Regular Article

PHYSICAL CHEMISTRY RESEARCH
Published by the
Iranian Chemical Society
www.physchemres.org
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Phys. Chem. Res., Vol. 5, No. 3, 519-529, September 2017
DOI: 10.22036/pcr.2017.78175.1359

Adsorption Properties of Folic Acid onto Functionalized Carbon Nanotubes: Isotherms and Thermodynamics Studies

Sh. Hamedani[a]* and Z. Felegari[b]

[a]*Department of Chemistry, Abhar Branch, Islamic Azad University, Abhar, Iran*
[b]*Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran*

(Received 16 February 2017, Accepted 13 April 2017)

In the present research, we report the results of a systematic study on the adsorption properties of folic acid (FA) over functionalized single walled carbon nanotubes (SWCNTs) using the various factors, such as adsorbent dose, contact time, temperature, and initial FA concentration. Our results reveal that SWCNTs is an excellent adsorbent for folic acid, with an adsorption percentage of up to 76.2% at initial folic acid concentration of 20 ppm and temperature of 298.15 K. Interpreting equilibrium isotherms on the basis of various adsorption models, including Freundlich and Langmuir, shows that the Langmuir model can describe the adsorption process better than the other one. To further examine the adsorption behavior, we perform thermodynamic calculations which indicate that the adsorption reaction of FA onto SWCNTs is an exothermic and spontaneous procedure in the temperature range of 298.15-313.15 K. Based on our experiments , the functionalized SWCNTs are expected to be a potential efficient adsorbent and also can be used as a suitable drug delivery vehicle within biological systems.

Keywords: Adsorbent, Adsorbate, Isotherm models, Thermodynamic functions, Equilibrium

INTRODUCTION

Folic acid (FA) is an essential vitamin belonging to the B-vitamin group (B9). It consists of a pterin ring (PT) system, a *p*-amino-benzoic acid (PABA) portion, and glutamic acid (Glu) (Fig. 1). The human body cannot synthesize glutamate or *p*-aminobenzoic acid that is why the enrolling folic acid from food is necessary. To reduce the risk of serious birth defects of the brain and spina (such as brain anencephaly), folic acid is consumed mainly as part of a healthy diet. It may also be used as a supplement for the prevention of Alzheimer's disease, high blood pressure, protecting against neoplasia in ulcerative colitis, and some psychiatric disorders [1-4]. Low molecular weigth of FA is one of the featurs that render it an attractive ligand for targeting cell membranes and enhancing CNTs endocytosis by the folate receptor [5-7].

Different substrates have been proposed as adsorbent in adsorption processing of drug molecules, such as activated carbon, [8] silica, [9] and boron nitrides [10]. In most cases, the adsorbents have diameter in the range of submicron to micron and large internal porosities to ensure adequate surface area for adsorption. However, the diffusion limitation within the particles leads to decrease the available capacity and the adsorption rate. Accordingly, it is important and interesting to develop an adsorbent with a large surface area to volume ratio, a small diffusion resistance, and a high capacity for molecular adsorption.

The stability of SWCNTs results in some drawbacks in integrating the nanotubes with the current technology. The extraordinary structural, mechanical, physicochemical, and electronic properties of SWCNTs make this species particularly favorable for basic science studies and practical applications. SWCNTs have high potential in the field of biomedical, biomaterials, drug adsorbent, drug delivery

*Corresponding author. E-mail: sh_hamedani2004@yahoo.com

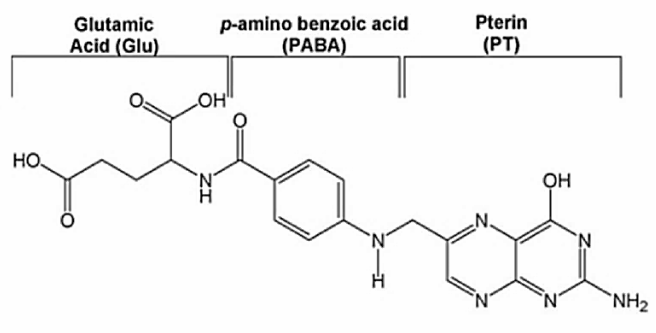


Fig. 1. The molecular structure of folic acid (FA).

systems, and even deliver therapeutic products [11-14]. Due to their large specific surface area along with remarkable optical, mechanical, and electrical properties, carbon nanotubes have been used as carriers for drug delivery [15, 16]. However, this huge potential can redound to effective usages, if SWCNTs are functionalized by different groups. Functionalization of SWCNTs is carried out by two different methods including the covalent and non-covalent linkages. There are many reports in the literature on the functionalization of nanotubes. For example, SWCNTs have been functionalized by carboxyl group [17], NH_2, phenol, thymine, $CONH_2$ groups [18], etc. for various applications.

