Information System for Adsorption Parameters Identification in NanoPorous Media

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Abstract
This paper presents the information system based on a mathematical model of complex adsorption prosses in a heterogeneous media of microporous particles, which allows for the identification of the diffusion coefficients in intraparticle space. The algorithm of identification is based on the gradient method, which was implemented and tested for efficiency on experimental data obtained using the nuclear magnetic resonance method. The obtained results were also tested for adequacy to experimental observations and used for numerical simulation and analysis of the kinetics of adsorption and concentration gradient fields.

Keywords 1
modeling, diffusion coefficients, gradient method, identification, numerical simulation

1. Introduction

Well-known, scientists often utilize experimental methods to monitor and evaluate the state of intricate physical objects, such as the complex adsorption systems used for mass transport in nanoporous media (such as zeolites). These methods are based on the most recent advancements in the fields of systems analysis and mathematical modeling [1-3].

Zeolites are currently employed in numerous industrial sectors (including medicine, petrochemistry, catalysis, and separations), owing to their multidimensional pore system, which can be broken down into two critical subsystems: a micro- and nano-pore system with exceptional adsorption capacity and a low degree of diffuse infiltration (intraparticle space), and a macropore system (voids between the particles of the medium), which is characterized by low spaciousness and rapid penetration (interparticle space) [4-7].

Previous papers have discussed the challenge of mathematically modeling the two-level adsorption mass transfer that occurs within catalytic media made up of microporous particles [8, 9]. However, an important issue that still requires attention is the identification of the kinetic parameters associated with the internal process. These parameters play a crucial role in the mass transfer flow and are instrumental in laying the groundwork for the development of new technologies.

The objective of this study was to identify diffusion coefficients while considering the developed theory of optimal control for complex systems, mathematical models of adsorption mass transfer in heterogeneous media consisting of nanoporous particles, and their analytical and numerical solutions [10], along with the results of experimental studies [11]. To achieve this goal, the direct and conjugate problems statements of the identification problem were established, and a gradient procedure was employed to identify the kinetics of the transfer. Ultimately, the distributions of diffusion coefficients for interparticle mass transfer in porous media were obtained.

2. Mathematical model

The mathematical model for one-component adsorption mass transfer can be described as the construction of a solution set of equations [12]:

$$\frac{\partial c_m}{\partial t} = D_{\text{inter}_m} \frac{\partial^2 c_m}{\partial z^2} - \frac{3(1-\varepsilon_{\text{inter}})}{\varepsilon_{\text{inter}}} \frac{D_{\text{intra}}}{R} \left(\frac{\partial q_m}{\partial r} \right)_{r=R},$$
(1)

$$\frac{\partial q_m}{\partial t} = D_{\text{intra}_m} \left(\frac{\partial^2 q_m}{\partial r^2} + \frac{2}{r} \frac{\partial q_m}{\partial r} \right)$$
(2)

in domain $I_m = \left\{ t > 0, r \in (0,R), z \in \bigcup_{m=1}^{n+1} (l_{m-1}, l_m); l_0 = 0; l_{m+1} \equiv l < \infty \right\}$,

with zero initial conditions:

$$c_m(t,z)\big|_{t=0} = 0; \qquad\qquad q_m(t,r,z)\big|_{t=0} = 0;$$
(3)

boundary conditions:

$$c_{n+1}(t,z)\big|_{z=l} = c_{\infty n+1}; \qquad\qquad q_m(t,r,z)\big|_{r=R} = K_m \cdot c_m(z,t);$$
(4)

$$\frac{\partial c_1}{\partial z}(t,z)\bigg|_{z=0} = 0, \qquad\qquad \frac{\partial q_m(t,r,z)}{\partial r}\bigg|_{r=0} = 0.$$
(5)

and contact conditions for coordinate z:

$$\left[c_k(t,z) - c_{k+1}(t,z) \right]\big|_{z=l_k} = 0; \qquad \left[\frac{\partial}{\partial z} c_k(t,z) - \frac{\partial}{\partial z} c_{k+1}(t,z) \right]\bigg|_{z=l_k} = 0, \quad m = \overline{1,n}.$$
(6)

3. Problem solution

The solution of a defined mathematical model can be found by applying numerical methods.

