



Adsorption of reactive blue 29 dye from aqueous solution by multiwall carbon nanotubes

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Received 30 September 2011; Accepted 4 March 2013

ABSTRACT

Industrial effluents that carry dyestuff into natural water systems are serious environmental concern. The complex aromatic structures of dyes make them more stable and more difficult to remove from the effluents discharged into water bodies. Dyes are known pollutants that not only affecting esthetic merit but also reducing light penetration and photosynthesis, and some are considered toxic and even carcinogenic for human health. This study examined the feasibility of removing reactive blue 29 dye (RB29) from aqueous solutions using multiwall carbon nanotubes (MWCNTs) and oxidized MWCNTs. The effects of RB29 dye concentration, MWCNT and MWCNT-COOH dosage, and pH on adsorption of RB29 by both MWCNTs and MWCNT-COOH were also evaluated. Also, the adsorption isotherms of this dye on to carbon nanotubes (CNTs) and related constants were studied. Results showed that adsorption capacity of pristine MWCNTs was higher than oxidized MWCNTs due to negative charge put on the surface of MWCNT-COOH. The adsorption capacities of MWCNTs and MWCNTs-COOH in the best conditions were 49 and 34 mg/g, respectively. The results also demonstrated that adsorption capacity of RB29 on CNTs was higher in lower pHs due to significantly high electrostatic attraction exists between the positively charged surface of the adsorbent and negatively charged anionic dye. And finally the Freundlich isotherm showed the best conformity to the equilibrium data.

Keywords: Adsorption; Reactive blue 29 dye; MWCNTs; Isotherm; Oxidized MWCNTs

1. Introduction

Many industries, including textile companies, dye manufacturers, food-processing companies, paper and pulp mills, and electroplating factories, release waste-

water containing dyes and thereby contaminate water resources [1].

Dyes are color organic compounds that can be used as color-agent for the colorization of other substances, such as textile, string and clothes in textile industries. The complex aromatic structures of dyes

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make them more stable and more difficult to remove from the effluents discharged into water bodies [2].

The waters containing color compounds are esthetically objectionable for drinking and other purpose [3]. Dyes can cause allergy, dermatitis, skin irritation [4], and also provoke cancer [5] and mutation in humans [6,7].

Nonetheless, dyes are extensively used in textiles, paper, rubber, plastics, leather, cosmetics, pharmaceuticals, and food industries, resulting in a steadily growing demand and production. Due to the regulations worldwide have grown stricter, the effluents of textile and related industry have to be treated carefully before discharge [8,9].

There are several methods to remove dyes, such as physical chemical and biological processes, to treat wastewaters including organic pollutant and dyes [10,11]. Examples of these processes including coagulation/flocculation [12], ozone treatment [13], chemical oxidation [14], membrane filtration [15], ion exchange [16], photocatalytic degradation [17], and adsorption [18]. Although chemical and biological approaches are effective in removing dyes, they require special equipment and are usually energy intensive; additionally, these processes often generate large amounts of byproducts [19]. The most commonly used methods for color removal are biological oxidation and chemical precipitation. However, these processes are effective and economic only in the case where the solute concentrations are relatively high.

Among all existing techniques, the adsorption processes has proven to be an effective and attractive process for the treatment of these dye-bearing waste waters. The adsorption characteristics of dyes on various adsorbents have been extensively investigated for many purposes involving separation and purification [20].

It is well known that adsorption is based on equilibrium separation process. The common adsorbents primarily include activated carbons, zeolites, clays, industrial by-products, agricultural wastes, biomass, and polymeric materials [21]. However, these adsorbents described above suffer from low adsorption capacities and separation inconvenience. Therefore, efforts are still needed to carry out investigation for new promising adsorbents. Among the adsorbent, carbon nanotube (CNT) materials have been proposed for the successful removal of dyes from aqueous effluents [1].

According to the grapheme layer, CNTs can be classified into single-wall CNTs (SWCNTs) and multi-wall CNTs (MWCNTs) [22].

Due to their large specific surface area, small size, and hollow and layered structures, CNTs have been proven to possess great potential as superior

adsorbents for removing many kinds of organic and inorganic contaminant [23].

Understanding the kinetic and equilibrium of the adsorption is critical for the development of more efficient adsorbents suitable for real environmental applications.

