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ISSN: 0973-4945; CODEN ECJHAO
E-Journal of Chemistry
2012, **9(4)**, 2371-2383

Kinetics and Equilibrium Studies on Adsorption of Acid Red 18 (Azo-Dye) Using Multiwall Carbon Nanotubes (MWCNTs) from Aqueous Solution

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Received 12 August 2011; Accepted 04 October 2011

Abstract: Azo dyes are one of the synthetic dyes that are used in many textile industries. Adsorption is one of the most effective techniques for removal of dye-contaminated wastewater. In this work, efficiency of multiwalled carbon nanotubes (MWCNTs) as an adsorbent for removal of Acid Red 18 (azo-dye) from aqueous solution was determined. The parameters affecting the adsorption process such as contact time, pH, adsorbent dosage, and initial dye concentration were studied. Experimental results have shown by increasing the adsorbent dosage, the rate of dye removal was increased, but the amount of adsorbed dyes per mass unit of MWCNTs was declined. pH as one of the most important influencing factors on the adsorption process was evaluated. The best pH for adsorption process was acidic pH of about 3. To describe the equilibrium of adsorption, the Langmuir, Freundlich and Temkin isotherms were used. The Langmuir isotherm (R^2=0.985) was the best fitted for experimental data with maximum adsorption capacity of 166.67 mg/g. A higher correlation value of the kinetic's model was observed close to pseudo second order (R^2=0.999) compared to other kinetic models.

Keywords: Adsorption, Acid Red 18 (azo dye), MWCNTs, Kinetics and Equilibrium.

Introduction

There are more than 1,00,000 types of dyes commercially available, with over 7×10^5 tonnes of dyestuff produced annually, which can be classified according to their structure as anionic and cationic[1]. The treatment and disposal of dye-contaminated wastewater is one of the most serious environmental problems faced by the textile, dyeing, printing, ink and related industries[2].Azo dyes are one of the synthetic dyes that used in many textile industries. Azo dyes and their intermediate products are toxic, carcinogenic and mutagenic to aquatic life[3]. Many treatment methods have been adopted to remove dyes from wastewater, which can be divided into physical, chemical and biological methods[4]. Moreover, in order to treat wastewater dyes, many researchers have been investigated the effect of advanced oxidation processes (AOPs). Applicable example of this technology can be expressed as decolorization and degradation of dyes by photocatalytic and nanophotocatalytic processes[5-7].

Among the advanced chemical and physical treatment processes, adsorption is considered to be superior to other techniques. This is attributed to its easy availability, simplicity of design, ease of operation, biodegradability, insensitivity to toxic substances and ability to treat dyes in more concentrated forms. Physical adsorption has been proven to be the most efficient method for quickly lowering the concentration of dissolved dyes in an effluen[t8,9]. Carbon nanotubes (CNTs) are an attractive alternative in removal of organic and inorganic contaminants such as heavy metal, trihalomethanes (THMs), fluoride and dyes from water and wastewater[10-14], because of their small sizes, large surface areas, unique hollow structures, high mechanical strength and remarkable electrical conductivities[15-17]. In this study, the adsorption behavior of multiwalled carbon nanotubes (MWCNTs), its removal capacity and other adsorption condition of an azo dye such as AR18 from aquatic solution have been investigated. The influence of contact time, pH, adsorbent dosage and initial dye concentration was studied. Furthermore, in order to find out the relation between adsorbent and adsorbed AR18, the isotherm and kinetics of adsorption were evaluated.

Experimental

All reagent and material were obtained in laboratory grade (Merck, Germany).

Characterization of MWCNTs

The MWCNTs being synthesized in the Iranian Research Institute of Petroleum Industry (RIPI), was purchased and was used without any purification for this study. The purity of MWCNTs was more than 95%. Table 1 presents the characteristics of prepared multiwalled carbon nanotubes. These nanotubes were synthesized by using chemical vapor deposition (CVD) of hydrocarbons. Furthermore, the size and morphology of MWCNTs were characterized by scanning electron microscope (SEM) and transmission electron microscopy (TEM) using a Philips XL 30 ESEM). Figure 1 and 2 shows the TEM and SEM images of $MWCNT_S$.

