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Equilibrium and kinetic studies of cadmium(II) and lead(II) ions biosorption onto *Ficus carcia* leaves

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Abstract

Background: *Ficus carcia* leaves (fig leaves) for the removal of cadmium(II) and lead(II) ions from aqueous solutions have been investigated.

Results: The biosorption of cadmium(II) and lead(II) ions was found to be dependent on the solution pH, initial metal ion concentrations, biosorbent dose, contact time, and temperature. The experimental equilibrium biosorption data were analyzed by two widely used two parameters, Langmuir and Freundlich isotherm models.

Conclusions: Langmuir isotherm model provided a better fit with the experimental data than Freundlich model by high correlation coefficients R^2. Kinetic studies showed that pseudo-second-order described the biosorption experimental data better than the pseudo-first-order kinetic model.

Keywords: Biosorption, *Ficus carcia* leaves, Cadmium(II), Lead(II), Equilibrium isotherms, Kinetic

Background

Cadmium(II) and lead(II) ions have been released to the environment through phosphate fertilizers, electrical wiring, manufacturing batteries, air conditioning tubing, plumbing, electroplating, and pigments. There is a growing demand to find relatively efficient, low-cost, and easily available adsorbents for the adsorption of toxic heavy metals. Different agrowastes have been investigated for the biosorption of Cd(II) and Pb(II) ions such as *Caladium bicolor* [1], neem leaf [2]; heartwood powder of *Areca catechu* [3]; *Ulmus carpinifolia* and *Fraxinus excelsior* tree leaves [4]; green coconut shell powder [5]; mango peel waste [6]; banana, lemon, and orange peel [7]; chemically modified *Moringa oleifera* tree leaves [8]; maize leaf [9]; *Scolymus hispanicus* [10]; processed walnut shell [11]; sugar cane residue or bagasse [12]; pomegranate peel [13], walnut, hazelnut, almond, pistachio, and apricot stone [14]; *Iagenaria vulgaris* shell [15]; grape stalk waste [16]; rice husk [17]; paper mulberry [18]; *Eucalyptus camaldulenis* tree leaves [19]; *Saraca indica* leaf powder [20]; and olive tree pruning waste [21].

In the present work, we have studied the potential of cadmium(II) and lead(II) biosorption on an agromaterial which *Ficus carcia* leaves (FL) coming from fig fruit tree waste. Results from this study can be used to assess the utility of FL for cadmium(II) and lead(II) removal from aqueous solution.

Methods

Preparation of biosorbent

The raw FL were collected from a local plantation in Jordan. This agricultural waste was thoroughly rinsed with water to remove dust and soluble material. Then it was allowed to dry at room temperature. The dried leaves were grounded to a fine powder in a grinding mill (Retsch RM 100, Thermo Fisher Scientific, NH, USA) and sieved to get size fraction <44 μm and then dried in an oven at 60°C for 4 h.

Preparation of Cd(II) and Pb(II) stock solutions

All the chemicals used were of analytical reagent (AR) grade purchased from Merck, Germany. Stock solutions of 1,000 mg/L of cadmium(II) and lead(II) were prepared from cadmium nitrate [Cd $(NO_3)_2 \cdot 4H_2O$] and lead nitrate [Pb $(NO_3)_2$], respectively, using double distilled water. Desired test solutions of Cd(II) and Pb(II) ions were

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prepared using appropriate subsequent dilutions of the stock solution. The range of concentrations of Cd(II) and Pb(II) ions prepared from standard solution varies between 10 and 100 mg/L. Before mixing the adsorbent, the pH of each test solution was adjusted to the required value with 0.1 M NaOH or 0.1 M HCl.

Analysis

The concentrations of Cd(II) and Pb(II) ions in the solutions before and after equilibrium were determined by AAS6300 atomic absorption spectrometer (Shimadzu, Japan). The pH of the solution was measured with a WTW pH meter using a combined glass electrode. Fourier transform infrared spectroscopy (FTIR) IR Prestige-21 (Shimadzu, Tokyo, Japan) was used to identify the different chemical functional groups present in the FL. FTIR analyses were also used to determine the functional groups which are responsible for the metal binding with FL. The analysis was carried out using KBr, and the spectral range varies from 4,000 to 400 cm^{-1}.

