



## Modeling and Simulation for Dynamics of Packed Bed Adsorption

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### Abstract

Understanding the dynamics of fixed-bed adsorption columns for modeling is a demanding task due to the strong nonlinearities in the equilibrium isotherms, interference effects of competition of solutes for adsorbent sites, mass transfer resistances between fluid phase and solid phase, and fluid-dynamic dispersion phenomena. The interplay of these effects produces steep concentration fronts, which move along the column during the adsorption process, which has to be accounted for in modeling. In this study, a mathematical model is studied for a fixed bed isothermal adsorption column with porous adsorbent. Simulations are carried out to understand the influence of axial dispersion, external film resistance, and solid diffusion resistance on adsorption using the above model. The mathematical equations are solved simultaneously using finite difference explicit scheme. The effect of flow rate, mass of adsorbent, and initial concentration of adsorbate are studied. Rapid occurrence of breakthrough time is observed for higher flow rates of effluent, lower mass of adsorbent, and high initial concentration of effluent. The model parameters studied are solid diffusion coefficient,  $D_s$ , axial dispersion coefficient,  $D_L$ , and external mass transfer coefficient,  $k_f$ . The values of  $D_s$  and  $D_L$  are found to be in the order of  $10^{-4}$  to  $10^{-5}$  and  $10^{-2}$  cm<sup>2</sup>/s, respectively. There is no effect of  $D_s$  and  $D_L$  on the breakthrough curve. The value of  $k_f$  is found to be in order of  $10^{-2}$  to  $10^{-4}$  cm<sup>2</sup>/s. The effect of external mass transfer coefficient on the breakthrough curve is found out.

**Keywords:** *adsorption; modeling; axial dispersion; solid diffusion control; mass transfer; breakthrough curve.*

### Introduction

Use of adsorption contacting systems for industrial and municipal wastewater treatment applications has become more prevalent during recent years. Both the design and operation of adsorption contactors are related to the characteristic breakthrough curves in which readily measured effluent concentration is plotted as a function of elapsed time. Depending on the ultimate objective of the process, either breakthrough point or saturation point represents the design and or operational target. This is the primary fact that wastewaters have an extremely complex

composition, which, in turn, substantially complicates modeling and simulation procedures. Adsorption of a fluid mixture components flowing through a fixed bed of a porous adsorbent material forms the basis of several important applications in chemical engineering [1].

Several features of the dynamics of fixed-bed adsorption columns make the modeling task particularly demanding. These include strong nonlinearities in the adsorption equilibrium isotherms, interference effects due to the competition of solutes for adsorbent sites, mass transfer resistances between the fluid phase and the solid

phase and fluid-dynamic dispersion phenomena [2]. The interplay of these effects produces steep concentration fronts, which move along the column during the adsorption process. This particular property of the fixed bed adsorption processes must be accounted by the mathematical model and constitutes a serious difficulty for the solving procedure [3].

The characteristic shape of breakthrough curve depends on the inlet flow rates, concentration and other properties such as column diameter, bed height, etc. [4]. The fixed bed of certain dimensions has a definite capacity to adsorb the solute, which is equivalent to saying that the adsorbent packed in the bed would remove pollutant not only until that time when an equilibrium relationship is attained but also upon the transfer mechanism and upon the rate of adsorption. The sharpness of the curve indicates linear or non-linear behavior of equilibrium isotherm. It indicates a rate process proportional to the solute concentration in mass transfer controlling phase.

The present study focused on understanding of mechanisms of adsorption in fixed bed columns for single-component adsorption on porous adsorbents. The mathematical model is governed by a set of partial differential equations, which were solved numerically using finite difference explicit scheme.

### Mathematical Model

The dynamics of a fixed bed is described by a set of convection diffusion equations, coupled with source terms due to adsorption and diffusion inside the adsorbent particles [5]. Prediction of the breakthrough curves is based on correct mathematical model formulation of a fixed bed adsorber. The system considered is an isothermal adsorption column packed with porous adsorbent. At time zero, a step change in the concentration of an adsorbate was introduced in the flowing stream. The adsorption column is subjected to axial dispersion, external film resistance, and solid diffusion resistance. The following assumptions are made in the analysis:

1. Isothermal adsorption of a single component.
2. Negligible concentration gradient in the radial direction.
3. The Linear Driving Force (LDF) model was used for presenting mass transfer into the pellets.
4. Constant cross section and uniform properties of the adsorbent bed throughout the column.

