

A Non-Linear Model for Solute Transport, Accounting for Sub-diffusive Concentration Decline and Sorption Saturation

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Abstract. Solute transport in porous media is very often complicated by solute immobilization on a solid matrix of porous media. Usually, immobilization is accounted by the mobile/immobile media approach (MIM). However, solute immobilization is very complicated phenomena with a variety of specific features. Therefore, in the literature there have been a lot of specific MIM-type models. Usually each model is constructed for to account one specific feature. Examples are the power decline of concentration in the large time limit at small concentration and the limitation of the immobilization process at high concentrations. Both effects have been evidenced by experiments. The present paper develops a hybrid nonlinear fractional MIM model potentially able to describe the above two features. A step-by-step process of constructing the nonlinear fractional MIM model is presented, and the main properties of the new model are discussed. Two limiting cases describe power law decline and sorption saturation have predicted by the new model equations. Numerical simulations illustrate limiting cases and the capabilities of new nonlinear fractional model.

Keywords and phrases: transport in porous media, immobilization, MIM approach

Mathematics Subject Classification: 76S05, 60J60, 35Q70

1. Introduction

Passive transport (diffusion) of a solute is usually described based on linear Fick's law [1,2]. It is assumed that the diffusive flux is proportional to the gradient of solute concentration. However, solute spreading in a number of physical systems deviates from Fick's law. One of such systems is a porous medium. Porous media have a rather complex spatial structure, and some experiments [3–5] show that diffusion in a porous medium is a slower process than that predicted by Fick's law. This effect is caused by solute immobilization when the solute particles stick to the solid matrix of the porous medium.

The immobilization is often modelled using the MIM (mobile/immobile media) approach [6]. It is assumed that the total solute concentration is divided into two phases. The first is called the mobile

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concentration and is related to the solute that is moving with the flow. The second is the immobile concentration associated with the particles adhered to the solid matrix or with the trapped fluid. Mathematically, the transport of the mobile solute is modelled by the classical diffusion equation, which incorporates an additional term to describe an influx of the solute into the immobile phase. The solute transition between the phases is described by additional “kinetic equation”. This equation governs the choice of the specific model which will be used to describe the immobilization process.

The simplest model of this type was proposed in [7], where the phase transition kinetics was described by the linear relationship ($C = \xi Q$) between the immobile (Q) and mobile (C) concentrations of the solute. This form of kinetic equation leads to a decrease of diffusivity by a factor of $1 + \xi$ in compliance with the classical diffusion model. The proposed relationship gives a poor fit to the experimental data. Another model was proposed in [8] and was developed in [6]. In these papers the immobilization is described by a linear dependence of the solute flux into the immobile phase (first derivative of Q with respect to time) on the solute concentrations in both phases. The model of this type is often called a linear sorption model or standard MIM model. The dependence of concentration on time, which is obtained within the standard MIM was confirmed by some experimental works [4, 9].

The problem of localized concentration peak dissolution is often considered in experimental investigations. For this problem the standard MIM model predicts an exponential decline of concentration with time at large times. However, the results of some thorough experimental studies have shown that the concentration decrease is governed by the power law. This fact is indicative of the sub-diffusion nature of solute transport in porous media. The explanation of this power law dependence is presented in [10]. It is assumed that a solute in porous media immobilizes within random time intervals and the distribution of such random variable does not have a mean value. The resultant kinetic equation is represented by the linear relation between the influx to the immobile phase and the fractional Caputo derivative of mobile phase concentration with respect to time. This model is often called fractional mobile/immobile model (fMIM).

All previously discussed models are based on the assumption that the influx to the immobile phase depends linearly on concentration. This assumption is appropriate for low solute concentrations, but if the solute concentration is significant, it is necessary to consider the effect of porous matrix saturation. The surface of the solid matrix of porous media is finite and in the case when a considerable part of the surface is occupied by the solute, the solute flux into the immobile phase diminishes. Due to this fact the kinetic equation should be written in the nonlinear form and the simplest form is the Lengmure-type second-order kinetic model [11, 12]. The linear limit of the latter model is the standard MIM model.

In the literature, there has been a great variety of the MIM-type models, which however, cannot take into account both the effect of solid matrix saturation and the effect of power asymptote of concentration decline at large times. For example another nonlinear model with subdiffusive behaviour at long-term limit is developed in the [13] for the case when the power of asymptote of concentration decline is depended on space coordinate. The objective of this paper is to develop a model, which can properly describe these two effects.

The paper consists of four parts: the first part is an overview of the MIM - type models and construction of the unified scheme for obtaining the equations and solutions. In the second part we derive a nonlinear analogue to the fractional MIM model and discuss its properties. A numerical solution of the one-dimensional localized peak dissolution problem is derived in the third part. The obtained results show the characteristic features of the model and its possible applications. The conclusions are formulated in the fourth part.

