

# Equilibrium, Kinetic and Thermodynamics of Biosorption of Lead (II) Copper (II) and Cadmium (II) Ions from Aqueous Solutions onto Olive Leaves Powder

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**Abstract** Biosorption of lead (II), copper (II) and cadmium (II) ions from aqueous solutions onto olive leaves powder has been investigated. The biosorption of lead (II), copper (II), and cadmium (II) was found to be dependent on 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. The Langmuir model gave a better fit than the Freundlich model. The kinetic studies indicated that the biosorption process of the metal ions followed well pseudo-second-order model. The thermodynamic parameters Gibbs free energy,  $\Delta G^\circ$ , enthalpy,  $\Delta H^\circ$ , and entropy,  $\Delta S^\circ$  were also calculated, and the values indicated that the biosorption process was endothermic and spontaneous in nature. It was concluded that olive leaves powder can be used as an effective, low cost, and environmentally friendly biosorbent for removal of Pb(II), Cu(II) and Cd(II) ions from aqueous solution.

**Keywords** Biosorption, Olive leaves, Lead, Copper, Cadmium, Adsorption Isotherms, Kinetic, Thermodynamic

## 1. Introduction

Heavy metal ions are present in the wastewater of several industries, such as metal cleaning and plating baths, refineries, paper and pulp, fertilizer, and wood preservatives. Different methods have been used on metal content reduction from water and industrial waste such as chemical precipitation, ion exchange, membrane filtration, electrolytic methods, reverse osmosis, solvent extraction and activated carbon adsorption [1-6]. These conventional techniques can reduce metal 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. Among these various treatment techniques, activated carbon adsorption [7] is one of the most commonly used due to its high efficiency and easy operation. In recent years, considerable attention has been focused on removal of metal ions from aqueous solution using adsorbents derived from low-cost agro-wastes [8-16].

In the present work, we have studied the potential of lead (II), copper (II), and cadmium (II) biosorption on an agro material which olive leaves (OL) coming from olive tree waste. Results from this study can be used to assess the utility

of live leaves powder (OL) for lead (II), copper (II), and cadmium (II) removal from water and industrial wastewaters.

## 2. Experimental

### 2.1. Adsorbent

The raw olive leaves (OL) was collected from a local plantation. 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 waste was grounded to a fine powder in a grinding mill (Retsch RM 100) and sieved to get size fraction  $< 44 \mu\text{m}$ , and then dried in an oven at  $60^\circ\text{C}$  for 24 h.

### 2.2. Materials

All chemicals used were of analytical reagent (AR) grade. Stock solutions of 1000 mg/L of lead (II), copper (II) and cadmium (II) were prepared from nitrates of lead, copper and cadmium which was purchased from Fluka AG using double distilled water. Desired test solutions of metal ions were prepared using appropriate subsequent dilutions of the stock solution. The range of concentrations of metal 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.

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### 2.3. Analysis

The concentrations of Pb (II), Cd(II) and Cu(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 olive leaves powder (OL). FTIR analyses also used to determine the functional groups which are responsible for the metal binding with OL. The analysis was carried out using KBr and the spectral range varying from 4000 to 400  $\text{cm}^{-1}$ .

### 2.4. Biosorption Experiments

Batch biosorption experiments were conducted by mixing biosorbent with metal 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 metal ions 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:

$$q_e = \frac{C_o - C_e}{M} \times V \quad (1)$$

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).

