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Adsorption of Lead(II) from Aqueous Solution by Using Leaves of Date Trees As an Adsorbent

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ABSTRACT: The efficiency of date tree leaves as a low cost adsorbent for removing lead ions from aqueous solution has been investigated in this paper. Batch experiments were conducted to study the effects of the main parameters such as contact time, initial concentration of Pb(II), adsorbent dose, solution pH, agitation speed, ionic strength, and temperature on the adsorption of Pb(II) by date tree leaves. The maximum removal of lead(II) is found to be 94 % at pH 5.8, initial Pb(II) concentration of 10 $mg \cdot L^{-1}$, adsorbent dose of 1 $g \cdot L^{-1}$, agitation speed of 200 rpm, ionic strength of 0.005 M, and temperature of 25 °C. Dynamics of the adsorption process were studied, and the values of rate constants of pseudofirst-order and pseudosecond-order were calculated. Equilibrium isotherms for the adsorption of Pb(II) were analyzed by the Langmuir, Freundlich, and Temkin isotherm models. The Temkin isotherm model was found to represent better the data of Pb(II) sorption onto date tree leaves. Different thermodynamic parameters, namely, changes in standard Gibbs energy, enthalpy, and entropy, were also evaluated from the temperature dependence, and the results suggest that the adsorption reaction is spontaneous and endothermic in nature.

INTRODUCTION

The existence of heavy metals in aquatic systems can be detrimental to a variety of living species.[1] They are important contaminants of liquid wastes discharged from a number of industries such as electroplating, dyes and dye intermediates, textiles, tanneries, oil refineries, electroplating, mining, smelters, and so forth. The most common toxic metals found in industrial wastewater are Cr, Ni, Mn, Hg, Cd, Cu, Zn, and Pb.[2] These metals are non iodegradable and tend to accumulate in living organisms, causing various disorders. Accordingly, improved and innovative methods of water and wastewater treatment are continuously being developed to treat water containing metals.[3] Pb(II) is a metal which is considered to be an environmental concern. The problem of Pb(II) pollution is due to the use of Pb in service pipes and particularly in soft water is the first recognized metal pollutant. Other sources of Pb(II) pollution are the battery industry, auto-exhaust, paints, ammunition, and the ceramic glass industries.[4] The permissible level of lead in drinking water is 0.05 $mg \cdot L^{-1}$. The permissible limit of Pb(II) in wastewater, given by the Environmental Protection Agency (EPA), is 0.05 $mg \cdot L^{-1}$, and that of the Bureau of Indian Standards (BIS) is 0.1 $mg \cdot L^{-1}$.[5]

Major health effects due to Pb(II) poisoning are nervous and renal breakdown, weakness, headache, brain damage, convulsions, behavioral disorders, and constipation. For lead in wastewater, current abatement and remediation procedures include pH adjustment with lime or alkali hydroxides, coagulation—sedimentation, reverse osmosis, and ion exchange.

Adsorption of heavy metals from aqueous solutions is a relatively new process that has proven to be very promising in the removal of contaminants from aqueous effluents. Adsorbent materials derived from low-cost agricultural wastes can be used for the effective removal and recovery of heavy metal ions from wastewater streams.[6,7]

The adsorption capacity of lignocellulosics for metal ions is generally described as adsorption. The major advantages of the adsorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive adsorbent materials. The major advantages of adsorption over conventional treatment methods include: low-cost, high efficiency, minimization of chemical and/or biological sludge, regeneration of adsorbent, no additional nutrient requirement, and the possibility of metal recovery.[8] The cost advantage of the adsorption technology would guarantee a strong penetration of the large market of heavy metal polluting industries.

The removal of heavy metal ions using low-cost abundantly available adsorbents: agricultural wastes such as tea waste and coffee,[9] hazelnut shells,[10] peanut hull,[11] red fir[12] and maple[13] sawdusts,[14] pinus bark[15] and different bark samples,[16] palm kernel husk[17] and coconut husk,[18,19] peanut skins,[20] modified cellulosic materials,[21,22] chemically modified cotton,[23] corncobs[24] and modified corncob,[25] rice hulls,[26] apple wastes,[27] activated carbon developed from coffee residue,[28] bark,[29,30] wool fibers,[31] tea leaves,[32] and wool, olive cake, pine needles, almond shells, cactus leaves, charcoal,[33] modified lignin,[34] banana and orange peels,[35] modified sugar beet pulp,[36] palm fruit bunch,[37] maize leaf[8] and different agricultural byproducts[38] have been used and investigated.

The objective of this study is to investigate the feasibility of metallic ion removal from aqueous solution by date tree leaves. The kinetics of the process is determined, especially in relation to the effects of various factors on the removal. The investigated factors include aqueous metal ion concentration, agitation speed, contact time, pH of solution, adsorbent concentration, temperature, and ionic strength. The second objective of this study is the modelization of the isotherms of lead(II) sorption from aqueous solutions onto date tree leaves. The representation of the adsorption isotherms onto date tree leaves can be based on

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Table 1. Physical and Chemical Characteristics of the Date Tree Leaves Used

parameter	value
surface area/$m^2 \cdot g^{-1}$	24.9
porosity/%	0.435
pH	4.2
conductivity/$\mu S \cdot m^{-1}$	41
particle size /μm	63

models with two parameters. The goal of this part is to apprehend the interactions, Pb—date tree leaves, through the validity of the isotherm models. In the case of the models, the Langmuir and Freundlich equations are largely used. Additionally, other models such as the Temkin equation exist and allow the determination of the energy of sorption and interaction energy between sorbed molecules.