3.1.   Numerical solution of the model

Let's put in domain I_m uniform orthogonal grid

$$I_m^* = \left\{ (t_k, z_i, r_{ij}) : t_k = k \cdot \Delta t, k = \overline{1,N}; z_i = i \cdot \Delta z, i = \overline{1,M}; r_{ij} = j \cdot \Delta r, j = \overline{1,L}; \Delta t = \frac{t}{N}, \Delta z = \frac{z}{M}, \Delta r = \frac{r}{L} \right\},$$

and approximate equation of system (1) - (6) with the Crank-Nicolson scheme (where $N, M, L \in \mathbb{N}$ - parameters of the partition area, $\Delta t, \Delta Z, \Delta X$ − grid steps for variables t, Z, X, $m = \overline{1,n+1}$) [13].

$$\frac{C_{m_i}^{k+1} - C_{m_i}^k}{\Delta t} = \frac{D_{\text{inter}}}{2 \cdot \ell^2} \left[\frac{C_{m_{i+1}}^{k+1} - 2 \cdot C_{m_i}^{k+1} + C_{m_{i-1}}^{k+1}}{(\Delta Z)^2} + \frac{C_{m_{i+1}}^k - 2 \cdot C_{m_i}^k + C_{m_{i-1}}^k}{(\Delta Z)^2} \right] -$$
$$- \Gamma_m \left[\frac{1}{2} \left[\frac{N_{m_{iL}}^{k+1} - N_{m_{iL-2}}^{k+1}}{\Delta X} + \frac{N_{m_{iL}}^k - N_{m_{iL-2}}^k}{\Delta X} \right] + \frac{1}{2} \left[N_{m_{iL}}^{k+1} + N_{m_{iL}}^k \right] \right]$$
(7)

$$\frac{N_{m_{ij}}^{k+1} - N_{m_{ij}}^k}{\Delta t} = \frac{D_{\text{intra}}}{2R^2} \left[\frac{N_{m_{ij+1}}^{k+1} - 2 \cdot N_{m_{ij}}^{k+1} + N_{m_{ij-1}}^{k+1}}{(\Delta X)^2} + \frac{N_{m_{ij+1}}^k - 2 \cdot N_{m_{ij}}^k + N_{m_{ij-1}}^k}{(\Delta X)^2} \right].$$
(8)

Here, $C_{m_i}^k$ - concentration for the i-th node of k-th time layer in the m-dimensional space segment of interparticle space; $N_{m_{ij}}^k$ - concentration for the j-th node of k-th time layer interparticle space in the m-dimensional segment of the media ($Q_m = \dfrac{N_m}{X}$).

After a few algebraic manipulations, the system of equations (7) - (8) can be reduced to:

$$a_m^c \cdot C_{m_{i-1}}^{k+1} + d_m^c \cdot C_{m_i}^{k+1} + b_m^c \cdot C_{m_{i+1}}^{k+1} = f_{m_i}^c, \tag{9}$$

$$a_m^q \cdot N_{m_{ij-1}}^{k+1} + d_m^q \cdot N_{m_{ij}}^{k+1} + b_m^q \cdot N_{m_{ij+1}}^{k+1} = f_{m_{ij}}^q, \tag{10}$$

where: $a_m^c = \sigma_{1_m}$; $a_m^q = \sigma_{2_m}$; $b_m^c = \sigma_{1_m}$; $\qquad b_m^q = \sigma_{2_m}$; $\qquad\qquad d_m^c = -\left(1 + 2 \cdot \sigma_{1_m}\right)$;
$d_m^q = -\left(1 + 2 \cdot \sigma_{2_m}\right)$;

$$\sigma_{1_m} = \frac{\Delta t}{\left(\Delta Z\right)^2} \cdot \frac{D_{\text{inter}_m}}{2 \cdot \ell^2}; \qquad\qquad \sigma_{2_m} = \frac{\Delta t}{\left(\Delta X\right)^2} \frac{D_{\text{intra}_m}}{2 \cdot R^2},$$

$$\overline{N}_{m_i}^{k+1} = \Gamma_m \frac{\Delta t}{\Delta x}\left[\left(1 + \Delta x\right)\left(N_{m_{iL}}^{k+1} + N_{m_{iL}}^k\right) - \left(N_{m_{iL-2}}^{k+1} + N_{m_{iL-2}}^k\right)\right]$$

$$f_{m_i}^c = \sigma_{1_m} \cdot \left(2 \cdot C_{m_i}^k - C_{m_{i+1}}^k - C_{m_{i-1}}^k\right) - C_{m_i}^k + \overline{N}_{m_i}^{k+1};$$

$$f_{m_{ij}}^q = \sigma_{2_m} \cdot \left(2 \cdot N_{m_{ij}}^k - N_{m_{ij+1}}^k - N_{m_{ij-1}}^k\right) - N_{m_i}^k;$$

To determine the concentrations for interparticle and intraparticle spaces at the (k+1)-th time layer in the m-th segment of the heterogeneous catalytic media from known concentrations at the k-th layer, the system of equations (9) - (10) needs to be solved, using the Thomas algorithm [13].

