Original Article

Application of Multi-Walled Carbon Nanotubes in the Removal of Reactive Red 120 from Aqueous Solutions

***Edris Bazrafshan**[1] Ferdos Kord Mostafapour[1] Ali Reza Hoseini[1] Mohammad Ali Zazouli[2]

1- Health Promotion Research Center, Zahedan University of Medical Sciences, Zahedan, Iran
2- Department of Environmental Health Engineering, School of Health AND Health Sciences Research Center, Mazandaran University of Medical Sciences, Sari, Iran

***e_Bazrafshan@yahoo.com**

(Received: 15 Sep 2014; Revised: 4 Nov 2014; Accepted: 9 Feb 2015)

Abstract

Background and purpose: Textile effluents are very difficult to treat satisfactorily due to high variations in their compositions. Strong color is one of the main characteristics of textile effluent and, if not eliminated, it can cause serious problems to the environment. In the present study, multi-walled carbon nanotubes (MWCNTs) were used as an adsorbent for the removal of Reactive Red-120 (RR-120) textile dye from aqueous solutions.

Materials and Methods: The influence of key parameters including pH (2-12), concentration of dye (10 to 200 mg/L), contact time (30-270 min), adsorbent dosage (0.01-0.07 g/L) have been investigated in order to find the optimum adsorption conditions (sample size = 48).

Results: Optimum pH for removing of RR-120 dye was found to be 5 and for this condition maximum adsorption capacity was obtained as 3453.4 mg/g. Experimental results have shown that 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. It was found that the data fitted to Langmuir better than BET and Freundlich model.

Conclusion: Results suggest the potential of using the MWCNTs as an adsorbent for effective treatment of dye-contaminated wastewaters.

*[*Bazrafshan E, Kord Mostafapour F, Hoseini AR, Zazouli MA.* **Application of Multi-Walled Carbon Nanotubes in the Removal of Reactive Red 120 from Aqueous Solutions**. *IJHS 2015; 3(1): 33-43] http://jhs.mazums.ac.ir*

***Key words*:** Reactive Red-120 dye, Adsorption, Multi-walled carbon nanotubes

1. Introduction

Textile industries are one of the biggest consumers of water and complex chemicals during textile processing at different processing phases. The unused materials from the processes are discharged as wastewater that is high in color, biochemical oxygen demand, chemical oxygen demand (COD), pH, temperature, turbidity, toxic chemicals, and other impurities. The direct discharge of this wastewater into the water resources like lakes, rivers, etc., pollutes the water and affects the flora and fauna. Effluent from textile industries contains various types of dyes, which because of high molecular weight and complex structures, shows very low biodegradability (1-3). Furthermore, the direct discharge of this industrial effluent into sewage networks produces disturbances in biological treatment processes. These effluents produce high concentrations of inorganic salts, acids, and bases in biological reactors leading to the increase of treatment costs (4,5). The common dyes include reactive, disperse, acid, and direct dyes. Usually, the dyes are low in toxicity, easy to dissolve in water and can be applied for various industrial uses, including inks, cosmetics, soap, and foods (6).

Inappropriate treatment and disposal of dye-contaminated wastewaters from textile, dyeing, printing, ink, and related industries have provoked severe environmental concerns all over the world (7,8). Many methods have been described in the literature for color removal from dye-containing wastewater. These include adsorption (e.g. on active carbon), coagulation-flocculation, chemical oxidation (chlorination, ozonization, etc.), electrocoagulation and photodegradation (ultraviolet [UV]/H_2O_2, UV/TiO_2, etc.) (9,10). The routine treatment process of textile effluents involves several steps because of the features of the production process (11).

Conventional treatment involves a process of coagulation/flocculation. In fact, chemical coagulation is one of the most common and practical methods for removing the colloidal forms of pollution from wastewater and for COD abatement. This consists in destabilizing colloids, aggregating, and binding them together into flocculates; the resulting flocs can finally be removed either by settling or by flotation. This is a flexible process, which can be used alone or combined with biological treatments, as a way of removing suspended solids and organic material, as well as promoting the extensive removal of dyes from textile industry effluents (9,12,13). Nevertheless, this method presents the disadvantage of producing a large volume of sludge. This sludge is rich in various dyes, in addition to other substances used in the textile process. This is a problem, as the produced sludge must be discharged appropriately to avoid environmental challenges (11). In addition, enzymatic and biological treatment (14-17), chemical oxidation and photocatalytic processes (18), sonochemical processes and nanoparticles (19,20), and membrane processes (21), were used for color removal from textile effluents. Nonetheless, some of these procedures are limited due to their high operational costs and operating difficulties.

One of the most effective techniques for the removal of color from wastewater is adsorption by activated carbon. Moreover, adsorption process has proven to be a reliable treatment approach due to its low capital investment cost, ease of design, simplicity of operation and insensitivity to toxic substances, but the high cost of activated carbon limits its use, thus necessitating the development of suitable low-cost adsorbents (22).

Many studies have been conducted to evaluate adsorption of various dyes onto wide range of natural and synthetic, organic and inorganic sorbents (23-25). Carbon nanotubes (CNTs), which are considered to be extremely superior adsorbents due to their high specific surface area and large micropore volume,

have been utilized for the sorption of a number of different organic compounds and inorganic ions (26-29), since the first report of their successful removal of dioxin (30).

