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# Batch adsorption of cadmium ions from aqueous solution by means of olive cake

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#### Abstract

The use of natural adsorbent such as olive cake to replace expensive imported synthetic adsorbent is particularly appropriate for developing countries such as Jordan. In this study, batch adsorption experiments were carried out for the removal of cadmium ions from its aqueous solution using olive cake as adsorbent. Parameters effects such as temperature, pH and adsorbent dose on the adsorption process were studied. The adsorbent used in this study exhibited as good sorption at approximately pH 6 at temperatures 28, 35 and 45 °C. The removal efficiency was found to be 66% at pH 6 and temperature 28 °C. The equilibrium data were analyzed using Langmuir and Freundlich isotherm models to calculate isotherm constants. The experimental results were in a good agreement with these models. Results show that when an increasing in temperature from 28 to 45 °C, the maximum adsorption capacity ( $q_{max}$ ) is decreased from 65.4 to 44.4 mg/g and Freundlich constant ( $K_f$ ) decreased from 19.9 to 15.7. The thermodynamic parameters for the adsorption process data were evaluated using Langmuir isotherm. The free energy change ( $\Delta G^{\circ}$ ) and the enthalpy change ( $\Delta H^{\circ}$ ) showed that the process was feasible and exothermic, respectively. The dynamic data fitted to the first order, Lagergren-first order and pseudo second-order kinetic models. The experimental results indicated that the pseudo second-order reaction model provided the best description for these data with a correlation coefficient of 0.99. The adsorption rate constant was calculated as  $8.4 \times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$  at  $28 \, ^{\circ}\text{C}$ .  $\bigcirc$  2007 Elsevier B.V. All rights reserved.

Keywords: Cadmium(II); Olive cake; Adsorption isotherms; Kinetics; Thermodynamics

# 1. Introduction

The removal of cadmium, Cd(II), ions gaining wide interest from both environmental and economical viewpoints, due to its serious hazardous impacts on humans, animals and plants. There are several industries are responsible for polluting the environment with high level of Cd(II) ions. These industries and operations may include the casting of various cadmium alloy products used for coating telephone cables, metallurgical alloying, ceramics, metal plating, photograph, pigment works, textile printing industries, lead mining and sewage sludge, alkaline batteries and electroplating [1].

Because of good performance for removing the dissolved heavy metal, the adsorption technique has gained important over the other techniques such as precipitation, flotation, ion

0304-3894/\$ - see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.jhazmat.2007.05.069 exchange, solvent extraction, membrane processing and electrolytic [2,3].

Many studies have recently devoted to use different adsorbent materials in processes involving the removal of Cd(II) ions from aqueous effluents with the aim of finding cheaper replacements for expensive conventional sorbent materials in different situations [4]. For example, the use of activated carbon [5–10] as adsorbent is considered particularly competitive and effective process for removing of Cd(II) ions from aqueous solutions but it is not suitable in developing countries due to its high cost which is associated with the production and regeneration of spent carbon. Therefore, many investigators have used inexpensive sorbent materials such as, chitin [11], anaerobic sludge [12], apple residue [13], sawdust [14], rice polish [15], clay [16], zeolite [17], fly ash [18], chitosan [19], waste tea [20,21], seaweeds [22] and others.

The solid waste namely; olive cake used as an adsorbent in this study was generated during the squeezing the olive to get the oil. Olive cake is an abundant and a low-cost adsorbent

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material on a large scale in many Mediterranean countries especially in Jordan. Jordan has a strong agricultural foundation that leaves behind 80,000 tonnes annually of olive cake wastes [23], with manure possibly being the most problematic one. However, existing research into the use of olive cake as adsorbent for removing of heavy metals from aqueous solution is extremely limited [24–26].

The goal of this work is to study the capacity of using untreated olive cake to treat wastewater contaminated by the cadmium ion under different operating conditions (temperature, dose and pH). The equilibrium studies to determine the thermodynamics parameter are also carried out. Then to study the kinetic models that fits the experimental finding.