This will yield the concentrations in the i-th and j-th nodes at the (k+1)-th time layer. $C_{m_i}^{k+1} = \alpha_{m_i}^c \cdot C_{m_{i+1}}^{k+1} + \beta_{m_i}^c$; $\qquad N_{m_{ij}}^{k+1} = \alpha_{m_{ij}}^q \cdot N_{m_{ij+1}}^{k+1} + \beta_{m_{ij}}^q$; $\qquad$ (11)

Coefficients $\alpha_{m_i}^c, \beta_{m_i}^c$ and $\alpha_{m_{ij}}^q, \beta_{m_{ij}}^q$ are determined at the direct sweep of the Thomas algorithm by formulas:

$$\alpha_{1_1}^c = -\frac{b_1^c + a_1^c}{d_1^c} \qquad \beta_{1_1}^c = \frac{f_{1_1}^c}{a_1^c} \qquad \alpha_{m_i}^c = -\frac{b_m^c}{a_m^c \cdot \alpha_{m_{i-1}}^c + d_m^c} \qquad \beta_{m_i}^c = \frac{f_{m_i}^c + \beta_{m_i}^c}{a_m^c \cdot \alpha_{m_{i-1}}^c + d_m^c}$$

$$\alpha_{m_{i1}}^q = -\frac{b_m^q + a_m^q}{d_m^q} \qquad \beta_{m_{i1}}^q = \frac{f_{m_{i1}}^q}{a_m^q} \qquad \alpha_{m_{ij}}^q = -\frac{b_m^q}{a_m^q \cdot \alpha_{m_{ij-1}}^q + d_m^q} \qquad \beta_{m_{ij}}^q = \frac{f_{m_j}^q + \beta_{m_j}^q}{a_m^q \cdot \alpha_{m_{ij-1}}^q + d_m^q} \tag{12}$$

Hence, when implementing the algorithm to construct the numerical solution of the mathematical model of adsorption mass transfer in a heterogeneous media consisting of catalytic particles with a microporous structure, a sweep method is utilized to calculate the concentration values for nodes in the (k+1)-th time layer. This method solves systems of equations for all n segments of the media simultaneously. To calculate the coefficients in the direct sweep, formulas (12) and (14) are used, while for the reverse sweep, formulas (13) and (11) are employed.

3.2. Parameters Identefication
3.2.1. Functional-residual

By assuming the diffusion coefficients D_{inter_m}, D_{intra_m} of (1) - (6) are unknown and on the surfaces, we have traces of known solutions (concentrations).

$$c_m(t,z)\big|_D = f_m(t,z)\big|_D, \quad \overline{q}_m(t,z)\big|_D = g_m(t,z)\big|_{.}, \tag{15}$$

where $\overline{q}_m(t,0,z) = \dfrac{1}{R}\displaystyle\int_0^R q_m(t,r,z)dr$ - is the average concentration of diffusion components in the micropores of the particles going from the particle's center ($r = 0$).

As a result, we obtain the problem (1) - (5), (15), which consists in finding functions $D_{intra} \in D$, $D_{inter} \in D$, where $D = \{v(t,z): v\big|_z \in C(z), v > 0\}$.

Functional-residual determines the deviation of the desired solution of its traces on the surface can be formulated as [17]:

$$J\left(D_{inter_m}, D_{intra_m}\right) = \frac{1}{2}\int_0^T \left(\left\|c_m\left(\tau,z,D_{inter_m},D_{intra_m}\right) - f\right\|_{L_2(D)}^2 + \left\|\overline{q}_m\left(\tau,0,D_{inter_m},D_{intra_m}\right) - g_m\right\|_{L_2(D)}^2\right)d\tau, \tag{16}$$

where $\|\varphi\|_{L_2(D)}^2 = \int_D \varphi^2 dD$ - squared norm, and in the current case is equal:

$$\|\varphi\|_{L_2(D)} = \big|\varphi(t,z)\big|_{z=D}.$$

3.2.2. Initial problem in increments

Applying the increments to the diffusion coefficients $D_{intra}^n + \Delta D_{intra}^n$, we have the corresponding gains for concentrations $q + w$. Consequently, the next boundary problem in increments can be formulated:

$$\frac{\partial}{\partial t}w(t,r,z) = D_{intra}^n \frac{\partial^2}{\partial r^2}w + \Delta D_{intra}^n \frac{\partial^2}{\partial r^2}w, \quad r \in (0,R), z \in (0,\ell), t \in (0,T). \tag{17}$$

with initial conditions on time

$$w(t,r,z)\big|_{t=0} = 0, \tag{18}$$

and boundary conditions on variable r

$$D_{i\,intra}^n \frac{\partial}{\partial r}w\big|_{r=0} = -\Delta D_{intra}^n \frac{\partial}{\partial r}w\big|_{r=0}0,$$

$$\left(D_{i\,intra}^n + \Delta D_{intra}^n\right)\frac{\partial(q+\theta)}{\partial r}\bigg|_{r=0} = 0, \qquad \theta\big|_{r=R} = 0, \tag{19}$$

