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

Samir E Samra$^1$, Bakir Jeragh$^2$, Ahmed M EL-Nokrashy$^3$ and Ahmed A El-Asmy$^{1,2}$

$^1$Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt
$^2$Chemistry Department, Faculty of Science, Kuwait University, Kuwait
$^3$Central Laboratory of drinking water, Dakahliya Comp. for Water, Mansoura, Egypt

Abstract

Removal of Pb$^{2+}$ 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 Pb$^{2+}$, 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 ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) were also calculated. Under the optimum experimental conditions employed, the removal of ~85% of Pb$^{2+}$ was attained. The procedure was successfully applied to remove Pb$^{2+}$ 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, Pb$^{2+}$ is transferred into animals and human beings [8]. The major biochemical effect of Pb$^{2+}$ 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 Pb$^{2+}$ 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 Pb$^{2+}$ 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 stopped 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 Pb$^{2+}$ stock solution 1002 ± 2 mg l$^{-1}$ was prepared from [Pb(NO$_3$)$_2$] in HNO$_3$ 0.5 mol l$^{-1}$ (Merck, Germany). The working solutions were made by diluting with deionized water. Further dilutions 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...
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 carried out at room temperature (25 ± 2°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 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:

\[
\% \text{Adsorption} = \left(\frac{C_i - C_r}{C_i}\right) \times 100
\]

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:

\[
q = \left(\frac{C_i - C_r}{m}\right) \times V
\]

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 pre-filtered 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 ν(C–H) of aliphatic acids. The band at 1728 cm⁻¹ due to ν(C=O) is attributed to the non-ionic carboxyl groups ν(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 ν(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
Citation: Samra SE, Jeragh B, EL-Nokrashy AM, El-Asmy AA (2014) Biosorption of Pb\textsuperscript{2+} from Natural Water using Date Pits: A Green Chemistry Approach. Mod Chem appl 2: 131. doi:10.4172/2329-6798.1000131

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

**Kinetics of the adsorption process**

The adsorption of Pb\textsuperscript{2+} 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 Pb\textsuperscript{2+} concentration attributing to higher collision between the Pb\textsuperscript{2+} 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\textsubscript{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 Pb\textsuperscript{2+} adsorbed (mg/g) and K\textsubscript{d} is the initial rate of intraparticle diffusion (mg g\textsuperscript{-1} min\textsuperscript{-0.5}). This indicates that an intra-pore diffusion mechanism was involved in the adsorption of Pb\textsuperscript{2+} 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 Pb\textsuperscript{2+} by DP [24,25]. The data agree with those of Juang et al. [26]. The value of the rate constant K\textsubscript{d} is 0.037 mg g\textsuperscript{-1} min\textsuperscript{-0.5}, which gives indication about the mobility of the Pb\textsuperscript{2+} toward the DP surface. The kinetic data was examined by Bangham equation [27]:

$$ \log \log \left[ C_i / (C_i - q_m) \right] = \log (K_m / 2.303V) + a \log t $$

Plot of Log log [C\textsubscript{i} / (C\textsubscript{i} - q\textsubscript{m})] vs. log t gives a straight line (Figure 5). The results show that the diffusion of Pb\textsuperscript{2+} into DP pores played a role in the adsorption process and is similar to those described elsewhere [28]. The calculated K\textsubscript{m} and a constants are 0.0037 and 0.148, respectively. The kinetic data obtained in Figure 5 for Pb\textsuperscript{2+} adsorption by DP were tested by Lagergren equation, as cited by Gupta and Shukla [29]:

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

where q\textsubscript{e} is the amount of Pb\textsuperscript{2+} adsorbed (mg g\textsuperscript{-1}) at equilibrium and K\textsubscript{ads} is the pseudo-first order reaction rate constant for adsorption (g mg\textsuperscript{-1} min\textsuperscript{-1}). The linear plot of \( \log (q_t - q) \) versus t (Figure 6) shows the first-order nature of the process. The K\textsubscript{ads} is 0.0925 g mg\textsuperscript{-1} min\textsuperscript{-1}. The pseudo second order kinetic model may be expressed by the equation:

$$ \frac{t}{q_t} = \frac{1}{K_s q_e^2} + \frac{1}{q_e} t $$

where K\textsubscript{s} (g mg\textsuperscript{-1} min\textsuperscript{-1}) is the equilibrium rate constant for the pseudo-second-order adsorption and can be obtained from the plot of t/q\textsubscript{t} against t (Figure 7) and it is calculated to be 0.493 (g mg\textsuperscript{-1} min\textsuperscript{-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\textsubscript{t}) vs. (ln t). It is represented by [10]:

$$ q_t = \frac{1}{\beta} \ln(q_0) + \frac{1}{\beta} \ln t $$

Where q\textsubscript{0} (mg g\textsuperscript{-1} min\textsuperscript{-1}) and \( \beta \) (mg g\textsuperscript{-1} min\textsuperscript{-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⁻¹ min⁻¹ and 11.521 mg g⁻¹ min⁻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 Pb²⁺ 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 Pb²⁺ adsorption data in Figure 2 was:

\[
\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max} k_L} \frac{1}{C_e}
\]

