Journal of Hazardous Materials 164 (2009) 1004–1011

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Kinetic and equilibrium studies of biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (*Amanita rubescens*) biomass

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ARTICLE INFO

Article history:
Received 15 April 2008
Received in revised form 28 August 2008
Accepted 1 September 2008
Available online 5 September 2008

Keywords:
Macrofungus
Amanita rubescens
Biosorption
Pb(II)
Cd(II)

ABSTRACT

The biosorption characteristics of Pb(II) and Cd(II) ions from aqueous solution using the macrofungus (*Amanita rubescens*) biomass were investigated as a function of pH, biomass dosage, contact time, and temperature. Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models were applied to describe the biosorption isotherm of the metal ions by *A. rubescens* biomass. Langmuir model fitted the equilibrium data better than the Freundlich isotherm. The maximum biosorption capacity of *A. rubescens* for Pb(II) and Cd(II) was found to be 38.4 and 27.3 mg/g, respectively, at optimum conditions of pH 5.0, contact time of 30 min, biomass dosage of 4 g/L, and temperature of 20 °C. The metal ions were desorbed from *A. rubescens* using both 1 M HCl and 1 M HNO_3. The recovery for both metal ions was found to be higher than 90%. The high stability of *A. rubescens* permitted ten times of adsorption–elution process along the studies without a decrease about 10% in recovery of both metal ions. The mean free energy values evaluated from the D–R model indicated that the biosorption of Pb(II) and Cd(II) onto *A. rubescens* biomass was taken place by chemical ion-exchange. The calculated thermodynamic parameters, ΔG°, ΔH° and ΔS° showed that the biosorption of Pb(II) and Cd(II) ions onto *A. rubescens* biomass was feasible, spontaneous and exothermic under examined conditions. Experimental data were also tested in terms of biosorption kinetics using pseudo-first-order and pseudo-second-order kinetic models. The results showed that the biosorption processes of both Pb(II) and Cd(II) followed well pseudo-second-order kinetics. Based on all results, It can be also concluded that it can be evaluated as an alternative biosorbent to treatment wastewater containing Pb(II) and Cd(II) ions, since *A. rubescens* is low-cost biomass and has a considerable high biosorption capacity.

1. Introduction

The presence of heavy metals contaminated in aqueous streams, arising from the discharge of untreated metal containing effluent into water bodies. They are non-degradable in the environment and can be harmful to a variety of living species. Besides the toxic and harmful effects to organisms living in water, heavy metals also accumulate throughout the food chain and may affect human beings [1]. For that reason, the removal of these metals from waters and wastewaters is important in terms of protection of public health and environment [2].

Heavy metals such as cadmium (Cd) and lead (Pb) often present in industrial wastewaters, are hazardous to the aquatic ecosystem and pose possible human health risk. High levels of Pb(II) can be traced to industrial discharges from variety of sources, such as batteries, paints, pigments and ammunition, petrol, cables, alloys and steels, plastics, the glass industry. The lead contamination is also due to effluents of vehicular traffic and the mixing of roadside runoffs. The presence of Pb(II) in drinkable water is known to cause various types of serious health problems [3]. Although the inorganic form of lead is a general metabolic poison and enzyme inhibitor, organic forms are even more poisonous [4,5]. On the other hand, cadmium is also a dangerous pollutant originating from metal plating, metallurgical alloying, mining, ceramics and other industrial operations [6]. Cadmium toxicity may be observed by a variety of syndromes and effects including renal dysfunction, hypertension, hepatic injury, lung damage and teratogenic effects [7].

The most widely used methods for removing heavy metals from wastewaters include ion-exchange, chemical precipitation, reverse osmosis, evaporation, membrane filtration, adsorption biological treatment [8]. Most of these methods suffer from some drawbacks, such as high capital and operational cost or the disposal of the residual metal sludge, and are not suitable for small-scale industries [9]. Biosorption plays an important role in the elimination of metal ions from aqueous solutions in water pollution control [10,11]. The main advantages of this technique are the reusability of biomaterial, low

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doi:10.1016/j.jhazmat.2008.09.002

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 [12]. Various biomasses have been used for removal of Pb(II) and Cd(II) ions from aqueous solution [13–16].

Macrofungi are edible fungi of commercial importance and their cultivation has emerged as a promising agro-based land-independent enterprise. More than 2000 species of macrofungi exist in nature but only about 22 species are extensively cultivated for commercial purposes [17]. The consumption of wild edible macrofungi is increasing, even in the developed world, due to a good content of proteins as well as a higher content of trace minerals [18]. Fungal biomass is better suitable for the removal of metals from wastewater than biomass because of their great tolerance towards heavy metals and other adverse conditions such as low pH, high cell wall binding capacity and high intracellular metal uptake capacity [19]. Several fungal biosorbents, *Penicillium* [20], *Rhizopus arrhizus* [21], *Rhizopus oryzae and Aspergillus oryzae* [22], and *Aspergillus niger* and *Mucor rouxii* [23,24] were studied as a potential biosorbent in heavy metals removal from aqueous solution. As far as the authors are aware, there is no investigation reported in the literature on the biosorption of Pb(II) and Cd(II) using the macrofungus, *A. rubescens*.

The objective of the present work is to investigate the biosorption potential of *A. rubescens* biomass in the removal of Pb(II) and Cd(II) ions from aqueous solution. Optimum biosorption conditions were determined as a function of pH, biomass dosage, contact time, and temperature. The Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models were used to describe equilibrium isotherms. Biosorption mechanisms of Pb(II) and Cd(II) ions onto *A. rubescens* biomass were also evaluated in terms of thermodynamics and kinetics.

