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MATHEMATICAL MODELING OF COMPETITIVE ADSORPTION AND DESORPTION OF GASES IN NANOPOROUS MEDIA USING LANGMUIR'S EQUILIBRIUMS

The theoretical bases of mathematical modeling of nonisothermal competitive adsorption and desorption in nanoporous zeolite media for the extended Langmuir's equilibrium are given. They most fully determine the mechanism of adsorption equilibrium for nanoporous particles media. The effective scheme of linearization of a nonlinear model is implemented. High-speed analytical solutions of the system of linearized boundary problems of adsorption and desorption in nanoporous media are justified and obtained using the Heaviside's operational method.

Key words and phrases: Heaviside's operational method, Competitive adsorption and desorption of gases, mathematical modelling, extended Langmuir's equilibrium, Laplace integral transformation.

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INTRODUCTION

The main anthropogenic sources of atmospheric pollutants are the processes by which energy is generated for transport and industry. It has been demonstrated that the transport sector is the emission source that contributes the most to global warming at present, and it will probably remain so in the immediate future [1]. The quality of mathematical models of processes of adsorption and desorption of hydrocarbons in nanoporous catalytic media determines the effectiveness of technological solutions for neutralizing and reducing exhaust emissions which is rapidly increasing, contributing to global warming [2].

At present, many experimental and theoretical studies of such processes are carried out, especially studies on the improvement of their mathematical models, taking into account the influence of various factors that limit the internal kinetics of adsorption and desorption in nanopores of catalytic media [3, 4, 5, 6, 7, 8]. For the first time, it has been possible to specify

УДК 517.444

2010 *Mathematics Subject Classification:* 35B30, 44-XX.

all the processes along the columns during non-isothermal adsorption and desorption. The proposed work outlines the theoretical foundations for modeling nonisothermal competitive adsorption and desorption in nanoporous catalysts for a nonlinear isotherm obtained by the Nobel laureate I. Langmuir, which most fully determines the mechanism of adsorption equilibrium for nanopores systems of the zeolite. For the modeling we have used the Heaviside operational method and the Laplace transform, but the development of calculations is quite original. This methodology allows you to get high-speed analytical solutions that improve the quality of computational paralleling and the simulation of real process.

1 MATHEMATICAL MODEL OF NONISOTHERMAL ADSORPTION AND DESORPTION IN A NANOPOROUS PARTICLES MEDIA

The general hypothesis adopted in the model development is that the competitive adsorption interaction between adsorption molecules of two gases and active adsorption centres on the phase separation surface in crystallites nanopores is determined on the basis of the nonlinear competitive adsorption Langmuir equilibrium's with allowance of the following physical assumptions [6, 7, 8, 9]. The refined kinetics of non-isothermal competitive adsorption and desorption in nanoporous zeolites, taking into account the nonlinear function of adsorption equilibrium and the given physical justifications, is described by the following system of nonlinear partial differential equations [9, 10]:

$$\frac{\partial c_i(t, z)}{\partial t} + \frac{\partial a_i(t, z)}{\partial t} + u \frac{\partial c_i}{\partial z} = D_{inter_i} \frac{\partial^2 c_i}{\partial z^2}, i = \overline{1, 2}, \quad (1)$$

$$-H \frac{\partial T(t, z)}{\partial t} - u h_g \frac{\partial T}{\partial z} - Q_{ads} \left(\frac{\partial a_1}{\partial t} + \frac{\partial a_2}{\partial t} \right) - 2 \frac{\alpha_h}{R_{column}} T + \Lambda \frac{\partial^2 T}{\partial z^2} = 0, \quad (2)$$

$$\frac{\partial a_i}{\partial t} = \beta \left(c_i - \frac{1}{k'_{0i} \exp\left(-\frac{\Delta H}{RT}\right)} \frac{a_i/a_{full}}{1 - a_1/a_{full} - a_2/a_{full}} \right), i = \overline{1, 2}. \quad (3)$$

Initial conditions for adsorption are as follows:

$$c_i(t, z)|_{t=0} = 0; T(t, z)|_{t=0} = T_0^{(0)} \quad (4)$$

and for desorption:

$$c_i(t, z)|_{t=0} = c_{0i}^{(0)}; T(t, z)|_{t=0} = T_0^{(0)}. \quad (5)$$

Boundary conditions for adsorption are as follows:

$$c_i(t, z)|_{z=0} = c_{in}; \frac{\partial}{\partial z} c_i(t, z)|_{z=\infty} = 0; T(t, z)|_{z=0} = T_{in}; \frac{\partial}{\partial z} T(t, z)|_{z=\infty} = 0 \quad (6)$$

and for desorption:

$$c_i(t, z)|_{z=0} = c_{in}(t); \frac{\partial}{\partial z} c_i(t, z)|_{z=\infty} = 0; T(t, z)|_{z=0} = T_{in}(t); \frac{\partial}{\partial z} T(t, z)|_{z=\infty} = 0. \quad (7)$$

The meaning of the terms in conditions (1)-(7) is given in the Nomenclature section.

2 THE SCHEME OF NONLINEAR MODEL LINEARIZATION AND CONSTRUCTION OF SOLUTION FOR SYSTEM OF LINEARIZED PROBLEMS

Based on the development of the methodology [9, 12, 13] we perform some expansions in the series of elements of the nonlinear component $\frac{1}{\exp(-\frac{\Delta H}{RT})} \frac{a_i/a_{full}}{1-a_1/a_{full}-a_2/a_{full}}$ of the differential equation (3) in following form:

$$\begin{aligned} \frac{\partial a_1}{\partial t} &= \beta \left(c_1(t, z) - K_1 a_1(t, z) + \varepsilon a_1(t, z) \left(a_1(t, z) + \frac{1}{2} a_2(t, z) + \theta T(t, z) \right) \right); \\ \frac{\partial a_2}{\partial t} &= \beta \left(c_2(t, z) - K_2 a_2(t, z) + \varepsilon a_2(t, z) \left(\frac{1}{2} a_1(t, z) + a_2(t, z) + \theta T(t, z) \right) \right), \end{aligned} \quad (8)$$

where $K_i = \frac{1+\Delta H/R}{k'_{01} a_{full}} \exp\left(\frac{\Delta H}{RT_{eq,i}}\right)$, $i = \overline{1, 2}$ is the adsorption constants (according to Henry's law), $\varepsilon = \frac{1+\frac{\Delta H}{R}}{k'_{01} (a_{full})^2} \exp\left(\frac{\Delta H}{RT_{eq1}}\right) \ll 1$ is a small parameter that takes into account the nonlinear component of the competitive adsorption isotherm, $\theta = \frac{a_{full}}{1+\frac{\Delta H}{R}} \frac{\Delta H}{R} \frac{1}{T_{eq1}^2}$, $\frac{a_i}{a_{full}} < 1$, $i = \overline{1, 2}$.

