

## Thermodynamics and Kinetic Studies of Iron(III) Adsorption by Olive Cake in a Batch System

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**Abstract.** The adsorption of Fe(III) ions from the aqueous solution model using olive cake as an adsorbent has been investigated. The influences of the initial pH, temperature, contact time and dosage of the adsorbent on adsorption performance have been experimentally verified by a batch method. The adsorbent used in this study exhibited a good adsorption potential at initial pH 4.5 for temperatures 28, 35 and 45 °C. The removal efficiency and distribution coefficient have also been determined for the adsorption system as a function of dosage of the adsorbent. The experimental results are described by Langmuir, Freundlich and Dubinin-Kaganer-Radushkevich (DKR) isotherm models. Experimental results show that the kinetic model of pseudo-second order provided a good description of the whole experimental data more than the kinetic of the Lagergren-first order.

**Key words:** Adsorption, iron ions, olive cake, isothermal and kinetics models.

**Resumen.** Se investigó la adsorción de iones Fe(III) de la solución acuosa modelo utilizando el bagazo de oliva como adsorbente. La influencia del primer pH, temperatura, tiempo de contacto y la dosis de adsorbente en el rendimiento de la adsorción se verificó experimentalmente por el método de lote. El adsorbente utilizado en este estudio exhibió un buen potencial de adsorción inicial a pH 4.5 para temperaturas de 28, 35 y 45 °C. La eficiencia de eliminación y el coeficiente de distribución se determinaron también para el sistema de adsorción en función de la dosis de adsorbente. Los resultados se describen en modelos de isothermas de Langmuir, Freundlich y Dubinin-Kaganer-Radushkevich (DKR), los cuales muestran que el modelo de cinética de pseudo segundo orden describe adecuadamente la totalidad de los datos experimentales, aún más que la cinética de Lagergren de primer orden.

**Palabras clave:** Adsorción, iones Fe, bagazo de oliva, modelos de isothermas y de cinética.

### Introduction

The removal of heavy metals such as Pb, Fe, Cr, Cd, Co, etc., from ground and industrial water is a matter of great interest in the poor countries that have limited water resources. Of these, iron ions are attracting wide attention of researchers as one of the heavy metals and they are found in many manufacturing industries such as the metal finishing and galvanized pipe [1]. The presence of iron ions in ground and industrial water becomes toxic at high level and then may cause environmental and human health problems [2-3].

In general, there are various technological methods exist for removing heavy metal ions from water and wastewater including supercritical fluid extraction [4], bioremediation [5], and oxidation with oxidizing agent [6]. However, most of these technologies are either extremely expensive or too inefficient in reducing metal ion levels in effluent to concentrations that are required by governmental legislation. Among all methods, the adsorption is a cost-effective technique and simple to operate [7-10]. The adsorption process usually used natural organic or inorganic materials that are particularly abundant and inexpensive. Among these materials are palm kernel husk [11], modified cellulosic material [12], corn cobs [13], residual lignin [14, 15], wool, [16], apple residues [17], polymerized orange skin and banana husk [18], pine bark [19], sawdust [20], peanut hull [21-24].

In particular, the olive cake, which is used as an adsorbent in this study, is generated during the squeezing the olive to get the oil and it may constitute a promising low-cost adsorbent among biomaterials, since this substance is produced in great

quantities in the Mediterranean area. The existing research into the use of olive cake as adsorbent for removing of heavy metals from aqueous solution is extremely limited [25-28]. Nacèra Yeddou *et al.* [29] studied the sorption of Fe(III) onto eggshells with respect to solute concentration, contact time, adsorbent dose and temperature. Adsorption studies of iron (III) on chitin are investigated by Karathikeyan *et al.* [30]. They studied the influence of particle size, dosage of the adsorbent, contact time, initial concentration of the adsorbate and temperature. No study, to our knowledge, has been reported on the use of the olive cake for removing Fe (III) ions from ground and industrial water.

The general aim of this study is to investigate adsorption capability of olive cake in the removing of Fe(III) ions from a solution model of industrial and ground water. Particularly, to investigate the adsorption yield of Fe(III) ions by studying the influence of initial pH, temperature and mass of olive cake; to use the adsorption isotherms models (Langmuir, Freundlich and Dubinin-Kaganer-Radushkevich (DKR)) in order to correlate the experimental results; to study the adsorption kinetics models of Fe(III) examining the change in adsorption rate with time.

### Materials and Methods

#### Adsorbent

The mixture of green and black of olive cake used in the present investigation was collected from olive mills located in

Irbid city, Jordan. This adsorbent contained a mixture between pulp and olive stone. A sample of olive cake was washed several times with hot deionized water and then by cool deionized water. This sample was filtered out using Whatman No. 41 and then dried in an oven at 100 °C for 24 hours until no variation in the weight of the sample observed. After that, the dried sample was grounded and sieved into several size fractions, using standard ASTM sieves. The particle size of the olive cake that used throughout this experiment was 100  $\mu\text{m}$ . The synthetic sample of 100 ppm-Iron solution was prepared from  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ . All the chemicals were of analytical-reagent grade.

### Apparatus

Atomic Absorption Spectrophotometer, AAS, (Model AA 100, Perkin-Elmer) was used to analyze the iron ions concentration in aqueous solution. The pH of all solutions was recorded by pH meter (Oiron 520). The temperature was controlled using temperature controller (Gefellschaft Funn 1003,  $\pm 0.1$  °C). Isothermal shaker was also used (Gefellschaft Fur 978).

