



MATHEMATICAL MODELING. MATHEMATICS

МАТЕМАТИЧНЕ МОДЕЛЮВАННЯ. МАТЕМАТИКА

UDC 538.931

MODEL OF NANOPOROUS MEDIUM WITH CHARGED IMPURITIES

Ihor Boiko; Mykhailo Petryk; Dmytro Mykhalyk

Ternopil Ivan Puluj National Technical University, Ternopil, Ukraine

Summary. *Mathematical model of nanoporous medium with two-level process of particles mass transfer in the presence of positively charged impurities was constructed and investigated. For the considered model, the theory of the process of mass transfer has been developed by finding self-consistent solutions of the Fick-Nernst and Poisson equations, and the electric fields generated in a nanoporous medium depending on the concentration of absorbed charged particles are calculated.*

Key words: *nanoporous media, selfconsistent solution, mass transfer, absorption.*

Received 29.09.2017

Statement of the problem. Theoretical and experimental investigation of physical mass transfer processes in nanoporous medium [1 – 3] as well as the processes of adsorption [4] and desorption [5] connected with them are of vital importance for many branches of modern science and engineering. Transient mass transfer process in nanoporous medium saturated by zeolite molecules occurs due to internal concentration gradients in micro- and macropores of sorbent or adsorbent determined by temperature conditions within investigated medium. In case when external designative factors are neglected, the mass transfer process is considered to be steady. In such development mathematical models of adsorption are based on the main balance equations and boundary conditions and equilibrium conditions. It is assumed that mass transfer occurs along nanoporous medium stratum depth and here Fick-Nernst law is realized [6]. Under such conditions adsorbate phase transfer from nanopores medium to inter-particle space has equilibrium character and is determined on the basis of convex isotherm of Langmuir desorption. However consideration of dissipation process, particularly the influence of adsorbed particles space charge current on mass transfer process defines the need for modification of the investigated mathematical models.

Analysis of the latest researches and publications. It should be noticed that at present there is actually no papers where mass transfer models were modified in order to describe investigated processes more clearly. Related problems concerning the influence of space charge on mass transfer processes were investigated in papers [7, 8] but their results cannot be used directly for the problems connected with the processes in nanoporous medium.

The objective of the paper. The objective of the given paper is to construct and investigate the mathematical model of mass transfer in nanoporous medium with positively

charged adsorbate particles present in it. It provides more clear description of mass transfer process in nanoporous medium and enables to determine factors having the greatest influence on the given process.

Statement of the task. Let us consider complicated system of mass transfer for two diffusion component in catalytic medium formed by microparticles with nanoporous structure. Diffusion processes in the given system are characterized by two types of mass transfer: diffusion in macropores in intercrystallite space and diffusion in intraparticle space. It is assumed that the layer with thickness l consists of the large number of nanoporous particles approximated by microstructures of spherical shape of radius R ($0 < R < l < +\infty$) containing adsorbate components with charged impurities (Fig. 1). In such a case diffusion process for two gases occurs in axial direction z of the macropores space (from 1 to 0) and radial space for each microparticle (R to 0). Providing that diffusion process is steady it is also supposed that concentration gradients of transferred components in macropores and nanopores of nanoparticles slightly change till equilibrium is reached. This allows us to assume that thermal effects are slight, diffusion process occur according to Henry's law. In general case it is assumed that nanoporous particles have the same size and are closely-packed within each medium layer [1 – 3].