Problem (1)-(7), taking into account the approximated kinetic equations of Langmuir adsorption equilibrium's (8) containing a small parameter ε , is boundary problem for a nonlinear system of second-order partial differential equations. The solution of problem (1)-(7) will be sought using of asymptotic expansions [12, 13]:

$$\begin{aligned} c_i(t, z) &= c_{i_0}(t, z) + \varepsilon c_{i_1}(t, z) + \varepsilon^2 c_{i_2}(t, z) + \dots, \\ T(t, z) &= T_0(t, z) + \varepsilon T_1(t, z) + \varepsilon^2 T_2(t, z) + \dots, \\ a_i(t, z) &= a_{i_0}(t, z) + \varepsilon a_{i_1}(t, z) + \varepsilon^2 a_{i_2}(t, z) + \dots, \quad i = \overline{1, 2} \end{aligned} \quad (9)$$

In the result of substituting the asymptotic sum (9) into (1)-(7), considering (8), the initial nonlinear boundary value problem (1)-(7) is parallelized into two types of linearized boundary value problems:

Proposition 1. *The problem A_{i_0} , $i = \overline{1, 2}$ (zero approximation with initial and boundary conditions of the initial problem): to find a solution in the domain*

$D = \{(t, z) : t > 0, z \in (0, \infty)\}$ of a system of partial differential equations:

$$\frac{\partial c_{i_0}(t, z)}{\partial t} + \frac{\partial a_{i_0}(t, z)}{\partial t} + u \frac{\partial c_{i_0}}{\partial z} = D_{inter_i} \frac{\partial^2 c_{i_0}}{\partial z^2}, \quad i = \overline{1, 2}, \quad (10)$$

$$-H \frac{\partial T_0(t, z)}{\partial t} - u h_g \frac{\partial T_0}{\partial z} - Q_{ads} \left(\frac{\partial a_{1_0}}{\partial t} + \frac{\partial a_{2_0}}{\partial t} \right) - 2 \frac{\alpha_h}{R_{columnn}} T_0 + \Lambda \frac{\partial^2 T_0}{\partial z^2} = 0, \quad (11)$$

$$\frac{\partial a_{i_0}}{\partial t} = \beta (c_{i_0} - K_i a_{i_0}). \quad (12)$$

Initial conditions for adsorption:

$$c_{i_0}(t, z)|_{t=0} = 0; \quad T_0(t, z)|_{t=0} = T_0^{(0)} \quad (13)$$

and for desorption:

$$c_{i0}(t, z)|_{t=0} = c_{i0}^{(0)}; T_0(t, z)|_{t=0} = T_0^{(0)}. \quad (14)$$

Boundary conditions for adsorption:

$$c_{i0}(t, z)|_{z=0} = c_{in}; \frac{\partial}{\partial z} c_{i0}(t, z)|_{z=\infty} = 0; T_0(t, z)|_{z=0} = T_{in}; \frac{\partial}{\partial z} T_0(t, z)|_{z=\infty} = 0 \quad (15)$$

and for desorption:

$$c_{i0}(t, z)|_{z=0} = c_{iin}(t); \frac{\partial}{\partial z} c_{i0}(t, z)|_{z=\infty} = 0; T_0(t, z)|_{z=0} = T_{in}(t); \frac{\partial}{\partial z} T_0(t, z)|_{z=\infty} = 0. \quad (16)$$

Proposition 2. *The problem $A_n; n = \overline{1, \infty}$ (n -th approximation with zero initial and boundary conditions): to construct in the domain D a bounded solution of a system of equations*

$$\frac{\partial c_{in}(t, z)}{\partial t} + \frac{\partial a_{in}(t, z)}{\partial t} + u \frac{\partial c_{in}}{\partial z} = D_{inter} \frac{\partial^2 c_{in}}{\partial z^2}, i = \overline{1, 2} \quad (17)$$

$$-H \frac{\partial T_n(t, z)}{\partial t} - uh_g \frac{\partial T_n}{\partial z} - Q_{ads} \left(\frac{\partial a_{1n}}{\partial t} + \frac{\partial a_{2n}}{\partial t} \right) - 2 \frac{\alpha_h}{R_{column}} T_n + \Lambda \frac{\partial^2 T_n}{\partial z^2} = 0, \quad (18)$$

$$\frac{\partial a_{1n}}{\partial t} = \beta \left(c_{1n} - K_1 a_{1n} - \sum_{i=0}^{n-1} \left(a_{1i}(t, z) \left(a_{1, n-1-i}(t, z) + \frac{1}{2} a_{2, n-1-i}(t, z) + \theta T_{n-1-i}(t, z) \right) \right) \right), \quad (19)$$

$$\frac{\partial a_{2n}}{\partial t} = \beta \left(c_{2n} - K_2 a_{2n} - \sum_{i=0}^{n-1} \left(a_{2i}(t, z) \left(\frac{1}{2} a_{1, n-1-i}(t, z) + a_{2, n-1-i}(t, z) + \theta T_{n-1-i}(t, z) \right) \right) \right). \quad (20)$$

