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Abstract. *We discuss a new way to approximate the concentration profile inside the porous solids. It is an extension of the work of Liaw et al., who adopted a parabola (i.e., quadratic) profile, which is a function of pellet radius, while retaining the spherical symmetry. We extend their work by adding the quartic term. The inclusion of this new term still preserves the form of linear driving force approximation with some correction to Glueckauf's parameter. The presence of such a correction will affect the breakthrough curve, although its significance can only be determined experimentally. We plan to apply the result to the case of fixed-bed adsorber used for hydrogen/methane separation with activated carbon.*

Keywords: activated carbon, Glueckauf's parameter, hydrogen, linear driving force, methane

Introduction

Recently, gas separation has seen its wide and direct application in industry. Due to its importance, it has become inevitable that one needs a mathematical model able to simulate the process. Such mathematical model is a set of differential equations describing the dynamics of physical variables such as concentration and temperature of the system as the function of time and coordinate (i.e., adsorber length). This allows us to find a set of parameters that leads to an optimal results (e.g., product purity, etc).

In fixed-bed columns with porous solids, for example, there are three equations involved, i.e., (i) equation describing gas concentration in the the bulk, (ii) mass-transfer equation inside the porous solids (adsorbent), and (iii) equation at the adsorbent surfaces. Although this may look straightforward, solving these three equations simultaneously can be very demanding. Such a complication, however, can be reduced should one take some simplifying assumptions. To name a few, they are linear driving force (LDF) approximation [1, 2], nonlinear driving force, parabolic profile approach, etc.

One of techniques found in literature is the approach of Liaw et al. [3], in which they assume that the concentration profile inside the adsorbent is isotropic with a parabolic (i.e., quadratic) function. This comes from the fact that any well-behaved function can always be written in terms of power series of its variables, with higher-order terms being more and more negligible. With this assumption, the equation for gas inside the adsorbents can be eliminated, hence reducing the number of differential equations involved. The interesting thing with this approximation is that it could reproduce the Glueckauf's result of linear driving force [1, 2], and more importantly, it could yield breakthrough curves in a good agreement with those derived by exact solution [4], with considerably less computational time. For direct application of this approach, see [5] and references therein.

In present work, we shall extend the work of [3] by including the quartic term to the concentration profile inside the porous solids in hopes of getting close-to-experiment result; adding more term into a power series expansion, a priori, will give a more accurate function. For all we know, we believe that this addition has never been worked out before. The inclusion of this new term retains the form of linear driving force approximation with some correction to Glueckauf's parameter. The correction will affect the shape of breakthrough curves, but its value can only be determined experimentally, i.e., by fitting the function to data. It could be very interesting, although the detail will be preserved for future work, if we can apply the result to fixed-bed adsorber used to separate hydrogen/methane with activated carbon.

Methodology

As mentioned before, in doing simulation of a fixed-bed column there are three differential equations involved. The first is the equation governing the concentration inside the bulk:

$$v\frac{\partial c}{\partial z}+\frac{\partial c}{\partial t}=-\frac{1}{\eta}\frac{\partial \bar{q}}{\partial t}, \tag{1}$$

where c is the gas concentration side the bulk/column, v is the flow velocity, $\bar{q}$ is the mean gas concentration within the porous solids, and $\eta \equiv \epsilon/(1-\epsilon)$ with ϵ being the void parameter of the column.

Inside the porous solids, there exists an equation

$$\frac{\partial q}{\partial t}=\frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial q}{\partial r}\right), \tag{2}$$

with D and r denoting the diffusion coefficient and the adsorbate radial coordinate, respectively. These two equations are related to each other through

$$D\left(\frac{\partial q}{\partial r}\right)_{r=R}=k(c-q_R/K), \tag{3}$$

where q_R, as the symbol suggests, is the mole fraction at the surface of the adsorbent with radius R, k is the mass transfer coefficient, and K is the adsorption equilibrium constant.

One can see that in Equation (1), q (or $\partial q/\partial t$) is expressed in average form, which is defined as

$$\bar{q}=\frac{3}{R^3}\int_0^R qr^2dr. \tag{4}$$

It is then straightforward to find $\partial\bar{q}/\partial t$, that is

$$\frac{\partial \bar{q}}{\partial t}=\frac{3}{R^3}\int_0^R\left(\frac{\partial q}{\partial t}\right)r^2dr=\frac{3D}{R}\left(\frac{\partial q}{\partial r}\right)_{r=R}, \tag{5}$$

where we have used Equation (2). Equation (5) suggests that should we know the q dependence on radius, $\partial\bar{q}/\partial t$ can be determined. This is the essence of [3].

We assume that q can be expressed as a power series expansion

$$q=a_0+a_1r+a_2r^2+\ldots, \tag{6}$$

with $a_{n+1}r \ll a_n$. Thanks to the finiteness of q, there is no term with negative power of r, and therefore such series can be truncated at some power of r. We further assume that q is spherically symmetric function, meaning that all odd powers vanish or $a_{2n+1}=0$. In the present case we will keep up to $\mathcal{O}(r^4)$ term, so q takes the form of

$$q=a_0+a_2r^2+a_4r^4. \tag{7}$$

Results and Discussion

Armed with Equation (7), we find $(\partial q/\partial r)_{r=R}=2a_2R(1+2a_4R^2/a_2)$. Similar to [3], it would be more useful if one can state this derivative in terms of physical quantities q_R and $\bar{q}$, namely

$$q_R=a_0+a_2R^2+a_4R^4 \tag{8}$$

$$\bar{q}=a_0+\frac{3}{5}a_2R^2+\frac{3}{7}a_4R^4 \tag{9}$$

Taking into consideration that $(a_4/a_2)R^2$ is much less than 1, so it can be treated a perturbation parameter, we obtain

$$\left(\frac{\partial q}{\partial r}\right)_{r=R} = \frac{5}{R}(1+\beta)(q_R - \bar{q}), \tag{10}$$

with

$$\beta \equiv \frac{4}{7}\left(\frac{a_4 R^2}{a_2}\right). \tag{11}$$

From Equation (5), the linear driving force relation follows

$$\frac{\partial \bar{q}}{\partial t} = \frac{15D}{R^2}(1+\beta)(q_R - \bar{q}), \tag{12}$$