2. MIM approach

Transport of solutes into porous media is often complicated by solute immobilization. Many types of solutes interact with a solid matrix of the medium. Due to this fact the solute particles sometimes “steak” to the wall and do not move during some period of time. This is the reason why the solute is separated into two phases at each time moment. The first is a mobile phase, which is composed of moving

particles. The motion of such solute is described by the standard advection-diffusion equation (ADE). The second phase is called immobile and contains particles which stick to the solid matrix. This phase of solute does not move and its dynamics is described by the solute flux exchange between phases. This approach is known as the mobile/immobile media approach and was described for the first time in [8] and developed in [6]. In the MIM approach, the general equations of solute concentration evolution can be written as

$$\begin{aligned}\partial_t C + \partial_t Q &= \nabla \cdot (D \nabla C - \mathbf{V} C), \\ \partial_t Q &= \mathbf{R}(C, Q),\end{aligned}\tag{2.1}$$

where C, Q are the solute concentrations in the mobile and immobile phases, respectively, sign ∂_t denotes the time derivative, D is the effective solute diffusivity, \mathbf{V} is the vector of the filtration flow velocity. The first equation of (2.1) is ADE with the additional term ($\partial_t Q$) describing the solute influx to the immobile phase. The second equation (2.1) is the kinetic equation. It reflects the dependence of the solute influx on the solute concentrations in both phases or it can be interpreted as kinetics of phase transition. The function $\mathbf{R}(C, Q)$ is the kinetic function, which defines the specific type of the MIM model. In the following sections we analyze and compare some commonly used models.

2.1. Standard linear MIM model

The standard MIM model [6] is the linear model, in which the solute transfer into the immobile phase increases linearly with the growth of the mobile concentration and decrease of the immobile concentration. The kinetic equation for the standard MIM is

$$\partial_t Q(\mathbf{r}, t) = \mathbf{R}(C, Q) = aC(\mathbf{r}, t) - bQ(\mathbf{r}, t),\tag{2.2}$$

where a is the adsorption rate and b is the desorption rate. Equation (2.2) is also known as the equation of linear sorption kinetics. This is a heterogeneous, linear, ordinary differential equation and its general solution can be written as

$$Q(\mathbf{r}, t) = \exp(-bt) \left[A(\mathbf{r}) + a \int_0^t C(\mathbf{r}, t') \exp(bt') dt' \right].\tag{2.3}$$

where $\mathbf{r} = (x, y, z)$ is the position vector in space. The function $A(\mathbf{r})$ in solution (2.3) denotes the initial distribution of the solute in the immobile phase. Usually the initial value of the immobile concentration is zero and in view of equations (2.1) the evolution of the mobile concentration is described by the following integro-differential equation

$$\partial_t \left[C(\mathbf{r}, t) + a \int_0^t C(\mathbf{r}, t') \exp\{-b(t-t')\} dt' \right] = \nabla \cdot (D \nabla C(\mathbf{r}, t) - \mathbf{V} C(\mathbf{r}, t)).\tag{2.4}$$

Equation (2.4) is the evolution equation with memory. The memory integral in the right-hand side is the convolution of concentration with the exponential kernel. One of the simplest ways of obtaining the solution to (2.4) is the Laplace-Fourier transformation method [14]. Let $\tilde{F}(\mathbf{r}, s) = \int_0^\infty F(\mathbf{r}, t) \exp\{-st\} dt$ be the Laplace transform of the function $F(\mathbf{r}, t)$ varying in time and $\hat{F}(\mathbf{k}, t) = \iint\int_{-\infty}^\infty F(\mathbf{r}, t) \exp\{-i\mathbf{k} \cdot \mathbf{r}\} d\mathbf{r}$ is the Fourier transform of the function $F(\mathbf{r}, t)$ varying in space (here we should keep in mind that ‘‘space’’ is a three dimensional Euclidean space where \mathbf{r} is the position vector). In the last integral i is the imaginary unit and \mathbf{k} is the vector in the three dimensional Fourier space. Let us define the linear space operator as $LC(\mathbf{r}, t) = \nabla \cdot (D \nabla C(\mathbf{r}, t) - \mathbf{V} C(\mathbf{r}, t))$. By virtue of the convolution theorem [15] the Laplace-Fourier transform of equation (2.4) reads:

$$s\tilde{\widehat{C}}(\mathbf{k}, s) \left[1 + \frac{a}{s+b} \right] - \widehat{C}(\mathbf{k}, 0) = \widehat{L}(\mathbf{k}) \tilde{\widehat{C}}(\mathbf{k}, s), \quad (2.5)$$

where $\widehat{L}(\mathbf{k}) = i\mathbf{k} \cdot (i\mathbf{k}D - \mathbf{V})$ is the Fourier transform of the operator L [10] and $\widehat{C}(\mathbf{k}, 0)$ is the Fourier transform of the initial concentration distribution. The solution to equation (2.5) is

$$\tilde{\widehat{C}}(\mathbf{k}, s) = \widehat{C}(\mathbf{k}, 0) \left[\frac{s+b}{s^2 + (a+b - \widehat{L}(\mathbf{k}))s - b\widehat{L}(\mathbf{k})} \right], \quad (2.6)$$

and the inverse Laplace transformation describes the time behavior of the solution

$$\widehat{C}(\mathbf{k}, t) = \widehat{C}(\mathbf{k}, 0) \exp\left(\frac{\widehat{L}(\mathbf{k}) - a - b}{2}t\right) \left[\cosh(\gamma t) + 2\frac{b-a + \widehat{L}(\mathbf{k})}{\gamma} \sinh(\gamma t) \right], \quad (2.7)$$

where $\gamma = \frac{1}{2}\sqrt{(\widehat{L}(\mathbf{k}) - b - a)^2 + 4\widehat{L}(\mathbf{k})b}$. From solution (2.7) it follows that any initial perturbation ($\widehat{C}(\mathbf{k}, 0)$) will decline at large times according to the exponential law. The large time asymptotics is given as

$$\widehat{C}(\mathbf{k}, t)\Big|_{t \rightarrow \infty} \sim \exp\left(\frac{\widehat{L}(\mathbf{k}) - a - b - \gamma}{2}t\right). \quad (2.8)$$

This decrease is slower than the decline predicted by the classical diffusion model: $\widehat{C}(\mathbf{k}, t)\Big|_{t \rightarrow \infty} \sim \exp\left(\frac{\widehat{L}(\mathbf{k})}{2}t\right)$ (note that for $\mathbf{V} = 0$ the fourier transformation of L is $\widehat{L}(\mathbf{k}) < 0$), but in some experiments [5, 16] a power law decrease is observed. The fractional MIM model [10] was constructed with the view to explain this effect. The next section is devoted to the discussion of advantages of the fMIM model.

