Chemical Engineering Journal 146 (2009) 36–41

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Adsorption of methyl violet onto granular activated carbon: Equilibrium, kinetics and modeling

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ARTICLE INFO

Article history:
Received 24 January 2008
Received in revised form 6 May 2008
Accepted 13 May 2008

Keywords:
Adsorption
Kinetics
Equilibrium isotherm
Activated carbon
Stochastic simulation
Methyl violet

ABSTRACT

A batch system was applied to study the adsorption of methyl violet from aqueous solution by granular activated carbon. The adsorption studies include both equilibrium and kinetics. Equilibrium data were mathematically modeled using the Langmuir–Freundlich isotherm. The equilibrium data were fitted to the isotherm with $n = 1$ very well. Maximum adsorption capacity of 0.095 g/g at equilibrium was achieved. The kinetics of adsorption were evaluated by pseudo-first-order and pseudo-second-order models. Also extended geometric method has been applied to estimate the adsorption and desorption rate constants of Langmuir kinetics. By the obtained concentration-independent rate constants, the kinetics of adsorption were modeled by Langmuir kinetics. The stochastic numerical simulation has been applied to simulate the adsorption kinetic data of methyl violet at different concentrations.

1. Introduction

Dyes are the major pollutants of waste water from textile, cosmetic, paper and coloring industries. Entering of colored effluents into rivers, upset biological activity, so removal of dyes from waste effluents becomes environmentally important. Conventional treatment methods for removal of pollutants from aqueous solution, like photochemical degradation, biological degradation, coagulation, chemical oxidation and adsorption have been investigated with varying success [1,2]. Between the mentioned methods, adsorption is one of the potential methods for removal of dye compounds from water. Different adsorbents can be used for pollutants removal, but activated carbon ability to remove a large variety of compounds from waste water has led to its increased use [1,2].

Dye removal from aqueous solutions has been studied extensively. In this paper we just refer to removal of methyl violet by adsorption method. Different adsorbents have been tested on the possibility to remove methyl violet from aqueous solutions such as membranes [3], waste materials [4], chitosan [5], agricultural waste [6], sepiolite [7], fly ash [8], hydrogels [9], perlite [10,11] and powdered activated carbon [12].

Adsorption on solid surfaces is important from both scientific aspects and industrial (environmental) applications. For preliminary design of adsorption technologies, the adsorption equilibrium capacity of an adsorbent for a special adsorbate has to be estimated. As in any separation process, adsorption efficiency is a complex attribute dependent on the kinetic and equilibrium properties of the adsorbate/adsorbent system. The characteristic of the adsorption behavior is generally understood in terms of both equilibrium and kinetics. For kinetics, the amounts of adsorbate are measured at different times and thus the obtained experimental data are used to develop a proper kinetic model.

The aim of this work is to investigate both equilibrium and kinetics of adsorption of methyl violet onto granular activated carbon (GAC). Theoretical models were used for both equilibrium isotherm and adsorption kinetics, and the unknown parameters in the proposed model were evaluated by fitting to the experimental data.

2. Experimental

2.1. Materials

Granular activated carbon supplied by Merck Co. and sieved into particle size range of 0.85–1.00 mm. The specific surface area, BET, of this GAC is about 800 m^2/g according to the Merck Co. report. Methyl violet supplied by Merck Co. and were used as adsorbate in the present study. Methyl violet is used without further purification. Accurately weighted quantities of methyl violet were dissolved in bi-distillated water to prepare stock solution. Then the other desired concentrations of solutions were obtained by successive dilutions.

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doi:10.1016/j.cej.2008.05.024

2.2. Method

The concentrations of solutions were measured by a UV–vis spectrophotometer (PerkinElmer Model Lambda 45) at 586 nm. All experiments were carried out at constant temperature, 25.0 ± 0.1 °C, using a multi-temp III thermostat.

2.2.1. Equilibrium experiments

The equilibrium adsorption experiments have been undertaken to assess the efficiency of granular activated carbon to remove methyl violet dye from aqueous solution and also finding isotherm constants. The experiments were performed by using a set of 25 ml solutions of consecutively increasing concentrations which were brought into contact 0.04 g of GAC. Upon equilibrium (more than 3 days) the samples were filtered and analyzed using UV–vis spectrophotometer. The amount of methyl violet adsorbed onto GAC at equilibrium, q_e (g/g), was computed by

$$q_e = \frac{(C_0 - C_e)V}{WM_W} \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentrations (mol/l), respectively, V the volume of solution (l), W the weight of GAC (g) and M_W is the molar weight of methyl violet (g/mol).