According to literature review, no study has determined the parameters that govern adsorption of reactive blue dyes on to MWCNT and MWCNT-COOH. Therefore, the use of MWCNT and MWCNT-COOH for reactive blue dye adsorption requires new studies on this topic.

This study elucidates the equilibrium of adsorption of Reactive Blue 29 dye (RB29) by MWCNTs and MWCNT-COOH. The Langmuir and Freundlich Isotherms were utilized to fit equilibrium data of adsorption, and the adsorption rates were determined quantitatively.

The objectives of this study are to (1) determine the effects of initial dye concentration, effect of pH on adsorption of RB29 onto MWCNTs and MWCNT-COOH, (2) measure the coefficients of Langmuir and Freundlich isotherms, and (3) comparison efficiency of MWCNT and MWCNT-COOH in the removal of RB29 from aqueous solution.

2. Materials and methods

2.1. Materials

MWCNTs were prepared through a special Combustion chemical vapor deposition method in Research Institute of Petroleum Industry (RIPI), Tehran, Iran. The MWCNTs were synthesized from the CH_4/H_2 mixture by chemical vapor deposition method at 700°C using Ni particles as a catalyst. The outer diameter of MWCNTs was greater than 10 nm, and the mass ratio of amorphous carbon of MWCNTs was less than 5%. The Raman spectroscopy was used for the evaluation of amorphous carbon.

The commercial RB29 (Molecular structure, $\text{C}_{31}\text{Cl}_2\text{H}_{19}\text{N}_5\text{O}_9\text{S}_2\text{Na}_2$; relative molecular weight 788 g/mol; maximum absorption wavelength 589 nm) was supplied from sigma Aldrich Company and was used without any further purification. Fig. 1 displays the structure of RB29. The molecular formula of RB29 is $\text{C}_{29}\text{H}_{15}\text{Cl}_2\text{N}_5\text{Na}_2\text{O}_9\text{S}_2$. Double-distilled water was used to prepare all the solution.

2.2. Purification of MWCNTs

In order to purification and removal of the metal nanocatalysts from CNTs surfaces, the final products were dissolving in 37% hydrochloride acid solution

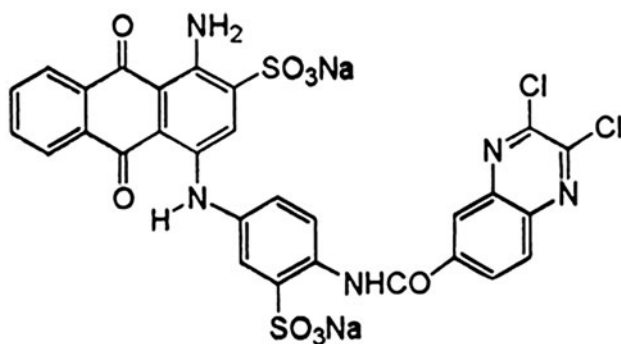


Fig. 1. Molecular structure of reactive blue 29 dye.

for about 16 h at ambient temperature and then washed several times with distilled water until the pH of the solution reached approximately neutral. Treated MWCNTs were dried in vacuum at 40°C overnight. For eliminate the amorphous carbons, all of the purified MWCNTs were placed in the furnace at 400°C for 30 min.

2.3. Functionalization of MWCNTs

In this work, for functionalization of CNTs, we used the H₂O₂ solution and ozone instead of acid treatment. This method previously reported by Naeimi et al. [24]. In this method, 1 g of purified MWCNTs was added to 150 mL of hydrogen peroxide (30%) and sonicated for 15 min. The temperature of the ultrasound bath was kept at 25°C with recirculation of water. The suspending mixture was then placed in a vertical held Pyrex reactor that equipped with a gas sparger (Mott Company, Multiple Elements Type 6400 Elements Side Mounted, stainless steel porous media, flow rate 6 gpm). A stream of ozone was continuously passed through the sample for 4 h. Then, the resulting mixture was filtered through the 0.2-mm poly carbonate membrane and washed with a large excess of methanol to remove any remaining H₂O₂. The product was dried in an oven at 120°C for 5 h.

2.4. Batch adsorption experiments

Adsorption kinetic experiments were conducted by preparing a 250-mL glass bottle containing 50 mg of MWCNT and different concentration of RB29 solution to determine the minimum time required for adsorption to reach a steady-state condition. The bottles were placed on a magnetic shaker and were shaken until reach to equilibrium.