As expected, the inclusion of the quartic coupling into the concentration profile leads to a correction to the Glueckauf's constant parameter. (In the work of Liaw et al., since they have quadratic function, $\beta = 0$, which is the reason why they end up like Glueckauf's LDF.) One may have noticed that the parameter β in Equation (11) is treated like constant. That is, both a_4 and a_2 have the same time dependence. One may argue that, in general, it is not always the case as each expansion coefficient a_i may have different time dependence. We justify it by noting that it is $\bar{q}$ that enters Equation (1). Therefore, $\bar{q}$ (or more precisely $\partial\bar{q}/\partial t$) consists of r and t functions that are always separable. This is the chief reason why each coefficient a_i has the same time dependence.

Despite the fact that the correction should be small, it is nevertheless useful to infer its value (and its significance) from experimental data. We preserve this for the future work.

Next, we would like to see how β will affect the breakthrough curves. Apart from β, Equation (12) pretty much looks like the one discussed in [3]. So we follow their procedure to eliminate q and to simplify Equation (1). We start by transforming variables z and t

$$x = z/(\eta v) \tag{13}$$

$$\theta = t - z/v \tag{14}$$

As a result, Equation (1) becomes

$$\frac{\partial c}{\partial x} = -\frac{\partial \bar{q}}{\partial \theta}, \tag{15}$$

or by using Equation (12) we get

$$\frac{\partial c}{\partial x} = -\frac{15D}{R^2}(1+\beta)(q_R - \bar{q}). \tag{16}$$

By taking derivative with respect to θ on both sides followed by using Equations (3) and (10), we can express $\bar{q}$ in terms of q_R and c

$$\bar{q} = \left(1 + \frac{Rk}{5D(1+\beta)K}\right) q_R - \frac{Rk}{5D}c. \tag{17}$$

Now we eliminate q_R by taking the derivative with respect to θ followed by using Equation (15). We finally get

$$\frac{\partial c}{\partial x} = -K\frac{\partial c}{\partial \theta} - \xi\frac{\partial^2 c}{\partial x \partial \theta}, \tag{18}$$

with

$$\xi \equiv R\left(\frac{K}{3k} + \frac{R}{15D(1+\beta)}\right) \simeq R\left(\frac{K}{3k} + \frac{R}{15D}(1-\beta)\right) \tag{19}$$

In above equation, we assume that $\beta \ll 1$, so that $1/(1+\beta) \simeq 1-\beta$. All fluid (gas) characteristics, including β, are contained in ξ.

To illustrate, in Figure 1 we show two breakthrough curves from two different ξ values. We consider at this moment that the change in ξ is solely caused by β. Red solid line is the curve with $\xi = 1$ and blue dashed line $\xi = 2$. We take $K = 1$ and $x = 80$ cm.

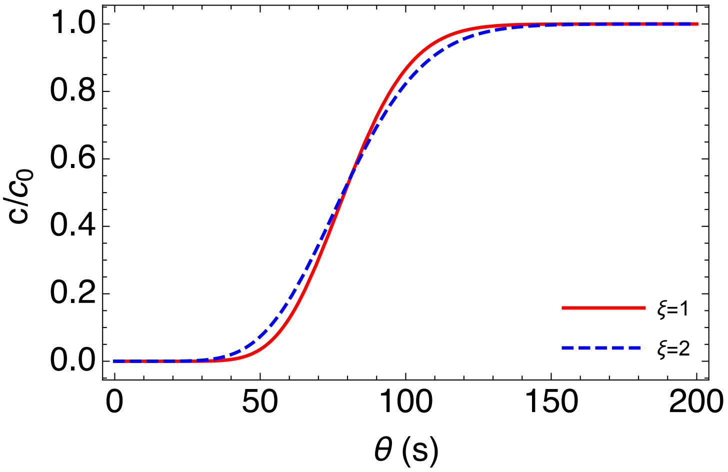

Figure 1: Breakthrough curves for the cases of $\xi = 1$ and $\xi = 2$. Note that the variation in ξ is solely determined by β.

From the figure, we can see that the curve with higher ξ will increase earlier compared to that of lower ξ. However, the curve with lower ξ will increase with higher slope, resulting in quicker saturation. Of course at this level, we still cannot determine whether the presence of β will raise or lower the ξ (the relative sign between a_2 and a_4 can be positive or negative). That is why this value can only be determined through experiment. We believe this approach will find its application, for instance, in fixed-bed column used to separate hydrogen/methane with activated carbon.

Conclusions and Outlook

We have extended the work of [3], where we add a quartic term to the concentration profile. The inclusion leads to a correction to Glueckauf's linear driving force parameter. Such correction is expected to be small but may affect the shape of breakthrough curves, although its significance will depend on experimental data. We hope to extend the result to separation of hydorgen/methane in fixed-bed column with activated carbon.

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