3.2.3. Conjugate problems

By applying the principle of Lagrange's to advanced functional, which contain sum of functional-residual and components that take into account the balance condition and initial boundary conditions, we obtain the formulation of the conjugate problem [12].

$$\frac{\partial}{\partial t}\psi_m(t,r,z) + \frac{\partial^2}{\partial r^2}D_{intra_m}^n \psi_m = \left(q_m\big|_{r=R} - f\right)\cdot\delta(r-R), \quad . \tag{20}$$

$$r \in (0,R), \quad z \in \bigcup_{m=1}^{n+1}(l_{m-1},l_m); l_0 = 0; l_{m+1} \equiv l < \infty, \; t \in (0,T)$$

time condition

$$\psi_m(t,r,z)\big|_{t=T} = 0 \tag{21}$$

boundary conditions

$$-D_{intra_m}^n \frac{\partial}{\partial r}\psi_m\big|_{r=0} = 0; \quad \psi_m\big|_{r=R} = 0, \; r \in (0,R), \tag{22}$$

The solution to the conjugate problem is constructed in a similar fashion, utilizing the Crank-Nicolson scheme [13].

3.2.4. Determination of functional analytical form

Following [10] analytical expression for the gradient of the functional component D_{intra}

$$\nabla J_{D_{int\,ra}} = \int_0^T \int_0^R \psi(t,r,z) \cdot \frac{\partial^2}{\partial r^2} q(t,r,z) dr dt, \tag{23}$$

3.3. Identification diffusion coefficients algorithm

The procedure of implementing the gradient method for the identification of diffusion coefficients D_{intra_m} based on the use of matrix system states $M\left(t_k, z_i, D_{intra_m}^\theta\right)$, which corresponds to the total accumulated mass of diffusion component in the pores of the particles [14].

Experimental studies, which produced the results shown in Figure 1, were conducted in the laboratory of the University of Pierre and Marie Curie Paris 6 with the participation of the authors, using the nuclear magnetic resonance method (NMR). The studies were carried out on systems of adsorption of benzene and hexane in zeolite ZSM-5 [9]. The results obtained are presented as profiles of the total accumulated mass of the diffusion component (benzene or hexane) along the studied experimental model. To track the evolution of the profiles over time, measurements were taken at different time intervals (shown in Figure 1 in hours).
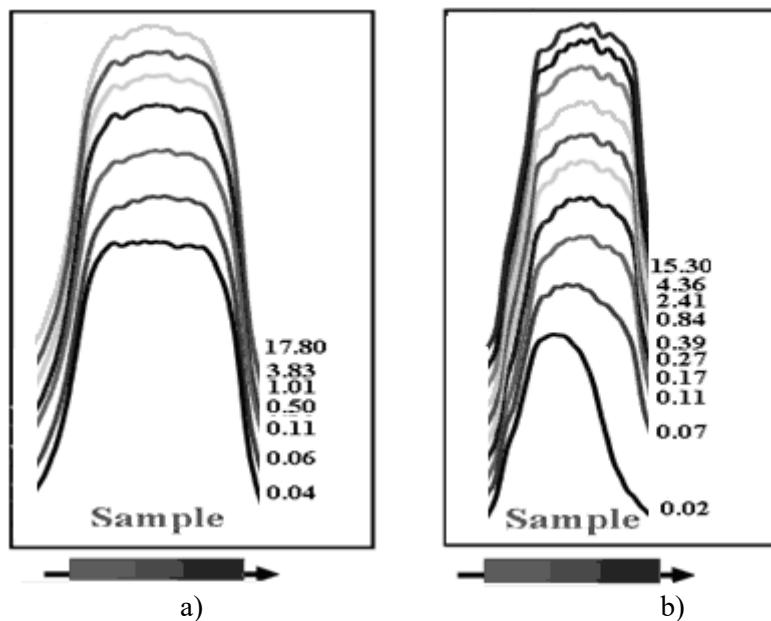

Figure 1: Experimental data of studies of adsorption in a microporous media:
a) - hexane, b) - benzene

In the matrix $M\left(t_k, z_i, D_{intra_m}^\theta\right)$ temporal and spatial variables t and z, are determine the specific status of the adsorption for which the identification of kinetic parameters are carry out.