After shaking and reaching to equilibrium time, the suspension was filtered through a 0.45-μm filter,

and the filtrate was analyzed by UV–vis spectrophotometer in wave length of 589 nm. The amount of RB29 dye adsorbed by MWCNTs was calculated from:

$$q = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where q is the amount of RB29 dye adsorbed by MWCNTs (mg/g); C_0 is the initial RB29 dye concentration (mgL⁻¹); C_e is the final RB29 dye concentration after a certain period of time (mgL⁻¹); V is the initial solution volume (l) and m is the MWCNTs dosage (g).

The influence of solution pH values on dye removal was also studied by adding defined amount of the MWCNT adsorbents in to the glass bottles containing 50 mL of different dye solution with pH values ranging from 2 to 12. Dye adsorption isotherms were determined at the optimum of pH, and the initial concentrations of reactive dyes were varied from 5 to 30 mg L⁻¹.

2.5. Determination of oxygen groups

The surface groups of the studied carbon materials were determined by the Boehm titration method. The acidic sites were determined by mixing small quantities (0.1 g) of each carbon material with 10 mL of different bases (0.1 M NaOH, 0.1 M NaHCO₃, or 0.05 M NaCO₃) in 25-mL beakers. The beakers were sealed and shaken for 24 h. The solutions were then filtered and titrated with 0.05 M H₂SO₄. Similarly, the basic sites were determined by mixing 0.1 g of each carbon material with 10 mL of 0.1 M HCl. The obtained solutions were titrated with 0.1 M NaOH.

3. Results and discussion

3.1. Properties of adsorbents

MWNTs were prepared with diameter ranging from 10 to 50 nm, lengths varying from 1 to 3 mm. The diameters and lengths of MWCNTs were determined by Raman spectroscopy and atomic force microscopy. SEM images and XRD spectra of MWCNTs and functionalized MWCNTs are shown in Figs. 2 and 3, respectively.

Fig. 3 indicates that XRD patterns of functionalized MWCNTs are similar to that of unmodified MWCNTs. It can be concluded that functionalized MWCNTs still had the same cylinder wall structure as unmodified MWCNTs. The peaks at 20, 24, and 43 relate to graphene structure of CNTs that were sharper in functionalized nanotubes.

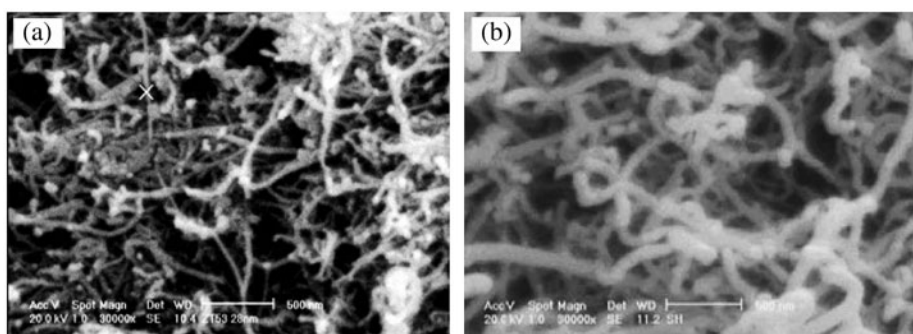


Fig. 2. SEM (30,000 \times) images of (a) pristine and (b) oxidized MWCNTs.

The amount of carboxylic groups on oxidized MWCNT which analyzed by Bohem titration method was increased from 0.7 mmol/g on pristine tubes to 5.2 mmol/g on oxidized MWCNTs.

3.2. Effect of pH on adsorption

The effect of pH on the adsorption of Reactive Blue dye by MWCNTs was studied by varying the pH of the dye solution from 2 to 12 for an initial concentration of 30 mg/L and MWCNTs dosage of 50 mg (Fig. 4).

