Mathematical Modeling of Fixed Bed Adsorption: Influence of Main Parameters on Breakthrough Curve

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Abstract

Dynamic modeling and simulation of fixed bed adsorption process and explaining the behavior of the breakthrough curve reported in this paper. Adsorption of sulfur compounds that present in road fuel, has posed a great challenge. A model of fixed bed adsorption from fuel was formulated with non-ideal plug flow behavior and considered velocity variation along a column. The model was solved using the Method of Lines (MOL) numerical solution - a technique for solving PDEs - in which all dimension was discretized except one; as a result, the set of ODEs solved by highly accurate methods and low computational cost. The effect of various factors, such as flow rate (4-10 cc/min), inlet concentration (125-500 ppm), and bed height (10-40 cm) on adsorption performance were investigated. The behavior of the breakthrough curve with some parameters such as the degree of bed utilization, breakpoint time, film mass transfer coefficient, and height of the adsorption zone was analyzed. High bed column, high flow rate, and high inlet concentration happened to be better conditions, in term of used overall bed capacity percentage for the adsorption system.

Keywords

Adsorption;
Benzothiophene;
Breakthrough Curve;
Fixed Bed;
Modeling

1. Introduction

Sulfur is one of the fuel impurities which causes serious problem for environmental and transportation equipment; for this reason, environmental rule limited the level of sulfur in fuel, for on-road vehicle, to 30 ppm and these components might deactivate the catalyst by poisoning active sites that lead to high cost [1]; [2]; [3]. A novel field, in near future, is a fuel cell that needs ultra-low sulfur (typically below 10 ppmw, but even lower concentrations would be plausible) which can generate ultra-clean fuel through fixed-bed selective adsorption [4]. Consequently, it is vital for human, combustion engine and refinery equipment to decrease sulfur levels of fuel and combustion sources.

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Conventional unit operations, such as HDS, distillation or absorption for desulfurization have inappropriate operation condition such as high temperature (300-400 °C), and pressure (30-130 bar). It should also be noted that HDS method is unsuitable for small-scale applications and it is not successful in removing thiophenic compounds [5]. An adsorption process, as desulfurization technique, is often better than conventional unit operations. In recent years, researchers have been interested in developing sorbents such as zeolite and activated carbon for selective adsorption from liquid fuel [6]; [7]. The adsorption process is usually a fixed bed operation that is packed with an adsorbent, in which a fluid containing adsorbate passes through a column in order to achieve separation[8].

Efficient performance of an adsorption bed depends on achieving the correct combination of process variables such as bed length, flow rate, inlet concentration. The interaction of this process variables is so complicated that it is difficult to arrive an optimal design simply by intuition and empiricism; a reliable mathematical simulation of the system is therefore required. Developing a numerical method helps us design an adsorption process without expensive experimental set-up [9]. In fact, this can be designed semi-industrial units without spending money amounts and predicts phenomena that occur within the bed.

Various models have been developed by making different assumptions, applying different equations, and solution methods to predict the breakthrough curves of packed bed adsorption. One of the popular assumptions for dynamic adsorption formulation is a linear driving force, which is proposed by Glueckauf and Coates[10]. Babu and Gupta took into account the variation of fluid velocity along the column[11]. Bautista et al. studied the adsorption of fixed bed and numerically solved a set of PDEs by reducing them to a set of ordinary differential equations using the orthogonal collocation method[12].

In order to design an efficient adsorption column, the key design and operating parameter which affects the column performance should be recognized; these parameters include height of bed, inner column diameter, particle diameter, flow rate, inlet concentration, Reynolds number, peclet number, and two dimensionless parameters, i.e. length-diameter ratio of bed and column diameter to particle diameter ratio mentioned by Wang at al. and Inglezakis [13]; [14].

Simulation of sulfur adsorption, in the liquid phase, on a fixed bed, has been reported in a few studies. The scope of the present study was related to mathematical adsorption modeling in a packed bed with a porous adsorbent which was carried out and solved by MOL numerical method. Upwind control volume method was employed to approximate the derivatives in the convection term which is obtained from the partial differential equation, governing the mass transfer step. This model considered film mass transfer resistance as well as non-ideal plug flow and fluid velocity variation along the bed. The effects of design and operation parameters (flow rate, inlet concentration, and bed height) on the degree of bed utilization were carried out.

