*Desalination and Water Treatment*
www.deswater.com

doi: 10.5004/dwt.2017.21454

92 (2017) 215–221
October

# Removal of cadmium(II) ion from wastewater by using Lebanese *Prunus avium* stem as adsorbents

Nour Al-Afy[a], Akram Hijazi[a], Hassan Rammal[a], Mohamad Reda[b], Rabih Nehme[a], Houssein Annan[a], Joumana Toufaily[a,b,c], Tayssir Hamieh[b,d,*]

[a]*Doctoral School of Science and Technology, Research Platform for Environmental Science (PRASE), Lebanese University, Lebanon, emails: nour.aliii2010@gmail.com (N. Al-Afy), hijazi_akram@hotmail.com (A. Hijazi), hasanrammal@hotmail.fr (H. Rammal), rabih.nehme@outlook.fr (R. Nehme), H.Annan@edst.edu.lb (H. Annan)*
[b]*Laboratory of Materials, Catalysis, Environment and Analytical Methods (MCEMA), LEADDER Laboratory, EDST, Lebanese University, Lebanon, emails: tayssir.hamieh@ul.edu.lb, tayssir.hamieh@univ-poitiers.fr (T. Hamieh), reda_mohamad75@hotmail.com (M. Reda), joumana.toufaily@ul.edu.lb (J. Toufaily)*
[c]*School of Mechanical and Materials Engineering, Washington State University, Washington, DC, USA*
[d]*Institut de Chimie, des Milieux et des Matériaux de Poitiers, UMR CNRS 7285, Université de Poitiers 4, rue Michel Brunet TSA51106, B27, 86073 Poitiers cedex 9*

Received 25 January 2017; Accepted 16 September 2017

**ABSTRACT**

The objective of this study was to investigate the possibility of using Lebanese *Prunus avium* stems as an alternative adsorbent for the removal of cadmium(II) ions from aqueous solutions. Different parameters such as the effect of initial metal ion concentration, pH, adsorbent dose and contact time were studied. Maximum adsorption capacity (90%) of Cd(II) ions was obtained at pH 10 with an initial Cd(II) concentration 150 mg/L after 1 h and at 25°C. Fourier transform infrared analysis pointed out the involvement of amine ($-NH_2$) and carboxylic (–COOH) groups in the adsorption process. The adsorption isotherm was better described by a Freundlich model rather than a Langmuir model. The paper discusses the thermodynamic parameters of the adsorption (the Gibbs free energy, entropy and enthalpy). Our results demonstrated that the adsorption process was spontaneous and exothermic under natural conditions. When the temperature decreases from 333 to 298 K, the standard free energy $\Delta G^0$ decreases thus indicating a spontaneous adsorption with an exothermic process $\Delta H^0 < 0$. Based on these results, it can be concluded that the stems of *Prunus avium* are effective as an alternative adsorbent for toxic Cd(II) ion remediation in waste water.

*Keywords:* *Prunus avium*; Cadmium(II); Adsorption; Langmuir and Freundlich isotherm models; Thermodynamics

## 1. Introduction

Heavy metals are one of the most important wide spread environmental problems in water resources [1]. These metals are toxic since they are non-biodegradable [2], so they must be removed. Cadmium is one of the top six deadliest and toxic materials known, it is most commonly found in 2+ oxidation state in nature [3]. It is frequently used in industrial processes such as alloys, painting, electroplating, smelting, batteries and mining industry [4]. When cadmium is absorbed into the body in quantities greater than 10 mg, adverse effects are acute and if it occurs over a long period of time, effects can be fatal [5]. Cadmium causes damage to kidneys, cardiac tissue, bones and is thought to be a carcinogen [6]. Symptoms of cadmium exposure are increased loss of small proteins in the urine, salivation, choking, vomiting, metallic taste, loss of sense of smell, joint pain and others [7]. Different physiochemical techniques

* Corresponding author.

are being used to remove cadmium from waste water such as ion exchange, chemical precipitation, reverse osmosis, electrodialysis, membrane filtration, flotation and activated carbon adsorption thus reduce the toxicity [8], but they have incomplete removal and high material cost.

Several researches were done in natural adsorbent to remove cadmium from aqueous solutions such as plants material like nut husk [9], juniper bark and wood [10], orange peel [11], orange waste [12], wheat stem [13], rice husk [14], agricultural waste biomass [15], wheat straw [16], coconut shell [17] and sugar beet pulp [18].