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 6: Plot of log (qe - q) vs. stirring time (t) for the adsorption of 5 mg L⁻¹ Pb²⁺ by 0.3 g DP at pH 6.](image)

![Figure 7: Plot of (t/q_e) vs. stirring time (t) for the adsorption of Pb²⁺ by 0.3 g DP at pH 6.](image)

![Figure 8: Plot of (t/q_e) vs. (ln t) for the adsorption of Pb²⁺ by 0.3 g DP at pH 6.](image)

![Figure 9: Langmuir plot for Pb²⁺ adsorption onto 0.3 g DP.](image)

| 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          | \(\alpha\) (mg g⁻¹ min⁻¹) | 0.8335  |
|                        | \(\beta\) (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     | \(K_o\)       | 0.0037  |
|                        | \(A\)         | 0.148   |
|                        | \(r^2\)       | 0.947   |

![Table 1: Kinetic model parameters for adsorption of Pb²⁺ onto DP.](image)
equilibrium constant (L mg⁻¹) and qmax is the maximum adsorption capacity (mg g⁻¹). Figure 9 shows that the plot of 1/q vs. 1/C gave a straight line suggesting the applicability of the Langmuir model. The values of maximum adsorption capacity (qmax), Langmuir cons. (kL) and the correlation coefficient (r) were 2.891 mg g⁻¹, 0.283 L mg⁻¹ and 1, respectively. Also, the equilibrium parameter RL 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 (RL) to predict the type of adsorption process, which is defined as: RL = 1/(1+KLC0). The values of RL indicate the type of isotherm to be irreversible (RL=0), favorable (0<RL<1), linear (RL = 1) or unfavorable (RL>1) [30]. The RL 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:

\[ \ln q_e = \ln k_f + \frac{1}{n} \ln C_e \]

Where Kf (L g⁻¹) and 1/n are the Freundlich isotherm constants 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 Kf 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].

Temkin isotherm is represented by the linear equation as follows:

\[ q_e = B \ln K_t + B \ln C_e \]

where Kt (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 Kt and B can be determined from a plot q vs. C (Figure 11) [10]. The equilibrium binding cons. (Kt) 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       | qmax (mg g⁻¹) | 2.891         |
|                         | kL (L mg⁻¹)   | 0.283         |
|                         | RL           | 0.0334        |
|                         | r²           | 1             |
| Freundlich isotherm     | Kf (mg g⁻¹)  | 0.589         |
|                         | N            | 1.216         |
|                         | r²           | 0.9983        |
| Temkin isotherm         | Kt           | 12.767        |
|                         | B (L g⁻¹)    | 0.3204        |
|                         | b (kJ mol⁻¹) | 7.742         |
|                         | r²           | 0.9239        |
| Dubinin-Radushkevich model | qmax (mol g⁻¹) | 2.4×10⁻⁶    |
|                         | β (mol² k J⁻²) | 0.199        |
|                         | E (kJ mol⁻¹)  | 1.585         |
|                         | r²           | 0.9542        |
Adsorption %

Figure 13: Effect of temperature on the sorption % of Pb²⁺ onto DP at different shaking times.

\[ \ln q_e = \ln q_m - \beta \frac{x}{T} \]

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 \( \beta \) is the activity-coefficient related to mean sorption energy (mol\(^2\) J\(^{-2}\)) and \( \varepsilon \) is the Polanyi potential described as: \( \varepsilon = R T \ln (1 + 1/C_e) \). The mean sorption energy, \( E (kJ \text{ mol}^{-1}) \), 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 \( \beta \) constant and was evaluated as 0.199 (mol\(^2\) J\(^{-2}\)). 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\(^{-1}\), sorption may be physical in nature.

The negative \( \Delta G^\circ \) values indicate that the adsorption of Pb²⁺ on DP is spontaneous thermodynamically. The calculated enthalpy change \( \Delta H^\circ \) was found to be 3.74 J mol\(^{-1}\). The positive value of \( \Delta H^\circ \) clarified that the sorption process is endothermic. The enthalpy change \( \Delta H^\circ \) and entropy change \( \Delta S^\circ \) were calculated from the slope and intercept of the plot of \( \ln K_d \) against \( 1/T \), respectively, as depicted in (Figure 14) and according to the following equation [31,36,37,38]:

\[ \ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \]