#### 2. Materials and methods

# 2.1. Olive cake

Olive cake used in this study was supplied by olive oil mill from Irbid city, Jordan. This sorbent of olive cake was dried in atmospheric environment during its disposal for almost 1 year. Stones and other heavy particles were removed from the collection sample. Defined weight of olive cake sample was washed many times with hot deioniozed water and then by deionized cooled water. This sample was dried at 100 °C for 24 h until no variation in the sample weight observed. After that, the dried sample was grounded and sieved into several size fractions, using standard ASTM sieves. The size of the dried sample used throughout this experiment was 100  $\mu$ m.

# 2.2. Adsorbate solution

Cadmium acetate dissolved in deionized water to prepare aqueous solution with required concentration of 100 ppm and using 1.0N of NaOH and HCl, for adjusting pH values.

#### 2.3. Experimental operations

In this study, the equilibrium and kinetics experiments were carried out.

#### 2.3.1. Equilibrium experiments

Batch equilibrium experiments were performed in a set of 250 ml-Erlenmeyer flasks. Each flask contains a solution of 0.05 g of olive cake and 200 ml aqueous solution of cadmium with a fixed concentration of 100 ppm. 1N of NaOH and HCl adjusts the initial pH of the solution within the range from 2 to 11 and it was recorded by pH meter (Orion,  $\pm 0.1$ ). The temperature of the solution was adjusted in the range of 28–45 °C using temperature controller (Gefellschaft Funn 1003,  $\pm 0.1$  °C).

The solution in an Erlenmeyer flask was shaken in an electric thermostated shaker (Gefellschaft Fur 978) for 24 h in order to reach the equilibrium, a series of such flasks were then agitated at constant speed of 100 rpm. At the end of the predetermined time interval, the flasks were removed from the shaker and the adsorbent was then filtered using filter paper (Whatman No. 41).

The filtrate was analyzed using atomic absorption spectrophotomatry (ASS). These procedures were repeated for others olive cake weights of 0.1, 0.2 and 0.3 g.

To ensure the accuracy, reliability and reproducibility of the collected data, all batch experiments were carried out in duplicated and the mean values of two data sets are presented. The experimental errors of data were in the range 1-4%.

The removal efficiency, %, of the olive cake on Cd(II) ions is defined as

$$\% = \frac{C_{\rm i} - C_{\rm e}}{C_{\rm i}} \times 100\%$$
(1)

where  $C_e$  and  $C_i$  are the equilibrium and initial concentrations of Cd(II) ions, respectively (mg/l).

#### 2.3.2. Kinetics experiments

A volume of 200 ml of Cd(II) ions solution with a concentration of 100 ppm was placed in a 1000 ml flask. The initial pH of the solution was adjusted to 6. An accurately weighted olive cake sample 0.3 g was added to a 1000 ml flask to get a solution of desired slurry (dose) concentration  $(1.5 \text{ g} \text{ l}^{-1})$ . A series of such flasks was agitated in isothermal shaker at stirrer speed of 100 rpm. The temperature of the solution is kept constant at 28 °C. Samples of 2 ml were withdrawal from the solution each 1 min for the first 5 min and 5 min for the first 25 min and then each 10 min until the end of the experiment. The samples were withdrawal using fritted glass tube to prevent any contact of the drain solution with the adsorbent particles outside the adsorption beaker. These samples were then analyzed by using atomic absorption spectrophotometry (ASS) for quantifying the change of solution concentration with time.

#### 2.4. Adsorption isotherms

The equilibrium distribution of cadmium ions between the olive cake and the solution is important in determining the maximum sorption capacity. Two isotherm models are used to describe the equilibrium sorption: Langmuir and Freundlich models [27,28]. The Langmuir model assumes that the uptake of metal ions on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. The Langmuir model for equilibrium ion removed is given by

$$q_{\rm e} = \frac{q_{\rm max}bC_{\rm e}}{1+bC_{\rm e}} \tag{2}$$

where  $q_e$  is the Cd(II) ions concentration on the olive cake at equilibrium (mg of cadmium ion/g of olive cake),  $q_{max}$  the maximum metal uptake per unit mass of olive cake (mg/g) and *b* is Langmuir constant (dm<sup>3</sup>/mol) related to energy of sorption which reflects quantitatively the affinity between the olive cake and Cd(II) ions.

