ADSORPTION PROPERTIES OF STEARIC ACID ONTO UNTREATED KAOLINITE

Ahmet Sari[*]and Ömer Iþýldak

Department of Chemistry, Gaziosmanpaşa University, 60240, Tokat, Turkey

ABSTRACT. The focus of the study is to investigate adsorption property and determine thermodynamic parameters for the adsorption of stearic acid onto untreated kaolinite at the temperatures of 25, 35 and 45 °C. The equilibrium adsorption isotherms were analyzed by linear Langmuir and Freundlich models. Adsorption experiments indicated that the sorption capacity of kaolinite decreased with increasing temperature. The calculated Langmuir equilibrium parameter, R_L indicated that the kaolinite was a good material for the sorption process of the stearic acid. The free energy change of adsorption, $\Delta G°_{ads}$, was found between -19.98 and -20.50 kJ/mol at examined temperatures and enthalpy of adsorption, $\Delta H°_{ads}$, and entropy of adsorption, $\Delta S°_{ads}$ were found as -12.30 kJ/mol and 0.0259 kJ/(mol.K), respectively. The calculated thermodynamic parameters ($\Delta H°_{ads}$ and $\Delta G°_{ads}$) showed that the adsorption process of stearic acid onto kaolinite was spontaneous and exothermic in nature. Furthermore, Fourier Transform infrared (FT-IR) spectroscopy was used to indicate the possible interaction between the stearic acid molecules and the surface groups of adsorbent.

KEY WORDS: Adsorption, Kaolinite, Stearic acid, Langmuir isotherm, Freundlich isotherm, Thermodynamic parameters

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. Moreover, stearic acid as a member of saturated fatty acids is attractive phase change material for thermal energy storage applications due to the properties of high latent heat storage, melting and solidifying at a nearly constant temperature, good chemical stability and non-toxicity [1-3]. These properties make it a significant industrial material for latent heat thermal energy storage.

Free fatty acids from the common vegetable and animal oils are normally derived breaking triglyceride ester bonds during the refining process in the industry. The use of adsorbent clay for bleaching of the oils can increase stearic acid content considerably [4]. There is limited number of study on adsorption of fatty acids in literature. Proctor and Palaniappan showed the ability of rice husk ash (RHA) to absorb free fatty acid from soy oil [5]. Adam and Saleh reported the fatty acids adsorbed on RHA could be easily eluted out by acetone and they suggested that the adsorption of fatty acids was taken place by physisorption [6]. Adam and Chua studied the adsorption of palmitic acid on RHA chemically modified with Al(III) ion using the sol-gel technique and they applied the Langmuir adsorption model to the experimental results [7]. Topallar and Bayrak investigated the adsorption isotherms of myristic, palmitic and stearic acid on RHA and they showed the adsorption of all fatty acids followed to the Langmuir isotherm [8].

As a result, the adsorption of a free saturated fatty acid by using a proper adsorbent is significant in terms of removing it from the main sources such as raw and edible soy, sunflower and olive oils.

_____

*Corresponding author. E-mail: asari@gop.edu.tr

Kaolinite is a 1:1 clay mineral including a tight interlayer structure with the ideal formula of $Al_2Si_2O_5(OH)_4$ [9]. The sorption properties of this clay are solely determined by the nature of its surface and edges. Kaolinite possesses a variable charge that can be related to the reactions between ionizable surface groups located at the edges and the ions present in aqueous solution [9-10]. It has been used as adsorbent material for the adsorption process of some organic substances and heavy metals [9-11].

This study aims to investigate the adsorption isotherms and thermodynamic parameters for the adsorption of stearic acid onto untreated kaolinite at 25, 35 and 45 ^{o}C.

EXPERIMENTAL

Materials

Kaolinite was obtained from Eczacıbaşı Natural Mineral Industry (Turkey) and Commercial firm (Eczacıbaşı, Turkey). Stearic acid (98% purity) was supplied from Merck (Germany). Sodium hydroxide (NaOH), potassium hydrogen phthalate (KHP), isooctane and 1-propanol were supplied from Aldrich (Germany).