The mathematical model describing kinetics of gas desorption in the investigated system taking into account physical factors which determine the given process is described by equation in partial derivatives expressed for concentrations $C_s(z, t)$, $Q_s(r, z, t)$ for areas $\Omega_T = (0, T) \times \Omega$, $\Omega = (0, l)$. Thus:

$$\frac{\partial C_s(z, t)}{\partial t} = \frac{D_{\text{inter}}^{(s)}}{l^2} \frac{\partial^2 C_s(z, t)}{\partial z^2} + e_{\text{iner}} K_s \frac{D_{\text{intra}}^{(s)}}{R^2} \frac{\partial Q_s(r, z, t)}{\partial r} \quad (1)$$

- being equation describing diffusion in intercrystallite space,

$$\frac{\partial Q_s(r, z, t)}{\partial t} = \frac{D_{\text{intra}}^{(s)}}{R^2} \left(\frac{\partial^2 Q_s(r, z, t)}{\partial r^2} + \frac{2}{r} \frac{\partial Q_s(r, z, t)}{\partial r} \right) \quad (2)$$

- being equation describing diffusion in intraparticle space.

Considering that the part of particles captured by micropores has charge, the total charge within the microparticle is as follows:

$$q_{\text{intra}}(x, r, t) = \frac{4}{3} \pi \eta q_{\text{intra}}^{(s)} Q_s(x, r, t) R^3, \quad (3)$$

where $0 \leq \eta \leq 1$ is the content of charged particles in separate microparticle, $q_{\text{intra}}^{(s)}$ – is the charge of particular charged particle.

In such a case the microparticles are considered to be charged and the electrical potential within each microparticle is determined by Poisson equation:

$$\frac{\partial^2 \varphi(r, z, t)}{\partial z^2} + \frac{\partial^2 \varphi(r, z, t)}{\partial r^2} = - \frac{\rho_{\text{intra}}(r, z, t)}{\varepsilon_{\text{intra}} \varepsilon_0}, \quad (4)$$

where

$$\rho_{\text{intra}}(r, z, t) = \eta q_{\text{intra}}^{(s)} Q_s(r, z, t) \quad (5)$$

- is the charge density within the microparticle.

For concentrations $C_s(z, t)$ i $Q_s(r, z, t)$ initials are realized:

$$C_s(z, t)|_{t=0} = C_{s0}; \quad Q_s(r, z, t)|_{t=0} = Q_{s\infty} \quad (6)$$

and homogeneous boundary conditions of macropores are:

$$C_s(z, t)|_{z=l} = 0; \quad \left. \frac{\partial C_s(z, t)}{\partial z} \right|_{z=0} = 0. \quad (7)$$

and symmetry boundary conditions for microparticles equilibrium are:

$$\left. \frac{\partial Q_s(r, z, t)}{\partial r} \right|_{r=R} = 0; \quad Q_s(r, z, t)|_{r=R} = Q_s(z, t). \quad (8)$$

Besides for potential $\varphi(r, z, t)$ proper boundary conditions connected with its and electric displacement vector finiteness are:

$$\varphi(r, z, t)|_{r=R} = \varphi_{\text{inter}}; \quad \varepsilon_{\text{inter}} \left. \frac{\partial \varphi(r, z, t)}{\partial r} \right|_{r=R} = \varepsilon_{\text{intra}} E_{\text{inter}}, \quad (9)$$

where

$$\begin{aligned} \varphi_{\text{inter}} &= \sum_{i=1}^N \varphi_{\text{inter}}(r_i) \delta(R - r_i) \approx \frac{1}{2} \frac{1}{V} \int_V \frac{\eta q_{\text{intra}}^{(s)} Q_s(r, z)}{4 \varepsilon_{\text{intra}} \varepsilon_0 r} dV = \\ &= \frac{\eta}{4 \varepsilon_{\text{intra}} \varepsilon_0 R^2 l} \int_0^R \int_0^\pi r \sin \theta d\theta Q_s(r, r \cos \theta); \\ E_{\text{inter}} &\approx \frac{\varphi_{\text{inter}}}{l} \end{aligned} \quad (10)$$

- being average values of potential and electric field strength in external medium, $\varepsilon_{\text{inter}}$ i $\varepsilon_{\text{intra}}$ - material dielectric permittivity of internal and external medium respectively.

