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A Kinetic Study for Malachite Green Removal of Adsorption over Multiwall Carbon Nanotubes

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Abstract

Current study was carried out to determine the adsorption ability of the Multiwall carbon nanotubes (MWCNTs) by adsorption Malachite Green dye from an aqueous solution. Crystal structure of the materials was measured using powder X-rays diffraction (PXRD), UV–Vis diffuse reflectance and specific surface area (BET). Many parameters that affecting the adsorption process such as contact time, pH, adsorbent dosage, initial dye concentration and temperature were studied. The outcome showed that an increasing occurred in the adsorbent dosage and the rate of dye removal, and the best efficiency for Malachite Green dye removal was amounted 99. 11 %. The results were obtained at optimal reaction conditions were pH = 5.5, catalyst weight 0.15 g, T = 298 K and reaction time = 1 h. In addition, the equilibrium adsorption isotherms and kinetics studies were investigated using Freundlich and Langmuir isotherms. The Freundlich isotherm (R_2=0.9506) was found to be the best fitted for experimental data of this study .A higher correlation value of kinetic model was observed close to pseudo-second-order (R_2=0.999) compared to other kinetic models.

Keywords: Adsorption, MWCNTs, Malachite Green, Kinetics, Isotherms

دراسة حركية لأزالة صبغة الملاكيت الاخضر من الامتزاز على الانابيب النانوية المتعددة الجدران

بشائر جواد كاظم

علوم الاغذية، جامعة الكوفة، محافظة النجف الاشرف ، العراق

الخلاصة

أجريت الدراسة الحالية لتحديد القدرة الامتزازية للأنابيب النانوية الكربونية متعددة الجدران عن طريق امتزاز صبغة الملكيت الخضراء من محلولها المائي . تم قياس التركيب البلوري للمواد باستخدام حيود (PXRD)الاشعة السينية ، وانعكاس الاشعة فوق البنفسجية– المرئية (UV–Vis)، ومساحة السطح المحددة (BET) . تمت دراسة العديد من العوامل التي تؤثر على عملية الامتزاز مثل الوقت ، درجة الحموضة ، وزن الممتز ،تركيز الصبغة الأولي ودرجة الحرارة. أظهرت النتائج حدوث زيادة في وزن الممتز ومعدل إزالة الصبغة ، وكانت أفضل كفاءة لإزالة صبغة الملكيت الخضراء 99.11٪. تم الحصول على النتائج في ظروف التفاعل المثلى كانت الأس الهيدروجيني = 5.5 ، ووزن المحفز 0.15غم، و 298 = T كلفن ، وزمن التفاعل = 1 ساعة. بالإضافة إلى ذلك ، تمت دراسة ايزوثيرم الاتزان ودراسات حركية التفاعل باستخدام ايزوثيرم فرندلش ولانكماير. ووجد ان ايزوثيرم فرندلش أفضل ملاءمة للبيانات التجريبية لهذه

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الدراسة. كما لوحظ ارتفاع قيمة معامل الارتباط بالنسبة للمرتبة الثانية الكاذبة (R=0.999) مقارنة بالنماذج الحركية الأخرى.

1. Introduction

Water constitutes 70 to 90 percent of the earth's surface. Life ceases to exist without it. . Recently, There have been a rising interest in studies investigating new methods for the reduction of contaminated dye wastewater for processing [1]. Azo dyes are the most powerful types of dyes used in water treatment [2].These dyes are widely used in the clothing, food and color printing industries. Azo coloring has a complex aromatic structure and is almost structurally complex with azo groups (-N=N-). The deep color of these paints comes from the presence of azo classes, so the color vanishes if these groups are removed. It is not easy to break these materials into smaller pieces under normal conditions due to their rigid structure [3]. The presence of dyes in water can cause some problems , such as decreasing the amount of water oxygen, interfering with the penetration of sunlight into water, delaying photosynthesis and interfering with the solubility of gas in water bodies [4].