2. Mathematical Modeling

The formulation and mathematical model help us to analyze and understand the physical adsorption system. It is very important to recognize the characteristics of a situation and to apply a model that is neither unnecessarily complicated nor oversimplified. Eq. 1 was derived considering the following assumptions:

1. Fluid and solid phase are in isothermal condition.
2. No pressure drops along the column.
3. No chemical reaction accrues in bed.
4. Radial dispersion is Negligible
5. Varying fluid velocity along the column.
6. Linear Driving Force (LDF) approximation used to describe mass transfer rate between fluid and solid phase.
7. The equilibrium of adsorption is described by Langmuir isotherm.

The general and component equations for mass balance which describes dynamics behavior of liquid fuel through a packed bed are presented in Eq. 1 and 2. These equations include axial dispersion term, convection flow term, accumulation in the fluid phase, and sink term of adsorption. [8][15]

$$\frac{\partial C_i}{\partial t} = D_Z \frac{\partial^2 C_i}{\partial z^2} - \frac{\partial (uC_i)}{\partial z} + \left(\frac{1-\varepsilon}{\varepsilon}\right)\rho_a \frac{\partial q_i}{\partial t} \qquad (1)$$

$$\frac{\partial C}{\partial t} = D_Z \frac{\partial^2 C}{\partial z^2} - \frac{\partial (uC)}{\partial z} + \left(\frac{1-\varepsilon}{\varepsilon}\right)\rho_a \frac{\partial q}{\partial t} \tag{2}$$

Initially, adsorbate-free column subjected and condition of fluid concentration was

$$t = 0 \rightarrow C_i = 0 \tag{3}$$

At the inlet of the column, feed concentration was known and outlet fluid condition was assumed that the diffusive flux is equal to zero:

$$\begin{cases} Z = 0 \rightarrow C_i = C_{feed} \\ Z = H \rightarrow \dfrac{\partial Ci}{\partial z} = 0 \end{cases} \tag{4}$$

where *Ci* and C represent the concentration of component and bulk, respectively, q_i is the concentration of a component in the solid phase. Z and t are the distance along the column length, and time, respectively. u, ε, ρ_a and D_z are fluid velocity, bed porosity, adsorbent density, and axial dispersion coefficient, respectively.

2.1. Mass transfer correlations

Axial dispersion coefficient correlation in Eq. 5 was applied to an adsorption column packed with porous adsorbent particles. Wakao and Funzakri suggested the following equation [16]:

$$\frac{\varepsilon D_z}{D_{AB}} = 20 + 0.5 Sc\,\mathrm{Re} \tag{5}$$

where Re, Sc, and D_{AB} are the Reynolds number, the Schmidt number, and the molecular diffusivity of adsorbate in solution, respectively. They were estimated using Wilke-chang Equation [17]:

$$D_{AB} = \frac{(117.3\times10^{-18})\,\mathrm{M}_B{}^{0.5}T}{\mu v_A{}^{0.6}} \tag{6}$$

$$\mathrm{Re} = \frac{u\,R_p}{\upsilon} \tag{7}$$

$$Sc = \frac{\upsilon}{D_{AB}} \tag{8}$$

Rate equation is used to describe mass transfer caused by molecular diffusion in film surrounded by the adsorbent particle. LFD model simplified the expression for the mass transfer rate presented in Eq. 12 [8]; [18]:

$$\frac{\partial q_i}{\partial t} = k\,(C_i - C_i{}^*) \tag{9}$$

where C_i^* is equilibrium component concentration in the adsorbate phase on the exterior surface of the particle and k is overall mass transfer rate coefficient. k can be written as [19]:

$$\frac{1}{k} = \frac{R_p}{3k_f} + \frac{R_p^2}{15D_p} \tag{10}$$

where k_f is film mass transfer coefficient which is an appropriate dimensionless group, Sherwood number, was defined by the following equation:

$$sh = \frac{2R_p k_f}{D_{AB}} \tag{11}$$

at low Reynolds number and liquid, Wilson and Geankoplis suggested Eq. 12 for Sherwood number [20]:

$$\mathrm{Sh} = \frac{1.09}{\varepsilon}\mathrm{Re}^{0.33}\mathrm{Sc}^{0.33} \tag{12}$$

This correlation is valid for Reynolds numbers, *Re*, ranging between 0.0015 and 55. which is broad enough to cover the liquid loading applied for this model.

Effective pore diffusion coefficient, D_P, is smaller than diffusivity in a straight cylindrical pore. This coefficient can be expressed in terms of tortuosity factor and particle porosity [21][22].

$$D_p = \frac{\varepsilon_p D_{AB}}{\tau} \tag{13}$$

$$\tau = \varepsilon_p + 1.5(1-\varepsilon_p) \tag{14}$$

Langmuir isotherm describes an adsorbate-adsorbent system. This isotherm was formulated on the basis of a dynamic equilibrium between the adsorbed and bulk phase [23]; [24].

$$\frac{q_i}{q_{\max}} = \frac{bC_i}{1+bC_i} \tag{15}$$

where q_{max} and b are maximum adsorption capacity and adsorption equilibrium parameter, respectively.

