Equilibrium, thermodynamic and kinetic studies on biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (*Lactarius scrobiculatus*) biomass

Ruhan Altun Anayurt, Ahmet Sari*, Mustafa Tuzen

Department of Chemistry, Gaziosmanpasa University, 60250 Tokat, Turkey

ARTICLE INFO

ABSTRACT

The equilibrium, thermodynamics and kinetics of the biosorption of Pb(II) and Cd(II) onto (*Lactarius scrobiculatus*) macrofungus from aqueous solution were investigated at different experimental conditions. Optimum experimental parameters were determined to be pH 5.5, contact time 60 min, biomass concentration 4 g/L of solution, and temperature 20 °C. The maximum biosorption capacity of *L. scrobiculatus* was found to be 56.2 mg/g for Pb(II) and to be 53.1 mg/g for Cd(II). The mean free energy values evaluated by using the Dubinin–Radushkevich (D–R) model indicated that the biosorption of the metal ions onto *L. scrobiculatus* biomass was taken place by chemical ion-exchange. The kinetic studies indicated that the biosorption process of the metal ions followed well pseudo-second order model. The calculated thermodynamic parameters (ΔG°, ΔH° and ΔS°) showed that the biosorption of Pb(II) and Cd(II) ions onto *L. scrobiculatus* biomass was feasible, spontaneous and exothermic in nature. The recovery of the metal ions from *L. scrobiculatus* biomass was found as higher than 95% using 1 M HCl and 1 M HNO₃. Furthermore, the reusability of the biosorbent was determined after six consecutive sorption-desorption cycles.

© 2009 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 livings 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 wastewater [2,3]. Cadmium is also a dangerous pollutant that created by metal plating, metallurgical alloying, mining, ceramics and other industrial operations [4]. Cadmium toxicity may be observed by a variety of syndromes and effects including renal dysfunction, hypertension, hepatic injury, lung damage and teratogenic effects [5].

The most widely used methods for heavy metal removal from wastewaters include chemical precipitation and filtration, electrochemical treatments, reverse osmosis, ion exchange, evaporation, preconcentration, adsorption and biosorption [6–8]. Among these methods, biosorption is an emerging and attractive method which involves sorption of dissolved substances by a biomaterial. In addition, the main advantages of this technique can be ordered as follows: 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 [9].

Studies on the mechanism of biosorption of heavy metals on fungi show that fungal cell walls mainly consisting of polysaccharides, proteins and lipids have many functional groups that are responsible for the binding of metals [10–12]. Several fungal biosorbents such as *Penicillium* [13], *Rhizopus arrhizus* [14], *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.

Lactarius scrobiculatus is a basidiomycete fungus and has many functional groups involving in the biosorption of heavy metal metals. This macrofungus is inedible and so, the use of this biosorbent for the heavy metal removal from aqueous solution is important from point of environment and of human health. *L. scrobiculatus* is a natural and readily available biosorbent. Therefore, this biomass could be used as an economical tool for the removal or recovery of metal ions from aqueous solutions. In addition, it was chosen as a biosorbent material because of a lack of information on its biosorption abilities in the removal of Pb(II) and Cd(II) ions from aqueous solution. In this study, the use of *L. scrobiculatus* as a biosorbent was tested for removing of Pb(II) and Cd(II) ions from aqueous solution. The effects of pH, biomass concentration, contact time, and temperature were discussed. The equilibrium isotherm models and kinetic models and thermodynamic parameters related with the process were performed.

---

* Corresponding author. Tel.: +90 356 2521616; fax: +90 356 2521585.
  E-mail address: asari@gop.edu.tr (A. Sari).

2. Experimental procedures

2.1. Biomass preparation

The macrofungus biomass was collected from the East Black Sea region of Turkey. The biomas samples were washed with deionized water and dried in an oven at 105 °C for 48 h. The dried samples was ground and sieved through different sizes and 200–300 μm fractions.

2.2. Reagents and equipments

All chemical reagents used in this study were of analytical grade. Double deionised water (Milli-Q Millipore 18.2 MΩ cm^{-1} conductivity) was used for all dilutions. Pb(II) and Cd(II) stock solutions were prepared as 1000 mg/L by dissolving 1.8307 g Pb(CH$_3$COOO)$_2$·3H$_2$O and 2.3709 g Cd(CH$_3$COOO)$_2$·3H$_2$O in a 1000 mL of deionized water, respectively. The pH of solutions was adjusted to desired values using 0.1 mol/L sodium phosphate buffer (for pH 2), 0.1 mol/L ammonium acetate buffers (for pH 4–6) and 0.1 mol/L ammonium chloride buffer (for pH 8).

A pH meter (Sartorius pp-15, Germany) was used for the measurement of pH values. A flame atomic absorption spectrometry (PerkinElmer AAnalyst 700, USA) with deuterium background corrector was used. Fourier transform infrared (FT-IR) spectra of unloaded and metal-loaded samples were recorded using a FT-IR spectrometer (JASCO-430, Japan) in wavenumber rage of 400–4000 cm^{-1}.

2.3. Batch biosorption procedure

Biosorption processes were carried out using batch method. In order to optimize the experimental conditions, the batch studies were performed for different metal concentrations (10–400 mg/L), contact times (5–90 min), pH (2–8), biosorbent dosages from (0.1 to 20 g/L), and temperatures (20–50 °C). The solutions (25 mL of 10 mg/L) including the metal ions and biosorbent were shaken during optimum contact time in an electrically thermostatic reciprocating shaker (Multimatic-55 model, Selecta Company, Spain) at 120 rpm. After the contents of the flask were filtered through 0.25 μm filters (Double rings, China), the metal concentration of filtrate was analyzed using flame AAS. Each determination was repeated three times and the results are given as average values. The error bars are also indicated wherever necessary.

The biosorption percent was calculated as follows:

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

where C_i and C_f are the initial and final metal ion concentrations, respectively.

