

The adsorption of malachite green (MG) as a cationic dye onto functionalized multi walled carbon nanotubes

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(Received 25 February 2013 • accepted 6 May 2013)

Abstract—Synthetic dyes are widely used by several industries to color their products. The discharge of colored wastewater into the hydrosphere causes serious environmental problems. We used functionalized multi wall carbon nanotubes as an adsorbent for the adsorption of cationic dye, malachite green, from aqueous solution. Based on information provided by the Iranian Research Institute of Petroleum Industry, carbon nanotubes are produced using a chemical vapor deposition (CVD) technique. These as-received MWCNTs were functionalized by acid treatment. The remaining dye concentration was read by UV-visible absorption spectroscopy at maximum adsorption wavelength. The effect of different operational parameters such as contact time, pH of solution, adsorbent dose and initial dye concentration were studied. The results showed that by increasing of contact time, pH and adsorbent dose the removal of dye increased, but by increasing initial dye concentration, the removal efficiency decreased. Adsorption isotherms and kinetics behavior of *f*-MWCNTs for removal of malachite green was analyzed, and fitted to various existing models. The experimental data were well correlated with the Langmuir isotherm with a maximum adsorption capacity (q_m) and regression coefficient (R^2) of 142.85 mg/g and 0.997, respectively. The results of this study indicate that functionalized multi wall carbon nanotubes can be used as an effective adsorbent for the removal of dyes.

Key words: Adsorption, Carbon Nanotube, Dye, Isotherm, Kinetic Study

INTRODUCTION

Synthetic dyes are widely used by several industries, such as textile companies, food-processing companies, dye manufacturers, paper and pulp mills, and electroplating factories, to color their products [18]. The discharge of colored wastewater into the hydrosphere not only causes serious environmental problems because of its high toxicity and possible accumulation in the environment, but also to human beings, by producing carcinogenic and mutagenic effects [27,38]. To minimize the risk of pollution and adverse health effects generated by such effluent, this effluent must be treated carefully before discharging into the environment [18]. Malachite green (MG) is a popular cationic dye and is used extensively. This dye is widely used for the dyeing of cotton, jute, silk, wool and leather products. It also finds applications in the fish farming industry, aquaculture and animal husbandry as fungicide, ectoparasiticide and disinfectant. It has been shown recently that MG is linked to an increased risk of cancer, acts as a liver tumor-enhancing agent and many other diseases. Malachite green is an important water-soluble dye belonging to the triphe-

nyl methane family. It may enter into the food chain, and due to its mutagenic and carcinogenic characteristics can cause severe effects on nervous system, reproductive system, liver, brain and kidney [7,33].

There are many processes available for dye removal such as coagulation, advanced oxidation, combined chemical and biochemical process, aerobic and anaerobic digestion, adsorption and membrane treatment; each of these has different removal efficiency, advantage, disadvantage, capital costs and operating rates. Adsorption is one of the cheapest and most effective techniques for wastewater treatment in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances. In addition, this technique can produce high-quality effluent without the formation of harmful substance like ozone and free radicals [1,14,15,24,31,35]. Numerous adsorbents and bioadsorbents such as neem sawdust [16], hen feathers [28], cyclodextrin-based [3], oil palm trunk fiber (OPTF) [9], bentonite clay [36], bagasse fly ash [25], bottom ash [8], de-oiled soya [29], *Cosmarium* sp. [4], *Pithophora* sp. [17] have been used for removal of malachite green from aqueous solution. More recently, Long and Yang [21] reported that MWCNTs could be more efficient than activated carbon for the removal of dioxin, so carbon nanotubes (CNTs) have attracted the attention of many researchers

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as new adsorbents.

Carbon nanotubes are divided into two general categories: single-wall carbon nanotubes (SWCNTs) and multi-wall carbon nanotubes (MWCNTs). Because of their relatively large specific surface areas, unique hollow structures, high mechanical strength, small size and remarkable electrical conductivities, CNTs can be used to remove many kinds of organic and inorganic contaminants [2,6], like trihalomethanes (THMs), heavy metal, fluoride and dyes from water and wastewater [5,19,22,32,35,39]. The aim of this work was 1) to study the adsorption capacity of carbon nanotubes for the removal of malachite green (MG) from aqueous solution, 2) to investigate the influence of different variable, including contact time, pH of solution, adsorbent dosage and initial dye concentration, 3) and to analyze adsorption isotherms and kinetics.

