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Biosorption of $\mbox{Pb}^{\mbox{\tiny 2+}}$ from Natural Water using Date Pits: A Green Chemistry Approach

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Abstract

Removal of Pb²⁺ ions from aqueous solutions by adsorption onto Date Pits (DP) has been investigated. The date pits (sorbent) may represent an environmental problem. The characteristic parameters (solution pH, initial concentration of Pb²⁺, sorbent dose, shaking time and temperature) influencing the adsorption process have been examined. pH=7 is found the best one having high floatability of 6 g l⁻¹ dose of DP. The Freundlich and Langmuir were applied. The change in Gibbs free energy change (Δ G°), enthalpy (Δ H°) and entropy (Δ S°) were also calculated. Under the optimum experimental conditions employed, the removal of ~95% of Pb²⁺ was attained. The procedure was successfully applied to remove Pb²⁺ from natural water samples. The SEM image of DP before and after lead adsorption shows complete adsorption.

Keywords: Heavy metals; Biosorption; Adsorption

Introduction

Heavy metal toxicity has become a major concern today due to its deleterious effects on health and environment [1,2]. Heavy metals are among the chief pollutants of surface and groundwater [3]. The contamination of natural waters with toxic metals has become one of the major concerns of environmental researchers in recent years due to water importance to environment and mankind [4]. Lead being the most toxic metal, ranks second in the list of prioritized hazardous substances issued by the US Agency for toxic substances and Disease Registry [5]. Lead is attracting wide attention of environmentalists as one of the most toxic heavy metals [6]. Lead has been a major focus in wastewater treatment because it is associated with many health hazards [7]. Lead is an important compound used as an intermediate in several industrial such as plating, paint and dyes, chemicals and allied products, lead acid storage batteries, ceramic and glass industries printing, ammunition, lead smelting and mine tailings, automobile industry, agricultural runoff, chemical spills and municipal wastewaters [2,8,9]. Through the food chain system of soil-plant-animal-human, Pb²⁺ is transferred into animals and human beings [8]. The major biochemical effect of Pb2+ is its interference with heme synthesis, which leads to hematological damage [7]. Lead poisoning in human caused severe damage to the kidneys, liver, brain, nervous and reproductive systems. Long term exposure may induce sterility, abortion, and neonatal death [10]. Due to the toxic effects of lead ions, the removal of them from waters and wastewaters is important in terms of protection of public health and environment [11]. Adsorption process was studied and emerged as one of the promising technique due to its low initial cost, simplicity of design, ease of operation and insensitivity to toxic substances [2]. It is necessary to have a low-cost material to treat large volumes of waste water. The use of low-cost sorbents has been thoroughly investigated instead of other more expensive materials, for example, natural and waste materials coming from industrial, agriculture and forestry activities have high capacity for removing metal ions [12]. The removal efficiency of new and inexpensive adsorbents can be tested first in model aqueous solutions (distilled water) and then in spiked ground and drinking water. One cheap and easily available material having possibilities as a suitable sorbent for Pb²⁺ ions is date pits. The date palm, *Phoenix dactylifera*, is the oldest tree known to be cultivated by man. Since ancient times, the date palm has been a significant source of food for both human and livestock [13]. The date tree (Phoenix dactylifera L.) is an important staple food and a strategic plant in many arid regions of the world. Date fruits are an important food item, with plenty vitamins and minerals. They are eaten fresh or are dried and stored for later consumption [14]. Individual date fruits contain a pit which, depending on the variety, accounts for about 10% to 18% weight of the fruits. The pits are generally used as complementary feed materials or as a conventional soil fertilizer also used for extracting oil for cosmetic and pharmaceutical purposes. Date pits contained 7.1-10.3% moisture, 5.0-6.3% protein; 9.9-13.5% fat; 65-69% neutral detergent fiber; and 1.0-1.8% ash. Total carbohydrate content of date pits is 71.9-73.4% and 3.8-5.8% total sugars [15,16]. We reported here the use of date pits as an adsorbent for removal of Pb²⁺ from aqueous solutions.

