Effect of Biot Number in Batch Studies of Adsorption

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Abstract

The Homogeneous Surface Diffusion Model (HSDM) which is based on mass transfer is widely used to analyze the adsorption phenomenon in batch studies. Different investigators used several approaches to find analytical solution using HSDM. They used dimensionless parameters for analyzing HSDM. The Biot number (Bi), a dimensionless parameter which relates external mass transfer coefficient with diffusion coefficient is used by few investigators. The Bi is expressed differently by different investigators based on their objectives of their study. The Bi used by Flora et al. for his successful analytical results is considered in the present study along with Distribution parameter (λ), another dimensionless parameter used by them. The relation between Bi and λ is studied and found that the product of these two parameters is a constant. The Bi considered in the study is found to be consisting of three different dimensional groups. The relationship among them is explored by conducting a parametric study using a wide range of values for the dependent parameters. The HSDM is discretized and analyzed in order to substantiate the results. The results obtained are in agreement with the theoretical trends of adsorption.

Introduction

The Homogeneous Surface Diffusion Model (HSDM) which is based on mass transfer is widely used [1, 5, 6, 9] to analyze the adsorption phenomenon in batch reactors. Flora et al. [5] used HSDM along with dimensionless parameters such as (i) time (ii) adsorbate concentration (iii) quantity adsorbed (iv) particle radius (v) Biot number (*Bi*) and (vi) Distribution parameter (λ) in their model. The usage of HSDM for batch studies is limited [11]. Al-Qodah [1] used HSDM for estimation of adsorption of dyes on shale oil ash. Hand et al. [6] developed few user-oriented solutions to the HSDM that are applicable to batch studies. They presented correlations and graphical solutions for estimating the diffusivity from the experiments. McKay [9] analyzed the model incorporating dimensionless time and dimensionless distance using Crank and Nicholson method. He performed experimental studies for adsorption of dyes onto activated carbon and applied the developed model. Markovska et al., [13], Slaney and Bhamidimarri [12], Basheer and Najjar [3] used HSDM for column studies of adsorption.

Flora et al.,[5] have verified their experimental results with those from analytical studies and reported encouraging trends. However, Ramakrishna [11] reported that the results reported by Flora et al. [5] are erratic and found that the erratic results that are obtained are primarily based on improper estimation of external mass transfer (k_f) and diffusion (D) coefficients. Babu and Ramakrishna [2], Ramakrishna [11] studied the various models available for estimation of the above two coefficients and observed that four models are available for this purpose:

- Models used by Buzanowski and Yang[4] and Liaw et al.[8] based on Linear Driving Force approach for uptake of adsorbate
- Model used by Kaguei et al. [7] which assumes that the rate of change of mass accumulation on the surface of adsorbent is proportional to the

change of concentration in liquid phase

- Model used by McKay and Allen [10]

The above four models give an indication of the range of mass transfer coefficients that are best suited for batch adsorption experiments. Babu and Ramakrishna [2] developed a code using 'C' language for estimating the mass transfer coefficients obtained from the above models for their use as initial guess values in simulation. They can be adjusted to fit to the actual experimental values. They used the experimental values reported by Flora et al., [5] as inputs to their code and compared with the values that are reported by Flora et al.[5]. They tested the code with the experimental results reported by Al-Qodah [1]. It is noticed that the results from only two these four models are close to that of the trends reported by Flora et al. [5]. A close examination of the results from these models revealed [2] that, (i) the specific surface of the adsorbate in the model is important for adsorption of adsorbate (ii) higher the specific surface, higher will be the adsorbate removal.

The usage of Biot number (*Bi*) in mass transfer studies as an analogous term to that used in heat transfer studies is available in literature [6,13]. Higher values of *Bi* indicate domination of k_f compared to that of *D*. The *Bi* is defined differently in the literature [5,6,13] based on the objectives of the study. Hand et al. [6] considered *Bi* based on surface diffusivity and porosity of the adsorbent. Markovska et al., [13] considered *Bi* based on radius of the particle and mass transfer coefficients. The *Bi* as defined by Flora et al., [5] depends not only on mass transfer coefficients, but also on adsorbent characteristics, and adsorption parameters at initial conditions. The Distribution parameter (λ), the other dimensionless parameter used by Flora et al., [5] depends upon ratio of adsorption capacity to amount adsorbed at initial conditions. Higher values of λ indicate higher adsorption under large adsorbent doses. The usage of λ in adsorption analysis is scarce [11]. Due to the similarity of these dimensionless parameters *Bi* and λ in terms of their independent variables, their relative dependency is investigated in the present study. The model given by Flora et al [5] is taken as the basis for the entire study.

