



Dominant Design Variables and Modeling Parameters for Adsorption in Batch Studies

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Abstract

The adsorption system is analytically modeled and simulated using the Homogeneous Surface Diffusion Model (HSDM) for batch studies of adsorption. The HSDM is discretized and solved using pure implicit scheme of finite difference method and Simpson's 1/3rd rule. The model is tested using two sets of literature data viz., Data-1 and Data-2. The model results are in good agreement with Data-1 and are not completely in agreement with Data-2 resulting in under-predicted values. To address this problem, four different existing models are identified for calculating the mass transfer coefficient (k_f) and diffusion coefficient (D). The values of these adjustable parameters (k_f and D) are determined using Data-2. Codes are developed in C language both for simulating the HSDM and calculating the above coefficients from experimental data. The values obtained from two of the available models are close to those reported in Data-2. The present study proved that, (i) keeping all other design variables constant, the parameters k_f and D are found to be the dominant design variables for adsorption studies for accurately estimating the adsorbate removal (ii) accurate estimation of the mass transfer coefficients is an important aspect in the simulation of analytical model for reliable results.

Keywords: *Adsorption; Modeling; External mass transfer coefficient; Diffusion coefficient; Homogeneous Surface Diffusion Model.*

Introduction

Adsorption is a simple technique used for removal of a wide range of pollutants from water and wastewater [1, 2]. Adsorbate (or pollutant) removal in adsorption depends on [1] several factors such as, operating parameters (pH, adsorbent dose, contact time, agitation speed etc), adsorbent characteristics (particle density, particle diameter, porosity, surface area etc.), and process parameters (rate constant, isotherm constants, mass transfer coefficients etc.). The key parameters for design of the adsorption system are the process parameters that are used for modeling the system for predicting the quality of

effluent under a wide range of operating conditions. The key process parameters in adsorption such as, isotherm constants and mass transfer coefficients are established by conducting batch studies of adsorption. Established isotherm models such as Langmuir and Freundlich are used for assessing the suitability of an adsorbent in adsorption system where, the experimental data is fitted to any one or both of these models. The isotherm constants are obtained from these models. Such studies are widely reported in literature [3, 4, 5].

Suitability of a relevant isotherm is essential to predict the adsorbate removal profiles either in

batch studies or column studies. Analytical models such as HSDM [6, 7] are used to simulate the adsorbate concentrations as a function of time. The adsorbate removal is basically a mass transfer operation and is primarily dependent upon the release of the adsorbate molecule from liquid phase and its accumulation & diffusion on solid adsorbent. The parameters, that are responsible for the above mass transfer operation are the external mass transfer coefficient (k_f) and diffusion coefficient (D). Established models are available for analytically modeling the adsorption system [6-11]. The present study focuses on identifying the dominant design variables and modeling parameters for batch studies in adsorption using Homogeneous Surface Diffusion Model (HSDM), an established analytical model.

Problem Formulation

The HSDM available in literature [6] for batch studies of adsorption is considered for predicting the adsorbate removal. The adsorption system considered in this study follows the Langmuir isotherm. The adsorption system is analytically modeled and simulated using the HSDM for batch studies of adsorption. The HSDM is discretized and solved using pure implicit scheme of finite difference method and Simpson's 1/3rd rule. A code is developed in C language to simulate the model. Two sets of experimental data reported in literature viz., Data-1 [6] and Data-2 [7] is considered for testing the model. Data-1 [6] comprises of experimental data for adsorption of mercury vapor on activated carbon using three different values of initial concentration (C_0) viz., 110 $\mu\text{g}/\text{m}^3$, 352 $\mu\text{g}/\text{m}^3$, and 1017 $\mu\text{g}/\text{m}^3$. The input parameters used for simulation are given in Table-1. Data-2 comprises [7] of experimental data pertaining to adsorption of dyes onto shale oil ash. The initial concentrations (C_0) and adsorbent dose (W/V) are varied in the experiments and the values of k_f and D are calculated and reported for each of the experimental runs.

