

Kinetics of adsorption of dyes from aqueous solution using activated carbon prepared from waste apricot

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Abstract

Adsorbent (WA11Zn5) has been prepared from waste apricot by chemical activation with $ZnCl_2$. Pore properties of the activated carbon such as BET surface area, pore volume, pore size distribution, and pore diameter were characterized by N_2 adsorption and DFT plus software. Adsorption of three dyes, namely, Methylene Blue (MB), Malachite Green (MG), Crystal Violet (CV), onto activated carbon in aqueous solution was studied in a batch system with respect to contact time, temperature. The kinetics of adsorption of MB, MG and CV have been discussed using six kinetic models, i.e., the pseudo-first-order model, the pseudo-second-order model, the Elovich equation, the intraparticle diffusion model, the Bangham equation, the modified Freundlich equation. Kinetic parameters and correlation coefficients were determined. It was shown that the second-order kinetic equation could describe the adsorption kinetics for three dyes. The dyes uptake process was found to be controlled by external mass transfer at earlier stages (before 5 min) and by intraparticle diffusion at later stages (after 5 min). Thermodynamic parameters, such as ΔG , ΔH and ΔS , have been calculated by using the thermodynamic equilibrium coefficient obtained at different temperatures and concentrations. The thermodynamics of dyes–WA11Zn5 system indicates endothermic process.

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1. Introduction

The textile industry discharges about 146,000 tonnes of dyes per year along with its wastewater [1]. The de-colorization of textile industry wastewater is a worldwide problem to which several treatment technologies have been applied, including adsorption onto solid substrates, chemical coagulation, disinfection, filtration and oxidation [2–4]. Adsorption has become a well-established separation technique to remove pollutants as well as having the potential for regeneration, recovery and recycling of the adsorbent materials.

The removal of organic color by adsorption onto agricultural residues has recently become the subject of considerable interest. There are reports on the removal of dyestuffs by sawdust [5], hardwood [6], bagasse pith [7], rice husk and bark [8], maize cob [9], and banana pith [10].

The characteristics of the adsorption behavior are generally inferred in terms of both adsorption kinetics and equilibrium isotherm. They are also important tool to understand the adsorption mechanism for the theoretical evaluation and interpretation of thermodynamic parameters.

1.1. Kinetic parameters of adsorption

Several kinetics models are used to examine the controlling mechanism of adsorption process such as chemical reaction, diffusion control and mass transfer. Applying those models are given in literature [11–15].

The pseudo-first-order equation is expressed [16] as

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

The integrated form of Eq. (1) becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (2)$$

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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 (min^{-1}).

The pseudo-second-order kinetic model of Ho and McKay [17,18] is

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

The integrated form of Eq. (3) becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where k_2 is the rate constant of pseudo-second-order adsorption ($\text{g}/(\text{mg min})$) and $h = k_2 q_e^2$, where h is the initial adsorption rate ($\text{mg}/\text{g min}$).

The Elovich equation is given as follows [19]:

$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t} \quad (5)$$

where α is the initial rate ($\text{mg}/\text{g min}$) because (dq_t/dt) approaches α when q_t approaches zero, and the parameter β is related to the extent of surface coverage and activation energy for chemisorptions (g/mg) [20].

Given that $q_t = 0$ at $t = 0$, integrated form of Eq. (5) is

$$q_t = \frac{1}{\beta} \ln(t + t_0) - \frac{1}{\beta} \ln t_0 \quad (6)$$

where $t_0 = 1/\alpha\beta$. If t is much larger than t_0 , Eq. (6) can be simplified as

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (7)$$

The rate parameter for intraparticle diffusion is determined using the following equation [21]:

$$q_t = k_{\text{int}} t^{1/2} + C \quad (8)$$

where C is the intercept and k_{int} is the intraparticle diffusion rate constant ($\text{mg}/\text{g min}^{-1/2}$). 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 [21].

Bangham equation [22] is given as

$$\log \log \left(\frac{C_0}{C_0 - q_t m} \right) = \log \left(\frac{k_0 m}{2.303 V} \right) + \alpha \log(t) \quad (9)$$

where C_0 is the initial concentration of the adsorbate in solution (mg/L), V the volume of solution (mL), q_t the amounts of dye adsorbed (mg/g) at time t , m the weight of the adsorbent used (g/L). α (<1) and k_0 ($\text{mL}/(\text{g}/\text{L})$) are constant.

The modified Freundlich equation was originally developed by Kuo and Lotse [23]:

$$q_t = k C_0 t^{1/m} \quad (10)$$

where q is the amount of adsorbed dye (mg/g) at time t , k the apparent adsorption rate constant ($\text{L}/(\text{g min})$), C_0 the initial dye concentration (mg/L), t the contact time (min) and m is the Kuo–Lotse constant. The values of k and m were used empirically to evaluate the effect of dye surface loading and ionic strength on the adsorption process.

Linear form of modified Freundlich equation is given as

$$\ln q_t = \ln(k C_0) + \frac{1}{m} \ln t \quad (11)$$

q_t (mg/g) was calculated by mass-balance relationship equation:

$$q_t = (C_0 - C_t) \frac{V}{W} \quad (12)$$

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 is the weight of the dry adsorbent used (g).

Finally, for research purposes the most widely used dye adsorbent and most readily available from commercial sources is activated carbon. Consequently an activated carbon prepared from waste apricot has been selected for this study. The kinetics, its mechanism and thermodynamic parameters at different temperatures are discussed in this study.

