ELSEVIER

PII: S0309-1708(96)00046-2

*Advances in Water Resources* 21 (1998) 237–249

0309-1708/97/$17.00

# Solution of the nonlinear transport equation using modified Picard iteration

**Kangle Huang,* Binayak P. Mohanty, Feike J. Leij & M. Th. van Genuchten**

*US Salinity Laboratory, Riverside, California, USA*

(Received 6 February 1996; accepted 13 May 1996)

The transport and fate of reactive chemicals in groundwater is governed by equations which are often difficult to solve due to the nonlinear relationship between the solute concentrations for the liquid and solid phases. The nonlinearity may cause mass balance errors during the numerical simulation in addition to numerical errors for linear transport system. We have generalized the modified Picard iteration algorithm of Celia *et al.*[5] for unsaturated flow to solve the nonlinear transport equation. Written in a 'mixed-form' formulation, the total solute concentration is expanded in a Taylor series with respect to the solution concentration to linearize the transport equation, which is then solved with a conventional finite element method. Numerical results of this mixed-form algorithm are compared with those obtained with the concentration-based scheme using conventional Picard iteration. In general, the new solver resulted in negligible mass balance errors ($< |10^{-8}|\%$) and required less computational time than the conventional iteration scheme for the test examples, including transport involving highly nonlinear adsorption under steady-state as well as transient flow conditions. In contrast, mass balance errors resulting from the conventional Picard iteration method were higher than 10% for some highly nonlinear problems. Application of the modified Picard iteration scheme to solve the nonlinear transport equation may greatly reduce the mass balance errors and increase computational efficiency.

*Key words:* solute, transport, nonlinearity, iteration, numerical method.

## INTRODUCTION

The specter of groundwater contamination looms over many industrialized, suburban, and rural areas. Mounting evidence indicates that leaching of environmental contaminants through the vadose zone to groundwater represents an increasing threat to the subsurface environmental quality and the public health. Contaminants may come from many sources, such as landfills, leaking underground storage tanks, spill sites, hazardous waste sites, septic tank systems, leaking industrial and municipal wastewater lagoons, and nonpoint source pollution associated with agricultural practices.[18] There is a strong demand for quantifying the movement and retention of solutes in the subsurface environment. Computer models are often used to predict the behavior of contaminants in the subsurface to better protect groundwater resource and plan effective remediation strategies. Solute transport problems are relatively difficult to solve due to their nonlinear and hyperbolic nature, space and time dependent boundary conditions, and nonhomogeneous parameters. Analytical solutions can rarely be obtained for such real world systems. Therefore in most cases transport equations have to be solved by numerical approximations.[5,34] However, numerically solving the transport problem is often challenged by numerical dispersion and oscillations, and frequently ends up with misleading results. Inaccurate results of numerical formulations may be a major cause for much confusion in the quantitative analyses of solute transport.

The development of efficient numerical solution methodologies for the convection–dispersion transport equation (CDE) has received considerable attention in recent years. Numerical instability resulting from the inherent hyperbolic nature of the equation is one of the major numerical problems. The convection term causes severe numerical oscillations and instability,

*Current address: Center for Geophysical Investigation of the Shallow Subsurface, Boise State University, Boise, Idaho 83725, USA.

especially when convection is dominant in the convection–dispersion transport equation and/or sharp concentration fronts exist. Algorithms specially designed for convection-dominated transport problems can be Eulerian,[1,2,10] Lagrangian,[7] or Lagrangian–Eulerian formulations.[17,20,32,34,35] These methods have significantly reduced numerical dispersion and oscillatory behavior associated with the standard numerical schemes.

Another major problem in solving the CDEs is the mass balance error pertaining to its nonlinear nature when transport involves physical and chemical reactions such as degradation, adsorption, and production. Although a good mass balance does not guarantee an accurate solution, mass conservation is an essential requirement for an accurate numerical algorithm. To reduce the mass balance error, small time steps and iterative procedures are usually required to solve a nonlinear equation or a system of coupled nonlinear equations, which in turn makes the solution very time-consuming. Numerical experience for some cases, depending on the nature and degree of the nonlinearity, shows that mass balance errors may not be effectively eliminated even when very small time steps are used. In flow and transport modeling, most attention has been paid to overcoming the nonlinearity of the flow problems and eliminating the numerical dispersion and spurious oscillations of the transport problems. In contrast, numerical problems related to the nonlinear nature of the solute transport equation have not been addressed sufficiently. Celia *et al.*[4] presented an optimal test function (OTF) method to solve the contaminant transport problem involving nonlinear reactions and biodegradation. One class of methods that has received much attention in the groundwater modeling literature for nonlinear transport is the operator splitting technique (OST).[6,15,23,31,33] The nonlinear system of advection–dispersion-reaction equations is split into a system of linear partial differential equations involving the advection–dispersion equations and a system of nonlinear ordinary differential equations involving the reaction equations. Although this technique was shown to be convergent[31] and may produce relatively accurate solutions, it may cause mass balance errors, especially for transport involving continuous mass flux boundary conditions.[25] Kaluarachchi and Morshed[14]showed that the OST may also produce significant mass balance errors if the transport equation includes a first-order decay reaction.

