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Equilibrium, thermodynamic and kinetic studies for the biosorption of aqueous lead(II), cadmium(II) and nickel(II) ions on *Spirulina platensis*

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Abstract

The biosorption of lead(II), cadmium(II) and nickel(II) ions from aqueous solution by *Spirulina platensis* was studied as a function of time, concentration, temperature, repetitive reactivity, and ionic competition. The kinetic results obeyed well the pseudo second-order model. Freundlich, Dubinin Radushkevich and Temkin isotherm models were applied in describing the equilibrium partition of the ions. Freundlich isotherm was applied to describe the design of a single-stage batch sorption system. According to the thermodynamic parameters such as ΔG°, ΔH° and ΔS° calculated, the sorption process was endothermic and largely driven towards the products. Sorption activities in a three metal ion system were studied which indicated that there is a relative selectivity of the biosorbent towards Pb^{2+} ions. The measurements of the repetitive reusability of *S. platensis* indicated a large capacity towards the three metal ions.
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1. Introduction

Toxic heavy metal contamination is a worldwide environmental problem and has necessitated the search to develop efficient methods for the removal of metal pollutants [1]. Traditional technologies such as chemical precipitation, ion exchange, activated carbon adsorption, and membrane separation processes have been applied widely for the removal of heavy metals from contaminated environmental waters [2]. As any method, most of these methods have several advantages and, at the same, drawbacks which have caused a great interest in the use of other sorbent materials [3]. Biological approaches, especially the use of biosorbents, have been evaluated as an alternative to these techniques [4]. Within this context, algae was reported to be one of the usable biosorbents by virtue of their low cost, relatively large surface area, high binding affinity and metal recovery [5,6]. In line with this trend in biotechnology, the usage of *Spirulina platensis* as a biosorbent is being viewed as a proper choice due primarily to its fast growth [7].

S. platensis, a member of blue-green algae, is an alternative source of protein for human food and feed purposes. Other than protein, it involves polysaccharides, lipids, and vitamins within [8]. These contain a variety of functional groups such as carboxyl, hydroxyl, sulphate and other charged groups which are responsible for metal binding [9]. Although biosorption has gained much attention, the exact interactions between the metal ions and the functional groups on the cell, the kinetics and the thermal properties of biosorption have not been well defined [10]. Literature reports reveal however, a large number of studies in which microorganisms have been used as biosorbents for heavy metals, and these studies may be useful for low cost industrial wastewater treatment where rapid removal of several heavy metals is needed [11–14]. Most studies have focused on the removal of Pb^{2+}, Cd^{2+}, and Ni^{2+} from wastewater by using various biosorbents. The mechanism of simultaneous metal removal (Cd^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+}) by three

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macrophytes biomass (*Spirodela intermedia*, *Lemna minor* and *Pistia stratiotes*) was investigated [15]. According to that study, Pb^{2+} and Cd^{2+} were reported to be more efficiently removed by the three adsorbents. *Azolla filiculoides* also has been shown to be able to effectively remove Pb^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} from aqueous solution [16]. In another study, the sorption behavior of Cu^{2+}, Cd^{2+}, and Pb^{2+} was investigated on four freshwater algae with different cell surface characteristics, *Oscillatoria limnetica*, *Anabena spiroides*, *Eudorina elegans* and *Chlorella vulgaris* [1]. The results showed all four freshwater algae to have great sorption capacity towards these metals, especially for Pb^{2+} in both one-metal and three-metal systems. Literature studies reported also that *S. platensis* can be a potential biosorbent for the removal and concentration of several metals [17–19].

In this study, kinetic and thermodynamic aspects of the sorption of Pb^{2+}, Cd^{2+}, and Ni^{2+} by *S. platensis* were examined. In addition, the competitive biosorption of the three metal ions, and the repetitive application of the biosorbent for five successive times were investigated.

2. Materials and methods

2.1. Preparation of the biosorbent

The cyanobacteria, *S. platensis* (Ege-Macc 31), was obtained from the culture collection of Ege University Microalgae Culture Collection, Ege-Macc. It was grown in Zarrouk's Medium under constant light (3000 lx) and temperature ($25 \pm 1\,^{\circ}C$). The culture was then filtered by Whatman No. 1 filter paper and washed with deionized water to remove the growing medium. Harvested cells were stored at $-24\,^{\circ}C$ and lyophilized accordingly with Christ alpha 1–4 Ld instrument.