Yang and *et al*. [19] functionalized SWCNTs with -CONH-C_6H_{12}-NH_3^+ and then used them as a DNA carrier. Poly ethylene glycol as a modifier in poly ethylene glycolated multi-walled carbon nanotubes (PEGylated MWCNTs) acts as a class of drug delivery system and supports drug releasing and adsorbing [20].

In this paper, we investigate the performance of functionalized SWCNTs in loading of folic acid as a molecular model [21-23]. Initially, SWCNT undergo oxidation process to become SWCNT-COOH. The next step, the carboxylated group of SWCNT reacts with oxalyl chloride, and subsequently resultant product reacts with alcohol or amine, such as 1,4-phenylenediamine ($C_6H_4(NH_2)_2$), to form SWCNT-CONH-C_6H_4-NH_2.

Finally, we use experimental observations to investigate the effect of some factors such as adsorbent dose, temperature, contact time, and initial concentration of folic acid on the adsorption efficiency of SWCNTs. In this regard, the Langmuir and Freundlich isotherm models are evaluated to explain the adsorption behavior.

MATERIALS AND METHODS

Materials

SWCNT-COOH with 2.73 wt% of COOH (outer diameter 1-2 nm; length about 5-30 nm, and specific surface area, SSA > 380 $m^2 g^{-1}$) was purchased at purity greater than 95% from US Research Nanomaterials, Inc. Folic acid ($C_{19}H_{19}N_7O_6$, molecular weight, 441.3975 g mol^{-1}), Oxalyl chloride ($(COCl)_2$, molecular weight, 126.93 g mol^{-1}), and 1,4-phenylenediamine ($(C_6H_4(NH_2)_2$, molecular weight, 108.1 g mol^{-1}) with high purity were supplied by Merck, Germany.

Chemical Functionalization of SWCNT-COOH

0.06 g of MWCNTs COOH in 50 ml dimethyl formamide (DMF) was sonicated for 30 min in a bottom flask. Then, 10 ml oxalyl chloride was added into the mixture while stirring at -10 °C for 2 h under nitrogen gas. The resulting mixture was stirred at room temperature for 12 h followed by heating at 70 °C for 12 h to remove the excess of oxalyl chloride. After adding 0.06 g of acylated SWCNTs to 50 ml DMF, 1,4-phenylenediamine (9 ml) was reacted to the mixture and sonicated for 45 min to produce SWCNT-CONH-(C_6H_4)-NH_2.

Batch Adsorption Experiments

Batch adsorption experiments were carried out to determine adsorption isotherms and thermodynamic properties for the adsorbed folic acid molecule over functionalized single walled carbon nanotube. First, a stock solution was prepared by dissolving 0.5 g folic acid in 500 ml double distilled water. The variation of folic acid

Table 1. Effect of Contact Time, Temperature, Adsorbents Dose and Initial Adsorbate Concentration on the Adsorption Percentage of Folic Acid over SWCNTs

Effect contact time		Effect of temperature		Effect of dose		Effect of concentration	
Time (min)	Adsorption percentage	T (K)	Adsorption percentage	Dose (g)	Adsorption percentage	Concentraion (mg l^{-1})	Adsorption percentage
10	45.23	298	75.88	0.025	43.56	2	45.12
20	55	303	69.24	0.05	54.57	5	54.33
30	62.45	308	62.67	0.075	64.23	15	70.63
40	67.31	313	60.45	0.1	76.11	20	76.2
50	72.12	-	-	0.15	75.79	25	76.23
60	76.86	-	-	-	-	-	-
70	76.79	-	-	-	-	-	-
80	77.32	-	-	-	-	-	-

concentration versus time in the aqueous solution was monitored under various conditions such as CNTs doses (0.025, 0.05, 0.075, 0.1, 0.15 g) and initial folic acid concentrations (2, 5, 10, 15, 20 and 25 mg l^{-1}).

The pH of solution was adjusted by adding 0.1 M phosphate buffer saline (PBS) solution. Adsorption experiments were conducted in 250 ml glass flask containing 0.10 g of the adsorbent and 100 ml of folic acid solution with the initial concentration of 20 mg l^{-1}. The mixture was shaken in a thermostatic orbit shaker at 180 rpm for different periods of time and at various temperatures (298.15, 303.15, 308.15 and 313.15 K). After a certain time, the samples were filtered using a 0.22 μm membrane.

The filtrates were immediately analyzed by UV-Vis spectrophotometer (Varian Cary 300) to determine the folic acid concentration. The adsorption percentage, A, and adsorption capacity at equilibrium, q_e (mg g^{-1}), were calculated by the Eqs. (1) and (2):

$$\text{Adsorption}, \% = \left(\frac{c_0 - c_e}{c_0}\right) \times 100 \quad (1)$$

$$q_e = \frac{(c_0 - c_e)}{m} \times V \quad (2)$$

where c_0 and c_e (mg l^{-1}) are the initial and equilibrium concentration of FA in solution, respectively, V (l) is solution volume, and m (g) is adsorbent mass.