Recently, Garcia-Fayos et al. [19] studied the biosorption ability of *Moringa oleifera* raw husk and tested for the removal of cadmium and copper from synthetic water. There are no previous studies of this part of the tree used as raw material for these metals. Their results allowed determining the maximum adsorption capacity of the biosorbent as a function of the mathematical linear regression following the isothermal models of Langmuir and Freundlich, and the kinetics using pseudo-first-order and pseudo-second-order models. This allowed determining if the biosorption process is suitable for removing heavy metals from contaminated waters.

Goswami et al. [20] characterized in another study, the cadmium removal from aqueous solution by biochar produced from *Ipomoea fistulosa* at different pyrolytic temperatures by developing a method to produce biochar through pyrolysis and to investigate the ability of Ipomoea-derived biochar to remove Cd(II) ions from aqueous solution.

In the present work, the stems of the Lebanese *Prunus avium* have been used as an adsorbent to remove Cd(II) ions from waste water by varying the experimental conditions such as contact time, initial metal ion concentration and pH. These parameters could be applied in the reduction of cadmium pollution in the environment.

## 2. Materials and methods

The raw *Prunus avium* (sweet cherry) stems were collected from a local Lebanese plantation. The stems were thoroughly rinsed with water and then dried at room temperature. After that, the dried stems were grinded to a fine powder in a grinding mill to get size of 0.25 mm.

### 2.1. Chemicals

The stock solution was prepared by dissolving 1 g of $CdCl_2.2H_2O$ in 1 L deionised water. All the required working solutions were prepared by diluting the stock solution with deionised water. A buffer solution with pH 6.0 was prepared from 0.1 mol/L disodium hydrogen phosphate. Samples for Fourier transform infrared (FT-IR) were prepared by diluting the adsorbent to 5% in KBr and cast in disks for analysis. Analysis of standards and simulated samples was done using an AA-140 atomic absorption spectrometer (AAS).

### 2.2. Batch experiments for Cd(II)

Batch experiments were carried out using a series of Erlenmeyer flask of 50 mL capacity. Batch experiments were performed to study the effect of initial Cd(II) ion concentration, pH, contact time and adsorbent dose on adsorption of the Cd(II) ions from its solution. All the adsorption experiments were carried out at room temperature except where the effect of temperature was being investigated. The initial pH was adjusted with $HNO_3$ (1 M) or NaOH (1 M) solutions.

#### 2.2.1. Effect of pH

The effect of pH on adsorption was investigated in the pH range 2–12 at 25°C ± 2°C. The initial pH of the Cd(II) solution was adjusted from pH 4 by adding few drops of $HNO_3$ (1 M) to get a pH 2. Solutions of pH between 6 and 12 were prepared by adding few drops of NaOH (1 M) to a pH 4.

#### 2.2.2. Effect of metal ion concentration

Adsorbent (0.5 g) was shaked with 50 mL of varying concentrations (25, 150, 300, 400 and 600 mg/L) of Cd(II) solution. The mixture was continuously agitated at 25°C ± 2°C with a shaker at 400 rpm. The pH of the solution was adjusted to a pH 6. After the established contact time (1 h) was reached, the suspension was filtered in two steps: first by Buchner filtration then by 0.45 μm filter. After that, the final concentration of Cd(II) in the filtrate was determined using AAS. The adsorbed amount was determined from the difference between the initial and residual concentrations of Cd(II) in the liquid phase.

#### 2.2.3. Effect of contact time

To find the effect of the contact time, experiment was performed with 50 mL of 150 mg/L Cd(II) solution at a pH 6. 0.5 g of adsorbent at 25°C ± 2°C was added to aqueous solution in respect to the following times: 30, 60, 120, 180, and 240 min and mixed with a shaker set at 400 rpm. After that, the samples were filtered and the filtrate was then analyzed by AAS in order to determine the adsorption capacity.

#### 2.2.4. Effect of temperature

To find the effect of temperature, experiment was also performed following the same procedure by fixing all other parameters and varying only the temperature ranges: 0 C, 25 C, 35 C, 50 C and 68 C.

#### 2.2.5. Effect of adsorbent dose

Adsorption dose experiments were performed following the same procedure as described earlier at pH 6, 150 mg/L Cd(II), 25°C ± 2°C, 400 rpm, with the following adsorbent masses: 0.2, 0.4, 0.6, 0.8, 1 and 1.2 g. After 1 h the samples were filtered and the filtrate was analyzed by AAS.