The Gibbs free energy change \( \Delta G^\circ \) was calculated by: \( \Delta G^\circ = -RT \ln K_d \) 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 \( \Delta H^\circ \) was found to be 3.74 J mol\(^{-1}\). The positive value of \( \Delta H^\circ \) clarified that the sorption process is endothermic. The entropy change \( \Delta S^\circ \) 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 \( \Delta G^\circ \) was calculated at 278, 283, 313, 333 K according to the following equation [31,36]:

\[ \ln K_d = q_e / C_e \]

The calculated entropy change \( \Delta S^\circ \) was calculated by: \( \Delta S^\circ = \Delta H^\circ / RT \). The negative \( \Delta G^\circ \) values indicate that the adsorption of Pb²⁺ on DP is spontaneous thermodynamically.
Application

To investigate the applicability of the recommended procedure, a series of experiments were performed to recover 5 mg l⁻¹ of Pb²⁺ 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

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 Pb²⁺ after its adsorption on DP (Figure 16b). To explain the morphological changes in the surface of the absorbents 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 15 (a): XRD of DP before treatment.

Figure 15 (b): XRD of DP after treatment with Pb²⁺.

Figure 16 (a): EDX of DP before treatment.

Figure 16 (b): EDX of DP after treatment with Pb²⁺.

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(II) ions from aqueous solutions. The parameters (solution pH, initial concentration of Pb(II), 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 ΔGº, ΔHº and ΔSº were calculated. The removal of ~95% of Pb(II) was attained. The procedure was successfully applied to remove Pb(II) from natural water samples.

