



## Dynamic analysis of sorption of Methylene Blue dye on granular and powdered activated carbon

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### ABSTRACT

Removal of dyes and pigments from wastewaters of dyeing and printing industries is a major environmental issue. Sorption rate and equilibrium parameters of Methylene Blue on granular and powdered activated carbons were investigated in a batch adsorber. Due to the significance of pore diffusion resistance and partial closure of pore mouths by dissociatively chemisorbed dyes, both sorption rate and sorption capacity values evaluated for granular carbon were lower than the corresponding values for powdered activated carbon. Concentration independent effective pore diffusivity values in the order of magnitude of  $10^{-9}$  cm<sup>2</sup>/s were obtained by the moment analysis of a proposed diffusion model (Model 1).

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### 1. Introduction

Dyes are used in large quantities in many industries including textile, leather, cosmetics, paper, printing, plastic, pharmaceuticals, food, etc. to color their products [1,2]. Over 10,000 dyes with an annual production over  $7 \times 10^5$  tons worldwide were reported to be commercially available [3]. It was also reported in the literature that up to 10% of the dyes used in industry were lost in the industrial effluents. This causes a major environmental issue. The dye and dyeing effluents contain large amount of suspended solids and also they have high chromaticity and high COD content [4]. Conventional methods for treating dye-containing wastewater include biological treatment, froth flocculation, adsorption, chemical oxidation, hyper-filtration, coagulation, etc. [5–13]. Among these treatment methods, high cost-effectiveness and wide range applicability of adsorption technology opened new opportunities for the treatment of effluent streams of dyeing industries [14]. Due to the biological and chemical stability of dyestuffs in number of conventional water treatment methods, adsorption is considered as an attractive and favorable alternate for the removal of dyes and other chemicals from wastewater streams. For an efficient adsorption process, rapid removal of the pollutants as well as a high ultimate adsorption capacity of the adsorbent is needed. Consequently, kinetic studies, which provide

information for the rate of removal of pollutants from solution and the adsorption equilibrium data, are essential for the design of water treatment units involving an adsorption process.

The use of activated carbon for treatment of wastewater has received a lot of interest in the literature [15]. Various commercial activated carbons with different properties are manufactured for different applications. The source material and preparation process are the most important factors determining the properties of the carbons. Basically, almost any carbonaceous material can be converted into activated carbon [16,17]. Most types of industrial activated carbons are produced from naturally occurring carbonaceous materials like coal, petroleum, peat, wood and agricultural wastes. Because of its availability and cheapness, coal is the most commonly used precursor for activated carbon production [18,19]. The surface area, pore volume and pore size distribution are among the important factors determining the adsorption capacities of activated carbons and adsorption rate values. Generally, activated carbons are mainly microporous, but in addition to micropores they also contain mesopores and macropores. In principle, there are two different processes for the preparation of activated carbon: physical and chemical. Possible contamination and equipment corrosion caused by the chemical agents are considered as important drawbacks for the chemical activation processes. Preparation of activated carbon with physical activation involves carbonization of carbonaceous materials followed by gasification of the resulting char using some mildly oxidizing gases such as carbon dioxide or steam [19–21].

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## Nomenclature

### Nomenclature

$C$	bulk concentration of adsorbate at any time (mg/l)
$C_A$	macropore concentration of adsorbate (mg/l)
$C_0$	initial bulk concentration of adsorbate (mg/l)
$C_e$	bulk concentration of adsorbate at equilibrium (mg/l)
$D_a$	macropore effective diffusivity ( $\text{cm}^2/\text{s}$ )
$K$	apparent adsorption equilibrium constant ( $\text{cm}^3/\text{g}$ )
$K_f$	constant in Freundlich equation
$n$	Freundlich exponent
$R_0$	adsorbent particle radius (cm)
$R^2$	determination coefficient
$q$	adsorbed concentration (mg/g)
$q_e$	adsorbed concentration at equilibrium
$q_m$	adsorbed concentration corresponding to monolayer coverage (mg/g)
$w_s$	mass of adsorbent divided by volume of solid free liquid ( $\text{g}/\text{cm}^3$ )

### Greek letters

$\varepsilon$	macroporosity
$\mu_0$	zeroth moment defined by Eq. (1)
$\rho_p$	apparent density of adsorbent ( $\text{g}/\text{cm}^3$ )