## 3. Results and discussion

When *Prunus avium* stems powder was tested for its ability to adsorb Cd(II) ion from aqueous solution, initial pH 6 was used for most experiments. The effects of the following experimental parameters (pH, initial concentration, contact time and adsorbent dosage) on adsorption were studied. The removal percentage of Cd(II) ion (% Re) was calculated by using the following equation:

$$\%\mathrm{Re} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where $C_i$ and $C_f$ are the initial and final concentrations of metal ion (mg/L). The adsorption capacity of Cd(II) is the concentration of Cd(II) over the adsorbent mass and it was calculated based on the mass balance principle according to the following equation:

$$q_m = \frac{V\left(C_i - C_f\right)}{m} \quad (2)$$

where $q_m$ (mg/g) is the amount of Cd(II) per dry weight of *Prunus avium*, $V$ is volume of solution (L) and $m$ is amount of sorbent (g) in the mixture.

### 3.1. FT-IR analysis of adsorbent

The FT-IR spectrum (Fig. 1) of *Prunus avium* was used to investigate the functional groups present on the *Prunus avium* that could be responsible for the removal of heavy metal species [21]. The spectrum of the adsorbent was measured within the range of 4,000–400 cm$^{-1}$ wave number. The comparison of the FT-IR spectra has been done before and after loading with Cd(II). The *Prunus avium* stems show a number of absorption peak that reflect its complex nature. Two peaks at 3,513 and 3,436 cm$^{-1}$ are due to the presence of N–H bond stretching (primary amine). A broad peak at 3,292 cm$^{-1}$ is due to the existence of OH groups. The absorption peak at 2,924 cm$^{-1}$ could be assigned to C–H stretching vibration, 1,736 cm$^{-1}$ to ester carbonyl, 1,608 cm$^{-1}$ to C=C, 1,520 cm$^{-1}$ to N–H, 1,066 cm$^{-1}$ to C–O.

After adsorption, a broad peak at 3,442 cm$^{-1}$ corresponds to the overlapping of OH and NH peaks. This phenomenon may be attributed to the water molecule directly interacting with amide.

After Cd(II) binding, a change of peak position occurs (3,437–3,442 cm$^{-1}$, 3,292–2,925 cm$^{-1}$, 1,736–1,745 cm$^{-1}$, 1,253–1,254 cm$^{-1}$, 1,066–1,069 cm$^{-1}$, 824–605 cm$^{-1}$, 536–565 cm$^{-1}$).

The shift in the wave number corresponds to the change in the energy of the functional groups that indicates the existence of Cd binding process done on the surface of *Prunus avium* stem powder [22].

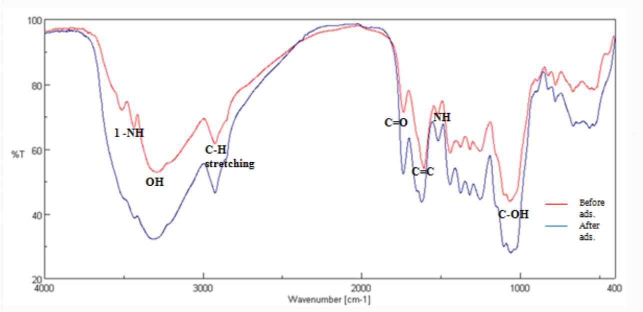


Fig. 1. FT-IR spectrum of *Prunus avium* stems before and after adsorption.

### 3.2. Adsorption of Cd(II)

#### 3.2.1. Effect of pH

The pH of an aqueous solution has been known as the most important variable affecting the Cd(II) ion adsorption onto biosorbents [22], because it affects the surface charge of adsorbents and the degree of ionization [23]. The effect of pH on the uptake of Cd(II) ions by *Prunus avium* stems is shown in Fig. 2. The removal percentage of $Cd^{2+}$ ions increases from pH 4 to alkaline region to reach maximum at pH 10 (90%), this could be associated with the formation of soluble hydroxylated complexes of $Cd(OH)_2$ and $Cd(OH)_4^-$ species which might be more attracted to the adsorbent rather than the positively charged $Cd^{2+}$ ions; where at lower pH, the surface of adsorbent became positively charged as the $OH^-$, $NH_2^-$ and other such groups become protonated. This will lead to an increase in electrical repulsion between the adsorbent surface and the species to be adsorbed, while at higher pH, the surface of the adsorbent was almost neutral and thus resulting in minimal repulsion between the adsorbent and the adsorbate. The pH will also greatly affect the Cd(II) solubility. Particularly, the solubility product of $Cd(OH)_2$ is so that $Cd(OH)_2$ precipitated for pH higher than 10. Therefore, for all experiments where the pH is greater than 10, the Cd(II) removal from the solution is probably due to the formation of $Cd(OH)_2$ more than to the uptake of Cd(II) by the stems.