In dealing with the nonlinear problem of water flow, Celia *et al.*[5] proposed a mass-conservative numerical scheme to solve the mixed-form Richards equation using 'modified Picard iteration'. Because of its perfect mass balance property, the modified Picard iteration technique proved to be a major improvement over earlier Picard methods. It also showed much promise in modeling unsaturated flow with steep wetting fronts where soil water flow is extremely nonlinear.[5,12] In dealing with the mass balance errors pertaining to the head-based formulation, Rathfelder and Abriola[22] showed that standard Picard iteration for the head-based form of the Richards equation could be equally good as the modified Picard iteration for the mixed form formulation, when the capacity coefficient is evaluated using a chord-slope approximation.

An alternative method for solving nonlinear flow and transport problems is Newton iterative scheme. However, the Newton approach is generally believed to be inferior to the Picard iteration method, as the latter preserves symmetry in the matrix.[16,21] In addition, evaluation for the partial derivatives involving nonlinear terms in the Newton method is often time-consuming and at times formidable for highly nonlinear problems.

In this work, we generalize the mixed-form algorithm of Celia *et al.*[5] to handle the nonlinearity of the transport equation. This is accomplished by linearizing a 'mixed-form' transport equation (proposed in this paper) rather than the conventional concentration-based transport equation, with the modified Picard iteration method. A conventional finite element method is then used to solve the linearized formulation to obtain the solution for concentration. The solution quality is evaluated based on mass balance errors and computational efficiency. Numerical experiments are presented to illustrate the promising solution performance of the proposed iteration method as compared with the conventional Picard scheme for various transport examples.

## BACKGROUND

### Transport equation

Contaminant migration in subsurface is the result of physical, chemical, and biological processes occurring in the soil or aquifer where fluids containing the contaminants percolate. We will focus on one-dimensional transport, since the extension to two- or three-dimensional systems is straightforward. The one-dimensional solute transport is generally described by the following convection–dispersion transport equation:

$$\frac{\partial \theta c}{\partial t} + \frac{\partial \rho s}{\partial t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial c}{\partial z}\right) - \frac{\partial qc}{\partial z} - \lambda_w \theta c - \lambda_s \rho s + \gamma_w \theta + \gamma_s \rho - S c_s \quad (1)$$

where $c$ is the solute concentration of the liquid phase ($ml^{-3}$), $s$ is the solute concentration of the solid adsorbed phase ($mm^{-1}$), $D$ is the dispersion coefficient ($l^2T^{-1}$), $q$ is the Darcy flux density ($lT^{-1}$), and $\lambda_w$ and $\lambda_s$ are first-order decay coefficients ($T^{-1}$) for the liquid and solid phases, respectively, $\gamma_w$ and $\gamma_s$ are zero-order rate constants for the liquid ($ml^{-3}T^{-1}$) and solid ($T^{-1}$) phases, respectively, $\rho$ is the soil bulk density ($ml^{-3}$), $S$ is

the source/sink term such as root water uptake (1/T), $\theta$ is the volumetric water content ($l^3l^{-3}$), and $c_s$ is the solute concentration of the water extracted by plant roots ($ml^{-3}$), $t$ is time (T), and $z$ denotes the vertical distance from the soil surface downward (l).

The dispersion coefficient, $D$ is defined as

$$D = \epsilon \frac{|q|}{\theta} + D_0 \tau \tag{2}$$

where $\epsilon$ is the dispersivity (l) of the medium, $D_0$ is the ionic or molecular diffusion coefficient in free water ($l^2T^{-1}$), and $\tau$ is a tortuosity factor. The tortuosity factor is evaluated as a function of the water content using the relationship of Millington and Quirk:[19]

$$\tau = \theta^{7/3}/\theta_s^2 \tag{3}$$

where $\theta_s$ is the saturated water content or, approximately, the porosity ($l^3l^{-3}$). The influence of sorption on contaminant transport is of particular importance because it may slow down the transport of contaminants from the surface to groundwater, thereby allowing more time for dissipation by microbial and chemical transformations. Sorption may also cause tailing effects, especially for nonlinear sorption.[24,28] Therefore sorption isotherms are essential for describing transport of solutes in soil and groundwater. Equation (1) requires an expression relating the adsorbed concentration, $s$, with the liquid concentration, $c$. In this study we assumed that the adsorbed and liquid concentrations are always in local equilibrium. A general expression for the adsorption isotherm is given by

$$s = f(c) \tag{4}$$

where $f(c)$ is an arbitrary function which is generally nonlinear; hence eqn (1) will also become nonlinear. Therefore an iterative solution scheme, similar to the one applied to the variably-saturated flow equation, must be used to solve such a nonlinear transport equation.