MATERIALS AND METHODS

1. Adsorbent

The CNTs used in this study were multi-wall carbon nanotubes. These CNTs have specific surface area 270 m²/g and electrical conductivity 1,500 S/m. The diameter and the length of the MWCNTs are in the ranges of 10-30 nm and 10 μm, respectively. The purity of CNTs was more than 95%. The CNTs were synthesized in the Iranian Research Institute of Petroleum Industry (RIPI) and were purchased. To remove the amorphous carbon and iron catalyst 2 g of the as-received CNTs was immersed in 4 M nitric acid for 2 h at room temperature and then washed by de-ionized water several times until the washing water showed no pH changes, then dried at 110 °C for 24 h. The clean CNTs were then oxidized by concentrated nitric acid, refluxed at 120 °C for 2 h. After cooling to room temperature the reaction mixture was diluted with 500 ml of de-ionized water and then vacuum-filtered through a filter paper (0.25 μm porosity). This washing operation was repeated until no pH changes in the washing water were detected, and was followed by drying in a vacuum oven at 110 °C for 24 h.

2. Adsorbate

Malachite green was purchased from Alvan Sabet Co (Hamedan, Iran), and was used without further purification. MG chemical formula, molecular weight and maximum adsorption wavelength (λ_{max}), were C₂₃H₂₆N₂O.HCl, 382.93 g/mol and 617 nm, respectively. The chemical structure of MG is shown in Fig. 1. Stock solutions of dye were prepared by dissolving accurately weighed dyes in distilled water to the desired concentration. The experimental solutions with different initial concentrations were obtained by diluting stock solu-

tion in required proportions and their absorbance was read by UV-Vis spectroscopy. After taking the measurements, we made a calibration curve to compute the concentration of each experiment. All other chemicals were analytical grade.

3. Experiments of Adsorption

To study the effect of parameters like contact time, pH, adsorbent dosage, and initial concentration for the color removal of MG, batch experiments were carried out in illuminated refrigerated incubator shaker (Innova 4340, USA) at a constant speed of 175 rpm at 298 K. Initial solution pH was adjusted using 0.1 N HCL and 0.1 N NaOH. The effect of various parameters such as contact time, solution pH, adsorbent dosage and initial dye concentration was investigated. By adding 0.04 g of *f*-MWCNTs to 100 mL of dye solution with 50 and 100 mg/L initial dye concentrations of the dye, the effect of contact time was evaluated. At different time intervals of the reaction, samples were taken from the suspension and were analyzed. To determine the effect of solution pH on the adsorption process, distinctive ranges of the solutions pH were investigated. The effect of adsorbent dose was evaluated by adding different amounts of adsorbent into the 75 mg/L initial concentration of MG solution, at pH 7.0 at the equilibrium time. To study the effect of initial concentration of MG on the adsorption process, 100 mL of MG solutions with different initial concentrations were prepared in a series of 250 mL Erlenmeyer flasks and 0.06 g/100 mL adsorbent doses were added to each flask at pH 7.0. At the end of equilibrium time in order to separate the adsorbents from the aqueous solutions, the samples were centrifuged at 4,000 rpm for 10 minutes, and then the supernatant of suspension was filtered with a 0.25 μm Millipore filter. The residual dye concentrations were analyzed by UV-visible spectrophotometer (Perkin-Elmer Lambda 25, USA) at maximum adsorption wavelength 617 nm. The percentage of dye removal, the amount of MG adsorbed at time *t* (*q_t*, mg/g) and at equilibrium (*q_e*, mg/g), respectively, was calculated through the following equations:

$$\text{Dye removal \%} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (1)$$

$$q_e = \frac{(C_o - C_e) \times V}{M} \quad (2)$$

$$q_t = \frac{(C_o - C_t) \times V}{M} \quad (3)$$

where *C_o* and *C_e* (mg/L) are the initial and equilibrium concentrations of MG solution; *M* (g), *V* (L), *C_t*, and *q_t* (mg/g) are the mass of *f*-MWCNTs, the volume of the solution, and the concentration of dye at any time, and the amount of adsorbed dye on *f*-MWCNTs at any time, respectively.