Optical image was obtained by using a trinocular light microscope (Olympus CH40). SEM characterization was carried out using Philips XL-30S FEG prior to analysis. Both the optical image and the SEM micro image show that *S. platensis* has a spiral shape as seen from the characteristic morphology (Fig. 1). The elemental composition of the alga was determined with LECO-932 elemental analyzer and according to the results *S. platensis* mainly involves 43.10% C, 9.90% N, 6.47% H, and 2.89% S by mass.

2.2. Biosorption studies

Aqueous Pb^{2+}, Cd^{2+}, and Ni^{2+} ions were prepared from analytical reagent grade lead nitrate, $Pb(NO)_3$ (Riedel, 99%, product code: 31137, CAS no. [10099-74-8]) cadmium chloride, $CdCl_2$ (Fluka, >99, product code: 20899, CAS no. [10108-64-2]) and nickel chloride, $NiCl_2 \cdot 6H_2O$ (Carlo Erba, 99%, product code: 464645, CAS no. [7791-20-0]), respectively. The stock solutions were prepared in deionized water at the initial concentrations of $100.0\,mg\,L^{-1}$ and $500.0\,mg\,L^{-1}$ for each of the metal ion. For equilibrium studies, 50-mL polyethylene centrifuge tubes were used. The pH of the solutions was adjusted to 6.0 with NH_3 and HNO_3 solutions. The mixtures were then mixed using GFL 1083 water bath shaker equipped with a microprocessor thermostat. In a typical run, 50.0 mg biosorbent was contacted with 10.0 mL
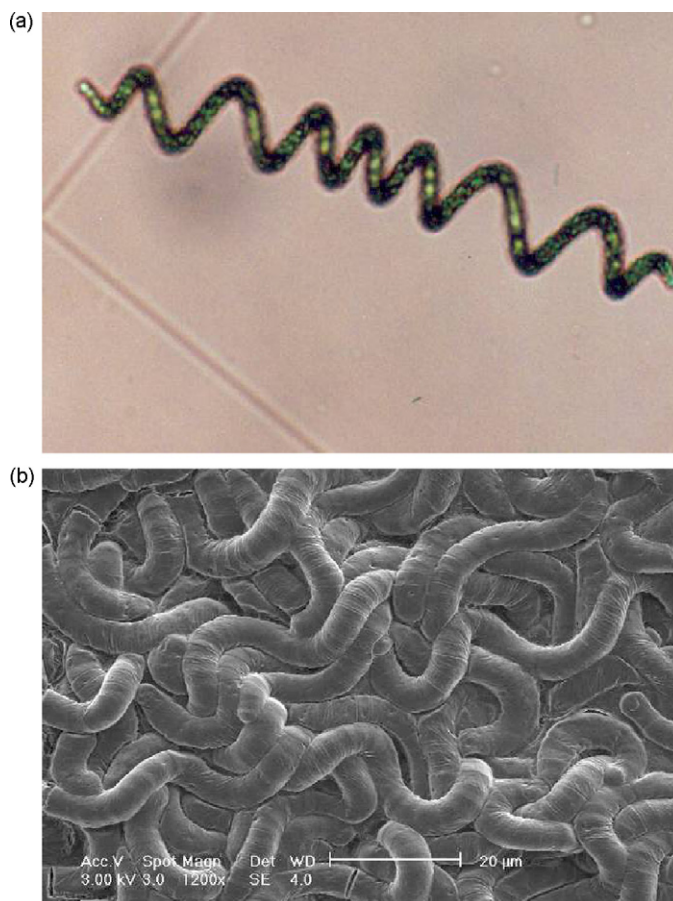

Fig. 1. Typical images of *Spirulina platensis* obtained with (a) optical microscope (100×) and (b) scanning electron microscope (1200×).

metal ion solution. The experiments were performed at $25\,^{\circ}C$ and $50\,^{\circ}C$ for contact periods of 5 s, 30 s, 1 min, 2 min, 15 min, 30 min, 60 min, 120 min, and 240 min. At the end of each mixing period, the biomass was removed by filtration through a $0.45\,\mu m$ cellulose acetate membrane filter and the filtrate was analyzed using a flame atomic absorption spectrometer (AAS), Thermo Elemental SOLAAR M6 Series instrument.