2. Experimental procedures

2.1. Biomass preparation

The macrofungus, *A. rubescens* was collected from the East Black Sea region of Turkey. Samples were washed with deionized water and dried in an oven at 105 °C for 48 h. The dried biomass was ground and sieved through different sizes and 200–300 μm fraction. Dried samples were homogenized using an agate homogenizer and stored in pre-cleaned polyethylene bottles until biosorption experiments.

2.2. Reagents and equipments

All chemicals 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 (Sartorius pp-15, Germany) was employed for measuring pH values in the aqueous phase. A flame atomic absorption spectrometer (PerkinElmer AAnalyst 700, USA) 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. Fourier Transform Infrared (FT-IR) spectra of dried unloaded biomass and Pb(II)-loaded biomass and Cd(II)-loaded biomass prepared as KBr discs were recorded at 400–4000 cm^{-1} wavenumber range using a FT-IR (JASCO-430, Japan) spectrometer.

2.3. Batch biosorption procedure

Biosorption experiments were optimized out at the desired pH value, contact time and biomass dosage level using the necessary biomass in a 250 mL stoppered conical flask containing 25 mL of test solution. A stock Pb(II) solution of 1000 mg/L was prepared was prepared by dissolving 1.8307 g $Pb(CH_3COOO)_2{\cdot}3H_2O$ in a 1000 mL of deionized water. A stock Cd(II) solution of 1000 mg/L was prepared was prepared by dissolving 2.3709 g $Cd(CH_3COOO)_2{\cdot}3H_2O$ in a 1000 mL of deionized water. The chemicals ($Cd(CH_3COOO)_2{\cdot}3H_2O$ and $Pb(CH_3COOO)_2{\cdot}3H_2O$) used for this study was analytical grades and they were supplied by Riedel-de Häen (Germany). Sodium phosphate buffer (0.1 mol/L) was prepared by adding an appropriate amount of phosphoric acid to sodium dihydrogen phosphate solution to result in a solution of pH 2. Ammonium acetate buffers (0.1 mol/L) were prepared by adding an appropriate amount of acetic acid to ammonium acetate solutions to result in solutions of pH 4–6. Ammonium chloride buffer solutions (0.1 mol/L) were prepared by adding an appropriate amount of ammonia to ammonium chloride solutions to result in solutions of pH 8.

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 (Selecta multimatic-55, Spain) at 120 rpm. The experiments were repeated at 20, 30, 40, and 50 °C. The time required for reaching the equilibrium condition was estimated by drawing samples at regular intervals of time till equilibrium was reached. The contents of the flask were filtered through 0.25 μm filters (Double rings, China) and the filtrate was analyzed for metal concentration by using flame AAS. Each determination was repeated three times and the results given are the average values. Standard deviations and error bars are indicated wherever necessary.

The percent biosorption of metal ion was calculated as follows:

$$\text{Biosorption } (\%) = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

where C_i and C_f are the initial and final metal ion concentrations, respectively. Biosorption experiments for the effect of pH were conducted by using a solution having 10 mg/L of Pb(II) and 10 mg/L of Cd(II) concentration with a optimum biomass dosage of 4 g/L. Throughout the study, the contact time was varied from 5 to 90 min, the pH from 2 to 8, the initial metal concentration from 10 to 400 mg/L, and the biosorbent dosage from 0.1 to 20 g/L.

2.4. Desorption procedure

A sample volume of 25 mL, containing 10 mg/L of Pb(II) and 10 mg/L of Cd(II) ions, was transferred into a beaker; 10 mL of buffer solution was added. After a fast shaking, 4 g/L of *A. rubescens* was added and the mixture was shaken again for 90 min at 100 rpm. The system was filtered with blue band filter paper. Then the filter and constituents were washed with distilled water. In order to elute the adsorbed analytes onto *A. rubescens*, 8–10 mL of 1 mol/L HNO_3 was used. The final volume was completed to 25.0 mL with 1 mol/L HNO_3. Analyte contents of the final solution were determined by flame atomic absorption spectrometry. The same procedure was applied to the blank solution. In order to use the *A. rubescens* for next experiment, *A. rubescens* was washed with excess of 1 mol/L HNO_3 and distilled water, sequentially.

3. Results and discussion

3.1. FT-IR analysis

The FT-IR spectroscopy method was used to obtain information on the nature of possible cell–metal ions interactions. The same procedure (drying at 105 °C at 48 h and followed by sieving) as biomass prepared for the FT-IR spectra of unloaded and metal ions-loaded biomass. The FT-IR spectra of unloaded and metal loaded

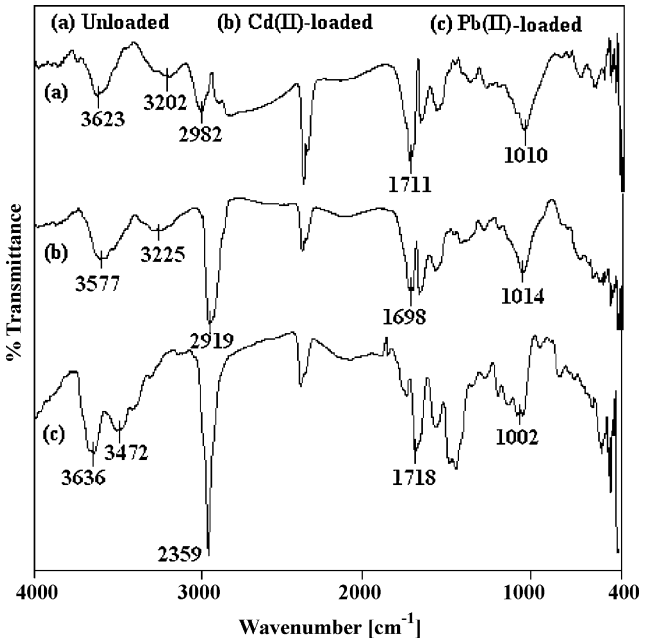

Fig. 1. FT-IR spectrum of unloaded, Cd(II)-loaded and Cd(II)-loaded biomass.

