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Fixed-bed adsorption with nonplug flow: Perturbation solution for constant pattern behavior

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ABSTRACT

Adsorption of a dilute solute from a fluid in nonplug flow through a fixed bed is investigated via a perturbation approach. The continuity equation for fixed-bed adsorption with axial dispersion is solved for the constant pattern concentration profile with the axial velocity characterized by a general axisymmetric function and the system having no resistances to external or intraparticle mass transfer. The isotherm is slightly favorable (i.e., concave downward) in order to justify the assumption that axial gradients of concentration are independent of the radial coordinate in the bed, as in the classical problem of Taylor diffusion. A series expansion of a general isotherm is used to treat adsorption equilibrium. The solution reveals the formation of a radial gradient of fluid-phase concentration and breakthrough behavior at the bed outlet dependent on the nonlinearity of the isotherm and the magnitude of the nonplug-flow-velocity profile. The results can be used to predict the breadth of the breakthrough wave of many chromatographic-type processes for packed beds and slightly favorable isotherms.

1. Introduction

A fundamental understanding of the factors that affect breakthrough behavior of a fixed bed is required in order to design and optimize an adsorption-based process. For many applications, such as those involving low breakthrough concentrations, a quantitative understanding of the phenomena that may alter the breadth of a breakthrough curve is necessary. These phenomena include, but are not limited to, external mass transfer resistances, intraparticle mass transfer resistances, the nonlinearity of adsorption isotherms, and dispersion in the axial and transverse directions.

A considerable amount of work has been performed in order to analyze phenomena that affect the breadth of the breakthrough curve for adsorption processes with plug flow. For example, Costa and Rodrigues (1985) demonstrate the significance of axial dispersion on the breadth of the breakthrough curve. As the Peclet number is increased the width of the breakthrough curve decreases, or tightens up. Coppola and LeVan (1981) indicate the influence that fluid–solid-adsorption equilibria has on the breakthrough curve for deep beds. As an adsorption bed begins to saturate, the velocity of the adsorption wave for a very favorable adsorption isotherm approaches the fluid velocity near the bed outlet and subsequently the breakthrough is abrupt.

However, breakthrough behavior for beds of moderate to large cross-sectional area, as well as for laboratory scale columns, is rarely as sharp as predicted by theory based on plug flow. Concentration waves passing through beds spread as the result of deviations from plug flow caused by both the nonuniformity of bed packings and wall effects in addition to the mechanisms of particle scale mass transfer and axial dispersion.

The scope of this paper involves investigating how adsorption processes described by constant pattern behavior are affected by small deviations from plug flow. Such deviations impact the breakthrough behavior at the bed outlet by saturating various radial positions of the adsorption bed at different times, in effect broadening the breakthrough curve. Deviations from plug flow exist in real adsorption beds due to nonuniform packings and channeling effects at the bed wall. Using laser-Doppler anemometry, Vortmeyer and Schuster (1983) have shown experimentally that the local fluid-phase velocity varies significantly across the cross section of the bed and is greater at the wall than at the centerline of the bed. Experiments and numerical analyses done by Miyabe and Guiochon (1999) and Astrath et al. (2007) also agree that the fluid-phase velocity is greater at the wall than the centerline in chromatography columns. In contrast, computational fluid dynamics simulations performed of HPLC chromatographic processes to determine numerical column profiles have predicted parabolic and other distorted concentration fronts advanced along the centerline of the column (Boysen et al., 2002).

In comparison to the amount of work that has dealt with constant pattern behavior for plug flow, there has been limited research

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concerning constant pattern behavior with deviations from plug flow. Tereck et al. (1987) discuss the relationship among concentrations for a constant pattern profile under nonplug-flow conditions for a cylindrical channel with adsorption at the wall. They demonstrate that a constant pattern profile can be approached for adsorption with nonplug-flow-velocity profiles. Rudisill and LeVan (1991) investigate adsorption of a dilute solute from fluid in nonplug flow through a porous structure of arbitrary but constant cross section. Avilés and LeVan (1991) create network models to describe nonuniform flow and nonlinear adsorption in packed beds. Although not solved for a system exhibiting constant pattern behavior, Vortmeyer and Michael (1985) numerically solve the nonplug-flow gas-phase continuity equation with adsorption rates modeled by a linear driving force. They note that the numerical model predicted distinct differences between the breakthrough curves near the wall and the center of the bed.

In this paper, we solve the continuity equation for fixed-bed adsorption with small deviations from plug flow, dispersion in the axial and transverse directions, and with adsorption equilibrium described by a slightly favorable isotherm. Both external mass transfer from interstitial fluid to particles and intraparticle mass transfer are assumed to be rapid giving local equilibrium between fluid and adsorbed phases. We begin by first assuming that the adsorbent bed is sufficiently long for a constant pattern adsorption wave to develop. Then, we decompose the continuity equation into a series of differential equations similar to Aris (1956). We use a perturbation analysis to obtain an approximate solution for the fluid-phase concentration. The results are general in the sense that the solution applies to perturbations of any axisymmetrical velocity profile and slightly favorable isotherm. We believe this to be the first analytical treatment of constant pattern behavior for a fixed-bed adsorber described by a nonplug-flow differential equation with axial and radial dispersion.