## 3. Results and Discussion

### 3.1. FT-IR Analysis

To investigate the functional groups of OL and copper loaded OL, a FT-IR study was carried out and the spectra are shown in fig. 1 and 2. The OL leaves displays a number of absorption peaks, reflecting the complex nature of the OL. A strong and broad peak at 3367  $\text{cm}^{-1}$  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 3298  $\text{cm}^{-1}$  in the spectrum of the copper loaded OL, fig. 2, indicates the binding of copper with amino and/or hydroxyl groups. The strong absorption peak at 2935  $\text{cm}^{-1}$  and 2916  $\text{cm}^{-1}$  could be assigned to -CH stretching vibrations of -CH<sub>3</sub> and -CH<sub>2</sub> functional groups. The shoulder peak in pure olive leaf powder at 1735  $\text{cm}^{-1}$  is shifted to lower frequency 1701  $\text{cm}^{-1}$  due to the involvement of carbonyl -CO group from carboxylic acids in the biosorption process of copper ions with olive leaf powder. The peak at 1654  $\text{cm}^{-1}$  indicates the fingerprint region of CO, C-O and O-H groups, which exists as functional groups of OL and shifting of this peak to 1604  $\text{cm}^{-1}$ , indicated involvement of these groups in copper binding. The region

between 1462 and 1000  $\text{cm}^{-1}$  is the fingerprint region, OH, and C-H bending vibration and C-O stretching vibration absorption bands. The absorption peaks at 1327, and 1088  $\text{cm}^{-1}$  could be attributed to the presence of C-O stretching. The intense band at 1088  $\text{cm}^{-1}$  can be assigned to the C-O of alcohols and carboxylic acids. The shift of the peak from 1083 to 1014  $\text{cm}^{-1}$  also suggests the involvement of C-O group in binding Cu (II). The shifts in the absorption peaks generally observed indicate the existence of a copper binding process taking place on the surface of the olive leaves powder.

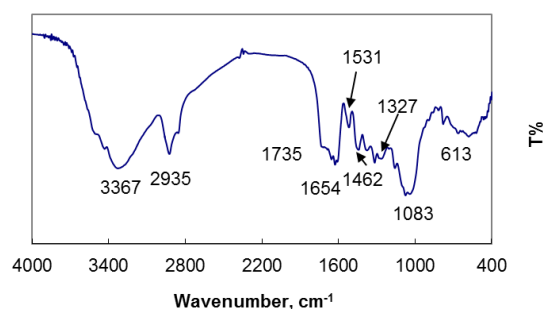


Figure 1. FT-IR of olive leaves powder

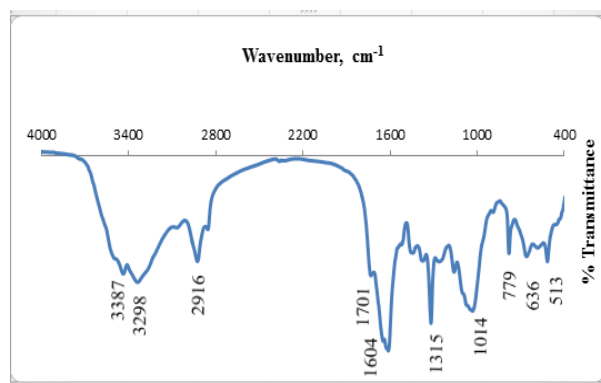


Figure 2. FT-IR of olive leaves powder loaded with Cu (II) ions

### 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. Generally, metal biosorption involves complex mechanisms of ion exchange, chelation, adsorption by physical forces, and spaces of the cell structural network of a biosorbent. The FTIR spectroscopic analysis showed that the olive leaves powder has a variety of functional groups, such as carboxyl, hydroxyl and amine and these groups are involved in almost all potential binding mechanisms. Moreover, depending on the pH values of the aqueous solutions these functional groups participate in metal ion bindings. The effect of pH on the biosorption of Pb(II), Cu(II) and Cd(II) ions onto olive leaves powder was studied at pH 1.0–8.0. The maximum biosorption was observed at pH 4.0, 6.0 and 5.0 for Pb(II), Cu(II) and Cd(II), respectively. Therefore, the

