Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.807479

52 (2014) 5343–5356
August

Taylor & Francis
Taylor & Francis Group

A novel kinetic model for batch aqueous-solution/porous-solid adsorption systems

Ahmad Baraka

Egyptian Armed Forces, Cairo, Egypt
Tel. +20 2 29283998; email: brkamtc@yahoo.com

Received 12 April 2013; Accepted 13 May 2013

ABSTRACT

In this work, a novel kinetic model is introduced to represent the batch adsorption for aqueous-solution/porous-solid systems. The model proposes that the rate of adsorption is controlled by three parameters: solute concentration, *n*-powered time, and what is called varying-resistance against adsorption. Applicability of the model was examined by investigating the performance of the model considering the batch adsorption of methylene blue from aqueous solution onto three different adsorbents: hybrid resin-gel (MFTAT), commercial exhausted black tea, and dried pea husk. The effect of initial concentration was studied to explore model behavior. According to results and determined data, the DB-model successfully estimated the adsorption capacities and the rate constants. In addition, the DB-model managed to recognize the relative contributions of diffusion in the adsorption processes.

Keywords: Adsorption; Porous; Kinetic; Diffusion; Binding

1. Introduction

Rapid increase in the number of industrial and workshop facilities causes increase in the amount of wastewater produced. Removing organic and inorganic pollutants from wastewater effluents is an important task to guarantee safe-water resources. Adsorption of such pollutants onto solid adsorbents, especially porous materials, is widely applied due to its efficiency and easiness. Batch adsorption is the usual applied technique in laboratory and small scale treatment applications. In this technique, polluted water and grains of the porous adsorbent are brought into contact for a specific period of time to guarantee considerable decrease of pollutant concentration. In most cases, this contact is performed under stirring or shaking to enhance adsorption rate. Determining the rate at which a pollutant adsorbs onto an adsorbent and also determining the adsorption capacity are crucial to design a versatile wastewater treatment system. Adsorption kinetic models should give the adsorption rate constant and estimate the adsorption capacity of considered adsorption system as practical usefulness [1]. Besides, studying the kinetics of adsorption through theoretically well-established models are necessary for understanding the contribution of different mechanisms in adsorption process [2].

Pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models, which are initially presented as empirical formulae, are usually applied for studying the rate of adsorption [3–5]. Recently,

1944-3994/1944-3986 © 2013 Balaban Desalination Publications. All rights reserved.

modified-pseudo-first-order and pseudo-n-order have been also applied [6]. PFO and PSO kinetic models have been lately theoretically verified [7,8]. It is well established that these models (specifically PSO) reflect the dependency of adsorption rate on the available active-sites on the surface of adsorbent rather than solute concentration [9]. In addition, and in general, these models are suggested to describe the chemical and/or physical binding interaction (i.e. surface reaction) between solute and active-sites of the adsorbent [9,10]. The wide success of these models to satisfactorily describe an adsorption process is suggested from both the goodness of fitting of experimental data points (which is concluded from the determination coefficient, R^2) and from the accuracy of model-estimated capacity with respect to experimental capacity [11,12].

However, successful application of these models on different adsorption systems did not adequately confirm, in many cases, that the rate of adsorption is dependent only on surface interaction [9,10]. It is a fact that diffusion mechanisms contribute in adsorption processes which utilize porous adsorbents [9,13]. These pseudo-models do not clearly reflect the role of diffusion mechanisms even after theoretical base has been given [9,10]. Moreover, the assumption that intraparticle diffusion is the rate-controlling step in the vast majority of adsorption cases has been widely accepted, especially when porous adsorbent is applied [9]. This means that surface reaction (binding: the transition of solute molecules or ions from solvated state into adsorbed state [1]) is not the sole event to represent the adsorption processes. In other words, these pseudo models do not necessarily identify the adsorption mechanism(s) in a precise way.

Introducing a kinetic model able to simply discover the relative contributions of diffusion and binding in addition to predicting adsorption rate constant and adsorption capacity would be useful. This work presents a novel empirical model that can give information about adsorption mechanism(s) in addition to essential data; adsorption rate constant and adsorption capacity. The basic assumptions of this new model and its differential and linear equation forms are introduced. In its linear form, the model describes the kinetics of adsorption through the change of expression of solute concentration, C_t, with n-powered time, t^n. For simplicity, the model is named DB-model to stand for Diffusion and Binding.

To verify the applicability of DB-model, kinetic studies of adsorption of methylene blue (MB) onto three different adsorbents (Hybrid resin-gel, commercial dried roasted tea and dried pea husk [DPH]) were carried out. There are several experimental conditions that should be considered to asses the model such as initial concentration, solution pH, temperature, and shaking speed. As a start, initial concentration of solute (MB) was considered the sole condition to study in this work due to its prime importance. For the three adsorption systems, DB-model showed accepted linearity according to the values of the coefficient of determination, R^2 [10]. Adsorption rate constants and significantly good-estimated adsorption capacities were easily determined. Besides, by a simple analysis, the model could give an indication about the contribution-degree of diffusion and binding with respect to time. It is important to mention that other conditions that always significantly affect the adsorption processes (such as, pH, temperature, and shaking speed) will be considered in separate future works.

2. Materials and methods

2.1. Chemicals and adsorbents

2.1.1. Chemicals

Analytical grade MB cationic dye ($C_{16}H_{18}ClN_3S$) was used in this work as pollutant. Its maximum absorbance in aqueous solution is at $\lambda_{max} = 664$ nm. Absorbance values at λ_{max} have been used to determine MB concentrations for adsorption experiments. The absorbances were determined using Shimadzu UV-160.

2.1.2. Hybrid resin-gel: melamine formaldehyde tartaric acid/acrylamide tartaric acid, MFTAT

Details of synthesis and characterization of the MFTAT hybrid resin-gel were presented in a previous work [14]. In brief, the synthesis includes reaction of several components [melamine (3.2 g), tartaric acid (4.5 g), acrylamide (1.4 g), and formaldehyde (6 ml)] at about 120˚C until formation of a white dense slurry product which then was transferred to a gamma radiation cell to receive a dose of 2 kGy. A solid MFTAT is formed after gamma irradiation. Then, MFTAT grains (355–710 μm) ready for adsorption were produced.

2.1.3. Commercial exhausted black tea

Commercial bags of roasted black tea (Egyptian local product of EL AROSA TEA Company) were purchased from a local market and boiled several times with fresh distilled water to remove its content of natural dye. Leaves were then oven-dried at 50˚C for 72 h producing exhausted black tea (EBT) material. EBT was stored in a tightly closed plastic vial until use for adsorption. EBT was used as it is without grinding (its size was about 1 mm).

2.1.4. Dried pea husk

Fresh pea husk was collected from a food canning company, (Egyptian local company, Kaha for food industries). The husk was exposed to sun for five days and then oven-dried at 50°C for 24 h producing DPH material. DPH was then ground and sieved to obtain the selected particle size fraction (355–710 μm). This fraction was stored in a tightly closed plastic vial until use for adsorption.

2.1.5. Porosity of adsorbents

BET analysis was performed for MFTAT, EBT, and DPH samples. The main data are given in Table 1. It can be concluded from table that meso- and macro-pores are the dominant pores for tested adsorbents for MFTAT and EBT, whereas it is about 75% for DPH.