Biosorption experiments

Batch biosorption experiments were conducted by mixing biosorbent with Cd(II) or Pb(II) ion solutions with desired concentration in 250 mL glass flask. The glass flasks were stoppered during the equilibration period and placed on a temperature-controlled shaker at a speed 120 rpm. The amount of biosorption was calculated based on the difference between the initial (C_o, mg/L) and final concentration (C_e, mg/L) in every flask, as follows:

$$q_e = \frac{C_o - C_e}{M} V \tag{1}$$

where q_e is the metal uptake capacity (mg/g), V the volume of the metal solution in the flask (L) and M is the dry mass of biosorbent (g).

Results and discussion

FTIR analysis

To investigate the functional groups of FL and metal loaded FL, a FTIR study was carried out and the spectra are shown in Figure 1 (a and b). The FL leaves display a number of absorption peaks, reflecting the complex nature of the FL. A strong and broad peak at 3,348 cm^{-1} results due to the stretching of the N-H bond of amino groups, which is indicative of bonded hydroxyl group. A change in peak position to 3,336 cm^{-1} in the spectrum of the metal-loaded FL indicates the binding of cadmium or lead with amino and hydroxyl groups [22-24]. The strong absorption peak at 2,927 cm^{-1} could be assigned to -CH stretching vibrations of -CH$_3$ and -CH$_2$ functional groups. The peak at 1,570 cm^{-1} indicates the fingerprint region of CO, C-O and O-H groups, which
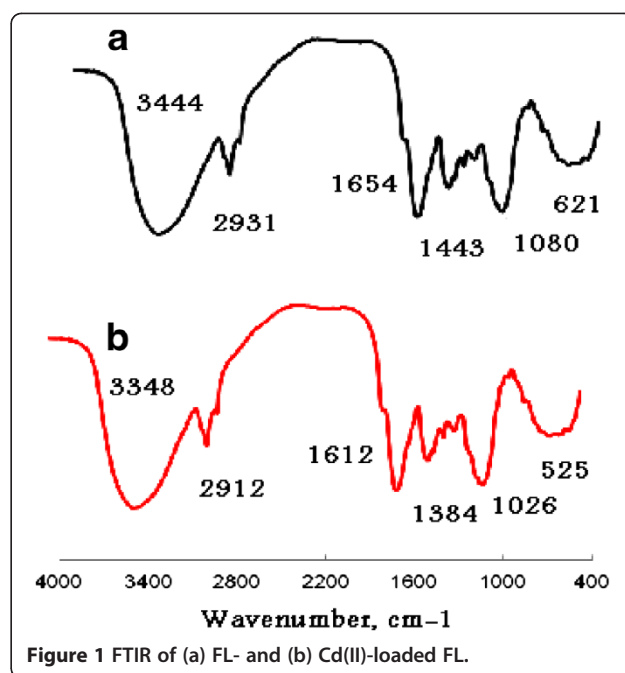

Figure 1 FTIR of (a) FL- and (b) Cd(II)-loaded FL.