Kaolinite was dried and sieved form 200-mesh, and then washed with distilled water several times to remove dust and other water-soluble impurities. The washed sample was dried in electric oven at 105 ^{o}C for 24 h and then placed in desiccator before adsorption experiment. Kaolinite, stearic acid and kaolinite loaded with stearic acid after adsorption were characterized by FT-IR spectrophotometer (Jasco 430 model, Japan). The FT-IR spectra were recorded as KBr disk.

Preparation of solutions

A 0.569 g stearic acid was dissolved in 1 L isooctane to prepare 2.00×10^{-3} M stock solution. 0.005 M aqueous solution NaOH was prepared and standardized by titrating with KHP. The solution was diluted to 0.0025 M with deionized water.

Batch adsorption procedure

Samples of kaolinite (predried at 105 ^{o}C 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 ± 0.1 mg and transferred to 50.0 mL conical flasks with glass stoppers. 20 mL stock solution of stearic acid was pipetted into each conical flask. The samples were shaken for 30 min by a mechanical shaker combined with a temperature controller (Arex, Velp Scientitica) at 25 ^{o}C and 100 rpm shaking speed. Subsequently, all samples were equilibrated at this temperature in a thermostated water bath (Lauda; KG. D-6970 model, Germany) for another 30 min until all adsorbent had settled to the bottom. At the end of 1-hour period, a 5.00 mL of the supernatant was pipetted into 10.0 mL neutralized 1-propanol and titrated with 0.0025 M NaOH. In addition, a blank titration on 5 mL of the untreated stock stearic acid solution was carried out. In order to determine the adsorption properties at different temperatures, the above experiments were repeated at 35 and 45 ^{o}C.

RESULTS AND DISCUSSION

Characterization of adsorbent

The chemical and mineralogical analyses were carried out by using X-ray powder diffractometry (Rigaku D-Max 2200 model, Japan) and the results are given in Table 1. The kaolinite mainly consists of 48.00 % SiO_2 and 36.56 % Al_2O_3 components. Its specific surface area was found to be 18.4 m^2/g by BET method using a surface analyzer (Quantachromosorb).

Table 1. Chemical and mineral composition of kaolinite.

Chemical composition (%)								
SiO_2	Al_2O_3	K_2O	MgO	Fe_2O_3	CaO	Na_2O	TiO_2	Ignition loss (at 1000 ^{o}C)
48.00	36.56	2.00	0.30	0.92	0.07	0.10	0.05	12.00
Mineral composition (%)								
Kaolinite		Mica			Feldspar		Other minerals	
83.00		13.00			2.00		2.00	

The micrographs were obtained by a scanning electron microscopy (SEM; Jeol 6400 model, Japan) to characterize the structure of untreated kaolinite. Figure 1a and 1b show SEM micrographs taken by 350 and 1500 magnifications, respectively. As it can be seen from the figures, it has isomorphic porous structure.
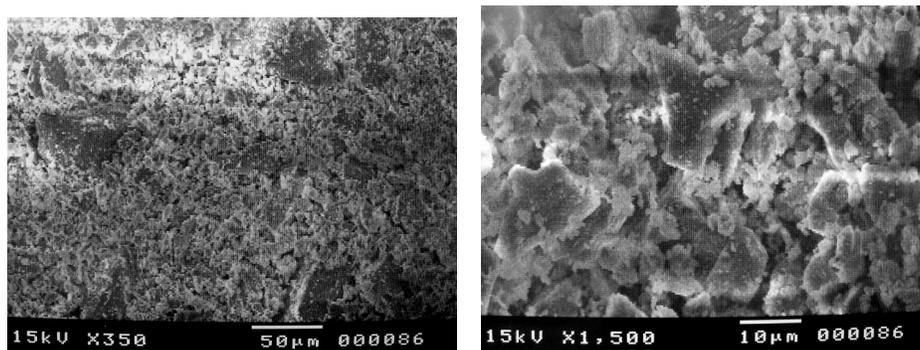
Figure 1. The SEM micrographs of untreated kaolinite (a) at x 350 magnification and (b) at x 1500 magnification.