Consequently, it is possible to efficiently extract dyes from contaminated aqueous solutions by adsorption processes.. Processes of dyes elimination are usually of low cost, quick to run, high recovery and simple design[5,6].

Carbon nanotubes (CNTs) appear to be a strong candidate as an adsorbent among a diverse array of adsorbents that can absorb wide range of organic contaminants from wastewater [7,8]. There are several types of carbon nanotubes such as single walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes, in addition to (MWCNTs)which were discovered by Iijima 1993 [5].This categorization is based on the number of sheets which are comprised in them[9]. In general, due to their ideal properties, such as high thermal stability, high electrical conductivity, high adsorption capacity, high power, and potential mechanical strength CNTs have many applications [10].

Thus, the aim of current research is extracting Malachite Green dye out of simulated industrial textile wastewaters via adsorption over multi-walled carbon nanotubes. Various factors, such as contact time effects, dosage of MWCNTs, pH, and temperature, that could influence the capacity of MWCNTs for adsorption will be investigated. Ultimately, experimental data will be undertaken to suit with kinetic and equilibrium model.

2. Materials and methods

MWCNTs with a diameter of 5.5 nm and a length of 10-30 μm were purchased from Sigma-Aldrich by Malachite Green dye and used without further treatment to provide a model of contaminated textile dye with a molecular formula $C_{23}H_{25}ClN_2$ and a molecular weight of 364.9g.mol^{-1}. The dye stock was prepared by dissolving the required dye weight in distilled water to get a concentration of 50 ppm. Solutions of different concentrations were obtained by diluting the stock dye solution to the necessary required concentrations in an acceptable quantity. Both Freundlich and Langmuir adsorption models have been applied in terms of adsorption isotherms. A series of experiments were conducted using a dye solution of 100 ml, 50 ppm with 0.15 g of MWCNTs at 25 °C for duration of one hour per run, 2 mL of reaction, then the mixture was regularly removed and then filtered off using a centrifuge .Using a 620 nm UV-Visible spectrophotometer, the absorbance of the supernatant liquid was measured. Also,with the following relationship, the quantity of dye adsorbed on the surface of the MWCNTs was calculated:

$$q_e = \frac{(C_0 - C_e) \times V}{W} \quad \textbf{(1)}$$

Where q_e refers to the quantity of Malachite Green adsorbed at equilibrium on the surface of MWCNTs, The initial and final dye concentrations are Co and C_e, respectively V represents the volume of the solution (L), and W is the weight of the adsorbent (g). Langmuir isothermal adsorption can be described in the following equation [11].

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad \textbf{2)}$$

Where q_m is the maximum amount of Malachite Green adsorbed by the Langmuir constant is the unit mass of the MWCNTs and K_L. The Freundlich model relies on the distinction between active adsorption sites and equilibrium aqueous phases of adsorbents molecules[12, 13]. In the following equation, the Freundlich model can be described.

$$log(q_e) = logK_F + \frac{1}{n} log\, C_e \quad \textbf{(3)}$$

Freundlich constants are (K_F) and (n).

2.1 Adsorption Kinetic modeling

To determine the rate of adsorption process two kinetic models were used, Pseudo-first order and pseudo-second order to analyze the kinetic data of the Malachite Green adsorption on the MWCNTs.

2.2 The pseudo-first order Kinetic model

The rate constant of adsorption was determined by using pseudo-first order equation described by Lagergren and Svenska [13]:

$$ln(q_t - q_e) = ln(q_e) - k_1 \quad \textbf{(4)}$$

Where q_e and q_t (mg/g) are the amounts of the Malachite Green adsorbed at equilibrium and at time t (min), respectively, and the adsorption rate constant is k1 (min^{-1}).