#### 3.2.2. Effect of adsorbent dose

The adsorbent dosage is another important parameter because this influences the extent of metal uptake from the solution and thus the effect as shown in Fig. 3. The percentage removal efficiency of Cd(II) increased from 58.77% to 100% when the adsorbent dosage increased from 0.2 to 0.8 g due to the limited availability of the number of adsorbing species for a relatively larger number of surface sites on the adsorbent at higher dosage of adsorbent. It is plausible that with higher dosage of adsorbent there would be greater availability of exchangeable sites from metal ions [24]. After that

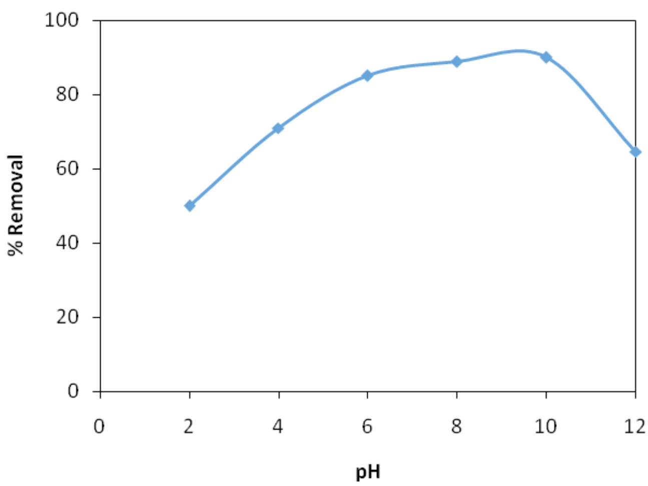


Fig. 2. Effect of pH on the adsorption of Cd(II) ions onto *Prunus avium* (with the following conditions: 50 mL of 150.0 mg L$^{-1}$ concentration of Cd(II), contact time of 60 min, agitation speed of 400 rpm and sorbent dose of 0.5 g).

as adsorbent dose increases from 0.9 to 1.2 g, the percentage removal remains constant approximately since equilibrium was reached [25] (Fig. 3).

### 3.2.3. Effect of contact time

The effect of contact time on the adsorption of Cd(II) from its solution is shown in Fig. 4. There is an increase in the % adsorption of Cd(II) with time. It can be seen that the adsorption yield of Cd(II) slowed down after 30 min to reach maximum 75%, so the equilibrium time was found at 30 min (Fig. 4). After this time, no significant change in cadmium concentration in the solution was observed. This was probably due to the larger surface area of the plants being available at beginning for the adsorption of $Cd^{2+}$ ions. As the surface adsorption sites become exhausted, the uptake rate was controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles [26].

### 3.2.4. Effect of Cd(II) concentration

To investigate the effect of the $Cd^{2+}$ concentration on the adsorption capacity, the process was carried out with initial $Cd^{2+}$ concentration between 25 and 600 mg/L while keeping the other four parameters constant.

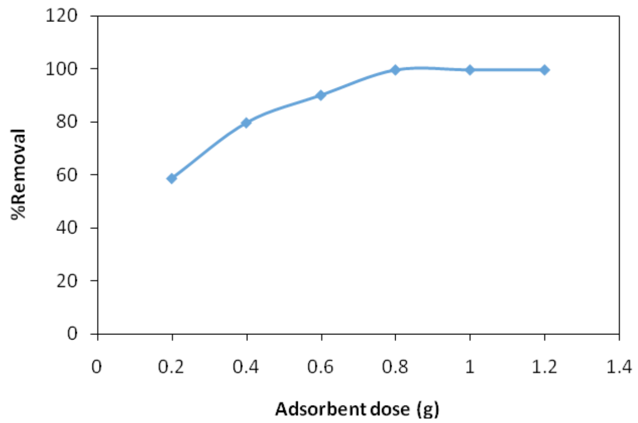


Fig. 3. Effect of the sorbent amount (the conditions used in this figure were the same of that of Fig. 2, except for sorbent amount).

