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Kinetic and adsorption studies of reactive black 5 removal using multi-walled carbon nanotubes from aqueous solution

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ABSTRACT

The removal of reactive black 5 (RB5) from aqueous solutions by adsorption onto multi-walled carbon nanotube (MWCNT) was studied. The effects of some operating parameters such as solution pH, initial dye concentration, adsorbent dosage and adsorption capacity on the adsorption of RB5 were investigated. It was found that RB5 removal by adsorption onto MWCNT was best achieved at natural pH. The adsorption efficiency of RB5 by MWCNT decreased with increasing initial dye concentration, while the increase of adsorbent dosage resulted in an increase of decolorization efficiency. The maximum adsorption capacity was reached at 36.2 mg/g after 90 min. The results obtained from kinetic studies reflected that RB5 removal fitted well with the second order model. Also, the isotherm data correlate well with the Freundlich model. The findings indicated that MWCNT can be used as a suitable adsorbent for removing dyes from wastewaters.

Keywords: Adsorption, Reactive Black 5, Multi-Walled Carbon Nanotubes

INTRODUCTION

Textile dyes are widely used in several industries like cosmetic manufacturing, paper and pulp and textile. All of these generate a huge amount of effluents containing various pollutants from organic matters and dyes to surface-active agents and textile additives employed during the process [1]. Textile dyes can be structurally different classified into three categories (1) anionic: acid, direct and reactive dyes applied to fibers such as silk, wool and nylon; (2) cationic: basic dyes mainly applied to acrylic fibers and (3) non-ionic: disperse dyes, which improves the fastness of the dye against water, light and perspiration [2]. Almost 45% of all textile dyes produced annually belong to the reactive dye class [3]. They are the most commonly applied among more than 10000 dyes applied in textile processing industries [4]. This widespread application can lead to release of a high amount of reactive dyes into water bodies. Discharge of dye-containing effluents into the environment, especially surface waters, has become an urgent environmental issue because they have adverse effects on aqueous ecosystem and are toxic to humans [5].

The human eyes can detect a concentration of 0.005 mg/L of reactive dyes in aqueous environments. Therefore, dye concentrations exceeding this limit would not be permitted aesthetically [4,5]. Most dyes are resistant to degradation by heat and light as well as biodegradation under aerobic processes [6]; of course, high level of textile dyes may be toxic to microorganisms, and their removal from effluents is difficult. Moreover, the technology that makes these dyes resistant to various factors causes them not to be removed from conventional wastewater treatment processes. Nowadays, many various chemical, physical and anaerobic biological processes have extensively been used to treat textile wastewaters [3,4,7]. Adsorption processes seem to be an alternative process for removing reactive dyes. Therefore, activated carbon, as an adsorbent, has been widely applied to remove pollutants from aqueous solution [8]. In recent years, nanotechnology has been considered as a promising technology to treat water. Multi-walled carbon nanotubes (MWCNTs) have shown an ability efficiently absorb various organic pollutants such as dioxins, polychlorinated dibenzo-furans and biphenyls from aqueous environments [9]. In this study, MWCNT was used as an adsorbent for the adsorption of reactive black 5 (RB5) from aqueous solutions. In addition, the effects of some parameters such as solution pH, initial dye concentration, adsorbent dosage and adsorption capacity on the adsorption of RB5 were studied.

MATERIALS AND METHODS

The preparation of dye
The dye: molecular formula: $C_{26}H_{21}N_5Na_4O_{19}S_6$, molecular weight: 991.82 g/mol was purchased from Alvan Sabet (Hamadan, Iran) and used without further purification. The RB9 is highly soluble (>50 g/L). Its molecule has a size of 3.15 nm × 1.23 nm × 0.92 nm [2]. All samples were taken in lab temperature using distilled water.

