

Investigation kinetics mechanisms of adsorption malachite green onto activated carbon

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Abstract

Lignite was used to prepare activated carbon (T3K618) by chemical activation with KOH. Pore properties of the activated carbon such as BET surface area, pore volume, pore size distribution, and pore diameter were characterized by *t*-plot based on N₂ adsorption isotherm. BET surface area of activated carbon is determined as 1000 m²/g. Adsorption capacity of malachite green (MG) onto T3K618 activated carbon was investigated in a batch system by considering the effects of various parameters like initial concentration (100, 150 and 200 mg/L) and temperature (25, 40 and 50 °C). The adsorption process was relatively fast and equilibrium was reached after about 20 min for 100, 150 mg/L at all adsorption temperature. Equilibrium time for 200 mg/L was determined as 20 min and 40 min at 298, 313 and 323 K, respectively. Simple mass and kinetic models were applied to the experimental data to examine the mechanisms of adsorption and potential rate controlling steps such as external mass transfer, intraparticle diffusion. Pseudo second-order model was found to explain the kinetics of MG adsorption most effectively. It was found that both mass transfer and pore diffusion are important in determining the adsorption rates. The intraparticle diffusion rate constant, external mass transfer coefficient, film and pore diffusion coefficient at various temperatures were evaluated. The activation energy (*E_a*) was determined as 48.56, 63.16, 67.93 kJ/mol for 100, 150, 200 mg/L, respectively. The Langmuir and Freundlich isotherm were used to describe the adsorption equilibrium studies at different temperatures. Langmuir isotherm shows better fit than Freundlich isotherm in the temperature range studied. The thermodynamic parameters, such as ΔG° , ΔS and ΔH° were calculated. The thermodynamics of dyes–T3K618 system indicates endothermic process. © 2006 Elsevier B.V. All rights reserved.

Keywords: Activated carbon; Adsorption; Reaction kinetics; Lignite; Malachite green

1. Introduction

The kinetic of adsorption and sorption in a complex porous media has been an important subject at the processes of separation and purification. Kinetic and velocity is the main subject while investigation of adsorption mechanism. Predicting the rate at which adsorption takes place for a given system is probably the most important factor in adsorption system design. However, while applying the process, existence of diffusion coefficient and mass transfer coefficient is an important parameter. In adsorption studies mostly active carbon is used as an absorbent, where textile dyes are preferred as an absorbent. In order to investigate the mechanism of adsorption, various kinetic models have been suggested. In recent years, adsorption mechanisms involving kinetics-based models have been reported. Numerous works

have models studies is given in literature related with activated carbon and dyes. Although some aspects have been understood, many are not very well known, for example, the role of texture (size and configuration) on the adsorption kinetic, especially the surface diffusion and the mass exchange between the intraparticle fluid phase and the adsorbed phase [1–3].

The textile industry is producing increasing amount of waste be cause of day by day growing dye consumption and usage of new kind of dyes. We face a big environment problem with approximately 10,000 registered different types of dyes and 7×10^5 tons consumption per year. When it is thought that roughly about 10–15% of these dyes are given to aqueous environments, it is obvious how great the rate of pollution is [4,5]. Since it is practically impossible to have adsorption and kinetic studies for each kind of dyes, generally studies on model dye compounds step forward.

A model kinetic study on active carbon and dye has a significant place in literature. Mall et al. studied Congo red's adsorption kinetic on to active carbon [6] and, Arslanoglu et al. reported

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on the adsorption of dark coloured compounds from peach pulp by using powdered activated carbon [7], Senthilkumaar et al. studied adsorption of methylene blue onto jute fiber carbon: kinetics and equilibrium studies [8], Juang et al. investigated phenol adsorption and desorption kinetic [9], Namasivayam and Kavitha studied Congo Red's adsorption kinetic [10], adsorption kinetics of various dyes onto industrial wastes was investigated by Jain et al. [11], rhodamine B's adsorption kinetic and various dyes and phenols adsorption kinetic were studied by Kadirvelu et al. [12] and by Wu and Tseng [13], respectively.

Mittal et al. used various adsorbents to Tartrazi's adsorption kinetic [14], Aksu and Kabasakal investigated 2,4-dichlorophenoxy-acetic acid's adsorption kinetic onto GAC [15], Rajgopal et al. studied MG's adsorption kinetic onto active carbon (AC) [16]. In their study, Senthilkumaar et al. [17] used AC as adsorbent for the adsorption of reactive Red2. The results of Wang and Li indicated dye adsorption kinetic by unburned carbon [18], Walker and Weatherley studied adsorption kinetics of acid dyes onto GAC [19].

2. Experimental

2.1. Materials

The dye, malachite green (MG), CI=42,000, chemical formula equal to $C_{50}H_{52}N_4O_8$, FW=927.03g/mol, and $\lambda_{max}=617$ nm (experimental obtained by us) was supplied by Merck (1398). One thousand milligram per liter stock solution was prepared by dissolving the required amount of dye in double distilled water. Working solutions of the desired concentrations were obtained by successive dilutions.

2.2. Preparation of activated carbon

Brought in containers from Tunçbilek-Kütahya (Turkey) lignite was dried under laboratory conditions for 3 h and then sieved to $-60+100$ mesh fraction and later stored in colorful plastic tubes. All experiments carried out with dried lignite at 105°C . Adsorbent (T3K618) were prepared from lignite by chemical activation with KOH, activation temperature and KOH/lignite ratio (impregnation ratio) was selected 800°C and 4:1, respectively. The impregnated sample was raised to the activation temperature under N_2 (100 mL/min) atmosphere with $10^\circ\text{C}/\text{min}$ flow rate and hold at impregnation temperature for 1h. After the activation, the sample was cooled down under N_2 flow and washed several times successively with hot distilled water until a neutral residue is obtained. The washed sample was dried at 110°C to prepare activated carbon. The adsorbent was powdered and sieved. An average particle size of 0.075 mm was used for the adsorption studies.