2.2. Batch adsorption experiments

All adsorption experiments were carried out using Companion SI-300R shaker where temperature was kept at 25°C. Prior to adsorption, the pH value of prepared MB-solutions was pre-adjusted using Hanna pH-meter (H18519) to be about 6.7 ± 0.02. Different MB-initial concentrations were applied; C_i: 6, 8, and 10 ppm. MB-adsorption onto any adsorbent constitutes MB-solution volume of 50 ml. Table 2 gives the other experimental adsorption conditions for each adsorption system.

Table 1
BET analysis of MFTAT, EBT and DPH

Character	MFTAT	EBT	DPH
Total surface area ($m^2\,g^{-1}$)	35.5	18.9	5.1
Micro-pores surface area ($m^2\,g^{-1}$)	0.2	0.9	1.3
Meso- and macro-pores (%)	99.4	95.2	74.5
Total average pore diameter (nm)	13.4	–	–

Table 2
Experimental adsorption conditions for adsorption systems

MB-adsorption onto	MFTAT	EBT	DPH
Adsorbent mass (g)	0.25	0.1	0.25
Shaking speed (rpm)	125	150	100
MB-absorbance measurement each at (min)	10	5	10
C_f determination at (min)	120	65	100
C_e determination at (h)	24	8	48

2.3. Introduction to and assumptions of DB-model and method of application

2.3.1. Introduction to DB-model

For a vast majority of different adsorption systems, the known kinetic models (PSO- and PFO-model) are frequently successful to determine adsorption rate constant and capacity which are the main objective of a model. Their linear forms relate an expression constituting q_t vs. t. Nevertheless, these models can not predict the diffusion(s) that may contribute in the adsorption process. These models theoretically consider that binding–interaction is the essential event of adsorption and considered to be the main controlling step [15]. On the other hand, however, the important linear equation of Webber–Morris model relates q_t directly with 0.5-powered time, $t^{0.5}$ [16]. Webber–Morris model is always applied successfully for the determination of diffusion types that may contribute in an adsorption process. However, this model is not suitable to determine adsorption capacity. In brief, each of these model-types is not solely suitable to adequately represent the adsorption process in many cases [10].

Most of adsorbents that are being utilized for the removal of pollutants from waters are porous materials. For these adsorbents, diffusions phenomena essentially and naturally occur during the course of an adsorption process [9,15]. It is not suitable to neglect the effect of diffusions on adsorption rate and to focus on binding–interaction as a sole predominant step [9,15]. Consequently, a kinetic model that deals with adsorption process on a porous material has to include parameters that reflect the different effective mechanisms in the adsorption process. Besides, it may be reasonable to accept that rate of intraparticle diffusion may change during adsorption process [16]. This is due to regular change of adsorption events with pore size from macro- to meso- to micro-pores, respectively [17].

Both of diffusion and binding should be considered when proposing a model that can represent adsorption on porous materials. Assumptions of DB-model considered this approach suggesting that dependency of an adsorption process would be on diffusion and binding. Their inter-relative weights (degree of effectiveness) in the process would judge the total performance of an adsorption system. In addition, the model takes into consideration that each adsorption system has its own inherent character which is introduced in model's equation as (C_fC_e/C_i) where C_i, C_f, and C_e are respectively the initial concentration, final concentration (concentration by the end of kinetic experiment) and equilibrium concentration (concentration after longer period of time to guarantee complete equilibration) of solute.

2.3.2. Assumptions of DB-model

In this work, rate of adsorption, r_{ads}, is defined as $-dC_t/dt$. The DB-model proposes that rate of adsorption is dependent on the following parameters:

1. *Solute concentration, C_t*, which by time causes decrease of adsorption rate due to its decrease as time of adsorption process elapses until equilibration.
2. *Time powered to a variable l, t^l*. As time, t, elapses, t^l increases and adsorption rate naturally decreases. As a rule, time should not be considered as a variable. However, in this work, due to the fact that involving adsorption steps have different rates, it is supposed that normal time scale can be optimized to represent these mechanisms as if having same modified time scale [18]. Powering the time normalizes the different rates of the mechanisms involving in the adsorption process, diffusions, and binding, with respect to time. In the present work, the linear form of DB-model is given as an expression of C_t vs. t^n. A similar empirical diffusion-chemisorption kinetic model was developed by Sutherland in 2004 *[19]*. In its linear form, $(q_e^2)/(q_e - q_t) = K_{DC}\ t^n + q_e$, an expression of q_t is give to be determined vs. t^n. Also, recently, Sutherland's model was applied on adsorption of cesium onto chemically modified pine cone powder [20]. By applying the non-linear forms of this model and PSO-model, the results indicated that Sutherland's model represented the adsorption process better than PSO-model for the modified pine cone case.
3. *A parameter named the varying-resistance against adsorption (VRA)* which is defined as the difference between solute concentration at any time during adsorption, C_t, and a constant A, i.e. $(C_t - A)$. The constant A is named *the conditioned balancing factor* (CBF) and equals (C_fC_e/C_i). CBF is considered as inherent character of an adsorption system. VRA parameter has the expression $(C_t - (C_fC_e/C_i))$. This parameter might be considered as a barrier which should be overcome at any time of adsorption process to achieve the final concentration. As the numerical difference between solute concentration, C_t and A decreases due to decrease of C_t, barrier becomes weaker, then C_t suffers higher rate of decrease and adsorption rate tend to increase. In other words, VRA parameter resembles a resistance against adsorption and as time elapses, C_t decreases, VRA also decreases and hence adsorption process faces less resistance. Accordingly, this parameter causes increase of adsorption rate.

According to the previous proposals, the model considers that rate of adsorption ($r_{ads} = -dC_t/dt$) is:

1. Directly proportional to solute concentration at time t, C_t.
2. Inversely proportional to l-powered time, t^l.
3. Inversely proportional to VRA, $(C_t - (C_fC_e/C_i))$.

Mathematically, the dependence of rate of adsorption on the three parameters can be written as follows:

$$r_{ads} = -\frac{dC_t}{dt} \propto \frac{C_t}{\mathrm{VRA} \times t^l} \tag{1}$$

$$r_{ads} = -\frac{dC_t}{dt} \propto \frac{C_t}{(C_t - (C_fC_e/C_i)) \times t^l} \tag{2}$$

$$r_{ads} = -\frac{dC_t}{dt} = k_{BD} \times \frac{C_t}{(C_t - (C_fC_e/C_i)) \times t^l} \tag{3}$$

$$-\int \frac{C_t - (C_fC_e/C_i)}{C_t} dC_t = k_{DB} \int \frac{1}{t^l} dt \tag{4}$$

By integrating Eq. (4) under the conditions: $C_t = C_i$ at $t = 0$ and $C_t = C_t$ at $t = t$, a linear equation form is produced:

$$\frac{C_fC_e}{C_i} \ln C_t - C_t = \frac{k_{DB}}{1-l} t^{1-l} - D, \tag{5}$$

where k_{DB} is the DB-model adsorption rate constant and D is the integration constant.

