SIMULTANEOUS EFFECT OF AXIAL DISPERSION AND ADSORPTION KINETICS ON A FORM OF THE BREAKTHROUGH CURVE OF AN ADSORBER

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The model of an adsorption bed is described in which the effect of axial dispersion and overall adsorption kinetics on a shape of the breakthrough curve is considered simultaneously. Separation of the effects of convection and axial dispersion from the effect of overall kinetics was achieved applying the method of statistical moments. On the basis of relations derived for the moments, several further characteristics of the breakthrough curves were expressed.

A number of papers have been published during the past 15 years which describe the form of the breakthrough curve of an adsorber by means of the statistical moment. The authors[1-7] used the method of statistical moments for analysis of a number of kinetic effects which are of importance in the sorption process on a fixed bed.

This paper provides results which are of special interest in the adsorption from the gas phase and it represents an extension of our previous paper[8], where only the influence of simultaneous convection and sorption kinetics was considered. The reresults enable one to predict a shape of the breakthrough curve assuming that the static capacity of the bed and the adsorption kinetics, measured for a sample of the column packing are known. The simple criteria derived are useful for a rapid estimation of the importance of various effects on the shape of the breakthrough curves, efficiency of the adsorber, *etc.*.

An advantage of this method is that no detailed knowledge of rate mechanism is needed. It is sufficient to know the time dependence of accumulation of the component sorbed by the sorbent. This information represents a response of the sample to the unit step change of sorbate concentration at the external surface of the sorbent. Usually it is obtained by the gravimetric method.

Such a kinetic measurement must be carried out under conditions close to those of the breakthrough curve. The main difficulty consists in establishing similar hydrodynamic conditions both in the kinetic experiment and in the sorption bed. An experimental arrangement which meets this condition sufficiently well was proposed by Timofeev[9].

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1) It is assumed that the adsorption bed is of constant cross-section and that the geometrical arrangement of the adsorbent packing possesses the following properties: Size and shape distribution of the sorbent particles can be rather general. It can be, however, regarded as homogeneous in the following sense – when selecting a volume element in the bed which is small with respect to the volume of the column but at the same time large enough so that the intergranular porosity α can be defined in it (α is the ratio of the free volume between particles in the given volume element to the volume of this element), one finds the same porosity value for any arbitrarily chosen volume element. The kinetic curve, which one would measure with any of these adsorbent elements would then be identical.

2) An incompressible carrier medium flows with the linear velocity u in the direction of z axis (parallel to the column axis).

3) The adsorption isotherm of the given sorbate–sorbent system is linear

$$a = K \,.\, c\,, \qquad (1)$$

where c is the concentration of the sorbate in the intergranular volume (in mol/cc), a the concentration of the sorbate within the grains of the adsorbent (expressed as the amount of sorbate per a unit volume of granules-including the micropores),

4) The concentration c of the sorbate in the mobile phase is so low that the concentration changes resulting from the sorption do not affect the flow rate of the carrier medium in the intergranular space.

5) It is assumed that the bed is operated under isothermal conditions.

6) The pressure drop along the column is negligible.

7) Axial dispersion characterized by the coefficient D_z (generally depending on hydrodynamic conditions) plays a role in the intergranular space.

The density of the mass-flow in the case of axial dispersion is given by a relation:

$$i_D = -D_z(\partial c/\partial z)\,. \qquad (2)$$

8) It is assumed that the external diffusion can either be neglected or, on contrary, its contribution can be included in the overall adsorption kinetics (*i.e.* that comparable hydrodynamic conditions can be ensured in both types of experiments).

In addition, the following two general conditions must be fulfilled:

A) The adsorber behaves as a linear system (the linearity of the adsorption isotherm is a condition necessary, not satisfactory).

B) All reactions occurring in the system are reversible (admitted are only reactions within the sorbent particles).