■ MATERIALS AND METHODS

Adsorbate and Analytical Measurements. All of the compounds used to prepare reagent solutions were of analytical reagent grade. The mother solution of Pb(II) (1000 $mg \cdot L^{-1}$) was prepared by dissolving a weighed quantity of lead nitrate in distilled water. The concentrations of metal solutions ranged from (10 to 90) $mg \cdot L^{-1}$. Before mixing with the date tree leaves, the pH of each solution was adjusted to the required value for the sorption of Pb(II) ions, by adding 0.1 M NaOH or 0.1 M HNO_3. A Schimadzu AA6500 atomic absorption spectrophotometer (AAS) equipped with a Zeeman atomizer and a SSC-300 autosampler was used to determine the concentration of unadsorbed Pb(II) ions in the solution. All of the instrumental conditions are optimized for maximum sensitivity as indicated by the manufacturer.

Adsorbent and Characterization. The leaves of the date tree used in the present study are collected from the Saoura region (southern Algeria). The collected leaves are washed with distilled water several times to remove dirt particles and water-soluble materials. The washing process is continued until the wash water contained no color. The washed materials are then completely dried in an oven at 50 °C for 2 days. The dried leaves are ground and sieved to obtain a particle size range of 63 μm. The obtained material is dried in an air circulating oven at 50 °C for 3 days and stored in a desiccator until use. A measurement of specific area has been made by nitrogen adsorption at 77 K using a Brunauer—Emmett—Teller (BET) surface analyzer (Nova Station A). The apparent density was calculated by filling a calibrated cylinder with a given weight of date tree leaves and tapping the cylinder until a minimum volume was recorded. This density was referred to as the tapping or bulk density of the adsorbent. For the real density we use the pycnometer method, which consists of filling a pycnometer with the date tree leaves, then adding a solvent (methanol) to fill the void; at each step the weight was determined. The pore volume and the porosity are determined by using a volumetric method which consists of filling a calibrated cylinder with a volume V_1 of date tree leaves (mass m_1) and solvent (methanol) until volume V_2 (total mass m_2) was reached. Knowing the density of solvent, the porous volume and porosity of the adsorbent are easily calculated. The pH of the date tree leaves was measured as follows: the suspension was prepared in a ratio of 10 mL of water to 1 g of date tree leaves; this mixture was stirred and the pH measured several times until a constant value was reached. The used pH meter was a Jenway 3305.[39,40] The physical and chemical characteristics of the date leaves are presented in Table 1.

Batch Sorption Procedure. The experiments were performed in a batch reactor (3 L) with a range of stirring speed [(100 to 400) rpm]. A known weight of date tree leaves was left in contact with 1000 mL of each solution [(10 to 90) $mg \cdot L^{-1}$] during 2 h, and the initial pH value of the solution was adjusted with nitric acid (0.1 $mol \cdot L^{-1}$) or sodium hydroxide (0.1 $mol \cdot L^{-1}$). The pH value was chosen so that metallic species are present in their divalent form (3−7). Small-volume liquid samples were withdrawn at different time intervals. Samples were filtered through glass-filter paper to remove adsorbent particles. The amount of Pb(II) ions in the solution was estimated by atomic absorption spectrophotometry (AAS) at a 283.3 nm wavelength. To obtain the sorption capacity, the amount of ions sorbed per mass unit of date tree leaves (q_e) is evaluated using the following expression:

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

where C_0 is the initial metal ion concentration ($mg \cdot L^{-1}$), C_e the equilibrium metal ion concentration ($mg \cdot L^{-1}$), V the volume of the aqueous phase (L), and m is the weight of date tree leaves used (g).

The sorption percentage (removal (%)) of metal ions from aqueous solution is computed as follows:

$$\text{removal}(\%) = 100\frac{(C_0 - C_e)}{C_0}$$

■ RESULTS AND DISCUSSION

Effect of Contact Time and Initial Concentration of Pb(II). The rate of metal removal is of great significance for developing a sorbent-based water technology. To establish the equilibrium time for maximum uptake and to know the kinetics of the sorption process, the sorption of Pb(II) by date tree leaves was carried out using contact times ranging from (5 to 180) min, and the results are shown in Figure 1. It is observed that metal sorption occurs rapidly. The sorption efficiency of Pb(II) increases gradually with increasing contact times and reaches a plateau afterward. An increase in the initial Pb(II) concentration leads to an increase in the sorption capacity of lead by date tree leaves. Equilibrium uptake increases with the increasing of the initial metal ion concentration over the range of experimental concentration. This is a result of the increase in the driving force of the concentration gradient, with an increase in the metal ion initial concentration. The equilibrium time required for the metal ion is short because the majority of Pb(II) is removed within the first 50 min. According to the results, the equilibrium time is fixed at 2 h for the rest of the batch experiments to make sure that equilibrium is reached. Similar results have also been reported for the removal of Pb(II) ions.[4] The sorbed amount of Pb(II) is found to be 9 $mg \cdot g^{-1}$ at the initial concentration of 10 $mg \cdot L^{-1}$ and 51 $mg \cdot g^{-1}$ at 90 $mg \cdot L^{-1}$.