For simplicity; consider $1 - l = n$, then Eq. (5) becomes:

$$\frac{C_fC_e}{C_i} \ln C_t - C_t = St^n - D, \quad \text{and slope, } S = k_{DB}/n \tag{6}$$

Eq. (6) is considered linear by relating $((C_fC_e/C_i) \ln C_t - C_t)$ against t^n. The constant D, the integration constant, can be determined by applying the initial condition $C_t = C_i$ at $t = 0$ on Eq. (6), then:

$$D = \frac{C_f C_e}{C_i} \ln C_i - C_i \tag{7}$$

2.3.3. Method of applying DB-model

When an adsorption system obeys DB-model, applying Eq. (6) on system's kinetic data points should give a linear plot of $((C_f C_e/C_i) \ln C_t - C_t)$ against t^n. The linearity is produced under the condition of properly selecting the value of the power n. By using a data sheet program, linear regression can be applied on the experimental result, $((C_f C_e/C_i) \ln C_t - C_t)$ against t^n. The proper selection of n-value should give a line of the highest determination coefficient, R^2, *and in the same time* the program-calculated value of the constant D should be equal or very close to $((C_f C_e/C_i) \ln C_i - C_i)$ according to Eq. (7). The adsorption rate constant, k_{DB}, can be determined from line-slope according to the following expression:

$$K_{DB} = S \times n \quad (\text{mg l}^{-1} \text{ min}^{-n}) \tag{8}$$

The estimated adsorption capacity by this model, q_{DB}, can also be determined using the following expression:

$$q_{DB} = S \times t^n \times \frac{V}{m} \quad (\text{mg g}^{-1}) \tag{9}$$

where V and m are respectively the solution volume and used adsorbent mass. In this study, the solute concentrations, solution volumes, adsorbent masses, and time have the next units respectively; ppm, l, g, and min. The unit of rate constant (k_{DB}) should be $\text{mg l}^{-1} \text{min}^{-n}$.

Throughout this work, DB-model is assessed by considering determination coefficients (R^2) and its estimated capacities [1,10]. Estimated capacity assessment was performed by calculating the relative error percentage with respect to experimental data according to the following relation [6]:

$$\text{RE}_{DB} (\%) = 100 \times \frac{q_{BD} - q_{EXP}}{q_{EXP}} \tag{10}$$

where q_{DB} and q_{EXP} are DB-model capacity and experimental capacity respectively.

2.4. PSO model

PSO-model was applied on the same experimental-adsorption data sets of points on which DB-model was applied. The aim is to compare DB-model outputs with a well known and widely used model, PSO [10]. The following linear form of PSO-model was applied in this work [21]:

$$\frac{t}{q_t} = \frac{1}{k_{PSO} q_f^2} + \frac{t}{q_{PSO}} \tag{11}$$

where q_{PSO} and q_t (mg g^{-1}) are adsorption capacity at the end of kinetic adsorption experiment and at time t, respectively, and k_{PSO} ($\text{g mg}^{-1} \text{min}^{-1}$) is the PSO-model adsorption rate constant. Assessment of PSO-model was regarded through determination coefficient (R^2) and relative error percentage of its estimated capacity with respect to experimental capacity in the same way as for DB-model according to following relation:

$$\text{RE}_{PSO} (\%) = 100 \times \frac{q_{PSO} - q_{EXP}}{q_{EXP}} \tag{12}$$

where q_{PSO} is PSO-model capacity.

3. Results and discussion (DB-model performance)

3.1. Adsorption of MB onto MFTAT

Fig. 1 shows the MB-removal percentage ($R\%$) by MFTAT against time of different MB-initial concentrations: 6, 8, and 10 ppm. From figure; it is obvious that MB-removal increases steadily and then started to slow down considerably around the minute 80. Fig. 2 shows the plots of DB-model for MB-adsorption onto MFTAT for mentioned concentrations by selecting $n = 0.7$ according to fitting performed using regression program, Microsoft® Excel™. From figure, the model does not give a linear relation over the whole time period of experiment (from 0 to 120 min). Multi-linearity concept was applied in the same manner as frequently Morris-Webber model was applied [17]. The model was applied considering two stages; the first from 0 to 80 min and the second from 80 to 120 min. Linearity is satisfactorily accepted according to R^2-values of linear fitting ($R^2 > 0.97$, except for second stage of 8 ppm condition $R^2 = 0.8303$, Table 3). Fig. 2 may indicate that DB-model successfully draws or simulates adsorption process on similarity basis with Fig. 1. It can be suggested the success of DB-model to represent the adsorption kinetics of MB onto MFTAT. As mentioned before, PSO-model was selected for comparison because of its wide use. Fig. 3 shows the plots of PSO-model for the same data sets. From figure, it is clear that PSO-model produced accepted linearity according to R^2-values of linear fitting ($R^2 > 0.96$, Table 3). However, as it is linear over the whole time

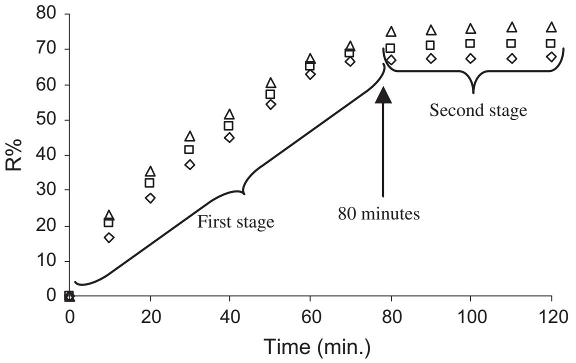

Fig. 1. Removal percentage of MB, R%, by MFTAT with respect to time for initial concentrations (◇) 10, (□) 8, and (Δ) 6 ppm.

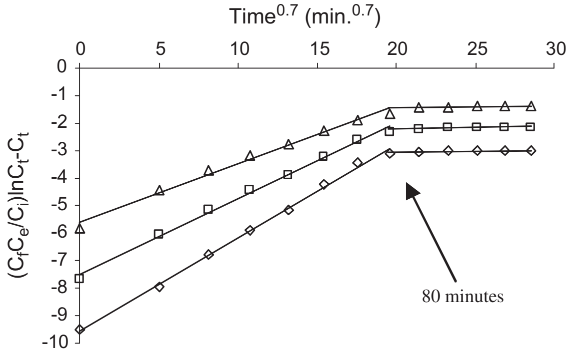

Fig. 2. DB-model plots of MB-adsorption onto MFTAT for initial concentrations (◇) 10, (□) 8, and (Δ) 6 ppm.

period of adsorption process, PSO-model does not show capability to simulate adsorption stages according to Fig. 1.

Referring to the present state of knowledge, adsorption process passes through the following consecutive steps: (1) migration of solute from solution bulk towards adsorbent outer surface (bulk diffusion), (2) diffusion of solute across liquid-film surrounding outer surface of the adsorbent (film diffusion), (3) diffusion of solute through the liquid inside the pores (intra-particle diffusion), and finally (4) binding of solute onto inner surface of the adsorbent along the pores' walls [1,10,13,15]. Yet, under shaking conditions, steps (1) and (2) can be neglected [10]. In this study, due to shaking, the intraparticle diffusion can be suggested to be the sole diffusion mechanism amongst the three diffusion mechanisms that can contribute, with binding, in the adsorption process [10,17]. Considering DB-model, for the three MB-initial concentrations, the adsorption rate was fast in the first 80 min and then considerably slowed down. This may be explained by suggesting that the first stage

Table 3
Characteristics of MB-adsorption onto MFTAT according to DB-model and PSO-model

C_i (ppm)	EXP.	DB-model						PSO-model		
	q_{EXP}	n	k_{DB}	q_{DB} (First stage) q_{DB} (Second stage)	q_{DB} (Total)	$RE_{DB}\%$	R^2	q_{PSO}	$RE_{PSO}\%$	R^2
6	0.919	0.7	0.1479 0.0059	0.827 (97.7%) 0.019	0.846	7.94	0.9894 0.9787	1.234	34.28	0.9896
8	1.145	0.7	0.1917 0.0089	1.072 (98.5%) 0.016	1.088	4.98	0.9956 0.8303	1.567	36.86	0.9817
10	1.356	0.7	0.2363 0.0074	1.321 (98.9%) 0.020	1.336	1.47	0.9980 0.9772	1.981	46.09	0.9641