2.2.2. Kinetic experiments

The kinetic experiments were carried out in a 250 ml stirred tank. The tank was equipped with a two-bladed agitator and was rotated with high speed (1100–1200 rpm) to prevent bulk diffusion as controlling step of adsorption kinetics. The volume of solution was 50 ml and concentration of GAC was 1.6 g/l as like as equilibrium experiments. At appropriate time intervals, 3 ml of solution were taken from the tank and were analyzed by UV–vis spectrophotometers to determine the residual methyl violet concentration in the solution and then returned to tank quickly to prevent any change in the volume of solution.

The kinetic experiments were carried out at different concentrations and each experiment was repeated three times but the average values were reported here. The amount of methyl violet adsorbed at any time q_t (g/g) was computed by

$$q_t = \frac{(C_0 - C)V}{WM_W} \tag{2}$$

where C is the concentration of methyl violet at any time (mol/l).

3. Result and discussion

3.1. Equilibrium adsorption

The most common representation of the adsorbate concentration and quantity of material adsorbed is the adsorption isotherm. The equilibrium adsorption isotherm is fundamental in describing the interactive behavior between solutes and adsorbent, and is important for the design of adsorption system.

Fig. 1 (open circles) shows the adsorption isotherm of methyl violet at 25 °C using the GAC. The equilibrium adsorption capacity, q_e, increased with increase in dye concentration. These data show that about 99–53% of dye has been removed by GAC depending on the initial concentration of methyl violet. This indicates that GAC is an effective adsorbent for removal of methyl violet from aqueous solution. As it is clear from Fig. 1, the shape of the isotherm indicated L-behavior according to Giles et al. [13] classification. This confirms a high affinity between the carbon and the dye molecule.

In this study the Langmuir–Freundlich isotherm equation was used for modeling of experimental data. This isotherm can be derived from the corresponding adsorption rate equation [14]:

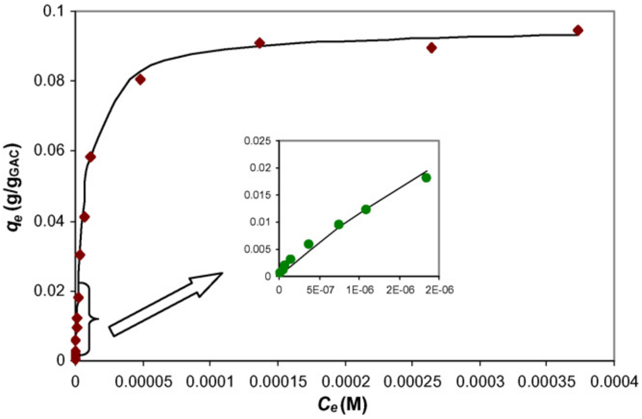

Fig. 1. Adsorption isotherm of methyl violet onto GAC at 25 °C. Open circles are experimental values and the solid line is the predicted values by Langmuir isotherm.

$$\frac{d\theta}{dt} = k_a C(1-\theta)^n - k_d \theta^n \tag{3}$$

where $\theta = q/q_m$ is the surface fractional coverage of adsorbate, and k_a and k_d are the adsorption and desorption rate constants, respectively. q_m is the maximum amount of adsorbate on the surface. At equilibrium $d\theta/dt = 0$ and therefore Eq. (3) converts to the Langmuir–Freundlich isotherm equation [14]:

$$\frac{q_e}{q_m} = \frac{(KC_e)^{1/n}}{1 + (KC_e)^{1/n}} \tag{4}$$

where $K = k_a/k_d$ is the equilibrium constant. It is clear that for $n = 1$, Eq. (4) simplifies to the Langmuir isotherm.

