

Removal of Pb(II) from Aqueous Solution by *Portulaca oleracea* Leaves: Kinetic, Equilibrium and Thermodynamic Studies

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Received May 4, 2013; revised June 5, 2013; accepted June 20, 2013

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ABSTRACT

Portulaca oleracea leaves are tested as an agriculture adsorbent material for reducing Pb(II) from aqueous solutions. The pH of solution, adsorbent dose, shaking speed and particles size of adsorbent were constants at all adsorption experiments. Effects of contact time on adsorption capacity of Pb(II) onto *Portulaca oleracea* leaves were studied. The adsorption capacity increased as the contact time increased and reached equilibrium at one hour. Kinetic models including a first-order, pseudo-second-order and intra-particle diffusion equations were selected to follow the adsorption process. The process follows a pseudo-second-order kinetic and the intra-particle diffusion is the main step to interpret the mechanism of adsorption. Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models were applied to describe adsorption equilibrium data. Results proved that the Langmuir isotherm model gave an acceptable fit to the experimental data more than Freundlich isotherm model. Maximum adsorption capacities obtained were 192.3, 333.3 and 434 mg/g at 295, 303 and 310 K, respectively. According to D-R isotherm data, the adsorption process is classified as physical adsorption. Thermodynamically, the adsorption process is non spontaneous, endothermic and random in nature.

Keywords: *Portulaca oleracea*; Langmuir; Freundlich; Isotherm; Lead; Adsorption

1. Introduction

Different toxic heavy metals are frequently discharged into the water environment due to industrial activities of humans. There are different industrial sources of heavy metals including mining, plating, textile, storage batteries, electroplating, metal finishing and lead smelting. The presence of these toxic heavy metals in the water environment is of important concern due to their health effects on human and other living organisms. Therefore, removal of toxic heavy metals from water media is very important [1]. There are several methods for elimination of toxic heavy metals from aqueous solutions such as ion exchange, chemical precipitation, coagulation, membrane process and electrochemical techniques [2]. Among the previous methods, adsorption onto low cost agriculture materials was studied. These agriculture materials include sawdust [1], olive orange waste [2], almond green hull [3], olive cake ash [4], walnut shell [5] and rice bran [6]. In the present work, an agriculture material, *i.e.* *Portulaca oleracea* leaves were tested as a low cost adsorb-

ent for the elimination of Pb(II) from aqueous solutions.

2. Materials and Methods

2.1. Preparation of Adsorbent

The leaves of *Portulaca oleracea* were collected from Samno village, Sebha, Libya. They were cleaned from dust and undesirable materials, washed twice with distilled water and dried at 100°C for two hours. The dried leaves were grounded in a mortar to a very fine powder and sieved through a 125 µm copper sieve. The pH of Pb(II) solution was 4, the doses of *Portulaca oleracea* leaves in all experiments were 0.05 g and the shaking speed was constant at 300 rpm.

2.2. Reagents

Analytical grade reagents were used in the experimental studies. Lead acetate, xylenol orange, hexamethylene tetra amine and ethylene di amine tetra acetic acid (EDTA) were delivered from MERCK, Germany. Hy-

drochloric acid, sulfuric acid and sodium hydroxide were supplied from FLUCA, Germany.

2.3. Apparatus

A pH meter, model 3505, Jenway Felsted. Dumow, Essex C.46 SLB, UK was employed for testing the pH of Pb(II) solutions. The batch experiments were carried out using a mechanical shaker, model 501, delivered from Stuart Scientific, UK.

2.4. Preparation of Pb(II) Solutions

A stock solution of 2000 mg/l was prepared by dissolving the 3.14 g of lead acetate in one liter double distilled water.

All working solutions were prepared by diluting the stock solution with double distilled water.

The pH values of the working solutions were adjusted with 0.1 M hydrochloric acid or 0.1 M sodium hydroxide and kept constant at pH 4.

The concentrations of Pb(II) were determined by titration with EDTA in the presence of xylenol orange as indicator.

2.5. Batch Adsorption

In batch experiments, 0.05 g of *Portulaca oleracea* leaves was added into several 250 ml Erlenmeyer flasks with plastic stopper, each containing 100 ml of Pb(II) solution. The flasks were then shaken at 300 rpm. After shaking, the Pb(II) solutions were filtered and their concentrations were determined.

In order to investigate the kinetics of adsorption, the effect of contact time (10 - 60 minutes) on adsorption capacity of *Portulaca oleracea* leaves was studied. The isotherm studies were performed by varying the initial Pb(II) concentration from 100 to 1000 mg/l at 295, 303 and 310 K.

