

## Equilibrium and thermodynamic studies of stearic acid adsorption on Celtek clay

AHMET SARI<sup>1</sup> and MUSTAFA SOYLAK<sup>2\*</sup>

<sup>1</sup>Department of Chemistry, Gaziosmanpaşa University, 60240, Tokat and <sup>2</sup>Department of Chemistry, Erciyes University, 38039, Kayseri, Turkey (e-mail: soylak@erciyes.edu.tr)

(Received 14 April, revised 9 August 2006)

**Abstract:** This paper presents the equilibrium and thermodynamic parameters of the adsorption of stearic acid on Celtek clay as a function of temperature. It was found that the adsorption of stearic acid on Celtek clay decreased with increasing temperature from 293 to 313 K. The equilibrium modelled data fitted well with the linear forms of both the Langmuir and the Freundlich models ( $R^2 = 0.99$  in both cases). The  $R_L$  and  $1/n$  values determined from the isotherm models proved that Celtek clay is a suitable adsorbent for stearic acid. The Dubinin–Radushkevich (D–R) isotherm was applied to describe the nature of the adsorption of stearic acid on Celtek clay and it was found that the adsorption occurred physically. Thermodynamic parameters of adsorption, such as Gibbs free energy change ( $\Delta G^0$ ), enthalpy change ( $\Delta H^0$ ) and entropy change ( $\Delta S^0$ ) were also calculated. These parameters showed that the adsorption of stearic acid on Celtek clay was feasible, spontaneous, and exothermic in nature. On the basis of the results, it can be concluded that Celtek clay has considerable potential for the removal of stearic acid from the main sources, such as raw and edible soybean, sunflower and olive oils.

**Keywords:** stearic acid, Celtek clay, adsorption, isotherm, thermodynamic parameter.

### INTRODUCTION

Fatty acids are widely used in the pharmaceutical and food industry. Many drugs and foods contain fatty acids and they are often subjected to thermal treatment during processing and storage. Free fatty acids from common vegetable and animal oils are normally resulted from the scission of the ester bonds of triglycerides during the industrial refining process. The adsorption method can be used for the bleaching of the oils, which can increase the content of stearic acid.<sup>1</sup> The number of papers on the adsorption of fatty acids is limited in the literature. Proctor and Palaniappan<sup>2</sup> investigated the ability of rice husk ash (RHA) to adsorb free fatty acid from soy oil. Adam and Saleh<sup>3</sup> reported that the adsorption of fatty acids on RHA took place physically, and suggested that the adsorbed fatty acids could

\* Corresponding author.

easily be recovered from the surface of RHA using acetone. Adam and Chua<sup>4</sup> studied the adsorption of palmitic acid on RHA modified with Al(III) ions using the sol-gel technique and the Langmuir adsorption model was applied to the experimental results. Topallar and Bayrak<sup>5</sup> examined the adsorption isotherms of myristic, palmitic, and stearic acid on RHA and indicated that the adsorptions of the fatty acids followed Langmuir isotherm. These studies proved that the adsorption of a free saturated fatty acid using a proper adsorbent is important for its removal from the main sources, such as raw and edible soybean, sunflower and olive oils.

Clay is a natural, earthy, fine-grained material composed largely of a group of minerals. Clays have been used for thousands of years and they still keep their position as very important industrial materials.<sup>6,7</sup> Clays have also been used for chemical studies for various purposes, including the adsorption of various organic, inorganic substances, radioactive specimens and heavy metals.<sup>8-11</sup>

Celtek clay was chosen as the adsorbent material in this study. The clay was collected from the Celtek Town of Amasya City in Turkey. This material has commonly been used as an industrial raw material for the construction of ceramics and bricks in the middle Anatolia-Turkey. According to our literature survey, Celtek clay has not been used as an adsorbent for organic substances from various samples.

The aim of this work was to investigate the equilibrium and thermodynamic parameters of the adsorption of stearic acid on Celtek clay as a function of temperature and determine the type of the adsorption (physical or chemical).

## EXPERIMENTAL

### *Preparation of the adsorbent material*

Celtek clay was first dried and sieved through a 200-mesh sieve, then washed with distilled water several times to remove any dust and other water-soluble impurities. The washed sample was dried in an electric oven at 378 K for 24 h.