Adsorption of organic molecules from aqueous solutions on various adsorbents has been investigated by number of researchers. Robinson et al. [22] have shown that two agricultural waste residues, corncob and barley husks, were efficient adsorbents of textile dyes from dye effluent. McKay et al. [23,24] investigated the adsorption of acidic, basic, disperse and direct dyes from aqueous solutions on activated carbon. Adsorption capacities of number of natural adsorbents, such as wood, rice husk, coal, teakwood bark, cotton waste, sawdust, waste solids from sugar industry and different types of clays such as bentonite, kaolinite, etc. for removal of different dyes were investigated by number of researchers [22–25]. Khare et al. [26] investigated the removal of Victoria Blue from aqueous solutions by fly ash. Gupta et al. [27] reported data for the removal of Omega Chrome by fly ash and coal combinations as mixed adsorbents. Significance of surface modification of silica on the adsorption of dyes was investigated by Khokhlova et al. [28]. Girgis et al. [29] reported a study on activated carbon prepared from discarded olive stones using column and batch techniques for removal of Direct Red 99 and Reactive Orange 11 from aqueous solutions. Chemically activated carbon (by treatment with  $\text{H}_3\text{PO}_4$ ) has been shown to be more effective in removing direct and reactive dyestuffs than the  $\text{CO}_2$ -activated carbon. Similarly, sugarcane bagasse was reported to be a possible alternative to activated carbon for removal of Basic Blue 69 and Acid Blue 25 from aqueous solutions [30]. In some studies, white-rot fungi have also been shown to be capable of decolorizing dyes. These fungi include *Trametes versicolor* [31,32], *Coriolus versicolor* [33,34], and *Funalia trogi* [35,36].

**Table 2**  
Physical properties of the adsorbents

Adsorbent	Powdered activated carbon (PAC)	Granular activated carbon (GAC)
Type	Norit SA3 (Aldrich Cat. No.: 26,001-0)	Nuchar WWH (Westvaco, USA)
Particle size (cm)	0.0147	0.0864
Density $\rho_p$ ( $\text{g}/\text{cm}^3$ )	0.76	1.09
BET surface area ( $\text{m}^2/\text{g}$ )	741	747
Langmuir surface area ( $\text{m}^2/\text{g}$ )	1070	1252

**Table 1**

Some physical properties of Methylene Blue [2,41]

Bulk density	400–600 $\text{kg}/\text{m}^3$
Solubility in water	50 g/l (at 20 °C)
Odour and form	Odourless and Dark Blue

Detailed information about the ultimate adsorption capacity, as well as information about the adsorption rate, is needed for the design of adsorption equipment. Adsorption rate data obtained from the experimental concentration decay curves in a batch adsorber or from the breakthrough curves obtained in a fixed bed flow system may be analyzed by using number of different adsorption rate models. Some of these models do not consider the effects of pore diffusion resistances. For instance in the conventional pseudo-first-order [37] and pseudo-second-order [38] adsorption rate models, diffusional effects were neglected. However, diffusional effects may be quite important in number of adsorption processes involving porous adsorbents and consequently the observed rate constants evaluated from the first- and second-order adsorption rate models are expected to be significantly dependent on the pore diffusion rate. Another approach for the description of adsorption rate of an adsorbate on a porous adsorbent is the use of diffusion models proposed for these systems [2,39].

Adsorption capacities of a natural zeolite (clinoptilolite) and Amberlite for the removal of dyes such as Methylene Blue and Basic Yellow 28 and also the adsorption rate data for these dyes were presented in our recent publications [1,2]. In the present study, granular and powdered activated carbons granulated activated carbon (GAC) and powdered activated carbon (PAC) were used as adsorbents for the removal of Methylene Blue in a batch adsorber and differences of their performances were illustrated. Adsorption rate and equilibrium data were obtained and analyzed by using different models. Significance of pore diffusion resistance on the adsorption rate was illustrated and effective diffusivities of the dye were evaluated. Importance of particle size on the diffusion resistance and consequently on the sorption rate and capacity was investigated.