forms of biosorbent in the range of 400–4000 cm^{-1} were taken and presented in Fig. 1. The broad and strong bands at 3202–3623 cm^{-1} were due to bounded hydroxyl (–OH) or amine (–NH) groups. The peaks at 1711 cm^{-1} were attributed to stretching vibration of carboxyl group (–C=O). The bands observed at 1010 cm^{-1} were assigned to C–O stretching of alcohols and carboxylic acids. The peaks observed at 2982 cm^{-1} can be assigned to the –CH group.

The asymmetrical stretching vibration at 3202–3623 cm^{-1} shifted was to 3472–3636 and 3225–3557 cm^{-1} for Pb(II)-loaded and Cd(II)-loaded biomass, respectively. The carboxyl peak was shifted to 1718 cm^{-1} for Pb(II)-loaded biomass and to 1698 cm^{-1} for Cd(II)-loaded biomass. The peak of C–O group was shifted to 1002 and 1014 cm^{-1} to for Pb(II)-loaded and Cd(II)-loaded biomasses, respectively. The results indicated that the chemical interactions as ion-exchange between the hydrogen atoms of carboxyl (–COOH), hydroxyl (–OH), and amine (–NH) groups of the biomass and the metal ions were mainly involved in the biosorption of Pb(II) and Cd(II) onto *A. rubescens* biomass. In addition, the disappearance of the band at 784 cm^{-1} indicated that there was also clear possibly belonging to monosubstituted aromatic protons of the biosorbent indicating possibly the involvement of aromatic amino acids in the biosorption of Pb(II) and Cd(II) ions. The similar FT-IR results were reported for Pb(II), Cd(II) and Cu(II) biosorption onto *Botrytis cinerea* fungal biomass [25,26], and Cd biosorption onto *Lentinus edodes* fungal biomass [27].

3.2. Effect of pH

One of the more important factors affecting biosorption of metal ions is acidity of solution. This parameter directly related with competition ability of hydrogen ions with metal ions to active sites on the biosorbent surface [28]. Generally, metal biosorption involves complex mechanisms of ion-exchange, chelation, adsorption by physical forces, and ion entrapment in interand intrafibrillar capillaries and spaces of the cell structural network of a biosorbent [29,30]. The FT-IR spectroscopic analysis showed that the macrofungus has a variety of functional groups, such as carboxyl, hydroxyl, and amine and these groups are involved in almost all potential binding mechanisms. Moreover, depending on the pH

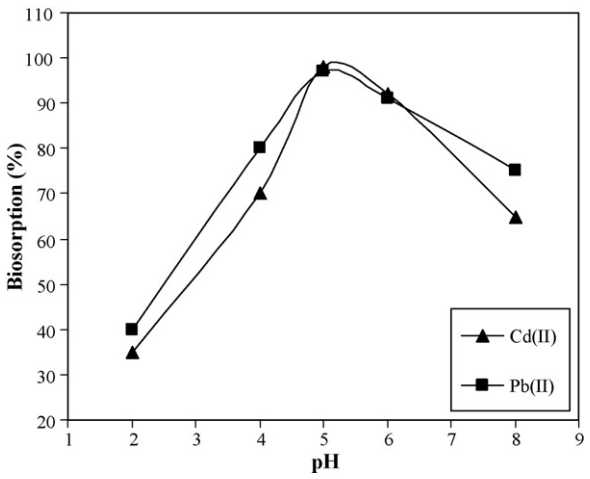

Fig. 2. Effect of pH on the biosorption of Pb(II) and Cd(II) onto *A. rubescens* biomass (metal concentration: 10 mg/L; temperature: 20 °C).

value of the aqueous solution these functional groups participate in metal ion bindings.

The effect of pH on the biosorption of Pb(II) and Cd(II) ions onto *A. rubescens* biomass was studied at pH 2–8 for initial metal concentration of 10 mg/L Pb(II) and 10 mg/L Cd(II) solution. The results regarding the pH effect on the biosorption yield of the metal ions were presented in Fig. 2. The biosorption efficiency was increased from 40% to 80% for Pb(II) biosorption and from 35% to 70% for Cd(II) ion, respectively, as pH was increased from 2 to 4. The maximum biosorption was found to be 98% for Pb(II) and 97% for Cd(II) ions at pH 5. Therefore, all the biosorption experiments were carried out at pH 5.

The biosorption mechanisms are related to physicochemical interaction of the species in solution [28,31,32]. At highly acidic pH (pH < 2.0), the overall surface charge on the active sites became positive and metal cations and protons compete for binding sites on cell wall, which results in lower uptake of metal [33,34]. When the pH of solution increased from 2 to 6, biosorbent surface were more negatively charged and the functional groups of the biomass were more deprotonated and thus available for metal ions. Especially, carboxyl groups have the highest affinity for metal ions, since they are deprotonated in a wide range of pH. Decrease in biosorption at higher pH (pH > 6) is not only related the formation of soluble hydroxilated complexes of the metal ions (lead ions in the form of $Pb(OH)_2$, and cadmium ions in form of $Cd(OH)_2$) [32] but also to the ionized nature of the cell wall surface of the biomass under the studied pH [35]. In addition, several researchers have investigated the effect of pH on biosorption of heavy metals by using different kinds of fungal biomass and reported almost same pH dependent and maximum biosorption was obtained in the pH range 5.0–7.0 [25,26].

