

# Biosorption of Cadmium and Lead from Aqueous Solutions by *Chlorella vulgaris* Biomass: Equilibrium and Kinetic Study

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**Abstract** Biosorption of cadmium and lead from aqueous solution was investigated using green algae *Chlorella vulgaris* at room temperature and at pH adjusted to 7.0. Various sorption parameters such as contact time, initial metal ion concentration and biomass quantity were studied. The equilibrium experimental data are well represented by Langmuir model among two-parameter models. It was noted that the maximum adsorption capacity for cadmium and lead was 149.9 and 178.5 mg (metal) g<sup>-1</sup> biomass, respectively. The kinetic data were fitted by models including pseudo-first order and pseudo-second order. It was observed that, the pseudo-first-order kinetic model describes the biosorption of cadmium and lead ions onto *C. vulgaris* biomass.

**Keywords** Biosorption · Cadmium · Lead · Heavy metals · *Chlorella vulgaris*

## الخلاصة

تتناول هذه الدراسة التحقق من إمكانية الامتصاص الحيوي لعنصري الكاديوم والرصاص من المحاليل المائية باستخدام الطحالب الخضراء من فصيلة الكلوريللا فولجارييس في درجة حرارة الغرفة وعند رقم هيدروجيني 7.0. وقد تمت دراسة العوامل المختلفة التي تؤثر في عملية الامتصاص مثل زمن التلامس، والتركيز الابتدائي لأيون المعدن وكمية الكتلة الحيوية. وقد أظهرت النتائج المعملية تمثيلا جيدا بتطبيقها في نموذج لانجمير من بين النماذج التي تم اختبارها. وقد لوحظ أن قدرة الامتزاز الأقصى للكاديوم والرصاص كانت 149.9 و 178.5 ملجم لكل جرام من الكتلة الحيوية على الترتيب. وكذلك تمت دراسة حركية عملية الامتصاص الحيوي لكلا العنصرين، وأظهرت النتائج أن عملية امتصاص الكاديوم والرصاص بوسط طحالب الكلوريللا فولجارييس تتبع نموذج حركية من الرتبة الأولى.

## 1 Introduction

Contamination of the aqueous environment by heavy metals due to the release of metal-containing effluents into the water bodies is one of the most serious environmental issues of the century. In addition to the toxic effect of the heavy metals even at low concentration, they can accumulate along the food chain which results in serious ecological and health hazards [1].

According to the WHO, the metals of the most concern are Al, As, Cd, Cr, Co, Cu, Fe, Pb, Hg, Ni, and Zn. Cadmium and lead were chosen for biosorption studies for their wide variety use in commercial applications.

Cadmium is frequently used in metallurgical alloying, ceramics, metal plating, photograph development, pigment works, textile printing industries, lead-zinc mining, alkaline batteries, and electroplating [2,3]. Cadmium is not biodegradable [4] and is likely to cause a number of acute and chronic disorders, such as itai-itai disease; renal damage; emphysema; hypertension; testicular atrophy [5]; damage to the kidneys, lungs, and liver [6]; and carcinogenesis [7]. Therefore, the maximum concentration limit for Cd(II) in drinking water has been strictly regulated. The World Health Organization (WHO) and the American Water Works Association (AWWA) have recommended that the concentration of cadmium in drinking water should not exceed 0.005 mg L<sup>-1</sup>.

Lead in the environment is commonly originated from various kinds of industrial activities such as mining, smelting and metal plating, battery manufacturing, ammunition production, paint production and paper and pulp processing. Lead has been identified as one of the most toxic heavy metals due to its detrimental effects on human nervous system, blood circulation system, kidneys and reproductive system [8,9]

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The conventional processes used to eliminate heavy metal ions from wastewater include various techniques such as solvent extraction, chemical precipitation, ion exchange, activated carbon adsorption, chelation, reverse osmosis, coagulation–precipitation, electrochemical operation and filtration. However, those physicochemical technologies possess significant disadvantages of being expensive and environmentally troublemaking, requiring input of external chemical additives or energy, as well as generating concentrated toxic sludge that must be disposed [10, 11]. These disadvantages are especially apparent at low metal concentrations often encountered in wastewaters. Therefore, it is urgent to develop efficient and environmentally compatible means able to remove or detoxify heavy metals in an economical way [12].