In the present work, multi-walled CNTs (MWCNTs) were chosen as sorbent for elimination of Reactive Red-120 (RR-120) dye. RR-120 is one of the frequently used dyes and is a potential threat to the aquatic environment due to its poor biodegradability. The main objective of this work was to investigate the adsorption of RR-120 dye on MWCNTs under various conditions. Afterward, the influence of several operating parameters such as initial pH of the solution, initial dye concentration, contact time, and MWCNTs dosage and was investigated

2. Materials and Methods

The studied textile dye (RR-120) was purchased from Merck Company. The key properties of the investigated dye are given in table 1 and figure 1. All chemicals and reagents used were analytical grade. Stock solution of RR-120 (1000 mg/L) was prepared by dissolving 1 g of dye in 1 L distilled water. Immediately, the solution was stirred for 1 h at 80°C, in order to ensure complete hydrolysis of the dye. The dye concentrations used in the adsorption process (10-200 mg/L) were obtained from dilution of the stock solution.

Table 1. Characteristics of the RR-120 dye

Characteristic	RR-120
Molecular formula	$C_{44}H_{24}C_{l2}N_{14}Na_6O_{20}S_6$
Color index name	RR-120
Molecular weight	1469,34 g/mol
Water solubility	70 (g/L)
λmax	515
Class	Diazo (-N=N- bond)

RR-120: Reactive red-120

MWCNTs (provided from Research Institute of Petroleum Industry, Tehran, Iran) were selected as adsorbents to study the adsorption characteristics of RR-120 from aqueous solutions. On the basis of the information provided by the manufacturer, the MWCNTs were synthesized by catalytic chemical vapor deposition method. Figures 2 and 3 show the scanning electron microscopy and transmission electron microscopy images of MWCNTS. The size of the outer diameter for the MWCNTs was 10-30 nm. The length of MWCNTs was 10 µm. Furthermore, specific surface area of MWCNTs was more than 270 m^2/g, and the mass ratio of the amorphous carbon of MWCNTs was <5%.

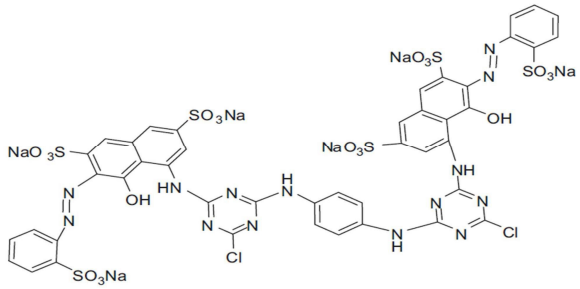

Figure 1. Chemical structure of the Reactive Red-120

In order to functionalize MWCNTs, 0.3 g of the MWCNTs was dispersed in 25 ml of nitric acid (65 wt %) in a 100 ml round bottom flask equipped with a condenser and the dispersion was refluxed under magnetic mixing for 48 h. Next, the resulting dispersion was diluted in distilled water and filtered. The resulting solid was washed up to neutral pH, and the sample was dried in a vacuum at 40°C overnight.

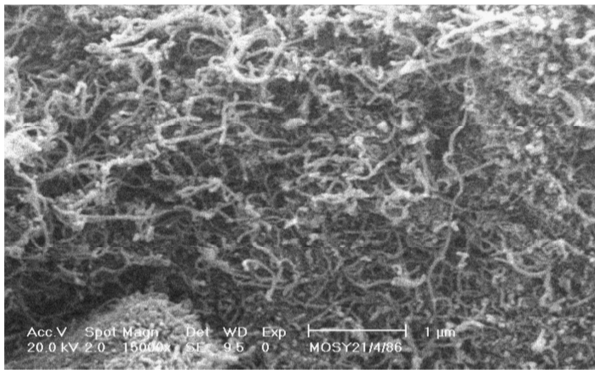

Figure 2. Scanning electron microscopy image of multi-walled carbon nanotubes sample used for this study