2. Experimental

2.1. Materials

Three dyes were used in the study. The dyes, Methylene Blue (MB) (1608, CI=52,015, chemical formula = $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{SH}_2\text{O}$, MW = 337.85 g/mol, $\lambda_{\text{max}} = 660 \text{ nm}$) was supplied by Panreac; Malachite Green (MG) (1398, CI=42,000, chemical formula = $\text{C}_{50}\text{H}_{52}\text{N}_4\text{O}_8$, MW = 927.03 g/mol, $\lambda_{\text{max}} = 617 \text{ nm}$); Crystal Violet (CV) (101458, CI=42,555, chemical formula = $\text{C}_{25}\text{H}_{30}\text{ClN}_3$, MW = 407.99 g/mol, $\lambda_{\text{max}} = 594 \text{ nm}$) were supplied by Merck. One thousand milligrams per liter of 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 (WA11Zn5)

Brought containers, waste apricot supplied by Malatya apricot plant were dried under laboratory conditions and then dried again at 100°C (Model FN 400, Nüve) until it reaches a constant weight. Starting material was stored in plastic tubes after grounding.

In the first step of activation, the starting material was mixed with ZnCl_2 at the ZnCl_2 /starting material weight ratio of 1:1 and the mixture was kneaded with adding distilled water. The mixture was then dried at 110°C to prepare the impregnated sample.

In the second step, the impregnated sample was placed on a quartz dish, which was then inserted in a quartz tube (i.d. = 60 mm). The impregnated sample was heated up to activation temperature (500°C) under N_2 flow (100 mL min^{-1}) at the rate of $10^\circ\text{C min}^{-1}$ and hold at the activation temperature for

1 h. After activation, the sample was cooled down under N_2 flow and 0.5N HCl was added on to activated sample. Activated sample was washed sequentially several times with hot distilled water to remove residual chemical until it did not give chloride reaction with $AgNO_3$. The washed sample was dried at $110^\circ C$ to prepare activated carbon.

2.3. Instrumentation

A Tri Star 3000 (Micromeritics, USA) surface analyzer was used to measure nitrogen adsorption isotherm at 77 K in the range of relative pressure 10^{-6} to 1. Before measurement, the sample was degassed at $300^\circ C$ for 2 h. The BET surface area, total pore volume, average pore radius, micropore area were obtained from the adsorption isotherms. Mesopore volume was determined by subtracting the micropore volume from total pore volume.

The spectrophotometric determination of dyes was done on a Shimadzu UV–vis spectrophotometer (model UV-2100S, Japan).

2.4. Adsorption experiments

To monitor the adsorption process at different temperatures (30 and $40^\circ C$) batch techniques was employed. Adsorption isotherms were recorded over the concentration range 50 – 400 mg/L of dye solutions in a series of 100 mL graduated conical flasks containing 50 mL solution of each concentration. A known amount (0.1 g WA11Zn5/50 mL dye solution of desired concentration) of activated carbon is then added into the solution and conical flask is stirred with thermostatic bath operating at 400 rpm.

3. Results and discussion

3.1. Characterization of the prepared activated carbon (WA11Zn5)

Nitrogen adsorption, because the relatively small molecule diameter of nitrogen is frequently used at 77 K to probe porosity and surface area and to be a standard procedure for the characterization of porosity texture of carbonaceous adsorbents also. The adsorption isotherm is the information source about the porous structure of the adsorbent, heat of adsorption, characteristic of physic and chemistry and so on. Adsorption isotherm may be grouped six types. As illustrated in Fig. 1, nitrogen adsorption at 77 K is standard method used in characterization of the adsorbents. WA11Zn5 exhibited adsorption isotherm of type IV

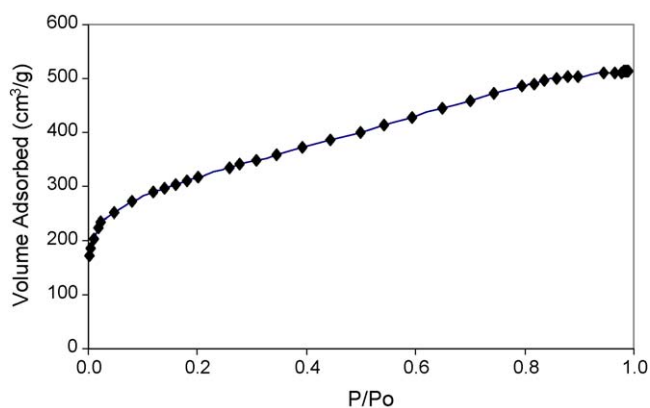


Fig. 1. Adsorption isotherm of nitrogen at 77 K for activated carbon (WA11Zn5).

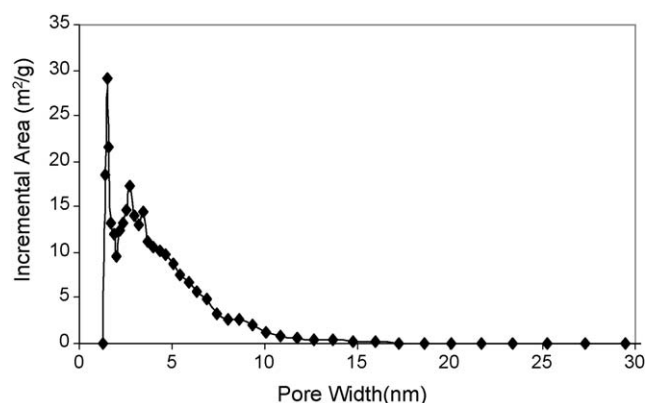


Fig. 2. Pore size distribution of the WA11Zn5.

according to IUPAC [24]. The type IV isotherm represents the micro–mesoporous structure of the adsorbents. The initial part of the isotherm follows the same path as the corresponding type II isotherm and therefore the result of monolayer–multilayer adsorption on the mesopore walls [25]. Characterization of activated carbon used in this study is investigated by Akmil Başar [26]. The BET surface area (S_{BET}), external surface area (including only mesopores 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 are listed in Table 1.

Fig. 2 shows the pore size distribution was calculated by using DFT plus software (with BJH method) [16]. It appears that activated carbon include micropores and mesopores. Percentages of micropores and mesopores area are 36 and 74%, respectively.