Results and Discussion

The model results are in good agreement with that of the data used for validation, i.e., Data-1 [6]. The input parameters to the model are given in Table-1 and a plot showing actual experimental values and predicted values of fractional adsorbate removal

(i.e., C/C_0) for one set of the operating parameters is shown in Fig. 1. The model is tested in this study using Data-2 [7]. The data that is considered for testing comprises of the data points that are available for the changes in W/V keeping C_0 constant i.e., $W/V = 0.5, 1.0, 2.0$ for $C_0 = 200 \text{ mg}/\text{L}$. Same values of k_f and D (i.e., $2.5 \times 10^{-6} \text{ m}/\text{s}$ and $1.0 \times 10^{-10} \text{ m}^2/\text{s}$ respectively) are reported [7] for $W/V=0.5 \text{ kg}/\text{m}^3$ and $2.0 \text{ kg}/\text{m}^3$. The k_f and D values reported [7] are $2.5 \times 10^{-6} \text{ m}/\text{s}$ and $1.10 \times 10^{-10} \text{ m}^2/\text{s}$ respectively for $W/V = 1.0 \text{ kg}/\text{m}^3$. Simulation is carried out with these values and an under-prediction of experimental data points is noted in all three cases of W/V values. Typical results for one of the data sets used for testing are shown in Fig. 2.

To address the problem of under-prediction of experimental results, four different existing models are identified [8-11] for calculating the values of k_f and D . The details of the models are given in Table-2. The values of k_f and D are determined [12] by developing a code in C for all the four models using Data-2. The k_f and D values calculated from each of these four models are given in Table-3. The k_f and D values reported in literature [6] are also given in Table-2 for comparison. It is noted from Table-3 that the k_f and D values are similar for two the four models viz., KM (Kaguei et al. Model, 1989) and MAM (McKay and Allen Model, 1980). The values obtained from the other two models are very low. Since the results are being under-predicted for the data considered from literature [7], the values obtained by the last two models in Table-3 are considered for simulation. These values are used as inputs in the model and the simulated results obtained are shown in Fig. 2. The errors are reduced compared to those obtained using the earlier reported values [7] of k_f and D . The k_f and D values from the above two models viz., KM and MAM are showing encouraging results (Fig. 2).

The four models considered in the study are examined for the resemblance of trends for only two of the models (viz., MAM and KM) with that of the experimental values in the simulation. The study reveals that, the MAM incorporates the specific surface of the adsorbate in the equation, which is important for adsorption of adsorbate. Higher the specific surface, higher will be the adsorbate removal. The KM incorporates the change in the concentration at any time with respect

to equilibrium concentration (i.e., $C-C_e$), which is indicative of the agreement of the model with the isotherm. The solution given by LM (Liaw et al. Model, 1979) is an approximation for the actual numerical solution, which is complex. BYM (Buzanowski and Young Model, 1989) incorporates calculation of the change in the accumulation of adsorbent at any time with the average value of accumulation of mass (i.e., $q-q_{avg}$). This assumption is found to be not accurate in predicting the actual profile of adsorbate removal in the present study. Hence, the first two models discussed above satisfy the trends in the present study.

The present study revealed that-

- For accurately estimating the adsorbate removal by simulation, accurate prediction of the parameters k_f and D is essential.
- Selection of appropriate model that determines the k_f and D values that can closely predict the actual adsorbate removal from experimental data is necessary.
- McKay and Allen Model, 1980 (MAM) and Kaguei et al. Model (KM) predicted the k_f and D , values more accurately for the given set of experimental values.
- Keeping all the other design variables fixed, the close resemblance of actual and predicted adsorbate removal for the variation of k_f and D values indicated that, k_f and D are the dominant design variables in adsorption system.

Conclusions

Selection of appropriate model for accurate estimation of k_f and D is essential for prediction of adsorbate removal by simulation. The adsorbate removal highly depends on k_f and D keeping all the other parameters constant. Hence, these two variables are the dominant design variables in adsorption system.

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Nomenclature

k_f	External mass transfer coefficient, m/s
D	Diffusion coefficient, m ² /s
C_o	Initial concentration, kg/m ³
W/V	Adsorbent dose, kg/m ³
C/C_o	Fractional adsorbate removal, dimensionless
ρ	Mass density of adsorbent, kg/m ³
r	Adsorbent particle radius, m
q	Accumulation on the surface of adsorbent, kg/kg
C_e	Concentration of adsorbate at equilibrium, kg/m ³
q_{avg}	Average accumulation on the surface of adsorbent, kg/kg
K_L	Langmuir isotherm constant, m ³ /kg (= ab , refer Table-1)
S_s	Specific surface, m ² /m ³
t	Contact time, s

