

Original Article**Adsorption of Nile Blue A from Wastewater Using Magnetic Multi-Walled Carbon Nanotubes: Kinetics and Equilibrium Studies***Mehrnaz Ghoochian***Received: 12.09.2015**Accepted: 19.10.2015***ABSTRACT**

Background: Synthetic dyes are serious pollutants and wide ranges of methods have been employed for their removal from aquatic systems. We studied the adsorption of "Nile blue A" (NBA), an anionic dye, from aqueous solution by oxidized multi-walled carbon nanotubes (MWCNTs).

Methods: Scanning electron microscope and Fourier transform infrared spectroscopy were used to characterize function groups produced at MWCNTs surface. Kinetics and adsorption isotherms of NBA, the effect of temperature, pH, contact time and initial dosage of nanotubes on the adsorption capacity were also assessed. The experimental data were analyzed by Langmuir and Freundlich models.

Results: Most of the dye was removed in the first 5 min and best adsorption percentage was at pH 7.0. The equilibrium reached at 45 min. The experimental data were analyzed by Langmuir and Freundlich models and the results fitted well with the Freundlich model. The adsorption kinetic data were analyzed using first-order and the pseudo-second order model and the adsorption kinetic data of NBA dye onto MWCNTs fitted the pseudo-second order model. The maximum adsorption capacity was obtained as 169.49 mg g⁻¹.

Conclusion: Freundlich model suggested that the adsorption process followed heterogeneous distribution onto MWCNTs and pseudo-second model of adsorption implied that chemical processes controlled the rate-controlling step. Oxidized MWCNTs could be used as an effective adsorbent for the removal of "Nile Blue A" dye. Oxidization of MWCNTs by nitric acid, improves the efficiency of NBA removal due to increases in functional groups and total number of adsorption sites.

Keywords: Carbon Nanotubes, Chemical Water Pollution, Nile Blue, Waste Water.

IJT 2016 (3): 7-12**INTRODUCTION**

Due to high concentration of oxidable materials, persistence, low biodegradability, interference with the photosynthetic action and even potentially mutagenic and carcinogenic effects, synthetic dyes are one of the serious pollutants [1, 2]. Thus, decolorization of dye effluents prior to discharge is an important issue [3].

A wide range of methods have been employed for the removal of dyes and pigments from aquatic systems, including adsorption methods, chemical oxidation, coagulation, photocatalytic degradation, ozone and hypochlorite treatment [4-6]. Adsorption is superior to other techniques, attributed to its

simplicity, easy availability and effectiveness in treating organic dyes [6]. Among various types of natural and synthetic adsorbents, carbon nanotubes, due to their small size, large specific surface area, light mass density and hollow structure, are one of the most effective adsorbents used for removal of dyes and pigments from water and wastewaters [7]. Gong et al. studied magnetic multi-walled carbon nanotubes (MWCNTs) nano-composite as adsorbent for cationic dyes: methylene blue, neutral red and brilliant cresyl blue in aqueous solutions [8]. MWCNTs could be more efficient for the removal of dioxin than activated carbon [9]. Oxidation of multiwalled carbon nanotubes

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with nitric acid has improved adsorption capability for Cd (II), Cu (II) and Pb (II) from water [10]. The adsorption equilibrium, kinetics and thermodynamics of carbon nanotubes (CNTs) for reactive dye Procion Red MX-5B have been investigated by Wu [11].

In the present study, we studied adsorption of "Nile blue A" (NBA) dye from aqueous solution by oxidized multi-walled carbon nanotubes (MWCNTs). Additionally, kinetics and adsorption isotherms of NBA, the effect of temperature, pH, contact time and initial dosage of nanotubes on the adsorption capacity were also assessed.

MATERIALS AND METHODS

Chemicals

All chemicals used were of analytical reagent grade (Merck). Double distilled water (DDW) was used throughout this study. MWCNTs (purity > 95%) were purchased from Merck (Germany) with 10-20 nm and 5-10 nm outside and inside diameters, respectively. To prepare oxidized MWCNTs, 10 g of MWCNTs was added to 100 ml concentrated HNO₃ solution, and the mixture was refluxed for 48 h at 120 °C. After cooling at room temperature, the suspension was filtrated through 0.45 μm filter membrane and then rinsed with deionized water until the pH reached neutral. Finally, the samples were dried in an oven for 2 h at 100 °C [12].