## 2. Experimental work

In this study, granulated activated carbon (GAC) and powdered activated carbon (PAC) are used as adsorbents for the removal of Methylene Blue from aqueous solutions. Methylene Blue is a monovalent cationic dye having a formula of  $\text{C}_{16}\text{H}_{18}\text{ClN}_3 \cdot x\text{H}_2\text{O}$  ( $x=2-3$ ). Some physical properties of Methylene Blue are reported in Table 1. The activated carbon samples used in dye adsorption experiments were commercial products Norit SA3 (Aldrich Cat. No.: 26,001-0, powdered activated carbon) and Nuchar WWH (Westvaco, USA; granulated activated carbon). Their surface area values, apparent densities and the pore structure characteristics were determined using nitrogen adsorption surface area analysis (Quantachrome) and mercury porosimetry (Micrometrics 9310) equipment. Some physical properties of these adsorbents are given in Table 2. The surface area values correspond essentially to the meso- and macropores. Adsorbent samples were stored under vacuum before using in the adsorption experiments. As reported in Table 2, these activated carbon samples have comparable surface

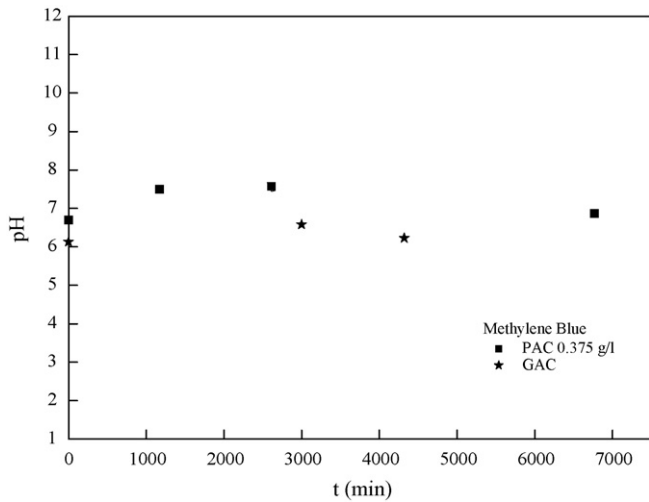


Fig. 1. pH change during the adsorption of Methylene Blue on GAC and PAC.

areas (around 745 m<sup>2</sup>/g), while the particle size of granular activated carbon was about 5.9 times higher than the particle size of powdered activated carbon.

Adsorption rate experiments were carried out in a 500 ml batch adsorption vessel. In most experiments, 250 ml of dye solution with an initial concentration of 12 mg/l was charged into the adsorption vessel. Adsorption rate experiments were repeated with different amounts of activated carbon charged into the adsorption vessel. The mixture in the adsorption vessel was stirred at a rate of 120 rpm using a magnetic stirrer. Adsorption rate experiments were started by charging predetermined amounts of adsorbent into the adsorption vessel. At predetermined time intervals, 3 ml samples were taken from the adsorption vessel and immediately analyzed spectrophotometrically (Pharmacia LKB-Novaspec II) at a wavelength of 665 nm. The pH of the solution was monitored during the adsorption experiments. The pH was around 7 throughout the adsorption experiments (Fig. 1).

The equilibrium values of the adsorbed concentrations of Methylene Blue corresponding to different fluid phase concentrations were also determined using a bottle-point procedure to construct the adsorption isotherms. In these experiments different amounts of adsorbents were added into each of six to ten bottles. The bottles were then filled with Methylene Blue solution and were left to shake in a constant temperature bath. Upon equilibration, samples were taken from each bottle and fluid phase concentration of Methylene Blue was determined spectrophotometrically.

### 3. Moment analysis of concentration decay curves

The zeroth moment, which corresponds to the area under the decay curve of dimensionless concentration in a batch adsorber, can be evaluated by the numerical integration given in Eq. (1) using the experimental adsorption rate data.

$$\mu_0 = \int_0^\infty \frac{(C - C_e)}{(C_0 - C_e)} dt \quad (1)$$

Here,  $C_0$  and  $C_e$  correspond to the initial and the equilibrium concentrations of adsorbate. The experimental zeroth moments evaluated from the concentration decay curves obtained in a batch adsorber may then be compared with the moment expressions which are derived for this system using different models.

Adsorption rate of an adsorbate by a porous adsorbent is generally controlled by diffusion of adsorbing molecules into the pores of adsorbent. For a batch-adsorbing vessel, rate of decrease of con-

centration of adsorbate may be evaluated from the diffusion rate into the pores of the adsorbent charged into this vessel.

$$\frac{dC}{dt} = - \left( \frac{w_s}{\rho_p} \right) \left( \frac{3}{R_0} \right) D_A \left[ \frac{\partial C_A}{\partial R} \right]_{R=R_0} \quad (2)$$

To evaluate the diffusion rate into the porous particles, different models may be proposed for the pseudo-homogeneous species conservation equation for these adsorbent particles. The simplest model corresponds to the Fick's second law containing a single parameter, namely effective diffusivity.

$$\frac{D_A}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial C_A}{\partial R} \right) = \frac{\partial C_A}{\partial t} \quad (\text{Model 1}) \quad (3)$$

$$\frac{\partial C_A}{\partial R} = 0 \quad \text{at } R = 0 \quad (4)$$

$$C_A = C \quad \text{at } R = R_0 \quad (5)$$

The zeroth moment expression corresponding to this model was reported in our earlier publication [2] as

$$\mu_0 = \frac{R_0^2}{15D_A(1 + (w_s/\rho_p))}. \quad (\text{Model 1}) \quad (6)$$

Effective diffusion coefficient values can then be evaluated from Eq. (6) using the experimental zeroth moment values.