RESULTS AND DISCUSSION

Effect of Contact Time

Aiming to optimize the contact time of adsorption, 0.1 g of adsorbent (functionalized SWCNTs) was added to 100 ml of folic acid solution with concentration of 20 mg l^{-1} at 25 °C. The obtained results from FA adsorption over the adsorbent show that the percentage of adsorbed molecule is increased with increasing the contact time (Table 1) and the time of 60 min is sufficient to achieve equilibrium (Fig. 2 and Table 1). Accordingly, 60 min contact time is selected as the equilibrium time for adsorbent functionalized SWCNT in all experiments.

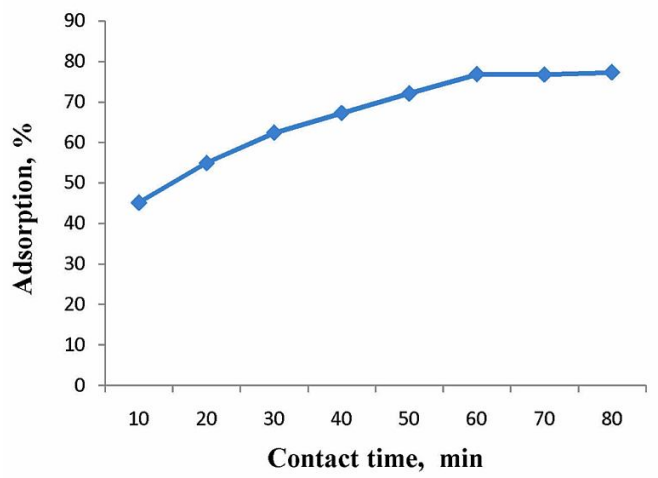


Fig. 2. Effect of contact time: Initial FA concentration = 20 mg l^{-1}, pH = 7, adsorbent dose = 0.1 g, contact time = 60 min, and temp. = 25 °C.

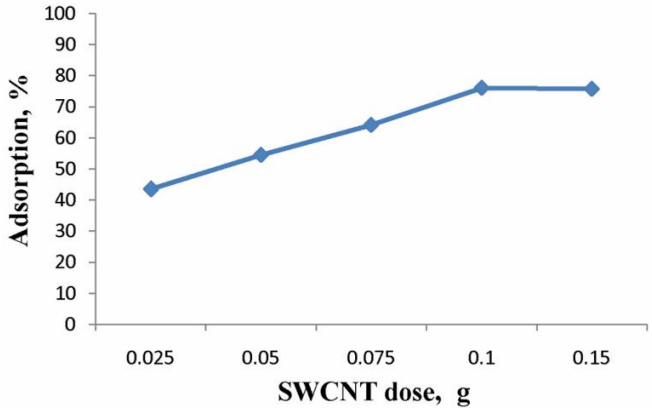


Fig. 3. Effect of CNTs dose on adsorption percentage: Initial FA concentration = 20 mg l^{-1}, pH = 7, temp. = 25 °C, contact time = 60 min.

Effect of Adsorbent Dose

To study the effect of functionalized SWCNT quantity on the adsorption of folic acid, the experiments are carried out under the conditions described in previous section with contact time of 60 min and a range of functionalized SWCNT dose (0.025, 0.05, 0.075, 0.1 and 0.15 g) (Fig. 3). Increase in adsorbent dose from 0.025 to 0.1 g brings up about 33% enhancement of the adsorption percentage onto functionalized SWCNT, from 43.56% to 76.11%. So, 0.1 g of functionalized SWCNT could be used as an appropriate dose in the next experiments of this work (Table 1). After optimum dose, all active sites are entirely exposed and the adsorbent surface is saturated.

Effect of Temperature on Molecule Adsorption

The adsorption experiments were performed at fixed initial concentration of folic acid, 20 mg l^{-1}, adsorbent dose of 0.1 g, and pH = 7, while varying temperature, 298.15, 303.15, 308.15 and 313.15 K, to investigate the effect of temperature on the adsorption behavior. Figure 4

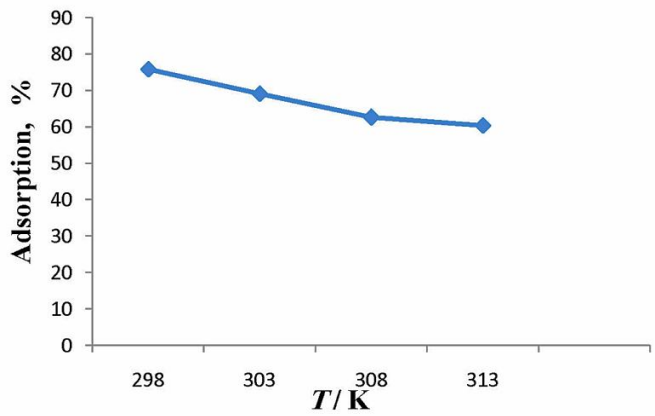


Fig. 4. Effect of temperature on percentage of adsorption: Initial FA concentration = 20 mg l^{-1}, pH = 7, adsorbent dose = 0.1 g, contact time = 60 min.