2.3 The pseudo-second order Kinetic model

The pseudo-second order equation based on equilibrium adsorption is expressed in the following equation [14]:

$$\frac{t}{q_t} = \frac{1}{k_2\, q_e^2} + \frac{t}{q_e} \quad \textbf{(5)}$$

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

3. Results and discussion

The effect of MWCNTs mass on the efficiency of Malachite Green dye removal was investigated via performing a series of experiments using different doses of MWCNTs with the initial dye concentration of 50 ppm. The obtained results are presented in Figure 1 and showed that the efficiency of dye removal increases with increasing of adsorbent dosage from 10 to 50 mg. Under these conditions, the percentage of dye removal was increased from 49.40 to 99.11% after 60 min of adsorption time. These results are attributed to the increase of the available number of adsorption sites directly with increase the amount of MWCNTs used [15,16].

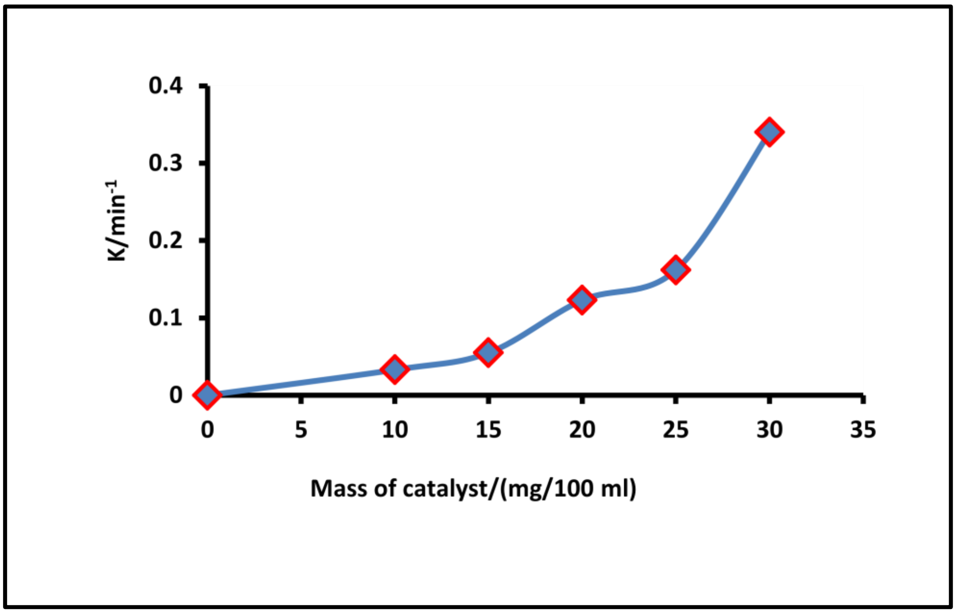

Figure 1-The influence of MWCNTs doses on removing the Malachite Green efficiency over MWCNTs

The effect of contact time on the removal efficiency of Malachite Green over MWCNTs is shown in Figure 2. It can be noticed from these results that the sum of malachite green color adsorbed MWCNTs at pH 5, 15 mg of MWCNTs and 298.15 K increased with an improvement in adsorption time for all doses of MWCNTs used.
The increase of loading capacity of CNTs with increase of time is likely due to greater interaction between the Malachite Green dye molecules and the active sites of the used adsorbent [17]. Results also showed rapid increase in efficiency of dye removal during the first 20 minutes [18]. This result is in agreement with what Toor et al. (2012) reported.