To identify the distribution of diffusion coefficients was used one of the gradient methods, mathematical basis of which to the problem of parametric identification of multi-distributed systems are presented in [14]. Due to the nature of the problem, the most suitable is method of minimal errors.

According to this method, for the determination of $(\theta+1)$-th approximation of the diffusion coefficient in interparticle space, are used the following gradient-identification procedure [12]:

$$D^{\theta+1}_{intra_m} = D^{\theta}_{intra_m} - \nabla J\left(D_{intra}\right)\frac{\left\|e^{\theta}_m\right\|^2}{\left\|\nabla J\left(D^{\theta}_{intra_m}\right)\right\|^2}; \qquad (32)$$

3.4. Numerical modeling and parameters identification

The identification procedure was performed based on the determination of diffusion coefficients of a system of one-component adsorption using the gradient method described above.

During the identification process, the experimental data $\left[M_{exp_{k_i}}\right]^{i=\overline{1,M}}_{k=\overline{1,N}}$ matrix were populated with the total absorbed mass values along coordinate z for various times of the adsorption process [15, 16].

The identification results are shown in the figures below and represent different thicknesses of the nanoporous medium and different adsorption process duration correlated with physical experiment results.
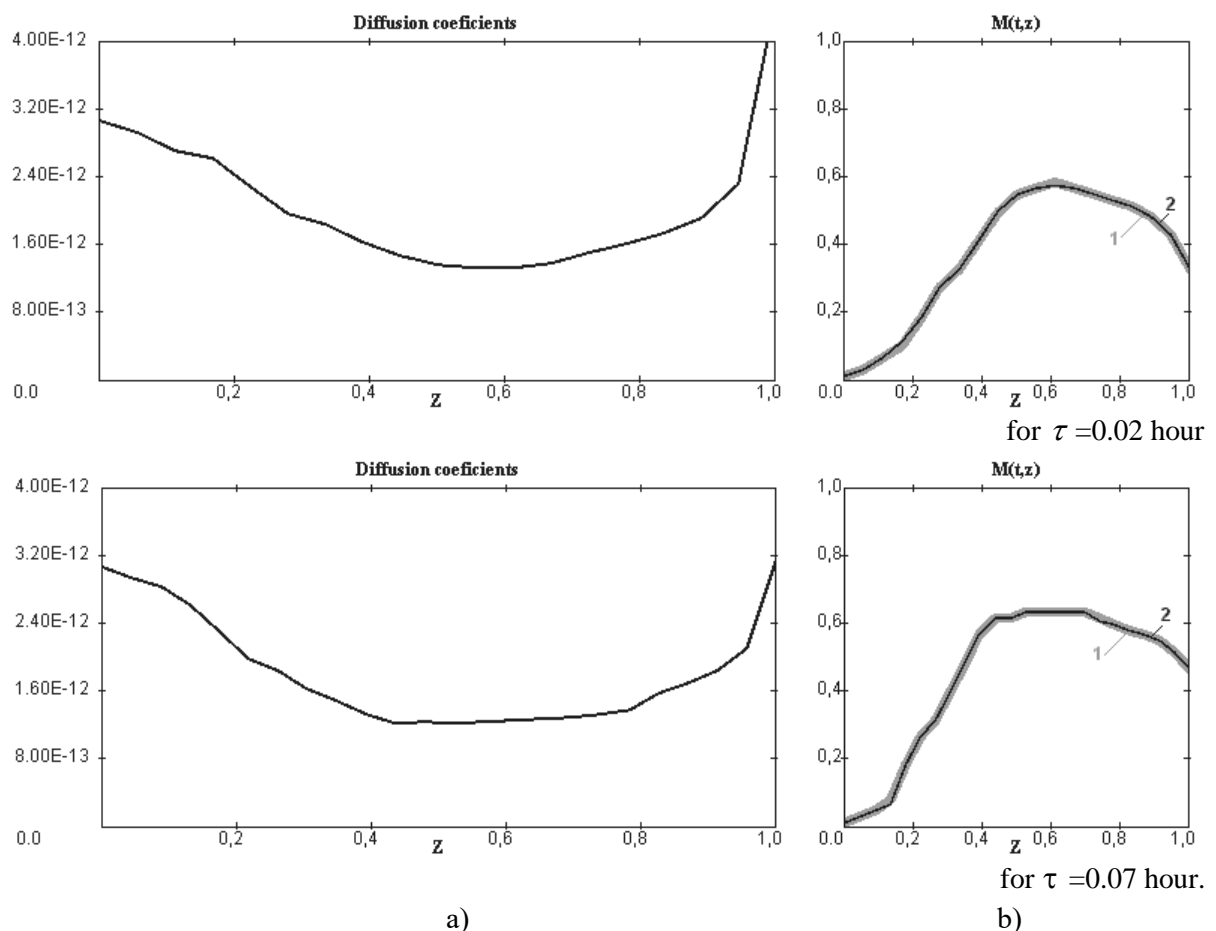

for τ =0.02 hour

for τ =0.07 hour.