Table 1
Porous structure parameters of the activated carbon (WA11Zn5)

S_{BET} (m^2/g)	S_{ext}^a		S_{mic}		V_t (cm^3/g)	V_{mic}		V_{meso}		D_p^b (nm)
	(m^2/g)	S_{ext} (%)	(m^2/g)	S_{mic} (%)		(cm^3/g)	V_{mic} (%)	(cm^3/g)	V_{meso} (%)	
1060	778	74	282	36	0.79	0.15	19	0.64	81	2.98

^a $S_{ext} = S_{meso}$.

^b $4V/A$ by BET.

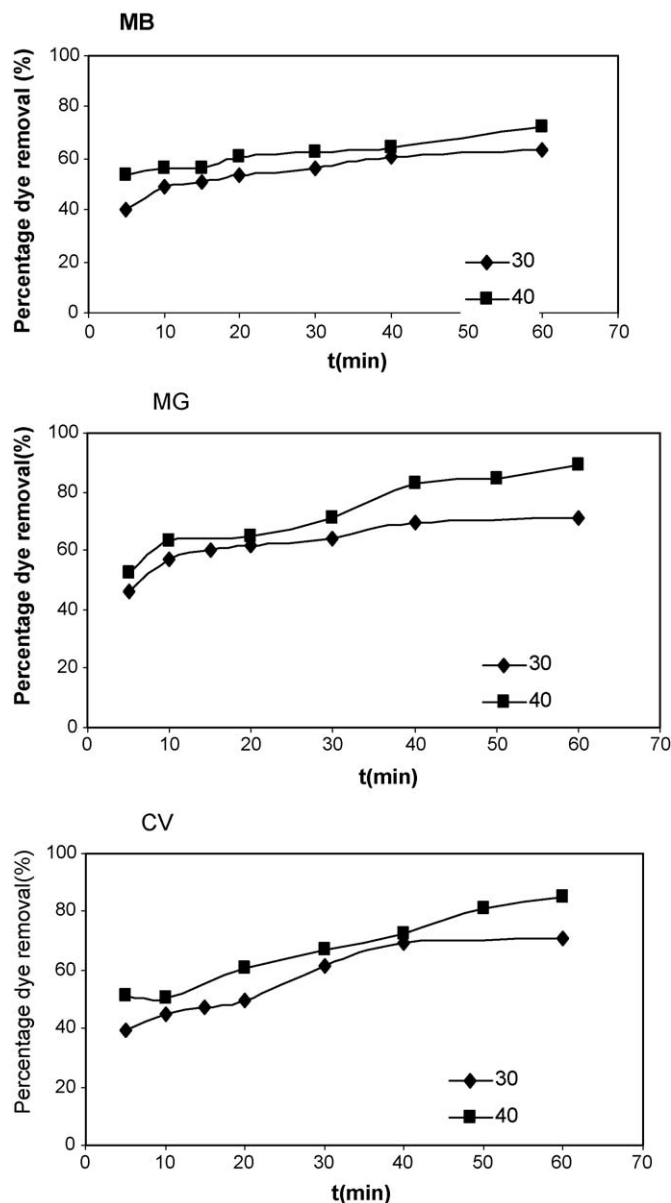


Fig. 3. Effect of contact time and temperature on the adsorption of MG, MB and CV.

3.2. Effect of contact time and temperature on adsorption

Adsorption experiments were carried out for different contact time at different temperatures with a fixed adsorbent dosage of 0.1 g at natural pH. The results are presented in Fig. 3. Similar plots were determined for three dyes. From the figures it was observed that percentage of dye removal gets increased with increase in contact time. Also maximum amount of dye was observed with in 40 min (~60–85% of total dye adsorbed) and thereafter the adsorption proceeds at slower rate till equilibrium and steady state was after equilibrium. The equilibrium time was 60 min for all adsorption temperature. Furthermore, adsorption increased with an increase in temperature, indicating that the process is endothermic.

3.3. Adsorption kinetics

Six kinetic models, which are pseudo-first-order, pseudo-second-order, the Elovich, the intraparticle diffusion, the Bangham and the modified Freundlich, have been applied for the experimental data to analyze the adsorption kinetics of MB, MG and CV dyes.

A simple kinetic analysis of adsorption is the first-order equation. The values of $\log(q_e - q_t)$ were calculated from the kinetic data of Fig. 3. The plots of $\log(q_e - q_t)$ versus t for the pseudo-first-order model given in Eq. (2) were given at temperatures of 30–40 °C in Fig. 4 for MB, MG and CV. The k_1 values were calculated from slope of this plot. The kinetic parameters for six kinetic model and correlation coefficient (R) were calculated and listed in Table 2. The values of first-order rate constant ($k_1 = 5.45 \text{ min}^{-1}$ for MB, 6.97 min^{-1} for MG, 4.81 min^{-1} for CV at 30 °C and $k_1 = 2.50 \text{ min}^{-1}$ for MB, 6.05 min^{-1} for MG, 4.58 min^{-1} for CV at 40 °C) indicate that the rate of removal is fastest for the MG followed by that for the other dyes. The correlation coefficient (R^2) is low, ranging from 0.979 to 0.897. Moreover, the experimental $q_{e(\text{exp})}$ values do not agree with the calculated ones. This shows that the adsorption of MB, MG and CV onto WA11Zn5 is not the first-order reaction.

On the other hand, the plots of (t/q_t) versus t for the pseudo-second-order model given in Eq. (4) were drawn at different temperatures in Fig. 5. q_e and k_2 values were calculated from slope and intercept of this plots, respectively. As can be seen from Table 2, the correlation coefficient (R^2), for the second-order kinetic model are between 0.992 and 0.999 and the experimental $q_{e(\text{exp})}$ values agree with the calculated ones. These results imply that the adsorption system studied follows to the pseudo-second-order kinetic model at all time intervals.