The experimental adsorption equilibrium data of methyl violet onto GAC were fitted to Eq. (4) by non-linear fitting method. The results of fitting were presented in Table 1. The best fitting were obtained by $n = 1$. So the equilibrium adsorption data of this system obeys Langmuir isotherm. For further clarity we also used the most popular linear form of Langmuir isotherm [15]:

$$\frac{C_e}{q_e} = \frac{1}{Kq_m} + \frac{C_e}{q_m} \tag{5}$$

This equation shows that if the system obeys Langmuir isotherm then the plot of C_e/q_e vs. C_e should be linear with $1/q_m$ and $1/Kq_m$ as slope and intercept, respectively. Such plot for the present system has been shown in Fig. 2. The obtained linear plot with a good correlation coefficient confirms that the Langmuir isotherm is a suitable isotherm for adsorption of methyl violet onto GAC. The obtained constants of Langmuir isotherm (K and q_m) from Fig. 1 were listed in Table 1. The Langmuir constants which derived by non-linear fitting and also Eq. (5) are very close to each other as indicated in Table 1. The solid line in Fig. 1 represents the predicted values by the Langmuir isotherm. The results show that the maximum capacity (q_m) for adsorption of methyl violet is 0.095 g/g of GAC.

Table 1
The constants of Langmuir isotherm for adsorption of methyl violet onto GAC at 25 °C, which is calculated by different methods

Method	q_m (g/g$_{GAC}$)	K (M^{-1})	r^2
Non-linear fitting	0.095	1.3×10^5	0.9985
Eq. (5)	0.095	1.5×10^5	0.9992

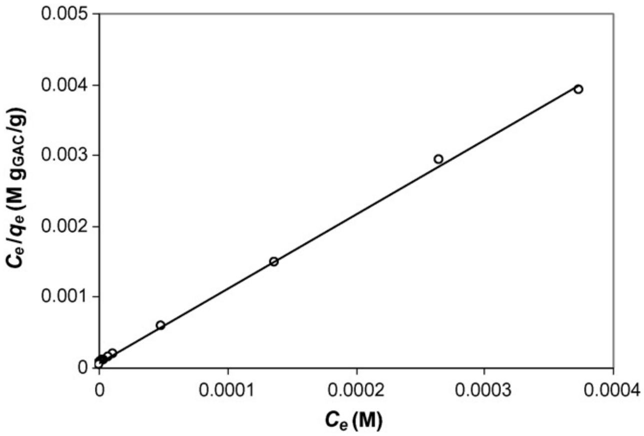

Fig. 2. Linear plot of Langmuir isotherm for methyl violet onto GAC.

3.2. Adsorption kinetics

To investigate the kinetics of adsorption, three different initial concentrations of methyl violet were chosen, 2.77×10^{-6}, 5.13×10^{-6} and 7.49×10^{-6} mol/l. Fig. 3 (open circles) shows the effect of contact time on the adsorption of methyl violet by GAC. The figures reveal that increased agitation time increased the uptake of methyl violet and attained equilibrium in 400 min. The majority of methyl violet was removed within the first 100 min. Fig. 3 also shows that the increase in the initial dye concentration increases the amount of dye adsorbed.

The kinetics of adsorption is described by the solute uptake rate. The adsorption kinetics ultimately controls the process efficiency. The adsorption kinetics of methyl violet onto GAC was examined with different kinetic models.

One of the simplest and oldest kinetic models of adsorption is pseudo-first-order model [16]:

$$\frac{dq}{dt} = k_1(q_e - q) \tag{6}$$

where q_e is the amount of adsorbed dye at equilibrium and k_1 is the rate constant of pseudo-first-order adsorption. After integration Eq. (6) becomes

$$\ln(q_e - q) = \ln q_e - k_1 t \tag{7}$$

If the adsorption kinetics obey pseudo-first-order model, then the plot of $\ln(q_e - q)$ vs. t should be linear. Fig. 4 shows the plot for adsorption of methyl violet on GAC. The constants of Eq. (7) were obtained from Fig. 4 at different concentrations and were listed in Table 2 including the correlation coefficients, r^2. As it is clear from Fig. 4 and Table 2, the fitting of experimental data to the pseudo-first-order model is not so good.

Another simple kinetic model is pseudo-second-order model [17]:

$$\frac{dq}{dt} = k_1(q_e - q)^2 \tag{8}$$

where k_2 is the pseudo-second-order rate constant. After integration of Eq. (8) and then rearrangement to a linear form, one obtains:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{9}$$

The pseudo-second-order model were used extensively in literature but it remains empirical up to 2004 where we derived [18] the first theoretical interpretation on this equation on the basis of theory of activated adsorption/desorption (TAAD) approach. Then we developed this model for heterogeneous adsorbents [19].