Table 1. The characteristics of MWCNTs.

characteristic	value	unit
Specific surface area (BET)	270	m^2/g
Length	10	µm
Diameter	10– 30	nm
Thermal conductivity	1500	w/mV

Adsorbate

Since AR18 has an azo group band (-N=N-), then it is in the group of azo dyes. The molecular structure of AR18 is shows in Figure 3, which is provided by Merck Company (Germany). Molar mass of AR18 is 604.47 g mol^{-1} with molecular formula of $C_{20}H_{11}N_2Na_3O_{10}S_3$. The AR18 dye was made with high purity of dye and was applied without further purification. The dye stock solution was prepared by dissolving 500 mg of acid red 18 (AR18) in 1000 mL deionized water. The lesser concentrations of dye was fabricated with dilution of stock dye.

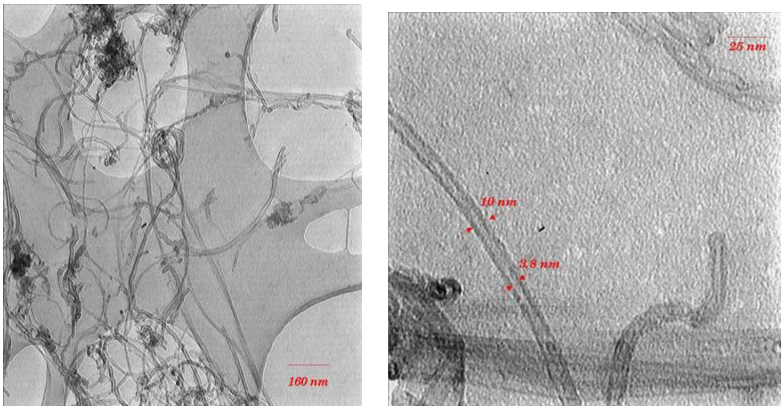

Figure 1. TEM of MWCNTs.

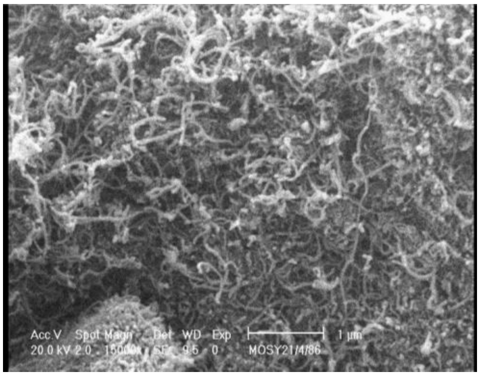

Figure 2. SEM of MWCNTs.

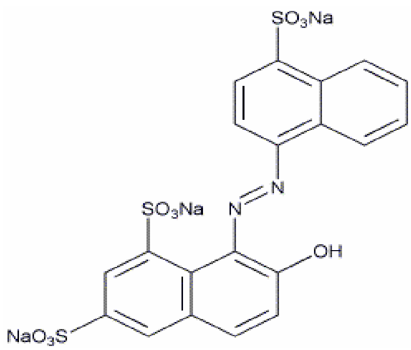

Figure 3. Structure of the azo dye Acid Red 18.

Batch Adsorption Experiments

In order to contact between adsorbent and dye solution, all tests were conducted in a closed Erlenmeyer flasks with 250 mL capacity as a batch system. Different doses of MWCNTs were applied by adding 0.02, 0.04, and 0.06 g of adsorbent per 100 mL of dye solution. Furthermore, the pH was adjusted to the desired value with 1 N HCl and NaOH (Merck, Germany). In this study, various parameters such as contact time ranges from (5-240 minute), pH 3 to 9, adsorbent dosage (0.2, 0.4, 0.6 g/L), initial dye concentrations (25, 50, 75, and