The preparation of MWCNTs
MWCNTs were obtained from Merck (Darmstadt, Germany). The preparation of MWCNTs was accomplished by stirring them in nitric acid for 12 h (70 ˚C). Next, they were filtered off, washed with distilled water and then dried at 110˚ C for 6 h. Then, MWCNTs were refluxed with 50% nitric acid for 12 h under stirring conditions. The product was then filtered and washed with doubly distilled water and finally dried in the oven [10].

Table 1. The characteristics of MWCNTs

Appearance	Black powder
External diameter	20-30 nm
Length	30 µm
Purity carbon	95%
specific surface area	110 m^2/g
Density	2.1 g/cm^3

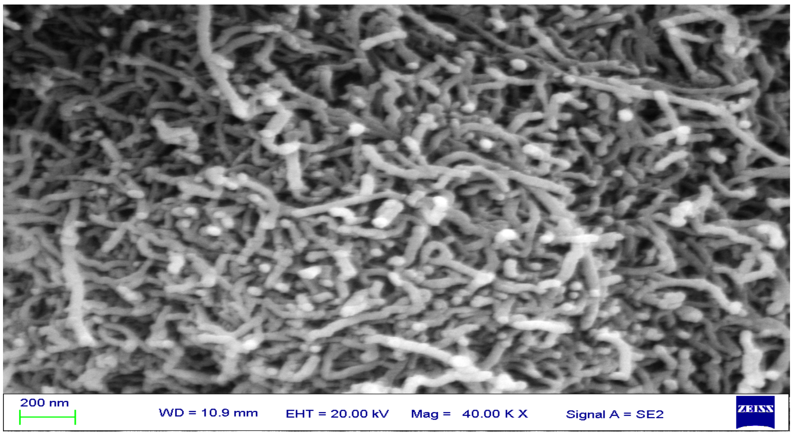

Figure 1. SEM image of MWCNTs

Characterization of MWCNTs
In order to determine the surface area of the adsorbents, scanning electron microscopy (SEM) was used. The SEM photograph of MWCNTs is shown in figure 1. Also, the surface functional groups of MWCNTs were obtained by

FTIR spectroscopy. The point of zero charge (pH_{pzc}) of MWCNTs was determined using the pH drift method. To determine pH_{pzc} of MWCNT, NaCl solution (0.01 M) was used as an inert electrolyte. The quantities of MWCNT (8 mg) were added to each flask. The flasks were placed in the shaker (Model GFL 3017) with a speed of 200 rpm for 48 h. Then, the contents of each flask were filtered using 0.45 µm and final pH was measured using a pH meter (Hatch Sinsion1).

Batch experiments

The adsorption experiments were carried out in a batch reactor. First, a stock solution of RB5 (1000 mg/L) was prepared. Then, working solutions were obtained by diluting the dye stock solution to the required contents. In this study, the effect of some parameters such as pH, initial dye concentration, adsorption dosage and adsorption capacity was examined in different contact times (30-120 min). In the first step of experiments, the effect of pH on the adsorption efficiency was tested in the range of 4-10 (under the selected conditions: initial dye concentration= 50 ppm and adsorbent dosage= 0.5 g/L). The pH of the solution was adjusted from 4 to 10 using HCl (1M) and NaOH (1N). In the next step, after the optimum pH was indicated, the effect of various concentrations of RB5 (from 50 to 200 mg/L) on the absorption efficiency was evaluated. In order to determine optimum dosage of MWCNTs in the adsorption process, various dosages of MWCNTs were examined in the range of 0.05 to 0.5 g/L. The sample solutions containing the adsorbent and dye were stirred using a magnetic stirrer at 120 rpm. To separate the adsorbents from the solution, the samples were centrifuged using a centrifuge (Sigma-301, Germany) with a speed of 1400 rpm for 15 min. The final pH was measured by using a pH-meter (Sension 1 model). All samples were withdrawn from the middle of the reactor in different contact times (15, 30, 60 and 120 min).

