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Adsorption Isotherms and Thermodynamics Studies for the Removal Methyl Orange from Wastewaters Using Multiwalled Carbon Nanotubes†

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In this study, the adsorption of methyl orange on multiwalled carbon nanotubes from aqueous solutions was investigated in a batch stirred cell. The equilibrium adsorption data were analyzed using two common adsorption models: Langmuir and Freundlich. The results showed that Langmuir isotherm fit the experimental results well. Different thermodynamic parameters like enthalpy (ΔH°), Gibb's free energy (ΔG°) and entropy (ΔS°) of the undergoing process were also evaluated through two adsorption models. The thermodynamic parameters (ΔH° , ΔS° and ΔG°) calculated from the temperature dependent adsorption isotherms indicated that the adsorption process of methyl orange on multiwalled carbon nanotubes was endothermic and spontaneous.

Keywords: Adsorption, Carbon nanotube, Methyl orange, Thermodynamics.

INTRODUCTION

Dyes are widely used in industries such as the pulp mill, textile, paper, dye synthesis, printing, food, leather and plastics industries. Increasing environmental pollution caused by toxic dyes owing to their hazardous nature is a matter of great concern. Hence, developing a sustainable competitive method of effluent management for the dyeing industry has long been an important task for the environmental protection. The conventional physicochemical processes for the removal of dyes from wastewater include electrochemical treatment¹, biodegradation^{2,3}, membrane separation, reverse osmosis, coagulation and the adsorption is one of the most effective methods that have been successfully employed for colour removal from wastewater⁴⁻⁶.

Carbon nanotubes (CNTs) have attracted great interest in multidisciplinary areas owing to their unique hollow tube structure and various potential applications⁷. Carbon nanotubes have been proposed for different applications such as sensors, hydrogen storage devices and so on⁸. Because of their easily modified surfaces and large surface areas, extensive experiments have been conducted on the adsorption of organic or inorganic contaminants on CNTs⁹. Therefore, CNTs might be ideal sorbents for the removal of dyes from water.

Methyl orange is a water-soluble azo dye, which is widely used in the textile, pharmaceutical, food industries, printing,

paper manufacturing and also in research laboratories. Azo dyes are well known carcinogenic organic substances. Like many other dyes of its class methyl orange on inadvertently entering the body through ingestion, metabolizes into aromatic amines by intestinal microorganisms¹⁰. Therefore, the safe removal of such a dye is the prime aim of our present research and this is accomplished by using CNTs.

EXPERIMENTAL

Multiwalled carbon nanotubes were prepared according to a method described in a previous study¹¹. Methyl orange ($C_{14}H_{14}N_3O_3Na$, molecular weight 327.33), purchased from Shanghai Reagents Co. (Shanghai, China), was used without further purification. All other chemicals were purchased in analytical purity and used without further purification and all solutions were prepared with Milli-Q water under ambient conditions.

Analysis methods: The adsorbate concentrations in the initial and final aqueous solutions were measured by using UV-visible spectrophotometer at 464 nm. The amount of methyl orange adsorbed on MWCNTs was calculated from the difference between the initial concentration and the equilibrium one. The adsorption percentage [adsorption % = $(C_0 - C_e)/C_0 \times 100\%$] was derived from the difference of the initial concentration (C_0) and the final one (C_e) in supernatant

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after centrifugation. All experimental data were the average of triplicate determinations and the relative errors were 5 %.