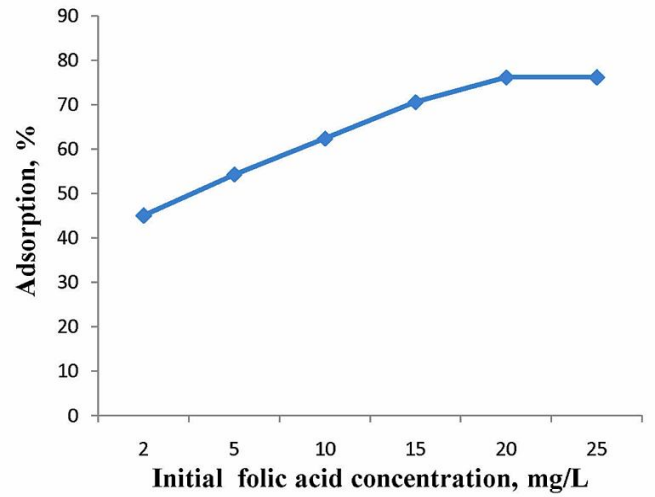


Fig. 5. Effect of initial FA concentration on percentage of adsorption: CNTs dose = 0.1 g, contact time = 60 min, temp. = 25 °C.

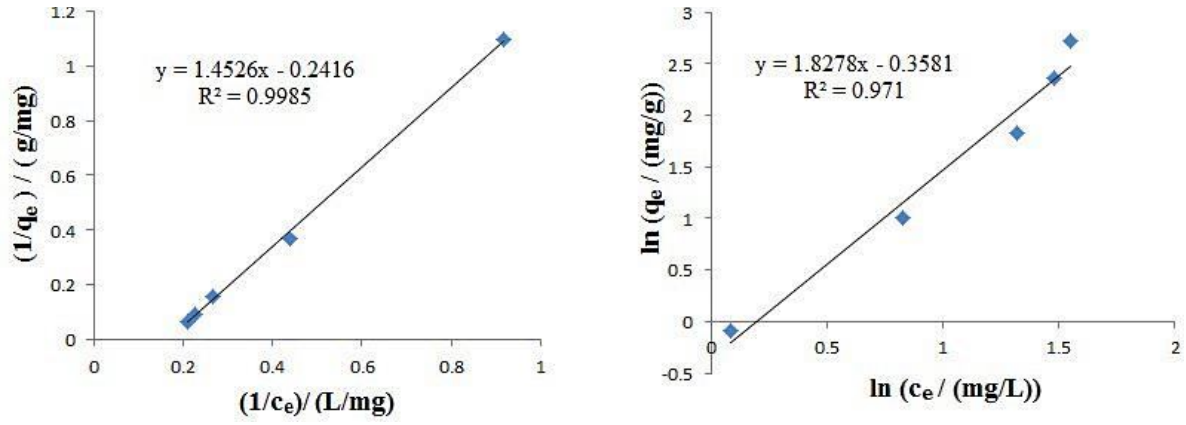
demonstrates adsorption percentage of folic acid as a function of temperature.

As reported in Fig. 4 and Table 1, the adsorption of folic acid onto adsorbent shows a ~15% decrease, from 75.88% to 60.45%, with increasing temperature. This phenomenon can be explained by the fact that the adsorbent sites are more active at lower temperatures. In this situation, the contact between the adsorbate molecule and the adsorbent active site is sufficient, leading to an increase in adsorption efficiency.

Effect of Initial Folic Acid Concentration

We get ahead the strategy applied in the previous stages to study the effect of initial concentration of folic acid on its adsorption over single-walled carbon nanotube. 0.1 g of nanotube is added to 100 ml of folic acid solution with initial concentration varying between 2 to 25 mg l^{-1} at pH = 7 and 25 °C.

As shown in Fig. 5 and Table 1, ~31% enhancement of the percentage of folic acid adsorption, from 45.12% to 76.2%, takes place through increasing the initial folic acid



(a) **(b)**

Fig. 6. The linearized Langmuir (a), Freundlich (b) isotherm of FA adsorption onto SWCNTs.

concentration from 2 to 25 mg l^{-1}. The percentage adsorption at higher concentration levels shows an increasing trend. At higher concentrations, all folic acid molecules present could interact with the binding sites, and thus the percentage of adsorption is higher than those at lower initial folic acid concentrations. In this condition, higher adsorption yield is due to the saturation of adsorption sites [24-26].

