CADMIUM AND LEAD BIOSORPTION BY CHLORELLA VULGARIS

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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 dosage were studied. It was noted that the maximum biosorption capacity for cadmium and lead is 6.7943 and 14.932 mg/g, respectively. The equilibrium experimental data are very well represented by Langmuir model among two parameter models. 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 *Chlorella vulgaris* biomass.

 Keywords: Biosorption, Cadmium, Lead, heavy metals, *Chlorella vulgaris*

1. INTRODUCTION

Contamination of the aqueous environment by heavy metals due to the discharge 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; Tobin & Roux [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 as they are being used in a wide variety of commercial processes.

Cadmium is frequently used in metallurgical alloying, ceramics, metal plating, photograph development, pigment works, textile printing industries, lead–zinc mining, alkaline batteries, and electroplating; Kadirevlu et al. [2], Mohapatara & Anand [3].

Cadmium is not biodegradable; Anayurt et al. [4], and is likely to cause a number of acute and chronic disorders, such as itai-itai disease; renal damage; emphysema; hypertension; testicular atrophy; Leyva et al. [5], damage to the kidneys, lungs, and liver; Bedoui et al.[6] and carcinogenesis; Brown et al.[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 0.005mg\L.

Lead in the environment 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; Tunali et al. [8], Li et al. [9].

The conventional processes used to remove heavy metal ions from the contaminated environments include solvent extraction, chemical precipitation, ion exchange, activated carbon adsorption, chelation, reverse osmosis, coagulation–precipitation, electrochemical operation and filtration. However, those physicochemical technologies possess significant drawbacks of being expensive and environmentally disruptive, requiring input of external chemical additives or energy, as well as generating concentrated toxic sludge or other wastes that must be disposed, Chen et al. [10], Yu et al. [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; Huang et al. [12].

Biosorption using microbial biomass as the adsorbent has emerged as a potential alternative technique to the existing methods for metal removal; Ozturk [13]. The use of biological material, including living and non-living microorganisms, in the removal and possibly recovery of toxic or precious 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; Sahin & Ozturk [14], Alluri et al. [15]. Microorganisms including bacteria, algae, fungi and yeast uptake metal either actively (bioaccumulation) and/or passively (biosorption); Yan & Virarghavan [16].

The biosorption mechanism, which is complex and still understood, depends on whether the organism are living or dead, the type of microorganism and the element species; Madrid & Camara [17]. The use of non-living microbial cells as a biosorbents has been shown to be an effective means for removal or recovery of heavy metals from aqueous systems; Taniguchi et al [18].

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

2.1Microorganisms, reagents and equipments

The microorganisms employed in the present study was the algal strain *Chlorella vulgaris*, it was obtained from Botany department, faculty of science, Alexandria

University. The species was cultivated in Bristol culture medium for 36 h (middle of logarithmic phase) at $23^{o}C$. The composition of liquid growth medium were (mg/L of deionized water): 750 $NaNO_3$, 25 $CaCl_2.2H_2O$, 75 $MgSO_4.7H_2O$, 20 FeEDTA, 75 K_2HPO_4, 175 KH_2PO_4, 20 NaCl, and 1 ml of trace mineral solution. The trace mineral solution consisted (mg/L of deionized water): 2860 H_3BO_3, 1810 $MnCl_2.4H_2O$, 220 $ZnCl_2.7H_2O$, 80 $CuSO_4._5H_2O$, 36 MoO_3 85%, 90 $CoSO_4.7H_2O$

The medium was sterilized by autoclaving at $121^{o}c$ for 20 minutes and the pH was adjusted to 7.0 with 0.1 $molL^{-1}$ solutions of HNO_3 and NaOH. Growth experiments were carried out in 1.0 L Kontes culture vessel that was fitted with baffles and filled with 500 mL of culture medium and air containing 0.04% CO_2 was bubbled through fritted glass bubbles at a flow rate of 200 mL/min.