Maximum adsorption occurs at acidic pH (pH 2). The lower adsorption of RB 29 at alkaline pH is because of the presence of excess OH^- ions competing with the dye anions for the adsorption sites. At pH 2, a significantly high electrostatic attraction exists between the positively charged surface of the adsorbent and negatively charged anionic dye [25]. As the pH of the system increases, the number of negatively charged sites increases and the number of positively charged sites decreases. A negatively charged surface site on the adsorbent did not favor the adsorption of anionic dye due to electrostatic repulsion. A similar

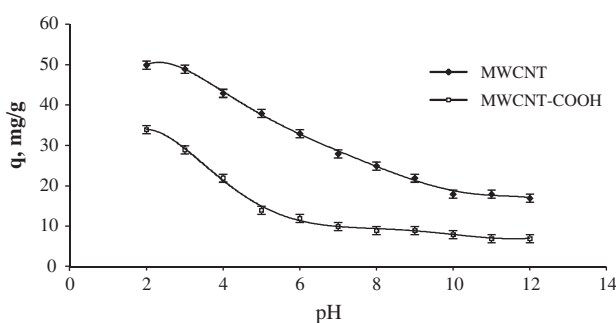


Fig. 4. Effect of pH for the adsorption of RB 29 dye onto MWCNT and MWCNT-COOH.

result was observed for the adsorption of acid red 14 by soy meal hull [26] and Congo red by baggese fly ash [27].

3.3. Effect of contact time and initial concentrations

Figs. 5 and 6 present the effect of initial concentration for the adsorption of RB29 on MWCNTs and MWCNTs-COOH. As shown in these figures, the amount of RB29 adsorbed on to CNTs increased with contact time for all RB29 concentrations.

The curves reveal that the adsorption kinetics of reactive dye 29 on CNTs mainly consists of two stages: an initial rapid stage related to the instantaneous external surface adsorption of metal ions. The second slower stage is the gradual adsorption stage that takes place before metal ion uptake attains equilibrium. The high adsorption rate during the initial period of 15 min is due to the number of available adsorption sites of the bare surface of adsorbents. As these sites became progressively covered, the rate of adsorption decreased.

According to Figs. 5 and 6 in low initial concentrations, the slight differences in amount of adsorption between both adsorbents were observed. But the

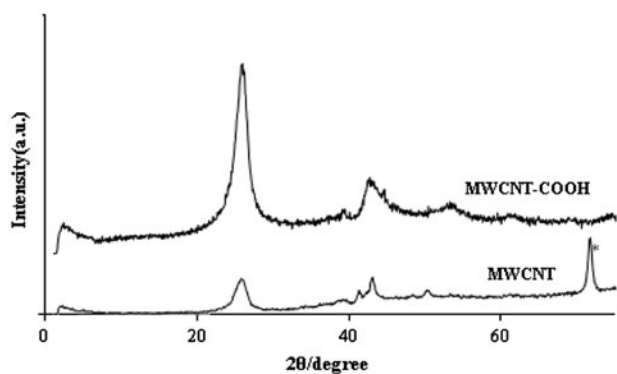


Fig. 3. XRD spectra of (a) pristine MWCNTs and (b) oxidized MWCNTs.

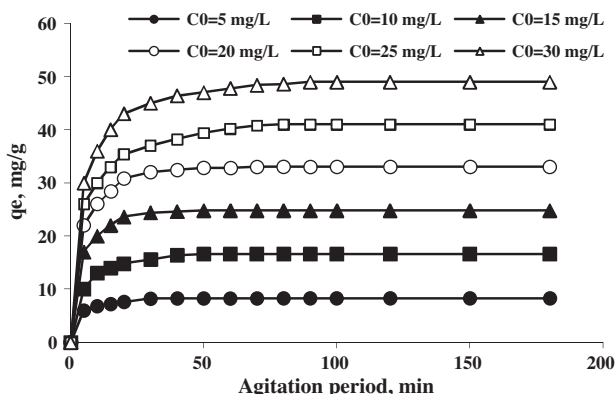


Fig. 5. Effects of initial concentration on the adsorption of RB 29 dye on MWCNTs (CNT dosage = 50 mg and $T = 25^\circ\text{C}$).

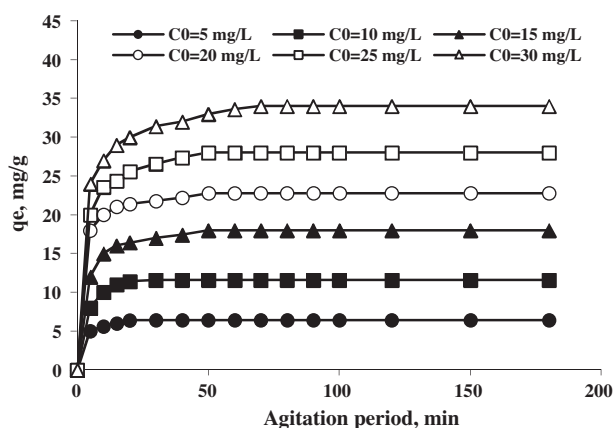


Fig. 6. Effects of initial concentration on the adsorption of RB 29 dye on MWCNTs-COOH (CNT-COOH dosage = 50 mg and $T = 25^\circ\text{C}$).