100 mg/L) were investigated in different experiments. In all experiments, the temperature was kept constant (25^0C). For better mixing, the Erlenmeyer flasks which contain 100 mg/L of dye solution were placed in the illuminated refrigerated incubator shaker (Innova 4340, USA) and were agitated at 175 rpm. At the end of equilibrium time the suspensions were centrifuged for 10 min at 4000 rpm and then the supernatant of suspension was filtered using a 0.2 µm Millipore filter. The final dye concentrations (AR18) were evaluated by UV-visible spectrophotometer (Lambda 25, USA) at maximum wavelength (506 nm). After taking these measurements, the concentrations of residual dye were determined by calibration curves. Removal efficiency, adsorption capacity (q) and Distribution coefficients were calculated using the following equations[19]:

$$\text{Removal efficiency } \% = \frac{(\mathrm{C_o} - \mathrm{C_f})}{\mathrm{C_o}} X100 \tag{1}$$

$$\mathrm{q} = \frac{(C_o - C_{\mathrm{f}})\mathrm{X\,V}}{M} \tag{2}$$

Isotherm Analysis

For analyzing the experimental data, adsorption isotherm models were used to determine the homogeneous and heterogeneous characteristics. To evaluate the adsorption isotherm, three equilibrium isotherms were studied: (A) Langmuir, (B) Freundlich, and (C) Temkin. Analysis of isotherms was used to describe the experimental adsorption data, and then best results can be obtained when correlation coefficients (R^2) come close to 1. High values of R^2 (close or equal to 1) indicate the conformity among experimental data with model isotherm or kinetic. The equations of these three isotherms and their linear forms are as below:

A- Langmuir equation:

$$\mathrm{q_e} = \frac{\mathrm{q_m K_c C_e}}{1 + \mathrm{K_c C_e}} \tag{3}$$

First, the Langmuir isotherm was used in order to describe the equilibrium of gas molecules onto the metal surface[18]. The linear form of Langmuir equation is expressed as the following Eq. (4):

$$\frac{\mathrm{C_e}}{\mathrm{q_e}} = \frac{1}{K_c q_m} + \frac{\mathrm{C_e}}{\mathrm{q_m}} \tag{4}$$

B- Freundlich equation:

$$\mathrm{q_e} = \mathrm{K_f C^{1/n}} \tag{5}$$

Freundlich In 1906 presented his isotherm as an empirical model, which later was known with his name. This model can be applied to non ideal sorption on heterogeneous surfaces as well as multilayer sorption[20]. Linearizing the Freundlich equation Eq. (6) gives:

$$\log q_e = \log(K_F) + \frac{1}{n}\log(C_e) \tag{6}$$

C- Temkin equation:

$$q_e = B_1 \ln(k_t C_e) \tag{7}$$

Temkin isotherm contains a factor that explicitly takes into the account the adsorptive-adsorbent interactions[21]. Linearizing the Temkin equation Eq. (8) gives:

$$q_e = B_1 \ln k_t + B_1 \ln C_e \tag{8}$$

Kinetic Analysis

In order to investigate the capacity of dye mass transfer[22] to MWCNTs sites, kinetics of adsorption was evaluated. The analysis of the isotherm data is important to develop an equation which accurately represents the results and could be used for design purposes[23]. Therefore, in this paper, three models of kinetic for 50 and 100 mg/L of dye were studied. These models are such as: (A) pseudo first-order, (B) pseudo second-order, (C) Weber-Morris (or intraparticle diffusion). The models of kinetic and their applied forms are as following equations:

A- Pseudo first-order Equation:

$$\frac{dq_t}{dt} = k_1\left(q_e - q_t\right) \tag{9}$$

The linearized Pseudo first-order equation is given as:

$$\log\left(\mathrm{q_e} - \mathrm{q_t}\right) = \log\left(\mathrm{q_e}\right) - \frac{\mathrm{k_1}}{2.303}t \tag{10}$$

B- Pseudo second-order Equation:

$$\frac{dq_t}{dt} = k_2\left(q_e - q_t\right)^2 \tag{11}$$

The linearized Pseudo second-order equation is given as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \tag{12}$$

C- Weber-Morris Equation;

$$\mathrm{q_t} = \mathrm{k_{id}}\ (\mathrm{t})^{\mathrm{a}} + C \tag{13}$$

The linearized Weber-Morris Equation is given as:

$$\log \mathrm{q_t} = \log \mathrm{k_{id}} + \mathrm{a} \log(\mathrm{t}) \tag{14}$$

Results and Discussion

Effect of Contact Time

To evaluate the effect of contact time on adsorption process, minimal dose of adsorbent was selected and was added to different dye concentrations (25, 50, 75, 100). pH of solutions was adjusted to 5 that was much close pH to the actual pH of solutions. Solutions were placed in the illuminated refrigerated incubator shaker (Innova 4340, USA) and the samples were taken at different time intervals. The effect of contact time on adsorption of dye is shown on Figure 4. As shown in Figure 4 adsorption of dye was increased by increasing the contact time. The adsorption process was faster in the initial 30 min and then became slowly until reached to equilibrium at 120 minutes. For investigation of other parameters, the equilibrium time was used .