Adsorption Experiments

To evaluate the equilibrium studies, batch experiments were conducted in 25 ml glass flasks. For each experiment, 0.02 g of MWCNTs was added to 30 mg/l of NBA, and HCl or NaOH were used to adjust the pH solution at 7.0. Then the obtained suspension was immediately stirred for 10 min and was filtered through 0.2 μm membrane filters. Residual dye concentration was analyzed using spectrophotometer (Jenway-6305, Japan) with the λ_{max} at 600 nm. Various amount of adsorbent in the range of 0.001–0.09 g and different time from 10 to 240 min were investigated. In order to study the effect of temperature on the adsorption of dye on MWCNTs, thirty mg/l of initial dye stirred for 45 min with 0.02 g of adsorbent at a pH of seven. The removal percentage was determined with following expression:

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

Where, C₀ and C_e are the initial and final dye concentrations (mg/g). All adsorption experiment was performed in triplicates to insure the repeatability of our results.

Adsorption Isotherms

Adsorption isotherms are introduced for the design of adsorption systems. Correlation of equilibrium data by either theoretical or empirical equation is important for practical operation. Langmuir and Freundlich equations were employed to describe the equilibrium adsorption. The Langmuir isotherm is expressed as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b_1} \quad (2)$$

Where, K_L is the Langmuir adsorption equilibrium constant (L mg⁻¹), C_e is the equilibrium dye concentration (mg/L), q_e is the amount of dye adsorbed per unit of adsorbent (mg g⁻¹) at equilibrium concentration C_e, and q_m is the maximum adsorption capacity (mg g⁻¹), which depends on the number of adsorption sites.

Freundlich adsorption model takes the following form:

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_f \quad (3)$$

Where, K_f is the Freundlich isotherm constant (L/mg), and n is Freundlich constant depending on the intensity of adsorption. When 1/n is in the range 0.1 < 1/n < 1, the adsorption process is favorable [13].

Adsorption Kinetics

In order to investigate the mechanism of adsorption, the first-order and pseudo-second order kinetics models were applied to fit the experimental data [14], which can be expressed as the following equations:

$$\ln(q_e - q_t) = \ln(q_e) - \frac{k_1 t}{2.303} \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

Where, q_e and q_t are the adsorption capacity (μg g⁻¹) at equilibrium and at time t (min), k is the rate constant, and h k²q_e² is the initial adsorption rate in pseudo-second order kinetics model.

RESULTS

Characterization of the Adsorbent

The Fourier transform infrared spectroscopy (FTIR) spectrum of MWCNTs showed a peak at $3432\text{ (cm}^{-1}\text{)}$ which could be assigned to the O-H stretch of the hydroxyl groups, while $1729\text{ (cm}^{-1}\text{)}$ and $1588\text{ (cm}^{-1}\text{)}$ peaks are associated with the stretching vibrations of inner-surface carboxylate anion and carbonyl group, respectively. Furthermore, the $1729\text{ (cm}^{-1}\text{)}$ peak could be due to C=C stretch of the graphite structure of MWCNTs, the C=O bonds, but the peak at $1588\text{ (cm}^{-1}\text{)}$ was from the C-H bonds of the alkyl chain. These peaks depicted that oxidation by nitric acid could provide numerous oxygen functional groups on the inner-surfaces of MWCNTs, which would increase adsorption sites. Because of hydrophilic properties of these functional groups, dispersion of MWCNTs in aqueous solution improves with oxidation. The morphology of oxidized MWCNTs was investigated using scanning electron microscopy (SEM), as depicted in Figure 1.

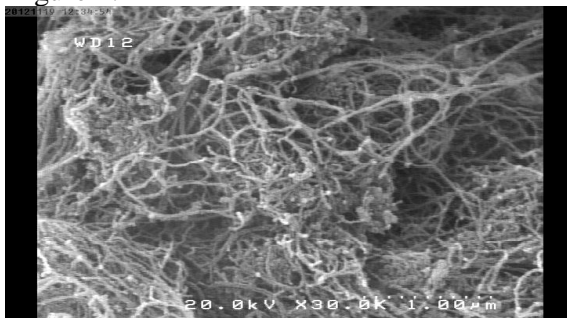


Figure 1. The SEM spectra of oxidized MWCNTs.

Effect of Ph

The initial pH of the solution played an important role in the adsorption process of dye molecules. The effect of initial pH of the solution was investigated in a range of 4-11 using 0.5 M HCl or NaOH solutions. The results are depicted in Figure 2.