Analysis

After adsorption process, the concentration of residual RB5 was determined at 598 nm using a UV spectrophotometer (HACH DR 5000, USA) [7]. Percentage of dye removal was calculated according to Eq. (1):

$$E = C_i - {}^{C_f}/_{C_i} \times 100 \qquad (1)$$

Where C_i is initial concentration of the dye (mg/L), C_f is instant concentration of the dye and E is the percentage of dye removal.

Adsorption isotherms

Langmuir and Freundlich isotherm models were used to describe the equilibrium at lab temperature. The Langmuir model can be described by Eq. (2) [11]:

$$q_e = \frac{q_{max} K_l C_e}{1 + K_l C_e} \qquad (2)$$

Where q_e is the amount adsorbed per gram of the adsorbent (mg/g) and C_e is the equilibrium concentration of adsorbed in the solution (mg/L). q_{max} and K_L are the Langmuir constants related to the maximum adsorption capacity and energy of adsorption, respectively.

The Freundlich isotherm model can also be described by Eq. (3) [11]:

$$q_e = K_f C_e^{1/n} \qquad (3)$$

Where q_e is the amount of adsorbed (mg/g), C_e is the equilibrium concentration of adsorbed in the solution (mg/L), and K_f and n are constants.

RESULTS AND DISCUSSION

Characteristic of MWCNT

The FTIR spectra of raw MWCNTs were studied. The FTIR photograph is shown in figure. 2. As revealed, there were various functional groups detected on the surface of adsorbents before adsorption. A broad peak at 3434 cm^{-1}

indicated the presence of carboxylic O–H stretch groups and H–bonded, which cover the N-H groups and confirm the presence of carbonyl groups on the surface of adsorbents. The second peak appearing at 2919 cm^{-1} indicated the presence of S-H_2, the peak around 1576 cm^{-1} indicated the presence of carbonyl C=O bonds. The peak around 1271 cm^{-1} corresponding to the C-O bond may be attributed to the bonded cysteine bonds, and the formation of second types of amides. XRD pattern of MWCN is shown in figure. 3 presenting a peak around 25 indicated the presence of carbon element and the peak around the 43 indicated the presence of oxygen element.