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 concentration. The biosorption efficiency for Pb(II) and Cd(II) ions as a function of biomass dosage was investigated (Fig. 3). The percentage of the metal biosorption steeply increases with the biomass loading up to 4 g/L. 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 [36]. Moreover, the maximum biosorption, 98% for Pb(II) and 96% for Cd(II), of the metal

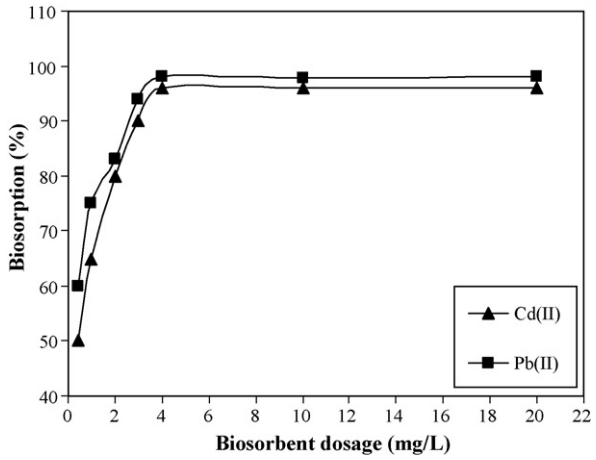

Fig. 3. Effect of biomass dosage on the biosorption of Pb(II) and Cd(II) onto *A. rubescens* biomass (metal concentration: 10 mg/L; pH: 5; temperature: 20 °C).

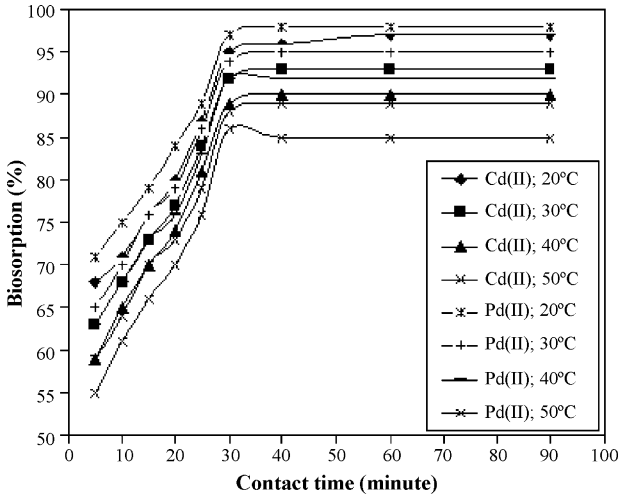

Fig. 4. Effect of contact time and temperature on the biosorption of Pb(II) and Cd(II) onto *A. rubescens* biomass (metal concentration: 10 mg/L; biomass dosage: 4 g/L; pH: 5).

ions was attained at biomass dosage, 4 g/L. However, the biosorption capacity becomes nearly constant above this dosage value. It is due to high biomass dosage resulted aggregates of biomass. This problem may cause interference between binding sites at higher biomass dosage or insufficiently of metal ions in the solution with respect to available binding sites [37]. It is likely that protons will then combine with metal ions for the ligands and thereby decrease the interaction of metal ions with the cell components [38,39]. The similar results were reported for cadmium biosorption in an aqueous solution by *Saccharomyces cerevisiae*. Therefore, the optimum biomass dosage was taken as 4 g/L for further experiments [39].

3.4. Effects of contact time and temperature

Contact time is one of the important parameters for successful use of the biosorbents for practical application and rapid sorption is among desirable parameters [40]. Fig. 4 shows the effect of contact time on the biosorption of Pb(II) and Cd(II) ions onto *A. rubescens*. The biosorption yield of Pb(II) and Cd(II) increased considerably with increasing contact time up to 30 min and after then, it was nearly constant. For instance, during 30 min (at 20 °C), when the biosorption efficiency was 97% and 98% for Pb(II) and Cd(II), respectively, it was 95% and 97%, respectively, during 90 min (at 20 °C). Therefore, the optimum contact time was selected as 30 min for further experiments.

Temperature of the medium affects on the removal efficiency of the pollutant from aqueous solution. Fig. 4 also shows the biosorption of Pb(II) and Cd(II) ions as a function of the temperature. The biosorption percentage decreased from 97% to 88% for Pb(II) and from 95% to 86% for Cd(II) as temperature was increased from 20 to 50 °C for the equilibrium time, 30 min. These results indicated the exothermic nature of Pb(II) and Cd(II) biosorption onto *A. rubescens* biomass. A decrease in the biosorption of Pb(II) and Cd(II) ions with the rise in temperature may be due to increasing tendency to desorb metal ions from the interface to the solution [41]. Optimum temperature was selected as 20 °C for further biosorption experiments.

3.5. Biosorption isotherm models

The capacity of a biomass can be described by equilibrium sorption isotherm, which is characterized by certain constants whose values express the surface properties and affinity of the biomass. The biosorption isotherms were investigated using three equilibrium models, which are namely the Langmuir, Freundlich and Dubinin–Radushkevich isotherm models were analyzed.

The Langmuir sorption isotherm has been successfully applied to many pollutant biosorption processes and has been the most widely used isotherm for the biosorption of a solute from a liquid solution. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the sorbent. This model can be written in non-linear form [42].