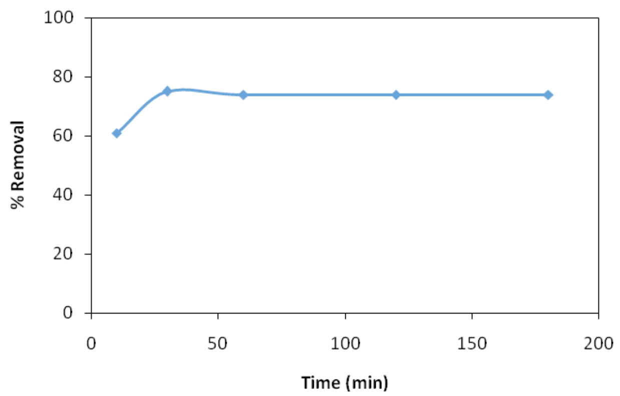


Fig. 4. Effect of contact time on adsorption of Cd(II) ions onto *Prunus avium* (conditions were the same as in Fig. 2, except for contact time).

As can be seen from Fig. 5, there is a sharp increase in adsorption of Cd(II) from 50% to 76.38% at 400 mg/L, that is due to the interactions between the metal ions and the active sites of the adsorbent. Thereafter, the adsorption levels off, remains almost constant. The leveling of the curve after 400 mg/L can be attributed to the saturation of adsorption active sites [3].

### 3.3. Biosorption isotherms

Adsorption isotherms are essential for understanding the mechanism of an adsorption system. Since they represent the amount of compounds adsorbed on a surface as a function of concentration at a constant temperature [27], two isotherms models were tested as given below.

### 3.3.1. Freundlich isotherm

Freundlich isotherm model is the well-known earliest relationship, which describes the adsorption process. It can be applied to non-ideal sorption on heterogeneous surfaces as well as multilayer sorption [28]. This isotherm is expressed by the following linear equation:

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

where $K_F$ is the Freundlich constant related to the bonding energy (L/mg), $1/n$ 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 $\log q_e$ vs. $\log C_e$ (Fig. 6), basis on the linear of Freundlich equation [3]. Where the $n$ value indicates the degree of non-linearity between solution concentration and adsorption as follows: if $n = 1$, the adsorption is linear; if $n < 1$, the adsorption is a chemical process; if $n > 1$, the adsorption is a physical process. The $n$ value in Freundlich equation was found to be 1.079 for *Prunus avium* (Table 1). Since $n$ is greater than 1, this indicates the physical biosorption of Cd(II) onto *Prunus avium*. The values of correlation coefficients $R^2$ are done as a measure of goodness of fit of the experimental data to the isotherm models [29].

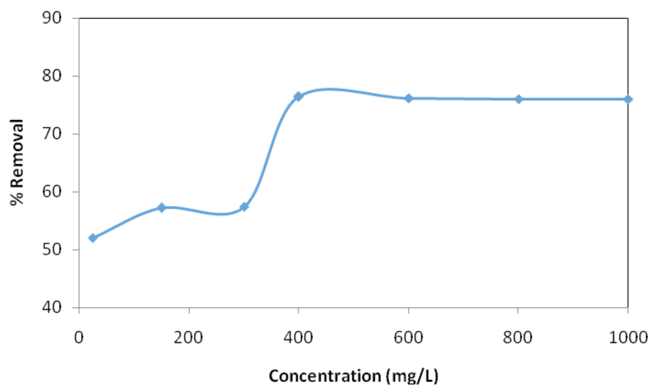


Fig. 5. Effect of the concentration on the % removal of Cd(II) ions by *Prunus avium* stems.

### 3.3.2. Langmuir isotherm

Langmuir isotherm model assumes the formation of an adsorbed solute monolayer on a uniform surface with a finite number of adsorption sites [30]. When a site is filled, no further sorption can take place at that site. Therefore, the surface will 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:

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

where $q_{\max}$ is the maximum adsorption capacity (mg/g) and $K_L$ is the Langmuir constant related to the energy of adsorption (L/g). Values of Langmuir parameters $q_{\max}$ and $K_L$ were calculated from the slope and intercept of the linear plot of $C_e/q_e$ vs. $C_e$ as shown in Fig. 7. Values of $q_{\max}$, $K_L$ and correlation coefficient $R^2$ are listed in Table 1. These values for *Prunus avium* biosorbent indicated that Langmuir model describes the biosorption phenomena favorable.

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:

$$R_L = \frac{1}{\left(1 + K_L C_i\right)} \tag{5}$$

where $K_L$ is the Langmuir constant (L/mg). There are four possible values for $R_L$: to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$) [27]. The $R_L$ was found to be 0.013 for concentration of 25–600 mg/L of Cd(II). They are in the range of 0–1 which indicates the favorable biosorption.