remaining all biosorption experiments were carried out at this pH values. The biosorption mechanisms on the olive leaves powder surface reflect the nature of the physicochemical interaction of the solution. At highly acidic pH ( $\text{pH} < 1.0$ ), the overall surface charge on the activesites 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 olive leaves powder were more deprotonated and thus available for the metal ions. Decrease in biosorption yield at higher pH ( $\text{pH} > 6$ ) is not only related the formation of soluble hydroxylated complexes of the metal ions (lead ions in the form of  $\text{Pb}(\text{OH})_2$ , copperions in form of  $\text{Cu}(\text{OH})_2$ , and cadmium ions in the form of  $\text{Cd}(\text{OH})_2$ ) but also to the ionized nature of the cell wall surface of the olive leaves 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  $\text{Pb}(\text{II})$ ,  $\text{Cd}(\text{II})$  and  $\text{Cu}(\text{II})$  was investigated. The biosorption yield of  $\text{Pb}(\text{II})$ ,  $\text{Cd}(\text{II})$  and  $\text{Cu}(\text{II})$  increased considerably until the contact time reached 120 min. Further increase in contact time did not enhance the biosorption, so, the optimum contact 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  $\text{Pb}(\text{II})$ ,  $\text{Cd}(\text{II})$  and  $\text{Cu}(\text{II})$  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. Moreover, the maximum biosorption, 74.9% for  $\text{Cu}(\text{II})$ , 85.2% for  $\text{Cd}(\text{II})$  and 94.5% for  $\text{Pb}(\text{II})$ , ions 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 describes the fraction of sorbate molecules that are partitioned between liquid and solid phases at equilibrium. Adsorption of metal ions onto OL particles was modeled using adsorption isotherms.

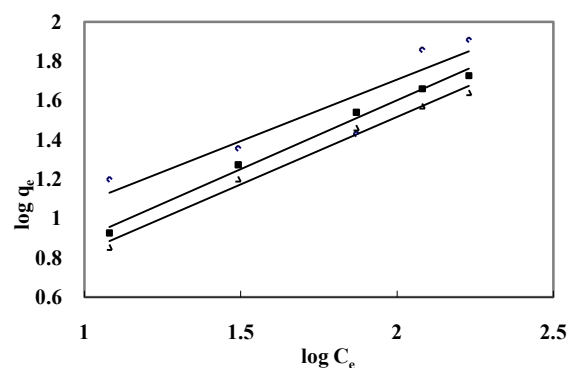
#### 3.5.1. Freundlich Isotherm

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 [17]:

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

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  $\log C_e$ , fig. 3 on the basis of the linear of Freundlich equation (2). 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 1.45-1.59 for OL, Table 1. Since  $n$  lie between 1 and 10, this indicate the physical biosorption of copper (II) onto OL. 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 adsorption isotherm of  $\diamond$ ,  $\text{Pb}(\text{II})$ ;  $\blacksquare$ ,  $\text{Cd}(\text{II})$ ;  $\triangle$ ,  $\text{Cu}(\text{II})$  onto OL 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 [18]. 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:

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

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 fig. 4. Values of  $q_{\max}$ ,  $K_L$  and regression coefficient  $R^2$  are listed in Table 1. These values for OL biosorbent indicated that Langmuir theory 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:

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

where  $K_L$  is the Langmuir constant and  $C_o$  is the initial concentration of copper (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 10–100 mg/L of metal ions. They are in the range of 0-1 which indicates the favorable biosorption.

**Table 1.** Langmuir and Freundlich constants for biosorption of Cd(II) onto olive leaves powder at different temperatures

Metal ions	$q_m$ (mg/g)	$K_L$ (mg/g)	$R^2$
Langmuir			
Pb(II)	119.05	0.013	0.9999
Cd(II)	90.09	0.008	0.9998
Cu(II)	71.43	0.009	0.9998
$n$	$K_f$	$R^2$	
Freundlich			
Pb(II)	1.59	2.84	0.8566
Cd(II)	1.43	1.58	0.9909
Cu(II)	1.45	1.58	0.9894