The values of  $q_{\text{max}}$  and b are the characteristics of the Langmuir model. They can be determined by linearizing Eq. (2) as shown in the following equation:

$$\frac{C_{\rm e}}{q_{\rm e}} = \frac{1}{q_{\rm max}b} + \frac{1}{q_{\rm max}}C_{\rm e} \tag{3}$$

Therefore, a plot of  $C_e/q_e$  versus  $C_e$ , gives a straight line of slope  $1/q_{max}$  and intercept  $1/(q_{max}b)$ .

The value of  $q_e$  is given from the following relation:

$$q_{\rm e} = \frac{C_{\rm i} - C_{\rm e}}{m/v} \tag{4}$$

where  $C_i$  is the initial concentration of Cd(II) ions in the solution (mg/l), v the initial volume of Cd(II) ions solution used (l) and m is the mass of olive cake used (g). The does (slurry) concentration is expressed by m/v.

On the other hand, the Freundlich model is chosen to estimate the adsorption intensity of the sorbent towards the olive cake. The equation is commonly represented by

$$q_{\rm e} = K_{\rm f} C_{\rm e}^{1/n} \tag{5}$$

where  $K_{\rm f}$  and *n* are Freundlich constants, indicating the adsorption capacity and the adsorption intensity, respectively.

The above equation is rearranged in linear form to give:

$$\ln q_{\rm e} = \ln K_{\rm f} + \frac{1}{n} \ln C_{\rm e} \tag{6}$$

where  $K_{\rm f}$  and *n* are, respectively, determined from the intercept and slope of plotting ln  $q_{\rm e}$  versus ln  $C_{\rm e}$ .

### 3. Results and discussions

#### 3.1. Equilibrium relation

#### 3.1.1. Effect of initial pH value

The solubility of metal ions depends on the pH of the solution, and as know the pH parameter plays an important role for the adsorption process of heavy metal ions from aqueous solution. To examine the effect of pH on the cadmium ions removal efficiency, several experiments were performed at different pH ranges from 2 to 11 at different temperatures (28, 35 and 45 °C) as shown in Fig. 1. For the three temperatures, it can be seen that the uptake of Cd(II) ions depends on pH, where the Cd(II) ions removal efficiency increases at pH ranges from 2 to 6, and



Fig. 1. Effect of initial pH on the removal efficiency, %, of Cd(II) ions at different temperatures (initial concentration of Cd(II): 100 ppm; agitation speed: 100 rpm; mass of olive cake: 0.3 g; dose: 1.5 g/l; contact time: 24 h).

then declining at higher pH (from 6 to 11). The optimal metal removal efficiency occurs at pH 6. This result is consistent with results reported by Ozer et al. for the adsorption of cadmium on the sugar beet pulp [29] and they found the optimum pH was 6.3. Bhattachary and Venkobachar also found the optimum pH was 6.6 for removal of cadmium on Gridih coal [30]. Mathialagan and Viraraghava [31] observed that the optimum pH for cadmium adsorption by perlite was 6.

Fig. 1 shows that at temperature 28 °C, the removal efficiency increases from 42% to 66% as pH increases from 2 to 6, and thereafter the removal efficiency decreases from 66% to 60% with the increasing of pH from 6 to 11. This behavior in decreasing of Cd(II) ions removals at very low pH is apparently due to the higher concentration of H<sup>+</sup> ions present in the solution that compete with Cd<sup>2+</sup> for the adsorption sites of olive cake, leaving cadmium ions free in the solution. This means that at higher H<sup>+</sup> ions concentration, the olive cake becomes more positively charged thus reducing the attraction between olive cake surface and cadmium cations.

The increase in the removal of cadmium ions at the range of pH from 2 to 6 is due to the concentration of the  $H^+$  ions exist in the solution will be decreased as pH increased and hence will not give the chance to compete with cadmium ions on the adsorption sites of olive cake. Thus, the surface of the olive cake becomes more negatively charged which attracts the positive charge of Cd<sup>+</sup> and Cd(OH)<sup>+</sup> ions hook up the free binding sites.