exists as functional groups of FL. Shifting of this peak to 1,666 cm^{-1} indicated involvement of these groups in metal binding. The regions between 1,481 and 1,000 cm^{-1} are the fingerprint region, OH and C-H bending vibration, and C-O stretching vibration absorption bands. The absorption peaks at 1,384 and 1,119 cm^{-1} could be attributed to the presence of C-O stretching. These peaks were shifted to 1,477 and 1,014 cm^{-1}, respectively. The intense band at 1,014 cm^{-1} can be assigned to the C-O of alcohols and carboxylic acids. The shift of the peak from 1,084 to 1,014 cm^{-1} also suggests the involvement of the C-O group in binding Cd(II) [22-24].The shifts in the absorption peaks generally observed indicate the existence of a metal binding process taking place on the surface of the *F. carcia* leaves.
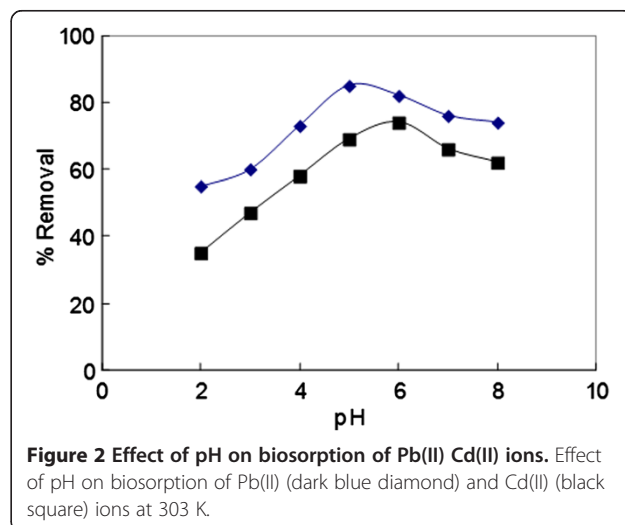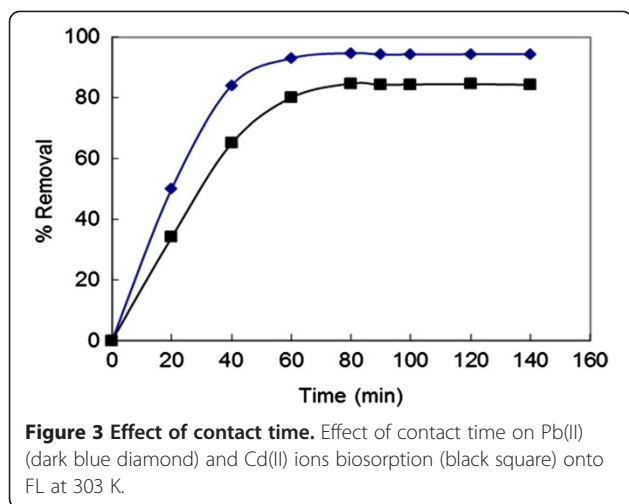

Figure 2 Effect of pH on biosorption of Pb(II) Cd(II) ions. Effect of pH on biosorption of Pb(II) (dark blue diamond) and Cd(II) (black square) ions at 303 K.

Figure 3 Effect of contact time. Effect of contact time on Pb(II) (dark blue diamond) and Cd(II) ions biosorption (black square) onto FL at 303 K.

Effect of pH

The effect of pH on the biosorption of Cd(II) and Pb(II) ions onto FL was studied at pH 2 to 8 conditions. The maximum biosorption was observed at pH 5.0 for Pb(II) ions and pH 6.0 for Cd(II) ions, as shown in Figure 2. At lower pH values Cd(II) and Pb(II) removal was inhibited, possibly as a result of the competition between hydrogen and metal ions on the sorption sites, with an apparent preponderance of hydrogen ions, which restricts the approach of metal cations as a consequence of the repulsive force. As the pH increased, the active sites in FL would be exposed, increasing the negative charge density on the FL surface, increasing the attraction of metal ions with positive charge, and allowing the biosorption onto the FL surface. In this study, the Cd(II) and Pb(II) ions at pH 5.0 to 6.0 would be expected to interact more strongly with the negatively charged binding sites in the biosorbent, as shown in Figure 2. The decrease in Cd(II) and Pb(II) biosorption above pH 5.0 to 6.0 was probably due to the precipitation of Cd(II) and Pb(II) ions as

