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Equilibrium and Thermodynamic Studies of Stearic Acid Adsorption on Sepiolite

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This study presents the equilibrium and thermodynamic parameters of the adsorption of stearic acid on sepiolite as a function of temperature. The equilibrium data were applied to linear Langmuir and Freundlich models and the coefficients of determination (r^2 = 0.849-0.935 for linear Langmuir model and r^2 = 0.990-0.995 for linear Feundlich model), indicating that the second model was more applicable in the evaluation of equilibrium data at studied conditions. Thermodynamic parameters such as free energy (ΔG°), enthalpy (ΔH°) and entropy of adsorption (ΔS°) were also calculated. These parameters revealed that the adsorption of stearic acid on sepiolite was feasible, spontaneous and exothermic in nature. On the basis of the results, it can be concluded that the sepiolite has a considerable potential for removal of stearic acid from the main sources such as raw and edible soybean, sunflower and olive oils.

Key Words: Sepiolite, Stearic acid, Adsorption 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. Free fatty acids from the common vegetable and animal oils is normally derived breaking triglyceride ester bonds during the refining process in industry. Adsorption method can be used for bleaching of the oils and can increase the stearic acid content[1]. The number of study on adsorption of fatty acids has been limited in literature. The ability of rice husk ash (RHA) to absorb free fatty acid was investigated in literature[2-5]. These studies proved that the adsorption of a free saturated fatty acid using a proper adsorbent is proper method for removing it from the main sources such as raw and edible soybean, sunflower and olive oils.

Sepiolite is a good adsorbent for organic species because it exhibits a variety of attractive properties such as high specific surface area, high porosity and surface activity[6]. Sepiolite is a fibrous, naturally occurring, hydrated magnesium silicate belonging to the clay family with ideal formula $Si_{12}Mg_8O_{30}(OH)_4(H_2O)_4 \cdot 8H_2O$. In general, the selectivity of fibrous clay minerals for sorption of organic compounds can be used for separating mixed components. Such selectivity plays a prominent role in the decolourization of oils and in separation processes such as refining of crude petroleum oils[6].

This work aimed to investigate the equilibrium and thermodynamic parameters of the adsorption of stearic acid on sepiolite as a function of temperature.

EXPERIMENTAL

Sepiolite was obtained from Eczacibasi Natural Mineral Industry and Commercial firm (Turkey). Sepiolite was dried and sieved through 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 378 K for 24 h and then placed in desiccator before adsorption experiment. Chemical were supplied from Aldrich company and used without further purification.

Characterization of the adsorbent (Sepiolite): The mineral analyis of sepiolite clay was carried out by using X-ray powder diffractometry (Rigaku D-Max 2200 model). The clay mineral mainly consists of 49.9 % SiO_2, 13.2 % MgO, 0.6 % Al_2O_3, 0.284 % Fe_2O_3, 0.178 % CaO, 1-2 % dolomite, 85 ± 5 % sepiolite, smectite and 5-10 % illite and 2-3 % salts, oxides and silicates. The specific surface area of the clay was found to be 72.4 m^2/g by BET method using a surface analyzer (Quantachromosorb).

Preparation of solutions: A 0.569 g stearic acid was dissolved in 1 L isooctane to prepare 2×10^{-3} mol/L stock solution. 5×10^{-3} mol/L NaOH solution was prepared and standardized by titrating with potassium hydrogen phosphate and then, it was diluted to 2.5×10^{-3} mol/L with deionized water.

Adsorption procedure: 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 and 0.8 g adsorbent were weighed with the accuracy of ± 0.1 mg and transferred to 50 mL conical flasks with glass stoppers. 20 mL stock solution of stearic acid was pipetted into each conical flask. The samples were shaken for 2 h by a mechanical shaker combined with a temperature controller (Arex, Velp Scientitica) at 100 rpm shaking speed. Subsequently, all samples were kept for 1 h until all adsorbent had settled to the bottom. After then, a 5 mL of the supernatant was pipetted into 10 mL neutralized propan-1-ol and titrated with NaOH solution. The titration was repeated in triplicate and average titrant volume was recorded. In order to determine the adsorption properties at different temperatures, the procedure were repeated at 293, 298, 303 and 308 K.

RESULTS AND DISCUSSION

Adsorption equilibrium data are generally described by Langmuir and Freundlich models. The experimental data were conformed the linear form of Langmuir model expressed as the following equation[7]

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

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 adsorbent. q_m (mg/g) and K_L (L/mg) are Langmuir constants which is determined from the slope and the intercept of the linear plot of C_e/q_e *vs.* C_e.