Substitution of eqn (4) into eqn (1) leads to the final form of the solute transport equation considered in this paper:

$$\frac{\partial \theta R c}{\partial t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial c}{\partial z}\right) - \frac{\partial q c}{\partial z} - \lambda \theta c + \Gamma \tag{5}$$

where the retardation factor is defined as

$$R = 1 + \frac{\rho}{\theta}\frac{f(c)}{c} \tag{6}$$

and the decay function is given by

$$\lambda = \lambda_w + \frac{\rho k c^{\eta - 1}}{\theta}\lambda_s \tag{7}$$

and the synthetical production term is given by

$$\Gamma = \gamma_w \theta + \gamma_s \rho - S c_s \tag{8}$$

Note that the retardation factor, $R$, according to eqn (6), is related to the ratio $f(c)/c$ instead of the isotherm slope $\partial f(c)/\partial c$ of the conventional definition.[28] Both $\lambda$ and $R$ are nonlinear coefficients of the concentration $c$. Equation (5) is considered to be a 'concentration-based formulation'. Almost all current numerical methods solve eqn (5) directly for the solution of concentration, $c$, using the numerical approaches available for nonlinear differential equations. Among others, the Picard iteration method has been widely used to deal with the nonlinearity. The modified Picard iteration method, however, has been shown to be one of the best approaches for solving nonlinear problems.[5,12]

**Modified Picard iteration algorithm**

The modified Picard iteration method of Celia *et al.*[5] was developed for solving the mixed-form Richards equation for water flow in a variably-saturated porous medium

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left(K \frac{\partial h}{\partial z}\right) - \frac{\partial K}{\partial z} - S \tag{9}$$

where $h$ is the pressure head (L), $\theta$ is the volumetric water content ($l^3l^{-3}$), and $K$ is the hydraulic conductivity [$lT^{-1}$]. $\theta$ and $K$ both are a function of $h$. $S$ is the source/sink term defined in eqn (1). The mixed-form of the Richards equation is considered to possess the mass conservative property inherent in the water content-based equation (not present here), while providing solutions in terms of the pressure head, $h$.

Using a fully implicit (backward Euler) time approximation and representing the water content, $\theta^{n+1,m+1}$, by the first-order approximation

$$\theta^{n+1,m+1} \approx \theta^{n+1,m} + \left(\frac{d\theta}{dh}\right)^{n+1,m}(h^{n+1,m+1} - h^{n+1,m}) \tag{10}$$

the modified Picard iteration scheme of Celia *et al.*[5] for the mixed form flow eqn (9) is given as follows:

$$C_h^{n+1,m}\frac{h^{n+1,m+1} - h^{n+1,m}}{\Delta t} + \frac{\theta^{n+1,m} - \theta^n}{\Delta t} - \frac{\partial}{\partial z}\left[K^{n+1,m}\left(\frac{\partial h^{n+1,m+1}}{\partial z} - 1\right)\right] = 0 \tag{11}$$

where $C_h = d\theta/dh$ is the specific soil water capacity ($l^{-1}$), the superscripts $n$ and $m$ denote time level and iteration level, respectively, and where, for simplicity, the sink term, $S$, has been ignored. The second term on the left-hand side of eqn (11) corresponds to the time derivative and is the key term for maintaining perfect mass balance.

Celia *et al.*[5] claimed that the mass-conservative property of eqn (11) holds for all types of boundary conditions and all numerical approximations that maintain spatial symmetry. The numerical performance

of the modified Picard iteration method was further improved by Huang *et al.*[12] by implementing a new convergence criterion and tested for comprehensive infiltration scenarios including highly nonlinear soil hydraulic properties, very dry soil conditions, layered soil, and two dimensions. In all tests, mass balance errors produced by implementing the modified Picard iteration method were almost zero ($< |10^{-8}|\%$).

Generalization of the modified Picard iteration algorithm to solve the nonlinear solute transport solution is fairly straightforward, and will be discussed in the following section by observing the physical and mathematical similarity between the flow eqn (9) and the 'mixed-form' transport equation to be defined below.

## IMPLEMENTATION

We first rewrite the governing eqn (5) into a 'mixed-form'

$$\frac{\partial M}{\partial t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial c}{\partial z}\right) - \frac{\partial qc}{\partial z} - \lambda\theta c + \Gamma \tag{12}$$

where $M$ is the solute content, i.e. the total concentration of solute per unit volume of soil ($ml^{-3}$), defined as

$$M = \theta c + \rho f(c) \tag{13}$$

The similarity between the transport eqn (12) and the flow eqn (9) is obvious if we compare the components of one equation with the other (see Table 1).

