



Using Tobacco Leaves as Adsorbent for the Orange-G Dye Removal from its Aqueous Solutions

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Abstract

The removal of commercial orange G dye from its aqueous solution by adsorption on tobacco leaves (TL) was studied in respect to different factor that affected the adsorption process. These factors including the tobacco leaves does, period of orange G adsorption, pH, and initial orange G dye concentration. Different types of isotherm models were used to describe the orange G dye adsorption onto the tobacco leaves. The experimental results were compared using Langmuir, and frundlich adsorption isotherm, the constants for these two isotherm models was determined. The results fitted frundlich model with value of correlation coefficient equal to (0.981). The capacity of adsorption for the orange G dye was carried out using various kinetic models like pseudo first order-kinetic, pseudo second order –kinetic, Elovich, and inter particle diffusion model, the rate constants for these models were evaluated. The data suggested that tobacco leaves are suitable sorbent for the orange - G dye removal from its solution.

Keywords: Adsorption, Orange G, Tobacco leaves.

Introduction

There are several harmful chemicals that composed the industrial wastes. Heavy metal phenol, and colure compounds are the major water pollutants that affecting the aquatic environment [1]. A dye one of colored substance that used in different industries as food cosmetics, dyeing paper and pharmaceutical industrial [2] these compound are aromatic molecular structural with chromophare and non-colored groups that intensity or influence the color, called auxochromes [3].

A different technique which was divided into three main types including physical, biological and chemical [4]. The quest for using –friendly method and cost effective, has been going one. Adsorption is an important process that has advantages in term of simplicity; flexibility, low cost and dose not release a harmful substance [5]. Natural adsorbents are used successfully for the removal of dye by adsorbed the dye at the surface such as natural clay, banana pith lemon peel, orange peel [6], peanut hull [7],

agricultural solid [8], jack fruit peel [9] and natural precursor [10].

In this research, an attempt has been achieved to use one kind of agricultural waste, tobacco leaves as a low - cost and friendly adsorbent for the treatment of the solutions that containing orange (G) dye. To evaluate the properties of the adsorption process in the batch experiments, Langmuir and Frundlich isotherm were applied. In addition different kinetic models including first and second order kinetic, Elovich and intrapartical to estimate the kinetic of the orange - G dye sorption.

Experimental Part

Material

Orange - G is a synthetic azo dye disodium salt with appearance of orange crystal or powder. C.I number 16230 and C.I name acid orange 10. The formula weight empirical formula is $C_{16} H_{10} N_2 O_7 S_2 Na_2$; λ_{max} value (maximum adsorbent wavelength) of orange G is 482 nm.

The UV-VIS of orange G dye were recorded from (200-800nm) its show only two color in aqueous solution brilliant orange in neutral

and red in pH 9. Figure (1) shown the chemical form of orange - G dye.

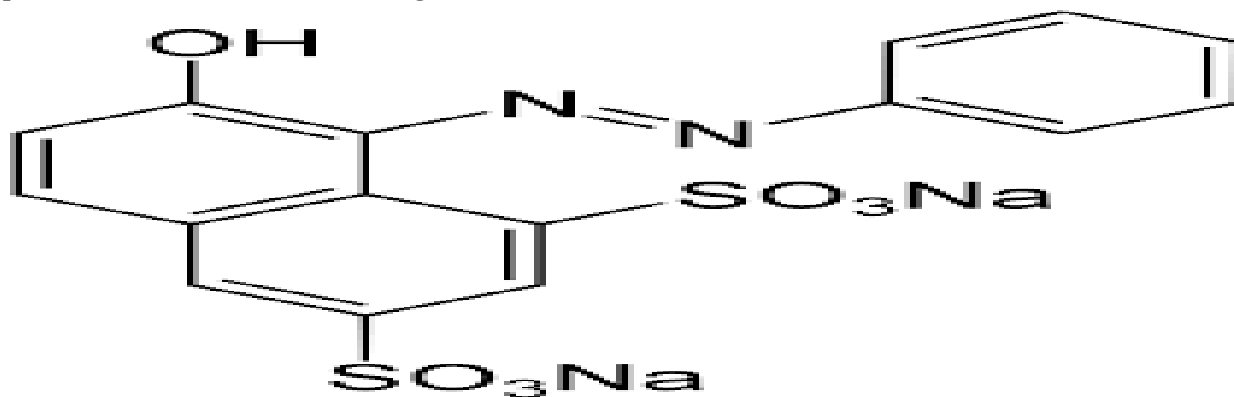


Figure 1: Chemical form for orange - G dye

Orange - G solution with concentration from 10 ppm to 40 ppm was prepared from the stock solution of 1000 mg/L. The leaves of tobacco collected from Iraqi tobacco company, Jadria, Baghdad were washed with excess quantity of distilled water, then heated with distilled water for one hour, the leaves was separated and dried under sun light for one day. The dried leaves were ground in mill then sieved in the particles size range from (150-250) μm .

