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SOLUTION OF INVERSE PROBLEMS IN CONTAMINANT TRANSPORT WITH ADSORPTION

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Abstract. In this paper, solution of inverse contaminant transport problems is studied, including nonlinear sorption in equilibrium and non-equilibrium mode. A precise numerical solver for the direct problem is discussed. The method is based on time stepping and operator splitting with respect to the nonlinear transport, diffusion and adsorption. The nonlinear transport problem corresponds to a multiple Riemann problem and is solved by modified front tracking method. The diffusion problem is solved by a finite volume scheme and the sorption part is solved by an implicit numerical scheme. The solution of the inverse problem is based on an iterative approach. The gradient of the cost functional with respect to the determined parameters is constructed by means of solution of the corresponding adjoint system. Numerical examples are presented for a 1D situation and for a dual-well setting with steady-state flow between injection and extraction wells.

1. Mathematical model

Contaminant transport with dispersion and adsorption is modelled by the following system:

$$\begin{aligned} \partial_t\varphi(C) + \operatorname{div}(\bar v \cdot C - D\nabla C) &= -\frac{\theta_n}{\theta_0}\partial_t S, \\ \partial_t S &= \kappa(\psi_n(C) - S) \end{aligned} \tag{1}$$

where $x \in \Omega \subset R^d$, $t \in (0,T) := I$, $d = 2,3$. The boundary conditions are:

$$\begin{aligned} C &= C_0(t) && \text{on } \partial\Omega_1, \\ (\bar v \cdot C - D\nabla C)\cdot\nu &= 0 && \text{on } \partial\Omega_2, \\ -D\nabla C\cdot\nu &= 0 && \text{on } \partial\Omega_3. \end{aligned} \tag{2}$$

where $\partial\Omega_i \subset \partial\Omega$ $(i = 1,2,3)$ are nonintersecting. The initial condition is

$$C(x,0) = 0, \qquad S(x,0) = 0 \tag{3}$$

The unknown $C(x,t)$ represents the volumetric contaminant concentration in the ground water and $S(x,t)$ is the volume of contaminant per unit volume of the corresponding porous material (rock or soil).

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The vector $\bar{v}$ represents the groundwater velocity and D is the dispersivity tensor given by:

$$D_{ij} = \left\{ (D_0 + \alpha_T|v|)\delta_{ij} + \frac{v_i v_j}{|v|}(\alpha_L - \alpha_T) \right\}$$

where δ_{ij} is Kronecker symbol, D_0 is molecular diffusion coefficient and α_L and α_T are longitudinal and transversal dispersivities.

The function $\varphi(C)$ is of the form $\varphi(C) = C + \dfrac{\theta_e}{\theta_0}\psi_e(C)$. Functions $\psi_e(C)$ and $\psi_n(C)$ are sorption isotherms characterizing equilibrium and nonequilibrium adsorption process. Constants θ_e and θ_n are volumetric ratios of the materials adsorbing in equilibrium and nonequilibrium modes in the considered porous medium. κ is the sorption rate coefficient for nonequilibrium sorption and θ_0 is porosity.

2. Numerical solution of the direct problem

The numerical scheme is based on time stepping and operator splitting approach. Let us discretize the time interval I, $t_0 = 0, t_1, \dots, t_{n-1}, t_n = T$. Then in each time step, the original problem (1)–(3) can be split in three subproblems – nonlinear transport, diffusion and adsorption. The transport problem is represented by an equation of the form:

$$\partial_t \varphi(\phi) + \mathrm{div}(\bar{v}\phi) = 0, \qquad t \in (t_k, t_{k+1}), \qquad \phi(t_k) = C^k \tag{4}$$

with the boundary condition $\phi(x,t) = C_0(t)$ at the inflow boundary. Let $\mathcal{T}_C(t)c_0$ be the operator that generates the solution of the transport problem with some initial condition c_0 in time t. Let us use the notation $C^{k+1/3} := \mathcal{T}_C(t_{k+1} - t_k)C^k$. Further let us consider the diffusion problem

$$\partial_t \varphi(\phi) + \mathrm{div}(D\nabla\phi) = 0, \qquad t \in (t_{k+1}, t_k), \qquad \phi(t_k) = C^{k+1/3} \tag{5}$$