Stock metal solutions were prepared by dissolving 2.744 g of cadmium nitrate $Cd(NO_3)_2.4H_2O$, and 1.598 g of lead nitrate $Pb(NO_3)_2$ in 1000 ml of distilled water to obtain a solution having 1000 mgL^{-1} of each metal ion. 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

The culture for the experiments was prepared in 2000 ml Erlenmeyer flasks containing 1500 ml of the culture medium. The microorganism was grown for 48 h (end of the logarithmic phase) at $30^{o}C$. The algal biomass was deactivated by heating in an autoclave at $121^{o}C$ for 10 minutes; Schiewer & Volesky [19]. Then the biomass was harvested by filtering the cultured medium through cellulose nitrate membrane filters (Whatman) with pore size of 45 μm, and washed with deionized water. After washing, the biomass was dried at 55° C for 24 h, powdered in a mortar and ground with 100 mesh size. Thus, a uniform powdered biomass material was produced and stoked 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 25 ml of solutions having metal concentrations of 10, 25, 50, 100, 200 and 300 mgL^{-1} for lead and cadmium, whereas for mercury, 3 initial concentrations were studied (100, 200 and 300 mgL^{-1}). The flasks were agitated at 150 rpm in an incubator shaker at $30^{o}C$ for 1 h. After attaining equilibrium, the algal biomass was separated from the metal solution by filtration through 0.2 μm 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:

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

Where R is the percentage of metal adsorbed by biomass, C_o is the initial metal concentration in mgL^{-1}, and C_t is the remaining concentration at time t in mgL^{-1}. 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 mg (metal) g^{-1} biomass, V is the volume of metal-containing solution in contact with the biosorbent in ml, C_i and C_e are the initial and equilibrium concentration of metals in the solution in mgL^{-1}, respectively, and x is the amount of added biomass on dry basis in g; Gksungur et al. [20].

3. RESULTS AND DISCUSSION

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

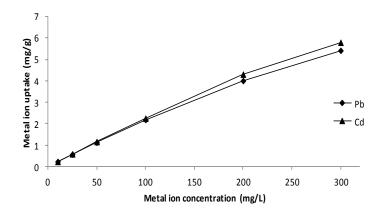### 3.1 Influence of initial metal concentration

Figure 1. Effect of initial metal concentration on its uptake by chlorella vulgaris

The biosorption capacity of Chlorella vulgaris as a function of initial metal concentrations of cadmium and lead have been studied at six different concentrations of 5, 10, 25, 100, 200 and 300 mgL^{-1} in batch experiment. Fig. 1 indicates that the metal biosorption 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 Chen et al. [21], Riaz et al. [22]

3.2 Influence of contact time

As the adsorption process proceeds, the sorbent reaches the saturation state and then the sorbed solute tends to desorbs 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; Sari & Tuzen [23].

The adsorption rate tests were performed on an equilibrium batch basis.1g/L of the biomass was contacted with a solution bearing a metal concentration of 100 and 300 mgL $^{-1}$ at 30° C and the optimum pH.
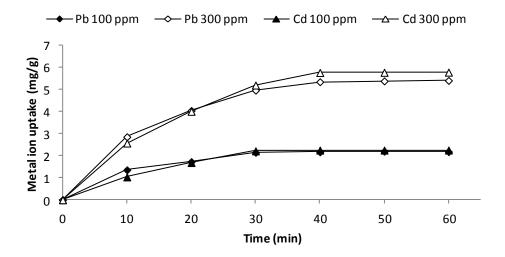

Figure 2. Effect of contact time between metal ions and biomaterial on metal adsorption

From the experimental data represented in Fig. 2, the process of biosorption reaches the equilibrium state after approximately 50 minutes of contact. The reaction rate is rather fast at first and 90% of total biosorption of cadmium, and lead occurs in the first 20 minutes and thereafter it proceeds at a lower rate and finally no further significant adsorption is noted beyond 50 minutes .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

Biosorbent dosage has a great influence on the biosorption process and determines the potential of biosorbent 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.
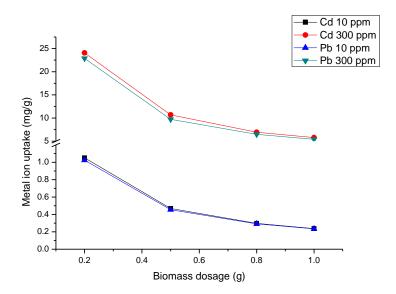
Figure 3. Effect of biomass dosage on biosorption of Cd and Pb at contact time of 1 h

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 biosorption of metals by increasing the biomass dosage is due to an increase in the number of active sites and available surface area. Similar trends was observed for lead removal using *S. cumini L.* as biosorbent; Ozsoy et al. [24].

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; Alyuz & Veli [25]. 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; Basha & Murthy [26]:

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

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

Where q_e and q_t are the amounts of metal adsorbed at equilibrium and time t (min) in mg/g, respectively, and k_1 (min^{-1}) and k_2 (g/mg.min) are the pseudo-first order and pseudo second 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 was collected for initial concentrations of metal (C_o= 50 and 100 mgL^{-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 models parameters (q_e, k_1, k_2 and h) and relevant statistical indicators such as correlation coefficient (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.