FT-IR spectroscopic analysis

FT-IR spectroscopic technique can be used to prove the possible interaction between the stearic acid molecules and the surface groups of adsorbent during an adsorption process [7]. Figure 2 show that FT-IR spectra of the stearic acid, kaolinite, and kaolinite loaded with stearic acid after adsorption. The C=O stretching frequency of the stearic acid appears at 1697.05 cm^{-1}. After adsorption this strong band disappears. Instead a weaker band at 1628.03 cm^{-1} appears. This is a very big shift of 69.02 cm^{-1} and it can be interpreted as possible interaction between the stearic acid molecule and the hydroxyl of silanol group on the surface of kaolinite (Scheme 1).
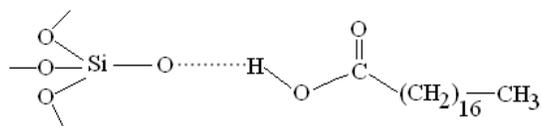
Scheme 1

In addition, the hydrophobic chain of the stearic acid is not involved in the adsorption process because the C-H vibrations frequencies at 2923.56 and 2856.06 cm^{-1} remain essentially unchanged on adsorption compared to the free stearic acid. Such a type interaction was proved for the sorption of different fatty acids on RHA ash by using FT-IR spectroscopic method [7].
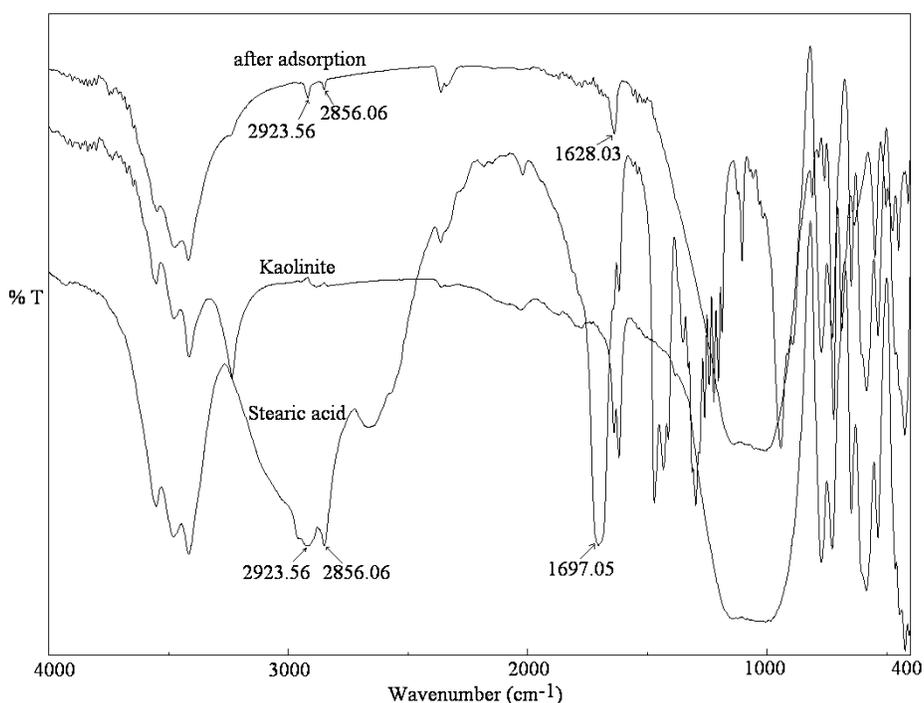
Figure 2. The FT-IR spectra of the stearic acid, kaolinite, stearic acid and kaolinite.

