ADSORPTION AND DESORPTION KINETICS BEHAVIOUR OF METHYLENE BLUE ONTO ACTIVATED CARBON

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Abstract. In the present work investigations on a potential use of activated carbon for the removal of Methylene Blue (MB) from wastewater are presented. Adsorption kinetics of methylene blue has been studied using reaction-based and diffusion-based models. Three kinetic models, namely, pseudo-first-order, pseudo-second-order and the Elovich are analyzed at the temperature of 298 K for the reaction-based model. The kinetic studies showed that the data were well described by the pseudo-second-order kinetic model. Intraparticle diffusion, external-film diffusion, and internal-pore diffusion models characterizing MB were obtained. The results suggested that the activated carbon has a high potential to be used as an effective adsorbent for methylene blue adsorption. Pseudo first-order, pseudo second-order and the Elovich models were employed to describe the desorption mechanism. The experimental results showed that the pseudo second-order equation is the best model. About 99% of activated carbon has been regenerated by desorption.

keywords: activated carbon, adsorption, desorption, kinetic studies, methylene blue

1. Introduction

Environmental pollution is a problem both in developed and devoloping countries. Factors such as population growth, and urbanization, invariably place greater demands on the world. Industrial revolution brought, with technological progress such as discovery of how to make synthetic dye, virtually universal use by different industries. Cheaper to produce, more brighter color, fast and easy to apply to fabric, the new dyes changed world. The chemicals used to produce dyes today are often highly toxic, carcinogenic, or even explosive. Harmful chemicals are used in the dying process, including aniline, dioxin, toxic heavy metals (such as chrome, copper, zinc, formaldehyde). Almost all industrial dye processes involve a solution of a dye in water in which the fabrics are soak. So, the textile factories across the world are dumping millions of Mg of dye effluent into rivers. Therefore, it is necessary to remove them from the wastewater before discharging. For the removal of these materials, several methods such as physical, chemical and biological have been investigated. Among the methods, removal of dyes by adsorption is regarded as one of the competitive methods

because of high efficiency, economic feasibility and simplicity of design/operation (Chen et al., 2010; Rafatullah et al., 2010; Haque et al., 2011). Activated carbons, because of their large surface area and relatively high sorption capacity, for a wide variety of dyes, have become the most promising and effective adsorbent. Nevertheless, their applications are restricted, because activated carbons are prepared from natural materials such as wood or coal, which are expensive. Recently, low cost and easily available other carbonaceous materials have been used, for example apricot stone, almand barks, coffee seeds, tea waste, rice husk etc.) (Diao et al., 2001; Wei-Lung et al., 2011). Textile waste containing cotton, nylon and polymers creates a problem in the world. Activated carbon prepared from these wastes could be important for the regional economy. Because high value products are obtained from low cost materials, they simultaneously bring solution to the problem of wastes (Altenor et al. 2009).

Methylene blue (MB) is one of the well known basic/cationic dyes and has been widely used in wood, silk, cotton, pharmaceutical industries. In this work, activated carbon has been prepared from a mixture of textural waste by chemical activation with $ZnCl_2$ in the flow of N_2 at 500°C. The prepared activated carbon is used as an adsorbent to remove methylene blue from aqueous solutions. The kinetics and diffusion parameters of the adsorption and desorption processes have been investigated.

2. Materials and methods

2.1. Materials

The solute selected for this work was MB (chemical formula = $C_{16}H_{18}N_3SCl$, MW =320 g/mol). A stock solution of 1000 mg/dm^3 was prepared by dissolving the required amount of methylene blue in distilled water. The spectrophotometric determination of MB was carried out using a Shimadzu UV/Vis spectrophotometer at 662 nm (model UV-2100S, Japan).