RESULTS AND DISCUSSION

1. Effect of Contact Time

The adsorption mechanism of cationic dyes by *f*-MMWCNTs may be derived from two reasons. One reason might be due to the electrostatic attraction between the positive cationic dyes and the negative charged *f*-MMWCNTs adsorbent surface. The other one might be based on van der Waals interactions occurring between the hexagonally arrayed carbon atoms in the graphite sheet of *f*-MMWCNTs and the aromatic backbones of the dyes [6]. The effect of contact

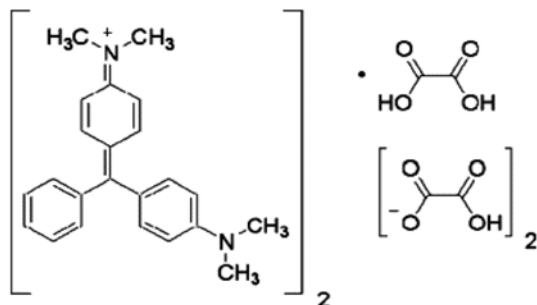


Fig. 1. Chemical structure of malachite green.

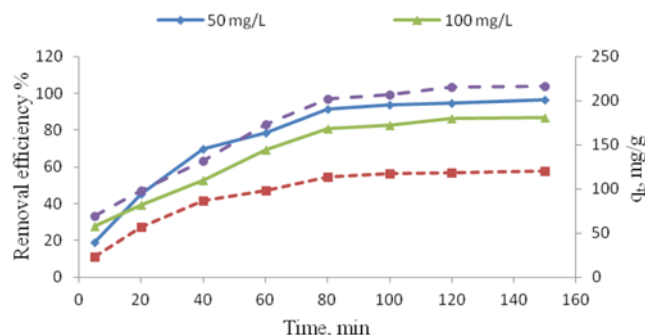


Fig. 2. Effect of contact time on the removal of MG dye by *f*-MWCNTs (condition: adsorbent dose=.04 g, T=25 °C, pH=7).

time on the removal of MG by *f*-MMWCNTs at different initial dye concentrations (50 and 100 mg/L) is presented in Fig. 2. As shown, by increasing the contact time, the removal efficiency of dye by *f*-MMWCNTs at any time was increased. The results show that removal of MG is faster in initial stages and then becomes slow and finally reaches equilibrium at approximately 80 minutes. These observations show initial dye concentration has no effect on required time for equilibrium. During initial stages, a large number of vacant sites are available on the surface of adsorbent and then the adsorption rate of dye is high. The adsorption process becomes less efficient due to gradual occupancy of these sites. With increasing time, the occupation of the remaining vacant sites due to increased repulsive forces between dye molecules and bulk solution is more difficult [23,30].

2. Effect of Solution pH

One of the most important parameters that affect the adsorption of dye molecules is pH of solution. The effect of solution pH on adsorption of dye on *f*-MMWCNTs was studied by varying the pH of the dye solution for an initial concentration of 50 mg/L while the adsorbent dosage, contact time, agitation speed and temperature were fixed at 0.04 g, 80 minute, 175 rpm and 25 °C, respectively. Dye removal efficiency increased when the pH increased from 3 to 11, indicating that pH significantly affected MG removal percentage, particularly under alkaline conditions. The influence of pH on adsorption of MG dye is presented in Fig. 3. When pH increased from 3 to 11, the removal efficiency increased from 66 to 98 percent. Because there was no significant difference in removal efficiency

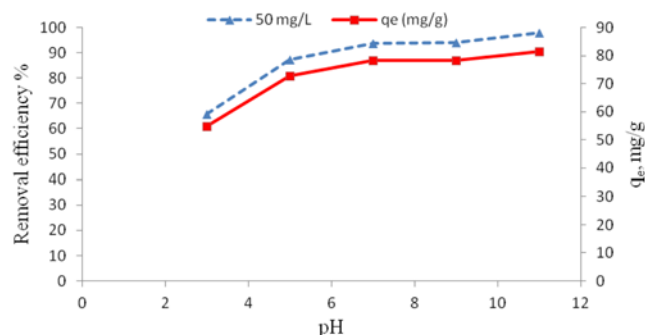


Fig. 3. Effect of initial pH on the removal of MG dye by *f*-MWCNTs (condition: adsorbent dose=.04 g, T=25 °C, MG concentration=50 mg/L).