The other kinetic models including Elovich, intraparticle diffusion, Bangham and modified Freundlich were also tested to identify the mechanism.

Elovich equation is used successfully to describe second-order kinetics assuming that the actual solid surfaces are energetically heterogeneous [27]. Fig. 6 shows a plot of q_t versus $\ln t$ for the adsorption of MB, MG and CV for the Elovich equation at different temperatures. The parameters of the Elovich equation are shown in Table 2. When the temperature of the solution increased, the constant α was observed to increase and constant β decreased [28].

The constant β is related to the extent of surface coverage, then increasing of the initial rate of adsorption depended on temperature will decrease the available of adsorption surface for the adsorbate. The results indicate that the rate could be enhanced by increasing the adsorption temperature. The trend concerning β is consistent with those found in conventional activated chemisorption systems, which show that β is an indication of the number of sites available for the adsorption [29,30].

The intraparticle diffusion rate, obtained from the plots q_t versus $t^{1/2}$. The plots are shown in Fig. 7. The plot may present multilinearity, indicating that three steps take place. The first portion (stage 1) attributed to the diffusion of adsorbate through the solution to the external surface of adsorbent. The external surface sorption (stage 1) is absent because of completion before

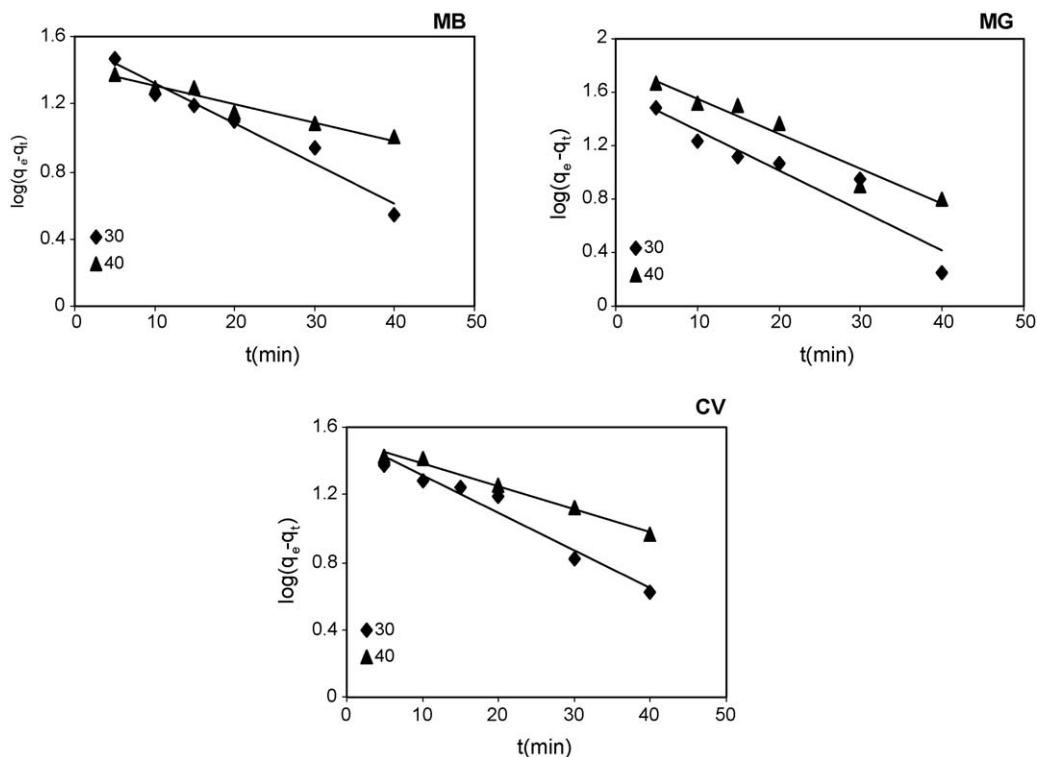


Fig. 4. The pseudo-first-order adsorption kinetics of MB, MG and CV at different temperatures.

Table 2

Kinetic parameters for the effect of temperatures on the adsorption of MB, MG and CV onto WA11Zn5

	MB		MG		CV	
	30 °C	40 °C	30 °C	40 °C	30 °C	40 °C
$q_{e(\text{exp})}$ (mg/g)	79.30	90.5	88.75	111.6	52.86	63.53
Pseudo-first-order equation						
q_e (mg/g)	35.90	26.30	42.10	32.73	32.89	41.33
k_1 ($\times 10^2 \text{ min}^{-1}$)	5.45	2.50	6.97	6.05	4.81	4.58
R^2	0.961	0.962	0.897	0.954	0.959	0.979
Pseudo-second-order equation						
q_e (mg/g)	83.30	93.45	93.45	106.38	60.24	70.42
k_2 ($\times 10^3 \text{ g/mg min}$)	2.98	2.41	2.86	2.73	1.90	1.95
h (mg/g min)	20.67	21.05	24.98	30.89	6.89	9.67
R^2	0.998	0.992	0.998	0.999	0.985	0.992
The Elovich equation						
α (mg/g min)	218.18	260.31	352.00	374.59	26.57	46.76
β (g/mg)	0.0884	0.0829	0.0829	0.0712	0.0952	0.0873
t_0 (min)	0.0518	0.0463	0.0343	0.0374	0.395	0.245
R^2	0.982	0.919	0.966	0.971	0.917	0.923
Intraparticle diffusion equation						
k_{int} (mg/g min ^{1/2})	4.298	5.066	4.7192	5.715	4.884	5.186
C	47.993	49.864	55.827	62.927	17.566	25.468
R^2	0.929	0.920	0.963	0.961	0.949	0.947
The Bangham equation						
k_0 (mL/(g/L))	8.724	10.664	10.817	11.935	5.970	7.670
α	0.262	0.256	0.265	0.315	0.399	0.434
R^2	0.979	0.949	0.955	0.975	0.928	0.923
The modified Freundlich						
m	5.672	6.44	6.071	5.934	3.688	4.297
k (L/g min)	0.157	0.186	0.186	0.210	0.119	0.164
R^2	0.964	0.916	0.947	0.948	0.955	0.922