Effect of pH

The effect of pH on the adsorption process by MWCNTs was evaluated by different value of initial pH. As shown on Figure 5, different pH condition in four ranges of 3, 5, 7, and 9 were applied for the initial concentrations of 25, 50, 75, and 100 mg/L. Higher efficiency of dye adsorption observed at acidic pH of 3 for any concentration of dye, while a decrease in adsorption rate was occurred with an increase in pH from acidic to neutral and alkaline ranges. In low pH, the surface of carbon material was charged with H^+ ion and this leads to a significantly strong electrostatic attraction between the positively charged carbon surface and anionic dye molecules which caused an increasing rate in dye sorption[24]. Furthermore, initial dye concentration affected the adsorption efficiency. Maximum adsorptions obtained with different concentrations of 25, 50, 75, and 100 mg/L at pH 3 equal to 98.71%, 96.97%, 78.79%, and 66.97%, respectively.

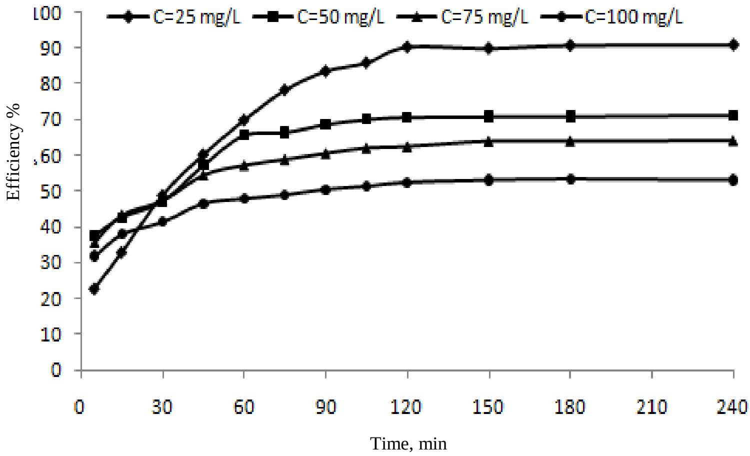

Figure 4 Effect of contact time on adsorption of AR18 to MWCNTs in different dye concentrations (pH=5, MWCNTs= 0.2 g/L, T=25^{o}C).

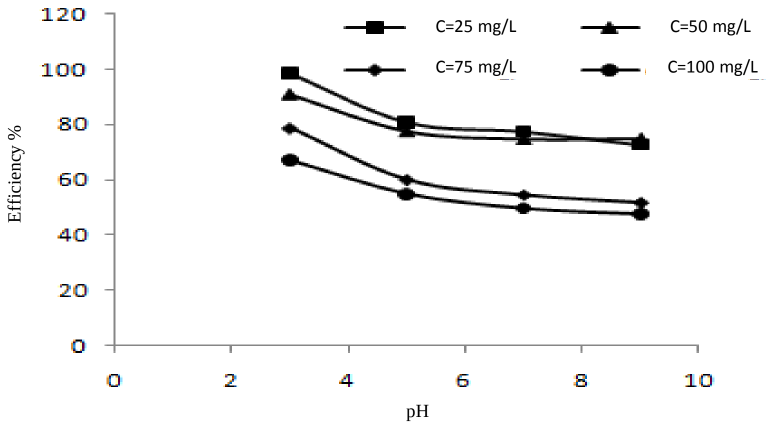

Figure 5. Effect of pH on the adsorption of AR18 onto MWCNTs in different dye concentration (adsorbent dosage =0. 04 g/100 mL, contact time= 120 min, T= 25°C).