2.3. Instrumentation

The spectrophotometric determination of dye was done on a Shimadzu UV-vis spectrophotometer (Model UV-2100S). The pore structures of active carbon were investigated by using the standard Micromeritics DFT plus software. Nitrogen adsorption

was recorded at 77 K by means of a TriStar 3000 (three port) surface analyzer (Micromeritics, USA). BET equation was used to calculate the specific surface area. Before the measurement, all samples were degassed at 300°C for 3 h.

2.4. Adsorption experiments

Dye solutions were prepared in distilled water at desired concentrations (100, 150, 200 mg/L). Adsorption experiments were carried out by agitating 0.1 g of T3K618 with 50 mL dye solutions of desired concentration and temperature ($25, 40, 50^\circ\text{C}$) in a thermostatic bath operating at 400 rpm (at natural pH). The amount of dye adsorbed onto T3K618, q_t (mg/g), was calculated by mass-balance relationship Eq. (1):

$$q_t = (C_0 - C_t) \frac{V}{W} \quad (1)$$

where C_0 and C_t are the initial and time t liquid-phase concentration of the dye (mg/L), respectively, V the volume of the solution (L), and W the weight of the dry T3K618 used (g).

3. Results and discussion

3.1. Characterization of the prepared adsorbent

Fig. 1 shows N_2 adsorption isotherm of the activated carbon (T3K618) obtained using KOH reagent. N_2 adsorption isotherm is classified as type I, characteristics of microporous solids, in IUPAC classification [22]. Table 1 contains the BET surface area (S_{BET}), external surface area (including mesopores and macropores area S_{ext}), micropores surface area (S_{mic}), total pore volume (V_t) and average pore diameter (D_p) results obtained by applying the BET equation to N_2 adsorption at 77 K and DR equation to N_2 adsorption at 77 K. It was found that the activated carbon had a remarkable BET surface area, which was primarily contributed by micropores. The average pore diameter was 2.3776 nm, indicative of its micropores character.

Fig. 2 shows the pore size distribution was calculated in the standard manner by using BJH method [20]. It appears that activated carbon was dominantly micropores. Percentage of micropores area is 84.8%.

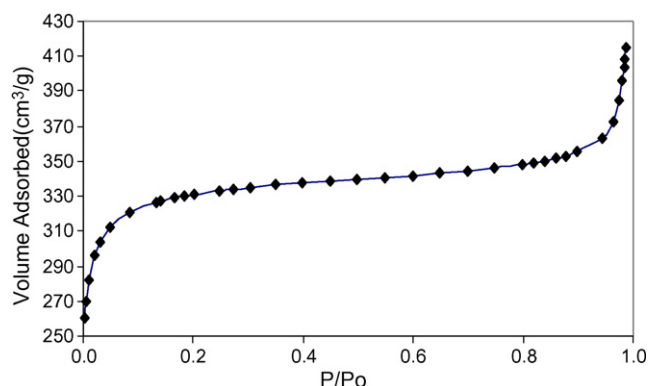


Fig. 1. Adsorption isotherm of nitrogen at 77 K for activated carbon (T3K618).

Table 1
Surface area and porosity of the activated carbon

S_{BET} (m^2/g)	S_{ext}		S_{mic}		V_t (cm^3/g)	V_{mic}		D_p (nm)
	(m^2/g)	% of S_{ext}	(m^2/g)	% of S_{mic}		(cm^3/g)	% of V_{mic}	
1000	153	15.3	848	84.8	0.59	0.44	74.6	2.27

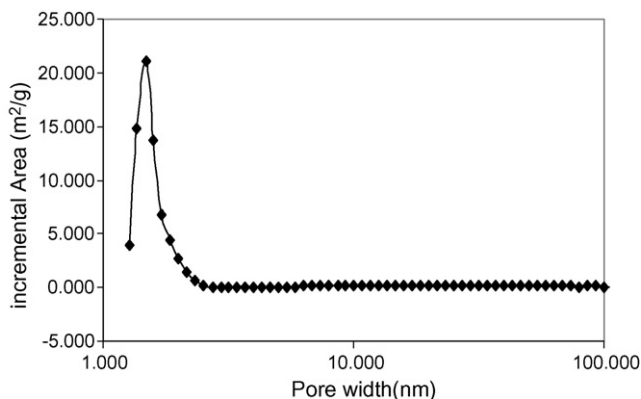


Fig. 2. Pore size distribution of the T3K618.

3.2. Effect of temperature and initial dye concentration on MG adsorption

The temperature has two important effects, which are known to increase the rate of diffusion of the adsorbate molecules across the boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution.

The curve in Fig. 3 relate amounts of malachite green adsorbed onto T3K618 for 100, 150, 200 mg/L initial dye concentration at 25, 40 and 50 °C. The removal of MG from aqueous solution by adsorption on T3K618 increases with time for all concentration, till the equilibrium is attained in 60 min. The MG adsorbed by activated carbon increased linearly with time in the beginning. Initial adsorption of MG occurred rapidly and the majority of MG removal occurred within 20 min except for 200 mg/L at 298 K (within 40 min) (Fig. 3). Ninety-nine percent of total adsorbed amount of MG was removed by adsorption in the first 20 min of contact for 100 mg/L, 150 mg/L dye concentration at all studied temperatures, for 200 mg/L at 313, 323 K, and in the first 40 min of contact for 200 mg/L at 298 K. In general, as the concentration of MG increased MG removal increased without regard to temperature.

3.3. Kinetic modelling

In present study, the sorption data were analyzed using two simplest kinetic models, first and second-order models that are explained as follows.