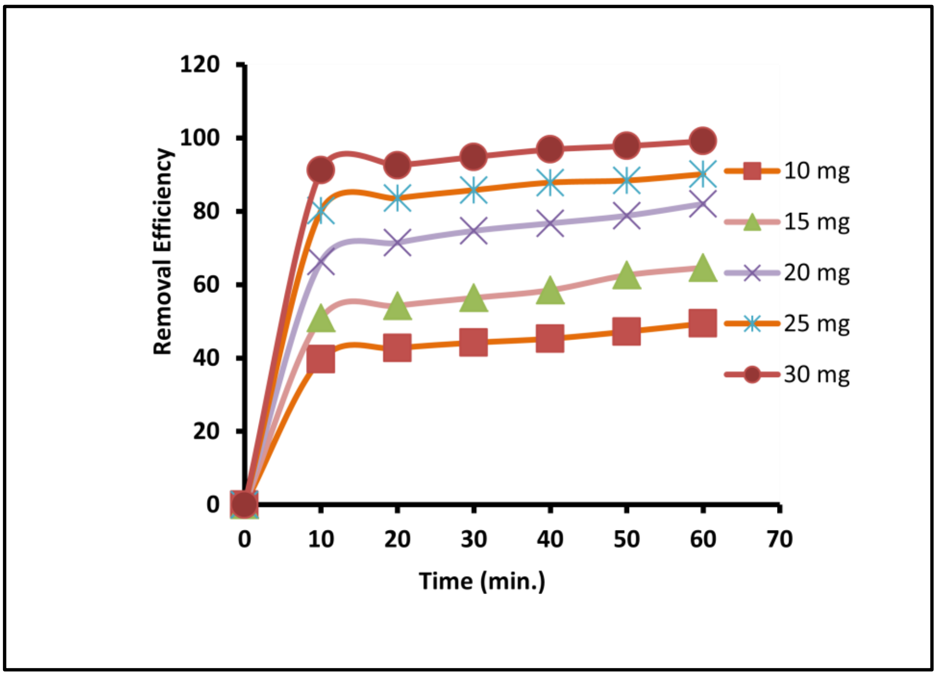

Figure 2-The effect of the length of touch on the removal of Malachite Green dye over MWCNTs

The pH value of the mixture may have a significant impact on the adsorption of dye molecules at the active sites on the surface of the adsorbent. The pH value can have an impact on the surface charge; in addition, it can effect ionization of different pollutants [19]. The effect of pH on adsorption of Malachite Green dye over MWCNTs was studied using different pH values from (2-10) with 50 ppm fixed initial dye concentration and 15 mg adsorbent dose for 60 minutes. Figure 3 shows that the adsorption of Malachite Green dye increased with an increase in the pH of the solution from (2 – 5), and then decreased gradually with pH values above 5.5.It is common knowledge that Multiwall carbon nanotubes contain carboxylic and hydroxyl groups after the purification method by acid treatment. The ionization of these functional groups would be influenced by the change in solution pH, and this can affect adsorption of dye molecules at MWCNTs' active surface sites. These results are in agreement with kinetics and Equilibrium studies on adsorption of acid red 18 (Azo-Dye) using multiwall carbon nanotubes (MWCNTs) from aqueous solution [20,21].