Method

A 25ml volume of different orange G dye concentration was placed into 100ml conical flask containing 0.25gm of tobacco leaves powder. The flasks were then shaken at 110 rpm using a mechanical shaker after shaking the sample was separate by centrifugation. The filtrate was analyzed by a UV-Visible spectro-photo-meter at maximum lambda 482 Nano meter. The equilibrium amount of orange G (q_e) in (mg/g) was estimated as follows

$$q_e = v[C_{in} - C_e]/m \dots\dots\dots(1)$$

C_e, C_{in} : the equilibrium and initial orange G concentration [mg. L^{-1}],

V : in litter is the volume of shaken dye solution,

m : in gram is the weight of the tobacco leaves powder .

The value of removal ability was found from the relationship:

$$\text{Removal \%} = [C_{in} - C_e / C_{in}] \times 100 \dots\dots\dots (2)$$

Results and Discussions

Tobacco Leaves (TL) Dose

The amount of TL leaves verify from (0.1-0.3) gm .From the Figure (2) it is observed that the removal ability increase as the TL leaves increased. This result attribution to the presence of more adsorption sites in the TL surface that cause to increase TL surface area [11].

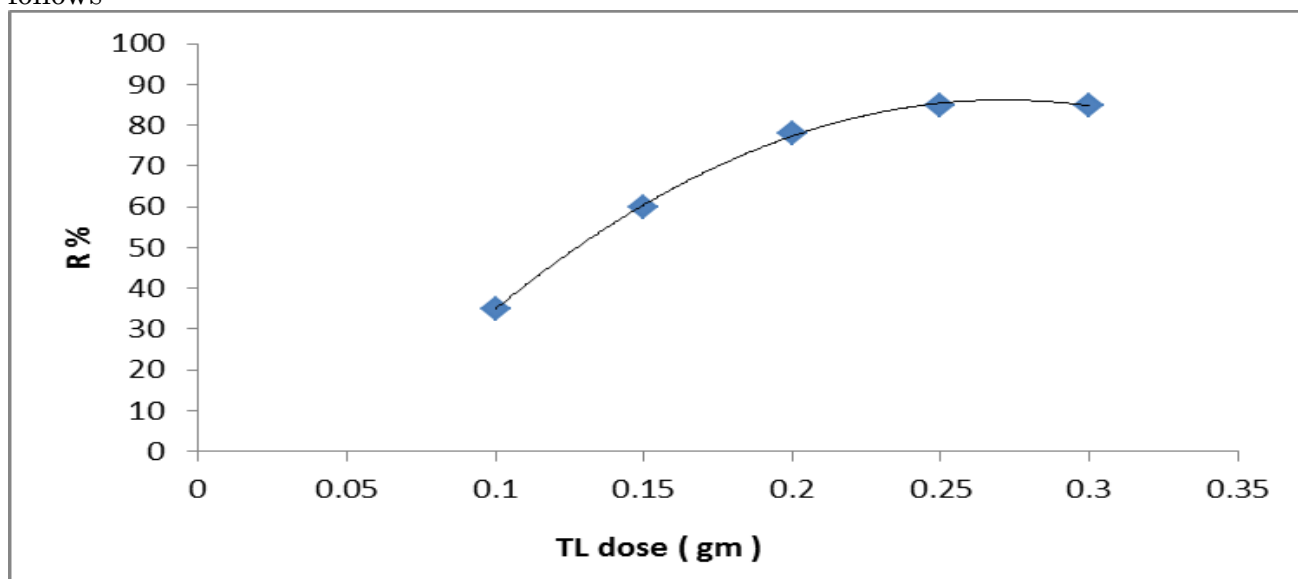


Figure 2: Influence of TL onto the adsorption process

Period of Adsorption

Figure (3) shows that uptake of the orange G dye was rapid at the first time and become slow in the last stage till it reaches saturation at 140 min.

This can be attributed to that at the beginning there are many sites qualified to be occupied by dye molecules, when the time progress, the site that are eligible for the adsorption were blocked that causes to slowed the rate.