Perceiving the similarity between the solute transport equation and water flow equation, it is not surprising to motivate the generalization of the modified Picard iteration scheme to the nonlinear transport equation. The procedures for implementing this scheme are basically the same as those for water flow equation, which are described in the preceding section. First, the implicit backward time scheme is applied to eqn (12)

$$\frac{M^{n+1,m+1} - M^n}{\Delta t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial c^{n+1,m+1}}{\partial z}\right) - \frac{\partial qc^{n+1,m+1}}{\partial z} - (\lambda\theta c)^{n+1,m} + \Gamma \tag{14}$$

Note that no iterations are required for the total source term $\Gamma$. Second, following the modified Picard philosophy, we perform the Taylor expansion for $M^{n+1,m+1}$ with respect to $c$ at $c^{n+1,m}$

$$M^{n+1,m+1} \approx M^{n+1,m} + \left(\frac{\partial M}{\partial c}\right)^{n+1,m} \times (c^{n+1,m+1} - c^{n+1,m}) \tag{15}$$

Substituting eqn (15) into eqn (14) yields the modified Picard iteration formulation for the mixed-form transport equation

$$C_s^{n+1,m}\frac{c^{n+1,m+1} - c^{n+1,m}}{\Delta t} + \frac{M^{n+1,m} - M^n}{\Delta t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial c^{n+1,m+1}}{\partial z}\right) - \frac{\partial qc^{n+1,m+1}}{\partial z} - (\lambda\theta c)^{n+1,m} + \Gamma \tag{16}$$

where $C_s$, similar to the specific water capacity, is the specific solute capacity ($l^3l^{-3}$) defined as

$$C_s = \frac{\partial M}{\partial c} = \theta + \rho\frac{\partial f(c)}{\partial c} \tag{17}$$

Equation (16) describes the proposed modified Picard iteration method for the nonlinear transport equation. The degree of nonlinearity in the adsorption isotherm,

**Table 1. Similarity between the transport eqn (12) and the flow eqn (9)**

| Transport equation | Flow equation |
|---|---|
| Concentration $c$ | Pressure head $h$ |
| Solute content $M(c)$ | Water content $\theta(h)$ |
| Convectional transport | Gravitational flow |
| Hydrodynamic dispersion | Hydraulic conduction |
| Decay and Production terms | Sink and source terms |
| Specific solute capacity $dM/dc$ | Specific water capacity $d\theta/dh$ |

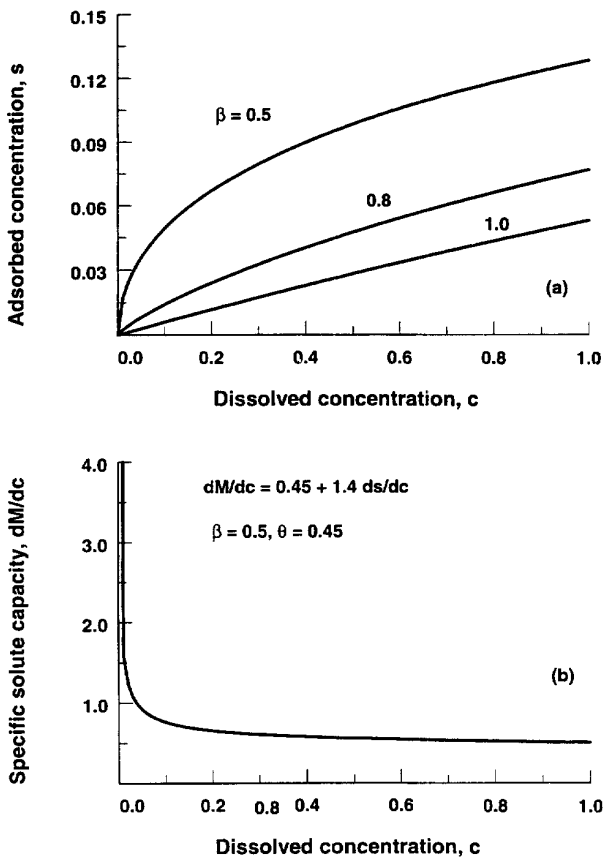


**Fig. 1.** Langmuir–Freundlich isotherm (eqn (19)) with different exponent $\beta$ (a), and the specific solute capacity curve for $\beta = 0{\cdot}5$, assuming $\theta = 0{\cdot}45\,cm^3\,cm^{-3}$ (b).

invoked by the exponent $\beta$, is demonstrated in Fig. 1a. It can be seen from the Fig. 1b that the specific solute capacity function according to eqn (17) can be highly nonlinear for a solute undergoing a nonlinear adsorption described by the Langmuir–Freundlich isotherm (eqn (19)). The high nonlinearity is characterized by significant changes in the solute capacity, $\partial M/\partial c$, in the lower concentration range.