Under conditions *1*–*8*, the mass balance equation for a volume element of the adsorber can be written as:

$$\partial C(z,t)/\partial t + u\,\partial C(z,t)/\partial z + (1/\alpha - 1)\,K\,\partial A(z,t)/\partial t$$
$$= D_z\,\partial^2 C(z,t)/\partial z^2\,, \qquad (3)$$

$C(z, t) = c(z, t)/c_0$, c_0 is the concentration of the sorbate in the mobile phase at the inlet of the adsorber, $A(z, t) = \bar{a}(z, t)/a_0$ is the instantaneous value of relative saturation of the adsorbent at a given place of the column, $a_0 = K \,.\, c_0$; t is a time coordinate, measured from the moment when a step change in concentration of the sorbed compound was applied to the inlet of the sorption bed.

As a result of the validity of condition (*A*), the expression $\partial A(z, t)/\partial t$ can be expressed by means of convolution of the function $C(z, t)$ and the function

$$\gamma(\tau) = [m(\tau) - m(\mathrm{o})]/[m(\infty) - m(\mathrm{o})]\,, \qquad (4)$$

This is a kinetic curve showing the time dependence of saturation of the adsorbent sample, assuming that at $\tau = 0$ a concentration step change was applied to the surface of the adsorbent. $m(\tau)$, $m(\mathrm{o})$, $m(\infty)$ denote the amount of the sorbate present in the given sample of the bed packing at the corresponding time.

We can therefore write:

$$\partial A(z,t)/\partial t = \frac{\partial}{\partial t}\int_0^t \partial\gamma(t-\tau)/\partial t\; C(z,\tau)\,\mathrm{d}\tau\,. \qquad (5)$$

The initial and boundary conditions for the adsorption in the bed (free of sorbate at $t = 0$), are

for $t = 0\,,\quad z > 0\quad$ is $\quad C(z, t) = A(z, t) = 0\,, \qquad (6)$

for $t < 0\quad$ is $\quad C(0, t) = 0\,,\quad$ for $\quad t > 0\,,\quad C(0, t) = 1\,, \qquad (7)$

for $t > 0\,,\quad z \to \infty\quad$ is $\quad C(z, t) = 0\,. \qquad (8)$

The condition (*B*) can be formulated as:

for $0 < z < \infty:\quad \lim_{t\to\infty} C(z,t) = \lim_{t\to\infty} A(z,t) = \lim_{\tau\to\infty} \gamma(\tau) = 1\,. \qquad (9)$

Applying the Laplace transform to the system of equations (3), (5), (6), (7), (8) and solving the corresponding boundary-value problem for the ordinary differential equation of second order we obtain solution of the problem in the Laplace domain:

$$s\tilde{C}(z, s) = \exp\{zu/2D_z - z\sqrt{[(u/2D_z)^2 + \omega(s)/D_z]}\}, \tag{10}$$

where

$$\tilde{C}(z, s) = \int_0^\infty e^{-st} C(z, t)\, dt, \tag{11}$$

$$\omega(s) = s\{1 + (1/\alpha - 1) K[s\tilde{\gamma}(s)]\}, \tag{12}$$

$$\tilde{\gamma}(s) = \int_0^\infty e^{-st} \gamma(t)\, dt, \tag{13}$$

where s denotes a complex variable.

As in paper[6] we applied the operational calculus for the straightforward calculation of normal statistical moments of the breakthrough curve $C(z, t)$, using the known relation[10]:

$$\mu'_n = (-1)^n \lim_{s \to 0} \frac{d^n}{ds^n} [s\tilde{C}(z, s)], \quad n = 0, 1, 2, \ldots \tag{14}$$

Applying this relation to equation *(10)* and introducing the normal moments of the kinetic curve $\gamma(\tau)$ according to *(15)*

$$\lambda_n = \int_0^\infty \tau^n (d\gamma/d\tau)\, d\tau = \lim_{s \to 0} \frac{d^n}{ds^n} [s\tilde{\gamma}(s)] \tag{15}$$

we obtain (using the well-known relation between normal and central moments[10]) final expressions for the central moments μ_n of the break through curves.