### *Materials and solutions*

Stearic acid (98 % purity) was supplied by Merck. Sodium hydroxide (NaOH), potassium hydrogen phthalate (KHP), isooctane and propan-1-ol were obtained from Aldrich. Stearic acid (0.569 g) was dissolved in 1 L isooctane to prepare a  $2.00 \times 10^{-3}$  mol/L stock solution. A NaOH solution (0.005 mol/L) was prepared and standardized by titrating with KNP and then diluted to 0.0025 mol/L with deionized water.

### *Instrumentation*

The chemical and mineral composition of dry Celtek clay was determined by X-ray powder diffractometry (XRD; Rigaku D-Max 2200 model). The dry adsorbent sample was also characterized by Fourier Transform Infrared (FT-IR) spectroscopy (Jasco model 430 instrument) and scanning electron microscopy (SEM; Jeol model 6400). The specific surface analysis was determined using a surface analyzer (Quantachromosorb) and the Brunauer-Emmett-Teller (BET) method.

### *Adsorption procedure*

Samples of Celtek clay (predried at 378K for 24 h and desiccated) of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 and 0.8 g were weighed with the accuracy of  $\pm 0.1$  mg and transferred to 50 mL conical flasks with glass stoppers. The stock solution of stearic acid (20 mL) was pipetted into each conical flask.

The samples were shaken for 120 min using a mechanical shaker combined with a temperature controller (Arex, Velp Scientifica) at 298 K and 100 rpm shaking speed. Subsequently, all samples were equilibrated at this temperature in a thermostated water bath (Lauda; KG. D-6970 model) for another 60 min until all the adsorbent had settled on the bottom of the flask. After the 3-hour adsorption period, 5 mL of the supernatant was pipetted into 10 mL neutralized propan-1-ol and titrated with 0.0025 mol/L NaOH. The titration was repeated in triplicate and the mean titrant volume was recorded. In addition, a blank titration of 5 mL of untreated stock stearic acid solution was carried out. In order to determine the adsorption properties at different temperatures, the above experiments were repeated at 293, 298, 303, 308 and 313 K.

## RESULTS AND DISCUSSION

### *Characterization of Celtek clay*

The chemical and mineral compositions of Celtek clay obtained by XRD analysis are given in Table I. Its specific surface area was found to be 69.0 m<sup>2</sup>/g by the BET method. The microstructure of the clay was investigated by SEM analysis and the micrographs obtained at 350 and 1500 magnifications are given in Fig. 1a and Fig. 1b, respectively. As can be seen from the Figures, Celtek clay has a heterogeneous porous structure.

TABLE I. Chemical and mineral composition of Celtek clay obtained by XRD analysis

Chemical composition/%									
SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	Fe <sub>2</sub> O <sub>3</sub>	CaO	SO <sub>3</sub>	Na <sub>2</sub> O	TiO <sub>2</sub>	Ignition los (at 1273 K)
59.5	14.9	2.5	2.0	5.2	4.8	0.1	1.0	0.7	8.7
Mineral composition/%									
Kuvars		Calcite		Anortite		Illite		Chlorite	
16.6		8.1		11.5		42.6		21.1	

The Celtek clay was also characterized by FT-IR spectroscopy at room temperature (Fig. 2). The broad bands at 3417, 3621, and 3696 cm<sup>-1</sup> are due to the O–H stretching vibration of the silanol (Si–OH) groups and the HO–H vibration of water molecules adsorbed on the silica surface. The strong band observed at 1029 cm<sup>-1</sup> represents the Si–O–Si groups of the tetrahedral sheet, and the bands observed at 796, and 694 cm<sup>-1</sup> are due to the deformation and bending modes of the Si–O bonds.