Model Formulation

The Biot number (*Bi*) is mathematically expressed as [5]:

$$Bi = \left(\frac{k_f}{D}\right)\left(\frac{r}{\rho}\right)\left(\frac{C_0}{q_0}\right) \quad \text{----- (1)}$$

where, k_f = external mass transfer coefficient, m/s
D = diffusion coefficient, m^2/s
r = radius of adsorbent particle, m
ρ = adsorbent particle density, kg/m^3
C_0 = initial concentration of adsorbate, kg/m^3
q_0 = dimensionless
= amount adsorbed for $C = C_0$ (from isotherm equation) and is calculated as-

$$q_0 = \frac{(abC_0)}{1+bC_0} \quad \text{for Langmuir Isotherm} \quad \text{---------(2)}$$

The distribution parameter (λ) is mathematically expressed as:

$$\lambda = \left(\frac{W}{V}\right)\left(\frac{q_0}{C_0}\right) \quad \text{------- (3)}$$

Where, W = mass of adsorbent, kg
V = volume of adsorbent, m^3

Combining Eqs. (1) and (3):

$$(Bi)(\lambda) = \left(\frac{k_f}{D}\right)\left(\frac{r}{\rho}\right)\left(\frac{W}{V}\right) \text{ --- (4)}$$

Eq. (4) is taken as governing equation for the present study. Eq. (4) indicates that,

- *Bi* is inversely proportional to λ
- the product of $[(Bi)(\lambda)]$ is a constant
- there are three terms, which are not dimensionless, on the right hand side of Eq. (4) on which the product of $[(Bi)(\lambda)]$ is dependant

The present study focused mainly on examining the above relations based on available data.

Results and Discussion

A set of values identified[11] for validating the code developed using Al-Qodah experimental data is considered for studying the relationship between *Bi* and λ and the other dependant parameters as per Eq. (4). The range of values are primarily identified (Refer Table-1) based on their ranges used for successful validation of experimental data of Al-Qodah [1]. Additional ranges of these parameters that are reported in literature [5] are also included in the study.

The values of *Bi* and λ are calculated using Eq. (4) and values of these parameters as per Table-1 and are plotted. The slope of the plot (Fig. 1) yielded a slope (i.e., $[(Bi)(\lambda)]$) of 0.002, a constant value, for *W/V* = 1.0 kg/m^3. Similarly, for a *W/V* value of 0.1 kg/m^3 and the resulting slope (i.e., $[(Bi)(\lambda)]$) is equal to 0.0002. The values of $[(Bi)(\lambda)]$ are calculated for a set of values given in Table-1.

Table1: Ranges of parameter values used in the present study

S.No.	Variable Parameter	Ranges of values	Unit
1	External mass transfer coefficient, k_f	$0.5\text{x}10^{-6}$; $2.5\text{x}10^{-6}$; $5.0\text{x}10^{-6}$; $10.0\text{x}10^{-6}$	m/s
2	Diffusion coefficient, *D*	$1.0\text{x}10^{-10}$; $2.5\text{x}10^{-10}$; $5.0\text{x}10^{-10}$; $10.0\text{x}10^{-10}$	m^2/s
3	Initial concentration of adsorbate, C_0	50; 250; 500	mg/L
4	Adsorbent dose, *W/V*	1.0; 0.1	kg/m^3
5	Adsorbent particle density, ρ	500; 841	kg/m^3
6	Particle diameter, *d(=2r)*	100; 200	mm

The above study showed the inter-dependence of *Bi* and λ, the two dimensionless parameters used in the study. However, the *Bi* for mass transfer in its conventional form is expressed [13] as:

$$Bi = \left[\left(\frac{k_f}{D}\right)(r)\right] \text{ ----- (5)}$$

The values of *Bi* are calculated based on the range of values given in Table-1. The calculated values are given in Table-2. It can be noted from Table-2 that *Bi* increases with either increase in k_f or decrease in *D* indicating higher values of *Bi* reflect the relative dominance of k_f over *D*. This is clearly in agreement with the definition of *Bi* [13].

