KINETIC CURVES FOR A BIPOROUS SORBENT WITH LINEAR SORPTION ISOOTHERMS WITH ALLOWANCE FOR SORPTION IN TRANSPORT PORES

2. GENERAL FORMULAS FOR SPHERICAL GRANULES

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In [1], an analytical solution was discussed for sorption kinetics on a biporous sorbent with linear sorption isotherms and comparable sorption values in transport pores and micropores. It was proposed that the kinetic function of the microporous zones was exponential, and granules in the form of membrane, cylinder, and coaxial cylinder were discussed in detail. In the present work the case of spherical granules is analyzed. Furthermore, we discuss the important practical question of the determination of characteristic diffusion relaxation times $\tau_1$ and $\tau_2$ in a biporous sorbent from the first two moments of the kinetic curve.

For spherical sorbent granules the fundamental equations and conditions of kinetic sorption for the case under consideration can be written [1] as follows:

$$\frac{\partial a}{\partial t} + \frac{\partial c}{\partial t} = D_1 \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right)$$

$$a = k_1 c + A k_2 \int_0^l q'(t - \sigma) c(r, \sigma) d\sigma$$

$$c(R, t) = c_0, \quad c(r, 0) = a(r, 0) = 0, \quad \left( r^2 \frac{\partial c}{\partial r} \right)_{r=0} = 0$$

Let us introduce some new dependent variables:

$$c_1(r, t) = r \cdot c(r, t), \quad a_1(r, t) = r \cdot a(r, t)$$

Then (1)-(3) take the form

$$\frac{\partial c_1}{\partial t} + \frac{\partial a_1}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial r^2}$$

$$a_1 = k_1 c_1 + A k_2 \int_0^l c_1(r, \sigma) q'(t - \sigma) d\sigma$$

$$c_1(R, t) = Rc_0, \quad c_1(r, 0) = a_1(r, 0) = 0, \quad \left[ r \frac{\partial c_1}{\partial r} - c_1 \right]_{r=0} = 0$$

In the case under consideration

$$q(t) = 1 - \exp\left(-t/\tau_2\right)$$

Allowing for the fact that $a_1(r, t)$ approaches a limit as $r \to 0$, we will look for a solution of (5)-(8) as follows [2]:

$$c_1(r, t) = r c_0 + \sum_{n=1}^{\infty} \left( A_n e^{-\delta n^2 t} + A_n^{-} e^{-\delta n^{-} t} \right) \sin \frac{\mu_n r}{R}$$

or,

$$c(r, t) = c_0 + \sum_{n=1}^{\infty} \left( A_n e^{-\delta n^2 t} + A_n^{-} e^{-\delta n^{-} t} \right) \frac{\sin \frac{\mu_n r}{R}}{r}$$
Using the first condition of (7), we obtain

\[ \mu_n = n \cdot \tau_n, \quad n = 1, 2, 3, ... \]  

(11)

Let us substitute (9) into (5) and take (6) into account. After the transformation we find (\( p = A \kappa_2/\tau_a \)):

\[
\begin{align*}
[prc_0 + \sum_n \left( \frac{A_n^+}{1 - \delta_n^+ \tau_a} + \frac{A_n^-}{1 - \delta_n^- \tau_a} \right) \sin \frac{\mu_n r}{R} ] e^{-\frac{t}{\tau_a}} + \\
+ \sum_n \left[ -(1 + k_1) \delta_n^+ + p - \frac{p}{1 - \delta_n^+ \tau_a} + \frac{D \mu_n^2}{R^2} \right] A_n^+ e^{-\delta_n^+ t} \sin \frac{\mu_n r}{R} + \\
+ \sum_n \left[ -(1 + k_1) \delta_n^- + p - \frac{p}{1 - \delta_n^- \tau_a} + \frac{D \mu_n^2}{R^2} \right] A_n^- e^{-\delta_n^- t} \sin \frac{\mu_n r}{R} = 0
\end{align*}
\]

(12)

From (12) it is easy to obtain:

\[ prc_0 + \sum_n \left( \frac{A_n^+}{1 - \delta_n^+ \tau_a} + \frac{A_n^-}{1 - \delta_n^- \tau_a} \right) \sin \frac{\mu_n r}{R} = 0 \]  

(13)

\[ -(1 + k_1) \delta_n^+ + p - \frac{p}{1 - \delta_n^+ \tau_a} + \frac{D \mu_n^2}{R^2} = 0 \]  

(14)

\[ -(1 + k_1) \delta_n^- + p - \frac{p}{1 - \delta_n^- \tau_a} + \frac{D \mu_n^2}{R^2} = 0 \]  

(15)

Furthermore, the second condition of (7) gives

\[ r c_0 + \sum_n (A_n^+ + A_n^-) \sin \frac{\mu_n r}{R} = 0 \]  

(16)

From (14) and (15) we find

\[
\delta_n^\pm = \frac{1}{2q} \left( \frac{1}{\tau_a} + \frac{\mu_n^2}{\tau_i} \right) \pm \sqrt{\frac{1}{4q^2} \left( \frac{1}{\tau_a} + \frac{\mu_n^2}{\tau_i} \right)^2 - \frac{\mu_n^2}{\tau_i \tau_a q}}
\]

(17)

\[ q = \frac{1 + k_1}{4 + 1}, \quad \tau_i = \frac{R^2 (1 + \Gamma)}{D_4}, \quad \Gamma = k_1 + A \kappa_2
\]

The coefficients \( A_n^+ \) and \( A_n^- \) are determined from (13) and (16):

\[
A_n^\pm = \frac{\delta_n^\pm (1 - \delta_n^\pm \tau_a)}{(\delta_n^+ - \delta_n^-)} \cdot \frac{2c_0 R \cos \mu_n}{\mu_n}
\]

(18)

Thus, (10), (17), and (18) give the solution to the problem.

The concentration \( a(r, t) \) is determined, with allowance for (2) and (10), by the expression