2.2. Preparation of activated carbon (WZ)

Textural waste, provided by different textile fabrics in Malatya, Turkey, was used in this study as a source of activated carbon. The raw material was subjected to two steps of activation as follows.

a) The raw material was mixed with $ZnCl_2$ ($ZnCl_2$: waste=0.5/1), and the mixture was kneaded by adding distilled water. The mixture was then dried at 110°C to prepare the impregnated sample.

b) The impregnated sample was placed on a quartz dish, which was then inserted within a quartz tube (internal diameter = 60 mm). The impregnated sample was heated at the rate of 10°C/min up to the activation temparature (500°C) under N_2 flow (100 cm^3/min) and held at the activation temperature for 1 h. After activation, the sample was cooled under N_2 flow. The sample was washed sequentially several times with hot

distilled water to remove any residual chemical and until a pH of 7 was reached. The washed sample was dried at 110°C to prepare activated carbon.

2.3. Adsorption experiments

MB solutions were prepared in distilled water at the desired concentrations. Adsorption experiments were carried out by agitating 0.1 g of WZ with 50 cm^3 solutions of the desired concentration (50, 75 and 100 mg/dm^3) at different values of time (1 to 60 min) and 25°C in a thermostatic bath operating at 400 rpm. The amount of MB adsorbed onto WZ, q_t (mg/g), was calculated by the mass balance relationship represented by equation:

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

where C_0 and C_t are the initial and final (at time t) liquid and phase concentrations of MB (mg/dm^3), respectively, V is the volume of the solution (dm^3), and W is the weight of the dry WZ used (g).

The normalized standard deviation Δq_e (%) was calculated using Eq. (2):

$$\Delta q_e(\%) = 100\sqrt{\frac{\sum\left[(q_{e,\exp} - q_{e,cal})/q_{e,\exp}\right]^2}{N-1}},$$ (2)

where N is the number of data points, $q_{e,\exp}$ and $q_{e,cal}$ (mg/g) are the experimental and calculated equilibrium adsorption capacities value, respectively.

2.4. Desorption experiments

For the desorption study, 0.5 g of activated carbon was added to 250 cm^3 of MB solutions (50, 75 and 100 mg/dm^3) and the mixture was stirred at 60 min. After mixing, the supernatant MB solution was discarded and the activated carbon alone was separated. Then, the MB-adsorbed activated carbon was added into 250 cm^3 of ethanol mixture (*v/v*, ethanol/water= 10/100). Ethanol and activated carbon (saturated with MB) solution samples were taken at specific time intervals (3, 5, 10, 60 min). The amount of MB desorbed from WZ, q_t (mg/g), was calculated at different values of time (1 to 60 min) and all concentrations and temperature of 25°C by the Eq. (1).

3. Results and discussion

3.1. Effect of initial concentration of methylene blue

Initial dye concentration provides an important driving force to overcome the mass transfer resistance of dye between the aqueous solution and activated carbon surface. Adsorption kinetic studies were performed by measuring methylene blue concentration and the results are illustrated in Fig. 1. The adsorption capacity

increased from 23.11 to 46.31 mg/g as the initial dye concentrations increased from 50 to 100 mg/dm³. It can be seen that a rapid adsorption of MB by activated carbon occurred, after approximately 30 min for all concentrations. It was particularly interesting that the process showed an extraordinarily fast initial rate of adsorption, which can be verified by the fact that the amount of adsorbed MB onto activated carbon within 5 min almost achieved 90% of that at the equilibrium.
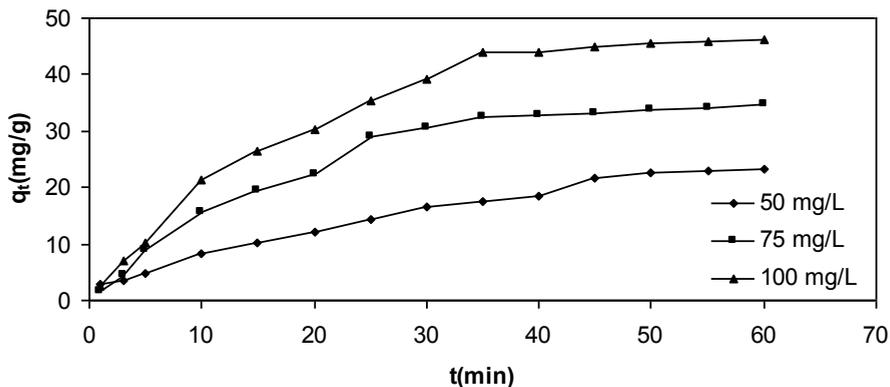