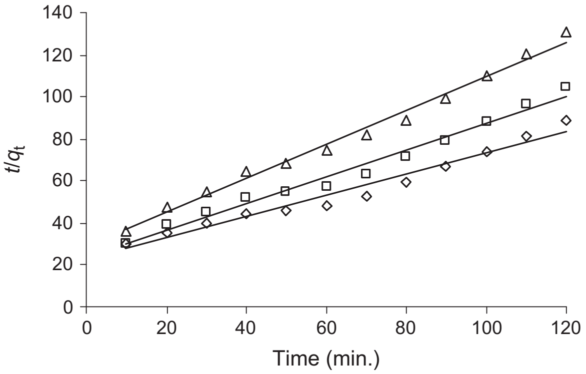

Fig. 3. PSO-model plots of MB-adsorption onto MFTAT for initial concentrations (◇) 10, (□) 8, and (Δ) 6 ppm.

involves: (1) solute binding onto active sites directly available over the outer surface of the adsorbent and (2) diffusion of solute into open-external pores accompanied by direct binding [22]. In the second stage, where pores are suggested to become narrower, the diffusion rate decreased and became the controlling step of the adsorption process [22]. In short, the first stage is binding controlled and the second stage is intraparticle diffusion controlled due to lesser size of pores. This estimation can not be determined from plots of PSO-model.

Table 1 indicates that MFTAT has the highest surface area (with dominant meso- and macro-pores) amongst the three adsorbents, however its capacity is considerably lower than that of EBT as will be shown (referring to Tables 3 and 4 for comparison). This again may support the suggestion that most of bindings of MB occurs with active sites available on outer surface (direct binding) and within external opened pores (fast diffusion then binding) where first stage shows removal amount (mg g^{-1}) > 97%, Table 3. Fig. 4 shows SEM image of MFTAT which may suggest this behavior. It is observed that surface is highly configured with open pores.

For the tested initial concentrations, Table 3 summarizes: the experimental capacities (q_{EXP}), the DB-model rate constants (k_{DB}), the selected-values of the power (n) of DB-model, the estimated capacities by DB-model (q_{DB}), and their error percentages (RE_{DB}%), the estimated capacities by PSO-model (q_{PSO}) and their error percentages (RE_{PSO}%), the coefficients of determination (R^2) for both models.

From the table, the values of determination coefficient suggest that both models can well represent the adsorption kinetics of this adsorption system. However, q_{DB} values are closer to experimental values than being q_{PSO} values. This can be derived by comparing the calculated error percentages of both models;

Table 4
Characteristics of MB-adsorption onto EBT according to DB-model and PSO-model

C_i (ppm)	EXP.	DB-model						PSO-model		
	q_{EXP}	n	k_{DB}	q_{DB} (First stage) q_{DB} (Second stage) q_{DB} (Third stage)	q_{DB} (Total)	RE_{DB}%	R^2	q_{PSO}	RE_{PSO}%	R^2
6	2.870	0.2	0.5954	2.711 (96.5%)	2.809	2.13	0.9998	2.982	3.90	0.9998
			0.1015	0.093			0.9123			
			0.0162	0.005			0.8999			
8	3.796	0.25	0.8463	3.580 (93.7%)	3.819	0.61	0.9987	3.960	4.32	0.9999
			0.1186	0.100			0.8893			
			0.0694	0.139			0.8056			
10	4.784	0.4	0.9784	4.432 (90.1%)	4.917	2.78	0.9987	5.311	11.02	0.9998
			0.2907	0.421			0.9877			
			0.0967	0.064			0.9376			

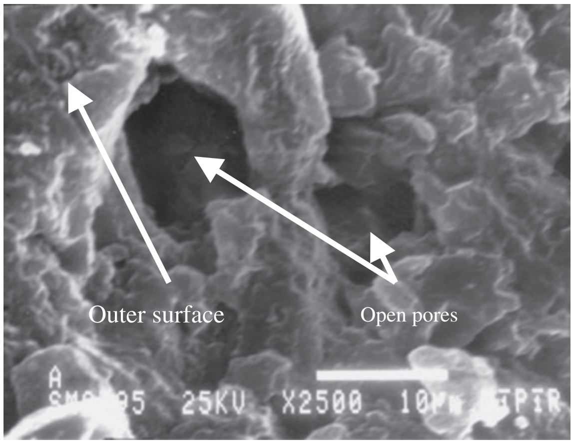

Fig. 4. SEM image of the outer surfaces of MFTAT [14], (open pores are easily observed).

($RE_{DB}\%$) < ($RE_{PSO}\%$). It is apparent that $RE_{PSO}\%$ values are significantly higher than $RE_{DB}\%$ values. For the first stage of adsorption it is clear that values of k_{DB} increases with C_i [11]. The power $n = 0.7$ does not change with initial concentration, C_i. This indicates that t^n parameter does not obviously respond to the change of C_i for MB/MFTAT adsorption system. If DB-model is accepted to reflect both of diffusion and binding, this stable performance of DB-model for the studied concentration range can suggest that degree of contribution of each step in the adsorption process does not change for this system. It is believed that power n normalizes the rate of intraparticle diffusion with binding [18]. In other words, changing time scale from t to t^n cancels the effect of the difference between diffusion rate and binding rate. This belief has to be verified and more experimental work should be performed for this objective. It is also clear from the table that most MB-removal occurs in the first 80 min, where (q_{DB} (First stage)/q_{DB} (Total)) > 97%, i.e. the first 80 min is the effective duration of the adsorption process. Prediction of the effective period of adsorption is an advantage of DB-model. This prediction can not be derived from PSO-model.

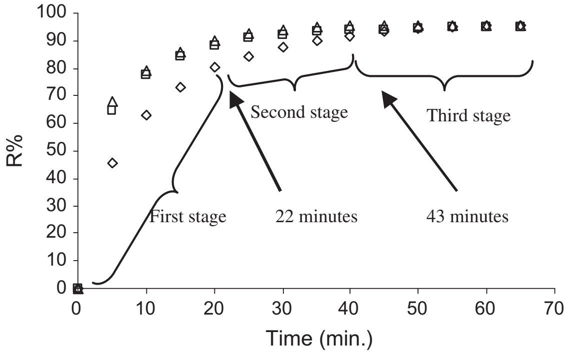

Fig. 5. Removal percentage of MB by EBT with respect to time for initial concentrations (◇) 10, (□) 8, and (Δ) 6 ppm.

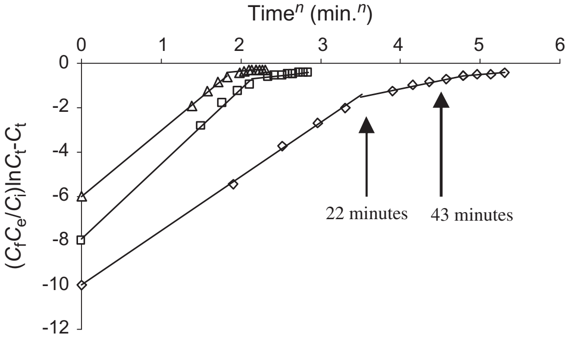

Fig. 6. DB-model plots of MB-adsorption onto EBT for initial concentrations (◇) 10, (□) 8, and (Δ) 6 ppm.

