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## Biosorption of Lead (II) Ions From Aqueous Solutions by Biological Activated Dates Stems

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**Abstract:** In this research, we investigated a biological activation method of dates stems, an abundant agricultural waste by-product in Algeria, to improve their biosorption capacity for lead (II) ions. Batch experiments were carried out to determine  $Pb^{2+}$  sorption capacity and the efficiency of the sorption process under different pH, contact time, initial  $Pb^{2+}$ , dates stems concentrations and temperature. The biosorption capacity was found to increase in the five parameters studied. The biosorption for  $Pb^{2+}$  onto activated dates stems obeys to the Langmuir and Freundlich isotherms models. Three kinetic models are the pseudo-first-order, pseudo-second-order and intraparticle diffusion model were selected to interpret the biosorption data. Kinetic parameters and related coefficients, for each cognate were calculated and discussed. It was indicated that the biosorption for  $Pb^{2+}$  onto activated dates stems could be described by the pseudo-second-order kinetic. Various thermodynamic parameters such as standard enthalpy ( $\Delta H^\circ$ ), standard entropy ( $\Delta S^\circ$ ) and standard free energy ( $\Delta G^\circ$ ) were evaluated.

**Key words:** Biosorption, lead, agricultural waste, isotherm, kinetic

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### INTRODUCTION

The increasing contamination of urban and industrial wastewaters by toxic metal ions is a worrying environmental problem. These inorganic micro-pollutants are of considerable concern because they are non-biodegradable, if directly discharged into the sewage system they may seriously damage the operation of biological treatment as well as making the activated sludge unsuitable for application to agricultural land (Cimino and Conisti, 1990; Madoni *et al.*, 1996), these toxic metals include arsenic (As), chromium (Cr), lead (Pb), mercury (Hg), copper (Cu), zinc (Zn), cadmium (Cd), nickel (Ni) and manganese (Mn), etc. Lead is used in many industries such as acid battery manufacturing, metal plating and finishing printing, photographic materials, explosive manufacturing and tetraethyl lead manufacturing and ceramic and glass industries.

The traditional techniques for the removal of metal ions from aqueous effluents are incapable of reducing concentration to the levels required by law (process of reduction or lime precipitation) or prohibitively expensive (process of ion exchange, activated carbon adsorption, electrolytic removal). The use of micro-organisms such as bacteria, fungi and algae in treating wastewaters containing toxic metal ions is an attractive technique but as yet not suitable for applications on large scale (Kapoor and Viraraghavan, 1995, 1997).

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In recent years the most promising alternative method for removal of these metal ions uses the sorption by activated waste organic materials, which are low cost and abundant like sawdust (Ayyappan *et al.*, 2005), sugar cane bagasse (Zhang *et al.*, 2005), fruit stones (Malik *et al.*, 2002), apricot stone (Kobyta *et al.*, 2005), pyrolysed coffee (Boonamnuayvitaya *et al.*, 2004), pecan shell (Bansode *et al.*, 2003), palm shell (Issabayeva *et al.*, 2006), nut shells (almond, walnut, pecan) (Ahmedna *et al.*, 2004), almond shells, olive stone and peach stones (Ferro-Garcia *et al.*, 1990). There are two different ways for the preparation of activated adsorbent, which are physical and chemical activation. In this research, we propose a new biosorbent, which is (stems of dates), an abundant agricultural wast in our country Algeria, with such new technical activating methods, which is the biological activation.

Experiments have been carried out to estimate the sorption capacity and kinetics of lead (II) ions from aqueous solution using activated stems of dates.

The factors studied include the influence of temperature, pH, contact time, initial lead (II) and adsorbent concentration on the sorption kinetics of the system. The biosorption isotherm, kinetic and thermodynamic parameters were deduced from the adsorption measurements.

Equilibrium data mostly known as adsorption isotherms are basic requirements to understand the mechanism of the adsorption. Well known adsorption isotherm models, Langmuir and Freundlich, are used to describe the equilibrium between biosorbed lead (II) ions onto activated stems of dates ( $q_e$ ) and lead (II) ions in solution ( $C_e$ ) at a constant temperature.

The linear forms of Langmuir and Freundlich (Gerçel, 2007) adsorption isotherm equation can be written following:

$$\text{Langmuir equation : } \frac{C_e}{q_e} = \frac{1}{b \cdot q_m} + \frac{C_e}{q_m} \quad (1)$$

$$\text{Freundlich equation : } \ln q = \ln K + \left(\frac{1}{n}\right) \ln C_e \quad (2)$$

where,  $q_m$  ( $\text{mg g}^{-1}$ ) is the maximum amount of lead (II) ions per unit weight of biosorbent to form a complete monolayer on the surface bound at high  $C_e$  and  $b$  ( $\text{L mg}^{-1}$ ) is a constant related to the affinity of binding sites.  $q_m$  and  $b$  can be determined from the linear plot  $C_e/q_e$  versus  $C_e$ . The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimension - less constant separation factor for equilibrium parameter,  $R_L$  (Çabuk *et al.*, 2007) which is defined by:

$$R_L = \frac{1}{1 + b \cdot C_0} \quad (3)$$

The parameter,  $R_L$  indicates the shape of isotherm as follows (Table 1).  $K_f$  and  $n$  are the Freundlich constant characteristics of the system.

