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Experimental study of methylene blue adsorption from aqueous solutions onto carbon nano tubes

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In this work, batch adsorption experiments were carried out for the removal of methylene blue as a basic dye from aqueous solutions using carbon nanotubes (CNTs). The effects of major variables governing the efficiency of the process such as, temperature, initial dye concentration, CNTs dosage, and pH were investigated. Experimental results have shown that, the amount of dye adsorption increased with increasing the initial concentration of the dye, CNTs dosage, and temperature. The dye removal using 400 mg L-1 of CNTs was more than 90%. This dosage (400 mg L-1) was considered as the optimum dosage of CNTs to remove methylene blue. The adsorption kinetic data were analysed using pseudo-first-order, pseudo-second-order and Elovich models. It was found that the pseudo-second-order kinetic model was the most appropriate model, describing the adsorption kinetics. Adsorption isotherm of methylene blue onto the CNTs was determined at 290, 300 and 310 K with 10 mg L-1 as initial concentration of methylene blue. Adsorption equilibrium was attained within 120 min. Equilibrium data were fitted to the Langmuir, Freundlich, Temkin and Sips isotherm models and isotherm constants were determined. The equilibrium data were best represented by the Sips isotherm model. Thermodynamic parameters such as changes in the free energy of adsorption ($\Delta G\circ$), enthalpy ($\Delta H\circ$) and entropy ($\Delta S\circ$) were calculated. The negative values of $\Delta G\circ$ indicate that the methylene blue adsorption process is spontaneous in nature and the positive value of $\Delta H\circ$ shows the endothermic nature of the process.

Key words: Carbon nanotubes, methylene blue, basic dye, adsorption, equilibrium, kinetic, thermodynamics.

INTRODUCTION

Synthetic dyes are one of the main pollutant groups of water and wastewater. Dye contamination in wastewater causes problems in several ways: the presence of dyes in water, even in very low quantities, is highly visible and undesirable; color interferes with penetration of sunlight into waters; retards photosynthesis; inhibits the growth of aquatic biota and interferes with gas solubility in water bodies (Garg et al., 2004; Robinson et al., 2002; Wang et al., 2005a; Hamdaoui, 2006; O¨zer and Dursun, 2007). These materials are the complicated organic compounds and they resist against light, washing and microbial invasions. Thus, they cannot be decomposed easily

(Wang et al., 2008b; Baldez et al., 2008). Direct discharge of dyes containing effluents into municipal environment may cause the formation of toxic carcinogenic breakdown products. The highest rates of toxicity were found amongst basic and diazo direct dyes (Lata et al., 2007; Wang et al., 2008a). Therefore, it is highly necessary to reduce dye concentration in the wastewater. The conventional methods for treating dye-containing wastewaters are electrochemical treatment (Fan et al., 2008; G¨urses et al., 2002), coagulation and flocculation (Tak-Hyun et al., 2004), chemical oxidation (Oguz and Keskinler, 2007), liquid–liquid extraction (Muthuraman et al., 2008) and adsorption (Wang et al. 2005a; Wang et al., 2005b; Mohan et al., 2002; G¨urses et al., 2006). Adsorption has been shown to be an effective way for removing organic matter from aqueous solutions in terms of initial cost, simplicity of design, ease

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of operation and insensitivity to toxic substances (Lata et al., 2007; Wang et al., 2005b). A considerable amount of work has also been reported in the literature regarding the adsorption of MB on various adsorbent surfaces such as, activated carbon (Shaobin et al., 2005; El Qada et al., 2008), rice husk (Vadivelan and Vasanth Kumar, 2005), peanut hull (Renmin et al., 2005), glass fibers (Sampa and Binay, 2005), Indian rosewood sawdust (Garg et al., 2004), neem leaf powder (Bhattacharyya and Sharma 2005), perlite (Doğan et al., 2004), fly ash (Wang et al., 2005b), yellow passion fruit peel (Pavan et al., 2008), chitosan-g-poly (acrylic acid) /montmorillonite super adsorbent nanocomposite (Wang et al., 2008b), sand (Bukallah et al., 2007), silica nano-sheets derived from vermiculite (Zhao et al., 2008), natural phosphate (Barka et al., 2009), cyclodextrin polymer (Crini, 2008) etc. The adsorbents with amorphous nanoporous surfaces and high surface area, such as carbon nanotubes, can be used in industry to decrease the dosage of adsorbent, particularly where selective adsorption of one fluid component from a mixture is important. (Zhao and Liu, 2008) Carbon nanotubes (CNTs) were first reported by Iijima in 1991. CNTs include single-wall (SWCNTs) and multi-wall (MWCNTs) depending on the number of layer comprising them. CNTs can be thought of as cylindrical hollow micro-crystals of graphite. They have exceptional mechanical properties, unique electrical property, highly chemical stability and large specific surface area (Iijima, 2002; Iijima, 1991), So CNTs have attracted researchers' interest as a type of adsorbent and offer an attractive option for the removal of organic and inorganic contaminates from water (Wu, 2007).

In the present work, commercial CNTs, supplied by the Iranian Research Institute of Petroleum Industry (R.I.P.I), Iran, were selected as an adsorbent to remove methylene blue from aqueous solution. Methylene blue (MB) is the most commonly used substance for dyeing cotton, wood and silk. Although, MB is not strongly hazardous, but it can cause several harmful effects where acute exposure to MB will cause increased heart rate, nausea, vomiting, shock, cyanosis, jaundice, and quadriplegia and tissue necrosis in humans (Kumar and Kumaran, 2005; Öner et al., 2007). The main objective of this research was to evaluate the adsorption aptitude of carbon nanotubes for the removal of methylene blue as a model compound for basic dyes. The effects of pH, contact time, initial dye concentration and CNTs dosage on adsorption capacity were investigated. Moreover, kinetic and equilibrium models were used to fit experimental data and the adsorption thermodynamic parameters were determined.