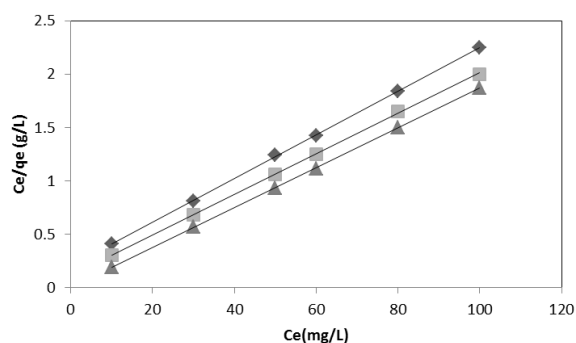
### 3.6. Adsorption Kinetic

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

#### 3.6.1. Pseudo First-Order Kinetics

The pseudo-first order equation of Lagergren [19] is generally expressed as follows:

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



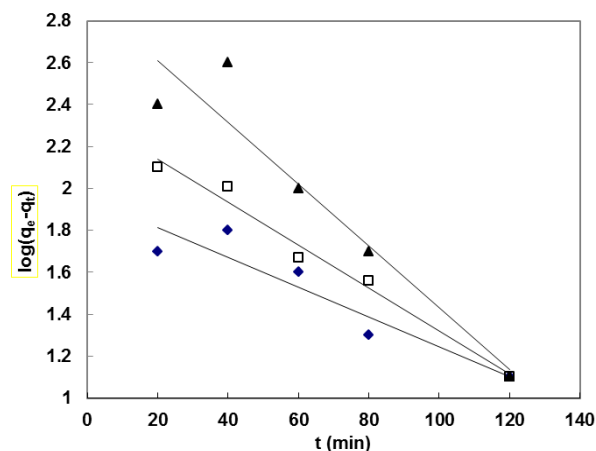
**Figure 4.** Langmuir adsorption isotherms for  $\blacklozenge$ , Pb(II);  $\blacksquare$ , Cd(II);  $\blacktriangle$ , Cu(II) ions onto OL at 303 K

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  $q_t = q_e$  at  $t = 0$  to  $t = t$ ; the integrated form of equation (5) becomes:

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

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 (6) to experimental data, the equilibrium sorption capacity,  $q_e$  must be known. In many cases 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 minutes 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,  $t$ . Fig. 5 shows the Lagergren pseudo-first order kinetic plot for the adsorption of metal ions onto OL powder. The calculated values and their corresponding linear regression correlation coefficient values are shown in Table 2. The linear regression correlation coefficient value found 0.8764, 0.9807 and 0.9007 for Pb(II), Cd(II) and Cu(II) ions, respectively which shows that this model cannot be applied to predict the adsorption kinetic model.



**Figure 5.** Pseudo-first order kinetic model for  $\blacklozenge$ , Pb(II);  $\square$ , Cd(II);  $\blacktriangle$ , Cu(II) biosorption onto OL 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:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (7)$$

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 (7) becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \quad (8)$$

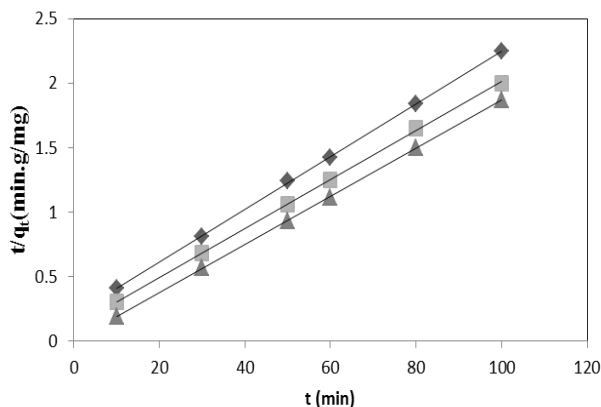
Equation (8) can be rearranged to obtain:

$$q_t = \frac{t}{\frac{1}{kq_e^2} + \frac{t}{q_e}} \quad (9)$$

The linear form of equation (9)

$$\frac{t}{q_e} = \frac{1}{kq_e^2} + \frac{1}{q_e} t \quad (10)$$

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 (10) should give a linear relationship, from which  $q_e$  and  $k$  can be determined from the slope and intercept of the plot, fig.6. The pseudo-second order rate constant  $k$ , 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 ♦, Pb(II); ■, Cd (II); ▲, Cu(II) biosorption onto OL at 303 K