The adsorption capacity (q_e) of *Portulaca oleracea* leaves was calculated according to the following equation [7]:

$$\frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentration of Pb(II) (mg/l), respectively. V is the volume of Pb(II) solution and W is the weight of *Portulaca oleracea* leaves.

3. Results and Discussion

3.1. Effect of Contact Time

Figure 1 shows the influence of contact time on adsorption capacity of Pb(II) at 295 K. C_0 was 300 mg/l for all cases. The experimental data indicate that the adsorption

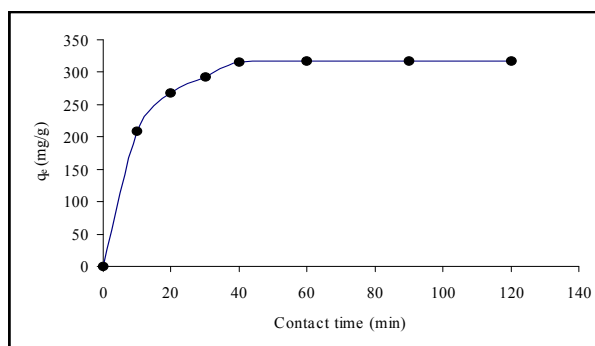


Figure 1. Effect of contact time.

capacity increased rapidly at initial contact time of less than 10 minutes and reached to equilibrium at one hour.

3.2. Kinetic Study

In order to suggest the mechanism of adsorption, kinetic models such as first-order, pseudo-second-order and intra-particle diffusion are probably used to test the experimental data.

The first-order rate Lagergren model is [8]:

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

where q_t is the amount of adsorbed Pb(II) on the adsorbent at time t and K_1 is the rate constant of the first-order (min^{-1}). K_1 and q_e can be calculated respectively from the slope and intercept of the plot $\log(q_e - q_t)$ versus t (**Figure 2**). It is found from **Table 1** that the q_e value obtained by first-order kinetic model ($q_{cal.}$) differ from the measured experimentally ($q_{exp.}$), suggesting the adsorption is not first-order reaction. The value of correlation coefficient (R^2) is 0.8755, indicating also that the adsorption is not first-order reaction.

The best fit for the obtained experimental data was carried out by application of pseudo second-order according to the following equation [8]:

$$t/q_t = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where K_2 is the rate constant of second-order adsorption ($\text{g/mg} \cdot \text{min}$). q_e ($q_{cal.}$) and K_2 can be calculated respectively from the slope and the intercept of the plot t/q_e versus t (**Figure 3**). R^2 for pseudo second-order was equal to 1 and the $q_{cal.}$ is agree with $q_{exp.}$ (**Table 2**). Both parameters suggest that the adsorption of Pb(II) followed the pseudo second-order kinetic model.

The intra-particle diffusion model is the most common model could be used to confirm the mechanism of adsorption. This model of Weber and Morris can be written as follows [9]:

$$q_t = K_p t^{1/2} + C \quad (4)$$

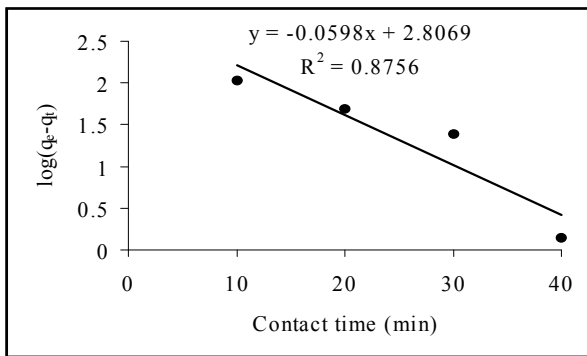


Figure 2. The first-order (Lagergren) plot.

Table 1. The first-order (Lagergren) parameters.

| $q_{exp.}$ (mg/g) | $q_{cal.}$ (mg/g) | K_1 (l/min) | R^2 |
|-------------------|-------------------|---------------|--------|
| 316 | 630 | 0.138 | 0.8756 |

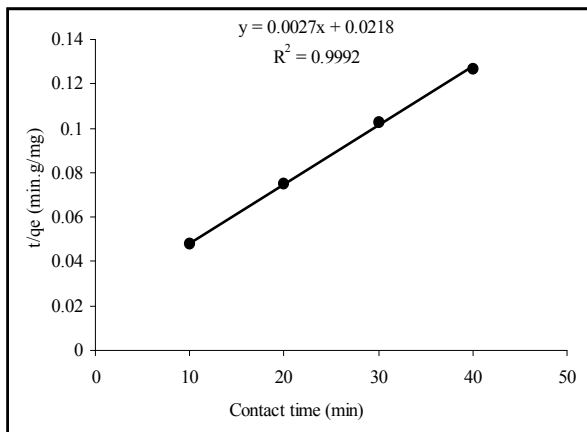


Figure 3. The pseudo second-order plot.

