HNO_3.

2.3. Biosorption experiments for single-metal systems

The factors that affect the biosorption capacity of the biosorbent were examined in a batch system. All batch experiments were carried out in 250 ml conical Erlenmeyer flasks with 100 ml metal solution on a rotary shaker.

The effect of pH on the sorption capacity of *P. simplicissimum* for Cd(II), Zn(II) and Pb(II) was evaluated in the pH range of 1.0–6.0. The initial pH of each metal solution was adjusted to the required pH value by using 1 mol l^{-1} NaOH or 1 mol l^{-1} HNO_3. Then 0.1 g of dried biosorbent was added to the metal solution and the reaction mixture was shaken on an orbital shaker at 120 rpm and 28 °C for 12 h, which was enough for adsorption equilibrium. Similarly, the biomass dose (0.1–0.6 g), initial metal ion concentration (0–300 mg l^{-1}), contact time (0–12 h) and temperature (20–40 °C) on the metals species sorption were performed. In the biosorption experiments, unless otherwise conditions stated, the initial metal concentration, temperature, and biomass dose were 50 mg l^{-1}, 28 °C and 0.1 g, respectively.

In kinetic studies, samples were taken out at different time. Samples were taken at given time intervals and centrifuged at 5000 rpm for 10 min, then the supernatant fractions were separated and analyzed for the remaining metal ions. All the experiments were conducted in triplicate and average values were used in the data analysis.

2.4. Biosorption experiments for multiple-metal systems

To determine the adsorption characteristics of metal ions in binary and ternary metal mixtures, the initial concentrations of the selected metal ions were 50 mg l^{-1}. All the experiments for the multiple-metal systems were conducted at pH 5.0, temperature 28 °C, and biomass dose 0.1 g for 12 h.

The amount of heavy metal adsorbed by the biomass was calculated using the following equation:

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

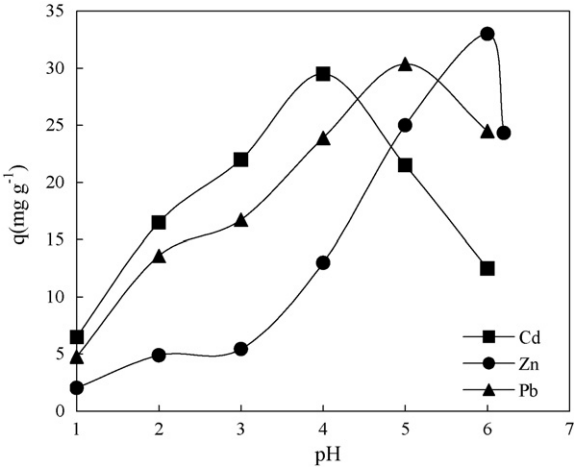

Fig. 1. Effects of pH on biosorption of Cd(II), Zn(II) and Pb(II) ions by *P. simplicissimum* (initial concentration, 50 mg l^{-1}; biomass dose, 0.1 g; contact time, 12 h; temperature 28 °C).

where q is the amount of metal adsorbed by biomass (mg g^{-1}), C_0 is the initial concentration of metal ion (mg l^{-1}), C_e is the final concentration of metal ion (mg l^{-1}), m is the mass of the biomass in the adsorption medium (g), V is the initial volume of the adsorption medium (l).

The concentrations of residual Cd(II), Zn(II) and Pb(II) ions in the solution were determined by an atomic adsorption spectrophotometer (PE AA700 USA).