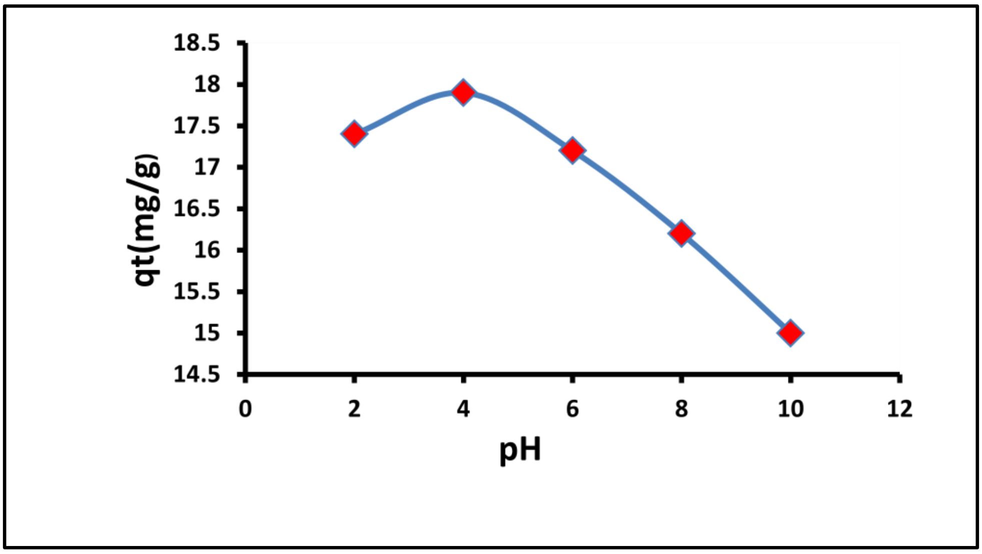

Figure 3-The effect of initial solution pH on adsorption of Malachite Green over MWCNTs

To investigate the effect of temperature on dye adsorption on MWCNTs, several experiments were conducted at a range of temperatures from 298.15 to 323 K Figure 4 shows that temperature changes can affect the dye adsorption efficiency over MWCNTs. The equilibrium adsorption capacity of the Malachite Green onto MWCNTs was found to increase when temperature increases. This fact indicates that when the temperature rises, the mobility of dye molecules can increase. In addition, with the increase in temperature, the viscosity of the dye solution decreases and as a consequence, the rate of diffusion of dye molecules will increase from the bulk of the active surface sites of MWCNTs, which contributes to an increment in the efficiency of dye adsorption when the applied temperature increase, which agrees with the findings of some studies[22].Adsorption isotherms were studied using adsorption models from Langmuir and Freundlich. Figures 5 and 6 indicate these isotherms, respectively.

Table 1 results indicated that the value obtained from the model of the Freundlich correlation factors[R_2 =0.9506] is greater than that of the Langmuir isotherm[R_2 =0.9362] thus, this method agrees with the model of Freundlich. The values of K_f and n were calculated from the slope and interception of the plot log q_e versus log Ce (Figure 6), and the obtained values of K_f and n are shown in Table 1.According to the n value, chemical adsorption is favorable, as the value of n is $n<1$.The truth is that the Freundlich isotherm fits the experimental data very well may be due to the heterogeneous distribution of active sites on the MWCNTs surfaces, since the Freundlich equation assumes that the surface of a catalyst is heterogeneous; this outcome is agreed with resent studies[22].

Table 1-The adsorption constants of Langmuir and Freundlich isotherms

Isotherms	Constants/Correlation Coefficients	Values
Langmuir	R^2	0.9362
	qm	0.651
	KL	0.021
Freundlich	R^2	0.9506
	KF	4.246
	n	0.157

