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Adsorption Isotherms of Oleic Acid on Carbon Nanotube

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The purpose of this research is to study the adsorption behaviour of oleic acid on the multi-wall carbon nanotube as a function of temperature and initial concentration of adsorbate through adsorption isotherms and evaluating the thermodynamic parameters (ΔG, ΔS and ΔH). The amount of oleic acid adsorbed on carbon nanotube surface increased with the concentration at constant temperature and decreased with the increase of temperature at constant concentration. The amount of oleic acid adsorbed nanotube surface was related to the concentration of adsorbate and temperature of the solution. The decrease in the values of ΔG with the increase of temperature demonstrated that the adsorption was supported by the high temperature and the positive value of ΔS showed that the oleic acid in a more randomic condition in the adsorbed state than in solution. The experimental results obtained at 295, 300 and 305 K showed that experimental data were well represented by the Langmuir, Freundlich and Temkin isotherms models.

Key Words: Adsorption, Oleic acid, Thermodynamic parameters, Carbon nanotube.

INTRODUCTION

Since the discovery of carbon nanotubes[1] (CNTs) these compounds highly developed in chemical and physical areas. The way of synthesis of this compound developed quickly[2]. Carbon nanotubes can adsorb so many of atoms and molecules on their surface such as absorption of metallic elements like lithium[3], potassium[4], rubidium[5], cesium[6] and non-metallic such as hydrogen[7], oxygen[8], nitrogen[9] and methanol[10].

Absorption characteristics of carbon nanotubes for adsorption of gases such as hydrogen and other gases[11]. All of the compounds on the surface of carbon nanotubes are absorbed and show two main covalent bonds and non covalent bonds[12,13]. Absorption takes places on the surface of the carbon walls while non covalent absorption which is the kind of physically absorption takes place on the carbon nanotubes walls. One of the characteristics of non covalent bonds adsorption on carbon nanotubes is that the structure of carbon nanotubes doesn't change after this absorption and separating the absorption[14,15].

Basically, essential fatty acid exists in liquid oil and that have many double bonds. The most important fatty acid is omega 9 (oleic acid) that is only finding in olive oil and is given a unique characteristic to olive oil. In fact the fat which exists in olive oil, is the best one, because the essential fatty acid not only don't increase the blood cholesterol, but decrease the fatty acids which have double bonds, provides only 7 to 8 % of total calorie to human body.

Essential fatty acids have a share in phospho lipids structure and usually phospho lipids play a role in cellular structure, if the phospho lipids lack, energy metabolism disordered. Metabolism takes place in the mitochondria walls and the lock of phospho lipids results in disordered in cellular metabolism. Essential fatty acid such as omegas is a kind of fatty acids which body is not able to produce them and should be provided by food. Omega 9 is an unsaturated fatty acid with the formulation of $C_{18}H_{34}O_2$ and is insoluble in water. According to role of fatty acids obtained by breakdown of existent fatties in nutrition regime and its importance in energy metabolism, a lot researches has been done about how they adsorbed. The role of oleic acid as an unsaturated fatty acid in preventing of cardiac diseases is demonstrated[16,17]. Also oleic acid prevents of heart-failure are decreased resistance to insulin in diabetes according to unique charocteristion of carbon nanotubes adsorption of oleic acid (omega 9) as an unsaturated fatty acid is very important.

The purpose of this work is to study of adsorption behaviour of oleic acid on multi-wall carbon nanotubes as a function of temperature and early concentration of adsorption isotherms and their thermodynamic parameters, enthalpy variation (ΔH), entropy variation (ΔS) and Gibbs free energy variation (ΔG) in solutions.

EXPERIMENTAL

Ethanol with purity of 97.7 % was purchased from Merck Co., Germany, while technical grade oleic acid with purity of 88 % was purchased from Merck Co., Germany. Carbon nanotube was purchased from Merck Co., Germany.

Fourier transform infrared (FTIR) analysis was performed using a Nexus670 FTIR spectrometer (Thermo Nicolet, Madison) equipped with a KBr beam splitter (KBr, FTIR grade). Spectra were acquired in the 4000-400 cm^{-1} wavenumber.