a)   b)

Figure 2: Identification of diffusion coefficients for benzene τ = 0.02 and = 0.07: a) coefficients distribution; b) adsorbed mass curves comparison for model (2) and experimental (1) results

At the fig. 2. shown the identified distributions of the diffusion coefficient D_{intra} (a) along with adsorbed mass curves (b) on coordinate z (the direction of mass flow) for benzen adsorption process. Two case are present for the kinetics $\tau = 0.02$ hour and $\tau = 0.07$ hour from the start of adsorption. As can be seen from fig. 2, b) profiles of adsorption mass (1), represent the experimental data, have heterogeneous characteristic along the catalytic bed. Since, time slice $\tau = 0.02$ hour filling of pore's subsystem placed in the entrance of the porous media is about $0.35 \div 0.5$ units. Here we can observe exponential growth of the adsorbed mass of the layer. Zone close to the center of porous media (position of coordinates of the thickness z = $0.8 \div 0.5$), has filling $0.5 \div 0.58$ units. Mass peak (the highest volume of benzene molecules) is concentrated in the area of a bed (coordinate z = $0.65 \div 0.6$) and equal to 0.58 unit. Further (position coordinates of the thickness z = $0.4 \div 0.0$) are observed almost linear decrease values of adsorbed mass from 0.3 to 0.01 units. Finally, the lowest adsorbed mass volume corresponds to the working area exaust.

Futher analyze of the reduced diffusion coefficients D_{intra} profiles (Fig. 2, a) for time $\tau = 0.02$ hour shows three characteristic regions. And regions have quite opposite character. The first one, around z = $1.0 \div 0.8$, has sharp decrease in diffusion coefficient's value from $4.0 \cdot 10^{-12}$ to $1.6 \cdot 10^{-12}$ m/s^2 - exponential decay area. The next one, around z= $0.8 \div 0.7$, has a more linear decrease to a value of $1.5 \cdot 10^{-12}$ m/s^2. And next segment of the layer (z = $0.7 \div 0.5$) has static diffusion coefficient with insignificant convexity at the center. The lowest diffusion coefficient is $1.35 \cdot 10^{-12}$ m/s^2 corresponds a peak of the adsorption mass curve (Fig. 2, b).
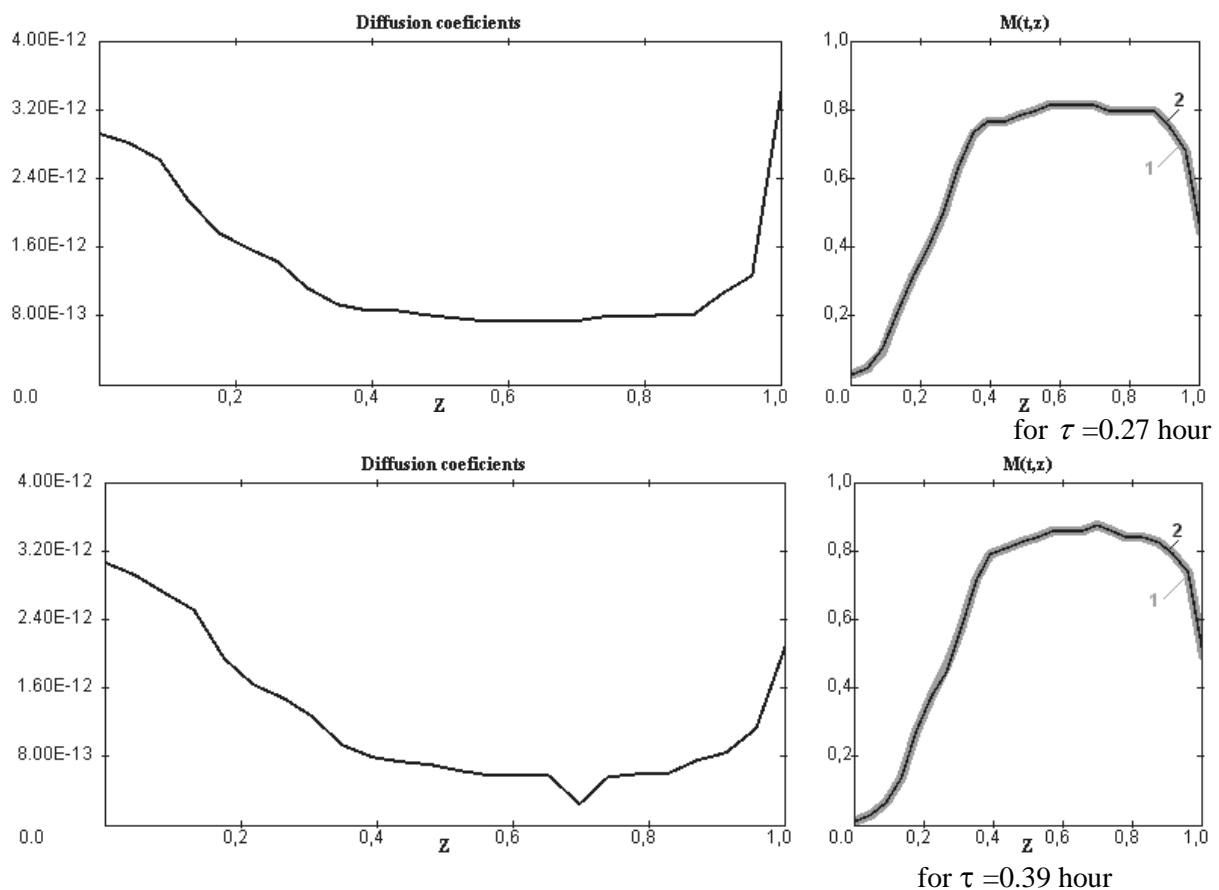