MATERIALS AND METHODS

Adsorbent

Multi-walled carbon nanotubes, which were purchased from Research Institute of Petroleum Industry, Iran with outer diameter (dp) < 10 nm (the average dp was 8 nm), surface area of 280 m2/g

and purity above 95%, were selected as an adsorbent to study the adsorption characteristics of dye from solution. The length of CNTs was in the range of 5 - 15 μm.

Adsorbate

A cationic dye, methylene blue, having molecular formula C16H18N3SCl was chosen as adsorbate. Methylene blue (Basic Blue 9) was purchased from Merck with Water solubility as 50 g L–1 (20°C) and molecular weight as 319.85 g. The MB was chosen in this study because of its known strong adsorption onto solids. The dye stock solution was prepared by dissolving accurately weighted methylene blue in distilled water to the concentration of 100 mg L-1. The experimental solutions were obtained by diluting the dye stock solution in accurate proportions to required initial concentrations.

Adsorption equilibrium experiments

For equilibrium studies, the batch technique was used because of its simplicity. Solutions of 10 mg L-1 methylene blue, as the initial concentration, were treated with 20, 40, 60, 80, 100, 120, 200 and 400 mg L-1 of MWCNTs respectively. The mixtures were agitated on shaker incubator (Amperetabelle Multitrun II) continuously for 120 min, as the equilibrium time, at 290, 300 and 310 K. After 120 min, the suspension was filtered using a 0.2 μm Millipore filter (Schleicher and Schuell, Ref. No.104 62 200) and the filtrates were analysed for residual Methylene blue concentration by UV-visible spectrophotometer (Varian, cary50) at 660 nm. The amount of methylene blue uptake by CNTs in each flask was calculated using the mass balance equation:

$$q = \frac{(C_0 - C_e)V}{W}$$

(1)

The dye percent removal (%) was calculated using the following equation:

$$\text{Removal}(\%) = \frac{C_0 - C_e}{C_0} \times 100$$

(2)

Where; q is the amount of methylene blue adsorbed by CNTs (mg g-1), C0 and Ce are the initial and final dye concentrations (mg L–1), respectively, V is the volume of solution (L), and W is the adsorbent weight (g).

Adsorption kinetic experiments

For kinetic studies, solutions of 5, 10, 20, 30 and 40 mg L-1 methylene blue, as the initial concentration each, were treated with 80 mg L-1 of MWCNTs at a constant temperature of 300 K. The mixtures were then subjected to agitation using shaker incubator at 180 rpm. In all cases, the working pH was that of solution and was not controlled. Mixtures were taken from the shaker at appropriate time intervals (1, 5, 10, 15, 30, 45, 60, 90 min) and the left out concentration in the methylene blue solution was estimated as have been explained before.

Effect of pH experiments

To study the effect of pH on MB adsorption, 80 mg L-1 of CNTs was added to solutions containing 10 mg L-1 of methylene blue ions. The initial pH values were adjusted from 2 – 12 using HCl and

Table 1. The values of parameters and correlation coefficients of kinetic models.

	T = 300 K				
	C = 5 mg L^{-1}	C = 10 mg L^{-1}	C = 20 mg L^{-1}	C = 30 mg L^{-1}	C = 40 mg L^{-1}
Pseudo-first order model					
K_1	0.036	0.028	0.0315	0.055	0.04
Q_e	23.45	51.42	78.88	97.51	105.95
R^2	0.989	0.945	0.92	0.975	0.98
Pseudo-second order model					
K1	0.0037	0.0014	0.001	0.0007	0.0009
Qe	60.24	93.458	136.99	166.67	178.57
R^2	0.999	0.998	0.999	0.999	0.999
Elovich model					
α	61.75	46.85	51.377	55.09	109.7
β	0.106	0.064	0.039	0.033	0.035
R^2	0.978	0.992	0.986	0.993	0.989

NaOH. After the suspensions were shaken for 120 min, equilibrium time, at the temperature of 300 K, they were filtered through 0.2 µm membrane filters and analysed for residual methylene blue concentration.

ADSORPTION ISOTHERMS AND KINETIC MODELS

Kinetic models

The adsorption kinetics shows the evolution of the adsorption capacity through time and it is necessary to identify the types of adsorption mechanism in a given system. The following models are used to describe the adsorption kinetics behavior:

Pseudo-first order model (Hamdaoui and Chiha, 2007)

The adsorption kinetics can be described by a pseudo-first order equation as suggested by Lagergren.

$$\frac{dq}{dt} = k_1(q_e - q_t)$$

(3)

Where; k_1 (min^{-1}) is the rate constant of the pseudo-first order model, q_t (mg g^{-1}) denotes the amount of adsorption at time t (min), and q_e (mg g^{-1}) is the amount of adsorption at equilibrium. After definite integration by application of the conditions t = 0 to t = t and q = 0 to q = q_e, Equation (3) becomes

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

(4)

The adsorption rate constant, k_1, can be experimentally determined by the slope of linear plots $\ln(q_e - q_t)$ vs. t.
Pseudo-second order model (Hamdaoui and Chiha 2007).The pseudo-second order equation developed by Ho can be written as

$$\frac{dq}{dt} = k_2(q_e - q_t)^2$$

(5

Where; k_2 (g mg^{-1} min^{-1}) is the rate constant of the pseudo-second order. Integrating Equation (5) for the boundary conditions t = 0 to t = t and q = 0 to q = q_e gives

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t$$

(6)

Which has a linear form of

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

(7)

k_2 and q_e can be obtained from the intercept and slope of plotting $\frac{t}{q_t}$ vs. t. (Table 1).