Table 2. The pseudo second-order parameters.

| $q_{exp.}$ (mg/g) | $q_{cal.}$ (mg/g) | K_2 (g/mg.min) | R^2 |
|-------------------|-------------------|------------------|--------|
| 316 | 370 | 0.00034 | 0.9992 |

where K_p is the intra-particle diffusion rate constant (mg/g min). The linear portion of the plot of q_t versus $t^{1/2}$ is displayed in **Figure 4**. The adsorption of Pb(II) onto *Portulaca oleracea* leaves could be interpreted by intra-particle diffusion because of the high value of R^2 (0.9993). The plot is not passed through the origin point, suggesting that the pore diffusion may not be the only rate controlling step in the adsorption process [10].

3.3. Adsorption Equilibrium

The adsorption isotherms are the equilibrium relationships between the concentrations of adsorbent metal and metal in solution at given temperature. The adsorption isotherms of Pb(II) onto *Portulaca oleracea* leaves are

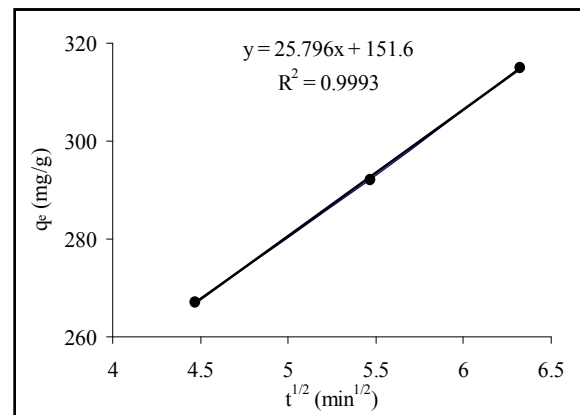


Figure 4. The intra-particle diffusion plot.

presented in **Figure 5**.

In the present work, Langmuir, Freundlich and D-R isotherm models were applied to describe the equilibrium data.

The Langmuir isotherm model is based on the hypothesis that adsorption occurs on a homogenous surface by monolayer sorption without interaction between adsorbed molecules [11]. This model is expressed as follows [12]:

$$\frac{C_e}{q_e} = \frac{1}{q_0 \times K} + \frac{C_e}{q_0} \quad (5)$$

where q_0 is the adsorption maximum of Pb(II) onto *Portulaca oleracea* leaves and K (l/mg) is the Langmuir adsorption constant which will be used later to determine the Gibbs free energy (ΔG°).

Linear plot of C_e/q_e versus C_e as presented in **Figure 6** was employed to determine the value of q_0 and K . The obtained data as well as R^2 values were illustrated in **Table 3**. The high values of R^2 (0.9920 - 0.9950) suggests that the Pb(II) adsorbed by *Portulaca oleracea* leaves from monolayer coverage on the surface of the adsorbent.

The dimensionless constant separation factor (R_L) can be determined according to the following equation [13]:

$$R_L = \frac{1}{1 + K(C_0)} \quad (6)$$

Accordingly, values of R_L at different temperatures were observed to be positive, lying between 0 and 1 (0.154 - 0.833). These results confirmed the favorability of the adsorption isotherm. The diagnostic criterion about the shape of isotherm, is as follows [13]: $R_L > 1$, unfavorable isotherm, $R_L = 1$, linear isotherm, $0 < R_L < 1$, favorable isotherm and $R_L = 0$, irreversible isotherm.