Experimental

Sorbent samples and solutions

The date pits samples used in this study were obtained from some date's factories located in Mansoura city, Egypt. The samples were collected, washed with water and dried for 2 h in large trays in an oven at 125°C, allowed to cool, crushed and sieved with size (25-63 µm). The samples were packed into stoppered bottles and stored in a desiccator for future use. All the solutions were prepared from certified reference materials. Aqueous solutions were prepared in deionized water. The Pb²⁺ stock solution 1002 \pm 2 mg/l was prepared from [Pb(NO₃)₂] in HNO₃ 0.5 mol/l (Merck, Germany). The working solutions were prepared daily as required.

Apparatus

A VWR model 3500 digital shaker was used for shaking solutions. Sartotius digital balance was used for all weights, the infrared spectroscopy was undertaken via a Mattson 5000 FT-IR

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spectrophotometer using the KBr disc method. The measurements were carried out using Atomic Absorption Spectrophotometer AA240FS (Varian, Australia). Also, the stirring of solutions was performed with a magnetic stirrer, Jenway 1000. The pH was measured using pH meter (symphony, USA) provided with a glass electrode.

Procedure

Unless stated otherwise, all batch sorption experiments were done at room temperature ($25 \pm 2^{\circ}$ C). Known volumes of Pb²⁺ stock solution were pipetted into quick-fit glass bottles containing 0.3 g of DP sorbent in 50 ml aqueous solution to give concentrations ranging from 1 mg l⁻¹ to 30 mg l⁻¹. Since the pH of any resulting solution was 3.0, no further controlling of pH was necessary since it was suitable for most adsorption experiments. The resulting solution was then shaken at 250 rpm and samples were taken at fixed time periods (1, 3, 5, 10, 15, 30, 60, 120 min) in order to study the kinetics of the adsorption process. Preliminary experiments showed that 60 min was sufficient for adsorption of Pb²⁺ onto DP. The samples were subsequently filtered



Figure 1: Adsorption % of 5 mg l^{-1} Pb^{2*} by 0.3 g DP vs. shaking time at different pH.



Figure 2: Amount of $Pb^{2\ast}$ concentration (mg $l^{\cdot1})$ adsorbed on DP at different shaking times.

off and the residual Pb(II) concentration in the filtrate was determined by atomic absorption spectrometry (at wavelength of 217 nm, lamp current 5 mA, slit width 1 nm, acetylene as fuel, air as support). The percentage adsorption of Pb²⁺ from the solution was calculated from the relationship:

Page 2 of 8

% Adsorption = $(C_i - C_r)/C_i \times 100$

Where C_i corresponds to the initial concentration of Pb²⁺ ions and C_r is the residual concentration in the filtrate after shaking for a definite time period. The metal uptake q (mg/g) was calculated as:

 $q = [(C_i - C_r)/m].V$

Where m is the quantity of sorbent (g) and V is the volume of the suspension (L). To assess the applicability of the procedure, another series of experiments was conducted on 50 ml of clear and prefiltered natural water samples with an initial pH adjusted to 3.0. These suspensions contained 5 mg l^{-1} Pb²⁺, ES 0.3 g and were shaken for the optimum time (60 min) at 250 rpm.

Results and Discussion

The IR spectrum of date pits showed bands at 3340-3440 cm⁻¹ indicating the stretching of inter and intramolecular hydrogen bonding in cellulose and lignin. The band at 2924 cm⁻¹ indicates symmetric or asymmetric v(C–H) of aliphatic acids. The band at 1728 cm⁻¹ due to v(C=O) is attributed to the non-ionic carboxyl groups v(COOH or – COOCH₃), and may be assigned to the carboxylic acids or their esters. Asymmetric stretching vibrations of ionic carboxylic groups (–COO–), appeared at 1632, and that at 1084 cm⁻¹ is assigned to v(C–OH) of alcoholic groups and carboxylic acids [17,18].