Adsorption experiments: A stock solution of about 100 mg/L oleic acid was prepared. The range of oleic acid concentration used is from 2 to 30 mg/L. Equilibrium adsorption experiments were performed using 40 mL screw-capped glass centrifuge tubes as batch reactor systems. Each tube containing 0.05 g carbon nanotubes was filled with 25 mL oleic acid solution of different concentrations. All tubes were immediately sealed with PTFE-lined caps and were then mechanically shaken for 24 h in a thermostated rotary shaker at 295 ± 1 K, except for the thermodynamic experiments, in which temperatures of 300 and 305 K were adjusted. After equilibration, all tubes were placed vertically for 4 h at the same temperature to ensure complete sedimentation of carbon nanotubes from the bulk solutions.

Adsorption isotherms: The adsorption isotherm described the relationship between the amount of a substance adsorbed and its remaining amount in the solution in equilibrium and was the method used to evaluate the mechanism of adsorption[18].

Langmuir model: This model of adsorption is used more ordinary and is expressed by eqn. 1.

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} C_e \qquad (1)$$

In this equation, q_e (mg g^{-1}) is amount of absorbed material in absorbent surface and q_m is equilibrium constant of adsorption and b is the capacity of adsorption in saturated single layer and C_e (mg L^{-1}) is solution in equilibrium state.

Freundlich model: This model is on experiential equation is used more for comprehension of metallic ions adsorption upon heterogeneous surface with multi layer adsorption and also for adsorptions that the adsorption amount is increased unlimited with increasing intension. This model is specified with eqn. 2.

$$q_e = k_f C_e^{1/n} \longrightarrow \ln q_e = \ln k_f + \frac{1}{n} \ln C_e \qquad (2)$$

In this equation, q_e (mg g^{-1}) is amount of absorbed material in absorbent surface, K, n in arrangement are adsorption capacity and adsorption intensification.

Temkin model: Temkin isotherm presents the reaction between absorbent and absorbed particles clearly. This model is specified with eqn. 3.

$$q_e = \frac{RT}{b} \ln(A C_e) \longrightarrow q_e = B \ln A + B \ln C_e \qquad (3)$$

In this relation, A is equivalent of bond constant with maximum of connect energy, b is constant of Temkin isotherm and B is adsorption temperature.

Thermodynamic parameters associated with the adsorption processes: The values of the thermodynamic parameters, enthalpy variation (ΔH) and entropy variation (ΔS), were calculated from the curve relating the distribution coefficient (K_D) as a function of the temperature using the equation:

$$\ln K_D = \Delta S/R - \Delta H/RT \qquad (4)$$

where K_D is the distribution coefficient (cm^3 g^{-1}), defined as:

$$K_D = q_e/C_e \qquad (5)$$

with q_e the amount adsorbed (mg adsorbate/g adsorbent) described by the equation:

$$q = V (C_i - C_e)/m \qquad (6)$$

where C_i and C_e are the initial and equilibrium concentrations of the solute, respectively (mg cm^{-3}), V is the volume of the solution (L) and m is the adsorbent mass (g). The value of ΔG (Gibbs free energy variation) was calculated by the classic thermodynamic relation:

$$\Delta G = \Delta H - T\Delta S \qquad (7)$$

RESULTS AND DISCUSSION

Fig. 1 shows the surface groups on carbon nanotube analyzed by FTIR. The peaks at 1186, 1160 and 1134 cm^{-1} of carbon nanotube corresponded to C=O (stretching), C-O-C (antisymmetrical stretching) and C-O-C (symmetrical stretching), respectively. The peak at 3700-3300 cm^{-1} (low intensity) corresponding to -OH (stretching) might be caused by moisture in the samples. However, the characteristic peak at 1750-1700 cm^{-1} corresponding to -COOH (stretching) was observed in these sample.

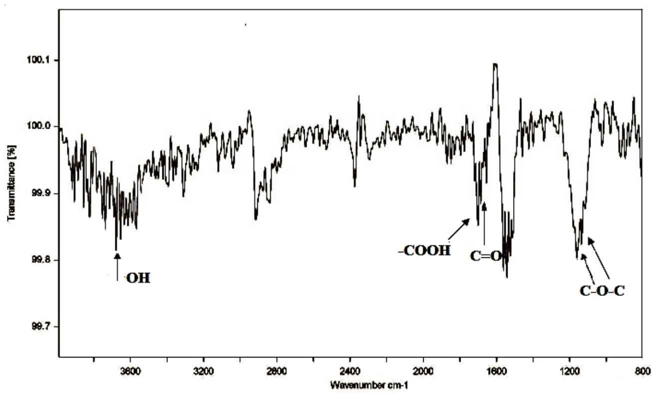

Fig. 1. Surface functional groups of carbon nanotube analyzed by FTIR

Thermodynamic parameters: The distribution coefficients (K_D) as a function of temperature of the adsorption process of the oleic acid on carbon nanotube are shown in Fig. 2. It was observed that the distribution coefficients decreased with the increase of temperature[16,17].