2.2. Numerical solution

There are several ways to formulate the discretized form of PDE, some of them are better than others. The convection-diffusion equation solved using central differencing scheme. This method has a faster convergence rate than some other methods. For hydrodynamic calculation with Peclet number higher than 2, central differencing is not a suitable discretization due to numerically unstable[25].

The numerical procedure for solving the partial differential equation (results in adsorption fixed-bed modeling) is the method of lines that reduces nonlinear parabolic PDE to ordinary differential equations of the time domain. Method of lines was presented to solve the one-dimensional advection-diffusion equation. For this aim, fourth order Runge–Kutta scheme used to solve the gained system of ordinary differential equations. Studies have shown that this method is very simple and can be easily used for the solution of time-dependent partial differential equations[26].

In this phenomena, the substance transport in packed bed is a combination of molecular diffusion and convection. Therefore, properties of substance is considered for advection phenomenon.

Nonlinear approximation of convective term, calculated by second upwind differences with flux conserving formulation, was derived. Used Superbee flux limiter in this algorithm in order to smooth solution and prevent overshoots and excessive oscillation [27-28].

The bed length was discretized to 80 equal intervals, in the axial directions, and PDE was transformed into a set of ODEs, with time as an independent variable.

Boundary value predicts derivative that was replaced with algebraic approximations. The resulting system of stiff ODEs in initial value variables was integrated numerically using MATLAB (The Mathworks, Inc) [29]. The unknown variables were solved in a set of ODE using ODE15s solver that is proper for stiff equations.

2.3. Model validation

In order to validate the proposed model, a case study was selected from an article and the experimental breakthrough curves were compared with numerical results of this work. Sotelo et al. reported the adsorption of benzothiophene (BT), as a model heterocyclic and aromatic sulfur with faujasite structure. Several zeolites were applied to dynamic liquid phase adsorption experiments[30]. Breakthrough curves of BT over different adsorbents help us to investigate model more carefully.

The operational conditions and model parameters of the case studies are presented in Table 2. Sotelo et al. reported Benzothiophene adsorption isotherm onto several adsorbents are shown in Table 1.

Table 1. Langmuir adsorption isotherm parameters[30].

Adsorbent	q_{max} (mg/g)	B (ppm^{-1})
A-NaY	44.1±3.6	0.015±0.004
A-NaX	48.3±1.0	0.076±0.006
A-NaLSX	35.5±0.5	0.079±0.005

Table 2. Model parameters' value for simulation[30].

Parameter	Value
Column length	0.3 m
Column diameter	4.9 mm
Bed density	0.53 gr/cm^3
Feed density	0.779 gr/cm^3
Benzothiophene weight fraction	250 ppmw
Particle radius	0.3 mm
Flow rate	5 cc/min
Temperature	298

2.4. Column operations

Fig. 1 shows a schematic diagram of the fixed-bed adsorption process. During the adsorption process, the fluid passed through a pack of adsorbent to transfer the adsorbate from the feed to solid . As the fluid drains continuously, the adsorbent saturates from the adsorbate molecules and creates an absorption zone in the bed, as seen in Fig. 1. Adsorption zone passes through the packed bed and causes an increase in the degree of bed saturation. Concentration pattern of the fluid phase in adsorption is the so-called breakthrough curve. Considering the idealized breakthrough curve of Fig. 2, the adsorption zone is constant in height and part of bed during concentration change, from breakpoint to exhaust point, is time dependent. The degree of column utilization at breakpoint can be obtained using Eqs. 17-20 [26].

$$f = \frac{U}{t_a} \tag{16}$$

$$t_f = (1-f)t_a \tag{17}$$

$$H_a = H\,\frac{t_a}{t_e - t_f} \tag{18}$$

$$Degree\ of\ saturation: \frac{H - f\,H_a}{H} \tag{19}$$

where t_a is the time required for adsorption zone to move its own height down,t_f is the time required for formation adsorption zone and f is the fractional capacity of adoptions zone.

3. Result and Discussion

In this research, removal of benzothiophene from cyclohexane by zeolite with faujasite structure was studied [30]. Experimental results are compared with numerical results in Fig. 2.

