

# Modeling and Simulation of Fixed Bed Adsorption Column: Effect of Operating Variables

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## Abstract

The kinetics in a fixed-bed adsorption system is explained using a mathematical model that takes into account of external and internal mass-transfer resistances with a nonideal plug flow behavior. The variation of fluid velocity along the column is an important aspect, which has not been accounted so far in these models. In the present study, a mathematical model is proposed for explaining the kinetic behavior of adsorption phenomena incorporating the fluid velocity variation along the column length also. Internal mass-transfer resistances due to pore diffusion mechanism are considered in the model. The proposed mathematical model for fixed-bed adsorption is solved numerically and compared with earlier model reported in literature. The results show that the breakpoint is obtained earlier, which represents the realistic behavior in adsorption phenomena. Simulations are carried out using the present model for a systematic parametric study. The effects of various important and influencing parameters such as flow rate, bed height, inlet adsorbate concentration and particle diameter on breakthrough curve are studied in detail.

*Keywords:* adsorption; modeling; pore diffusion control; breakthrough curve; mass transfer

## 1. Introduction

Use of adsorption contacting systems for industrial and municipal wastewater treatment has become more prevalent during recent years (Babu and Gupta, 2004). An adsorption process is often used at the end of a treatment sequence for pollution control due to the high degree of purification that can be achieved. Adsorption is an important step in industrial downstream processing. It is required to stop the adsorption stage before the saturation of the adsorbent is completed, for which a thorough understanding of adsorption characteristics is essential (Bautista et.al, 2003). At industrial scale, the time of stopping the operation must be determined after an economic and, eventually, environmental evaluation of the process. Because not only the amount of solute adsorbed but the operating time has an important impact on the effective use of the column and on

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the final throughput of the process, too. The optimization of this and other operating conditions can be accomplished with the help of reliable mathematical models. The adsorption kinetics can be described by various models depending upon the mechanism of transport (pore diffusion, solid diffusion, and both mechanisms in parallel) assumed inside the particles.

Ma et al. (1996) described the pore and surface diffusion models for fixed-bed adsorption system. Liao and Shiau (2000) described an axial dispersion model for the operation of a fixed-bed adsorber with a linear adsorption isotherm. Sotelo et al. (2004) studied the adsorption of methyl ethyl ketone and trichloroethene from aqueous solutions onto activated carbon fixed-bed adsorbers. Bautista et al. (2003) proposed the kinetic mechanism for the adsorption of  $\alpha$ -amylase from *Aspergillus oryzae* in a fixed bed. The above models have not incorporated the fluid velocity variation along the bed, which makes a significant effect on breakthrough curve for high inlet adsorbate concentration (Ruthven, 1984). In the present study, the effect of various operating variables (flow rate, bed height, inlet adsorbate concentration, and particle diameter) on the process of fixed-bed adsorption is studied. Furthermore, the kinetics is studied using a mathematical model that takes into account of both the external and internal mass-transfer resistances, nonideal plug flow along the column, and the variation of fluid velocity along the column.

## **2. Mathematical Modeling**

To formulate a generalized model corresponding to the pore diffusion mechanism, following assumptions are made:

1. The system operates under isothermal conditions.
2. The equilibrium of adsorption is described by Langmuir isotherm.
3. Intraparticle mass transport is due to Fickian diffusion, and it is characterized by the pore diffusion coefficient,  $D_p$ .
4. Mass transfer across the boundary layer surrounding the solid particles is characterized by the external-film mass transfer coefficient,  $k_f$ .
5. The macroporous adsorbent particles are spherical and homogeneous in size and density.

Based on the preceding assumptions, for the control volume,  $\Delta z$ , for limiting situation  $z \rightarrow 0$ , net rate of accumulation or depletion is given by Eq. 1:

$$-D_L \frac{\partial^2 C_b}{\partial z^2} + V \frac{\partial C_b}{\partial z} + C_b \frac{\partial V}{\partial z} + \frac{\partial C_b}{\partial t} + \rho_p \left( \frac{1-\varepsilon}{\varepsilon} \right) \frac{\partial q_p}{\partial t} = 0 \quad (1)$$