2.2. Fractional MIM

The power law asymptotics at large times and low rates of the solute transport in porous media is indicative of a sub-diffusion nature of this process. The authors of [10] assumed that the time of solute particle immobilization is a random variable, which is distributed according to the one-sided Levy stable law of the exponent $\alpha < 1$. This assumption leads to the following expression for the relationship between the mobile and immobile concentrations:

$$Q(\mathbf{r}, t) = \lambda I_{0,+}^{1-\alpha} = \frac{\lambda}{\Gamma(1-\alpha)} \int_0^t \frac{C(\mathbf{r}, t')}{(t-t')^\alpha} dt' \quad (2.9)$$

where $I_{0,+}^{1-\alpha}$ is the fractional Riemann-Liouville integral, Γ is the Euler gamma function, $0 < \alpha < 1$ is the exponent of the Levy stable law and λ is the mobility parameter. The mobility parameter denotes the portion of the immobile concentration in the total concentration. The exponent of the Levy stable law describes the relaxation of the system to the state of dynamical equilibrium between phases. For $\alpha = 0$ the kinetic equation reads $\partial_t Q = \lambda C$, which means that the time to relaxation is infinite, the process of mobilization is blocked and equilibrium cannot be reached. This value is the singularity of the model and because of this $\alpha > 0$. If $\alpha = 1$, the operator $I_{0,+}^{1-\alpha} = Id$ corresponds to the unit operator and $Q = \lambda C$ is a rigid equilibrium dependence corresponding to the instantaneous relaxation. The relationship (2.9) allows us to write the diffusion equation for the fMIM model as

$$\partial_t \left[C(\mathbf{r}, t) + \frac{\lambda}{\Gamma(1-\alpha)} \int_0^t \frac{C(\mathbf{r}, t')}{(t-t')^\alpha} dt' \right] = \nabla \cdot (D \nabla C(\mathbf{r}, t) - \mathbf{V} C(\mathbf{r}, t)). \quad (2.10)$$

The obtained equation, like the previous one (2.4), is the evolution equation with memory, but the memory integral is a convolution of concentration with a power kernel. A decrease in the mobile phase concentration can be evaluated in the way common to the standard MIM model (see [10,14]). The solution for $C(\mathbf{r}, t)$ in the Laplace-Fourier space is

$$\tilde{\tilde{C}}(\mathbf{k}, s) = \hat{C}(\mathbf{k}, 0) \left[\frac{1}{s + \lambda s^\alpha - \hat{L}(\mathbf{k})} \right], \quad (2.11)$$

and the inverse Laplace transformation describes the time behavior of the solution [17]

$$\tilde{\tilde{C}}(\mathbf{k}, t) = \frac{\hat{C}(\mathbf{k}, 0)}{\pi} \int_0^\infty \frac{\exp(-ht) h^\alpha \sin(\pi\alpha) dh}{(\hat{L}(\mathbf{k}) + h)^2 + \lambda^2 h^{2\alpha} - 2(\hat{L}(\mathbf{k}) + h) \lambda h^\alpha \cos(\alpha\pi)}. \quad (2.12)$$

Finally, a decline of the mobile concentration at large times [10,17] is

$$\hat{C}(\mathbf{k}, t) \Big|_{t \rightarrow \infty} \sim \frac{\lambda \alpha t^{-\alpha-1}}{\Gamma(1-\alpha)}. \quad (2.13)$$

Although these results have been confirmed by many experiments [5,16], the fMIM model cannot describe the experimental results [18] obtained for high solute concentrations. In particular, some experimental data support the view that the Langmuir isotherm [11,12,19] is best suited for describing the dynamic equilibrium between the mobile and immobile phases (when C and Q do not depend on time). Due to this fact a nonlinear kinetic equation is introduced in the MIM approach. The next section is devoted to a nonlinear MIM model.

2.3. Nonlinear MIM model

To describe the phenomena of solute transport in porous media in the presence of considerable solute concentration it is necessary to take into account the effect of saturation of the immobile phase (the concentration of immobilized solute should not exceed some limiting value). This effect was considered in [12] in the framework of the second-order kinetic model, in which the adsorption rate (see eq. (2.2)) linearly depends on the difference between the limiting saturation concentration of porous medium and the concentration of immobile solute. This kinetic equation can be written in the following form:

$$\partial_t Q = \omega(Q_0 - Q)C - bQ, \quad (2.14)$$

where ω is the adsorption parameter, Q_0 is the concentration of medium saturation and b is the desorption rate. If $Q \ll Q_0$ then the linear limit of this equation is the kinetic equation of the standard MIM model (see eq. (2.2)) with $a = \omega Q_0$. In the stationary case when $\partial_t Q = 0$, we obtain the Langmuir-type adsorption isotherm [18,19]

$$Q = \frac{\omega Q_0 C}{\omega C + b}. \quad (2.15)$$

The solution to equation (2.14) can be obtained exactly in the same manner as the solution to eq. (2.2) and is expressed as