References

1. Li X, Zheng W, Wang D, Yang Q, Cao J, et al. (2010) Removal of Pb (II) from aqueous solutions by adsorption onto modified areca waste: Kinetic and thermodynamic studies. Desalination 258: 148-153.
2. Wang XS, Liu Y, Adie Gilbert U, Emmanuel Mc K (2011) Kinetics of Pb (II) adsorption on black carbon derived from wheat residue. Chemical Engineering Journal 166: 986-993.
3. Ucurum M (2009) A study of removal of Pb heavy metal ions from aqueous solution using lignite and a new cheap adsorbent (lignite washing plant tailings). Fuel 88: 1460-1465.
4. Prado AGS, Moura AO, Holanda MS, Carvalho TO, Andrade RDA, et al. (2010) Thermodynamic aspects of the Pb adsorption using Brazilian sawdust samples: Removal of metal ions from battery industry wastewater. Chemical Engineering Journal 160: 549-555.
5. Reddy DHK, Harinath Y, Seshaih K, Reddy AVR (2010) Biosorption of Pb(II) from aqueous solutions using chemically modified Moringa oleifera leaf extracts. Chemical Engineering Journal 162: 626-634.
6. Liu D, Cao Q, Cao X, Luo F (2009) Removal of Pb(II) using the modified lawny grass: mechanism, kinetics, equilibrium and thermodynamic studies. J Hazard Mater 186: 239-247.
7. Martín-Lara MA, Rodríguez IL, Blázquez G, Calero M (2011) Factorial experimental design for optimizing the removal conditions of lead ions from aqueous solutions by three wastes of the olive-oil production. Desalination 278: 132-140.
8. Liu Y, Liu Z, Gao J, Dai J, Han J, et al. (2011) Selective adsorption behavior of Pb(II) by mesoporous silica SBA-15-supported Pb(II)-imprinted polymer based on surface molecularly imprinting technique. J Hazard Mater 186: 197-205.
9. Adie Gilbert U, Emmanuel I, Adeyemo Adebanjo A, Olalere G (2011) Biosorptive removal of Pb(II) and Cd(II) onto novel biosorbent: Defatted Carica papaya seeds. Biomass and Bioenergy 35: 2517-2525.
10. Momcilovic M, Purenovic M, Bojic A, Zarubica A, Randelovic M (2011) Removal of lead(II) ions from aqueous solutions by adsorption onto pice cone activated carbon. Desalination 278: 53-59.
11. Ünlü N, Ersöz M (2006) Adsorption characteristics of heavy metal ions onto a low cost biopolymeric sorbent from aqueous solutions. J Hazard Mater 136: 272-290.
12. Palma G, Freer J, Baeeza J (2003) Removal of metal ions by modified Pinus radiata bark and tannins from water solutions. Water Res 37: 4974-4989.
13. Adthaheri A, Alhadrani A, Aboainaga N, Wasti I, Eriod M (2004) Chemical composition of date pits and reproductive hormonal status of rats fed date pits. Food Chemistry 86: 93-97.
14. Waew-Zadeth M, Ghazanfar A, Noorbakhsh S (2010) Finite element analysis and modeling of water absorption by date pits during a soaking process. J Zhejiang Univ Sci B 11: 482-488.
15. Saad EM, Mansour RA, El-Asmy A, El-Shahawi MS (2008) Sorption profile and chromatographic separation of uranium (VI) ions from aqueous solutions onto date pits solid sorbent. Talanta 76: 1041-1046.
16. Hamada JS, Hashimi BS, Sharif FA (2002) Preliminary analysis and potential uses of date pits in foods. Food Chemistry 76: 135-137.
17. Al-Ghouli MA, Li J, Salamah Y, Al-Laqtaeh N, Walker G, et al. (2010) Adsorption mechanisms of removing heavy metals and dyes from aqueous solution using date pits solid adsorbent. J Hazard Mater 160: 510-520.
18. Izgal M, Saeed A, Zafar SI (2009) FTIR spectrophotometry, kinetics and adsorption isotherms modeling, ion exchange, and EDX analysis for understanding the mechanism of Cd(II) and Pb(II) removal by mango peel waste. J Hazard Mater 164: 161-171.
19. Pehlivan E, Yanik BH, Ahmetli G, Pehlivan M (2008) Equilibrium isotherm studies for the uptake of cadmium and lead ions onto sugar beet pulp. Biosour Technol 99: 3520-3527.
20. Al-Ghouli MA, Li J, Salamah Y, Al-Laqtaeh N, Walker G, et al. (2010) Adsorption mechanisms of removing heavy metals and dyes from aqueous solution using date pits solid adsorbent. J Hazard Mater 176: 510-520.
21. Liu D, Zheng W, Li X, Yang Q, Yue X, et al. (2010) Removal of lead(II) from aqueous solutions using carbonate hydroxyapatite extracted from eggshell waste. J Hazard Mater 177: 126-130.
22. Crank J (1965) The Mathematics of Diffusion. Carlelond Press, Oxford, London.
23. McKay G, Otterbern MS, Sweeney AG (1980) The removal of colour from effluent using various adsorbents—Il. Silica: Rate processes. Water Research 14: 15-20.
24. Ghazy SE, Ragab AH (2007) Removal of copper from water samples by sorption onto powdered limestone. Indian Journal of Chemical Technology 14: 507-514.
25. Weber WJ, Morris JC (1963) Intraparticle diffusion during the sorption of surfactants onto activated carbon. J Sanit Eng Div Am Soc Civ Eng 89: 53-61.
26. Jiang RS, Wu FC, Tseng RL (2000) Mechanism of Adsorption of Dyes and Phenols from Water Using Activated Carbons Prepared from Plum Kernels. J Colloid Interface Sci 227: 437-444.
27. Ghazy SE, Ragab AH (2007) Removal of Lead from Water Samples by Sorption onto Powdered Limestone. Separation Science and Technology 42: 653-667.
28. Qadeer R, Hanif J (1994) Kinetics of Uranium (VI) Ions Adsorption on Activated Charcoal from Aqueous Solutions. Radiochimica Acta 65: 259-264.
29. Gupta GS, Shukla SP (1996) An inexpensive adsorption technique for the treatment of carpet effluents by low cost materials. Adsorp Sci Tech 13: 15-26.
30. Krika F, Azzouz N, Ncibi M (2011) Adsorptive removal of cadmium from aqueous solution by cork biomass: Equilibrium, dynamic and thermodynamic studies. Arabian Journal of Chemistry.
31. Erdem M, Altundogan HS, Tumen F (2004) Removal of hexavalent chromium by using heat-activated bauxite. Minerals Engineering 17: 1045-1052.
32. Sari A, Tuzen M, Soyak M (2007) Adsorption of Pb(II) and Cr(III) from aqueous solution on Celite clay. J Hazard Mater 144: 41-46.
33. Al-Asheh S, Banat F (2001) Adsorption of Pb(II) and Cu(II) from aqueous solution using Montmorillonite. Adsorption Science & Technology 19: 117-129.
34. Al-Asheh S, Banat F (2001) Adsorption of Zinc and Copper Ions by the Solid Waste of the Olive Oil Industry. Adsorption Science & Technology 19: 117-129.
35. Yubin T, Fangyan C, Honglin Z (1998) Adsorption of Pb²⁺ and Cu²⁺ onto To Waste Fluidized Catalytic Cracking (FCC) Catalyst. Adsorption Science & Technology 16: 595-606.
36. Mane VS, Desai MV, Chandra Srivastava V (2007) Kinetic and equilibrium isotherm studies for the adsorptive removal of Brilliant Green dye from aqueous solution by rice husk ash. J Environ Manag 84: 390-400.
37. Donat R, Akdogan A, Erdem E, Cetisli H (2005) Thermodynamics of Pb²⁺ and Ni²⁺ adsorption onto natural bentonite from aqueous solutions. J Colloid Interface Sci 286: 43-52.
38. Gupta SS, Bhattacharyya KG (2005) Interaction of metal ions with clays: I. A case study with Pb(II). Applied Clay Science 30: 199-208.