Adsorption Isotherms

One of the most important investigations to optimize the design of an adsorption process is to establish the adsorption isotherm. Adsorption isotherm studies are done using different initial folic acid concentrations ranging from 2-25 mg l^{-1}, with adsorbent dose 0.1 g at T = 25 °C and pH = 7.

Equilibrium data of adsorption process can be analyzed on the basis of Freundlich, [27] and Langmuir [28] models. The Langmuir isotherm is valid for monolayer adsorption on a surface with homogeneous binding sites, equivalent sorption energies, and no mutual interaction between adsorbed ions. The Langmuir isotherm is represented by the following equation:

$$q_e = \frac{K_L q_m c_e}{1 + K_L c_e} \qquad \text{(Langmuir model)} \qquad (3)$$

Equation (3) can be transformed into a linear equation as follow:

$$\frac{1}{q_e} = \left(\frac{1}{K_L q_m}\right)\frac{1}{c_e} + \frac{1}{q_m} \qquad \text{(Linear Langmuir model)} \qquad (4)$$

where q_m (mg g^{-1}) is the maximum adsorption capacity corresponding to complete monolayer coverage, K_L (l mg^{-1}) is the Langmuir constant including the affinity of binding sites, and c_e (mg l^{-1}) is the equilibrium solute concentration.

The values of Langmuir parameters introduced in equation 4, q_m and K_L, are determined from the intercept and the slope of the linear plots of $1/q_e$ against $1/c_e$, respectively (Fig. 6a).

The Freundlich equation is an empirical approach to describe heterogeneous surface, in which it is assumed that the adsorption occurs at sites with different adsorption energies. This isotherm is applicable to both monolayer (chemisorption) and multilayer (physisorption) adsorptions. It can be described as follows:

$$q_e = K_F c_e^{1/n} \qquad \text{(Freundlich model)} \qquad (5)$$

$$\ln q_e = (\frac{1}{n})\ln c_e + \ln K_F \qquad \text{(Linear Freundlich model)} \qquad (6)$$

The Freundlich constants, K_F (l g^{-1}) and n that indicate relative capacity and adsorption intensity, are calculated from the slope and intercept of plots of $\ln q_e$ *vs.* $\ln c_e$, respectively. Figure 6b shows the linearized Freundlich adsorption isotherm of FA molecule. Obtained isotherm

Table 2. The Langmuir and Freundlich Adsorption Isotherm Parameters for Adsorption of Folic Acid onto SWCNTs

Isotherm model	Langmuir			Freundlich		
Parameters	q_m (mg g^{-1})	K_L (l mg^{-1})	R^2	n	K_F (l mg^{-1})	R^2
	4.139	0.169	0.9985	0.547	1.430	0.971

Table 3. The Separation Factor or Equilibrium Parameter *R*L for Adsorption of Folic Acid onto SWCNTs Adsorbent

Initial folic acid concentration (mg l^{-1})	Separation factor R_L
2	0.747
5	0.542
10	0.371
15	0.282
20	0.228
25	0.191

Table 4. Thermodynamic Parameters for Folic Acid Adsorption onto SWCNTs

Temperature (K)	K_0	ΔG^o (kcal mol^{-1})	ΔH^o (kcal mol^{-1})	ΔS^o (cal mol^{-1} K^{-1})
298	3.149	-0.679		
303	2.250	-0.487		
308	1.680	-0.317	-9.074	-28.23
313	1.528	-0.263		

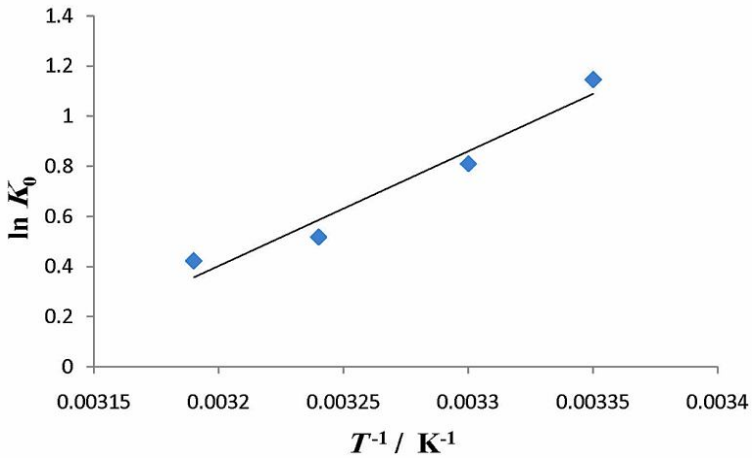


Fig. 7. lnK_0 *vs*. 1/*T* plot for the thermodynamic parameters.

parameters and correlation coefficients are reported in Table 2.

