DYNAMICS OF ADSORPTION OVER A WIDE RANGE OF BREAKTHROUGH CONCENTRATIONS.

COMMUNICATION 7. DYNAMICS OF ADSORPTION ON A BIPOROUS ADSORBENT

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In [1, 2] we have discussed the rules governing the dynamics of adsorption in the case of mixed-diffusion kinetics when all the resistance to internal mass transfer is determined by diffusion in the transport pores of the adsorbent granules. The present communication discusses the more general case of a biporous adsorbent, when the diffusion resistance is created in the transport pores as well as in the individual microporous zones [3]. As before, we shall consider the isotherm as approximately sharply convex and rectangular; this is justified, for instance, in the adsorption of organic substances by active carbons and zeolites.

In order to simplify the problem, we shall neglect the influence of longitudinal effects, which can be taken into account implicitly in the effective coefficient of external mass exchange. Besides this, the amount of substance present in the space between the granules will be considered as negligibly small in comparison with the amount of substance adsorbed, since the concentration of the component in the adsorbent is usually higher by several orders of magnitude than in the gas stream.

With account of the above limitations the mathematical model for the dynamics of adsorption can be written as follows:

\[ \frac{\partial a}{\partial t} = - v \frac{\partial C}{\partial x} = \beta_0 (C - C_0) \]  
\[ (1 - \varepsilon_i) \frac{\partial a_i}{\partial t} = \varepsilon_i D_t \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_i}{\partial r} \right) \]  
\[ \frac{\partial a_i'}{\partial t} = D_a \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left( \rho^2 \frac{\partial a_i'}{\partial \rho} \right) \]

\[ a_i = \frac{3}{r_0^3} \int_0^{r_0} \rho^2 a_i' d\rho, \quad a = (1 - \varepsilon)(1 - \varepsilon_i) \int_0^R r^2 a_i' dr \]

where \( a, a_i, \) and \( a_i' \) are the mean sorption with respect to the unit volume and the local sorption within the granule and in the microporous zone; \( C, C_0, \) and \( C_i \) are the concentrations of the adsorbed substance in the stream, on the surface of the granules, and in the transport pores; \( x \) and \( t \) are the coordinates of the layer and time; \( v \) is the velocity of the stream with respect to the entire cross section of the layer; \( \beta_0 \) is the coefficient of external mass exchange; \( D_t \) and \( D_a \) are the coefficients of diffusion in the transport pores and the microporous zones; \( \varepsilon \) is the porosity of the layer; \( \varepsilon_i \) is the fraction of transport pores in the volume of the granules; \( r_0 \) and \( R \) are the radii of the microporous zones and the granules.

Equations (1) describe the material balance and the external mass exchange. The diffusion in the transport and microporous zones is described by Eqs. (2) and (3), respectively. The internal mass transfer takes place as follows. The sorption front extends from the surface of the granules toward the center, in which the concentration in the transport pores \( C_i \) changes from \( C_0 \) on the surface to 0 at the internal boundary of the front with the coordinate \( r = r_1 \). Since the isotherm is rectangular, in the moment \( t = t_1 \), as the front approaches a spherical layer within the granule, the sorption on the surface of the microporous zones located on this sphere, increases suddenly to its limiting value. Thus, at this moment the microporous zones become "included" and participate in the process, regardless of the character...
of changes in concentration in the transport pores. For \( t \geq t_1 \), Eq. (3) gives the following solution:

\[
\gamma_i = \frac{a_i}{a_0} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-n^2 \pi^2 D_a r_i^2 (u - t_1)}
\]  

(5)

By introducing dimensionless parameters and variables with account of (5), instead of the system (1)-(4) we can write

\[
\frac{\partial \gamma}{\partial \tau} + \frac{\partial \gamma}{\partial \xi} = 0
\]  

(6)

\[
\frac{\partial \gamma}{\partial \tau} = Bi (y - y_s)
\]  

(7)

\[
\frac{\partial \gamma}{\partial h} = \omega \frac{\partial^2 \gamma}{\partial h^2}
\]  

(8)

where

\[ \gamma = a/a_0 ; \quad y = C/C_0 ; \quad h = r/R ; \quad \tau = D_a t/r_0^2 ; \quad \xi = D_a a_0 x/(r_0^2 v C_0) ; \quad Bi = \beta_r C_0 r_0^2/(a_0 D_a) ; \]

\[ \omega = (1 - e) r_0^2 D_a \sigma^2 / (R^2 a_0 D_a) . \]

By integrating Eq. (8) twice with respect to \( h \), we obtain

\[
\frac{\partial y_i}{\partial h} \bigg|_{h=1} (1 - h) - h y_s + h y_i = \frac{1}{\omega} \frac{\partial}{\partial \tau} \left( \frac{1}{h} \int_{h_1}^{h} y h \gamma_i dh \right) - h \frac{1}{\omega} \frac{\partial}{\partial \tau} \left( \frac{1}{h} \int_{h_1}^{h} \gamma_i dh \right)
\]  

(10)

The latter equation is valid at any value of \( h \). In particular, when \( h = 0 \), we have

\[
\frac{\partial y_i}{\partial h} \bigg|_{h=1} = \frac{1}{\omega} \frac{\partial}{\partial \tau} \left( \frac{1}{h} \int_{h_1}^{h} y h \gamma_i dh \right) - \frac{1}{\omega} \frac{\partial}{\partial \tau} \left( \frac{1}{h} \int_{h_1}^{h} \gamma_i dh \right)
\]  

(11)

where \( h_1 \) is the internal boundary of the sorption front at which \( y_i = 0 \). When \( h = h_1 \), we obtain from (10) with account of (11) and rearrangements

\[
y_i = \frac{1}{\omega} \frac{\partial}{\partial \tau} \left( \frac{1}{h} \int_{h_1}^{h} y h \gamma_i dh \right) - \frac{1}{3 \omega} \frac{\partial \gamma}{\partial \tau}
\]  

(12)

By eliminating \( y_s \) from (7) and (12), we obtain

\[
y = \left( \frac{1}{Bi} - \frac{1}{3 \omega} \right) \frac{\partial \gamma}{\partial \tau} + \frac{1}{\omega} \frac{\partial}{\partial \tau} \left( \frac{1}{h} \int_{h_1}^{h} y h \gamma_i dh \right)
\]  

(13)

Substitution of \( y \) in the material balance equation (6) and integration with respect to \( \tau \) gives

\[
\gamma + \left( \frac{1}{Bi} - \frac{1}{3 \omega} \right) \frac{\partial \gamma}{\partial \xi} + \frac{1}{\omega} \frac{\partial}{\partial \xi} \left( \frac{1}{h} \int_{h_1}^{h} y h \gamma_i dh \right) = 0
\]  

(14)

Here the integration constant is equal to 0. The obtained equation describes the movement of the internal boundary of the sorption front within the granule. For this purpose we can use the operation method. Thus, the image of \( \gamma_i \) takes the form.