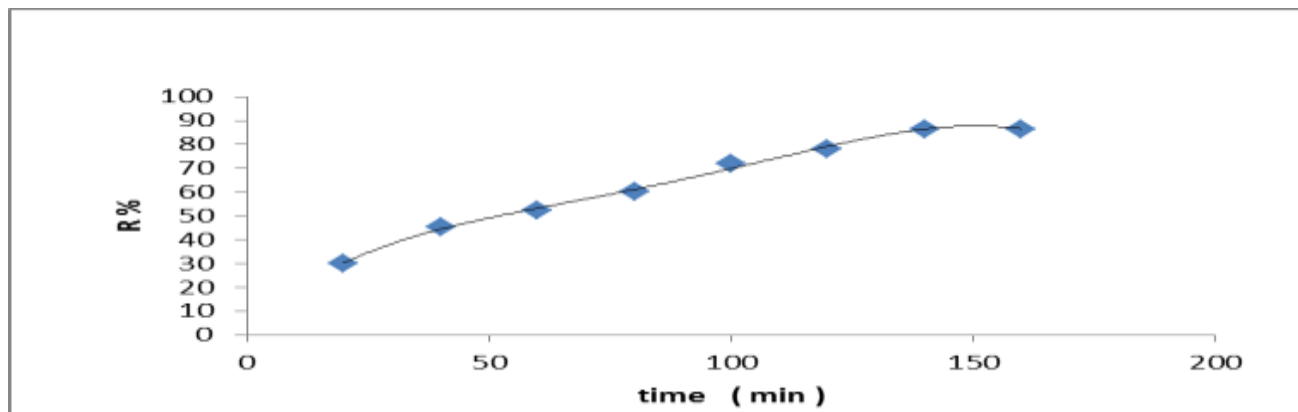


Figure 3: Influence of the period of adsorption

The Influence of pH

Adsorption of orange G onto TL is affected with the pH of the aqueous solution. Figure (4) shows that the maximum removed for the dye when the pH range from 9 to 10. At lower

values of pH the surface of TL becomes positively charged, this cause to remains high hydrogen ion concentrations and the H ions compete with orange G dye (cationic dye) for the empty site that qualified for the adsorption on the surface [12].

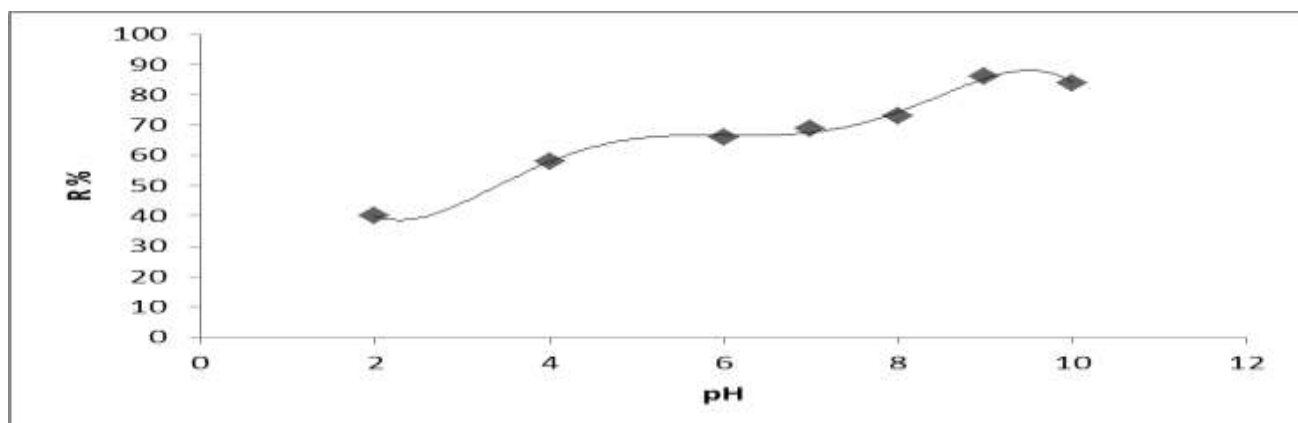


Figure 4: The influence of the (pH) on the adsorption of orange G onto TL surface

Influence of Initial Concentrations of Orange - G Dye

Figure (5).Shows that removal ability of the dye decrease when the initial orange G

increase. At higher initial orange G concentration the available adsorption sites being fewer that make the removed ability of the dye decrease [13].

