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Biosorption of Pb(II) and Cd(II) from aqueous solution using green alga (*Ulva lactuca*) biomass

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Abstract

The biosorption characteristics of Pb(II) and Cd(II) ions from aqueous solution using the green alga (*Ulva lactuca*) 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 *U. lactuca* biomass. Langmuir model fitted the equilibrium data better than the Freundlich isotherm. The monolayer biosorption capacity of *U. lactuca* biomass for Pb(II) and Cd(II) ions was found to be 34.7 mg/g and 29.2 mg/g, respectively. From the D–R isotherm model, the mean free energy was calculated as 10.4 kJ/mol for Pb(II) biosorption and 9.6 kJ/mol for Cd(II) biosorption, indicating that the biosorption of both metal ions was taken place by chemisorption. The calculated thermodynamic parameters (ΔG°, ΔH° and ΔS°) showed that the biosorption of Pb(II) and Cd(II) ions onto *U. lactuca* 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 metal ions followed well pseudo-second-order kinetics.
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Keywords: Green alga; *Ulva lactuca*; Lead(II); Cadmium(II); Biosorption; Isotherm; Thermodynamics; Kinetics

1. Introduction

The release of different pollutants into environment has increased noticeably as a result of industrialization, and thereby lowered the quality of the environment to alarming levels [1]. Of such pollutants, heavy and toxic metals are most important because of their non-biodegradability, with lead and cadmium ions being the toxic and hazardous [2]. Lead has special industrial significance since it is employed in batteries, paints, pigments and ammunition, petrol, cables, alloys and steels, plastics, the glass industry and the metal industry [3]. As a consequence, lead contamination is due to effluents of these industries, and also vehicular traffic and the mixing of roadside run-offs [4]. On the other hand, cadmium toxicity may be observed by a variety of syndromes and effects including renal dysfunction, hypertension, hepatic injury, lung damage and teratogenic effects [5]. Numerous processes such as ion exchange, precipitation, phytoextraction, ultrafiltration, reverse osmosis and electrodialysis have been used for the removal of heavy metal ions from aqueous solution [6]. However, technical or economic factors limit sometimes the feasibility of such processes.

Biosorption, which uses the ability of biological materials, is a relatively new technology to remove heavy metals from industrial wastewater. The major advantages of the biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive biosorbent materials such as naturally abundant algae or by products of fermentation industries as biosorbents [7]. Different types of biomass have been investigated for the biosorption characteristics of lead (Pb(II)) and cadmium (Cd(II)) ions from aqueous solution [8,9].

Among the biological materials marine algae otherwise known as seaweeds have been reported to have high metal binding capacities due to the presence of polysaccharides, proteins or lipid on the cell wall surface containing functional groups such as amino, hydroxyl, carboxyl and sulphate, which can act as binding sites for metals [10]. The green alga, *Ulva lactuca*, is particularly useful in these respects because of its wide distribution and relatively simple structure [11]. *U. lactuca* has a

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sheet-like thallus which is two cells thick, resulting in a relatively high surface area of structurally uniform and physiologically active cells [12]. *U. lactuca* is widespread along the shores of Turkey, grows well along the Black Sea coasts [13]. Some investigations have been carried out for the removal of different heavy metals using *U. lactuca* [12,14]. However, according to authors' survey, there is no extensive study on the biosorption of Pb(II) and Cd(II) using this algal biomass in literature. In addition, this new material was chosen as biosorbent in this study due to being of its natural, renewable and thus low-cost biomass.

The present work focused on the potential use of *U. lactuca* biomass for removal of Pb(II) and Cd(II) ions from aqueous solution. Experimental parameters affecting the biosorption process such as pH, contact time, biomass dosage and temperature were studied. The equilibrium biosorption data were evaluated by Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models. The biosorption mechanisms were also investigated in terms of thermodynamics and kinetics.

2. Experimental procedures

2.1. Biomass preparation

The green alga (*U. lactuca*) biomass was used as biosorbent for the biosorption of Pb(II) and Cd(II) ions. Samples of the biomass were collected from the East Black Sea coast of Turkey. Samples were washed several times using deionized water to remove extraneous and salts. They were then dried in an oven at 60 °C for 48 h. The dried algae biomass was chopped, sieved and the particles with an average of 0.5 mm were used for biosorption experiments.