2.4. Desorption and reusability studies

The desorption studies of Pb(II) and Cd(II) from *L. scrobiculatus* was carried out by using 10 mM HNO$_3$ and 10 mM HCl. After determination of metal contents of the final solutions, the biosorbent was washed with excess of the acid solution and distilled water in order to reuse for next experiment. Consecutive sorption-desorption cycles were repeated six times to establish the reusability of the biosorbent.

3. Results and discussion

3.1. FT-IR analysis

The FT-IR spectroscopy method was used to obtain information on the nature of possible biosorbent-metal ions interactions. Fig. 1
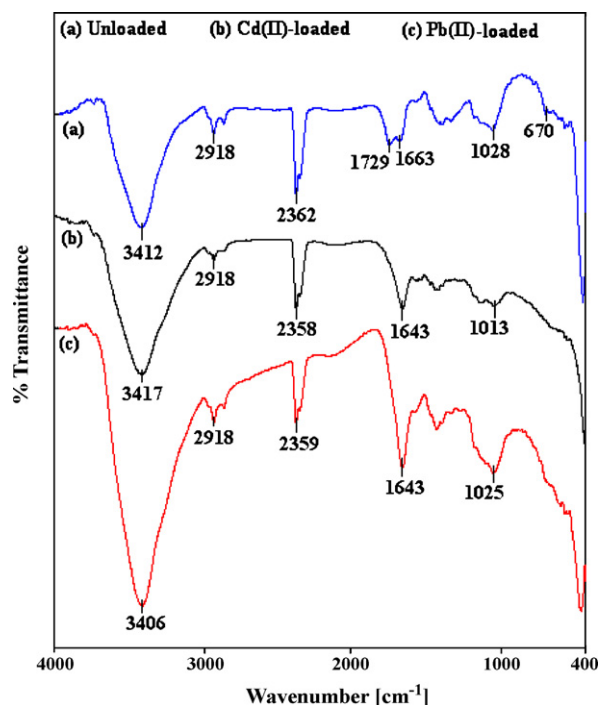

Fig. 1. FT-IR spectrum of unloaded, Cd(II)-loaded and Cd(II)-loaded biomass.

shows the FT-IR spectra of unloaded and metal-loaded biomass samples. The peak at 3412 cm^{-1} was due to bounded hydroxyl (–OH) or amine (–NH) groups. The peak at 2918 cm^{-1} can be assigned to the –CH groups of unloaded biomass sample. The peaks at 1729 cm^{-1} were attributed to stretching vibration of carboxyl group (–C=O). The band observed at 1028 cm^{-1} was assigned to C–O stretching of alcohols and carboxylic acids.

The asymmetrical stretching vibration at 3412 cm^{-1} was shifted to 3406 and 3417 cm^{-1} after the biosorption of Pb(II)-loaded and Cd(II), respectively. The changes in OH adsorption peak of indicated that the hydroxyl group had been changed from multimer to monopolymer or even dissociative state [17] which showed that the degree of the hydroxyl polymerization in lignocellulose was decreased by binding of Pb(II) and Cd(II). It offered more opportunity for Pb(II) and Cd(II) to be bound to the hydroxyl or amine groups. The carboxyl peak at 1729 cm^{-1} was observed at 1643 cm^{-1} for both Pb(II) and Cd(II)-loaded biomass. The peak of C–O group was shifted to 1025 after Pb(II) soprtion and 1013 cm^{-1} after Cd(II) sorption. These results indicated that the free carboxyl groups changed into carboxylate, which occurred during the reaction of the metal ions and carboxyl groups of the biosorbent. Moreover, the ion-exchange process occurred when the metal ions in the solution was transferred from solution to biomass and chemical bonds were formed between the metal ions and the carboxyl (–C=O), hydroxyl (–OH), and amine (–NH) groups of the biomass. The similar FT-IR results were reported for the biosorption Pb(II), Cd(II) and Cu(II) onto *Botrytis cinerea* fungal biomass [18,19], and Cd(II) biosorption onto *Lentinus edodes* fungal biomass [20].

3.2. Effect of pH

The pH parameter has been identified as one of the most important parameter that is effective on metal sorption. It is directly related with competition ability of hydrogen ions with metal ions to active sites on the biosorbent surface. The effect of pH on the biosorption of Pb(II) and Cd(II) onto *L. scrobiculatus* biomass was
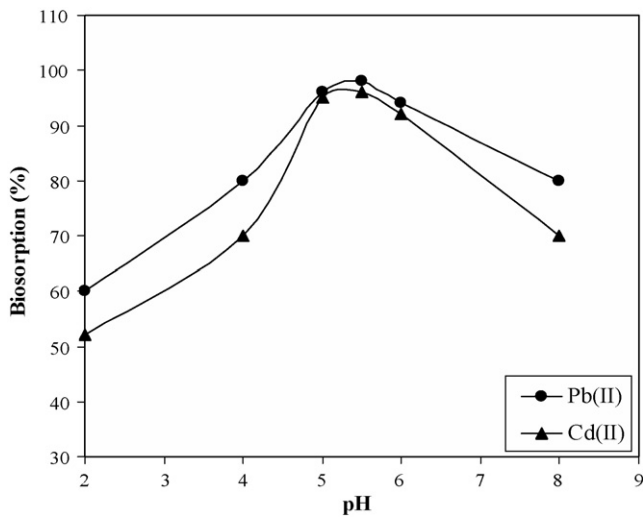
Fig. 2. Effect of pH on the biosorption of Pb(II) and Cd(II) onto *L. scrobiculatus* biomass (biomass concentration: 4 g/l, volume of solution: 25 mL, initial concentration: 10 mg/L, temperature: 20 °C).

studied at pH 2–8 and the results are given in Fig. 2. The biosorption efficiency was increased from 60% to 96% for Pb(II) and from 52% to 95% for Cd(II) ion as pH was increased from 2 to 5. The maximum biosorption was found to be 98% for Pb(II) and 96% for Cd(II) ions at pH 5.5. Therefore, the remaining all biosorption experiments were carried out at this pH value.

