Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2017, 9(4):226-231

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

A Kinetic Study for Removal of Bismarck Brown G by Adsorption over Multiwall Carbon Nanotubes

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ABSTRACT

In this work, Multiwall carbon nanotubes (MWCNTs) were used in the adaptive removal of Bismarck Brown G (BBG) dye from an aqueous solution. Crystal structure of the materials was investigated using X-rays diffraction XRD, specific surface area (BET) and UV–Vis diffuse reflectance. The effects of contact time, MWCNT dosage, pH and temperature on adsorption of BBG dye by MWCNTs were investigated. The adsorption study was analyzed kinetically, and the results revealed that the adsorption followed pseudo-second order kinetics with good correlation coefficients. The equilibrium adsorption data was analyzed using two common adsorption models: Langmuir and Freundlich.

Keywords: Adsorption; MWCNTs; Bismarck brown R; Kinetics; Isotherms

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INTRODUCTION

Water represents 70 to 90% of surface of the earth and the humans can't continue in living without pure water. Currently water pollution is the research topic and one of the most important pollution sources is the synthetic dyes [1]. In this context, azo dyes seem to be the most effective type as these dyes are used widely such as textile industries, food, and color paper printing industry [2]. Generally, azo dyes have a complex aromatic structure, and they are almost have complex structural azo groups (-N=N-). The deep color of these dyes comes from the presence of the azo groups in such dyes, and hence if these groups are broken then the color can be disappeared. Due to the rigid structure of these compounds, so that is not easy to break these materials into smaller fragments under normal condition [3]. The presences of dyes in water can cause some problems such as reducing oxygen levels in water; interfering with penetration of sunlight into waters; retarding photosynthesis and interfering with gas solubility in water bodies [4]. In this context, removing these dyes using adsorption processes can be used effectively for removing dyes from polluted aqueous solutions. Generally, these processes are not expensive, easily of operation, high recovery and simplicity of design [5,6]. Among wide range of adsorbents, carbon nanotubes (CNTs) are seemed to be good candidate adsorbent that can absorb wide spectrum of organic pollutants from wastewater [7,8]. CNTs are made up of concentric of rolled graphene sheets and it can be existed in different types such as single walled carbon nanotubes (SWCNTs) and multiwall carbon nanotubes (MWCNTs). This sorting is depending on the number of sheets that comprise them [9]. Generally, CNTs have many applications because of their perfect properties such as high thermal stability, high electrical conductivities, high strength, good mechanical and their high adsorption ability [10].

The present work involves investigation of kinetics study for removal of BBG dye from simulated industrial textile wastewaters by adsorption over multi walled carbon nanotubes. Different factors that can effect on adsorption ability of MWECNTs would be investigated. These factors involve effects of contact time, MWCNTs dosage, pH and temperature. Also a Kinetic and equilibrium models would be undertaken to fit experimental data.

EXPERIMENTAL SECTION

Multiwall carbon nanotubes (MWCNTs) that were used in this work was purchased from Aldrich and it have an average diameter of 5.5 mm and a length of 10-30 μm and used as provided without and further treatment. Bismarck Brown G (BBG) dye was used as a model of polluted textile dye with a molecular formula $C_{21}H_{24}N_8.2HCl$ and molecular weight as 461.39g mol^{-1}, this dye was purchased from Sigma-Aldrich. The dye stock solution was prepared by dissolving a required weight of the dye in distilled water to the concentration of 50 pm. The experimental solutions were obtained by diluting the dye stock solution in accurate proportions to the required initial concentrations. In terms of adsorption isotherms, both Freundlich and Langmuir adsorption model was undertaken. In this case, a series of experiments were performed using 100 ml, 50 ppm of dye solution with 0.05 g of MWCNTs at 25°C for a period of one hour for each run. Periodically, 2 mL of reaction mixture were withdrawn and then filtered off using a centrifuge. The absorbance of the supernatant liquid was recorded using UV-visible spectrophotometer at 468 nm. The amount of dye that was adsorbed on the surface was calculated using the following relation:

$$q_e = (C_o – C_e) \times V)/W \qquad (1)$$

From this relation, qe is refers to the amount of BBG that is adsorbed on the surface of MWCNTs at equilibrium, C_o and C_e are the initial and final dye concentrations, respectively, V is the volume of solution (L), and W is the adsorbent weight (g). Langmuir adsorption isotherm can be presented in the following equation [11].