The values of the thermodynamic parameters, enthalpy variation (ΔH) and entropy variation (ΔS) calculated from eqn. 4 and Gibbs free energy variation (ΔG) described by eqn. 7, of the adsorption process of the oleic acids, is shown in Table-1.

In all adsorption processes studied, being, initial concentration of the solutions and temperature, the negative values of ΔG showed that there is a reduction in the Gibbs free energy as expected in a spontaneous process. The decrease in the values of ΔG, with the increase in temperature, demonstrated that the adsorption process was facilitated by the higher temperatures.

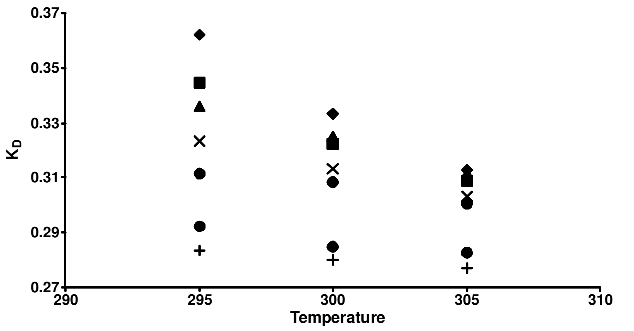

Fig. 2. Distribution coefficient as a function of the temperature of the adsorption of solutions of oleic acid on carbon nanotube: (◆ 2 mg/L); (■ 5 mg/L); (▲ 10 mg/L); (× 15 mg/L); (o 20mg/L); (● 25mg/L); (+ 30mg/L)

TABLE-1
THERMODYNAMIC PARAMETERS OF THE OLEIC ACID ADSORPTION

C_i (mg L^{-1})	ΔS (J mol^{-1} k^{-1})	ΔH (J mol^{-1})	ΔG (J mol^{-1})		
			295 K	300 K	305 K
2	0.447939	-107.498	-239.64	-241.880	-244.12
5	0.360162	-80.3861	-186.634	-188.435	-190.236
10	0.277872	-55.6375	-137.61	-138.999	-140.388
15	0.254465	-47.7668	-122.834	-124.106	-125.379
20	0.185424	-26.5622	-81.2625	-82.190	-83.1167
25	0.183416	-24.2686	-78.3763	-79.293	-80.2105
30	0.164910	-18.1688	-66.8171	-67.642	-68.4662

The entropy variation is related to variations of the order-disorder in a system. The positive value of ΔS showed that the oleic acid in a more randomic condition in the adsorbed state than in solution. The negative values of ΔH indicate an exothermic process, as is common in most of the cases[21,22].

Adsorption isotherms: The Langmuir, Freundlich and Temkin isotherms of the adsorption process of oleic acid on carbon nanotube are shown in Figs. 3-5. It was observed that the experimental data were well represented by Langmuir Freundlich and Temkin models.

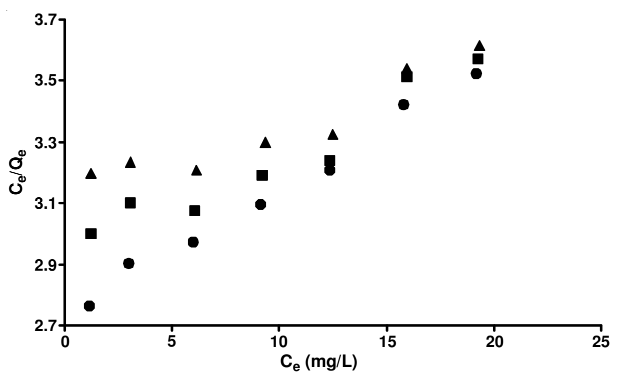

Fig. 3. Langmuir isotherm of oleic acid on carbon nanotube: ● 295 K (R^2 = 0.9883); ■ 300 K (R^2 = 0.9215); ▲ 305 K (R^2 = 0.8811)