Adsorption isotherms

The Langmuir and Freundlich adsorption isotherms are widely used to characterize the adsorption phenomena from solution. The Langmuir isotherm can be described by the linear form [12] as shown in the equation

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

(1)

where C_e (mg) 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) is the amount of adsorbate adsorbed to form a monolayer coverage on the solid particles. K_L is the Langmuir adsorption equilibrium constant.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter R_L [7, 8] by the following equation

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

where C_o is the initial amount of adsorbate and R_L value between the 0 and 1 indicates the suitability of the adsorbent for the adsorbate at the studied temperature.

The linear Freundlich adsorption isotherm [13] can be written as

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

where q_e and C_e are the same parameters as described in equation (1). K_F and n are the Freundlich constants.

Figure 3 shows the adsorption isotherms of stearic acid from isooctane solution at 25, 35 and 45 ^{o}C. The curves are reached to almost a constant value of q_e (mg/g) at the studied three temperatures and the surface of adsorbent is covered with a monolayer of stearic acid molecules. The same adsorption type was observed for the different fatty acids on the RHA [8] and the modified RHA with Al(III) ion [7]. Moreover, the adsorption pattern of stearic acid onto untreated kaolinite is not influenced by temperature, but the adsorption capacity decreases with increasing temperature.
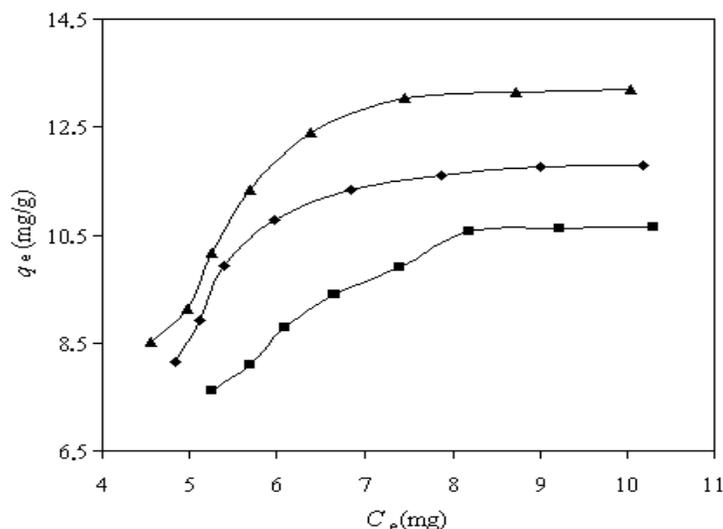
Figure 3. The adsorption isotherm plots of qe (mg/g) versus Ce (mg) at different temperatures; (▲) 25 ^{o}C, (◆) 35 ^{o}C, (■) 45 ^{o}C.
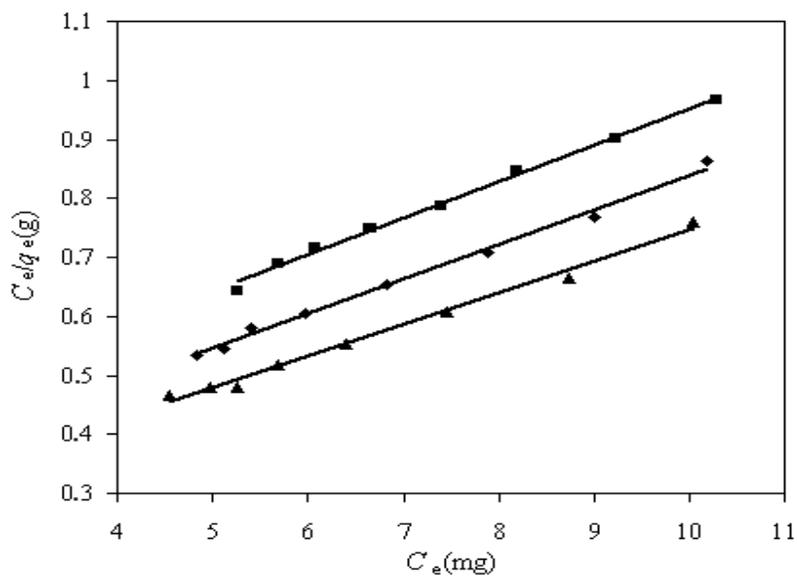
Figure 4. Langmuir isotherms at different temperatures; (▲) 25 ^{o}C, (◆) 35 ^{o}C, (■) 45 ^{o}C.
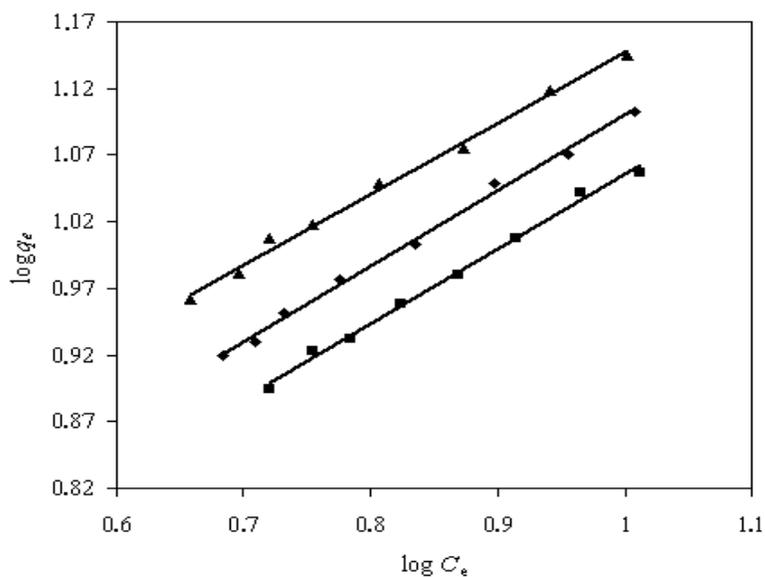
Figure 5. Freundlich isotherms at different temperatures; (▲) 25 ^{o}C, (◆) 35 ^{o}C, (■) 45 ^{o}C.