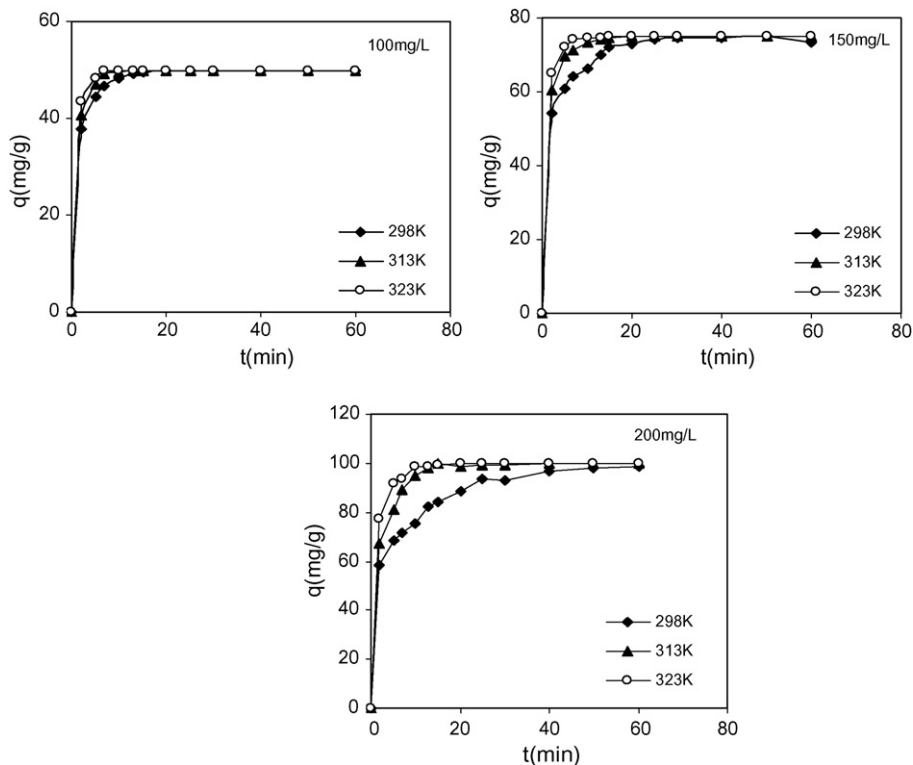


Fig. 3. The adsorption curves of malachite green obtained for 100, 150 and 200 mg/L at different temperatures (pH: natural, 0.1 g/50 mL activated carbon, 400 rpm).

Table 2
Kinetic parameters for the effects of solution temperature and concentration

Concentration (mg/L)	Temperature (K)	E_a (kJ/mol)	$q_{e.exp}$ (mg/g)	First-order kinetic equation			Second-order kinetic equation		
				q_e (mg/g)	$k_1 \times 10^2$ (min ⁻¹)	r^2	q_e (mg/g)	$k_2 \times 10^3$ (g/mg min)	r^2
100	298	48.56	49.75	12.53	17.8	0.878	50.3	48	0.999
	313		49.73	28.51	50.5	0.960	50.0	114	1
	323		49.81	38.46	60.4	0.954	50.0	222	1
150	298	63.16	73.37	2.71	23.0	0.942	75.8	14.3	0.999
	313		74.81	24.16	28.0	0.880	75.2	45.3	1
	323		74.90	44.88	26.0	0.920	75.2	104.0	1
200	298	67.93	98.74	42.65	7.30	0.954	103.9	3.3	0.999
	313		99.77	28.68	15.6	0.970	101.0	13.2	0.999
	323		99.89	24.47	22.0	0.972	101.0	27.2	0.999

$q_{e.exp}$: obtained as experimental.

3.3.1. Pseudo first-order and second-order

The pseudo first-order equation is expressed [21,22] as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2}$$

After integration, the integrated form of Eq. (2) becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{3}$$

where q_e and q_t are amounts of dye adsorbed (mg/g) at equilibrium and time t (min), respectively, and k_1 is the rate constant of pseudo first-order adsorption (min⁻¹). The values of $\log(q_e - q_t)$ were calculated from the kinetic data of Fig. 3. The k_1 values and q_e were calculated from slope and intercept from the plots of $\log(q_e - q_t)$ versus t (figures not shown) for different concentra-

tion and temperatures, respectively. The k_1 values, q_e calculated and correlation coefficient is given in Table 2.

The $q_{e.exp}$ values do not agree with calculated ones, obtained from the plots. This results show that the adsorption of MG onto T3K618 is not a first order reaction.

The pseudo second-order kinetic model of Ho and McKay [23,24] is:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{4}$$

The integrated form of Eq. (4) becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{5}$$

where k_2 is the rate constant of pseudo second-order adsorption (g/mg min). The plots of (t/q_t) versus t for the pseudo second-