The decrease in the adsorption rate at the range of pH from 6 to 11 might be attributed to the formation of  $Cd(OH)_3^-$  ions taking place as a result of dissolution of  $Cd(OH)_2$ . The hydrolysis and precipitation of metal ions affect adsorption by changing the concentration to form soluble metal species that are available for adsorption. Reed and Matsumoto [32] reported that the principal species of Cd(II) are formed according to the following reactions:

$Cd^{2+} + H_2O \Leftrightarrow Cd(OH)^+ + H^+$	$pK_1=9$
$Cd^{2+} + 2H_2O \Leftrightarrow Cd(OH)_2 + 2H^+$	$pK_1 = 19.1$
$Cd^{2+} + 3H_2O \Leftrightarrow Cd(OH)_3 + 3H^+$	$pK_1 = 30.3$
$Cd^{2+} + 2H_2O \Leftrightarrow Cd(OH)_{2(s)} + 2H^+$	$pK_1 = 30.3$

Depends on these equilibrium constants, Reed and Matsumoto [32] constructed a speciation diagram that shows the Cd(II) ion predominates at pH below 7 and it begins to precipitate out as Cd(OH)<sub>2</sub> at pH values just above 9. At pH 8, the species distribution is approximately 90% Cd(II) and 10% Cd(OH)<sup>+</sup>. This means that all the species occurring at pH values of 8 and below carry a positive charge either as Cd<sup>2+</sup> or Cd(OH)<sup>+</sup>. Generally, the adsorption mechanisms can be explained based on H<sup>+</sup>–Cd<sup>2+</sup> exchange reaction [33].

Fig. 1 also shows that the removal efficiency of cadmium ions decreases with the increasing of the solution temperature from 28 to 45  $^{\circ}$ C, which indicates to the adsorption process, is an exothermic one. This decreasing in adsorption may be attributed to many parameters: the relative increase in the escaping tendency of the cadmium ions from the solid phase to the bulk



Fig. 2. Effect of dosage on the removal efficiency of Cd(II) ions at different temperatures (initial concentration of Cd(II): 100 ppm; agitation speed: 100 rpm; pH: 6; contact time: 24 h).

phase; deactivating the adsorbent surface or destructing some active sites on the adsorbent surface due to bond ruptures [34]; or due to the weakness of adsorptive forces between the active sites of the adsorbents and the adsorbate species and also between the adjacent molecules of adsorbed phase [35]. Our results are in a good agreement with those obtained for removal of cadmium ions using activated carbon [36–38] and they are in agreement with the thermodynamics point of view.

#### 3.1.2. Effect of dose

The dependence of Cd(II) ions sorption on the dose concentration was studied at different amounts of olive cake 0.05, 0.1, 0.2 and 0.3 g and at different temperatures of 28, 35 and 45 °C. The initial pH was adjusted at 6. Fig. 2 presents the removal efficiency as a function of the amount of olive cake. It is clear that the removal efficiency is generally improved with the increasing amount of olive cake over the temperature ranges from 28 to 45 °C. This is expected because the higher dose of adsorbent in the solution, the greater availability of exchangeable sites for the ions. Our results showed that the maximum removal efficiency was obtained at 0.3 g of olive cake for temperature 28 °C.

#### 3.1.3. Adsorption isotherm

The equilibrium removal of metal ion consideration can be mathematically expresses in terms of adsorption isotherms of the Langmuir (Eq. (3)) and Freundlich (Eq. (6)). These models were performed by exposing 0.05, 0.1, 0.2 and 0.3 g of olive cake to 100 ppm cadmium solution. The initial pH was adjusted at 6.

Table 1 Langmuir and Freundlich constants for adsorption of Cd(II) ions on olive cake



Fig. 3. The linearized Langmuir adsorption isotherms for Cd(II) ions adsorption by olive cake at different temperatures (initial concentration of Cd(II): 100 ppm; agitation speed: 100 rpm; pH: 6; contact time: 24 h).