The pseudo- first-order, pseudo-second-order kinetic models and intraparticle diffusion model have been applied for the experimental data to the biosorption kinetics. The first-order (Panday *et al.*, 1985) and pseudo-second-order (Ho and McKay, 1998) equations are expressed as:

**Table 1: Dimensionless equilibrium parameter,  $R_L$**

$R_L$ value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$R_L = 1$	Irreversible
$0 < R_L < 1$	Favorable

$$\text{Pseudo - first - order equation : } \text{Log} \frac{(q_e - q_t)}{q_e} = -\frac{k_1}{2.3} t \quad (4)$$

$$\text{Pseudo - second - order equation : } \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where,  $q_t$  is the amount of the lead (II) ions adsorbed at various times  $t$  ( $\text{mg g}^{-1}$ ) and  $k_1$ , the first-order rate constant ( $\text{min}^{-1}$ ) of adsorption;  $q_e$ , the maximum adsorption capacity ( $\text{mg g}^{-1}$ );  $k_2$ , is the equilibrium rate constant of pseudo-second-order adsorption ( $\text{mg g}^{-1} \text{min}^{-1}$ ).

Intraparticle diffusion model based on the theory proposed by Weber and Moris (Gerçel, 2007) was tested to identify the diffusion mechanism. According to this theory:

$$q_t = k_p t^{0.5} \quad (6)$$

where,  $k_p$  ( $\text{mg g}^{-1} \text{min}^{0.5}$ ) is the intraparticle diffusion rate constant.

By using this model, the plot of uptake,  $q_t$ , versus the square root of time ( $t^{0.5}$ ) should be linear if the intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin then the intraparticle diffusion is the rate-controlling step (Gerçel, 2007). When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and this further shows that the intraparticle diffusion is not the only rate-limiting step, but also other kinetic models may control the rate of biosorption, all of which may be operating simultaneously. The slope of linear portion from the figure can be used to derive values of the rate parameter,  $k_p$ , for the intraparticle diffusion.

The concept of thermodynamic assumes that in an isolated system where energy can not be gained or lost, the entropy change is the driving force (Kumar and Kumaran, 2005).

The thermodynamic parameters that must be considered to determine the process are changes in standard enthalpy ( $\Delta H^\circ$ ), standard entropy ( $\Delta S^\circ$ ) and standard free energy ( $\Delta G^\circ$ ) due to transfer of unit mole of solute from solution into the solid-liquid interface the value of  $\Delta H^\circ$  and  $\Delta S^\circ$  were computed using the following equation:

$$\ln K_d = \left( \frac{\Delta S^\circ}{R} \right) - \left( \frac{\Delta H^\circ}{RT} \right) \quad (7)$$

where,  $R$  ( $8.314 \text{ J mol}^{-1} \text{ K}$ ) is the universal gaz constant  $T$  (K) the absolute solution temperature and  $k_d$  is the distribution, coefficient which can be calculated as:

$$K_d = \frac{C_{Ae}}{C_e} \quad (8)$$

where,  $C_{Ae}$  ( $\text{mg L}^{-1}$ ) is the amount adsorbed on solid at equilibrium and  $C_e$  ( $\text{mg L}^{-1}$ ) is the equilibrium concentration

The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were calculated from the slope and intercept of plot between  $\ln k_d$  versus  $1/T$ .  $\Delta G^\circ$  can be calculated using the relation below:

$$\Delta G^\circ = -RT \ln K_d \quad (9)$$

## MATERIALS AND METHODS

### Preparation and Characterization of Activated and Raw Dates Stems

Stems of date were dried at  $60^\circ\text{C}$  for 24 h, ground in a crusher mill and sieved to within a size range of 0.3-0.8 mm using successive sieving.

Activated dates stems were prepared by silting a part of the raw date stems in a static condition, crushed in nitrate enriched solution ( $200 \text{ mg L}^{-1}$ ) with a daily renewed environment, this device enable to enhance the development of micro-organisms already existing on the organic support without the contribution of exterior biomass, we obtain out of 5 days an output of denitrification. rate of 88% witch corresponds to an optimal development of denitrifying micro flora. Along with time, We point out a considerable drop in the efficiency of the denitrification. Considering the fact that the nitrates are acceptors of electrons and the organic matter in stems of dates is a donor of electrons, it is necessary that the contribution in organic matter become sufficient for complete denitrification. If the organic matter become limiting, denitrification stops. We process to a filtration of the stems of dates, treated in a likewise, the stems in matter are next washed with distilled water and dried in  $60^\circ\text{C}$ , 48 h during.