3. Results and discussion

It is well known that pH of the medium is among the most important factors that influence the biosorption process. Therefore, preliminary experiments have been performed to find out the optimum pH for maximizing the metal removal for algae, before investigating the kinetic and thermodynamic aspects of biosorption. An optimum pH is closely related with the chemical speciation of metal ion, speciation of the functional groups on the algae, and the nature of interaction of the metal ion with the algae functional groups. It is reported that at pH 5.0 algal cells have generally a net negative charge on the surface that favors the binding of metal ions to the surface ligands [20]. A decrease in metal sorption by algae has been frequently observed at low pHs (<2). High concentration of H^+ ions at low pH values is thought to be effective in excluding metal ions from binding to the sites on cell surface [21].

The experiments aiming at investigating the effect of pH on adsorption were conducted over a wide pH range. As a general trend, an increase in adsorbed metal amount was observed with the increase in pH. In this study, pH values in the alkaline range were not preferred due to the possible precipitation of metal hydroxides. The experiments performed within this context for Pb^{2+}, Cd^{2+} and Ni^{2+} ions at pH values of 2.0, 4.0, and 6.0 resulted, respectively, in % biosorption values of 5, 80, and 92 for Pb^{2+}; 14, 86, and 87 for Cd^{2+}; and 12, 47, and 59 for Ni^{2+} at initial metal ion concentration of $100.0\,mg\,L^{-1}$. In light of these results, pH 6.0 was chosen for the further experiments as an optimum condition.

3.1. Kinetics of sorption

Kinetic studies of sorption on *S. platensis* were carried out at the initial metal concentrations of $100.0\,mg\,L^{-1}$ and $500.0\,mg\,L^{-1}$ for times of contact that ranged from 5 s to 240 min. The experiments were conducted at two preset temperatures; namely 25 °C and 50 °C.

The time required to reach equilibrium was in all cases less than 1 h for each of Pb^{2+}, Cd^{2+} and Ni^{2+} ions. The kinetic plots for the three cations are demonstrated in Fig. 2. The experimental kinetic data showed best correlation with the pseudo-second-order rate equation given by the equation [22]:

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

where q_t is the concentration of sorbed ion on the solid at time t ($\mu mol\,g^{-1}$), q_e is the concentration of sorbed ion at equilibrium ($\mu mol\,L^{-1}$), and k_2 is the pseudo-second-order rate constant ($\mu g\,\mu mol^{-1}\,min^{-1}$), respectively. The values of q_t in the equation above were calculated using the mass balance equation:

$$q = (C_0 - C)\frac{V}{M} \tag{2}$$

where C_0 is the initial metal concentration ($\mu mol\,L^{-1}$), C is the equilibrium concentration of metal solution ($\mu mol\,L^{-1}$), V is the volume of solution (L), and M is the mass of the solid (g).

Fig. 2 shows the kinetic plots as predicted by the pseudo-second-order kinetics. These plots were constructed using the model parameters obtained from the linear regression analysis. The linear regression plots of t/q_t against t (insets in Fig. 2) provided the rate constants, k_2, which are given in Table 1, together with q_e and the linear correlation coefficients, R.