$$\begin{aligned}
Q(\mathbf{r}, t) &= \omega Q_0 \int_0^t C(\mathbf{r}, t') \exp \left[- \int_{t'}^t (\omega C(\mathbf{r}, \tau) + b) d\tau \right] dt' \\
&+ Q(\mathbf{r}, 0) \exp \left[- \int_0^t (\omega C(\mathbf{r}, \tau) + b) d\tau \right],
\end{aligned} \tag{2.16}$$

where $Q(\mathbf{r}, 0)$ is the initial solute distribution in the immobile phase. A comparison between (2.16) and (2.3) discloses another limiting case of the nonlinear MIM model: if $\omega C_{max} \ll b$, then we can use the standard linear MIM, where C_{max} is the maximal or typical value of concentration. The above condition requires that the value of mobile concentration be small. Usually a small value of immobile concentration is the consequence of this condition (it is true for zero initial immobile concentration ($Q(\mathbf{r}, 0)$), which is an ordinary initial condition).

The experiments, which have verified the fact of power law decline of concentration with time usually correspond to large times when the deviation of concentration from zero is very small. Due to this fact the results of such experiments cannot be described by the nonlinear MIM model because in this case the model turns into a standard MIM and the above-discussed decline becomes exponential. All of the preceding is considered to be the motives for construction of the hybrid nonlinear fractional MIM model.

3. Nonlinear fractional model

The nonlinear fractional MIM model should be constructed as a fractional version of the nonlinear MIM (2.14). The relationship between the immobile and mobile concentrations in the linear fMIM can be obtained by substituting the exponential kernel of the memory integral by the power kernel. We try to follow the same way in obtaining the fractional version of nonlinear MIM model. First, the evolution equation in nonlinear MIM model with zero initial immobile concentration can be written in the following form:

$$\begin{aligned}
\partial_t \left[C(r, t) + \omega Q_0 \int_0^t C(\mathbf{r}, t') \exp \left(- \int_{t'}^t (\omega C(\mathbf{r}, \tau) + b) d\tau \right) dt' \right] \\
= \nabla \cdot (D \nabla C(r, t) - \mathbf{V} C(r, t)).
\end{aligned} \tag{3.1}$$

Second, we extract the kernel of the memory integral and use the following substitution:

$$\exp \left[-b \int_{t'}^t \left(\frac{\omega}{b} C(\mathbf{r}, \tau) + 1 \right) d\tau \right] \rightarrow \left[\int_{t'}^t \left(\frac{\omega}{b} C(\mathbf{r}, \tau) + 1 \right) d\tau \right]^{-\gamma}. \tag{3.2}$$

Third, it is convenient to redefine such parameters as $\omega Q_0 = \Lambda$ and $\omega/b = \sigma$. Finally, after normalization of the model at the initial point $t = 0$ by the factor in the form of the Euler gamma function (see eq. (2.9) and [10]) one can obtain the following equation:

$$\begin{aligned}
\partial_t \left[C(r, t) + \frac{\Lambda}{\Gamma(1-\gamma)} \int_0^t C(\mathbf{r}, t') \left[\int_{t'}^t (\sigma C(\mathbf{r}, \tau) + 1) d\tau \right]^{-\gamma} dt' \right] \\
= \nabla \cdot (D \nabla C(r, t) - \mathbf{V} C(r, t)).
\end{aligned} \tag{3.3}$$

Equation (3.3) includes the following new parameters: Λ is the mobility parameter, γ is the power of memory integral kernel and σ is the parameter of nonlinear interaction between the mobile and immobile phases. The parameters Λ and γ have the same physical meaning as λ and α , which has been explained in

Section 2.2. The parameter $1/\sigma = C^*$ is the characteristic concentration of the solute. If $C \gtrsim C^*$, then the term $\sigma C(\mathbf{r}, \tau)$ has the magnitude comparable with 1 and we should take into account a nonlinear term. The relationship between the mobile and immobile concentrations within this model is

$$Q = \frac{\Lambda}{\Gamma(1-\gamma)} \int_0^t C(\mathbf{r}, t') \left[\int_{t'}^t (\sigma C(\mathbf{r}, \tau) + 1) d\tau \right]^{-\gamma} dt'. \quad (3.4)$$

The limiting cases give two experimentally substantiated characteristic types of the concentration behaviour. First, if the solute concentration is low $C \ll C^*$, $\sigma C(\mathbf{r}, \tau) \ll 1$ and the relationship (3.4) reads

$$Q \approx \frac{\Lambda}{\Gamma(1-\gamma)} \int_0^t C(\mathbf{r}, t') \left[\int_{t'}^t d\tau \right]^{-\gamma} dt' = \frac{\Lambda}{\Gamma(1-\gamma)} \int_0^t \frac{C(\mathbf{r}, t')}{(t-t')^\gamma}. \quad (3.5)$$

The last expression, which provides the power law decline of the mobile concentration (see Section 2.2) corresponds to the linear fMIM model. Second, in the case of stationary distribution of the mobile concentration ($C = C_{eq}(\mathbf{r})$) in the presence of high solute concentration we have

$$\begin{aligned} Q &\approx \frac{\Lambda}{\Gamma(1-\gamma)} \int_0^t C_{eq}(\mathbf{r}) \left[\int_{t'}^t (\sigma C_{eq}(\mathbf{r}) + 1) d\tau \right]^{-\gamma} dt' \\ &= \frac{\Lambda C_{eq}(\mathbf{r})}{(\sigma C_{eq}(\mathbf{r}) + 1)} \frac{1}{\Gamma(1-\gamma)} \int_0^t [t-t']^{-\gamma} dt', \end{aligned} \quad (3.6)$$

where $C_{eq}(\mathbf{r})$ is the time independent space distribution of the mobile concentration. The expression (3.6) does not describe the equilibrium given by (2.15). The immobile concentration grows as $t^{1-\gamma}$. This growth is slow for certain values of γ (usually $0.8 < \gamma < 1$ see [20]). The Langmuir-type isotherm can be obtained from (3.6) as a limit at $\gamma \rightarrow 1$. Note that $\lim_{\gamma \rightarrow 1} \int_0^t [t-t']^{-\gamma} dt' = \Gamma(1-\gamma)$ see [14]. In a porous media, a slow increase of the immobile concentration in the absence of equilibrium can be responsible for the effect of pore blocking by solutes.