Considering the size of Methylene Blue molecules, strong interaction of these molecules with the pore surfaces is expected during the diffusion process. The effective diffusivity of Model 1 involves the contributions of pore diffusion and also the adsorption terms. In this model, migration of adsorbing molecules into the adsorbent particles was described with a single parameter namely effective diffusion coefficient  $D_A$ . In another model, adsorption and pore diffusion terms were considered as separate terms.

$$\frac{D_A}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial C_A}{\partial R} \right) = (\varepsilon_A + \rho_p K) \frac{\partial C_A}{\partial t} \quad (\text{Model 2}) \quad (7)$$

The zeroth moment expression corresponding to this model was also reported in our recent publication [2].

$$\mu_0 = \frac{R_0^2(\varepsilon_A + \rho_p K)}{15D_A(1 + (w_s/\rho_p)(\varepsilon_A + \rho_p K))} \quad (\text{Model 2}) \quad (8)$$

In the derivation of this model, a linear adsorption relation was assumed between adsorbed concentration  $q$  and the fluid phase concentration  $C_A$  in the pores. It was shown by Doğu et al. [40] that the observed adsorption equilibrium constant  $K$  which appear in Eq. (8) may be estimated from the slope of the adsorption isotherm at  $C_e$ . For Freundlich and Langmuir type adsorption isotherms  $K$  may be estimated from the following expressions:

$$\text{Freundlich isotherm : } q = K_f C_e^{1/n}, \quad K = \frac{K_f}{n} C_e^{(1-n)/n} \quad (9)$$

$$\text{Langmuir isotherm : } \frac{q}{q_m} = \frac{K_A C_e}{1 + K_A C_e}, \quad K = \frac{q_m K_A}{(1 + K_A C_e)^2} \quad (10)$$

## 4. Results and discussions

### 4.1. Comparison of adsorption rates of Methylene Blue on GAC and PAC

Typical adsorption data obtained at 20 °C, for the time dependence of Methylene Blue concentration in the adsorption vessel, using different amounts of GAC and PAC are reported in Figs. 2 and 3, respectively. Comparison of the data presented in these two figures showed that adsorption rate values obtained with PAC were much higher than the corresponding values obtained with GAC. As it is

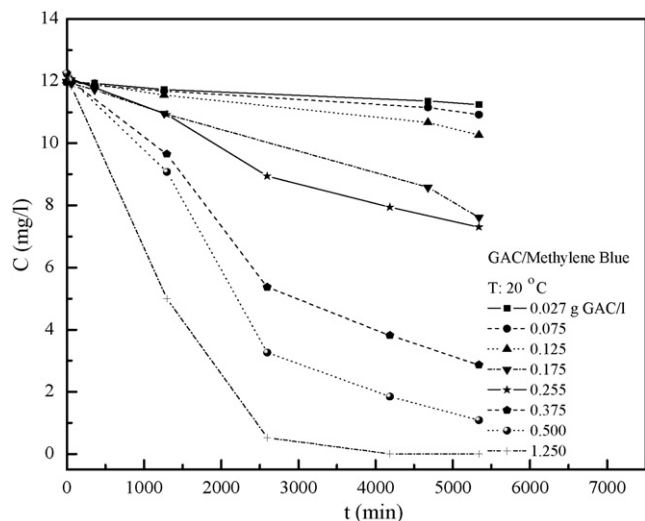


Fig. 2. Batch adsorber adsorption data, for Methylene Blue on granular activated carbon.

shown in Fig. 3, concentration of Methylene Blue approached to the equilibrium value at about 4000 min, for small amounts of PAC, in the range of 0.01–0.1 g/l, charged to the adsorber. Much longer times were needed to reach equilibrium with GAC (Fig. 4) and also much higher amounts of activated carbon were needed to achieve similar sorption capacities as PAC.