The Freundlich isotherm is probably used to describe the multilayer sorption of metal ion on a heterogeneous surface of adsorbent according to the following equation [14]:

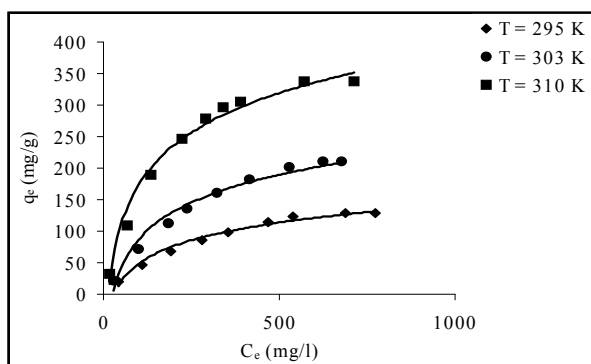


Figure 5. Adsorption isotherm of Pb(II) onto *Portulaca oleracea* leaves at different temperatures.

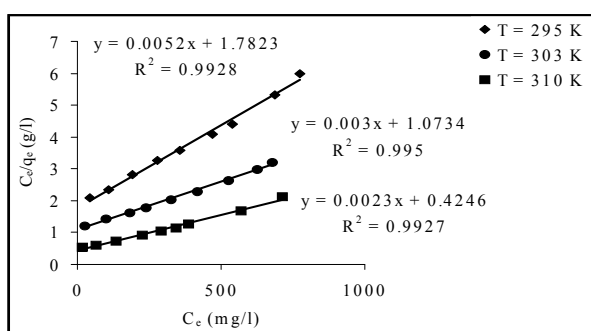


Figure 6. Linearized langmuir isotherm plots (C_0 , 100 - 1000 mg/l; contact time, 2 hours and adsorbent, 0.5 g).

Table 3. Langmuir isotherm parameters for Pb(II) uptake by *Portulaca oleracea* leaves.

| Temp. (T) | q_e (mg/g) | K | R^2 |
|-----------|--------------|--------|--------|
| 295 | 192.3 | 0.0029 | 0.9928 |
| 303 | 333.3 | 0.0026 | 0.9950 |
| 310 | 434 | 0.0055 | 0.9927 |

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (7)$$

where n and K_F are the Freundlich constants which determined respectively from the slope and intercept of the plot of $\log q_e$ against $\log C_e$ (Figure 7). The Freundlich isotherm parameters are displayed in Table 4. The R^2 values (0.9475 - 0.9722) indicated that the isotherm data is fitted with Freundlich isotherm model but less than Lungmuir isotherm model. From Table 4 it is apparent that the obtained values of n indicate favorable adsorption, as they lie between 1 and 10 [5].

The equilibrium data were also investigated in order to decide the nature of adsorption process. The following equation can be used to calculate the parameters of Dubinin-Radushkevich (D-R) isotherm model [15]:

$$\ln q_e = \ln q_{\max} - \beta \epsilon^2 \quad (8)$$

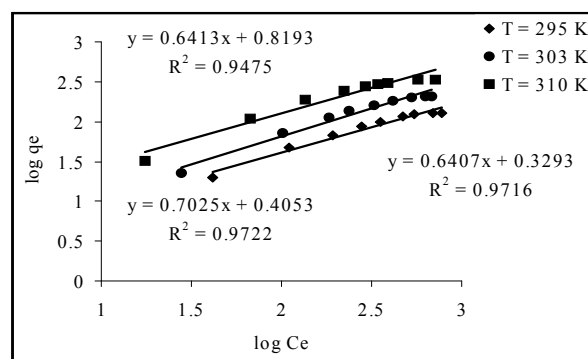


Figure 7. Freundlich isotherm plots (C_0 , 100 - 1000 mg/l; contact time, 2 hours and adsorbent, 0.5 g).

Table 4. Freundlich isotherm parameters for Pb(II) uptake by *Portulaca oleracea* leaves.

| Temp. (T) | K_F | n | R^2 |
|-----------|-------|-------|--------|
| 295 | 2.13 | 1.560 | 0.9716 |
| 303 | 2.54 | 1.423 | 0.9722 |
| 310 | 6.59 | 1.559 | 0.9475 |

where β is the activity coefficient ($\text{mol}^2 \cdot \text{J}^{-2}$) which can be calculated from the slope of the plot of ϵ^2 against $\ln q_e$ (Figure 8) and ϵ is the Polanyi Potential.

The values of ϵ can be calculated by the use of the following equation [15]:

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (9)$$

The mean free energy (E ; $\text{KJ} \cdot \text{mol}^{-1}$) is determined by the use of β value according to the following equation [15]:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (10)$$

The values of E give an idea about absorption of mechanism whether if physical or chemical. If the values lies between 8 and 16 $\text{KJ} \cdot \text{mol}^{-1}$, the adsorption process is classified as chemical adsorption [15].