Elovich model (G¨unay et al., 2007)

In reactions involving chemisorption of adsorbate on a solid surface without desorption of products, adsorption rate decreases with time due to an increased surface coverage. One of the most useful models for describing such 'activated' chemisorption is the Elovich equation (G¨unay et al., 2007). The Elovich equation can be written as (Hamdaoui and Chiha 2007):

$$q = \frac{1}{\alpha} \ln(\alpha\beta) + \frac{1}{\alpha} \ln t$$

(8)

Where; α is the initial adsorption rate, and β is the desorption constant during each experiment.

Adsorption isotherms

Adsorption isotherms are important for the description of how adsorbates will interact with an adsorbent and are critical in optimizing the use of adsorbent (Wang et al., 2005a). Thus, the correlation of equilibrium data using either a theoretical or empirical equation is essential for adsorption data interpretation and prediction. Several mathematical models can be used to describe experimental data of adsorption isotherms. Four famous isotherm equations, the Langmuir, Freundlich, Temkin and Sips, were employed for further interpretation of the obtained adsorption data.

Langmuir isotherm

The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent and has found successful application to many sorption processes of monolayer adsorption (Wang et al., 2005a). The Langmuir isotherm can be written in the form (Hameed et al., 2009):

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

(9)

Where; q_m and K_L are Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. For the Langmuir equation the favorable nature of adsorption can be expressed in terms of dimensionless separation factor of equilibrium parameter, which is defined by:

$$R_L = \frac{1}{1 + K_L C_0}$$

(10)

Where; K_L is the Langmuir constant and C_0 is the initial concentration of the adsorbate in solution. The values of R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$) (Hamdaoui 2006). R_L values for methylene blue adsorption onto carbon nanotubes at different temperature were less than 1 and greater than zero indicating favorable adsorption.

Freundlich isotherm

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems (Wang et al., 2005a) .

The Freundlich equation is

$$q_e = K_F C_e^{\frac{1}{n}}$$

(11)

K_F is a constant indicative of the adsorption capacity of the adsorbent (mg1−(1/n) L1/n g−1) and n is an empirical constant related to the magnitude of the adsorption driving force. The magnitude of 1/n quantifies the favorability of adsorption and the degree of heterogeneity of the CNTs surface. According to Halsey (Halsey 1952):

$$K_F = \frac{q_m}{C_0^{\frac{1}{n}}}$$

(12)

To determine the maximum adsorption capacity (q_m), it is necessary to operate with constant initial concentration C0 and variable weights of adsorbent.

Temkin isotherm

Temkin and Pyzhev considered the effects of some indirect sorbate/adsorbate interactions on adsorption isotherms and suggested that because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly with coverage (Temkin and Pzhev, 1940).

The Temkin isotherm has been used in the following form

$$q_e = \frac{RT}{b} \ln(K_T C_e)$$

(13)

Where; K_T is the equilibrium binding constant (L g-1), b is related to heat of adsorption (J/mol), R is the universal gas constant (8.314 J/mol K) and T is the absolute temperature (K).

Equation 13 can be written as the following form:

$$q_e = B_1 \ln(K_T C_e)$$

(14)

Sips isotherm

Sips isotherm is a combination of the Langmuir and Freundlich isotherm type models and expected to describe heterogeneous surfaces much better. At low adsorbate concentrations it reduces to a Freundlich isotherm, while at high adsorbate concentrations it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm (G¨unay et al. 2007). The model can be written as (G¨unay et al., 2007):

$$q_e = \frac{q_m a_s C_e^{\frac{1}{n}}}{1 + a_s C_e^{\frac{1}{n}}}$$

(15)

Where; q_m is monolayer adsorption capacity (mg g-1) and a_s is Sips constant related to energy of adsorption and parameter n could be regarded as the parameter characterizing the system heterogeneity.

RESULTS AND DISCUSSION

Adsorption rate

Effect of contact time and initial Methylene Blue concentration :The effect of initial dye concentration and contact time on the adsorption rate of MB onto CNTs is shown in Figure 1. As shown, when the initial MB concentration is increased from 5 to 40 mg L-1 the amount
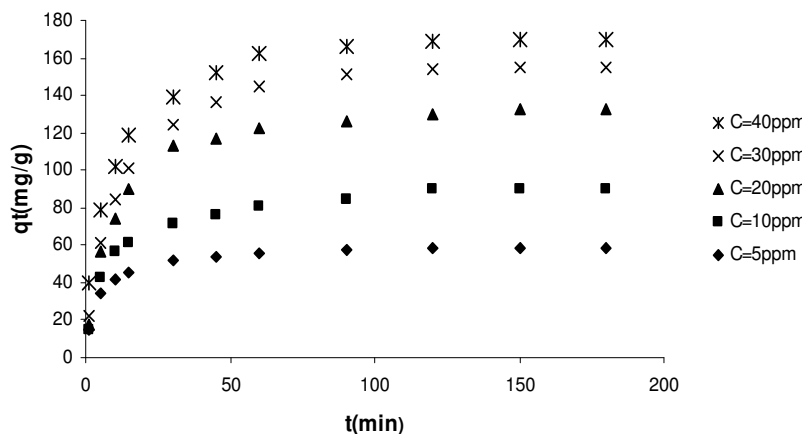
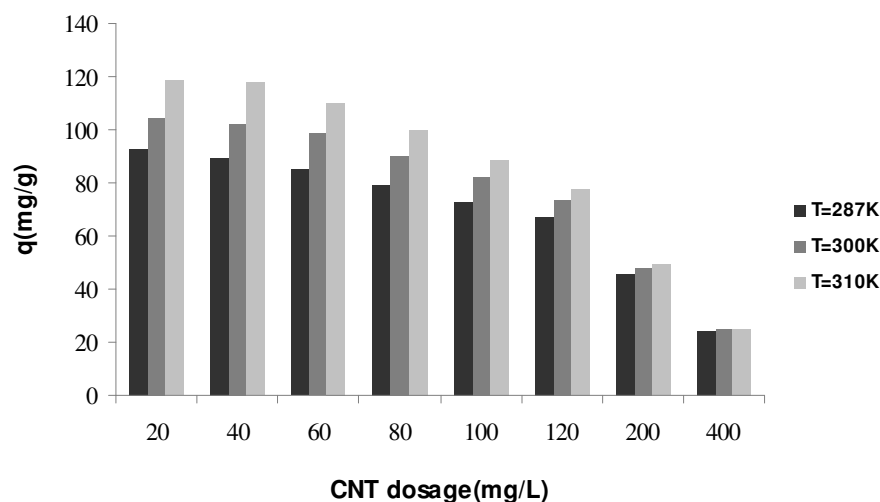**Figure 1.** Effect of contact time on the adsorption of MB by CNTs.

