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Biosorption of Cadmium (II) from Aqueous Solutions by *Prunus Avium* Leaves

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Abstract A new biosorbent from *Prunus avium* (sweet cherry) leaves was used to remove cadmium(II) from aqueous solutions. The biosorption of cadmium(II) was found to be dependent on solution pH, initial metal ion concentrations, biosorbent dose, and contact time. The experimental equilibrium biosorption data were analyzed by two widely used two-parameters, Langmuir and Freundlich isotherm models. The Langmuir model gave a better fit than the Freundlich model. The kinetic studies indicated that the biosorption process of the cadmium ions followed well pseudo-second-order model. It was concluded that *Prunus avium* leaves powder can be used as an effective, low cost, and environmentally friendly biosorbent for the removal of Cd(II) ions from aqueous solution.

Keywords Biosorption, *Prunus avium* Leaves, Cadmium(II) Ions, BiosorptionIsotherms, Kinetic

1. Introduction

The major sources of Cd(II) release into the environment by waste streams are electroplating, smelting, alloy manufacturing, pigments, plastic, battery, mining and refining processes. Cadmium is one of the toxic heavy metals, which is regarded as an element of high toxicity. Different methods have been used on cadmium content reduction from water and industrial waste such as chemicalprecipitation, ion exchange, membrane filtration, electrolytic methods, reverse osmosis, solvent extraction, and activated carbon adsorption[1]. These conventional techniques can reduce cadmium ions, but they do not appear to be highly effective due to the limitations in the pH range as well as the high material and operational costs. Different biosorbentmaterials have been investigated for removal of cadmium ions from aqueous solutions such as plant materials like wheat straw[2], agricultural waste biomass[3], rice husk[4], orange peel[5], nut husk[6], sugar beet pulp[7], orange waste[8], coconut shell[9], juniper bark and wood[10] and wheat stem[11].In recent years, considerable attention has been focused on the removal of cadmium ions from aqueous solution using adsorbents derived from low-cost tree leaves such as loquat leaves[12], *sidiumguajava* eaves[13], maize leaf[14], ulmus leaves[15], Scolymus hispanicus.[16], Ulmus carpinifolia and Fraxinus excelsior tree leaves[17],

In the present work, We have studied the potential of cadmium(II) ions biosorption on *Prunus avium* (sweet cherry) coming from *P. avium* tree leaves. Results from this study can be used to assess the utility of *P. avium* leaves powder for cadmium(II) ions removal from water and industrial wastewaters.

2. Materials and Methods

2.1. Adsorbent

The raw *Prunus avium* (sweet cherry) leaves were collected from a local plantation. The leaves were thoroughly rinsed with water to remove dust and soluble materials. Then it was allowed to dry at room temperature. The dried leaves was grounded to a fine powder in a grinding mill (Retsch RM 100) and sieved to get size fraction < 44 μm, and then dried in an oven at 60 °C for 24 h.

2.2. Materials

All the chemicals used were of analytical reagent (AR) grade. Stock solutions of 1000 mg/L of cadmium(II) ionswere prepared from nitrates of cadmium which was purchased from Fluka AG using double distilled water. Desired test solutions of cadmium ions were prepared using appropriate subsequent dilutions of the stock solution. The range of concentrations of cadmium ions prepared from standard solution varies between 10 and 100 mg/L. Before mixing the adsorbent, the pH of each test solution was

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adjusted to the required value with 0.1 M NaOH or 0.1 M HCl.

2.3. Analysis

The concentrations of Cd(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, Japan) was used to identify the different chemical functional groups present in the *P. avium* leaves powder. FTIR analyses also used to determine the functional groups which are responsible for the cadmium binding with *P. avium* leaves powder. The analysis was carried out uing KBr and the spectral range varying from 4000 to 400 cm^{-1}.