The biosorption mechanisms on the biomass surface reflects the nature of the physicochemical interaction of the species in solution and the biosorptive sites of sorbent [21,22]. 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 [23]. The biosorbent surface was more negatively charged as the pH of solution increased from 2 to 5.5. The functional groups of the biomass were more deprotonated and thus available for the metal ions. Especially, carboxyl, amine and phosphate groups are important functional groups involved in biosorption of heavy metals [24,10]. Decrease in biosorption yield at higher pH (pH >5.5) 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)$_2$ [22] but also to the ionized nature of the cell wall surface of the biomass under the studied pH [25]. In addition, several studies reported the similar pH effect on biosorption of heavy metals by using different kinds of fungal biomass [18,19].

3.3. Effect of biomass concentration

The biosorption efficiency for Pb(II) and Cd(II) ions as a function of biomass concentration was investigated. The biosorption yield steeply increases with concentration as the biomass concentration was increased from 0.1 to 4 g/L. This result can be explained by the fact that for optimum biosorption, extra sites must be available for biosorption reaction, whereas by increasing the biomass concentration, number of sites available for biosorption site increases [26]. The maximum biosorption percentage reached 98% for Pb(II) and 96% for Cd(II) as biomass concentration was 4 g/L. A further increase in biomass concentration over 4.0 g/L did not lead to a significant improvement in biosorption yield due to the saturation of the biosorbent surface with the metal ions. Therefore, the optimum biomass concentration was taken as 4 g/L for further batch experiments.

3.4. Effects of contact time and temperature

The rate of biosorption is important for designing batch biosorption experiments. Therefore, the effect of contact time on the biosorption of Pb(II) and Cd(II) was investigated. The biosorption yield of Pb(II) and Cd(II) increased considerably until the contact time reached 60 min. Further increase in contact time did not enhance the biosorption yield, so, the optimum contact time was selected as 60 min for further experiments.

The temperature of solution affects on the removal efficiency of the heavy metals from aqueous solutions. The biosorption decreased from 98% to 90% for Pb(II) and from 95% to 88% for Cd(II) as temperature was increased from 20 to 50 °C during the equilibrium time, 60 min. These results indicated the exothermic nature of Pb(II) and Cd(II) biosorption onto *L. scrobiculatus* biomass. A decrease in the biosorption of Pb(II) and Cd(II) ions with the rise in temperature may be due to increasing metal desorption tendency from the interface to the solution [27]. 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 isotherms which express the surface properties and affinity of the biomass. In this study, the biosorption isotherms were investigated using three equilibrium models, which are namely the Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models were analyzed.

The Langmuir sorption isotherm has been successfully applied to the biosorption processes of heavy metal ions. The 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 [28].

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2}$$

where q_e is the equilibrium metal ion concentration on the sorbent (mg/g), C_e is the equilibrium metal ion concentration in the solution (mg/L), q_m is the monolayer sorption capacity of the sorbent (mg/g), and K_L is the Langmuir sorption constant (L/mg) related with the free energy of sorption. Nonlinear regression analysis was carried out in SigmaPlot software (SigmaPlot 2001, SPSS Inc., USA) in order to determine K_L and q_m values.

Fig. 3 indicates the non-linear Langmuir isotherm plots. The coefficients of determination (R^2) were found to be 0.997 and 0.992
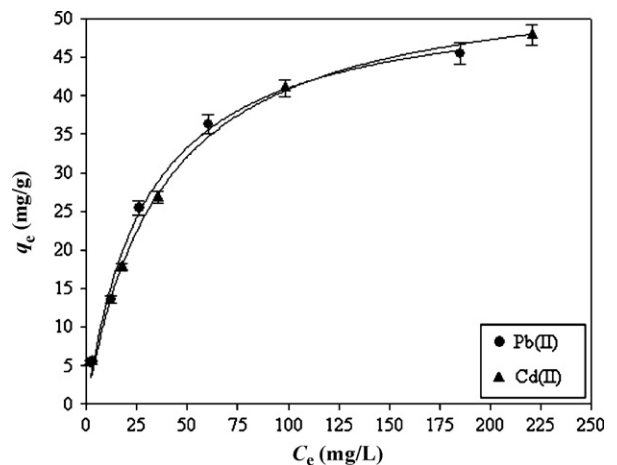
Fig. 3. Langmuir isotherm plots for the biosorption of Pb(II) and Cd(II) onto *L. scrobiculatus* biomass (pH: 5.5, biomass concentration: 4 g/l, volume of solution: 25 mL, initial concentration: 10 mg/L, temperature: 20 °C).

Table 1
Comparison of biosorption capacity (mg/g) of *L. scrobiculatus* biomass for Pb(II) and Cd(II) with that of different biosorbents.

| Biosorbent	Pb(II)	Cd(II)	Reference
Rhizopus arrhizus	–	26.8	[29]
Streptomyces noursei	–	3.4	[30]
Mucor rouxii (NaOH pretreated)	–	20.3	[31]
Phanerochaete chrysosporium	–	15.2	[32]
Spirulina sp.	–	159.0	[33]
Sargassum sp.	–	120.0	[34]
Fucus vesiculosus	–	73.0	[35]
Najas graminea (Aquatic plant)	–	28.0	[36]
Bifurcaria bifurcata	–	61.0	[37]
Gracillaria sp.	–	33.7	[38]
Fontinalis antipyretica (Aquatic moss)	–	28.0	[39]
H. splendens	–	32.5	[40]
Ulva lactuca	34.7	29.2	[41]
Phanerochaete chrysosporium	69.8	23.0	[42]
Zoogloea ramigera	10.4	–	[43]
Rhizopus arrhizus	15.5	–	[43]
Penicillium simplicissimum	76.9	–	[44]
Streptomyces longwoodensis	100.0	–	[45]
Phellinus badius	170.0	–	[46]
Cephalosporium aphidicola	36.9	–	[47]
Aspergillus flavus	13.5	–	[48]
Lactarius scrobiculatus	56.2	53.1	Present study