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

where q_e is the equilibrium metal ion concentration on the adsorbent (mg/g), C_e is the equilibrium metal ion concentration in the

Table 1
Comparison of biosorption capacity of *A. rubescens* biomass for Pb(II) and Cd(II) with that of different biosorbents

Biosorbent	Pb(II)	pH	Cd(II)	pH	Reference
Rhizopus arrhizus	–	–	26.8	6–7	[43]
Streptomyces noursei	–	–	3.4	6.0	[44]
Mucor rouxii (NaOH pretreated)	–	–	20.3	6.0	[45]
Phanerochaete chrysosporium	–	–	15.2	4.5	[46]
Ulva lactuca	34.7	5.0	29.2	5.0	[47]
Phanerochaete chrysosporium	69.8	6.0	23.0	6.0	[48]
Zoogloea ramigera	10.4	4.5	–	–	[49]
Rhizopus arrhizus	15.5	5.0	–	–	[49]
Streptomyces longwoodensis	100.0	3.0	–	–	[50]
Phellınus badıus	170.0	5.0	–	–	[51]
Cephalosporium aphidicola	36.9	5.0	–	–	[52]
Aspergillus flavus	13.5	5.0	–	–	[53]
Amanita rubescens	38.4	5.0	27.3	5.0	Present study

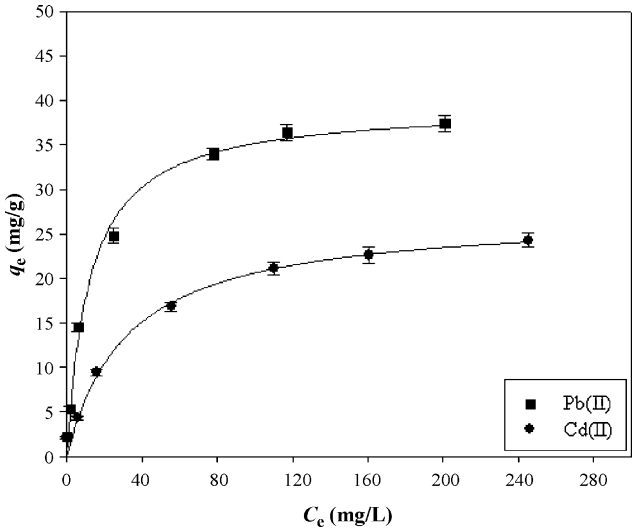

Fig. 5. Langmuir isotherm plots for the biosorption of Pb(II) and Cd(II) onto *A. rubescens* biomass (biomass dosage: 4 g/L; contact time: 30 min; pH: 5; temperature: 20 °C).

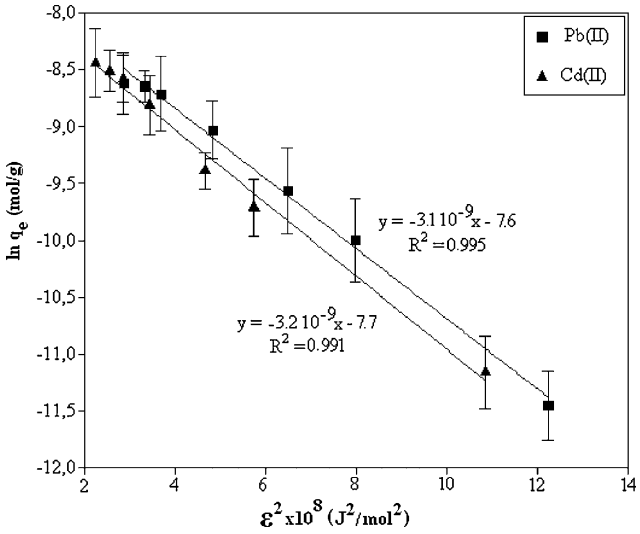

Fig. 6. D–R isotherm plots for the biosorption of Pb(II) and Cd(II) onto *A. rubescens* biomass (pH: 5; adsorbent dosage: 4 g/L; contact time: 30 min; temperature: 20 °C).

solution (mg/L), q_m is the monolayer biosorption capacity of the adsorbent (mg/g), and K_L is the Langmuir biosorption constant (L/mg) related with the free energy of biosorption.

Fig. 5 indicates the non-linear relationship between the amount (mg) of Pb(II) and Cd(II) ions sorbed per unit mass (g) of *A. rubescens* biomass against the concentration of Pb(II) and Cd(II) ions remaining in solution (mg/L). The coefficients of determination (R^2) were found to be 0.993 and 0.990 for Pb(II) and Cd(II) biosorption, respectively. These results indicate that the biosorption of the metal ions onto *A. rubescens* biomass fitted well the Langmuir model. In other words, the sorption of Pb(II) and Cd(II) ions onto *A. rubescens* was taken place at the functional groups/binding sites on the surface of the biomass which is regarded as monolayer biosorption. The maximum biosorption capacity (q_m) of *A. rubescens* biomass was found to be 38.4 mg/g for Pb(II) and 27.3 mg/g for Cd(II). Moreover, the K_L value was found as 0.083 L/mg for Pb(II) ion and 0.085 L/mg for Cd(II) ion.

On the other hand, Table 1 presents the comparison of biosorption capacity (q_m; mg/g) of *A. rubescens* biomass for Pb(II) and Cd(II) ions with that of various biomasses reported in literature [43–53]. The biosorption capacity of *A. rubescens* biomass for Pb(II) and Cd(II) is higher than that of the majority of other biomasses mentioned. Therefore, it can be noteworthy that the *A. rubescens* biomass has important potential for the removal of Pb(II) and Cd(II) ions from aqueous solution.