Effect of Adsorbent Dose. The dose of adsorbent (m) was varied from (0.3 to 1.5) $g \cdot L^{-1}$ keeping all other experimental variables (viz. pH 5.8, initial concentration/$mg \cdot L^{-1}$ = 10, contact time/h = 2 and agitation speed/rpm = 200) constant. Figure 2 presents the adsorbent dose profile versus Pb(II) removal percent. It may be observed that on increasing the

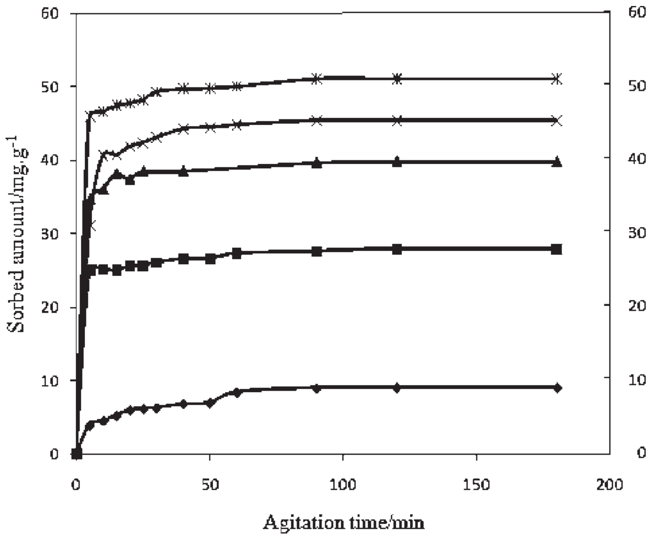

Figure 1. Effect of agitation time and initial concentration of Pb(II) on the sorption of lead by date tree leaves. Conditions: pH 5.8; agitation speed = 200 rpm; ionic strength = 0.005 M, and temperature = 25 °C. —◆—, 10 mg·L^{-1}; —■—, 30 mg·L^{-1}; —▲—, 50 mg·L^{-1}; —×—, 70 mg·L^{-1}; —∗—, 90 mg·L^{-1}.

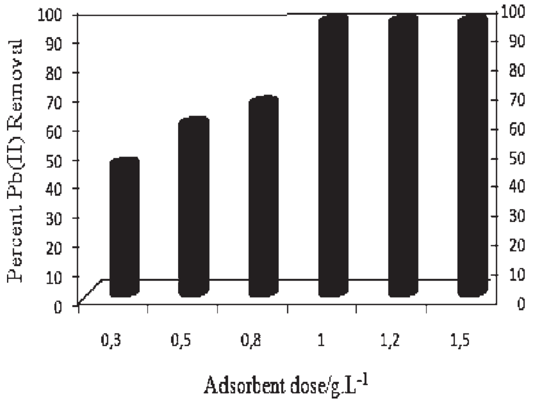

Figure 2. Effect of adsorbent dosage on Pb(II) removal. Conditions: pH 5.8; initial concentration of Pb(II) = 10 mg·L^{-1}; agitation time = 2 h; agitation speed = 200 rpm; ionic strength = 0.005 M, and temperature = 25 °C.

adsorbent dose, the percentage of removal of Pb(II) increases up to a date tree leaves dose of 1 g·L^{-1}. This may be attributed to an increased sorbent surface area and availability of more sorption sites resulting from the increased dose of the sorbent. At an amount of adsorbent higher than 1 g·L^{-1}, the incremental Pb(II) removal becomes very low, as the surface Pb(II) concentration and the solution Pb(II) concentration come to equilibrium with each other. The percentage of removal of Pb(II) increases from (45 to 94) % with an increase of the amount of adsorbent from (0.3 to 1.5) g·L^{-1}, respectively (Figure 2).

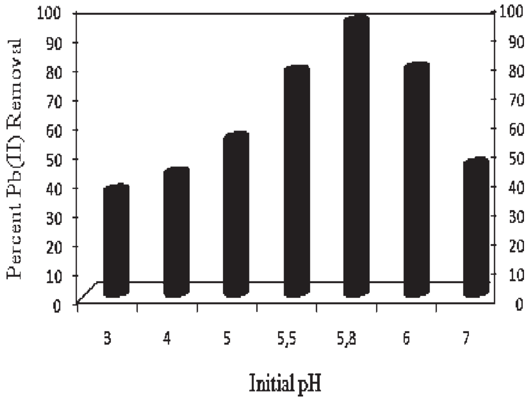

Figure 3. Effect of pH on Pb(II) removal. Conditions: adsorbent dose = 1 g·L^{-1}; initial concentration of Pb(II) = 10 mg·L^{-1}; agitation time = 2 h; agitation speed = 200 rpm; ionic strength = 0.005 M, and temperature = 25 °C.

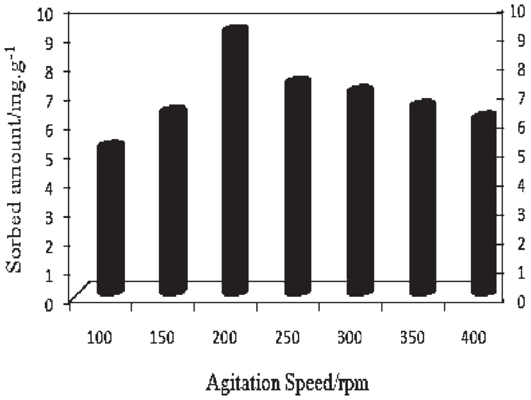

Figure 4. Effect of agitation speed on the sorption of lead by date tree leaves. Conditions: pH 5.8; initial concentration of Pb(II) = 10 mg·L^{-1}; agitation time = 2 h; ionic strength = 0.005 M, and temperature = 25 °C.