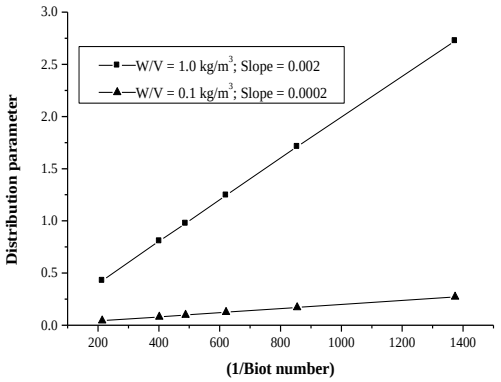

Figure 1: Plot of Biot number *vs*. Distribution parameter

Table 2: Values of Conventional Biot Number

S. No.	Variable Parameter			Biot Number $Bi = [(k_f)(r)/(D)]$
	k_f (m/s)	D (m^2/s)	r (mm)	
1	0.5×10^{-6}	1.0×10^{-10}	100	500
2	2.5×10^{-6}	1.0×10^{-10}	100	1250
3	0.5×10^{-6}	2.5×10^{-10}	100	200
4	2.5×10^{-6}	2.5×10^{-10}	100	1000

Comparing Eqs. (1) and (5) it can be observed that, the *Bi* defined by Flora et al., [5] is having additional terms such as particle density and adsorption parameters in the equation. These parameters are not used by other[6] researchers. It is hence decided to study the *Bi* as defined by Flora et al., [5] in detail and examine its applicability in understanding the trends of adsorption phenomenon in batch studies. Further, based on the encouraging results obtained in the study for proving $[(Bi)(\lambda)]$ as constant, an analysis is further carried out based on the three functional groups involved in the *Bi* for their inter-dependence.

Study of the functional groups in Biot number

As discussed above, the Biot number comprises of three dimensional functional groups viz.,

- mass transfer coefficients, $\left(k_f / D\right)$ with dimensions of (L^{-1})
- adsorbent characteristics, $\left(r / \rho\right)$ with dimensions of (L^4M^{-1})
- adsorption parameters $\left(C_0 / q_0\right)$ with dimensions of (ML^{-3})

The inter-dependence of these three functional groups is studied using a selected range of values (Table-3). Two of the three functional groups are kept constant while the third functional group is varied. The ranges of these values are selected based on the values adopted for initial parametric study (Refer Table-2).

Effect of k_f/D: The value of k_f is initially kept same (2.5×10^{-6} m/s) for the ratio of k_f/D = 0.25×10^4 m^{-1} and 1.0×10^4 m^{-1}. The trends of adsorbate removal indicate (Fig. 2) that the effect of reduction in D value for the above ratios is negligible. The k_f value is then increased for k_f/D = 2.0×10^4 m^{-1} onwards (k_f = 5.0×10^{-6}, 6×10^{-6}, and 10×10^{-6} m/s respectively) while there is a marginal reduction of D value for k_f/D = 3.0×10^4 m^{-1}. The trends show increased adsorbate removal for the last three combinations. This could be largely attributed to the increase of k_f value in the k_f/D ratios since the effect of D is found negligible in the first two cases. It is evident from the results that, k_f is dominant compared to D in this analysis.