The following initial conditions (Eqns. 2 & 3) are considered

$$C_b = C_{b0} \quad z = 0, t = 0 \quad (2)$$

$$C_b = 0 \quad 0 < z \leq L, t = 0 \quad (3)$$

The contour conditions at both ends of the column are given by Eqns. 4 & 5:

$$D_L \frac{\partial C_b}{\partial z} = -V_0 (C_{b0} - C_b), \quad z = 0, t > 0 \quad (4)$$

$$\frac{\partial C_b}{\partial z} = 0, \quad z = L, t \geq 0 \quad (5)$$

The superficial velocity,  $V$  in fixed-bed adsorption is not constant because of adsorption. The following equation is used to estimate  $(dV/dz)$ , the variation of velocity of bulk fluid along the axial direction of the bed. For liquid adsorption, assuming the liquid density to be constant, the total mass balance gives Eq. 6:

$$\rho_l \frac{\partial V}{\partial z} = -(1-\varepsilon) \rho_s \frac{\partial q_p}{\partial t} \quad (6)$$

Velocity boundary conditions are given by Eqns. 7 & 8:

$$V = V_0, \quad z = 0, t > 0 \quad (7)$$

$$\frac{\partial V}{\partial t} = 0, \quad z = L, t > 0 \quad (8)$$

The inter-phase mass transfer rate may be expressed as given by Eq. 9

$$\rho_s \frac{\partial q_p}{\partial t} = \frac{3k_f}{a_p} (C_b - C_s) \quad (9)$$

The intra-pellet mass transfer is due to the diffusion of adsorbate molecules through the pore. The macroscopic conservation equation is given by Eq. 10

$$\varepsilon_p \frac{\partial c}{\partial t} + (1-\varepsilon_p) \rho_p \frac{\partial q}{\partial t} = D_p \left( \frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right) \quad (10)$$

Then rearranging Eq. 3, we get Eq. 11

$$\frac{\partial c}{\partial t} = \frac{1}{\left[1 + \rho_p \left(\frac{1 - \varepsilon_p}{\varepsilon_p}\right) \frac{\partial q}{\partial c}\right]} D_p \left( \frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right) \quad (11)$$

The following initial condition considered is shown by Eq. 12:

$$c = 0, \quad q = 0, \quad 0 < r < a_p, \quad t = 0 \quad (12)$$

The symmetry condition at the center of the particles and continuity condition on the external surface of the adsorbent bed are expressed as given by Eqns. 13 & 14:

$$\frac{\partial c}{\partial r} = 0, \quad r = 0, \quad t > 0 \quad (13)$$

$$k_f (C_b - C_s) = D_p \frac{\partial c}{\partial r}, \quad r = a_p, \quad t > 0 \quad (14)$$

The adsorption isotherm was favorable and nonlinear, and it described by Langmuir isotherm (Eq. 15):

$$q = \frac{q_m bc}{1 + bc} \quad (15)$$

### 3. Simulation Technique

Since nonlinear adsorption equilibrium is considered, the preceding set of partial differential equations (Eqns. 1-15) are solved numerically by a reduction to set of ordinary differential equations using the Explicit Finite Difference technique. Finite difference technique has successfully been applied to solve such type of partial differential equations in other studies by Babu and Chaurasia (2003a; 2003b; 2004a; 2004b; 2004c; 2004d). A mathematical algorithm to solve these coupled equations is developed and implemented into a computer program using MATLAB (v.6.1) software. The same parameters reported by Bautista et al. (2003) are used for simulation in the present study, which are given in Table-1.

### 4. Results and Discussion

The model used, as described above, determines the outlet adsorbate concentration at different times based on different operating conditions. In the present model, linear velocity variation along the bed is considered and the obtained results are compared with

the previous model given by Bautista et al. (2003). Same parameters, as given by Bautista et al. (2003) are used and some parameters (see Table-1) are assumed which are not given in literature. The results show that the breakpoint is obtained earlier (Fig. 1). Initially the sharp front of the breakthrough curve is seen followed by broadening of tail of the breakthrough curve as shown in Fig. 1 (Ruthven, 1984). These obtained results are more justifiable with theoretical phenomena occurring in the adsorption system. The fluid velocity along the bed is a decreasing function of bed length (Ruthven, 1984). The velocity continuously decreases inside the bed with respect to bed length. This phenomenon is validated by the mass balance (Eq. 6) for velocity variation. This establishes the fact that the effect of velocity variation on breakthrough curve is significant. This fact is also in agreement with the results reported in the literature (Ruthven, 1984). Based on the successful implementation of velocity variation in the model, and supporting evidence in the literature, the simulations are carried out using the present model to carryout a systematic parametric study. The present model is studied by varying different important parameters such as flow rate, bed height, inlet adsorbate concentration and particle diameter.