with the corresponding boundary conditions of the form (2) . The corresponding operator is denoted by $\mathcal{D}_C(t)c_0$. Then we have $C^{k+2/3} := \mathcal{D}_C(t_{k+1} - t_k)C^{k+1/3} = \mathcal{D}_C(t_{k+1} - t_k)\mathcal{T}_C(t_{k+1} - t_k)C^k$. The adsorption problem reads:

$$\begin{gathered} \partial_t \varphi(\phi) + \frac{\theta_n}{\theta_0}\partial_t S = 0, \qquad \partial_t S = \kappa(\psi_n(\phi) - S) \\ t \in (t_k, t_{k+1}), \qquad \phi(t_k) = C^{k+2/3}, \qquad S(t_k) = S^k \end{gathered} \tag{6}$$

Let $\mathcal{A}_C(t)c_0$ be the operator generating the solution (the concentration of contaminant in the water) of the adsorption problem. Then we finally set

$$\begin{aligned} C^{k+1} &= \mathcal{A}_C(t_{k+1} - t_k)C^{k+2/3} = \mathcal{A}_C(t_{k+1} - t_k)\mathcal{D}_C(t_{k+1} - t_k)\mathcal{T}_C(t_{k+1} - t_k)C^k \\ S^{k+1} &= S(t_{k+1}) \end{aligned}$$

2.1. Numerical approximation of (4)

The crucial point is to construct a precise approximation with low numerical dispersion and consequently to project it to a discretization grid used for the numerical approximation of the diffusion problem. Generally, we use implicit Godunov type higher order approximation. In case of Freundlich or Langmuir sorption isotherms the function $\varphi(C)$ is convex or concave which makes construction of an entropy solution for the corresponding Riemann problems easier, especially after additional dimensional splitting.

2.2. Numerical approximation of (5)

In order to solve the dispersion problem, we use standard finite volume approximation and solve the resulting nonlinear algebraic system by means of Newton iterations. In the case of larger time steps we can use a relaxation method instead of finite volumes (see [**4**] for details.)

2.3. Numerical approximation of (6)

Integrating (6) and using initial conditions we obtain:

$$\varphi(\phi(t)) + S(t) = \varphi(C^k) + S^k, \qquad t \in (t_k, t_{k+1})$$

$$S(t) = S^k \, \mathrm{e}^{-\kappa t} + \kappa \int_{t_k}^{t} \mathrm{e}^{-\kappa(t-s)} \, \psi_n(\phi(s)) \; \mathrm{d}s, \qquad t \in (t_k, t_{k+1})$$

and hence, after elimination of S, we solve the resulting nonlinear integral equation by time discretization with a time substep $\sigma = (t_{k+1} - t_k)/m$. We approximate the unknown function $\psi_n(\phi(t))$ by a piecewise linear function, linear on each of the time subintervals (σ_{j-1}, σ_j). Then, successively for $j = 1, \dots, m$ we determine $\phi_j \approx \phi(\sigma_j)$ using Newton method (see [**8**]).

3. Solution of the inverse problem

By an inverse problem we mean the problem of parameter identification, that means we try to determine some of the unknown values of the model parameters according to measurements in a real site and results obtained by simulations. Let $\mathbf{p}$ be the vector of parameters to be determined. Essentially, we want to minimize the cost functional

$$\mathcal{F}(C, \mathbf{p}) = \int_0^T \int_{\partial\Omega_3} \bar{v}.\nu (C - C_*)^2 \, \mathrm{d}x \, \mathrm{d}t \tag{7}$$

where $C_*(x,t)$ is the concentration measured at the outflow boundary and $C(x,t,\mathbf{p})$ is the numerical solution of direct problem with parameter vector $\mathbf{p}$.