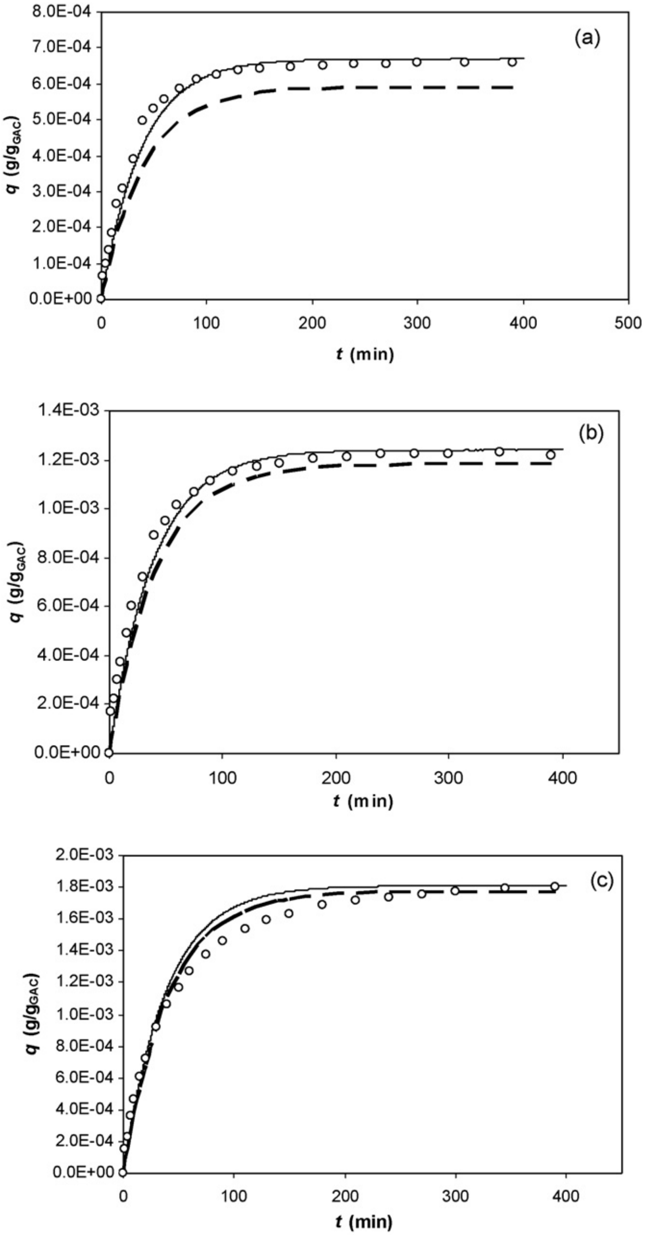

Fig. 3. Adsorbed amount of methyl violet as a function of time at different concentrations. (a) $C_0 = 2.77 \times 10^{-6}$ mol/l, (b) $C_0 = 5.13 \times 10^{-6}$ mol/l and (c) $C_0 = 7.49 \times 10^{-6}$ mol/l. Open circles are experimental values. Dashed lines and solid lines are the predicted values by extended geometric method and numerical simulation, respectively.

If the adsorption kinetics obeys pseudo-second-order model then the plot of t/q vs. t, will be a straight line with slope $1/q_e$ and intercept $1/k_2 q e_e^2$. Fig. 5 shows the plot of t/q vs. t for adsorption of methyl violet onto GAC at different initial concentrations of solute. The values of q_e and k_2 were obtained from the slopes and intercepts of plots in Fig. 5. These constants and also the correlation coefficients were listed in Table 2. Although the correlation coefficients are good but as it can be seen in Fig. 5 there is a deviation from this model for short times (when t is less than 50 min) at all three concentrations.

The main disadvantage of both pseudo-first-order and pseudo-second-order models is dependency of their rate constants (k_1 and

Table 2
The obtained constants of pseudo-first-order and pseudo-second-order kinetic models with correlation coefficients (r^2), at different initial concentrations

C_0 (M)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	q_e (g/g_{GAC})	k_1 (min^{-1})	r^2	q_e (g/g_{GAC})	k_2 ($g_{GAC}/g\,min$)	r^2
2.77×10^{-6}	4.68×10^{-4}	0.020	0.9704	7.06×10^{-4}	69.85	0.9982
5.13×10^{-6}	8.79×10^{-4}	0.019	0.9870	1.31×10^{-3}	40.13	0.9989
7.49×10^{-6}	1.42×10^{-3}	0.014	0.9886	1.96×10^{-3}	16.36	0.9996