Effect of Solution Initial pH. pH is one of the most important environmental factors influencing not only site dissociation but also the solution chemistry of the heavy metals: on the one hand, hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, and precipitation are strongly influenced by pH, and on the other hand, pH strongly influences the speciation and adsorption availability of heavy metals.[41] To study the effect of this parameter on the metal sorption by date tree leaves, the solution initial pH was varied within the range 3 to 7. This pH range was chosen to avoid metal solid hydroxide precipitation. The effect of solution initial pH on the sorption kinetics for Pb(II) on date tree leaves is shown in Figure 3. The experiments were performed for an initial concentration of 10 mg·L^{-1}, 1 g·L^{-1} adsorbent dose, and 25 °C. The results indicate that the maximum uptake of these ions is obtained at pH 5.8.

At low pH values, there is excessive protonation of the date tree leaves surface resulting in a decrease in the sorption of Pb(II) ions. This is consistent with the results obtained by Kobya et al.[42] On increasing the pH of Pb(II) solutions from 3, the removal percentage increases and becomes quantitative over the pH range 5 to 5.8. The increase in metal removal as pH increases can be explained on the basis of a decrease in competition between protons (H^+) and positively charged metal ions at the surface sites. According to the Pb(II) speciation diagram[43] and in this range of pH, the dominant species of sorption are Pb(II). The minimal sorption amount obtained at higher pH (pH > 5.8) is due to metal hydrolysis and the onset of precipitation.

Subsequent studies were conducted at pH 5.8.

Effect of Agitation Speed. The quality of dispersion of the solid in sorption is a significant factor as in all processes of mass transfer. Stirring influences the distribution of the aqueous solution and can also act on the formation of an external film of separation. The experiments were undertaken with different

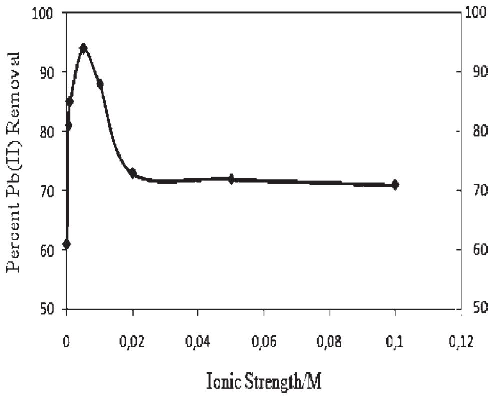

Figure 5. Effect of ionic strength on Pb(II) removal. Conditions: pH 5.8; adsorbent dose = 1 g·L^{-1}; initial concentration of Pb(II) = 10 mg·L^{-1}, agitation time = 2 h; agitation speed = 200 rpm, and temperature = 25 °C.

agitation speeds of (100, 150, 200, 250, 300, 350, and 400) rpm keeping constant the other process variables. Results (Figure 4) show that the high amount of lead sorbed at equilibrium (9.10 mg·g^{-1}) is obtained with an agitation speed of 200 rpm which assures good diffusion of ions toward date tree leaf particles. The sorbed amount of Pb(II) increases with an increase of the agitation speed from (100 to 200) rpm, and at higher stirring speed (>200 rpm), the sorbed amount of Pb(II) decreases. When increasing the agitation speed (< 200 rpm), the diffusion rate of metal ions from the bulk liquid to the liquid boundary layer surrounding sorbent particles becomes higher because of an enhancement of turbulence and a decrease of the thickness of the liquid boundary layer. At higher stirring speeds (> 200 rpm), the decrease of the sorbed amount of Pb(II) is attributed to the rejection of the adsorbent part, which is found plated against the internal walls of the reactor.

Effect of Ionic Strength. In water, salt is present over a wide range of concentration depending on the source and the quality of the water. The presence of salt or co-ions in solution can affect the sorption of metal ions. The effect of salt concentration (ionic strength) on the removal percentage of Pb(II) by date tree leaves was analyzed over the NaCl concentration range from (0 to 0.1) M. Sorption kinetics are carried out for a lead initial concentration of 10 mg·L^{-1}, solution volume of 1 L, and a sorbent mass of 1 g. The obtained results are shown in Figure 5. Higher metal ion removal takes place when the ionic strength of solution is increased from (0 to 0.005) M. According to the electrostatic double layer (EDL) theory,[44,45] the EDL of the date tree leaves is compressed when ionic strength of the solution is increased. Consequently, more sorption of metal ions from the aqueous solution is achieved. At an ionic strength greater than 0.005 M, it is seen that the increase in the salt concentration (> 0.005 M) results in a decrease of lead sorption by date tree leaves, which can be attributed to the competitive effect between lead ions and cations from the salt (Na^+) for sites available for the sorption process.[46,47] As the concentration of salt is increased from (0.005 to 0.1) M, the percentage of removal of Pb(II) by date tree leaves decreases from (94 to 71) %. Another reason is the influence of the great ionic strength on the activity coefficient of lead which reduces its transfer to the sorbent surface.

Effect of Temperature. The temperature dependence of lead ion sorption onto date tree leaves was studied at various initial lead ion concentrations and at various temperatures [(25, 35, 40, and 60) °C]. The temperature has two main effects on sorption processes. Increasing temperature is known to increase the diffusion rate of the sorbate within the pores as a result of decreasing solution viscosity and also modifies the equilibrium capacity of the sorbent for a particular sorbate. Table 2 shows the variation of the adsorbed amount versus various temperatures. The results obtained with an initial metal ion concentration of 90 mg·L^{-1} show that by increasing temperature from (25 to 60) °C, the equilibrium sorption capacity slightly increases from (51 to 58) mg·g^{-1}, respectively.