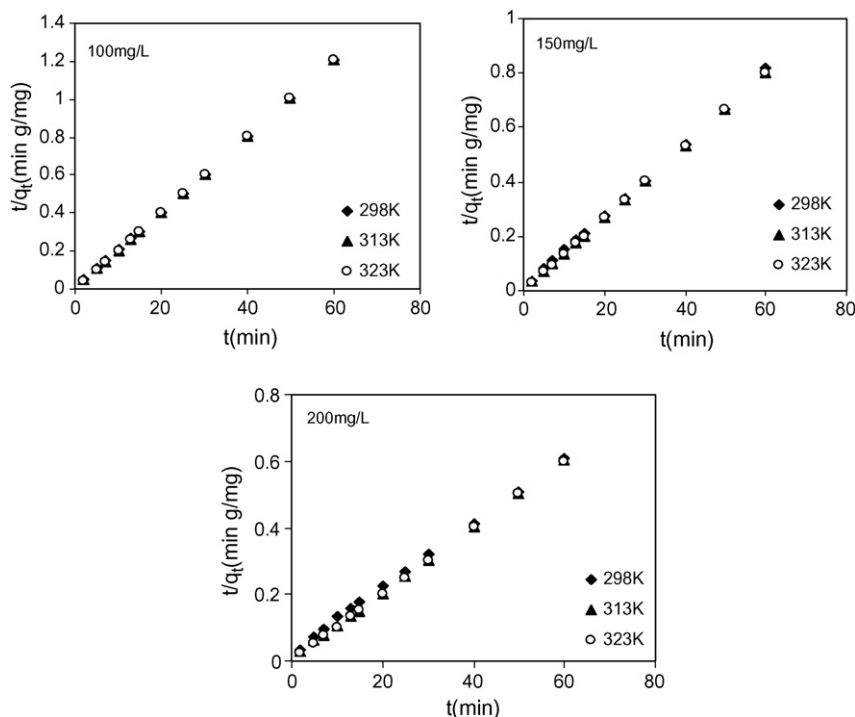


Fig. 4. The pseudo second-order adsorption kinetics plots of MG at different temperatures (pH: natural, 0.1 g/50 mL activated carbon, 400 rpm).

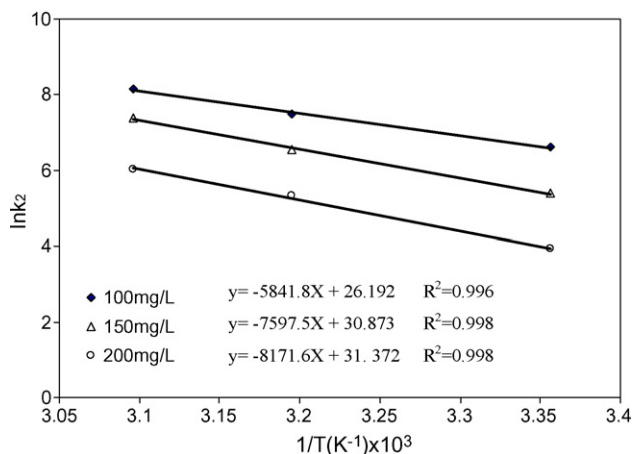


Fig. 5. Arrhenius plot for adsorption of malachite green on T3K618.

order model given in Eq. (5) were drawn at different solution temperature in Fig. 4. The q_e and k_2 values were calculated from slope and intercept of this plots, respectively. Table 2 shows that the correlation coefficients of second-order kinetic model are greater than first order kinetic. Also, the calculated q_e values agree very well with the experimental data ($q_{e,exp}$). These indicate that the adsorption perfectly complies with pseudo second-order reaction [25].

The activation energy was calculated from linearized Arrhenius Eq. (6):

$$\ln k_2 = \ln k_0 - \frac{E_a}{RT} \quad (6)$$

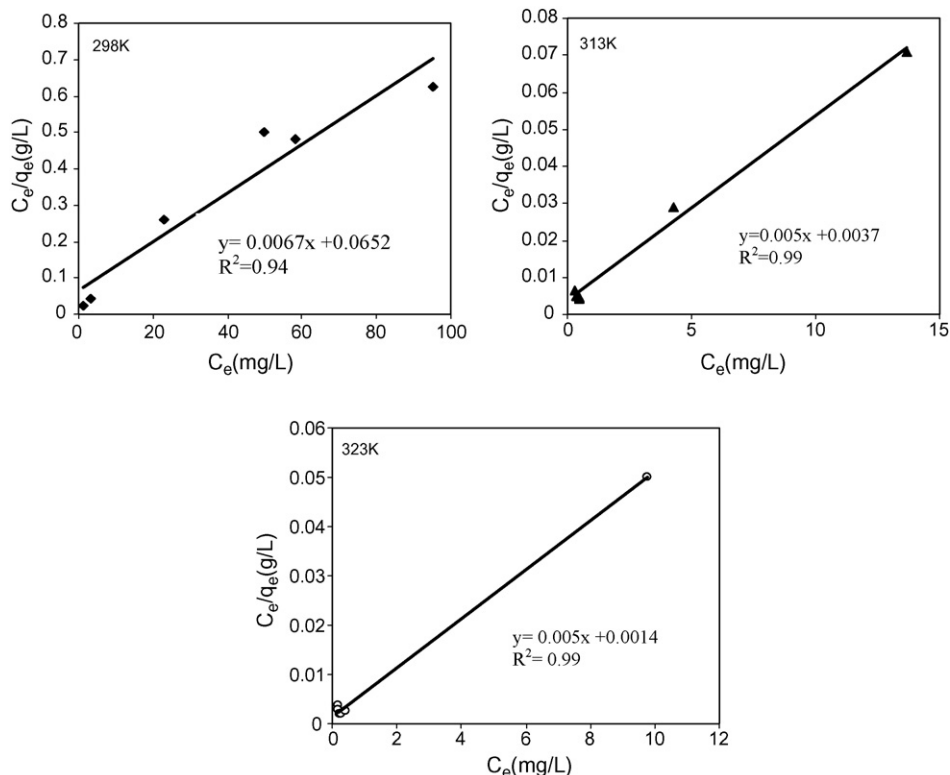


Fig. 6. Langmuir isotherm plots for the removal of MG (contact time = 60 min, pH: natural, 0.1 g/50 mL activated carbon, 400 rpm).

where k_2 is the rate constant of adsorption (g/mol s), k_0 is the temperature independent factor (g/mol s), E_a is the activation energy (kJ/mol), R is the gas constant (J/mol K) and T is the adsorption temperature (K). The plots of $\ln k_2$ versus the absolute temperature $1/T$ give straight line for all concentration, as shown in Fig. 5. The activation energy values are given in Table 2. The activation energy values fall above 42 kJ/mol the adsorption process. The type of adsorption of MG on the T3K618 was defined as chemical adsorption [26–28].