The Freundlich model assumes a heterogeneous adsorption surface and active sites with different energy. The Freundlich model [54] is

$$q_e = K_f C_e^{1/n} \quad (3)$$

Table 2
Influence of various eluents on the desorption of Pb(II) and Cd(II) ions from *A. rubescens*

Eluent	Recovery (%)	
	Pb(II)	Cd(II)
0.5 mol L^{-1} HCl	60 ± 2	70 ± 2
1 mol L^{-1} HCl	80 ± 3	85 ± 3
0.5 mol L^{-1} HNO_3	75 ± 3	80 ± 3
1 mol L^{-1} HNO_3	90 ± 3	90 ± 3

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 values of K_f and $1/n$ were found to be 8.2 and 0.3 for Pb(II) biosorption and 3.5 and 0.4 for Cd(II) biosorption. The $1/n$ values were between 0 and 1 indicating that the biosorption of Pb(II) and Cd(II) onto *A. rubescens* biomass was favourable at studied conditions. However, the R^2 values were found to be 0.954 for Pb(II) biosorption and 0.962 for Cd(II) biosorption. These results indicate that the Freundlich model was not able to adequately to describe the relationship between the amounts of sorbed metal ions and their equilibrium concentration in the solution. Therefore, it can be concluded that the Langmuir isotherm model best fitted the equilibrium data since it presents higher R^2 values.

The equilibrium data were also subjected to the D–R isotherm model to determine the nature of biosorption processes as physical or chemical. The D–R sorption isotherm is more general than Langmuir isotherm, as its derivation is not based on ideal assumptions such as equipotent of the sorption sites, absence of steric hindrance between sorbed and incoming particles and surface homogeneity on microscopic level [55]. The linear presentation of the D–R isotherm equation [56] is expressed by

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \quad (4)$$

where q_e is the amount of metal ions adsorbed on per unit weight of biomass (mol/L), q_m is the maximum biosorption capacity (mol/g), β is the activity coefficient related to biosorption mean free energy (mol^2/J^2) and ε is the Polanyi potential ($\varepsilon = RT\ln(1 + 1/C_e)$).

The D–R isotherm model well fitted the equilibrium data since the R^2 value was found to be 0.995 and 0.991 for Pb(II) and Cd(II), respectively (Fig. 6). The q_m value was found using the intercept of the plots to be 4.9×10^{-4} mol/g for Pb(II) biosorption and 4.4×10^{-4} mol/g for Cd(II) biosorption. The biosorption mean free energy (E; kJ/mol) is as follow:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (5)$$

The E (kJ/mol) value gives information about adsorption mechanism, physical or chemical. If it lies between 8 and 16 kJ/mol, the adsorption process takes place chemically and while $E < 8$ kJ/mol, the adsorption process proceeds physically [57]. The mean biosorption energy was calculated as 12.8 and 12.5 kJ/mol for the

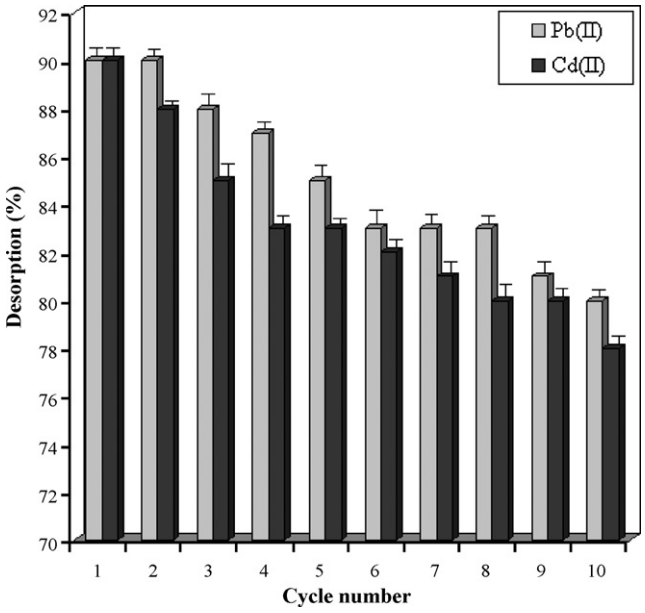

Fig. 7. Desorption efficiency of *A. rubescens* biomass with cycle number.

biosorption of Pb(II) and Cd(II) ions, respectively. These results suggest that the biosorption processes of both metal ions onto *A. rubescens* biomass could be taken place by chemical ion-exchange mechanism because the sorption energies lie within 8–16 kJ/mol.

3.6. Desorption efficiency

Desorption of adsorbed analyte ions onto *A. rubescens* were also studied by using HCl and HNO_3 at various concentrations in Table 2. For these studies, 10 mL of each eluent was used. Analyte ions were desorbed from *A. rubescens* with both 1 M HCl and 1 M HNO_3. The highest recovery for both metal ions was found to be 90% using 1 M HNO_3 and 80% using 1 M HCl. The effects of volume of 1 M HNO_3 as eluent were also investigated in the range of 5.0–10.0 mL. The highest recovery values (90%) were obtained for both metal ions after 8.0 mL of 1 M HNO_3. Subsequent elution with 10 mL 1 M HNO_3 readily strips the sorbed metal ions from *A. rubescens*. In addition, as it can be seen from Fig. 7, the high stability of *A. rubescens* permitted ten times of adsorption–elution process along the studies without a decrease about 10% in recovery of both metal ions.