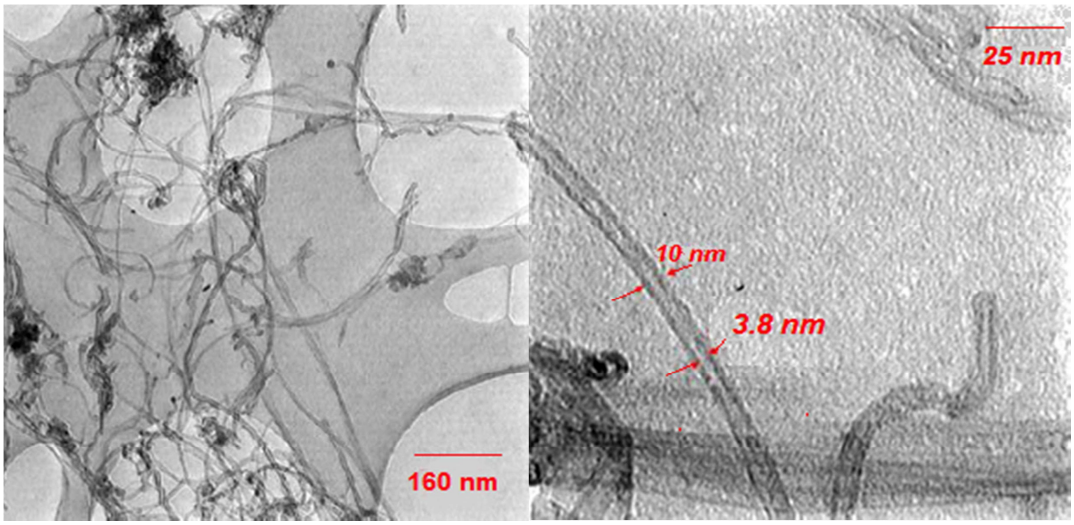

Figure 3. Transmission electron microscopy image of multi-walled carbon nanotubes sample used for this study

Adsorption was determined by the batch method. The parameters considered for the study were pH, adsorbent dose, initial concentration of adsorbate (RR-120) and contact time. Adsorption experiments were conducted in which aliquots of dye solution of known concentration were introduced into glass bottles 250 ml (containing 100 ml solution) containing predetermined amounts of MWCNTs. The pH of the solution was adjusted using 0.1 NHCl or NaOH solutions. The bottles were shaken at 21-23°C (room temperature) for a prescribed time. After the mixing time elapsed, the suspension was allowed to settle, and the supernatant after centrifugation at 4000 rpm was analyzed for the residual dye. RR-120 dye concentration was determined spectrophotometrically at λmax = 515 nm according to the Lambert–Beer law using a UV-VIS spectrophotometer (T80 PG Instruments Ltd.). Then the amount of dye (RR-120 dye) adsorbed, qe (mg/g), was obtained as follows:

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

where C0 and Ce are the initial and equilibrium liquid phase concentration of dye (mg/L), respectively. V is the volume of the solution (L) and M is the amount of adsorbent used (g).

To express the dye removal efficiency, the following equation was used:

$$\text{Removal efficiency (\%)} = \frac{(C_0 - C_f)}{C_0} \times 100 \quad (2)$$

Where C0 and Cf represent the initial and final (after adsorption) dye concentrations, respectively. All tests were performed in duplicate to insure the reproducibility of the results; the mean of the two measurements is reported.

3. Results

3.1. Effect of initial pH

Figure 4 shows the effect of initial pH of the solution on RR-120 dye adsorption onto MWCNTs. The adsorption of RR-120 dye onto MWCNTs is intimately dependent on solution pH. The adsorption capacity of RR-120 dye increases with increasing solution pH from 2 (2759.7 mg/g) to 5 (3453.4 mg/g) and changes slightly when solution pH is above 5. The maximum adsorption capacity of the MWCNTs was 3453.4 mg/g at pH 5, initial concentration of 50 mg/L and 22±1°C, when 69.07% of the dye was removed. As it can be

seen from figure 4, more increase of pH decreased adsorption capacity, and minimum capacity was attained at pH 12 (2552.9 mg/g). In addition, as presented in figure 4, dye removal efficiency increase with rise of pH and maximum removal efficiency (69.07%) was achieved at initial pH 5 and minimum efficiency achieved at pH 12 (51.06%).

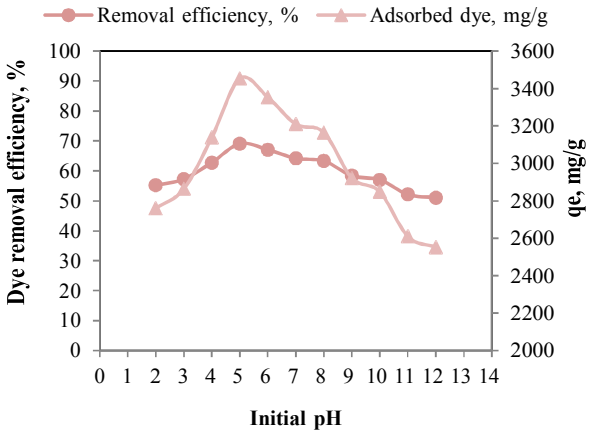

Figure 4. Effect of initial pH on the adsorption of Reactive Red-120 to multi-walled carbon nanotubes (C_0 = 50 mg/L, contact time = 180 min, adsorbent dosage = 0.01 g/L)

3.2. Effect of the amount of adsorbent (MWCNTs)

The effect of adsorbent dose on removal of RR-120 was studied by varying the dose of adsorbent from 1 to 7 g/L. The experiment was carried out at fixed dye concentration of 50 mg/L, at a fixed pH of 5 (optimum pH) for contact time 180 min.

From figure 5, it is evident that adsorbent dose significantly influences the amount of dye adsorbed. In fact, the percentage of RR-120 removal steeply increases with the adsorbent loading up to 0.05 g/L. The maximum adsorption efficiency of RR-120 onto MWCNTs at adsorbent dosage 0.05 g/L was found to be 92.79% (927.85 mg/g). Furthermore, dye adsorbed decreased as the dose of adsorbent increases from 1 to 7 g/L. In addition, minimum removal efficiency was achieved at adsorbent dose 0.01 g/L (~71%). Nevertheless, highest adsorption rate was obtained in 0.07 g of MWCNTs that was 93.31%.