The linear form of Freundlich model is given by following equation[8]

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (2)$$

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

Figs. 1 and 2 show the linear plots of Langmuir and Freundlich isotherms of the adsorption of stearic acid on sepiolite at 293, 298, 303 and 308 K. The results obtained from these models were given in Table-1. The higher coefficients of determination (r^2) obtained for the linear Feundlich model (r^2 = 0.990-0.995) than that obtained for the linear Langmuir model (r^2 = 0.849-0.935) indicated that the linear Freundlich model is more applicable to the equilibrium data. The values of Langmuir constants decreased from 14.9 to 13.4 mg/g and 0.36 to 0.25 L/mg with increasing temperature.

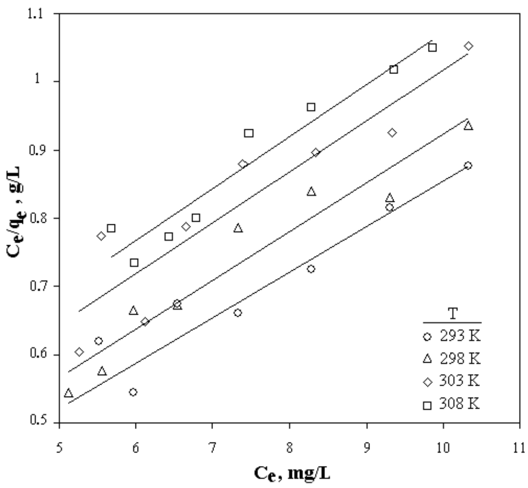

Fig. 1. Linear plots of Langmuir isotherm of adsorption of stearic acid on sepiolite at different temperatures

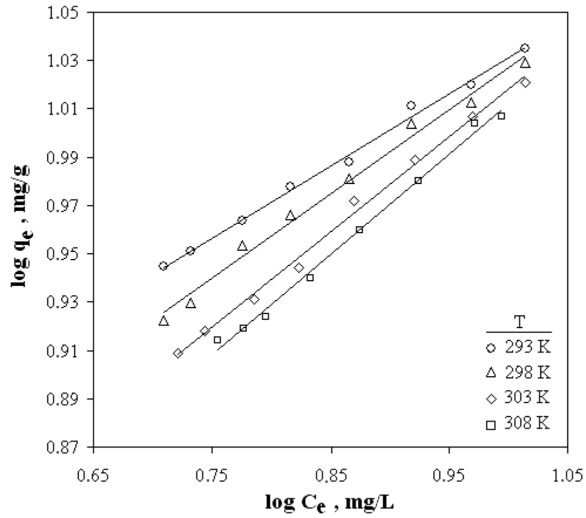

Fig. 2. Linear plots of Freundlich isotherms of adsorption of stearic acid on sepiolite at different temperatures

TABLE-1
LANGMUIR AND FREUNDLICH CONSTANTS DETERMINED FOR THE ADSORPTION OF STEARIC ACID ON SEPIOLITE AT DIFFERENT TEMPERATURES

Langmuir isotherm				Freundlich isotherm		
Temp. (K)	q_m (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)	n	R^2
293	14.9	0.36	0.906	5.4	3.4	0.995
298	13.9	0.35	0.932	4.8	2.9	0.990
303	13.5	0.27	0.849	4.3	2.5	0.994
308	13.4	0.25	0.935	4.0	2.4	0.995

On the other hand, adsorption capacity (K_F) and adsorption intensity (n) decrease from 5.4 to 3.9 mg/g and from 3.4 to 2.4, respectively with increasing temperature, indicating that the adsorption of stearic acid on sepiolite is exothermic in nature and less favourable with temperature rise.

Thermodynamic parameters: The free energy of adsorption (ΔG^o) is calculated using the following equation

$$\Delta G^o = -RT \ln K_o \tag{3}$$

where, R is the universal gas constant and T is the Kelvin temperature. K_o is the thermodynamic equilibrium constant of adsorption process determined by plotting ln (q_e/C_e) *vs.* C_e and extrapolating to zero C_e[9] as shown in Fig. 3.

