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# SUBSTANCE TRANSFER IN A POROUS MEDIUM SATURATED WITH MOBILE AND IMMOBILE LIQUIDS

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*Consideration has been given to the problem of transfer of a substance in a porous medium consisting of two zones: a) with transit pores (with a mobile liquid) and b) with an immobile liquid (with bound water) with allowance for the effects of convective transfer, hydrodynamic dispersion, substance adsorption, and internal mass transfer between both zones. The fields of substance concentration, adsorption, and internal mass transfer for different cases determined by the character of adsorption and internal mass exchange have been determined. It has been established that the presence of zones with an immobile liquid significantly influences the general characteristics of substance transfer in the porous medium.*

***Keywords:*** *substance adsorption, internal mass transfer, hydrodynamic dispersion, zones with a mobile and immobile liquid, substance transfer, porous medium.*

**Introduction.** The issues of utilization of different contaminants (impurities) by injecting them into underground reservoirs (permeable beds) together with water have acquired an increasingly greater importance in recent times. Technical implementation of this method is closely connected with the development of methods for evaluation and calculation of the indices of the process, which in turn makes it possible to evaluate waste-utilization risk in terms of environmental safety. Studying substance (solute) transfer in a porous medium is also important from the viewpoint of the analysis and development of secondary and tertiary methods of extraction of oil, determination of the characteristics of underground water-bearing beds by injection of different tracers and underground leaching of beds, and others [1–5]. Adequate mathematical modeling allowing for the basic characteristic features of the process is of great importance for qualitative and quantitative evaluation of the characteristics of substance transfer in porous media. The issues of mathematical modeling of substance transfer in porous media have been the focus of [6–9].

As the practice of development of oil fields with inhomogeneous reservoirs and water production from inhomogeneous beds shows, fluids can remain immobile or be of low mobility even at appreciable pressure gradients in certain zones with poor transport and storage properties. Such zones are usually considered to be stagnant, and pores in these zones are assumed to be "dead-end." Mathematical modeling of the processes of substance transfer in such media was first effected in [10, 11]. Mass exchange between zones with a mobile and immobile liquid was described, in these models, using the kinetic equation of first order

$$m_2\alpha \frac{\partial N}{\partial t} = c - N \, .$$

Further analysis with alternative approaches using a certain geometry of zones with an immobile liquid and a diffusion equation for them [12, 13] has shown that the model approach [10, 11] produces good results in some cases. The problem of transfer of a substance with allowance for its diffusion into the stationary water-saturated part of the bed has been considered in [14] on the basis of the model of [10]. Solution of the problem was used in describing results of experiments specially conducted in an artificial porous medium. A 0.01 N $CaCl_2$ solution was used as a filtered liquid and an $\alpha$ value of 1900.8 sec was obtained. We note that $1/\alpha$ was used instead of $\alpha$ in [14]. The model was also experimentally checked in [15–18] with assessment of $\alpha$ values. As applied to the problems of migration of

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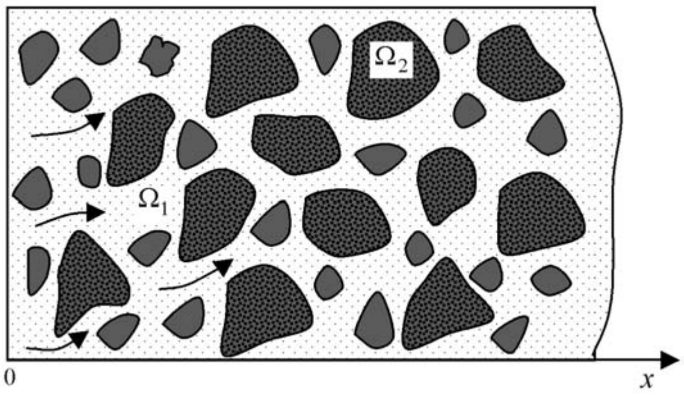

Fig. 1. Porous medium with two zones: with transit pores ($\Omega_1$) and with a bound immobile liquid ($\Omega_2$).

salts in soil washing, this approach has been used in [19, 20]. In these woks, pores in the zone with a mobile liquid were considered to be transit, whereas the zone with an immobile liquid was treated as being saturated with immobile bound water. In the present work, we consider the problem of transfer of a substance in a two-zone bed with allowance for substance adsorption in the zone with a mobile liquid. The adsorption is considered to be nonequilibrium and described by the kinetic equation of first order [21–23].