### Adsorption experiments

#### Equilibrium studies

Batch equilibrium experiments were performed by shaking 200 ml aqueous solution containing 100 ppm of Fe (III) ions with 1.0 g of olive cake. The solution in 250 ml-Erlenmeyer flasks was shaken using an isothermal shaker for 24 hours in order to ensure that adsorption equilibrium was established. The shaken speed was controlled at constant speed of 100 rpm. Three temperatures of the solution were studied (28, 35 and 45 °C). The initial pH of the solution was adjusted within the range from 2 to 8 by using 1N of NaOH and 1N of HCl.

At the end of the equilibrium time, the flasks were removed from the shaker and the adsorbent was then filtered using filter paper (Whatman No. 41). The filtrate was analyzed using AAS. An optimum value of initial pH was selected for isotherm and kinetic studies. All the reported results are the average of at least triplicate measurements. Average and standard deviation values from triplicates shown in the tables are calculated using OriginPro 7 software. The error bars shown in the figures represent the standard deviation values.

The Fe(III) ions adsorbed by the olive cake at equilibrium is determined using a mass balance equation

$$q_e = \frac{(C_i - C_e)S}{m} \quad 1$$

where  $q_e$  is the Fe(III) ions concentration adsorbed on the olive cake at equilibrium (mg of iron ion/g of olive cake),  $C_i$  is the initial concentration of Fe(III) ions in the solution (mg/l) and  $C_e$  is the equilibrium concentration or final concentration of Fe(III) ions in the solution (mg/l). The does (slurry) concentration,  $S$ , is expressed by

$$S = \frac{m}{v} \quad 2$$

Where  $v$  is the initial volume of Fe(III) ions solution used (L) and  $m$  is the mass of olive cake used (g).

The percent adsorption (%) and distribution ratio ( $K_d$ ) are calculated using the following equations

$$\% \text{ adsorption} = \frac{C_i - C_e}{C_i} \times 100\% \quad 3$$

$$K_d = \frac{\text{amount of Fe(III) in adsorbent}}{\text{amount of Fe(III) in solution}} \times \frac{1}{S} \quad 4$$

The percent adsorption and  $K_d$  (L/g) can be correlated by the following equation [28]

$$\% \text{ adsorption} = \frac{100 K_d}{K_d + 1/S} \quad 5$$

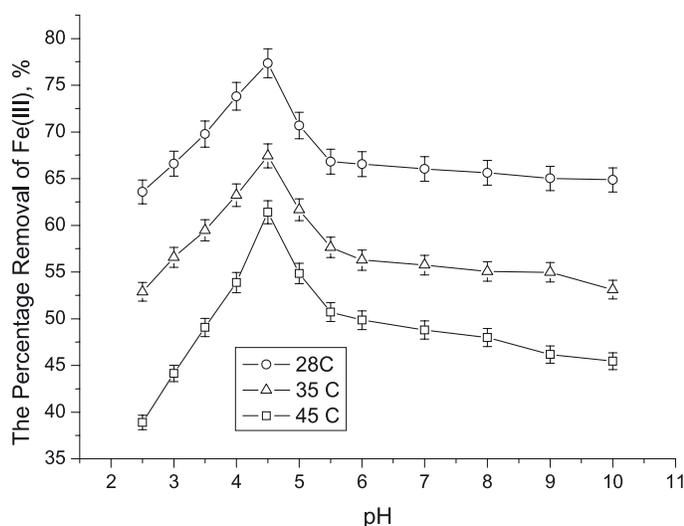
### Kinetic studies

Batch kinetic studies were investigated by placing 200 mL of Fe (III) ions solution with a concentration of 100 ppm in a 1000 ml-Erlenmeyer flask. The initial pH of the solution was adjusted at the optimum value. 1 g of olive cake was added to a 1000 mL flask. A series of such flasks was agitated in isothermal shaker at shaking 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 minute for the first 5 minutes and 5 minutes for the first 25 minutes and then each 10 minutes until the end of the experiment. The samples were withdrawal and then filtered using filter paper (Whatman No. 41). These filter samples were then analyzed using AAS for quantifying the change of solution concentration with time.

## Results and Discussions

### Effect of initial pH

In order to evaluate the effect of initial pH on removal of Fe (III) ions from aqueous solution, several experiments were performed at different initial pH values that ranges from 2 to 8 and at different temperatures of 28, 35 and 45 °C. The initial concentration of Fe(III) ions and speed of the shaker were fixed at 100 ppm and 100 rpm respectively. The amount of the olive cake was taken 1 g. Figure 1 represents the removal efficiency of Fe (III) ions versus the initial pH over temperatures of 28, 35 and 45 °C. For the three temperatures, it can be seen that there are no important differences among optimal initial pH values corresponding to these temperatures. It can also be observed that the removal efficiency increases with increasing initial pH and it almost reaches a peak value around 4.5 and then decreases with increasing initial pH. Then the optimal Fe (III) removal efficiency occurs at pH 4.5. This result is considerably consistent with eggshells and chitin adsorbents [29, 30].