3.7. Biosorption kinetics

The prediction of biosorption rate gives important information for designing batch biosorption systems. Information on the kinetics of pollutant uptake is required for selecting optimum operating conditions for full-scale batch process. In order to clarify the biosorption kinetics of Pb(II) and Cd(II) ions onto *A. rubescens* biomass two kinetic models, which are Lagergren's pseudo-first-order and pseudo-second-order model were applied to the experimental data.

The linear form of the pseudo-first-order rate equation by Lagergren [58] is given as

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

where q_t and q_e (mg/g) are the amounts of the metal ions biosorbed at equilibrium (mg/g) and t (min), respectively, and k_1 is the rate constant of the equation (min^{-1}). The biosorption rate constants (k_1) can be determined experimentally by plotting of $\ln(q_e - q_t)$ vs t.

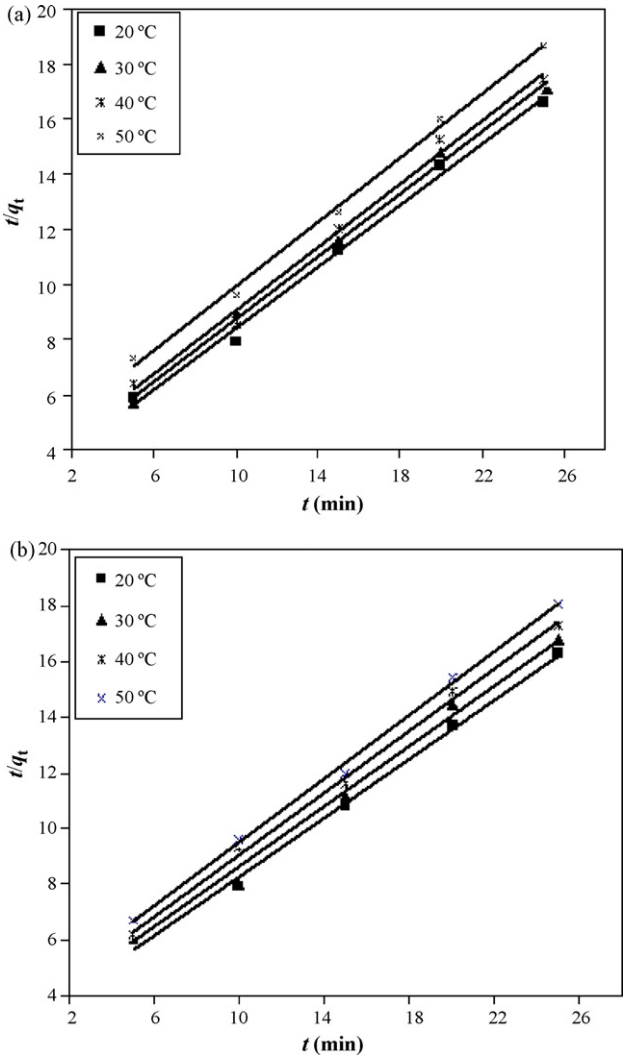

Fig. 8. Pseudo-second-order kinetic plots at different temperatures; (a) for Pb(II) biosorption and (b) for Cd(II) biosorption (metal concentration: 10 mg/L; pH: 5; biomass dosage: 4 g/L).

The plots of $\ln(q_e - q_t)$ vs t for the pseudo-first-order model were not shown as figure because the coefficients of determination for this model at studied temperatures is low. It can be concluded from the R^2 values in Table 3 that the biosorption mechanisms of Pb(II) and Cd(II) ions onto *A. rubescens* biomass does not follow the pseudo-first-order kinetic model. Moreover, from Table 3, it can be seen that the experimental values of $q_{e,exp}$ are not in good agreement with the theoretical values calculated ($q_{e1,cal}$) from Eq. (6). Therefore, the pseudo-first-order model is not suitable for modeling the biosorption of Pb(II) and Cd(II) onto *A. rubescens*.

Experimental data were also tested by the pseudo-second-order kinetic model which is given in the following form [59]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \quad (7)$$

where k_2 (g/mg min) is the rate constant of the second-order equation, q_t (mg/g) is the amount of biosorption time t (min) and q_e is the amount of biosorption equilibrium (mg/g).

This model is more likely to predict kinetic behavior of biosorption with chemical sorption being the rate-controlling step [60]. The linear plots of t/q_t vs t for the pseudo-second-order model for the biosorption of Pb(II) and Cd(II) ions onto *A. rubescens* at 20–50 °C

Table 3
Kinetic parameters obtained from pseudo-first-order and pseudo-second-order for Pb(II) and Cd(II) bisorption onto *A. rubescens* biomass at different temperatures

Temperature (°C)	Pseudo-first-order				Pseudo-second-order		
	$q_{e,exp}$ (mg/g)	k_1 (1/min)	$q_{e1,cal}$ (mg/g)	R^2	k_2 (g/mg min)	$q_{e2,cal}$ (mg/g)	R^2
Pb(II)							
20	1.89	9.4×10^{-2}	1.16	0.918	9.4×10^{-2}	1.89	0.996
30	1.86	8.9×10^{-2}	1.14	0.934	9.2×10^{-2}	1.84	0.991
40	1.78	8.4×10^{-2}	1.12	0.905	8.8×10^{-2}	1.79	0.997
50	1.72	7.9×10^{-2}	1.09	0.849	8.5×10^{-2}	1.79	0.996
Cd(II)							
20	1.82	8.8×10^{-2}	1.18	0.983	10.9×10^{-2}	1.80	0.999
30	1.66	8.2×10^{-2}	1.15	0.967	10.7×10^{-2}	1.76	0.999
40	1.61	7.5×10^{-2}	1.13	0.863	10.1×10^{-2}	1.74	0.998
50	1.58	5.9×10^{-2}	1.12	0.856	8.2×10^{-2}	1.72	0.999