3. Results and discussion

3.1. Effect of initial pH

Solution initial pH is a critical parameter for adsorption experiments [13]. The solution pH strongly influences the solution chemistry of the metals, the activity of functional groups (carboxylate, phosphate and amino groups) on the cell wall as well as the competition of metallic ions for the binding site [10]. Fig. 1 shows the effects of the initial pH on biosorption of Cd(II), Zn(II) and Pb(II) ions in aqueous solution. Maximum biosorption capacities were obtained at pH 4.0, 6.0 and 5.0 for Cd(II), Zn(II) and Pb(II), respectively. At low pH (<1.0) the biosorption capacity for all metal ions is very low, because large quantity of hydrogen ions competes with metal ions at sorption sites. As the pH increasing, more negatively charged cell surface become available thus facilitating greater metal uptake [14]. However, metal precipitates at high pH values (>7.0) inhibit the contact of metal with the most fungal biomass. Consider the comparability of a single metal biosorption and competitive biosorption at same conditions and to ensure no interference from metal precipitation, subsequent experiments were carried out at pH 5.0. Similar results appeared in previous studies related to the biosorption of Cd(II), Zn(II) and Pb(II) on *Trametes versicolor* [15] and *L. taylorii* [16].

3.2. Effects of biomass dose and initial metal ion concentration

The influences of biomass dose and initial metal ion concentration on biosorption were studied at temperature of 28 °C and pH 5.0. Fig. 2 shows that all the curves have the same trend, i.e. an initial quick decrease followed by a final stability, with the increasing of biomass dose. This was due to the interference between binding sites and higher biomass dose or insufficiency of metal ions in solution with respect to available binding sites [17].

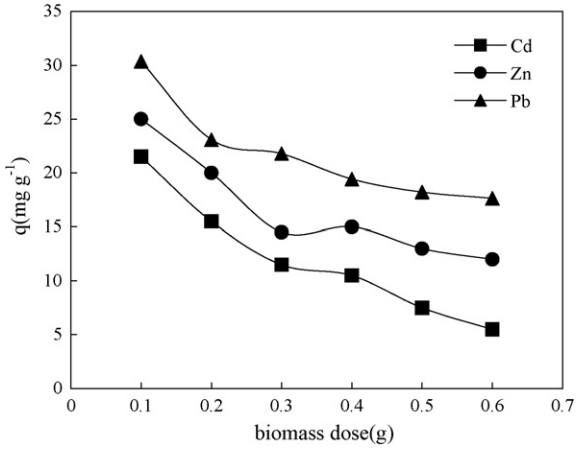

Fig. 2. Effects of biomass dose on biosorption of Cd(II), Zn(II) and Pb(II) ions by *P. simplicissimum* (pH 5.0; initial concentration, 50 mg l^{-1}; contact time, 12 h; temperature, 28 °C).

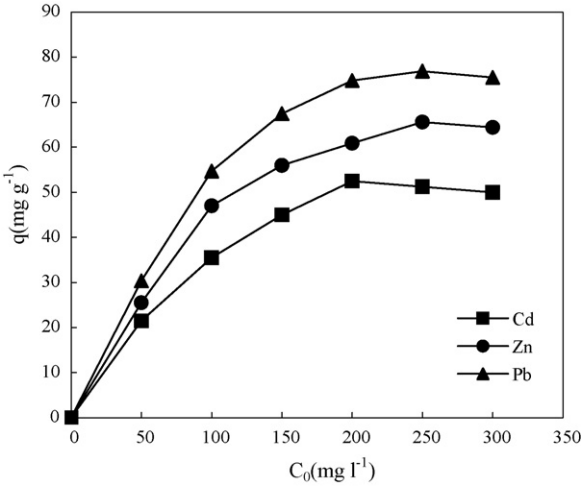

Fig. 3. Effects of initial concentration on biosorption of Cd(II), Zn(II) and Pb(II) ions by *P. simplicissimum* (pH 5.0; biomass dose, 0.1 g; contact time, 12 h; temperature, 28 °C).

The biosorption of Cd(II), Zn(II) and Pb(II) ions by *P. simplicissimum* increased with increasing initial metal concentration, and became saturated at 200 mg l^{-1} for Cd(II), 250 mg l^{-1} for Zn(II) and Pb(II) (Fig. 3). The maximum Cd(II), Zn(II) and Pb(II) uptake capacity were determined as 52.50, 65.60 and 76.90 mg g^{-1}, respectively. These results may be explained that the initial metal concentration provides a driving force to overcome all mass transfer resistances between the biosorbent and biosorption medium. Hence higher sorption capacities were obtained at higher initial metal concentration for the three metal ions.