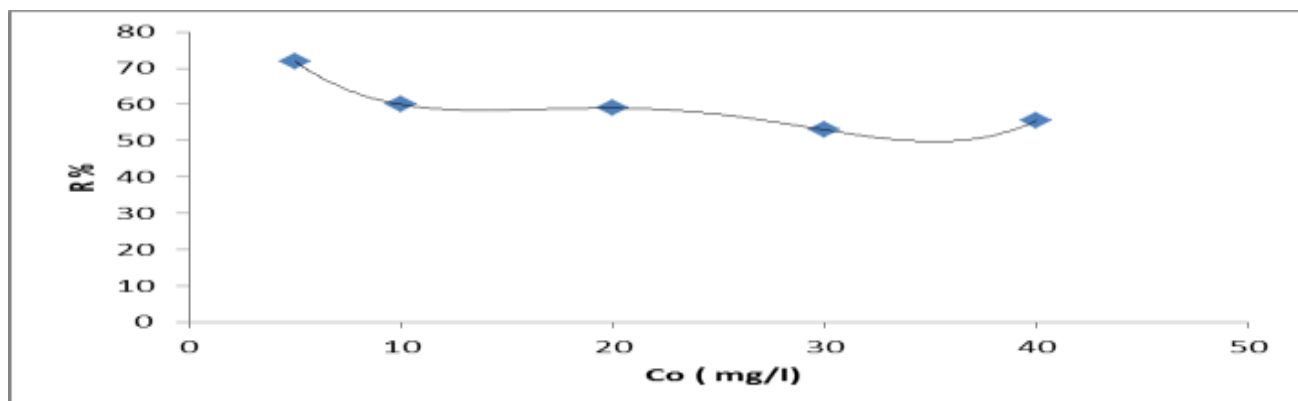


Figure 5: Influence of initial concentration of orange G onto adsorption process

Isotherm Models

By using the equilibrium data three type of adsorption isotherm were analyzed.

Langmuir Model

The Langmuir theory is based on assumption that sorption take place at specific active sites within the adsorbent [14]. The Langmuir model was express as:

$$C_e / q_e = C_e / q_o + 1/q_o b \dots\dots\dots (3)$$

Where q_o , b are Langmuir constants in (mg/g) and (L/mg) respectively q_o related to adsorption capacity and b related to adsorption energy.

Values of b , q_o evaluated from the intercept and slope of linear relation between C_e/q_e and C_e as showing in Figure (6). Table (1) summarized the values of Langmuir constants.

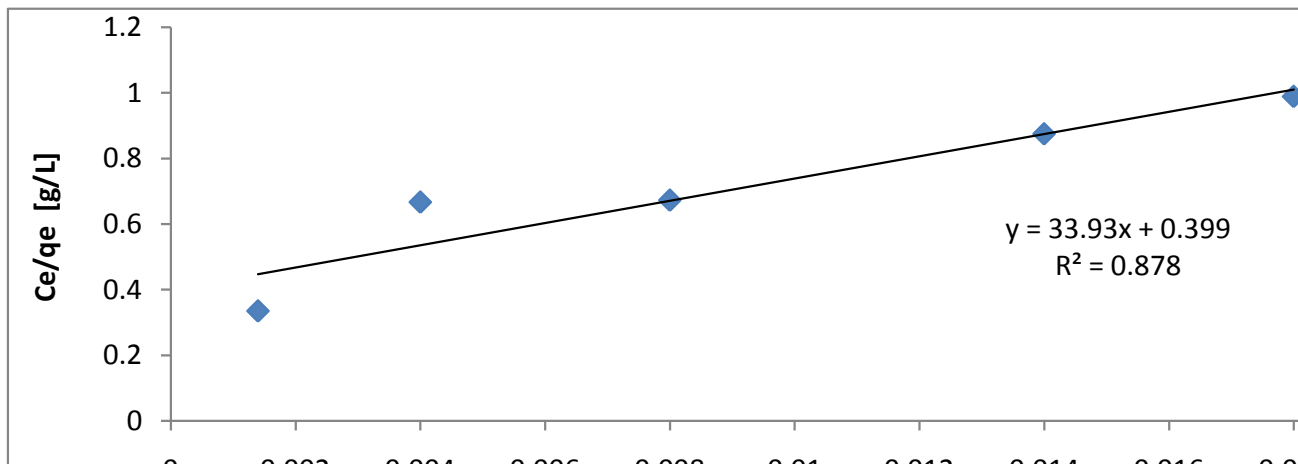


Figure 6: Langmuir isotherm orange - G adsorption into TL surface

Langmuir isotherm can be described in terms of a (dimensionless constant) K_s which can be represented as

$$K_s = 1 / (1 + K_m C_{it}) \dots\dots\dots (4)$$

Where: K_m is the Langmuir constant in (L/mg), C_{it} is the initial concentration of the orange G dye in (mg/L). The parameter K_s shows the shape of the adsorption isotherm as:

Values of K_s	$K_s > 1$	$K_s = 0$	$K_s = 1$	$0 < K_s < 1$
Type of isotherm	Un-favorable	Irreversible	Linear	Favorable

Values of the calculated K_s are listed in Table (1). The values of K_s for orange - G at different concentration are shown in Figure (7). K_s values indicated that orange - G dye adsorption onto TL Leaves was more favorable for the higher C_{it} initial

concentration than the lower C_{it} . K_s values for orange - G dye adsorption of orange G dye onto TL leaves were greater than [0] and less than [1], this indicated a favorable - sorption process.

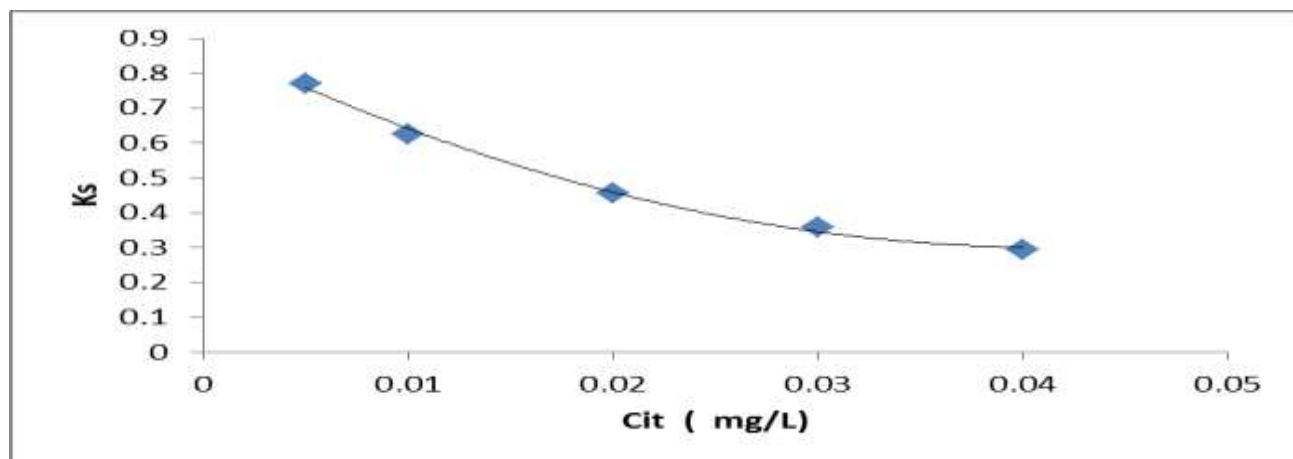


Figure 7: Values of the (separation constant) K_s for adsorption of orange G onto TL surface

Frundlich Model

This model can be used in adsorption from diluted aqueous solution, the linear form of this model [15]

$$\ln q_e = \ln K_f + (1/n) \ln C_e \dots\dots\dots (5)$$

Where n, K_f frundlich constants which are roughly on indicator of surface hetrogency and adsorption capacity. The values of frundlich constants K_L , n estimated from the intercepted and slope of the curve plotted between $\ln K_q_e$ and $\ln C_e$, Figure (8).

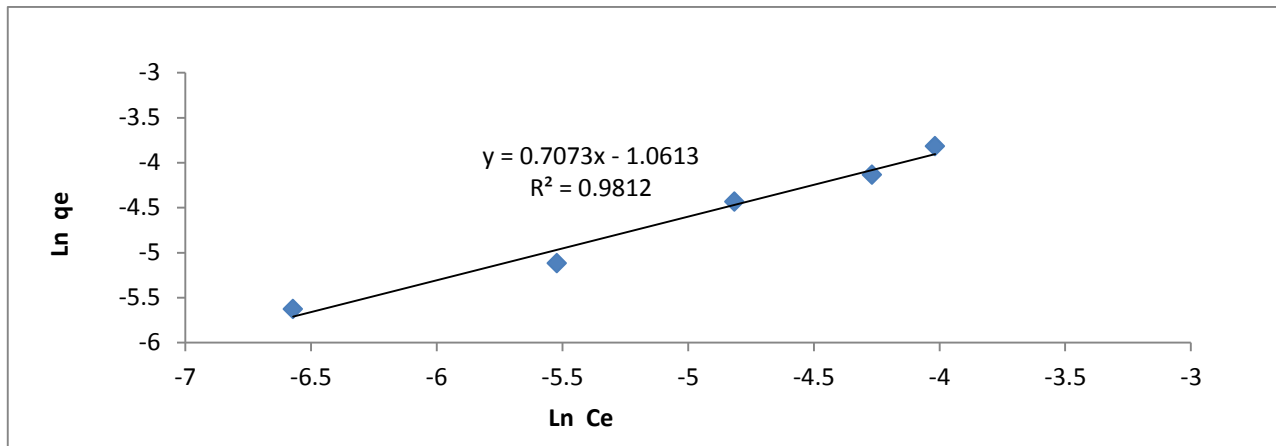


Figure 8: Frundlich isotherm model for the adsorption of orange G into TL surface