2.4. Biosorption Experiments

Batch biosorption experiments were conducted by mixing biosorbent with cadmium 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 r/min. The effect of pH on the equilibrium biosorption of Cd(II) was investigated by mixing, 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:

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

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). Percent removal (% R) of cadmium ions was calculated from the following equation:

$$\%R = \frac{C_o - C_e}{C_o} x100 \tag{2}$$

3. Results and Discussion

3.1. FT-IR Analysis

To investigate the functional groups of *P. avium* and cadmium loaded *on P. avium*, a FT-IR study was carried out and the spectra are shown in Figures. 1. and 2. The *P. avium* leaves display a number of absorption peaks, reflecting their complex nature. A strong and broad peak at 3356cm^{-1} results due to the stretching of the N–H bond of amino groups and indicative of bonded hydroxyl group of alcohols and phenols. A change in peak position to 3375 cm^{-1} in the spectrum of the cadmium loaded *P. avium*, Fig.2, indicates the binding of cadmium with amino and/or hydroxyl groups. The absorption peaks at 2939 cm^{-1} and 2893cm^{-1} could be assigned to –CH stretching vibrations of $-CH_3$ and $-CH_2$ functional groups. The shoulder peak in pure *P. avium* leaves powder at 1701 cm^{-1} is shifted to lowe frequency 1696 cm^{-1} due to the involvement of carbonyl –CO group from carboxylic acids in the biosorption process of cadmium ions with *P. avium* leaves powder. The peak at 1635cm^{-1} indicates the fingerprint region of CO, C–O and O–H groups, which exist as functional groups of *P. Avium* and shifting of this peak to 1631cm^{-1}, indicated involvement of these groups in cadmium binding. The band at 1377 cm^{-1} corresponding of C-O stretching was shifted to 1404 cm^{-1}. The region between 1284 and 1000 cm^{-1} is the fingerprint region, OH, and C-H bending vibration and C-O stretching vibration absorption bands. The intense band at 1029 cm^{-1} can be assigned to the C-O of alcohols and carboxylic acids. The shift of the peak from 1029 to 1010 cm^{-1} also suggests the involvement of C–O group in binding Cd(II). The shifts in the absorption peaks generally observed indicate the existence of a cadmium binding process taking place on the surface of the *P. avium* leaves powder.

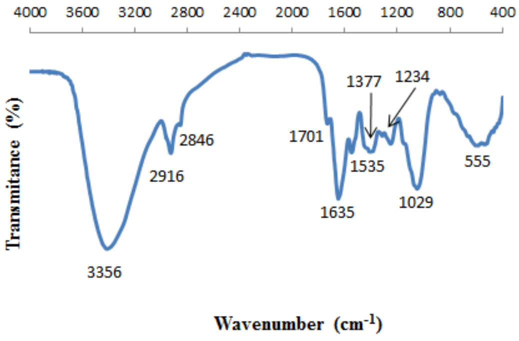

Figure 1. FTIR of *P. avium* leaves powder

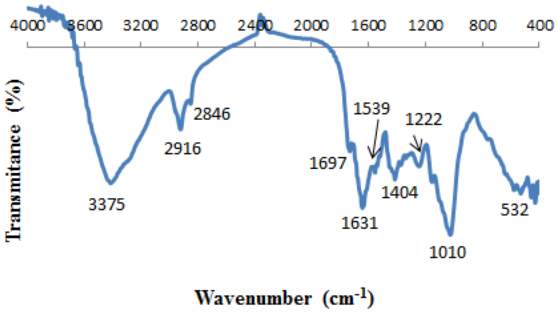

Figure 2. FTIR of P. avium leaves powder loaded with cadmium

3.2. Effect of PH

The pH has been identified as one of the most important parameter that is effective on metal sorption. It is directly related with competition ability of hydrogen ions with metal ions to active sites on the biosorbent surface. The effect of pH on the biosorption of Cd(II) ions onto *P.avium* leaves powder was studied at pH 1.0–8.0. The maximum biosorption was observed at pH 6.5 for Cd(II). Therefore, the remaining all biosorption experiments were carried out at this pH values. The biosorption mechanisms on the *P.avium* leaves powder surface reflect the nature of the physicochemical interaction of the solution. At highly acidic pH (pH < 1.0), the overall surface charge on the active sites became positive and metal cations and protons complete for binding sites on cell wall, which results in lower uptake of metal. The biosorbent surface was more negatively charged as the pH solution increased from 1.0 to 6.0. The functional groups of the *P. avium* leaves powder were more deprotonated and thus available for the metal ions. Decrease in biosorption yield at higher pH (pH > 6) is not only related the formation of soluble hydroxylated complexes of the metal ions (cadmium ions in the form of $Cd(OH)_2$) but also to the ionized nature of the cell wall surface of the bark powder under the studied pH.