Effect of pH

One of the most important parameters in adsorption process is the pH of the medium. Moreover, the sorption of Pb²⁺ by DP is also influenced by the surface properties of the sorbent and lead species present in aqueous solution. Variation in pH can affect the surface charge of the adsorbent and the degree of ionization and speciation of the metal adsorbate [19]. Pb2+ uptakes on DP may involve coordination, ion exchange and adsorption [20]. The pH dependence of the binding showed that ion exchange, electrostatic interactions, hydrogen bond and other phenomena are involved in the binding mechanism [20]. Figure 1 illustrates the effect of pH on Pb²⁺ adsorption by DP. In the ion-exchange mechanism, metal ions bind to anionic sites by displacing protons from acidic groups. In the complexation mechanism, metal ions sequestration is viewed as the coordination of metal ions to surface functional groups [20]. It was confirmed that DP is dominated by negatively charged sites that are largely hydroxyl groups. Pb2+ may form complexes with surface functional groups of DP such as cellulose-OH and phenolic-OH through ion-exchange reactions.

Effect of Pb²⁺ concentration and sorbent dose

The effect of initial Pb²⁺ concentration (1-30 mg l⁻¹) on its adsorption by DP (0.3 g) after shaking from 1 to 120 min was shown in Figure 2. It was found that the increase of initial Pb²⁺ concentration, the q [metal uptake (mg/g)] increases. The increase of q with increasing C_0 [initial metal ion concentration] was expected due to the increase of the sorbed ion concentration per unit weight of DP. Moreover, increasing the Pb²⁺ concentration increases the diffusion of Pb²⁺ in the boundary layer resulting in higher sorption by DP. Varying the amounts of DP from 0.05 to 1 g, on the adsorption of Pb²⁺ [5 mg l⁻¹] of pH 6 was depicted in Figure 3. The data show that the adsorption increases as the amount of DP increases. This agrees well with the data shown in



Figure 2. Moreover, 6 g l^{-1} dose of DP was an optimum one for further experiments.

Kinetics of the adsorption process

The adsorption of Pb²⁺ is quite rapid at the first stage suggesting that the adsorption occurs mainly at the surface of the sorbent and to some extent by the internal macro-pores, transitional pores and micro-pores. The uptake increases with increasing the initial Pb²⁺ concentration attributing to higher collision between the Pb²⁺ and sorbent. One hour of shaking was found suitable for maximum adsorption. When the data in Figure 2 were re-plotted against the square root of the shaking time (t^{1/2}), the obtained linear correlation (Figure 4) may verify the Morris-Weber equation:

 $q = K_{d}(t)^{1/2}$

where q is the amount of Pb²⁺ adsorbed (mg/g) and K_d is the initial rate of intraparticle diffusion (mg g⁻¹min^{-0.5}). This indicates that an intra-pore diffusion mechanism was involved in the adsorption of Pb²⁺ by DP. Figure 4 shows two distinct regions: an initial linear portion due to the boundary layer effect [21,22] and a second due to intra-particle diffusion effect [23]. However, the fact that the line depicted in Figure 4 is nonlinear indicating that intra-pore diffusion is not the controlling step in sorption of Pb²⁺ by DP [24,25]. The data agree with those of Juang et al. [26]. The value of the rate constant K_d is 0.037 mg g⁻¹min^{-0.5}, which gives indication about the mobility of the Pb²⁺ toward the DP surface. The kinetic data was examined by Bangham equation [27]:

 $\text{Log log } [C_i / (C_i - q_m)] = \log (K_o m / 2.303V) + \alpha \text{ Log t}$

Plot of Log log $[C_i/(C_i \cdot q_m)]$ vs. log t gives a straight line (Figure 5). The results show that the diffusion of Pb²⁺ into DP pores played a role in the adsorption process and is similar to those described elsewhere [28]. The calculated K_o and α constants are 0.0037 and 0.148, respectively. The kinetic data obtained in Figure 5 for Pb²⁺ adsorption by DP were tested by Lagergren equation, as cited by Gupta and Shukla [29]:

$$\log (q_e - q_t) = \log q_e - K_{ads} t / 2.303$$

where q_t is the amount of Pb²⁺ adsorbed (mg g⁻¹) at any given time t (min), qe is the amount of metal ion adsorbed (mg g⁻¹) at equilibrium

and K_{ads} is the pseudo-first order reaction rate constant for adsorption (g mg⁻¹min⁻¹). The linear plot of log (q_e – q) versus t (Figure 6) shows the first-order nature of the process. The K_{ads} is 0.0925 g mg⁻¹min⁻¹. The pseudo second order kinetic model may be expressed by the equation:

Page 3 of 8

$$t/q_{t} = 1/k_{2}q_{e}^{2} + 1 t/q_{e}$$

where k_2 (g mg⁻¹ min⁻¹) is the equilibrium rate constant for the pseudo-second-order adsorption and can be obtained from the plot of t/qt against t (Figure 7) and it is calculated to be 0.493 (g mg⁻¹ min⁻¹).