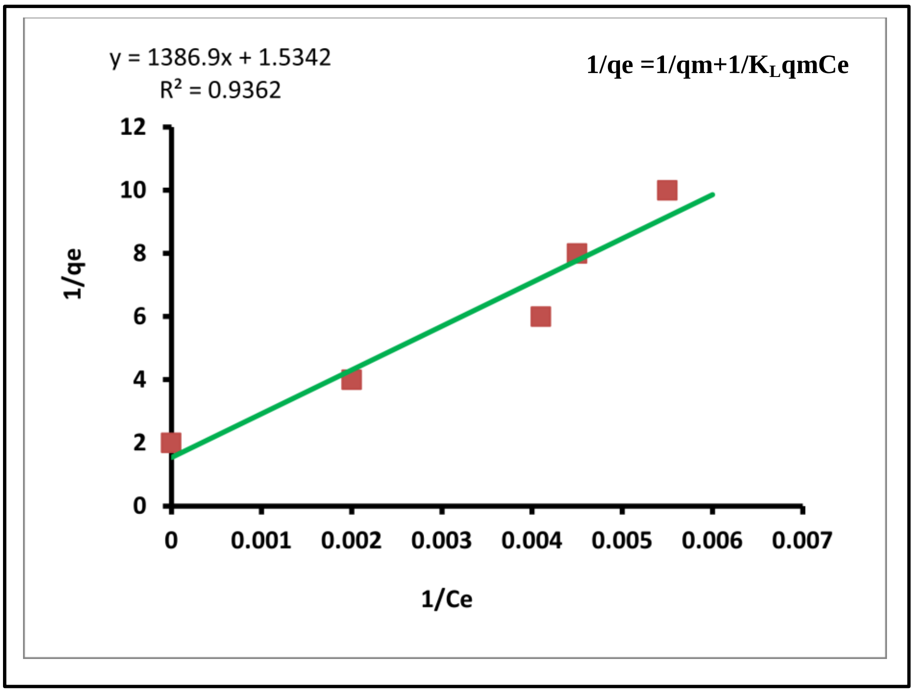

Figure 4-The effect of temperature on Malachite Green adsorption by MWCNTs

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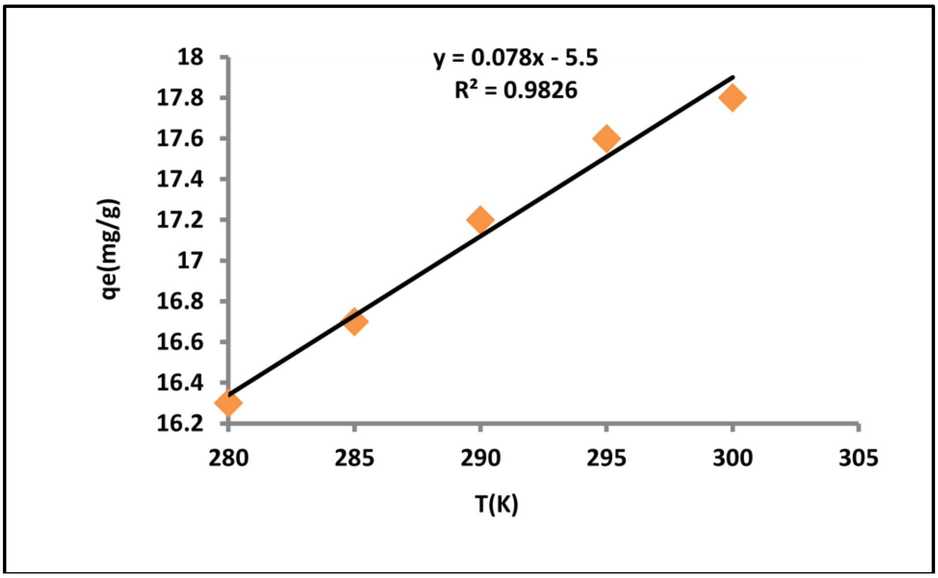