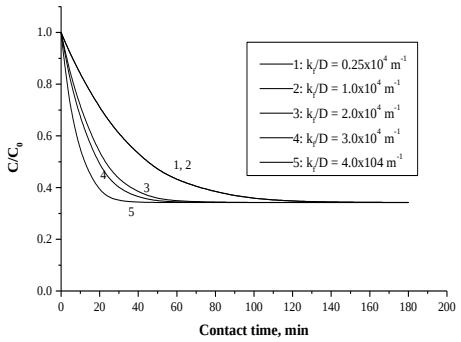

Figure 2: Effect of contact time on adsorbate removal for various parameter values of k_f/D; Operating parameters: C_0 = 250 mg/L; W/V = 1.0 kg/m^3; d = 100 µm; ρ = 500 kg/m^3

To further ascertain the domination of k_f over D, the HSDM is discretized and analyzed by developing a code in 'C' language. Variation of k_f and D are studied independently and exhaustively [11] by changing the other independent parameters. The results are discussed below:

Variation of k_f with respect to adsorbent dose

The variation of k_f with respect to adsorbent dose (i.e., W/V) is studied for a wide range of parameters keeping D, d, ρ, and C_0 as constants. It is observed that the trends of adsorbate removal curves are similar for a specific value of C_0 and W/V values. The adsorbate removal is increasing with increase of k_f value indicating the increased release rate of the adsorbate from the liquid (Refer Fig.3). The amount adsorbed (q) on the adsorbent is increased with decrease of W/V values. This is clear from Eq. 6 given below, which indicates the higher accumulation of adsorbate when the W/V value is reduced. This is important since, the efficiency of adsorbent is judged from its dosage into the system and the corresponding accumulation of adsorbate on adsorbent. In view of this aspect, study of W/V values for less than 1.0 is useful.

$$q = \left(\frac{V}{W}\right)(C_0 - C) \qquad \text{------- (6)}$$

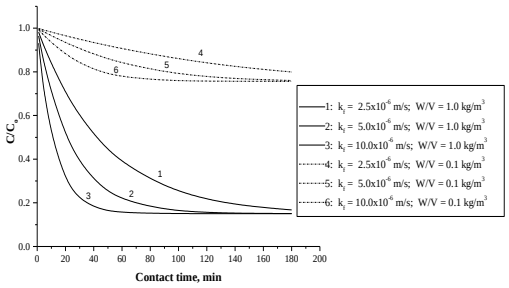

Figure 3: Effect of contact time on adsorbate removal for various parameter values of k_f and W/V. Operating parameters: D = 5x10^{-10} m^2/s; C_0 = 50 mg/L; ρ = 500 kg/m^3; d = 100µm

The study showed that, the adsorption system is dependent on W/V value and the accumulation is inversely proportional to the ratio of W/V value. Studies on the effect of k_f with respect to particle radius and density indicated that adsorbate removal increased with decrease in particle size (Refer Fig.4). This indicates the availability of higher specific surface of the adsorbent (Eq. 7) when the particle size is reduced.

$$S_s = \left(\frac{6}{d}\right)\left(\frac{1}{\rho}\right)\left(\frac{W}{V}\right) \qquad \text{------ (7)}$$

The adsorbate removal is reduced with decrease of particle density (Refer Fig.4). This also indicates the availability of higher specific surface on the adsorbent (Eq. 7). The lower values of particle diameter and density together resulted in higher adsorbate removal validating [11] the above assumption.

It may be further noted that, the equilibrium time is reduced with

increase in either C_0 or k_f (Refer Figs. 3 & 4). This is understandable since, increase of C_0 increases amount of adsorbate available for adsorption and increase of k_f indicates the rapid release of adsorbate from liquid. This has resulted in achieving equilibrium in shorter durations at higher values of these two parameters. Further, the rapid release of adsorbate from the liquid resulted in a steep slope of the linear portion of the curves while the lower values of k_f showed a relative flatter slope. Hence, the linear portion of the curve is shifting close to the axis indicating a steep slope or rapid adsorption while the curve is shifting away from the axis indicating a slower adsorption.