2.2. Reagents and equipments

All chemicals used in this work, were of analytical reagent grade and were used without further purification. A Perkin Elmer AAnalyst 700 flame atomic absorption spectrometer with deuterium background corrector was used. All measurements were carried out in an air/acetylene flame.

2.3. Batch biosorption procedure

Biosorption experiments were carried out at the desired pH value, contact time and biomass dosage level using the necessary biomass in a 100 mL stoppered conical flask containing 25 mL of test solution. Initial solutions with different concentration of Pb(II) and Cd(II) were prepared by proper dilution from stock 1000 mg/L Pb(II) and Cd(II) standards. 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 at 100 rpm. The experiments were repeated at 20, 30, 40, and 50 °C. The time required for reaching the equilibrium condition estimated by drawing samples at regular intervals of time till equilibrium was reached. The contents of the flask were filtered through filter paper and the filtrate was analyzed for metal concentration by using flame AAS. 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 biomass dosage of 20 g/L. Throughout the study, the contact time was varied from 5 to 120 min, the pH from 2 to 8, the initial metal concentration from 10 to 400 mg/L, and the biosorbent dosage from 2 to 40 g/L.

3. Results and discussion

3.1. Effect of pH

Algal biomasses contain high content of carboxyl groups from mannuronic and guluronic acids on the cell wall polysaccharides, which suggests that the biosorption process could be affected by changes in the solution pH [15]. The effect of pH on the biosorption of Pb(II) and Cd(II) ions onto *U. lactuca* biomass was studied by changing pH values in the range, 2–8 and the results were presented in Fig. 1. The maximum biosorption was found to be 95% for Pb(II) and 90% for Cd(II) ions at pH 5. Therefore, all the biosorption experiments were carried out at pH 5. At higher pH values, the biosorption yield for Cd(II) was dramatically decreased. At pH range, 2–4, the biosorption

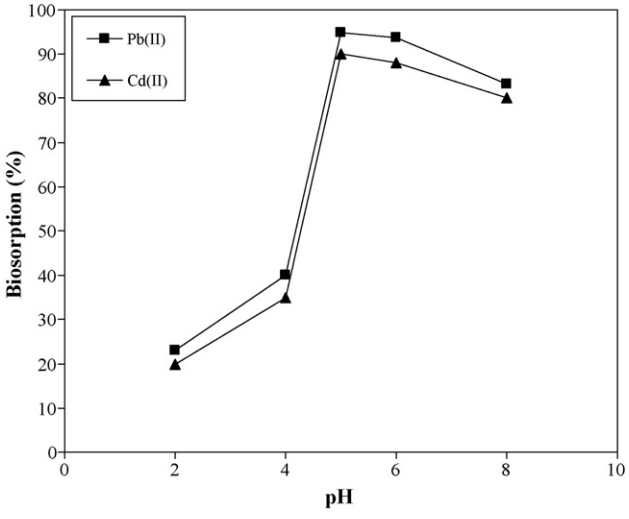

Fig. 1. Effect of pH on biosorption of Pb(II) and Cd(II) onto *U. lactuca* biomass (metal concentration:10 mg/L; temperature: 20 °C).

yield was in the range of 20–40% for both Pb(II) and Cd(II) ions. Increased positive charge (protons) density on the sites of biomass surface at low pH values (pH 2–4) restricted the approach of metal cations as a result of repulsive force. In contrast, when the pH value increased, biomass surface was more negatively charged and the biosorption of the metal ions with positive charge (Pb^{2+} and Cd^{2+}) was reached maximum around pH 5. Decrease in biosorption at higher pH (pH > 5) is due to the formation of soluble hydroxilated complexes of the metal ions and their competition with the active sites, and as a consequence, the retention would decrease.

3.2. Effect of biomass dosage

The effect of biomass dosage on the biosorption of Pb(II) and Cd(II) ions was studied using different biomass dosage in the range, 2–40 g/L (Fig. 2). Results showed that the biosorption efficiency is highly dependent on the increase in biomass dosage of the solution. The maximum biosorption of the metal ions was attained at about biomass dosage, 20 mg/L and it was almost same at higher dosages. This trend could be explained as a consequence of a partial aggregation of biomass at higher biomass concentration, which results in a decrease in effective surface area for the biosorption [16]. Therefore, the optimum biomass dosage was selected as 20 g/L for further experiments.