Figure 2. Effect of temperature on the amount of MB adsorption onto CNTs.

of MB adsorbed per unit weight of the CNTs (mg g-1), at equilibrium conditions and the constant temperature as 300 K, increased from 59 (94 %) to 170 (34 %). Therefore, the adsorption percentage decreases and the extent of adsorption increase with increasing initial dye concentration. This is obvious from the fact that the initial MB concentration provides an important driving force to overcome all of mass transfer resistance. Furthermore, the increase of loading capacity of CNTs with increasing initial MB concentration may be due to higher interaction between MB and adsorbent. For constant dosage of adsorbent, at higher initial concentrations, the available adsorption sites of adsorbent became fewer and hence the removal of MB depends upon the initial concentration. The removal of dye by adsorption onto CNTs was found to be rapid at the initial period of contact time, and then to become slow with the increase of contact time. Fast diffusion onto the external surface was followed by fast

pore diffusion into the intraparticle matrix to attain rapid equilibrium.

Effect of temperature

To study the effect of temperature on the adsorption of dye adsorption by CNTs, the experiments were performed at temperatures of 290, 300, and 310 K. Figure 2, shows the influence of temperature on the adsorption of dye onto CNTs. As it was observed, the equilibrium adsorption capacity of MB onto CNTs was found to increase with increasing temperature, especially in higher equilibrium concentration, or lower adsorbent dose because of high driving force of adsorption. This fact indicates that the mobility of dye molecules increased with the temperature. The adsorbent shows the endothermic nature of adsorption.
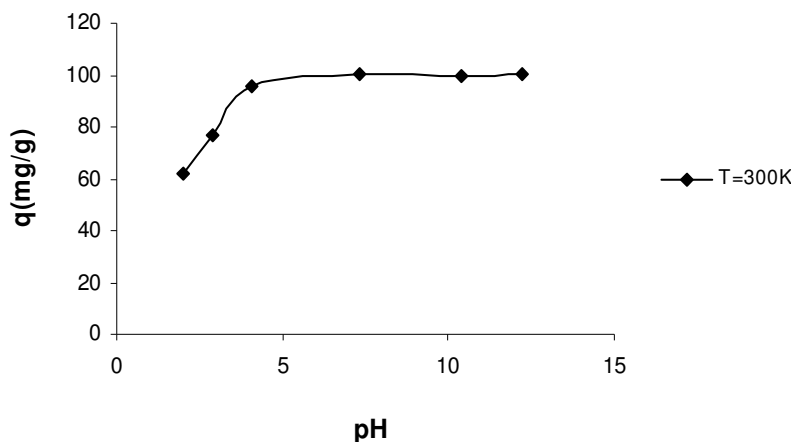
Figure 3. Effect of initial solution pH on the adsorption amount of MB onto CNTs.

Effect of pH

The pH of the dye solution plays an important role in the whole adsorption process, particularly on the adsorption capacity (Jain and Shrivastava, 2008). As shown in Figure 3, a consistent increase in adsorption capacity of the CNTs was noticed as the pH increased from 2 - 4, whereas in the range 4 - 12, the adsorption amount was only slightly affected by pH. As pH of the system decreased, the number of negatively charged adsorbent sites decreased and the number of positively charged surface sites increased, which did not favor the adsorption of positively charged dye cations due to electrostatic repulsion. In addition, lower adsorption of methylene blue at acidic pH might be due to the presence of excess H+ ions competing with dye cations for the available adsorption sites (Vadivelan and Kumar, 2005; Bestani et al., 2008). Some authors have reported that methylene blue adsorption usually increases as the pH is increased (Gupta et al., 2004; Singh et al., 2003).

Effect of adsorbent dose

In order to study the effect of adsorbent mass on the adsorption of methylene blue, a series of adsorption experiments was carried out with different adsorbent dosages at initial dye concentration of 10 mg L^{-1}. Figure 4 shows the effect of adsorbent dose on the removal of methylene blue. Along with the increase of adsorbent dosage from 20 - 600 mg L-1, the percentage of dye adsorbed increased from 20.8 - 98.91%. Above 400 mg L-1 of adsorbent dose, the adsorption equilibria of dyes were reached and the removal ratios of dyes kept almost invariable.

Adsorption kinetics

Three kinetic models; pseudo-first order, pseudo-second order and Elovich models were used to fit experimental data to examine the adsorption kinetics. The straight-line plots of ln (qe-qt) versus t for the pseudo-first order reaction (Figure 5), t/qt versus t for the pseudo-second order reaction (Figure 6) and qt versus ln t for the Elovich equation (Figure 7) for adsorption of MB onto CNTs have also been tested to obtain the rate parameters. The kinetic parameters of MB under different conditions were calculated from these plots and are given in Table 1. It is seen that the pseudo-second order model well represented the experimental data (R^2 >0.99). Similar results have been observed in the adsorption of methylene blue onto dehydrated wheat bran carbon (Ö̈zer and Dursun 2007), montmorillonite super adsorbent nanocomposite (Wang et al., 2008b), and agricultural by-products (Wang et al., 2008a).