Biosorption using microbial biomass as the adsorbent has emerged as a potential alternative technique to the existing methods for metal removal [13]. The use of biological material, including living or non-living microorganisms, in the removal and possibly recovery of toxic or valuable metals from industrial wastes, has gained important credibility during recent years, because of the good performance, minimization of chemical/biological sludge and low cost of these materials [14, 15]. Some plants as *Phragmites australis* show a great tendency to adsorb heavy metals as Zn, Cu, Cd and Pb [16]. Removal of heavy metals (cobalt, cadmium, and zinc) from waste water was also possible using biological wastes as black tea waste [17].

Microorganisms including bacteria, algae, fungi and yeast uptake metal either actively (bioaccumulation) and/or passively (biosorption) [18].

The biosorption mechanism, which is complex and still less understood, depends on whether the organisms are living or dead, the type of microorganism and the element species [19]. The use of non-living microbial cells as biosorbents has been shown to be an effective means for removal or recovery of heavy metals from aqueous systems [20].

In the present study, the ability of the dead cells of *Chlorella vulgaris* to eliminate Cd(II) and Pb(II) ions from synthetic wastewater and the effect of various parameters such as contact time, initial metal concentration and biomass dosage have been investigated. Equilibrium modeling was carried out using Langmuir and Freundlich adsorption isotherm. Also, the nature of the biosorption process has been investigated with respect to its kinetic aspects.

## 2 Materials and Methods

### 2.1 Microorganisms, Reagents and Equipments

*Chlorella vulgaris* stored on agar was obtained from Carolina Biological Supply (Burlington, North Carolina, Catalogue

No. 15-2075) and grown on Bold's Basal Medium [21] having the following composition in  $\text{mgL}^{-1}$  of deionized water: 75  $\text{K}_2\text{HPO}_4$ , 175  $\text{KH}_2\text{PO}_4$ , 75  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 250  $\text{NaNO}_3$ , 25  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , 25  $\text{NaCl}$ , 50  $\text{EDTA Na}_4$ , 31  $\text{KOH}$ , 5  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 11.4  $\text{H}_3\text{BO}_3$ , 1.4  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , 0.24  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ , 0.25  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , and 0.2  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ . After stirring, the pH of the medium is measured and it was  $6.9 \pm 0.1$ .

The growth experiments were carried out in a 4-L working volume enclosed cylindrical glass photobioreactor with an outer diameter of 10.8 cm and height of 70 cm. The operation conditions were defined as following: temperature set at  $29.0^\circ\text{C}$  and air containing 0.04 %  $\text{CO}_2$  was bubbled through fritted glass bubbles at a flow rate of  $200 \text{ mL min}^{-1}$ . Eight fluorescent lamps of 20 W were fitted outside the photobioreactor with the illumination cycle of 12:12. The photobioreactor was inoculated directly from the stock algal slope on nutrient agar after mixing its content with 2 mL of BBM solution.

Stock metal solutions of  $1,000 \text{ mg L}^{-1}$  of Cd(II) and Pb(II) were prepared by dissolving 2.744 g of cadmium nitrate  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , and 1.598 g of lead nitrate  $\text{Pb}(\text{NO}_3)_2$  in 1,000 mL of distilled water that contains few drops of  $\text{HNO}_3$  to avoid precipitation. The stock solutions were diluted to obtain test solutions of desired strength. All chemicals used in this study were analytical grade (Merck).

### 2.2 Biosorption Experiments

Batch biosorption experiments were performed in 250-mL Erlenmeyer flasks containing 100 mL metal solution. The algal biomass was harvested by filtering the cultured medium through cellulose nitrate membrane filters (Whatman) with pore size of  $0.45 \mu\text{m}$ , and washed with deionized water. After washing, the biomass was dried at  $55^\circ\text{C}$  for 24 h stocked in the refrigerator for further study, which will be referred to as "pretreated biomass".