3.3. Effects of contact time and temperature

Contact time is one of the important parameters for successful biosorption application. Fig. 3 shows the biosorption efficiency of Pb(II) and Cd(II) ions by *U. lactuca* as a function of contact time and temperature. As can be seen from Fig. 3, the biosorption efficiency increases with rise in contact time up to 60 min at 20–50 °C and after then it is almost constant. Therefore, the optimum contact time was selected as 60 min for further experiments.

On the other hand, the biosorption yield decreased from 95 to 73% for Pb(II) ion and from 91 to 70% for Cd(II) ion with

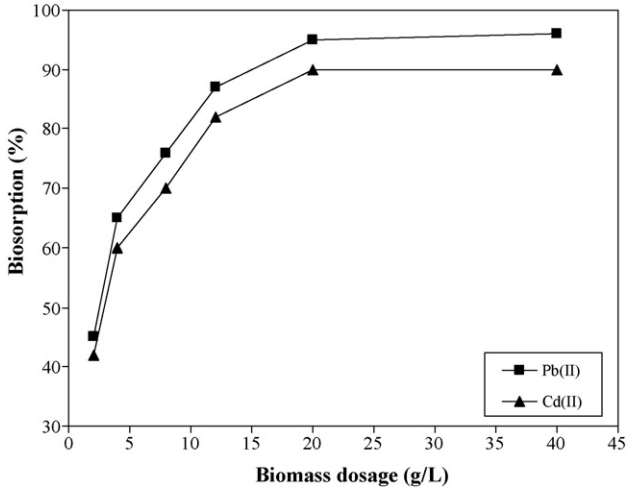

Fig. 2. Effect of biomass dosage on biosorption of Pb(II) and Cd(II) onto *U. lactuca* biomass (metal concentration: 10 mg/L; pH: 5; temperature: 20 °C).

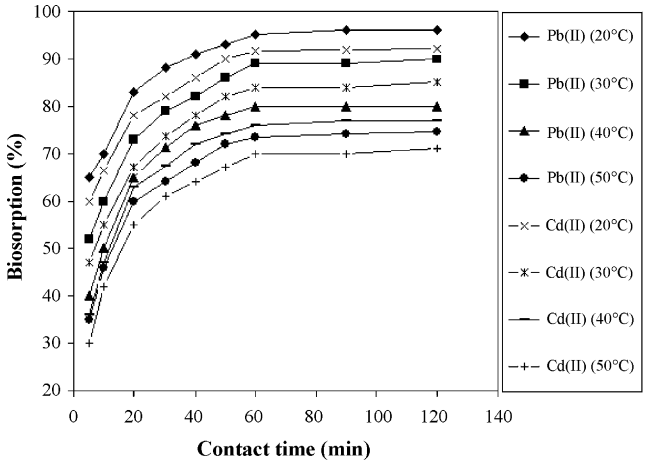

Fig. 3. Effect of contact time and temperature on biosorption of Pb(II) and Cd(II) onto *U. lactuca* biomass (metal concentration:10 mg/L; biomass dosage: 20 g/L; pH: 5).

increasing temperature from 20 to 50 °C during a 60 min-contact time. This result indicated the exothermic nature of Pb(II) and Cd(II) biosorption onto *U. lactuca* biomass. A decrease in the biosorption of Pb(II) and Cd(II) ions with the rise in temperature may be due to either the damage of active binding sites in the biomass [17] or increasing tendency to desorb metal ions from the interface to the solution [18]. The optimum solution temperature was selected as 20 °C for further biosorption experiments.

3.4. Biosorption isotherm models

The sorption capacity of a biosorbent can be described by equilibrium sorption isotherm, which is characterized by definite constants whose values express the surface properties and affinity of the biosorbent. In this study, three important sorption isotherm models were selected to fit experimental data, which are namely Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models. The Langmuir model assumes that biosorption occurs at specific homogeneous sites on the biosorbent and is used successfully in many monolayer biosorption processes. This model can be written as follows [19]

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

where q_e is the equilibrium metal ion concentration on the biosorbent (mg/g), C_e is the equilibrium metal ion concentration in the solution (mg/L), q_m is the monolayer biosorption capacity of the biosorbent (mg/g), and K_L is the Langmuir biosorption constant (L/mg) relating the free energy of biosorption.