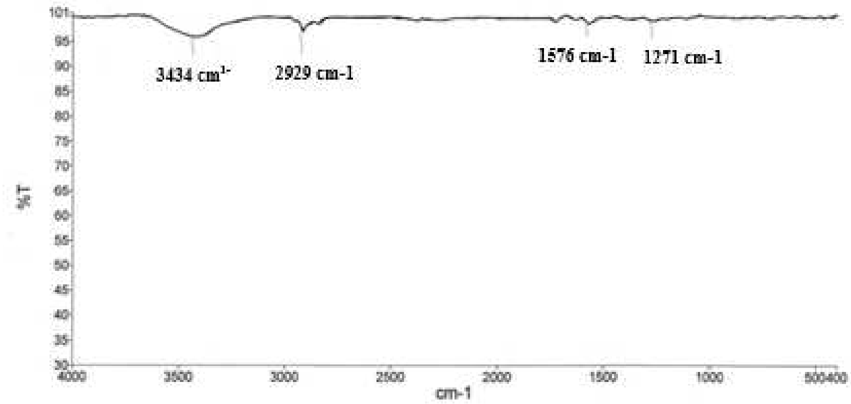

Figure 2. FTIR spectra of raw MWCNTs

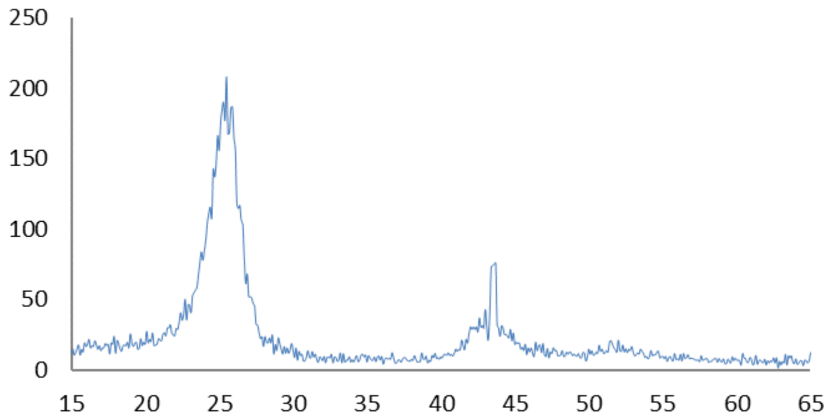

Figure 3. XRD pattern of MWCNTs

Effect of pH

Solution pH affects the nature of the adsorbent surface, the solubility of the dye and adsorption capacity. Since pH is one of the significant factors influencing the adsorption process, the effect of initial pH of the solution (at three different pH values; 4, 7 and 10) on the adsorption process under the selected conditions was studied in this part of present study. The results of this part have been shown in figure 4. The maximum adsorption efficiency of RB5 was seen at pH 7 after 120 min. Thus, when pH of the solution increased from 4 to 7, the adsorption of the dye onto MWCNTs increased from 90 to 95%. In contrast, at pH 10, the adsorption efficiency decreased to 85%. As shown in Figure 4, the dye removal by adsorption onto MWCNTs was best achieved at pH 7, which can be attributed to the influence of solution pH on the surface of MWCNT. At pH values lower than 7, a negative charge is present on the surface, so, it is expected that the adsorption of negatively charged dye ions onto such surface is difficult. On the other hand, lower adsorption capacity in alkaline condition (at pH values higher than 7) is due to the competition between hydroxyl ions and negatively charged dye ions for the adsorption sites. Therefore, it decreases the adsorption efficiency of RB5. This observation supports the results of copper ions removal from water solution using chemical modified MWCNT [12]. In the current study, an increase in the adsorption of copper was observed with increasing solution pH from1.5 to 6. In a similar study, the optimum pH in the adsorption of chromium (VI) for the normal activated carbon was found to be 4, while that for the MWCNT supported by activated carbon was 2 [13], which are inconsistent with our results. This can be attributed to the influence of activated carbon that is coated with MWCNTs. In addition, the obtained results showed that the pH_{pzc} of GAC was 7.2. Previous studies have suggested that in adsorption process at pH values lower than pH_{pzc} the adsorbent surface is positively charged. Thus, the electrostatic force of attraction between negatively charged dye ions and positively charged adsorbent surface ultimately leads to higher RB5 adsorption.

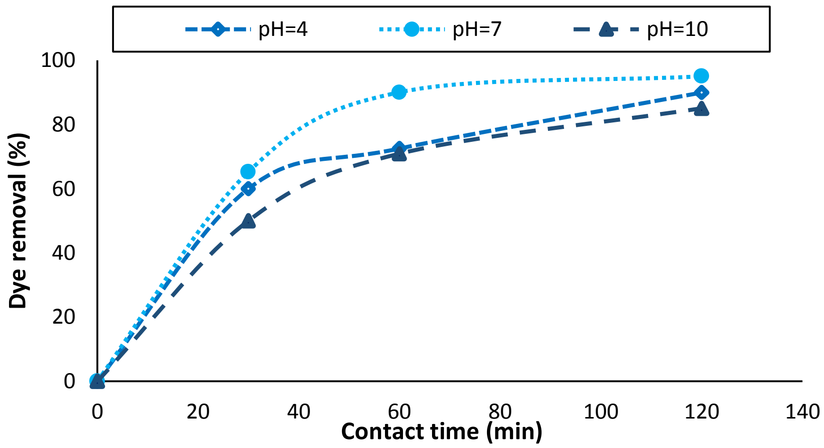

Figure 4. The effect of pH on the adsorption of RB5 (conditions: Initial dye concentration= 50 mg/L and adsorbent dose= 0.5 g/L)