4. The dissolution of localized peak

To illustrate the capabilities of the nonlinear fMIM model, we solve a simple one dimensional problem of dissolution of the localized concentration peak. We consider a diffusion transport in a thin cell of porous media of length l . The fields of concentrations are the functions of one space variable x and time t ($C(x, t)$ and $Q(x, t)$). The coordinate x and time t can vary within the intervals $0 \leq x \leq l$ and $0 \leq t \leq T$ where T is the maximal time of calculations. For the sake of simplicity, equation (3.3) was non-dimensionalized. We use l and $\tau = l^2/D$ as the scales of time and length. The dimensionless evolution equation of the nonlinear fMIM model reads

$$\begin{aligned} \partial_t \left[C(x, t) + \frac{\Lambda (l^2/D)^\gamma}{\Gamma(1-\gamma)} \int_0^t C(x, t') \left[\int_{t'}^t (\sigma C(x, \tau) + 1) d\tau \right]^{-\gamma} dt' \right] \\ = \nabla \cdot \left(\nabla C(x, t) - \frac{Vl}{D} C(x, t) \right). \end{aligned} \quad (4.1)$$

where V is the filtration flow speed in the x direction, which in the examined problem is assumed to be zero, $V = 0$. This problem contains three dimensionless parameters, which are written as $\beta = \Lambda (D/l^2)^\gamma$, γ and σ .

The initial concentration peak is located within a small interval Δx near the center of the cell (in the next section a small length Δx will be used as a mesh size of the numerical space grid). For the above concentration peak we set the following initial conditions $Q(x, 0) = 0$ and $C(0, x) = A[\Theta(x - 0.5 - \Delta x) - \Theta(x - 0.5)]$. The boundary conditions are assumed to be homogeneous and are written as $C(0, t) = Q(0, t) = 0$.

Equation (4.1) is nonlinear and therefore it is difficult to find an analytical solution even for a simple one dimension problem. Due to this fact, to find a numerical solution of the boundary value problem in the framework of the nonlinear fMIM model, we use the numerical semi-implicit finite difference method, which is described in the next Section

4.1. Numerical method

The discretization of all fields for the one dimensional problem is carried out in following manner: $F(x, t) \approx F(n\Delta x, m\Delta t) = F_n^m$ where Δx and Δt are the space and time steps, $0 < n < N$ and $0 < m < M$ are the integer space and time indexes, wherein $N = l/\Delta x$ and $M = T/\Delta t$. The grid step is assumed to meet the following conditions $n\Delta x \leq x < (n+1)\Delta x$ and $m\Delta t \leq t < (m+1)\Delta t$. For the above grid the relationship (3.4) can be written in the discrete form

$$Q_n^m = \frac{\Lambda \Delta t^{1-\gamma}}{2\Gamma(1-\gamma)} \left[\frac{\sigma C_n^m + \sigma C_n^{m-1} + 2}{2} \right]^{-\gamma} \frac{C_n^m + C_n^{m-1}}{(1-\gamma)} + \frac{\Lambda \Delta t^{1-\gamma}}{2\Gamma(1-\gamma)} \sum_{j=0}^{m-2} [C_n^{j+1} I_n^{-\gamma}(j+1, m) + C_n^j I_n^{-\gamma}(j, m)] + O(\Delta t^{2-2\gamma}), \quad (4.2)$$

where the function $\Delta t I_n(j, m)$ is

$$\Delta t I_n(j, m) = \int_{j\Delta t}^{m\Delta t} (\sigma C(n\Delta x, t) + 1) d\tau = \Delta t (m - j) + \frac{\Delta t \sigma}{2} \sum_{h=j}^{m-1} (C_n^{h+1} + C_n^h) + O(\Delta t^2). \quad (4.3)$$

The applied numerical method is a semi-implicit finite difference method of the first order of accuracy in time and second order of accuracy in space. A discrete analogue to equation (3.3) at the $m+1$ time step is

$$\Delta t \frac{V\Delta x - 2D}{2\Delta x^2} C_{n+1}^{m+1} + \left(1 - \frac{\Delta t D}{\Delta x^2} \right) C_n^{m+1} - \Delta t \frac{V\Delta x + 2D}{2\Delta x^2} C_{n-1}^{m+1} = C_n^m - Q_j^m + Q_j^{m-1}, \quad n = 1 \dots N - 1. \quad (4.4)$$

4.2. The results

In this Section we present and discuss some concentration profiles and breakthrough curves, which have been obtained as solution of the problem of localized peak dissolution. The parameters β and γ are set at the following values: $\beta = 1$ and $\gamma = 0.9$. These values are the same to the values obtained in [6, 20, 21] while performing identification of the standard MIM and fMIM models parameters. The ‘‘height’’ of the concentration peak is $A = 10$. This value corresponds to a high value of concentration and allows us to get a deeper insight into the above effect. During computation the parameter σ is varied.