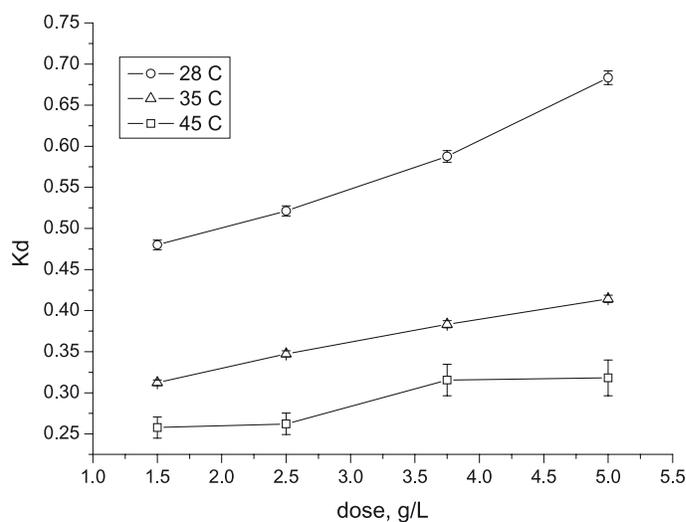
**Fig. 1.** Effect of initial pH on the removal efficiency, %, of Fe(III) ions at different temperatures. (Initial concentration of Fe (III): 100 ppm, Agitation speed: 100 rpm, Mass of olive cake: 1 g, Dose: 5 g/L, Contact time: 24 h).

At low pH, the concentration of proton is high, so iron ions binding sites become positively charged and then metal cations and protons compete for binding sites of olive cake which results in lower uptake of iron ions. As pH increases in the ranges from 2 to 4.5, the concentration of proton exist in the solution will be decreased and hence will not give the chance to compete with iron ions on the adsorption sites of olive cake thus facilitating greater Fe(III) ions uptake. After pH 4.5 the removal efficiency decreases as pH increases, which is inferred to insoluble iron hydroxide starts precipitating from the solution. Therefore, at these pH values, both adsorption and precipitation are the effective mechanisms to remove the iron (III) in aqueous solution. The iron cations in aqueous solution convert to different hydrolysis products [31].

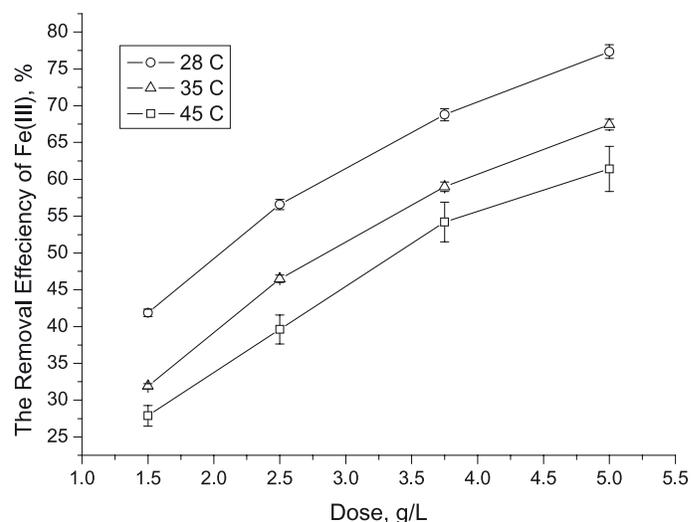
#### Effect of dosage

The effect of varying the dosage of the adsorbent on the distribution ratio,  $K_d$ , and on the removal efficiency of Fe(III) ions from aqueous solution are shown in Figs. 2 and 3 respectively. The initial pH was adjusted at 4.5. Figure 2 shows that  $K_d$  values increase with the increasing of the dose concentration over the three temperatures of solution (28, 35 and 45 °C).

Figure 3 shows that the removal efficiency is generally increased as the dose concentration increases over the three temperature values. At 28 °C, it is observed that 42% removal is achieved at 1.5 g/L while 77% is achieved at 5 g/L. This can be explained by the fact that more mass available, more the contact surface offered to the adsorption. These results are qualitatively in a good agreement with those found in the literature [30]. Our results showed that the best removal efficiency was obtained at 1 g (dose concentration = 5g/L) and 28 °C of olive cake and temperature respectively.



**Fig. 2.** Effect of dosage of olive cake on the distribution ratio of Fe (III) ions: (Initial concentration of Fe(III): 100 ppm, Agitation speed: 100 rpm, pH: 4.5, Contact time: 24 h).



**Fig. 3.** Effect of dosage of olive cake on the removal efficiency of Fe (III) ions at different temperatures: (Initial concentration of Fe (III): 100 ppm, Agitation speed: 100 rpm, pH:4.5, Contact time: 24 h).

#### Adsorption isotherms

To conduct the isotherm studies, the above procedures as shown in Sec. 2.3.1 were repeated except the initial pH of solution which was adjusted at the optimum value (pH = 4.5) and the mass of olive cake which was taken as 0.3, 0.5, 0.75 and 1 g at different temperatures of 28, 35 and 45 °C.