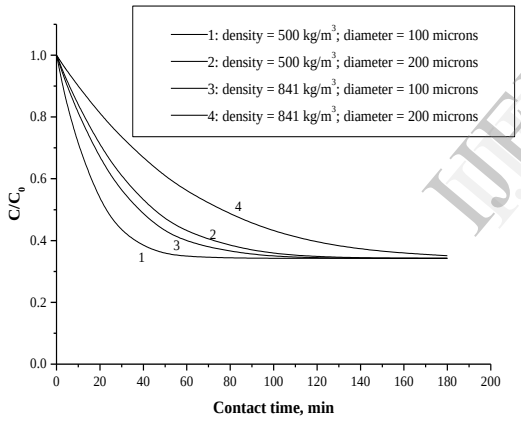

Figure 4: Effect of contact time on adsorbate removal for various parameter values of ρ and d; Operating parameters: $k_f = 2.5\text{x}10^{-6}$ m/s; $D = 5\text{x}10^{-10}$ m^2/s; C_0 = 250 mg/L; W/V = 1.0 kg/m^3

Variation of D with respect to adsorbent dose: The variation of D with respect to adsorbent dose (i.e., W/V) is studied for a wide range of parameters keeping k_f, d, ρ, and C_0 as constants. It is observed that, adsorption is independent with respect to the variations of D. Further the removal is higher for higher values of k_f (Refer Fig. 5 and 6). This indicates that, external mass transfer (i.e., k_f) is the dominant parameter in adsorbate removal of the system considered. Further, it may also be noted from Fig. 5 and 6 that, the accumulation is increasing with decrease in W/V value.

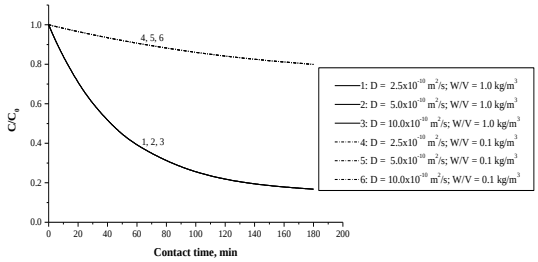

Figure 5: Effect of contact time on adsorbate removal for various parameter values of D and W/V. Operating parameters: $k_f = 2.5\text{x}10^{-6}$ m/s; C_0 = 50 mg/L; ρ = 500 kg/m^3; d = 100µm

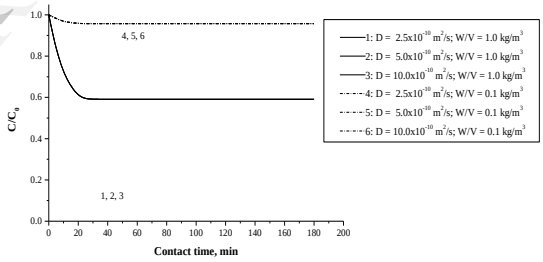

Figure 6: Effect of contact time on adsorbate removal for various parameter values of D and W/V. Operating parameters: $k_f = 5.0\text{x}10^{-6}$ m/s; C_0 = 250 mg/L; ρ = 500 kg/m^3; d = 100µm

Effect of ρ/r: The adsorbent particle density is doubled (500 and 1000 kg/m^3) in the first two combinations while the particle radius is reduced 2.5 times (500 and 200 µm). This indicates that ρ/r value is increased 5 times. Since the changes made in adsorbent particle density and particle radius are almost same (i.e., 2 and 2.5), a similar trend of adsorbate removal (Fig. 7) is obtained. Further, in the second combination,

particle radius is decreased resulting in availability of higher specific surface of adsorbent. The adsorbate removal is hence increased with decrease in particle size. In the third and fourth combinations, radius of adsorbent is kept constant (50 μm) while the particle density is doubled (500 and 1000 kg/m^3). The relatively higher adsorbate accumulation in the third combination compared to that of the fourth is due to the availability of more specific surface of the adsorbent (Eq. 6) since the density is decreased. The results obtained are in agreement with those discussed earlier. Hence, it is concluded that, lower values of adsorbent particle density *(ρ)* and particle diameter *(d)* favor adsorbate removal in adsorption.