Under the above assumptions, the governing equations and appropriate initial and boundary conditions can be written as follows:

Fluid phase mass balance

$$-D_L \frac{\partial^2 c}{\partial z^2} + \frac{\partial}{\partial z}(uc) + \frac{\partial c}{\partial t} + \left( \frac{1-\varepsilon}{\varepsilon} \right) \frac{\partial \bar{q}}{\partial t} = 0 \quad (1)$$

Initial and boundary conditions:

$$\text{at } t = 0, \quad c = 0 \quad (2)$$

$$\text{at } z = 0, \quad c_{in} = c - \frac{D_L}{v} \frac{\partial c}{\partial z} \quad (3)$$

$$\text{at } z = L, \quad \frac{\partial c}{\partial z} = 0 \quad (4)$$

By introducing the dimensionless coordinates

$$Y = \frac{z}{L}, \quad \theta = \frac{tv}{L}$$

Eq. (1) to Eq. (4) becomes

$$-\frac{1}{Pe} \frac{\partial^2 c}{\partial Y^2} + \frac{\partial c}{\partial Y} + \frac{\partial c}{\partial \theta} + \left( \frac{1-\varepsilon}{\varepsilon} \right) \frac{\partial \bar{q}}{\partial \theta} = 0 \quad (5)$$

$$\text{at } \theta = 0, \quad c = 0 \quad (6)$$

$$\text{at } Y = 0, \quad c_{in} = c - \frac{1}{Pe} \frac{\partial c}{\partial Y} \quad (7)$$

$$\text{at } Y = 1, \quad \frac{\partial c}{\partial Y} = 0 \quad (8)$$

Where, Peclet number  $Pe = \frac{Lv}{D_L}$

The uptake rate expressed on the basis of unit adsorbent volume, is given by

$$m = \frac{d\bar{q}}{dt} \quad (9)$$

In terms of external mass transfer,  $m$  may be written as

$$m = \frac{3k_f}{R_p} (c - c_s) \quad (10)$$

The uptake rate in terms of the intra-particle diffusion can be obtained from the solution of the appropriate intra-particle diffusion equation. The uptake rate expression based on the linear driving force (LDF) model for solid diffusion is

$$m = \frac{15D_s}{R_p^2} (q_s - \bar{q}) \quad (11)$$

$q_s$  and  $c_s$  are the adsorbed phase and fluid phase concentration, respectively, at the fluid-pellet interface. They are in equilibrium and defined by the Langmuir equation

$$q_s = \frac{q_m K c_s}{1 + K c_s} \quad (12)$$

After combining all the above equations the final fluid phase balance equation become

$$-\frac{1}{Pe} \frac{\partial^2 c}{\partial Y^2} + \frac{\partial c}{\partial \theta} + \frac{\partial c}{\partial z} + 3Bi_i T \left( \frac{1-\varepsilon}{\varepsilon} \right) \quad (13)$$

$$\left( c_b - \frac{q_s K \rho_p}{q_m K - q_s K} \right) = 0$$

Solid phase mass balance

$$\frac{dq_s}{d\theta} = \frac{\left( 3Bi_i T \left( \frac{1-\varepsilon}{\varepsilon} \right) \left( c_b - \frac{q_s K \rho_p}{q_m K - q_s K} \right) + \left( \frac{Bi}{5} \right) \left( \frac{\partial c}{\partial \theta} \right) \right)}{1 + \left( \frac{Bi}{5} \right) \left( \frac{K}{q_m K - q_s K} \right)^2} \quad (14)$$

Where,  $Bi = \frac{k_f R_P}{D_s}$  is Biot number.

$T = \frac{D_s L}{R_P^2 v}$  is constant.

## Results and discussion

The model equations (13) and (14) are solved using explicit method of Finite Difference technique with the appropriate initial and boundary conditions. A code is developed in Matlab to simulate the model. Data reported in literature [5] is used for simulations in the present study. The outlet concentration at different times is determined and adsorption curves are generated. The unknown model parameters *viz.*, solid diffusion coefficient,  $D_s$ , axial dispersion coefficient,  $D_L$  and external mass transfer coefficient,  $k_f$  are adjusted to give the best-fit curve.

### Effect of flow rate

The effects of flow rate and inlet dye concentration for adsorption on natural zeolite were investigated in a packed-bed column. The effect of flow rate is

studied at 35 and 50 ml/min, while the inlet dye concentration in each run is kept constant at 100 mg/l. The characteristic curves are shown in Fig.1, as the flow rate increases, the breakthrough curve becomes steeper. The break point time and adsorbed dye concentration decreases. If the residence time of the solute in the column is not long enough for adsorption equilibrium to be reached at that flow rate, the dye solution leaves the column before equilibrium occurs. Thus, at higher flow rate the contact time of dye with natural zeolite is very short, causing a reduction in removal efficiency, which is evident from Fig.1.

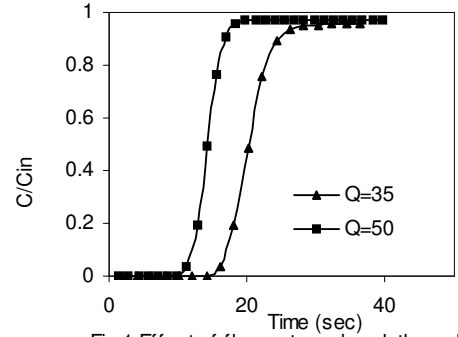


Fig.1 Effect of flow rate on breakthrough curve

### Effect of bed height

Fig. 2 shows the effect of bed height on dye removal. An increase in the bed height from 10 to 15 cm increases the breakthrough time.