Fig. 1. Effect of initial dye concentration on the adsorption of MB as a function of time at 298 K

3.2. Adsorption kinetics

Kinetic mechanism of dye adsorption occurs through three consecutive steps:
1. external diffusion of dye molecules across the liquid film surrounding the porous adsorbent
2. adsorption of the dye on the adsorption site
3. internal diffusion of dye within the particle.

Due to the nature of adsorption, kinetic model for dyes could be divided into two types, namely reaction-based models and diffusion based models (Ho et al., 2000; Al-Degs et al., 2006).

3.2.1. Reaction-based models

To investigate the adsorption kinetics of MB three kinetic models, namely, pseudo first-order, pseudo second-order and Elovich models were analyzed at the temperature of 298 K.

The rate constant for the adsorption of MB onto activated carbon determined by the pseudo first-order equation is expressed as (Barrett et al.,1971):

$$\frac{dq_t}{dt} = k_1(q_e - q),$$
(3)

where k_1 (min^{-1}) is the pseudo first-order rate constant. Integrating Eq. (3) with respect to the integration conditions $q = 0$ to $q = q_t$ at $t = 0$ to $t = t$, the kinetic rate expression becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t ,$$ (4)

where q_e and q_t are the amounts of MB adsorbed (mg/g) at equilibrium and time t (min), respectively.

The adsorption kinetics have also been determined by the pseudo second-order model using equation (Ho and McKay, 1998):

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

where k_2 is the second order-rate constantn, g/(mg·min); and $h = k_2 q_e^2$, where h is the initial adsorption rate, mg/(g·min).

The Elovich model equation is generally expressed as (Low, 1960):

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t).$$ (6)

To simplify the the Elovich equation, Chian and Clayton (1980) assumed that $\alpha\beta t \gg t$ and by applying boundary conditions $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_0$. Then, Eq. (6) becomes (Chien and Clayton, 1980):

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

where α is the initial adsorption rate, mg/(g·min) and β is the desorption constant (g/mg).

The plot of log (q_e-q_t) versus t should give a linear relationship, from which k_1 and q_e can be obtained from the slope and intercept of the plot, respectively. The k_1 values, calculated q_e values, and correlation coefficients are provided in Table 1. The coefficient of correlation for the pseudo first-order kinetic model is not high for all concentrations. Moreover, the determined values of q_e calculated from the equation differ from the experimental values showing that adsorption of methylene blue onto WZ is not a first-order reaction and had low correlation coefficients (R^2<0.88).

The plot of (t/q_t) versus t of Eq. (5) should give a linear relationship, from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively. The results are illustrated in Table 1. The experimental results were applied to the pseudo-second order model straight lines with high correlation coefficients (R^2=0.982). They indicate that adsorption of MB follows the pseudo-second order kinetic model. From the analysis of all kinetic models one can predict experimental behaviour of the MB-WZ system.