**Formulation of the Problem.** We consider a porous medium consisting of two zones: 1) the zone with a porosity $m_1$ where the pores are transit for the liquid, i.e., the zone with a mobile liquid, and 2) the zone with an immobile liquid (with immobile bound water) of porosity $m_2$ (Fig. 1). The medium is considered to be seminfinite and one-dimensional; the zone $\Omega_2$ is assumed to be uniformly distributed in $\Omega_1$. The latter assumption enables us to make no assumptions for the geometric shape of the aggregates of the $\Omega_2$ zone. The elements of the $\Omega_2$ zone with a certain geometric shape and the issues of substance transfer have been investigated in [12, 13]. Also, we assume that the adsorption of the substance occurs only in the $\Omega_1$ zone, although in a more general case it is necessary to allow for adsorption phenomena in both zones in which the adsorption kinetics may significantly differ [11]. In the $\Omega_1$ zone, we usually have the hydrodynamic dispersion of the substance due to the nonuniform distribution of the velocity of motion of the liquid in the pores, which leads to the linear dependence of the dispersion coefficient on the liquid velocity in the pores [6, 7]. Here for the sake of simplicity a constant dispersion coefficient $D$ is taken which, apparently, should be read as a certain effective coefficient.

Within the framework of the assumptions made, the equation of substance transfer in $\Omega_1$ can be written in the form

$$m_1 \frac{\partial c}{\partial t} + v \frac{\partial c}{\partial x} + m_2 \frac{\partial N}{\partial t} + \beta \frac{\partial S}{\partial t} = D \frac{\partial^2 c}{\partial x^2} . \tag{1}$$

Let a liquid with a constant concentration of the substance $c_0$ be injected into the medium initially saturated with pure (without a substance) liquid from the initial instant of time. We consider such periods of time when the concentration field does not reach the right-hand boundary of the medium, $x = \infty$. Under the above assumptions, the initial and boundary conditions for the problems have the form

$$c(0, x) = 0 , \quad N(0, x) = 0 , \quad S(0, x) = 0 , \quad c(t, 0) = c_0 , \quad c(t, \infty) = 0 . \tag{2}$$

It is necessary to determine the concentration fields of the substance, including the adsorbed substance and that diffused from $\Omega_1$ into $\Omega_2$.

**Solution of the Problem.** We consider several cases depending on the form of adsorption and internal-mass-exchange kinetics.

*Linear Kinetics of Adsorption and Internal Mass Exchange.* In (1), the term with $\frac{\partial N}{\partial t}$ characterizes intradiffusion mass exchange from the zone $\Omega_1$ to $\Omega_2$. To evaluate it we can use the solution of the problem of diffusion from $\Omega_1$ into $\Omega_2$, representing these zones as geometric bodies of a certain shape (cylinders, spheres, and others) [12, 13]. Here we use the approach where mass exchange is determined as a kinetic process of first order [10, 11, 19, 24]. Thus, intradiffusion mass exchange is determined by the kinetic equation

$$\alpha \frac{\partial N}{\partial t} = kc - N \,, \tag{3}$$

where $k$ and $\alpha$ are const.

In the $\Omega_1$ zone, we have nonequilibrium substance adsorption whose kinetics is determined, just as intradiffusion mass exchange, by the equation of first order [21, 22]

$$\frac{\partial S}{\partial t} = k_1 \frac{m_1}{\beta} c - k_2 S \,, \tag{4}$$

where $k_1$ and $k_2$ are const.