Table 2. Effect of Temperature on the Adsorbed Amount of Lead by Date Tree Leaves (mg·g^{-1}) at Different Initial Concentrations (Conditions: pH 5.8; Agitation Speed = 200 rpm; Agitation Time = 2 h, and Ionic Strength = 0.005 M)

t/°C	10 mg·L^{-1}	30 mg·L^{-1}	50 mg·L^{-1}	70 mg·L^{-1}	90 mg·L^{-1}
25	9.09 ± 0.24	27.96 ± 0.23	39.81 ± 0.08	45.44 ± 0.22	51.09 ± 0.40
35	9.73 ± 0.14	27.17 ± 0.33	41.46 ± 0.38	46.87 ± 0.21	53.26 ± 0.35
45	9.18 ± 0.17	28.72 ± 0.39	42.76 ± 0.12	48.45 ± 0.55	55.13 ± 0.25
60	9.63 ± 0.20	28.26 ± 0.34	43.46 ± 0.24	49.91 ± 0.53	57.25 ± 0.56

Sorption Kinetic Study. Most sorption processes take place by a multistep mechanism comprising: (i) diffusion across the liquid film surrounding the solid particles (a process controlled by an external mass transfer coefficient), (ii) diffusion within the particle itself assuming a pore diffusion mechanism (intraparticle diffusion), and (iii) physical or chemical adsorption at a site.[48] The transient behavior of the batch sorption process at different temperatures and Pb(II) concentrations is analyzed using the Lagergren first-order kinetic model and the pseudosecond-order model.

Pseudofirst-Order Model. The differential equation of the pseudofirst-order model is given as:

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \qquad (1)$$

where q_t/mg·g^{-1} is the amount of sorbate sorbed at time t/min, q_e/mg·g^{-1} is the sorption capacity at equilibrium, K_1/min^{-1} is the pseudofirst-order rate constant, and t/min is the contact time.

The integration of eq 1 for the boundary conditions: $t = 0$ to t and $q_t = 0$ to q_t leads to:[49]

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \qquad (2)$$

Values of the rate constant (K_1), equilibrium sorption capacity (q_e(cal)), and the coefficient of determination (R^2) calculated from the plots of log($q_e - q_t$) versus t (not shown here) at different initial concentrations and different temperatures are summarized in Table 3. One can see that the rate constant K_1 ranges between (1.6·10^{-2} and 5.110^{-2}) min^{-1}. Namasivayam and Kadirvelu[50] have reported K_1 values of (1.9658·10^{-2}, 2.653·10^{-2}, 3.2232·10^{-2}, and 3.4112·10^{-2}) min^{-1} for the initial Cu(II) concentration of (20, 30, 40, and 50) mg·L^{-1}, respectively. For the removal of copper(II) by adsorption onto peanut hull carbon, Periasamy and Namasivayam[51] have reported K_1 values of (3.26·10^{-2}, 3.52·10^{-2}, and 3.37·10^{-2}) min^{-1} for the initial concentration of (10, 15, and 20) mg·dm^{-3}, respectively. As shown in Table 3, the coefficient of determination (R^2) of the linear regression of eq 2 is low, ranging from 0.802 to 0.979, and the calculated q_e(cal) values do not agree with the experimental q_e(exp) data. These results suggest that the pseudofirst-order model does not describe the sorption kinetics of the system

Table 3. Sorption Kinetic Model Rate Constant of Date Tree Leaves at Different Temperatures

		pseudofirst-order kinetic				pseudosecond-order kinetic			
t	C_0	K_1	q_e(exp)	q_e(cal)		K_2	q_e(exp)	q_e(cal)	
°C	mg·L^{-1}	min^{-1}	mg·g^{-1}	mg·g^{-1}	R^2	g·mg^{-1}·min^{-1}	mg·g^{-1}	mg·g^{-1}	R^2
25	10	0.043	9.10	8.60	0.914	0.007	9.10	10.10	0.987
	30	0.027	27.97	4.01	0.958	0.018	27.97	28.57	0.999
	50	0.035	39.82	4.51	0.925	0.020	39.82	41.66	0.999
	70	0.051	45.44	11.01	0.938	0.010	45.44	47.62	0.999
	90	0.037	51.10	12.95	0.931	0.006	51.10	52.63	0.999
35	10	0.029	9.73	3.51	0.900	0.019	9.73	10.10	0.997
	30	0.016	27.18	2.45	0.836	0.026	27.18	27.77	0.999
	50	0.031	41.47	3.16	0.802	0.057	41.47	41.66	1.000
	70	0.044	46.87	6.51	0.962	0.017	46.87	47.62	0.999
	90	0.036	53.27	8.17	0.948	0.010	53.27	55.55	0.999
45	10	0.029	9.19	3.09	0.859	0.021	9.19	9.52	0.999
	30	0.022	28.73	4.77	0.930	0.014	28.73	29.41	0.999
	50	0.035	42.76	2.80	0.857	0.035	42.76	43.48	1.000
	70	0.020	48.46	5.46	0.979	0.012	48.46	50.00	0.999
	90	0.024	55.13	3.87	0.905	0.020	55.13	55.55	0.999
60	10	0.030	9.63	3.34	0.958	0.020	9.63	10.00	0.999
	30	0.024	28.27	4.71	0.970	0.015	28.27	28.57	0.999
	50	0.030	43.47	3.73	0.961	0.021	43.47	45.45	0.999
	70	0.018	49.91	4.47	0.978	0.015	49.91	50.00	0.999
	90	0.022	57.26	5.83	0.906	0.011	57.26	58.82	0.999