In Table 1, the values which are tabulated at two different temperatures indicate that while the k_2 values increased as temperature was increased in the cases of Pb^{2+} and Ni^{2+}, a decrease in the k_2 value was observed in the case of Cd^{2+} sorption. This means that, unlike Pb^{2+} and Ni^{2+}, the increase in temperature is causing a delay in the attainment of equilibrium for Cd^{2+}. Generally speaking, the effect of temperature on the rate constants in liquid–solid sorption systems is likely a complicated issue. Literature resources have reported many cases in which the increase in temperature caused a decrease in the rate constants of different adsorbate ions [23]. From a physicochemical perspective that is based on the behavior of gases, the rate constant is expected
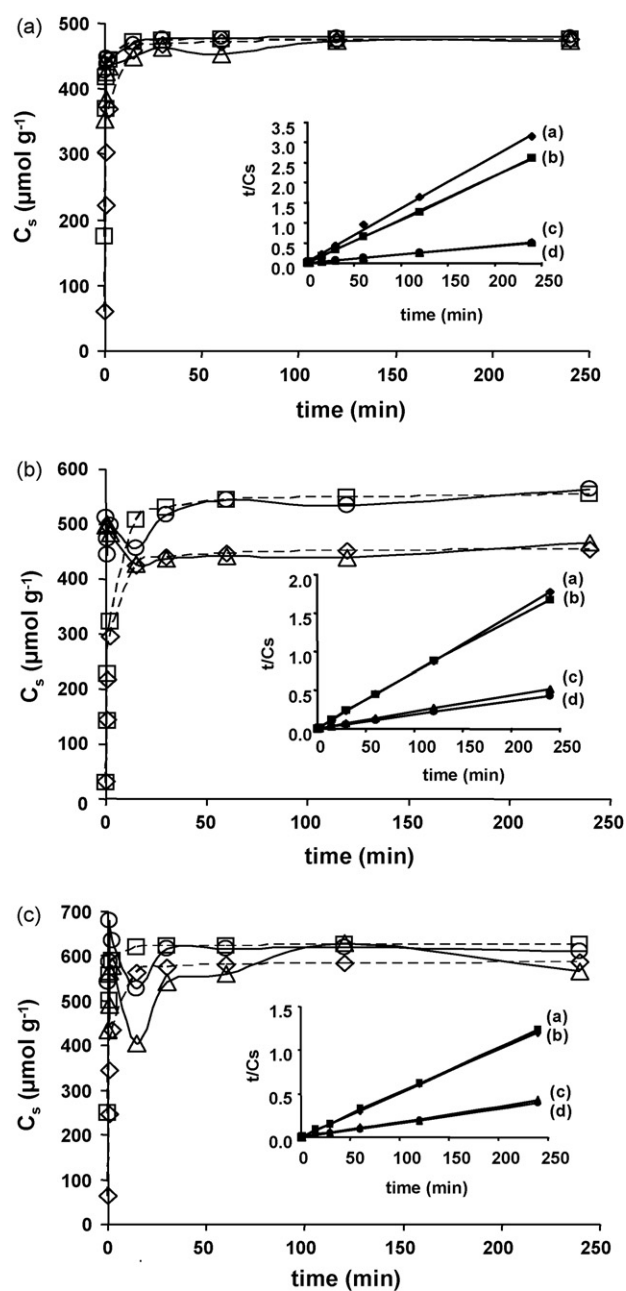

Fig. 2. Theoretical and experimental variations of the sorbed amount of (a) Pb^{2+}, (b) Cd^{2+} and (c) Ni^{2+} ($\mu mol\,g^{-1}$) with time at 25 °C and 50 °C on *Spirulina platensis*. (($\triangle$) 25 °C $500.0\,mg\,L^{-1}$ experimental, ($\bigcirc$) 50 °C $500.0\,mg\,L^{-1}$ experimental, ($\diamond$) 25 °C $500.0\,mg\,L^{-1}$ theoretical, ($\square$) 50 °C $500.0\,mg\,L^{-1}$ theoretical). The insets show the linear regression plots (a) 25 °C $100.0\,mg\,L^{-1}$, (b) 50 °C $100.0\,mg\,L^{-1}$, (c) 25 °C $500.0\,mg\,L^{-1}$, (d) 50 °C $500.0\,mg\,L^{-1}$.

to usually increase as the temperature is increased [24]. This is usually caused by the fact that the increase in temperature, in a medium where the intermolecular forces are very weak, leads to an increase in the kinetic energy of gas molecules/atoms and thus enhances the rate of reactions. In liquid–solid sorption systems, however, the situation is much more complicated as the behavior of ions in solution or on the solid would be subject to factors like the inter-ionic forces, the hydration energy, the availability of sorption sites and the relative stability of sorbed ions at these sites [25]. The signs of the observed energy of activation, E_a,

Table 1
Kinetic parameters obtained from linear fits of the experimental data for Pb^{2+}, Cd^{2+}, Ni^{2+} biosorption on *Spirulina platensis* (metal ion concentrations = 500.0 mg L^{-1}, amount of biomass = 50.0 mg, solution volume = 10.0 mL)

Sample	T (°C)	$[q]_e$ (μmol g^{-1})	k_2 (g μmol^{-1} min^{-1})	R	h (μmol g^{-1} min^{-1})	E_a (kJ mol^{-1})
Pb^{2+}-loaded *S. platensis*	25	476	3.68×10^{-3}	>0.9999	8.33×10^2	+44
	50	476	1.47×10^{-2}	0.9999	3.33×10^3	
Cd^{2+}-loaded *S. platensis*	25	455	2.01×10^{-3}	0.9991	4.16×10^2	−16
	50	556	1.24×10^{-3}	0.9993	3.83×10^2	
Ni^{2+}-loaded *S. platensis*	25	588	2.41×10^{-3}	0.9969	8.33×10^2	+54
	50	625	1.28×10^{-2}	0.9998	5.00×10^3	

which are provided in Table 1 reflect the effect of temperature on the rate constants. According to literature resources, when the value of E_a is between 8.4 and 83.7 kJ/mol, the adsorption is said to be activated chemical type which means that the rate varies with temperature according to finite activation energy in the Arrhenius equation [26,27]. However, since the values of E_a are not purely determined by the intrinsic sorption step, but might include also contributions from ionic dehydration effects in addition to plausible contributions dependent on the nature of the adsorbent, it is unlikely to provide mechanistic speculations about the sorption process.