Table 1. Kinetic paramaters of adsorption

Concentration (mg/dm^3)	50	75	100
$q_{e,\exp}$ (mg/g)	32.11	43.56	64.30
Pseudo-first order			
$q_{e,\text{cal}}$ (mg/g)	34.84	72.45	111.55
k_1 (min^{-1})	0.072	0.080	0.091
R^2	0.839	0.858	0.878
Δq_e (%)	40.2	31.1	28.0
Pseudo-second order			
$q_{e,\text{cal}}$ (mg/g)	32.36	42.63	68.49
k_2 (g·mg^{-1}·min^{-1})	0.00081	0.00078	0.00072
h (mg·g^{-1}·min^{-1})	0.848	1.417	3.377
R^2	0.915	0.962	0.982
Δq_e (%)	11.1	9.90	5.69
Elovich			
α (mg·g^{-1}·min^{-1})	3.947	6.537	8.864
β (g.mg^{-1})	0.178	0.106	0.079
R^2	0.900	0.953	0.958
Δq_e (%)	28.8	26.1	18.2

A comparison of the three kinetic models with experimental values for all concentrations can be seen in Figs. 2a-c. The normalized standard deviations Δq_e (%) are used to see the fit between the experimental data and theoretical values of MB onto activated carbon. It is clear from the figures and standard deviations (<11.10 %) that for pseudo-second-order (Table 1), there is a good agreement between the experimental and predicted values.

3.2.2. Diffusion-based models

Various diffusion models can be used to describe adsorption. These diffusion models have been developed to predict the dynamic character of adsorption. This work used the intraparticle diffusion, external-film diffusion, and internal-pore diffusion models to characterize adsorption of MB.
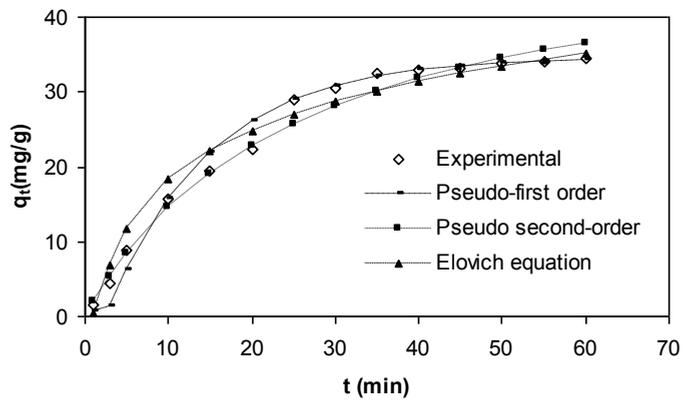
The intraparticle diffusion equation (Srivastova et al., 1989; Weber et al., 1973) can be written as follows:
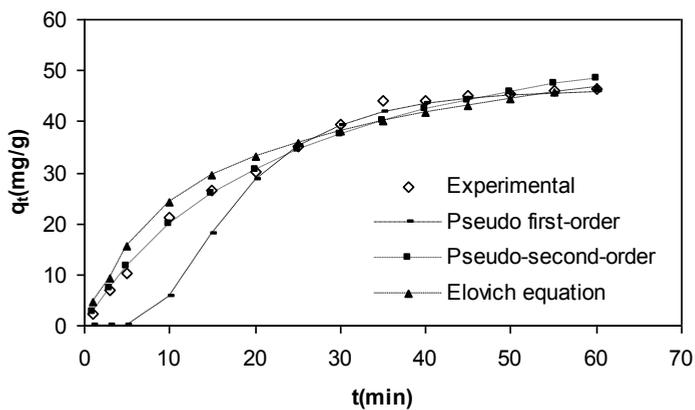
$$q_t = k_{\text{int}} t^{1/2} + c , \tag{8}$$