Fig. 4 indicates the linear relationship between the amount (mg) of Pb(II) and Cd(II) ions sorbed per unit mass (g) of *U. lactuca* 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 0.992 and 0.997 for Pb(II) and Cd(II) biosorption, respectively, indicating that the biosorption of the metal ions onto *U. lactuca* biomass fitted well the Langmuir model. In other words, the sorption of metal ions onto *U. lactuca* was taken place at the functional groups/binding sites

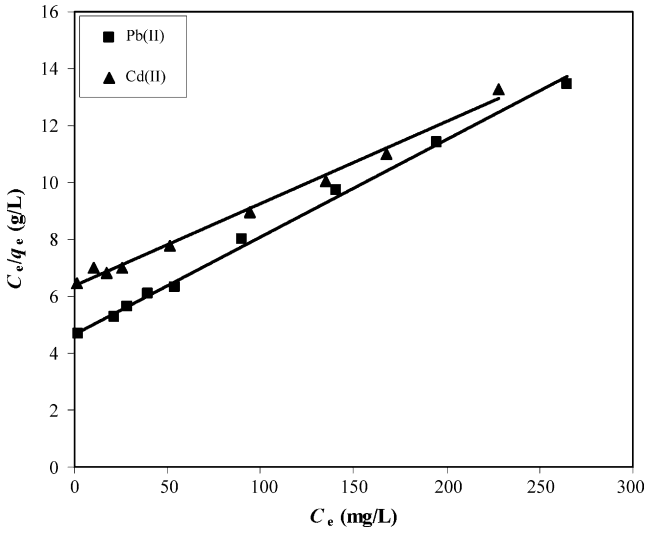

Fig. 4. Langmuir isotherm plots for biosorption of Pb(II) and Cd(II) onto *U. lactuca* biomass (biomass dosage: 20 g/L; contact time: 60 min; pH: 5; temperature: 20 °C).

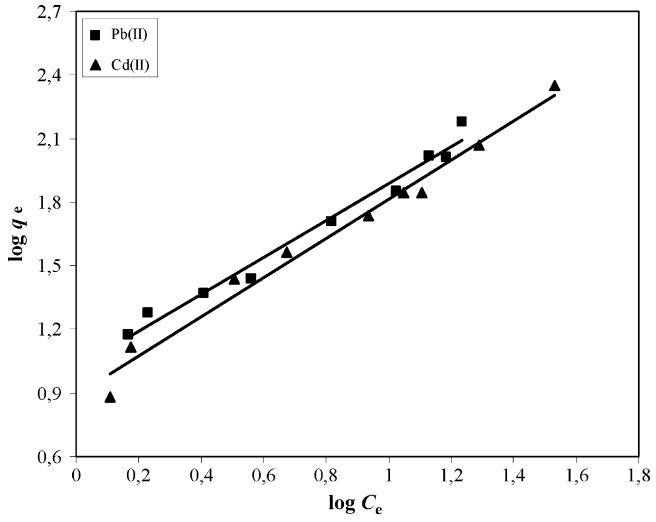

Fig. 5. Freundlich isotherm plots for biosorption of Pb(II) and Cd(II) onto *U. lactuca* biomass (biomass dosage: 20 g/L; contact time: 60 min; pH: 5; temperature: 20 °C).

on the surface of the biomass which is regarded as monolayer biosorption.

The K_L value was found as 5.0×10^{-2} L/mg for Pb(II) ion and 7.0×10^{-2} L/mg for Cd(II) ion. The maximum biosorption capacity (q_m) was found to be 34.7 mg/g for Pb(II) ion and 29.2 mg/g for Cd(II) ion. In addition, Table 1 presents the comparison of biosorption capacity of *U. lactuca* biomass for the Pb(II) and Cd(II) with those of various biomasses in literature [9,20–25]. The biosorption capacity of *U. lactuca* biomass for these metal ions is higher than that of the majority of other biomasses given in Table 1. Therefore, it can be noteworthy that the *U. lactuca* biomass has important potential for removal of Pb(II) and Cd(II) ions from aqueous solution.

The Freundlich model can be applied for non-ideal sorption on heterogeneous surfaces and multilayer sorption. The Freundlich model [26] is

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

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.