The experimental and theoretical variations of the sorbed amounts of Pb^{2+}, Cd^{2+}, Ni^{2+} on *S. platensis* at temperatures of 25 °C and 50 °C is provided in Fig. 2a–c, respectively.

3.2. Thermodynamic parameters

The experimental data obtained at different temperatures were used in calculating the thermodynamic parameters of sorption; $\Delta H°$, $\Delta G°$, and $\Delta S°$ utilizing the well-known equations:

$$\Delta G° = -RT \ln R_d \tag{3}$$

$$\Delta H° = R \ln \frac{R_d(T_2)}{R_d(T_1)} \left[\frac{T_1 T_2}{T_2 - T_1} \right] \tag{4}$$

$$\Delta S° = \frac{\Delta H° - \Delta G°}{T} \tag{5}$$

The distribution ratio, R_d (mL g^{-1}), is defined as q_e/C_e, and reflects the extent of distribution of the adsorbate ion between the solid and liquid phases at equilibrium. R_d is valid at a particular initial concentration and reaction conditions. The obtained 'apparent' values of $\Delta H°$, $\Delta S°$ and $\Delta G°$ of sorption for each metal ion uptake on the biosorbent are summarized in Table 2.

The $\Delta H°$ values demonstrate that the sorption process is of endothermic nature in all cases. This behavior indicates that

higher temperatures are more preferred for higher sorption, with the sequence of preference being $Pb^{2+} > Cd^{2+} > Ni^{2+}$. The calculated values are described as 'apparent' values because they include plausible energy contribution from the adsorbent and forces of dehydration of the adsorbate ions in addition to the energy associated with the intrinsic adsorption step. The endothermic nature of biosorption was reported in earlier studies. Tsezos and Volesky [28] reported a slight increase in cation sorption by seaweed biomass with increase in temperature from 4 to 55 °C. Similarly, Aksu [26] recorded increase in Ni^{2+} biosorption by dried biomass of *Chlorella vulgaris* with enhancement of temperature from 15 °C to 45 °C. On the contrary, some studies indicate exothermic nature of metal sorption by algae. For instance, it is stated that Cd^{2+} sorption by *Sargassum* sp. biomass decreased slightly with an increase in temperature [29]. Some other studies also support this observation [30,31]. In the sorption studies of heavy metals, the observed enthalpy is comprised of contributions from the energetic effects associated with intrinsic adsorption step, dehydration effects of the metal ions inside the aqueous solution, in addition to any plausible contribution from the physical/chemical changes that the sorption sites might undergo as a result of sorption. Due to the complex nature of the adsorption process in liquid–solid systems, it is usually not easy to depict correlations between different sorption systems, especially if the experimental conditions do not match.

The calculated negative standard Gibbs energy changes depict that the sorption reactions are largely driven towards the products, with the same sequence of preference as given above.

The calculated values of $\Delta S°$ refer to the entropy change of the adsorption system (not the total entropy change), which can have positive or negative values. As shown in Table 2, positive values are reported in all cases. Positive values mean, theoretically, that more disorder is associated with the adsorption process. This might be intuitively explained based on the

Table 2
Values of $\Delta H°$, $\Delta S°$ and $\Delta G°$ calculated from the sorption data of Pb^{2+}, Cd^{2+}, Ni^{2+} on *Spirulina platensis* (metal ion concentrations = 500.0 mg L^{-1}, amount of biomass = 50.0 mg, solution volume = 10.0 mL)

Sample	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})	$\Delta G°$ (kJ mol^{-1})	
			298 K	323 K
Pb^{2+} – *S. platensis*	36	194	−21.8	−26.6
Cd^{2+} – *S. platensis*	16	97.7	−13.1	−15.6
Ni^{2+} – *S. platensis*	5	53.7	−11.4	−12.7

increase in the dehydration steps of the adsorbate ions, which are known to possess relatively high energies of solvation, and thus are stabilized by water sheaths in the absence of the adsorbent.