where c is the intercept of the line, which is proportional to the thickness of the boundary layer and k_{int} is the intraparticle diffusion rate constant, mg/(g·min$^{-1/2}$). The intraparticle diffusion model rate constant, k_{int}, is obtained from the slope of the straight line of q_t versus $t^{1/2}$ (Fig. 3).
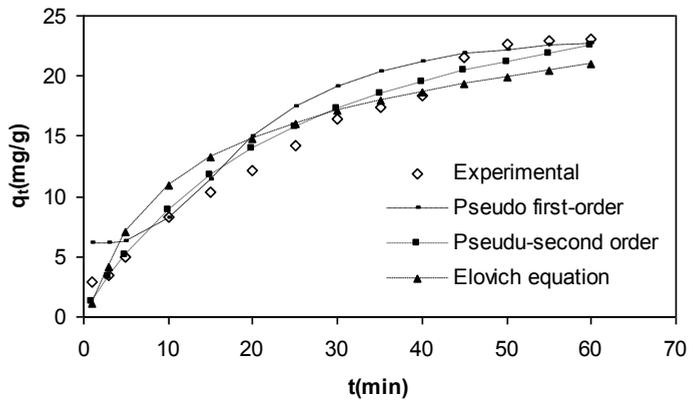
(a)

(b)

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Fig. 2. Comparison of kinetic models at 298 K (a) Concentration of MB solutions: 50 mg/dm^3, (b) Concentration of MB solutions: 75 mg/dm^3 and (c) Concentration of MB solutions 100 mg/dm^3
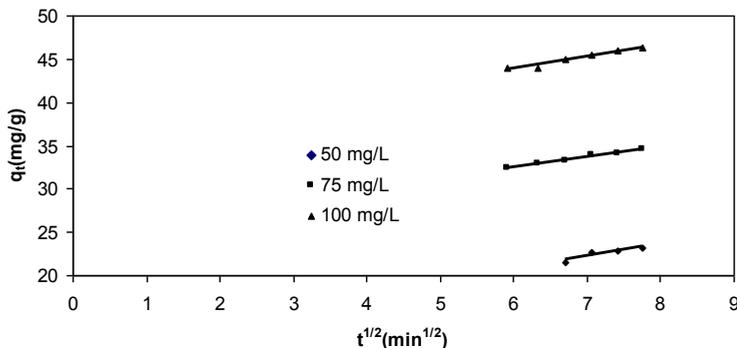
Fig. 3. Intraparticle diffusion plots of MB adsorption

During the initial adsorption period, description can be simplified by assuming that the concentration at the activated carbon surface tends toward zero (intraparticle diffusion negligible). External diffusion resistance is predominant and controls the adsorption of MB. Thus, the external diffusion models can be considered as follows (Dutta et al. 2011):

$$\left[\frac{d(C_t / C_0)}{dt} \right]_{t=0} = -k_f \frac{A}{V}. \tag{9}$$

and in the integrated form:

$$\ln \frac{C_t}{C_0} = -k_f \frac{A}{V} t, \tag{10}$$

where C_0 is the initial MB concentration (mg/dm^3), C_t MB concentration at time t (min), k_f external surface diffusion coefficient (m/min), A external surface area of the activated carbon (1750 m^2/g), V volume of solution (dm^3). Parameter k_f can be estimated from the slope of the $\ln(C_t/C_0)$ versus t curve at time $t{\rightarrow}0$.

The internal-pore diffusion can be calculated by using equations which are derived from Fick's law (Hajjaji et al., 2001; Streat et al., 1995)

$$F(t) = \frac{C_0 - C_t}{C_0 - C_e} = \frac{q_t}{q_e} = \left[1 - \exp\left(-\frac{\pi^2 D t}{r^2} \right) \right]^{1/2}, \tag{11}$$

or

$$\ln\left[1 - F(t)^2 \right] = -\frac{\pi^2 D}{r^2} t, \tag{12}$$

where C_e is the MB equilibrium concentration (mg/dm^3), D is the internal-pore diffusion coefficient (m^2/min) and r is the particle radius assuming spherical geometry $(2.10^{-6}$ m). A plot of ln[1-F(t)^2] versus time t should be linear with a slop of $-\pi^2 \cdot D/r^2$, which is commonly known as the diffusional rate constant.

