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Thermodynamic Study of Chrysene Adsorption by Multi-Walled Carbon Nanotubes

MEHDI VADI* and MINA ZAKERI

Department of Chemistry, Firoozabad Branch, Islamic Azad University, Firoozabad, Fars (Iran).
E-mail: mahdi_vadi@iaufasa.ac.ir

ABSTRACT

The present work investigates the equilibrium adsorption of Chrysene on multi-walled carbon nanotubes at 293, 303 and 313°K, and determines the equilibrium adsorption isotherms and thermodynamic parameters (ΔG, ΔH and ΔS). The values of ΔH and ΔG suggested that the adsorption of Chrysene onto MWCNTs was endothermic and nonspontaneous. The experimental data were analyzed using Langmuir, Freundlich and Temkin isotherm equations. The experimental results showed that a well conformity between experimental data and isotherm models.

Key words: Multi-walled carbon nanotubes, Adsorption isotherm, Chrysene, Thermodynamic parameters.

INTRODUCTION

Fullerenes, single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs) are novel and interesting carbon materials. Since their first discovery[1-3], carbon nanotubes (CNTs) have attracted special attention to their potential applications in areas such as purification of air and water as adsorbents due to their large surface area[4,5]. This fascinating new class of materials has shown promising application in many areas. The rapid growth in production and applications of CNTs will inevitably increase their release and exposure into the environment[6,7].

However, there is serious concern over their health and environmental risks once they are released to the environment[8-10]. The primary risk of these materials comes from their toxicity. Because of the nanosize, they can enter into cells[11-13], causing damage to plants, animals, and humans. Previous researchers have explored the toxicity of carbon nanomaterials to animal and human cells[14-20]. It was suggested that the toxicity of carbon nanomaterials is not only from their own harmful nature but also from the toxic substances sorbed by them[8-10]. Therefore, knowledge of toxic compound adsorption by carbon nanomaterials is critical and useful for risk assessment of these nanomaterials. Numerous

studies suggest CNTs as effective adsorbents for organic chemicals after compared with C18 [21, 22] and activated carbon (AC)[23-24]. These organic chemicals include non polar aliphatic (e.g., cyclohexane), polar aliphatic (e.g., trihalomethanes), nonpolar aromatics (e.g., polycyclic aromatic hydrocarbons (PAHs) and benzene), polarandnonionic aromatics (e.g., toluene, chlorobenzenes, and nitrobenzenes), and polar and ionizable aromatics (e.g., aniline derivates, phenolic chemicals and natural organic matter). Peng *et al.,* [25] examined the adsorption of 1,2-dichlorobenzene by carbon nanotubes, suggesting that they can be used as adsorbents for removal of chlorobenzenes from water. The Freundlich model was used in their study to describe the isotherms. Another study showed that MWCNTs had potential applications for trihalomethane removal from drinking water, and both Langmuir and Freundlich models fitted the isotherms well[26]. Cheng *et al,* [27-28] investigated the adsorption-desorption of naphthalene and 1,2-dichlorobenzene by different aggregates of fullerene (C60). They used the linear model to describe the isotherms of large C60 aggregates and thin C60 films, and the Freundlich model was used to describe the isotherms of small C60 aggregates.

PAHs are hydrophobic pollutants of high toxicity (*29*, *30*), their bioavailability depends very much on the nature of sorbents in a given medium[31]

Therefore, in this work, the adsorption isotherms and thermodynamics of CHRY on MWCNTs were studied. The aim of this work was to understand the thermodynamic behavior of CHRY adsorption on MWCNTs and determination of the equilibrium adsorption isotherms.