#### **4.1 Effect of flow rate**

The results for different solution flow rates are plotted for a bed height of 0.163 m and an inlet adsorbate concentration of 2.5 mg/ml in Fig. 2. Fig. 2 shows that as the flow rate increases from 3.0 to 4.0 ml/min, the breakthrough curve becomes steeper. The break point time decreases from 190 to 160 sec without considering the velocity variation along the bed and 140 to 105 sec with velocity variation. This is because of the residence time of the solute in the column, which is not long enough for adsorption equilibrium to be reached at high flow rate. So at high flow rate the adsorbate solution leaves the column before equilibrium occurs. Furthermore, a fixed saturation capacity of bed based on the same driving force gives rise to a shorter time for saturation at higher flow rate.

#### **4.2 Effect of bed height**

The effect of bed height on the effluent adsorbate concentration is presented for flow rate of 4 ml/min and inlet adsorbate concentration of 2.5 mg/ml in Fig. 3. It is observed that as the bed height increases from 0.163 to 0.173 m, the break point time increases from 160 to 185 sec without considering the velocity variation and 105 to 135 sec with velocity

variation along the bed. This shows that at smaller bed height the effluent adsorbate concentration ratio increases more rapidly than for a higher bed height. Furthermore, the bed is saturated in less time for smaller bed heights. Smaller bed height corresponds to lesser amount of adsorbent. Consequently, a smaller capacity for the bed to adsorb adsorbate from solution and a faster increase in rate of adsorbate adsorption is expected.

#### **4.3 Effect of Inlet concentration**

The effect of inlet adsorbate concentration on effluent concentration is shown in Fig. 4. During these simulations other parameters such as bed height and flow rate are kept constant. It is observed that as the inlet adsorbate concentration increases from 2.5 to 5 mg/ml, the break point time decreases from 160 to 145 sec without considering the velocity variation and 105 to 95 sec with velocity variation along the bed. For larger feed concentration, steeper breakthrough curves are found, because of the lower mass-transfer flux from the bulk solution to the particle surface due to the weaker driving force. In addition, at high concentration, the isotherm gradient is lower, yielding a higher driving force along the pores. Thus the equilibrium is attained faster for values of higher adsorbate concentration.

#### **4.4 Effect of particle radius**

The effect of particle size on effluent concentration is shown in Fig. 5. During these simulations other parameters such as flow rate, bed height, and inlet adsorbate concentration are kept constant. Figure 5 reveals that as the particle radius increases from  $4.1 \times 10^{-4}$  to  $5.1 \times 10^{-4}$  m, the steepness of the breakthrough curve decreases. The break point time increases from 160 to 210 sec without considering the velocity variation and 105 to 150 sec with velocity variation along the bed. As the diameter of the particle increases, the thickness of stagnant film around the particles increases, and also the total length of the path inside the pores increases. Under these conditions, the overall kinetics of the process is slow, because the time for a molecule of adsorbate to reach the adsorption site is more, as the diffusional path along the pores is large.

### **5. Conclusions**

Following conclusions are drawn from present study based on the results discussed above:

1. There is a significant effect of velocity variation through the bed on breakthrough curve, wherein the break point is obtained earlier.
2. As the flow rate is increased, the breakthrough curve becomes steeper. The break point time is obtained earlier and effluent adsorbate concentration ratio increases more rapidly.
3. For smaller bed height, the effluent adsorbate concentration ratio increases more rapidly than for a higher bed height.
4. For larger feed concentration, steeper breakthrough curves are obtained and break point time is achieved sooner.
5. With decrease in particle radius, the breakthrough curve becomes steeper and the break point time decreases.

These results improve the understanding of adsorption phenomena with reference to pore diffusion, and are very useful in the design of adsorption columns.

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### Nomenclature

$a_p$	radius of the adsorbent pellets, m
$A$	area of cross section, $m^2$
$b$	Langmuir isotherm parameter, ml/mg
$c$	solute concentration in the liquid phase inside the pores, mg/l
$C_b$	bulk phase dye concentration, mg/ml
$C_s$	liquid phase concentration in equilibrium with $q_s$ on the surface, mg/ml
$C_{in}$	inlet adsorbate concentration, mg/ml
$D_L$	axial dispersion coefficient, $m^2/s$
$D_p$	pore diffusion coefficient, $m^2/s$
$k_f$	external film mass transfer coefficient, m/s
$L$	column length, m
$q$	average adsorbed phase dye concentration, mg/g
$q_m$	Langmuir isotherm parameter, mg/g
$q_s$	concentration on the surface of the pellet, mg/g
$Q$	flow rate, ml/min
$r$	radial coordinate, m
$t$	time, sec
$V$	superficial velocity, m/s
$V_o$	initial superficial velocity, m/s
$V_i$	interstitial velocity inside the bed, m/s
$z$	axial coordinate, m