Effect of initial dye concentration

Initial dye concentration is another significant factor in the adsorption process. Therefore, in the present study, to investigate the effect of variation of initial dye concentration on the adsorption efficiency in removal of RB5, the dye concentration was varied from 50 to 200 mg/L. The adsorption of RB5 on MWCNT vs. contact time at different initial concentrations has been presented in figure 5. It was observed that the adsorption of RB5 onto MWCNT decreased with increasing initial dye concentration. According to the results, the adsorption efficiency of RB5 at initial dye concentration of 50 and 200 mg/L was 93 and 37.2%, respectively, after 120 min. This is due to the limitation of free places available on MWCNT for RB5 adsorption resulting from the increased initial dye dose. Previous studies have observed similar results for removing Reactive Orange 12, Reactive Red 2 and Reactive Blue 4 [4]. Based on the results, adsorption increased with increasing contact time.

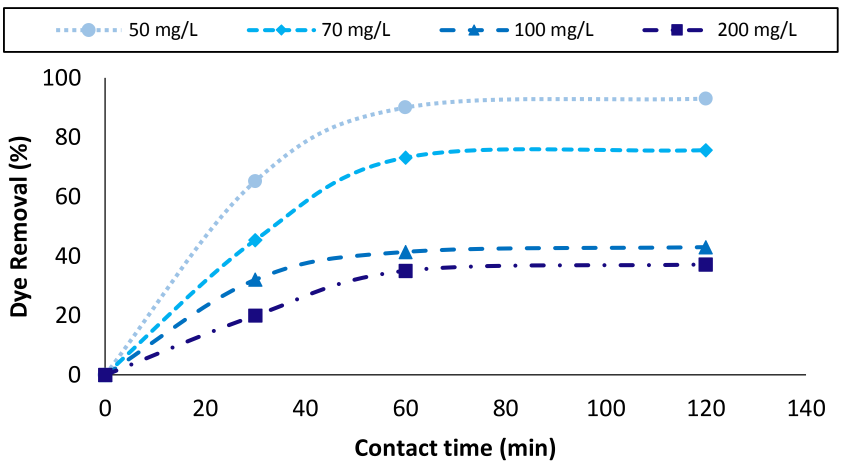

Figure 5. The effect of initial dye concentration on the adsorption of RB5 (conditions: pH= 7 and adsorbent dose= 0.5 g/L)

Effect of adsorbent dosage

To examine the effect of adsorbent dosage on the removal efficiency of RB5, adsorption experiments were carried out with different concentrations of MWCNTs (0.05, 0.1 and 0.5 g/L). The adsorption of RB5 on MWCNT vs.

contact time at adsorbent dosage has been presented in figure 6. As shown, the adsorption efficiency of RB5 in the presence of 0.05 and 0.5 g/L of MWCNT was 13.8 and 93%, respectively, after 120 min. Therefore, the adsorption efficiency of RB5 increased with increasing adsorbent dosage. This can be attributed to the greater availability surface site stemming from the increased adsorbent dosage. This observation accords with the results of Reactive Orange 12 removal with coir pith activated carbon conducted by Santhy and Selvapathy [4]. These findings were also consistent with Zhang et al. who studied the adsorption of copper ions from Water using chemical modified MWCNTS [12].