Problem (1)–(4), even if linear, is difficult to solve analytically, since it is necessary to find three fields simultaneously. Therefore, here we use the finite-difference method [25]. In the domain $\Omega = \{(t, x),\ 0 \le t \le T,\ 0 \le x < \infty\}$ in question, we introduce a grid uniform in directions:

$$\overline{\omega}_{\tau h} = \left\{ (t_j, x_i) \,;\, t_j = \tau j \,,\, x_i = ih \,,\, \tau = \frac{T}{J} \,,\, i = \overline{0, I} \,,\, j = \overline{0, J} \right\} ,$$

where $I$ is a fairly large integer selected so that the segment $[0, x_I]$ overlaps the range of calculated variation in the $c$, $S$, and $N$ fields.

In the open grid domain

$$\omega_{\tau h} = \left\{ (t_j, x_i) \,;\, t_j = \tau j \,,\, x_i = ih \,,\, \tau = \frac{T}{J} \,,\, j = \overline{1, J} \,,\, i = \overline{1, I-1} \right\}$$

we approximate Eqs. (1), (3), and (4) as follows:

$$m_1 \frac{c_i^{j+1} - c_i^j}{\tau} + v \frac{c_{i+1}^{j+1} - c_{i-1}^{j+1}}{2h} + m_2 \frac{N_i^{j+1} - N_i^j}{\tau} + \beta \frac{S_i^{j+1} - S_i^j}{\tau} = D \frac{c_{i-1}^{j+1} - 2c_i^{j+1} + c_{i+1}^{j+1}}{h^2} \,, \tag{5}$$

$$\alpha \frac{N_i^{j+1} - N_i^j}{\tau} = kc_i^j - N_i^{j+1} \,, \tag{6}$$

$$\frac{S_i^{j+1} - S_i^j}{\tau} = k_1 \frac{m_1}{\beta} c_i^j - k_2 S_i^{j+1} \,, \tag{7}$$

where $c_i^j$, $N_i^j$, and $S_i^j$ are the grid values of the functions $c(t, x)$, $N(t, x)$, and $S(t, x)$ at the point $(t_j, x_i)$.

From the explicit grid equations (6) and (7), we determine $N_i^{j+1}$ and $S_i^{j+1}$:

$$N_i^{j+1} = p_1 N_i^j + p_2 \,, \tag{8}$$

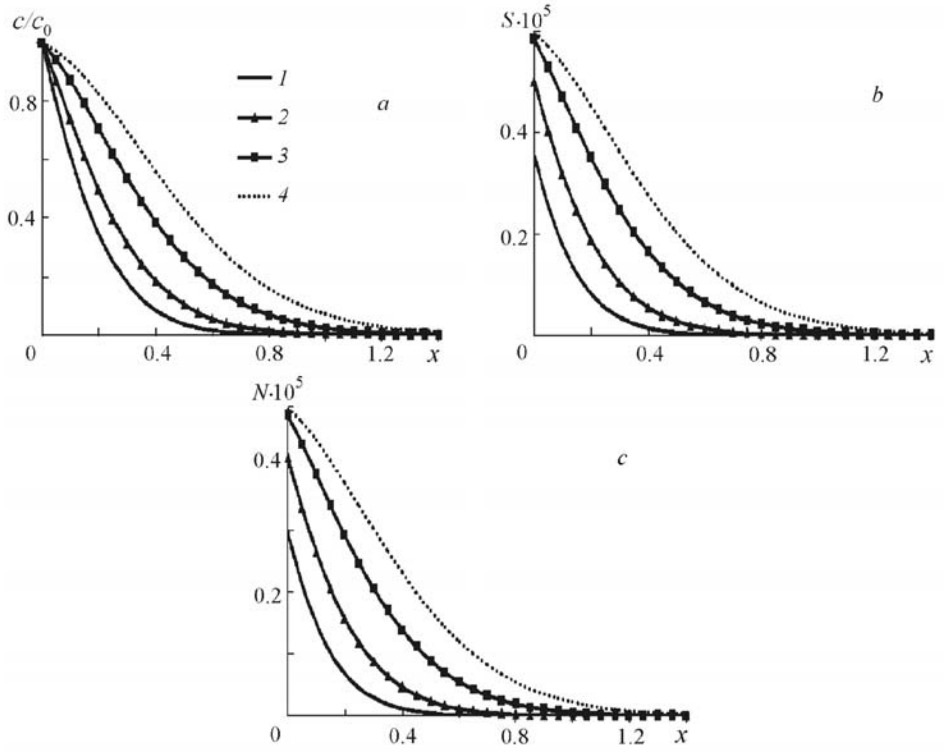

Fig. 2. Profiles of the concentrations $c/c_0$ (a), $S$ (b), and $N$ (c) for $k$ = $5\cdot 10^{-4}$ sec$^{-1}$, $k_1$ = $2\cdot 10^{-3}$ sec$^{-1}$, $k_2$ = $5\cdot 10^{-4}$ sec$^{-1}$, $\alpha$ = 2000 sec, and $\beta$ = 2000 kg/m$^3$ at different instants of time $t$: 1) 1800, 2) 3600, 3) 7200, and 4) 10,800 sec.

$$S_i^{j+1} = q_1 N_i^j + q_2 \,, \quad i = \overline{0, I} \,, \tag{9}$$

where

$$p_1 = \alpha\,(\alpha + \tau)^{-1} \,; \quad p_2 = \tau k c_i^j\,(\alpha + \tau)^{-1} \,; \quad q_1 = (1 + k_2 \tau)^{-1} \,; \quad q_2 = \frac{\tau k_1 m_1}{\beta\,(1 + \tau k_2)}\, c_i^j \,.$$

The grid equations (5) are reduced to the form

$$\gamma_1 c_{i-1}^{j+1} - \gamma_2 c_i^{j+1} + \gamma_3 c_{i+1}^{j+1} = -\,F_i^j \,, \quad i = \overline{1, I-1} \,, \tag{10}$$

where

$$\gamma_1 = \frac{Dv}{h^2} + \frac{\tau v}{2h} \,; \quad \gamma_2 = \frac{2D\tau}{h^2} + m_1 \,; \quad \gamma_3 = \frac{Dv}{h^2} - \frac{\tau v}{2h} \,; \quad F_i^j = m_1 c_i^j - m_2\,(N_i^{j+1} - N_i^j) - \beta\,(S_i^{j+1} - S_i^j) \,.$$

In the calculations, we have used the following values of the initial parameters: $v$ = $5\cdot 10^{-5}$ m/sec, $D$ = $3\cdot 10^{-6}$ m$^2$/sec, $m_1$ = 0.3, $m_2$ = 0.2, and $c_0$ = 001 and different vales of $k$, $k_1$, $k_2$, $\alpha$, and $\beta$.

We establish the following order of calculation of solutions. We determine $N_i^{j+1}$ and $S_i^{j+1}$ from (8) and (9) and then, by the marching method, $c_i^{j+1}$ in solving the system of linear equations (10). Since we have $p_1$ and $q_1 < 1$, schemes (8) and (9) are stable, and the conditions of stability of the marching method are satisfied for (10). Certain calculation results for one set of values of the initial parameters are given in Fig. 2. An analysis of the plots shows that three fields (of $c$, $S$, and $N$) which move forward in the bed with time are formed in the medium due to the arrival of the substance. We can observe an increase in the concentration of the adsorbed substance and in the internal