with zero initial boundary conditions. Developing the methodologies [12, 13] and supposing that the sought and determined functions of the system (10)-(16), (17)-(20) are Laplace originals, we obtained limited analytical solutions of boundary value problems using Heaviside operational method [14, 15]. The analytic solution of the zero approximation problem, which describes the dependence of the absorptive concentration in the gas phase (interparticle space), of the temperature and of adsorbate concentration in nanoporous particles along the coordinate of the catalytic bed and in time for the adsorption ($c_{i0}(t, z)|_{t=0} = 0; c_{i0}(t, z)|_{z=0} = c_{iin}; T_0(t, z)|_{z=0} = T_{in}$) and desorption cycles ($c_{i0}(t, z)|_{t=0} = c_{i0}^{(0)}; c_{i0}(t, z)|_{z=0} = c_{iin}(t); T_0(t, z)|_{z=0} = T_{in}(t)$):

$$\begin{aligned} c_{i0}(t, z) = & c_{iin}(0) e^{\frac{u}{2D_{inter_i}} z} \Phi_{c_i}^0(t, z) + e^{\frac{u}{2D_{inter_i}} z} \int_0^t \frac{d}{d\tau} c_{iin}(\tau) \Phi_{c_i}^0(t - \tau, z) d\tau + \\ & + c_{i0}^0 \frac{K_i}{K_i + 1} \left(1 + \frac{1}{K_i} e^{-\beta(K_i+1)t} - \frac{K_i + 1}{K_i} e^{\frac{u}{2D_{inter_i}} z} \Phi_{c_i}^0(t, z) \right) + \\ & + \beta c_{i0}^0 e^{\frac{u}{2D_{inter_i}} z} \int_0^t e^{-\beta(K_i+1)(t-s)} \Phi_{c_i}^0(\tau, z) d\tau \end{aligned} \quad (21)$$

$$\begin{aligned}
 T_0(t, z) &= T_{in}(0) \Phi_T^0(t, z) + \int_0^t \frac{d}{d\tau} T_{in}(\tau) \Phi_T^0(t - \tau, z) + \\
 &+ \frac{1}{\Lambda} \int_0^t \int_0^\infty [HT_0^0 \mathcal{H}_T(t - \tau; z, \xi) - \\
 Q_{ads}\beta &\left(\mathcal{H}_T(t - \tau; z, \xi) - \beta K_1 \int_0^{t-\tau} e^{-\beta K_1(t-\tau-s)} \mathcal{H}_T(\tau - s; z, \xi) ds \right) c_1(\tau, \xi) - \\
 -Q_{ads}\beta &\left(\mathcal{H}_T(t - \tau; z, \xi) - \beta K_2 \int_0^{t-\tau} e^{-\beta K_2(t-\tau-s)} \mathcal{H}_T(\tau - s; z, \xi) ds \right) c_2(\tau, \xi) \Big] d\xi d\tau,
 \end{aligned} \tag{22}$$

$$a_{i_0}(t, z) = \beta \int_0^t e^{-\beta K_i(t-\tau)} c_{i_0}(\tau, z) d\tau. \tag{23}$$

The analytic solution of the problem A_{i_n} , $n = \overline{1, \infty}$ describing the temporal spatial distributions n -th approximations of adsorption condensations in the gas phase $c_{i_n}(t, z)$, of temperature $T_n(t, z)$ and of adsorption (the adsorbate concentration in particle nanopores) $a_{i_n}(t, z)$ for desorption adsorption stages:

$$\begin{aligned}
 c_{1_n}(t, z) &= \frac{\beta}{D_{inter_1}} \int_0^\tau \int_0^\infty \left[\mathcal{H}_{c_1}(t - \tau; z, \xi) - \beta K_1 \int_0^{t-\tau} e^{-\beta K_1(\tau-s)} \mathcal{H}_{c_1}(s; z, \xi) ds \right] \times \\
 &\times \sum_{i=0}^{n-1} a_{1_i} \left(a_{1,n-1-i} + \frac{1}{2} a_{2,n-1-i} + \theta T_{n-1-i} \right) (\tau, \xi) d\xi d\tau; \\
 c_{2_n}(t, z) &= \frac{\beta}{D_{inter_2}} \int_0^\tau \int_0^\infty \left[\mathcal{H}_{c_2}(t - \tau; z, \xi) - \beta K_2 \int_0^{t-\tau} e^{-\beta K_2(\tau-s)} \mathcal{H}_{c_2}(s; z, \xi) ds \right] \times \\
 &\times \sum_{i=0}^{n-1} a_{2_i} \left(\frac{1}{2} a_{1,n-1-i} + a_{2,n-1-i} + \theta T_{n-1-i} \right) (\tau, \xi) d\xi d\tau,
 \end{aligned} \tag{24}$$

$$\begin{aligned}
 T_n(t, z) &= \frac{Q_{ads}\beta}{\Lambda} \int_0^t \int_0^\infty \left[\left(\mathcal{H}_T(t - \tau; z, \xi) - \beta K_1 \int_0^{t-\tau} e^{-\beta K_1(t-\tau-s)} \mathcal{H}_T(s; z, \xi) ds \right) \times \right. \\
 &\times \left[\sum_{i=0}^{n-1} a_{1_i} \left(a_{1,n-1-i} + \frac{1}{2} a_{2,n-1-i} + \theta T_{n-1-i} \right) (\tau, \xi) - c_{1_n}(\tau, \xi) \right] + \\
 &+ \left(\mathcal{H}_T(t - \tau; z, \xi) - \beta K_2 \int_0^{t-\tau} e^{-\beta K_2(t-\tau-s)} \mathcal{H}_T(s; z, \xi) ds \right) \times \\
 &\times \left. \left[\sum_{i=0}^{n-1} a_{2_i} \left(\frac{1}{2} a_{1,n-1-i} + a_{2,n-1-i} + \theta T_{n-1-i} \right) (\tau, \xi) - c_{2_n}(\tau, \xi) \right] \right] d\xi d\tau
 \end{aligned} \tag{25}$$

$$\begin{aligned}
a_{1_n}(t, z) &= \beta \int_0^t e^{-\beta K_1(t-\tau)} \left(c_{1_n}(\tau, z) - \sum_{i=0}^{n-1} a_{1_i} \left(a_{1,n-1-i} + \frac{1}{2} a_{2,n-1-i} + \theta T_{n-1-i} \right) (\tau, z) \right) d\tau; \\
a_{2_n}(t, z) &= \beta \int_0^t e^{-\beta K_2(t-\tau)} \left(c_{2_n}(\tau, z) - \sum_{i=0}^{n-1} a_{2_i} \left(\frac{1}{2} a_{1,n-1-i} + a_{2,n-1-i} + \theta T_{n-1-i} \right) (\tau, z) \right) d\tau.
\end{aligned} \tag{26}$$