Scamming Electron Microscopy (SEM) analysis was carried out for the raw and prepared activated date stems to study the surface morphology and to verify the presence of porosity. In addition, the surface functional groups of the raw and prepared activated stems of dates were detected by Fourier Transform Infrared (FTIR) spectroscope (FTIR\_2000\_pek,in\_Elmer)the spectra were recorder from  $4000$  to  $400 \text{ cm}^{-1}$ .

### **Preparation of Metal Solutions**

Pb (II) solution used in this study was prepared by dilution of  $1000 \text{ mg L}^{-1}$  stock solution, obtained by dissolving  $\text{pb}(\text{NO}_3)_2$  in deionized water. Fresh dilutions were used in each experiment

### **Biosorption Experiments**

To determine the optimum pb (II) biosorption condition, the batch adsorption experiments were conducted with  $10 \text{ g L}^{-1}$  of raw and activated date stems in Erlenmeyer flasks. biosorbent was added to medium and the reaction mixture was shaken on an orbital shaken at  $600 \text{ rpm}$ . The effect of contact time on adsorption was investigated in the time range of  $2$ - $120 \text{ min}$ .

The effect of pH on the adsorption capacity of activated date stems for pb (II) was investigated at several pH values ( $1.8, 2.4, 3.5, 4, 4.5$  and  $5.4$ ) by using know volume of  $50 \text{ mg L}^{-1}$  pb (II) solutions. The pH of the solutions was adjusted to required values using  $0.1 \text{ N HCl}$  and  $0.1 \text{ N NaOH}$ . Also the effect of biosorbent concentration was studied in the concentration range of  $2.5$ - $30 \text{ g L}^{-1}$ . Similarly above, pb (II) solutions with there concentration values ( $50, 100$  and  $150 \text{ mg L}^{-1}$ ) were used to assess the effect of initial Pb (II) ion concentration.

The biosorption of lead (II) ions onto activated date stems was evaluated at constant temperatures of  $12, 25, 40$  and  $63^\circ\text{C}$ .

The final lead (II) ion concentrations of the solutions were determined by using an atomic absorption spectrophotometer (SOLAAR. MAA. report) with an air acetylene flame. The instrument calibration was periodically checked by using standard metal solutions for every 10 reading.

The amount of adsorption at equilibrium,  $q_e$  ( $\text{mg g}^{-1}$ ) and at time  $t$ ,  $q_t$  ( $\text{mg g}^{-1}$ ) was calculated, respectively by:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (10)$$

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (11)$$

where,  $C_0$ ,  $C_e$  and  $C_t$  ( $\text{mg L}^{-1}$ ) are the liquid-phase concentrations of lead (II) ions at initial, equilibrium and at any time  $t$ , respectively.  $V$  is the volume of solution (L) and  $m$  is the mass of biosorbent used (g).

## RESULTS AND DISCUSSION

### Textural Characterization of Prepared Activated Dates Stems

It can be shown from Fig. 1, the porous structure of the activated dates stems. Figure 2 shows the FT-IR spectra obtained:

- 3446.94  $\text{cm}^{-1}$  : O-H stretching vibrations
- 2919.49  $\text{cm}^{-1}$  : C-H stretching vibrations of cellulose
- 1736.56  $\text{cm}^{-1}$  : C = O stretching vibrations of cellulose
- 1634.14  $\text{cm}^{-1}$  : Stretching vibrations in aromatic rings; (indicative of amide bond in N-acetyl glucosamine polymer or of the protein peptide bond)
- 1408.82  $\text{cm}^{-1}$  : C-H indicative of bending of  $\text{CH}_3$
- 1244.00  $\text{cm}^{-1}$  : Stretching vibrations

The FT-IR spectra of activated dates stems Fig. 3 shows the intensity of the band at 3436.7  $\text{cm}^{-1}$  due to the O-H stretching vibrations was decrease and a peak appearance at 2146.3  $\text{cm}^{-1}$ , due to the C = O stretching vibrations.