### *Adsorption isotherms*

Adsorption equilibrium data generally described by either the Langmuir or the Freundlich model. The Langmuir model represents one of the first theoretical treatments of non-linear sorption and suggests that the uptake occurs on a homogenous surface by monolayer sorption without interaction between the adsorbed molecules. Moreover, the model assumes uniform energies of sorption onto the surface and no transmigration of the adsorbate. The experimental data were fitted to the linear form of the Langmuir model, expressed by the following equation:<sup>12</sup>

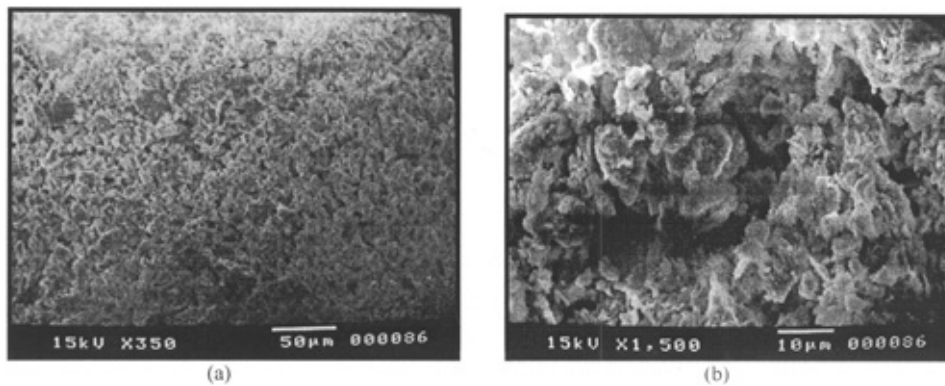


Fig. 1. SEM Micrographs of Celtek clay (a) at  $\times 350$  magnification (b) at  $\times 1500$  magnification.

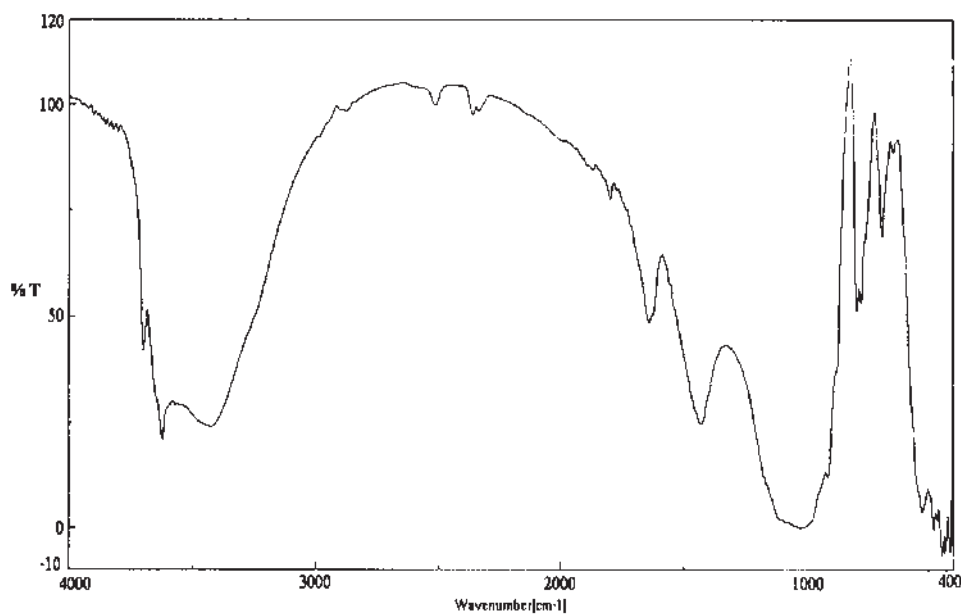


Fig. 2. FT-IR Spectrum of Celtek clay at room temperature.

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (1)$$

where,  $C_e$  (mg/L) is the amount of adsorbate in the solution at equilibrium and  $q_e$  (mg/g) is the amount of adsorbate adsorbed onto the adsorbent.  $q_m$  (mg/g) and  $K_L$  (L/mg) are Langmuir constants related to the adsorption capacity and the energy of adsorption, respectively. These constants can be determined from the slope and the intercept of the linear plot of  $C_e/q_e$  versus  $C_e$ .