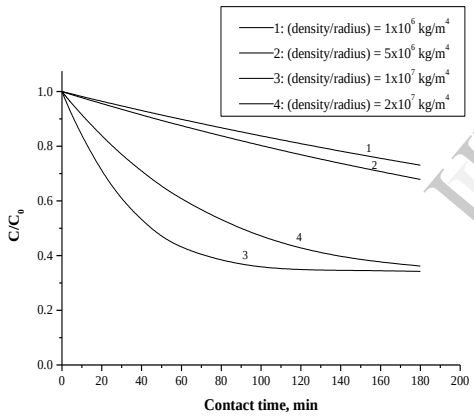

Figure 7: Effect of contact time on adsorbate removal for various parameter values of *ρ/r*, Operating parameters: k_f = 2.5x10^{-6} m/s; *D* = 5x10^{-10} m^2/s; C_0 = 250 mg/L; *W/V* = 1.0

Effect of q_0/C_0: This study is conducted with five different adsorbate concentrations viz., 100, 150, 200, 750, and 1000 mg/L respectively. The corresponding values of q_0 are calculated using Eq. 2. It should be noted that, the percentage adsorbate removal is increasing with decrease in q_0/C_0 value (Fig. 8). The value of q_0 calculated from Eq. 2 is increasing with increase of C_0. It indicates that, the accumulation of adsorbate is increasing with increase of C_0. The results obtained are in agreement with this assumption.

The present study revealed that:

- HSDM is useful in analyzing adsorption phenomenon in batch studies.
- Dimensionless parameters such as Biot number (*Bi*) and Distribution parameter (λ) are useful in understanding the relative importance of mass transfer coefficients and adsorption parameters in batch studies of adsorption.
- The product of *Bi* and λ is found to be a constant.
- Large values of *Bi* indicate higher values of external mass transfer coefficient which is proved in the present study.
- *Bi* as defined by Flora et al.[5] is helpful in understanding the trends of adsorption.
- External mass transfer coefficient (k_f) is relatively dominant in batch studies of adsorption phenomenon than diffusion coefficient (*D*). This is ascertained by conducting parametric study with a wide range of values.
- Adsorbate removal efficiency is higher when *W/V* ratio, particle diameter (*d*=2*r*) and density *(ρ)* are low.
- Accumulation of adsorbate on adsorbent is high with increase of *Co.*
- The percentage adsorbate removal is increasing with decrease in q_0/C_0 value
- The equilibrium time is reduced with increase in either C_0 or k_f.

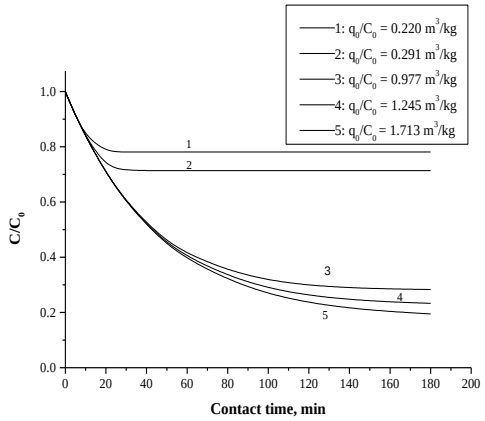

Figure 8: Effect of contact time on adsorbate removal for various parameter values of q_0/C_0 Operating parameters: k_f = 2.5x10^{-6} m/s; D = 5x10^{-10} m^2/s; ρ =500 kg/m^3; d = 100 µm; W/V = 1.0 kg/m^3

Summary and Conclusions

The effect of Biot number (*Bi*) on Distribution parameter (λ) in batch studies of adsorption is studied. It is found that *Bi* is inversely proportional to λ and the product of [(*Bi*)(λ)] is a constant. The inter-dependence of the three functional groups (viz., mass transfer coefficients, adsorbent characteristics, and adsorption parameters) in the Biot number is studied exhaustively using a selected range of values and Homogeneous Surface Diffusion Model. The results indicate that,

- k_f is dominant compared to D in the analysis.
- lower values of adsorbent particle density (ρ) and particle diameter (d) favor adsorbate removal in adsorption.
- accumulation of adsorbate is increasing with increase of C_0.

References

[1] Al-Qodah Z. (2000). "Adsorption of Dyes using Shale Oil Ash", Water Research, 34 (17), 4295-4303.

[2] Babu B.V. and V. Ramakrishna (2004). "Dominant Design Variables and Modeling Parameters for Adsorption in Batch Studies", CHEMCON, Mumbai.