Table 2 shows that the intraparticle diffusion model rate constant, k_{int}, which increases as the initial MB concentration increases. This could be attributed to the driving force of diffusion. The driving force changes with the MB concentration in the solution. The linear plots at various concentration do not pass through the origin, which shows that the intraparticle diffusion is not the only rate-controlling step (Fig. 3). If the plot is straight line passing through the origin, then the adsorption rate is governed by particle diffusion mechanism. Otherwise, it is governed by the film diffusion (Sarkar et al., 2003). The values of c are related to the boundary layer resistance. It is relatively high, and the greater is the contribution of the surface adsorption in the rate limiting step.

The values of external diffusion coefficient, k_f, increase by the increasing initial MB concentration (Table 2). The change in k_f, depends on the surface area and pore distribution of activated carbon. The activated carbon has micropores and external diffusion is more diffucult with the increasing initial concentration of MB.

The internal pore diffusivities were determined using Eq. (12). The adsorption data in Table 2 show that the internal pore diffusion coefficients is increasing with the increasing initial dye concentration.

A comparison of the adsorption capacities of MB adsorption estimated from the kinetic studies on various adsorbents is presented in Table 3. The variation in adsorption capacities and affinities can be mainly attributed to the differences in experimental condition and properties of the adsorbent. From Table 3, it can be observed, that the values of q_e of WZ for MB adsorption for the same initial concentration were higher than that for agricultural by-products (wood sawdust, rejected tea, carrot powder etc), zeolite, and activated carbon. The results demonstrated that WZ's could be employed as promising adsorbents.

Table 2. Diffusion parameters of adsorption

Concentration (mg/dm^3)	50	75	100
İntraparticle diffusion			
k_{int} (mg·g^{-1}·min$^{-1/2}$).	1.12	1.18	1.42
c	12.29	25.46	35.42
R^2	0.898	0.970	0.989
External-film diffusion			
$k_f \cdot 10^8$ (m/min)	13.10	14.50	15.10
R^2	0.976	0.980	0.993
Internal-pore diffusion			
$D \cdot 10^{15}$ (m^2/min)	22.31	27.18	28.27
R^2	0.893	0.963	0.939

Table 3. Adsorption capacities of MB for adsorbents

Adsorbent	C_o (mg/dm^3)	q_e (mg/g)	Ref.
Wood sawdust	120	16.21	(Ofomaja, 2008)
Cotton stalk	475	104.82	(Deng et al., 20011)
	825	211.35	
Cotton stalk	950	240.96	(Deng et al., 20011)
(with H$_2$SO$_4$)	1415	381.68	
Cotton stalk	950	173.01	(Deng et al., 20011)
(with H$_3$PO$_4$)	1415	242.13	
Rejected tea	50	20.80	(Nasuha et al., 2010)
	100	40.50	
	200	80.00	
Kenaf care fibers	50	44.84	(Sajab et al., 2011)
	100	96.15	
	150	142.80	
Activated carbon	250	50.09	(Durala et al., 2011)
(from posidonia oceonica)	500	101.40	
	750	153.55	
Wheat straw	100	96.40	(Han et al., 2010)
Palm kernel fiber	20	7.67	(El-Sayed et al., 2011)
	40	7.22	
	80	27.22	
	160	31.26	
Peanut husk	80	35.52	(Song et al., 2011)
Carrot leaves powder	10	4.10	(Kushwaha et al., 2011)
Carrot stem powder	10	4.34	(Kushwaha et al., 2011)
J. curcas cake residue	200	160.85	(Kurniawan et al. 2011)
	500	282.31	
Titanate nanotubes	50	94.15	(Xionga et al. 2010)
	100	129.17	
NaOH-modified rejected	50	2.44	(Nasuha et al. 2011)
tea	100	3.99	
	200	19.80	
	300	71.42	
Lotus leaf powder	50	46.00	(Han et al., 2011)
	100	91.00	
Zeolite	30	4.81	(Han et al., 2009)
	55	8.27	
	113	14.90	
Jack fruit peel	35	10.58	(Hameed, 2009)
	80	25.48	
	130	40.70	
Tea waste	50	24.76	(Udin et al., 2009)
Activated carbon	50	32.36	This work
(from textural waste)	75	42.63	
	100	68.49	