Compared with many reported literatures, the results obtained from this study were found to be promising (Table 1).

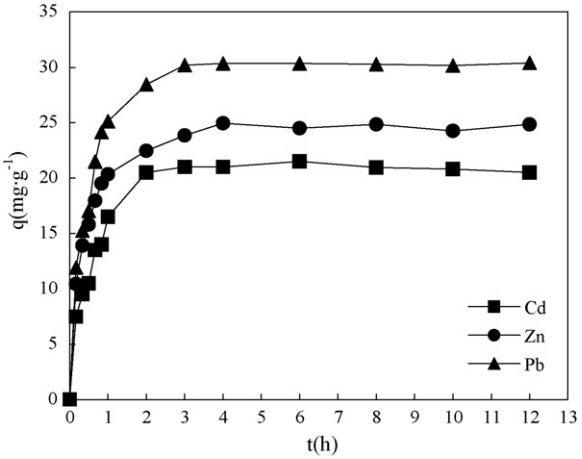

Fig. 4. Effects of contact time on biosorption of Cd(II), Zn(II) and Pb(II) ions by *P. simplicissimum* (pH 5.0; initial concentration, 50 mg l^{-1}; biomass dose, 0.1 g; temperature, 28 °C).

3.3. Effects of contact time and temperature

The effects of contact time on Cd(II), Zn(II) and Pb(II) uptake capacity by *P. simplicissimum* were given in Fig. 4. The biosorption capacity increased with increasing contact time and a large amount of metal ions was removed in the first 1 h. Equilibrium was reached in 3 h for Cd(II), 4 h for Zn(II) and Pb(II), respectively. After the equilibrium time, no more Cd(II), Zn(II) and Pb(II) were adsorbed.

It was shown that the uptake amount of all metal ions increased with increasing temperature from 20 to 40 °C (Fig. 5). So the biosorption of Cd(II), Zn(II) and Pb(II) was endothermic in the extent. The sorption of Cd(II), Zn(II) and Pb(II) ions may involve not only physical but also chemical sorption. This effect may be caused by the increasing of active sites due to bond rupture at higher temperatures.

3.4. Biosorption from binary and trinary metal solution

Simultaneous biosorption of Cd(II), Zn(II) and Pb(II) ions by *P. simplicissimum* was studied using a medium that contained 50 mg l^{-1} of each metal ion. The results of the biosorption of the binary system and the ternary system

Table 1
Previously reported adsorption capacities for various adsorbents for metal ion adsorptions

Biosorbent	Adsorption capacity (mg g^{-1})		pH	Temperature (°C)	Concentration (mg l^{-1})	Biomass (g l^{-1})	Reference
Mucor rouxii	Cd(II)	20.31	6.0	–	10	0.67	[18]
Pantoea sp.	Cd(II)	52.00	6.0	25	95.8	1.0	[19]
C. vulgaris	Cd(II)	67.00	4.0	30	200	0.75	[20]
P. simplicissimum	Cd(II)	52.50	5.0	28	200	1.0	This study
P. digitatum	Zn(II)	9.70	5.5	25	25	7.0	[21]
Mucor rouxii	Zn(II)	53.85	6.0	–	10	0.67	[18]
Botrytis cinerea	Zn(II)	12.98	5.0–6.0	25	100	2.0	[22]
P. simplicissimum	Zn(II)	65.60	5.0	28	250	1.0	This study
A. niger	Pb(II)	32.60	4.0	35	250	1.0	[23]
P. putida	Pb(II)	180.41	5.5	25	270.62	1.0	[24]
C. aphidicola	Pb(II)	36.91	5.0	30	100	2.0	[25]
P. simplicissimum	Pb(II)	76.90	5.0	28	250	1.0	This study

Table 2
Effect of co-ions on biosorption of Cd(II), Zn(II) and Pb(II) by *P. simplicissimum*