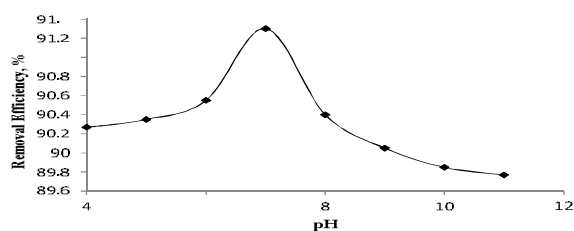


Figure 2. The effect of pH on the adsorption of dye on MWCNTs.

Effect of Adsorbent Dosage

The effect of the adsorption percentage of dye was studied by adding various amount of adsorbent in the range of 0.001–0.09 g into 30 mg/l solution of dye and the pH of the solutions was fixed at 7.0 (Figure 3).

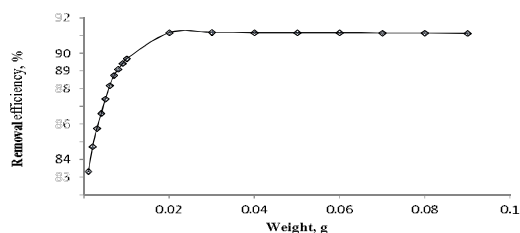


Figure 3. Percentage of dye removal at different MWCNTs dosage.

Effect of Contact Time

The adsorption percentage of dye onto oxidized MWCNTs was studied to obtain the time taken by MWCNTs to remove 30 mg L^{-1} of initial dye at pH 7 and with 0.02 g of adsorbent. It was observed that most of the dye was removed in the first 5 min of contact time. Therefore, the optimum contact time to achieve the equilibrium and complete adsorption was established at 45 min (Figure 4).

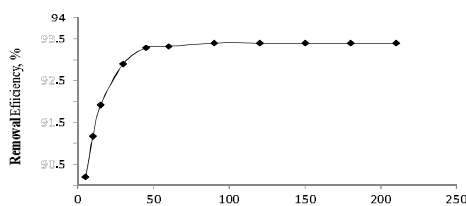


Figure 4. The effect of contact time on the adsorption of dye on MWCNTs.

Effect of Temperature

Dye adsorption decreased as the temperature increased (Figure 5).

Adsorption Isotherms

The Langmuir adsorption isotherm applies for the monolayer adsorption onto a homogenous surface. On the other hand, there

was no interaction between the dye molecules and the adsorption is localized in a monolayer. The Langmuir plots (C_e/q_e vs. C_e) are shown in Figure 6 and the correlation coefficients are shown in Table 1.

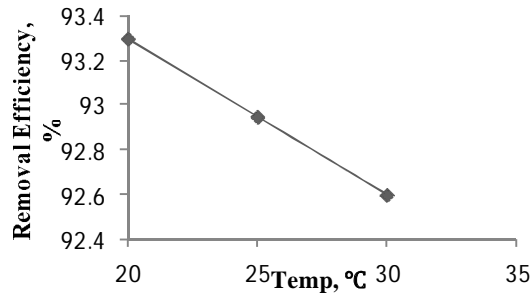


Figure 5. The effect of temperature on the adsorption of dye on MWCNTs.

The Freundlich isotherm shows monolayer adsorption but not a saturation-type isotherm and is suitable for adsorption over heterogeneous surfaces. The linear plot of $\ln q_e$ vs. $\ln C_e$ of our result is illustrated in Figure 7. Freundlich correlation coefficients and constants are shown in Table 1.

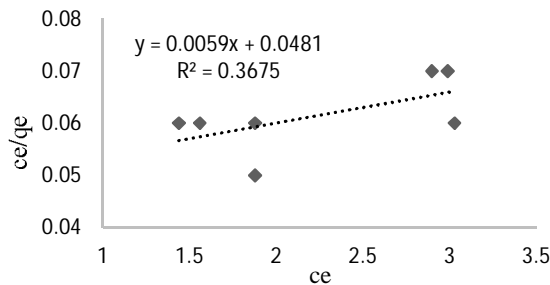


Figure 6. Langmuir isotherm plot of NBA on MWCNTs (MWCNTs dosage = 0.02 g, pH = 7, contact time 45 min, initial dye concentration 30 mg L⁻¹).