Comparison of correlation coefficients, R^2, for Langmuir and Freundlich models, (0.998 and 0.971), confirms that the Langmuir model can be a proper approach in all conditions.

The basic features of the Langmuir isotherm [28] can be expressed by means of a dimensionless constant related to the separation factor, R_L, which is defined as,

$$R_L = \frac{1}{1 + K_L c_0} \quad (7)$$

The equilibrium parameter R_L was observed to be between 0 and 1, therefor, the adsorption process is quite favorable. The calculated R_L values are tabulated in Table 3.

Adsorption Thermodynamics

Thermodynamic parameters are determined in the temperature range of 298.15-313.15 K, at initial FA concentration of 20 mg l^{-1} to find whether the reaction occurs spontaneously or not. The desired parameters, including Gibbs free standard energy ($\Delta G°$), standard enthalpy ($\Delta H°$), and standard entropy ($\Delta S°$) are calculated using the following equations [29-31]:

$$K_0 = \frac{a_s}{a_e} = \frac{q_e}{c_e} \quad (8)$$

$$\Delta G^\circ = -RT\ln K_0 \quad (9)$$

$$\Delta G° = \Delta H° - T\,\Delta S° \quad (10)$$

$$\ln K_0 = -\frac{\Delta H^\circ}{R}\frac{1}{T} + \frac{\Delta S^\circ}{R} \quad (11)$$

where the equilibrium constant values, K_0, are obtained by plotting $\ln(q_e/c_e)$ *vs*. q_e and extrapolating q_e to zero, and subsequently, ΔH^o and ΔS^o parameters, are determined from the slope and intercept of the plot of lnK_0 *vs*. 1/*T* using the Eq. (11) (Fig. 7). The values of K_0, $\Delta G°$, ΔH^o and ΔS^o parameters are reported in Table 4.

Based on the results (Table 4), the negative values of $\Delta G°$ at different temperatures reveal that the adsorption reaction occurs spontaneously. The decrease in $\Delta G°$ with the temperature decrement reflects a more energetically favorable adsorption at lower temperatures [32]. The negative value of $\Delta H°$ indicates that the interaction of folic acid adsorbed on SWCNTs is an exothermic process, which is the reason for the increase in adsorption at lower temperatures. In addition, the negative value of the standard entropy change, ΔS^o, shows a random decrease at adsorbent-adsorbate interface during the adsorption of FA onto SWCNTs [33].

CONCLUSIONS

In this article, we report the results of a detailed

experiment searching for the vital factors, including adsorbent dose, contact time, and temperature, that are responsible for the changes in the adsorption ability of SWCNTs to adsorb FA.

Each part of the study conducted to explore the influence of the above mentioned factors through fixing the other conditions, and their influences on the adsorption behavior of folic acid are identified by analyzing the adsorption isotherms and thermodynamic properties. On the basis of the experimental results the amount of adsorbed molecule on functionalized SWCNTs is increased with time. It was found that maximum adsorption takes place after 60 min, and after which, no change was observed in the adsorbed amount. In addition, maximum adsorption was observed at adsorbent dose of 0.1 g. Based on the results, after optimum dose, all active sites are entirely exposed and the adsorption on the surface is saturated.

The Langmuir isotherm model indicated the best fits to predict the adsorption for FA onto SWCNTs, and thermodynamic parameters obtained from the adsorption process revealed spontaneous and exothermic nature of phenomenon. Furthermore, the results confirmed that the decrease in ΔG° with the decrease in temperature represents a favorable adsorption at lower temperatures.

REFERENCES

[1] La Vecchia, C.; Negri, E.; Pelucchi, C.; Franceschi, S., Dietary folate and colorectal cancer. *Int. J. Cancer.* **2002**, *102*, 545-547, DOI: 10.1002/ijc.10720.

[2] Wang, X.; Qin, X.; Demirtas, H.; Li, J.; Mao, G.; Huo, Y.; Sun, N.; Liu, L.; Xu, X., Efficacy of folic acid supplementation in stroke prevention: a meta-analysis. *The Lancet.* **2007**, *369*, 1876-1882, DOI: 10.1016/S0140-6736(07)60854-X.

[3] Zhang, X.; Meng, L.; Lu, Q.; Fei, Z.; Dyson, P. J., Targeted delivery and controlled release of doxorubicin to cancer cells using modified single wall carbon nanotubes. *Biomaterials.* **2009**, *30*, 6041-6047, DOI: 10.1016/j.biomaterials.2009.07.025.