The simplest model used in the literature for the sorption rate of an adsorbate assumes a first-order adsorption rate process. For this model, the following relation was used for the variation of adsorbed concentration with respect to time [1,2,15].

$$\ln(q_e - q) = \ln q_e - k_1 t \tag{11}$$

This is the well-known Lagergren equation which was proposed for the description of adsorption rate on an adsorbent. In this model, the observed rate constant  $k$  is expected to depend upon the adsorbate concentration in the liquid, as well as the mass of adsorbent charged to the adsorber per unit liquid volume ( $w_s$ ) [2]. Also, this model does not consider diffusional effects on the observed rate. In the case of significant pore diffusion effects, observed adsorption rate constant is also expected to be dependent on the effective pore diffusivity and particle size of the adsorbent. This model may

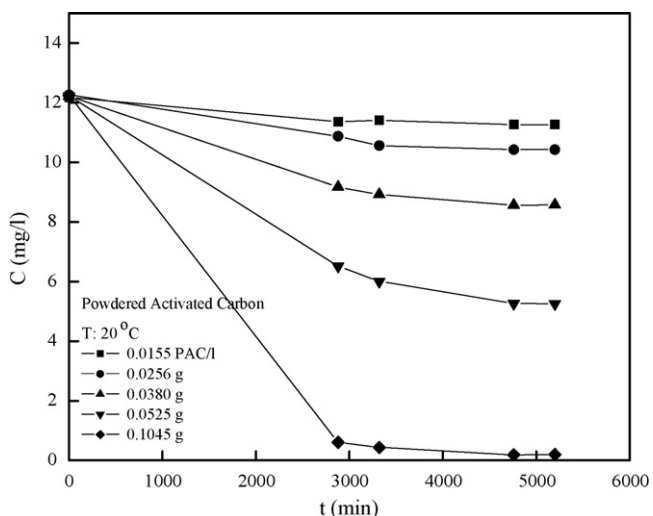


Fig. 3. Batch adsorber adsorption data, for Methylene Blue on powdered activated carbon.

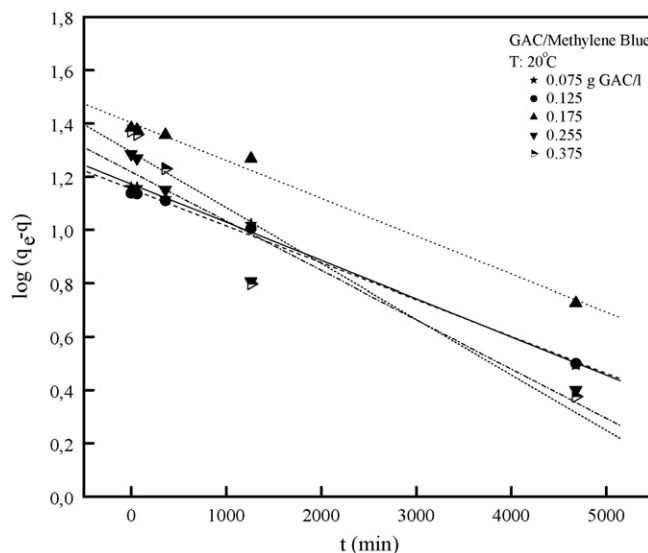


Fig. 4. Typical Lagergren plots for adsorption of Methylene Blue on GAC at 20 °C.

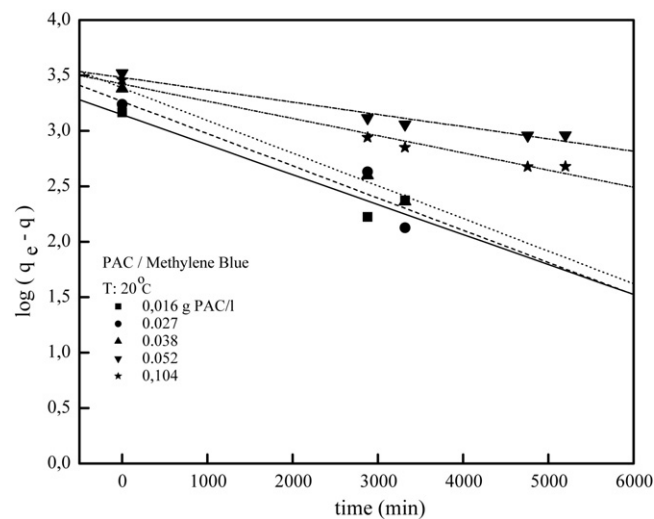


Fig. 5. Typical Lagergren plots for adsorption of Methylene Blue on PAC at 20 °C.

be used for the estimation of observed adsorption rate constant in dilute systems. One should also keep in mind that the observed rate constant evaluated from this model includes the diffusional effects.