MATERIALS AND METHODS

Materials

N-hexane and carbon nanotubes were purchased from Merck Co., Germany. Chrysene (CHRY, 99+ %) was purchased from Supelco Chemical Co., USA

Adsorption experiments

Adsorption experiments were performed using 50ml glass bottles with addition of 50mg CNTs and 25ml of CHRY solution of increased initial concentrations (C_i) from 0.2 to 2.5 mg/L. The glass

bottles were sealed with Teflon and then mounted on a HZQ-C shaker and shaken, for 24 h at 293 ±1°K, except for the thermodynamic experiments, in which temperatures of 303 and 313 K were used. After equilibrium the solution, all vials were placed vertically on a flat surface for 5 h at the same temperature to ensure separation between solutions and CNTs. The supernatant solution was analyzed spectrophotometrically using a Genesys 5 doubling beam UV/vis spectrophotometer (32, 33). The amount of CHRY adsorbed by CNTs was calculated as follows:

$$q_e = V \, (C_i - C_e)/m \qquad \qquad ...(1)$$

Where q_e the amount adsorbed (mg g^{-1}), C_i and C_e are the initial and equilibrium concentrations of CHRY (mg L^{-1}), respectively, V is the volume of the solution (L) and m is the CNTs dosage (g).

Adsorption isotherms

The adsorption isotherm described the relationship between the equilibrium concentrations of adsorbate in the solution and the amount of adsorbate on adsorbent. Which indicates how adsorbate molecules are distributed between the liquid phase and solid phase when the adsorption process reaches equilibrium[34, 35]. In this study, three isotherms were used for describing the experimental results, namely the Freundlich isotherm, the Langmuir isotherm and the Temkin isotherm.

Langmuir isotherm

The Langmuir model assumes that the ideal monolayer adsorption takes place at specific homogeneous sites within the adsorbent, i.e. once a molecule occupies a sit and no further adsorption takes place (36).The Langmuir equation may be written as

$$\frac{c_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} c_e \qquad \qquad ...(2)$$

Where q_e is the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg g^{-1}), Ce the equilibrium concentration of the solute in the bulk solution (mg L^{-1}), q_m the maximum adsorption

capacity (mg g^{-1}), and *b* is the constant related to the free energy of adsorption (L mg^{-1})

Freundlich isotherm

The Freundlich isotherm was broadly used to describe adsorption phenomenon in liquid and for adsorption on heterogeneous surface with multi layer adsorption. This isotherm assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increase[37,38]. The Freundlich isotherm is expressed by the following empirical equation:

$$\ln q_e = \ln k_f + \frac{1}{n}\ln c_e \qquad ...(3)$$

where q_e and C_e are the equilibrated concentration of the adsorbate in sorbent and solution, respectively, where K_F is a constant indicative of the relative adsorption capacity of the adsorbent (mg$^{1-(1/n)}$ L$^{1/n}$ g^{-1}), and *n* is adsorption intensity related to the surface heterogeneity.

Temkin model

The Temkin isotherm equation assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the binding energies, up to some maximum binding energy[39,40]. It is expressed by the relation:

$$q_e = B_1 \ln kT + B_1 \ln Ce \qquad ...(4)$$

where constant *B=RT/b* is related to the heat of adsorption, *R* the universal gas constant (J mol^{-1} K^{-1}), *T* the temperature(K), *b* the variation of adsorption energy (J mol^{-1}) and K_T is the equilibrium binding constant (L mg^{-1}) corresponding to the maximum binding energy.

Thermodynamic parameters

Thermodynamic parameters provide additional in-depth information regarding the inherent energetic changes involved during sorption. The values of the thermodynamic parameters, such as enthalpy variation (ΔH) and entropy variation (ΔS), were calculated from the variation of the distribution coefficient (K_D) with the change in temperature.

The equilibrium distribution constant K_D, ΔS and ΔH *are* calculated by

$$K_D = qe/Ce \qquad ...(5)$$

$$\text{Ln } K_D = \Delta S/R - \Delta H/RT \qquad ...(6)$$

Free energy changes *ΔG* for any interaction can be calculated using the relationship

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

Where R is the universal gas constant (8.314, Jmol^{-1} K^{-1}), T is the temperature in Kelvin.