### 3.3.3. Adsorption thermodynamics

The thermodynamic parameters for the adsorption of Cd(II) ions on the surface of *Prunus avium* stems, such as free energy ($\Delta G^0$), enthalpy change ($\Delta H^0$) and entropy change ($\Delta S^0$), were determined using the following equations:

$$\Delta G^0 = -RT \ln K_L = \Delta H^0 - T\Delta S^0 \tag{6}$$

where $T$ is the absolute temperature in Kelvin (K) and $R$ the gas constant ($8.314 \times 10^{-3}$ kJ/mol K). $\Delta H^0$ and $\Delta S^0$ were obtained from the slope and intercept of Vant'Hoff plots of $\ln K_L$ vs. $1/T$ (Fig. 8) using the following equation:

$$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{7}$$

The results of the thermodynamic calculations of the Langmuir constants, enthalpy, entropy and Gibbs free energy are given in Table 2:

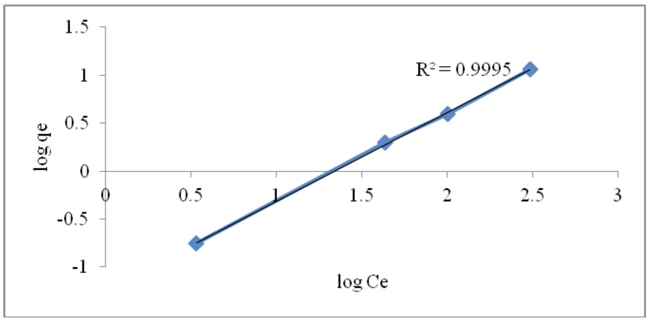


Fig. 6. Freundlich isotherm for Cd(II) ion biosorption into *Prunus avium* stems.

Table 1
Freundlich and Langmuir constants for Cd(II) ions biosorption by *Prunus avium* stems

| Freundlich isotherm | | |
|---|---|---|
| $K_F$ | $n$ | $R^2$ |
| 0.0577 | 1.079 | 0.9995 |
| Langmuir isotherm | | |
| $K_L$ | $q_{\max}$ | $R^2$ |
| 0.013 | 9.662 | 0.9927 |

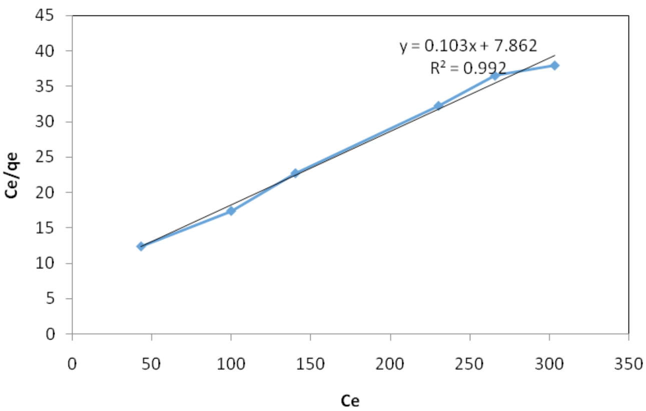


Fig. 7. Langmuir isotherm for Cd(II) biosorption onto *Prunus avium* stems.

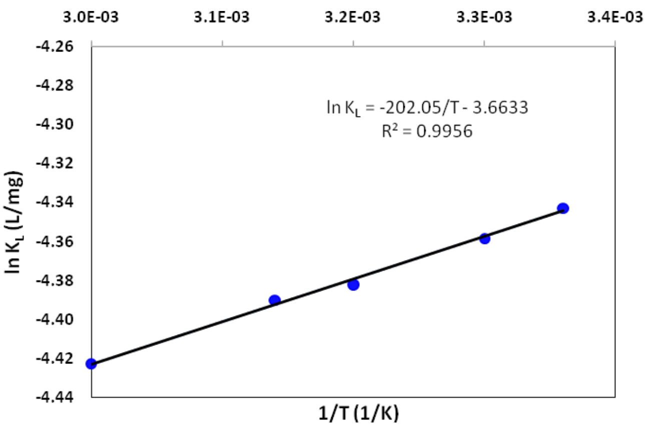


Fig. 8. Plot of $\ln K_L$ vs. $1/T$.