Figure 3: Identification of diffusion coefficients for benzene for time τ = 0.27 and τ = 0.39: a) coefficients distribution; b) adsorbed mass curves comparison for model (2) and experimental (1) results

Further segments z = 0.5 ÷ 0.4 and z = 0.4 ÷ 0.2 is characterized by a linear increase of diffusion coefficient to $1.6 \cdot 10^{-12}$ m/s^2 and $2.8 \cdot 10^{-12}$ m/s^2, respectively. And at the last section of the layer (z = 0.2 ÷ 0), has diffusion coefficient increase.

As is evident from the compare the experimental (1) and model (2) curves of the adsorbed mass (Fig. 2b) curves are sufficiently consistent with each other. Such results confirm the efficiency of proposed method of identification and ensure the adequacy of the model and experimental study. Looking ahead, we must say that the picture is similar for all other distributions considered below.

A further picture of the adsorption kinetic is followed by the next time slices shown in fig. 4 (τ = 0.27 hour, τ = 0.39 hour). These times reflect the middle adsorption phase. At time slice τ = 0.27 hour the interval z = 1.0 ÷ 0.8 filling equal 0.45-0.75 units. and diffusion coefficients vary from $3.51 \cdot 10^{-12}$ m/s^2 to $1.068 \cdot 10^{-12}$ m/s^2, which is 25-30% smaller than the corresponding values at the previous time period. Accordingly, layer z = 0.8 ÷ 0.4 filling is 0.76 ÷ 0.82 units. Diffusion coefficients vary from $8.26 \cdot 10^{-13}$ to $7.45 \cdot 10^{-13}$ m/s^2. For the time slice τ = 0.39 hour (layer z = 1.0 0.8) filling is 0.5-0.79 units., the diffusion coefficients vary from $2.138 \cdot 10^{-13}$ to $8.62 \cdot 10^{-13}$ m/s^2, which is 40-45% lower than the at previous time slice. For the layer z = 0.8 ÷ 0.4 filling is 0.81-0.88, and the diffusion coefficients vary from $2.49 \cdot 10^{-13}$ to $7.549 \cdot 10^{-13}$ m/s^2.