3.4. Adsorption isotherms

The adsorption equilibrium data were analyzed using Langmuir, Freundlich isotherm expression. As the Freundlich isotherm poorly fits the equilibrium data, the data fitting Langmuir alone are presented in this study. The Langmuir expression [29] is given by:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (7)$$

where C_e is the dye concentration at equilibrium (mg/L), q_e is the adsorption capacity in equilibrium (mg/g), b is the Langmuir adsorption constant (L/mg), Q_0 signifies adsorption capacity (mg/g). Fig. 6 shows the Langmuir (C_e/q_e versus C_e) plots for the removal of MG at different temperatures. The isotherms of dye, namely MG were found to be linear over the whole concentration range studies and the correlation coefficients were extremely high as shown in Table 3. The value of Q_0 increases with temperature increase, thereby confirming that the process

Table 3
Langmuir adsorption isotherm of MG at different temperatures

Temperature (K)	Concentration (mg/L)	$R_L \times 10^3$	Q_0 (mg/g)	b (L/mg)	r^2
298	100	88.7	149	0.103	0.96
	150	60.9			
	200	46.4			
	250	37.4			
	300	31.4			
	400	23.7			
313	100	7.34	200	1.351	0.99
	150	4.91			
	200	3.69			
	250	2.95			
	300	2.46			
	400	1.85			
323	100	2.79	200	3.571	0.99
	150	1.86			
	200	1.39			
	250	1.18			
	300	0.93			
	400	0.69			

is endothermic [30,31]. At 40, 50 °C, the maximum adsorption capacities were determined as 200 mg/g. To determine if adsorption process is favorable or unfavorable, for the Langmuir type adsorption process, isotherm can be classified by a term ‘ R_L ’, a dimensionless constant separation factor, which is defined as below [32].

$$R_L = \frac{1}{(1 + bC_0)} \tag{8}$$

The R_L values are found in the range of 0.00069–0.0887 for MG at 30, 40 and 50 °C, respectively, showing favorable adsorption.

3.5. Adsorption mechanism

The rate parameter for intraparticle diffusion is determined using the following equation [33]:

$$q_t = k_{int}t^{1/2} + C \tag{9}$$

where C is the intercept and k_{int} is the intraparticle diffusion rate constant (mg/g min^{-1/2}). The plot may present multilinearity, indicating that three steps take place. The first, sharper portion is attributed to the diffusion of adsorbate through the solution to the external surface of adsorbent or the boundary layer diffusion of solute molecules. The second portion describes the gradual adsorption stage, where intraparticle diffusion is rate limiting. The third portion is attributed to the final equilibrium stage [34]. The intra particle diffusion rate constant obtained from the slope of linear gradients of the plots q_t versus $t^{1/2}$. The plots are shown in Fig. 7. From Fig. 7, it was noted that the adsorption process tends to be followed by two phases. The two phases in the intraparticle diffusion plots suggest that the adsorption process proceeds by surface adsorption and intraparticle diffusion. Further, the linear plots at each concentration and temperatures did not pass through the origin and this indicates that intraparticle diffusion was not only rate controlling step [35]. The intra particle diffusion rate constant k_{int} values for 100, 150, 200 mg/L dye concentration at 25, 40, 50 °C is given in Table 4.

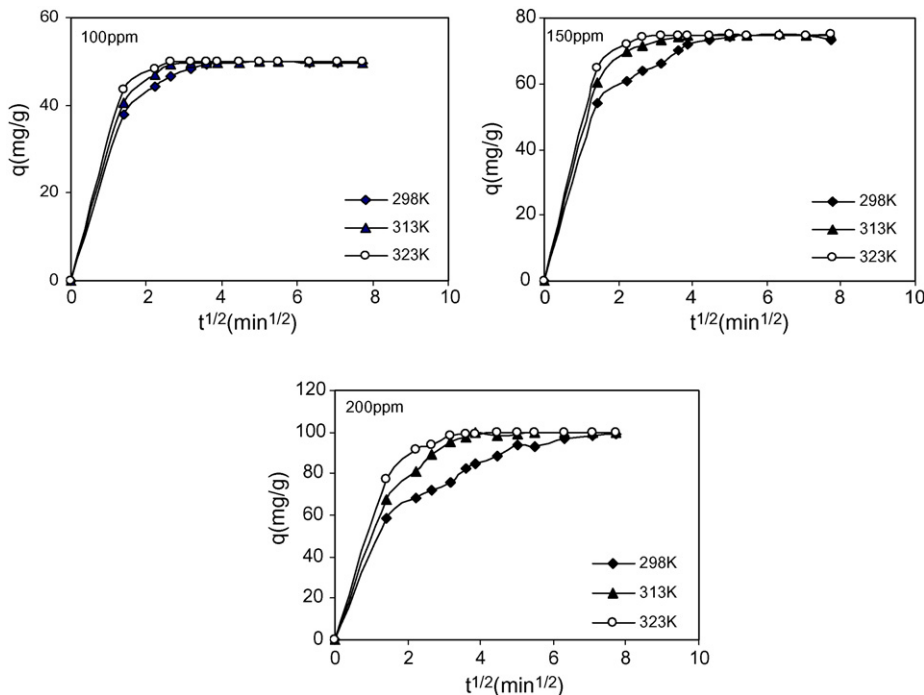


Fig. 7. q vs. $t^{1/2}$ plots obtained at 100, 150, 200 mg/L initial dye concentration and at different temperatures (contact time = 60 min, pH: natural, 0.1 g/50 mL activated carbon, 400 rpm).