cadmium and lead hydroxides, but not due to biosorption. As a result, the optimum pH for cadmium and lead ions biosorption was found as 5.0 and 6.0, respectively; and the other biosorption experiments were performed at this pH value.
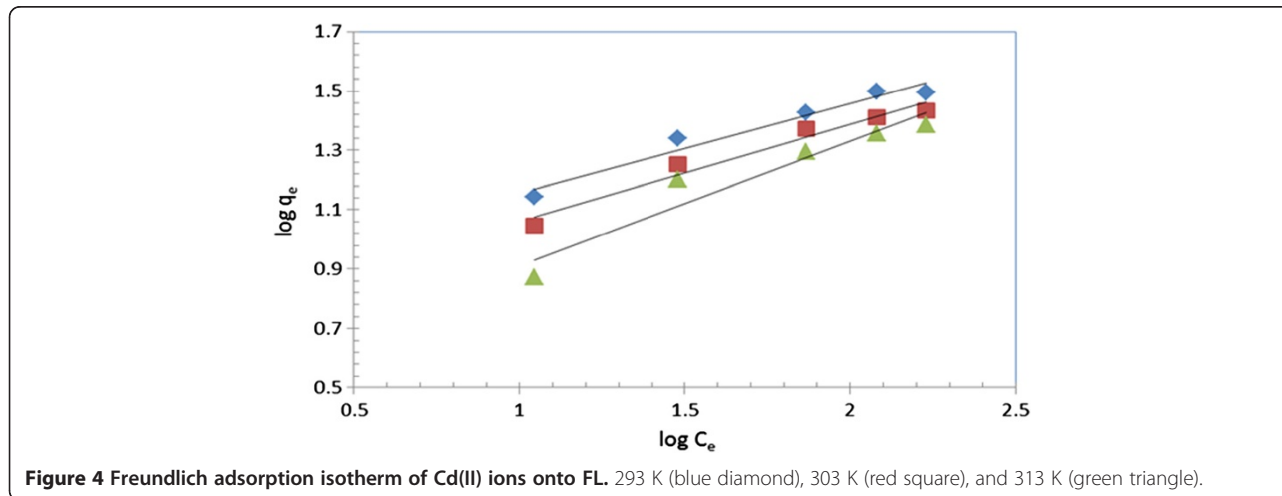
Effect of contact time

The rate of biosorption is important for designing batch biosorption experiments. Therefore, the effect of contact time on the biosorption of metals was investigated. The biosorption of Cd(II) and Pb(II) ions increased considerably until the contact time reached 80 min at 30°C. Further increase in contact time did not enhance the biosorption process; so, the optimum contact time was selected as 80 min for further experiments (Figure 3).

Effect of the adsorbent concentration

The adsorbent concentration effect on the percentage removal at equilibrium conditions was investigated. It was observed that the amount of Cd(II) and Pb(II) biosorbed varied with varying adsorbent concentration. The amount of Cd(II) and Pb(II) adsorbed increases with an increase in adsorbent concentration from 0.1 to 0.5 g/0.1L. The percentage of metal removal was increased from 58.44% to 98.58% for an increase in FL concentration from 0.1 to 0.5 g/0.1L at initial concentration of 40 mg/L. The increase in the adsorption of the amount of solute is obvious due to the increasing FL surface area.

Biosorption isotherms

An adsorption isotherm describes the fraction of sorbate molecules that are partitioned between liquid and solid phases in equilibrium. The adsorption of Cd(II) and Pb(II) ions onto FL particles was modeled using two adsorption isotherms: Freundlich and Langmuir isotherms.
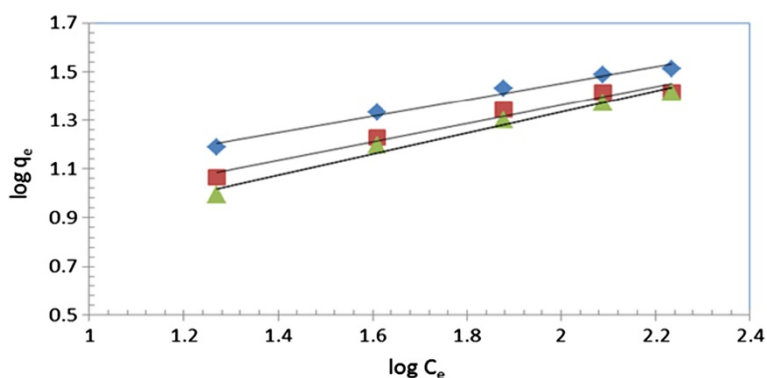

Figure 4 Freundlich adsorption isotherm of Cd(II) ions onto FL. 293 K (blue diamond), 303 K (red square), and 313 K (green triangle).