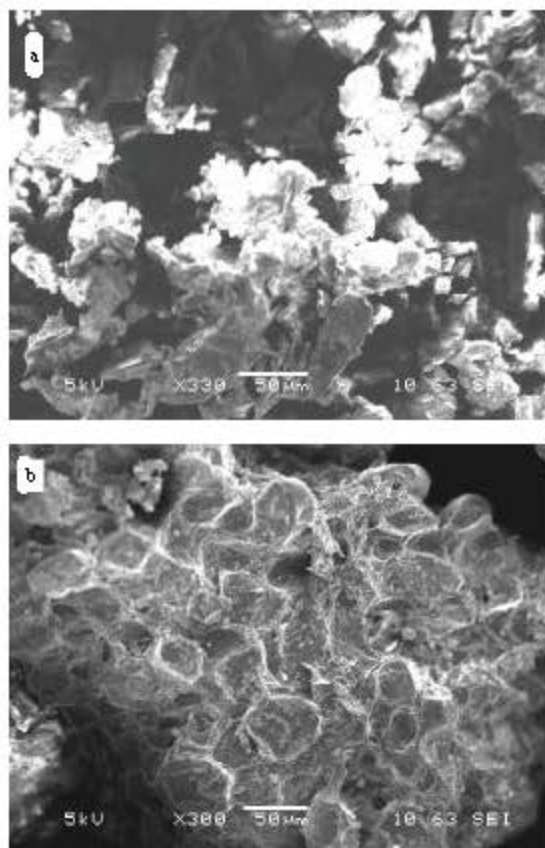


Fig. 1: SEM microscopic pictures of raw (a) biological activated and (b) dates stems

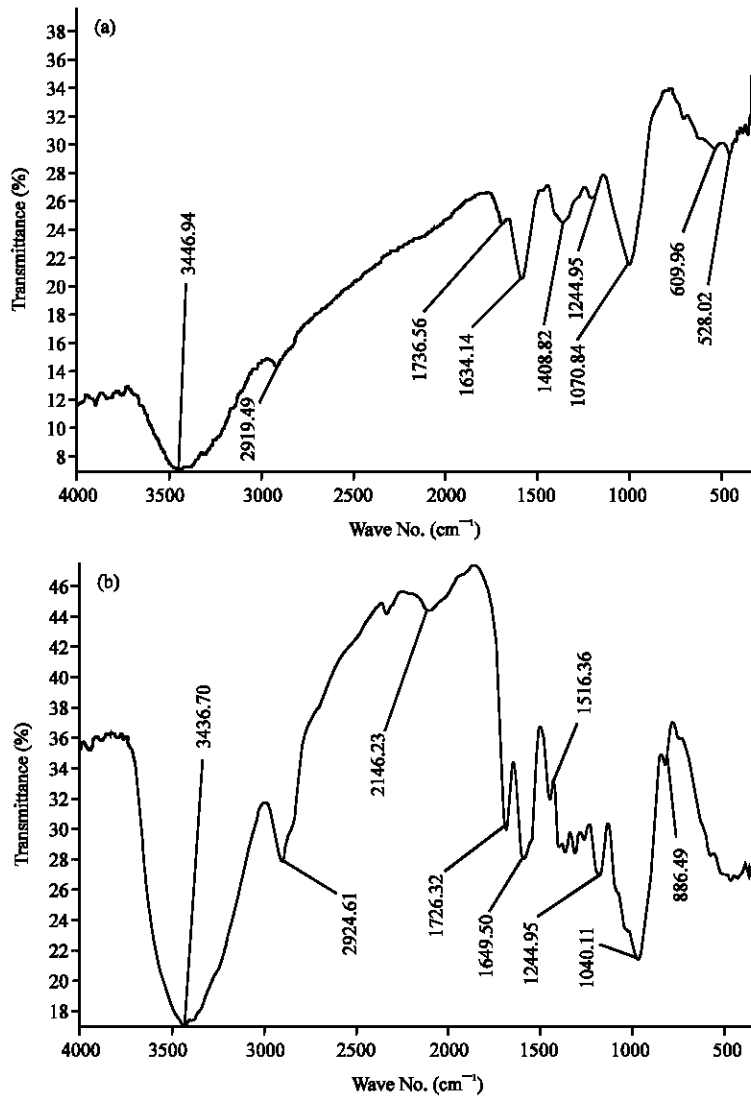


Fig. 2: The FT-IR spectrum patterns of raw (a) biological activated and (b) dates stems

**Effect of Contact Time**

It has been determined that rapid adsorption Pb (II) ions by dates stems was observed in first 10 min with raw dates stems and 5 min with activated ones, this was caused by strong attractive forces between the Pb (II) ions and adsorbent; then the Pb (II) concentration did not significantly change and attained the final equilibrium plateau corresponding to 63.8 and 97% with raw and activated date stems respectively within 60 min (Fig. 3). The results demonstrate that the maximum adsorption is a significant parameter for large-scale application in industrial processes, this finding was attributed to highly porous and meshes structure of adsorbent, which provides ready access and large surface area for the sorption metals on the binding sites (Çabuk *et al.*, 2007).

As it can be shown from Fig. 1 the porous structure of the dates stems eliminates the problem of diffusion limitation as would be expected to occur for biosorption of Pb (II) on stems of dates.