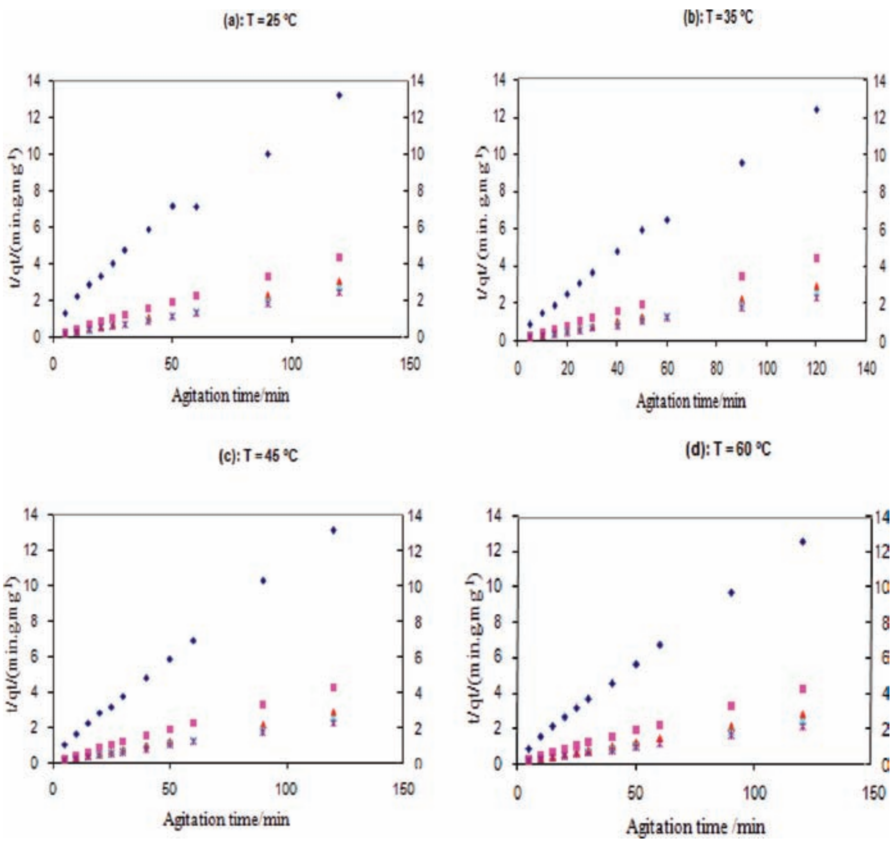

Figure 6. Pseudosecond-order kinetics at different temperatures. ◆, 10 mg·L^{-1}; ■, 30 mg·L^{-1}; ▲, 50 mg·L^{-1}; ×, 70 mg·L^{-1}; ∗, 90 mg·L^{-1}.

Table 4. Langmuir, Freundlich, and Temkin Constants for Sorption of Lead on Date Tree Leaves at Different Temperatures Using the Linear Method

	Langmuir constants			Freundlich constants				Temkin constants		
t	q_{mon}	K_L		K_F					A	
°C	$mg \cdot g^{-1}$	$mg \cdot g^{-1}$	R^2	$mg^{1-1/n} \cdot L^{1/n} \cdot g^{-1}$	$1/n$	n	R^2	B	$L \cdot mg^{-1}$	R^2
25	55.56	0.353	0.996	15.911	0.343	2.915	0.815	8.779	8.339	0.945
35	58.81	0.321	0.991	15.705	0.375	2.667	0.748	10.310	5.349	0.887
45	58.82	0.340	0.989	16.395	0.365	2.740	0.794	9.914	7.020	0.927
60	58.85	0.85	0.996	24.167	0.276	3.623	0.741	8.019	39.645	0.906

studied. Kinetic data were further treated with the pseudosecond-order kinetic model.

Pseudosecond-Order Model. The differential equation of the pseudosecond-order model is represented as:[52]

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \tag{3}$$

where $K_2/g \cdot mg^{-1} \cdot min^{-1}$ is the equilibrium rate constant of the pseudosecond-order sorption.

Integrating eq 3 for the boundary conditions $t = 0$ to t and $q_t = 0$ to q_t gives:

$$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{1}{q_e} t \tag{4}$$

Figure 6 shows the plots of t/q_t versus t for sorption of Pb(II) on the surface of date tree leaves at different initial concentrations and different temperatures. The values of K_2 and q_e(cal) can be obtained from the slope and intercept of the line, respectively. The results are summarized in Table 3 for each initial concentration and each temperature. It can be seen that the calculated coefficient of determination (R^2) is very close to unity and that the calculated (q_e (cal)) values agree well with the experimental ones. These results suggest that the pseudosecond-order model describes the sorption kinetics of the system studied more appropriately than the pseudofirst-order model. A similar phenomenon has been observed in the sorption of Cr(VI) by used tires and sawdust, congo red on coir pith carbon, and phosphate on calcined alunite and $ZnCl_2$-activated coir pith carbon.[53] From Table 3 it can be also seen that the variation of K_2 with the initial Pb(II) concentration can be divided into two regions. The first region where the initial Pb(II) concentration is less than 50 $mg \cdot L^{-1}$ exhibited an increase in value of K_2 which corresponds to the monolayer adsorption of lead onto date tree leaves. The second region corresponding to higher concentrations [(50 < Pb(II) < 90) $mg \cdot L^{-1}$] exhibited a decrease of K_2 which is due to the repulsion effect between the adsorbed and the nonadsorbed Pb(II).