3.3 Desorption kinetics

Desorption characteristics or regeneration of spent activated carbon is extremely important. Desorption experiments were carried out using activated carbon at 25°C and initial concentration of 50, 75 and 100 mg/dm^3. As shown in Fig. 4 the desorption capacity at equilibrium of MB desorption increased from 0.08 to 0.23 mg/dm^3 with an increase in the initial dye concentration. The desorption reaches equilibrium with solid phase concentration of q_t at the shortest time of about 6 min. On the other hand, the

longest equilibrium time of about 12 min is needed for the case with the highest q_t values (Tseng et al., 2009). These values show that more than 99% of MB has been desorbed.
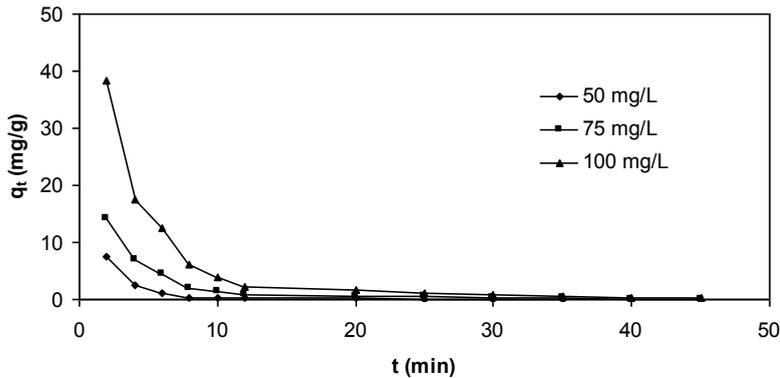

Fig. 4. Effect of initial dye concentration on the desorption of MB from activated carbons at 298 K

Desorption kinetics for activated carbon has not been determined in studies conducted to date. In this work, the kinetics of desorption has been considered using the pseudo-first order, pseudo-second order and Elovich model. Plots of the kinetic equation are shown in Figs. 5-7. The experimental results for the three kinetic illustrated equations are presented in Table 4. The behavior of k_1, k_2 and β could be attributed to the decrease in dye concentration in activated carbon. The R^2 values of the pseudo second-order model were >0.93, which is higher than the R^2 values obtained for the pseudo-first-order and the Elovich model. Therefore, the desorption kinetics could be better described by the pseudo-second-order kinetic model for MB desorption from activated carbon.

Table 4. Kinetic parameters of desorption

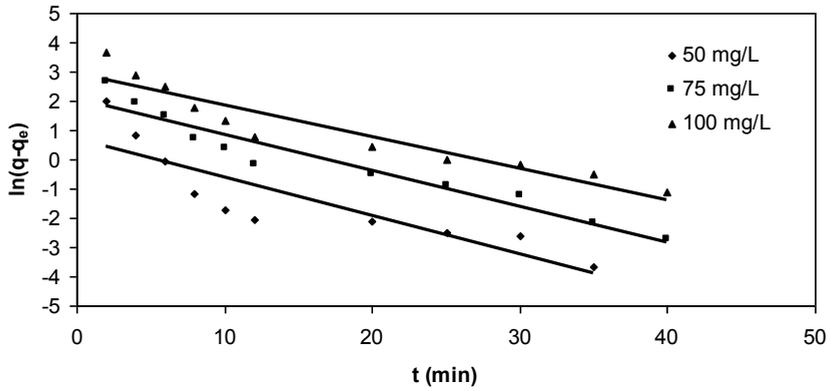| Concentration (mg/dm^3)	50	75	100
$q_{e,\exp}$ (mg/g)	0.08	0.09	0.23
Pseudo-first order			
$q_{e,\mathrm{cal}}$ (mg/g)	2.00	8.03	18.88
k_1 (min^{-1})	0.13	0.12	0.10
R^2	0.756	0.929	0.892
Pseudo-second order			
$q_{e,\mathrm{cal}}$ (mg/g)	0.11	0.29	0.51
k_2 (g·mg^{-1}·min^{-1})	2.11	0.61	0.31
h (mg·g^{-1}·min^{-1})	0.025	0.051	0.081
R^2	0.978	0.934	0.941
Elovich			
α (mg·g^{-1}·min^{-1})	38.67	102.4	305.27
β (g/mg)	0.32	0.22	0.09
R^2	0.800	0.875	0.849