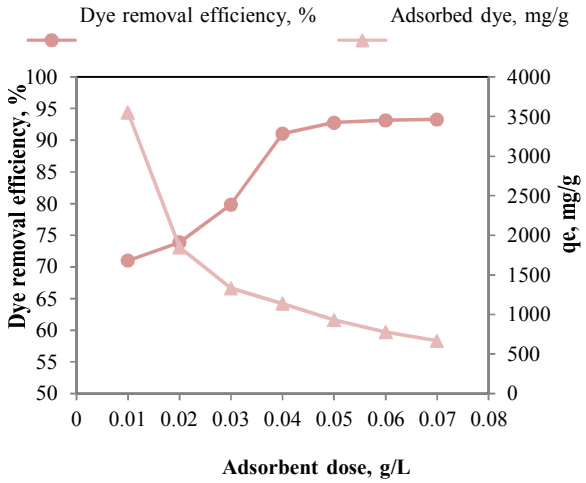

Figure 5. Effect of adsorbent dosage on Reactive Red-120 adsorption onto multi-walled carbon nanotubes (C_0 = 50 mg/L, contact time = 180 min, pH = 5)

3.3. Effect of contact time on RR-120 adsorption onto MWCNTs

Figure 6 shows the effect of contact time (30-270 min) on the adsorption capacity and percent removal efficiency of RR-120 dye onto the MWCNTs at a constant initial dye concentration (50 mg/L) and 0.05 g/L adsorbent dosage.

The uptake of RR-120 dye on MWCNTs, as shown in figure 6, depicts that the sorption is quite rapid initially, gradually slows down and then reaches the equilibrium. Nearly, 50-55% of the ultimate adsorption occurred within 30 min of contact. On the other hand, according to Figure 6, the RR-120 was rapidly adsorbed in the first 30 min (53.62%), and then the adsorption rate decreased gradually from 30 to 270 min and finally reached equilibrium in about 180 min (93.47%).

3.4. Effect of initial RR-120 dye concentration

To determine the effect of initial dye concentration on the adsorption process, the initial concentration of RR-120 was varied from 10 to 200 mg/L at a fixed pH equal 5 and

fixed amount of adsorbent 0.05 g/L for contact time 180 min. As presented in figure 7, dye removal efficiency decreased with increasing of dye concentration, so minimum efficiency was achieved at initial dye concentration 200 mg/L (50.36%).

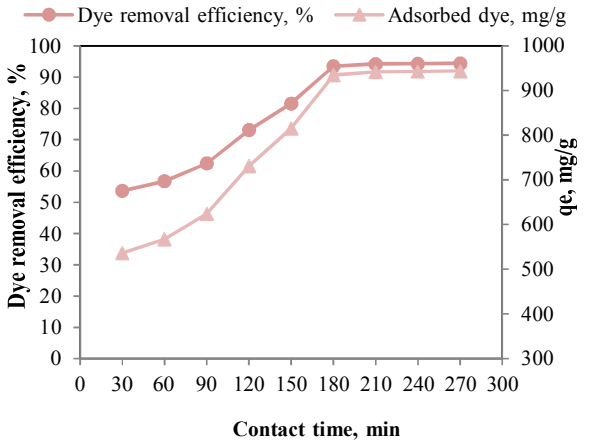

Figure 6. Effect of contact time on Reactive Red-120 adsorption onto multi-walled carbon nanotubes (C_0 = 50 mg/L, adsorbent dosage = 0.05 g/L, pH = 5)

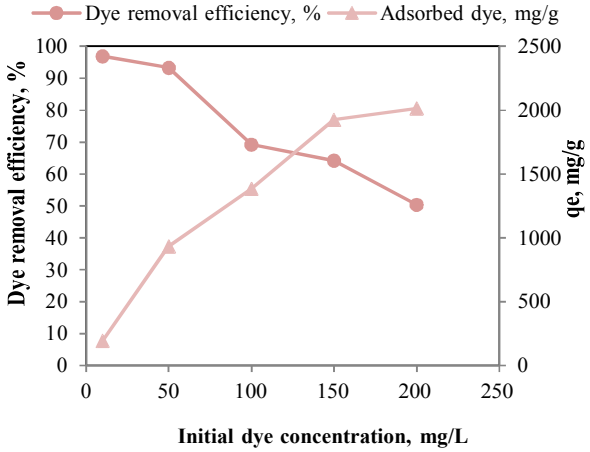

Figure 7. Effect of initial dye concentrations on Reactive Red-120 adsorption onto multi-walled carbon nanotubes (adsorbent dosage = 0.05 g/L, contact time = 180 min, pH= 5)

3.5. Adsorption isotherms

To optimize the use of MWCNTs adsorbent, it is important to establish the most appropriate adsorption isotherm. Furthermore, the isotherm provides a relationship between the dye concentration in solution (RR-120) and the amount of dye adsorbed on the solid phase when both phases are in equilibrium. At current work, equilibrium adsorption data were evaluated using the Langmuir, Freundlich and BET isotherm models (Figures 8-10). In addition, analyses of isotherms were used to describe the experimental adsorption data, and then best findings can be attained when correlation coefficients (R^2) come close to 1 (31). The liner form of used isotherm models (Langmuir, Freundlich, and BET) are as below:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_l}\frac{1}{C_e} \quad (3)$$