**Table 2.** Biosorption kinetic model for metal ions onto OL at 303 K

Metal ions	$k_1$	$q_e$	$R^2$
Pseudo first order			
Pb(II)	0.016	0.024	0.8764
Cd(II)	0.024	221.26	0.9807
Cu(II)	0.034	799.28	0.9097
	$k_2$	$q_e$	$R^2$
Pseudo -second order			
Pb(II)	0.002	47.85	0.9998
Cd(II)	0.003	52.63	0.9998
Cu(II)	0.119	53.76	0.9999

### 3.7. Thermodynamic Parameters

In order to describe thermodynamic behaviour of the biosorption of Pb(II), Cd(II) and Cu(II) ions onto olive leaves powder, thermodynamic parameters including the change in free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) were calculated from following equations:

$$\Delta G^\circ = -RT \ln K_D \quad (11)$$

where  $R$  is the universal gas constant ( $8.314 \times 10^{-3}$  kJ/mol K),  $T$  is the temperature (K) and  $K_D$  is the distribution coefficient.

The thermodynamic equilibrium constant ( $K_D$ ) of the adsorption is defined as:

$$K_D = \frac{C_a}{C_e} \quad (12)$$

where,  $C_a$  is mg of adsorbate adsorbed per liter and  $C_e$  is the equilibrium concentration of solution, mg/L. According to thermodynamics, the Gibb's free energy change is also related to the enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) at constant temperature by the van't Hoff equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (13)$$

Equations (11) and (13) can be written as:

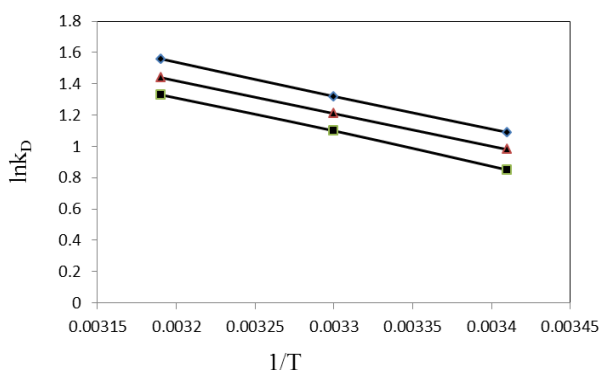
$$-RT \ln K_D = \Delta H^\circ - T\Delta S^\circ \quad (14)$$

or

$$\ln K_D = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (15)$$

According to Eq. 15, the values of enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) were calculated from the slope and intercept of the plot of  $\ln K_D$  vs.  $1/T$ , Fig 7. The calculated values of thermodynamic parameters  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  for the biosorption of Pb(II), Cd(II) and Cu(II) onto olive leaves powder are reported in Table 3. A positive value of  $\Delta H^\circ$  as 17.76, 17.38 and 18.14 kJ/mol for lead, cadmium and copper removal with OL, indicated the endothermic nature of the process. A negative value of the free energy ( $\Delta G^\circ$ ) [-2.66, -2.38 and -2.07 kJ/mol for Pb(II), Cd(II) and Cu(II), respectively] at 293 K indicated the spontaneous nature of the biosorption process. It was also noted that the change in free energy, increases with increase