The effect of biomass concentrations on the removal of metal ions was studied employing 0.2, 0.5, 0.8 and 1 g of biomass. Biosorption experiments were conducted by introducing a known weight of biomass into a series of Erlenmeyer containing 100 mL of solutions with metal concentrations of 10, 25, 50, 100, 200 and  $300 \text{ mg L}^{-1}$  for lead and cadmium individually. The flasks were agitated at 150 rpm in an incubator shaker at  $30^\circ\text{C}$  for 1 h. After attaining equilibrium, the algal biomass was separated from the metal solution by filtration through  $0.45 \mu\text{m}$  filters. Filtered samples were analyzed for the residual metal concentration using by flame atomic absorption spectrometry (SOLAAR M5).

Metal removal by dry biomass was determined according to:

$$R (\%) = \frac{C_o - C_t}{C_o} \times 100$$



where  $R$  is the percentage of metal adsorbed by biomass,  $C_o$  is the initial metal concentration in  $\text{mgL}^{-1}$ , and  $C_t$  is the remaining concentration at time  $t$  in ppm. At equilibrium, metal uptake by biomass was determined according to:

$$q = V \frac{C_i - C_e}{x}$$

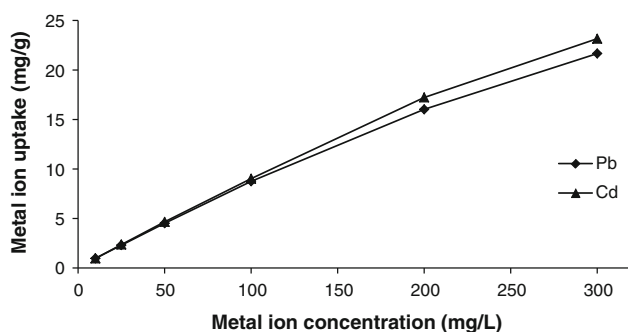
where  $q$  is the metal uptake in  $\text{mg (metal) g}^{-1}$  biomass,  $V$  is the volume of metal-containing solution in contact with the biosorbent in L,  $C_i$  and  $C_e$  are the initial and equilibrium concentration of metals in the solution in  $\text{mgL}^{-1}$ , respectively, and  $x$  is the amount of added biomass on dry basis in g [22].

### 3 Results and Discussion

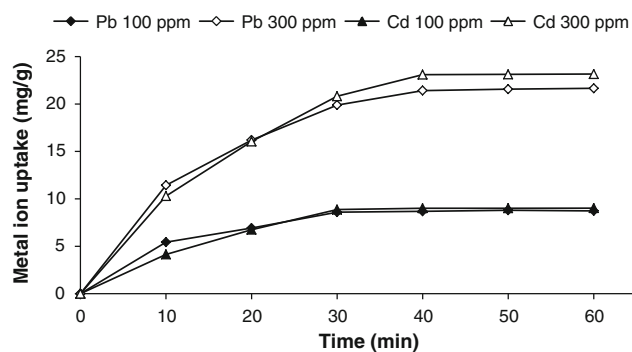
In the present study, the effect of initial metal concentration, contact time and biomass dosage on biosorption process was studied.

#### 3.1 Influence of Initial Metal Concentration

The adsorption capacity of *C. vulgaris* as a function of initial metal concentrations has been studied at six different concentrations.  $1 \text{ gL}^{-1}$  of the biomass was contacted with a solution bearing a metal concentration of 5, 10, 25, 100, 200 and  $300 \text{ mgL}^{-1}$  in batch experiment at  $30^\circ\text{C}$  and the optimum pH. Figure 1 indicates that the metal adsorption capacity increases with an increase in the initial metal ion concentration. This is due to the fact that an increase in initial ion concentration provides a larger driving force to overcome all mass transfer resistance between solid and aqueous phase, thus resulting in higher metal ion adsorption. Similar results have been reported by Mohammed [17], Chen et al. [23] and Riaz et al. [24].