Figure 5 Freundlich adsorption isotherm of Pb(II) ions onto FL. 293 K (blue diamond), 303 K (red square), and 313 K (green triangle).

Freundlich isotherm

The Freundlich isotherm model is the well-known earliest relationship describing the adsorption process. This model applies to adsorption on heterogeneous surfaces with the interaction between adsorbed molecules, and the application of the Freundlich equation also suggests that sorption energy exponentially decreases on completion of the sorption centers of an adsorbent. This isotherm is an empirical equation and can be employed to describe heterogeneous systems and is expressed as follows in linear form [25]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e, \qquad (2)$$

where K_F (mg/g)(L/mg)$^{1/n}$ is the Freundlich constant related to the bonding energy; $1/n$ is the heterogeneity factor and n (L/g) is a measure of the deviation from linearity of adsorption. Freundlich equilibrium constants were determined from the plot of log q_e versus log C_e, Figures 4 and 5, on the basis of the linear of Freundlich equation (Equation 1). The n value indicates the degree of nonlinearity between solution concentration and adsorption as follows: if $n = 1$, then adsorption is linear; if $n < 1$, then adsorption is a chemical process; if $n > 1$, then adsorption is a physical process. The n value in Freundlich equation was found to be 2.39 to 3.96 for FL, Table 1. Since n lies between 1 and 10, this indicates the physical biosorption of cadmium(II) and lead(II) onto FL.

Langmuir isotherm

The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites [26]. Once a site is filled, no further sorption can take place at that site. As such, the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved. The linear form of the Langmuir isotherm model is described as

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{1}{q_{max}} Ce, \qquad (3)$$

where K_L is the Langmuir constant related to the energy of adsorption and q_{max} is the maximum adsorption capacity (mg/g). Values of Langmuir parameters q_{max} and K_L were calculated from the slope and intercept of the linear plot of C_e/q_e versus C_e as shown in Figures 6 and 7. Values of q_{max}, K_L, and regression coefficient R^2 are listed in Tables 1 and 2. These values for FL biosorbent indicated that Langmuir theory describes the biosorption phenomena as favorable.

The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and sorbent using separation factor
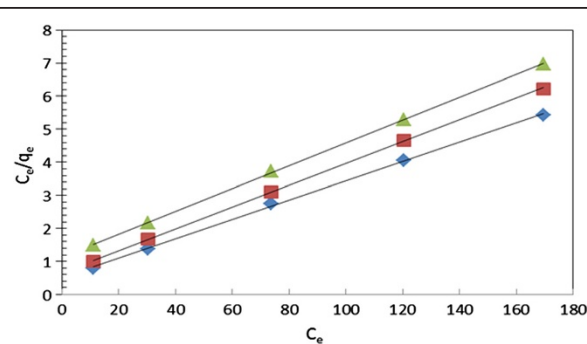
Table 1 Langmuir and Freundlich constants for biosorption of Cd(II) onto FL at different temperatures

T(°C)	Langmuir			Freundlich		
	q_{max}	K_L	R^2	n	K_F	R^2
20	34.13	0.057	0.9994	3.31	7.15	0.9575
30	30.30	0.049	0.9998	3.06	5.43	0.9639
40	28.98	0.030	0.9999	2.39	3.11	0.9234