Here:

$$u_{1_i} = \frac{u}{D_{inter_i}};$$

$$\mathcal{H}_T(\tau; z, \xi) = e^{-\frac{u_2}{2}(z-\xi)} (\Phi_T(\tau, |z-\xi|) - \Phi_T(\tau, z+\xi));$$

$$\mathcal{H}_c(\tau; z, \xi) = e^{-\frac{u_1}{2}(z-\xi)} (\Phi_c(\tau, |z-\xi|) - \Phi_c(\tau, z+\xi));$$

$$\Phi_{c_i}^0(t, z) = \frac{1}{\pi} \int_0^\pi e^{-\varphi_{1_i}(\nu)z} \frac{\sin(\nu t - z\varphi_{2_i}(\nu)^2)}{\nu} d\nu + e^{-\frac{u}{2D_{inter_i}}z};$$

$$\Phi_{A_i}(t, z) = \frac{1}{2\pi} \int_0^\infty \frac{\varphi_{1_i}(\nu) \cos(\nu t - \varphi_{2_i}(\nu)z) + \varphi_{2_i}(\nu) \sin(\nu t - \varphi_{2_i}(\nu)z)}{(\Gamma_{1_i}^2(\nu) + \nu^2 \Gamma_{2_i}^2(\nu))^{1/2}} d\nu;$$

$$\Phi_T^0(t, z) = \frac{1}{\pi} \int_0^\infty e^{-\varphi_1(\nu)z} \frac{\sin(\nu t - z\varphi_2(\nu)^2)}{\nu} d\nu + e^{-\frac{u}{2\Lambda}z};$$

$$\Phi_T(t, z) = \frac{1}{2\pi} \int_0^\infty \frac{\varphi_1(\nu) \cos(\nu t - \varphi_2(\nu)z) + \varphi_2(\nu) \sin(\nu t - \varphi_2(\nu)z)}{(\Gamma_{T_1}^2(\nu) + \nu^2 \Gamma_{T_2}^2(\nu))^{1/2}} d\nu;$$

$$\varphi_{1,2_i}(\nu) = \left[\frac{(\Gamma_{1_i}^2(\nu) + \nu^2 \Gamma_{2_i}^2(\nu))^{1/2} \pm \Gamma_{1_i}^2(\nu)}{2} \right]^{1/2}; \quad \Gamma_{1_i}(\nu) = \frac{u^2}{4D_{inter_i}^2} + \frac{\nu^2 \beta}{D_{inter_i}^2 (\nu^2 + \beta^2 K_i^2)};$$

$$\Gamma_{2_i}(\nu) = \frac{\nu^3 + \nu\beta^2 (K_i + 1) K_i}{D_{inter_i} (\nu^2 + \beta^2 K_i^2)}, \quad i = \overline{1, 2}; \quad \Gamma_{T_1}(\nu) = \frac{u^2 + 8 \frac{\alpha_h}{R_{column}}}{4\Lambda^2}; \quad \Gamma_{T_2}(\nu) = \frac{H\nu}{\Lambda}. \tag{27}$$

3 NUMERICAL MODELLING AND DISCUSSION

The objective of this computer modelling is to study the capabilities of the proposed model to its use in gas separation technologies, in catalysis, for the purification of air, in particular for the elimination of carbon emissions into the atmosphere from industry and transport (propane, CO_2 and other combustion products). Propane was chosen as the adsorbate because it corresponds to approximately 30% by volume of the total gas flow emitted by car engines [2]. Using the developed mathematical theory and technology oriented to parallel multicore computer calculations, the modeling and calculation of concentration

dependencies of non-isothermal adsorption and desorption curves in a zeolite ZSM-5 bed are carried out.

Computational calculations were performed with such experimental papers [6, 7, 11]: Geometric dimensions of the column: length: $l = 1.2 \cdot 10^{-2} \text{ m}$ and radius $R_{\text{column}} = 2,3 \cdot 10^{-3} \text{ m}$. Thermal and mass transfer characteristics: $Q_{\text{ads}} = 2800 \text{ kJ/kg}$; $\Lambda = 0.5 \text{ kJ}/(\text{m}^2 \cdot \text{s})$; $h_g = 1.2 \text{ kJ}/\text{m}^3 \cdot \text{s}$ (for propane at 3 bar); $\rho_a = 650 \text{ kg}/\text{m}^3$ (bulk density of zeolite material); $H = 0.96 \text{ kJ}/\text{kg} \cdot \text{K}$; $D_{\text{inter}} = 5.0 \cdot 10^{-6} \text{ m}^2/\text{s}$; $\beta = 0.95 \text{ s}^{-1}$ [6, 10]. Initial gas flow temperature: for adsorption $T = 20^\circ\text{C}$, for desorption $T = 300 - 350^\circ\text{C}$. In order to analyze the effect of changes in flow velocity, a range of 0.2 -2m/s was considered (adsorption, desorption). To ensure the process of the propane desorption from the nanopores of the zeolite, the column with zeolite sample was heated to a temperature of 300-350°C.