3.3. 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 d Cd(II) was investigated. The biosorption yield of Cd(II) increased considerably until the contact time reached 120 min. Further increase in contact time did not enhance the biosorption, so, the optimum conta ct time was selected as 120 min for further experiments

3.4. Effect of Adsorbent Dose on Biosorption

The biosorbent dosage is an important parameter because this determines the capacity of a biosorbent for a given initial concentration. The biosorption efficiency for Cd(II) ions as a function of biosorbent dosage was investigated. The percentage of the metal biosorption steeply increases with the biosorbent loading up to 0.5 g/0.1 L. This result can be explained by the fact that the biosorption sites remain unsaturated during the biosorption reaction whereas the number of sites available for biosorption site increases by increasing the biosorbent dose. The maximum biosorptio n 94.44% for Cd(II) was attained at biosorbent dosage, 0.5 g/0.1 L. Therefore, the optimum biosorbent dosage was taken as 0.5 g/0.1 L for further experiments.

3.5. Biosorption Isotherms

An adsorption isotherm descris the fraction of sorbate molecules that are partitioned between liquid and solid phases at equilibrium. Two isotherm models were tested:

3.5.1. 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[18]:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{3}$$

where K_F is the Freundlich constant related to the bonding energy. 1/n is the heterogeneity factor and n (g/L) 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, Figure 3 on the basis of the linear of Freundlich equation (3).The n value indicates the degree of non-linearity 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 1.15 for *P. avium* , Table 1. Since n lie between 1 and 10, this indicate the physical biosorption of cadmium (II) onto *P. avium*. The values of regression coefficients R^2 are regarded as a measure of goodness of fit of the experimental data to the isotherm models.

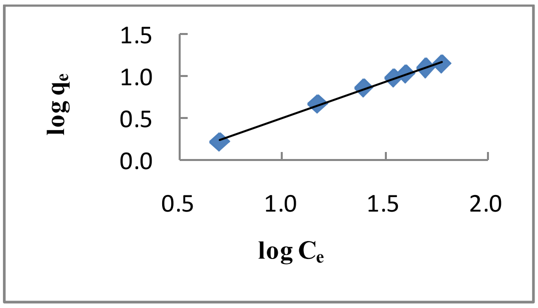

Figure 3. Freundlich isotherm for Cd(II) biosorption onto *P. avium* leaves powder at 303 K

3.5.2. Langmuir isotherm

The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites[19]. 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:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{1}{q_{\max}} Ce \tag{4}$$

where K_L is the Langmuir constant related to the energy of adsorption and qmax is the maximum adsorption capacity (mg/g) . Values of Langmuir parameters qmax and K_L were calculated from the slope and intercept of the linear plot of C_e/qe versus C_e as shown in Figure 4. Values of q*max*, K_L and regression coefficient R^2 are listed in Table 1. These values for *P. avium* biosorbent indicated that Langmuir model describes the biosorption phenomena favarouble.

The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and sorbent using separation factor or dimensionless equilibrium parameter, R_L expressed as in the following equation:

$$R_L = \frac{1}{(1 + K_L C_o)} \tag{5}$$

where K_L is the Langmuir constant and C_o is the initial concentration of cadmium (II) 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 0.64-0.88 for concentration of 10–40 mg/L of Cd(II). They are in the range of 0-1 which indicates the favourable biosorption.

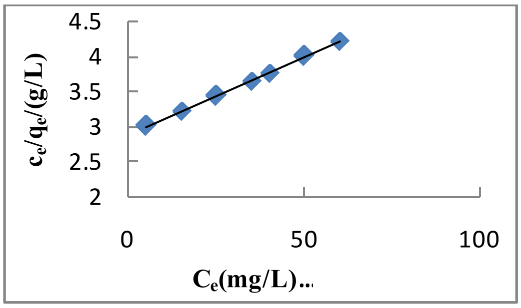

Figure 4. Langmuir isotherm for Cd (II) biosorption onto *P. avium* leaves powder at 303 K

Table 1. Freundlich and Langmuir constants`for Cd(II) ions biosorption by *P. avium* at 303 K

Freundlich isotherm		
K_F	n	R^2
2.32	1.15	0.997
Langmuir isotherm		
K_L	q_{max}	R^2
0.008	45.45	0.999

3.6. Biosorption Kinetics

Parameters from two kinetic models, pseudo first-order and pseudo second-order were fit to experimental data to examine the biosorption kinetics of cadmium (II) uptake by *P. avium* leaves powder.