Fig. 3 represents the experimental data that were fitted by the linear form of Langmiur model,  $(C_e/q_e)$  versus  $C_e$ , at temperature 28, 35 and 45 °C. The values of  $q_{\text{max}}$  and b were evaluated from the slope and intercept, respectively, for the three isothermal lines and they are listed in Table 1.

Because the regression coefficients,  $R^2$ , values presented in Table 1, are higher than 0.98 then the Langmuir isotherm is applicable for the experimental results. The sorption capacity,  $q_{\text{max}}$ , which is a measure of the maximum adsorption capacity corresponding to complete monolayer coverage found to be 65.36 mg/g for the experiments carried out at 28 °C. The values of  $q_{\text{max}}$  decreased from 65.36 to 44.44 mg/g, when the solution temperature increased from 28 to 45 °C. We also observed that the adsorption coefficient, *b*, value which is related to the apparent energy of adsorption also decreased from 0.0710 to 0.0628 l/mg as the solution temperature increased from 28 to 45 °C.

The decreasing in these values of  $q_{\text{max}}$  and b with temperature indicates that the cadmium ions are favorably adsorbed by olive cake at lower temperatures, which shows that the adsorption process is an exothermic one.

Our experimental data of values  $q_{max}$  are compared with other adsorbents in order to validate olive cake as an adsorbent for Cd(II) ions adsorption. Table 2 shows the value of  $q_{max}$  for the adsorption of Cd(II) ions on different adsorbents cited in the literature compared with that of the present study. It can be observed that the uptake of cadmium ions on olive cake is greater than other adsorbents materials that reported in Table 2 except for sugar can material. It can also be seen that our experimental data

Temperature (°C)	Langmuir const	Langmuir constants			Freundlich constants		
	b (l/mg)	$q_{\rm max} \ ({\rm mg/g})$	$R^2$	1/n	$K_{ m f}$	$R^2$	
28	0.0710	65.3595	0.9867	0.2367	19.8737	0.7929	
35	0.0699	60.6060	0.9894	0.2281	19.1098	0.8154	
45	0.0628	44.4444	0.9914	0.1949	15.7478	0.8753	

Table 2
Langmuir constant for different adsorbents

Adsorbent	Langmuir constant, $q_{\text{max}}$ (mg/g)	References
Groundnut husk	42.71	Okieimen et al. [39]
Commercial activated carbon (F. 400)	8.21	Ramos et al. [40]
Seaweeds		
Padina tetrastomatica (brown)	64	Hashim and Chu [41]
Chaetomorpha linum (green)	58.6	
Gracilaria salicornia (red)	19.6	
Lignite	40.25	Allen and Brown [42]
Activated bentonite	16.5	Paradas et al. [43]
Sugar Can (SA-SC)	149.93	Anoop Krishnan and Anirudhan [44]
Olive cake	65.4	Present study



Fig. 4. The linearized Freundlich adsorption isotherms for Cd(II) ions adsorption by olive cake at different temperatures (initial concentration of Cd(II): 100 ppm; agitation speed: 100 rpm; pH: 6; contact time: 24 h).

of values  $q_{\text{max}}$  are considerably consistence with those that generated from the adsorption of Cd(II) onto the seaweeds of Padina tetrastomatica (brown) and Chaetomorpha linum (green).

The applicability of Freundlich model was also analyzed by plotting  $\ln q_{\rm e}$  versus  $\ln C_{\rm e}$  as shown in Fig. 4. The constants *n* and  $K_{\rm f}$  can be determined as a function of temperature from the slope and intercept, respectively. These values of  $K_{\rm f}$ , *n* and  $R^2$  are listed in Table 1.