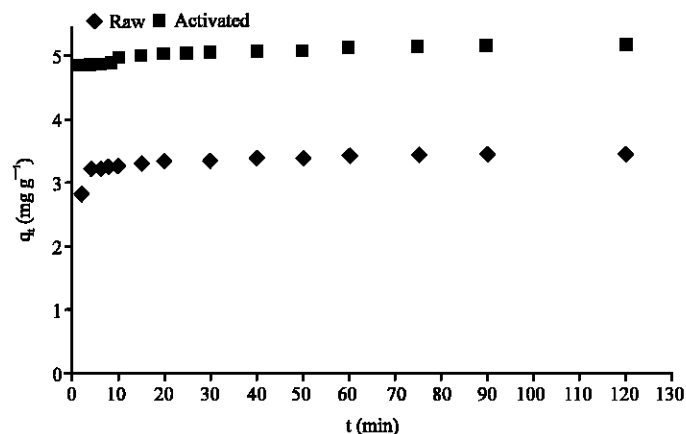


Fig. 3: Effect of contact time on the Pb (II) biosorption onto raw and activated dates stems, ( $T = 25^{\circ}\text{C}$ ,  $C_0 = 50 \text{ mg L}^{-1}$ ,  $\text{pH} = 4.5$ ,  $m = 10 \text{ g L}^{-1}$ )

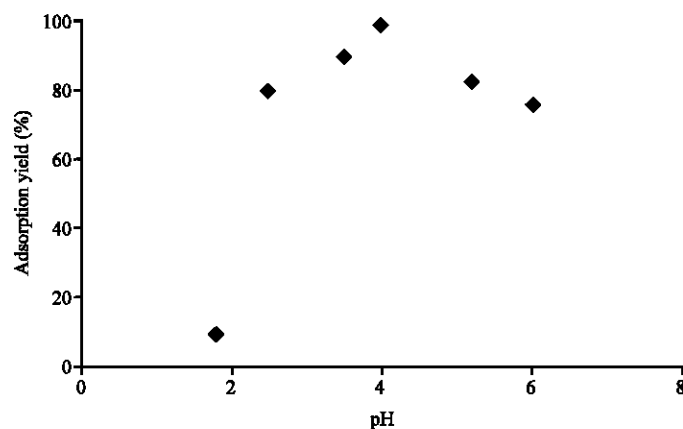


Fig. 4: Effect of pH on the Pb(II) biosorption onto activated dates stems, ( $T = 25^{\circ}\text{C}$ ,  $C_0 = 50 \text{ mg L}^{-1}$ ,  $m = 10 \text{ g L}^{-1}$ )

### Effect of pH

The pH of solution has been identified as the most important variable governing metal adsorption on the adsorbent. Figure 4 shows the effect of pH on the removal of lead (II) ions onto activated stems of dates from aqueous solutions that the biosorption of metal ion was low for pH less than 2. The heavy metal removal capacity increased very sharply with an increase in pH from 2 to 4.

The low metal biosorption at pH 2 has been attributed to the competition that metal ions face from hydrogen ions for the available adsorption sites. With an increase in the pH, the negative charge density on the activated stems of dates surface increases due to deprotonation of the metal binding and thus increases adsorption. At the values of greater than 4, the heavy metal removal capacity decreased due to the fact that with the pH values of 5 the metal precipitation appeared and interfered with the accumulation or a adsorbent deterioration.

### Effect of Biosorbent Dosage

To determine the effect of biosorbent dosage on metal removal, the amounts of biosorbent added into metal solution were varied from 2.5 to 30  $\text{g L}^{-1}$  and the results are shown in Fig. 5. The amount



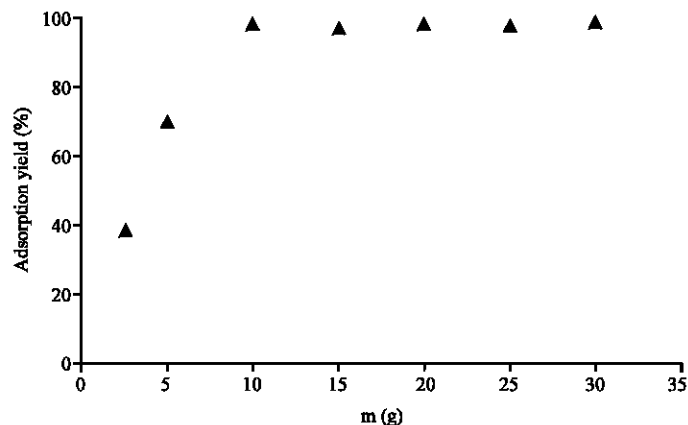


Fig. 5: Effect of biosorbent concentration on the Pb (II) adsorption onto activated dates stems, (T = 25°C, C<sub>0</sub> = 50 mg L<sup>-1</sup>, pH = 4.5)