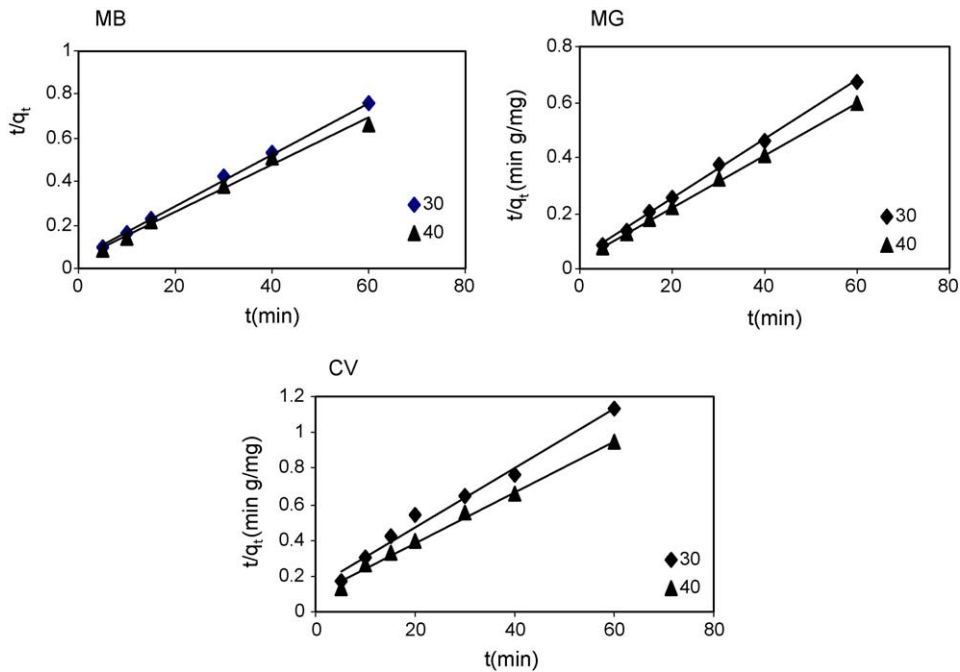


Fig. 5. The pseudo-second-order adsorption kinetics of MB, MG and CV at different temperatures.

5 min. The second portion (stage 2, up to 5 min) describes the gradual adsorption stage, where intraparticle diffusion is rate limiting [31]. The second linear portion (stage 2) followed by a plateau (stage 3 is not shown) is attributed to the final equilibrium stage. k_{int} values are determined from the slope of second linear portion of this plot. The values of intercept, C give an idea about the boundary layer thickness, i.e., the larger the intercept,

the greater is the boundary layer effect. At a certain time limit (up to 10 min), the curves reveal a linear characteristic that the intraparticle diffusion controls the adsorption process. Values of C and k_{int} , the intraparticle diffusion rate constant, are given in Table 2 for three dyes.

Fig. 8 presents a plot of $\log \log(C_0/(C_0 - q_t m))$ versus $\log t$ for all three dyes at 30 and 40 °C adsorption temperature. The

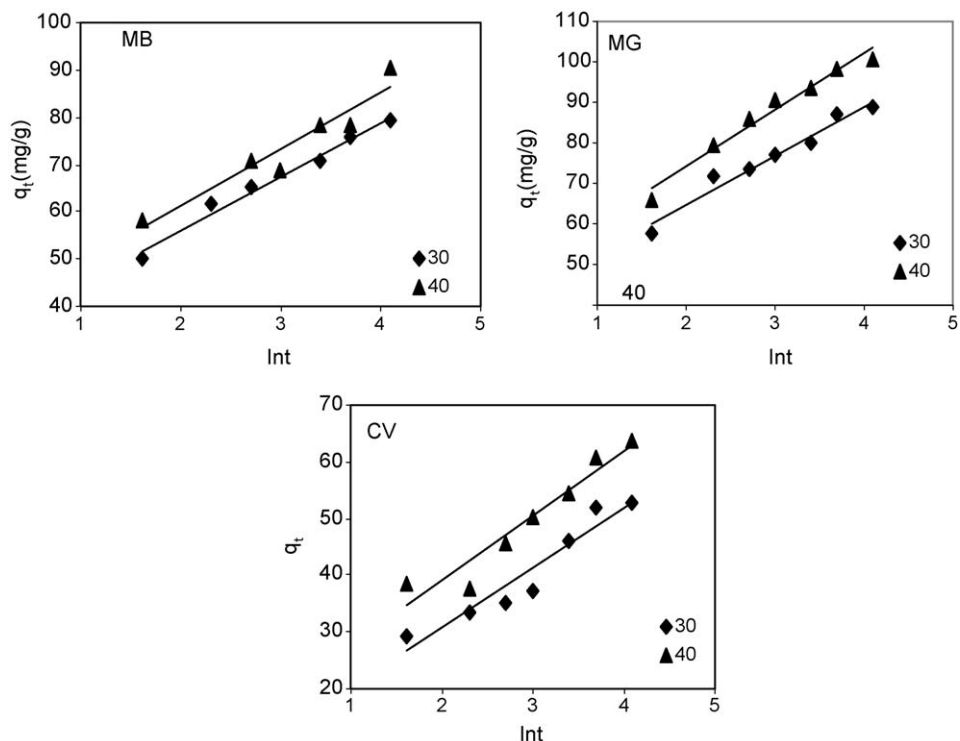


Fig. 6. The Elovich equation for adsorption of MB, MG and CV at different temperatures.