Typical Lagergren plots corresponding to the first-order adsorption rate model (Eq. (11)) obtained with GAC and PAC are given in Figs. 4 and 5, respectively. Observed first-order adsorption rate constant values of Methylene Blue on GAC and PAC were then evaluated from the slopes of the linear Lagergren plots (Figs. 4 and 5). Typical values are reported in Table 3. In this analysis, data obtained at early times of adsorption were used. As it is seen in Table 3, first-order

**Table 3**  
Adsorption rate constants of Methylene Blue on GAC and PAC for first-order adsorption rate model ( $T = 20\text{ °C}$  and  $C_0 = 12\text{ mg/l}$ )

Granulated activated carbon		Powdered activated carbon	
Adsorbent Amount (g/l)	$k_1$ ( $\text{min}^{-1}$ )	Adsorbent Amount (g/l)	$k_1$ ( $\text{min}^{-1}$ )
0.075	0.00033	0.016	0.00062
0.125	0.00032	0.027	0.00067
0.175	0.00033	0.038	0.00068
0.255	0.00043		
0.375	0.00048		



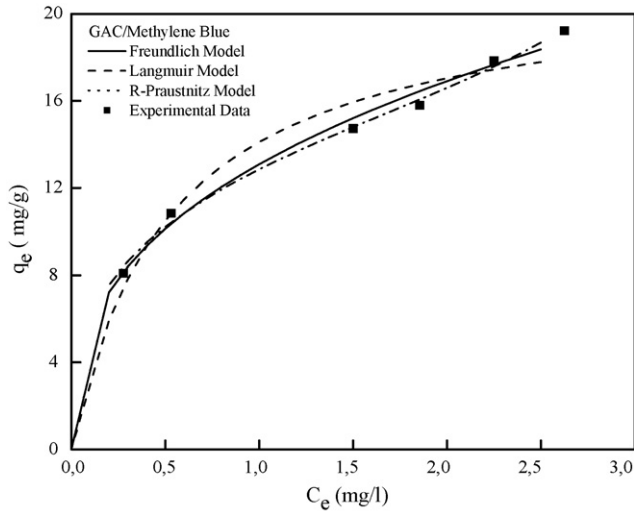


Fig. 6. Different adsorption models for Methylene Blue adsorption on granular activated carbon.

adsorption rate constants ( $k_1$ ) obtained with PAC were about twice the values obtained with GAC. Although the surface area values of PAC and GAC were about the same, both adsorption rate and the adsorption capacity of PAC were found to be higher than GAC. A possible explanation for this observation is the higher significance of pore diffusion and pore mouth closure in GAC.

The first-order adsorption rate constant values obtained with GAC were found to be quite consistent for adsorbent amounts less than 0.175 g/l charged into the adsorber. Deviations were observed at higher amounts of adsorbent (Table 3). In the case of PAC, consistent  $k_1$  values were at much lower adsorbent amounts. As it was discussed in our recent publication [2], the observed pseudo-first-order rate constant is expected to be dependent upon the amount of adsorbent as well as the concentrations of adsorbate. This constant is also influenced by the diffusional effects.

#### 4.2. Adsorption isotherms of Methylene Blue on GAC and PAC

Using the data obtained at very long times of contact, equilibrium values of fluid phase concentration and the corresponding values of the adsorbed concentration of the dye were determined.

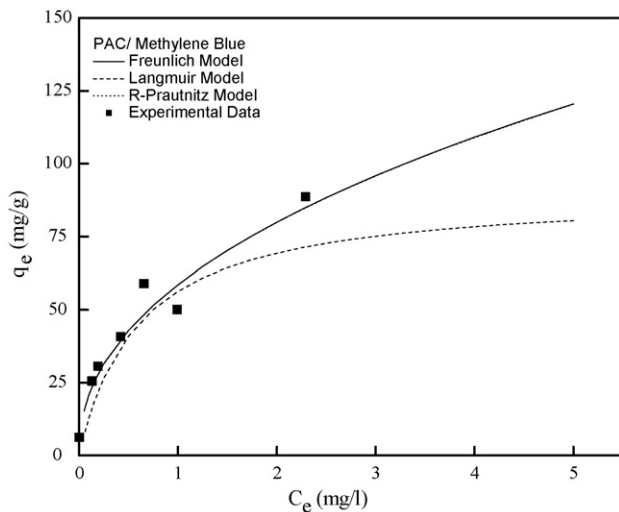


Fig. 7. Different adsorption models for Methylene Blue adsorption on powdered activated carbon.