were shown in Fig. 8a and b, respectively. The rate constants (k_2), the R^2 and q_e values are given in Table 3. It is clear from these results that the R^2 values are very high (in range of 0.991–0.996 for the Pb(II) biosorption and 0.998–0.999 for the Cd(II) biosorption). In addition, the theoretical $q_{e2,cal}$ values were closer to the experimental $q_{e,exp}$ values (Table 3). In the view of these results, it can be said that the pseudo-second-order kinetic model provided a good correlation for the biosorption of Pb(II) and Cd(II) onto *A. rubescens* in contrast to the pseudo-first-order model.

3.8. Biosorption thermodynamics

In order to describe thermodynamic behavior of the biosorption of Pb(II) and Cd(II) ions onto *A. rubescens* biomass, thermodynamic parameters including the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated from following equations

$$\Delta G^\circ = -RT \ln K_D \quad (8)$$

where, R is the universal gas constant (8.314 J/mol K), T is temperature (K) and K_D (q_e/C_e) is the distribution coefficient [61,62].

The enthalpy (ΔH°) and entropy (ΔS°) parameters were estimated from the following equation

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

According to Eq. (9), the ΔH° and ΔS° parameters can be calculated from the slope and intercept of the plot of $\ln K_D$ vs $1/T$ yields, respectively (Fig. 9). Gibbs free energy change (ΔG°) was calculated to be −20.7, −17.8, −16.9, and −15.3 kJ/mol for Pb(II) biosorption and −18.3 −17.2, −16.1, and −14.5 kJ/mol for the biosorption of Cd(II) at 20, 30, 40, and 50 °C, respectively. The negative ΔG° values indicated thermodynamically feasible and spontaneous nature of the biosorption. The decrease in ΔG° values with increase in temperature shows a decrease in feasibility of biosorption at higher temperatures. The ΔH° parameter was found to be −57.1 and −53.2 kJ/mol for Pb(II) and Cd(II) biosorption, respectively. The negative ΔH° indicates the exothermic nature of the biosorption processes at 20–50 °C. The ΔS° parameter was found to be −129.1 J/mol K for Pb(II) biosorption and −119.1 J/mol K for Cd(II) biosorption. The negative ΔS° value suggests a decrease in the randomness at the solid/solution interface during the biosorption process.

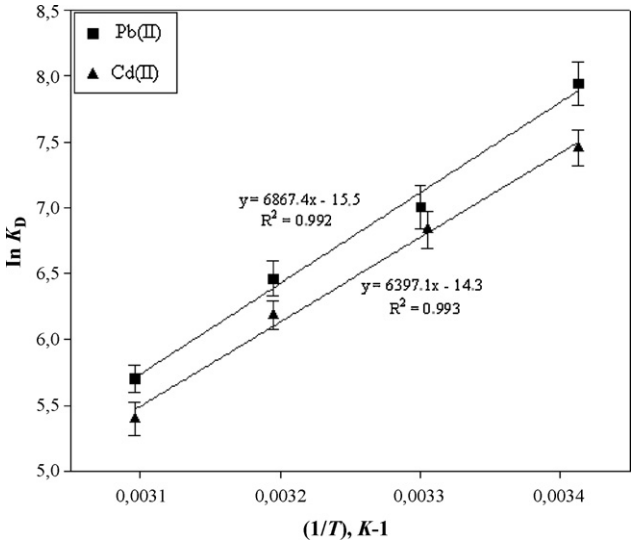

Fig. 9. Plot of $\ln K_D$ vs $1/T$ for the estimation of thermodynamic parameters for biosorption of Pb(II) and Cd(II) onto *A. rubescens* biomass.

4. Conclusions

This study focused on the biosorption of Pb(II) and Cd(II) ions onto *A. rubescens* biomass from aqueous solution. The operating parameters, pH of solution, biomass dosage, contact time, and temperature, were effective on the biosorption efficiency of Pb(II) and Cd(II). The biosorption capacity of *A. rubescens* biomass was found to be 38.4 mg/g for Pb(II) and 27.3 mg/g for Cd(II), respectively, at optimum conditions of pH 5.0, contact time of 30 min and temperature of 20 °C. The mean free energy values evaluated from the D–R model indicated that the biosorption of Pb(II) and Cd(II) onto *A. rubescens* biomass was taken place by chemical ion-exchange. The kinetic data signified that the biosorption of Pb(II) and Cd(II) ions onto *A. rubescens* followed well the pseudo-second-order kinetic model. The thermodynamic calculations showed the feasibility, exothermic and spontaneous nature of the biosorption of Pb(II) and Cd(II) ion onto *A. rubescens* biomass at 20–50 °C. Taking into consideration present findings, it can be stated that *A. rubescens* is a good adsorbent for Pb(II) and Cd(II) removal from aqueous solution. Furthermore, it can be evaluated as an alternative biosorbent to treatment wastewater containing Pb(II) and Cd(II) ions, since *A. rubescens* is low-cost biomass and has a considerable high biosorption capacity.

Acknowledgements

The authors are grateful for the financial support of the Unit of the Scientific Research Projects of Gaziosmanpasa University. The authors also would like to thank D. Cıtak for his helps in experimental studies and Dr. Ertugrul Sesli for identification of macrofungus.

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