Also, the kinetics of the adsorption was examined by linear form of Elovich model which describes a number of reaction mechanisms including bulk and surface diffusion and the activation and deactivation of catalytic surfaces. It gives a straight line by plotting (q_e) vs. (ln t). It is represented by [10]:

$$qt = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(\alpha\beta)$$

Where α (mg g⁻¹min⁻¹) and β (mg g⁻¹min⁻¹) are the constants of the adsorption and are determined from a plot depicted in Figure 8. Elovich













model is based on a kinetic principle assuming that, the adsorption sites increase exponentially with adsorption which implies a multilayer adsorption. The Elovich coefficients related to initial adsorption rate (a) and surface coverage (b) were calculated to be 0.834 mg g⁻¹min⁻¹ and 11.521 mg g⁻¹min⁻¹ respectively. All kinetic data for the adsorption of Pb²⁺ onto DP, calculated from the related plots, are summarized in Table 1.

Adsorption isotherms

Adsorption isotherms can be generated based on numerous theoretical models where Langmuir and Freundlich models are the most commonly used. The Langmuir model assumes that the uptake of Pb^{2+} occurs on a homogenous surface by monolayer adsorption without any interaction between the adsorbed ions. The linear form of the Langmuir equation applied to the Pb^{2+} adsorption data in Figure 2 was:

$$1/q_e = 1/q_{max} + (1/q_{max}k_L) 1/C_e$$

Where q_e is the amount of Pb²⁺ (mg g⁻¹) adsorbed at equilibrium, C_e is the final equilibrium concentration (mg L⁻¹), k_L is the Langmuir



Figure 8: Plot of (q_t) vs. (In t) for the adsorption of Pb²⁺ by 0.3 g DP at pH 6.

Kinetic model	Parameter	Value
Pseudo-first-order	K _{ads} (g mg⁻¹ min⁻¹)	0.0925
	q _{e (exp)} (mg g ⁻¹)	0.660
	q _{e (theo)} (mg g ⁻¹)	0.473
	r ²	0.9947
Pseudo-second-order	K ₂ (g mg ⁻¹ min ⁻¹)	0.493
	q _{e (exp)} (mg g ⁻¹)	0.660
	q _{e (theo)} (mg g ⁻¹)	0.679
	r ²	0.9997
Elovich model	α (mg g ⁻¹ min ⁻¹)	0.8335
	β (mg g ⁻¹ min ⁻¹)	11.521
	r ²	0.9788
Intraparticle diffusion model	K _d (g/mg min)	0.039
	r ²	0.90
Bangham's equation	K	0.0037
	Å	0.148
	r ²	0.947

Table 1: Kinetic model parameters for adsorption of Pb2+ onto DP.







equilibrium constant (L mg⁻¹) and q_{max} is the maximum adsorption capacity (mg g⁻¹). Figure 9 shows that the plot of $1/q_e vs. 1/C_e$ gave a straight line suggesting the applicability of the Langmuir model. The values of maximum adsorption capacity (q_{max}) Langmuir cons. (k_L) and the correlation coefficient (r) were 2.891 mg g⁻¹, 0.283 L mg⁻¹ and 1, respectively Also, the equilibrium parameter R_L was found to be 0.0334 indicating that the adsorption process is favorable.

The essential feature of the Langmuir isotherm can be expressed in terms of dimensionless separation cons or equilibrium parameter (R_L) to predict the type of adsorption process, which is defined as: R_L= 1/ (1+K_L C₀). The values of R_L indicate the type of isotherm to be irreversible (R_L=0), favorable (0<R_L<1), linear (R_L= 1) or unfavorable (R_L>1) [30]. The R_L value was found to be 0.0334, less than 1 and greater than 0.