Table 4
Intraparticle rate parameters, external mass transfer and diffusion coefficients at different temperatures and concentration

Concentration (mg/L)	Temperature (K)	$k_L \times 10^5$ (cm/s)	k_{int} (mg/g min ^{0.5})	$D_1 \times 10^9$ (cm ² /s)	$D_2 \times 10^9$ (cm ² /s)
100	298	1.322	5.1312	3.407	7.465
	313	3.104	5.4122	3.840	14.28
	323	6.045	5.3167	4.099	15.86
150	298	0.596	7.1162	2.965	5.713
	313	1.860	7.3487	3.741	7.562
	323	4.271	7.5776	4.020	8.583
200	298	0.194	10.361	2.049	2.045
	313	0.733	13.194	2.806	3.892
	323	1.511	13.757	3.582	5.685

The values of k_{int} increase with increase of temperature, that is why mobility of dye molecules increases with increase of the initial dye concentration due to greater driving force. The increasing trend of intraparticle rate constant with initial dye concentration and temperature has been reported by various investigators [15,36,37].

Both the film diffusion (D_1 , cm²/s) and diffusion within the adsorbent (D_2 , cm²/s) control the intraparticle diffusion process. Assuming adsorbent particle to be sphere of radius ‘a’ and that the diffusion follows Fick’s law, the relationship between uptake and time is given by [38]:

$$\frac{q_t}{q_e} = 6 \left(\frac{Dt}{a^2} \right)^{1/2} \left\{ \pi^{-1/2} + 2 \sum_{n=1}^{\infty} ierfc \frac{na}{Dt^{1/2}} \right\} - 3 \frac{Dt}{a^2} \quad (10)$$

At small times, D is replaced by D_1 and Eq. (10) reduces to:

$$\frac{q_t}{q_e} = 6 \left(\frac{D_1}{\pi a^2} \right)^{1/2} t^{1/2} \quad (11)$$

Fig. 8 shows the plots of q_t/q_e versus $t^{1/2}$. The film diffusion coefficient (D_1) values for different initial dye concentration and temperatures are calculated from the slope of these plots. For moderate and large times, the relation between weight uptake and diffusion equation is:

$$\frac{q_t}{q_e} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left(\frac{-Dn^2\pi^2t}{a^2} \right) \quad (12)$$

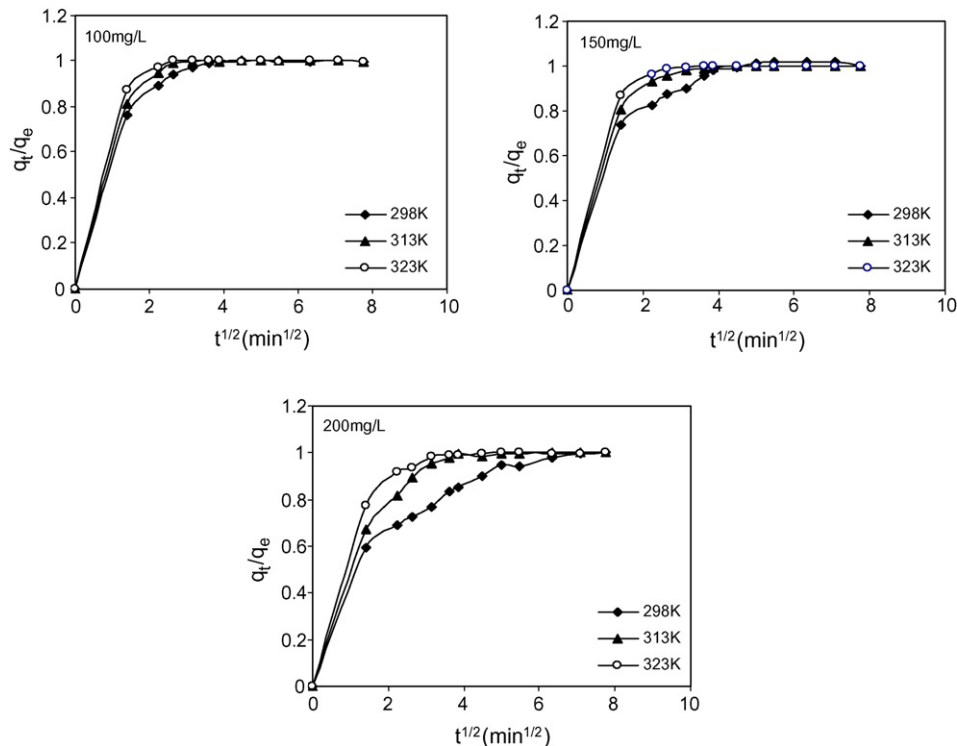


Fig. 8. Determination of diffusion coefficient (D_1) for the initial concentration 100, 150, 200 mg/L at 25, 40 and 50 °C.