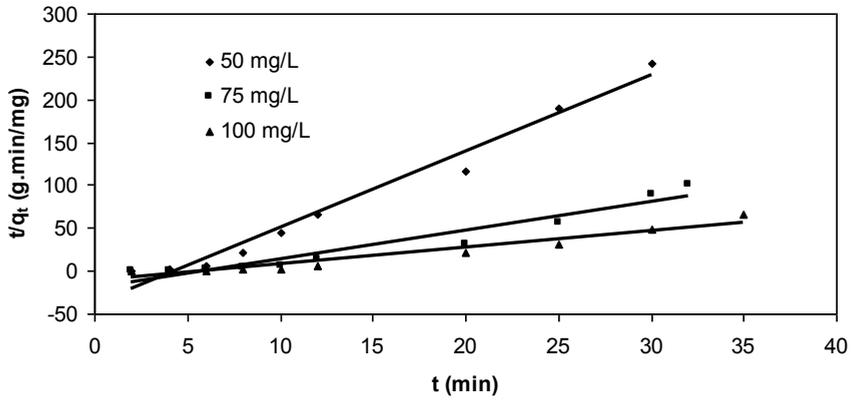Fig. 5. Pseudo-first-order kinetics for the desorption of MB

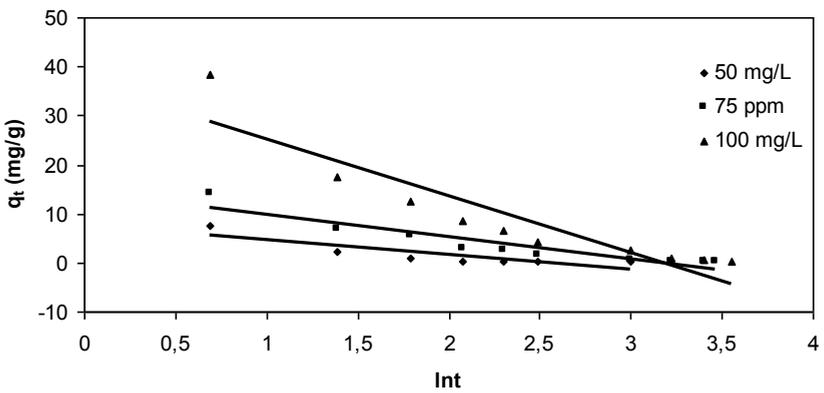Fig. 6. Pseudo-second-order kinetics for the desorption of MB

Fig. 7. The Elovich kinetics model for the desorption of MB

4. Conclusion

Activated carbon (WZ) can be used as adsorbent for removal of MB from its aqueous solution.

The kinetics of MB adsorption onto activated carbon was examined using the pseudo-first-order, pseudo-second-order and Elovich kinetics models. The adsorption kinetics followed the pseudo-second-order kinetic model.

The adsorption of MB onto activated carbon was controlled by external diffusion. The rate of adsorption of MB was very high during the first ten minutes. This was followed by a slower rate, and gradually approached a plateau.

Regeneration efficiency of activated carbon (or desorption of MB) was calculated to be 99%. The desorption kinetics followed the pseudo-second-order kinetic model.

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