On the other hand, the Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface. The equation is commonly represented by:

 $\ln q_e = \ln k_F + 1/n \ln C_e$

Where $K_{\rm F}$ (l g⁻¹) and 1/n are the Freundlich isotherm constants characteristic of the system, which indicate the adsorption capacity and the adsorption intensity (n), respectively. Figure 10 shows the applicability of this equation on the adsorption of Pb²⁺ on DP. The parameters $K_{\rm F}$ and n for Pb²⁺ adsorption onto DP were calculated from intercept and the slope of the figure giving values of 0.589 l g⁻¹ and 1.216, respectively with a correlation coefficient r=0.998. It was known that favorable adsorption occurs when 1/n>1 [31].

Page 5 of 8

Temkin isotherm is represented by the linear equation as follows:

$$q_e = B \ln K_t + B \ln C_e$$

where K₁ (L g⁻¹) is the equilibrium binding constant corresponding to the maximum binding energy and constant B=RT/b represents the heat of adsorption, while R is the universal gas constant, T is the absolute temperature in Kelvin and 1/b indicates the adsorption potential of the adsorbent. Both K₁ and B can be determined from a plot q_e versus C_e (Figure 11) [10]. The equilibrium binding cons. (K₁) and the heat of adsorption (b) were calculated from the intercept and slop giving the values of 12.767 L g⁻¹ and 7.742 kJ mol⁻¹ respectively. The isotherm parameters for the adsorption of Pb²⁺ onto DP are given in Table 2. The sorption data was modeled by Dubinin-Radushkevich (D–R) isotherm

Equilibrium model	Parameter	Value
Langmuir isotherm	q _{max} (mg g ⁻¹)	2.891
	k _L (I mg ⁻¹)	0.283
	RL	0.0334
	r ²	1
Freundlich isotherm	K _F (mg g ⁻¹)	0.589
	N	1.216
	r ²	0.9983
Temkin isotherm	K _T	12.767
	B (I g ⁻¹)	0.3204
	b (kJ mol ⁻¹)	7.742
	r ²	0.9239
Dubinin-Radushkevich model	q _{max} (mol g ⁻¹)	2.4×10-6
	β (mol ² k J ⁻²)	0.199
	E (K J mol ⁻¹)	1.585
	r ²	0.9542





Page 6 of 8

equation (Figure 12) to determine the adsorption type (physical or chemical). The linear form of this model is expressed by [27,32]:

 $\ln q_e = \ln q_m - \beta \epsilon^2$

Where q_e is the amount of the metal adsorbed per unit dosage of DP (mol l⁻¹), q_m the monolayer capacity (mol g⁻¹), and β is the activity-coefficient related to mean sorption energy (mol² J⁻²) and ϵ is the Polanyi potential described as: ϵ =RT ln (1 +1/C_e). The mean sorption energy, E (kJ mol⁻¹), can be calculated by the equation [24,32]:

 $E = (2 \beta)^{-1/2}$

As seen in Figure 12, the slope of the D–R plot gives β constant and was evaluated as 0. 199 (mol² kJ⁻²). The sorption energy (E) was found to be 1.585 kJ mol⁻¹. It is generally assumed that if the sorption energy is below 8 kJ mol⁻¹, the sorption can be affected by physical forces such as Vander Der Walls forces, while if E is between 8 and 16 kJ mol⁻¹, the sorption is governed mainly by ion exchange. Sorption may be governed by particle diffusion if E > 16 kJ mol⁻¹ [33]. Therefore, the E value calculated for the adsorption of Pb²⁺ onto DP showed that the sorption may be physical in nature.

Effect of temperature and thermodynamic parameters

The temperature has two major effects on the sorption process. Increasing the temperature is known to increase the rate of diffusion of the sorbate; changing the temperature will change the equilibrium capacity of the sorbent for a particular sorbate. In this study, a series of experiments were conducted on the adsorption of 5 mg l⁻¹ Pb²⁺ onto 0.3 g of DP at 278, 283, 298, 313 and 333 K to investigate the effect of temperature on the sorption dynamics at different stirring times. The results depicted in (Figure 13) showed that the sorption increases as the temperature increases confirming that the process is endothermic in nature. Such results may either be attributed to the creation of some new active sites on the sorbent or to the acceleration of some originally slow adsorption steps. Moreover, the enhancement of mobility of Pb2+ from the bulk of solution towards the adsorbent surface should also be taken into consideration. This agrees well with the literature data [34,35]. Moreover, there was a decrease in the equilibration time to reach to a 100% for lead adsorption.

