ISOTHERMAL ADSORPTION BY BIPOROUS SPHERICAL PARTICLES IN A RESTRICTED VOLUME

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A finite-difference method is used in examining the isothermal one-component adsorption by spherical particles in a restricted volume on the assumptions of nonlinear equilibrium and nonlinearity in the diffusion coefficient.

One can simulate the adsorption by a microporous sorbent by means of a system of equations incorporating the characteristic nonlinear equilibrium, bidisperse pore distribution, and concentration dependence of the diffusion coefficient.

Most models dealing with adsorption on biporous sorbents are restricted to the assumption of isotherm linearity [1-3]; the effects of nonlinearity in the equilibrium relationship have been examined only for a rectangular isotherm [4, 5]. The published models also relate to a particular expression for constant diffusion coefficients. Accumulation in the macropores is usually neglected.

Microporous sorbents are widely used, which requires detailed research on the adsorption kinetics and simulation for various conditions, which requires more accurate models that reflect the mechanism more fully.

Here we present numerical results on isothermal one-component adsorption by spherical particles in a vessel of restricted volume. The model incorporates the following basic features: a) the bidisperse pore distribution; b) the concentration dependence of the diffusion coefficient; c) nonlinear equilibrium of any type of the particles; d) accumulation in the macropores; e) a variable boundary condition at the particle surfaces with allowance for external mass transfer; and f) spherical shapes for the particles and microparticles.

The model is described by the following equations:

1) diffusion in the micropores

$$\frac{\partial \tilde{c}_z}{\partial \tau} = \frac{1}{\tilde{r}^2}\frac{\partial}{\partial \tilde{r}}\left(\tilde{r}^2 \tilde{D}_z(\tilde{c}_z)\frac{\partial \tilde{c}_z}{\partial \tilde{r}}\right),\ 0<\tilde{r}<1, \tag{1}$$

with the boundary conditions

$$\left.\frac{\partial \tilde{c}_z}{\partial \tilde{r}}\right|_{\tilde{r}=0} = 0, \tag{2}$$

$$\tilde{c}_z|_{\tilde{r}=1} = f(\tilde{c}_p); \tag{3}$$

2) mass transfer in the macropores

$$\frac{1}{\delta}\frac{\partial \tilde{c}_p}{\partial \tau} - \nu \left.\frac{\partial \tilde{c}_z}{\partial \tilde{r}}\right|_{\tilde{r}=1} = \frac{1}{\tilde{R}^2}\frac{\partial}{\partial \tilde{R}}\left(\tilde{R}^2\frac{\partial c_p}{\partial \tilde{R}}\right),\ 0<\tilde{R}<1, \tag{4}$$

where the mean accumulation of the adsorbed component in the microparticles is defined as

$$\frac{\partial c_{z\,\mathrm{m}}}{\partial t} = \frac{3}{r_z} D_z(c_z) \left.\frac{\partial c_z}{\partial r}\right|_{r=r_z}.$$

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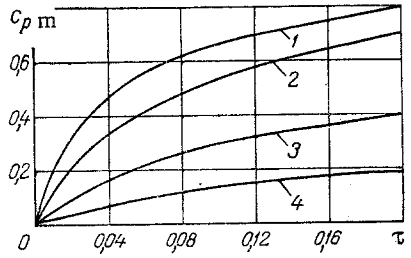

Fig. 1

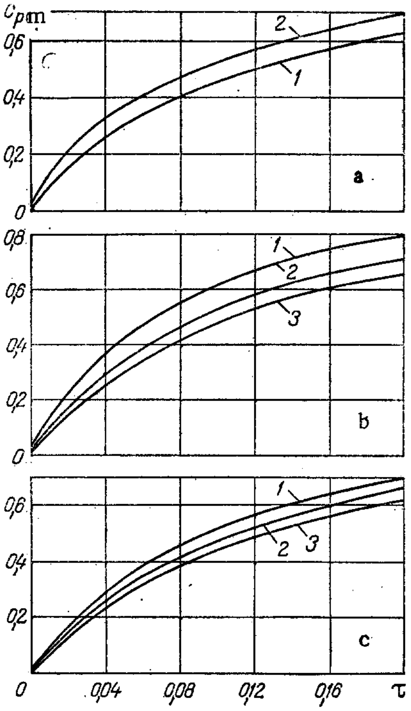

Fig. 2

Fig. 1. Effects on kinetic curves from diffusion resistance in the micropores and macropores.