for Pb(II) and Cd(II) biosorption, respectively. These results indicate that the biosorption of the metal ions onto *L. scrobiculatus* biomass fitted well the Langmuir model. The maximum biosorption capacity (q_m) of *L. scrobiculatus* biomass was found averagely to be 56.2 mg/g for Pb(II) and 53.1 mg/g for Cd(II). The K_L value was found averagely as 0.02 L/mg for Pb(II) ion and 0.03 L/mg for Cd(II) ion. Table 1 also presents the comparison of biosorption capacity of *L. scrobiculatus* for Pb(II) and Cd(II) ions with that of various biosorbents. The biosorption capacity of *L. scrobiculatus* for Pb(II) and Cd(II) was found to be comparable and moderately higher than those of many corresponding sorbents in literature [29–48]. Therefore, it can be noteworthy that the *L. scrobiculatus* biomass has a considerable potential for the removal of Pb(II) and Cd(II) ions from aqueous solution.

The Freundlich model assumes a heterogeneous sorption surface. The Freundlich model [49] is

$$q_e = K_f C_e^{1/n} \tag{3}$$

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. K_f and $1/n$ values were determined using nonlinear regression analysis by SigmaPlot software (SigmaPlot 2001, SPSS Inc., USA). Fig. 4 indicates the non-linear Freundlich isotherm plots. From the plots, the K_f were found to be 6.26 and 6.54 and the $1/n$ values were found as 0.39 and 0.38 for Pb(II) and Cd(II) biosorption, respectively. The $1/n$ values between 0 and 1 indicated that the biosorption of Pb(II) and Cd(II) onto *L. scrobiculatus* biomass was favorable at studied conditions. The R^2 values were found as 0.965 and 0.942 for Pb(II) Cd(II) biosorption, respectively. These results indicate that the Freundlich model was not able to adequately describe the relationship between the amounts of sorbed metal ions and their equilibrium concentrations in the solution.

The D–R isotherm model was also performed to the equilibrium data in order to determine the nature of biosorption processes as physical or chemical. The D–R sorption isotherm is more general than the Langmuir isotherm as its derivation is not based on ideal assumptions such as equipotent of the sorption sites, absence of stoic hindrance between sorbed and incoming particles and surface homogeneity on microscopic level [50]. The linear presentation of
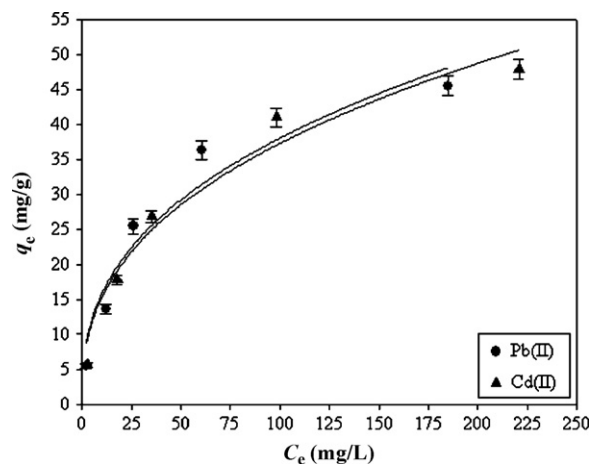
Fig. 4. Freundlich isotherm plots for the biosorption of Pb(II) and Cd(II) onto *L. scrobiculatus* biomass (pH: 5.5, biomass concentration: 4 g/l, volume of solution: 25 mL, initial concentration: 10 mg/L, temperature: 20 °C).

the D–R isotherm equation [51] is expressed by

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{4}$$

where q_e is the mole amount of metal ions adsorbed on per unit weight of biomass (mol/g), 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 because of the high R^2 values 0.991 for Pb(II) and 0.993 for Cd(II) (Fig. 5). The q_m value was found using the intercept of the plots to be 9.5×10^{-4} mol/g for Pb(II) biosorption and 10.1×10^{-4} mol/g for Cd(II) biosorption. The biosorption mean free energy (E; kJ/mol) is as follow:

$$E = \frac{1}{\sqrt{-2\beta}} \tag{5}$$

The E (kJ/mol) value gives information about sorption mechanism, physical or chemical. If it lies between 8 and 16 kJ/mol, the sorption process takes place chemically, while, $E < 8$ kJ/mol, the sorption process proceeds physically [52].

The mean biosorption energy was calculated as 10.3 and 10.1 kJ/mol for the biosorption of Pb(II) and Cd(II) ions, respectively. These results suggest that the biosorption processes of both metal ions onto *L. scrobiculatus* biomass could be taken place by chemical
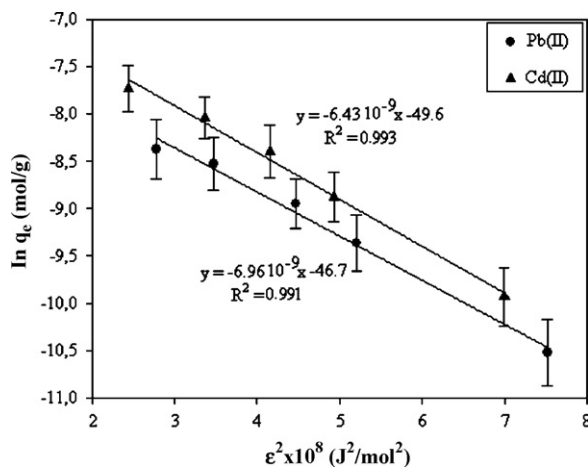
Fig. 5. D–R isotherm plots for the biosorption of Pb(II) and Cd(II) onto *L. scrobiculatus* biomass (pH: 5; adsorbent dosage: 4 g/L; contact time: 60 min; temperature: 20 °C).
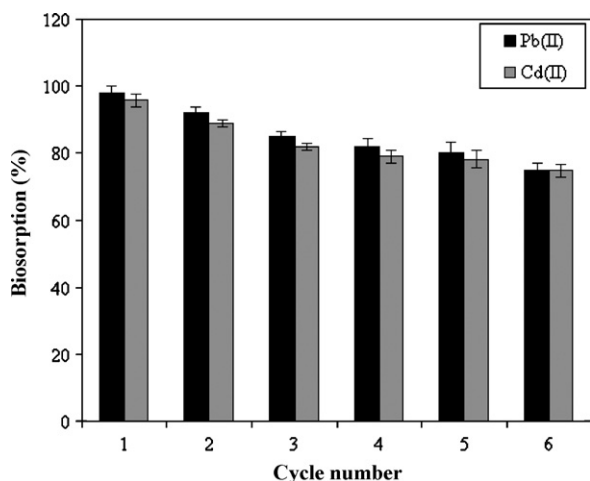
Fig. 6. Reusability of *L. scrobiculatus* biomass with repeated sorption–desorption cycle (pH: 5.5, biomass concentration: 4 g/l, volume of solution: 25 mL, initial concentration: 10 mg/L).