Figure 4 and 5 show the plots of Langmuir and Freundlich isotherms in linear form for the adsorption of stearic acid on untreated kaolinite at 25, 35 and 45 ^{o}C. The plots point out that adsorption isotherms of stearic acid on kaolinite are well in agreement with the Langmuir and Freundlich models at the examined temperatures. The determined Langmuir and Freundlich parameters are summarized in Table 2. The linear correlation coefficient (r^2) is in the range of 0.9913-0.9954 for Langmuir model and 0.9944-0.9954 for Freundlich model. These values exhibit that the adsorption data for both isotherms follow a straight line. The decreases in the K_L, K_F and q_m values with rise in temperature signify that the adsorption of stearic acid on kaolinite is an exothermic process in nature. It is concluded that stearic acid is significantly adsorbed onto kaolinite when the qm value, 18.80 mg/g at 25 ^{o}C in Table 2 is compared with the value of 37.27 mg/g and 15.48 mg/g which are found for the adsorption of stearic acid and palmitic acid on RHA, respectively, at the same temperature [7, 8]. Furthermore, the Langmuir equilibrium parameter, R_L was found as 0.29, 0.27 and 0.23 for the temperature of 25, 35 and 45 ^{o}C, respectively. The kaolinite is good adsorbent for the adsorption of stearic acid from isooctane solution at the studied temperatures since it is between 0 and 1.

Table 2. Langmuir and Freundlich constants and other derived parameters for 25, 35, and 45 ^{o}C.