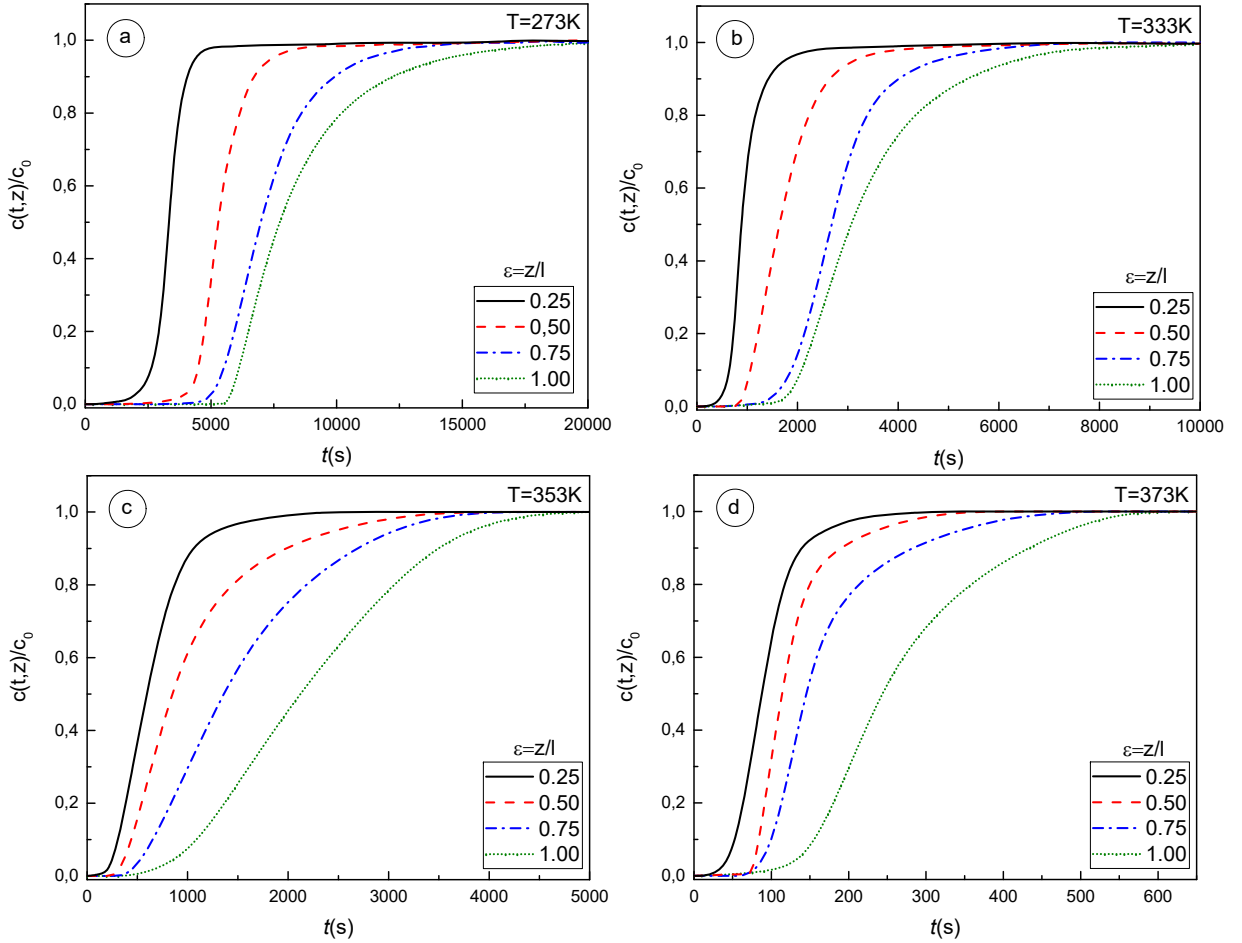


Figure 1: Calculated adsorbate concentrations for breakthrough curves, which are calculated as a function of time t for different temperature values 273K (a), 333K (b), 353K (c), 373K (d).

Using the equations (24) and (26), the adsorbate concentrations in inter- and intracrystallites spaces were calculated. In Fig. 1a, b, c, d of the concentration, $c(t, z)$, in such column and at the temperatures 30 °C, 60 °C, 100°C, 350°C of the bed are shown as function on time t . Direct calculations were performed for various geometric configurations of the

adsorption column, characterized by its relative height $\varepsilon = z/l$ relative to its true size l . The presented simulation results clearly demonstrate the effect of temperature and magnitude of ε on the change in the concentration of propane in the inter-crystalline space. As can be seen from Fig. 1a, b, c, d for all values and for all calculated values of temperature, the behavior of the dependence of the relative value $c(t, z)/c_0$ is qualitatively the same: in a certain time interval differently for the values of temperature and ε there is a rapid increase in the value of concentration with its subsequent reaching saturation. However, it should be noted that for different values of temperature, the value of the interval in which the time evolution of concentration occurs rapidly decreases with increasing of temperature. In particular, the calculated time intervals for the concentration to saturate at temperatures of 273K and 373K. In addition, an important observed effect is that, with an increase in ε , the saturation of $c(t, z)/c_0$ value is reached each time later. This, firstly, indicates that in different geometrical positions of the adsorption column, the saturation concentration does not occur simultaneously, and, secondly, this makes it possible to establish the characteristic value of the value of the time required to achieve a uniform propane concentration in the space of the zeolite sample in the adsorption column.