For convenience of comparison, the standard Picard iteration method for the transport eqn (5) with mass-lumped algorithm is given below

$$\theta R^{n+1,m}\frac{c^{n+1,m+1}-c^{n}}{\Delta t}=\frac{\partial}{\partial z}\left(\theta D\frac{\partial c^{n+1,m+1}}{\partial z}\right)-\frac{\partial q c^{n+1,m+1}}{\partial z}-\theta\lambda^{n+1,m}c^{n+1,m+1}+\Gamma \tag{18}$$

where $R^{n+1,m}$ and $\lambda^{n+1,m}$ are nonlinear functions of concentration $c$ as defined in eqns (6) and (7), respectively.

## PERFORMANCE EVALUATION

The performance of the modified Picard iteration method to solve the nonlinear transport equation is evaluated for several examples. Solutions are obtained by solving the discretized transport eqn (16) using the mass-lumped linear Galerkin finite element method which has been proved to be superior to consistent formulations in terms of mass conservation.[5] The general Langmuir–Freundlich model[11] is used to describe the adsorption isotherm for the numerical tests in this study

$$s=\frac{Q(kc)^{\beta}}{1+(kc)^{\beta}} \tag{19}$$

where $Q$ is the total amount of surface sites or the maximum sorption capacity, $k$ ($mm^{-1}$) is an 'overall affinity' coefficient, and $0<\beta<1$ is a dimensionless fitting parameter. Note that for $\beta=1$, eqn (19) reduces to the Langmuir sorption scenario, while the Freundlich isotherm is the limiting case of the general model (19) when $1/k \gg c$

$$s=k_f c^{\beta} \tag{20}$$

where $k_f=Qk^{\beta}$.

Numerical results were obtained by implementing the proposed modified Picard iteration algorithm into the computer code HYDRUS.[29] The HYDRUS code simulates one-dimensional water flow, solute transport, and heat movement in variably-saturated porous media using a linear finite element method. In all examples, a maximum permitted number of iterations of 20 was used for each time step. Simulations were run on a Pentium 16 bit, 90 MHZ personal computer.

For simplicity, an initial solute free distribution condition was assumed in each simulation. To ensure better mass conservation nature at the influx boundary, a flux boundary condition, as suggested by van Genuchten and Parker,[27] was used at the soil surface ($z=0$ cm). All examples were run by assuming free-drainage at the bottom boundary, leading to a unit-hydraulic gradient condition for water flow and a zero-concentration gradient condition for solute transport, respectively.

The proposed algorithm was evaluated based on the mass balance error (MBE) and the solution accuracy. According to the mass continuity equation, the MBE for solute was defined as the difference between the net amount of solute added to the system and the change in the amount of solute stored in the system after a given elapsed time. Although focus of this study will be primarily on the discussion on the mass balance error, the computational efficiency will also be investigated.

### Verification of the proposed method

We verified our numerical solutions by comparison with 'exact solutions'. Since it is very difficult or essentially impossible to obtain an analytical solution for nonlinear convection–dispersion transport problems, we obtained the 'exact solutions' by the method of characteristics (MOC). This method incorporates the nonlinear decay and equilibrium-controlled sorption into the convection–dispersion transport equation.[9] The MOC code implements the particle tracking technique which is generally considered to be the most advanced and accurate method for solving the convection–dispersion transport problems.[20,34] Two benchmark problems of Goode and Konikow[9] were simulated: (1) an 80-s pulse of solute subject to a Freundlich adsorption into a 12-cm homogeneous, solute free soil column having a uniform pore-water velocity, $v=q/\theta=0{\cdot}1\,cm\,s^{-1}$; (2) an 80-s pulse of solute under the same flow condition, but subject to a Langmuir adsorption. A source concentration $C_0=0{\cdot}05\,mg\,l^{-1}$ was used for both pulse experiments. Other transport parameters used for the simulations include: dispersion coefficient $D=0{\cdot}01\,cm^2\,s^{-1}$, the porosity $P=0{\cdot}37$, and the soil bulk density $\rho=1{\cdot}587\,g\,cm^{-3}$. For Freundlich adsorption, equilibrium coefficient $k_f=0{\cdot}3\,cm^3\,g^{-1}$ and slope exponent $\beta=0{\cdot}7$, while for Langmuir adsorption, equilibrium coefficient $k=100\,cm^3\,g^{-1}$, maximum sorption capacity $Q=0{\cdot}003\,g\,g^{-1}$, and $\beta=1{\cdot}0$ were used. Simulations were carried out for solute transport with or without decay. The decay rate constants are 0·01 and $0{\cdot}1\,L\,s^{-1}$ for Freundlich and Langmuir isotherms, respectively. As adopted in the MOC modeling, the solution domain was discretized into 120 elements using a uniform increment $\Delta z=0{\cdot}1$ cm and a constant time step, $\Delta t=0{\cdot}25$ s, was used. We assumed that a convergent solution is achieved when the difference between the solved concentration values at