RESULTS AND DISCUSSION

The adsorption isotherm shows how the adsorption molecules distribute between the solid phase and the liquid phase when the adsorption process gets to an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important study to find the suitable model that can be used for design purpose¹². The isotherm data are fitted to the Langmuir and Freundlich isotherm models. The Langmuir and Freundlich isotherm models are used to simulate the adsorption isotherms and to establish the relationship between the amount of methyl orange adsorbed on MWCNTs and the concentration of methyl orange remained in solution. The Langmuir model assumes that adsorption occurs in a monolayer with all adsorption sites identical and energetically equivalent¹³. Its form can be described by the following equation:

$$q_e = \frac{bq_{\max}C_e}{1 + bC_e} \quad (1)$$

eqn. 1 can be expressed in linear form:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{bq_{\max}} \quad (2)$$

where C_e is the equilibrium concentration of methyl orange remained in the solution (mg L^{-1}); q_e is the amount of metal ions adsorbed on per weight unit of solid after equilibrium (mg g^{-1}); $q_{\max}$, the maximum adsorption capacity, is the amount of adsorbate at complete monolayer coverage (mg g^{-1}) and b (L mg^{-1}) is a constant that relates to the heat of adsorption. When C_e/q_e was plotted against C_e , straight line with slope $1/q_{\max}$ was obtained (Fig. 1A), indicating that the adsorption of methyl orange on MWCNTs follows the Langmuir isotherm. Langmuir constants b and $q_{\max}$ were calculated from this isotherm and their values are listed in Table-1.

TABLE-1				
PARAMETERS FOR THE LANGMUIR AND FREUNDLICH FITTING OF METHYL ORANGE ADSORPTION ON MWCNTS				
Correlation parameters		T = 293 K	T = 303 K	T = 313 K
Langmuir	q _{max} (mg g ⁻¹)	59.88	63.29	68.03
	b (L mg ⁻¹)	0.38	0.41	0.44
	R ²	0.994	0.992	0.995
Freundlich	k _F (mg ¹⁻ⁿ L ⁿ g ⁻¹)	17.46	18.76	19.87
	n	2.4	2.47	2.5
	R ²	0.925	0.91	0.929

The Freundlich isotherm model allows for several kinds of adsorption sites on the solid surface and represents properly the adsorption data at low and intermediate concentrations on heterogeneous surfaces¹⁴. The equation is represented by the following equation:

$$q_e = k_F C_e^{1/n} \quad (3)$$

eqn. 3 can be expressed in linear form:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad (4)$$

Fig. 1. Langmuir (A) and Freundlich (B) isotherms for methyl orange dye adsorption onto MWCNTs at different temperatures

where k_F ($\text{mg}^{1-n} \text{g}^{-1} \text{L}^n$) represents the adsorption capacity when metal ion equilibrium concentration equals to 1 and n represents the degree of dependence of adsorption with equilibrium concentration. The plot of $\ln q_e$ versus $\ln C_e$ (Fig. 1B) gives straight lines with slope $1/n$. Fig. 1B indicates that the adsorption of methyl orange on MWCNTs also follows the Freundlich isotherm. Hence, Freundlich constants (K_F and n) are calculated and listed in Table-1.

The thermodynamic parameters (ΔH° , ΔS° and ΔG°) for adsorption of methyl orange on MWCNTs can be determined from the temperature dependence. Free energy change (ΔG°) is calculated from the relationship:

$$\Delta G^\circ = -RT \ln K \quad (5)$$

where K is the adsorption equilibrium constant. Values of $\ln K$ obtained by plotting $\ln K_d$ versus q_e for adsorption of methyl orange on MWCNTs and extrapolating q_e to zero are 10.74 ($T = 293 \text{ K}$), 10.83 ($T = 303 \text{ K}$) and 10.92 ($T = 313 \text{ K}$), respectively. Standard entropy change (ΔS°) is calculated using the equation:

$$\left(\frac{\partial \Delta G^\circ}{\partial T} \right)_p = -\Delta S^\circ \quad (6)$$

The average standard enthalpy change (ΔH°) is then calculated from the expression:

$$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ \quad (7)$$

The values obtained from eqns. 5-7 are tabulated in Table-2. The values of Gibbs free energy change (ΔG°) are negative