Table 1
Comparison of biosorption capacity of *U. lactuca* biomass for Pb(II) and Cd(II) ions with that of different biomasses

Biosorbent	Biosorption capacity (mg/g)		
	Pb(II)	Cd(II)	Reference
Pinus sylvesteris	22.2	19.1	[9]
Syzygium cumini	32.5	–	[20]
Mucor rouxii	35.7	8.5	[21]
Caulerpa lentillifera	28.7	4.7	[22]
Chlorella minutissima	9.74	11.1	[23]
Rhizopus arrhizus	56.0	27.0	[24]
Cystine-modified biomass	45.9	11.6	[25]
U. lactuca	34.7	29.2	Present study

The Fig. 5 shows the Freundlich isotherms obtained for the biosorption of Pb(II) and Cd(II) ions onto *U. lactuca* biomass using Eq. (3). The values of K_f and $1/n$ were found to be 10.5 and 0.9 for Pb(II) biosorption and 7.8 and 0.9 for Cd(II) biosorption. The $1/n$ values were between 0 and 1, indicating that the biosorption of Pb(II) and Cd(II) onto *U. lactuca* biomass was favourable at studied conditions. However, compared to the R^2 values, 0.980 for Pb(II) and 0.981 for Cd(II) ion, with that obtained from the Langmuir model, it can be remarkably noted that the Langmuir isotherm model is better fitted the equilibrium data.

The equilibrium data were also applied to the D–R isotherm model to determine the nature of biosorption processes as physical or chemical. The linear form of the D–R isotherm equation [27] is:

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

where q_e is the amount of metal ions sorbed on per unit weight of biomass (mol/L), q_m is the maximum biosorption capacity (mol/g), β is the activity coefficient related to mean biosorption 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 0.993 for Pb(II) biosorption and 0.997 for Cd(II) biosorption (Fig. 6). From the intercept of the plots, the q_m value was found to be 2.0×10^{-4} mol/g for Pb(II) biosorption and 3.7×10^{-4} mol/g for Cd(II) biosorption. The mean biosorption energy (E, kJ/mol) is as follow:

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

The mean free energy of biosorption gives information about biosorption mechanism, physical or chemical. If E value is between 8 and 16 kJ/mol, the biosorption process follows chemically and if $E < 8$ kJ/mol, the biosorption process is of a physically [28]. The mean biosorption energy was calculated as 10.4 and 9.6 kJ/mol for the biosorption of Pb(II) and Cd(II)

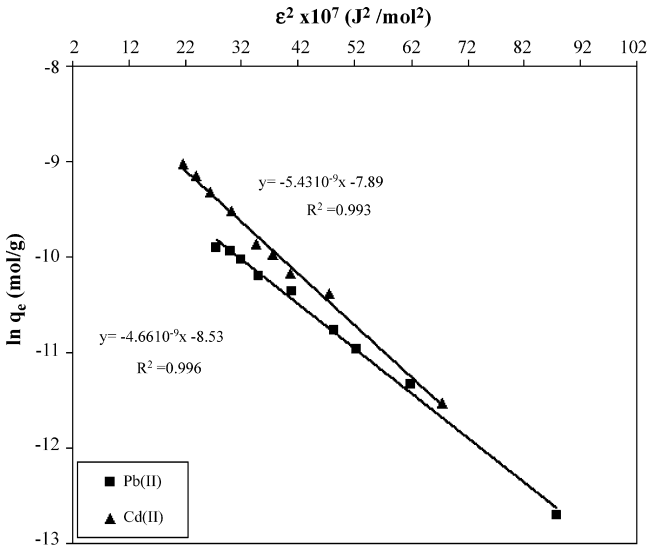

Fig. 6. D–R isotherm plots for biosorption of Pb(II) and Cd(II) onto *U. lactuca* biomass (pH: 5; biosorbent dosage: 20 g/L; contact time: 60 min; temperature: 20 °C).

ions, respectively. These results indicated that the biosorption processes of both metal ions onto *U. lactuca* biomass may be carried out via chemisorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate [29].

3.5. Biosorption kinetics

The biosorption kinetics involves the search for a best model that well represents the experimental data. Several kinetic models are available to understand the behavior of the biosorbent and also to examine the controlling mechanism of the biosorption process and to test the experimental data. In this study, the biosorption equilibrium data were analyzed using two simplest kinetic models, pseudo-first-order and pseudo-second-order model.

The linearized form of the pseudo-first-order rate equation by Lagergren [30] 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 $\ln(q_e - q_t)$ versus t.

The plots of $\ln(q_e - q_t)$ versus 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 ($R^2 = 0.962$–0.982 for the Pb(II) biosorption and $R^2 = 0.970$–0.980 for Cd(II) biosorption, as seen in Table 2). It can be concluded from the R^2 values that the biosorption of Pb(II) and Cd(II) ions onto *U. lactuca* biomass does not fit a pseudo-first-order kinetic model.