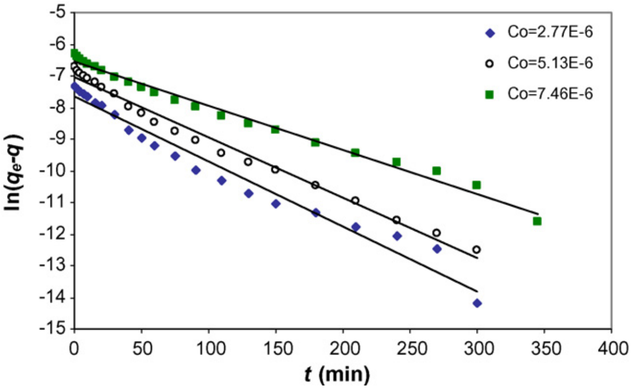

Fig. 4. The linear plot of pseudo-first-order kinetic model at three different initial concentration of methyl violet.

k_2) to the initial concentration solute so they are really pseudo-constants. This dependency has been shown both experimentally [20] and theoretically [18].

One of the best models for analysis of adsorption kinetics is Eq. (3), but there is no analytical solution for this equation because of n exponent. Most recently we proposed an approximation method [21] for derivation of rate constants of Eq. (3). This method was called “extended geometric method” [21]. On the basis of this method for Eq. (3) the rate constant of adsorption (forward) can be computed by

$$k_a \cong \frac{k_0}{C_0(1-t_L/t_e)-\beta k_0 t_L((1/2)-(n/3)k_0 t_L+(n(n-1)/8)k_0^2 t_L^2)} \quad (10)$$

where k_0 is the initial slope of θ vs. t plot (linear region), C_0 the initial concentration of solute, t_L the initial time of adsorption where θ vs. t is linear, t_e the equilibrium time, n the exponent in Eq. (3) which can be easily found from the adsorption isotherm, Eq. (4), and β is $Wq_m/M_W V$. So the input data of Eq. (10) can be easily obtained from the experimental data of θ vs. t and also adsorption isotherm. Desorption rate constant (k_d in Eq. (3)) can be easily computed by

$$k_d = \frac{k_a}{K} \quad (11)$$

where K is the equilibrium constant. It is clear that for $n = 1$, Eqs. (3) and (4) convert to Langmuir kinetic model and Langmuir isotherm, respectively. In this case Eq. (10) simplifies to [21]:

$$K_a \cong \frac{k_0}{C_0(1-t_L/t_e)-\beta k_0 t_L((1/2)-(1/3)k_0 t_L)} \quad (12)$$

Equilibrium studies on the adsorption of methyl violet onto GAC showed that the present system obeys Langmuir isotherm and therefore $n = 1$. So we can estimate the k_a from Eq. (12). Some of the input data of Eq. (12) for the present system are $\beta = 3.86 \times 10^{-4}$ mol/l, $t_L = 10$ min and $t_e = 390$ min. The values of C_0, k_0 and the calculated k_a were listed in Table 3. As it is shown in Table 3, the obtained k_a values at different concentrations are very close to each other and their small different is due to the experimental errors and also approximations used in the method. So the average values of k_a and k_d for methyl violet onto GAC at 25 °C are 62.5 mol/l min and 4.46×10^{-4} min^{-1}, respectively. The interesting point is that the obtained rate constants are independent of initial concentration.

Now by having k_a and k_d from extended geometric method one can calculate the value of q as a function of time for Langmuirian kinetics as [18]:

$$q = \frac{q_m \zeta_e^{\lambda t+\tau} - \nu}{2a(1-e^{\lambda t+\tau})} \quad (13)$$

where

$$\lambda = \sqrt{b^2 - 4af} \quad (14)$$

$$\nu = b - \lambda \quad (15)$$

$$\zeta = b + \lambda \quad (16)$$

$$\tau = \ln\frac{\nu}{\zeta} \quad (17)$$

$$a = k_a \beta \quad (18)$$

$$b = \left(\beta + C_0 + \frac{1}{K}\right) k_a \quad (19)$$

$$f = k_a C_0 \quad (20)$$

Fig. 3 (dashed line) shows the variation of calculated q with time for a Langmuirian kinetics using extended geometric method. Although the calculated values do not exactly match to the experimental data due to the reasons explained following, but this method as an approximate analytical method gives reasonable data.