$$K_L\ Ce\ 1+ qm\ K_L\ Ce/\ q_e \qquad (2)$$

Whereas qm represents a maximum amount of BBG that is adsorbed per unit mass of the MWCNTs and K_L is the Langmuir constant. Freundlich model is based on the distribution of an adsorbate molecules between adsorbent active sites and the aqueous phases at equilibrium [12,13]. Freundlich model can be represented in the following relation:

$$\log (qe) = \log K_F + 1\backslash n \log C_e \qquad (3)$$

Whereas: K_F and n are Freundlich constants. To determine the rate of adsorption process two kinetic models were used pseudo first order and pseudo second order models were investigated to analyze the kinetic data of the BBG adsorption onto the MWCNTs. The rate constant of adsorption was determined by using pseudo-first order equation given by Lagergren and Svenska [13]:

$$\ln (qt – qe) = \ln (qe) – k1\ t \qquad (4)$$

Whereas: *qe* and *qt* (mg/g) are the amounts of BBG molecules that are adsorbed at equilibrium and at time t (min) respectively, and the adsorption rate constant is k_1 (min^{-1}). The pseudo-second order equation based on equilibrium adsorption can be presented following equation [14]:

$$t/q_t= t/k_2q_e^2 + t/q_e \qquad (5)$$

Whereas: k_2 is the rate constant of the second order equation (g/mg min).

RESULTS AND DISCUSSION

The effect of MWCNTs mass on the efficiency of BBG dye removal was investigated via performing a series of experiments using different doses of MWCNTs under constant other conditions with use initial dye concentration of 50 ppm. The obtained results are presented in Figure 1. These results showed that the efficiency of dye removal was increased with increasing of adsorbent dosage from 10 to 50 mg. Under these conditions, percentage of dye removal was increased from 87.97 to 96.45% after 60 min of adsorption time. This result are attributed to the increase of the available number of adsorption sites directly with the increase of the amount of the used MWCNTs [15,16].

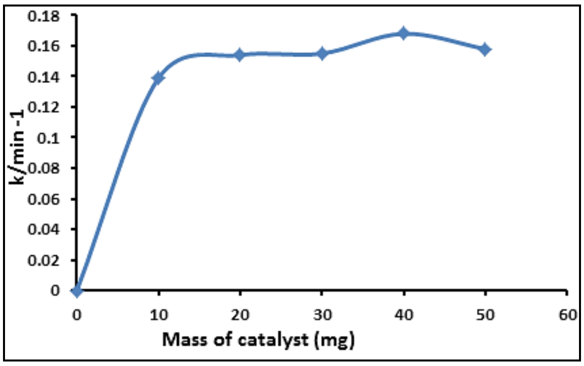

Figure 1: Effect of MWCNTs doses on the removal efficiency of BBG over MWCNTs

The effect of contact time on efficiency of removing of BB G over MWCNTs is shown in Figure 2. From these results it can be seen that, the amount of BBG dye adsorbed onto MWCNTs at pH value 5, 20 mg of MWCNTs and at 298.15 K was increased with increase of adsorption time for all the used doses of the used MWCNTs. The increase of loading capacity of CNTs with increase of time is probably due to higher interaction between BBG dye molecules and the active sites of the used adsorbent [17]. These results showed rapid increase in efficiency of dye removal was achieved during the first 20 minutes [18].

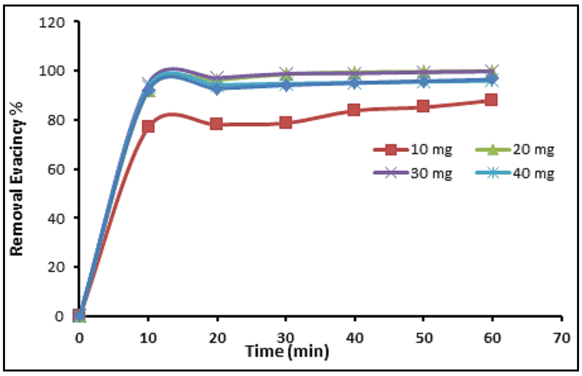

Figure 2: Effect of contact time on the removal of BBG dye over MWCNTs

The value of pH of reaction mixture can effect significantly of the efficiency of adsorption of dye molecules on the active site at the surface of the used adsorbent. The value of pH can effect on the charge of the surface beside that it can effect of ionization of different pollutants [19]. The effect of pH on the adsorption of BBG dye over MWCNTs was investigated under different values of pH from (2-10) with 50 ppm fixed initial dye concentration and adsorbent dosage 20 mg for 60 min. The obtained results are shown in Figure 3. From these results, adsorption of BBG dye over MWCNTs was increased with increase the value of pH of solution from 2 to 5 and then it was decreased slightly when the pH values were over 5.5. These observations are probably due to the presence of carboxyl and hydroxyl groups at the surface of MWCNTs after purification method by acid treatment. The change in solution pH will effect on the ionization of these functional groups and this can effect on adsorption of dye molecules at the active sites of surface of MWCNTs [20,21].