Table (1) shows the experimental isotherm data for the adsorption of orange G onto TL leaves. From these data it was clear that the Frundlich model isotherm has a higher

correlation factor ($R^2=0.981$). These results confirm the existence of interaction between various adsorption species [16]. That agreed well with Frundlich model isotherm.

Table 1: Isotherm data for the adsorption of orange G onto TL surface

Langmuir isotherm			Frundlich isotherm		
Q_o	b	R^2	K_f	n	R^2
	(L/mg)				
0.0383	59.7935	0.878	0.362	1.4143	0.981
Values of K_s (Separation constant)					
C_o (mg/L)	0.005	0.01	0.02	0.03	0.04
K_s	0.7699	0.6258	0.4554	0.3579	0.2948

Kinetic Model

Elovich Models

The Roginsky –Zelovich model is given by the equation [17].

$$q_t = \ln [\alpha \cdot \beta] / \beta + [\ln t / \beta] \dots\dots\dots (6)$$

Where, α : the initial orange G sorption rate in (mg/g/ min), β (g^*1/mg) the desorption constant, q_t is the amount of orange G adsorbed in ($mg.g^{-1}$) the constants α and β were calculated from the linear plot of q_t and $[\ln t]$ Figure (9).

The evaluated constants of Elovich model are shown in Table (2). These values indicated

that the adsorption surface is high hetrogenous.

Pseudo first order model

[lagergrens equation] the linearized form of this equation represented as [18].

$$\ln (q_e - q_t) = \ln q_e - (k_1 * t) \dots\dots\dots (7)$$

Where q_t , q_e is amount of orange G dye at time in minute, and at equilibrium in (g^*1/g) respectively and k_1 in (1/min) is the pseudo - first -order rate constant, the values of q_e , k_1 were obtained from the linear plot of $[\ln q_e - q_t]$ vs. (t) Figure (10).