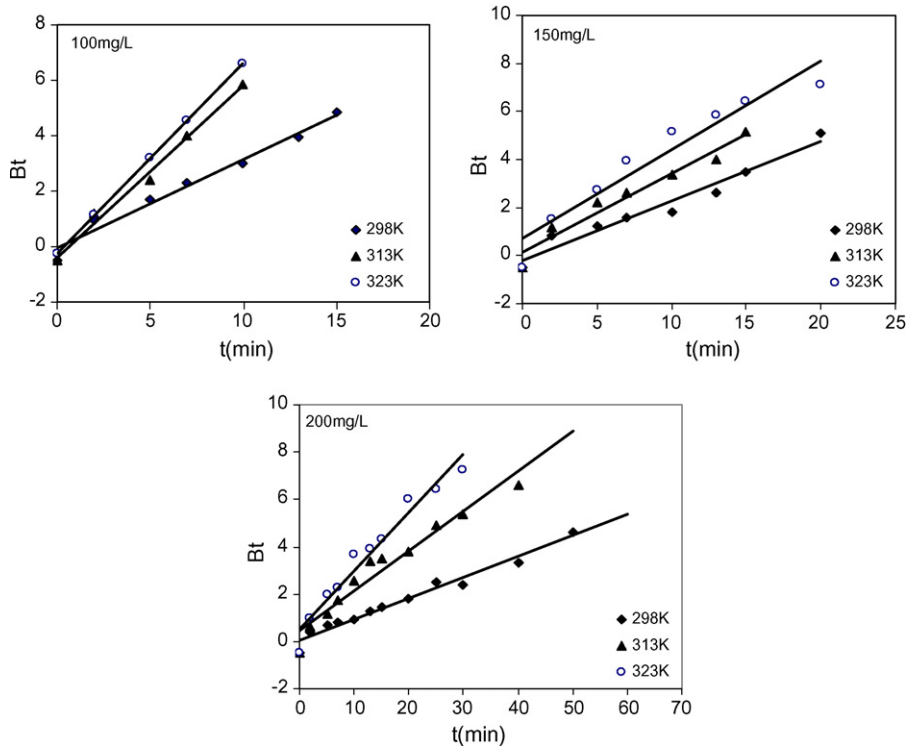


Fig. 9. Bt vs. t plots for the adsorption of MG onto T3K618.

As t tends to large times, Eq. (12) can be written in the form:

$$\left(1 - \frac{q_t}{q_e}\right) = \frac{6}{\pi^2} \exp\left(\frac{-D_2\pi^2}{a^2} t\right) \quad (13)$$

If $B = (D_2\pi^2/a^2)$, Eq. (13) can be simplified as:

$$\left(1 - \frac{q_t}{q_e}\right) = \frac{6}{\pi^2} \exp(-Bt) \quad (14)$$

$$Bt = -0.4977 - \ln\left(1 - \frac{q_t}{q_e}\right) \quad (15)$$

Eq. (15) is used to calculate Bt values at different temperature and initial dye concentration. The calculated Bt values were plotted against time as shown in Fig. 9 that is used to identify whether external transport or intraparticle transport control the rate of adsorption. If the plot of Bt versus t (having slope B) is straight line passing through the origin, then the adsorption rate is governed by particle diffusion mechanism; otherwise, it is governed by film diffusion [37,39,40]. As can be seen from Fig. 9, the plot at 100, 150, 200 mg/L is linear and does not pass through the origin except for 200 mg/L at 298 K. The plot is linear and also passes through the origin for 200 mg/L at 298 K, indicating the rate controlling step to be particle diffusion. The calculated B values were used to calculate the pore diffusion coefficient (D_2) using the $B = (D_2\pi^2)/(a^2)$. Both the film diffusion (D_1) and pore diffusion (D_2) coefficient values are given in Table 4. The data in Table 4 show that the film and pore diffusion coefficients decreased with raise in initial MG concentration, and increased with increasing adsorption temperature. These results are explained by increasing mobility of dye molecules with raise in temperature and by decreasing available open sites to adsorb

with increasing initial dye concentration. Similar observation was also reported in literature [17,41–44].

External diffusion across the boundary layer surrounding each adsorbent particle and internal diffusion into the porous particle are two main mass transfer resistances. Based on the film-pore diffusion model for describing the process [45], external mass transfer is:

$$N_t = k_L A (C_t - C_e) \quad (16)$$

where N_t is the diffusion rate across the film layer surrounding the adsorbent particle, k_L is the external mass transfer coefficient, A is the external surface area of adsorbent, C_t and C_e is the adsorbate concentration at time t and equilibrium time, respectively. Diffusion rate can be also written by using the Eq. (1) as:

$$N_t = -V \frac{dC_t}{dt} = m \frac{dq_t}{dt} \quad (17)$$

at initial conditions (i.e., $C_t = C_0$ and $C_e = 0$ at $t = 0$), therefore

$$(N_t)_{t \rightarrow 0} = k_L A C_0 \quad (18)$$

Combining Eqs. (4), (17), (18), the external mass transfer coefficient, k_L , can be written as follows:

$$k_L = \frac{mk_2q_e^2}{C_0A} \quad (19)$$

where m is mass of adsorbent (g), k_2 is the second-order rate constant (g/mg min), q_e is the dye adsorbed (mg/g), C_0 is the initial dye concentration (mg/m³), A is the external surface area of adsorbent (15.3 m² for 0.1 g adsorbent from Table 1); and k_L

values (cm/s) for 100, 150, 200 mg/L at 25, 40 and 50 °C are calculated by using Eq. (19). Table 4 gives the obtained values of k_L ranging from 0.194×10^{-5} to 6.045×10^{-5} cm/s. Tsai et al. [46] conducted the adsorption of acid dyes onto activated bleaching earth during the external transport process. The value of external mass transfer coefficient is ranging from 8.97×10^{-6} to 1.29×10^{-4} , which was obtained by film-pore diffusion model, indicating that the values of k_L decreased with increase of initial adsorbate concentration. Rajgopal et al. [16] investigated the adsorption behavior of malachite green on the different adsorbents. They found that the values of k_L increased with increase of the temperature. Hsu et al. [47] investigated the adsorption of basic dyes. Their results showed that the values (10^{-4} to 10^{-5} cm/s) of external mass transfer coefficient were found to be lower at higher initial concentration. Aksu and Kabasakal [15] determined the external mass transfer coefficients increase with increase temperature, and decrease with increase initial dye concentration.