Minimization of the functional (7) is realized by means of some optimization technique (conjugated gradients, Levenberg-Marquardt method) and requires the gradient of $\mathcal{F}$. This gradient can be computed numerically by approximating the derivatives by finite differences. In cases when we want to determine more than one or two parameters, this strategy can be quite costly. In that case, using Lagrange method via the solution of an adjoint system seems to be a better alternative. Let us illustrate the technique on the case when the sorption parameters are the ones to be determined, i.e. the functions $\varphi(C,\mathbf{p_1})$, $\psi_n(C,\mathbf{p_2})$ and the parameter κ, where $\mathbf{p_1}$ and $\mathbf{p_2}$ represent the isotherm parameters. The adjoint system to (1)–(3) is then of the following form:

$$\nabla_{\mathbf{p_1}}\varphi(C,\mathbf{p_1})\partial_t\Psi + \bar{v}\cdot\nabla\Psi + \operatorname{div}(D\nabla\Psi) - \frac{\theta_n}{\theta_0}\kappa\nabla_{\mathbf{p_2}}\psi_n(C,\mathbf{p_2})(\Psi-\eta) = 0$$
$$\frac{d}{\mathrm{d}t}\eta = \kappa(\eta-\Psi)$$
$$\frac{d}{\mathrm{d}t}\xi = \kappa(\xi-\eta-\Psi)$$

with the boundary and initial conditions:

$$\begin{aligned} \Psi(x,t) &= 0 && \text{on } \partial\Omega_1\\ D\nabla\Psi\cdot\nu &= 0 && \text{on } \partial\Omega_2\\ \bar{v}\Psi + (D\nabla\Psi)\cdot\nu &= 2\bar{v}\cdot\nu(C-C_*) && \text{on } \partial\Omega_2 \end{aligned}$$
$$\Psi(x,T)=0, \qquad \eta(T)=0, \qquad \xi(T)=0$$

The derivatives of $\mathcal{F}$ with respect to $\mathbf{p_1}$, $\mathbf{p_2}$ and κ can be now expressed as:

$$\nabla_{\mathbf{p_1}}\mathcal{F} = \int_0^T\int_\Omega \nabla_{\mathbf{p_1}}\varphi(C,\mathbf{p_1})\partial_t\Psi\,\mathrm{d}x\,\mathrm{d}t + \int_\Omega \nabla_{\mathbf{p_1}}\varphi(C_0,\mathbf{p_1})\Psi(x,T)\,\mathrm{d}x$$
$$\nabla_{\mathbf{p_2}}\mathcal{F} = -\frac{\theta_n}{\theta_0}\kappa\int_0^T\int_\Omega \nabla_{\mathbf{p_2}}\psi_n(C,\mathbf{p_2})(\Psi-\eta)\,\mathrm{d}x\,\mathrm{d}t$$
$$\partial_\kappa\mathcal{F} = -\frac{\theta_n}{\theta_0}\kappa\int_0^T\int_\Omega \psi_n(C,\mathbf{p_2})(\Psi-\eta-\xi)\,\mathrm{d}x\,\mathrm{d}t$$

4. Dual-well application

This application was extensively discussed and treated in [**1**]. The dual-well system is a practical tool for evaluating properties of a groundwater aquifer. It consists of two monitor wells and the procedure is based on injecting some tracer in one of the wells and monitoring its concentration in the other well. According to such measurements, we are able to determine values of various model parameters as was described in Section 3.

In our computations, we apply Dupuit-Forchheimer approximation to the underlying groundwater flow, that means we neglect the vertical component of the flow. Moreover we assume that the dual-well system generates a steady-state flow in the aquifer. The wells are considered to be fully penetrable and the injection and extraction is uniformly distributed over the depth of the well.

Now let us consider that the injection well with radius r_1 is situated at point $(d,0)$ and the extraction well with radius r_2 at point $(-d,0)$ in the (x,y)-plane. We have to solve the corresponding convection-diffusion-adsorption problem in the domain consisting of whole plane except the inner space of the wells. The problem is symmetric along the x-axis and therefore we can consider only one half-plane of the original domain. Moreover, let us consider a new coordinate system with coordinates u, v:

$$x = \frac{\delta}{2}\frac{\sinh v}{\cosh v - \cos u}, \quad y = \frac{\delta}{2}\frac{\sin u}{\cosh v - \cos u}$$

where

$$\sqrt{r_1^2 + \frac{1}{4}\delta^2} + \sqrt{r_2^2 + \frac{1}{4}\delta^2} = 2d$$

In these new coordinates, the original half-plane domain corresponds to a rectangle $\widetilde{\Omega} = (0, \pi) \times (v^{(1)}, v^{(2)})$ where

$$\sinh v^{(1)} = -\frac{\delta}{2r_1}, \qquad \sinh v^{(2)} = \frac{\delta}{2r_2}$$