The reason for deviation of calculated values of q from experimental data in Fig. 3 are (i) we used the average value of k_a for all concentrations; (ii) there are two approximations in the extended geometric method, (iii) experimental errors and (iv) adsorbate–adsorbate interactions. It is important to notice that the extended geometric method provides an easy way to estimate the

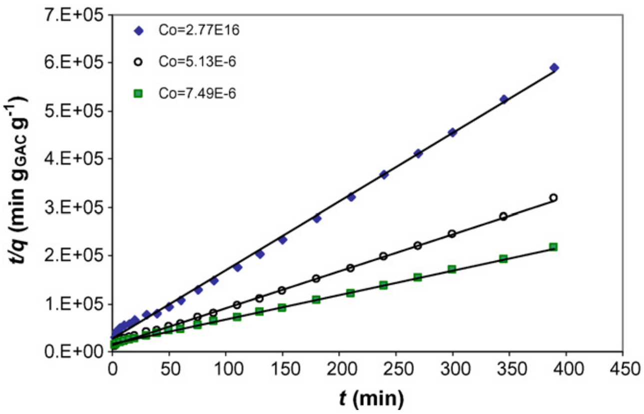

Fig. 5. The linear plot of pseudo-second-order kinetic model at three different initial concentration of methyl violet.

Table 3
The adsorption rate constant (k_a) of Eq. (3) which is obtained by extended geometric method and numerical simulation

C_0 (M)	k_0 (min^{-1})	k_a (M^{-1} min^{-1}) by extended geometric method	k_a (M^{-1} min^{-1}) by numerical simulation
2.77×10^{-6}	1.54×10^{-4}	63.1	70
5.13×10^{-6}	2.73×10^{-4}	60.2	70
7.49×10^{-6}	4.22×10^{-4}	64.1	60

concentration-independent rate constants of adsorption. We used this method successfully for analysis of kinetics of adsorption of methyl orange onto GAC [21].

In addition to the above analytical methods for derivation of adsorption rate constants and modeling of the adsorption kinetics of methyl violet onto GAC, we applied numerical simulation too. We applied the stochastic modeling technique for numerical simulation. For simulations the CKS package developed by Houle and Hinsberg [22] were applied. The program was run on a personal computer. This method has been used for numerical simulation and analysis of several chemical kinetics processes [22–26]. The input data for simulations are initial concentration of solute, number of vacant sites and adsorption/desorption rate constants. In our system the values of rate constants of adsorption/desorption at first were taken from extended geometric method, then this constants were adjusted until a reasonable reproduction of the experimental q vs. time were obtained. The values of adjusted rate constants of adsorption were listed in Table 3. The average values of k_a and k_d for adsorption and desorption of methyl violet onto GAC which obtained by numerical simulation are 66.7 l/mol min and 4.76×10^{-4} min^{-1}, respectively. Fig. 3 (solid lines) shows the simulated values of q at different times by using the average values of k_a and k_d.

It is clear that there is a good agreement between the experimental and simulated values of q at different times. Comparison of the average values of k_a and k_d obtained by extended geometric method and numerical simulation, shows that the extended geometric method as an easy analytical method can provide reasonable values of adsorption rate constants. The results of kinetic modeling suggested that the removal of methyl violet by GAC is chemisorption controlled.

To examine the validity of extended geometric method and also stochastic numerical simulation, two other examples were modeled by these methods. The adsorption kinetics of methyl orange onto GAC at different concentrations were studied recently by us [21]. The analysis of kinetic data by the extended geometric method for adsorption of methyl orange onto GAC led to the derivation of concentration-independent rate constants and also the results of modeling were close to the experimental data. Since the equilibrium data of methyl orange onto GAC follows Langmuir–Freundlich isotherm with $1/n = 0.5$, so we applied Eq. (3) with $n = 2$ for both extended geometric method and stochastic numerical simulation. The obtained rate constants from the extended geometric method and numerical simulation are $k_a = 19.2$, $k_d = 2.5 \times 10^{-4}$ and $k_a = 18.7$ l/mol min, $k_d = 2.4 \times 10^{-4}$ min^{-1}, respectively. It is clear that the obtained rate constants by different methods are close to each other. Fig. 6 compares the experimental kinetic data of adsorption of methyl orange onto GAC with the calculated values based on extended geometric method and stochastic numerical simulation. This figure shows the results of both methods are close to the experimental data.