	Adsorption capacity ($mg\,g^{-1}$)				
	Single	Co-ions			
		Cd(II) + Zn(II)	Cd(II) + Pb(II)	Pb(II) + Zn(II)	Cd(II) + Zn(II) + Pb(II)
Cd(II)	21.50	13.61	10.19	–	6.94
Zn(II)	25.54	19.41	–	20.03	18.72
Pb(II)	30.37	–	16.98	24.23	13.38

on biomass were shown in Table 2. In binary Cd(II) + Pb(II) system, the presence of Cd(II)/Pb(II) ions resulted in the inhibition in Cd(II)/Pb(II) uptake, and this observation was much more significant than those in the presence of Cd(II) + Zn(II) or Zn(II) + Pb(II) system. The biosorption capacities of in the presence of the binary and trinary metal mixture were lower than that of noncompetitive conditions. The results clearly showed that the combined action of multiple ions was antagonistic. The most likely reason for the antagonistic effect was the competition for adsorption sites on the cell surfaces and/or the screening effect by the competing metal ions. Results showed that Cd(II) exerted the most inhibitory effect on the biosorption of other metals, followed by Pb(II) and Zn(II).

A similar phenomenon had been observed in the binary adsorption Pb(II) and Cu(II) biosorption onto *Aspergillus flavus*, where it was shown that Pb(II) and Cu(II) strongly competed with each other, the biosorption capacities of the binary metal mixture were lower than that of noncompetitive conditions and the uptake capacities of Pb(II) ions were smaller influence than Cu(II) ions [26].

3.5. Biosorption isotherm

In this study, Langmuir, Freundlich, Redlich–Peterson (R–P) and Dubini–Radushkevich (D–R) isotherms were applied to describe the equilibrium between adsorbed metal ions and metal ions in solution. The Langmuir isotherms equation is valid for monolayer sorption on to surface containing finite number of identical sorption sites which is described by the following equation [27]:

$$q_{eq} = \frac{q_{max} b C_{eq}}{1 + bC_{eq}} \quad (2)$$

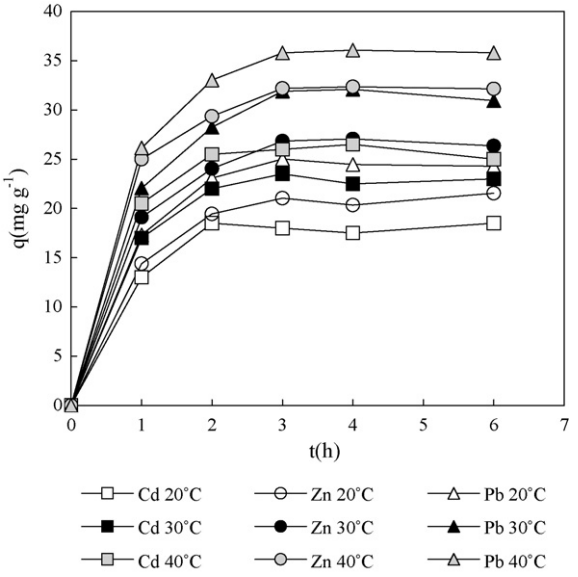

Fig. 5. Effects of temperature on biosorption of Cd(II), Zn(II) and Pb(II) ions by *P. simplicissimum* (pH 5.0; initial concentration, 50 $mg\,l^{-1}$; biomass dose, 0.1 g; contact time, 6 h).

where q_{eq} ($mg\,g^{-1}$) and C_{eq} ($mg\,l^{-1}$) are the amount of adsorption and the residual concentration in solution at equilibrium, respectively. q_{max} ($mg\,g^{-1}$) and b ($l\,mg^{-1}$) are maximum adsorption capacity and a constant related to adsorption energy of adsorption, respectively, which can be determined by the linearized Langmuir isotherm as follows:

$$\frac{C_{eq}}{q_{eq}} = \frac{C_{eq}}{q_{max}} + \frac{1}{bq_{max}} \quad (3)$$

The Freundlich equation is purely empirical based on sorption on a heterogeneous surface, which is commonly presented as:

$$q_{eq} = K_F C_{eq}^{1/n} \quad (4)$$

where K_F ($(mg\,g^{-1})(mg\,l^{-1})^n$) and n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively [27].