An important characteristics of dissolution is the dependence of concentration on the coordinate or profiles of the mobile and immobile concentrations. These profiles at time $t = 0.5$ for different values of σ is presented in Fig.1.

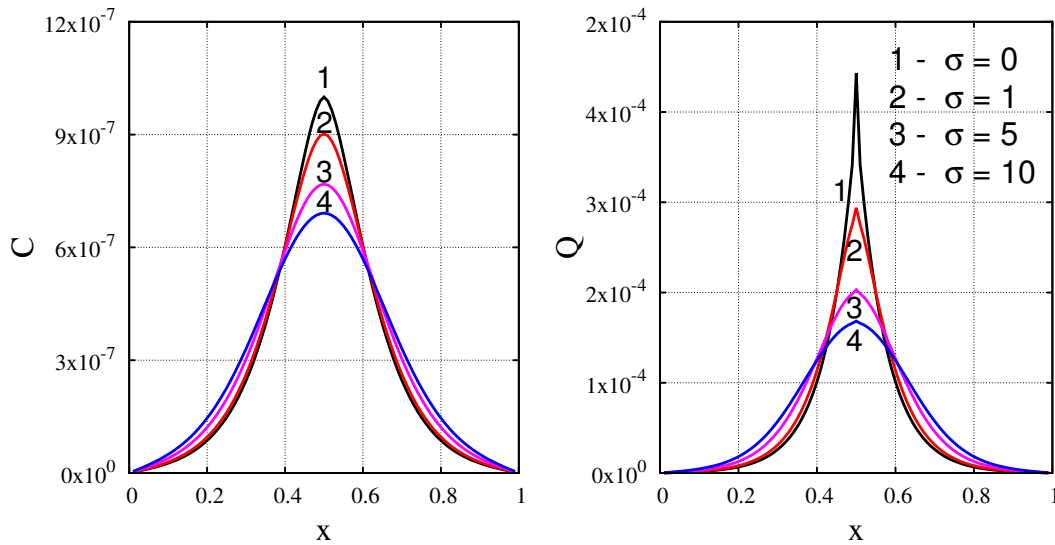


FIGURE 1. The profiles of mobile (C) and immobile (Q) concentrations at time $t = 0.5$ for different values of σ indicated in the legend. The calculations are performed for the initial peak at point $x = 0.5$.

The Fig. 1 shows that a wider concentration profile corresponds to a greater value of σ . This effect can be explained by the fact that at a large value of σ the concentration of solid matrix saturation is small, which is the cause of poor solute immobilization. The major part of solute is kept in the mobile phase and solute spreads more easily into the cell. Because of that the profile of concentration distribution is wide. At $\sigma = 0$ the shape of the concentration profile is similar to the shape of the profile typical for the sub-diffusive distribution with a break at the point of initial peak [10, 14].

The dependence of concentration on time at the point of initial peak ($x = 0.5$) is plotted in Fig. 2.

The breakthrough curves shown in Fig. 2 are yet another illustration of this effect. One can see that with the growth of σ the mobile concentration increases and the immobile concentration diminishes. The panel c in Fig. 2 shows the breakthrough curves plotted in the log-log coordinates. It is seen that at time $t > 0.1$ these plots are parallel straight lines, which indicates a large-time asymptote in the form of power law $C \sim t^{-\gamma-1}$. The effect of diffusion acceleration with increasing σ is also confirmed by Fig. 3.

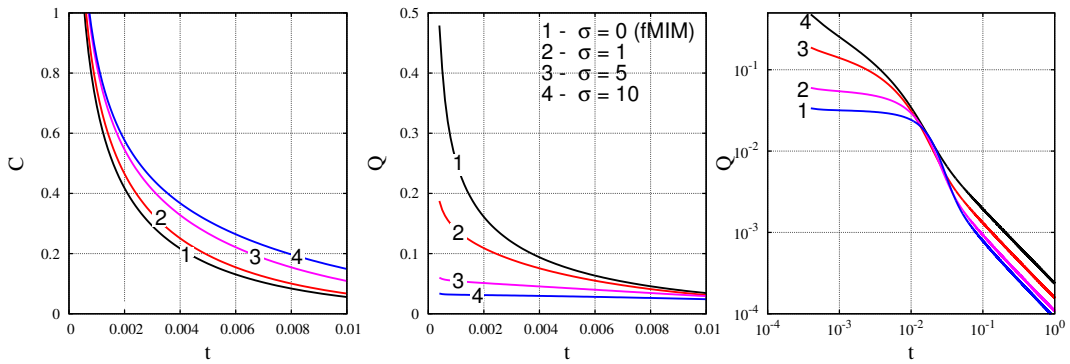


FIGURE 2. The breakthrough curves for mobile (C) and immobile (Q) concentrations at the point $x = 0.5$ for different values of σ indicated in the legend. The breakthrough curve for the immobile concentration is plotted in the log-log coordinates in right panel. The calculations have been started from the initial peak at point $x = 0.5$.