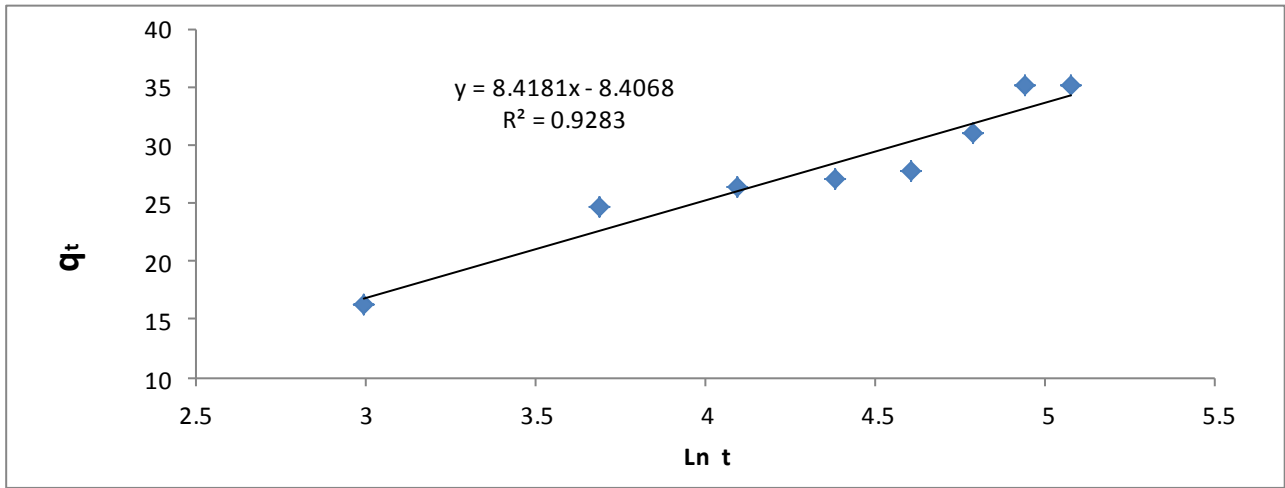


Figure 9: Elovich kinetic model for the adsorption of orange G onto TL surface

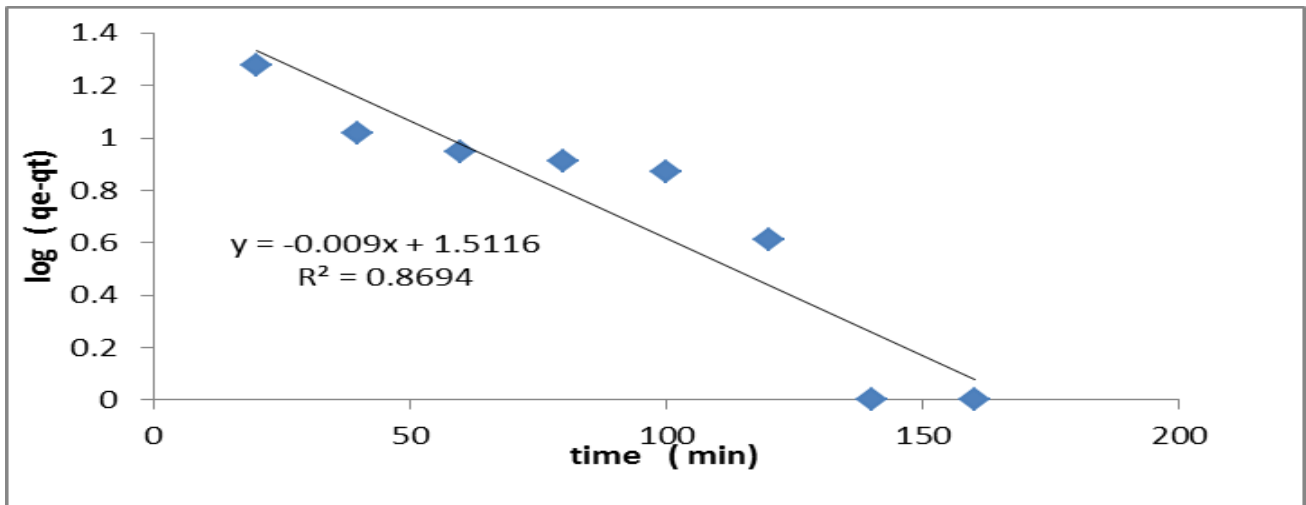


Figure 10: Pseudo first order plot for the adsorption of orange G onto TL leaves

Pseudo Second Order Model

This model can be written as shown below:

$$t/q_t = [1/k_2q_e^2] + [t/q_e] \dots\dots\dots(8)$$

Where, k_2 : the rate constant in [g/mg .min] for pseudo second order model. This constant was calculated from the linear relationship between $[t/q_t]$ and $[t]$ Figure (11).

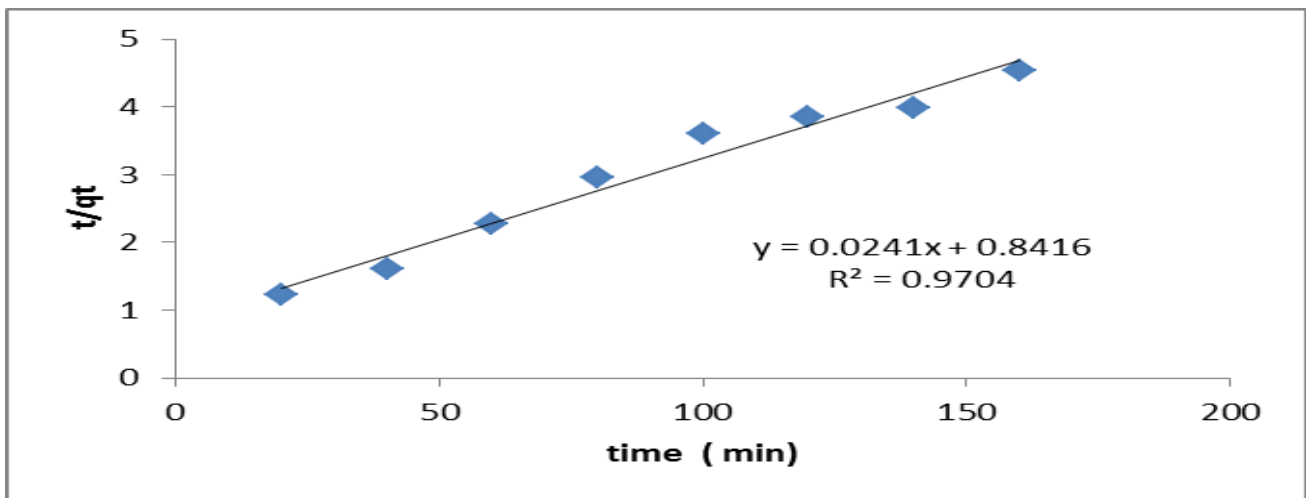


Figure 11: Pseudo-second order plot for the adsorption of orange G onto TL surface