Temperature (^{o}C)	Langmuir isotherm			Freundlich isotherm			
	q_m (mg/g)	K_L (mg^{-1})	r^2	R_L	K_F	n	r^2
25	18.80	0.25	0.9913	0.29	4.14	1.89	0.9944
35	16.95	0.23	0.9933	0.27	3.42	1.77	0.9955
45	16.12	0.19	0.9954	0.23	3.11	1.78	0.9945

Thermodynamic parameters

The free energy change of adsorption (ΔG^o_{ads}) is calculated by using following equation

$$\Delta G^o_{ads} = -RT \ln K_o$$

(4)

where R is the universal gas constant and T is the Kelvin temperature. K_o is the thermodynamic equilibrium constant for the adsorption process determined by plotting ln (q_e/C_e) versus C_e and extrapolating to zero C_e as suggested by Khan and Singh [14, 15] (Figure 6).

The other thermodynamic parameters, the enthalpy of adsorption, ΔH^o_{ads}, and the entropy of adsorption, ΔS^o_{ads}, are calculated from the slope and intercept of the plot of ln K_o against 1/T, respectively, (Figure 7) from the following equation

$$\ln K_o = \frac{\Delta S^o_{ads}}{R} - \frac{\Delta H^o_{ads}}{RT}$$

(5)

The calculated thermodynamic functions (K_o, ΔG^o_{ads}, ΔH^o_{ads} and ΔS^o_{ads}) for the temperature of 298, 308 and 318 K are given in Table 3. The Gibbs free energy change of adsorption (ΔG^o_{ads}) is between -19.98 and -20.50 kJ/mol. Based on ΔG^o_{ads} values, the adsorption process is spontaneous and physical characteristic in nature [16]. Moreover, the negative value of ΔH^o_{ads} (-12.30 kJ/mol) exhibits the exothermic nature of the adsorption process of stearic acid onto kaolinite. These results are in contrary with the data given in the literature [7, 8]. It may be due to that the energy released after the adsorption is higher than that needed for extracting the solvent molecules from the pores of kaolinite by stearic acid during the adsorption. On the other hand, the positive ΔS^o_{ads} (0.0259 kJ/mol.K) means that the disorder of the system is increased due to the physical interaction of stearic acid with the adsorption sites of kaolinite.
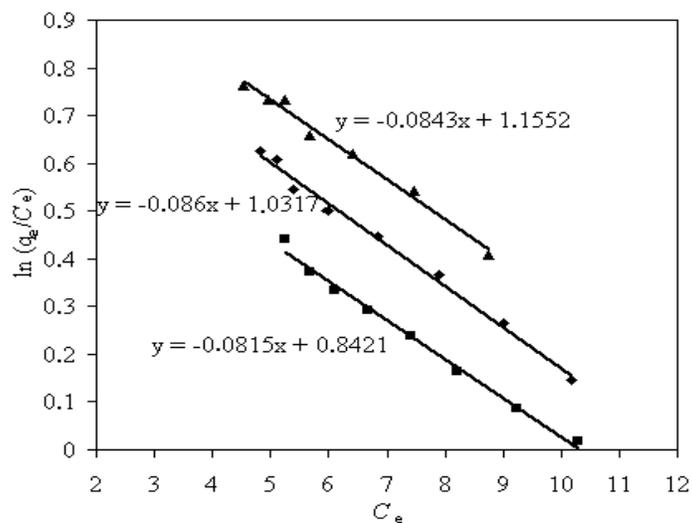
Figure 6. Plots of ln (q_e/C_e) versus C_e at different temperatures; (▲) 298, (◆) 308, (■) 318 K.
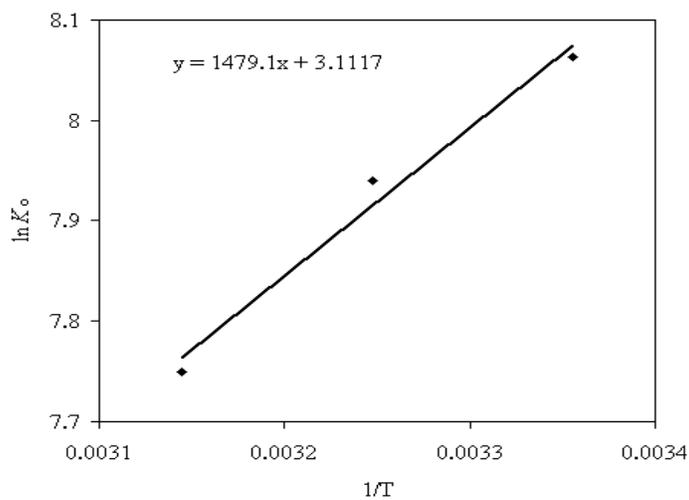
Figure 7. Plots of ln K_o versus 1/T.