**Fig. 1** Effect of initial metal concentration on its uptake by *Chlorella vulgaris*



**Fig. 2** Effect of contact time between metal ions and biomaterial on metal adsorption

#### 3.2 Influence of Contact Time

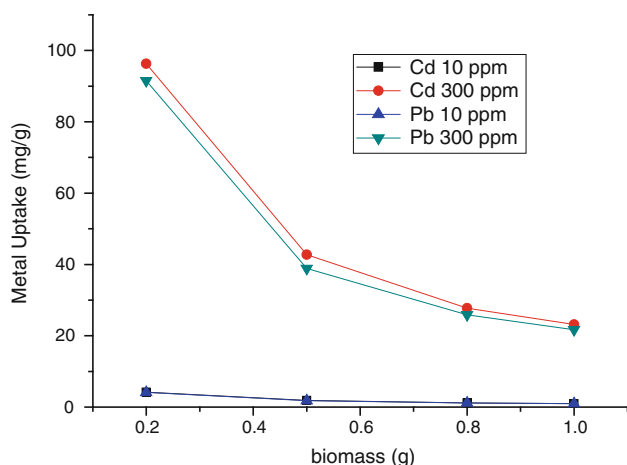
As the adsorption process proceeds, the sorbent reaches the saturation state and then the sorbed solute tends to desorb back into the solution. Eventually, the rates of adsorption and desorption will be equal at equilibrium. When the system reaches sorption equilibrium, no further net adsorption occurs. The time at which adsorption equilibrium occurs was determined [25].

The adsorption rate tests were performed on an equilibrium batch basis.  $1 \text{ gL}^{-1}$  of the biomass was contacted with a solution bearing a metal concentration of 100 and  $300 \text{ mgL}^{-1}$  at  $30^\circ\text{C}$  and the optimum pH. From the experimental data represented in Fig. 2, the process of biosorption reaches the equilibrium state after approximately 50 min of contact. The reaction rate is rather fast at first and 90% of total biosorption of cadmium and lead occurs in the first 20 min and thereafter it proceeds at a lower rate and finally no further significant adsorption is noted beyond 50 min. The very fast sorption and settling of the biomass make this material suitable for continuous flow water treatment systems.

#### 3.3 Influence of Biomass Dosage

Adsorbent dosage has a great influence on the adsorption process and determines the potential of adsorbent through the number of binding sites available to remove metal ions at a specified initial concentration.

The effect of biomass dosage on Cd and Pb ion removal is indicated in Fig. 3. At equilibrium, metal uptake decreases with an increase in biomass dosage from 0.5 to 5 g. This decrease can be attributed to the concentration gradient between the sorbent and the sorbate; an increase in biomass concentration causes a decrease in the amount of metal sorbed onto a unit weight of the algae. Moreover, the increase in adsorption of metals by increasing the biomass dosage is due to an increase in the number of active sites and available



**Fig. 3** Effect of biomass dosage on biosorption of Cd and Pb at contact time of 1 h

surface area. Similar trends were observed for lead removal using *S. cumini* L. as biosorbent [26].

### 3.4 Kinetic Study

Kinetic study provides valuable information about the mechanism of adsorption and subsequently investigation of the controlling mechanism of the biosorption process as either mass transfer or chemical reaction in order to obtain the optimum operating conditions for industrial-scale batch processes [27]. In batch systems, adsorption kinetics is described by a number of models based on adsorption equilibrium such as the pseudo-first-order and the pseudo-second-order kinetic models. The linearized pseudo-first-order and pseudo-second-order kinetic models take the following forms [28]:

$$q_t = q_e - q_e \exp(-k_1 t) \quad (1)$$

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

where  $q_e$  and  $q_t$  are the amounts of metal adsorbed at equilibrium and time  $t$  (min) in  $\text{mg g}^{-1}$ , respectively, and  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) are the pseudo-first-order and pseudo-second-order reaction rate constants.