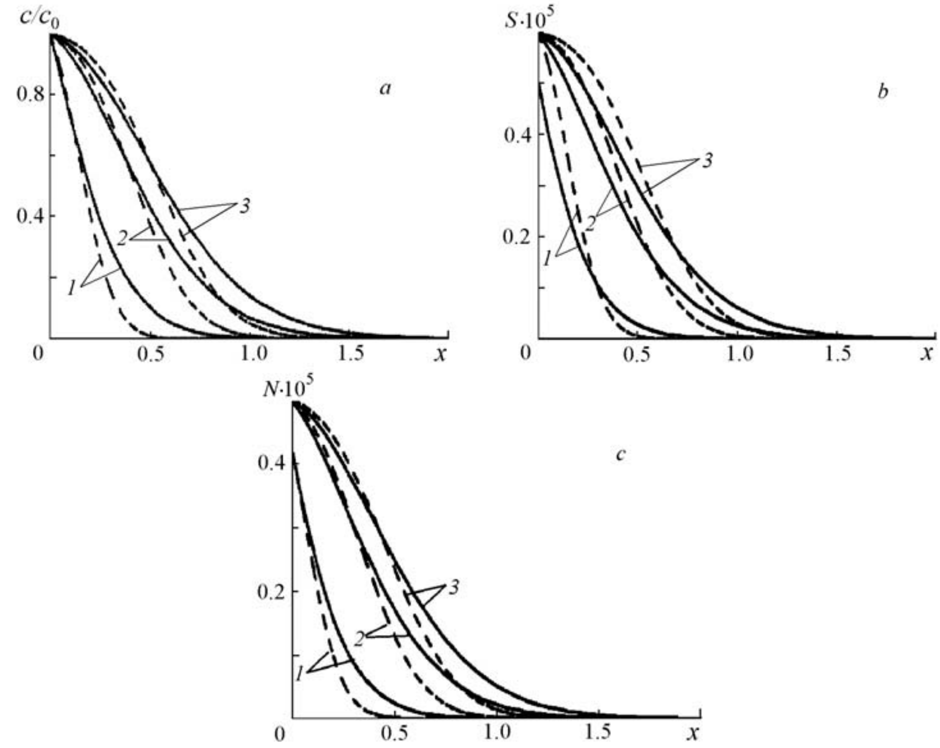

Fig. 3. Profiles of the concentrations $c/c_0$ (a), $S$ (b), and $N$ (c) for equilibrium adsorption (dashed curves) and nonequilibrium adsorption (solid curves) at different instants of time $t$: 1) 3600, 2) 10,800, and 3) 14,400 sec. The values of $k$, $k_1$, $k_2$, $\alpha$, and $\beta$ are the same as those in Fig. 2.

mass exchange at each point of the bed, including the point $x = 0$. The substance entering the medium together with the carrier liquid can be in a suspended state ($c(t, x)$ field), be adsorbed ($S(t, x)$ field), or diffuse into the zone with an immobile liquid ($N(t, x)$ field). Comparing the plots constructed for different values of the parameter $\alpha$ (other parameters being invariant), we can note the delayed dynamics of $N$ profiles. The transient process is delayed with increase in the value of $\alpha$. As the parameter $k_1$ grows, we note the relative increase in the concentrations of the adsorbed substance. Accumulation of the substance in the bed by adsorption leads to a decrease in $c(t, x)$ and consequently in $N(t, x)$. As a consequence, the advance of the $c$, $S$, and $N$ fronts in the direction of motion of the liquid slows down. The relative decrease in the adsorption can be found as the $k_2$ values increase. Simultaneously the advance of the profiles in the direction of motion of the liquid is accelerated. Generalizing the aforesaid, we can infer that the influence of $k_1$ and $k_2$ on the process of adsorption and on the entire substance transfer is mutual.

At $t \to \infty$, Eq. (4) yields

$$S = k_3 \frac{m_1}{\beta} c\,, \quad k_3 = \frac{k_1}{k_2}\,, \tag{11}$$

i.e., the equilibrium linear law of adsorption. The characteristic time of transition from (4) to (11) is $k_2^{-1}$.

At long $t$, Eq. (3) yields

$$N = kc \tag{12}$$

i.e., the linear equilibrium law of internal mass exchange. The characteristic time of transition from (3) to (12) is $\alpha$.