Adsorption mechanism

In order to gain insight into the mechanisms and rate controlling steps affecting the kinetics of adsorption, the kinetic experimental results were fitted to the Weber's intraparticle diffusion (Weber and Morris 1963). The initial rate of the intraparticle diffusion is expressed as,

$$q_t = K_p t^{1/2}$$

(16)

Where; K_p is the intraparticle diffusion rate constant (mg g-1 min-1/2), which can be evaluated from the slope of the linear plot of q_t versus $t^{1/2}$ (Weber and Morris, 1963) as shown in Figure 8. If the regression of q_t versus $t^{1/2}$ is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step (Poots et al., 1976).

   As seen in previous studies such plots may present a multilinearity, which indicates that two or more steps occur. The first, sharper portion is the external surface
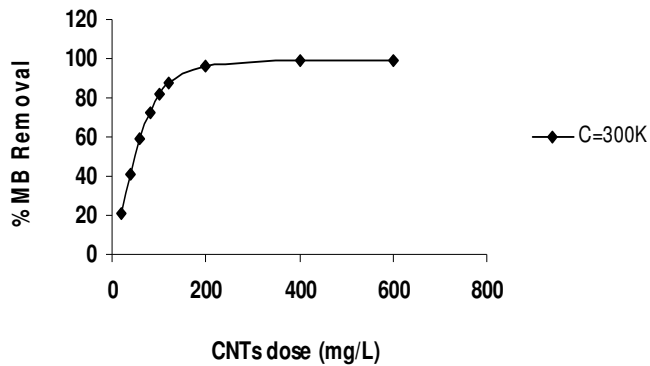
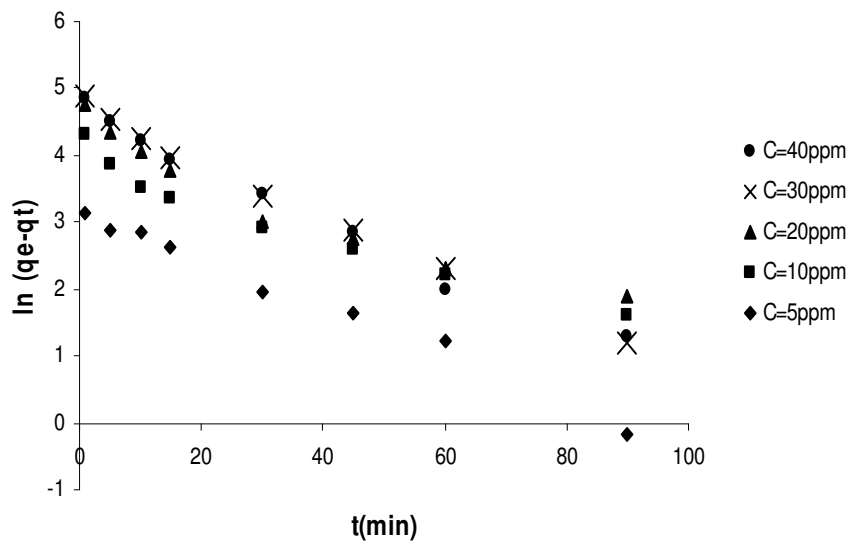**Figure 4.** Effect of adsorbent dose on the adsorption percentage of MB onto CNTs.

Figure 5. Modeling MB adsorption kinetics by CNTs (pseudo-first order model).
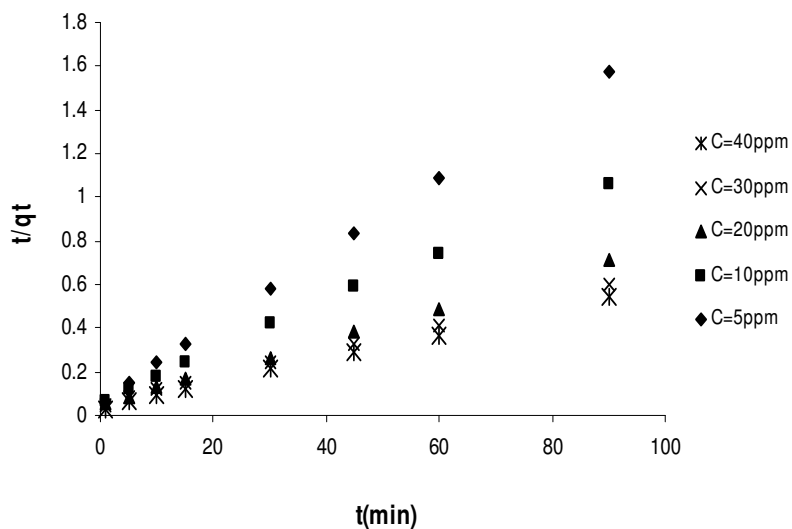

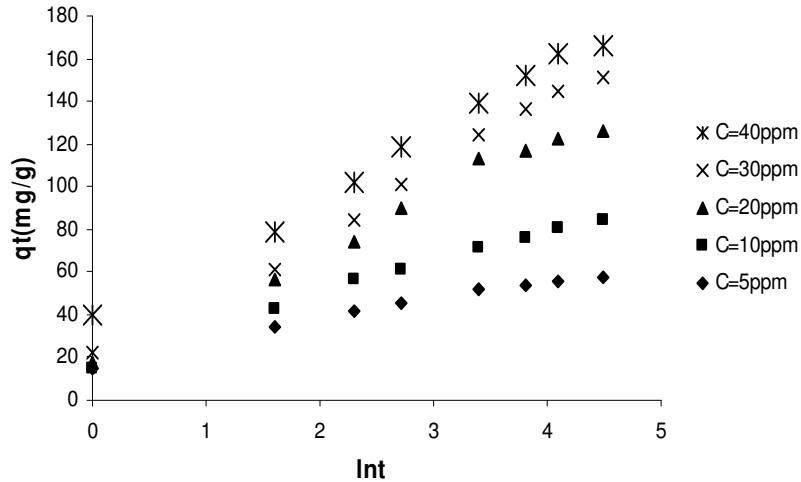**Figure 6.** Modeling MB adsorption kinetics by CNTs (pseudo-second order model).