Figure 6 Langmuir adsorption isotherms for Cd(II) ions onto FL. 293 K (blue diamond), 303 K (red square), and 313 K (green triangle).
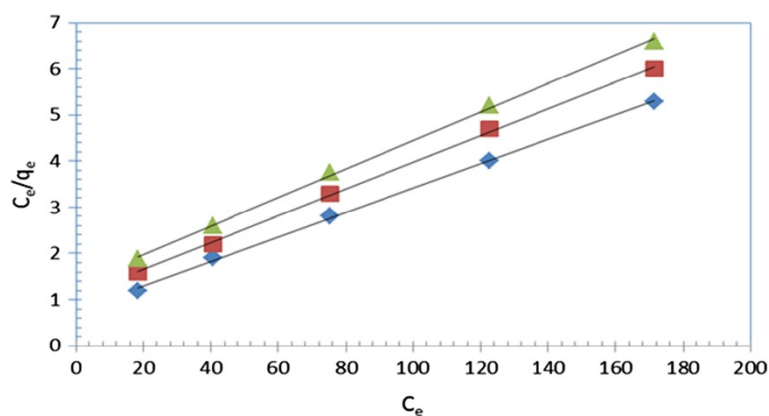
Figure 7 Langmuir adsorption isotherms for Pb(II) ions onto FL. 293 K (blue diamond), 303 K (red square), and 313 K (green triangle).

or dimensionless equilibrium parameter, R_L, expressed as in the following equation:

$$R_L = \frac{1}{(1 + K_L C_o)} \qquad (4)$$

where K_L is the Langmuir constant and C_o is the initial concentration of metal ions. The value of separation parameter R_L provides important information about the nature of adsorption. The value of R_L indicated the type of Langmuir isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$). The R_L was found to be 0.21 to 0.67 for concentrations of 10 to 100 mg/L of Cd(II) and Pb(II). They are in the range of 0 to 1 which indicates the favorable biosorption.

Adsorption kinetic
Parameters from two kinetic models, pseudo-first-order and pseudo-second-order, were fit to experimental data to examine the adsorption kinetics of cadmium(II) and Pb(II) uptake by FL.

Pseudo-first-order kinetics
The pseudo-first-order equation of Lagergren [27] is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t), \qquad (5)$$

Table 2 Langmuir and Freundlich constants for biosorption of Pb(II) onto FL at different temperatures
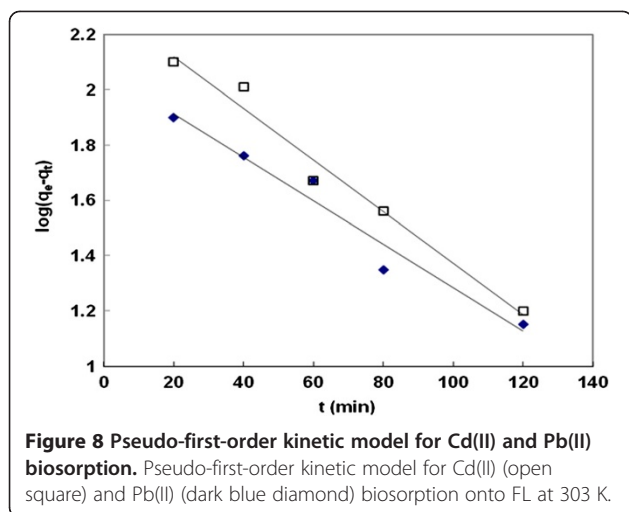
T(°C)	Langmuir			Freundlich		
	q_{max}	K_L	R^2	n	K_F	R^2
20	37.74	0.034	0.9992	3.96	5.44	0.9825
30	34.36	0.027	0.9991	2.64	3.82	0.9648
40	32.36	0.022	0.9990	2.41	3.02	0.9678

where q_e and q_t are the sorption capacities at equilibrium and at time t, respectively (mg/g), and k_1 is the rate constant of pseudo-first-order sorption (1/min). After integration and applying boundary conditions, $q_t = 0$ to $q_t = q_t$ at $t = 0$ to $t = t$, the integrated form of Equation 5 becomes