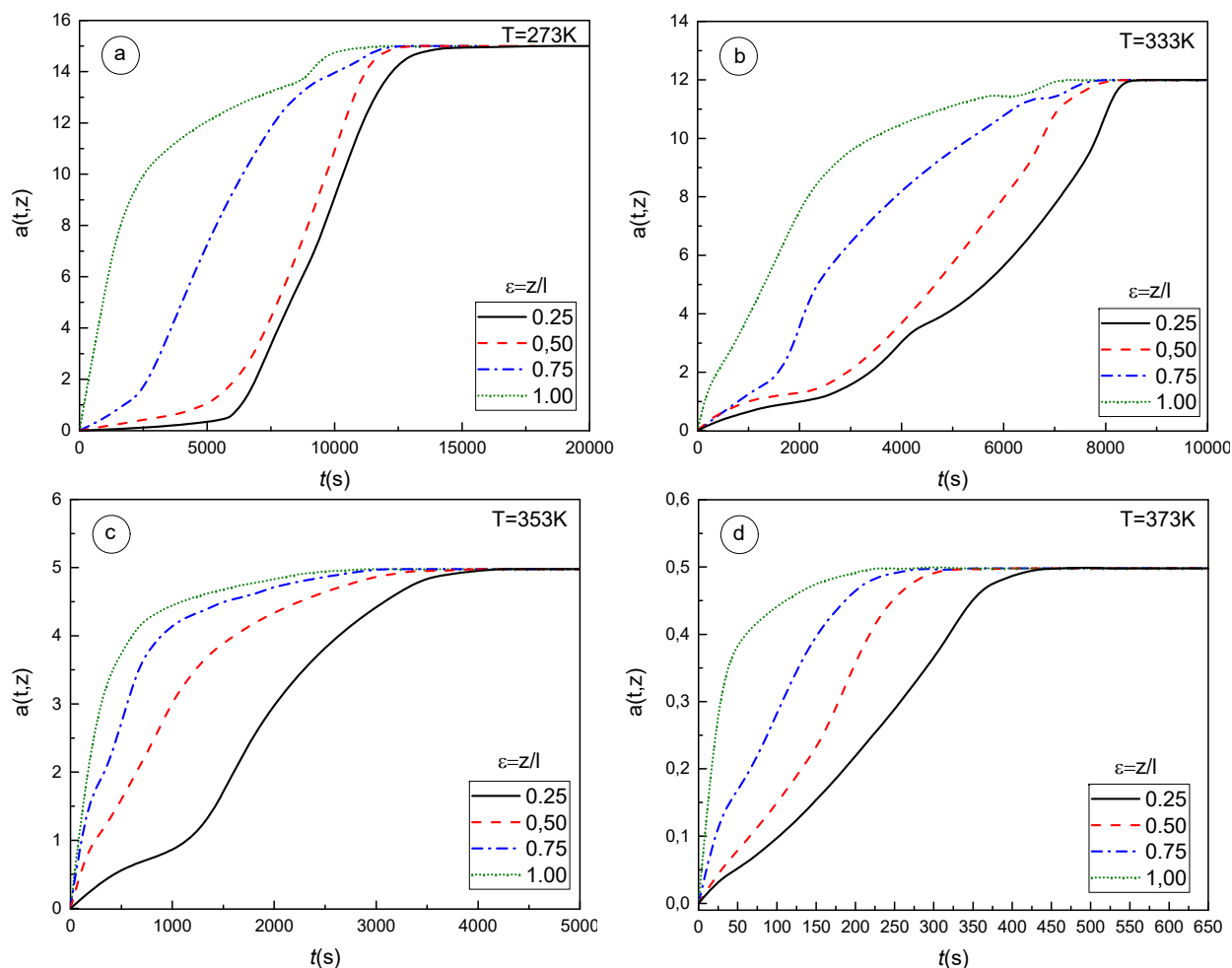


Figure 2: The adsorbate concentration in the intraparticle space as a function of time t , calculated for temperature values 273K (a), 333K (b), 353K (c), 373K (d)

In Fig. 2a, b, c, d are shown the time dependencies for the adsorbate concentration $a(t, z)$ in the intraparticle space ((25)), the calculations of which within the developed mathematical model were performed with similar calculations for $c(t, z)$ values of temperature ((??)) and relative height ε of the adsorption column. As can be seen from Fig. 2, the time dependencies $a(t, z)$ grow, reaching their maximum values corresponding to the saturation of the propane concentration in the pores of the zeolite. In this case, in contrast to the dependencies $c(t, z)$, the achievement of the maximum concentration value occurs in the order of decreasing ε . In addition, all concentration values $a(t, z)$ calculated for a fixed temperature value reach the same maximum values regardless of the value of ε .