Fig. 2. Effects on the kinetic curves from accumulation in the macropores (a), isotherm nonlinearity (b), and variable diffusion coefficient in the micropores (c).

The boundary conditions for (4) take the form

$$\left.\frac{\partial \tilde{c}_p}{\partial \tilde{R}}\right|_{\tilde{R}=0} = 0, \tag{5}$$

$$\frac{\partial \tilde{c}}{\partial \tau} = -\lambda \left.\frac{\partial \tilde{c}_p}{\partial \tilde{R}}\right|_{\tilde{R}=1}, \quad \tilde{c} = \tilde{c}_p|_{\tilde{R}=1}. \tag{6}$$

The boundary condition of the type of (6) represents mass transfer in the vessel with ideal mixing in the finite volume V.

To allow for mass transfer via the layers around the particles, we have to replace (6) by

$$\left.\frac{\partial \tilde{c}_p}{\partial \tilde{R}}\right|_{\tilde{R}=1} = \mathrm{Bi}\,(\tilde{c} - \tilde{c}_p)_{\tilde{R}=1}, \tag{7}$$

where the concentration in the surrounding medium is calculated from the balance in the adsorbed material:

$$Wc_{p\mathrm{m}} = V(c_0 - c), \; W = N\pi \frac{4}{3} R_p^3. \tag{8}$$

The mean accumulation in a grain is defined by

$$c_{p\mathrm{m}} = \frac{3}{R_p^3} \int_0^{R_p} c_{z\mathrm{m}} R^2 dR, \quad c_{z\mathrm{m}} = \frac{3}{r_2^3} \int_0^{r_z} c_z r^2 dr.$$

The system was solved by a finite-difference method with a six-point inexplicit scheme for approximating the derivatives. As the isotherm is nonlinear and the diffusion coefficient is variable, we use an interative procedure, with the following linearization for the equilibrium

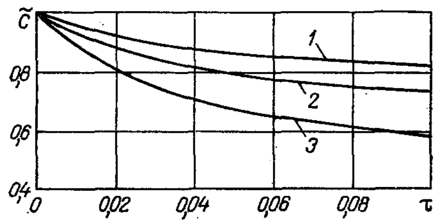

Fig. 3

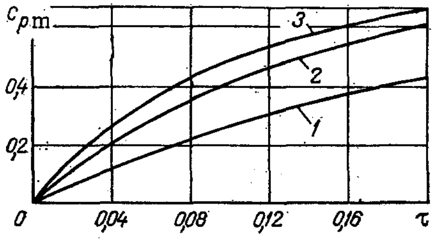

Fig. 4

Fig. 3. Effect of restricted gas volume around particles on mean concentration in vessel.

Fig. 4. Effects of external mass transfer on kinetic curves.

dependence: $\tilde{c}_{z(it+1)} = f\,(\tilde{c}_{p(it)} + [\tilde{c}_{p(it+1)} - \tilde{c}_{p(it)}]\left(\dfrac{\partial f}{\partial \tilde{c}_p}\right)_{it}$. Numerical experiments were performed to examine the effects of the parameters; Figs. 1-4 show the results. The kinetic curves in Fig. 1 enable one to examine the assumptions. Curve 1 corresponds to a monoporous sorbent ($\nu = 0$). The values of ν give curves 2 and 4 to correspond to the kinetic curves for the cases of predominant diffusion in the micropores ($\nu \to 0$, curve 2) and in the macropores ($\nu \to \infty$, curve 4). The general case incorporates comparable effects from the diffusion resistance in the macropores and micropores, and this is represented by curve 3.

Figure 2a shows the solution with allowance for accumulation in the macropores (curve 1) and without it (curve 2), the variable being the dimensionless δ. The difference between the kinetic curves in the limiting cases of Figs. 1 and 2a confirms that it is necessary to use models with bidispersed pores. Neglect of the biporous structure in interpreting the experiments leads to differences in the diffusion coefficients by several orders of magnitude [3, 6].