Sorption Isotherms. The analysis and design of sorption separation processes requires the relevant sorption equilibrium, which is the most important piece of information in understanding the sorption process. The different parameters and the underlying thermodynamic assumption of these equilibrium models often provide some insight into both the sorption mechanism and the surface properties and affinity of sorbent.

In the present study, the sorption capacity and equilibrium isotherm for lead ions onto date tree leaves are estimated using three equilibrium models: Langmuir, Freundlich, and Temkin isotherm equations.

Linear Method. The Langmuir isotherm is based on the monolayer sorption of lead ions on the surface of date tree leaves sites and is represented by the following equation:[54]

$$q_e = q_{mon} \frac{K_L C_e}{1 + K_L C_e} \tag{5}$$

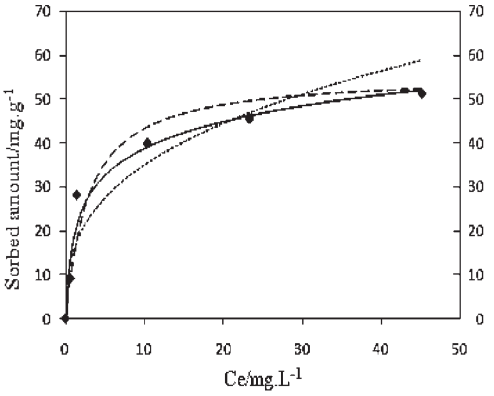

Figure 7. Sorption isotherms for lead onto date tree leaves (linear method). Conditions: pH 5.8; agitation speed = 200 rpm; agitation time = 2 h; ionic strength = 0.005 M, and temperature = 25 °C. ◆, experiment; — — —, Langmuir; —, Temkin; - - -, Freundlich.

where C_e is the concentration of the Pb(II) ion solution at equilibrium ($mg \cdot L^{-1}$), q_e is the amount of sorbed lead at equilibrium ($mg \cdot g^{-1}$), and q_{mon} and K_L are the Langmuir constants related to sorption capacity and the energy of sorption, respectively. The linear form of eq 5 can be written as:

$$\frac{C_e}{q_e} = \frac{1}{q_{mon} K_L} + \frac{1}{q_{mon}} C_e \tag{6}$$

The Freundlich isotherm describes the heterogeneous surface energies by multilayer sorption and is expressed by the equation:[55]

$$q_e = K_F {C_e}^{1/n} \tag{7}$$

where K_F and $1/n$ are the Freundlich constants related to sorption capacity and sorption intensity, respectively.

The Freundlich isotherm has been derived by assuming an exponentially decaying sorption site energy distribution. The linearized form of eq 7 can be obtained by taking logarithms on both sides:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{8}$$

The Temkin isotherm based on the heat of sorption of the ions, which is due to the sorbate and adsorbent interactions, is

Table 5. Langmuir, Freundlich, and Temkin Constants for Sorption of Lead on Date Tree Leaves at Different Temperatures Using the Nonlinear Method

	Langmuir constants			Freundlich constants				Temkin constants		
t	q_{mon}	K_L		K_F					A	
°C	$mg \cdot g^{-1}$	$mg \cdot g^{-1}$	R^2	$mg^{1-1/n} \cdot L^{1/n} \cdot g^{-1}$	$1/n$	n	R^2	B	$L \cdot mg^{-1}$	R^2
25	49.93	0.605	0.970	20.022	0.257	3.891	0.815	8.778	8.339	0.952
35	55.28	0.435	0.967	20.801	0.267	3.745	0.900	10.309	5.349	0.902
45	53.63	0.594	0.956	20.000	0.292	3.426	0.945	9.923	7.020	0.929
60	53.68	1.889	0.947	28.052	0.211	4.739	0.924	8.017	39.645	0.821

given by:[56]

$$q_e = B \ln A + B \ln C_e \tag{9}$$

where:

$$B = \frac{RT}{b} \tag{10}$$

B is related to the heat of sorption, and A is the equilibrium binding constant corresponding to the maximum binding energy.

The Langmuir, Freundlich, and Temkin isotherm constants as well as the coefficients of determination were obtained (Table 4) using the linear method which consisted of plotting C_e/q_e versus C_e, $\log(q_e)$ versus $\log(C_e)$, and q_e versus $\ln(C_e)$, respectively. From Table 4, it was observed that the coefficients of determination for the Freundlich isotherm equation are lower. These relatively lower values suggest that the equilibrium data do not follow the Freundlich isotherm equation. In all cases, the Langmuir isotherm exhibited the highest coefficient of determination, and the q_{mon} value is higher than experimental q_e. Figure 7 shows plots comparing the experimental data points and the three theoretical isotherms plotted on the same graph. The Temkin isotherm was found to be the most suitable model for the lead sorption system using date tree leaves even though the coefficients of determinations were lower than that obtained with Langmuir isotherm model.

Nonlinear Method. The abilities of the Langmuir, Freundlich, and Temkin isotherms, to model the equilibrium sorption data were also examined by using the nonlinear method. For this method, a trial and error procedure, which is applicable to computer operations, was developed to determine the isotherm parameters using an optimization routine to maximize the coefficient of determination in the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel.[57] The Langmuir, Freundlich, and Temkin isotherm constants as well as the coefficients of determination obtained by using the nonlinear method are presented in Table 5. From Tables 4 and 5, it was observed that the Langmuir and Freundlich isotherm constants calculated by linear and nonlinear methods, respectively, were high but the difference between Temkin isotherm constants determined by the linear and nonlinear methods was very low. Figure 8 obtained by using the nonlinear method shows that the Temkin isotherm represents well the sorption of lead onto date tree leaves.