The transient processes have different durations depending on the characteristic times $k_2^{-1}$ and $\alpha$. However, here we have a complex process of substance transfer where transition to the steady state of the concentration $c$ is determined, among other factors, by the kinetics of internal mass exchange (3) and adsorption of the substance (4). To

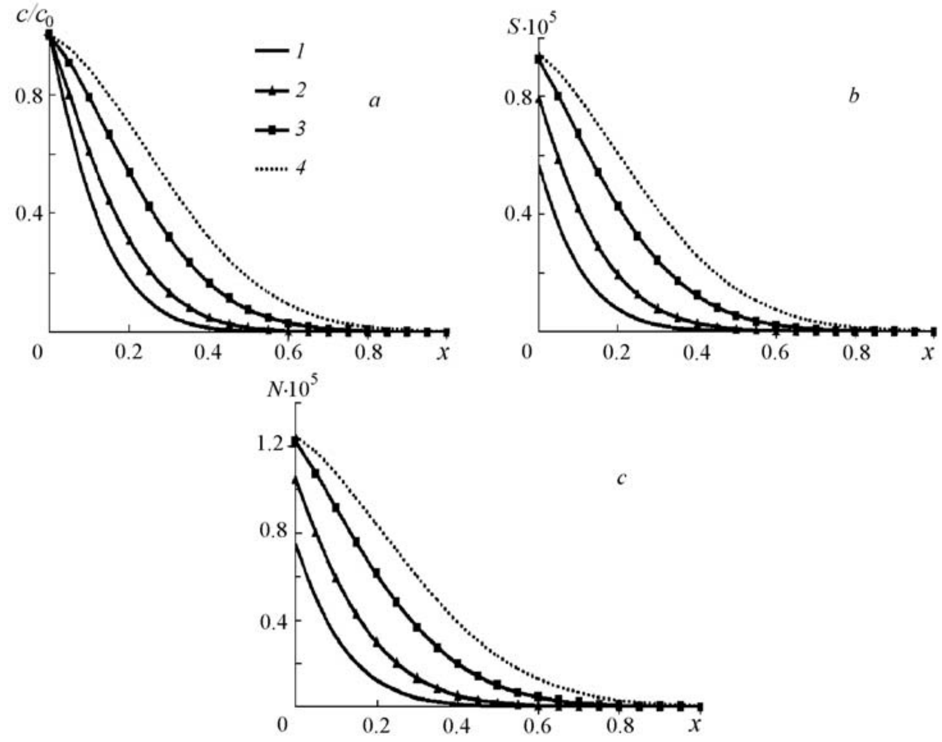

Fig. 4. Profiles of the concentrations $c/c_0$ (a), $S$ (b), and $N$ (c) for $m = 0.8$ and $n = 0.9$ at different instants of time. The values of 1–4 and $k$, $k_1$, $k_2$, $\alpha$, and $\beta$ are the same as those in Fig. 2.

investigate the influence of the adsorption kinetics on the characteristics of substance transfer we have solved the problem with equilibrium adsorption (11) instead of (4). Even at $t$ times much longer than the characteristic times $k_2^{-1}$ and $\alpha$, there is a marked discrepancy in the values of equilibrium and nonequilibrium adsorption (Fig. 3). In turn this is reflected on the $c$ and $N$ plots, which shows the above-noted complex character of the transient process where the dynamics of establishment of the $c$, $S$, and $N$ fields interact.

*Nonlinear Kinetics of Adsorption and Linear Kinetics of Internal Mass Exchange.* Here, instead of the linear adsorption kinetics (4), we consider

$$\frac{\partial S}{\partial t} = k_1 \frac{m_1}{\beta} c^n - k_2 S\,, \quad 0 < n < 1\,, \tag{13}$$

i.e., the nonlinear kinetics.

At $t \to \infty$, expression (13) yields

$$S = k_3 \frac{m_1}{\beta} c^n\,, \quad k_3 = \frac{k_1}{k_2}\,, \tag{14}$$

i.e., the Freundlich isotherm.

Results of numerical solution of Eqs. (1), (3), and (13) show that the values of adsorption in the medium increase with decrease in $n$. The advance of the concentration profiles $c$, $S$, and $N$ in the medium slows down due to the accumulation of the substance in the bed, as in the case of linear adsorption kinetics. The obtained results show that, all other things being equal, the adsorption is more intense in the case of nonlinear kinetics than that in the case of linear kinetics. The complex features of the transient process that have been noted for the linear kinetics of adsorption are totally preserved in the case of nonlinear kinetics.