3.2. Adsorption of MB onto EBT

Fig. 5 shows the MB-removal percentage (R%) by EBT against time for different MB-initial concentrations: 6, 8, and 10 ppm. From figure; removal increases regularly but steeply at the beginning (first 20 min). It is difficult to suggest adsorption stages of distinguished rates. Fig. 6 shows the plots of DB-model for MB adsorption onto EBT for mentioned concentrations by selecting, respectively $n = 0.2$, 0.25 and 0.4, 0.7 according to fitting performed using regression program, Microsoft® ExcelTM. For each initial concentration, the model was applied considering three stages. These stages were clearly observed when applying DB-model by the regression program. From figure, linearity is satisfactorily accepted ($R^2 > 0.88$, except for $C_i = 8$ ppm (second stage), Table 4). This suggests the success of DB-model to represent the adsorption kinetics of MB onto EBT. Fig. 7 shows the corresponding plots given by PSO-model. From figure, PSO-model produced an excellent linearity ($R^2 > 0.9990$, Table 4).

Considering DB-model, for the three MB-initial concentrations, the adsorption rate was fast in the first 22 min (first stage) and then noticeably slowed down for the next 21 min (second stage) and again slowed down for the last 22 min (third stage). This may be explained in the same manner as for MB/MFTAT adsorption system. Moreover, the second and third stages can represent two different intra-particle rates due to progressive decrease in pore size [17]. In summary, the first stage is controlled by binding, the second stage is controlled by intra-particle diffusion, and the third is controlled by slower intraparticle

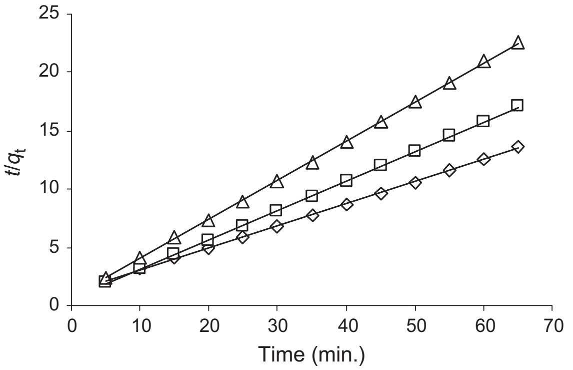

Fig. 7. PSO-model plots of MB-adsorption onto EBT for initial concentrations (◇) 10, (□) 8, and (Δ) 6 ppm.

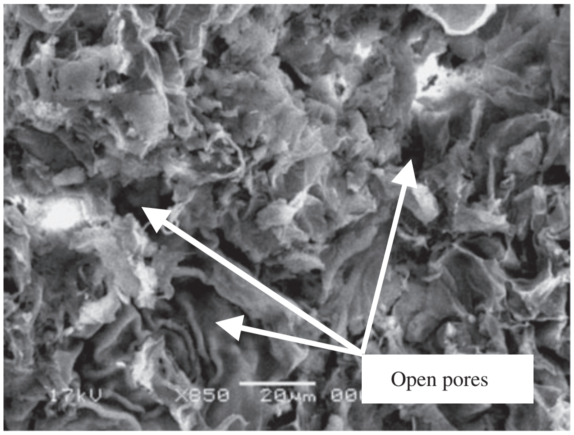

Fig. 8. SEM image of the outer surfaces of EBT.

diffusion. Again, this estimation can not be determined from plots of PSO-model, Fig. 7. Fig. 8 shows SEM image of EBT. The surface is highly configured with open routes that allow migration of MB molecules though the EBT grains. This may also explain the high capacity of EBT (refer to Table 4). The inner pores of EBT grains are suggested to decrease in size and consequently the adsorption shows regular decrease in rate.

For MB/EBT adsorption system, it can be suggested that plots of DB-model managed to clarify the details of adsorption process which is not clear from removal percentage, Fig. 5. According to Fig. 7, PSO-model cannot estimate stages of adsorption for MB/EBT adsorption system.

Table 4 gives the same summary as Table 1, but for adsorption of MB onto EBT. From the table, the values of determination coefficient suggest that PSO-model well represent the adsorption kinetics of this adsorption system. DB-model can be suggested to adequately represent the adsorption kinetics of this adsorption system. However, The capacity values estimated by DB-model are more accurate than those given by PSO-model according to calculated error percentages; $(RE_{\mathrm{DB}}\%) < (RE_{\mathrm{PSO}}\%)$.

From the table, the power n increases with initial concentration, C_i. This means that the power n is dependent on the initial concentration which is a different behavior compared to the case of MB/MFTAT adsorption system. This change in performance of DB-model from adsorption system to another reflects the flexibility of the model to reflect the nature of adsorption system under study. In addition, model's response to change of applied condition for certain adsorption system, C_i, is another important character. It can be suggested for this particular case, adsorption of MB onto EBT, that change of initial concentration causes a change in degree of contribution of binding and intraparticle diffusion in the adsorption process. For the time being, no further explanation can be given and more experimental work is needed to explore what occurs in details. From the table, it is clear that most MB-removal occurs in the first 20 min where $(q_{\mathrm{DB}}\text{ (First stage)}/q_{\mathrm{DB}}\text{ (Total)}) > 90\%$, i.e. the first 20 min is the effective duration of the adsorption process.

3.3. Adsorption of MB onto DPH

Fig. 9 shows the MB-removal percentage (R%) by DPH against time for different MB-initial concentrations: 6, 8, and 10 ppm. From figure; removal increases regularly and smoothly with time and the minute 60 is suggested to represent the start of slowing down adsorption stage. Fig. 10 shows the plots of DB-model for MB adsorption onto DPH for mentioned concentrations by selecting $n = 0.22$ according to fitting performed using the regression program. For each initial concentration, the model was applied consider-

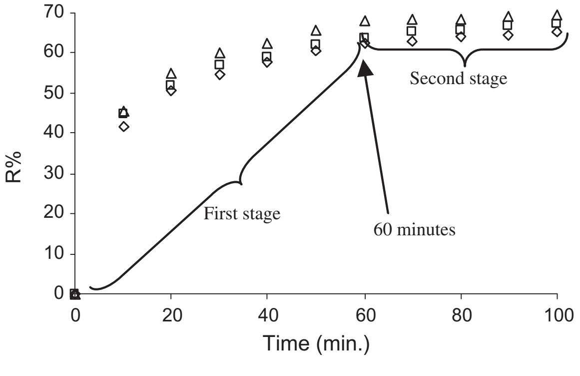

Fig. 9. Removal percentage of MB by DPH with respect to time for initial concentrations (◇) 10, (□) 8, and (Δ) 6 ppm.