Based on further analysis of the Langmuir equation, the dimensionless parameter of the equilibrium or the adsorption intensity ( $R_L$ ) can be expressed by:

$$R_L = \frac{1}{1 + K_L C_0} \tag{2}$$

where,  $C_0$  (mg/L) is the initial amount of adsorbate. The  $R_L$  parameter is considered as a reliable indicator of the adsorption. There are four probabilities for the value of  $R_L$ : (i) for favorable adsorption,  $0 < R_L < 1$ , (ii) for unfavorable adsorption,  $R_L > 1$ , (iii) for linear adsorption,  $R_L = 1$ , (iv) for irreversible adsorption,  $R_L = 0$ .<sup>4,5,13,14</sup>

The Freundlich model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between the adsorbed molecules. The linear form of the Freundlich model is given by the following equation:<sup>15</sup>

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \tag{3}$$

where,  $1/n$  and  $K_F$  can be determined from the slope and the intercept of the linear plot of  $\log q_e$  versus  $\log C_e$ , respectively.

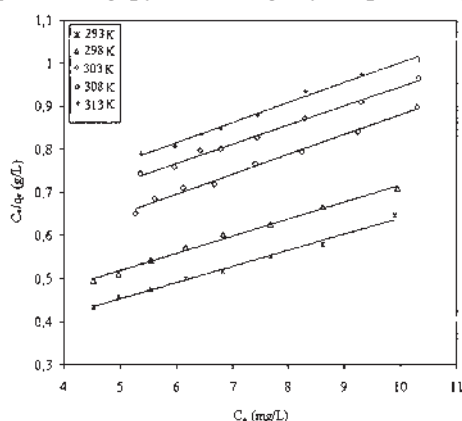


Fig. 3. Linear plots of Langmuir isotherms of the adsorption of stearic acid on Celtek clay at different temperatures.

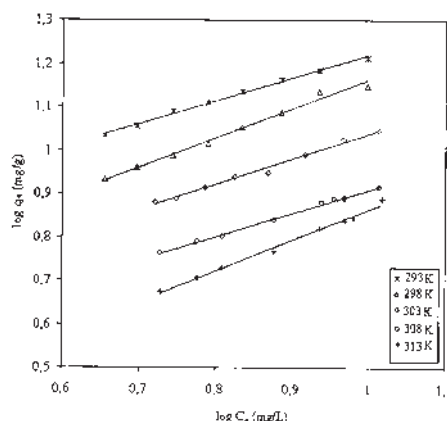


Fig. 4. Linear plots of the Freundlich isotherms of the adsorption of stearic acid on Celtek clay at different temperatures.

The linear plots of Langmuir and Freundlich isotherms obtained for the temperatures of 293, 298, 303, 308 and 313 K are shown in Figs. 3 and 4, respectively and the results are given in Table II. The adsorption pattern for stearic acid adsorption onto Celtek clay is fitted well with the linear Langmuir and Freundlich models at the examined temperatures, as can be seen by the high coefficient of determination ( $R^2 = 0.99$  for both models). The values of the Langmuir constants  $q_m$  and  $K_L$  decreased from 26.7 to 21.3 mg/g and 0.14 to 0.08 L/mg with increasing temperature. The adsorption intensity ( $R_L$ ) ranged from 0.39–0.50 at the studied temperatures, suggesting that Celtek clay is a suitable adsorbent for the adsorption of stearic acid.

On the other hand, the adsorption capacity ( $K_F$ ) and the adsorption intensity ( $n$ ) decreased from 4.92 to 1.41 mg/g and from 1.90 to 1.41, respectively, with in-

creasing temperature, which indicates that the adsorption of stearic acid on Celtek clay is exothermic in nature and less favorable at higher temperatures.

TABLE II. Langmuir and Freundlich constants and other parameters determined for the adsorption of stearic acid on Celtek clay at different temperatures

$T$ K	Langmuir isotherm			Freundlich isotherm			
	$q_m$ mg/g	$K_L$ L/mg	$R_L$	$R^2$	$K_F$ mg/g	$n$	$R^2$
293	26.7	0.14	0.39	0.99	4.9	1.9	0.99
298	25.2	0.12	0.42	0.99	3.1	1.8	0.99
303	23.0	0.10	0.47	0.99	2.8	1.7	0.99
308	22.2	0.09	0.49	0.99	2.3	1.5	0.99
313	21.3	0.08	0.50	0.99	1.4	1.4	0.99