two successive iteration levels satisfies a given criterion, i.e. $\delta_c = |c^{n+1,m+1} - c^{n+1,m}| < 0{\cdot}0001\,\mathrm{mg\,l^{-1}}$ for all finite element nodes. Here an $L_\infty$-norm, or max ($\delta_c$), criterion is implied.

Figure 2 illustrates the simulated breakthrough curves (BTCs) for the pulse subject to Freundlich adsorption, obtained using the method of characteristics, and the standard and modified Picard iterations. The standard Picard iteration method, as expected, produced almost identical results to those of MOC and the proposed method, for the linear sorption case ($\beta = 1$). The pulse for the nonlinear adsorption ($\beta = 0{\cdot}7$) is apparently more retarded than for linear adsorption, resulting in late breakthrough. The BTCs also exhibit long tailing due to relatively strong sorption at lower concentrations. Decay further reduces the concentration, most noticeably around the peak after approximately 4·5 pore volumes have been leached through. The results obtained with the proposed scheme agree well with those calculated by MOC for both linear or nonlinear sorption cases with almost zero mass balance errors ($\pm 10^{-8}$%). For nonlinear transport with or without decay reaction, however, the predicted BTCs by the standard Picard method deviated largely from those produced by both MOC and the proposed algorithm, with a mass balance error ranging from 5 to 15%. The BTCs simulated using the standard method also exhibit a lower peak and greater spreading than those calculated by MOC and the modified Picard iteration scheme.

The comparison of the simulated BTCs for the Langmuir sorption scenario [eqn (19) with $\beta = 1$] is illustrated in Fig. 3. the nonlinear nature of the isotherm produced a sharp breakthrough. The tailing phenomenon in this case is not as distinct as that of Freundlich sorption, due to lesser nonlinearity. The proposed method almost duplicated the BTCs of the MOC for both transport with and without decay. For this mildly nonlinear transport problem, the standard Picard iteration method also predicted the data fairly well in the absence of decay, with about 1% mass balance error. However, noticeable discrepancies between the BTCs produced by the standard iteration scheme and those obtained with the proposed method or the MOC can be observed when decay reaction is incorporated, with a mass balance error of 5% resulting from the conventional iteration method.

Generally speaking, for a stable and convergent numerical algorithm, an 'exact solution' may be obtained by using relatively small discretizations and a strict convergence criterion for the iteration. We generated such an 'exact solution' for solute transport involving highly nonlinear Freundlich sorption ($\beta = 0{\cdot}5$) by the proposed algorithm, using a relatively small temporal step, $\Delta t = 0{\cdot}01$ h, and a relatively strict convergence tolerance ($\delta_c \leq 10^{-4}\,\mathrm{g\,l^{-1}}$). A solution of concentration $C_0 = 1{\cdot}0\,\mathrm{g\,l^{-1}}$ was applied at a constant rate of $q = 2{\cdot}0\,\mathrm{cm\,h^{-1}}$ to a homogeneous soil column under saturated steady-state flow condition for a duration of 5 h, followed by a leaching with solute free water ($C_0 = 0{\cdot}0\,\mathrm{g\,l^{-1}}$). Transport parameters used in this test problem are: $D = 0{\cdot}01\,\mathrm{cm^2\,h^{-1}}$, $\theta = 0{\cdot}45\,\mathrm{cm^3\,cm^{-3}}$, $\rho = 1{\cdot}587\,\mathrm{g\,cm^{-3}}$, and $k_f = 0{\cdot}3$. In this and subsequent examples, the soil column is assumed to be 200-cm long discretized with a uniform spatial step, $\Delta z = 1$ cm.