BYM Buzanowski and Young Model, 1989

LM Liaw et al. Model, 1979

KM Kaguei et al. Model, 1989

MAM McKay and Allen Model, 1980

Table-1: Model input parameters for simulation

Parameter	Value [6]	Value [7]
Particle density, kg/m ³	500	841
Particle radius, m	372 x 10 ⁻⁶	200 x 10 ⁻⁶
Volume of adsorbate, m ³	0.0125	1.0
Mass of adsorbent, kg	0.0001	1.0
External mass transfer coefficient (k_f), m/s	12 x 10 ⁻²	2.5 x 10 ⁻⁶
Diffusion coefficient (D), m ² /s	2.29 x 10 ⁻¹¹	1.10 x 10 ⁻¹⁰
Langmuir constant (b), m ³ /kg	6.15 x 10 ⁶	30.478
Langmuir constant (a), kg/kg	123 x 10 ⁻⁶	0.2275

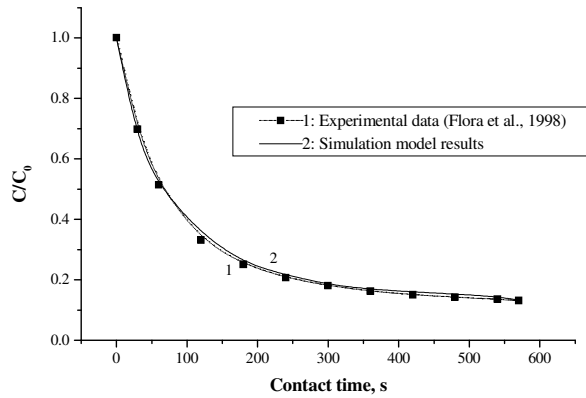


Fig. 1: Comparison of simulation results with experimental data for an initial concentration (C_0) of 110 µg/m³

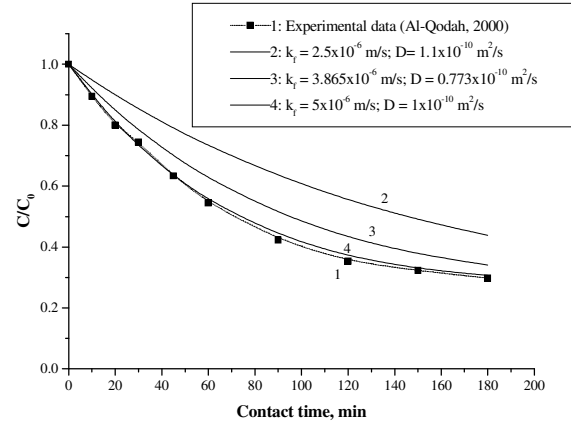


Fig. 2: Validation of simulation results for $W/V = 1.0$ kg/m³

Table-2 Nomenclature of models used for estimation of mass transfer coefficient values

Model Equation	Model name	Reference
$\frac{dq_{avg}}{dt} = \frac{3k_f}{r} (q - q_{avg})$	Buzanowski and Young Model, 1989 (BYM)	[8]
$\left(1 - \frac{q}{q_e}\right) = \frac{6}{\pi^2} \exp\left(\frac{-\pi^2 D t}{r^2}\right)$	Liaw et al. Model, 1979 (LM)	[9]
$\frac{\partial q_{avg}}{\partial t} = \frac{3k_f}{\rho r} (C - C_e)$	Kaguei et al. Model, 1989 (KM)	[10]
$\frac{C}{C_0} = \left(\frac{1}{1 + K_L(W/V)}\right) + \frac{K_L(W/V)}{1 + K_L(W/V)} \exp\left(\frac{-(1 + K_L(W/V))}{K_L(W/V)} k_f S_s t\right)$	McKay and Allen Model, 1980 (MAM)	[11]

Table-3 Comparison of mass transfer coefficient values

S.No.	W/V, kg/m ³	Experimental data [7]		BYM		LM		KM		MAM	
		k_f	D	k_f	D	k_f	D	k_f	D	k_f	D
1	0.5	2.5	1.0	0.00217	0.00043	0.01230	0.00240	3.54	0.707	3.138	0.627
2	1.0	2.5	1.1	0.00567	0.00110	0.01878	0.00375	4.96	0.991	3.865	0.773
3	2.0	2.5	1.0	0.01250	0.00250	0.02700	0.00540	6.16	1.230	5.560	1.112

k_f : External mass transfer coefficient, m/s (x10⁻⁶)

D : Diffusion coefficient, m²/s (x10⁻¹⁰)