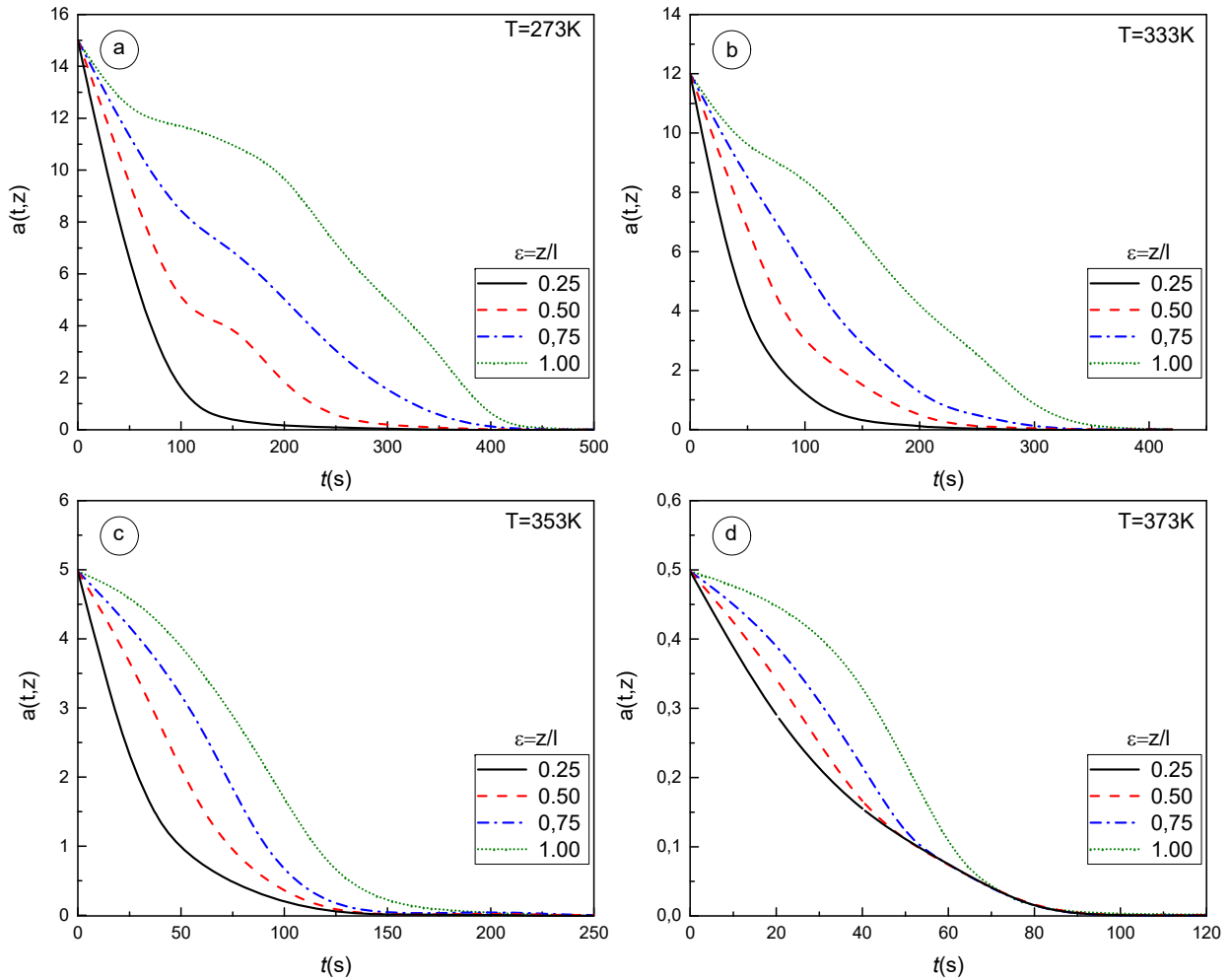


Figure 3: The adsorbate concentration in the intraparticle space as a function of time during the desorption process, calculated for temperature values 273K (a), 333K (b), 353K (c), 373K (d)

In Fig. 3a, b, c, d are shown the time dependencies calculated in the developed model for the propane concentrations in the intraparticle space, which correspond to the desorption process. The beginning of the desorption process, which is shown in Fig. 3 corresponds to the moment of completion of the process shown in Fig. 2, in particular, the initial values of the concentrations $a(t, z)$ correspond to their saturation values during adsorption in the

intraparticle space. It can be seen from the given dependencies that the process of propane desorption from zeolite micropores occurs more intensively with increasing temperature. Each of the curves $a(t, z)$ successively, with decreasing ε , reaches the values $a(t, z) \rightarrow 0$. Also, in this case, there is a clear tendency for the $a(t, z)$ dependencies to converge for different values of ε with increasing temperature. This effect is can be explained by the equalization of the intensity of the desorption kinetics for different ε at high temperatures and low propane concentrations. In particular, for the dependencies shown in Fig. 3c, first the merging of the $a(t, z)$ curves for different ε is observed, and then the curve formed by their merging goes to zero.

4 CONCLUSIONS

Proposed mathematical modeling research has confirmed the effectiveness of the proposed model and software for adsorption-desorption technology to absorb gases, in particular carbon oxides that cause global warming. The spatial distribution of the adsorbate concentrations in inter-particle space and in micropores of solid are obtained with the achievement of equilibrium conditions, as well as the distributions of the gas flow temperature over time and the coordinates of the column length. It also allows evaluating the behavior of concentration dependencies, achieving their equilibrium from temperature and gas flow rate for different coordinate positions along the column length and other factors. But this was not only the main goal of this study. Analytical solutions of the proposed mathematical model of the gas adsorption on microporous bed is based on the original mathematical apparatus and an efficient high-performance algorithm using the Heaviside operational method and the Laplace transform using the generalized Langmuir equilibrium equation, which most fully describes the processes of phase transformations. The development of calculations is quite original. The result allows instantly getting the dynamics of the kinetics of the process in columns during non-isothermal adsorption and desorption - the current adsorbate concentrations in interparticle space and in micropores of the bed and the temperature of gas flow. This original mathematical treatment can serve as a model for many applications related to this type of process, mainly to clean atmospheres, which will help reduce the impact of global warming.

The theoretical foundations of mathematical modeling of nonisothermal competitive adsorption and desorption in nanoporous catalysts for the nonlinear Langmuir isotherm that best describes the mechanism of adsorption equilibrium for micro- and nanoporous systems of the ZSM-5 zeolite class are outlined. An effective linearization scheme for the nonlinear model is realized. High-speed analytical solutions of the system of linearized boundary-value problems of competitive adsorption and desorption in nanoporous media are substantiated and obtained using the Heaviside operational method.

5 NOMENCLATURE

$c_i, i = \overline{1, 2}$ - concentrations of absorptive i in the gas phase in the column, (mol/m^{-3});
 a_i - concentration of moisture absorptive i in the solid phase;

T - temperature of gas phase flow, (K);
 u - velocity of gas phase flow, (m/s);
 ρ_{ads} density of adsorbent, (kg/km^3);
 M_{ads} - molar mass of adsorbent, kg/mol ;
 D_{inter} - effective longitudinal diffusion coefficients, (m^2/s);
 Λ - coefficient of thermal diffusion along the columns, ($kJ/kg \cdot m^2/s$);
 h_g - gas heat capacity, ($kJ/kg \cdot K$);
 h - total heat capacity of the adsorbent and gas, ($kJ/kg \cdot K$);
 ΔH - energy of activity, (kJ/mol);
 $Q = \Delta H/M_{ads}$ - specific heat of adsorption (adsorption heat capacity), (kJ/kg);
 R - universal gas constant;
 α_h - heat transfer coefficient, ($kJ/(kg \cdot K \cdot m \cdot s)$);
 K_1, K_2 - Henry constants;
 β - mass transfer coefficient, (m/s);
 z - distance from the top of the bed for mathematical simulation, (m);
 in - index of parameter names (concentration, temperature) in the inlet of the column.