Moreover, the streamlines and equipotential curves are parallel with the coordinate axes and the contaminant transport is now realized only in v-direction. Therefore, instead of the original two-dimensional transport problem we can now solve a set of one-dimensional problems corresponding to the individual streamlines.

The original problem (1)–(3) is now transformed to the following form:

$$\begin{aligned} \partial_t \varphi(C) - G\partial_v C - g\{\partial_u(a\partial_u C) + \partial_v(b\partial_v C)\} &= \frac{\theta_n}{\theta_0}\partial_t S \\ \partial_t S &= \kappa(\psi_n(C) - S) \end{aligned} \tag{8}$$

and the boundary conditions are now of the form:

$$C(u, v^{(1)}, t) = C_0(t) \;\text{ on } \Gamma_1, \quad \partial_u C = 0 \text{ on } \Gamma_2 \cup \Gamma_4, \quad \partial_v C = 0 \;\text{ on } \Gamma_3$$

where $\Gamma_1 := (0, \pi) \times \{v = v^{(2)}\}$, $\Gamma_2 := \{0\} \times (v^{(1)}, v^{(2)})$, $\Gamma_3 := (0, \pi) \times \{v^{(1)}\}$ and $\Gamma_4 := \{\pi\} \times (v^{(1)}, v^{(2)})$. The coefficients g, G, a, b in the transformed equation (8) depend on the coordinates u, v, on model parameters α_L, α_T, D_0, θ_0 and on the saturation of the aquifer.

4.1. Inverse problem in $\widetilde{\Omega}$

Let $C_{\mathbf{p}}(u, v^{(1)}, t)$ be the contaminant concentration at the border of the extraction well, assuming that the values of model parameters are given by vector $\mathbf{p}$. The average concentration in the extraction well is then expressed as:

$$C_{\mathbf{p}}^{(1)}(t) = \frac{1}{\pi}\int_0^\pi C_{\mathbf{p}}(u, v^{(1)}, t)\,\mathrm{d}u$$

The actual average concentration in the well can be obtained by measurements, let $C_M^{(1)}(t)$ represent the measured values. Then our cost functional is given by:

$$\mathcal{F}(\mathbf{p}, C_{\mathbf{p}}) = \int_0^T (C_{\mathbf{p}}^{(1)}(t) - C_M^{(1)}(t))^2 \;\mathrm{d}t$$

The gradient of $\mathcal{F}$ is obtained by means of the solution of the adjoint system as described in Section 3.

5. Convergence of the operator splitting method

In [**9**], the convergence of the splitting method described in Section 2 was proved for a 1D problem of the following form:

$$
\begin{aligned}
\partial_t\varphi(C) - F(v)\partial_v C - g(v)\partial_v(b(v)\partial_v C) + \partial_t S &= 0 \\
\partial_t S &= \kappa(\psi_n(C) - S)
\end{aligned} \tag{9}
$$

where $\varphi(C) = C + \psi_e(C)$, $v \in \langle v^{(1)}, v^{(2)}\rangle$, $t \in \langle 0, T\rangle$. The technique of the proof is based on the ideas presented in [**2**], [**3**], [**6**], [**7**].