[4] Castillo, J. J.; Svendsen, W. E.; Rozlosnik, N.; Escobar, P.; Martínez, F.; Castillo-León, J., Detection of cancer cells using a peptide nanotube-folic acid modified graphene electrode. *Analyst*. **2013**, *138*, 1026-1031, DOI: 10.1039/c2an36121c.

[5] Hamedani, S.; Moradi, S.; Aghaie, H., Adsorption of folic acid on the Single-walled Carbon Nanotubes: AIM and NBO Analysis *via* DFT. Chin. *J. Struct. Chem.* **2015**, *34*, 1161-1169, DOI: 10.14102/j.cnki.0254-5861.2011-0677.

[6] Hamedani, S., Structural and electronic properties of folic acid adsorption on the carbon nanotubes: a density functional theory study. *Orient. J. Chem.* **2015**, *31*, 345-351, DOI: 10.13005/ojc/310140.

[7] Hamedani, S.; Aghaie, H., Molecular structure and theoretical thermodynamic study of folic acid based on the computational approach. *Chin. J. Struct. Chem.* **2015**, *34*, 1307-1316, DOI: 10.14102/j.cnki.0254-5861.2011-0688.

[8] Tseng, R. -L.; Wu, K. -T.; Wu, F. -C.; Juang, R. -S., Kinetic studies on the adsorption of phenol, 4-chlorophenol, and 2,4-dichlorophenol from water using activated carbons. *J. Environ. Manage.* **2010**, *91*, 2208-2214, DOI: 10.1016/j.jenvman.2010.05.018.

[9] Oleszczuk, P.; Pan, B.; Xing, B., Adsorption and desorption of oxytetracycline and carbamazepine by multiwalled carbon nanotubes. *Environ. Sci. Technol.* **2009**, *43*, 9167-9173, DOI: 10.1021/es901928q.

[10] Weng, Q.; Wang, B.; Wang, X.; Hanagata, N.; Li, X.; Liu, D.; Wang, X.; Jiang, X.; Bando, Y.; Golberg, D., Highly water-soluble, porous, and biocompatible boron nitrides for anticancer drug delivery. *ACS nano.* **2014**, *8*, 6123-6130, DOI: 10.1021/nn5014808.

[11] Felegari, Z.; Monajjemi, M., AIM and NBO analyses on the interaction between SWCNT and cyclophosphamide as an anticancer drug: A density functional theory study. *J. Chem. Theory. Comput.* **2015**, *14*, 1550021, DOI: 10.1142/S0219633615500212.

[12] Wong, B. S.; Yoong, S. L.; Jagusiak, A.; Panczyk, T.; Ho, H. K.; Ang, W. H., Carbon nanotubes for delivery of small molecule drugs. *Adv. Drug Deliv. Rev.* **2013**, *65*, 1964-2015, DOI: 10.1016/j.addr.2013.08.005.

[13] Felegari, Z., Structural and stability investigation of the anticancer drug Cyclophosphamide *via* quantum chemical calculations: A nanotube drug delivery. *Orient. J. Chem.* **2014**, *30*, 1865-1875, DOI: 10.13005/ojc/300447.

[14] Safari, J.; Zarnegar, Z., Advanced drug delivery systems: Nanotechnology of health design A review. *J. Saudi Chem. Soc.* **2014**, *18*, 85-99, DOI: 10.1016/j.jscs.2012.12.009.

[15] Peymani, S.; Izadyar, M.; Nakhaeipour, A., Functionalization of the single-walled carbon nanotubes by bulfur dioxide and electric field effect, a theoretical study on the mechanism. *Phys. Chem. Res.* **2016**, *4*, 553-565, DOI: 10.22036/pcr.2016.15614.

[16] Vashist, S. K.; Zheng, D.; Pastorin, G.; Al-Rubeaan, Kh., Delivery of drugs and biomolecules using carbon nanotubes. *Carbon*. **2011**, *49*, 4077-4097, DOI: 10.1016/j.carbon.2011.05.049.

[17] Kar, T.; Akdim, B.; Duan, X.; Pachter, R., Open-ended modified single-wall carbon nanotubes: A theoretical study of the effects of purification. *Chem. Phys. Lett.* **2006**, *423*, 126-130, DOI: 10.1016/j.cplett.2006.02.089.

[18] Veloso, M. V.; Filho, A. G. S.; Filho, J. M.; Fagan, S. B.; Mota, R., *Ab initio* study of covalently functionalized carbon nanotubes. *Chem. Phys. Lett.* **2006**, *430*, 71-74, DOI: 10.1016/j.cplett.2006.08.082.