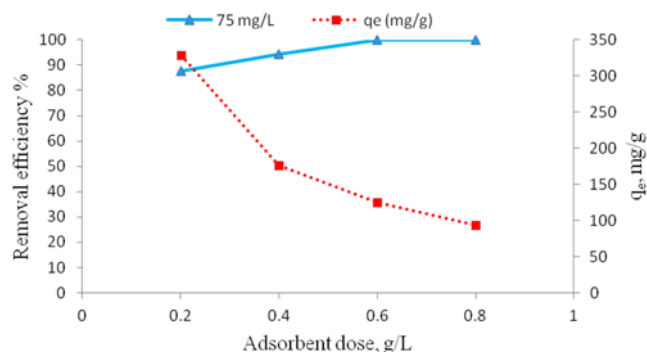


Fig. 4. Effect of adsorbent dosage on the removal of MG dye by *f*-MWCNTs (condition: MG concentration=75 mg/L T=25 °C, pH=7).

beyond pH 7, this pH was selected for other experiments. The lower removal of malachite green as a cationic dye, at acidic pH, is because of the presence of excess H⁺ ions competing with the dye cations for the adsorption sites. At pH 11, a significantly high electrostatic attraction exists between the negatively charged surface of the adsorbent and positively charged cationic dye [23,38].

3. Effect of Adsorbent Dosage

Adsorbent dosage is another important parameter in the determination of adsorption capacity. The effect of the adsorbent dose was investigated for 75 mg/L initial MG concentration by adding various amounts of *f*-MWCNTs in 100 mL dye solution; other parameters were kept constant. Fig. 4 shows the removal of MG as a function of *f*-MWCNTs dosage. The removal efficiency increased from 87.7% to 99.9% by increasing adsorbent dose from 0.02 to 0.08 g. This phenomenon can be attributed to an increase in the adsorbent specific surface area and availability of more adsorption sites. However, if the adsorption capacity was expressed in mg adsorbed per gram of adsorbent, the capacity decreased with the increasing amount of sorbent [18,23]. In the present study, when the adsorbent dose increased from 0.02 to 0.08 g, the amount of adsorbed dye per mass unit of *f*-MWCNTs (adsorption capacity) decreased from 328 to 94 mg/g. Wu and colleagues employed multi-wall carbon nanotubes to adsorb reactive dye and obtained similar results [39]. Similar results were also obtained for Brazilian pine-fruit shell as a biosorbent by [20], and for activated carbon prepared from agricultural waste by [34]. In the present study, the adsorbent dose 0.08 g per 100 ml is the optimal value for the removal of MG dye.

4. Effect of Initial Dye Concentration (C₀)

The effect of initial dye concentration on the removal of MG by *f*-MWCNTs is shown in Fig. 5. It is evident that with the increase in the initial dye concentration the amount of MG adsorbed per unit mass of *f*-MWCNTs increased; however, the percentage of MG removal decreased with the increase in C₀. By increasing MG concentration from 25 to 100 mg/L, the removal percentage of dye decreases from 99 to 77% at 0.06 g/100 mL adsorbent dosage. The amount of MG adsorbed at equilibrium increased from 41.57 mg/g for 25 mg/L to 128.59 mg/g for 100 mg/L. This was expected due to a greater driving force, resulting from the greater concentration gradient between MG in solution and MG on the adsorbent surface at higher initial dye concentration [10]. A similar finding was observed for the adsorption of MG from aqueous solution by bagasse

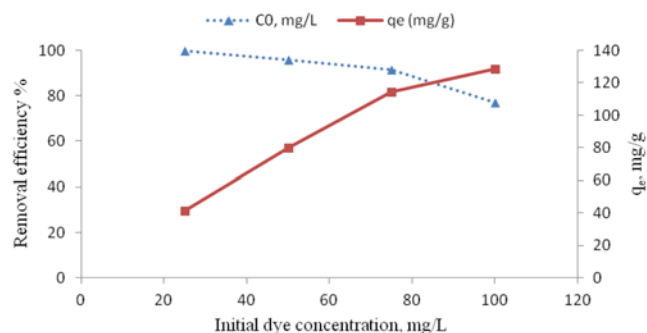


Fig. 5. Effect of initial dye concentration on the removal of MG by *f*-MWCNTs (condition: adsorbent dose=.06 g, T=25 °C, pH=7).

fly ash and activated carbon [25], and oil palm trunk fiber [9].