2. Theory

We examine mass transfer for axisymmetrical flow of fluid through a deep bed of packed adsorbent particles, so that the fluid-phase concentration c is a function of time, bed radius, and axial position only. The material balance for this system may be written

$$\rho_b \frac{\partial n}{\partial t} + \varepsilon' \frac{\partial c}{\partial t} + \varepsilon \vec{v} \frac{\partial c}{\partial z} = \varepsilon D_r \frac{1}{r} \frac{\partial}{\partial r}\left(r \frac{\partial c}{\partial r}\right) + \varepsilon D_z \frac{\partial^2 c}{\partial z^2} \tag{1}$$

with boundary conditions in the radial direction of

$$\left.\frac{\partial c}{\partial r}\right|_{r=0} = 0, \quad \left.\frac{\partial c}{\partial r}\right|_{r=R_{bed}} = 0$$

where $\vec{v}$ is the local velocity, which may vary across the cross section of the bed but not axially, R_{bed} is the radius of the bed, and the adsorbed-phase concentration n is described by a slightly favorable (i.e., concave downward) adsorption isotherm. D_r and D_z in Eq. (1) are molecular diffusion or dispersion coefficients in the radial and axial directions. We let

$$\xi = \frac{r}{R_{bed}}, \quad z_a = \frac{z}{R_{bed}}, \quad t_1 = \frac{\langle v \rangle t}{R_{bed}}$$
$$u(\xi) = \frac{\varepsilon \vec{v}(\xi)}{\langle v \rangle}, \quad c^* = \frac{c - c'}{c'' - c'}, \quad n^* = \frac{n - n'}{n'' - n'}$$
$$Pe_r = \frac{2\langle v \rangle R_{bed}}{\varepsilon D_r}, \quad Pe_a = \frac{2\langle v \rangle R_{bed}}{\varepsilon D_z} \tag{2}$$

where $\langle v \rangle$ is the mean superficial velocity, c' and n' are presaturated concentrations (zero for an initially clean bed), c'' is the feed concentration, and n'' is the corresponding adsorbed-phase concentration. Eq. (1) becomes

$$\rho_b \frac{n'' - n'}{c'' - c'} \frac{\partial n^*}{\partial t_1} + \varepsilon' \frac{\partial c^*}{\partial t_1} + u(\xi) \frac{\partial c^*}{\partial z_a} = \frac{2}{Pe_r} \frac{1}{\xi} \frac{\partial}{\partial \xi}\left(\xi \frac{\partial c^*}{\partial \xi}\right) + \frac{2}{Pe_a} \frac{\partial^2 c^*}{\partial z_a^2} \tag{3}$$

A new coordinate is defined in order to follow the stoichiometric front of the adsorption wave. We let

$$\zeta = z_a - \frac{t_1}{\Lambda + \varepsilon'} \tag{4}$$

where Λ, the partition ratio, is given by

$$\Lambda = \rho_b \frac{n'' - n'}{c'' - c'} \tag{5}$$

Assuming that the bed length L is large, a constant pattern profile will develop. Furthermore, for $\Lambda \gg 1$, Coppola and LeVan (1981) show that the fluid-phase accumulation term in Eq. (3) is negligible, transforming the continuity equation to

$$-\frac{\partial n^*}{\partial \zeta} + u(\xi) \frac{\partial c^*}{\partial \zeta} = \frac{2}{Pe_r} \frac{1}{\xi} \frac{\partial}{\partial \xi}\left(\xi \frac{\partial c^*}{\partial \xi}\right) + \frac{2}{Pe_a} \frac{\partial^2 c^*}{\partial \zeta^2} \tag{6}$$

with boundary conditions in the axial direction of

$$c^* \to 1 \text{ as } \zeta \to -\infty, \quad c^* \to 0 \text{ as } \zeta \to +\infty \tag{7}$$

We describe the local velocity by a small perturbation from plug flow using

$$u(\xi) = 1 + \gamma f(\xi) \tag{8}$$

where γ is the perturbation parameter for which $\gamma \ll 1$, and $f(\xi) = O(1)$ is an axisymmetric term such that

$$\int_0^1 f(\xi) \xi \, d\xi = 0 \tag{9}$$

We solve Eq. (6) using a perturbation method with an assumed solution of the form

$$c^* = \sum_{k=0}^{\infty} \gamma^k c_k^* = c_0^* + \gamma c_1^* + \cdots \tag{10}$$

Substituting Eq. (10) into Eq. (6) gives the zero-order differential equation

$$-\frac{\partial n_0^*}{\partial \zeta} + \frac{\partial c_0^*}{\partial \zeta} = \frac{2}{Pe_a} \frac{\partial^2 c_0^*}{\partial \zeta^2} \tag{11}$$

where $n_0^* = n^*(c_0^*)$.

We solve this equation following the method outlined by Coppola and LeVan (1981) resulting in

$$d\zeta = \frac{2}{Pe_a} \frac{dc_0^*}{(c_0^* - n_0^*)} \tag{12}$$

which they integrated for Langmuir (constant separation factor) and Freundlich isotherms.

The first and second-order differential equations are obtained by first writing the dimensionless adsorbed-phase concentration n^* in a Taylor series expansion of the form

$$n^* = n^*(c_0^{*\prime}) + \left.\frac{dn^*}{dc^*}\right|_{c_0^{*\prime}} \frac{(c^* - c_0^{*\prime})}{1!} + \left.\frac{d^2 n^*}{dc^{*2}}\right|_{c_0^{*\prime}} \frac{(c^* - c_0^{*\prime})^2}{2!} + \cdots \tag{13}$$

where $c_0^{*\prime}$ is the point at which the loading is centered. The subsequent examples, with profiles centered about the plug-flow solution,