TABLE-2
VALUES OF THERMODYNAMIC PARAMETERS FOR
THE ADSORPTION OF METHYL ORANGE
ADSORPTION ON MWCNTS

T (K)	ΔG° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	ΔH° (kJ mol ⁻¹)
293	-26.17	109.50	5.91
303	-27.28	109.50	5.89
313	-28.36	109.50	5.92

and the standard entropy changes (ΔS°) are positive, which shows that the adsorption reaction is spontaneous. The value of ΔG° becomes more negative with increasing temperature, implying more efficient adsorption at higher temperatures. The positive value of entropy change (ΔS°) indicates some structural changes in sorbate and sorbent during the adsorption process.

From Table-1, the adsorption could be better described by the Langmuir model better than by the Freundlich model. As also seen in Table-2, thermodynamic analyses indicated that the adsorption of methyl orange direct dyes onto MWCNTs is endothermic and spontaneous. Similar sorption behaviours of methyl orange on various kinds of adsorbents were reported by Mohammadi *et al.*¹⁵, Asuha *et al.*¹⁶ and Chen *et al.*⁵.

Conclusion

The adsorption of methyl orange onto MWCNTs is favoured at higher temperature. The equilibrium data were analyzed using the Langmuir and Freundlich isotherm models. The maximum monolayer adsorption capacities were found to be 59.88, 63.29 and 68.03 mg/g at 293, 303 and 313 K, respectively. Equilibrium data fitted very well with Langmuir isotherm equation. The results of methyl orange adsorption on MWCNTs indicate that methyl orange adsorption on MWCNTs is spontaneous and endothermic process.

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REFERENCES

1. Z.M. Shen, D. Wu, J. Yang, T. Yuan, W.H. Wang and J. Jia, *J. Hazard. Mater.*, **131**, 90 (2006).
2. J.-S. Chang, C. Chou, Y.-C. Lin, P.-J. Lin, J.-Y. Ho and T.L. Hu, *Water Res.*, **35**, 2841 (2001).
3. N.C.G. Tan, F.X. Prenafeta-Boldu, J.L. Opsteeg, G. Lettinga and J.A. Field, *Appl. Microbiol. Biotechnol.*, **51**, 865 (1999).
4. N. Mohammadi, H. Khani, V.K. Gupta, E. Amereh and S. Agarwal, *J. Colloid Interf. Sci.*, **362**, 457 (2011).
5. S.H. Chen, J. Zhang, C.L. Zhang, Q.Y. Yue, Y. Li and C. Li, *Desalination*, **252**, 149 (2010).
6. T.A. Saleh and V.K. Gupta, *J. Colloid Interf. Sci.*, **371**, 101 (2012).
7. N. de Jonge, Y. Lamy, K. Schoots and T.H. Oosterkamp, *Nature*, **420**, 393 (2002).
8. M.S. Mauter and M. Elimelech, *Environ. Sci. Technol.*, **42**, 5843 (2008).
9. G.P. Rao, C. Lu and F. Su, *Sep. Purif. Technol.*, **58**, 224 (2007).
10. A. Mittal, A. Malviya, D. Kaur, J. Mittal and L. Kurup, *J. Hazard. Mater.*, **148**, 229 (2007).
11. G.D. Sheng, D.D. Shao, X.M. Ren, X.Q. Wang, J.X. Li, Y.X. Chen and X.K. Wang, *J. Hazard. Mater.*, **178**, 505 (2010).
12. B.H. Hameed and A.A. Ahmad, *J. Hazard. Mater.*, **164**, 870 (2009).
13. I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).
14. H.M.F. Freundlich, *J. Phys. Chem.*, **57**, 385 (1906).
15. N. Mohammadi, H. Khani, V.K. Gupta, E. Amereh and S. Agarwal, *J. Colloid Interf. Sci.*, **362**, 457 (2011).
16. S. Asuha, X.G. Zhou and S. Zhao, *J. Hazard. Mater.*, **181**, 204 (2010).