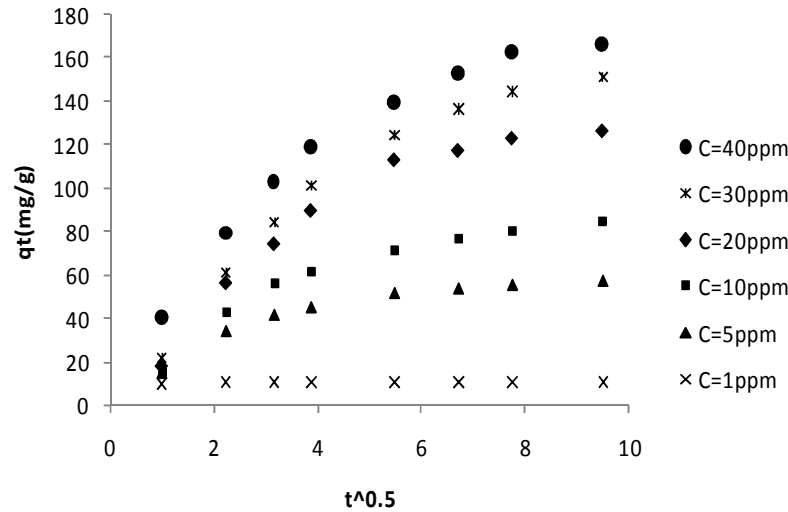**Figure 7.** Modeling MB adsorption kinetics by CNTs (Elovich model).

Figure 8. Mechanism of MB adsorption onto CNTs (intraparticle diffusion model).

adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage, where the intraparticle diffusion is rate controlled. The third portion is the final equilibrium stage where the intraparticle diffusion starts to slow down due to extremely low solute concentrations in the solution (Wu et al., 2001; Wang et al., 2008a; Hameed, 2009).

Adsorption isotherms

Figures 9 - 12 display the adsorption isotherms and experimental data at various temperatures. Table 2 summarized the coefficients of the isotherms at different temperatures. The validity of the models was determined by calculating the average relative error (ARE) using:

$$ARE = \frac{100}{p} \sum_{i=1}^{p} \left[\frac{\left| q_{cal} - q_{exp} \right|}{q_{exp}} \right]$$

(17)

Where the subscripts exp and cal refer to the experimental and the calculated data, and p is the number of data points. It can be seen from this table that most of R^2 values exceed 0.9 and the ARE values are smaller than 13% for all isotherm models, suggesting that all models closely fitted the experimental results. However, the regression results show that the Sips isotherm fitted experimental data better than the others. An adsorption isotherm is characterized by certain coefficients the values of which express the surface properties and affinity
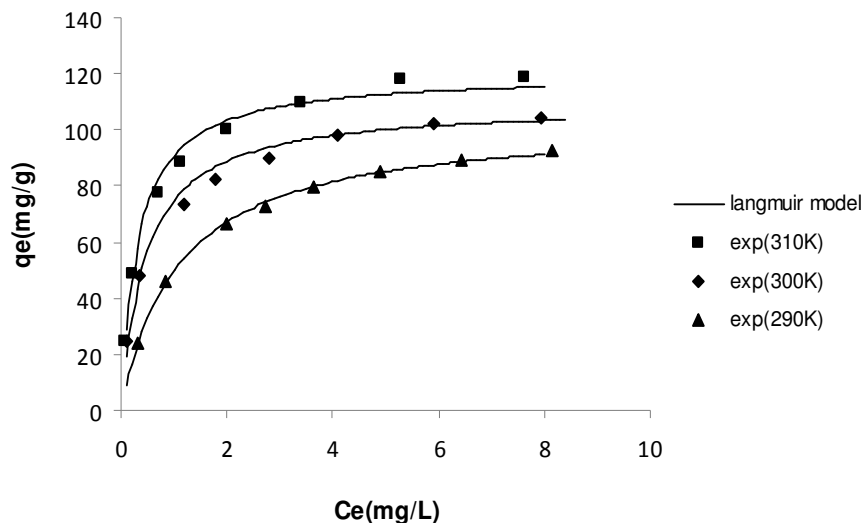
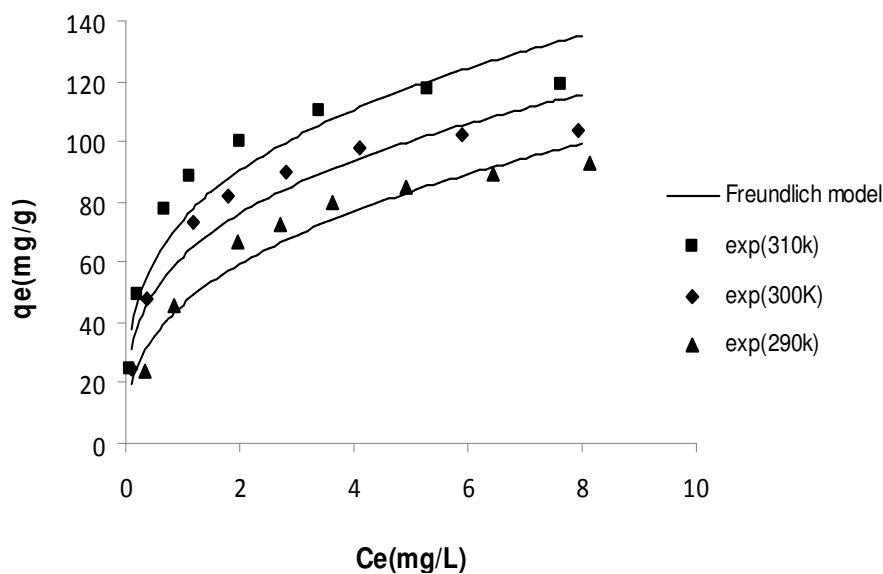**Figure 9.** Langmuir isotherm for MB adsorption onto CNTs.