Table 1. Critical parameters of adsorption kinetics

Metal	C_o (mg/L)	$q_{e\,(exp.)}$ (mg/g)	Pseudo first-order kinetic model				Pseudo second -order kinetic model			
			$q_{e\,(cal.)}$ (mg/g)	k_1 (min^{-1})	R^2	*MSE*	$q_{e\,(cal.)}$ (mg/g)	k_2 (g/mg.min)	R^2	*MSE*
Cd	50	1.439	1.506	0.0702	0.992	0.0174	1.868	0.0394	0.947	0.0272
	100	2.715	2.855	0.0684	0.999	0.0381	3.553	0.0200	0.978	0.0539
Pb	50	1.735	1.853	0.0551	0.997	0.0372	2.4347	0.0205	0.963	0.0451
	100	8.875	9.001	0.0407	0.996	0.0703	10.760	0.0088	0.923	0.0976

According to the correlation coefficient (R^2) value listed in the table, the pseudo-first order kinetics equation (R^2 = 0.992 and 0.997 for cadmium and 0.997 and 0.996 for lead) could better fit the test data than the pseudo-second order kinetics equation (R^2 = 0.947 and 0.978 for cadmium and 0.963 and 0.923 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 mg/L. This indicates that a solution with a lower concentration is likely to equilibrate much faster. This is consistent with the previously observed zinc adsorption on Chinese loss; Tang et al. [27]. The predicted adsorption amounts per unit mass of algae were 1.506, 2.855, 1.853, and 9.001 mg/g for solutions with initial concentration of 50 and 100 mg/L 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 two-parameters isotherm models: Langmuir, Freundlich, and Temkin models. The constants mean squared error (*MSE*) and correlation coefficient (R^2) of the three parameter models are given in Table 2 for cadmium and lead. All model parameters were evaluated by non-linear regression using software (Polymath).

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

Two-parameters models	Cadmium	Lead
Langmuir		
q_m (mg/g)	6.7943	14.932
k (L/mg)	0.0617	0.0181
R^2	0.9858	0.9865
MSE	0.0613	0.0917
Freundlich		
K_f (L/g)	0.5359	0.4307
n	1.536	1.3910
R^2	0.9474	0.9513
Temkin		
B (mg/g)	1.4888	1.2678
K_T (L/g)	1.1901	1.0442
R^2	0.7667	0.7754
MSE	0.3512	0.2344

The Langmuir isotherm model is expressed as follows:

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

Where q_m is the maximum metal biosorption and k_l (L/mg) is the Langmuir constant. These constants are related to monolayer adsorption capacity and energy of adsorption; Vijayaraghavan et al. [28]. Maximum monolayer adsorption capacity (q_m) was obtained as 6.7843 and 14.932 mg/g for cadmium and lead respectively. The k_l values of cadmium and leas biosorption process were estimated from the isotherms to be 0.0167 and 0.0181 L/mg respectively.

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; Gunay et al. [29]. The k_f and n values in the Freundlich model were estimated to be 0.5359 L/g, 0.4307 L/g, 1.536 and 1.391 for cadmium and lead respectively.

The Timken isotherm model is expressed as follows:

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

Where B (mg/g) and k_t (L/mg) represent the isotherm constants, which have been estimated from the isotherm to be 1.4888 mg/g, 1.2678 mg/g, 1.1901 L/g and 1.0442 L/g for cadmium and lead respectively.

The fitting of the data to the Langmuir, Freundlich and Timken 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 correlation factor R^2

(0.9858 compared to 0.9574 and 0.7667 for cadmium and 0.9865 compared to 0.9513 and 0.7754 for lead). Experimental q_e value obtained was lower than q_m , this trend agrees with cases reported in the literature; Ozer & Ozer [30], Lawala et al. [31]. These results suggested that adsorption takes place as monolayer phenomena; Vijayaraghavan et al. [28].

The fitness of the biosorption data of cadmium and lead ions to the Langmuir isotherm 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 & Volesky [32] 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 0.0617 and 0.0181 L/g, and 6.7943 and 14.932 mg/g 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; Katircioglu et al. [33], and the adsorption of lead on *S. cumini L.* where 0.075 and 32.47 were reported for k_l and q_m, respectively; king et al. [34]. 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 *Chlorella 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. The rapid biosorption process of cadmium and lead onto *Chlorella vulgaris* stimulates the use of such strain in a continuous wastewater treatment processes.

ACKNOWLEDGEMENTS

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