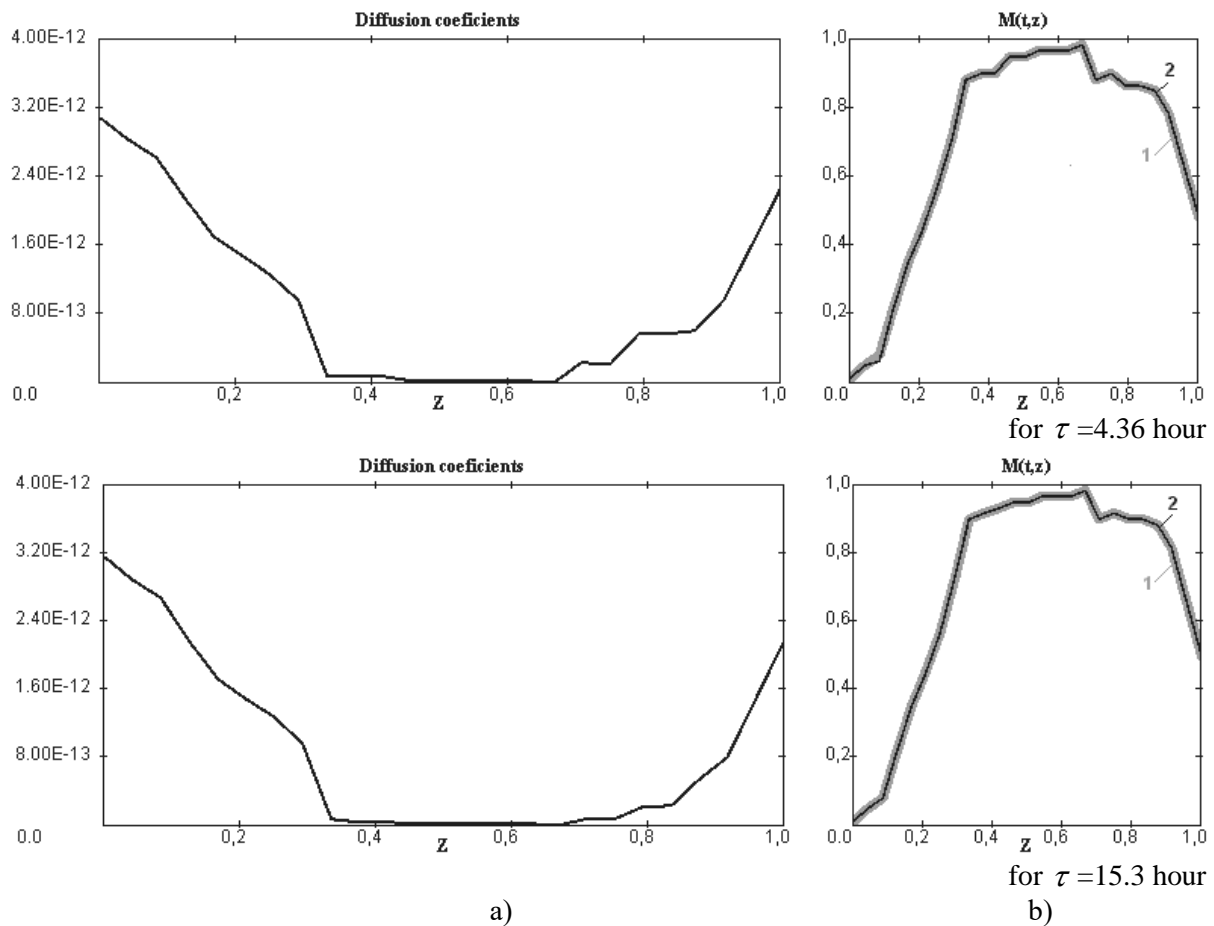a)   b)

Figure 4: Identification of diffusion coefficients for benzene for time τ = 4.36 and τ = 15.3 (equilibrium) a) coefficients distribution; b) adsorbed mass curves comparison for model (2) and experimental (1) results

4. Discussion

Comparing the results of different time slices we can observe little but distinct evolutions of absorbed mass curves in the direction of growth, and in same time diffusion coefficients going to be decreased, due to the accumulation of absorbed benzene molecules in the absorbent.

A key stage of adsorption kinetics modeling is masstransfer system evolution towards equilibrium. It cleary observable by changes in the form of curves of adsorbed mass. Based on the conducted numerical experiments, can be observed that starting from time $\tau = 4.36$h, the shape of the curve is stabilized and further continuation of the adsorption has low variations. Another important timepoint was around $\tau = 15.3$ hour has an almost identical profile of the adsorbed mass in the micropores and confirms equilibrium condition achievement.

One more important fact of equilibrium confirmation is the diffusion coefficients evolution. Moreover, the diffusion coefficients decrease with time $\tau = 4.36$ hour is practically unchanged, which is also on the other hand confirms that the system reached equilibrium.

5. Conclusion

An information system for identifying and studying of parameters of complex adsorption and diffusion processes in heterogeneous media of microporous particles has been implemented. The direct and conjugate problems of coefficient identification in intraparticle space are formulated. The identification algorithm of kinetic parameters using the gradient method and numerical solutions obtained from the considered adsorption complex model is implemented.

The adequacy of the results obtained from the identification process was tested against experimental observations. Furthermore, numerical simulation and analysis of the kinetics of adsorption, as well as the concentration gradient fields were conducted.

The results obtained from this study enable efficient simulation of adsorption process kinetics and can be utilized for investigating the equilibrium conditions in complex adsorption systems under the influence of many various factors.

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