For the first normal moment of the breakthrough curve we obtain:

$$\mu'_1 = (\mu'_1)_v + (\mu'_1)_a, \tag{16}$$

where $(\mu'_1)_v = z/u$ *(17)* signifies the mean residence time of the molecule in the mobile phase during its motion through the bed and

$$(\mu'_1)_a = (z/u)(1/\alpha - 1) K \tag{18}$$

is the mean residence time of the molecule in the stationary phase.

For the second central moment we get:

$$\mu_2 = (2D_z/U^2)(\mu'_1)_v + 2\lambda_1(\mu'_1)_a = (2D'_z/U^2)\,\mu'_1 + 2\lambda_1(\mu'_1)_a \tag{19}$$

and

$$D'_z = D_z/[1 + (1/\alpha - 1)K], \tag{20}$$

$$U = u[1 + (1/\alpha - 1)K]^{-1}. \tag{21}$$

With respect to the fact that $U = z/\mu'_1$, U in fact represents the mean effective velocity of the motion of the sorbed molecule along the sorbent bed.

In order to explain the meaning of the quantity $2D'_z/U^2$ let us carry out the following consideration, based on the model of Glueckauf[11].

If the sorbent bed is replaced by a number N_D of identical, ideally mixed vessels, in which the adsorption equilibrium between the mobile and stationary phase is established instantaneously in each of the vessels, the substitute system must meet two conditions. First, the overall capacity of the mobile and stationary phase in the system of replaced vessels must equal the corresponding capacity of the adsorber. Second, the total number of vessels must be chosen such that μ_2 in the breakthrough curves of the adsorber and substitute model system are equal.

The mass balance of the sorbate component in the substitute system is expressed by a system of difference-differential equations of the type

$$C_{n-1} - C_n = (\Delta z/u)\,[1 + (1/\alpha - 1)K]\left(\frac{dC_n}{dt}\right), \quad n = 1, 2, 3, \ldots, N_D \tag{22}$$

where $\Delta z = z/N_D$.

For further calculation one can substitute the function $C_n(t)$, defined only in the points $n = 0, 1, 2, \ldots, N_D$ by a function continuous in z; then it is possible to use the Taylor expansion in the neighbourhood of an arbitrary point of the given sequence:

$$C(z - \Delta z, t) - C(z, t) = -\Delta z\,\partial C(z, t)/\partial z + (\Delta z^2/2)\,\partial^2 C/\partial z^2 \tag{23}$$

thus, after the transformation, equation (22) obtains the form:

$$\partial C/\partial t + U\,\partial C/\partial z = [(\Delta z U)/2]\,\partial^2 C/\partial z^2. \tag{24}$$

It can be shown that in agreement with the above formulated equivalence criterion between the original equilibrium column and the substitute model system of mixers (requiring equal μ_2 values of the breakthrough curves) it must hold that

$$D'_z = (\Delta z U)/2. \tag{25}$$

The expression $2D'_z/U^2$ in equation (*19*) has a dimension of time and it will therefore be denoted by a symbol

$$2D'_z/U^2 = \tau_D . \qquad (26)$$

Using equations (*25*), (*20*) and (*21*) we obtain for τ_D:

$$\tau_D = (\Delta z/u)\left[1 + (1/\alpha - 1) K\right] = \mu'_1/N_D . \qquad (27)$$

We can see that τ_D has the meaning of the residence time of a molecule on one mixer.

Equation (*19*) can be therefore rewritten to a form

$$\mu_2 = \mu'_1(\tau_D + 2\lambda_1 f_a) , \qquad (28)$$

where $f_a = (\mu'_1)_a/\mu'_1$ represents a fraction of the time the molecule spends in the adsorbent.

In an analogous way, expressions for the third- and higher order central moments are obtained from the Laplace transform of the breakthrough curves. We present the final expressions only for μ_3 since the practical importance of higher order values is low due to large errors encountered in their experimental estimation.

$$\begin{aligned}\mu_3 &= 3\mu'_1\{(2D'_z/U^2)^2 + (2D'_z/U^2) \,.\, 2\lambda_1 f_a + \lambda_2 f_a\} = \\ &= 3\mu'_1\{(\tau_D)^2 + 2\lambda_1 f_a \tau_D + \lambda_2 f_a\} . \qquad (29)\end{aligned}$$

The equality requirement of μ_2 in the breakthrough curves of the adsorption bed and of the cascade model must hold even for a case where the cascade consists of only one vessel. In such case we obtain a limiting value of μ_2 for the so-called mixed flow adsorber (Carberry reactor).