5. Adsorption Isotherms

An adsorption isotherm describes how the adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models helps us to find a suitable model that can be used for design purpose. We used three adsorption isotherms for describing experimental results: Langmuir, Freundlich and Temkin. The most widely used adsorption isotherm for the adsorption of a solute from a liquid solution is the Langmuir adsorption isotherm. Langmuir isotherm assumes that the single adsorbate binds to a single site on the adsorbent, and once a dye molecule occupies a site, no further adsorption takes place at that site. So, all surface sites on the adsorbents have the same affinity for the adsorbate. The saturation monolayer can be represented by the expression [37]:

$$q_e = \frac{q_m K C_e}{1 + K C_e} \quad (4)$$

The linear form of the Langmuir equation is:

$$\frac{C_e}{q_e} = \frac{1}{K q_m} + \frac{C_e}{q_m} \quad (5)$$

where q_e is the amount of dye adsorbed per gram of *f*-MWCNTs (mg/g); C_e is the equilibrium concentration of dye in a solution (mg/L); k is the Langmuir constant (L/mg), which is related to the affinity of binding sites, and q_m is the theoretical saturation capacity of the monolayer (mg/g). The values of q_m and k were calculated from the linearized form of Eq. (5) by plotting C_e/q_e versus C_e . The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant called the equilibrium parameter or separation factor (R_L). The value of R_L is used to determine if the adsorption process is favorable or unfavorable. The parameter is defined by:

$$R_L = \frac{1}{1 + k C_0} \quad (6)$$

Where k is the Langmuir constant and C_0 is the highest initial MG concentration (mg/L). The R_L value indicates adsorption process is favorable ($0 < R_L < 1$), linear ($R_L = 1$), unfavorable ($R_L > 1$) or irreversible $R_L = 0$.

The Freundlich isotherm is an empirical equation and corresponds

to heterogeneous adsorbent surfaces. The presence of different functional groups on the surface and several adsorbent-adsorbate interactions can cause the heterogeneity.

The Freundlich equation expressed as [11,39]:

$$q_e = k_f C_e^{1/n} \quad (7)$$

The linear form of the Freundlich equation is:

$$\log q_e = \log(k_f) + 1/n \log(C_e) \quad (8)$$

where q_e is the amount of MG adsorbed per unit mass of adsorbent (mg/g), C_e is the concentration of MG in solution at equilibrium (mg/L), k_f and n are the Freundlich constants, which correspond to the adsorption capacity and the adsorption intensity of the adsorbent, respectively. The values of k_f and $1/n$ can be calculated from the intercept and slope of the logarithmic plot of q_e vs C_e . Higher