Table 3. Thermodynamic parameters calculated for 298, 308 and 318 K.

Temperature (K)	K_o (kg^{-1})	ΔG^o_{ads} (kJ/mol)
298	3174	-19.98
308	2806	-20.33
318	2321	-20.50
ΔH^o_{ads} (kJ/mol)	-12.30	
ΔS^o_{ads} (kJ/(mol.K))	0.0259	

CONCLUSION

The adsorption of the stearic acid onto untreated kaolinite at 25, 35 and 45 ^{o}C confirms to the Langmuir and Freundlich isotherms. The FT-IR spectroscopy method proves that the adsorption is carried out by possible interaction between the stearic acid molecule and the hydroxyl of silanol group on the surface of kaolinite. The equilibrium parameter, RL, shows that the kaolinite is a suitable adsorbent for the stearic acid. The free energy change of adsorption (ΔG^o_{ads}) was found between -19.98 and -20.50 kJ/mol at examined temperatures and enthalpy of adsorption (ΔH^o_{ads}) and entropy of adsorption (ΔS^o_{ads}) were found to be -12.30 kJ/mol and 0.0259 kJ/(mol.K), respectively. ΔH^o_{ads} and ΔG^o_{ads} values calculated for the temperatures above demonstrate that the adsorption process of stearic acid onto kaolinite is spontaneous and exothermic in nature. It is finally concluded that the kaolinite used in this study is a suitable adsorbent for the adsorption of stearic acid from isooctane solution at room temperature.

ACKNOWLEDGEMENTS

REFERENCES

1. Abhat, A. *Solar Energy* **1983**, 30, 313.
2. Sarý, A.; Kaygusuz, K. *Solar Energy* **2002**, 71, 365.
3. Sarý, A, *Energy Convers Manage* **2003**, 44, 2277.
4. Proctor, A.; Adhikara, C.; Blyholder, G.D. *J. Am. Oil Chem. Soc*. **1995**, 72, 331.
5. Proctor, A.; Palaniappan, S. *J. Am. Oil Chem. Soc.* **1990**, 67, 15.
6. Adam, F.; Saleh, M.I. *J. Am. Oil Chem. Soc*. **1994**, 71, 1363.
7. Adam, F.; Chua, J.H. *J. Colloid Interface Sci.* **2004**, 280, 55.
8. Topallar, H.; Bayrak, Y. *Turkish J. Chem.* **1999**, 23, 193.
9. Ikhsan, I.; Johson, B.B.; Wells, J.D.; Angove, M.J. *J. Colloid. Interface Sci.* **2004**, 273, 1.
10. Angove, M.J.; Johson, B.B.; Wells, J.D. *Coll. Surf. A: Phys. Eng. Asp.* **1997**, 126, 137.
11. Adebowale, K.O.; Unuaabonah, I.E.; Olu-Owolabi, B.I. *App. Clay Sci*. **2005**, 29, 145.
12. Langmuir, I. *J. Am. Chem. Soc.* **1918**, 40, 1361.
13. Freundlich H. *Colloid and Capillary Chemistry,* Methuen: London; **1926**.
14. Khan, A.A; Singh, R.P. *Colloids. Surf.* **1987**, 24, 33.
15. Tahir, S.S.; Rauf, N. *J. Chem. Thermodynamics* **2003**, 35, 2003.
16. Özcan, S.F.; Erdem, B.; Özcan, A. *J. Colloid Interface Sci.* **2004**, 280, 44.