in which exhibits an increase in adsorption with rise in temperature. This could be possibly because of activation of more sites on the surface of OL with increase in temperature or that the energy of biosorption sites has an exponential distribution and a higher temperature enables the energy barrier of biosorption to be overcome. The physical adsorption the free energy change ( $\Delta G^\circ$ ) ranges from (–20 to 0) kJ/mol and for chemical adsorption it ranges between (–80 and –400) kJ/mol<sup>–1</sup>. The  $\Delta G^\circ$  for Pb(II), Cd(II) and Cu(II) biosorption onto OL was in the range of (–2.07 to –4.06) kJ/mol<sup>–1</sup> and so the adsorption was predominantly physical biosorption. A positive value of  $\Delta S^\circ$  as 69.63 J/mol K showed increased randomness at solid solution interface during the adsorption of Pb(II), Cd(II) and Cu(II) ions onto olive leaves powder.



**Figure 7.** Plot of  $\ln K_D$  for biosorption of  $\blacklozenge$ , Pb(II);  $\blacktriangle$ , Cd(II);  $\blacksquare$ , Cu(II) onto olive leaves powder

**Table 3.** Thermodynamic parameters for biosorption of Pb(II), Cd(II) and Cu(II) onto olive leaves powder

Metal ion	T(K)	$K_D$	$\Delta G^\circ$ (KJ/mo l)	$\Delta H^\circ$ (KJ/mo l)	$\Delta S^\circ$ (J/mol K)
Pb(II)	293	2.86	-2.66	17.76	69.62
	303	3.74	-3.33		
	313	4.76	-4.06		
Cd(II)	293	2.66	-2.38	17.38	67.43
	303	3.35	-3.05		
	313	4.22	-3.75		
Cu(II)	293	2.34	-2.07	18.14	68.95
	303	3.01	-2.52		
	313	3.78	-3.46		

### 3.8. Desorption and Regeneration Studies

In order to investigate biosorption on metal ions from copper-loaded OL, the copper-loaded biosorbent was treated with HCl. Desorption studies were performed with different hydrochloric acids concentration. Complete elution of the loaded metal 98.44% could be achieved by using 0.1N

HCl. To keep the biosorption process cost down, our results indicate that OL biosorbent could be used repeatedly in Cu(II) biosorption.

## 4. Conclusions

The potential of olive leaves (OL) powder for the removal of Pb(II), Cu(II) and Cd(II) ions from aqueous solutions and wastewater was dependent on biosorption process such as solution pH, initial metal ions concentration, biosorbent dose, contact time and temperature. The Langmuir biosorption isotherms were demonstrated to provide the best correlation for the biosorption of Pb(II), Cd(II) and Cu(II) ions onto OL. The kinetic results provided the best correlation of the experimental data of biosorption of metal ions onto OL by pseudo second-order equation. Thermodynamic parameters of the biosorption confirmed the endothermic nature of sorption process as did the positive heat of enthalpy  $\Delta H^\circ$ , accompanied by a positive value of entropy change  $\Delta S^\circ$ . The standard Gibbs free energy change  $\Delta G^\circ$  during adsorption process was negative, corresponding to feasible, spontaneous biosorption. It can be concluded that since the OL 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 lead (II), copper(II) and cadmium (II) ions.

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## REFERENCES

- [1] P. Vasudevan, V. Padmavathy, S.C. Dhingra, Kinetics of biosorption of Cadmium on Baker's yeast, *Bioresour. Technol.* 89 (2003) 281–287.
- [2] Y. Goksungur, S. Uren, Biosorption of lead and cadmium ions by ethanol and waste baker's yeast biomass, *Bioresour. Technol.* 96 (2005) 103–109.
- [3] P. Loderio, B. Cordero, J.L. Barriada, M.E. Herrero, Sastre de Vicente, Biosorption of cadmium by biomass of brown marine macroalgae, *Bioresour. Technol.* 96 (2005) 1796–1803.
- [4] P. Sharma, P. Kumari, M.M. Srivastava, S. Srivastava, Removal of cadmium from aqueous system by shelled *Moringa oleifera* Lam. Seed powder, *Bioresour. Technol.* 97 (2006) 299–305.
- [5] Y. Liu, X. Chang, Y. Guo, S. Meng, Biosorption and preconcentration of lead and Cadmium on waste Chinese herb *Pang Da Hai*, *J. Hazard Mater.* B135 (2006) 389–394.