RESULTS AND DISCUSSION

Adsorption isotherms
The adsorption data were analyzed according to the linear form of the isotherms

The linear plots are shown Fig. 1, 2 and 3. The fitting results, i.e. Isotherm parameters and the coefficient of determination, R^2, presented in Table 1. The value of correlation coefficient (313°K) for Freundlich equation ($R^2 = 0.993$) is higher than Langmuir ($R^2 = 0.988$) and Temkin ($R^2 = 0.983$) suggesting that equilibrium data are well described

Table 1: The parameters for Langmuir, Freundlich and Temkin isotherms at three different temperatures

T(°K)	Langmuir			Freundlich			Temkin		
	b(L.mg$^-$)	q$_m$(mg.g$^-$)	R^2	n	K$_F$(L.g$^-$)	R^2	K$_T$(L.mg$^-$)	B	R^2
293	1.955	0.33	0.977	2.4	0.205	0.98	23.258	0.067	0.965
303	2.529	0.37	0.973	2.825	0.248	0.985	37.491	0.070	0.94
313	3.922	0.404	0.988	3.428	0.304	0.993	88.076	0.069	0.983

by Freundlich isotherm.

Thermodynamic parameters

As shown in Eq (6) predicts a linear plot of ln K_D versus $1/T$ for adsorption of CHRY on MWCNTs. The slope of Eq. (6) is $-\Delta H/R$, and the intercept is $\Delta S/R$ (Fig. 4). ΔG (J/mol), ΔH (KJ/mol), and ΔS [J/(mol K)] values are listed in Table 2.

The ΔG values were positive for CHRY at all three temperatures, indicating that the adsorption

of CHRY on MWCNTs was nonspontaneous. The observed positive ΔH suggested an endothermic adsorption, which was supported by the observation that adsorption of CHRY on MWCNTs increased with increasing sorption temperature (Fig. 4). The rise in adsorption capacity was due to the increase in collision frequency between adsorbent and adsorbate molecules[34, 41].

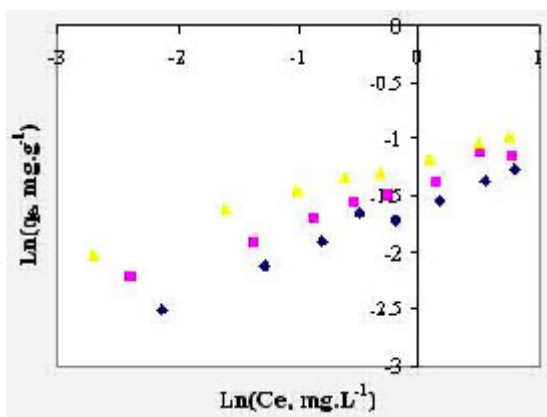The entropy variation is related to variations of the order–disorder in a system. The entropy will

Fig. 1: Freundlich isotherm of CHRY on CNT: of CHRY on CNT: ◆, 293°K (R² =0.98); ■, 303°K (R² =0.985); ▲, 313°K (R² =0.993)
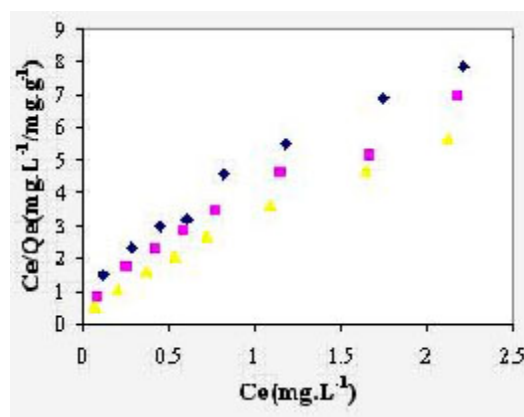

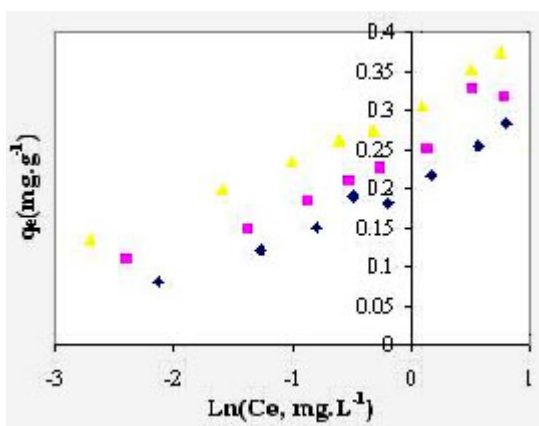**Fig. 2: Langmuir isotherm, ◆, 293°K (R² 0.977); ■, 303°K (R² =0.973); ▲, 313°K (R² =0.988)**