Table 4

Adsorption isotherm models used for Methylene Blue adsorption on GAC and PAC ( $T = 20^\circ\text{C}$ )

Isotherm	Powdered activated carbon	Granular activated carbon
Langmuir: $q_e = \frac{q_m K_A C_e}{1 + K_A C_e}$	$q_m$ : 91 mg/g $K_A$ : 1.66 l/mg $R^2$ : 0.87	$q_m$ : 21.5 mg/g $K_A$ : 1.90 l/mg $R^2$ : 0.97
Freundlich: $q_e = K_f (C_e)^{1/n}$	$K_f$ : 65 $n$ : 2.23 $R^2$ : 0.96	$K_f$ : 13.08 $n$ : 2.7 $R^2$ : 0.99
Radke-Prausnitz: $q_e = \frac{abC_e}{1 + bC_e}$	$a$ : 65 $b$ : $1.22 \times 10^5$ $c$ : 0.63 $R^2$ : 0.99	$a$ : 13.08 $b$ : $3.08 \times 10^5$ $R^2$ : 0.99

These data were used to construct the adsorption isotherms. The data obtained for Methylene Blue at  $20^\circ\text{C}$  using GAC and PAC adsorbents are reported in Figs. 6 and 7, respectively. These adsorption equilibrium data are fitted to the Langmuir, Freundlich and Radke-Prausnitz adsorption isotherms and the results are summarized in Table 4. As it is seen in this table, the ultimate adsorption capacity of PAC corresponding to the monolayer coverage of all the sites by the adsorbate ( $q_m$  value of Langmuir adsorption isotherm) is much higher than the corresponding value obtained with GAC, indicating a higher adsorption capacity of this adsorbent.

Among these isotherms, Langmuir isotherm was the poorest to fit the experimental adsorption equilibrium data. Considering that Langmuir isotherm assumes a monolayer coverage and uniform activity distribution on the adsorbent surface, this is an expected result. Adsorption of Methylene Blue is quite a complex process, probably forming multilayers and even closing some of the pores. Also, a variation of sorption activity is expected with surface coverage. Both Freundlich and Radke-Prausnitz isotherms gave very good fit to the adsorption data of Methylene Blue on both GAC and PAC. Among these two isotherms, Freundlich isotherm is a two-parameter model, while Radke-Prausnitz is a three-parameter model. As shown in Table 4, the value of parameter "b", which appears in the denominator of Radke-Prausnitz isotherm, is very high. For such a high value of "b", Radke-Prausnitz isotherm approaches to Freundlich isotherm. Consequently, it was concluded that the adsorption equilibrium data of Methylene Blue could be described by Freundlich isotherm quite successfully.

#### 4.3. Diffusional effects on adsorption rate of Methylene Blue

Adsorption rates of Methylene Blue on GAC were also evaluated using the diffusion models described in the previous section (Models 1 and 2). In order to estimate the effective diffusivity values from these models, experimental values of zeroth moments are needed. The zeroth moment values were evaluated by the numerical integration of Eq. (1), using the concentration decay data reported in Fig. 2 for GAC. These experimental zeroth moment values were then used for the evaluation of effective diffusion coefficient of Methylene Blue from Model 1 (Eq. (6)) and from Model 2 (Eq. (8)). In the case of Model 2, the observed adsorption equilibrium parameter  $K$  should be known in order to estimate the value of  $D_A$  from Eq. (8).  $K$  values were evaluated from Eq. (9) considering Freundlich adsorption isotherm model and the results are summarized in Table 5. The values of effective diffusion coefficients were then evaluated for GAC using Eqs. (6) and (8) (Models 1 and 2) and the results are also reported in Table 5.

As it is seen in Table 5, effective diffusion coefficients evaluated from Model 1 are almost independent of the amount of

**Table 5**Effective diffusivity values of Methylene Blue evaluated from Model 1 to Model 2 in granular activated carbon at 20 °C ( $K$  values are evaluated from Freundlich Model)