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t. \qquad (6)$$

The equation applicable to experimental results generally differs from a true first-order equation in two ways: the parameter $k_1(q_e - q_t)$ does not represent the number of available sites, and the parameter log q_e is an adjustable parameter which is often not found equal to the intercept of a plot of log $(q_e - q_t)$ against t, whereas in a true first-order sorption reaction, log q_e should be equal to the intercept of $\log(q_e - q_t)$ against t. In order to fit Equation 5 to the experimental data, the equilibrium sorption capacity q_e must be known. In many cases, q_e is unknown and as chemisorption tends to become unmeasurably slow, the amount sorbed is still significantly smaller than the equilibrium amount. In most cases in the literature, the pseudo-first-order equation of Lagergren does not fit well for the whole range of contact time and is generally applicable over the initial 20 to 60 min of the sorption process. Furthermore, one has to find some means of extrapolating the experimental data to $t = \infty$, on treating q_e as an adjustable parameter to be determined by trial and error. For this reason, it is therefore necessary to use trial and error to obtain the equilibrium sorption capacity, in order to analyze the pseudo-first-order model kinetics.

The pseudo-first-order rate constant can be obtained from the slope of plot between log $(q_e - q_t)$ against time, t. Figure 8 shows the Lagergren pseudo-first-order kinetic plot for the biosorption of Cd(II) and Pb(II) ions onto FL. The pseudo-first-order rate constant values were

Figure 8 Pseudo-first-order kinetic model for Cd(II) and Pb(II) biosorption. Pseudo-first-order kinetic model for Cd(II) (open square) and Pb(II) (dark blue diamond) biosorption onto FL at 303 K.

Figure 9 Pseudo-second-order kinetic model for Cd(II) and Pb(II) biosorption. Pseudo-second-order kinetic model for Cd(II) (open square) and Pb(II) (blue diamond) biosorption onto FL at 303 K.

calculated from the slope of Figure 8. The calculated values and their corresponding linear regression correlation coefficient values are shown in Table 3. The linear regression correlation coefficient values show that this model cannot be applied to predict the adsorption kinetic model.

Pseudo-second-order kinetics

The pseudo-second-order rate expression, which has been applied for analyzing chemisorption kinetics rate, is expressed as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2, \tag{7}$$

where q_e and q_t are the sorption capacity at equilibrium and at time t, respectively (mg/g); and k_2 is the rate constant of pseudo-second-order sorption, (g/mg/min). For the boundary conditions, $q_t = 0$ to $q_t = q_t$ at $t = 0$ to $t = t$, the integrated form of Equation 7 becomes
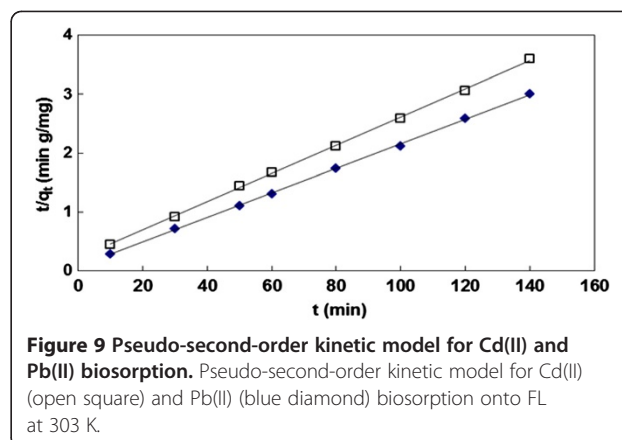
$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e}e + k_2 t. \tag{8}$$

Equation 8 can be rearranged to obtain

$$q_t = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}}. \tag{9}$$

The linear form of Equation 9

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t, \tag{10}$$

where t is the contact time (min), q_e (mg/g) and q_t (mg/g) are the amount of the solute adsorbed at equilibrium and at any time, t. If pseudo-second-order kinetics is applicable, the plot of t/q_t versus t of Equation 9 should give a linear relationship, from which q_e and k can be determined from the slope and intercept of the plot, Figure 9. The pseudo-second-order rate constant k_2, the calculated q_e value, and the corresponding linear regression correlation coefficient value are given in Table 3. At all initial metal concentrations, the linear regression correlation coefficient R^2 values were higher. The higher