Figure 5-Isotherm of Langmuir adsorption for Malachite Green adsorption

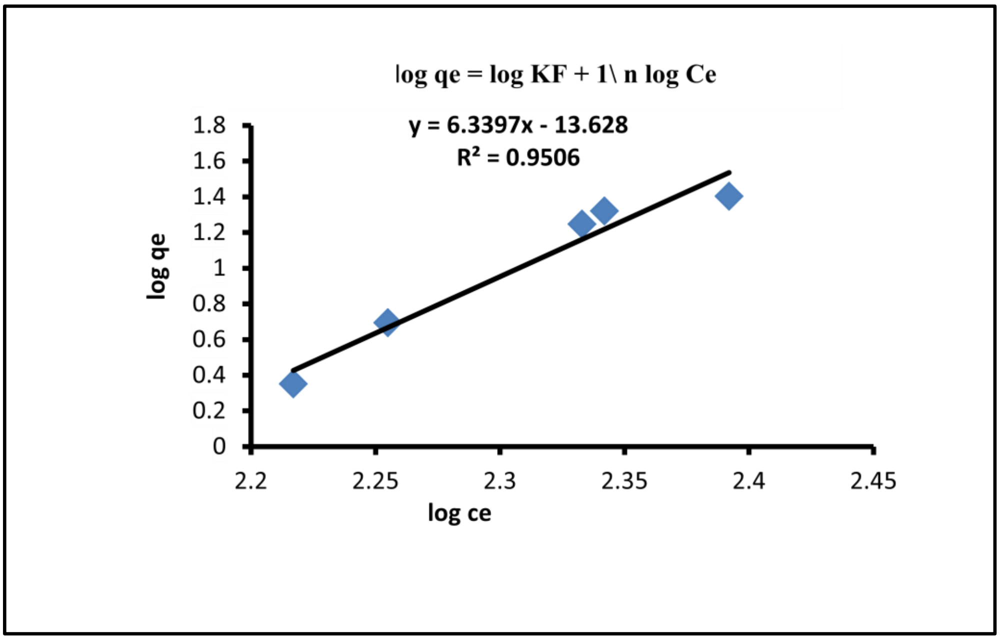

Figure -6 Freundlich adsorption isotherm for Malachite Green dye adsorption over MWCNTs

Results of Table 2 showed that the kinetic pseudo-second-order model was used with correction factor value of (0.9860-0.9997) and it was higher than that of the first false correction factors. Through this result, it is obvious that Malachite Green dye adsorption mechanism follows the kinetic structures of the pseudo-first order and the pseudo-second order. A similar phenomenon has been observed in previous literatures [23]. Tables 2 and 3 present the findings obtained (Figures 7 and 8).

Table 2-Pseudo-first-order kinetics parameters for Malachite Green dye adsorption over MWCNTs

Pseudo-first-order kinetic				
Adsorbent dose (g/100 ml)(	**qe,(experimental) (mg/g)**	**qe,(calculated) (mg/g)**	**K1 (min^{-1})**	**R^2**
0.01	24.70	27.45	0.035	0.966
0.015	21.54	23.17	0.043	0.864
0.02	22.05	24.56	0.021	0.992
0.025	18.02	21.97	0.051	1.000
0.03	16.51	10.46	0.046	0.965

Table 3-Pseudo second order the kinetic parameters for Malachite Green dye adsorption over MWCNTs

Pseudo-second-order kinetic				
Adsorbent dose (g/100 ml)	**qe,(experimental) (mg/g)**	**qe,(calculated) (mg/g)**	**K1 (min^{-1})**	**R^2**
0.01	24.70	25.00	0.5	0.994
0.015	21.54	21.73	0.4	0.992
0.02	22.05	27.72	0.18	0.986
0.025	18.02	18.51	1.87	0.999
0.03	16.51	16.49	1.45	0.999