Let us first define the weak solution for the problem (9). Let us consider a test function $\phi(v,t) \in C^\infty(\Omega)$, $\Omega = \langle v^{(1)}, v^{(2)}\rangle \times \langle 0, T\rangle$, with compact support in $\langle v^{(1)}, v^{(2)}\rangle$, $\phi(v,T) = 0$ a $\zeta(v,t) \in C^\infty(\Omega)$, $\zeta(v,T) = 0$. The we obtain the variational formulation:

$$
\begin{aligned}
&\int_0^T \int_{v^{(1)}}^{v^{(2)}} \Big[\varphi(C)\partial_t\phi - C\partial_v(F(v)\phi) + C\partial_v(b(v)\partial_v(g(v)\phi)) + S\partial_t\phi\Big] \,\mathrm{d}v\,\mathrm{d}t \\
&\qquad + \int_{v^{(1)}}^{v^{(2)}} \phi(v,0)\varphi(C(v,0))\,\mathrm{d}v + \int_{v^{(1)}}^{v^{(2)}} \phi(v,0)S(v,0)\,\mathrm{d}v = 0
\end{aligned} \tag{10}
$$

$$
\int_0^T \int_{v^{(1)}}^{v^{(2)}} \Big[S\partial_t\zeta + \kappa(\psi_n(C) - S)\zeta\Big] \,\mathrm{d}v\,\mathrm{d}t + \int_{v^{(1)}}^{v^{(2)}} \zeta(v,0)S(v,0)\,\mathrm{d}v = 0 \tag{11}
$$

Let us recall the operators $\mathcal{T}_C(t)$, $\mathcal{D}_C(t)$ and $\mathcal{A}_C(t)$ corresponding to the three parts of the operator splitting process and similar operators $\mathcal{T}_S(t)$, $\mathcal{D}_S(t)$, $\mathcal{A}_S(t)$ for the unknown S. The whole process of solving the problem can then be expressed in the following way:

$$
\begin{aligned}
C^{k+1} &= [\mathcal{A}_C(\tau_k) \circ \mathcal{D}_C(\tau_k) \circ \mathcal{P} \circ \mathcal{T}_C(\tau_k)]\, C^k \\
S^{k+1} &= \mathcal{A}_S(\tau_k) S^k \\
C^0 &= C(v,0) \\
S^0 &= S(v,0)
\end{aligned} \tag{12}
$$

for $k = 1 \dots n-1$, where $\mathcal{P}$ is the projection operator.

While using a numerical method, we obtain an approximate solution (C^k, S^k) in every point t_k of the time discretization. Anyway, in order to obtain convergence results we need functions that are defined on the whole interval $\langle 0, T\rangle$. Let us therefore define the following sequences:

$$
C_\nu(v,t) = \begin{cases}
\mathcal{T}_C(3(t-t_k))C^k(v) & t \in \langle t_k, t_{k+1/3}) \\
\mathcal{D}_C(3(t-t_{k+1/3}))C^{k+1/3}(v) & t \in \langle t_{k+1/3}, t_{k+2/3}) \\
\mathcal{A}_C(3(t-t_{k+2/3}))C^{k+2/3}(v) & t \in \langle t_{k+2/3}, t_{k+1})
\end{cases}
$$

$$
S_\nu(v,t) = \begin{cases}
\mathcal{T}_S(3(t-t_k))S^k(v) \equiv S^k & t \in \langle t_k, t_{k+1/3}) \\
\mathcal{D}_S(3(t-t_{k+1/3}))S^k(v) \equiv S^k & t \in \langle t_{k+1/3}, t_{k+2/3}) \\
\mathcal{A}_S(3(t-t_{k+2/3}))S^k(v) & t \in \langle t_{k+2/3}, t_{k+1})
\end{cases}
$$

The parameter ν corresponds to time, resp. space discretization. The definition of the sequences formally corresponds to the operator splitting procedure.

The convergence proof consists of several basic steps:

- We prove that C_ν, S_ν are uniformly bounded.
- We show that C_ν, S_ν have bounded total variation in the space variable.
- We prove that C_ν, S_ν are L_1-Hölder continuous in time with coefficient 1/2.
- Applying Riesz-Frechet-Kolmogorov's compactness criterion we prove the existence of convergent subsequences of C_ν, S_ν converging for $\nu \to 0$ in L_1 to some $C(v,t)$, $S(v,t)$.
- We show that the limits $C(v,t)$, $S(v,t)$ satisfy the variational formulation (10)–(11).