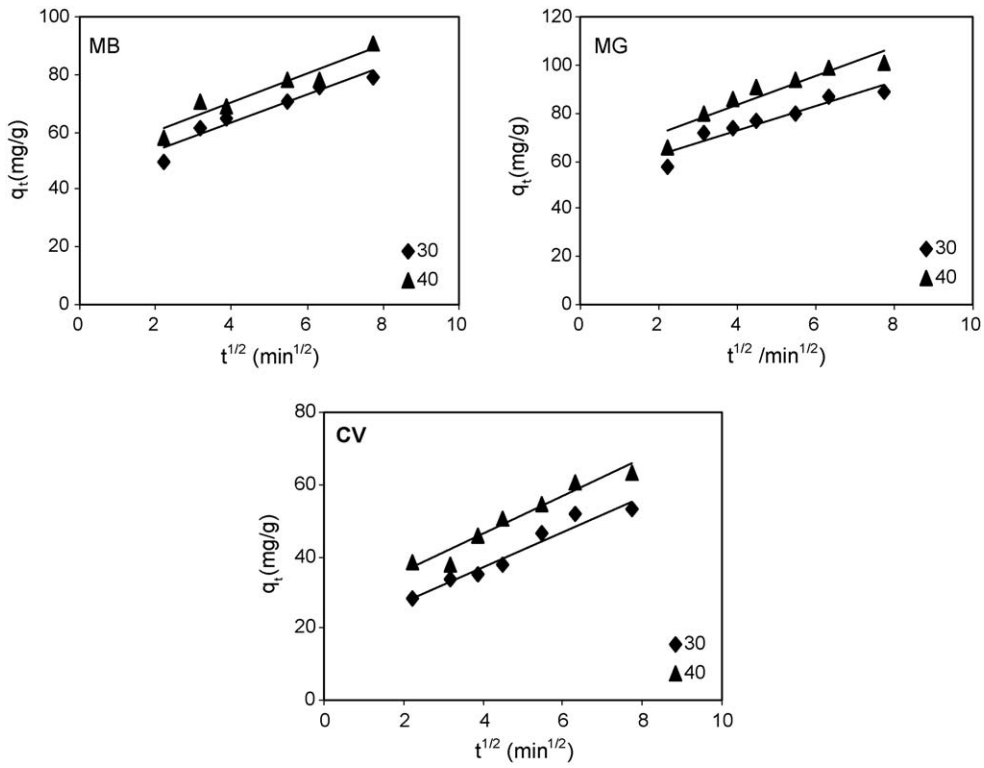


Fig. 7. Plots of the intraparticle diffusion kinetics equation for adsorption of MB, MG and CV onto WA11Zn5 at different temperatures.

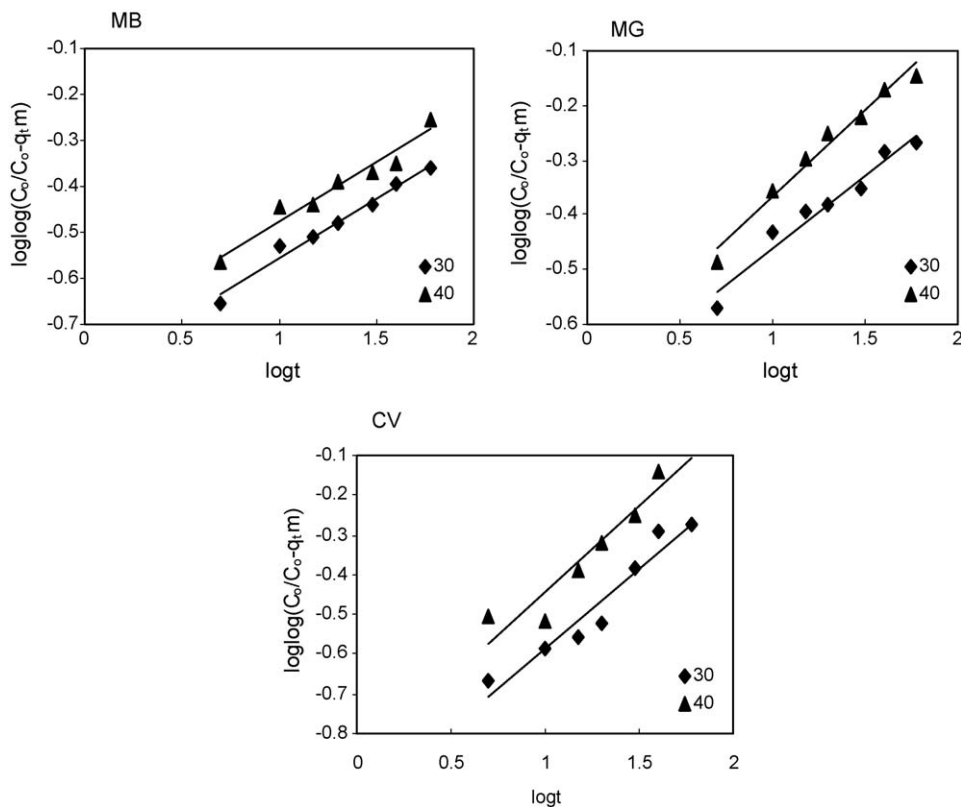


Fig. 8. Bangham's plot of $\log \log(C_0/C_0 - q_t/m)$ vs. $\log t$ for MB, MG and CV adsorption.