3.3. Sorption isotherm models

Sorption isotherms are mathematical models that describe the distribution of the adsorbate species among solid and liquid phases, and are thus important from the view point of chemical design. The data of Pb^{2+}, Cd^{2+}, and Ni^{2+} biosorption on *S. platensis* were examined by using three types of the most common isotherms; Freundlich, Dubinin–Radushkevich (D–R), and Temkin isotherm models.

Freundlich isotherm model is given by the equation:

$$q_e = kC_e^n \tag{6}$$

Non-linear fits of sorption data of Pb^{2+}, Cd^{2+} and Ni^{2+} are given in Fig. 3. The values of Freundlich constants, "k" and "n", are obtained from linear fits of sorption data and given in Table 3. The "n" values indicate that the biosorption process is highly non-linear, while the "k" values show that the affinity of the biosorbent towards the adsorbate ions follows the sequence $Ni^{2+} > Pb^{2+} > Cd^{2+}$.

D–R isotherm model is described by the equation:

$$q_e = q_m \exp(-K\varepsilon^2) \tag{7}$$

where

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right)$$

The magnitude of D–R parameter, q_m, corresponds to the sorption monolayer capacity and K gives information about sorption energy E, perceived as the amount of energy required to transfer one mole of the adsorbate ion from infinity in the bulk of the solution to the site of sorption. It is calculated using D–R constant, K, according to the relation $E = (2K)^{-1/2}$. The values of q_m and K are evaluated from the intercepts and slopes of plot of $\log q$ versus ε^2. The obtained constants are given in Table 4.

Temkin isotherm is given as:

$$q_e = B \ln(K_T C_e) \tag{8}$$

It can be expressed in the linear form as:

$$q_e = B \ln K_T + B \ln C_e \tag{9}$$

where $B = RT/b$

Fig. 3. Non-linear fits of isotherm models for (a) Pb^{2+}, (b) Cd^{2+} and (c) Ni^{2+} sorbed by *Spirulina platensis* (($\diamond$) experimental, ($\square$) Freundlich, ($\triangle$) Temkin, ($\bigcirc$) D–R isotherms).

Table 3
Freundlich parameters n, k obtained from the plots of Pb^{2+}, Cd^{2+}, Ni^{2+} sorbed by *Spirulina platensis* at 25 °C (amount of biomass = 10.0 mg, solution volume = 10.0 mL)

Sample	Freundlich constants		
	n	k	R
Pb^{2+} – *S. platensis*	0.2174	0.00419	0.8554
Cd^{2+} – *S. platensis*	0.2169	0.00254	0.9308
Ni^{2+} – *S. platensis*	0.4785	0.0162	0.9201

Table 4
D–R parameters, K, q_m and E obtained from the plots of Pb^{2+}, Cd^{2+}, Ni^{2+} sorbed by *Spirulina platensis* at 25 °C (amount of biomass = 10.0 mg, solution volume = 10.0 mL)

Sample	D–R constants			R
	K (mol kJ^{-1})^2	q_m (mol g^{-1})	E (kJ mol^{-1})	
Pb^{2+} – *S. platensis*	0.0018	0.0015	16.7	0.8869
Cd^{2+} – *S. platensis*	0.0022	0.0011	15.1	0.9463
Ni^{2+} – *S. platensis*	0.0057	0.0032	9.4	0.9022

Table 5
Temkin parameters K_T and B obtained from the plots of Pb^{2+}, Cd^{2+}, Ni^{2+} sorbed by *Spirulina platensis* at 25 °C (amount of biomass = 10.0 mg, solution volume = 10.0 mL)

Sample	Temkin constants		R
	K_T (L mol^{-1})	B	
Pb^{2+} – *S. platensis*	3.3×10^6	0.0001	0.9333
Cd^{2+} – *S. platensis*	4.4×10^5	0.0001	0.9367
Ni^{2+} – *S. platensis*	1.6×10^4	0.0003	0.8523

A plot of q versus $\ln C$ enables the determination of the isotherm constants B and K_T from the slope and the intercept, respectively. Temkin constants are given in Table 5. K_T is the equilibrium binding constant corresponding to the maximum binding energy and constant B is related to the heat of adsorption.

3.4. Sorption activities in a three metal ion system: competitive biosorption

Competitive biosorption was investigated at three different initial concentrations of Pb^{2+}, Cd^{2+} and Ni^{2+}; namely, 10.0, 50.0, and 100.0 mg L^{-1} contacted in each trial with 10.0 mg doses of the biomass. The results of competitive runs, expressed as %biosorption, are provided in Table 6, in line with the data that were obtained for biosorption of single components. In general, the presence of competing ions leads to a decrease in the biosorption. The extent of this decrease is, however, dependent on the concentration, and is also different for different ions. As the initial concentration is increased, less biosorption is observed, as expected. The most prominent result here is the apparent relative selectivity of the biosorbent towards Pb^{2+} ions, as can be seen at the ion concentrations of 50.0 and 100.0 mg L^{-1}.