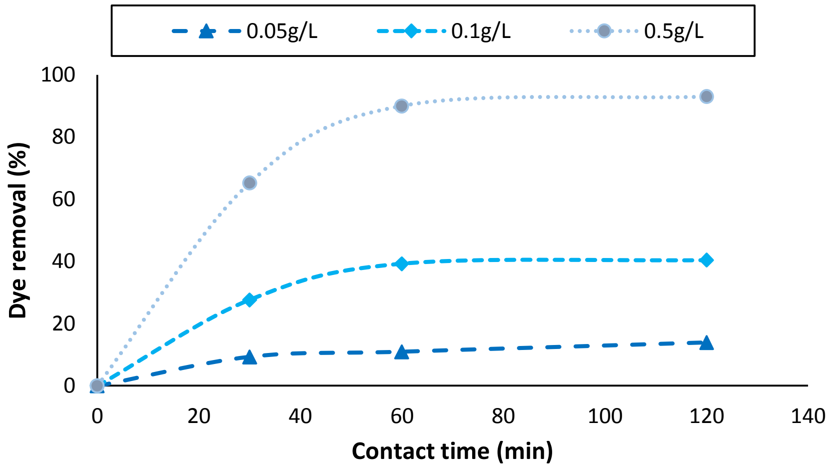

Figure 6. The effect of adsorbent dosage on the adsorption of RB5 (conditions: initial dye concentration= 50 mg/L, pH= 7 and adsorbent dose= 0.5 g/L)

Variation of adsorption capacity and equilibrium time

The variation in dye adsorption capacity in adsorption process by MWCNT has been shown in figure 7. The adsorption capacity increased sharply with increasing contact time from 15 to 45 min, and then increased slightly, even with increasing contact time to 90 min. Therefore, maximum adsorption capacity was found to be 36.2 mg/g in 90 min. This figure is higher than the maximum adsorption capacities reported for some other active carbon as adsorbents in previous studies [14,15,16]. This result is important because the adsorption capacity is one of the considerations for economical application in the removal of pollutants from water and wastewater for greater scales.

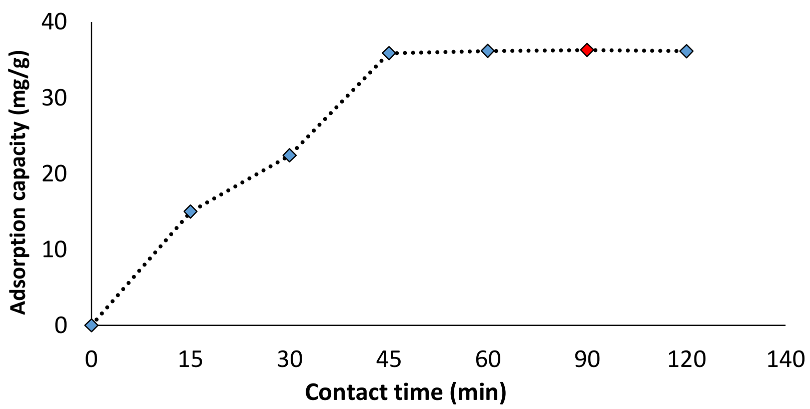

Figure 7. The variation of adsorption capacity with the increasing contact time (conditions: initial dye concentration= 50 mg/L, pH= 7 and adsorbent dose= 0.5 g/L)

Kinetics analysis

The adsorption kinetic models are used to determine the adsorption rate and adsorption system design. The adsorption rate coefficients are important physicochemical parameters to assay the quality of adsorbents [17]. In this study, in order to analyze adsorption kinetic onto MWCNT, three simplified kinetic models of pseudo zero-order, pseudo first-order and pseudo second-order were used. The results obtained revealed that the adsorption process followed the second-order kinetic model with a correlation coefficient values of 0.91(figure. 8).