Table 2
Thermodynamics data for Cd(II) ions biosorption by *Prunus avium* stems

| $T$ (K) | $K_L$ (L/mg) | $\ln K_L$ | $\Delta G^0$ (kJ/mol) | $\Delta H^0$ (kJ/mol) | $\Delta S^0$ (J/mol K) |
|---|---|---|---|---|---|
| 333 | 0.0120 | –4.423 | 12.245 | –1.815 | –42.2 |
| 318 | 0.0124 | –4.390 | 11.607 | –1.815 | –42.2 |
| 313 | 0.0125 | –4.382 | 11.403 | –1.815 | –42.2 |
| 303 | 0.0128 | –4.358 | 10.979 | –1.815 | –42.2 |
| 298 | 0.0130 | –4.343 | 10.760 | –1.815 | –42.2 |

The positive values of $\Delta G^0$ imply that the adsorption of Cd(II) ions on the surface of *Prunus avium* stems is not spontaneous. However, when the temperature decreases from 333 to 298 K, the free standard energy, $\Delta G^0$, decreases. This indicates a spontaneous adsorption by decreasing the temperature, because the spontaneous adsorption is inversely proportional to the temperature. On the other hand, the standard enthalpy change, $\Delta H^0$, is negative, therefore, the process is exothermic; consequently, an increase in the temperature leads to a lower adsorption of Cd(II) ions on the surface of *Prunus avium* stems at equilibrium, and physical by nature and involves weak forces of attraction. The negative values of $\Delta S^0$ suggest that the system exhibits random behavior and the decrease of the system disorder, thus promoting the adsorption process and decreasing the degree of freedom. This thermodynamic behavior was also observed by Tosun [31] in the adsorption of ammonium on clinoptilolite.

## 4. Conclusion

This study investigated the adsorption of Cd(II) ions from aqueous solutions onto dried *Prunus avium* stems that is dependent on biosorption process such as initial metal ions concentration, pH, adsorbent dose and contact time. The Langmuir and Freundlich biosorption isotherms were demonstrated to provide best correlation for biosorption of Cd(II) ions onto *Prunus avium* stems. The adsorption process was also thermodynamically spontaneous under natural conditions. From this study, it was observed that stems of *Prunus avium* can be used as an alternative low cost, eco-friendly and effective adsorbent for treatment of waste water containing Cd(II) ions. The thermodynamic study showed that adsorption process of Cd(II) ions on *Prunus avium* stems was non-spontaneous and adsorption rate increased with a decrease in the temperature, thus showing the exothermic nature of the adsorption. Other heavy metals adsorbed by stems of *Prunus avium* are under study.

## References


[1] H. Benhima, M. Chiban, F. Sinan, P. Seta, M. Persin, Removal of lead and cadmium ions from aqueous solution by adsorption onto micro-particles of dry plants, Colloids Surf., B, 61 (2008) 10–16.

[2] T.A. Saleh, V.K. Gupta, Processing methods, characteristics and adsorption behavior of tire derived carbons: a review, Adv. Colloid Interface Sci., 211 (2014) 93–101.

[3] C.M. Zvinowanda, J.O. Okonkwo, P.N. Shabalala, N.M. Agyei, A novel adsorbent for heavy metal remediation in aqueous environments, Int. J. Environ. Sci. Technol., 6 (2009) 425–434.

[4] K.S. Low, C.K. Lee, Cadmium uptake by the moss, *Calymperes delessertii*, Besch, Bioresour. Technol., 38 (1991) 1–6.

[5] P.A. Balch, Prescription for Nutritional Healing. Penguin Group, New York, 2006.

[6] N. Johri, G. Jacquillet, R. Unwin, Heavy metal poisoning: the effects of cadmium on the kidney, Biometals, 23 (2010) 783–792.

[7] P. Russell, A. Williams, The Nutrition and Health Dictionary, Jones & Bartlett Learning, LLC, Auburn, 1995.

[8] S. Doyurum, A. Celik, Pb (II) and Cd(II) removal from aqueous solutions by olive cake, J. Hazard. Mater., 138 (2006) 22–28.

[9] F.E. Okieimen, E.U. Okundia, D.E. Ogbeifun, Sorption of cadmium and lead ions on modified groundnut (*Arachis hypogea*) husks, J. Chem. Technol. Biotechnol., 51 (1991) 97–103.

[10] E.W. Shin, K.G. Karthikeyan, M.A. Tshabalala, Adsorption mechanism of cadmium on juniper bark and wood, Bioresour. Technol., 98 (2007) 588–594.

[11] X. Li, Y. Tang, Z. Xuan, Y. Liu, F. Luo, Study on the preparation of orange peel cellulose adsorbents and biosorption of $Cd^{2+}$ from aqueous solution, Sep. Purif. Technol., 55 (2007) 69–75.

[12] A.B. Pérez-Marín, V.M. Zapata, J.F. Ortuno, M. Aguilar, J. Sáez, M. Lloréns, Removal of cadmium from aqueous solutions by adsorption onto orange waste, J. Hazard. Mater., 139 (2007) 122–131.