The R–P equation contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms [28]. The R–P isotherm can be described as follows:

$$q_{eq} = \frac{K_{RP} C_{eq}}{1 + a_{RP} C_{eq}^{\beta}} \quad (5)$$

Where K_{RP}, a_{RP} and β are the R–P parameters. β Lies between 0 and 1. For $\beta = 1$, the R–P equation convert to Langmuir form. When K_{RP} and a_{RP} are much greater than unity, the equation can transform Freundlich form. The integrated form of Eq. (5) is

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{K_{RP}} + \frac{a_{RP} C_{eq}^{\beta}}{K_{RP}} \quad (6)$$

The D–R isotherm is more general than the Langmuir isotherm, because it does not assume a homogeneous surface or constant sorption potential. The D–R equation is [29]:

$$q_{eq} = q_{max} \exp(-B[RT \ln(1 + 1/C_{eq})]^2) \quad (7)$$

Where B is a constant related to the adsorption energy, R ($8.314\,J\,mol^{-1}\,K^{-1}$) is the gas constant, and T (K) is the absolute temperature.

The constant B ($mol^2\,kJ^{-2}$) gives the mean free energy E ($kJ\,mol^{-1}$) of sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and

Table 3
Adsorption isotherm parameters for adsorption of Cd(II), Zn(II) and Pb(II) by *P. simplicissimum*

	Cd(II)	Zn(II)	Pb(II)
Langmuir			
q_{max} ($mg\,g^{-1}$)	61.35	77.52	87.72
b ($l\,mg^{-1}$)	0.023	0.025	0.035
R^2	0.981	0.992	0.993
Freundlich			
K_F ($(mg\,g^{-1})(mg\,l^{-1})^n$))	9.032	8.248	11.600
n	2.68	2.50	2.45
R^2	0.900	0.887	0.884
Redlich–Peterson			
K_{Rp} ($l\,g^{-1}$)	0.901	0.098	1.422
a_{RP} ($(l\,mg^{-1})^{\beta}$)	0.005	0.004	0.006
β	1.340	1.244	1.195
R^2	0.995	0.992	0.997
Dubini–Radushkevich			
q_{max} ($mg\,g^{-1}$)	168.62	189.60	248.64
B ($10^{-3}\,mol^2\,kJ^{-2}$)	4.6	4.8	3.7
E ($kJ\,mol^{-1}$)	10.43	10.21	11.62
R^2	0.921	0.915	0.907

can be computed using the relationship [30]:

$$E = \frac{1}{(2B)^{0.5}} \quad (8)$$

This parameter gives information about chemical or physical adsorption. The magnitude of E is between 8 and 16 kJ mol^{-1}, the biosorption process follows chemical ion-exchange, while for the values of $E < 8$ kJ mol^{-1}, the biosorption process is of a physical nature [25].

The R–P parameters were obtained by non-linear regression analysis and other parameters by linear regression analysis using SPSS 14.0. The adsorption constants in Table 3 show that the three-parameter R–P model describes the adsorption of metal ions better than that of Langmuir, Freundlich and D–R models. Indeed, the values of β were closer to unity than 0, which implied that the isotherm was more approaching the Langmuir than the Freundlich isotherm. Hence, the monolayer coverage process of heavy metal onto *P. simplicissimum* was approved by the best fit of equilibrium data in both R–P and Langmuir isotherm expressions.

In the Freundlich model, the n values in the range of 1–10 indicated favorable adsorption. All the E values from D–R model were between 8 and 16 kJ mol^{-1}, which may correspond to a chemical ion-exchange mechanism.

The values of q_{max} obtained from the Langmuir model for Cd(II), Zn(II) and Pb(II) on *P. simplicissimum* closed to the experimental values, and this could be evidence that the surface of the sorbent were homogenous. On the other hand, the sorption capacities q_{max} derived from D–R model for all metal ions biosorption were quite different to the q_{max} values at the Langmuir region. This may be attributed to the different assumptions considered in the formulation of the isotherms. The differences were also reported in other studies [31,32].