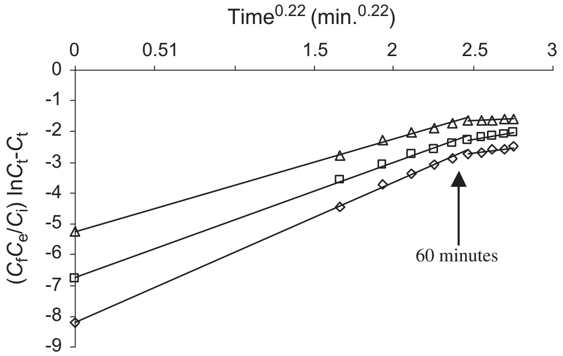

Fig. 10. DB-model plots of MB-adsorption onto DPH for initial concentrations (◇) 10, (□) 8, and (Δ) 6 ppm.

ing two stages. From figure, linearity is satisfactorily accepted ($R^2 > 0.9$, Table 5). This suggests the success of DB-model to represent the adsorption kinetics of MB onto DPH. Fig. 10 may indicate that DB-model successfully draws or simulates adsorption process on similarity basis with Fig. 9. Fig. 11 shows the corresponding plots given by PSO-model. From figure, PSO-model produced an excellent linearity ($R^2 > 0.999$, Table 5). Nevertheless, PSO-model does not show capability to simulate adsorption stages due to its linearity over the whole time period of adsorption process.

According to DB-model, for the three MB-initial concentrations, the adsorption rate was higher during the first 60 min than during the next 40 min. This is similar to MB/MFTAT adsorption system. Although DPH has a notable small surface area, adsorption capacities are almost similar to those of MB/MFTAT adsorption system (referring to Tables 3 and 5). This may be due to the openings (width ≈ 20 µm) that are available on surface as shown by SEM image of DPH, Fig. 12.

Table 5 gives the same summary as Table 1 but for adsorption of MB onto DPH. From the table, the values of determination coefficient suggest that both models well represent the adsorption kinetics of this adsorption system. The capacity values estimated by DB-model are less accurate than those given by PSO-model according to calculated error percentages; ($RE_{DB}\%$) > ($RE_{PSO}\%$). However, it is not that significantly high when opposite case of MB/MFTAT is regarded.

From the table, the power $n = 0.22$ does not change with initial concentration, C_i. This is a similar behavior of MB/MFTAT adsorption system. This indicates that t^n parameter does not respond to the change of C_i for MB/DPH adsorption system. This stable performance of DB-model for the studied concentration

Table 5
Characteristics of MB-adsorption onto DPH according to DB-model and PSO-model

C_i (ppm)	EXP.	DB-model						PSO-model		
	q_{EXP}	n	k_{DB}	q_{DB} (First stage) q_{DB} (Second stage)	q_{DB} (Total)	$RE_{DB}\%$	R^2	q_{PSO}	$RE_{PSO}\%$	R^2
6	0.833	0.22	0.3294	0.737 (98.4%)	0.749	10.08	0.9985	0.893	7.20	0.9997
			0.0460	0.012			0.9471			
8	1.078	0.22	0.4129	0.924 (95.5%)	0.968	10.20	0.9980	1.157	7.33	0.9994
			0.1667	0.044			0.9719			
10	1.306	0.22	0.5008	1.120 (96.2%)	1.164	10.87	0.9991	1.404	7.50	0.9997
			0.1662	0.044			0.9453			

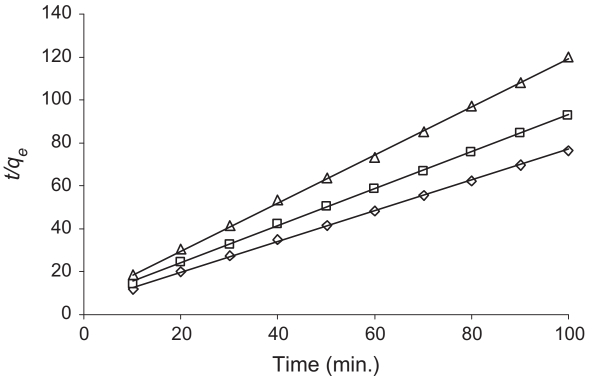

Fig. 11. PSO-model plots of MB-adsorption onto DPH for initial concentrations (◇) 10, (□) 8, and (Δ) 6 ppm.

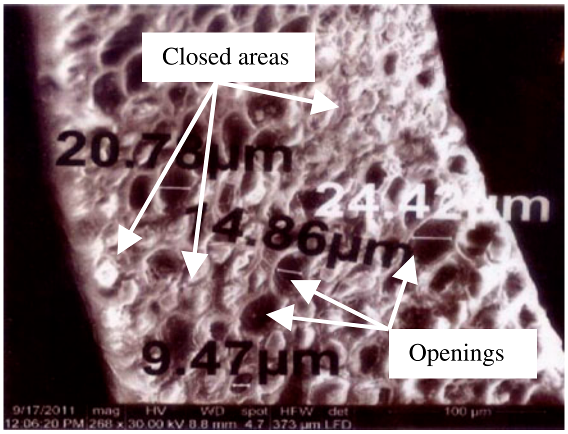

Fig. 12. SEM image of the outer surfaces of DPH.

range can suggest that degree of contribution of diffusion and binding in the adsorption process does not change for this system. It is also clear that most MB-removal occurs in the first 60 min, where (q_{DB} (First stage)/q_{DB} (Total)) > 92%, i.e. the first 60 min is the effective duration of the adsorption process. This is similar to the previous two adsorption systems.

3.4. Roles of DB-model parameters according to studied adsorption systems

DB-model is empirical model based on suggested parameters: solute concentration, the varying-resistance against adsorption, and time powered to a variable. It differs from other common kinetic models from three aspects:

3.4.1. Powered–time, t^n

Only two known kinetic models relate adsorption to powered time scale, Webber–Morris equation and power function equation [16,23]. These two models are simple and they relate the variable q_t directly to t^n ($n = 0.5$ for Webber–Morris equation). As a routine practice, contribution of diffusion mechanisms in an adsorption process is usually discussed by applying Webber–Morris equation on experimental data points [17]. DB-model may be the first kinetic model to relate C_t expression, ((C_fC_e/C_i) ln $C_t - C_t$), to t^n. The power n, in this model, can be thought as a normalizing factor for two different rates: intraparticle diffusion rate and binding rate. In simple words, by normalization, the two rates are thought to be having almost the same time scale according to the definition: "in the simple cases, normalization means adjusting values measured on different scales to a common scale" [18].

If the two rates are of the same speed then there is no scaling, $n = 1$, and the function should be related to t. But, by applying DB-model on three different adsorption systems, it was found that $n < 1$ and DB-model equation is related to t^n. This can suggest that intraparticle diffusion and binding have different rates (i.e. speeds). Now, if binding event can be supposed to be instantaneous once the solute molecule arrives to active site, then diffusion rate is said to be slower than that of binding. Consequently: (1) for MD/MFTAT adsorption system, $n = 0.7$ (nearest value to 1) means that the two rates are comparable with some predominance (more controlling) of diffusion, (2) for MD/EBT adsorption system, $n = 0.2$–0.4 means that the two rates are not comparable with notable predominance of diffusion, and (3) for MD/DPH adsorption system, $n = 0.22$ means again that the two rates are not comparable with notable predominance of diffusion. In summary, value of n reflects the role of diffusion with respect to binding; if n is close to 1, then diffusion is fast and of same order of binding and adsorption rate is mainly due to binding and if n is significantly lower than 1 then diffusion is slow and plays important role in the overall rate. Indeed, this explanation needs more evidences and future works are planned to investigate this concept especially by considering shaking speed [24] as a factor and by considering adsorbent porosity as experimental condition.