In order to investigate the thermodynamic parameters for the







Figure 14: Thermodynamic distribution coefficient (K_d) calculated for the adsorption of Pb^+ on DP as a function of temperature.

Sample (location)	Added (mg l ⁻¹)	Adsorbed (mg l ⁻¹)	Re %
Distilled water	5	3.95	79.0
Tap water (our laboratory)	5	4.52	90.5
Nile water (Mansoura City)	5	4.49	89.8
Underground water (Mansoura City)	5	4.38	87.6
Sea water (Sharm El-Sheikh)	5	4.32	86.4

Table 3: Recovery of Pb2+ added to some water samples using 0.3 g of DP sorbent.

adsorption of Pb^{2+} by DP, the distribution coefficient K_d (l g⁻¹) was calculated at 278, 283, 313, 333 K according to the following equation [31,36]:

$$K_d = q_e / C_e$$

The K_d values at 278, 283, 313, 333 K are 0.206, 0.236, 0.238, and 2.82 L g⁻¹ respectively. These results show that the K_d increases with temperature and revealing that the sorption of Pb²⁺ by DP may be endothermic. The enthalpy change (Δ H^{*}) and entropy change (Δ S^{*}) were calculated from the slope and intercept of the plot of ln K_d against 1/T, respectively, as depicted in (Figure 14) and according to the following equation [31,37,38]:

 $\ln K_d = \Delta S^{\circ}/R - \Delta H^{\circ}/RT$

The Gibbs free energy change (ΔG°) was calculated by: ΔG° = -RT ln K_d, where R is the universal gas constant (8.314 J mol⁻¹ K⁻¹) and T is the absolute temperature (K).

The calculated enthalpy change ΔH° was found to be 3.74 J mol⁻¹. The positive value of ΔH° clarified that the sorption process is endothermic. The entropy change (ΔS°) was found to be 0.105 J mol⁻¹ K⁻¹. According to Sari et al. [28], this result showed that Pb²⁺ in bulk phase (aqueous solution) is in a much chaotic distribution compared with the relatively ordered state of solid phase (sorbent surface). Moreover, the Gibbs free energy change (ΔG°) was -0.239, -0.243, -0.269, and -0.287 kJ mol⁻¹ for the adsorption of Pb²⁺ at 278, 283, 313 and 333 K, respectively. The negative ΔG° values indicate that the adsorption of Pb²⁺ on DP is spontaneous thermodynamically.









6

7

9

10

keV

Application

To investigate the applicability of the recommended procedure, a series of experiments were performed to recover 5 mg l^{-1} of Pb^{2+} added to aqueous and some natural water samples. The adsorption experiments were carried out using 50 ml clear and filtered. The results obtained are listed in Table 3.

XRD, EDX and SEM studies

Full Scale 3486 cts Cursor: 10.060 (17 cts)

Powered XRD studies help in understanding the changes

occurred on the structure of DP sorption. XRD data of DP before and after adsorption are shown in Figure 15a and b and it provided evidence of modification in the surface morphologies. The EDX graph was shown in Figure 16a and b which also show the presence of the Pb^{2+} after its adsorption on DP (Figure 16b). To explain the morphological changes in the surface of the adsorbents in the coverage of pores of the DP due to the adsorption of Pb(II), SEM image of DP before and after lead adsorption is shown in Figure 17 a and b.





Figure 17 (a): SEM of DP before treatment.



Figure 17 (b): SEM of DP after treatment with Pb2+.

Conclusion

Date pits were used to remove Pb^{2+} ions from aqueous solutions. The parameters (solution pH, initial concentration of Pb^{2+} , sorbent dose, shaking time and temperature) have been examined. pH=6 is found the best one having high floatability of 6 g l⁻¹ dose of DP. The change in ΔG° , ΔH° and ΔS° were calculated. The removal of ~95% of Pb²⁺ was attained. The procedure was successfully applied to remove Pb²⁺ from natural water samples.

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