Three adsorption isotherms models were used: Langmuir, Freundlich and Dubinin-Kaganer-Radushkevich (DKR) [32]. Langmuir's isotherm model suggests that the uptake occurs on homogeneous surface by monolayer sorption without interac-

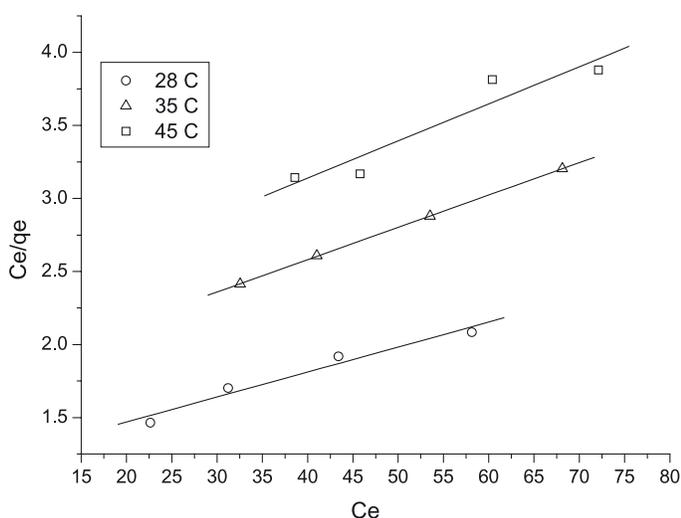
tion between adsorbed ions. The linear form of Langmuir isotherm equation is represented by the following equation

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{1}{q_{\max}} C_e \quad 6$$

Where  $q_{\max}$  is the maximum Fe(III) ions uptake per unit mass of olive cake (mg/g) related to adsorption capacity and  $b$  is Langmuir constant (L/mol) related to energy of sorption. Therefore, a plot of  $C_e/q_e$  versus  $C_e$ , gives a straight line of slope  $1/q_{\max}$  and intercept  $1/(q_{\max} b)$ .

Figure 4 shows the experimental data that were fitted by the linear form of Langmuir model, ( $C_e/q_e$ ) versus  $C_e$ , at temperatures of 28, 35 and 45 °C. The values of  $q_{\max}$  and  $b$  were evaluated from the slope and intercept respectively for the three isothermal lines. These values of  $q_{\max}$  and  $b$  are listed in Table 1 with their uncertainty and their determination coefficients,  $R^2$ .

Table 1 shows that the values of  $q_{\max}$  and  $b$  are decreased when the solution temperature increased from 28 to 45 °C. The



**Fig. 4.** The linearized Langmuir adsorption isotherms for Fe(III) ions adsorption by olive cake at different temperatures. (Initial concentration of Fe(III): 100 ppm, Agitation speed: 100 rpm, pH: 4.5, Contact time: 24 h).

decreasing in the values of  $q_{\max}$  and  $b$  with increasing temperature indicates that the Fe(III) ions are favorably adsorbed by olive cake at lower temperatures, which shows that the adsorption process is exothermic.

In order to justify the validity of olive cake as an adsorbent for Fe(III) ions adsorption, its adsorption potential must be compared with other adsorbents like eggshells [29] and chitin [30] used for this purpose. It may be observed that the maximum sorption of Fe(III) on olive cake is approximately greater 10 times than those on the chitin and eggshells.

The Freundlich model is a case for heterogeneous surface energies and it gives an exponential distribution of active sites. The linear form of this model is represented by

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad 7$$

The Freundlich constants  $K_f$  and  $n$ , which respectively indicating the adsorption capacity and the adsorption intensity, are calculated from the intercept and slope of plot  $\ln q_e$  versus  $\ln C_e$  respectively, as shown in Fig 5. These values of  $K_f$  and  $n$  are also listed in table 1 with their determination coefficients.

It can be observed that the values of  $K_f$  are decreased with increasing the temperature of solution from 28 to 45 °C. The decreasing in these values with temperature confirms also that the adsorption process is exothermic. It can be also seen that the values of  $1/n$  decreases as the temperature increases. Our experimental data of values  $K_f$  and  $1/n$  are considered qualitatively consistence with those that found in adsorption of iron (III) on eggshells [29] and chitin [30].

The Dubinin-Kaganer-Radushkevich (DKR) model has the linear form

$$\ln q_e = \ln X_m - \beta \varepsilon^2 \quad 8$$

where  $X_m$  is the maximum sorption capacity,  $\beta$  is the activity coefficient related to mean sorption energy, and  $\varepsilon$  is the Polanyi potential, which is equal to

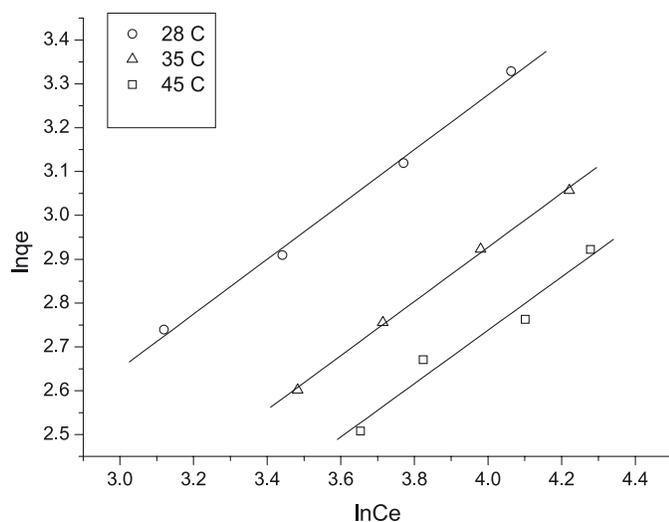
$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad 9$$

where  $R$  is the gas constant (kJ/kmol-K).