3.6. Thermodynamic parameters of adsorption

Effect of concentration and temperature on the MG adsorption is shown in Fig. 3. While temperature increases, the percentage of dye removal increases, indicating the adsorption to be endothermic. The change in standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of adsorption were calculated from the following equation:

$$\Delta G^\circ = -RT \ln K_c \quad (20)$$

where R is the gas constant (8.314 J/mol K), K_c is the equilibrium constant and T is temperature in K. The K_c value is calculated from Eq. (21):

$$K_c = C_{Ae}/C_{Se} \quad (21)$$

Table 5
Thermodynamic parameters for the adsorption of MG onto T3K618

Concentration (mg/L)	Temperature (K)	K_c	$-\Delta G^\circ$ (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
100	298	82.33	10.93	60.16	238
	313	315.25	14.97		
	323	522.83	16.81		
150	298	44.95	9.43	91.65	340
	313	391.16	15.53		
	323	736.10	17.73		
200	298	7.67	5.05	159.11	553
	313	439.81	15.84		
	323	934.89	18.37		
250	298	4.00	3.44	182.64	627
	313	488.14	16.11		
	232	966.11	18.46		
300	298	4.15	3.53	164.20	562
	313	69.19	11.03		
	323	747.12	17.767		
400	298	3.20	2.88	83.85	292
	313	28.20	8.69		
	323	39.94	9.90		

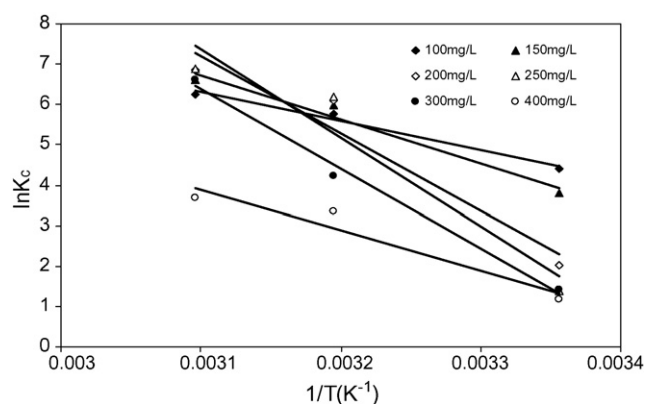


Fig. 10. Van't Hoff plots of MG adsorption onto T3K618 for different initial dye concentration.

where C_{Ae} and C_{Se} are the equilibrium concentration of dye ions on adsorbent (mg/L) and in the solution (mg/L), respectively.

Standard enthalpy (ΔH°) and entropy (ΔS°), of adsorption can be estimated from Van't Hoff equation given in:

$$\ln K_c = \frac{-\Delta H_{ads}^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (22)$$

The slope and intercept of the Van't Hoff plot is equal to $-\Delta H_{ads}^\circ/R$ and $\Delta S^\circ/R$, respectively. The Van't Hoff plot for the adsorption of MG onto T3K618 is given in Fig. 10. Thermodynamic parameters obtained are summarized in Table 5. The endothermic nature of process is well explained by positive value of the enthalpy change. The negative value of free energy suggests that the adsorption process is spontaneous and the affinity of the adsorbent for the dye is indicated by the positive value of entropy [11,48,49].

4. Conclusion

In this work, activated carbon, prepared from lignite by chemical activation with KOH, has been used successfully for the removal of the malachite green from aqueous solution. The N_2 adsorption isotherm is of type I. The values of S_{BET} , V_t and S_{mic} and V_{mic} are $1000 \text{ m}^2/\text{g}$, $0.59 \text{ cm}^3/\text{g}$ and $848 \text{ m}^2/\text{g}$, $0.44 \text{ cm}^3/\text{g}$, respectively. Results show that activated carbon is dominantly micropores. Percentage of micropores area is 84.8%.

Adsorption was investigated by various parameters such as initial dye concentration and temperature. Ninety-nine percent of total adsorbed amount of MG was removed by adsorption in the first 20 min of contact for all concentration at studied all temperatures. Adsorption of the dye onto T3K618 increased with an increase in temperature, indicating that the process is endothermic. The kinetics of adsorption of MG on T3K618 was studied by using two simple kinetic models. The adsorption of MG from aqueous solution onto T3K618 proceeds according to the pseudo second-order model which provides the best correlation of the data in all cases and the experimental $q_{e,exp}$ values agree with the calculated ones. The activation energy values fall above 42 kJ/mol the adsorption process. The type of adsorption of MG on the T3K618 was defined as chemical adsorption.

The adsorption isotherm followed Langmuir and Freundlich models. The Langmuir gave a better fit to all adsorption isotherms (at 20, 30, 40, 50°C) than the Freundlich. The value of Q_0 increases with temperature increase, thereby confirming that the process is endothermic. The R_L values are found in the range of 0.00069 – 0.0887 for MG at 25, 40 and 50°C for all initial dye concentration, respectively, showing favorable adsorption.

According to intraparticle diffusion, intraparticle diffusion was not only rate controlling step. Both the film diffusion (D_1 , cm^2/s) and diffusion within the adsorbent (D_2 , cm^2/s) coefficients are calculated for all initial dye concentration at 25, 40, 50°C . Further, kinetics studies apparently reveal that the adsorption mainly takes through a film diffusion process at all the concentration and temperature except for 200 mg/L at 298 K . The rate controlling step is the particle diffusion for 200 mg/L at 298 K . The value of external mass transfer coefficient is ranging from 8.97×10^{-6} to 1.29×10^{-4} , which was obtained by film-pore diffusion model.

The positive values of enthalpy change conform to the endothermic nature of the adsorption process. The parameters, ΔH , ΔS and ΔG , for the MG-activated carbon prepared from lignite interactions changed in away that made the adsorption thermodynamically feasible with high degree of affinity of the dye molecules for the T3K618 surface.

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