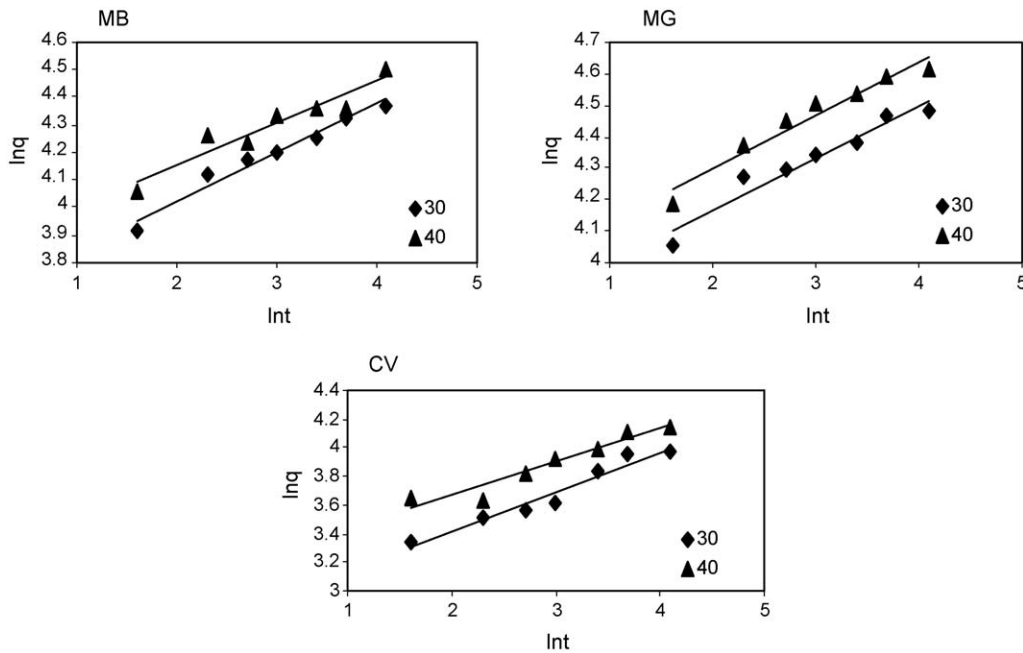


Fig. 9. The modified Freundlich plot of $\ln t$ vs. $\ln q_t$ for MB, MG and CV at different temperatures.

double logarithmic plot according to Eq. (9) did not yield linear curves for MB, MG and CV removal by WA11Zn5 showing that the diffusion of adsorbate into pores of the sorbent is not the only rate-controlling step [32,33]. It may be that both the film and pore diffusion were important to different extents in the removal of dyes. Values of k_0 and α (<1) are given in Table 2.

The modified Freundlich model fit the experimental data well, according to Fig. 9 and the R^2 values listed in Table 2. Modified Freundlich model parameter increases (adsorption rate k_0) with increasing temperature [34]. k_0 values of MG is 0.186 and 0.210 L/g min at 30 and 40 °C, respectively. A comparison of

the k_0 values reveals that MG is removed more effectively than MB and CV by WA11Zn5.

3.4. Adsorption thermodynamics

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

$$\Delta G^\circ = -RT \ln K_c \quad (13)$$

Table 3
Thermodynamic parameters of MB, MG and CV

Dyes	Concentration (mg/L)	ΔH (J/mol)	$-S$ (kJ/mol)	$-\Delta H$ (kJ/mol)			Equilibrium constant		
				303 K	313 K	323 K	303 K	313 K	323 K
MB	100	38.380	164.49	11.298	11.450	14.558	88.694	81.46	226.169
	200	39.828	141.28	3.031	4.353	5.878	3.332	5.327	8.926
	250	38.614	131.74	1.385	2.511	4.849	1.733	2.624	6.085
	300	29.278	99.136	0.780	0.977	2.504	1.363	1.455	2.540
	400	29.995	99.776	0.294	1.161	2.310	1.124	1.562	2.264
MG	100	34.350	147.52	10.336	11.913	13.290	60.546	97.318	141.04
	150	28.909	124.96	3.551	3.95	4.263	34.858	52.02	71.059
	200	36.269	134.52	1.763	2.309	2.654	5.835	10.074	14.213
	250	34.344	126.56	0.895	2.106	2.342	2.448	8.218	10.402
	300	40.768	144.99	0.799	1.924	2.196	2.225	6.848	8.990
CV	50	21.089	109.520	12.018	13.398	14.195	118.01	171.59	197.57
	100	56.422	200.74	7.084	6.150	8.629	16.649	10.627	24.863
	150	35.274	123.837	2.191	4.453	4.663	2.387	5.537	5.678
	200	38.537	130.538	0.923	2.713	3.518	1.443	2.836	3.706
	250	49.356	161.150	-0.587	2.396	2.644	0.791	2.512	2.677
300	29.429	94.147	-1.161	0.107	0.978	0.630	1.042	1.439	