Figure 10. Freundlich isotherm for MB adsorption onto CNTs.

of the adsorbent and can also be used to find the maximum adsorption capacity. Based on the coefficients of the Langmuir isotherm model, R_L values, for methylene blue adsorption onto carbon nanotubes at different temperatures, were less than 1 and greater than zero indicating favorable adsorption. The values of k_L were 0.93, 2.16 and 3.12 L mg-1 at 290, 300 and 310 K, respectively. It is observed that k_L increased with temperature, revealing that the adsorption of methylene blue on CNTs increased with temperature. The results obtained with the Freundlich isotherm show that the values of kF and 1/n increased and decreased with the

increasing of temperatures, respectively. The 1/n values were between 0 and 1 indicating that the adsorption of MB onto CNTs was favorable at studied conditions. Based on the coefficients of the Sips isotherm model, the parameter n is greater than unity, suggesting some degree of heterogeneity of this MB/ CNTs system.

Adsorption thermodynamics

The thermodynamic parameters, namely free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) have an important role to determine spontaneity and heat change
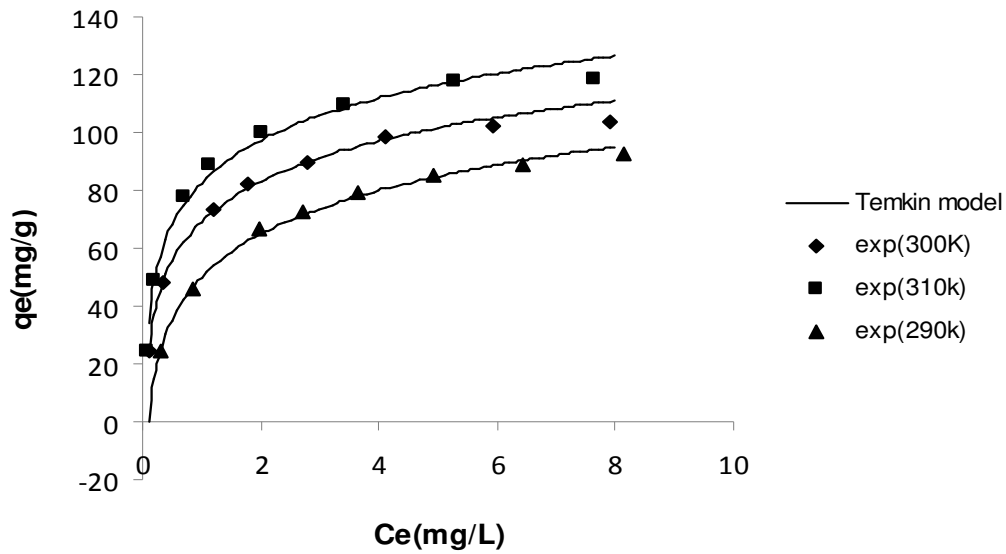
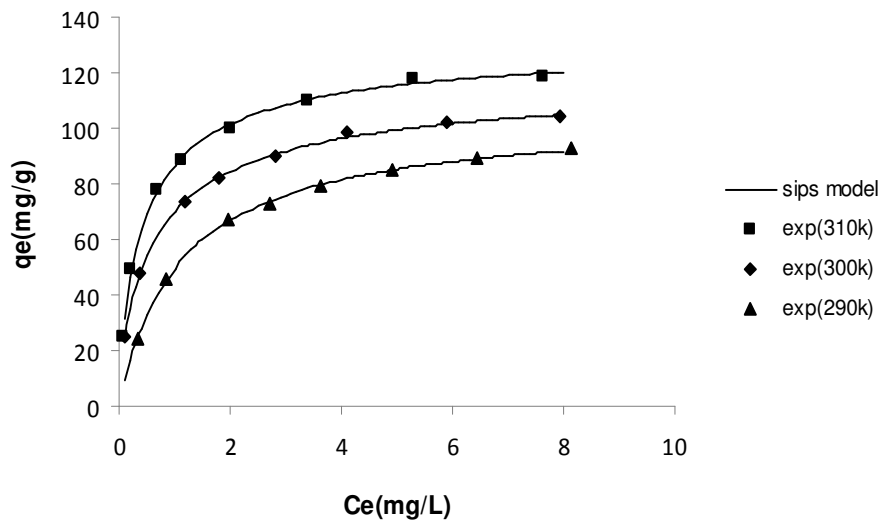**Figure 11.** Temkin isotherm for MB adsorption onto CNTs.

Figure 12. Sips isotherm for MB adsorption onto CNTs.

for the adsorption process. Assuming that the activity coefficients are unity at low concentrations (the Henry's law sense), thermodynamic parameters were calculated using the following relations (Karago¨z et al., 2008; Pehlivan and Arslan, 2007):

$$K_D = \frac{q_e}{C_e} \qquad (18)$$

$$\Delta G^\circ_= -RT\ln K_D \qquad (19)$$

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (20)$$

Where; K_D is the distribution coefficient of the adsorbate, q_e and C_e are the equilibrium concentration of methylene blue on the carbon nanotubes (mg g-1) and in the solution (mg L-1), respectively. R is the universal gas constant (8.314 J/mol K) and T is the temperature

Table 2. Parameter values of the isotherms for the MB adsorption onto CNTs.