In the present work, E value was calculated as 0.045 $\text{KJ} \cdot \text{mol}^{-1}$. This result suggest that the adsorption process may interpreted by physical mechanism because the value of $E < 8 \text{ KJ} \cdot \text{mol}^{-1}$.

4. Thermodynamic Study

The thermodynamic parameters such as Gibbs free ΔG° , enthalpy (ΔH°) and entropy (ΔS°) were estimated to evaluate the feasibility and nature of adsorption [16].

ΔG° for the adsorption of Pb(II) by *Portulaca oleracea* was calculated using the following equation [16]:

$$\Delta G^\circ = -RT \ln K \quad (10)$$

where R is gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$).

ΔH° and ΔS° can be determined respectively from the slop and intercept of the plot of $1/T$ versus $\ln K$ (**Figure 9**) using the following equation [16]:

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (11)$$

The calculated thermodynamic parameters are illustrated in **Table 5**. The positive values of ΔG° suggested the non spontaneous nature of the process. ΔH° and ΔS° can be determined respectively from the slop and intercept of the plot of $\ln K$ versus $1/T$. The positive value of ΔH° and ΔS° indicated that the Pb(II) adsorption process was endothermic in nature and random. It has been reported in literature that the value of ΔH° due to chemisorption should be in the range from 40 to 120 $\text{KJ}\cdot\text{mol}^{-1}$ [16]. In the present work, the value of ΔH° ($26.6 \text{ KJ}\cdot\text{mol}^{-1}$) confirmed the physisorption process. This result agrees with the results obtained from D-R isotherm model studies.

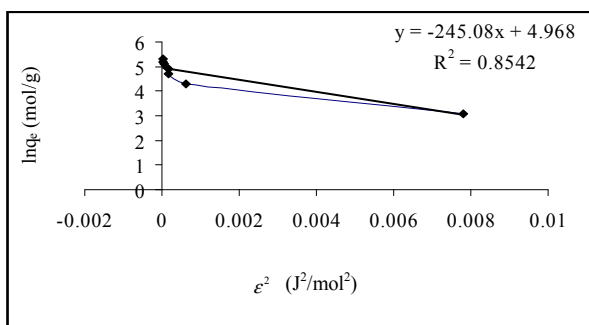


Figure 8. D-R isotherm plot (C_0 , 100 - 1000 mg/l; T , 303 K; contact time, 2 hours and adsorbent, 0.5 g).

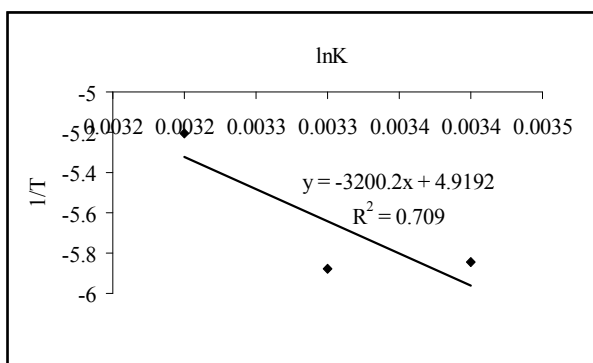


Figure 9. The plot of $1/T$ versus $\ln K$.

Table 5. The thermodynamic parameters of Pb(II) adsorption onto *Portulaca oleracea* leaves.

| ΔG° | | | ΔH° | ΔS° |
|------------------|-------|-------|------------------|------------------|
| 295 K | 303 K | 310 K | | |
| 9.51 | 13.4 | 14.7 | 26.6 | 0.041 |

5. Conclusion

In this work, the parameters including initial pH, adsorbent dose, particles size of adsorbent and shaking speed are kept constants. The adsorption of Pb(II) onto *Portulaca oleracea* leaves reached equilibrium after two hours. Batch lead ion uptake capacity tests have shown that the adsorption process can be better described by pseudo second-order model. The intra-particle diffusion may be one of the determining step in the adsorption process. The adsorption data fitted with the Langmuir and Freundlich models. However, Langmuir isotherm displayed a better fitting model than Freundlich isotherm because of the higher correlation coefficient, thus, indicating the adsorption of Pb(II) as a monolayer onto the surface of *Portulaca oleracea* leaves. The mean free energy value evaluated from D-R isotherm model explained that the adsorption of Pb(II) onto *Portulaca oleracea* leaves was carried out through physical adsorption mechanism. Thermodynamically, the adsorption process is non-spontaneous, endothermic and random.

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