Effect of Adsorbent Dosage

Figure 6. shows the effect of MWCNTs dosage on the adsorption process. In order to find the optimum dosage of MWCNTs, three doses of adsorbent were investigated. The tests were performed at equilibrium time of 120 min and pH 3. Highest adsorption rate was obtained in 0.06 g of MWCNTs. An increase in adsorption rate with adsorbent dosage can be attributed to increased surface area and the availability of more adsorption sites[25]. For kinetics and equilibrium studies the mean dosage (0. 4 g) of MWCNTs was selected as the optimum dose.

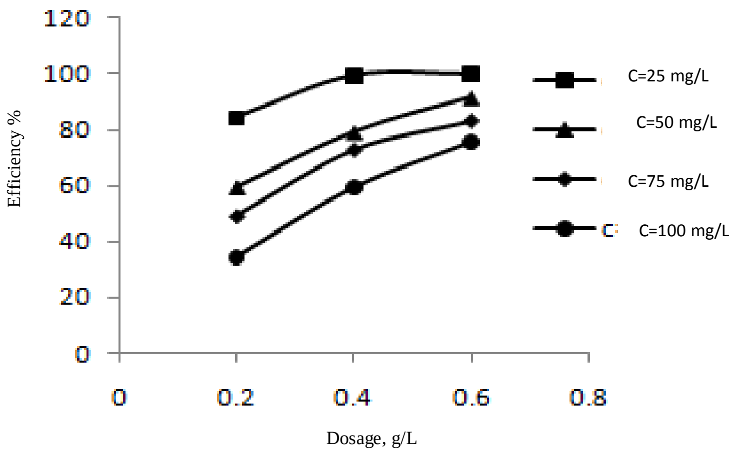

Figure 6. Effect of adsorbent dosage on the adsorption of AR18 in different dye concentration (contact time =120 min, pH= 3, T=25°C).

Effect of Initial Dye Concentration

The influence of initial dye concentration on adsorption of AR18 onto MWCNTs was investigated by adding of 0.04g of MWCNTs to 100 mL of dye solution and contact time equal to equilibrium time (120 min). As shown in Figure 7 by increasing the initial dye concentration, the adsorption of AR18 was decreased. The adsorption of dye was faster at initial stages and gradually decreased and became constant after equilibrium was reached. For constant dosage of adsorbent at lower initial dye concentration the large number of vacant surface sites was available for adsorption of dye. Mean while, by increase of dye concentration, adsorption sites of adsorbent became lower and due to repulsive forces between dyes molecules on $MWCNT_{S,}$ the occupation of remaining vacant surface sites were difficult. Removal of AR18 onto $MWCNT_S$ is dependent on initial dye concentration, at an initial concentration of 25 mg/L of AR18 and maximum removal efficiency was found to be (98.2%) and by increasing the AR18 concentration to 100 mg/L, the removal efficiency decreased to (63.8%). However, the amount of adsorbed AR18 per unit of $MWCNT_S$ mass increased from 61.38 to 159.5 mg/g. Therefore, the increase in initial dye concentration resulted in increase of the driving force for mass transfer.

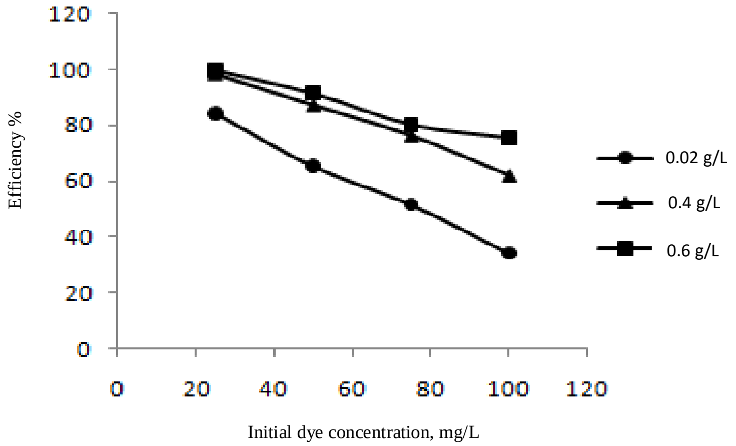

Figure 7. Effect of initial dye concentration on adsorption of AR18 onto $MWCNT_S$ (contact time = 120 min, pH = 3, T =25°C).