3.6.1. Pseudo First-Order Kinetics

The pseudo-first order equation of Lagergren[20] is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (6)$$

Where qe and qt 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 (6) becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (7)$$

The equation applicable to experimental results generally differs from a true first order equation in two ways: the parameter $k_1(qe - q_t)$ 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 (7) to experimental data, the equilibrium sorption capacity, q_e must be known. In many cases is unknown and as chemisorption tends to become un measurably 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 minutes of the sorption process. Furthermore, one has to find some means of extrapolating the experimental data to $t = \infty$, on treating qe 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 5 shows the Lagergren pseudo-first order kinetic plot for the adsorption of cadmium ions onto *P. avium* leaves powder. The calculated values and their corresponding linear regression correlation coefficient values are shown in Table 2. The linear regression correlation coefficient value found 0.9506,which shows that this model cannot be applied to predict the adsorption kinetic model.

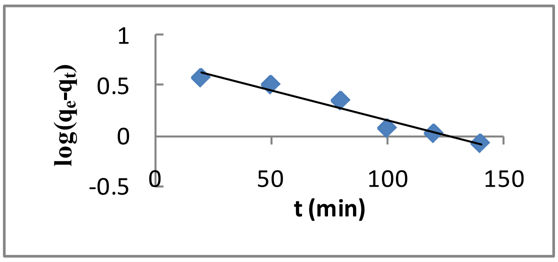

Figure 5. Pseudo-first order kinetic model for Cd (II) biosorption onto *P. avium* leaves powder at 303 K

3.6.2. Pseudo-Second Order Kinetics

The pseudo second-order rate expression, which has been applied for analyzing chemisorption kinetics rate[20] is expressed as:

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \qquad (8)$$

Where q_e and q_t are the sorption capacity at equilibrium and at time t, respectively (mg/g) and k is the rate constant of pseudo-second order sorption, (g/mg min). For the boundary conditions to $q_t = 0$ to $q_t = q_t$ at $t = 0$ to $t = t$; ; the integrated form of equation (8) becomes:

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e}t \qquad (9)$$

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_2 can be determined from the slope and intercept of the plot, Fig. 6. 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 2. At all initial metal concentrations, the linear regression correlation coefficient R^2 values were higher. The higher values confirm that the adsorption data are well represented by pseudo-second order kinetics.

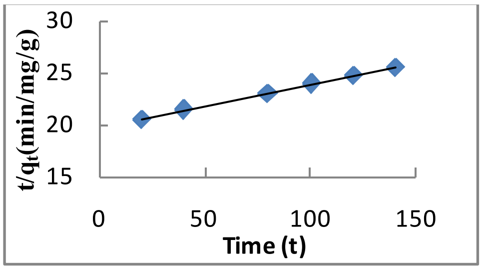

Figure 6. Pseudo-second order kinetic model for Cd(II) biosorption onto *P. avium* leaves powder at 303 K

Table 2. Biosorption kinetic parameters for Cadmium (II) ions by P. avium leaves at 303 K

	Pseudo-first order	
K_1	q_e (mg/g)	R^2
0.014	5.67	0.9506
	Pseudo-second order	
K_2	q_e (mg/g)	R^2
8.8E-05	24.04	0.9996

4. Conclusions

The potential of *P. avium* leaves powder for the removal of Cd(II) ions from aqueous solutions and wastewater was dependent on biosorption process such as pH, initial metal ions concentration, biosorbent dose, and contact time,. The Langmuir and Freundlich biosorption isotherms were demonstrated to provide best correlation for the biosorption of Cd(II) ions onto *P. avium* leaves powder. The kinetic results provided the best correlation of the experimental data of biosorption of cadmium ions onto *P. avium* leaves powder by pseudo second-order equation. it can be concluded that since the *P. avium* leaves are 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) ions.

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