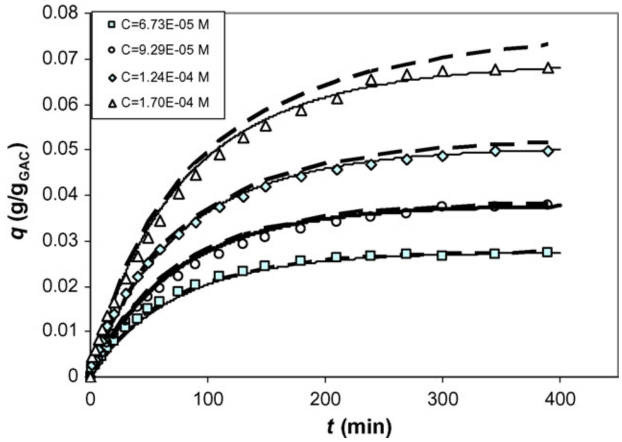

Fig. 6. Adsorbed amount of methyl orange as a function of time at different concentrations. Open circles are experimental values. Dashed lines and solid lines are the predicted values by extended geometric method and numerical simulation, respectively.

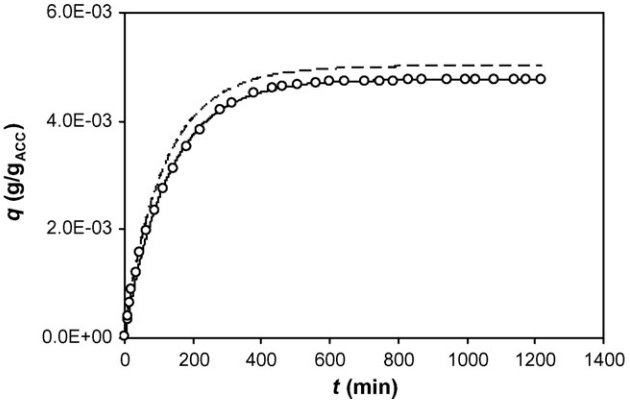

Fig. 7. Adsorbed amount of adsorbed AB92 dye as a function of time at $C_0 = 1 \times 10^{-5}$ mol/l. Open circles are experimental values. Dashed lines and solid lines are the predicted values by extended geometric method and numerical simulation, respectively.

As another example, the adsorption kinetic data of AB92 dye onto activated carbon cloth [27] were modeled by two methods. Since the equilibrium isotherm of this dye follows Langmuir isotherm [27], so for kinetic modeling we used Eq. (3) with $n = 1$. The obtained rate constants by extended geometric method and stochastic numerical simulation are $k_a = 93.8$, $k_d = 3.7 \times 10^{-4}$ and $k_a = 78.0$ l/mol min, $k_d = 3.0 \times 10^{-4}$ min^{-1}, respectively. The results of kinetic modeling are presented in Fig. 7. This figure shows that the results of stochastic numerical simulation completely matched with the experimental data. The extended geometric method provides good data at initial stage of adsorption but show small deviation at longer times.

4. Conclusions

The present study shows that the granular activated carbon is an effective adsorbent for removal of methyl violet from aqueous solution. Adsorption equilibrium followed Langmuir isotherm. The adsorption capacity was 0.095 g/g. The shape of isotherm indicated L-behavior, confirming high affinity between the carbon and the dye molecule. The rate of adsorption of methyl violet onto GAC was initially very high, then was followed by a slower rate and gradually approached a plateau. Although, the pseudo-fist-order and pseudo-second-order kinetics models are the simplest models for kinetic modeling of adsorption but in the present system, these models did not fit to experimental data very well and showed deviation from linear plots. Also, the concentration-dependent rate constant of these models is a disadvantage for them. Extended geometric method as an easy analytical method can provide a good estimate of concentration-independent adsorption/desorption rate constants of Langmuir or Langmuir–Freundlich kinetic models. The present study showed that the stochastic numerical simulation is a powerful tool for study of adsorption/desorption kinetics at solid/solution interface. By using stochastic numerical simulation it is possible to find more accurate rate constants of adsorption/desorption.

Acknowledgement

The authors acknowledge Dr. Ayranci, University of Akdenic (Turkey), for providing the experimental data of adsorption of AB92 dye onto activated carbon cloth.

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