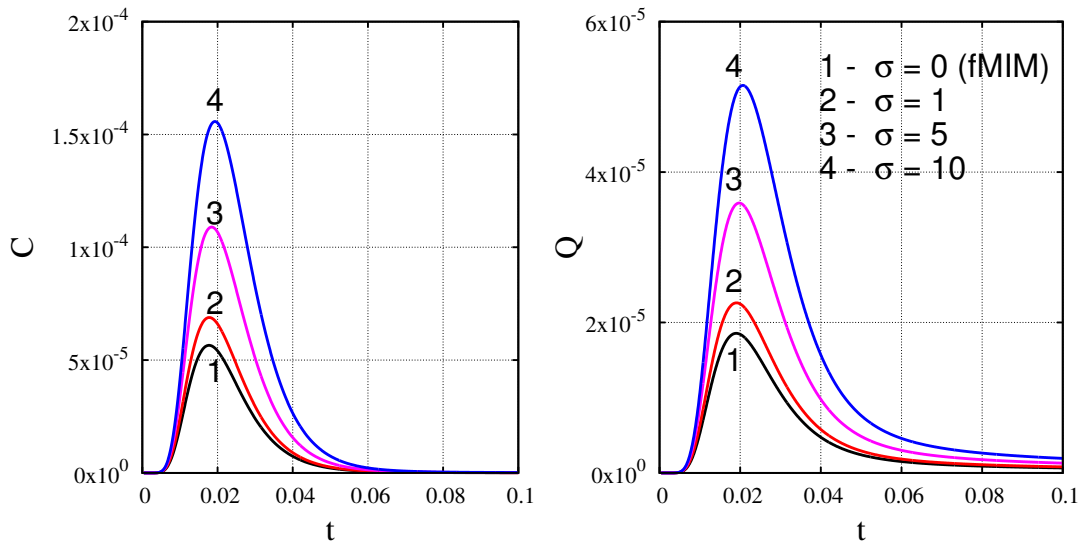


FIGURE 3. The breakthrough curves for mobile (C) and immobile (Q) concentrations at point $x = 0.99$ for different values of σ indicated in the legend. The calculations have been started from the initial peak at point $x = 0.5$.

The breakthrough curves plotted in Fig. 3 have been obtained at the end of the cell (coordinate $x = 0.99$). These curves have asymmetric form typical for the solute transport in porous media [3,4,6,10,16].

The breakthrough curves plotted in Fig. 2 and Fig. 3 show that near the initial peak the difference between the linear and nonlinear fMIM models is small, but at the end of the cell this difference is significant. However, the large time asymptotics for all curves plotted in the figures are similar. This property can be useful for describing solute transport in sand, because the description based on the linear

fMIM gives good fit of experimental data near the source and poor fit at some distance, but correctly predicts the decline of concentration. For the sake of illustration, we present in Fig. 4 the results of identification of the linear fMIM parameters.

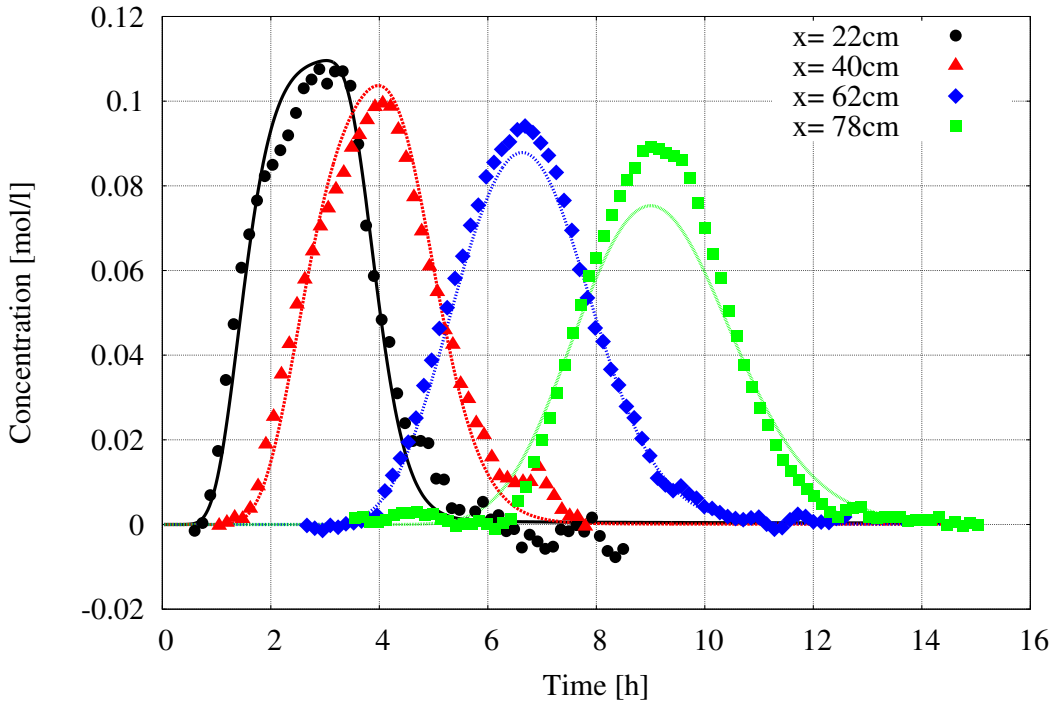


FIGURE 4. The breakthrough curves for total ($C+Q$) concentration at four fixed points. The source of solute is located at point $x = 0 \text{ cm}$. The points indicate the experimental result and lines denote the results of linear fMIM approximation. The dimensionless parameter for fMIM is assumed to be equal to $\beta \approx 1.8$, $\gamma \approx 0.9$ and $\sigma = 0$. The distance from the source to the investigated point is indicated in the legend. The data for this figure has been taken from the paper [21].