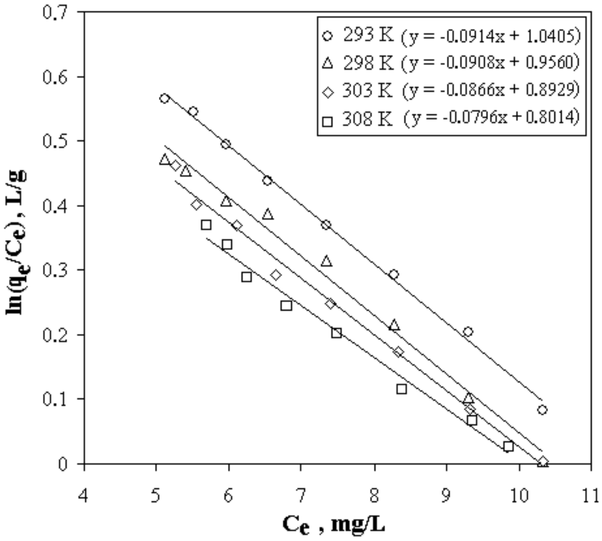

Fig. 3. Plots of ln (q_e/C_e) *vs.* C_e at different temperatures

The other thermodynamic parameters, the enthalpy of adsorption (ΔH°) and the entropy of adsorption (ΔS°) were calculated from the slope and intercept of the plot of ln K_o against 1/T, respectively[10,11] as shown in Fig. 4.

$$\ln K_o = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (4)$$

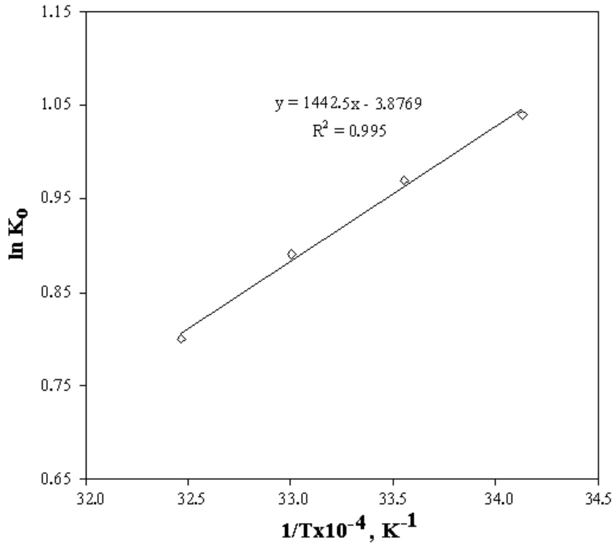

Fig. 4. Variation of the thermodynamic equilibrium constant in the adsorption of stearic acid on sepiolite as a function of temperature

The free energy of adsorption (ΔGº) was found to be in the range of -2.5, -2.4, -2.2 and -2.1 kJ/mol at 293, 298, 303 and 308 K, respectively. These results indicated that the adsorption of stearic acid on sepiolite was feasible and spontaneous. The enthalpy of adsorption (ΔHº) was found as -11.9 kJ/mol. The negative ΔHº confirmed that the adsorption of stearic acid on sepiolite was exothermic in nature. It also indicated that the energy released after the adsorption is higher than that needed for extracting the solvent molecules from the pores of sepiolite. The entropy of adsorption (ΔSº) was found to be -32.2 J/mol K. The negative value for the entropy of adsorption means that the adsorption system as a whole was in a high state of orderliness at equilibrium.

Conclusion

The results indicated that the adsorption capacity of stearic acid on sepiolite was affected considerably with temperature. The adsorption equilibrium data better fitted to the linear Freundlich model than the linear Langmuir model in the temperature range of 293-308 K. The thermodynamic parameters (ΔGº, ΔHº and ΔSº) determined with respect to the temperature variation revealed that the adsorption of stearic acid on sepiolite was feasible, spontaneous and exothermic in nature. In addition, it is concluded that the sepiolite can be used as an adsorbent to remove stearic acid from the main sources such as raw and edible soybean, sunflower and olive oils.

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REFERENCES

1. A. Proctor, C. Adhikara and G.D. Blyholder, *J. Am. Oil Chem. Soc.*, **72**, 331 (1995).
2. A. Proctor and S. Palaniappan, *J. Am. Oil Chem. Soc.*, **67**, 15 (1990).
3. F. Adam and M.I. Saleh, *J. Am. Oil Chem. Soc.*, **71**, 1363 (1994).
4. F. Adam and J.H. Chua, *J. Colloid Interf. Sci.*, **280**, 55 (2004).
5. H. Topallar and Y. Bayrak, *Turk. J. Chem.*, **23**, 193 (1999).
6. A. Askin and D.T. Yazici, *Chromatography*, **61**, 625 (2005).
7. I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).
8. H. Freundlich, *Z. Phys. Chem.*, **57**, 385 (1906).
9. V.K. Gupta, P. Singh and N. Rahman, *J. Colloid. Interf. Sci.*, **275**, 398 (2004).
10. A.A. Khan and R.P. Singh, *Colloids Surf.*, **24**, 33 (1987).
11. S.S. Tahir and N. Rauf, *J. Chem. Thermodyn.*, **35**, 2003 (2003).

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