*Linear Kinetics of Adsorption and Nonlinear Kinetics of Internal Mass Exchange.* We assume that the internal mass exchange between the zones of the bed with transit pores and the stagnant liquid occurs by the nonlinear kinetics

$$\alpha \frac{\partial N}{\partial t} = kc^m - N\,, \quad 0 < m < 1\,. \tag{15}$$

In the case $m = 1$ expression (15) yields the linear kinetics (3). Adsorption occurs by the linear kinetics (4). For the equilibrium internal mass exchange, from (15) we have

$$N = kc^m\,. \tag{16}$$

To evaluate the nonlinear kinetics of internal mass exchange we consider Eq. (1) together with (15) and (4). The problem is solved for conditions (2). From numerical calculations, we determine the $c$, $S$, and $N$ profiles for different values of the initial parameters. The relative increase in the internal mass exchange $N$ is noted with decrease in the exponent of nonlinearity $m$. Unlike the previous cases, the change in $c$ and $S$ due to the increase in $N$ is less pronounced. The nonlinear kinetics of internal mass exchange (the remaining parameters being the same) leads to an intensification of the internal mass exchange, whereas the unsteady transient process is delayed.

*Nonlinear Kinetics of Adsorption and Internal Mass Exchange.* We investigate the case where adsorption and internal mass exchange occur by the nonlinear kinetics. Equation (1) will be considered together with (13) and (15). Results of numerical calculations for one set of the initial parameters are given in Fig. 4. Increase in the $S$ values can be noticed with decrease in the exponent $n$. This is reflected on the $c$ and $N$ profiles. They relatively decrease and the intensity of their propagation in the medium becomes weaker. The case considered here is characterized by the intensity of the processes of adsorption and internal mass exchange compared to the previous cases. The use of the nonlinear adsorption kinetics compared to that linear leads to an intensification of the adsorption process (other parameters being equal).

**Conclusions.** From the presented results, it is clear that the adsorption of the substance in the porous medium with transit pores and a bound immobile liquid leads to a delayed development of the concentration field in a mobile liquid and of mass exchange between the zones. The nonlinear kinetics (other parameters being equal) enhances adsorption effects. The characteristic transient processes for the adsorption, mass exchange, and transfer of the substance, interacting with each other, generate a complex transient process. In particular, the delay of the steady-state regime is noted for the transient process that was expected to be completed faster than the remaining processes. In the case of nonlinear kinetics the internal mass exchange is intensified (other parameters being equal).

## NOTATION

$c_0$ and $c$, constant and running mass concentration of the substance, kg/m$^3$; $D$, coefficient of hydrodynamic dispersion, m$^2$/sec; $h$, step of the grid in the $x$ direction; $k$, coefficient of internal mass exchange; $k_1$ and $k_2$, coefficients of adsorption and desorption kinetics, which are independent of the running concentration, sec$^{-1}$; $I$, number of the grid's intervals in $x$; $J$, number of the grid's intervals in $t$; $m_1$ and $m_2$, porosities in the zones with a mobile and immobile liquid respectively; $m$, exponent in the nonlinear kinetics of internal mass exchange; $n$, exponent in the nonlinear kinetics of adsorption; $N$, concentration of the substance in the zone with an immobile liquid, kg/m$^3$; $S$, concentration of the adsorbed substance in the zone with a mobile liquid, kg/kg; $t$, time, sec; $T$, maximum time for which the process is investigated, sec; $v$, filtration velocity, m/sec; $x$, coordinate, m; $\alpha$, coefficient of internal-mass-exchange intensity, sec; $\beta$, total density of the porous medium, kg/m$^3$; $\tau$, time step of the grid; $\Omega_1$, zone with a mobile liquid; $\Omega_2$, zone with an immobile liquid.

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