Adsorption Isotherms

In this study, various isotherm models such as Langmuir, Freundlich, and Temkin were studied to describe the equilibrium characteristics of adsorption. Isotherm is the relationship between the equilibrium amount of dye (AR18) adsorbed on MWCNTs surface and residual concentration of dye in solution. Figure 8 illustrates Langmuir isotherm plot for experimental data (q_e/C_e *vs*. C_e). Referring to Table 2, R^2 value in this model is 0.985. Freundlich plot presented in Figure 9, has been drawn with Log q_e *vs*. Log C_e R^2 value of Freundlich isotherm was determined to be 0.971. Furthermore, in Figure 10, Temkin isotherms plot (Ln C_e *vs*. C_e) with R^2=0.982 is illustrated. In contrast, it can be found that the Langmuir isotherm with R^2=0.985 represents the best fit with the adsorption experimental data, and adsorption data of dye onto MWCNTs are confirmed with this model related to former models. Further detail of isotherms models are given in Table 2.

Table 3 illustrated the maximum adsorption capacity of some adsorbents that have been published on literature for various dyes in different conditions. According to this table CNTs have higher efficiency comparative to other adsorbent. But, due to variable experimental condition a direct comparison between different adsorbents cannot be made.

It is worth to mention that application of different enzymes has shown a good promise in removal of dyes from textile wastewaters and are as well as adsorption processes using $MWCNT_s$[36].

Kinetic Models

In this study, to express the mechanism of AR18 adsorption onto MWCNTs, the most three popular kinetic models were used. These models are Pseudo first order, Pseudo second order and Weber–Morris. The experimental data was obtained for two concentrations of 50, 100 mg/L, at equilibrium time 120 min, MWCNTs dosage 0.04g and pH 7. The plots of kinetic models are presented in Figures 11- 13. With regard to the plots of these models and with the help of Table 3, it can be seen, that higher R^2 has been achieved in Pseudo second order. With regard to pseudo second order R^2 value (0.999) for the concentrations of 50, and 100 mg/L, it can be seen that it is the best fit conformity in this model. Therefore, adsorption mechanism of AR18 was close to second order model and it is suggested for dye adsorption onto multiwall carbon nanotubes surface. Kinetic details of AR18 adsorption with the correlation coefficients are presented in Table 4.

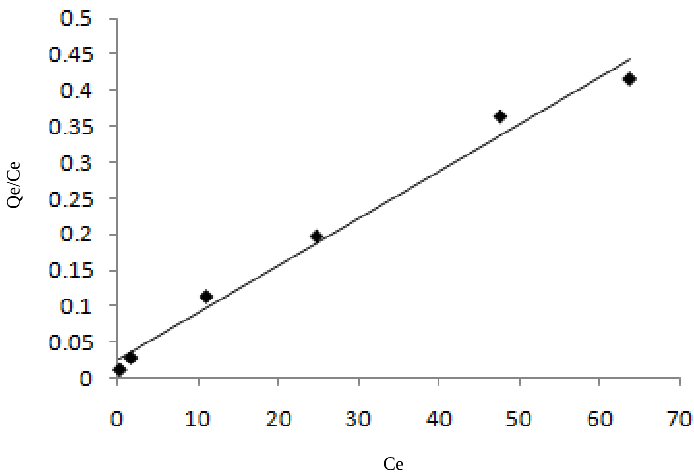

Figure 8. Langmuir isotherm for adsorption data of AR18 by MWCNTs; Time 120 min, dose: 0.04 g/100 mL, pH=7.