**Table 1.** Langmuir, Freundlich and DKR constants for adsorption of Fe(III) ions on olive cake.

T (°C)	Langmuir				Freundlich		DKR			
	b	$q_{\max}$	$R^2$	$1/n$	$k_f$	$R^2$	$\beta$	$X_m$	$E$	$R_2$
28	0.0152 ±0.00011	58.479 ±3.44	0.96	0.626	2.164 ±0.98	0.99	-0.00006	28.321 ±1.04	91.287	0.91
35	0.0130 ±0.00013	45.249 ±1.17	0.99	0.618	1.578 ±0.15	0.99	-0.00009	23.539 ±2.12	74.535	0.97
45	0.012 ±0.000144	39.370 ±2.07	0.91	0.609	1.354 ±0.12	0.96	-0.0001	20.816 ±1.01	70.711	0.95

$b$  in (L/mg),  $q_{\max}$  in (mg/g)  $b$  in (mol/J)<sup>2</sup>,  $X_m$  in (mg/g),  $E$  in (J/mol).

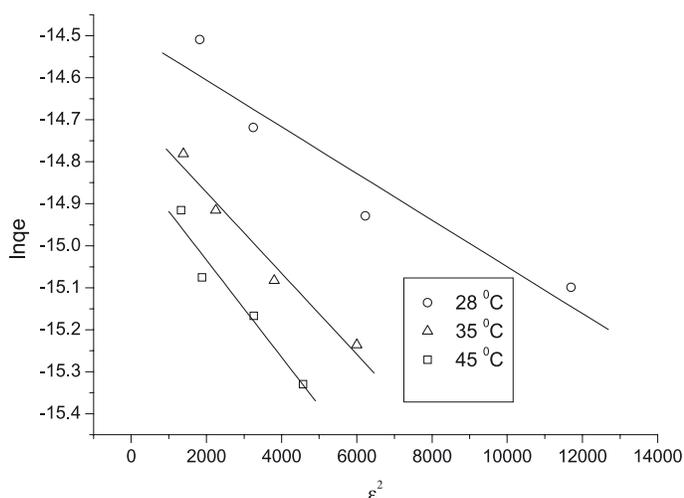


**Fig. 5.** The linearized Freundlich adsorption isotherms for Fe(III) ions adsorption by olive cake at different temperatures. (Initial concentration of Fe (III): 100 ppm, Agitation speed: 100 rpm, pH: 4.5, Contact time: 24 h).

The slope of the plot of  $\ln q_e$  versus  $\varepsilon^2$  gives  $\beta$  ( $\text{mol}^2/\text{J}^2$ ) and the intercept yields the sorption capacity,  $X_m$  ( $\text{mg}/\text{g}$ ) as shown in Fig. 6. The values of  $\beta$  and  $X_m$ , as a function of temperature are listed in table 1 with their corresponding value of the determination coefficient,  $R^2$ . It can be observed that the values of  $\beta$  increase as temperature increases while the values of  $X_m$  decrease with increasing temperature.

The values of the adsorption energy,  $E$ , was obtained from the relationship [33]

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



**Fig. 6.** The linearized Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherms for Fe(III) ions adsorption by olive cake at different temperatures. (Initial concentration of Fe(III): 100 ppm, Agitation speed: 100 rpm, pH: 4.5, Contact time: 24 h).

and then they are listed in table 1. It can be observed that the values of  $E$  decreases as the temperature increases indicating that the adsorption of Fe(III) ions onto olive cake may be physical (electrostatic) in nature.

The goodness of fit of the experimental data is measured by the determination coefficients,  $R^2$ . At all temperatures, the Freundlich model showed better fit followed by Langmuir model followed by Dubinin-Kaganer-Radushkevich (DKR) model.

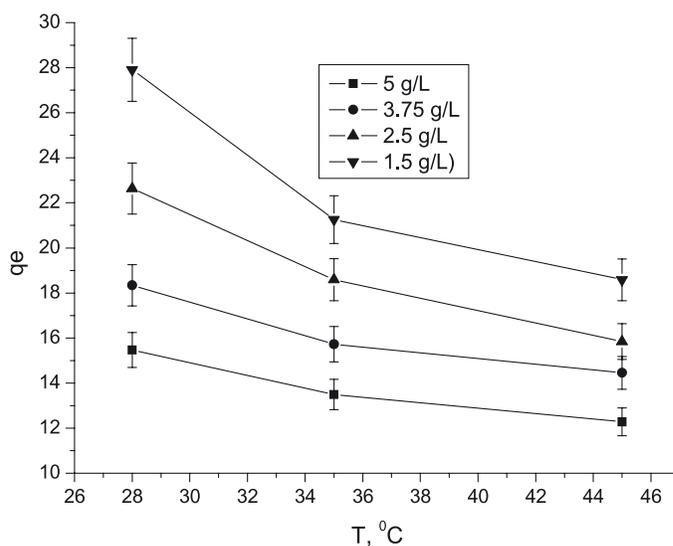
### Effect of temperature

Figure 7 shows the equilibrium removal of Fe(III) ions as a function of the temperature. The initial concentration was fixed at 100 ppm and initial pH was adjusted at 4.5. Over the dosage of the adsorbent values (namely 1.5, 2.5, 3.75 and 5 g/L), it can be seen that the  $q_e$  decreases as the temperature increases. For example, at dosage of 1.5 g/L of olive cake, it is found that  $q_e$  decreases from 27.9 mg/g to 18.6 mg/g as the solution temperature increases from 28 °C to 45 °C respectively. This behavior confirms that the adsorption process is exothermic process. Our results are in a good agreement with those obtained for removal of iron ions using eggshells [29] and chitin [30].