Fig. 3: Temkin isotherm of oleic acid on CNT: ◆,293°K (R² =0.965); ■, 303°K (R² =0.94); ▲,313°K (R² =0.983)
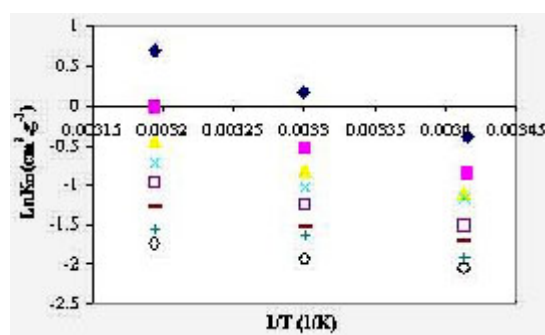

Fig. 4: Linear plot of ln K_D vs. 1/T for the adsorption of CHRY on MWCNTs at different concentrations: (◆,0.2 mg/L); (■,0.4mg/L); (▲,0.6mg/L); (×,0.8mg/L); (□,1mg/L); (▬,1.4mg/L); (+,2mg/L); (○,2.5mg/L)

Table 2: Thermodynamic parameters of CHRY adsorbed on MWCNTs.

C_i (mg-L^{-1})	ΔS(J.mol^{-1}-k^{-1})	ΔH(KJ-mol^{-1})	ΔG(J-mol^{-1})		
			293°K	303°K	313°K
0.2	135.792	40.718	930.594	-427.331	-1785.26
0.4	99.693	31.374	2164.442	1167.51	170.5783
0.6	74.094	24.429	2719.376	1978.433	1237.489
0.8	46.793	16.625	2914.368	2446.439	1978.511
1	57.732	20.613	3697.302	3119.978	2542.654
1.4	41.229	16.420	4340.016	3927.725	3515.434
2	34.224	14.650	4622.541	4280.303	3938.066
2.5	25.214	12.448	5060.058	4807.919	4555.78

be higher when the system tends to be more random. Therefore, the positive value of ΔS revealed the increase in randomness at the solid/solution interface during the adsorption process[35,41]

CONCLUSIONS

In this work, the adsorption of Chrysene onto MWCNT at three various temperatures was examined and determines thermodynamic parameters. The positive free energy changes accompanied by a positive entropy changes indicate that the adsorption reactions are nonspontaneous and adsorpfion is an endothermic reaction. The results indicate that the Freundlich adsorption isotherm fits the data better than the other two models which suggests heterogeneity in the sorption sites.