Denoting residence time of a molecule in the mixed flow reactor as τ_M, and using the equality:

$$\tau_M = \mu'_1 = \tau_D \qquad (30)$$

equation (*28*) gives after substitution

$$\mu_2 = \tau_M^2 + 2\lambda_1 f_a \tau_M \qquad (31)$$

or when expressing $f_a \tau_M$ by means of the dead volume V_t of the adsorber (volume not involving the sorbent particles) and by means of the volume flow rate v:

$$\mu_2 = \tau_M^2 + 2\lambda_1[\tau_M - (V_t/v)] . \qquad (32)$$

Such an approach cannot be applied for the derivation of the higher-order moments of the breakthrough curves of the mixed flow reactor. As follows from direct calculation of the moments by means of equation (*22*) (*i.e.* on basis of the discontinuous model), the contribution to μ_3 caused by mixing is:

$$(\mu_3)_D = 2\tau_M^3 \,. \tag{33}$$

The continuous model would give for a mixed flow reactor in equation (*33*) a coefficient 3, in contradiction with the experimental facts.

Using equations (*28*) and (*29*) we shall express some further characteristics of the adsorption bed.

The number of theoretical plates N of the column is defined by equation (*12*)

$$N = (\mu_1')^2/\mu_2 \,, \tag{34}$$

so that

$$N = \mu_1'[\tau_D + 2\lambda_1 f_a]^{-1} \,. \tag{35}$$

The height of the theoretical plate $H = z/N = z\mu_2/(\mu_1')^2$, measured as a function of μ_1' enables a most convenient experimental determination of the parameters τ_D and λ_1. In fact, by plotting H against $z/\mu_1' \equiv U$ we get an analogy of the van Deemter relation. The term τ_D decreases rapidly with rising U and the relation, after reaching its minimum approaches rapidly the asymptotic linear behaviour $H = 2\lambda_1 f_a U$; thus from the slope of this relation we obtain a quantity $\lambda_1 f_a$. As long as the value of the slope K of the adsorption isotherm K is greater than 100, one can usually regard $f_a \approx 1$, determine λ_1 and finally the quantity $\tau_D(U)$.

In the opposite case it is necessary to determine independently the intergranular porosity α.

Another important characteristics of the breakthrough curve is given by the coefficient of skewness S (ref.[13]).

$$S = \mu_3/\delta^3 \,, \tag{36}$$

where $\delta = \sqrt{\mu_2}$ is a standard deviation. The positive value of this coefficient indicates a breakthrough curve tailing in the positive direction of t. Thus, using equations (*28*), (*29*) and (*36*) we can write:

$$S = 3[\tau_D + B(\tau_D + A)^{-1}]\,[\mu_1'(\tau_D + A)]^{-1/2} \,, \tag{37}$$

where

$$A = 2\lambda_1 f_a \quad \text{and} \quad B = \lambda_2 f_a .$$

For the case of prevailing axial dispersion ($B = A = 0$):

$$S = 3(\tau_D/\mu_1')^{1/2} . \tag{38}$$

In contrast, for the case of prevailing effect of the overall kinetics ($\tau_D = 0$):

$$S = 3[B^2/(\mu_1' A^3)]^{1/2} . \tag{39}$$

The equations (*37*)–(*39*) reflect the well known fact that the increase of column length lowers the asymmetry of the breakthrough curves, proportionally to $z^{-1/2}$.

The presented examples illustrate the way in which the overall adsorption kinetics, represented by the moments of the kinetic curves, affects the behaviour of an adsorption bed under dynamic conditions.

In many cases the derived criteria allow to estimate fast the efficiency of the adsorption bed, the breakthrough time and the extent of utilization of capacity of the adsorption bed[14].

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