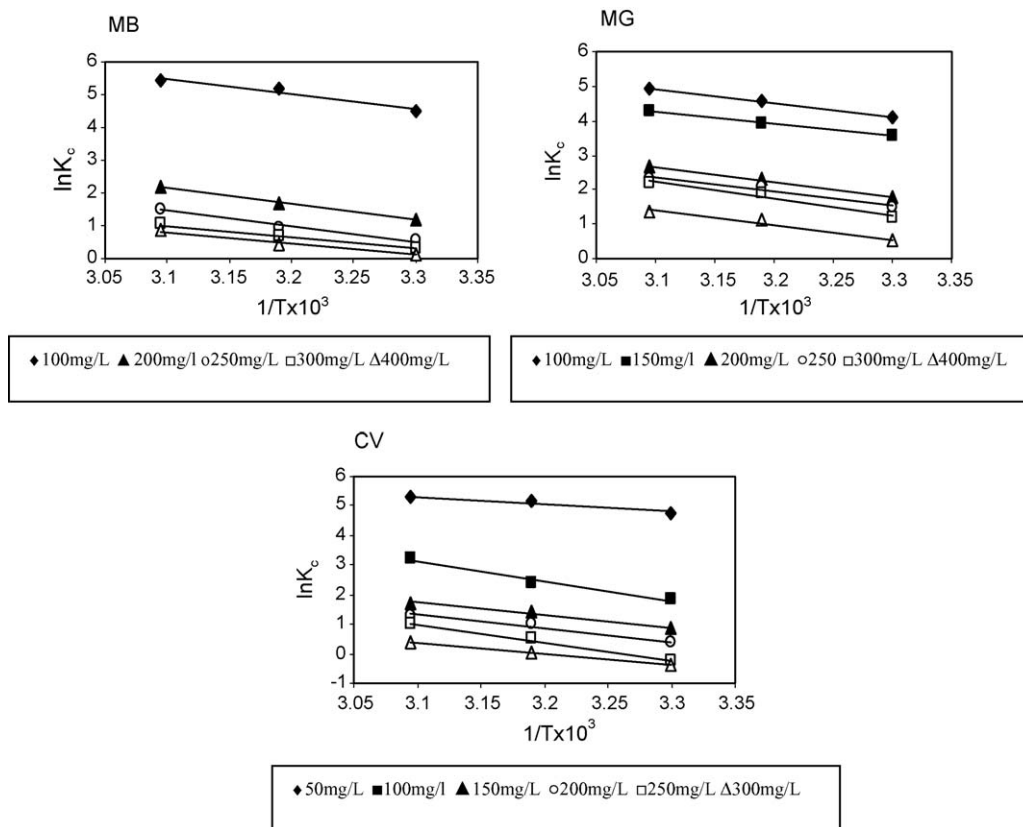


Fig. 10. Van't Hoff plots of MB, MG and CV adsorption onto WA11Zn5 for initial dye concentration.

where R is gas constant, K_c the equilibrium constant and T is temperature in K . The K_c value is calculated from Eq. (14):

$$K_c = \frac{C_{Ae}}{C_{Se}} \quad (14)$$

where C_{Ae} and C_{Se} is 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

$$\ln K_c = \frac{-\Delta H_{ads}^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (15)$$

The slope and intercept of the van't Hoff plot is equal to $-\Delta H_{ads}^\circ/R$ and $\Delta S^\circ/R$, respectively [16]. The van't Hoff plot for the adsorption of MB, MG and CV onto WA11Zn5 is given in Fig. 10. Thermodynamic parameters obtained are summarized in Table 3.

It is seen in Table 3 that the ΔH° values were in 29.995–39.828, 28.909–40.768 and 21.089–56.422 kJ/mol with a mean value of 35.219, 35.025 and 38.351 kJ/mol for MB, MG and CV, respectively. The positive values of enthalpy change conform to the endothermic nature of the adsorption process [35]. The positive values of ΔS° reflects the affinity of adsorbent material towards MB, MG and CV. The entropy (ΔS°) values vary from 99.136 to 164.49, 121.83 to 144.99 and 94.147 to 200.74 J/mol K for MB, MG and CV, respectively. Mean value of entropy is 127.28, 133.39 and 136.65 J/mol K for MB, MG and CV, respectively. Similar results for endothermic adsorption

of MG were also observed earlier on activated carbon prepared from de-oiled soya [11] and prepared from Tunçbilek lignite [36]. Despite being endothermic nature, the spontaneity of the adsorption process was decreased in the Gibbs energy of the system. The ΔG° values varied in range with the mean values showing a gradual increase from -3.357 to -6.019 , -2.944 to -4.339 and -3.411 to 5.771 kJ/mol for MB, MG and CV, respectively, in the temperature range of 30–50 °C in accordance with the endothermic nature of the adsorption process.

4. Conclusion

The results of this work can be summarized as follows:

- (1) The N_2 adsorption isotherm of WA11Zn5 is of type IV. The values of S_{BET} , V_t and S_{mic} and V_{mic} are 1060 m²/g, 0.79 cm³/g and 282 m²/g, 0.15 cm³/g, respectively. Results show that activated carbon includes micropores and mesopores.
- (2) The adsorption capacities of WA11Zn5 decreases in the order Malachite Green (MG) > Methylene Blue (MB) > Crystal Violet (CV). The amount of dye adsorbed onto WA11Zn5 for 250 mg/L initial dye concentration are 79.28 and 90.5 mg/g (for MB), 88.75 and 100.77 mg/g (for MG) and for 150 mg/L initial dye concentration is 52.86 and 63.53 mg/g (for CV) at 30 and 40 °C, respectively. Adsorption of all dyes onto WA11Zn5 increased with an increase in temperature, indicating that the process is endothermic.

- (3) The kinetics of adsorption of MB, MG, and CV on WA11Zn5 was studied by using six kinetic models. The adsorption of MB, MG and CV from aqueous solution onto WA11Zn5 proceeds according to the pseudo-second-order model which provides the best correlation of the data in all cases and the experimental $q_{e(\text{exp})}$ values agree with the calculated ones.
- (4) The dyes uptake process was found to be controlled by external mass transfer at earlier stages (before 5 min) and by intraparticle diffusion at later stages (after 5 min).
- (5) According to Elovich and Bangham model, the results show that the rate could be enhanced by increasing the adsorption temperature. The trend concerning β is consistent with those found in conventional activated chemisorption systems, which show that β is an indication of the number of sites available for the adsorption and MB, MG and CV removal by WA11Zn5 show that the diffusion of adsorbate into pores of the sorbent is not the only rate-controlling step.
- (6) It may be that both the film and pore diffusion were important to different extents in the removal of dyes, respectively.
- (7) The modified Freundlich kinetic model results and other data show that MG is removed more effectively than MB and CV by WA11Zn5.
- (8) The positive values of enthalpy change conform to the endothermic nature of the adsorption process. The parameters, ΔH , ΔS and ΔG , for the MB, MG and CV-activated carbon prepared from waste apricot interactions changed in away that made the adsorption thermodynamically feasible with high degree of affinity of the dye molecules for the WA11Zn5 surface.

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