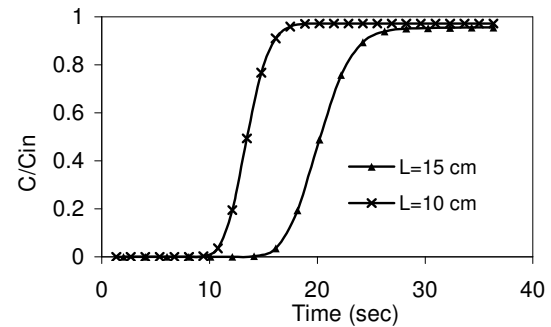


Fig.2:Effect of bed height on breakthrough curve

### Effect of Inlet concentration

The effect of inlet dye concentration on dye removal is shown in Fig. 3. An increase in the initial concentration from 100 to 200 mg/l makes breakthrough curve much steeper.

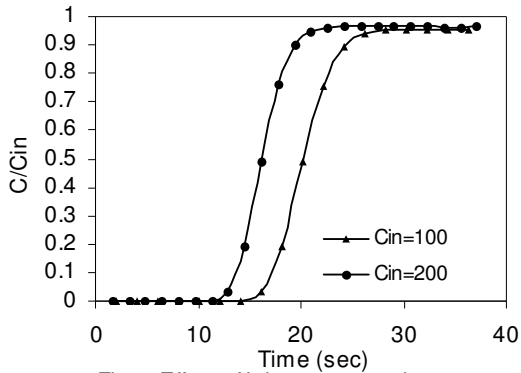


Fig.3: Effect of inlet concentration on breakthrough curve

### Effect of mass transfer coefficient

Fig.4 shows the effect of  $k_f$  on breakthrough curves. With a decrease in  $k_f$  value the concentration ratio ( $C/C_{in}$ ) approaches to unity. But when the  $k_f$  value is increased, the adsorbate removal ratio approaches to some constant value, which less than unity initially and asymptotically becomes constant after some time.

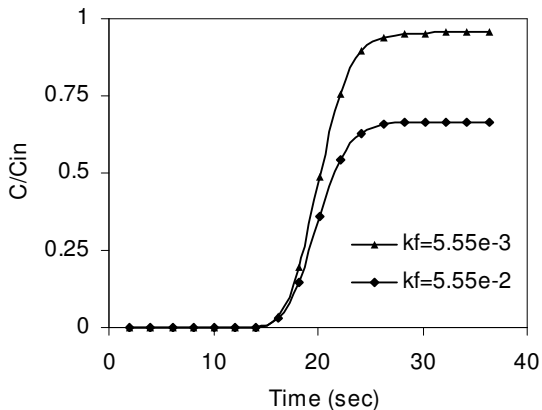


Fig.4: Effect of mass transfer coefficient on breakthrough curve

### Conclusions

The following conclusions are drawn from the present study:

1. The solid diffusion control model describing single solute adsorption in a fixed bed is based on the Linear Driving Force (LDF) model.
2. The adsorption capacity is strongly dependent on the flow rate, inlet dye concentration, and bed height and is greater under conditions of high contact time and lower concentration of dye.
3. As the flow rate is increased, the breakthrough curve becomes steeper while the break point time and adsorbed dye concentration decreased. Much sharper breakthrough curves were

obtained with adsorbent at higher inlet dye concentration.

4. The value of the external mass transfer coefficient has a significant effect on the breakthrough curve. For higher values of external mass transfer coefficient, the  $C/C_{in}$  (outlet concentration / initial concentration) ratio does not approach to unity and asymptotically becomes constant at a lesser value.

### Nomenclature

$Bi$  – Biot number

$c_b$  – bulk phase dye concentration, mg/l

$c_s$  – Liquid phase concentration in equilibrium with  $q_s$  on the surface, mg/l

$c_{in}$  – Inlet concentration, mg/l

$c$  – average liquid phase concentration, mg/l

$D_L$  – axial dispersion coefficient,  $cm^2/s$

$D_s$  – Solid diffusion coefficient,  $cm^2/s$

$k_f$  – mass transfer coefficient, cm/s

$K$  – Langmuir isotherm parameter, ml/mg

$L$  – column length, cm

$m$  – uptake rate of adsorption, mg/g.s

$q$  – average adsorbed phase dye concentration, mg/g

$q_s$  – concentration on the surface of the pellet, mg/g

$q_m$  – Langmuir isotherm parameter, mg/g

$R_p$  – radius of the adsorbent pellets, m

$t$  – time, s

$v$  – interstitial velocity, m/s

$Pe$  – Peclet number

$Y$  – dimensionless axial coordinate

$z$  – axial coordinate, m

### Greek letters

$\epsilon$  – bed porosity

$\epsilon_p$  – porosity of the adsorbent pellet

$\theta$  – dimensionless time variable

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