The adsorption equilibrium data were also modelled by the D-R model to determine the type of adsorption (physical or chemical).<sup>14,18,19</sup> The linear presentation of this model is expressed by the following equation:

$$\ln q_e = \ln X_m - \beta \varepsilon^2 \quad (4)$$

where,  $q_e$  and  $X_m$  are the equilibrium concentration (mol/L) and the monolayer capacity (mol/g), respectively.  $\beta$  is the constant of the sorption energy (mol<sup>2</sup>/J<sup>2</sup>), which is related to the average energy of sorption per mole of the sorbate as it is transferred to the surface of the solid from an infinite distance in the solution. The Polanyi potential,  $\varepsilon$  is described as:

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (5)$$

As can be seen from Fig. 5,  $\beta$  and  $X_m$  can be obtained from the slope and the intercept of the plot of  $\ln q_e$  versus  $\varepsilon^2$ . The mean energy of sorption ( $E$ , kJ/mol) can be calculated using Eq. (6):

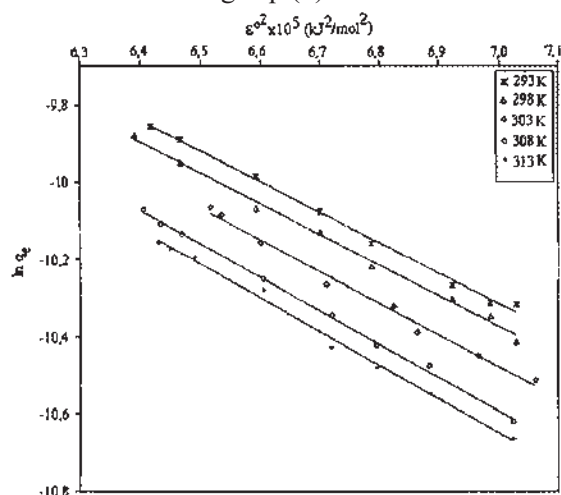


Fig. 5. D-R Isotherm plots of the adsorption of stearic acid on Celtek clay at different temperatures.

$$E = \frac{1}{\sqrt{-2\beta}} \quad (6)$$

TABLE III. D–R Parameters of the adsorption of stearic acid on Celtek clay at different temperatures

$T/K$	$X_m$	$\beta$	$E$	$R^2$
	mol/g	mol <sup>2</sup> /kJ <sup>2</sup>	kJ/mol	
293	$8.3 \times 10^{-3}$	$-7.9 \times 10^{-6}$	7.96	0.99
298	$8.2 \times 10^{-3}$	$-7.8 \times 10^{-6}$	7.90	0.99
303	$9.0 \times 10^{-3}$	$-8.3 \times 10^{-6}$	7.76	0.99
308	$10.8 \times 10^{-3}$	$-8.3 \times 10^{-6}$	7.58	0.99
313	$11.2 \times 10^{-3}$	$-8.8 \times 10^{-6}$	7.54	0.99

The D–R parameters and mean sorption energy were calculated for different temperatures by examination of the plots in Fig. 5, and the results are given in Table III. The monolayer sorption capacity ( $X_m$ ) was between  $8.3 \times 10^{-3}$  and  $11.2 \times 10^{-3}$  mol/g and the mean sorption energy ( $E$ ) was between 7.54 and 7.96 kJ/mol in the temperature range of 293–313 K. The magnitude of  $E$  is in the range 1–8 kJ/mol and 9–16 kJ/mol for physical and chemical adsorption, respectively.<sup>14,19</sup> The  $E$  values were found in the range of 1–8 kJ/mol, indicating that the adsorption of stearic acid on Celtek clay is essentially physical.

#### Thermodynamic parameters

The Gibbs free energy change of adsorption ( $\Delta G^0$ ) is calculated using the following equation

$$\Delta G^0 = -RT \ln K_0 \quad (7)$$

where,  $R$  is the gas constant and  $T$  is the temperature in Kelvin.  $K_0$  is the thermodynamic equilibrium constant of the adsorption process determined by plotting  $\ln(q_e/C_e)$  versus  $C_e$  and extrapolating to zero  $C_e$ <sup>4,16,17</sup> as shown in Fig. 6.