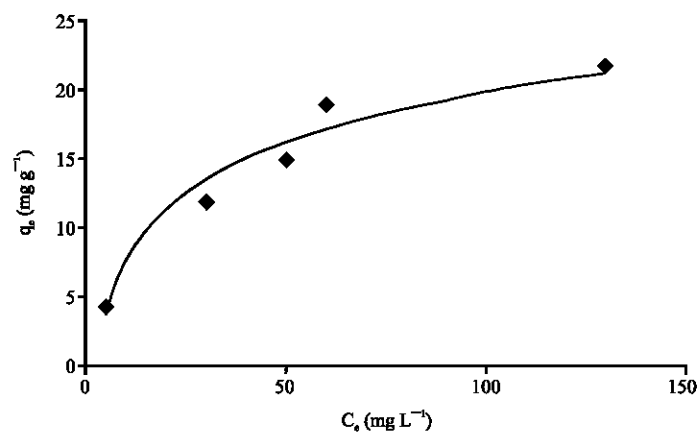


Fig. 6: Adsorption isotherm of Pb (II) ions on the activated stems of dates at 21°C

of biosorbed lead (II) ions removal increased with increasing of the activated stems of dates concentration as expected. With increase in the adsorbent dosage from 2.5 to 30 g L<sup>-1</sup>, the biosorption yield was changed from 39 to 98.2%. It is well known that, increasing the adsorbent dosage, the total removal of lead (II) from the solution increased because the availability of active sites for metal binding increased and that increasing this number had also no effect after equilibrium was reached.

After certain adsorbent dosage, the removal efficiency is not increased significantly. It is evident that the optimum of activated stem of dates for further adsorption experiments was selected as 10 g L<sup>-1</sup> and the removal of lead (II) ions was found to be 97.9%.

### Biosorption Isotherms

The equilibrium adsorption isotherms are one of the most important data to understand the mechanism of the biosorption. Figure 6 shows the adsorption isotherm of lead (II) ions on activated stems of dates obtained from the batch system at 21°C. As shown in this Fig. 6, q<sub>e</sub> increased with an increase in C<sub>e</sub>. These results demonstrated that lead (II) ions adsorption by activated stems of dates was chemically equilibrated mechanism whose uptake increased as long as binding sites were available.

Table 2: Parameters of a biosorption models for Pb (II) on activated steams of dates

Langmuir model			Freundlich model		
$q_m$ (mg g <sup>-1</sup> )	$b$ (L mg <sup>-1</sup> )	$R^2$	$K_f$ (L g <sup>-1</sup> )	$1/n$	$R^2$
27.03	0.032	0.978	2.11	0.502	0.979

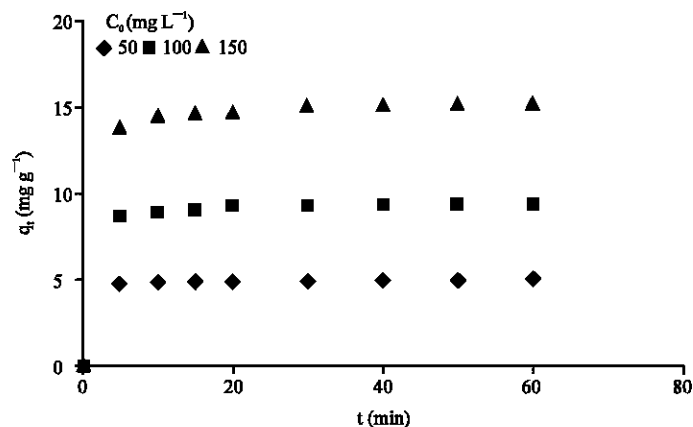


Fig. 7: The variation of biosorption capacity with adsorption time at various initial Pb (II) concentrations. (T = 25°C, pH = 4.5, m = 10 g L<sup>-1</sup>)

Langmuir and Freundlich isotherms were used for the modelling of the experimental biosorption data. The Langmuir and Freundlich constants were obtained by fitting the adsorption equilibrium data to the isotherm models and are shown in Table 2. It is evident from these data, Langmuir and Freundlich models fit well compared with the  $R^2$  values. The maximum adsorption capacity ( $q_m$ ) of adsorbent calculated from Langmuir isotherm equation defines the total capacity of the adsorbent for lead (II) ions is 27.03 mg g<sup>-1</sup>.

The value of  $R_L$  calculated from Eq. 3 is 0.08, between 0 and 1, indicate that the biosorption process is favourable.

The Freundlich constants  $K_f$  and  $n$  indicate the biosorption capacity of the biosorbent and a measure of the deviation from linearity of the biosorption, respectively. The values of  $K_f$  and  $n$  at equilibrium were 2.11 L g<sup>-1</sup> and 1.99, respectively. The value of  $n$  is greater than unity, indicating that lead (II) ions are favourably adsorbed by biological activated stems of dates.