The main result is summarized in the following theorem:

Theorem 5.1. *Let the functions $\psi_e(C)$, $\psi_n(C)$ be sorption isotherms, both nondecreasing and Lipschitz continuous. In addition, let us assume that functions $F(v)$, $g(v)$ and $b(v)$ are smooth and $g(v)$, $b(v)$ are positive. If both $C(v,0)$ and $S(v,0)$ are nonnegative, bounded and of bounded total variation, than the numerical solution $(C^n(v), S^n(v))$ obtained by the operator splitting scheme* (12) *converges to the weak solution of the convection-diffusion-adsorption problem* (9) *for $n \to \infty$.*

6. Numerical experiments

In order to verify the efficiency of the suggested numerical method, a great amount of numerical experiments has been realized. In 1D, it is possible to test the accuracy of the method by comparing the results with the analytical solution (in a simple case) or with a semi-analytical solution of a problem with only equilibrium adsorption. For such comparisons, see e.g. [**5**], [**9**].

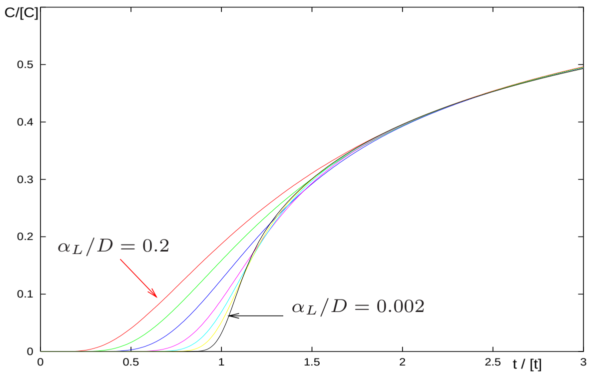

Figure 1. BTC-step input, $\alpha_L = 0.2$, 0.1, 0.05, 0.02, 0.01, 0.005 and 0.002.

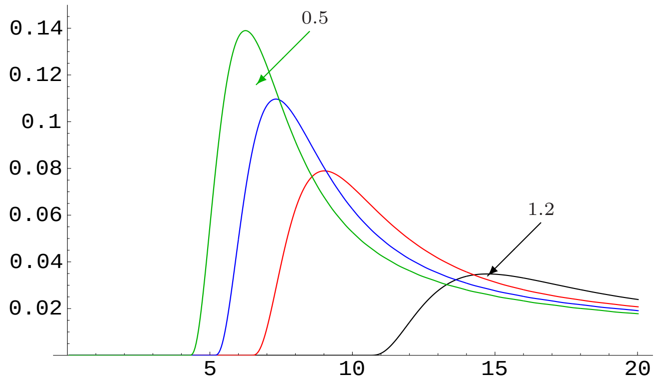

Figure 2. Breakthrough curves for $k = 0.5$, 0.8, 1.0, 1.2.

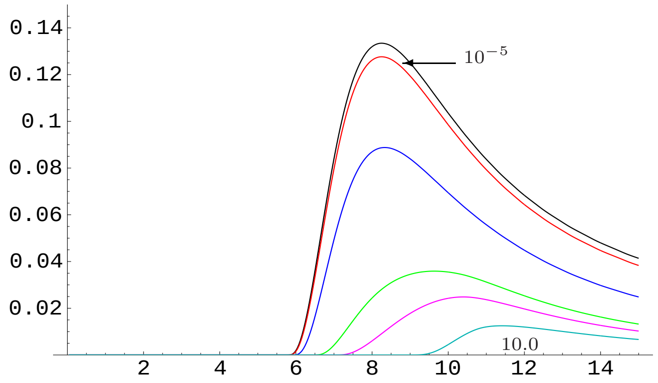

Figure 3. Breakthrough curves for $\kappa = 10^{-5}$, 0.01, 0.1, 0.5, 1.0, 10.0.

6.1. Numerical experiments for direct problems

In the following experiments, we will present some results obtained for a two-dimensional dual-well problem. Namely we will show some computed breakthrough curves for the extraction well to illustrate the influence of various model parameters on the solution. Such experiments are important when we want to test the applicability of the numerical method to inverse problems – only a method that is sensitive enough to changes of the parameters can be used for precise parameter determination.