REFERENCES

1. Kroto, H. W., Heath, J. R., O'Brien, S. C., Curl, R. F., Smalley, R. E.C60: Buckminsterfullerene. *Nature* (London) **318**: 162-163 (1985).
2. Iijima, S. Helical microtubules of graphic carbon. *Nature* (London), **354**: 56-58 (1991).
3. Iijima, S., Ichihashi, T. Single-shell carbon nanotubes of 1-nm diameter. *Nature.* (London) **363**: 603-605 (1993).
4. Mauter, M. S., Elimelech, M. Environmental applications of carbon-based nanomaterials. *Environ. Sci. Technol.* **42**: 5843-5859 (2008).
5. Pan, B., Xing, B. S. Adsorption mechanisms of organic chemicals on carbon nanotubes. *Environ. Sci. Technol.* **42**: 9005-9013 (2008).
6. Nowack, B., Bucheli, T. D. Occurrence, behavior and effects of nanoparticles in the environment. *Environ. Pollut.*, **150**: 5-22 (2007).
7. Mauter, M. S., Elimelech, M. Environmental applications of carbon-based nanomaterials. *Environ. Sci. Technol.*, **42**: 5843–5859 (2008).
8. Colvin, V. L. The potential environmental impact of engineered nanomaterials. *Nat. Biotechnol*, **21**: 1160-1170 (2003).
9. Brumfiel, G. Nanotechnology: A little knowledge. *Nature* (London) **424**: 246-248 (2003).
10. Borm, P. J. A. Particle toxicology: From coal mining to nanotechnology. *Inhalation Toxicol.*, **14**(3): 311-324 (2002).
11. Kam, N. W. S., Jessop, T. C., Wender, P. A., Dai, H. J. Nanotube molecular transporters: Internalization of carbon nanotubeprotein conjugates into mammalian cells. *J. Am. Chem. Soc.*, **126**(22): 6850-6851 (2004).
12. Lu, Q., Moore, J. M., Huang, G., Mount, A. S., Rao, A. M., Larcom, L. L., Ke, P. C. RNA polymer translocation with single-walled carbon nanotubes. *Nano Lett.* **4**(12): 2473-2477 (2004).
13. Foley, S., Crowley, C., Smaihi, M., Bonfils,

C., Erlanger, B. F., Seta, P., Larroque, C. Cellular localisation of a water-soluble fullerene derivative. *Biochem. Biophys. Res. Commun.*, **294**(1): 116-119 (2002).

14. Warheit, D. B., Laurence, B. R., Reed, K. L., Roach, D. H., Reynolds, G. A., Webb, T. R. Comparative pulmonary toxicity assessment of single-wall carbon nanotubes in rats. *Toxicol. Sci.*, **77**: 117-125 (2004).

15. Lam, C. W., James, J. T., McCluskey, R., Hunter, R. L. Pulmonary toxicity of single-wall carbon nanotubes in mice 7 and 90 days after intratracheal instillation. *Toxicol. Sci.*, **77**: 126-134 (2004).

16. Cui, D. X., Tian, F. R., Ozkan, C. S., Wang, M., Gao, H. J. Effect of single wall carbon nanotubesonhumanHEK293cells. *Toxicol. Lett.*, **155**(1): 73-85 (2005).

17. Shvedova, A. A., Castranova, V., Kisin, E. R., Schwegler-Berry, D., Murray, A. R., Gandelsman, V. Z., Maynard, A., Baron, P. Exposure to carbon nanotube material: Assessment of nanotube cytotoxicity using human keratinocyte cells. *J. Toxicol. Environ. Health-part A*, **66**(20): 1909-1926 (2003).

18. Monteiro-Riviere, N. A., Nemanich, R. J., Inman, A. O., Wang, Y. Y. Y., Riviere, J. E. Multiwalled carbon nanotube interactions withhumanepidermal keratinocytes. *Toxicol. Lett.*, **155**(3): 377-384 (2005).

19. Jia, G., Wang, H., Yan, L., Wang, X., Pei, R. Yan, T., Zhao, Y., Guo, X. Cytotoxicity of Carbon Nanomaterials: Single-Wall Nanotube, Multi-Wall Nanotube, and Fullerene. *Environ. Sci. Technol.*, **39**: 1378-1383 (2005).

20. Oberdorster, E. Manufactured nanomaterials (Fullerenes, C-60) induce oxidative stress in the brain of juvenile largemouth bass. *Environ. Health Perspec.,* **112**(10), 1058-1062 (2004).

21. Liu, G. H., Wang, J. L., Zhu, Y. F., Zhang, X. R. Application of multiwalled carbon nanotubes as a solid-phase extraction sorbent for chlorobenzenes. *Anal. Lett* , **37**: 3085–3104 (2004).

22. Pyrzynska, K., Stafiej, A., Biesaga, M. Sorption behavior of acidic herbicides on carbon nanotubes. *Microchim. Acta*, **159**: 293-298 (2007).

23. Su, F. S., Lu, C. S. Adsorption kinetics, thermodynamics and desorption of natural dissolved organic matter by multiwalled carbon nanotubes. *J. Environ. Sci. Health Part A* **42**: 1543-1552 (2007).