[3] Basheer A. I. and Y.M. Najjar. (1996)."Predicting Dynamic Response of Adsorption Columns with Neural Nets", Journal of Computing in Civil Engineering-ASCE, 10 (1), 31-39.

[4] Buzanowski M.A. and R.T. Yang. (1989). "Extended Linear Driving-Force Approximation for Intraparticle Diffusion Rate Including Short Times", Chemical Engineering Science, 44 (11), 2683-2689.

[5] Flora J.R.V., R.D. Vidic, W. Liu, and R.C. Thurnau. (1998). "Modeling Powdered Activated Carbon Injection for the Uptake of Elemental Mercury Vapors", Journal of Air & Waste Management Association, 48 (1998), 1051-1059.

[6] Hand D.W., J.C. Crittenden, and W.E. Thacker. (1983). "User-oriented Batch Reactor Solutions to the Homogeneous Surface Diffusion Model", Journal of Environmental Engineering-ASCE, 109 (1), 82-100.

[7] Kaguei S., N. Ono, and N. Wakao. (1989). "Parameter Estimation in Batch Adsorption with a Linear Isotherm", Chemical Engineering Science, 44 (11), 2565-2570.

[8] Liaw C.H., J.S.P. Wang, R.A. Greenkorn, and K.C. Chao. (1979). "Kinetics of Fixed-Bed Adsorption: A New Solution", American Institute of Chemical Engineers Journal, 25 (2), 376-381.

[9] McKay G. (1985). "The Adsorption of Dyestuffs from Aqueous Solutions Using Activated Carbon: An External Mass Transfer and Homogeneous Surface Diffusion Model", American Institute of Chemical Engineers Journal, 31 (2), 335-339.

[10] Mckay G. and S.J. Allen. (1980). "Surface Mass Transfer Processes Using Peat as an Adsorbent for Dyestuffs", The Canadian Journal of Chemical Engineering, 58 (1980), 521-526.

[11] Ramakrishna V. (2004). "Modeling of Adsorption for Wastewater Treatment using Analytical-, Regression-, and Neural Network- Approaches", PhD Thesis, Birla Institute of Technology and Science, Pilani.

[12] Slaney M. and R. Bhamidimarri. (1998). "Adsorption of Pentachlorophenol (PCP) by Activated Carbon in Fixed Beds: Application of Homogeneous Surface Diffusion Model", Water Science Technology, 38 (7), 227-235.
[13] Markovska L., V. Meshko, V. Noveski, and M. Marinkovski (2001). "Solid Diffusion Control of the Adsorption of Basic Dyes onto Granular Activated Carbon and Natural Zeolite in Fixed Bed Columns", Journal of Serbian Chemical Society, 66 (7), 463-475.

Nomenclature Used

HSDM	Homogeneous Surface Diffusion Model
Bi	Biot Number, Dimensionless
Co	Initial concentration of adsorbate, mg/L (or) kg/m^3
d	Particle diameter, m (or) μm
D	Diffusion coefficient, m^2/s
k_f	External mass transfer coefficient, m/s
q	Mass adsorbed on adsorbent, kg/kg
S_s	Specific surface area of adsorbate
W/V	Adsorbent dose, kg/m^3
λ	Distribution Parameter, Dimensionless
ρ	Mass density of particle, kg/m^3

Table 3 Range of values studied for inter-dependence of functional groups in Biot number

S. No.	Values of the independent functional groups		Values of the dependent functional group	
	Functional group	*Value*	*Functional group*	*Value*
1	q_0/C_0	0.804	k_f/D	$0.25x10^4$; $1.0x10^4$; $2.0x10^4$; $3.0x10^4$; $4.0x10^4$.
	ρ/r	$1x10^7$		
2	q_0/C_0	0.804	ρ/r	$1.0x10^6$; $5.0x10^6$; $1.0x10^7$; $2.0x10^7$.
	k_f/D	$2.0x10^4$		
3	ρ/r	$1.0x10^7$	q_0/C_0	0.220; 0.291; 0.977; 1.245; 1.713.