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \quad (4)$$

$$\frac{C_e}{(C_i - C_e)\, q_e} = \frac{1}{AX_m} + \frac{A-1}{AX_m} \quad (5)$$

where q_e is the amount of metal adsorbed per specific amount of adsorbent (mg/g), C_e is equilibrium concentration of RR-120 dye (mg/L), K_L is Langmuir constant and q_m is the maximum amount of RR-120 dye required to form a monolayer (mg/g). K_f and 1/n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. C_i is the initial concentration of dye in solution (mg/L), A is a constant to describe the energy of interaction between the solute and the adsorbent surface and Xm is the amount of solute adsorbed in forming a complete monolayer (mg/g).

Isotherm data were applied to three adsorption models, and the results of their linear regression were used to find out the fit model among them. Values of resulting parameters and regression coefficients (R^2) are listed in table 2. The R^2 values of Langmuir, Freundlich and BET models (Table 2) are 0.9981, 0.9332 and 0.9913, respectively, indicating that the Langmuir model is more suitable for describing the adsorption equilibrium of RR-120 dye onto MWCNTs.

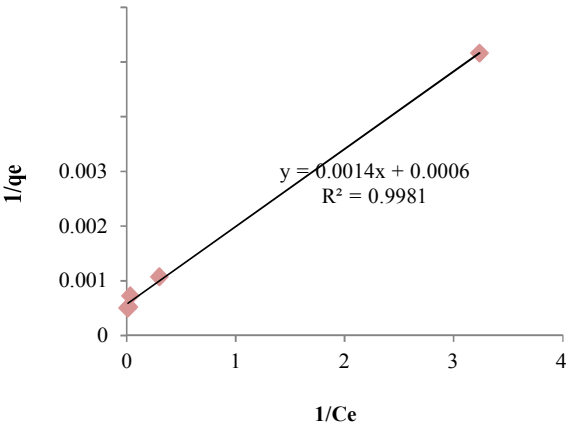

Figure 8. Langmuir isotherm for sorption of Reactive Red-120 onto multi-walled carbon nanotubes (R^2 = 0.9981)

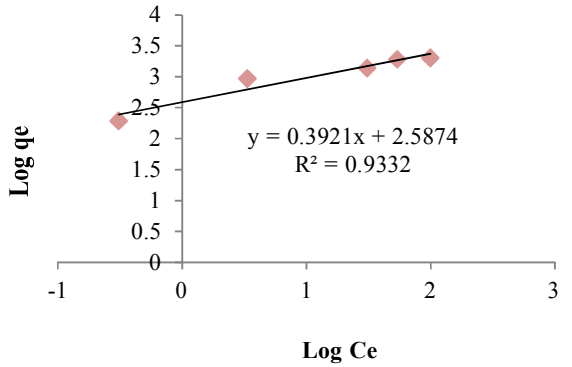

Figure 9. Freundlich isotherm for sorption of Reactive Red-120 onto multi-walled carbon nanotubes (R^2 = 0.9332)

4. Discussion

4.1. Effect of initial pH

It is known that the solution pH can affect the surface charge of the adsorbent, the degree of ionization of the different pollutants, the dissociation of functional groups on the active sites of the adsorbent as well as the structure of the dye molecule (28). On the other hand, the solution pH would affect both aqueous chemistry and surface binding sites of the adsorbent. Hence, the solution pH is an important parameter during the dye adsorption process. As presented in figure 4, optimum pH of 5 was achieved for RR-120 removal by MWCNTs. The higher adsorption of the dye at lower pH is apparently due to greater accessibility of the dye to the active sites and more facile diffusion. It is well-known that the surface charge of the adsorbent and the ionic charge of the dye molecule play an important role in the adsorption. In acidic solution (lower pH), there is increased protonation of the dye. The negative charge developed on the surface of the adsorbent especially by the hydroxyl groups serve as active sites and cause strong electrostatic attraction for the anionic dye in solution. This causes the preference of the dye for active sites and facilitates the diffusion and adsorption process. While, with an increase in alkaline conditions or pH, protonation of dye is reduced, thereby retarding diffusion and adsorption. Similar findings were reported by Shirmardi et al. (31).

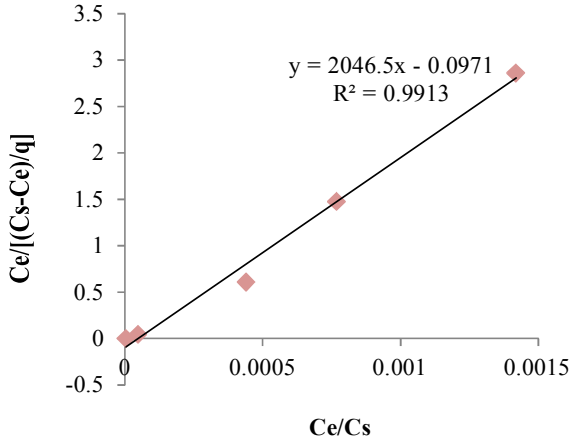

Figure 10. BET isotherm for sorption of Reactive Red-120 onto multi-walled carbon nanotubes (R^2 = 0.9913)