If the adsorption follows the pseudo-first-order rate equation, a plot of  $\ln(q_e - q_t)$  against time should give a straight line. Similarly,  $t/q_t$  should change linearly with time  $t$  if the adsorption process obeys the pseudo-second-order rate equation and the initial adsorption rate  $dq/dt = h$  at  $t = 0$  is given by  $q_e^2 k_2$ .

The data of the adsorption kinetic of cadmium and lead were collected for initial concentrations of metal ( $C_o = 50$  and  $100 \text{ mg L}^{-1}$ ) and the obtained data were fitted using both pseudo-first-order and pseudo-second-order models. Nonlinear regression software (Polymath) was used to determine model parameters ( $q_e$ ,  $k_1$ ,  $k_2$  and  $h$ ) and relevant statistical indicators such as coefficient of determination ( $R^2$ ) and the mean squared error (MSE). Usually a model with smaller MSE and  $R^2$  closer to unity presents the data more accurately than a model with larger MSE and  $R^2$  lower than 1.

Table 1 lists the critical parameters of adsorption kinetics. According to the coefficient of determination ( $R^2$ ) value listed in the table, the pseudo-first-order kinetics equation ( $R^2 = 0.993$  and  $0.996$  for cadmium and  $0.996$  and  $0.996$  for lead) could better fit the test data than the pseudo-second-order kinetics equation ( $R^2 = 0.936$  and  $0.948$  for cadmium and  $0.966$  and  $0.935$  for lead). In addition, a slight decrease in the rate constant  $k_1$  was observed when the initial concentration was increased from  $50$  to  $100 \text{ mg L}^{-1}$ . This indicates that a solution with a lower concentration is likely to equilibrate much faster. This is consistent with the previously observed lead adsorption on brown algae [29]. The predicted adsorption amounts per unit mass of algae were  $19.7$ ,  $36.6$ ,  $18.4$ , and  $36.1 \text{ mg g}^{-1}$  for solutions with initial concentration of  $50$  and  $100 \text{ mg L}^{-1}$  for cadmium and lead, respectively.

### 3.5 Biosorption Isotherm Models

For optimization of the biosorption design, it is necessary to develop an equation that can be used to compare different biosorbents under different operational conditions. Various sorption isotherm models are used for fitting data in order to examine the relationship between sorption and aqueous concentration at equilibrium. In this investigation, the relationship between metal biosorption capacity and metal ion concentration at equilibrium has been described by three

**Table 1** Critical parameters of adsorption kinetics

Metal	$C_o$ ( $\text{mg L}^{-1}$ )	Pseudo-first-order kinetic model				Pseudo-second-order kinetic model				
		$q_{e(\text{exp.})}$ ( $\text{mg g}^{-1}$ )	$q_{e(\text{cal.})}$ ( $\text{mg g}^{-1}$ )	$k_1$ ( $\text{min}^{-1}$ )	$R^2$	MSE	$q_{e(\text{cal.})}$ ( $\text{mg g}^{-1}$ )	$k_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	$R^2$	MSE
Cd	50	19.05	19.70	0.0689	0.993	0.198	24.29	0.0504	0.945	0.556
	100	35.6	36.61	0.0701	0.996	0.2674	45.07	0.0421	0.964	0.784
Pb	50	18.25	18.41	0.084	0.996	0.134	21.80	0.0808	0.923	0.741
	100	35.5	36.02	0.080	0.996	0.281	43.04	0.0741	0.911	0.822