As is evident from the structure of equations system (1) – (2), (4), then taking into account boundary and initial conditions (6) – (9) it is nonlinear. It is worthwhile to find its solution using the method of finite differences. Then the solution of the system of equations (1) – (2), (4) is found on trimetric uniform space-time network $\overline{\omega}_{hp\tau}$ in Ω_T . In order to do that we introduce one-dimensional networks:

$$\begin{aligned} \overline{\omega}_h &= \{r_i = ih, i = 0, 1, \dots, N_1\}; \\ \overline{\omega}_p &= \{z_p = jp, j = 0, 1, \dots, N_2\}; \\ \overline{\omega}_\tau &= \{t_k = k\tau, k = 0, 1, \dots, N_3\}, \end{aligned} \quad (11)$$

where

$$h = \frac{R}{N_1}; \quad p = \frac{L}{N_2}; \quad \tau = \frac{T}{N_3}, \quad (12)$$

then:

$$\overline{\omega}_{hp\tau} = \overline{\omega}_h \times \overline{\omega}_p \times \overline{\omega}_\tau = \{(ih, jp, k\tau), \quad i = 0, 1, \dots, N_1, \quad j = 0, 1, \dots, N_2, \quad k = 0, 1, \dots, N_3\}. \quad (13)$$

Approximating according to the method of finite differences [9] first-order and higher-order derivatives we get:

$$\begin{aligned} \frac{\partial C_s(z, t)}{\partial t} &\sim \frac{C_s^{(i, j, k)} - C_s^{(i, j, k+1)}}{\tau}; \quad \frac{\partial^2 C_s(z, t)}{\partial z^2} \sim \frac{C_s^{(i, j-1, k)} - 2C_s^{(i, j, k)} + C_s^{(i, j+1, k)}}{p^2}; \\ \frac{\partial Q_s(r, z, t)}{\partial x} &\sim \frac{Q_s^{(i+1, j, k)} - Q_s^{(i, j, k)}}{h}; \quad \frac{\partial Q_s(r, z, t)}{\partial t} = \frac{Q_s^{(i, j, k)} - Q_s^{(i, j, k+1)}}{\tau}; \\ \frac{\partial^2 Q_s(r, z, t)}{\partial r^2} &\sim \frac{Q_s^{(i-1, j, k)} - 2Q_s^{(i, j, k)} + Q_s^{(i+1, j, k)}}{h^2}; \quad \frac{\partial Q_s(r, z, t)}{\partial r} = \frac{Q_s^{(i+1, j, k)} - Q_s^{(i, j, k)}}{h}; \\ \frac{\partial^2 \varphi(r, z, t)}{\partial z^2} &\sim \frac{\varphi_s^{(i, j-1, k)} - 2\varphi_s^{(i, j, k)} + \varphi_s^{(i, j+1, k)}}{p^2}; \quad \frac{\partial^2 \varphi(r, z, t)}{\partial r^2} \sim \frac{\varphi_s^{(i-1, j, k)} - 2\varphi_s^{(i, j, k)} + \varphi_s^{(i+1, j, k)}}{h^2}. \end{aligned} \quad (14)$$

Approximation of initial and boundary conditions results in:

$$\begin{aligned} C_s^{(i, j, 0)} &= C_{s0}; \quad Q_s^{(i, j, 0)} = Q_{s\infty}; \\ C_s^{(i, N_2, k)} &= 0; \quad C_s^{(i, 0, k)} = C_s^{(i, 1, k)}; \\ Q_s^{(N_1-1, j, k)} &= Q_s^{(N_1, j, k)}; \quad Q_s^{(N_1, j, k)} = Q_s^{(0, j, k)}; \\ \varphi_s^{(N_1, j, k)} &= \varphi_{\text{inter}}; \quad \varphi_s^{(N_1, j, k)} - \varphi_s^{(N_1-1, j, k)} = \frac{\mathcal{E}_{\text{intra}}}{\mathcal{E}_{\text{inter}}} E_{\text{inter}}. \end{aligned} \quad (15)$$