3.6. Kinetic modeling

With respect to the kinetic modeling of Cd(II), Zn(II) and Pb(II) biosorption, the pseudo first-order and pseudo second-order rate equation have been used. The first-order rate equation of Lagergren based on solid capacity is expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_{eq} - q_t) \quad (9)$$

where q_t is sorption capacity at time t and k_1 is first-order rate constant. The integrated form of Eq. (9) is

$$\log(q_{eq} - q_t) = \log q_{eq} - \frac{k_1}{2.303}t \quad (10)$$

where value of k_1 can be determined from the slope of the plot of the $\log(q_{eq} - q_t)$ versus t. In most cases the first-order equation of Lagergren does not fit well over the entire adsorption period and is generally applicable over the initial 30–50 min of the sorption process [33].

Which is different to the pseudo first-order model, the pseudo second-order model predicts the behavior over the whole time adsorption and is in agreement with adsorption mechanism being the rate-controlling step. The pseudo second-order rate equation is expressed as:

$$\frac{dq_t}{dt} = k_2(q_{eq} - q_t)^2 \quad (11)$$

where k_2 is pseudo second-order rate constant. The integrated form of Eq. (11) is

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}}t \quad (12)$$

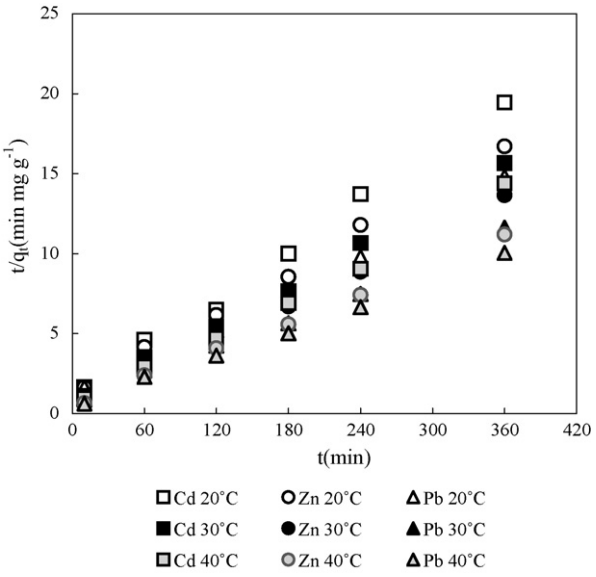

Fig. 6. Linearized pseudo second-order kinetic plots of Cd(II), Zn(II) and Pb(II) ions by *P. simplicissimum*.

where k_2 can be determined from the intercept of linearized plot of t/q_t versus t (Fig. 6).

The applicability of the first-order and second-order kinetic model was tested in the range of 20–40 °C. The results in Table 4 indicate that the second-order kinetic constants increase with increasing temperature. The correlation coefficients of the second-order kinetic model were greater than 0.994 for all cases, and the theoretical q_{eq} values were also agreed well with the experimental data. On the other hand, the correlation coefficients for the pseudo first-order kinetics were lower than those for the second-order. In addition, the values of k_1 obtained from the former had no obvious increase or decrease with increasing temperature. These imply that the biosorption of Cd(II), Zn(II) and Pb(II) on *P. simplicissimum* follows the pseudo second-order kinetics rather than the pseudo first-order one.

3.7. Thermodynamic parameters

Thermodynamic parameters such as Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) can be estimated using equilibrium constants changing with temperature. The Gibbs free energy change of the sorption reaction is given by

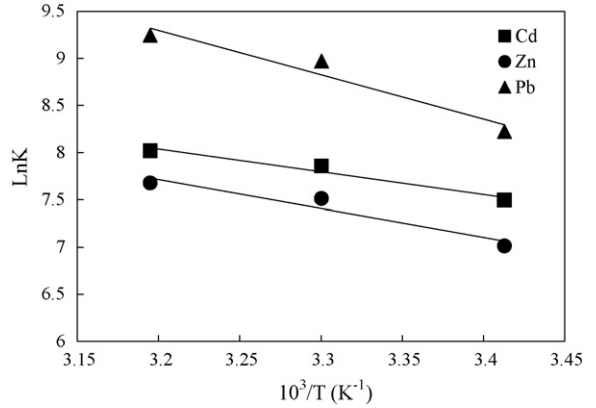

Fig. 7. The plot of van't Hoff plot of ln K against $10^3/T$.