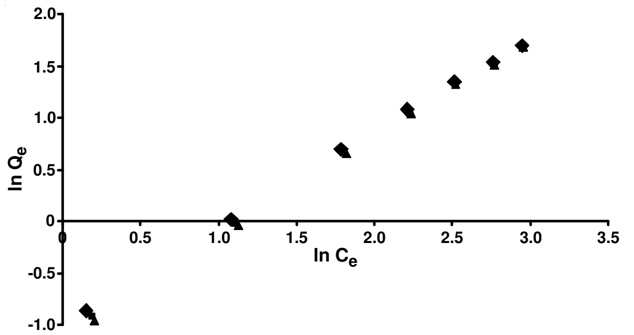

Fig. 4. Freundlich isotherm of oleic acid on carbon nanotube: ● 295 K (R^2 = 0.9990); ■ 300 K (R^2 = 0.9986); ▲ 305 K (R^2 = 0.9990)

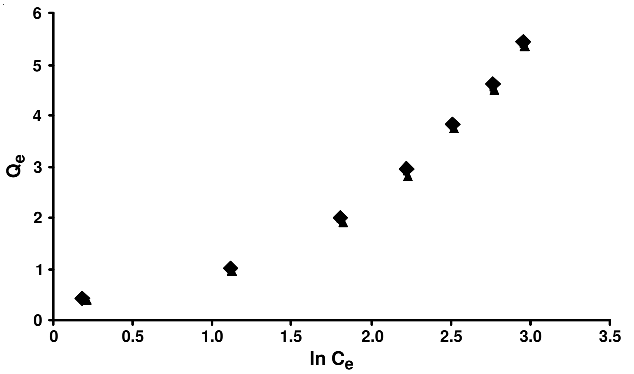

Fig. 5. Temkin isotherm of oleic acid on carbon nanotube: ● 295 K (R^2 = 0.9130); ■ 300 K (R^2 = 0.9118); ▲ 305 K (R^2 = 0.9073)

The values of the constants of the isotherms of Langmuir, q and b and of Freundlich, k and n and of Temkin, B and A and b, are shown in Table-2.

Conclusion

In this research the thermodynamic properties of oleic acid adsorption on carbon nanotube were studied. The negative values of ΔG and ΔH showed that the adsorption of oleic acid on carbon nanotube was a spontaneous and an exothermic process. The decrease in the values of ΔG, with the increase of temperature, demonstrated that the adsorption was benefited by the high temperature and the positive values of ΔS showed that the oleic acid molecules are in a more randomic condition in the adsorbed state than in solution. In the adsorption process of oleic acid on carbon nanotube, it was obtained a complete quantification of the experimental values, it was verified that the adsorption capacity decreased with the temperature and increased with initial concentration of acids in solution. These behaviours were expected because the adsorption process was exothermic and an increase in the driving force allowed more molecules of solute to transfer from the liquid phase to the solid surface. The increase of the temperature negatively influenced the adsorption capacity of the adsorbents due to desorption of the molecules of the interface (increase of the

TABLE-2
PARAMETERS OF LANGMUIR, FREUNDLICH AND TEMKIN ISOTHERMS OF THE OLEIC ACID ADSORPTION

Temp. (K)	Langmuir			Freundlich			Temkin			
	b	q	R^2	n	K ($L.g^{-1}$)	R^2	A ($L.mg^{-1}$)	B	b ($J.mol^{-1}$)	R^2
295	0.015157	24.1346	0.9883	1.090	0.3838	0.9990	0.8080	1.7660	13.694	0.913
300	0.010767	31.6012	0.9215	1.060	0.3838	0.9986	0.7905	1.7750	13.857	0.911
305	0.007451	43.0100	0.8811	1.040	0.3541	0.9990	0.7692	1.7780	14.065	0.907

solubility of the acids in aqueous solution). Similar behaviour of the concentration and temperature effects were observed by several authors[16,21-25]. The equilibrium experimental data were well represented by the Langmuir, Freundlich and Temkin isotherms models. The Langmuir, Freundlich and Temkin constants obtained in this work confirmed the observed behaviour.

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