3.4.2. The conditioned balancing factor (C_fC_e/C_i), constant

DB-model constitutes conditioned balancing factor (CBF) constant as inherent value that distinguishes an adsorption system from another. When examining different adsorption systems which involve same initial concentration (C_i), it is almost impossible to determine same final (C_f) and equilibrium (C_e) concentrations. Similarly, examining certain adsorption system which involve different initial concentrations (C_i), it is also almost impossible to determine same final (C_f) and equilibrium (C_e) concentrations. In this work, three different adsorption systems were examined with the same set of initial concentrations. For the three adsorption system, CBF constant is different for the three initial concentrations as given in Table 6. This means that CBF constant value reflects the behavior of an adsorption process.

The importance of CBF constant can be observed from the relations: $((C_fC_e)/C_i)$ vs. C_i and k_{DB} vs. $((C_fC_e)/C_i)$. From Table 6, as C_i increases, $((C_fC_e)/C_i)$ linearly increases. This can be explained by the phenomenal fact that: though the removed amount, q_{DB}, increases with C_i, the removal percent of solute, $R\%$, decreases with C_i, [22,25]. This means that higher values of remaining concentrations C_f and C_e are recorded as C_i increases. The increase of C_f and C_e relatively overweighs the increase of C_i and the resultant is that $((C_fC_e)/C_i)$ increase with C_i. This behavior indicates that $((C_fC_e)/C_i)$ reflects the influence of initial concentration on adsorption system, i.e. it represents the extent to which the adsorption system reaches final concentration states C_f (final state for kinetic experiment) and C_e (final equilibration state). From Table 6 and in addition, it is observed that k_{DB} increases with the increase of $((C_fC_e)/C_i)$ and the relation was found to be linear as well. Increase of k_{DB} with $((C_fC_e)/C_i)$ increase can be explained by noting that final states C_f (final state for kinetic experiment) and C_e (final equilibration state) increase with C_i which make it relatively faster to reach equilibrium.

Change of the rate constant of PSO-model, $k_{PSO,}$ with C_i was presented and it was a decrease relation in most cases. This relation has been verified experimentally and theoretically [8,11,26]. For DB-model, k_{DB} linearly increases with the increase of C_i (Table 6). This behavior drives the importance of initial concentration as a driving force for adsorption processes which has been mentioned in several works [24,27–33]. The previous discussion about CBF may now elucidate the meaning of driving force of initial concentration for adsorption processes. In general, it can be suggested that CBF constant is considered conditioned balancing factor for certain adsorption system tested with specific initial concentration at specific conditions (such as solution-temperature, solution-pH, and shaking speed).

3.4.3. Dependency of DB-model on solute concentration

For PSO-model, it is widely accepted that a sort of surface interaction between solute and active sites is

Table 6
Relation of k_{DB}, $((C_fC_e)/C_i)$ with C_i^*

Adsorption system	MB/MFTAT (same n-value = 0.7)			MB/EBT (different n-value)			MB/DPH (same n-value = 0.22)		
C_i	6	8	10	6	8	10	6	8	10
$(C_fC_e)/C_i$	0.099	0.162	0.207	0.005	0.008	0.009	0.420	0.596	0.782
k_{DB}	0.1479	0.1917	0.2363	0.5954	0.8463	0.9784	0.3294	0.4129	0.5008
$(C_fC_e)/C_i$ vs. C_i	$((C_fC_e)/C_i) = 0.027\ C_i - 0.06$; $R^2 = 0.9908$			–			$((C_fC_e)/C_i) = 0.0905\ C_i - 0.1247$; $R^2 = 0.9997$		
k_{DB} vs. $(C_fC_e)/C_i$	$k_{DB} = 0.8106\ ((C_fC_e)/C_i) + 0.0655$; $R^2 = 0.9898$			–			$k_{DB} = 0.4735\ ((C_fC_e)/C_i) + 0.1306$; $R^2 = 1$		
k_{DB} vs. C_i	$k_{DB} = 0.0221\ C_i + 0.0152$; $R^2 = 1$			–			$k_{DB} = 0.0429\ C_i + 0.0716$; $R^2 = 0.9998$		

*Only first effective stage is considered for this table.

the main event of adsorption process [7,10]. Lately, the behavior of PSO-model is shown to be dependent on initial concentration (which was theoretically verified, [8,11]) and this dependency presents itself through change of k_{PSO} with C_{i} (k_{PSO} decreases in most cases with C_{i}, [25,34–37]). For chemical reactions, it is a fact that rate constant is dependent only on temperature and change of initial concentration never has an effect on rate constant [15]. Accordingly, dependency of k_{PSO} on C_{i} has been recognized as: "the PSO equation is able to represent the kinetics of sorption in systems for which not only the rate of surface reaction governed the overall process rate"; W. Plazinski et al. [10] and "the main disadvantage of both PFO and PSO models is dependency of their rate constant to the initial concentration solute so they really pseudo-constants" Azizizn et al. [26]. These conclusions indicate that rate constant is changing with initial concentration due to the engagement of another mechanism(s) with surface reaction binding during the adsorption processes. Besides, it is accepted as a trend that higher value of q_{PSO} requires a longer time for the adsorption system to attain equilibration and this occurs with lower k_{PSO} value [10]. Higher value of q_{f} is achieved with higher value of C_{i}. Consequently, it is almost a fact that k_{PSO} decreases with C_{i} increase [10].

When considering DB-model, some analogies are observed: (1) the model gives higher value of q_{DB} with higher value of C_{i} and (2) k_{DB} changes (linearly increases) with C_{i} increase. k_{DB} increases with C_{i} meanwhile k_{PSO} decreases. This can be explained by observing that DB-model considers change of C_t (decreases) while PSO-model considers change of q_{t} (increases) with time and this is due to known relation: $q_{\mathrm{t}} = (C_{\mathrm{i}} - C_t) \times (V/m)$. This behavior can suggest same explanations that have been given for PSO-model, i.e. DB-model reflects more than one event that involve in adsorption process which have been presented through out this work. In addition, it can be suggested that k_{DB} is not intrinsic rate constant; however, it is also a pseudo rate constant [26].

4. Conclusions

A novel kinetic model (DB-model) is introduced to describe batch adsorption systems. The model was empirically developed considering that both diffusion and binding are controlling the adsorption process and degree of contribution of each depends on adsorption system and experimental conditions. The linear form of the model was applied on three different adsorption systems. The model was assessed with respect to solute initial concentration only as variable experimental condition. The linear form of the model managed to represent the three adsorption systems with accepted determination coefficient values. For all cases, the estimated capacities by DB-model are in general more representative of experimental capacities than those given by PSO-model. DB-model is successful to reflect the different stages of adsorption (MB/MFTAT and MB/DPH adsorption systems) or to discover it (MB/EBT adsorption system). For the first stages of studied adsorption systems, k_{DB} increases with initial concentration, C_{i}. This may indicate that adsorption process involves simultaneously diffusion and binding and it is suggested that they are working with relative degrees. The power n is sensitive parameter to adsorption system and initial concentration and can be regarded as diffusion representative. This behavior is thought to be related to porosity-nature of the adsorbent. It is suggested that t^n normalizes diffusion and binding rates during the first stages of adsorption and this is the reason of observed linearity. The model is sensitive to equilibrium stage that helps in determining the economically effective period of adsorption. It is important to mention that this model has to be examined with several adsorption systems for more understanding, verification, and validation of its performance. Experimental conditions such as shaking speed, solution-pH, and temperature should also be studied to assess its outputs with respect to other known kinetic models.

References

[1] W. Rudzinski, W. Plazinski, Theoritical descreption of the kinetics of solute adsorption at heterogenous solid/solution interfaces on possibility of distinguishing between the diffusional and the surface reaction kinetics models, Appl. Surf. Sci. 253 (2007) 5827–5840.