$C_e$ (mg/l)	$w_s$ (g/cm <sup>3</sup> )	$\mu_0$ (s)	$K$ (cm <sup>3</sup> /g)	$D_A$ Model 1 (cm <sup>2</sup> /s)	$D_A$ Model 2 (cm <sup>2</sup> /s)
11.3	$0.27 \times 10^{-4}$	$111.8 \times 10^3$	1052	$1.12 \times 10^{-9}$	$1.24 \times 10^{-6}$
11.0	$0.75 \times 10^{-4}$	$115.7 \times 10^3$	1070	$1.08 \times 10^{-9}$	$1.16 \times 10^{-6}$
10.4	$1.25 \times 10^{-4}$	$117.6 \times 10^3$	1109	$1.06 \times 10^{-9}$	$1.12 \times 10^{-6}$
8.0	$1.75 \times 10^{-4}$	$117.8 \times 10^3$	1308	$1.06 \times 10^{-9}$	$1.23 \times 10^{-6}$
7.5	$2.55 \times 10^{-4}$	$105.1 \times 10^3$	1362	$1.19 \times 10^{-9}$	$1.30 \times 10^{-6}$
3.7	$3.75 \times 10^{-4}$	$101.6 \times 10^3$	2125	$1.23 \times 10^{-9}$	$1.58 \times 10^{-6}$
1.9	$5.00 \times 10^{-4}$	$97.3 \times 10^3$	3230	$1.28 \times 10^{-9}$	$1.72 \times 10^{-6}$

adsorbent charged to the adsorber. Different values of adsorbent amount correspond to different adsorbate concentrations ( $C_e$ ) at equilibrium. This result shows the suitability of Model 1 to describe the adsorption rate of Methylene Blue in GAC. The average values of  $D_A$  evaluated from this model is  $1.15 \times 10^{-9}$  cm<sup>2</sup>/s. The diffusivity values estimated from this model are based on the pseudo-homogeneous particle assumption.

Weisz criterion [42,43] can be used to estimate the significance of diffusion resistance on the rate of a reaction or adsorption in porous solids. According to this criterion, the following relation should hold for negligible pore diffusion.

$$\left( \frac{R_0^2 r_{\text{obs}}}{D_A C_0} \right) < 1.0 \quad (12)$$

Here,  $r_{\text{obs}}$  is the observed adsorption rate. Considering that adsorption rate was highest at the initial times of adsorption process,  $r_{\text{obs}}$  was estimated using the first-order adsorption rate constant value reported for GAC in Table 3 and the corresponding  $C_0$ . The left hand side of Weisz criterion was then estimated to be in the order of magnitude of 9, which was an order of magnitude higher than one. This result proved that diffusion was the controlling step for the rate of sorption of Methylene Blue in GAC. In the case of PAC, particle size is about 5.9 times smaller than GAC and the left hand side of Eq. (12) is expected to be less than 1.0. For PAC diffusional effects are expected to be quite small. Consequently, the use of diffusion models was not recommended to describe the adsorption rate.

Effective diffusion coefficient of Methylene Blue in GAC was also estimated from Model 2. In this case, the effective diffusion coefficients were found to be concentration dependent (Table 5). Especially for large amounts of adsorbent charged to the adsorber (over 0.25 g/l),  $D_A$  values changed with the amount of adsorbent. In this model, adsorption and effective pore diffusion coefficients were considered as separate terms and migration rate into the GAC was described by two parameters. The values of effective diffusivities estimated from this model are three orders of magnitude higher than the corresponding values estimated from Model 1. In fact, the relation between the diffusion coefficients evaluated from these two models can be approximately expressed as

$$(D_A)_{\text{Model 1}} \approx \left[ \frac{(D_A)_{\text{Model 2}}}{\varepsilon + \rho_p K} \right]. \quad (13)$$

These results showed that Model 1 was a better representation of this system for applications in a large range of Methylene Blue concentrations. Model 1 is a single parameter model and also the effective diffusivity evaluated from this model is not dependent on the amount of adsorbent charged into the adsorber.

## 5. Conclusions

Results of adsorption studies carried out in a batch adsorber showed that the sorption capacity and the sorption rate of Methylene Blue on powdered activated carbon was much higher than granular activated carbon. In the case of using granular activated

carbon with a particle size of 0.0864 cm, pore diffusion was found to be the controlling mechanism for adsorption rate. A single parameter diffusion model was shown to represent the adsorption successfully. The effective diffusion coefficient corresponding to this pseudo-homogeneous model was found to be independent of amount of adsorbent charged into the adsorber and consequently the concentration of adsorbate. The order of magnitude of the effective diffusion coefficient evaluated from this model using the moment technique was found to be  $10^{-9}$  m<sup>2</sup>/g. It was also shown that, the adsorption equilibrium data of Methylene Blue on both granular and powdered activated carbon were successfully described by Freundlich isotherm.

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