We consider two wells with radii $r_1 = r_2 = 15$cm situated at points $(-5, 0)$ and $(5, 0)$ in the (x, y)-plane. The aquifer height is 10m and the piezometric head in the injection well is 15m. The porosity of the soil is $\theta_0 = 0.2$ and we consider

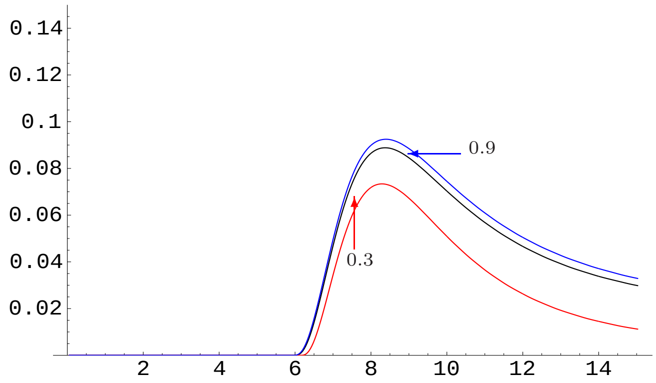

Figure 4. Breakthrough curves for q, $q = 0.3$, 0.75, 0.9.

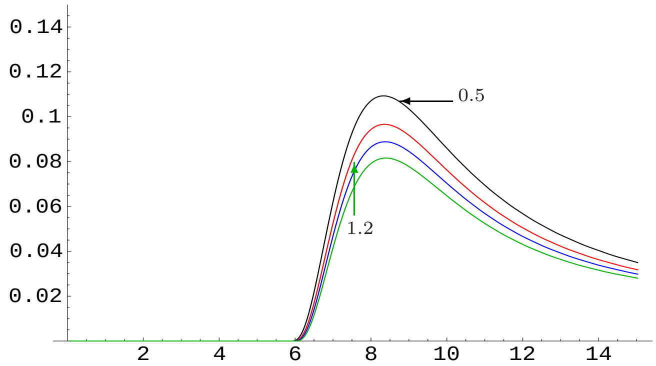

Figure 5. Breakthrough curves for a, $a = 0.5$, 0.8, 1.0, 1.2.

$\theta_e = \theta_n = \theta_0$. We consider the contaminant dispersion to be one-dimensional, i.e. $\alpha_T = 0$, $D_0 = 0$. The equilibrium sorption isotherm is of the form $\psi_e(C) = C^{0.75}$.

First we show an experiment for a step input (permanent injection of contaminant with $C_0(t) = 1$ in the injection well). Here the piezometric head in the extraction well was 10m. We apply the method in 80 strips, each with 200 inner space discretization points. The injected front is tracked with 10 moving grid points, and the time step of the operator splitting is 0.05 days. We consider that only equilibrium adsorption is present in the aquifer. The resulting breakthrough curves for the confined flow for 7 different values for α_L are plotted in Figure 1.

In the following experiments, we present the results obtained for pulse input – we inject contaminant with concentration $C_0(t) = 1$ during 2 days and afterwards the injection is stopped. We consider here nonequilibrium adsorption with sorption isotherm of the form $\psi_n(C) = aC^q$. To discretize the rectangular domain, we used a space grid of 80×400 grid points and the maximum time step was $\Delta t = 0.04$ days. The hydraulic head in the injection well was 4m.

The parameters that we are interested in are hydraulic conductivity k, sorption rate coefficient κ, and the parameters of nonequilibrium sorption isotherm q and a. Only one parameter is varied in each experiment, the rest of them have default values $k = 0.864$, $\kappa = 0.1$, $q = 0.75$, $a = 1$. In Figure 2, we show results for various values of k monitored during 20 days, Figures 3, 4 and 5 demonstrate the influence of changing κ, q and a, respectively, and the data was recorded during 15 days. All experiments confirm that the effect of variation of each particular parameter can be clearly recognized.

6.2. Experiments for inverse problems

Finally we show a few experiments illustrating application of the splitting method to problems of parameter determination.