[19] Yang, X. Y.; Liu, Z. F.; Mao, J.; Wang, Sh. J.; Ma, Y. F.; Chen, Y. Sh., The preparation of functionalized single walled carbon nanotubes as high efficiency DNA carriers. *Chin. Chem. Lett.* **2007**, *18*, 1551-1553, DOI: 10.1016/j.cclet.2007.10.006.

[20] Dinan, N. M.; Atyabi, F.; Rouini, M. R.; Amini, M.; Golabchifar, A. A.; Dinarvand, R., Doxorubicin loaded folate-targeted carbon nanotubes: Preparation, cellular internalization, *in vitro* cytotoxicity and disposition kinetic study in the isolated perfused rat liver. *Mater. Sci. Eng.* **2014**, *39*, 47-55, DOI: /10.1016/j.msec.2014.01.055.

[21] Kang, B.; Yu, D.; Dai, Y.; Chang, S.; Chen, D.; Ding, Y., Cancer-cell targeting and photoacoustic therapy using carbon nanotubes as "Bomb" agents. *Small.* **2009**, *5*, 1292-1301, DOI: 10.1002/smll.200801820.

[22] Xia, W.; Low, P. S., Folate-targeted therapies for cancer. *J. Med. Chem.* **2010**, *53*, 6811-6824, DOI: 10.1021/jm100509v.

[23] Castillo, J. J.; Rozo, C. E.; Castillo-León, J.; Rindzevicius, T.; Svendsen, W. E.; Rozlosnik, N.; Boisen, A.; Martínez, F., Computational and experimental studies of the interaction between single-walled carbon nanotubes and folic acid. Chem. *Phys. Lett.* **2013**, *564*, 60-64, DOI: 10.1016/j.cplett.2013.02.014.

[24] Dar, B. A.; Taher, A.; Wani, A.; Farooqui, M., Isotherms and thermodynamic studies on adsorption of copper on powder of shed pods of Acacia nilotica. *J. Environ. Chem. Ecotoxicol.* **2013**, *5*, 17-20, DOI: 10.5897/JECE12.013.

[25] Rajaei, G. E.; Aghaie, H.; Zare, K.; Aghaie, M., Adsorption of Cu(II) and Zn(II) ions from aqueous solutions onto fine powder of Typha latifolia L. root: kinetics and isotherm studies. *Res. Chem. Intermed.* **2013**, *39*, 3579-3594, DOI: 10.1007/s11164-012-0864-7.

[26] Madadi Mahani, N., A First-principles study on interaction between carbon nanotubes (10,10) and gallates derivatives as vehicles for drug delivery. *Phys. Chem. Res.* **2017**, *5*, 367-375, DOI: 10.22036/pcr.2017.63950.1317.

[27] Freundlich, H., Over the adsorption in solution. *J. Phys. Chem.* **1906**, *57*, e470.

[28] Langmuir, I., The Constitution and Fundamental Properties of Solids and Liquids. Part I. Solids. *J. Am. Chem. Soc.* **1916**, *38*, 2221-2295, DOI: 10.1021/ja02268a002.

[29] Wu, S.; Zhao, X.; Li, Y.; Du, Q.; Sun, J.; Wang, Y.; Wang, X.; Xia, Y.; Wang, Z.; Xia, L., Adsorption properties of doxorubicin hydrochloride onto graphene oxide: equilibrium, kinetic and thermodynamic studies. *Materials.* **2013**, *6*, 2026-2042, DOI: 10.3390/ma6052026.

[30] Guedidi, H.; Reinert, L.; Soneda, Y.; Bellakhal, N.; Duclaux, L., Adsorption of ibuprofen from aqueous solution on chemically surface-modified activated carbon cloths. *Arab. J. Chem.* **2014**, DOI: 10.1016/j.arabjc.2014.03.007.

[31] Xiong, Z. -H.; Wang, L.; Zhou, J. -G.; Liu, J. -M., Thermodynamics and kinetics of adsorption of diclofenac on magnetic multiwalled carbon nanotubes in an aqueous solution. *Acta Phys. -Chim. Sin.* **2010**, *26*, 2890-2898, DOI: 10.3866/PKU.WHXB20101130.

[32] Hamedani, S.; Felegari, Z., Adsorption properties and quantum molecular descriptors of the folic acid drug

adsorbed onto zigzag and armchair single walled carbon nanotubes: DFT simulations. *Chin. J. Struct. Chem*. **2017**, *36*, 503-510, DOI: 10.14102/j.cnki.0254-5861.2011-1331.

[33] Guedidi, H.; Reinert, L.; Lévêque, J. -M.; Soneda, Y.; Bellakhal, N.; Duclaux, L., The effects of the surface oxidation of activated carbon, the solution pH and the temperature on adsorption of ibuprofen. *Carbon*. **2013**, *54*, 432-443, DOI: 10.1016/ j.carbon.2012.11.059.