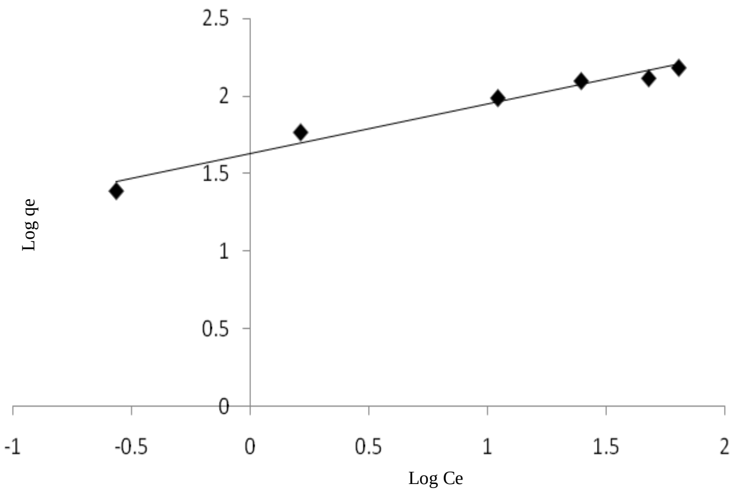

Figure 9. Freundlich isotherm for adsorption data of AR18 by MWCNTs; Time 120 min, dose: 0.04 g/100 mL, pH=7.

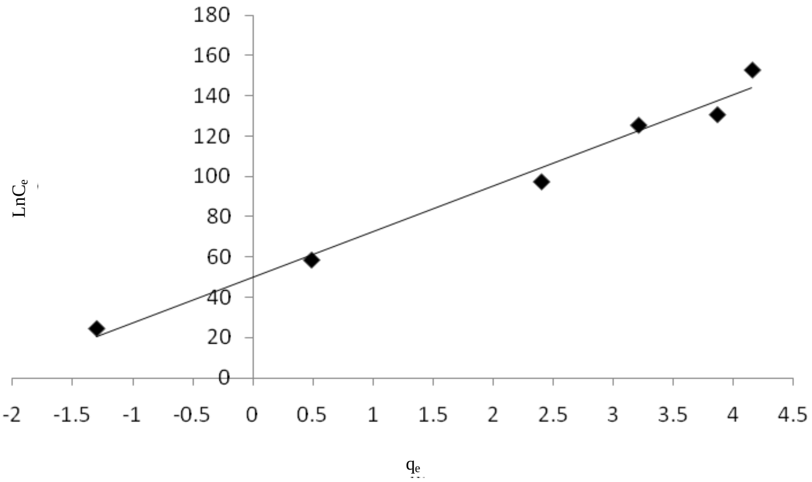

Figure 10. Temkin isotherm for adsorption data of AR18 by MWCNTs; Time 120 min, dose: 0.04 g/100 mL, pH =7.

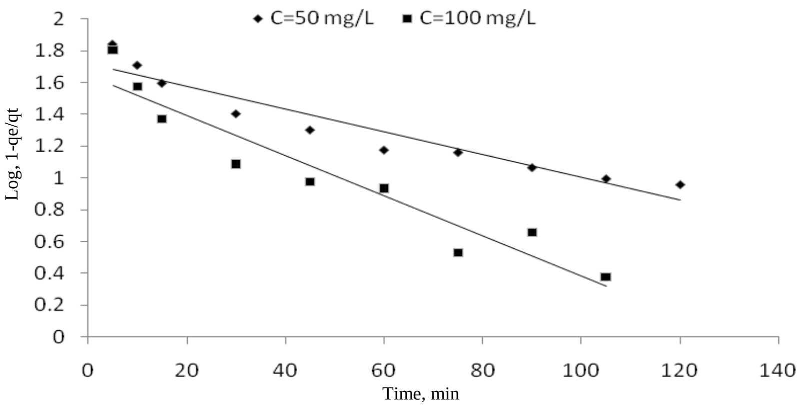

Figure 11. Pseudo-first order kinetic model; Time 120 min, dose: 0.04 g/100 ml, pH 7.

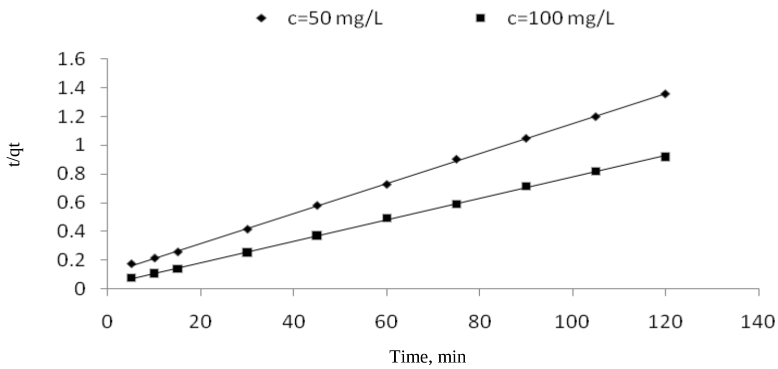

Figure 12. Pseudo-second order kinetic model; Time 120 min, dose: 0.04 g/100 mL, pH 7.