Experimental data were also tested by the pseudo-second-order kinetic model which is given in the following form [31]:

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

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 [31]. The linear plots of *t/qt* versus *t* for the pseudo-second-order model for the biosorption of Pb(II) and Cd(II) ions onto the alga biomass at 20–50 °C were shown in Fig. 7a and b, respectively. The rate constants (k_2), the R^2 and the q_e values are given in Table 2. It is clear from these results that the R^2 values are very high (in range, 0.995–0.999 for the Pb(II) biosorption and 0.998–0.999 for the Cd(II) biosorption). These results suggest that the biosorption of Pb(II) and Cd(II) ions onto *U. lactuca* biomass well follows the pseudo-second-order kinetic model and based on the assumption that the rate limiting step may be chemisorption.

3.6. Biosorption thermodynamics

Thermodynamic parameters including the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were used to describe thermodynamic behaviour of the biosorption of Pb(II) and Cd(II) ions onto *U. lactuca* biomass. These parameters were

Table 2
Pseudo-first-order and pseudo-second-order parameters for the biosorption of Pb(II) and Cd(II) onto *U. lactuca* biomass at different temperatures

Temperature (°C)	Pseudo-first-order			Pseudo-second-order		
	k_1 (1/min)	q_e (mg/g)	R^2	k_2 (g/mg min)	q_e (mg/g)	R^2
Pb(II)						
20	8.4×10^{-2}	0.56	0.977	0.29	1.01	0.999
30	7.5×10^{-2}	0.54	0.974	0.24	0.98	0.998
40	7.3×10^{-2}	0.44	0.982	0.22	0.88	0.999
50	4.1×10^{-2}	0.43	0.962	0.16	0.86	0.995
Cd(II)						
20	8.4×10^{-2}	0.63	0.970	0.25	0.99	0.999
30	8.0×10^{-2}	0.53	0.972	0.19	0.95	0.999
40	7.3×10^{-2}	0.44	0.971	0.17	0.90	0.998
50	5.0×10^{-2}	0.43	0.980	0.16	0.81	0.998

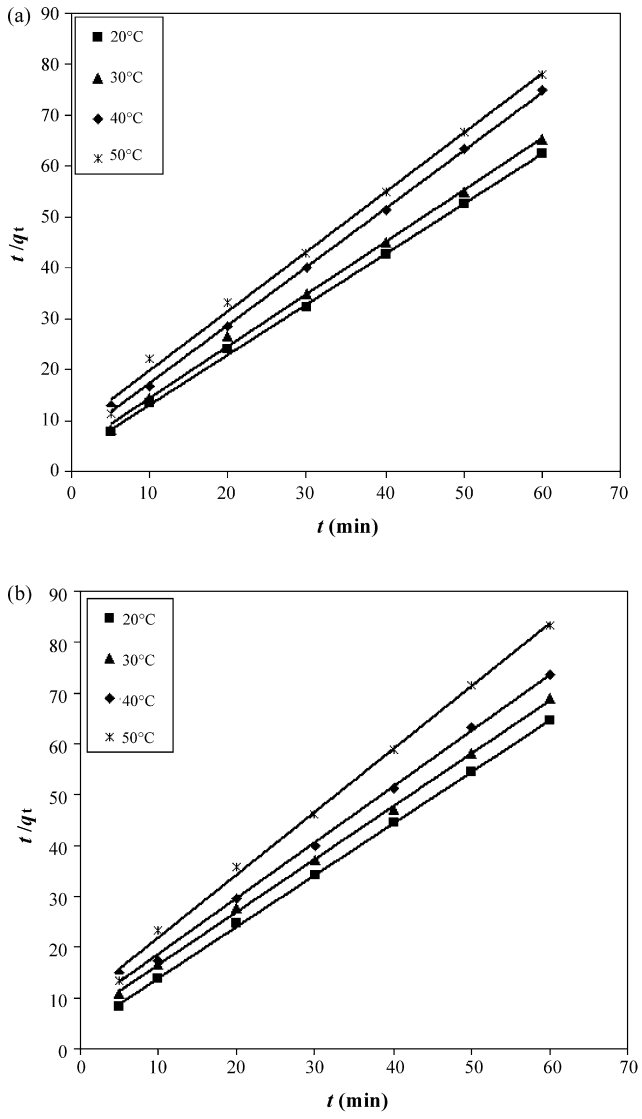

Fig. 7. Pseudo-second-order kinetic plots at different temperatures: (a) for Pb(II) biosorption (b) for Cd(II) biosorption.