[2] S. Azizian, A novel and simple method for finding the heterogeneity of adsorbents on the basis of adsorption kinetic data, J. Colloid Interface Sci. 302 (2006) 76–81.

[3] N. Chiron, R. Guilet, E. Deydier, Adsorption of Cu(II) and Pb (II) onto a grafted silica: Isotherms and kinetic models, Water Res. 37 (2003) 3079–3086.

[4] G. Blanchard, M. Maunaye, G. Martin, Removal of heavy metals from waters by means of natural zeolite, Water Res. 18 (1984) 1501–1507.

[5] Y.S. Ho, G. McKay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, Water. Res. 34 (2000) 735–742.

[6] S. Azizian, R.N. Fallah, A new empirical rate equation for adsorption kinetics as solid/solution interface, Appl. Surf. Sci. 256 (2010) 5153–5156.

[7] Y. Liu, New insight into pseudo-second-order kinetic equation for adsorption, Colloids Surf. A 320 (2008) 275–278.

[8] S. Azizian, Kinetic models of sorption: A theoretical analysis, J. Colloid Interface Sci. 276 (2004) 47–52.

[9] W. Rudzinski, W. Plazinski, Kinetics of metal ions adsorption at heterogeneous solid/solution interfaces: A theoretical treatment based on statistical rate theory, J. Colloid Interface Sci. 327 (2008) 36–43.

[10] W. Plazinski, W. Rudzinski, A. Plazinska, Theoretical models of sorption kinetics including a surface reaction mechanism: A review, Adv. Colloid Interface Sci. 152 (2009) 2–13.

[11] S. Azizian, B. Yahyaei, Adsorption of 18-crown-6 from aqueous solution on granular activated carbon: A kinetic modeling study, J. Colloid Interface Sci. 299 (2006) 112–115.

[12] C. Tan, M. Li, Y. Lin, X. Lu, Z. Chen, Biosorption of Basic Orange from aqueous solution onto dried A. filiculoides biomass: Equilibrium, kinetic and FTIR studies, Desalination 266 (2011) 56–62.

[13] S. Figaro, J.P. Avril, F. Brouers, A. Ouensanga, S. Gaspard, Adsorption studies of molasse's wastewater on activated carbon: Modelling with a new fractal kinetic equation and evaluation of kinetic models, J. Hazard. Mater. 161 (2009) 649–656.

[14] A. Baraka, Degradation of methylene blue adsorbed onto transparent adsorbent by UV-illumination (simple regeneration method), Desalin. Water Treat. 49 (2012) 172–180.

[15] D. Kumar, J.P. Gaur, Chemical reaction- and particle diffusion-based kinetic modeling of metal biosorption by a Phormidium sp.-dominated cyanobacterial mat, Bioresour. Technol. 102 (2011) 633–640.

[16] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solution, J. Saint Eng. Div. Am. Soc. Civ. Eng. 89 (1963) 31–39.

[17] G.F. Malash, M.I. El-Khaiary, Piecewise linear regression: A statistical method for the analysis of experimental adsorption data by the intraparticle-diffusion models, Chem. Eng. J. 163 (2010) 256–263.

[18] Y. Dodge, The Oxford Dictionary of Statistical Terms, Sixth ed., Oxford University Press, Oxford, 2006, (ISBN: 978-0-19-920613-1).

[19] C. Sutherland, Removal of heavy metals from waters using low-cost adsorbents: Process development. PhD Thesis. University of the West Indies, Trinidad, 2004, pp. 150–164.

[20] A.E. Ofomaja, A. Pholosi, E.B. Naidoo, Kinetics and competitive modeling of cesium biosortion onto chemically modified pine cone powder, J. Taiwan Inst. Chem. Eng. (2013). Available from: http://dx.doi.org/10.1016/j.jtice.2013.02.001

[21] Y.S. Ho, G. McKay, Pseudo-second-order model for sorption processes, Process Biochem. 34 (1999) 451–465.

[22] K.G. Bhattacharyya, S.S. Gupta, Pb(II) uptake by kaolinite montmorillonite in aqeous medium: Influence of acid activation of the clays, Colloids Surf., A 277 (2006) 191–200.

[23] D.L. Sparks, Kinetics of Soil Chemical Processes, Academic Press Inc., New York, 1989.

[24] L. Nouri, I. Ghodbane, O. Hamdaoui, M. Chiha, Batch sorption dynamics and equilibrium for the removal of cadmium ions from aqueous phase using wheat bran, J. Hazard. Mater. 149 (2007) 115–125.

[25] B.K. Nandi, A. Goswami, M.K. Purkait, Adsorption characteristics of brilliant green dye on kaolin, J. Hazard. Mater. 161 (2009) 387–395.

[26] S. Azizian, M. Haerifar, H. Bashiri, Adsorption of methyl violet onto granular activated carbon: Equilibrium, kinetics and modeling, Chem. Eng. J. 146 (2009) 36–41.

[27] A. Kara, L. Uzunb, N. Beşirli, A. Denizli, Poly(ethylene glycol dimethacrylate-n-vinyl imidazole) beads for heavy metal removal, J. Hazard. Mater. 106 B (2004) 93–99.

[28] F. Gode, E. Pehlivan, Sorption of Cr(III) onto chelating b-DAEG–sporopollenin and CEP–sporopollenin resins, Bioresour. Technol. 98 (2007) 904–911.

[29] M.A.M. Salleh, D.K. Mahmoud, E.A. Al-Maamary, Adsorption of basic dye from aqueous solution using mixture of agricultural solid wastes (Maw): Isotherm kinetic studies and process design, J. Adv. Sci. Eng. Res. 1 (2011) 76–97.

[30] A. Baraka, H. Hatem, I. Mamdouh, A. Zaki, Alkaline treatment of seashells and its use for the removal of Cu(II) from aqueous solution, Desalin. Water Treat. 16 (2010) 74–82, April.

[31] A. Özer, G. Dursun, Removal of methylene blue from aqueous solution by dehydrated wheat bran carbon, J. Hazard. Mater. 146 (2004) 262–269.

[32] F. Çiçek, D. Özer, A. Özer, A. Özer, Low cost removal of reactive dyes using wheat bran, J. Hazard. Mater. 146 (2007) 408–416.

[33] V.S. Mane, I.D. Mall, V.C. Srivastava, Kinetic and equilibrium isotherm studies for the adsorptive removal of Brilliant Green dye from aqueous solution by rice husk ash, J. Environ. Manage. 84 (2007) 390–400.

[34] I.A.W. Tan, A.L. Ahmad, B.H. Hameed, Adsorption of basic dye on high-surface-area activated carbon prepared from coconut husk: Equilibrium, kinetic and thermodynamic studies, J. Hazard. Mater. 154 (2008) 337–346.

[35] B.H. Hameed, A.L. Ahmad, K.N.A. Latiff, Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust, Dyes Pigm. 75 (2007) 143–149.

[36] B.H. Hameed, A.T.M. Din, A.L. Ahmad, Adsorption of methylene blue onto Bamboo-based activated carbon: Kinetics and equilibrium studies, J. Hazard. Mater. 141 (2007) 819–825.

[37] M. Wawrzkiewicz, Z. Hubicki, Removal of tartarzine from aqueous solutions by strongly basic polystyrene anion exchange resins, J. Hazard. Mater. 164 (2009) 502–509.