The mean absolute deviation of a data set was introduced as the error term between the experiment and model, as the following equation:

$$AAD = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{C_{\exp} - C_{\text{model}}}{C_0}\right| \tag{20}$$

where n is the number of data points. AAD ≤ 0.05 data are highly consistent at laboratory scale, AAD < 0.1 data are probably consistent, and AAD > 0.1 are probably not consistent [31]. In this study, AAD was 0.02.

3.1. Parametric study

The validated model was used to study the impact of operating and design parameters on adsorption column performance. When studying vital parameters on adsorption column, the other parameters were considered constant, but their effects will be discussed because the model's parameters are related to each other. Many factors influenced the unsteady-state circumstances of fixed bed adsorption which complicate some commutations in a general case.

3.2. Flow rate effect

The results of varying volumetric flow rate are plotted in Fig. 3. In order to investigate the effect of varying flow rate on the effluent concentration, two other parameters (bed height, inlet BT concentration) were fixed.

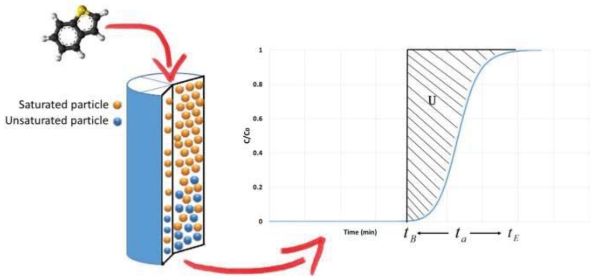

Figure 1. Adsorption process scheme and concentration profile

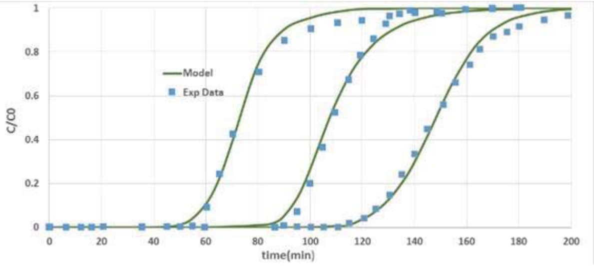

Figure 2. Comparison of model results and experiment data at different inlet concentrations

The results indicate that, with increasing the flow rate, the breakthrough curve slope became steeper and the breakpoint time decreased. An increase in this operation parameter caused a decrease in the resistance time and an increase in the mass transfer coefficient. A column operation in up-flow could lead to partial fluidization in high flow rates. Favorable LHSV and low contact time influenced equilibrium state and led to an unfavorable adsorption equilibrium at high flow rates. effect of varying flow rate on the fractional approach to saturation of the column at the breakpoint, film mass transfer coefficient, and breakpoint time are presented in Table 3.

For high flow rate, increase in the convective mass transfer coefficient led to the improvement of bed performance disregarding of internal mass transfer resistance against film resistance.

Table 3. Breakthrough curve parameters at different flow rates

Flow rate (cc/min)	**Degree of bed saturation**	**Breakpoint time (min)**	**Film mass transfer coefficient (cm/s)**
4	0.737	100	4.53×10^{-3}
5	0.806	85	4.2×10^{-3}
7	0.822	65	3.6×10^{-3}
10	0.86	48	3.34×10^{-3}

Table 4. Breakthrough curve parameters at different inlet concentration

Concentration (ppm)	**Degree of bed saturation**	**Breakpoint time (min)**	**Height of adsorption zone (cm)**
500	0.87	52	9.3
250	0.806	85	13.6
187.5	0.77	65	15.2
125	0.68	48	21.4

3.3. Concentration effect

As observed in Fig. 4, the breakpoint time decreased when the inlet concentration rose, the breakthrough curve became steeper. During this simulation, bed height of 30 cm and a flow rate of 5cc/min was kept constant.

The reason for this phenomena is high adsorbate concentration due to the stronger driving force which leads to high mass transfer flux from bulk to adsorbent particle. In addition, at high adsorbate concentration, the equilibrium will be achieved faster. Unfavorable effect of high initial concentration is increasing the height of the adsorption zone owing to a decrease in the percentage of bed utilization or overall adsorption capacity [32]; [33]; [34].

The value of breakpoint time, the degree of utilization, and height of the adsorption bed versus inlet concentration are presented in table 4.

3.4. Bed height effect

The result of varying bed height is plotted in Fig. 5. To investigate the effect of varying bed height on the effluent concentration, fixed flow rate and inlet BT concentration were determined 5 cc/min and 250 ppm, respectively.