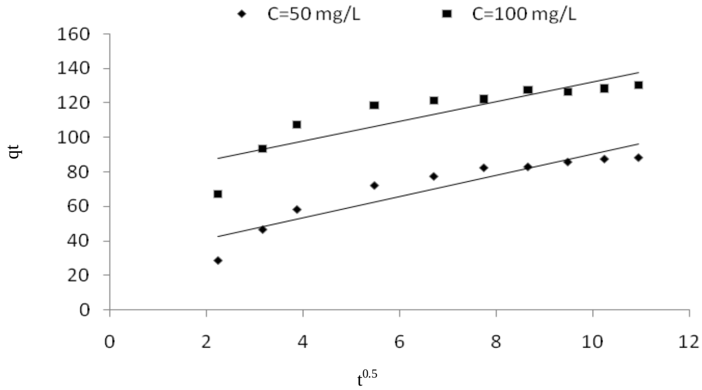

Figure 13. Weber–Morris kinetic model; Time 120 min, dose: 0.04 g/100 mL, pH 7.

Table 3. Maximum adsorption capacity of some adsorbents for different dyes.

Adsorbent	Adsorbate	Conditions	Maximum adsorption capacity, mg/g	References
$MWCNT_S$	Acid Red 18	-	166.67	Present work
$MWCNT_S$	Methylene Blue	290 ^{o}k 300 ^{o}k 310 ^{o}k	103.62 109.31 119.71	[26]
F-$MWCNT_S$	Direct Gongo Red Reactive Green HI-4BD Golden Yellow	- - -	148 152 141	[27]
$MWCNT_s$- Fe_20_3	Methylene Blue Neutral Red	- -	42.3 77.5	[28]
CNT_S	Procion Red MX-5B	301 ^{o}k PH= 6.5	39.84	[29]
Halloysite nanotubes	Neutral Red	298 ^{o}k 308 ^{o}k	54.85 59.24	[30]
Activated carbon	Acid Red 97	-	82.08	[31]
Activated carbon (poplar wood)	Acid Red 18	-	3.9	[3]
Activated carbon	Methylene Blue	298 ^{o}k 303 ^{o}k 318 ^{o}k	40.06 40.38 42.86	[32]
Activated rice husk carbon	Acid yellow 36	-	86.9	[33]
Commercial activated carbon	Acid yellow 23	-	56.5	[34]
Activated carbon	Reactive Yellow 15	-	116	[35]
Eggshell	Reactive Red 123	-	1.26	[19]

Table 4. Kinetic details of AR18 adsorption by MWCNTs.

Kinetic model	Parameters	Pseudo-first order	Pseudo second order	Weber-Morriss
Conc. (50 Mg/L)	R^2	0.915	0.999	0.864
	Constant	k_1=0.016	k_2=0.093	k_{id}=6.10
	q_e	51.88	100	-
Conc. (100 mg/L)	R^2	0.914	0.999	0.764
	Constant	k_1=0.0009	k_2=0.0015	k_{id}=5.70
	q_e	43.95	142.8	-

Conclusion

Dyes are one of the most-used materials in many industries. Azo dyes are toxic and carcinogenic to human and aquatic life. Therefore, these effluents should be treated prior to discharge**.** Adsorption process is considered, due to its easy availability, simplicity of design and other advantages. This study expressed a high-efficiency adsorbent for dye removal. MWCNTs as an adsorbent with high adsorption rate can be used for removal of Azo-dye from textile wastewaters. Using MWCNTs as a modern adsorbent can result in maximum adsorption capacity of AR18 to 166.67 mg/g. Dye adsorption using MWCNTs will follow the Langmuir isotherm and pseudo second order kinetic model.

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