results of the lower uptake amount for MWNTs-COOH in high initial concentration (high driving force) indicate that surface chemical properties rather than specific surface areas or pore volume are crucial factors to determine the final adsorption ability of MWNTs. These figures also show that the adsorption capacities of MWCNTs and MWCNTs-COOH in the best conditions were 49 and 34 mg/g, respectively.

According to results from XRD spectra and back titration method, functionalization of MWCNTs with H_2O_2 in the presence of ozone made the surface of MWCNTs negatively charged. Previous studies indicated that carboxylic groups on the surface of MWCNTs acted as electrons withdrawing groups localizing electron from π system of MWCNTs, which might be expected to interfere with and weaken π - π dispersion forces between the aromatic ring of reactive blue dyes and the graphitic structure of MWCNTs [28].

3.4. Isotherms studies

Adsorption kinetic studies are important in the treatment of aqueous effluents because they provide valuable information on the mechanism of the adsorption process.

In general, the adsorption isotherm describes how adsorbates interact with adsorbents, and this is critical in optimizing the use of adsorbents. Two commonly used isotherms, such as Langmuir and Freundlich, were selected for this study.

Although the Langmuir and Freundlich isotherms were firstly introduced about 90 years ago, they still remain the two most commonly used sorption isotherm equations. Their success undoubtedly reflects their ability to fit a wide variety of sorption data quite well.

The Langmuir model represents chemisorptions on a set of well-defined localized adsorption sites, having the same sorption energies independent of surface coverage and no interaction between adsorbed molecules. Langmuir isotherm assumes monolayer coverage of adsorbate onto sorbent. Freundlich isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. This isotherm does not predict any saturation of the adsorbent surface; thus, infinite surface coverage is predicted, indicating physisorption on the surface.

Theoretically, the adsorbent has a finite capacity to adsorb the adsorbate. Therefore, a saturation value is reached beyond which no further adsorption takes place [29]. The monolayer capacity can be represented by the expression:

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

The linear form of the above equation is represented as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (3)$$

where C_e is the concentration of the dye solution (mg/L) at equilibrium, q_e the amount of dye adsorbed per unit weight of adsorbent (mg/g), and K_L is the constant related to the free energy of adsorption (L/mg). Q_m is the maximum adsorption capacity. The values of Q_m and K_L were calculated from the slope and intercept of the linear plot.

An essential characteristic of Langmuir isotherm can be expressed in terms of a dimensionless constant called equilibrium parameter [30]:

Table 1
Isotherm model constants for the adsorption of RB29 on MWCNTs and MWCNTs-COOH

Adsorbent	C_0 (mg/l)	Freundlich			Langmuir		
		K_f (mg/g) (mg/L) ⁿ	n	R^2	q_m (mg/g)	b (L/mg)	R^2
MWCNTs	5–30	2.68	1.03	0.99	55.7	9.88	0.77
MWCNTs-COOH	5–30	1.77	1.84	0.99	35.6	3.4	0.70

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

where K_L is the Langmuir constant and C_0 is the highest initial dye concentration (mg/L). The value of R_L indicates the type of isotherm to be favorable ($0 < R_L < 1$), linear ($R_L = 1$), unfavorable ($R_L > 1$) or irreversible $R_L = 0$.

Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The Freundlich equation is commonly given by:

$$q_e = K_F C_e^{1/n} \quad (5)$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e the equilibrium concentration of solute in the bulk solution (mg/L), K_F the Freundlich constant indicative of the relative adsorption capacity of the adsorbent (mg/g), and $1/n$ is the heterogeneity factor.

The linearized of this equation can be described as the following:

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

A plot of $\log q_e$ vs. $\log C_e$ enables the constant K_F and exponent $1/n$ to be determined from the intercept and slope of the line, respectively.