The decreasing in adsorption as temperature increases may be due to the relative increase in the escaping tendency of the iron ions from the solid phase to the bulk phase; 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 [34].

### Thermodynamics parameters

It is important to study the thermodynamic parameters such as standards Gibbs free energy,  $\Delta G^\circ$ , enthalpy,  $\Delta H^\circ$  and entropy,  $\Delta S^\circ$  changes.



**Fig. 7.** Equilibrium concentration of Fe(III) ions as a function of solution temperatures (Initial concentration of Fe(III): 100 ppm, Agitation speed: 100 rpm, pH: 4.5).

When the adsorption reaches equilibrium state

$$G^0 = -RT \ln b \quad 10$$

where  $b$  denotes the equilibrium constant,  $R$  is universal gas constant and  $T$  is the absolute temperature in  $K$ . Therefore,  $\Delta G^0$  for an adsorption reaction will be estimated if Langmuir constant,  $b$ , for adsorption is known. The other useful relationships are  $\Delta H^0$  and  $\Delta S^0$  and they are given by:

$$\frac{\Delta G^0}{RT} = \frac{\Delta H^0}{RT} - \frac{\Delta S^0}{R} \quad 11$$

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

Thermodynamic parameters obtained from Eqs. 10 and 11 for the adsorption of Fe(III) ions on olive cake are given in table 2. As shown in the table, the negative value of  $\Delta G^0$  confirms the feasibility of the process and the spontaneous nature of sorption. The values of  $\Delta H^0$  and  $\Delta S^0$  are found to be  $-10.83$  kJ/mol and  $19.9$  J/mol-K respectively. The values of  $\Delta H^0$  was negative, indicating that the sorption reaction is exothermic. The positive value of  $\Delta S^0$  shows the increasing randomness at the solid/liquid interface during the sorption of Fe(III) ions onto olive cake.

### Kinetics study

The kinetic results obtained from batch experiments were analyzed using different kinetics models such as Lagergren pseudo first-order [35], pseudo second-order [36] models. Equation 10 gives the linear form of Lagergren pseudo first-order models

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad 12$$

Where  $q_t$  is Fe(III) ions concentration ions adsorbed on olive cake at any time (mg of Fe(III) ion/g of olive cake) and  $k_1$  is the adsorption rate constant ( $\text{min}^{-1}$ ). A linear plot of  $\ln(q_e - q_t)$  against  $t$  gives the slope =  $k_1$  and intercept =  $\ln q_e$ .

The equation that describes the pseudo-second order model is given in the following linear form

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad 13$$

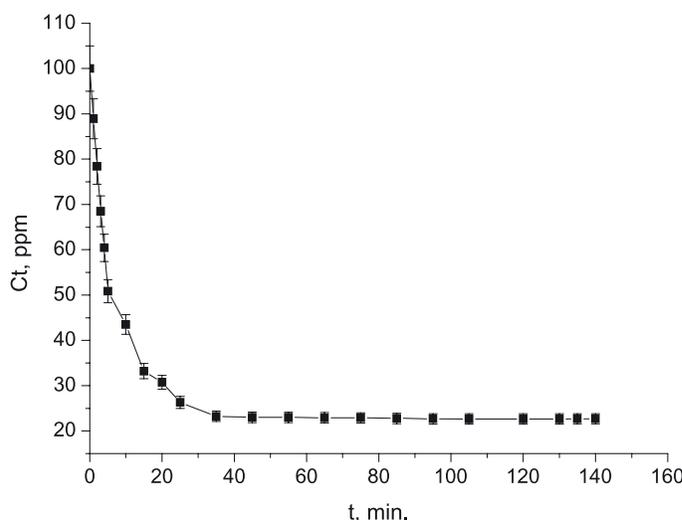
where  $k_2$  is the adsorption rate constant (g/mg-min). The  $k_2$  and  $q_e$  are found from the intercept and slope of  $t/q_t$  versus  $t$  linear plot such that  $q_e = 1/\text{slope}$  and  $k_2 = \text{slope}^2/\text{intercept}$ .