### Effect of Initial Pb (II) Ion Concentration and Biosorption Kinetics

Figure 7 shows the effect of initial Pb (II) ion concentration on the efficiency of Pb (II) ion removal. The removal of Pb (II) ion increases rapidly in the beginning (first 5 min) and then more slowly until the equilibrium. The kinetic of Pb (II) ion biosorption onto activated dates stems was analysed using pseudo-first order, pseudo-second-order and intraparticle diffusion models. The plots of linea form of the pseudo-first-order, pseudo-second-order (Fig. 8) and intraparticle diffusion (Fig. 9) for the adsorption of lead (II) ions were obtained at the initial concentrations of 50, 100 and 150 mg L<sup>-1</sup>. The kinetic parameters for the biosorption of lead (II) ions onto activated stems of dates are shown in Table 3. The plots of  $\text{Log} \frac{(q_b - q_t)}{q_b}$  versus t for the pseudo-first-order equation are not

shown as a figure since the calculated correlation coefficient are less than 0.977. From Table 3, it can be seen that pseudo-first-order equation provided poor description of the data. When second-order equation was used to model, the data a straight line and good fit ( $R^2 \geq 0.999$ ) were obtained. These data

Table 3: Kinetic parameters of the pseudo-first-order, pseudo-second-order and intraparticle diffusion equation for pb<sup>2+</sup> biosorption onto activated stems

C <sub>0</sub> (mg L <sup>-1</sup> )	Pseudo-first-order		Pseudo-second-order				Intraparticle diffusion	
	k <sub>1</sub>	R <sup>2</sup>	q <sub>e</sub> (mg g <sup>-1</sup> )	k <sub>2</sub> (g mg <sup>-1</sup> min <sup>-1</sup> )	h <sub>0</sub> (mg g <sup>-1</sup> min <sup>-1</sup> )	R <sup>2</sup>	K <sub>p</sub> (mg g <sup>-1</sup> min <sup>-0.5</sup> )	R <sup>2</sup>
50	0.05	0.469	5.15	51.5×10 <sup>-2</sup>	13.70	1	0.055	0.911
100	0.11	0.886	9.52	19.7×10 <sup>-2</sup>	17.87	1	0.128	0.888
150	0.10	0.879	15.62	9.5×10 <sup>-2</sup>	23.24	1	0.353	0.903

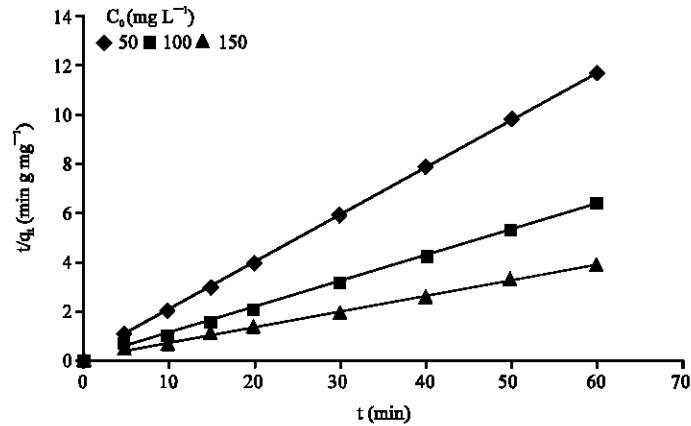


Fig. 8: Pseudo-second-order kinetic plots at various initial concentrations, (T = 25°C, pH = 4.5, m = 10 g L<sup>-1</sup>)

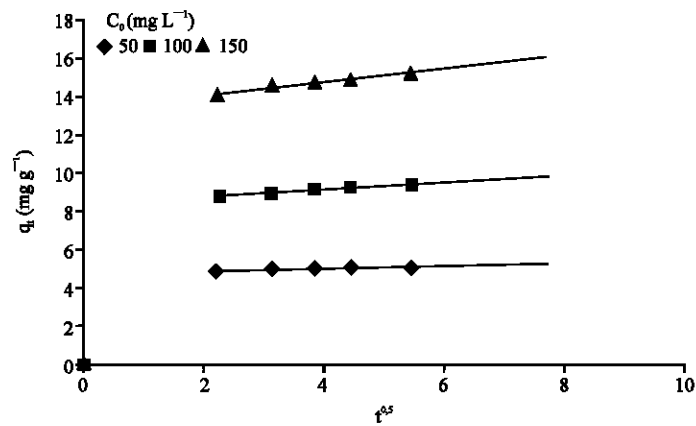


Fig. 9: Intraparticle diffusion plots at various initial concentrations (T = 25°C, pH = 4.5, m = 10 g L<sup>-1</sup>)

suggested that the adsorption system studied belong to the pseudo-second-order kinetic model. In this model, the rate-limiting step is a adsorption mechanism involving chemisorption, where metal removal from solution is due to purely physic-chemical interactions between adsorbent and metal solution (Aksu, 2001).

The parameters of Eq. 5 were obtained from the slope and intercept of straight line plots of t/q<sub>t</sub> versus t. The equilibrium sorption capacity, q<sub>e</sub> increases from 5.155 to 15.625 mg g<sup>-1</sup> when the initial concentration of Pb (II) increases from 50 to 150 mg L<sup>-1</sup>.