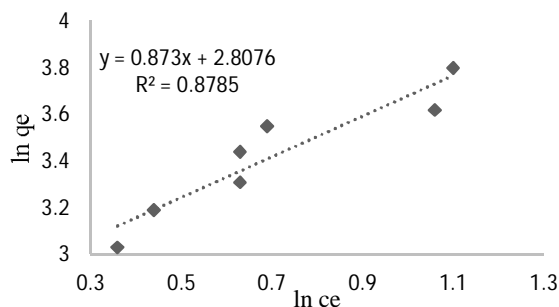


Figure 7. Freundlich isotherm plot of NBA on MWCNTs (MWCNTs dosage = 0.02 g, pH = 7, contact time 45 min initial dye concentration 30 mg L⁻¹).

Table 1. Isotherm model parameters for "Nile blue A" adsorption on MWCNTs.

Dye	Langmuir model			Freundlich model			
	q_{max}	b	K_L	R^2	K_f	1/n	R^2
NBA	169.49	0.048	0.122	0.367	16.24	0.873	0.878

The R^2 of Langmuir and Freundlich Eqs were 0.367, 0.878, respectively. Freundlich model was more suitable for describing the adsorption equilibrium of dye onto the MWCNTs. This result suggested that the adsorption process could be a heterogeneous distribution onto MWCNTs.

Adsorption Kinetics

The R^2 values of the first-order and pseudo-second order kinetics models were 0.437 and 1.0, respectively (Table 2). Accordingly, the adsorption of NBA by MWCNTs followed pseudo-second model (Plot of t/q_t vs. t) which suggested that chemical process controlled the rate-controlling step in the adsorption (Figure 8).

Table 3 shows the comparison our results with some other methods.

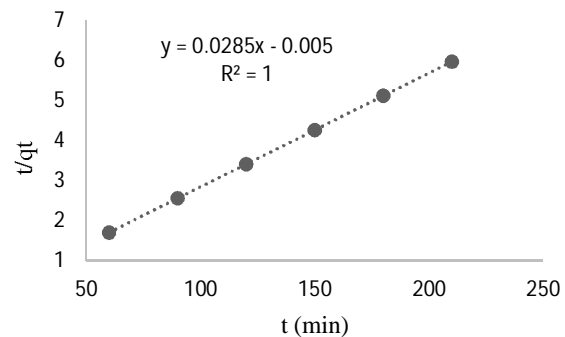


Figure 8. Plot of second-order model for adsorption of NBA onto MWCNTs.

Table 2. Kinetics model parameters for NBA sorption on MWCNTs.

Dye	first-order model			pseudo-second order model		
	K_1	$q_{e, Cal}$	R^2	K_2	$q_{e, Cal}$	R^2
NBA	0.002	35.05	0.243	0.156	35.71	1

Table 3. Comparison of the adsorption capacity of some synthetic dye on to various adsorbents.

Adsorbents	Adsorption capacity (mg g^{-1})			References
	MB	CR	Ic	
MMWCNTs	15.87	-	-	[15]
MWCNTs	-	148	-	[16]
Activated carbon	5.65	-	-	[17]
Maghemite nanoparticles	-	6.85	-	[18]
Brazil nut shells	7.81	-	1.09	[19]
Bottom ash	-	-	7.34	[20]

DISCUSSION

According to the results, dye removal gradually increased when the pH of solution increased from 4 to 7 and decrease at higher pHs. This can be due to protonation of electrons on the MWCNTs surface at lower pH. Therefore, positive charge density increases which causes a more electrostatic attraction between the positively charged MWCNTs surface and negatively charged of anionic dye [21]. The adsorption dose of dye determines the capacity of the adsorbent for a given initial concentration of dye solution. The adsorption percentage increases with increases in MWCNTs mass due to availability of sufficient adsorption sites [22, 23]. We observed that the adsorption capacity for the fixed concentration of dye reached at 0.02 g of adsorbent and further increases in adsorbent did not affect the removal of dye.

Dye adsorption decreased as the temperature increased, which was as a result of exothermic characteristic of adsorption and weak bonding forces between dye molecules and available sites of adsorbent [24, 25]. At higher temperatures, the mobility of the dye ions increases and the interaction of dye with the adsorbent decreases [26].

CONCLUSION

Oxidized MWCNTs can be used as an effective adsorbent for the removal of Nile blue A dye. Oxidization of MWCNTs by nitric acid, improves the efficiency of NBA removal due to increases in functional groups and total number of adsorption sites. The isotherm adsorption data fitted with the Freundlich model, and the kinetic data fitted with pseudo-second order model.

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