Table 2. Isotherm model parameters for the adsorption of RR-120 onto MWCNTs

Langmuir isotherm			Freundlich isotherm			BET isotherm		
q_m (mg/g)	k_L (L/mg)	R^2	k_f	n	R^2	A	Xm (mg/g)	R^2
1666.7	0.43	0.9981	386.72	2.55	0.9332	359.1	0.00049	0.9913

MWCNTs: Multi-walled carbon nanotubes, RR-120: Reactive Red-120

4.2. Effect of the amount of adsorbent (MWCNTs)

As it can be seen from figure 5, there was a non-significant increase in the percentage removal of RR-120 when the adsorbent concentration increases beyond the 0.05 g/L. This suggests that after a certain dose of biosorbent, the maximum adsorption is attained and hence the amount of pollutants remains constant even with a further addition of the dose of adsorbent (32). Furthermore, when the adsorbent dosage increased, percentage removal of RR-120 also increased but amount of adsorbed RR-120 of per gram adsorbent decreased due to the fact that fixed dye concentration (50 mg/L) led to unsaturated active site on adsorbent surface and increase in the adsorbent concentrations caused particle aggregation (33). Similar findings were reported by other researchers (34,35).

4.3. Effect of contact time on RR-120 adsorption onto MWCNTs

The contact time between adsorbate and adsorbent is one of the most important design parameters that affect the performance of adsorption processes. The adsorption capacity and percent removal of RR-120 dye onto the MWCNTs drastically increase during the initial adsorption stage and then continue to increase at a relatively slow speed with contact time until a state of equilibrium is attained. On the other hand, it is clear from figure 6 that the extent of adsorption is rapid in the initial stages and becomes slow in later stages till saturation is achieved. This is obvious from the fact that a large number of surface sites are available for adsorption at the initial steps and after a lapse of time, the remaining surface sites are difficult to be occupied because of repulsion between the solute molecules of the solid and bulk phases. The time required to attain equilibrium in the case of adsorption of dyes is 180 min. The uptake of dye molecules by the adsorbents, and the time required for the establishment of equilibrium suggest the effectiveness of these materials for wastewater treatment. The decrease in the amount of dye adsorbed with time may be due to aggregation of dye molecules around the adsorbent particles.

4.4. Effect of initial RR-120 dye concentration

The effect of initial dye concentration can be carried out by prepare adsorbent–adsorbate solution with fixed adsorbent dose and different initial dye concentration for different time intervals and shaken until equilibrium. To study the influence of initial dye concentration on the efficiency of decolorization, the experiments were performed at different initial concentration of RR-120 by maintaining the other parameters constant. According to figure 7, as the initial dye concentration increases, the efficiency of the decolorization process decreases. Remarkably, the adsorption capacity of RR-120 dye increases (Figure 7) but the percent removal of RR-120 dye decreases with the increase in initial concentration, suggesting that the adsorption of RR-120 dye onto MWCNTs is highly dependent on initial concentration. For example, increase in the concentration of dye from 10 to 200 mg/L decreases the decolorization from 96.9 to 50.4% at 180 min. In contrast, the adsorption capacity of MWCNTs increases when the initial dye concentration increases from 100 to 200 mg/L. Similar results have been reported in the literature (36,37).

The percentage removal of dye is highly dependent on the initial amount of dye concentration. The effect of the initial of dye concentration factor depends on the immediate relation between the concentration of the dye and the available binding sites on an adsorbent surface. In general, the percentage of dye removal decreases with an increase in the initial dye concentration, which may be due to the saturation of adsorption sites on the adsorbent surface (38). At a low concentration, there will be unoccupied active sites on the adsorbent surface, and when the initial dye concentration increases, the active

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

Adsorbent	Adsorbate	Maximum adsorption capacity, mg/g	References
Modified rice stem	Acid red 18	10.20	(45)
Azolla filiculoides	Acid black 1	145.00	(10)
Banana peel	Methyl orange	21.00	(46)
Orange peel	Methyl orange	20.50	(46)
Pinecone derived activated carbon	Methyl orange	404.40	(47)
Cumin herb wastes	Reactive Red-120	120.48	(37)
Calcined layered double hydroxides	Methyl orange	200.00	(48)
Moringa peregrina ash	Methyl orange	15.43	(22)
Moringa peregrina ash	RR-198	13.61	(22)
MWCNTS	RR-120	1666.70	Current study

MWCNTs: Multi-walled carbon nanotubes, RR-120: Reactive Red-120

sites required for adsorption of the dye molecules will lack (39). On the other hand, the increase in initial dye concentration will cause an increase in the loading capacity of the adsorbent and this may be due to the high driving force for mass transfer at a high initial dye concentration (40-43).