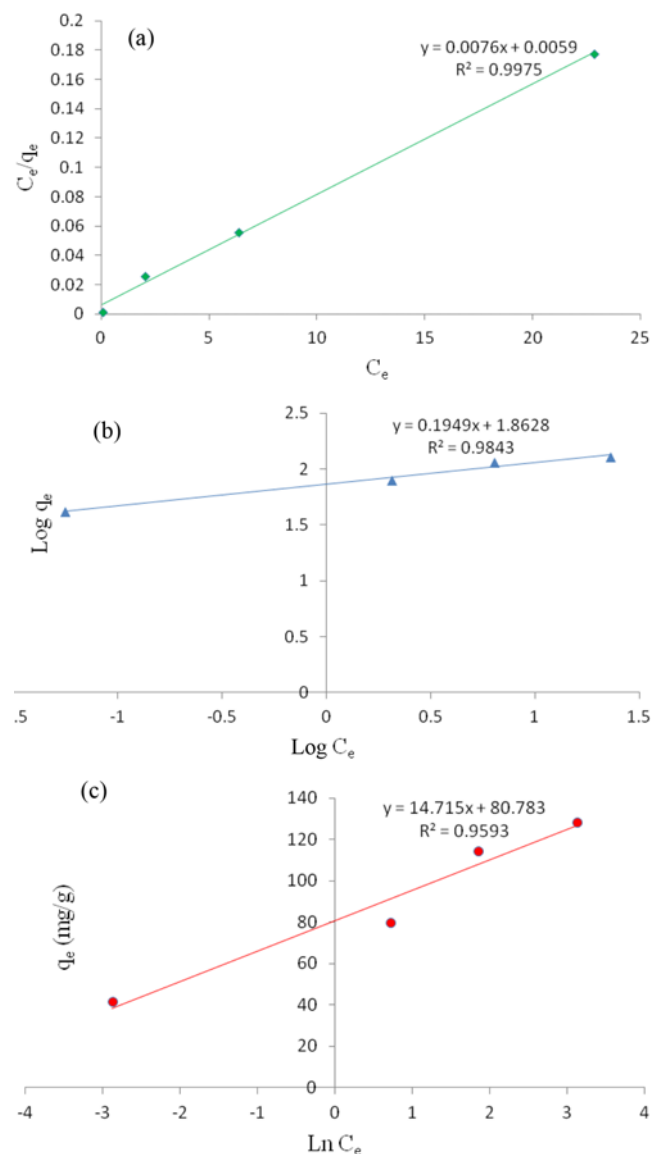


Fig. 6. Langmuir (a), Freundlich (b) and Temkin (c) isotherms plots for removal of MG by *f*-MWCNTs (conditions: initial dye concentration=25, 50, 75, 100 mg/L, adsorbent dose=.06 g, T=25 °C, pH=7).

affinity for adsorbate is related to higher value for k_f and the values of the empirical parameter $1/n$ lie between $0.1 < 1/n < 1$, indicating favorable adsorption. The Temkin isotherm [13,27] contains a factor that explicitly takes into account the adsorptive-adsorbent interactions:

$$q_e = B_1 \ln(k_f C_e) \quad (9)$$

The linear form of the Temkin isotherm is expressed as:

$$q_e = B_1 \ln k_f + B_1 \ln C_e \quad (10)$$

where $B_1 = RT/b$ and k_f are the constants. R is the gas constant (8.31 J/mol K) and T (K) is the absolute temperature, k_f is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy, and constant B_1 is related to the heat of adsorption. The isotherm constants k_f and B_1 can be obtained from the slope and intercept of plots of q_e versus $\ln C_e$, respectively. The applicability of the isotherm equation to describe the adsorption process was compared by judging the correlation coefficients, R^2 values. The adsorption isotherm data of MG onto *f*-MWCNTs was fitted with Langmuir, Freundlich and Temkin isotherms. Fig. 6(a)-(c) shows the fitted equilibrium data to Langmuir, Freundlich and Temkin isotherms. The isotherm constants for all above-mentioned isotherms were calculated from the linear form of each model. The obtained parameters of adsorption isotherms along with regression coefficients (R^2) are shown in Table 1. The calculated values of R_L and $1/n$ are less than 1, so they represent the favorable removal condition. Based on the correlation coefficient (R^2) (Table 1), the experimental data were well correlated with the Langmuir isotherm than the other two isotherms. The maximum adsorption capacity obtained from the Langmuir isotherm is 142.85 mg/g.

6. Adsorption Kinetics

The modeling of the kinetics of adsorption of MG on *f*-MWCNTs was investigated by two common models: the pseudo-first-order kinetic model and pseudo-second-order kinetic model. These models are widely used for describing dye sorption as well as other pollutants such as heavy metals on solid adsorbents. The best-fit model was chosen based on the linear regression correlation coefficient values (R^2). The pseudo-first-order model can be expressed as [26]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (11)$$

The linear form of pseudo-first-order rate equation is:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (12)$$

where q_e and q_t are the amounts of MG adsorbed (mg/g) at equilibrium and time t (min), respectively; k_1 is the rate constant of pseudo-first-order kinetic model (1/min). The parameters k_1 and q_e could be calculated from the slope and intercept of the plots of $\log(q_e - q_t)$ versus t for Eq. (12). Linear form of the pseudo-second-order kinetic model can be expressed as [12]:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (13)$$

where h is given by:

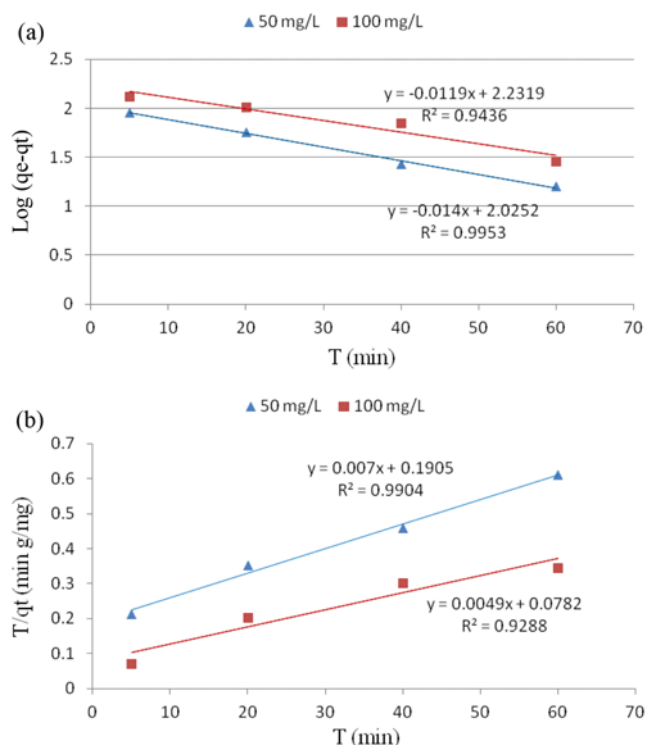


Fig. 7. (a) Pseudo-first-order kinetic (b) Pseudo-second-order kinetic plots for removal of MG by *f*-MWCNTs (condition: initial dye concentration=50 and 100 mg/L, adsorbent dose=.04 g, $T=25^\circ\text{C}$, $\text{pH}=7$).

Table 1. Constants of Langmuir, Freundlich and Temkin models for the adsorption of MG onto *f*-MWCNTs

Isotherm models	Parameters	Value
Langmuir	q_m (mg/g)	142.8571
	k (L/mg)	1.4
	R^2	0.997
	R_L	0.007
Freundlich	k_f (mg/g (L/mg) $^{1/n}$)	72.778
	n	5.154
	R^2	0.984
	R^2	0.984
Temkin	B	14.71
	k_f	5.49
	R^2	0.959

Table 2. Kinetic parameters for the adsorption of MG onto *f*-MWCNTs

Kinetic model	Dye concentration (mg/L)	
	50	100
Pseudo-first order		
q_e , exp (mg/g)	114.1128	202.3125
q_e , cal (mg/g)	105.92	170.2
k_1 (1/min)	0.0322	0.0253
R^2	0.995	0.943
Pseudo-second-order		
k_2 (g/mg min)	2.58×10^{-4}	2.05×10^{-4}
q_e , cal (mg/g)	142.85	250
R^2	0.99	0.928

$$h = k_2 q_e^2 \quad (14)$$

where k_2 (g/mg min) is the rate constant of the pseudo-second-order. The q_e and k_2 values can be obtained from the slope and intercept of plots of t/q_t versus t . Fig. 7(a) and (b) shows the linearized form of the pseudo-first-order model and pseudo-second-order model for f -MWCNTs adsorption at 50 and 100 mg/L initial MG concentrations. The calculated kinetics constants are given in Table 2. The correlation coefficients values were greater than 0.9 and the calculated q_e was near the experimental value for both kinetics models, but this value for the pseudo-first-order model is slightly greater than pseudo-second-order model, indicating that the adsorption of MG could follow the pseudo-first-order model.

CONCLUSION

The adsorption of malachite green dye onto f -MWCNTs as a novel adsorbent was carried out by using batch technique. The effects of different operational parameters such as contact time, pH of solution, adsorbent dose and initial MG concentration were evaluated. The results of the present study indicate that by increasing contact time, pH and adsorbent dosage, the removal percentage increased, but by increasing the initial MG concentration, the removal percentage decreased. Experimental data were fitted with the most common existing models. Based on correlation coefficient (R^2), the experimental data follows the Langmuir isotherm with maximum adsorption capacity of 142.85 mg/g. The results of this study indicate f -MWCNTs can be used as an effective adsorbent for dye removal.

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