3.5. Reusability

The repetitive reusability of the biosorbent was studied for the three metal ions at the initial concentrations of 10.0 mg L^{-1}. In these experiments the amount of the biosorbent was 10.0 mg, and each sample was tried repetitively for five successive runs. The results are shown in Fig. 4a–c. As seen, almost a total removal of Pb^{2+} ions can still be achieved even at the fifth trial of the same sample. In comparison to this, a steady decrease in the ability of sorption towards Ni^{2+} and Cd^{2+} was observed. However, this decrease is not steep, the thing that emphasizes the high capacity of the biosorbent at the applied conditions.
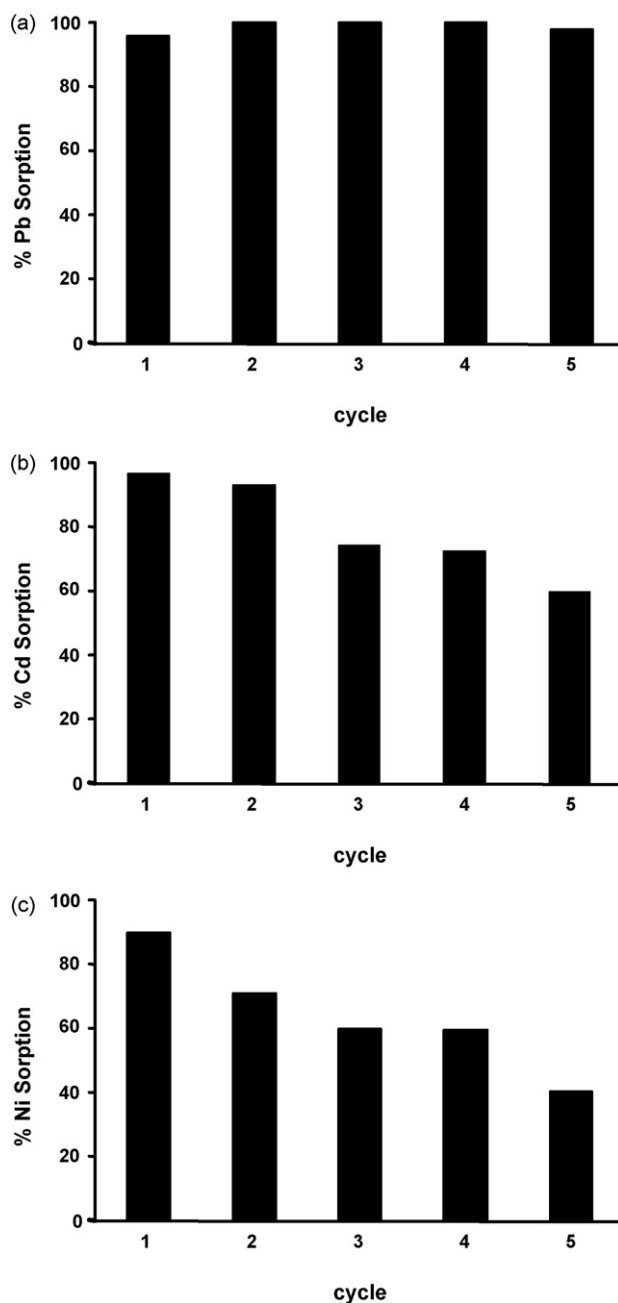

Fig. 4. Repetitive adsorption data for (a) Pb^{2+}, (b) Cd^{2+} and (c) Ni^{2+}.