ion-exchange mechanism because the sorption energy lies within 8–16 kJ/mol.

3.6. Desorption efficiency and reusability

The regeneration of the biosorbent is one of the key factors for assessing of its potential for commercial applications. Two different desorption agents, 1 M HCl (10 mL) and 1 M HNO$_3$ (10 mL), were used to recover the Pb(II) and Cd(II) ions from the biosorbent. Higher than 95% of the adsorbed Pb(II) ions were desorbed from the biosorbent. 1 M HNO$_3$ (10 mL) was selected as desorption agent for Pb(II) and Cd(II) ions from the biosorbent due to the attaining the best regeneration using this solution.

On the other hand, the reusability of the biosorbent was also tested during six consecutive biosorption-desorption cycles (Fig. 6). The lost in the biosorption capacity of the biomass for both metal ions was determined to be 5%. This might be due to the ignorable amount of biomass lost during the adsorption-desorption process. These results indicated that the *L. scrobiculatus* biomass offers potential to be used repeatedly in Pb(II) and Cd(II) biosorption studies without any detectable loss in the total biosorption capacity.

3.7. Biosorption kinetics

The prediction of biosorption rate gives important information for designing batch biosorption systems. The Lagergren's pseudo-first-order and pseudo-second-order model were performed to the experimental data to clarify the biosorption kinetics of Pb(II) and Cd(II) ions onto *L. scrobiculatus* biomass.

The linear form of the pseudo-first-order rate equation by the Lagergren [53] is given as

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{6}$$

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

The plots of $\ln(q_e - q_t)$ vs t for the pseudo-first-order model were not shown as figure because of low coefficients of determination that obtained at studied temperatures. The R^2 values in Table 2 indicated that the biosorption mechanisms of Pb(II) and Cd(II) ions onto *L. scrobiculatus* biomass does not follow the pseudo-first-order kinetic model. It can be also 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 Pb(II) and Cd(II) biosorption onto *L. scrobiculatus*.

Experimental data were also tested by the pseudo-second-order kinetic model which is given in the following form [54]:

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

where k_2 (g mg^{-1} min^{-1}) 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 [55]. Fig. 7a and b shows the linear plots of t/qt vs t for the pseudo-second-order model for the biosorption of Pb(II) and Cd(II) ions onto *L. scrobiculatus*. The rate constants (k_2), the R^2 and q_e values are also given in Table 2. The R^2 values are found very high (in range of 0.992–0.999 for Pb(II) and Cd(II) biosorption). In addition, the theoretical $q_{e2,cal}$ values were closer to the experimental $q_{e,exp}$ values. 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 *L. scrobiculatus* in contrast to the pseudo-first-order model.

3.8. Biosorption thermodynamics

Pb(II) and Cd(II) biosorption may be represented generally by the following reversible process

Metal(II) in solution ⇔ metal(II) − biosorbent
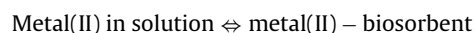
For such equilibrium reactions, K_D, the distribution constant, can be used to estimate the thermodynamic parameters due to its dependence on temperature. The changes in energy (ΔG°),

Table 2
Kinetic parameters obtained from pseudo-first-order and pseudo-second-order for Pb(II) and Cd(II) bisorption onto *L. scrobiculatus* biomass at different temperatures (pH: 5.5, sorbent concentration: 4 g/l, volume of solution: 25 mL, initial concentration: 10 mg/L).

Temperature (°C)	$q_{e,exp}$ (mg/g)	Pseudo-first-order			Pseudo-second-order		
		k_1 (1/min)	$q_{e1,cal}$ (mg/g)	R^2	k_2 (g mg^{-1} min^{-1})	$q_{e2,cal}$ (mg/g)	R^2
Pb(II)							
20	1.42	4.3×10^{-2}	0.46	0.956	0.25	1.56	0.992
30	1.38	4.0×10^{-2}	0.44	0.806	0.23	1.41	0.992
40	1.34	3.4×10^{-2}	0.41	0.867	0.21	1.37	0.995
50	1.30	3.1×10^{-2}	0.40	0.973	0.19	1.20	0.999
Cd(II)							
20	1.40	4.5×10^{-2}	0.58	0.785	0.61	1.41	0.993
30	1.36	4.4×10^{-2}	0.53	0.888	0.57	1.28	0.998
40	1.32	2.4×10^{-2}	0.48	0.965	0.47	1.18	0.999
50	1.28	1.9×10^{-2}	0.44	0.893	0.43	1.09	0.992