5. Conclusion

Solute transport in porous media is a very complicated phenomena, the specific features of which accounts for a large number of models in the literature that bring out and describe different aspects of this phenomenon [1, 6–8, 10–12]. Usually, each model is constructed for description of one specific feature. The most important characteristics are the power decline of concentration in the long-term limit when the concentration value is small (linear fMIM model [10]) and the limitation of immobilization process at sufficiently high concentration (nonlinear MIM model [12]). In the present paper, we have constructed the hybrid nonlinear fractional MIM model, which provides a framework for describing both features. It has been demonstrated that the asymptote of nonlinear fMIM model at small concentration values is a linear fMIM. Also, in the limit of integer exponent of memory kernel the equilibrium between the mobile and immobile phases is described by the Langmuir-type isotherm within the frame of the nonlinear fMIM. The latter result was the experimental finding, which was the main motive for constructing the nonlinear MIM model [12].

To illustrate the performance of the new nonlinear fMIM model we have solved the one dimensional problem of dissolution of the localized concentration peak. Since the analytical solution of this problem is difficult to obtain, we have applied and tested a numerical method based on the semi-implicit computational scheme of the first order of accuracy in time (see eqs. (4.2), (4.4)). The main results of the numerical simulation are presented in Section 4.2. These are the profiles of concentration and breakthrough curves, which demonstrate the main features of solute transport in porous media, such as a power decline of concentration with time at low concentration and limitation of the immobilization process at high concentration.

The new nonlinear fractional MIM model can be applied to the problems, in which solute concentration changes within a rather wide range. This type of problems requires consideration of both effects and therefore it appears unreasonable to investigate these effects within nonlinear MIM or linear fMIM model, which lead to inaccurate description of experimental data (see for example Fig. 4).

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References

- [1] L. Lapidus, N. R. Amundson. *Mathematics of Adsorption in Beds. VI. The Effect of Longitudinal Diffusion in Ion Exchange and Chromatographic Columns* J. Phys. Chem., 56 (1952), 984–988.
- [2] D. A. Nield, A. Bejan. *Convection in Porous Media*, Springer, New York, 2006.
- [3] B. D. Kay, D. E. Elrick. *Adsorption and movement of lindane in soil*. Soil Sci., 104 (1967), 314–322.
- [4] M. Bromly, C. Hinz. *Non-Fickian transport in homogeneous unsaturated repacked sand*. Water Resour. Res., 40 (2004), W07402.
- [5] P. Gouze, T. Le Borgne, R. Leprovost, G. Lods, T. Poidras, P. Pezard. *Non-Fickian dispersion in porous media: 1. Multiscale measurements using single-well injection withdrawal tracer tests*. Water Resour. Res., 44 (2008), W06426.
- [6] M. T. Van Genuchten, P. J. Wierenga. *Mass transfer studies in sorbing porous media I. Analytical solutions*. Soil. Sci. Soc. Am. J., 40 (1976), 473–480.
- [7] F. T. Lindstrom, R. Haque, V. H. Freed, L. Boersma. *Theory on movement of some herbicides in soils: Linear diffusion and convection of chemicals in soil* Environ. Sci. Technol., 2 (1967) 561–565.
- [8] H. A. Deans. *A mathematical model for dispersion in the direction of flow in porous media*. Soc. Pet. Eng. J., 3 (1963), 49–52.
- [9] D. E. Nielsen, J.W. Biggar. *Miscible displacement in soils I. Experimental Information*. Soil Sci. Soc. Am. Proc., 25 (1961), 1–5.
- [10] R. Schumer, D. A. Benson, M. M. Meerschaert, B. Baeumer. *Fractal mobile/immobile solute transport* Water Resour. Res., 39 (2003), 1296.
- [11] R.D. Harter, D.E. Baker. *Applications and misapplications of the Langmuir equation to soil adsorption phenomena*. Soil Sci. Soc. Am. J., 41 (1977), 1077–1080.
- [12] H. M. Selim, M. C. Amacher. *Reactivity and Transport of Heavy Metals in Soils*. CRC/Lewis, Boca Raton, Florida, 1997.
- [13] S. Falconer, A. Al-Sabbagh, S. Fedotov. *Nonlinear Tempering of Subdiffusion with Chemotaxis, Volume Filling, and Adhesion*. Math. Model. Nat. Phenom. Vol. 10 (2015), 48–60.
- [14] R. Metzler, J. Klafter. *The random walk's guide to anomalous diffusion: a fractional dynamics approach*. Phys. Rep., 339 (2000), 1–77.
- [15] R.J. Beerends. *Fourier and Laplace Transforms*. Cambridge University Press, Cambridge, 2003.
- [16] M. W. Becker, A. M. Shapiro. *Tracer transport in fractured crystalline rock: Evidence of nondiffusive breakthrough tailing*, Water Resour. Res., 36 (2000), 1677–1686.
- [17] R. Gorenflo, F. Mainardi. *Integral and differential equations of fractional order*. CISM lecture notes, 378 (1997), 223–274.
- [18] Z. Gerstl, Y. Chen, U. Mingelgrin, B. Yaron. *Toxic Organic Chemicals in Porous Media*. Ecological Studies Ser., Springer, Berlin, 1989.
- [19] D. G. Duff, David G., S. M. C. Ross, D. H. Vaughan. *Adsorption from Solution: An Experiment to Illustrate the Langmuir Isotherm*. J. Chem. Ed., 65(1988), 815.
- [20] B. Maryshev, A. Cartalade, C. Latrille, M. Joelson, M.-Ch. Neel. *Adjoint state method for fractional diffusion: parameter identification*. Comput. Math. Appl., 66 (2013), 630–638.
- [21] B. Maryshev, A. Cartalade, C. Latrille, M.-Ch. Neel. *Adjoint state method for fractional mobile-immobile model*, Proceedings (CD) of the 4th International Conference on Porous Media and its Applications in Science and Engineering, ICPM4, AIP, Potsdam, Germany, 2012.