Table 4
The first-order and second-order kinetics constants for biosorption of Cd(II), Zn(II) and Pb(II) ions by *P. simplicissimum*

T (°C)	First-order kinetic			Second-order kinetic		
	k_1 ($\times 10^{-2}$) (min^{-1})	q_{eq} (mg g^{-1})	r^2	k_2 ($\times 10^{-3}$) (g mg^{-1} min^{-1})	q_{eq} (mg g^{-1})	r^2
Cd(II)						
20	2.44	14.91	0.988	2.41	19.61	0.995
30	2.12	17.80	0.991	2.42	23.98	0.997
40	2.53	18.53	0.982	3.67	26.74	0.995
Zn(II)						
20	1.82	16.50	0.984	1.46	23.36	0.997
30	1.54	17.89	0.956	1.85	28.33	0.996
40	1.57	19.81	0.990	1.93	33.40	0.999
Pb(II)						
20	2.00	20.07	0.983	1.40	26.11	0.994
30	1.45	23.26	0.985	1.43	33.56	0.995
40	1.58	26.99	0.989	1.49	38.02	0.998

Table 5
The thermodynamic parameters of biosorption by *P. simplicissimum*

Metal ions	T (°C)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})
Cd(II)	20	−18.27	20.03	130.90
	30	−19.81		
	40	−20.88		
Zn(II)	20	−17.08	25.42	145.48
	30	−18.92		
	40	−19.98		
Pb(II)	20	−20.04	39.13	202.52
	30	−22.60		
	40	−24.06		

the following [34,35]:

$$\Delta G^\circ = -RT \ln K \quad (13)$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (14)$$

where K is the equilibrium constant, which can be obtain from Langmuir isotherms at different temperature (data not show). ΔH° and ΔS° were obtained from the slope and intercept of van't Hoff plot of $\ln K$ against $10^3/T$ (Fig. 7). The values of ΔG°, ΔH° and ΔS° were given in Table 4.

The negative ΔG° values of Cd(II), Zn(II) and Pb(II) at various temperatures approved the adsorption processes were spontaneous, and the values of ΔG° (Table 5) decreased with an increase in temperature, indicated that the spontaneous nature of adsorption of Cd(II), Zn(II) and Pb(II) were inversely proportional to the temperature. Enhancement of adsorption capacity at higher temperatures may be attributed to the enlargement of pore size and/or activation of the adsorbent surface. The positive value of ΔH° illuminated the endothermic nature of biosorption. The positive value of ΔS° suggested the increase randomness at the solid/solution interface during the biosorption of metal ions on *P. simplicissimum*.

4. Conclusion

The high potential of *P. simplicissimum* to remove Cd(II), Zn(II) and Pb(II) from aqueous solution was demonstrated in this study. The initial pH significantly influenced Cd(II), Zn(II) and Pb(II) uptake. The sorption capacities of Cd(II), Zn(II) and Pb(II) ions increased with initial metal ions concentration and temperature increased, but decreased with the biomass dose increased. The maximum loading capacity followed the order of Pb(II) > Zn(II) > Cd(II). In the case of binary and trinary metal mixture, the biosorption capacity of biomass decreased for each metal ion. Biosorption equilibrium data fitted very well to both the Redlich–Peterson and Langmuir model. Chemical ion-exchange was found to be an important process based on free energy value from D–R isotherm for all metal ions. For all heavy metal ion systems at the different temperature studied, the rate of adsorption was found to follow the pseudo second-order kinetics. The thermodynamics constants ΔG°, ΔH° and ΔS° of the adsorption process showed that biosorption of Cd(II), Zn(II) and Pb(II) ions on *P. simplicissimum* were endothermic and spontaneous. The results indicated that *P. simplicissimum* may be used as an inexpensive, effective and easily cultivable biosorbent for the removal of Cd(II), Zn(II) and Pb(II) from aqueous solutions.

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