Fig. 8. Plot of ln K_D vs $1/T$ for the estimation of thermodynamic parameters for biosorption of Pb(II) and Cd(II) onto *L. scrobiculatus* biomass.
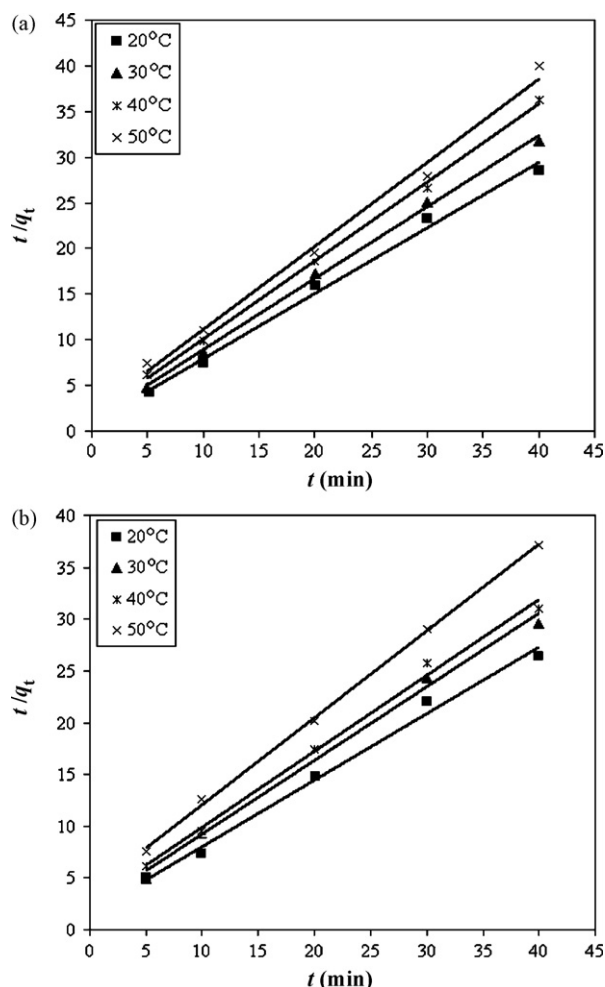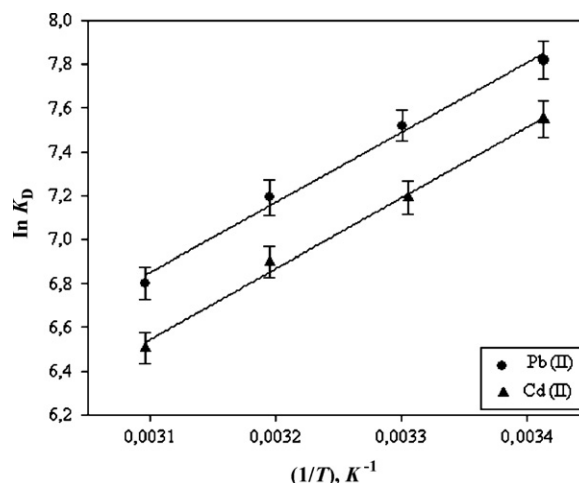
Fig. 7. Pseudo-second-order kinetic plots at different temperatures; (a) for Pb(II) biosorption (b) for Cd(II) biosorption (pH: 5.5, biomass concentration: 4 g/l, volume of solution: 25 mL, initial concentration: 10 mg/L).

enthalpy ($\Delta H°$) and entropy ($\Delta S°$) of biosorption process were determined by using following equations:

$$K_D = \frac{q_e}{C_e} \tag{8}$$

$$\Delta G° = -RT \ln K_D \tag{9}$$

$$\ln K_D = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{10}$$

A Van't Hoff plot of ln K_D as a function of $1/T$ (Fig. 8) yields a straight line [56] The $\Delta H°$ and $\Delta S°$ parameters were calculated from the slope and intercept of the plot, respectively. The Gibbs free energy change ($\Delta G°$) was calculated to be −19.1, −18.9, −18.7, and −18.3 kJ/mol for Pb(II) biosorption and −18.4, −18.1, −18.0, and −17.5 kJ/mol for Cd(II) biosorption at 20, 30, 40, and 50 °C, respectively. The negative $\Delta G°$ values indicated thermodynamically feasible and spontaneous nature of the biosorption. The decrease in $\Delta G°$ values shows a decline in feasibility of biosorption as temperature is increased. The $\Delta H°$ parameter was found to be −26.5 and −26.8 kJ/mol for Pb(II) and Cd(II) biosorption, respectively. The negative $\Delta H°$ indicates the exothermic nature of the biosorption processes at 20–50 °C. The $\Delta S°$ parameter was found to be −25.2 J/mol K for Pb(II) biosorption and −28.6 J/mol K for Cd(II) biosorption. The negative $\Delta S°$ value means a decrease in the randomness at the solid/solution interface during the biosorption process.

4. Conclusions

In this study, the use of *L. scrobiculatus* as a biosorbent was tested for removing of Pb(II) and Cd(II) ions from aqueous solution. The batch study parameters, pH of solution, biomass concentration, contact time, and temperature, were found to be effective on the biosorption efficiency of Pb(II) and Cd(II). The biosorption capacity of *L. scrobiculatus* biomass was determined as 56.2 mg/g for Pb(II) and 53.1 mg/g for Cd(II) at optimum conditions of pH 5.5, contact time of 60 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 *L. scrobiculatus* biomass was taken place by chemical ion-exchange. The FTIR spectroscopic analysis of metal-loaded biomass sample confirmed this result. The kinetic studies revealed that the biosorption process followed well the pseudo-second-order kinetic model. The calculated thermodynamic parameters showed the feasibility, exothermic and spontaneous nature of the biosorption of Pb(II) and Cd(II) ion onto *L. scrobiculatus* biomass. The recovery tests indicated that 1 M HNO$_3$ solution was able to elute 95% of Pb(II) and Cd(II) from the biomass. The reusability of the biosorbent was good after six consecutive sorption–desorption cycles based on all results, the *L. scrobiculatus* biomass as a natural and low-cost biomass can be used as alternative biosorbent for treatment of wastewaters containing Pb(II) and Cd(II) ions.