First we show two results obtained by using Levenberg-Marquardt (LM) minimization method and numerical differentiation for evaluating the gradient of cost functional. We consider the dual-well problem as in the previous section and the pulse input. In the first experiment, we determine sorption rate coefficient κ, we consider dispersivity $\alpha_L = 0.1$ and we use fixed space grid of 80×400 points. In the second experiment we determine nonequilibrium sorption isotherm parameters a, q, where $\psi_n(C) = aC^q$. We have $\alpha_L = 0.0$ and we use adaptive space grid of 80×250 points. All other parameters have default values as stated in Section 6.1. The results are shown in Table 1.

Table 1. Determination of $\kappa = 0.1$ with initial guess $\kappa = 0.6$ and of $\psi_n(C) = C^{0.75}$ with starting values $a = 1.2$, $q = 0.5$.

step	κ	cost
1	0.385136	0.168396
2	0.175589	0.0299582
3	0.108411	0.000558969
4	0.100648	3.49939e−06
5	0.100012	1.21477e−09
6	0.1	1.83997e−13

step	q	a	cost
1	0.511351	1.15679	0.0218165
2	0.529183	1.12295	0.0149195
3	0.546005	1.06303	0.00832204
4	0.605499	1.03455	0.00332059
5	0.669511	0.979249	0.000342218
6	0.705181	0.973469	0.00012843
7	0.728392	0.980453	5.59663e−05
8	0.73799	0.989019	4.03591e−05
9	0.741269	0.995396	1.79671e−05
10	0.744679	0.995711	1.3971e−05
11	0.74468	0.995711	1.39603e−05

In the following experiment, we applied the adjoint system method. We use an experiment, where the breakthrough curve is the result of the direct problem with the following parameters: $\alpha_L = 0.02$, equilibrium sorption isotherm $\Psi_e(C) = aC^q$ with $a = 0.1$ and $q = 0.8$, and where there are 100 measurement points during the time interval $(0, 18$ days$)$. Operator splitting is done every 0.1 days. At the inflow boundary there is an injection $C_0(t) = 1$ for $t \in (0,1)$, and 0 afterwards. Nonequilibrium adsorption is not present.

We reconstruct isotherm parameters a and q. We present the value of $\nabla_{\mathbf{p}} F$ ($\mathbf{p} = (a,q)$) calculated with the forward and central difference formula (FD and CD) and with the value arising from the adjoint method (AM). The variation of the parameters was ($\delta \mathbf{p} = 0.01$) and we stop the iterations when the cost functional $F < 0.0001$. The results are in Table 2. The first and fourth line are initial values, the rest are the minima as found by line search using the conjugate gradient method. We can see that FD does not in general give good values, and that the adjoint equation method gives values for the gradient which are comparable with a central difference formula. We conclude that using the adjoint method is as good, if not better, than using a CD formula for the gradient. However, AM includes solving a linear PDE in this case, and is obtained in a fraction of the time needed to solve the direct problem. For comparison, we also add the values obtained by Levenberg-Marquardt method with the same number of iterations.

Table 2. Determination of equilibrium sorption parameters $a = 0.1$, $q = 0.8$ and gradients of the cost functional.

(a,q) − AM	(a,q) − LM	FD	CD	AM
(0.2, 0.6)	(0.2, 0.6)	(0.095,-0.0065)	(0.0938,−0.00644)	(0.0874, −0.0068)
(0.094, 0.608)	(0.134 0.528)	(0.0074, −0.00057)	(0.00027 , −0.0006)	(0.00012, −0.00053)
(0.1016, 0.729)	(0.105 0.608)	Cost = 0.000091		
(0.1, 0.3)	(0.1, 0.3)	(0.0484, −0.0088)	(0.0382 , −0.00919)	(0.0349, −0.00899)
(0.0794, 0.305)	(0.098, 0.366)	(0.0107, −0.00497)	(0.00152 , −0.00531)	(−0.0028, −0.00514)
(0.0742, 0.474)	(0.096, 0.448)	(−0.0151, −0.00063)	(−0.023, −0.00074)	(−0.024, −0.00066)
(0.0926, 0.516)	(0.095, 0.547)	(0.0103, −0.00133)	(0.0031 , −0.00136)	(0.0023, −0.00121)
(0.1018, 0.769)	(0.096, 0.668)	Cost = 0.000038		

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