It was clear from the kinetic results listed in Table (2), that the pseudo-second order model agreed with the experimental adsorption data better than the pseudo-first-order models the correlation-coefficients of the

pseudo-second-order close to unity. Both results obtained from the Elovich and pseudo-second-order model related that the adsorption of orange G onto the TL surface followed chemisorption. In this type of

adsorption, it is assumed that the sorption capacity is proportional to the total number of the active –sites on the TL leaves that occupied with the dyes molecular.

Intra – Particle Diffusion Model

This model can be written as shown below [19]:

$$q_t = K_i [t]^{1/2} + C \dots\dots\dots(9)$$

The values of K_i (intra – particle diffusion constant in [mg /g.min^{0.5}]) and C were estimated from the slop of the linear plot between q_t and $[t]^{1/2}$, Figure (12).

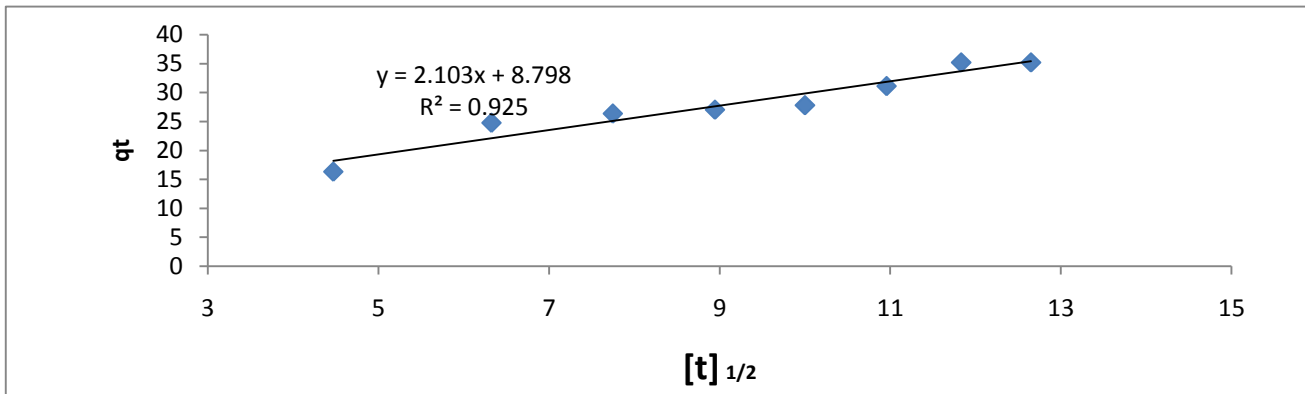


Figure 12: Intra particle diffusion plot for orange G adsorption of onto TL surface

Table 2: Different kinetic modles for orange G dye adsorption onto TL surface

Elovich model	α (mg g ⁻¹ min ⁻¹)	B (g mg ⁻¹)	R
	3.0966	0.1184	0.928
Pseudo first order	qe (cal.)	k1 (min) ⁻¹	R
	92.4339	0.0207	0.8694
Pseudo second order	qe (cal.)	k2 (g.mg ⁻¹ .min ⁻¹)	R
	41.666	6.849×10 ⁻⁴	0.9704
Intra particle model	Ki (mg/g.min ^{0.5})	C (mg/g)	R
	2.1033	8.7983	0.9256

As shown in Figure (12) the plot of (q_t) versus (t)^{1/2} is linear with some deviation from the origin. Such deviation from the origin indicates that the pore diffusion is not the rat-controlling step [20].

Conclusion

In this research, the adsorption of orange G onto tobacco leaves were studied by using batch tests conducted under different experimental conditions including the

tobacco Leaves dose, period of orange G adsorption, pH and initial orange G concentrations. The best removed obtained at (140) min, pH (10) and tobacco leaves dose equal to (0.25 gm). The experimental results gained were extremely well described by frundlich model. The kinetic study for the system pointed out the adsorption process can describe by pseudo second order model. It is evident that tobacco leaves as natural –low cost material are good adsorbent for orange G dye removal from waste solutions.

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