[13] G. Tan, D. Xiao, Adsorption of cadmium ion from aqueous solution by ground wheat stems, J. Hazard. Mater., 164 (2009) 1359–1363.

[14] U. Kumar, M. Bandyopadhyay, Sorption of cadmium from aqueous solution using pretreated rice husk, Bioresour. Technol., 97 (2006) 104–109.

[15] U. Garg, M.P. Kaur, G.K. Jawa, D. Sud, V.K. Garg, Removal of cadmium (II) from aqueous solutions by adsorption on agricultural waste biomass, J. Hazard. Mater., 154 (2008) 1149–1157.

[16] V.B.H. Dang, H.D. Doan, T. Dang-Vu, A. Lohi, Equilibrium and kinetics of biosorption of cadmium (II) and copper (II) ions by wheat straw, Bioresour. Technol., 100 (2009) 211–219.

[17] G.H. Pino, L.M.S. de Mesquita, M.L. Torem, G.A.S. Pinto, Biosorption of cadmium by green coconut shell powder, Miner. Eng., 19 (2006) 380–387.

[18] E. Pehlivan, B.H. Yanık, G. Ahmetli, M. Pehlivan, Equilibrium isotherm studies for the uptake of cadmium and lead ions onto sugar beet pulp, Bioresour. Technol., 99 (2008) 3520–3527.

[19] B. Garcia-Fayos, J.M. Arnal, J. Piris, M. Sancho, Valorization of *Moringa oleifera* seed husk as biosorbent: isotherm and kinetics studies to remove cadmium and copper from aqueous solutions, Desal. Water Treat., 57 (2016) 23382–23396.

[20] R. Goswami, J. Shim, S. Deka, D. Kumari, R. Kataki, M. Kumar, Characterization of cadmium removal from aqueous solution by biochar produced from *Ipomoea fistulosa* at different pyrolytic temperatures, Ecol. Eng., 97 (2016) 444–451.

[21] M.A. Wahab, S. Jellali, N. Jedidi, Ammonium biosorption onto sawdust: FTIR analysis, kinetics and adsorption isotherms modeling, Bioresour. Technol., 101 (2010) 5070–5075.

[22] L. Tribe, K.D. Kwon, C.C. Trout, J.D. Kubicki, Molecular orbital theory study on surface complex structures of glyphosate on goethite: calculation of vibrational frequencies, Environ. Sci. Technol., 40 (2006) 3836–3841.

[23] Z. Aksu, Application of biosorption for the removal of organic pollutants: a review, Process Biochem., 40 (2005) 997–1026.

[24] L. Tan, D. Zhu, W. Zhou, W. Mi, L. Ma, W. He, Preferring cellulose of *Eichhornia crassipes* to prepare xanthogenate to other plant materials and its adsorption properties on copper, Bioresour. Technol., 99 (2008) 4460–4466.

[25] M.E. Argun, S. Dursun, C. Ozdemir, M. Karatas, Heavy metal adsorption by modified oak sawdust: thermodynamics and kinetics, J. Hazard. Mater., 141 (2007) 77–85.

[26] X. Mi, G. Huang, W. Xie, W. Wang, Y. Liu, J. Gao, Preparation of graphene oxide aerogel and its adsorption for $Cu^{2+}$ ions, Carbon, 50 (2012) 4856–4864.

[27] O.S. Amuda, A. Giwa, I.A. Bello, Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon, Biochem. Eng. J., 36 (2007) 174–181.

[28] E. Malkoc, Y. Nuhoglu, M. Dundar, Adsorption of chromium (VI) on pomace—an olive oil industry waste: batch and column studies, J. Hazard. Mater., 138 (2006) 142–151.
[29] N.M. Salem, A.M. Farhan, A.M. Awwad, Biosorption of cadmium (II) from aqueous solutions by *Prunus avium* leaves, Am. J. Environ. Eng., 2 (2012) 123–127.
[30] H.B. Senturk, D. Ozdes, C. Duran, Biosorption of Rhodamine 6G from aqueous solutions onto almond shell (*Prunus dulcis*) as a low cost biosorbent, Desalination, 252 (2010) 81–87.
[31] I. Tosun, Ammonium removal from aqueous solutions by clinoptilolite: determination of isotherm and thermodynamic parameters and comparison of kinetics by the double exponential model and conventional kinetic models, Int. J. Environ. Res. Public Health, 9 (2012) 970–984.