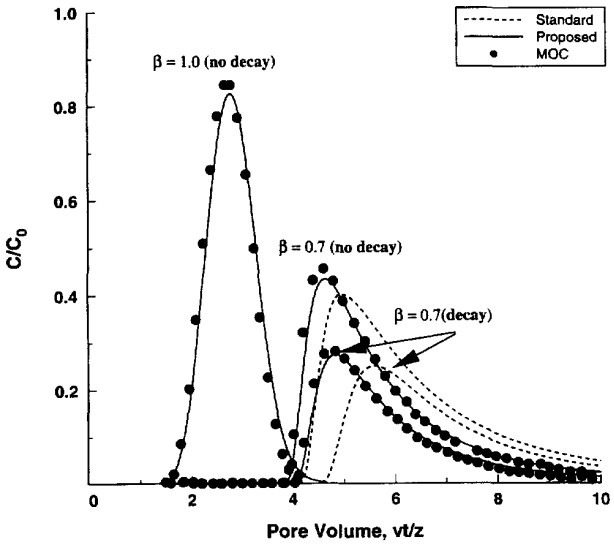


**Fig. 2.** Breakthrough curves (BTCs) predicted with the standard and the modified Picard iteration methods as well as the method of characteristics (MOC) for transport during steady-state flow with linear ($\beta = 1{\cdot}0$) and nonlinear ($\beta = 0{\cdot}7$) Freundlich sorption (example after Goode and Konikow[9]).

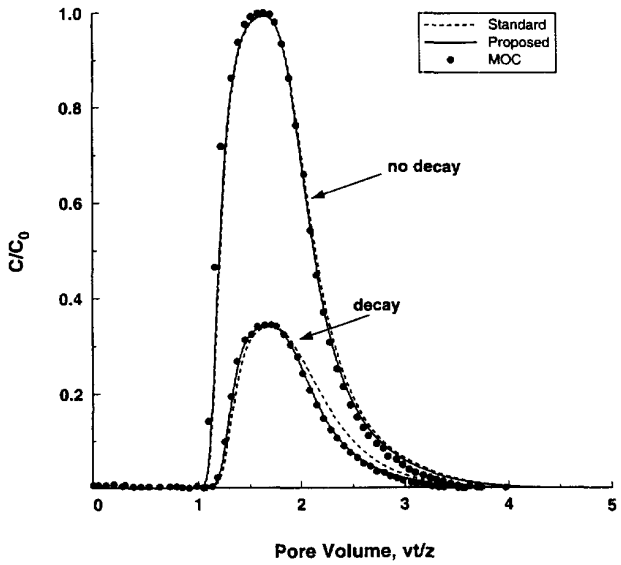


**Fig. 3.** Simulated BTCs at depth $z = 8$ cm with the standard and the modified iteration methods as well as the MOC for transport during steady-state flow with Langmuir sorption ($\beta = 1{\cdot}0$).

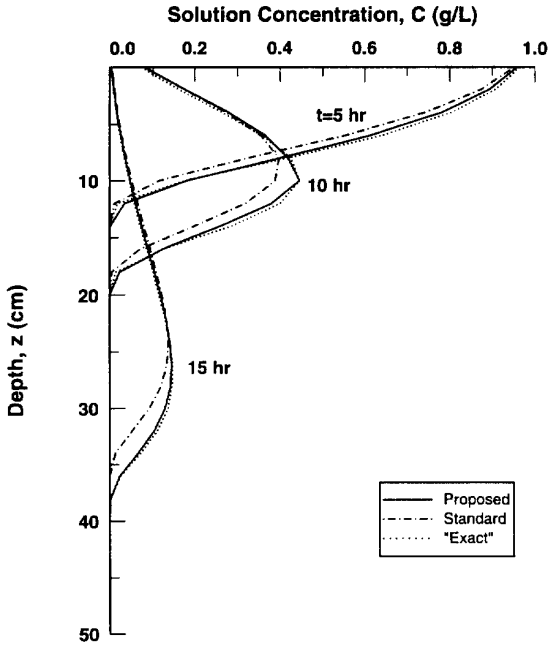


**Fig. 4.** Comparison of numerical solutions obtained with the proposed and the conventional Picard iteration methods with 'exact' solutions for transport under steady-state flow condition with Freundlich sorption ($\beta = 0{\cdot}5$).

Figure 4 shows the comparison of the concentration distributions simulated by the proposed iteration method using a relatively large time step, $\Delta t = 0{\cdot}1$ h, and a relaxed convergence criterion, $\delta_c = 0{\cdot}001\,\mathrm{g\,l^{-1}}$, with the 'exact solutions'. The solutions of the proposed method, having near zero mass balance errors, agree very well with the exact solutions. By comparison, the solutions produced by the standard Picard iteration method with the same time step and convergence criterion apparently deviate from the exact solutions, with a mass balance error of $2{\cdot}5 \sim 3{\cdot}0\%$ which increases with the elapsed time of transport.