Table 4 Biosorption of Pb(II) and Cd(II) ions by different biosorbents

Biosorbent	Pb(II)	Cd(II)	Reference
Pomegranate peel	13.87	-	[13]
Banana cortex	-	67.2	[7]
Orange cortex	-	28.8	[7]
Lemon cortex	-	12	[7]
Processed walnut shell	32	11.6	[11]
Rice husk	0.62	-	[17]
Olive tree pruning waste	33.39	-	[21]
Maize leaf	-	10.18	[9]
Moringa oleifera leaves	209.54	-	[8]
Scolymus hispanicus L	-	54.04	[10]
Ulmus tree leaves	201	80	[4]
Fraxinus tree leaves	172	67.2	[4]
Green coconut shell	-	285.7	[5]
Neem leaf	13.51	1.89	[2]
Heartwood of *Areca catechu*	-	10.66	[3]
Ficus carcia leaves	34.36	30.31	This work

Table 3 Biosorption kinetic model parameters for Cd(II) and Pb(II) by FL

T(°C)	Pseudo-first order			Pseudo-second order		
	k_1	q_e	R^2	k_2	q_e	R^2
Cd(II)	0.018	117.19	0.9766	0.11	41.67	0.9997
Pb(II)	0.018	201.51	0.9627	0.021	47.85	0.9995

values confirm that the adsorption data are well represented by pseudo-second-order kinetics.

Comparison of *F. carcia* leaves with other biosorbents

A comparative study of the maximum biosorption capacity (q_{max}) of *F. carcia* leaves with those of some other biosorbents reported in literature is given in Table 4. Differences in q_{max} are due to the nature and properties of each biosorbent such as surface area and the main functional groups in the structure of the biosorbent. A comparison with other adsorbents indicated a high Cd(II) and Pb(II) biosorption capacity of the *F. carcia* leaves.

Experimental

All the chemicals used were of analytical reagent (AR) grade purchased from Merck (Germany). All the solutions were prepared with double-distilled water with zero levels of dissolved oxygen. The cadmium(II) and lead(II) stock solutions were prepared from cadmium nitrate [$Cd(NO_3)_2$] and lead nitrate [$Pb(NO_3)_2$], respectively. *F.* carcia leaves were washed with distilled water several times to remove dust and soluble materials and then allowed to dry at room temperature. The dried leaves were grounded to a fine powder and sieved to get size fraction <44 μm and then dried in an oven at 60°C for 4h. Cadmium(II) and lead(II) concentrations were determined by AAS600 atomic spectrophotometer (Shimadzu, Japan). pH measurements were made with a WTW pH meter using a combined glass electrode. Fourier transform infrared spectroscopy IR prestige-21 (Shimadzu, Japan) was used to study the functional groups in biosorbent and biosorbent-loaded metal.

Conclusions

The potential of FL for the removal of Cd(II) and Pb(II) ions from aqueous solutions was dependent on biosorption process such as pH, initial metal ion concentrations, biosorbent dose, contact time, and temperature. The equilibrium data have been analyzed using Langmuir and Freundlich isotherms. The characteristic parameters for each isotherm and related correlation coefficients R^2 were determined. The Langmuir biosorption isotherms were demonstrated to provide the best correlation for the biosorption of Cd(II) and Pb(II) ions onto FL. The maximum monolayer biosorption capacity of FL was found to be 30.31 mg of Cd(II)/g of FL and 34.36 mg of Pb(II)/g of FL. The kinetic results provided the best correlation of the experimental data of biosorption of Cd(II) and Pb(II) onto FL by pseudo-second-order equation. It can be concluded that since the FL is an easily locally available low-cost adsorbent and has a considerable high biosorption capacity, it may be treated as an alternative adsorbent for treatment of wastewater containing cadmium(II) and lead(II) ions.

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