References

[1] T.K. Naiyaa, A.K. Bhattacharya, S. Mandal, S.K. Das, The sorption of lead(II) ions on rice husk ash, J. Hazard. Mater. 163 (2009) 1254–1264.
[2] M.K. Jamali, T.G. Kazi, M.B. Arain, H.I. Afridi, N. Jalbani, A.R. Menon, Heavy metal contents of vegetables grown in soil, irrigated with mixtures of wastewater and sewage sludge in Pakistan, using ultrasonic assisted pseudo-digestion, J. Agronomy Crop Sci. 193 (3) (2007) 218–228.
[3] M. Ghaedi, E. Asadpour, A. Vafaie, Simultaneous preconcentration and determination of copper, nickel, cobalt, lead, and iron content using a surfactant-coated alumina, Bulletin Chem. Soc. Jpn. 79 (2006) 432–436.
[4] T.G. Kazi, A.R. Memon, H.I. Afridi, M.K. Jamali, M.B. Arain, N. Jalbani, R.A. Sarfrz, 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. 389 (2008) 270–276.

[5] T.G. Kazi, N. Jalbani, N. Kazi, M.K. Jamali, M.B. Arain, H.I. Afridi, G.A. Kandehro, Z. Pirzado, Evaluation of toxic metals in blood and urine samples of chronic renal failure patients, before and after dialysis, Renal Failure 30 (2008) 737–745.

[6] M. Ghaedi, M. Montazerozohori, M. Soylak, Solid phase extraction method for selective determination of Pb(II) in water samples using 4-(4-methoxybenzylidenimine) thiophenole, J. Hazard. Mater. 142 (2007) 368–373.

[7] M. Ghaedi, Pyrimidine-2-thiol as selective and sensitive ligand for preconcentration and determination of Pb^{2+}, Chemia Analityczna 51 (2006) 593–602.

[8] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, Water Res. 33 (1999) 2469–2479.

[9] B. Volesky, Sorption and Biosorption, BV-Sorbex, Inc., St. Lambert, Quebec, 2003.

[10] A. Kapoor, T. Viraraghavan, Heavy metal biosorption sites in Aspergillus niger, Bioresour. Technol. 61 (1997) 221–227.

[11] F. Veglio, F. Beolchini, A. Gasbarro, Biosorption of toxic metals: an equilibrium study using free cells of Arthrobacter sp, Process Biochem. 32 (1997) 99–105.

[12] N.Md. Akthar, K.S. Sastry, P.M. Mohan, Mechanism of metal ion biosorption by fungal biomass, Biometals 9 (1996) 21–28.

[13] M. Galun, P. Keller, D. Malki, H. Feldstein, E. Galun, S. Siegel, B. Siegel, Recovery of uranium(VI) from solution using precultured Penicillium biomass, Water Air Soil Pollut. 20 (1983) 221–232.

[14] M. Tsezos, B. Velosky, The mechanism of uranium biosorption by Rhizopus arrhizus, Biotechnol. Bioeng. 29 (1982) 385–401.

[15] C. Huang, C.P. Huang, Application of Aspergillus oryzae and Rhizopus oryzae for Cu(II) removal, Water Res. 30 (1996) 1985–1990.

[16] M.D. Mullen, D.C. Wolf, T.J. Beveridge, G.W. Bailey, Sorption of heavy metals by the soil fungi Aspergillus niger and Mucor rouxii, Soil Biol. Biochem. 24 (1992) 129–135.

[17] R. Kellner, J.M. Mermet, M. Otto, Analytical Chemistry, WILEY-VCH Verlag GmbH Press, New York, 1998, p. 824.

[18] T. Akar, S. Tunali, I. Kiran, Botrytis cinerea as a new fungal biosorbent for removal of Pb(II) from aqueous solutions, Biochem. Eng. J. 25 (2005) 227–235.

[19] T. Akar, S. Tunali, Biosorption performance of Botrytis cinerea fungal by products for removal of Cd(II) and Cu(II) ions from aqueous solutions, Miner. Eng. 18 (11) (2005) 1099–1109.

[20] G. Chen, G. Zeng, L. Tang, C. Du, X. Jiang, G. Huang, H. Liu, G. Shen, Cadmium removal from simulated wastewater to biomass byproduct of Lentinus edodes, Bioresour. Technol. 99 (2008) 7034–7040.

[21] Z. Aksu, F. Gonen, Z. Demircan, Biosorption of chromium (VI) ions by Mow- ital B₃OH resin immobilized activated sludge in a packed bed: comparison with granular activated carbon, Process Biochem. 38 (2002) 175–186.

[22] M. Amini, H. Younesi, N. Bahramifar, A.A.Z. Lorestani, F. Ghorbani, A. Daneshi, M. Sharifzadeh, Application of response surface methodology for optimization of lead biosorption in an aqueous solution by Aspergillus niger, J. Hazard. Mater. 154 (2008) 694–702.

[23] M. Iqbal, R. Edyvean, Biosorption of lead, copper and zinc ions on loofa sponge immobilized biomass of Phanerochaete chrysosporium, Miner. Eng. 17 (2004) 217–223.

[24] A.Y. Dursun, 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. 28 (2006) 187–195.

[25] G. Yan, T. Viraraghavan, Heavy metal removal in a biosorption column by immobilized M. rouxii biomass, Bioresour. Technol. 78 (2001) 243–249.

[26] P. Vasudevan, V. Padmavathy, S.C. Dhingra, Biosorption of monovalent and divalent ions on Bakers yeast, Bioresour. Technol. 82 (2002) 285–289.

[27] A. Sarı, M. Tuzen, Ö.D. Uluözlü, M. Soylak, Biosorption of Pb(II) and Ni(II) from aqueous solution by lichen (Cladonia furcata) biomass, Biochem. Eng. J. 37 (2007) 151–158.

[28] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinium, J. Am. Chem. Soc. 40 (1918) 1361–1403.

[29] E. Fourest, J.C. Roux, Heavy metal biosorption by fungal mycelial by-products: mechanism and influence of pH, Appl. Microbiol. Biotechnol. 37 (1992) 399–403.