The values of  $K_f$  decreased from 19.9 to 15.7 with increasing the solution temperature from 28 to 45 °C. Since  $K_f$  is measuring the degree of strength of adsorption and the decreasing in these values with temperature confirms that the adsorption process is exothermic. The values of 1/n were found less than unity over the temperatures 28, 35 and 45 °C. These values represent good adsorption of cadmium ions on the olive cake. It can be also noticed that the values of 1/n decreases as the temperature

Table 3 Thermodynamic parameters for the adsorption process of Cd(II) ions increases indicating to the adsorption of cadmium ions on the olive cake decreases with increasing the temperature.

On comparing the regression coefficient values that generated from the Langmiur model with those of Freundlich model, we observed that Langmiur model has a better fitting model than Freundlich model as the former has a higher correlation regression coefficient than the later. This indicates to the applicability of monolayer coverage of the Cd(II) ions on the surface of the olive cake.

#### 3.1.4. Thermodynamics point view

In environmental engineering practice, both energy and entropy factors must be considered in order to determine what processes will occur spontaneously. Standard Gibb's free energy change  $\Delta G^{\circ}$  is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if  $\Delta G^{\circ}$  is a negative value. The very useful relationship between standard free energy change,  $\Delta G^{\circ}$ , and the Langmuir constant, *b*, is given by the following equation [45]:

$$\Delta G^{\circ} = -RT\ln b \tag{7}$$

where *R* is universal gas constant (8.314 J/mol K), and *T* is the absolute temperature in K. The other useful relationships are the change in standard enthalpy,  $\Delta H^{\circ}$ , and standard entropy,  $\Delta S^{\circ}$ , and they are given by

$$\frac{\Delta G^{\circ}}{RT} = \frac{\Delta H^{\circ}}{RT} - \frac{\Delta S^{\circ}}{R}$$
(8)

The enthalpy and entropy changes can be, respectively, determined from the slope and intercept of the plot  $\ln b$  against 1/T.

The values of  $\Delta G^{\circ}$ ,  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  for the adsorption process were calculated and they are listed in Table 3. The negative value of  $\Delta G^{\circ}$  confirms the feasibility of the process and the spontaneous nature of sorption. The value of  $\Delta H^{\circ}$  was negative, indicating that the sorption reaction is exothermic. The positive

$\overline{T(^{\circ}C)}$	<i>b</i> (l/mol)	$-\Delta G^{\circ}$ (kJ/mol)	$-\Delta H^{\circ}$ (kJ/mol)	$\Delta S^{\circ}$ (J/mol K)
28	7983.844	22.4967		
35	7865.14	22.9813	$6.0358 (R^2 = 0.897)$	54.8 ( $R^2 = 0.897$ )
45	7054.393	23.4393		



Fig. 5. Variation of the Cd(II) ions concentration with time (initial concentration of Cd(II): 100 ppm; agitation speed: 100 rpm; pH: 6; temperature  $28 \degree$ C).

value of  $\Delta S^{\circ}$  shows the increasing randomness at the solid/liquid interface during the sorption of Cd(II) ions onto olive cake.

### 3.2. Kinetics studies

The selecting optimum operating conditions for batch process can be generated from the information on the kinetics. Fig. 5 displays the concentration decay curve related to adsorption of cadmium ion on olive cake. The system variable includes time while keeping the other conditions constant. The initial concentration, amount of olive cake, temperature and agitation speed are 100 ppm, 0.3 g, 28 °C and 100 rpm, respectively. The initial pH is adjusted at 6. The pH of solution was not controlled after initiation of the batch experiments. From Fig. 5, the adsorption rate within the first 5 min was observed to be very high and thereafter the reaction proceeds at a slower rate until the time reached 120 min and then it is almost stayed constant.

Here, we attempted to analyze the adsorption data using pseudo first-order and pseudo second-order kinetic models. Legergen pseudo first-order model [46] assumes that the rate of change of solute uptake with time is directly proportional to the difference in the saturation concentration and the amount of solid uptake with time.

The general form of this model is expressed as

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_{1,\mathrm{ads}}(q_\mathrm{e} - q_t) \tag{9}$$

where  $q_t$  is the amount of cadmium adsorbed on the adsorbent at any time *t*, respectively (mg of ion/g of olive cake) and  $k_{1,ads}$ is the rate constant of adsorption (min<sup>-1</sup>).