**Table 2.** Thermodynamics parameters for the adsorption of Fe(III) ions on olive cake.

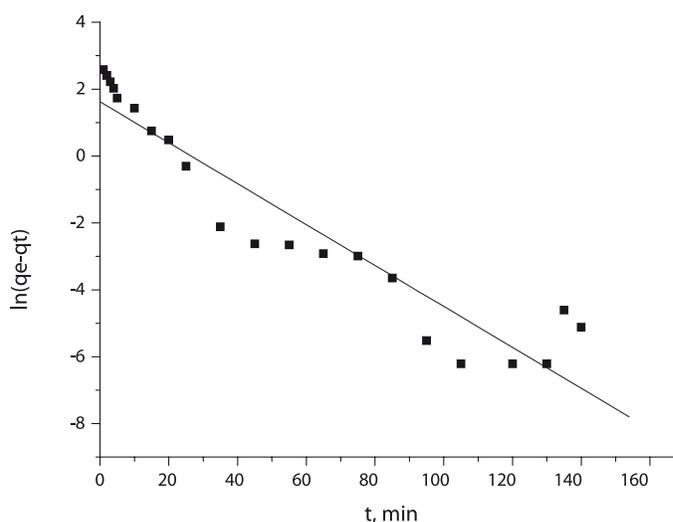
T(°C)	$b$ (L/mol)	$-\Delta G^0$ (kJ/mol)	$-\Delta H^0$ (kJ/mol)	$\Delta S^0$ (J/mol-K)
28	847.2174	16.8718		
35	727.8947	16.8755	10.83	19.9
45	667.7246	17.1953		

Figure 8 shows the change in the remaining concentration of Fe(III) ions as a function of time at 1 g of olive cake (dosage 5 g/L). The initial concentration, temperature and agitation speed are fixed at 100 ppm, 28 °C and 100 rpm respectively. The initial pH was adjusted at 4.5. It was observed that the remaining concentration of Fe(III) ions in the aqueous solution decreased rapidly at the incipient stage of adsorption and then reached almost equilibrium in about 35 minutes. Thereafter the reaction proceeds at a slower rate until equilibrium and then almost stayed constant when the time approximately reached 140 min.

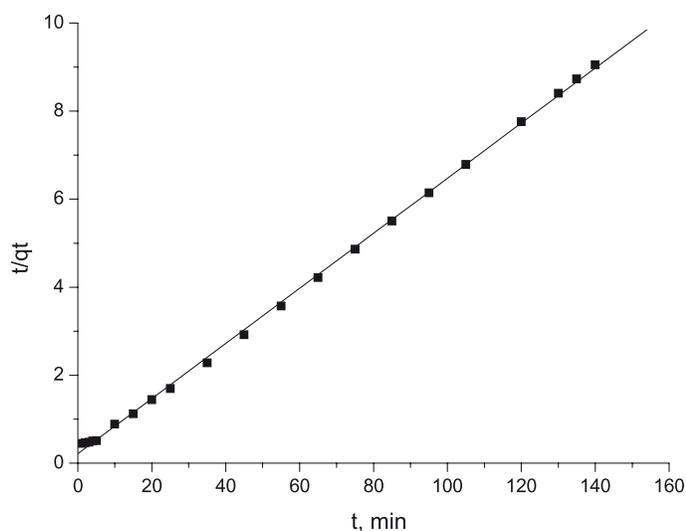
The parameters of the kinetics models (pseudo-first, pseudo-second) with their correspondent coefficients of determination are calculated from the slopes and intercepts of the linear plot of these models as shown in Figs. 9-10 and they are summarized in Table 3.



**Fig. 8.** Variation of the Fe(III) ions concentration with time. (Initial concentration of Fe(III): 100 ppm, Agitation speed: 100 rpm, pH: 4.5, temperature 28 °C).



**Fig. 9.** Pseudo-first-order kinetic plots for the adsorption of Fe(III) ions on olive cake. (Initial concentration of Fe(III): 100 ppm, Agitation speed: 100 rpm, dosage: 5 g/L, pH: 4.5, temperature: 28 °C).



**Fig. 10.** Pseudo-second-order kinetic plots for the adsorption of Fe(III) ions on olive cake. (Initial concentration of Fe(III): 100 ppm, Agitation speed: 100 rpm, dosage: 5 g/L, pH: 4.5, temperature: 28 °C).

**Table 3.** The adsorption kinetic model rate constants for adsorption of Fe(III) ions on olive cake.

Pseudo first-order		Pseudo second-order		
$k_1$	$R^2$	$k_2$	$q_e$	$R^2$
0.061	0.89	0.018	15.97	0.99

$k_1$  in (1/min),  $k_2$  in (g/mg-min),  $q_e$  in (mg/g).

The degree of goodness of linear plot of these kinetic models can be judged from the value of the determination coefficient of the plot, which can also be regarded as a criterion in the determination of the adequacy of kinetic model. From the determination coefficient values above, adsorption of Fe(III) ions on the olive cake is regarded as pseudo-second-order rather than pseudo-first-order.

## Conclusions

Based upon the experimental results of this study, the following conclusions can be drawn:

1. The maximum removal efficiency of Fe(III) ions occurs at initial pH of 4.5 and solution temperature of 28 °C.
2. The removal efficiency of Fe(III) ions increases as the dosage of the adsorbent increases.
3. The isotherm study indicates that the Langmuir, Freundlich and Dubinin–Kaganer–Radushkevich (DKR) isotherms models can adequately model sorption data.

4. The equilibrium removal of Fe(III) ions decreases as the temperature of solution increases.
5. The removal of Fe(III) ions by this olive cake is an exothermic process.
6. It is found that the pseudo-second order model is applicable for whole the range of contact time while not for the pseudo-first order.