4.5. Adsorption isotherms

In the Langmuir isotherm, it is assumed that the site energy for adsorption is the same for all surface sites and does not depend on the degree of coverage and that the largest capacity corresponds to only one monolayer. These assumptions are not valid for most adsorbents because, for example, activated carbon has a wide range of pore size that continues to adsorb organics as the concentration increases. While the BET isotherm does allow for multiple layers, it is assumed in the BET equation that site energy is the same for the first layer and equal to the free energy of precipitation for subsequent layers. In reality, the site energy of adsorption varies widely for most adsorbents because adsorbents like activated carbon are very heterogeneous, and the site energy varies considerably with surface coverage. The Freundlich equation is used to describe isotherm data for heterogeneous adsorbents (varying site energies) much better than the Langmuir or BET equations (44). According to findings of this study, it was found that the data fitted to Langmuir better than BET and Freundlich model. Maximum adsorption capacity of some adsorbents for removal of different dyes from aqueous environments is presented in table 3.

Acknowledgement

This project was supported by health research deputy of Zahedan University of Medical Sciences (Project Number: 2377). We are very grateful to the foundation and for the financial and technical support provided by Zahedan University of Medical Sciences, Zahedan, Iran.

References

1. Pala A, Tokat E. Color removal from cotton textile industry wastewater in an activated sludge system with various additives. Water Res 2002; 36(11): 2920-5.
2. Kim TH, Park C, Yang J, Kim S. Comparison of disperse and reactive dye removals by chemical coagulation and Fenton oxidation. J Hazard Mater 2004; 112(1-2): 95-103.
3. Gao BY, Yue QY, Wang Y, Zhou WZ. Color removal from dye-containing wastewater by magnesium chloride. J Environ Manage 2007; 82(2): 167-72.
4. Gholami M, Nasseri S, Alizadeh Fard MR, Mesdaghinia A, Vaezi F, Mahvi A, et al. Dye removal from effluents of textile industries by ISO9888 method and membrane technology. Iran J Public Health 2001; 30(1-2): 73-80.
5. Babu BR, Parande AK, Raghu S, Kumar TP. Cotton textile processing: waste generation and effluent treatment. Journal of Cotton Science 2007; 11(3): 141-53.

6. Lin YT, Weng CH, Chen FY. Effective removal of AB24 dye by nano/micro-size zero-valent iron. Separation and Purification Technology 2008; 64(1): 26-30.
7. Koyuncu I. Reactive dye removal in dye/salt mixtures by nanofiltration membranes containing vinylsulphone dyes: effects of feed concentration and cross flow velocity. Desalination 2002; 143(3): 243-53.
8. Liu HL, Chiou YR, Optimal decolorization efficiency of reactive red 239 by UV/ZnO photocatalytic process. J Chin Inst Chem Engrs 2006; 37: 289-98.
9. Zazouli MA, Balarak D, Mahdavi Y, Ebrahimi M. Adsorption rate of 198 reactive red dye from aqueous solutions by using activated red mud. Iranian Journal of Health Sciences 2013; 1(1): 36-43.
10. Zazouli MA, Yousefi Z, Yazdani-Charati J, Mahdavi Y. Application of azolla filiculoides biomass for Acid Black 1 dye adsorption from aqueous solution. Iranian Journal of Health Sciences 2014; 2(3): 24-32.
11. Bazrafshan E, Mahvi AH, Zazouli MA. Textile wastewater treatment by electrocoagulation process using aluminum electrodes. Iranian Journal of Health Sciences 2014; 2(1): 16-29.
12. Tunay O. Color removal from textile wastewaters. Water Sci Technol 1996; 34(11): 9-16.
13. Anjaneyulu Y, Sreedhara Chary N, Samuel Suman Raj D. Decolourization of industrial effluents-available methods and emerging technologie-a review. Rev Environ Sci Biotechnol 2005; 4(4): 245-73.
14. Gholami-Borujeni F, Mahvi AH, Naseri S. Faramarzi M A, Nabizadeh R, Alimohammadi M. Application of immobilized horseradish peroxidase for removal and detoxification of azo dye from aqueous solution. Res J Chem Environ 2011; 15(2): 217-22.
15. Gholami-Borujeni F, Mahvi AH, Nasseri S, Faramarzi MA, Nabizadeh R, Alimohammadi M. Enzymatic treatment and detoxification of acid orange 7 from textile wastewater. Appl Biochem Biotechnol 2011; 165(5-6): 1274-84.
16. Dehghani MH, Mesdaghinia AR, Nasseri S, Mahvi AH, Azam K. Application of SCR technology for degradation of reactive yellow dye in aqueous solution. Water Qual Res J Can 2008; 43(2-3): 183-7.
17. Kapdan IK, Kargi F. Simultaneous biodegradation and adsorption of textile dyestuff in an activated sludge unit. Process Biochemistry 2002; 37(9): 973-81.
18. Solozhenko EG, Soboleva NM, Goncharuk VV. Decolourization of azo dye solutions by Fenton's oxidation. Water Res 1995; 29(9): 2206-10.
19. Mahvi AH, Ghanbarian M, Nasseri S, Khairi A. Mineralization and discoloration of textile wastewater by TiO2 nanoparticles. Desalination 2009; 238(1-3): 309-16.
20. Maleki A, Mahvi A, Ebrahimi R, Zandsalimi Y. Study of photochemical and sonochemical processes efficiency for degradation of dyes in aqueous solution. Korean J Chem Eng 2010; 27(6): 1805-10.
21. Yu S, Liu M, Ma M, Qi M, Lu Z, Gao C. Impacts of membrane properties on reactive dye removal from dye/salt mixtures by asymmetric cellulose acetate and composite polyamide nanofiltration membranes. Journal of Membrane Science 2010; 350(1-2): 83-91.
22. Bazrafshan E, Zarei AA, Nadi H, Zazouli MA. Adsorptive removal of methyl orange and reactive red 198 dyes by Moringa peregrine ash. Indian J Chem Tech 2014; 21(2): 105-13.
23. Malik PK. Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics. J Hazard Mater 2004; 113(1-3): 81-8.
24. Chiou MS, Li HY. Equilibrium and kinetic modeling of adsorption of reactive dye on cross-linked chitosan beads. J Hazard Mater 2002; 93(2): 233-48.
25. Wang XS, Zhou Y, Jiang Y, Sun C. The removal of basic dyes from aqueous solutions using agricultural by-products. J Hazard Mater 2008; 157(2-3): 374-85.
26. Hu J, Chen C, Zhu X, Wang X. Removal of chromium from aqueous solution by using oxidized multiwalled carbon nanotubes. J Hazard Mater 2009; 162(2-3): 1542-50.
27. Zhang L, Xu T, Liu X, Zhang Y, Jin H. Adsorption behavior of multi-walled carbon nanotubes for the removal of olaquindox from aqueous solutions. J Hazard Mater 2011; 197: 389-96.