Applying the boundary condition  $q_t = 0$  at t = 0 and  $q_t = q_t$  at t = t and then integrate Eq. (9), we get

$$\ln(q_e - q_t) = \ln q_e - k_{1,ads}t \tag{10}$$

The rate constant  $k_{1,ads}$  and the equilibrium amount of cadmium,  $q_e$ , of Legergen pseudo first-order model can be, respectively, obtained from the slope and intercept of plot between  $\ln(q_e - q_l)$  versus time, *t* as shown in Fig. 6. The calculate values of the  $k_{1,ads}$ ,  $q_e$  and  $R_2$  are 0.0368 (min<sup>-1</sup>), 16.87 (mg/g) and 0.85,



Fig. 6. Pseudo first-order kinetic plots for the adsorption of Cd(II) on olive cake (initial concentration of Cd(II): 100 ppm; agitation speed: 100 rpm; pH: 6; temperature 28  $^{\circ}$ C).

respectively. This figure shows that Legergen model does not fit well for the whole range of the contact time. It might be due to the surfaces of the olive cake are not so homogenous.

The pseudo second-order model [47] is based on the sorption capacity of the solid phase. The general form of this model is given by

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_{2,\mathrm{ads}}(q_\mathrm{e} - q_t)^2 \tag{11}$$

where  $k_{2,ads}$  is the rate constant of adsorption (g/mg min).

The linear form of Eq. (11) (after integrating under the same boundary conditions of the pseudo first-order kinetics) is

$$\frac{t}{q_t} = \frac{1}{k_{2,\text{ads}}q_e^2} + \frac{1}{q_e}t$$
(12)

Fig. 7 shows the experimental data fitted to linear form of the pseudo second-order model where  $t/q_t$  plotted versus *t*. The values of  $q_e$  and  $k_{2,ads}$  can be determined from the slope and intercept of the plot, respectively. This figure represents good



Fig. 7. Pseudo second-order kinetic plots for the adsorption of Cd(II) on olive cake (initial concentration of Cd(II): 100 ppm; agitation speed: 100 rpm; pH: 6; temperature  $28 \,^{\circ}$ C).



Fig. 8. Theoretical and experimental Cd(II) concentration,  $q_t$ , of olive cake as a function of time. Long-dashed line corresponds to theoretical and circle symbols corresponds to experimental.

fit over the whole range of the time. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients,  $R^2$ , which is equal to 0.99. This indicates that this model successfully describes the kinetics of Cd(II) ions adsorption on the olive cake. The theoretical values of  $k_{ads}$  and  $q_e$  are found  $8.4 \times 10^{-3}$  g mg<sup>-1</sup> min<sup>-1</sup> and 44.25 mg/g. By inserting these values into Eq. (12) and then rearranging it, we get the theoretical relation of  $q_t$ 

$$q_t = \frac{k_{\text{ads}} q_e^2 t}{1 + k_{\text{ads}} q_e t} = \frac{16.447t}{1 + 0.372t}$$
(13)

Fig. 8 shows the comparison of experimental values of  $q_t$  with theoretical ones. It is clear from Fig. 8 that the experimental and theoretical  $q_t$  values are in accordance with each other. These results suggest that the adsorption of the Cd(II) on olive cake follows the second-order type kinetic reaction.

## 4. Conclusions

In general, the present study shows that olive cake is an effective adsorbent for removal of cadmium ions under suitable experimental conditions. The experimental data may prove to be helpful in the design and performance a wastewater treatment plant. Specifically, the following conclusions can be drawn from the results of this study:

- 1. The batch pH studies indicated that the optimum pH was 6 and the maximum cadmium removal at this pH was 66.6%.
- 2. The isotherm study indicates that the Langmuir and Freundlich models were adequately modeled our experimental data.
- 3. The thermodynamic studies confirm that the process was spontaneous and exothermic nature of the adsorption process.
- 4. The kinetics study of sorption at pH 6 and temperature 28 °C indicates that the pseudo second-order model provides better correlation of the sorption data than the pseudo first-order model.

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