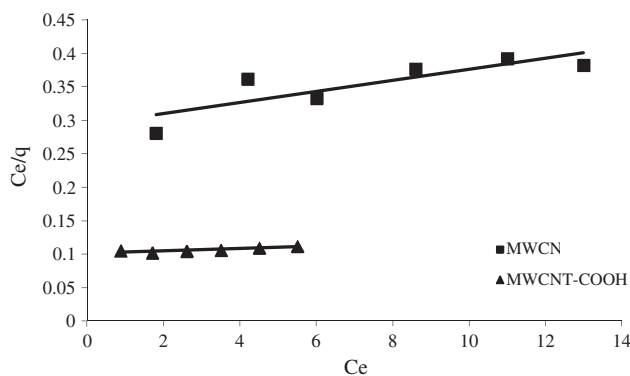


Fig. 7. Langmuir isotherm for adsorption of RB29 on MWCNTs and MWCNT-COOH.

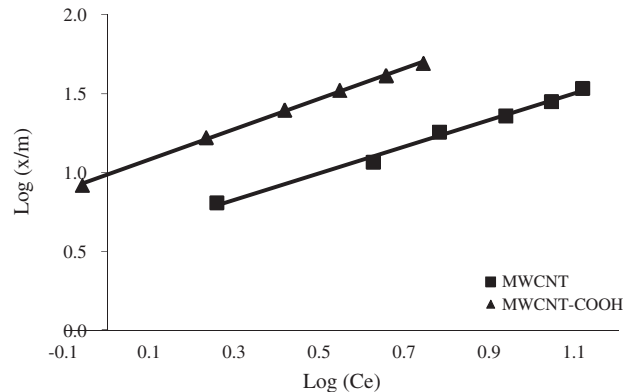


Fig. 8. Freundlich isotherm for adsorption RB29 on MWCNTs and MWCNT-COOH.

The magnitude of $1/n$ quantifies the favorability of adsorption and the degree of heterogeneity on the surface of CNTs. If $1/n$ is less than unity—suggesting favorable adsorption—adsorption capacity increases and new adsorption sites form. Higher value for K_F indicates higher affinity for adsorbate and the values of the empirical parameter $1/n$ lie between $0.1 < 1/n < 1$, indicating favorable adsorption [31].

Figs. 5 and 6 show the Adsorption Langmuir and Freundlich isotherms of RB29 on CNTs respectively. The isotherm parameters are shown also in Table 1.

Based on the linear isotherm equations and according to Figs. 7 and 8 and using the constants in Table 1, the correlation coefficients, R^2 , in the table indicate that the Freundlich isotherm data was appropriate to describe the adsorption characteristics of RB29 onto both MWCNTs and MWCNT-COOH.

The plots in Fig. 8 are typical and demonstrate that the Freundlich equation provides an accurate description of the experimental data, which is further confirmed by the extremely high values of the correlation coefficients for the dye-CNTs systems. The high degree of correlation for the linearized Freundlich relationship describes equilibrium on heterogeneous surfaces and hence does not assume monolayer capacity. These results are in accordance with PengLuo et al that examined adsorption of neutral red from

aqueous solution on to hollow site nanotubes and suggested that Freundlich isotherm is more appropriate for describe the adsorption of neutral red on to nanotubes [32]. Also Crittenden et al reported that the Freundlich model is used to describe the data for heterogeneous adsorbent such as activated carbon [33].

4. Conclusion

In this study, the performance of MWCNTs and MWCNTs-COOH to remove RB29 from aqueous solution has been investigated. Equilibrium isotherms have been measured and analyzed using Langmuir and Freundlich equations for this reactive dye.

The experimental observations are summarized below:

- Based on the results from our experiments, by increasing initial concentration of RB29, the adsorption of RB 29 dye per unit weight of MWCNTs increased.
- Due to negative charge created on the surface of MWCNTs due to hydrogen peroxide and ozone treatment, the adsorption capacity of MWCNTs-COOH was lesser than pristine MWCNTs.
- Adsorption capacity of RB29 on both MWCNTs and MWCNTs-COOH was higher in lower pH, because a significantly high electrostatic attraction exists between the positively charged surface of the adsorbent and negatively charged anionic dye.
- The Freundlich isotherm equation gave the best correlation for the adsorption of RB29 on MWCNTs and MWCNTs-COOH.

Acknowledgment

The authors are grateful to the Student Scientific Research Center, Tehran University of Medical Sciences for the financial support as well as all laboratory staffs of Department of Environmental Health Engineering, Tehran University of Medical Sciences.

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