28. Ai L, Zhang C, Liao F, Wang Y, Li M, Meng L, et al. Removal of methylene blue from aqueous solution with magnetite loaded multi-wall carbon nanotube: kinetic, isotherm and mechanism analysis. J Hazard Mater 2011; 198: 282-90.
29. Tuzen M, Saygi KO, Usta C, Soylak M. Pseudomonas aeruginosa immobilized multiwalled carbon nanotubes as biosorbent for heavy metal ions. Bioresour Technol 2008; 99(6): 1563-70.
30. Long RQ, Yang RT. Carbon nanotubes as superior sorbent for dioxin removal. J Am Chem Soc 2001; 123(9): 2058-9.
31. Shirmardi M, Mesdaghinia AR, Mahvi A.H, Nasseri S, Nabizadeh R. Kinetics and equilibrium studies on adsorption of acid red 18 (Azo-Dye) using multiwall carbon nanotubes (MWCNTs) from aqueous solution. E-J Chem 2012; 9(4): 2371-83.
32. Chakravarty P, Sarma NS, Sarma HP. Removal of lead (II) from aqueous solution using heartwood of Areca catechu powder. Desalination 2010; 256(1-3): 16-21.
33. Calvete T, Lima EC, Cardoso NF, Dias SLP, Pavan FA. Application of carbon adsorbents prepared from the Brazilian pine-fruit-shell for the removal of Procion Red MX 3B from aqueous solution-Kinetic, equilibrium, and thermodynamic studies. Chemical Engineering Journal 2009; 155(3): 627-36.
34. Gulnaz O, Sahmurova A, Kama S. Removal of Reactive Red 198 from aqueous solution by Potamogeton crispus. Chemical Engineering Journal 2011; 174(2-3): 579-85.
35. Cengiz S, Cavas L. Removal of methylene blue by invasive marine seaweed: Caulerpa racemosa var. cylindracea. Bioresour Technol 2008; 99(7): 2357-63.
36. Aksu Z, Akin AB. Comparison of Remazol Black B biosorptive properties of live and treated activated sludge. Chemical Engineering Journal 2010; 165(1): 184-93.
37. Bazrafshan E, Ahmadabadi M, Mahvi AH. Reactive Red-120 removal by activated carbon obtained from cumin herb wastes. Fresen Environ Bull 2013; 22(2a): 584-90.
38. Eren Z, Acar FN. Adsorption of Reactive Black 5 from an aqueous solution: equilibrium and kinetic studies. Desalination 2006; 194(1-3): 1-10.
39. Kannan N, Sundaram MM. Kinetics and mechanism of removal of methylene blue by adsorption on various carbons-a comparative study. Dyes and Pigments 2001; 51(1): 25-40.
40. Bulut Y, Aydin H. A kinetics and thermodynamics study of methylene blue adsorption on wheat shells. Desalination 2006; 194(1-3): 259-67.
41. Bazrafshan E, Kord Mostafapour F, Faridi H, Farzadkia M, Sargazi S, Sohrabi A. Removal of 2, 4-dichlorophenoxyacetic acid (2, 4-d) from aqueous environments using single-walled carbon nanotubes. Health Scope 2013; 2(1): 39-46.
42. Bazrafshan E, Kord Mostafapour F, Hosseini AR, Rakhsh Khorshid A, Mahvi AH. Decolorisation of reactive red (120) dye by using single-walled carbon nanotubes in aqueous solutions. J Chem 2013; (2013): 1-8.
43. Bazrafshan E, Kord Mostafapour F, Mahvi AH. Phenol removal from aqueous solutions using pistachio nut shell ash as a low cost adsorbent. Fresen Environ Bull 2012; 21(10): 2962-8.
44. Crittenden C, Turssel R, Hand D, Howe K, Tchobanoglous G. Water treatment: principles and design. New York, NY: John Wiley and Sons; 2005.