### Greek letters

$\varepsilon$	bed porosity
$\varepsilon_p$	porosity of the adsorbent pellet
$\rho_l$	solution density, $kg/m^3$
$\rho_p$	particle density, $kg/m^3$
$\rho_b$	bed density, $kg/m^3$

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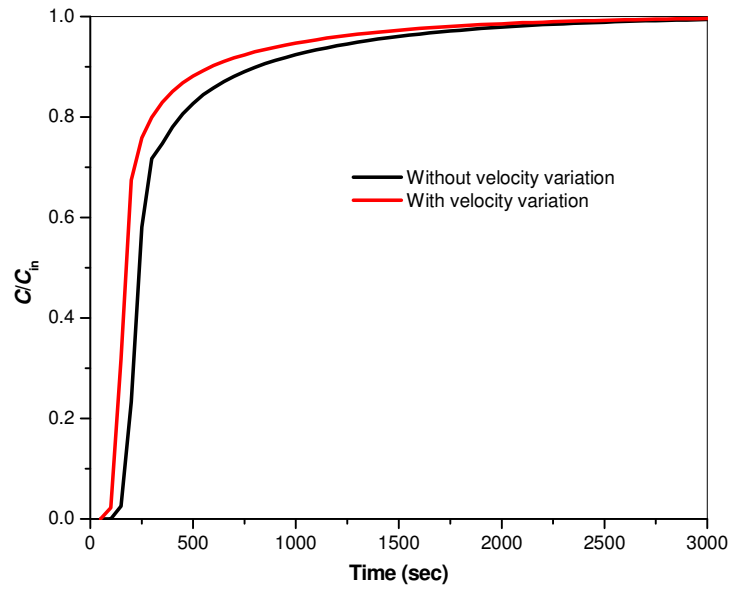


Figure 1: Effect of velocity variation on breakthrough curve

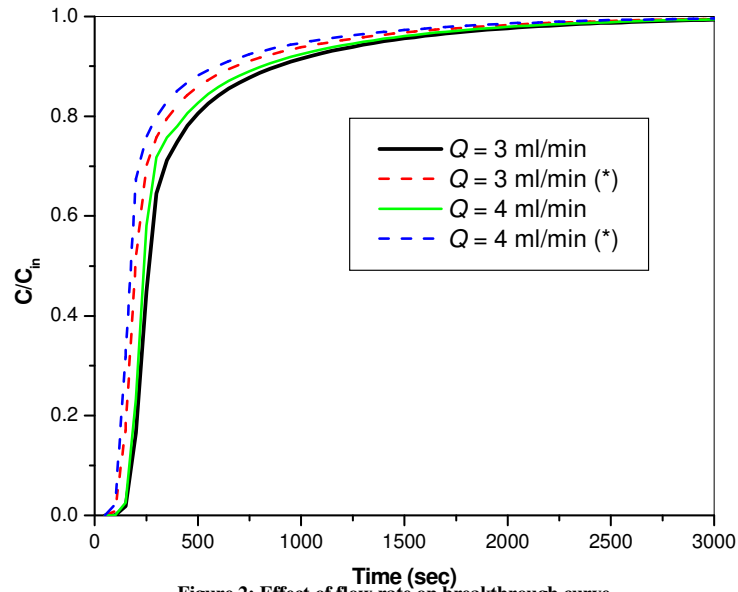
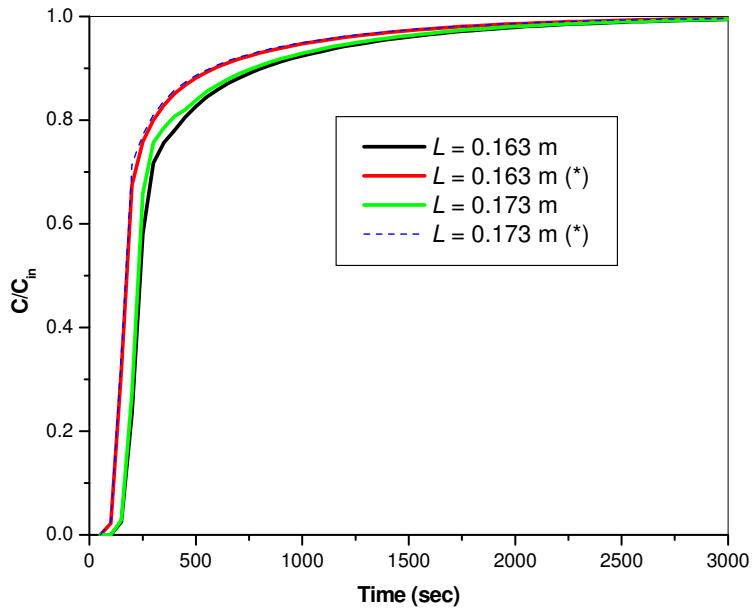
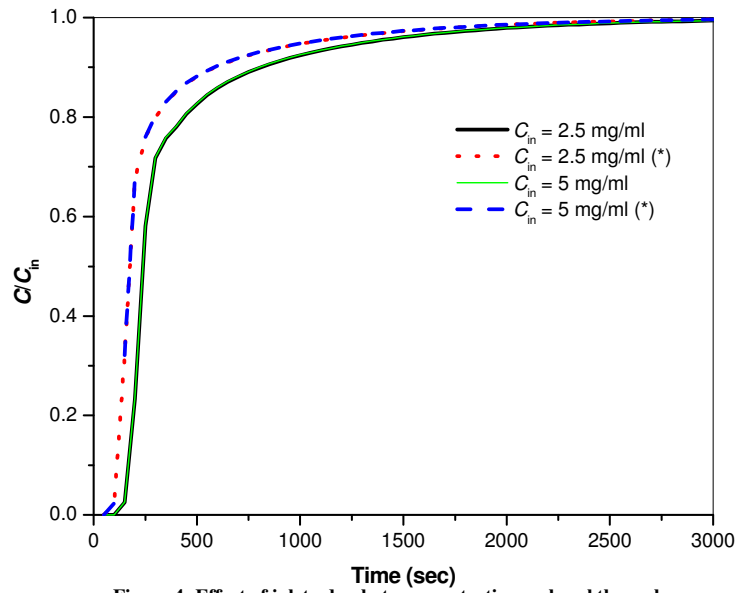