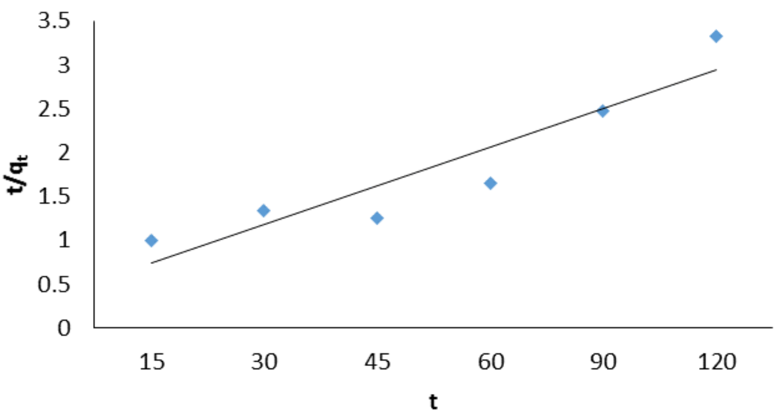

Figure 8. The results of kinetic study: second-order model

Isotherm analysis

To describe the dye uptake capacity and its adsorption behavior onto MWCNT, isotherm data were analyzed by using Langmuir and Freundlich isotherm models. The results illustrated that the isotherm data were fitted well with the Freundlich model with a correlation coefficient of 0.91. This can be due to different sites with several adsorption energies are involved. The results of isotherm studies have been shown in figure. 9.

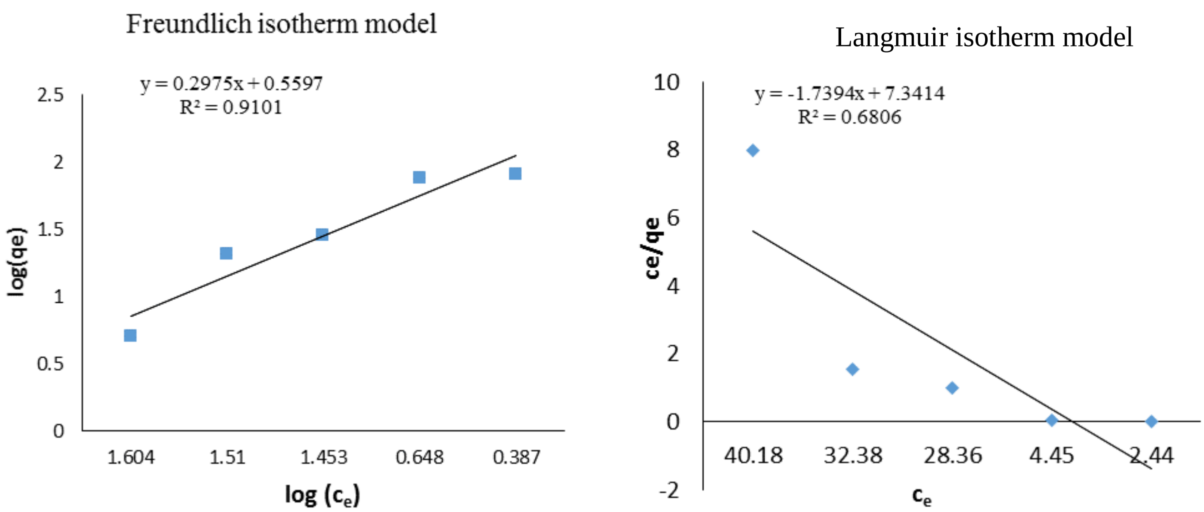

Figure 9. Isotherm models for adsorption of the dye onto MWCNT

CONCLUSION

In the present study, the efficiency of MWCNT in adsorption of RB5 from aqueous solution was studied. The effects of some parameters such as solution pH, initial dye concentration, adsorbent dosage and adsorption capacity on the adsorption of RB5 were investigated. It was found that RB5 removal by adsorption onto MWCNT was best achieved at pH 7. The adsorption efficiency of RB5 by MWCNT decreased with increasing initial dye concentration. The adsorption efficiency increased with increasing MWCNT dosage. The maximum adsorption capacity was found to be 36.2 mg/g after 90 min. The results obtained from kinetic studies showed that RB5 removal followed the second order model. Moreover, the isotherm data were fitted well with the Freundlich model. As a whole, it is concluded that MWCNT can be used as a suitable adsorbent for removing dyes from wastewater.

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