**Table 2** Isotherm constants of two-parameter models for cadmium and lead biosorption on *Chlorella vulgaris*

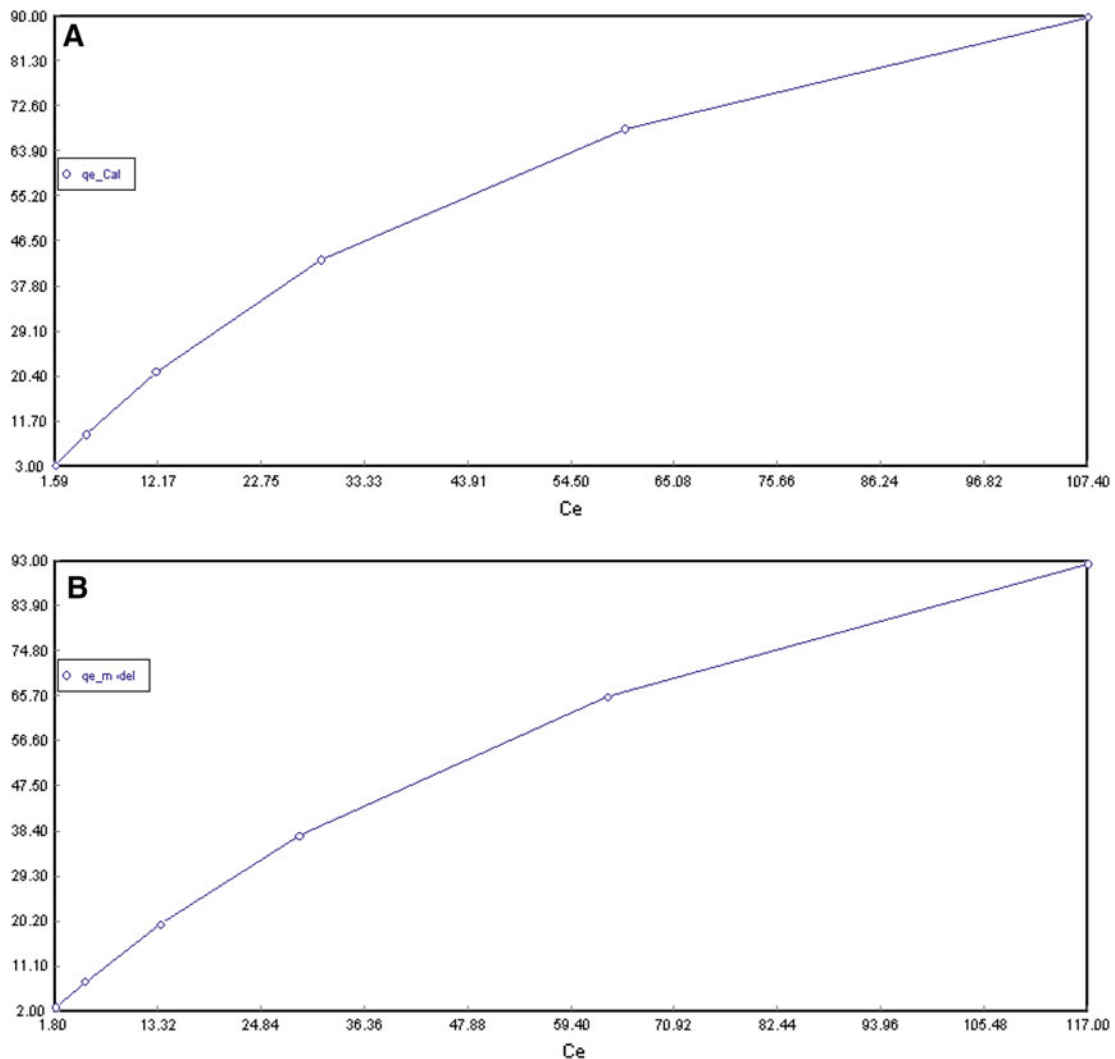
Two-parameter models	Cadmium	Lead
<b>Langmuir</b>		
$q_m$ (mg g <sup>-1</sup> )	149.9	178.5
$k$ (L mg <sup>-1</sup> )	0.013	0.009
$R^2$	0.989	0.996
MSE	0.714	0.727
<b>Freundlich</b>		
$k_f$ (L g <sup>-1</sup> )	0.122	0.233
$n$	1.436	1.133
$R^2$	0.947	0.951
<b>Temkin</b>		
$B$ (mg g <sup>-1</sup> )	88.2	101.3
$k_t$ (L g <sup>-1</sup> )	1.02	112
$R^2$	0.7667	0.7754
MSE	1.11	0.875

two-parameter isotherm models: Langmuir, Freundlich, and Temkin models. The constant mean squared error (MSE) and coefficient of determination ( $R^2$ ) of the three parameter models are given in Table 2 for cadmium and lead. All model parameters were evaluated by nonlinear regression using software (Polymath).