Figure 2: Effect of flow rate on breakthrough curve  
 (\*) indicates model results with velocity variation



**Figure 3: Effect of bed height on breakthrough curve**  
 (\*) indicates model results with velocity variation



**Figure 4: Effect of inlet adsorbate concentration on breakthrough curve**  
 (\*) indicates model results with velocity variation

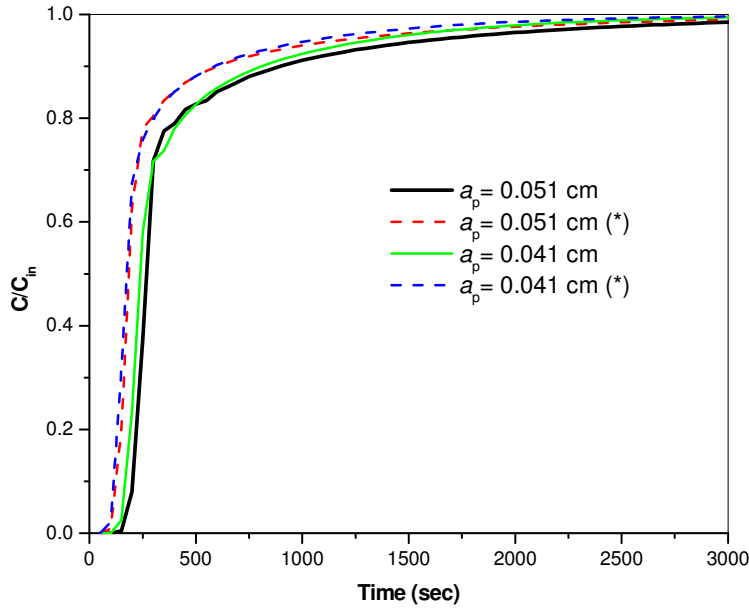


Figure 5: Effect of particle radius on breakthrough curve  
 (\*) indicates model results with velocity variation

Table-1: Model parameters value for simulation [Bautista et al., 2003]

Parameter	Value
$\varepsilon$ , Bed porosity, (-)	0.58
$\varepsilon_p$ , Particle porosity, (-)	0.53
$\rho_p$ , Particle density, $\text{kg/m}^3$	1970
$\rho_b$ , Bed density, $\text{kg/m}^3$ (§)	900
$\rho_l$ , Liquid density, $\text{kg/m}^3$ (§)	1000
$D_L$ , Axial dispersion coefficient, $\text{m}^2/\text{s}$ (§)	$5.9 \times 10^{-10}$
$q_m$ , Maximum adsorption capacity, $\text{mg/g}$	45.4
$b$ , Langmuir isotherm constant, $\text{ml/mg}$	0.84
$D_p$ , Pore diffusivity, $\text{m}^2/\text{sec}$	$2.4 \times 10^{-11}$
$k_f$ , External mass transfer coefficient, $\text{m/sec}$	$8.2 \times 10^{-6}$
$d$ , Bed diameter, $\text{m}$	0.016

(§) The values not reported in literature