- [6] N. Ahalya, T.V. Ramachandra, R.D. Kanamadi, Biosorption of heavy metals, *Res. J. Chem. Environ.*, 7 (2003) 71-78.
- [7] G. Issabayeva, M.K. Aroua, N.M.N. Suleiman, Removal of lead from aqueous solutions on palm shell activated carbon, *Bioresour. Technol.* 97 (2006) 2350-2355.
- [8] A.M. Awwad, N. M. Salem, Biosorption of Copper (II) and lead (II) ions from aqueous solutions by Modified Loquat (*Eriobotrya japonica*) leaves (MLL), *J. of Chem. Eng. and Mater. Sci.*, 3 (2012) 7-17.
- [9] H.N. Bahatti, R. Khalid, M.A. Hanif, Dynamic biosorption of Zn (II) and Cu (II) using pretreated *Rosa gruss an teplitz* (red rose) distillation sludge, *Chem. Eng. J.* 148(2009)434-443.
- [10] M.R. Sangi, A. Shahmoradi, J. Zolgharnein, G.H. Aimi, M. Ghorbandoost, Removal and recovery of heavy metals from aqueous solution using *Ulmus carpinifolia* and *Fraxinus excelsior* tree leaves, *Science Direct*. 155 (2008) 513-522.
- [11] V.S. Munagapati, V. Yarramuthi, S.K. Nadavala, S.R. Alla, Abburu K., biosorption of Cu (II), Cd (II) and Pb (II) by *Acacia leucocephala* bark powder: Kinetics, equilibrium and thermodynamics, *Chemical Engineering Journal*. 157 (2010) 357-365.
- [12] A.E. Ofomaja, E.B. Naidoo, Biosorption of copper from aqueous solutions by chemically activated pine cone: A kinetic study, *Chemical Engineering Journal*. 175 (2011) 260-270.
- [13] R.P. de Carvalho, J.R. Freitas, A.M.G. de Sousa, R.L. Moreira, V.B. Pinheiro, K. Krambrock. Biosorption of copper ions by dried leaves: chemical bonds and site symmetry, *Science Direct*. 71 (2003) 277-283.
- [14] H. Yazici, M. Kilic, M. Solak, Biosorption of copper (II) by *Marrubium globosum* subsp. *globosum* leaves powder: Effect of chemical pretreatment, *Science Direct*. 151(2008) 669-675.
- [15] R.P. de Carvalho, K.J. Guedes, M.V.B. Pinheiro, K. Krambrock, Biosorption of copper by dried plant leaves studied by electron paramagnetic resonance and infrared spectroscopy, *Hydrometallurgy* 59 (2001) 407-412.
- [16] N.A.A. Babarinde, O.O. Oyesiku, O.F. Dairo, Isotherm and thermodynamic studies of the biosorption of copper (II) ions by *Erythrodontium barteri*, *International Journal of Physical Sciences*. 2 (2007) 300-304.
- [17] H. Freundlich, Ueber die adsorption in loesungen, *Z. Phys. Chem.* 57 (1906) 385-470.
- [18] I. Langmuir, the adsorption of gases on plane surfaces of glass, mica and platinum, *J. Amer. Chem. Soc.* 40 (1918) 1361-1403.
- [19] S. Lagergren, Zur theorie der sogenannten adsorption geloster stoffe. *Kungliga Svenska Vetenskaps akademien, Handlingar* 24 (1998) 1-39.
- [20] Y.S. Ho, G. McKay, D.A.J. Wase, C.F. Foster. Study on the sorption of divalent metal ions onto peat, *Adsorpt. Sci. Technol.* 18 (2000) 639-650.