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 [32].

By considering Eq. (9), the enthalpy (ΔH°) and entropy (ΔS°) of biosorption were estimated from the slope and intercept of the plot of $\ln K_D$ versus $1/T$ yields, respectively (Fig. 8)

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

The free energy change (ΔG°) was calculated to be −16.7, −16.4, −15.7, and −15.4 kJ/mol for Pb(II) biosorption and −16.4, −16.0, −15.2, and −14.8 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

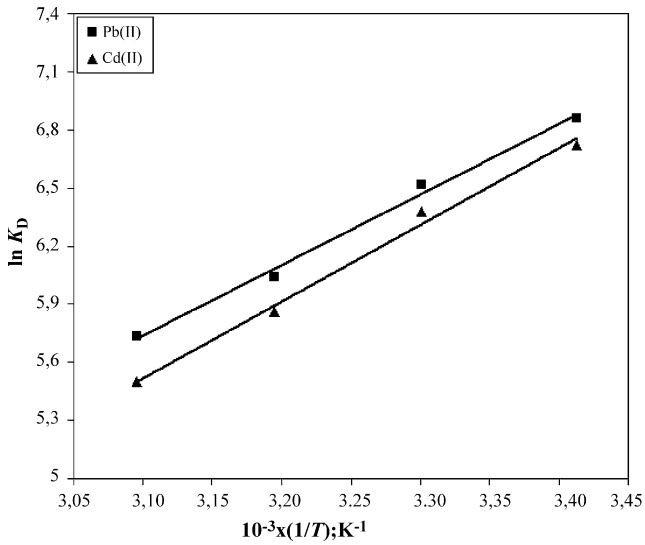

Fig. 8. Plot of $\ln K_D$ vs. $1/T$ for the estimation of thermodynamic parameters for biosorption of Pb(II) and Cd(II) onto *U. lactuca* biomass.

with increase in temperature shows a decrease in feasibility of biosorption at higher temperatures. The enthalpy of biosorption (ΔH°) was found to be −30.2 and −32.8 kJ/mol for Pb(II) and Cd(II) biosorption, respectively. The negative ΔH° is indicator of exothermic nature of the biosorption and also its magnitude gives information on the type of biosorption, which can be either physical or chemical. The enthalpy or heat of biosorption, ranging from 0.5 to 5 kcal/mol (2.1–20.9 kJ/mol) corresponds a physical sorption as it ranges from 20.9 to 418.4 kJ/mol in case of a chemical sorption [29]. The biosorption heats of Pb(II) and Cd(II) ions fall into the heat range of chemisorption. Therefore, the ΔH° values showed that the biosorption processes of Pb(II) and Cd(II) ions onto *U. lactuca* biomass were taken place via chemisorption. The mean biosorption energy values obtained from the D–R model also confirm this result. The ΔS° parameter was found to be −45.8 J/mol K for Pb(II) biosorption and −55.9 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.

4. Conclusions

This study focused on the biosorption of Pb(II) and Cd(II) ions onto algal biomass (*U. lactuca*) 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). Biosorption equilibrium was better described by the Langmuir isotherm model than the Freundlich model. The monolayer biosorption capacity of *U. lactuca* biomass for Pb(II) and Cd(II) was found to be 34.7 and 29.2 mg/g ions, respectively. From the D–R model, the mean energy was determined as 10.4 kJ/mol for Pb(II) biosorption and 9.6 kJ/mol for Cd(II) biosorption, indicating that the biosorption of both metal ions onto *U. lactuca* biomass may be carried out by chemisorption. Kinetic examination of the equilibrium data showed that the biosorption of Pb(II) and Cd(II)

ions onto *U. lactuca* followed well the pseudo-second-order kinetic model. The thermodynamic calculations indicated the feasibility, exothermic and spontaneous nature of the biosorption process at 20–50 °C. Based on all results, it can be also concluded that the *U. lactuca* is an effective and alternative biomass for the removal of Pb(II) and Cd(II) ions from wastewaters in terms of high biosorption capacity, natural and abundant available, and low cost.

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