The other thermodynamic parameters, the enthalpy change ( $\Delta H^0$ ) and the entropy change ( $\Delta S^0$ ), were calculated from the slope and intercept of the plot of  $\ln K_0$  against  $1/T$ , respectively, according to Eq. (8)<sup>4,14,18,19</sup> and shown in Fig. 7:

$$\ln K_0 = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (8)$$

The thermodynamic parameters of the adsorption of stearic acid on Celtek clay at the examined temperatures are presented in Table IV. The Gibbs free energy change of adsorption ( $\Delta G^0$ ) was found to be in the range of  $-2.6$  and  $-0.7$  kJ/mol, as the temperature changed between 293 and 313 K. These results indicated that the adsorption of stearic acid on Celtek clay is feasible and spontaneous.  $\Delta H^0$  and  $\Delta S^0$  were found as  $-30.4$  kJ/mol and  $-94.4$  J/mol K, respectively. The negative

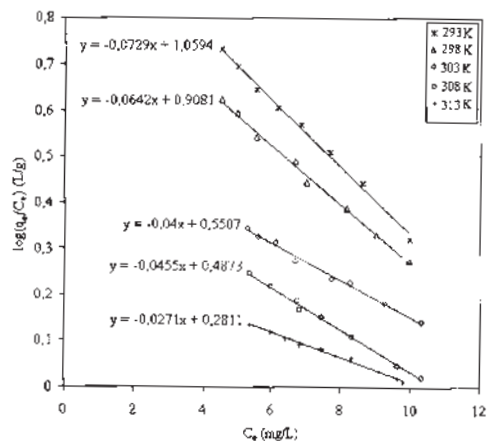


Fig. 6. Plots of  $\ln(q_e/C_e)$  versus  $C_e$  at different temperatures.

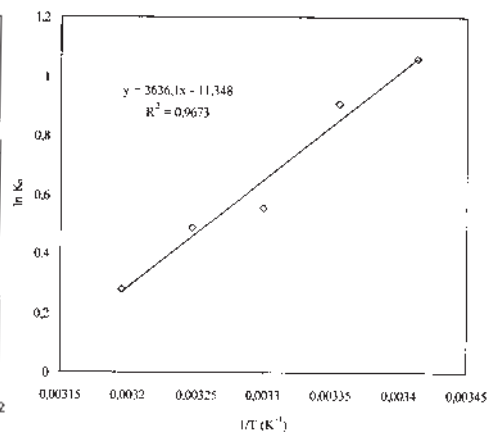


Fig. 7. The variation of the thermodynamic equilibrium constant of the adsorption of stearic acid on Celtek clay as a function of temperature.

value of  $\Delta H^0$  confirmed that the adsorption of stearic acid on Celtek clay is an exothermic process. These results are contrary to the data given in the literature.<sup>4,5</sup> This can be due to the energy released after the adsorption being higher than that needed to extract the solvent molecules from the pores of Celtek clay. The negative value of  $\Delta S^0$  suggests that the randomness in solid/solution interface decreased during the adsorption.

TABLE IV. Thermodynamic parameters of adsorption of stearic acid on Celtek clay at different temperatures

$T/K$	$K_0$	$\Delta G^0$
	L/g	kJ/mol
293	2.9	-2.6
298	2.5	-2.3
303	1.8	-1.4
308	1.6	-1.3
313	1.3	-0.7
$\Delta H^0 = -30.4$ kJ/mol		
$\Delta S^0 = -94.4$ J/mol K		

## CONCLUSIONS

The results obtained in this study indicate that the adsorption capacity of Celtek clay for stearic acid is considerably affected by temperature. The equilibrium data fitted well with both the Langmuir and Freundlich models. The  $R_L$  and  $1/n$  values show that Celtek clay is a suitable adsorbent for stearic acid. The D-R isotherm confirmed that the adsorption of stearic acid on Celtek clay proceeds physi-



cally. In addition, the thermodynamic parameters ( $\Delta G^0$ ,  $\Delta H^0$ , and  $\Delta S^0$ ) determined with respect to the temperature variation indicate that the adsorption of stearic acid on Celtek clay is feasible, spontaneous and exothermic in nature.

On the basis of the results, it is concluded that Celtek clay can be used as an adsorbent to remove stearic acid from the main sources, such as raw edible soybean, sunflower and olive oils.