The Langmuir isotherm model is expressed as follows:

$$q_e = q_m \frac{k_1 C_e}{1 + k_1 C_e}$$

where  $q_m$  is the maximum metal biosorption and  $k_1$  (L mg<sup>-1</sup>) is the Langmuir constant. These constants are related to monolayer adsorption capacity and energy of adsorption [30]. Maximum monolayer adsorption capacity ( $q_m$ ) was obtained as 149.9 and 178.5 mg g<sup>-1</sup> for cadmium and lead, respectively. The  $k_1$  values of cadmium and lead biosorption process were estimated from the isotherms to be 0.013 and 0.009 L mg<sup>-1</sup>, respectively.



**Fig. 4** Isotherms of cadmium (a) and Pb (b) at different initial concentrations

The Freundlich isotherm model is expressed as follows:

$$q_e = k_f C_e^{1/n}$$

where  $k_f$  is the Freundlich constant and  $n$  is the Freundlich exponent. Values of  $n$  greater than 1 show favorable nature of adsorption [31]. The  $k_f$  and  $n$  values in the Freundlich model were estimated to be 0.223, 0.197 L g<sup>-1</sup>, 0.311 and 0.278 for cadmium and lead, respectively.

The Temkin isotherm model is expressed as follows:

$$q_e = B \ln(k_t C_e)$$

where  $B$  (mg g<sup>-1</sup>) and  $k_t$  (L g<sup>-1</sup>) represent the isotherm constants, which have been estimated from the isotherm to be 37.6, 16.1 mg g<sup>-1</sup>, 1.322 and 1.0442 L g<sup>-1</sup> for cadmium and lead, respectively.

The fitting of the data to the Langmuir, Freundlich and Temkin isotherms suggests that the biosorption of cadmium and lead onto the treated biomass can be explained by the isotherms as outlined in Table 2. It is apparent that the Langmuir model explains the biosorption process better than the other models on the basis of determination coefficient  $R^2$  (0.989 compared to 0.938 and 0.796 for cadmium and 0.996 compared to 0.942 and 0.745 for lead). Experimental  $q_e$  value obtained was lower than  $q_m$ , this trend agrees with cases reported in the literature [32,33]. These results suggested that adsorption takes place as monolayer phenomena [30].

The fitness of the biosorption data of cadmium and lead ions to the Langmuir isotherm (Fig. 4) implies that the binding energy on the whole surface of the biomass was uniform. It also indicates that the adsorbed metal ions do not interact or compete with each other and that they are adsorbed by forming a monolayer. Kratochvil and Volesky [34] stated that a favorable biosorbent should have a low Langmuir constant  $k_l$  and a high  $q_m$  value. In this study,  $k_l$  and  $q_m$  values were found to be 0.013, 0.009 L g<sup>-1</sup>, 149.9, and 178.5 mg g<sup>-1</sup> for cadmium and lead, respectively, this compares favorably with the adsorption of cadmium on *Oscillatoria* sp. where 0.03 and 30.1 were reported for  $k_l$  and  $q_m$ , respectively [35], and the adsorption of lead on *C. vulgaris* 11.3 L mmol<sup>-1</sup> and 138.2 were reported for  $k_l$  and  $q_m$ , respectively [36]. The study indicates that the biomass tested is an encouraging biosorbent for cadmium and lead ions removal from aqueous solution.

## 4 Conclusion

In this study, the ability of cadmium and lead biosorption by pretreated cells of *C. vulgaris* biomass has been demonstrated. In this batch mode of studies, the biosorption was dependent on contact time, initial metal ion concentration and biomass dosage. It was investigated that biosorption

capacity decreases with an increase in biomass dosage and increases with an increase in the initial metal ion concentration. The results of the study revealed that the adsorption process seems to follow the pseudo-first-order kinetic model and the Langmuir isotherm model better which shows the existence of monolayer adsorption under the experimental conditions.

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