The result indicates that, as bed height increased, purification volume also increased because an increase in the weight of adsorbent and overall adsorption capacity shape of breakthrough curves in different bed height was kept same and heights of adsorption zone were the same in different bed height. Accordingly, the considered height of the bed to adsorption zone ratio should be a proper value to take up as much capacity as possible. In another word, it is better to consider a high degree of bed utilization; however high ratio of column height to diameter causes some problems, such as back-mixing[35].

The value of breakpoint time, the degree of utilization, and height of the adsorption zone versus bed height are presented in table 5.

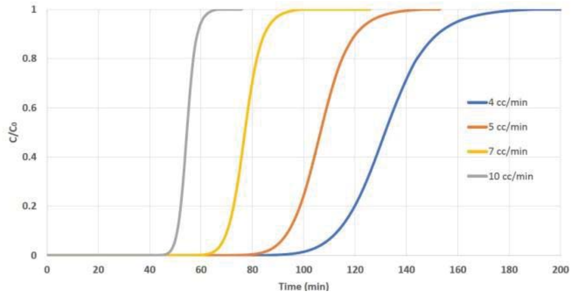

Figure 3. Effect of flow rate on the breakthrough curve

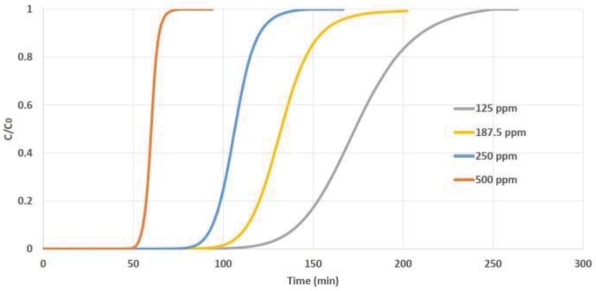

Figure 4. Effect of inlet adsorbate concentration on the breakthrough curve

Table 5. Breakthrough curve parameters at different bed height

Bed height (cm)	Degree of bed saturation	Breakpoint time (min)	Height of adsorption zone (cm)
10	0.48	16	13.6
20	0.68	47	13.6
30	0.806	85	13.6

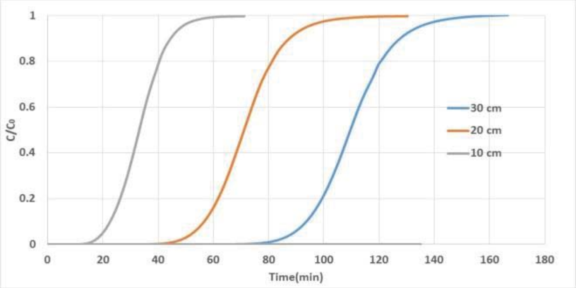

Figure 5. Effect of bed height on the breakthrough curve

4. Conclusions

Mathematical modeling results compared with experimental data in order to validate the simulation. The effect of flow rate, inlet concentration, and bed height on the behavior of breakthrough curve investigated and concluded that these parameters are important factors in the design and operation of the packed bed column. Solving PDE of adsorption bed with the method of lines has an accurate result. This method in addition to high accuracy has good convergence rate. The optimum value of flow rate depends on flow direction, bed dimension, and inlet concentration. Breakthrough curve slope becomes steeper and decreases the breakpoint time when increase flow rate. The high value of inlet concentration leads to the degree of bed saturation decrease which is not cost-effective. Varying bed height does not affect breakthrough curve shape. High bed length increases resistance time required to reach adsorption equilibrium.

Nomenclatures

b	Langmuir isotherm parameter
C	Bulk fluid phase concentration
C^*	Liquid phase concentration in equilibrium with q on the surface
D_{AB}	Diffusivity of A in very dilute solution in solvent B
D_p	Pore diffusion coefficient
D_z	Axial diffusion coefficient
f	Fractional capacity of adsorption zone
H	Column length
H_a	Adsorption zone length
k	Overall mass transfer coefficient
k_f	External film mass transfer coefficient
M_B	Solvent molecular weight
q	Average concentration on the pellet
q_{max}	Langmuir isotherm parameter
R_p	Particle radius
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number
T	Fluid temperature
t	Time
t_a	Time required for adsorption zone to move down owns height
t_e	Time required for adsorption zone to move out the bed
t_f	Time of initial formation
u	Superficial velocity
v_A	Solute molal volume at normal boiling point
X	Coded factors
Y	Predicted response
z	Axial coordinate

Greek letters

ε	Bed porosity
ε_p	Porosity of the adsorbent particle
β	Model parameters
τ	Tortuosity factor
ρ_a	Adsorbent density
μ	Liquid viscosity
ν	Kinematic viscosity of the fluid

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