*Acknowledgement:* The authors wish to thank Dr. Ömer Işildak for his help with the experiments, Dr. Tashin Unlu for the XRD analysis, Dr. Menderes Suiçmez for taking the SEM photographs and Dr. Beytullah Afsin for the BET analysis.

#### ИЗВОД

### ИСПИТИВАЊЕ ТЕРМОДИНАМИКЕ И РАВНОТЕЖЕ АДОРПЦИЈЕ СТЕАРИНСКЕ КИСЕЛИНЕ НА ГЛИНИ „CELTEK”

АХМЕТ САРИ<sup>1</sup> И МУСТАФА СОЈЛАК<sup>2</sup>

<sup>1</sup>Department of Chemistry, Gaziosmanspaşa University, 60240, Tokat и <sup>2</sup>Department of Chemistry, Erciyes University, 38039, Kayseri, Turkey

У раду је приказана зависност равнотежних и термодинамичких параметара адсорпције стеаринске киселине на глини „Celtek” у функцији температуре. Експериментални резултати показују да са порастом температуре од 293 К до 313 К долази до опадања количине адсорбоване стеаринске киселине на глини Celtek. Експериментални резултати се могу приказати као Лангмирова и Фројндлихова изотерма ( $R^2 = 0.99$  за оба модела). На основу добијених вредности  $R_L$  и  $1/n$  добијених из изотерми утврђено је да је глина Celtek погодан адсорбент за стеаринску киселину. Примена Dubinin–Radušković изотерме је показала да се стеаринска киселина физички адсорбује на глину Celtek. Такође су израчунати термодинамички параметри адсорпције,  $\Delta G^0$ ,  $\Delta H^0$  и  $\Delta S^0$ . Ти параметри показују да је адсорпција стеаринске киселине спонтани егзотерман процес. На бази ових резултата је закључено да Celtek глина може бити погодан адсорбент за отклањање стеаринске киселине из сојиног, сунцокретовог или маслиновог уља.

(Примљено 14. априла, ревидирано 9. августа 2006)

#### REFERENCES

1. A. Proctor, C. Adhikara, G. D. Blyholder, *J. Am. Oil Chem. Soc.* **72** (1995) 331
2. A. Proctor, S. Palaniappan, *J. Am. Oil Chem. Soc.* **67** (1990) 15
3. F. Adam, M. I. Saleh, *J. Am. Oil Chem. Soc.* **71** (1994) 1363
4. F. Adam, J. H. Chua, *J. Colloid Interface Sci.* **280** (2004) 55
5. H. Topallar, Y. Bayrak, *Turkish J. Chem.* **23** (1999) 193
6. B. Baran, T. Erturk, Y. Sarikaya, T. Alemdaroglu, *Appl. Clay Sci.* **20** (2001) 53
7. M. Ozer, F. Arslan, G. Onal, *Key Eng. Mater.* **264** (2004) 1439
8. M. Tuzen, E. Melek, M. Soylak, *J. Hazard. Mater.* **136** (2006) 597
9. A. E. Osmanlioglu, *Waste Manage.* **22** (2002) 481
10. H. Akcay, F. ĐKurtulmus, *J. Radioanal. Nucl. Chem. Lett.* **200** (1995) 529
11. N. L. Dias, W. L. Polito, Y. Gushikem, *Talanta* **42** (1995) 1031
12. I. Langmuir, *J. Am. Chem. Soc.* **40** (1918) 1361
13. T. W. Weber, R. K. Chakraborti, *J. Am. Inst. Chem. Eng.* **20** (1974) 228
14. J. Romero-Gonzalez, J. R. Peralta-Videa, E. Rodriguez, S. L. Ramirez, J. L. Gardea-Torredey, *J. Chem. Thermodyn.* **37** (2005) 343

15. H. Freundlich, *Z. Phys. Chem.* **57** (1906) 385
16. V. K. Gupta, P. Singh, N. Rahman, *J. Colloid Interface Sci.* **275** (2004) 398
17. A. A. Khan, R. P. Singh, *Colloids Surf.* **24** (1987) 33
18. S. S. Tahir, N. Rauf, *J. Chem. Thermodyn.* **35** (2003) 2003
19. R. Donat, A. Adkoğan, E. Erdem, H. Cetisli, *J. Colloid Interface Sci.* **286** (2005) 43.