REFERENCES

- [1] Berezansky Yu. M. Expansions in eigenfunctions of self-adjoint operators. Translations of Mathematical Monographs Vol. 17, Providence, R.I.: Am. Math. Soc., 1968, 809 p.
- [2] Puertolas B., Navarro M.V., Lopez J.M., Murillo R., Mastral A.M., Garcia T. *Modelling the heat and mass transfers of propane onto a ZSM-5 zeolite*. Separation and Purification Technology 2012, **107** (2), 126–136. doi:10.1016/j.seppur.2011.10.036
- [3] Barrer, R.M. Diffusion and Flow in Porous Zeolite, Carbon or Ceramic Media, Characterization of Porous Solids, Society of Chemical Industry, London, 1979.
- [4] Karger J. and Ruthven D. Diffusion in Zeolites and Other Microporous Solids, John Wiley and Sons, New York, 1992.
- [5] Karger J., Ruthven D., Theodorou D. Diffusion in Nanoporous Materials. John Wiley and Sons, Hoboken, 2012.
- [6] Krishna R., Van Baten J.M. *Investigating the Non-idealities in Adsorption of CO₂ -bearing Mixtures in Cation-exchanged Zeolites*. Separation and Purification Technology 2018, **206** (11), 208–217. doi:j.seppur.2018.06.009
- [7] Leclerc S., Petryk M., Canet D., Fraissard J. *Competitive Diffusion of Gases in a Zeolite Using Proton NMR and Slice Selection Procedure*. Catalysis Today 2012, **187** (1), 104–107. doi:10.1016/j.cattod.2011.09.007
- [8] Petryk M., Leclerc S., D. Canet, Sergienko I.V., Deineka V.S., Fraissard J. *The Competitive Diffusion of Gases in a zeolite bed: NMR and Slice Procedure, Modelling and Identification of Parameters*. The Journal of Physical Chemistry C 2015, **119** (47), 26519–26525. doi:10.1021/acs.jpcc.5b07974
- [9] Petryk M., Khimitch A., Petryk M.M. *Simulation of Adsorption and Desorption of Hydrocarbons in Nanoporous Catalysts of Neutralization Systems of Exhaust Gases Using Nonlinear Langmuir Isotherm*. J. Autom. Inf. Sci. 2018, **50** (18), 18–31. doi:/10.1615/JAutomatInfScien.v50.i10.20
- [10] Petryk M., Khimitch A., Petryk M.M., Fraissard J. *Experimental and computer simulation studies of dehydration on microporous adsorbent of natural gas used as motor fuel*. Fuel 2019, **239** (1), 1324–1330. doi:10.1016/j.fuel.2018.10.134

- [11] Lebovka N., Petyk M., Tatchenko M., Vygornitskii N. *Two-stage random sequential adsorption of discorrectangles and disks on a two-dimensional surface*. Physical Review E 2023, **108** (1), 024109. doi:10.1103/PhysRevE.108.024109
- [12] Petryk M., Boyko I., Fessard J., Lebovka N. *Modelling of non-isothermal adsorption of gases in nanoporous adsorbent based on Langmuir equilibrium*. Adsorption 2023, **29** (9), 141–150 . doi:10.1007/s10450-023-00389-9
- [13] M. R. Petryk, I. V. Boyko, O. M. Khimich, M. M. Petryk. *High-Performance Supercomputer Technologies of Simulation of Nanoporous Feedback Systems for Adsorption Gas Purification*. Cybernetics and Systems Analysis 2020, **56** (5), 835–847 . doi:10.1007/s10559-020-00304-y
- [14] Staines, J. *The Heaviside Operational Calculus: The Laplace Transform for Electrical Engineers*, Amazon, CreateSpace Independent Publishing Platform, Scotts Valley, California, 2013.
- [15] Doetsch, G. . *Handbuch der Laplace-Transformation: Band I: Theorie der Laplace-Transformation*, Springer, Basel AG, 1950.

Received 15.12.2023

Петрик М.Р., Бойко І.В., Петрик О.Ю. (in Ukrainian) *Математичне моделювання компетитивної адсорбції та десорбції газів у нанопористих середовищах з використанням рівноваги Ленгмюра* // Буковинський матем. журнал — 2023. — Т.11, №2. — С. 59–70.

Подані теоретичні основи математичного моделювання процесів компетитивних адсорбції і десорбції (двох газів) в нанопористих каталітичних середовищах, що ґрунтуються на механізмах рівноваги, описаних нелінійною неізотермічною залежністю Ленгмюра. Отримані результати найбільш повно визначають механізм адсорбційної рівноваги для середовищ нанопористих частинок типу цеоліт, що складають два простори: міжчастинковий і внутрічастинковий. Шляхом розкладу нелінійних залежностей опису адсорбційної рівноваги в точках фазового переходу (температури адсорбції/десорбції) та обґрунтування малого параметру реалізована ефективна схема декомпозиції вихідної нелінійної моделі на еквівалентну систему лінеаризованих моделей. З використанням операційного методу Гевісайда, інтегрального перетворення Лапласа та методу функцій впливу Коші обґрунтовані та побудовані високопродуктивні точні аналітичні розв'язки системи лінеаризованих крайових задач компетитивних адсорбції і десорбції в нанопористому середовищі. Це дало можливість отримати взаємозалежні часово-просторові розподіли концентрацій дифундованих компонентів адсорбату у міжчастинковому та внутрічастинковому просторах, а також температури газового потоку з урахування енергії активації (теплоти адсорбції) та інших лімітуючих чинників кінетики процесу. На основі цих отриманих аналітичних фізичних залежностей виконанні їх алгоритмічна реалізація, що дозволяє розпаралелювання обчислень та комп'ютерне моделювання режимних параметрів цих процесів, досліджені умови адсорбційної рівноваги компонентів адсорбату для міжчастинкового та внутрічастинкового просторів для циклів адсорбції та десорбції в широкому температурному діапазоні.