## Acknowledgments

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## References

1. Aksu, Z.; Calik, A.; Dursun, A. Y.; Demarcan, Z. *Process Biochemistry* **1999**, *34*, 483–491.
2. Das, B.; Hazarika, P.; Saikia, G.; Kalita, H.; Goswami, D. C.; Das, H. B.; Dube, S. N.; Dutta, R. K. *J. Hazard. Mater.*, in press.
3. Sarin, P.; Snoeyink, V. L.; Bebee, J.; Jim, K. K.; Beckett, M. A.; Kriven, W. M.; Clement, J. A. *Water Res.* **2004**, *38*, 1259–1269.
4. Ellis, D.; Bouchard, C.; Lantagne, G. *Desalination* **2000**, *130*, 255–264.
5. Andersen, W.C.; Bruno, T. J. *Anal. Chim. Acta* **2003**, *485*, 1–8.
6. Berbenni, P.; Pollice, A.; Canziani, R.; Stabile, L.; Nobili, F. *Technol.* **2000**, *74*, 109–114.
7. Uchida, M.; Ito, S.; Kawasaki, N.; Nakamura, T.; Tanada, S. *J. Colloid Interf. Sci.* **1999**, *220*, 406–409.
8. Pakula, M.; Biniak, S.; Swiatkowski, A. *Langmuir* **1998**, *14*, 3082–3089.
9. Huang, C.; Cheng, W. P. *J. Colloid Interf. Sci.* **1997**, *188*, 270–274.
10. Kato, M.; Kudo, S.; Hattori, T. *Bull. Chem. Soc. Jpn.* **1998**, *49*, 267.
11. Demirbas, A. *J. Hazard. Mater.* **2004**, *109*, 221–226.
12. Hawthorne-Costa, E. T.; Winkler-Hechenleitner, A. A.; Gómez-Pineda, E. A. *Sep. Sci. Technol.* **1995**, *30*, 2593–2602.
13. Elik, A. C.; Dost, K.; Sezer, H. *Environ. Bull.* **2004**, *13*, 124–127.
14. Lalvani, S. B.; Wiltowski, T. S.; Murphy, D.; Lalvani, L. S. *Environ. Technol.* **1997**, *18*, 1163–1168.
15. Balkose, D.; Baltacıoğlu, H. *J. Chem. Technol. Biotechnol.* **1992**, *54*, 393–397.
16. Lee, S. H.; Jung, C. H.; Chung, H.; Lee, M. Y.; Yang, J. *Process Biochem.* **1998**, *33*, 205–211.
17. Raghuvanski, P.; Deshmukh, A.; Dashi, A. *Asian J. Chem.* **2003**, *15*, 1531–1534.
18. Al-Asheh, S.; Duvnjak, Z. *J. Hazard. Mater.* **1997**, *56*, 35–51.
19. Taty-Costodes, V. C.; Fauduet, H.; Porte, C.; Delacroix, A. *J. Hazard. Mater.* **2003**, *B105*, 121–142.
20. Perisamy, K.; Namasivayam, C. *Waste Manage.* **1995**, *15*, 63–68.
21. Johnsona, P. D.; Watsona, M. A.; Brown, J.; Jefcoatb, I. A. *Waste Manage.* **2002**, *22*, 471–480.
22. Chamarthy, S.; Seo, C. W.; Marshall, W. E. *J. Chem. Technol. Biotechnol.* **2006**, *76*, 593–597.
23. Wafwoyo, W.; Seo, C. W.; Marshall, W. E. *J. Chem. Technol. Biotechnol.* **2006**, *74*, 1117–1121.
24. Bailey, S. E.; Trudy, J. O.; Bricka, R. M.; Adrian, D. D. *Water Res.* **1999**, *33*, 2469–2479.
25. Al-Asheh, S.; Banat, F. *Adsorp. Sci. Technol.* **2001**, *19*, 117–129.
26. Gharaibeh, S. H.; Abu-el-sha'r, W. Y.; Al-Kofahi, M. M. *Water Res.* **1998**, *32*, 498–502.

27. Pagnanelli, F.; Toro, L.; Vegliò, F. *Waste Manage.* **2002**, *22*, 901–907; Vegliò, F.; Beolchini, F.; Prisciandaro, M. *Water Res.* **2003**, *37*, 4895–4903.
28. Saad Ali Khan; Riaz-ur-Rehman; M. Ali Khan *J. Radioanal. Nucl. Chem.* **1996**, *207*, 19–37.
29. Yeddou, N.; Bensmaili, A. *Desalination* **2007**, *206*, 127–134.
30. Karthikeyan, G.; Muthulakshmi, N.; Anbalagan, K. *J. Chem. Sci.* **2005**, *117*, 663–672.
31. Ghimire, K. N.; Inoue, K.; Ohto, K.; Hayashida, T. *Bioresour. Technol.*, in press.
32. Dabrowski, A. *Adv. Colloid Interface Sci.* **2001**, *93*, 135–224.
33. Chien, S. H.; Clayton, W. R. *Soil Sci. Soc. Am. J.* **1980**, *44*, 265–268.
34. Meena, A. K.; Mishra, G. K.; Rai, P. K.; Rajagopal, C.; Nagar, P. N. *J. Hazard. Mater.* **2005**, *B122*, 161–170.
35. Lagergren, S. *Zur Theorie der sogenannten Adsorption gelöster Stoffe*. Kungliga Svenska Vetenskapsakademiens Handlingar, **1898**; Vol. *24*, 1–39.
36. Ho, Y. S.; McKay, G. *Process Biochem.* **1999**, *34*, 451–465.