Model	Temperature		
	290 K	300 K	310 K
Langmuir	$Q_m = 103.62$	$Q_m = 109.31$	$Q_m = 119.71$
	$K_L = 0.93$	$K_L = 2.16$	$K_L = 3.12$
	$R_L = 0.097$	$R_L = 0.044$	$R_L = 0.031$
	$R^2 = 0.999$	$R^2 = 0.986$	$R^2 = 0.987$
	ARE = 0.709	ARE = 4.344	ARE = 3.299
Freundlich	$K_F = 45.987$	$K_F = 61.88$	$K_F = 73.96$
	$N = 2.7$	$n = 3.32$	$n = 3.45$
	$q_m = 107.804$	$q_m = 123.75$	$q_m = 144.21$
	$R^2 = 0.944$	$R^2 = 0.939$	$R^2 = 0.921$
	ARE = 8.43	ARE = 9.22	ARE = 12.75
Temkin	$B_1 = 21.68$	$B_1 = 20.06$	$B_1 = 21.08$
	$K_T = 9.98$	$K_T = 31.45$	$K_T = 50.27$
	$R^2 = 0.994$	$R^2 = 0.990$	$R^2 = 0.989$
	ARE = 1.63	ARE = 1.72	ARE = 3.14
Sips	$q_m = 105.44$	$q_m = 121.27$	$q_m = 132.61$
	$a_s = 0.88$	$a_s = 1.37$	$a_s = 1.78$
	$n = 1.03$	$n = 1.33$	$n = 1.15$
	$R^2 = 0.999$	$R^2 = 0.999$	$R^2 = 0.998$
	ARE = 0.55	ARE = 0.78	ARE = 1.64
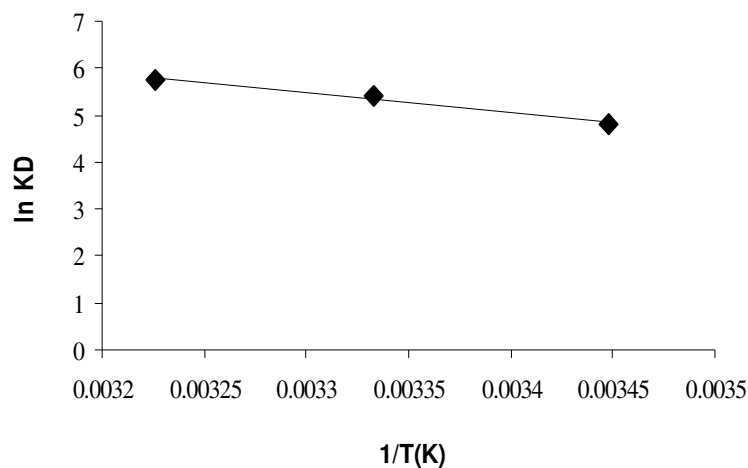
Figure 13. Plot of lnK versus 1/T for estimation of thermodynamic parameters.

(K). $\Delta H^°$ and $\Delta S^°$ parameters can be calculated from the slope and intercept of the plot $\ln K_D$ vs. 1/T, respectively (Figure 13). From Equation (19), $\Delta G^°$ were calculated using $\ln K_D$ values for different temperatures.

Results were summarized in Table 3. As it can be seen, $\Delta G^°$ values at the temperatures of 290, 300 and 310 K are negative. These indicate that the adsorption process was a spontaneous process. The decrease in $\Delta G^°$ with the increase of temperature indicates more efficient

Table 3. Thermodynamic parameter of MB adsorption onto CNTs.

H° (KJ/mol) [*]	35.2181Δ
S° (J/mol K) [*]	161.79Δ
G° (KJ/mol) Δ	
T=290 K	-11.641
T=300 K	-13.519
T=310 K	-14.866

[*] Average value

interface during adsorption and the positive value of ΔH° indicated the adsorption process was endothermic.

adsorption at higher temperature. The positive ΔH° value confirms that the adsorption process is endothermic for methylene blue, which is an indication of the existence of a strong interaction between CNTs and methylene blue. For methylene blue ions travel through solution and reach the adsorption sites, it is necessary for them first to be stripped out (at least partially) of their hydration shell, this process requires energy input. Thus the positive value of ΔH° indicates that the adsorption is increasing with temperature. Moreover, the positive value of ΔS° indicates that the degrees of freedom increased at the solid-liquid interface during the adsorption of MB onto CNTs and reflected the affinity of CNTs toward MB ions in aqueous solutions and may suggest some structural changes in adsorbents (Chen et al., 2007; Teker and Imamoglu 1999).

Conclusion

This study shows that carbon nanotubes have a high adsorptive capacity for MB. The equilibrium adsorption capacity of methylene blue increased with temperature. The adsorption amounts increase with an increase of initial concentration of methylene blue. 400 mg L-1 was considered as the optimum dosage of CNTs to remove methylene blue. pH has an important role in this process. The adsorption kinetics could be quite successfully fitted by a pseudo-second order kinetic equation and adsorption is dominantly by a three-step intraparticle diffusion process. The Langmuir, Freundlich, Temkin and Sips adsorption isotherm models were used to express the adsorption phenomenon of the methylene blue. The equilibrium data were well described by the Sips model with monolayer adsorption capacity of 132.6 mg g-1 at 310 K. The value of the separation factor, R_L, indicated that dye/CNTs system was a favorable adsorption. The negative value of ΔG° confirmed the spontaneous nature of adsorption process. The positive value of ΔS° showed the increased randomness at the solid-solution

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