[30] B. Mattuschka, G. Straube, Biosorption of metals by a waste biomass, J. Chem. Technol. Biotechnol. 58 (1993) 57–63.

[31] G. Yan, T. Viraraghavan, Heavy metal removal from aqueous solution by fungus Mucor rouxii, Water Res. 37 (2003) 4468–4496.

[32] Q. Li, S. Wu, G. Liu, X. Liao, X. Deng, D. Sun, Y. Hu, Y. Huang, Simultaneous biosorption of cadmium (II) and lead (II) ions by pretreated biomass of Phanerochaete chrysosporium, Separ. Purif. Technol. 34 (2004) 135–142.

[33] K. Chojnacka, A. Chojnacki, H. Gorecka, Biosorption of Cr^{3+}, Cd^{2+} and Cu^{2+} ions by blue–gren algae Spirulina sp.: kinetics, equilibrium and the mechanism of the process, Chemosphere 59 (2005) 75–84.

[34] C.C.V. Cruz, A.C.A. da Costa, C.A.V. Henriques, A.S. Luna, Kinetic modeling and equilibrium studies during cadmium biosorption by deadSargassumsp. Biomass, Bioresour. Technol. 91 (2004) 249–257.

[35] Z.R. Holan, B. Volesky, I. Prasetyo, Biosorption of cadmium by biomass of marine algae, Biotechnol. Bioeng. 41 (1993) 819–825.

[36] C.L. Lee, T.C. Wang, C.K. Lin, H.K. Mok, Heavy metals removal by a promising locally available aquatic plant, Najas graminea del., in Taiwan, Water Sci. Technol. 39 (1999) 177–181.

[37] P. Lodeiro, B. Cordero, J.L. Barriada, R. Herrero, M.E. Sastre de Vicente, Biosorption of cadmium by biomass of brown marine macroalgae, Bioresour. Technol. 96 (2005) 1796–1803.

[38] P.X. Sheng, Y.P. Ting, J.P. Chen, L. Hong, Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms, J. Colloid Interface Sci. 275 (2004) 131–141.

[39] R.J.E. Martins, R. Pardo, R.A.R. Boaventura, Cadmium(II) and zinc(II) adsorption by the aquatic moss Fontinalis antipyretica: effect of temperature, pH and water hardness, Water Res. 38 (2004) 693–699.

[40] A. Sarı, D. Mendil, M. Tuzen, M. Soylak, Biosorption of Cd(II) and Cr(III) from aqueous solution by moss (Hylocomium splendens) biomass: equilibrium, kinetic and thermodynamic studies, Chem. Eng. J. 144 (2008) 1–9.

[41] A. Sarı, M. Tuzen, Biosorption of Pb(II) and Cd(II) from aqueous solution using green alga (Ulva lactuca) biomass, J. Hazard. Mater. 152 (2008) 302–308.

[42] R. Say, A. Denizli, M.Y. Arıca, Biosorption of cadmium(II), lead(II) and copper(II) with the lamentous fungus Phanerochaete chrysosporium, Bioresour. Technol. 76 (2001) 67–70.

[43] Y. Sag, D. Ozer, T. Kutsal, A comparative study of the biosorption of lead (II) ions to Z. Ramigera and R. arrhizus, Process Biochem. 30 (1995) 169–174.

[44] T. Fan, Y. Liu, B. Feng, G. Zeng, C. Yang, M. Zhou, H. Zhou, Z. Tan, X. Wang, Biosorption of cadmium(II), zinc(II) and lead(II) by Penicillium simplicissimum: Isotherms, kinetics and thermodynamics, J. Hazard. Mater. 160 (2008) 655–661.

[45] N. Friis, P. Myers-Keith, Biosorption of uranium and lead by Streptomyces longwoodensis, Biotechnol. Bioeng. 28 (1986) 21–28.

[46] J.T. Matheıckal, Q. Yu, Biosorptıon of lead(II) from aqueous solutıons by Phellınus badıus, Minerals Eng. 10 (1997) 941–957.

[47] S. Tunali, T. Akar, A.S. Ozcan, I. Kiran, A. Ozcan, Equilibrium and kinetics of biosorption of lead(II) from aqueous solutions by Cephalosporium aphidicola, Separ. Purif. Technol. 47 (2006) 105–112.

[48] T. Akar, S. Tunali, Biosorption characteristics of Aspergillus flavusbiomass for removal of Pb(II) and Cu(II) ions from an aqueous solution, Bioresour. Technol. 97 (2006) 1780–1787.

[49] H.M.F. Freundlich, Über die adsorption in lösungen, Zeitschrift für Physikalische Chemie (Leipzig) 57A (1906) 385–470.

[50] U.R. Malik, S.M. Hasany, M.S. Subhani, Sorptive potential of sunflower stem for Cr(III) ions from aqueous solutions and its kinetic and thermodynamic profile, Talanta 66 (2005) 166–173.

[51] M.M. Dubinin, E.D. Zaverina, L.V. Radushkevich, Sorption and structure of active carbons. I. Adsorption of organic vapors, Zhurnal Fizicheskoi Khimii 21 (1947) 1351–1362.

[52] F. Helfferich, Ion Exchange, McGraw Hill, New York, USA, 1962, p. 166.

[53] S. Lagergren, Zur theorie der sogenannten adsorption geloster stöffe, Kungliga Sevenska Vetenskapsakademiens, Handlingar 24 (1898) 1.

[54] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.

[55] Y.S. Ho, G. McKay, D.A.J. Wase, C.F. Forster, Study of the sorption of divalent metal ions on to peat, Adsorption Sci. Technol. 18 (2000) 639–650.

[56] Y. Onal, C. Akmil-Basar, C. Sarıcı-Ozdemir, Investigation kinetics mechanisms of adsorption malachite green onto activated carbon, J. Hazard. Mater. 146 (2007) 194–203.