3.6. Design of batch sorption

The sorption isotherm relations were applied to predict the design of single-stage batch sorption systems [32,33]. In a batch

Table 6
Comparison of the amount of Pb^{2+}, Cd^{2+}, Ni^{2+} sequestered from multi-metal ion solutions by *Spirulina platensis* (amount of biomass = 10.0 mg, sample volume = 10.0 mL, n = 3)

Initial concentration of Pb^{2+} + Cd^{2+} + Ni^{2+}	%Pb^{2+} sorption		%Cd^{2+} sorption		%Ni^{2+} sorption	
	Single	Mixed	Single	Mixed	Single	Mixed
10.0 mg L^{-1}	99 ± 1	97 ± 2	99 ± 1	93 ± 2	95 ± 0	87 ± 2
50.0 mg L^{-1}	99 ± 0	95 ± 2	82 ± 2	36 ± 2	64 ± 3	34 ± 2
100.0 mg L^{-1}	75 ± 3	85 ± 1	54 ± 0	15 ± 2	31 ± 6	19 ± 2

Table 7
Linear equations of predicted amount of biosorbent (M) against sample volume (L) (metal ion concentration = $100.0\,\mathrm{mg\,L^{-1}}$, sample volume = 1–10 L) where y is the biosorbent amount and x is the solution volume in equation

Removal (%)	Pb^{2+}	Cd^{2+}	Ni^{2+}
90	$y = 0.8991x - 00034$	$y = 2.3815x - 0.0005$	$y = 6.0591x - 0.1758$
80	$y = 0.6876x$	$y = 1.8236x + 0.0001$	$y = 3.8291x - 0.0002$
70	$y = 0.5512x - 0.0003$	$y = 1.4614x - 0.0005$	$y = 2.7609x - 0.0002$
60	$y = 0.4443x$	$y = 1.1768x - 0.0002$	$y = 2.0613x - 0.0004$

operation with a solution volume V (L), the initial concentration of the adsorbate is decreased from C_0 to C_1 (mol L^{-1}). At the same time, the amount of adsorbate on the adsorbent of mass M will increase from q_0 to q_1. The mass balance equation for the sorption system can be written as:

$$V(C_0 - C_1) = M(q_0 - q_1) = Mq_1 \tag{10}$$

Under equilibrium conditions, $C_1 \rightarrow C_e$ and $q_1 \rightarrow q_e$.

Since the adsorption isotherm studies confirm that the equilibrium data for each metal ion correlated well with Freundlich isotherm, the isotherm equation can be used to calculate q_1 in the mass balance equation. This yields:

$$\frac{M}{V} = \frac{C_0 - C_1}{q_e} = \frac{C_0 - C_1}{K_f C_e^n} \tag{11}$$

The equation can be used to predict the amount of adsorbent required to achieve a specific percentage removal for a given initial metal ion concentration and solution volume. Table 7 presents the obtained linear equations that can be used for predicting the amount of biosorbent required to obtain 60–90% removal at the initial metal ion concentration of $100.0\,\mathrm{mg\,L^{-1}}$ and at different solution volumes of (1–10 L). For example, in order to have 90% removal of Pb^{2+} from a 2 L solution of $100.0\,\mathrm{mg\,L^{-1}}$, about 1.8 g (exact amount is 1.7948 g) *S. platensis* is required.

4. Conclusions

The present study has demonstrated that *S. platensis* is an effective biosorbent for the adsorption of Pb^{2+}, Cd^{2+}, and Ni^{2+} ions from aqueous solution. The uptake of metal ions by *S. platensis* seemed to be quite rapid and the experimental data obeyed well the pseudo-second-order model. Faster adsorption kinetics was observed for Pb(II) ions in comparison to Cd^{2+} ions. A decrease in k_2 value was observed in the case of Cd^{2+} sorption. Based on kinetic modeling, the apparent activation energy, E_a, were calculated and found to be 44 kJ/mol, -16 kJ/mol and 54 kJ/mol for Pb^{2+}, Cd^{2+}, and Ni^{2+}, respectively. The biosorption of metal ions by biosorbent was found to be endothermic. The equilibrium data fitted well to Freundlich, Dubinin–Radushkevich and Temkin isotherm models in the studied concentration range. Freundlich isotherm model was then used to predict the amount of *S. platensis* required to remove desired amount of Pb^{2+}, Cd^{2+}, and Ni^{2+} ions from solutions of initial concentration of $100.0\,\mathrm{mg\,L^{-1}}$. Competitive biosorption experiments showed that *S. platensis* had a relative selectivity towards Pb^{2+} ions. The reusability of the biosorbent

was investigated for three metal ions for several trials. A little decrease in the sorption of Cd^{2+} and Ni^{2+} ions was achieved in comparison to Pb^{2+} ions indicating that the biosorbent could still be suitable for the removal of metal ions even after five successive runs. Based on the obtained results, it is believed that the application of biosorption using *S. platensis* for the purification of industrial waste water from Pb^{2+}, Cd^{2+} and Ni^{2+} ions can be suitable in bioreactor design or large-scale batch biosorption systems.

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