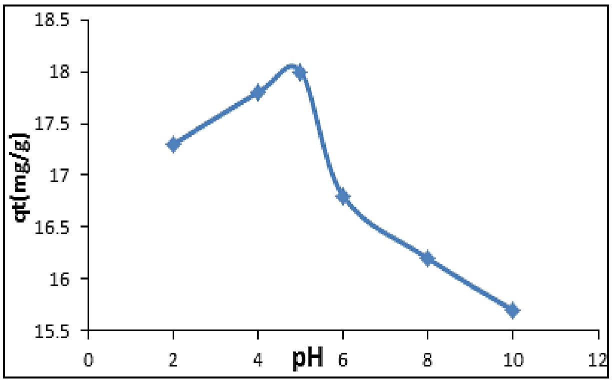

Figure 3: Effect of initial solution pH on adsorption of BBG over MWCNTs

To study the effects of temperature on the adsorption of dye over MWCNTs, a series of experiments were carried out at a range of temperatures from 298.15 to 323 K under constant other reaction conditions. The obtained results are shown in Figure 4. These results showed that change in temperature can effect on the efficiency of dye adsorption over MWCNTs. As it was observed, the equilibrium adsorption capacity of BBG onto MWCNTs was found to increase with increase of temperature. This fact indicates that the mobility of dye molecules can increase with increase of temperature. Beside that viscosity of dye solution reduces with rise in temperature and as a result the rate of diffusion of dye molecules can increase from bulk to the active sites at the surface of MWCNTs which leads to increase on the efficiency of dye adsorption with increase of the applied temperature [22]. Adsorption isotherms were investigated using Langmuir and Freundlich adsorption models. These isotherms are shown in Figures 5 and 6 respectively. Table 1 shows values of Langmuir and Freundlich adsorption isotherms constants.

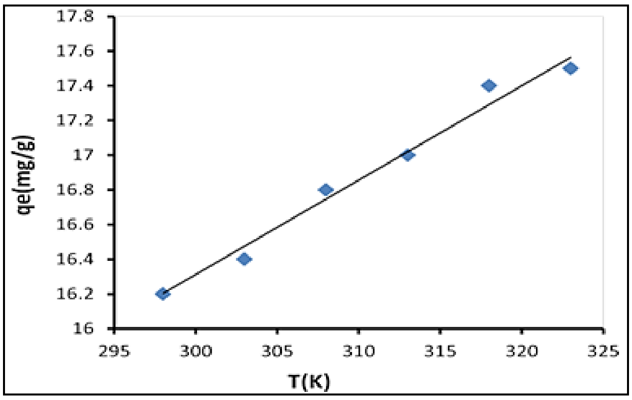

Figure 4: Effect of temperature on adsorption of BBG over MWCNTs

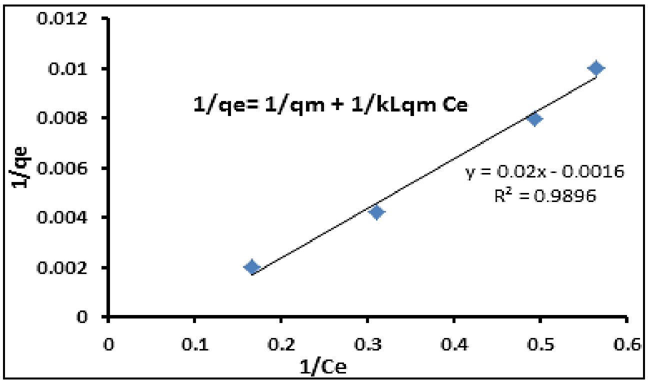

Figure 5: Langmuir adsorption isotherm for adsorption of BBG over MWCNTs

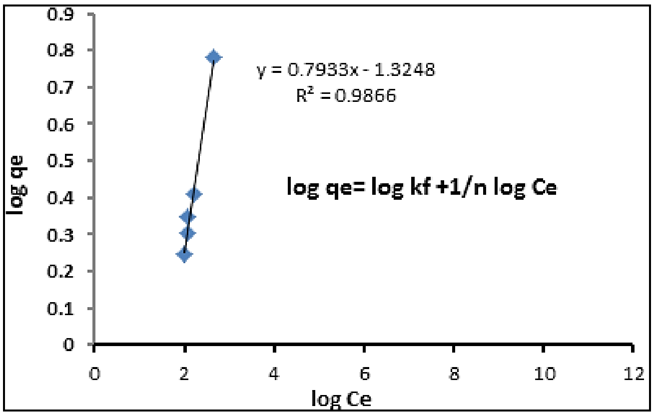

Figure 6: Freundlich adsorption isotherm for adsorption of BBG dye over

MWCNTs

From results that are summarized in Table 1, it can be seen that the value of the correlation factor (R^2) that are obtained from the Langmuir model is larger than that for Freundlich isotherm. This means that this process agrees with Langmuir model.