In spite of much higher coefficients of determination obtained using Langmuir isotherm, this model does not describe perfectly the equilibrium data because q_{mon} values are lower than that of experimental q_e. This result suggests that it is not appropriate to use the coefficient of determination of the linear regression method for comparing the best-fitting isotherms. The nonlinear method is a better way to obtain the isotherm constants.

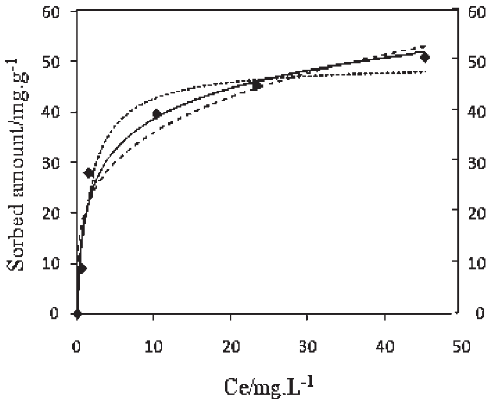

Figure 8. Sorption isotherms for lead onto date tree leaves (nonlinear method). Conditions: pH 5.8; agitation speed = 200 rpm; agitation time = 2 h; ionic strength = 0.005 M, and temperature = 25 °C. ◆, experiment; — — —, Langmuir; —, Temkin; - - -, Freundlich.

Table 6. Comparison of Monolayer Sorption Capacities of Various Sorbents for Lead Sorption

sorbent	$q_{mon}/mg \cdot g^{-1}$	ref
date leaves	58.83	present study
hazelnut shell	28.18	58
almond shell	8.08	58
rice husk	5.69	59
chitosan	8.31	59
pretreated arca shell	30.39	60
native salsola steams	34.3	61
hydrolyzed salsola steams	42.2	61
esterified salsola stems	10.1	61
native salsola leaves	44.2	61
hydrolyzed salsola leaves	52.2	61
esterified salsola leaves	10.8	61
orange peel	41.99	62

The sorption capacity of date tree leaves for the removal of Pb(II) has been compared with those of other sorbents reported in literature, and the values of sorption capacities have been summarized in Table 6. The values are reported in the form of monolayer sorption capacity. It should be noted that the values and comparisons reported for lead removal capacity have only a relative meaning because of different testing conditions (temperature, pH, stirring speed, and wastewater composition) and type of biomaterials.

The experimental data of the present investigation show that natural date tree leaves exhibit a reasonable capacity for Pb(II) sorption from aqueous solutions. This result reveals that natural date tree leaves are an effective sorbent for lead(II) ions from wastewater.

The heat of sorption ΔH, Gibbs energy change ΔG, and entropy change ΔS of the sorption of Pb(II) onto date tree leaves were determined using the following equations:[62]

$$\ln K = \ln K_0 - \frac{\Delta H}{RT} \qquad (11)$$

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (12)$$

$$\Delta G = -RT \ln K \qquad (13)$$

where K is the equilibrium constant related to the energy of adsorption, K_0 is the constant, and R and T/K are the gas constant and temperature, respectively.

Thus from $\ln K$ versus $1/T$ plot, the ΔH is calculated and found to be 21.59 $\text{kJ} \cdot \text{mol}^{-1}$. A positive value of ΔH confirms the endothermic nature of the process. The negative values (−7.37, −7.52, −7.92, and −10.83) $\text{kJ} \cdot \text{mol}^{-1}$ of ΔG indicate the spontaneous nature of sorption for lead at (25, 35, 45, and 60) °C, respectively. The positive values of ΔS (95.45 $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) suggest the increased randomness at the solid/solution interface during the sorption of lead(II) onto date tree leaves.

■ CONCLUSION

The present study shows that date tree leaves can be used as a sorbent for the removal of lead from aqueous solutions. A higher percentage of Pb(II) removal by date tree leaves is possible provided that the initial concentration in the solution is low.

The sorption of lead onto date tree leaves depends on solution pH, contact time, initial concentration of Pb(II), adsorbent dose, agitation speed, ionic strength, and temperature. The maximum sorption uptake is achieved at pH 5.8, and the results show that the capacity of sorption increases with a rise in initial concentration of lead in solution at any temperature and with the powdered date tree leaf dosage at 1 $\text{g} \cdot \text{L}^{-1}$. The time, agitation speed, and ionic strength corresponding to the maximum sorption are 50 min, 200 rpm, and 0.005 M, respectively.

The equilibrium data fit perfectly the Temkin model of sorption, showing that the heat of adsorption of all of the molecules in the layer decreases linearly with coverage due to adsorbent−adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the binding energies, up to some maximum binding energy. The value for maximum sorption is 57 $\text{mg} \cdot \text{g}^{-1}$ at 60 °C. The kinetics of lead(II) sorption in the date tree leaves follows the pseudosecond-order model.

The enthalpy change for the sorption process is 21.59 $\text{kJ} \cdot \text{mol}^{-1}$, which indicates very strong interaction forces between lead(II) ions and date tree leaves and indicates the endothermic nature of the process. The ΔG values are negative, which indicates that the sorption is spontaneous, and the positive value of ΔS (95.45 $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) suggests increased randomness at the solid/solution interface.

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