Isotherm nonlinearity was examined for the Langmuir equation

$$\tilde{c}_z|_{r=1} = \frac{\tilde{c}_p}{S + (1 - S)\,\tilde{c}_p},$$

where S varying in the range from 0 to 1 corresponds to the shape of the equilibrium curve varying from rectangular to linear. Figure 2b shows the results as $\tilde{c}_{p\,m} = f(\tau)$ curves for $S = 0.4$ (curve 1), $S = 0.8$ (curve 2), and $S = 1.0$ (curve 3). As the isotherm curvature increases, the kinetic curves become steeper and the grains are more rapidly filled.

The effects of variable diffusion coefficient were examined for a fractionally linear concentration dependence (Fig. 2c):

$$\tilde{D}_z = \frac{1}{1 - \left(\dfrac{1}{\varkappa} - 1\right)\tilde{c}_z};$$

where for $\kappa < 1$ the diffusion in a grain accelerates as the concentration increases (curve 1), while with $\kappa = 1$ the diffusion coefficient is constant (curve 2), and for $\kappa > 1$ the diffusion coefficient decreases as the concentration increases (curve 3).

The nonlinearity in the isotherm and the diffusion coefficient control the number of iterations required to produce convergence; usually, three or four iterations were sufficient for a given time step, but twice as many were required at the start.

We also examined the effects of the form of boundary condition. The assumptions of ideal mixing and restricted gas volume require a balance for the diffusion fluxes through the particle surfaces as boundary condition. The effects of the restricted volume are expressed by the dimensionless parameter λ. Figure 3 shows the concentration as a function of time in the surroundings for $\lambda = 0.5$ (curve 1), $\lambda = 0.8$ (curve 2), and $\lambda = 1.5$ (curve 3). The curves in Fig. 4 correspond to simultaneous effects from the restricted gas volume [Eq. (8)] and the external mass transfer around the particles [Eq. (7)]. The kinetic curves show the effects of external mass transfer for Bi = 4, with external-diffusion kinetic control (curve 1), Bi = 20, namely the joint effects from external and internal diffusion (curve 2), and Bi = 4000, i.e., negligibly small effect from external mass transfer (curve 3).

NOTATION

$\tilde c_z$, $\tilde c_p$, $\tilde c$, Dimensionless concentrations in micropores, macropores, and medium; $c_{p,m}$, mean concentration in a grain, dimensionless; $\tilde c_z = c_z/c_{z0}$, $\tilde c_p = c_p/c_0$, $\tilde c = c/c_0$; $c_{z,m}$, mean concentration in micropores, dimensionless; $\tilde r$, R, dimensionless radial coordinates in micropores and macropores, $\tilde r_z = r/r_z$, $\tilde R = R/R_p$; $\tau = tD_{z0}/r_z^2$; $\tilde D = D_z/D_{z0}$; $\nu = \frac{3(1-\varepsilon_p)}{\varepsilon_p}\frac{c_{z0}}{c_{p0}}\frac{1}{\delta}$; $\delta = D_p r_z^2/(R_p^2 D_{z0})$; $\lambda = 3\varepsilon_p W_p/(V\delta)$; Bi = Biot number, S, parameter in the Langmuir equation; κ, parameter in the linear-fractional concentration dependence; W, V, volumes of solid phase and medium; N, number of adsorbent particles; r_z, microcrystal radius; R_p, grain radius.

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MASS REMOVAL IN FORMATION OF INTERNAL CAVITIES IN METALS BY CHEMICAL ETCHING

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Mass removal in cavity formation within metals is studied and the principles governing the processes are established.

New methods for chemical etching of metal and alloy surfaces have recently been developed. Ever greater use is being made of forced supply of the liquid reagent to the surface being processed. Thus, for example, it was shown in [1-3] that use of a liquid jet not only allows control of the mass exchange process, but significantly increases the intensity of mass removal in the region of jet interaction with the surface.

The present study will establish the principles of mass removal governing application of a jet of chemically active liquid within a metallic specimen.

Experimental studies have shown that in this situation a cavity which grows in size with time is formed within the metal (Fig. 1). The experiments were performed with full size specimens of the alloy MA-8. Specimen diameter was 110 mm, with a height of 120 mm. Etching was performed by a 7.36% solution of sulfuric acid in distilled water. An orifice 10 mm in diameter was drilled into the specimen to a depth h_0, into which an atomizer with nozzle diameter of 3 mm was installed. To maintain constant flow conditions the distance from the nozzle to the depth h_0 was kept at 5 mm. The liquid was supplied through nozzle 1 and removed

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