The values of the rate constant were found to decrease from  $50.2 \times 10^{-2}$  to  $9.52 \times 10^{-2} \text{ g mg}^{-1} \text{ min}^{-1}$  for an increase in the initial concentration from 50 to 150  $\text{mg L}^{-1}$  and as expected the biosorption rate was higher for high initial Pb (II) concentration (Table 3).

According to the Eq. 6, a plot of  $q_t$  versus  $t^{0.5}$  should be a straight line with a slope  $k_p$  when adsorption mechanism follows the intraparticle diffusion process. The values of  $k_p$  as obtained from the slopes of straight lines are shown in Table 3. Because of the deviation of the curves from the origins and non-linear distribution of the plots, intraparticle diffusion cannot be accepted as only rate-determining step for the biosorption of lead (II) ions onto activated stems of dates. Although, the correlation coefficients for intraparticle diffusion model are also lower than that of the pseudo-second-order kinetic model.

### Effect of Temperature and Adsorption Thermodynamics

the temperature of adsorption medium could be important for energy-dependent mechanisms in the metal biosorption by activated stems of dates. Figure 10 shows the effect of temperature on the maximum adsorption capacity,  $q_e$ , at the initial lead (II) concentration of 50  $\text{mg L}^{-1}$ . Increasing the temperature increase the sorption capacity of activated stems of dates. Thus, when increasing the temperature from 12 to 63°C, the removal of the lead (II) increased from 96.8 to 99.9% indicating the endothermic nature of the biosorption reaction. The enhancement in the biosorption capacity might be due to the chemical interaction between adsorbates and biosorbent.

The calculated values of  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  are shown in Table 4. The positive value of  $\Delta H^\circ$  indicated the endothermic nature of the biosorption interaction. The positive value of  $\Delta S^\circ$  showed the affinity of the activated stems of dates for lead (II) and the increasing randomness at the solid-solution interface during the adsorption process. The negative value of  $\Delta G^\circ$  indicated the feasibility of the process and the spontaneous nature of the biosorption with a high preference lead (II) onto the activated stems of dates. Similar observations were reported for adsorption of arsenic onto coconut husk carbon (Manju *et al.*, 1998), adsorption of MB onto mango seed kernel powder (Ru-Ling and Tseng, 2005) and adsorption of MB onto oil palm fibre activated carbon (Tan *et al.*, 2007).

Table 4: Thermodynamic parameters for biosorption of lead (II) onto activated stems of dates

$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (kJ mol <sup>-1</sup> )	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )			
		285 k	298 k	313 k	336 k
59.24	0.23	-7.16	-9.64	-11.50	-18.49

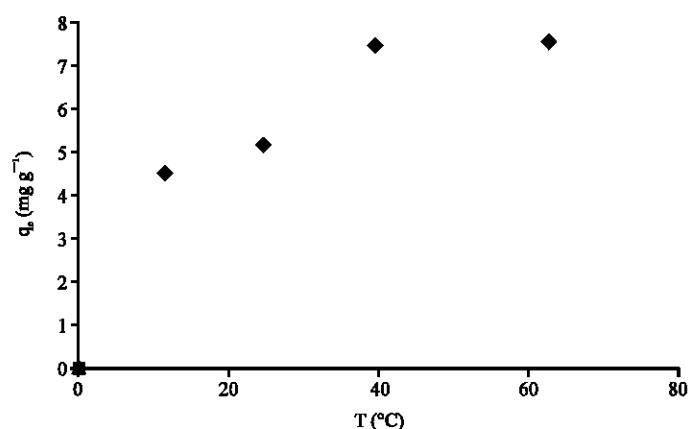


Fig. 10: Effect of temperature on metal uptake ( $C_0 = 50 \text{ mg L}^{-1}$ ,  $\text{pH} = 4.5$ ,  $m = 10 \text{ g L}^{-1}$ )

## CONCLUSION

The experimental biosorption capacities of lead (II) ions onto stems of dates were 3.48 and 5.15 mg g<sup>-1</sup> for raw and biological activated dates stems, respectively, for the initial concentration of 50 mg L<sup>-1</sup> and removal increases from 63.8 to 97%.

SEM study showed that the activated stems of dates were more porous than raw ones. The main surface functional groups in the raw and activated stems of dates were the hydroxyl groups.

Lead (II) ions biosorption was dependent on initial pH, initial Pb<sup>2+</sup>, stems of dates concentration and temperature.

The pseudo-second-order model described the kinetic data well and the chemisorption might be the rate-limiting step that controls the biosorption process; this is consisted by the best agreement with the Langmuir isotherm model. The equilibrium sorption data fitted both the Langmuir and Freundlich isotherms with high correlation coefficients suggesting that the adsorption process followed a monolayer sorption.

The biosorption process was found to be endothermic, spontaneous and can be explained with the pseudo-second-order type kinetic model.

It may be concluded that activated stems of dates may be used as a low and abundant source in Algeria, for the removal of lead (II).

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