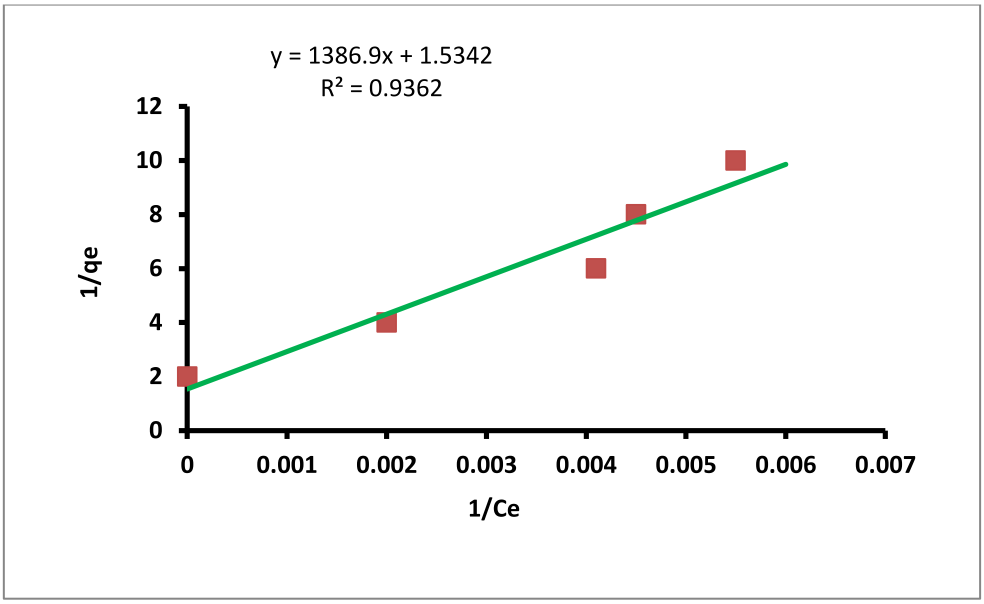

Figure 7-Pseudo-first-order of kinetic model for Malachite Green dye adsorption over MWCNTs

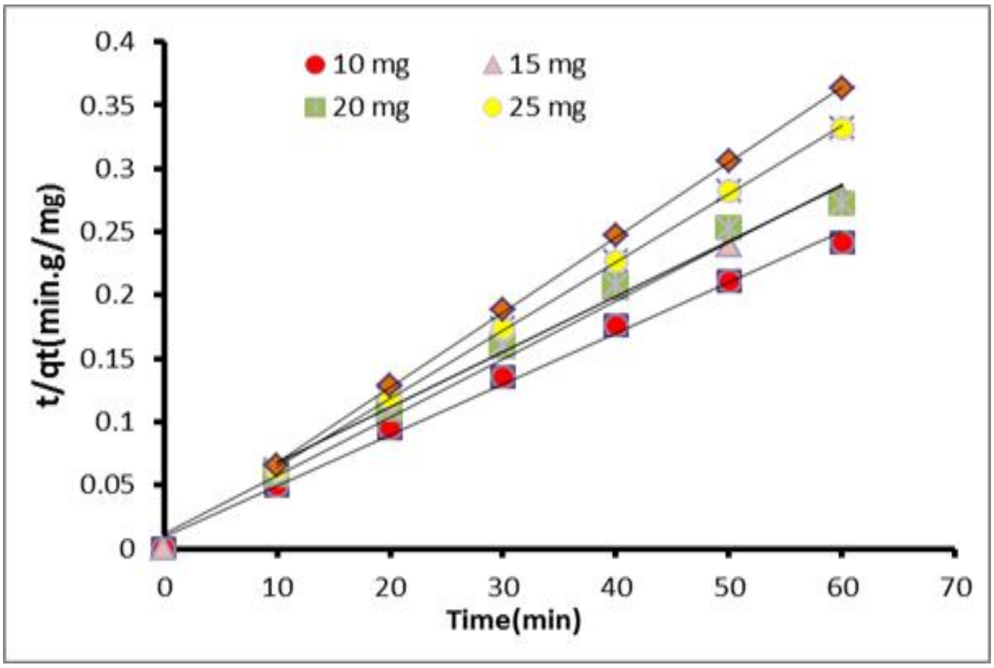

Figure 8-Pseudo-second-order kinetics adsorption model of Malachite Green dye over MWCNTs

Conclusion

This study indicates that MWCNT can be used efficiently to extract Malachite Green from the aqueous solution. The optimal dosage of MWCNTs for adsorbing BET is 15 mg, the initial Malachite Green concentration increased and Malachite Green's adsorption potential on MWCNTs was improved. Moreover, the temperature and the equilibrium adsorption capacity of Malachite Green were increased. The optimal time of contact and pH were 20 min and 5 respectively .A pseudo-second-order kinetic model was used to suit the adsorption kinetics. The Langmuir and Freundlich adsorption isothermal models have identified Malachite Green Adsorption on MWCNTs. Ultimately the equilibrium knowledge was equipped with the Langmuir isotherm.

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