Table 1: The adsorption constants of Langmuir and Freundlich isotherms constants

Isotherms	Constants/Correlation cofficients	Values
Langmuir	R^2	0.9896
	q_m	625
	K_L	0.08
Freundlich	R^2	0.9866
	K_F	21.125
	n	1.26

Through the results that are shown in the Table 2, it is found that the value of the correction factor for the pseudo second order kinetic model (0.9979-1.000) is higher than the value of the first false correction coefficient. Through this result, it is clear that the dye adsorption process of BBG follows the pseudo first order kinetic and pseudo second order kinetic models. The obtained results are presented in Tables 2 and 3 (Figures 7 and 8).

Table 2: **Pseudo-first-order kinetic parameters for adsorption of BBG dye over MWCNTs**

Pseudo-first-order kinetic				
Adsorbent dose(g/100 ml)	**qe,exp (mg/g)**	**qe,calc. (mg/g)**	**$K_{1\ (min-1)}$**	**R^2**
0.01	43.988	20.706	0.07	0.75
0.02	16.603	6.534	0.134	0.96
0.03	16.624	16.865	0.071	0.97
0.04	11.993	4.315	0.053	0.99
0.05	9.645	8.203	0.047	0.94

Table 3: **Pseudo second order kinetic parameters for adsorption of BBG dye over MWCNTs**

Pseudo-second -order kinetic				
Adsorbent dose(g/100 ml)	**qe,exp (mg/g)**	**qe,calc. (mg/g)**	**K2 (min^{-1})**	**R2**
0.01	43.988	45.454	0.372	1
0.02	16.603	16.949	1	1
0.03	16.624	16.949	1.512	1
0.04	11.993	12.048	3.61	1
0.05	9.645	9.708	1.241	1

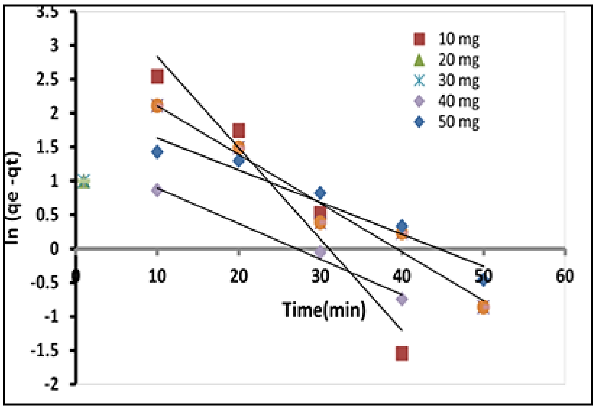

Figure 7: The pseudo first order kinetic model for adsorption of BBG dye over MWCNTs

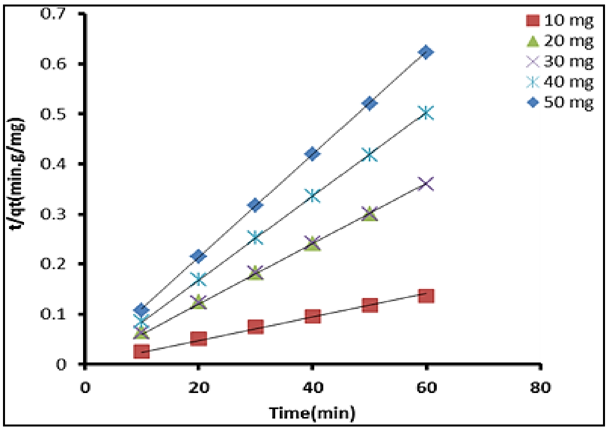

Figure 8: The pseudo second order kinetic model for adsorption of BBG dye over MWCNTs

CONCLUSION

This study shows that MWCNT can be used effectively for the removal of BBG from aqueous solution. 20 mg is the optimum dosage of MWCNTs to adsorb BBG. The adsorption capacity of the BBG on MWCNTs increased with the increasing of initial concentration of BBG. The equilibrium adsorption capacity of BBG increased with temperature. The optimum contact time and pH were 20 min and 5 respectively. The adsorption kinetics was fitted by a pseudo-second order kinetic model. The adsorption of BBG on MWCNTs has been described by the Langmuir and Freundlich adsorption isotherm models. The equilibrium data were fitted with the Langmuir isotherm.

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