24. Wang, S. G., Liu, X. W., Gong, W. X., Nie, W., Gao, B. Y., Yue, Q. Y. Adsorption of fulvic acids from aqueous solutions by carbon nanotubes. *J. Chem. Technol. Biotechnol.*, **82**: 698–704 (2007).

25. Peng, X., Li, Y., Luan, Z., Di, Z., Wang, H., Tian, B., Jia, Z. Adsorption of 1,2-dichlorobenzene from water to carbon nanotubes. *Chem. Phys. Lett.*, **376**: 154-158 (2003.

26. Lu, C., Chung, Y.-L., Chang, K.-F. Adsorption of trihalomethanes from water with carbon nanotubes. *Water Res.*, **39**: 1183-1189 (2005).

27. Cheng, X. K., Kan, A. T., Tomson, M. B. Naphthalene Adsorption and Desorption from AqueousC60 Fullerene. *J. Chem. Eng. Data*, **49**: 675-683 (2004).

28. Cheng, X. K., Kan, A. T., Tomson, M. B. Uptake and sequestration of naphthalene and 1,2-dichlorobenzene by C-60. *J. Nanopart. Res*, **7**: 555-567 (2005).

29. Walters, R. W., Luthy, R. G. Equilibrium adsorption of polycyclic aromatic hydrocarbons from water onto activated carbon. *Environ. Sci. Technol.*, **18**: 395-403 (1984).

30. May, W. E., Wasik, S. P. Determination of the solubility behavior of some polycyclic aromatic hydrocarbons in water. *Anal. Chem*, **50**: 997-1000 (1978).

31. Cornelissen, G., Gustafsson, O., Bucheli, T. D., Jonker, M. O., Koelmans, A. A., Van noort, P. M. Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: mechanisms and consequences for distribution, bioaccumulation, and biodegradation. *Environ. Sci. Technol.*, **39**: 6881-6895 (2005).

32. Peng, X., Y. Li, Z. Luan, Z. Di, H. Wang, B. Tian, and Z. Jia, Adsorption of 1, 2-dichlorobenzene from water to carbon nanotubes, *Chemical physics letters* **376**: 154-158 (2003).

33. Lu, C., Y.L. Chung, and K.F. Chang,

Adsorption of trihalomethanes from water with carbon nanotubes, *Water research* **39**: 1183-1189 (2005).

34.   Sheng, GD, DD Shao, XM Ren, XQ Wang, JX Li, YX Chen, and XK Wang, Kinetics and thermodynamics of adsorption of ionizable aromatic compounds from aqueous solutions by as-prepared and oxidized multiwalled carbon nanotubes, *Journal of hazardous materials* **178**: 505-516 (2010).

35.   Freitas, A.F., M.F. Mendes, and G.L.V. Coelho, Thermodynamic study of fatty acids adsorption on different adsorbents, *J. Chem. Thermodynamics* **39**: 1027-1037 (2007).

36.   I. Langmuir, The constitution and fundamental properties of solids and liquids, *J. Am. Chem. Soc.* **38**: 2221–2295 (1916).

37.   H.M.F. Freundlich, U¨ ber die adsorption in lo¨sungen, *Z. Phys. Chem.* **57**: 385-470 (1906).

38.   J. Zeldowitsch, Adsorption site energy distribution, *Acta Physicochim.* URSS **1**: 961-973 (1934).

39.   M.I. Temkin, Adsorption equilibrium and the kinetics of processes on nonhomogeneous surfaces and in the interaction between adsorbed molecules, *Zh. Fiz. Chim.* **15**: 296–332 (1941).

40.   Y. Kim, C. Kim, I. Choi, S. Rengraj, J. Yi, *Environ. Sci. Technol.* **38**: 924 (2004).

41.   Ahmad, R., R. Kumar, and SH. Haseeb, Adsorption of Cu2+ from aqueous solution onto iron oxide coated eggshell powder: Evaluation of equilibrium, isotherms, kinetics, and regeneration capacity, *Arabian Journal of Chemistry*, 1-7 (2010).