Taking into account (14) from self-consistent equation system (1), (2) and (4), initial and boundary conditions (6) – (9) we derive difference scheme:

$$\left[\begin{aligned} h\tau C_s^{(i, j-1, k)} - C_s^{(i, j, k)} i(j^2 + 2k) + j^2 k C_s^{(i, j, k+1)} + ik C_s^{(i, j+1, j)} - e_{\text{iner}} K_s \frac{D_{\text{intra}}^{(s)}}{R^2} (Q_s^{(i, j, k)} - Q_s^{(i+1, j, k)}) &= 0; \\ \frac{D_{\text{intra}}^{(s)} \tau}{R^2 h^2} Q_s^{(i-1, j, k)} - \left\{ 1 + 2 \frac{D_{\text{intra}}^{(s)} \tau}{R^2 h} \left(\frac{1}{h} + \frac{1}{r^{(p)}} \right) \right\} Q_s^{(i, j, k)} + Q_s^{(i, j, k+1)} + \frac{D_{\text{intra}}^{(s)} \tau}{R^2 h} \left\{ \frac{1}{h} + \frac{2}{r^{(p)}} \right\} Q_s^{(i+1, j, k)} &= 0; \\ p^2 \varphi_s^{(i-1, j, k)} - 2(h^2 + p^2) \varphi_s^{(i, j, k)} + h^2 \varphi_s^{(i, j-1, k)} + h^2 \varphi_s^{(i, j+1, k)} + p^2 \varphi_s^{(i+1, j, k)} &= - \frac{p^2 h^2 \rho_{\text{intra}}^{(i, j, k)}}{\mathcal{E}_{\text{intra}} \mathcal{E}_0}; \\ C_s^{(i, j, 0)} &= C_{s0}; \quad Q_s^{(i, j, 0)} = Q_{s\infty}; \\ C_s^{(i, N_2, k)} &= 0; \quad C_s^{(i, 0, k)} = C_s^{(i, 1, k)}; \\ Q_s^{(N_1-1, j, k)} &= Q_s^{(N_1, j, k)}; \quad Q_s^{(N_1, j, k)} = Q_s^{(0, j, k)}; \\ \varphi_s^{(N_1, j, k)} &= \varphi_{\text{inter}}; \quad \varphi_s^{(N_1, j, k)} - \varphi_s^{(N_1-1, j, k)} = \frac{\mathcal{E}_{\text{intra}}}{\mathcal{E}_{\text{inter}}} E_{\text{inter}}. \end{aligned} \right. \quad (16)$$

Here the solution of the difference scheme (16) is found by sweep method.

Conclusions.

The mathematical model which allows to consider the effect of captured particles on the given process is offered for the systems with double-level mass transfer process. Using the method of finite differences we get difference scheme describing the solution of the investigated mathematical model. These results provide the development of mass transfer theory in nanoporous medium taking into account the influence of internal and applied external fields.

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УДК 538.931

МОДЕЛЬ НАНОПОРИСТОГО СЕРЕДОВИЩА З ЗАРЯДЖЕНИМИ ДОМІШКАМИ

Ігор Бойко; Михайло Петрик; Дмитро Михалик

*Тернопільський національний технічний університет імені Івана Пулюя,
Тернопіль, Україна*

Резюме. Побудовано та досліджено математичну модель нанопористого середовища з дворівневим процесом масопереносу частинок за наявності позитивно заряджених домішок. Для моделі, яку розглядаємо, шляхом знаходження самоузгоджених розв'язків системи рівнянь Фіка-Нернста та Пуассона, розвинено теорію процесу масопереносу та проведено розрахунок електричних полів, що виникають у нанопористому середовищі, залежно від концентрації абсорбованих заряджених часток.

Ключові слова: нанопористе середовище, самоузгоджений розв'язок, масоперенос, абсорбція.

Отримано 29.09.2017