### Performance for transient flow conditions

It can be seen from the above examples that the proposed iteration method precisely conserved the mass and produced very accurate solutions, while the conventional Picard iteration scheme induced serious mass balance errors and, as a result, caused inaccurate predictions of concentration distributions both in space and in time, for highly nonlinear problems. The solute transport problems investigated in the previous sections involved steady-state flow with a uniform velocity. Most solute transport problems, however, involve transient flow conditions. Numerical simulations for solute transport under transient flow are generally much more complicated than that under uniform steady-state flow condition. We will therefore investigate the mass balance errors of the modified and the standard Picard iteration methods for solute transport under unsteady flow, and for different degrees of nonlinearity (different $\beta$ values) of the Langmuir–Freundlich isotherm with equilibrium coefficient $k = 0{\cdot}12\,\mathrm{g\,g^{-1}}$ and maximum sorption capacity $Q = 0{\cdot}5\,\mathrm{g\,g^{-1}}$. We may also include a decay reaction assuming $\lambda_w = 0{\cdot}01\,\mathrm{h^{-1}}$ and $\lambda_s = 0{\cdot}01\,\mathrm{h^{-1}}$. As stated earlier, all simulations invoked a solution domain of 200 cm with constant spatial increments ($\Delta z$) of 1 cm, and used a maximum permitted number of iterations of 20, and a convergence tolerance of $\delta_c = 0{\cdot}001\,\mathrm{g\,l^{-1}}$.

We considered a variably-saturated water infiltration assuming a constant rate of $2\,\mathrm{cm\,h^{-1}}$ into an initially dry soil (pressure head $h_i = -10^4$ cm of water) with water retention and hydraulic conductivity functions being described by[26]

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r} = \frac{1}{[1 + (\alpha|h|)^n]^{1-1/n}} \tag{21}$$

$$K = K_s S_e^{1/2}[1 - (1 - S_e^{n/(n-1)})^{1-1/n}]^2 \tag{22}$$

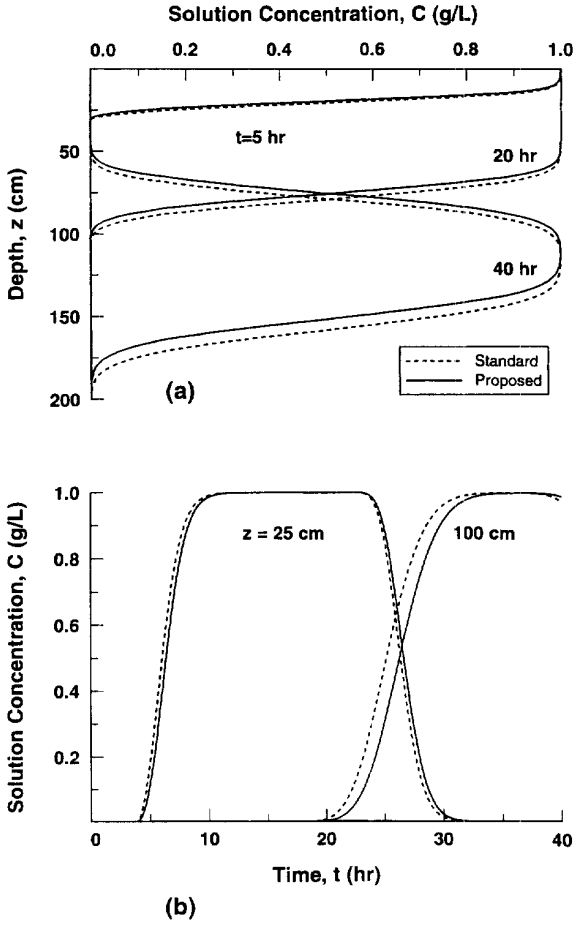


**Fig. 5.** Concentration profiles (a), and breakthrough curves (b) calculated using the standard and modified Picard iteration schemes for solute transport during infiltration into a dry soil subject to Langmuir–Freundlich sorption of $\beta = 1{\cdot}0$.

where $S_e$ is the effective saturation, $\theta_r$ and $\theta_s$ are the residual and saturated water contents ($l^3l^{-3}$), respectively, $K_s$ is the saturated hydraulic conductivity ($lT^{-1}$), and $\alpha(l^{-1})$ and $n$ are shape parameters. Except where mentioned otherwise, the following hydraulic parameters were used for transient flow simulations: $K_s = 2\,cm\,h^{-1}$, $\alpha = 0{\cdot}02\,cm^{-1}$, $n = 2{\cdot}0$, $\theta_s = 0{\cdot}45\,cm^3\,cm^{-3}$, and $\theta_r = 0{\cdot}05\,cm^3\,cm^{-3}$. The flow solutions were obtained by solving eqn (13), the mixed-form Richards equation implemented with the modified Picard iteration method. The time step ($\Delta t$) was automatically updated, within a given minimum and maximum, according to the convergence history of the previous simulation run. The dispersion coefficient was calculated according to eqn (2), assuming a dispersivity of 0·01 cm and negligible molecular diffusion.

Figure 5a and b presents the simulated concentration distribution profile and breakthrough curve, respectively, for a solute pulse injection and subsequent leaching for a typical Langmuir adsorption isotherm ($\beta = 1{\cdot}0$). For this mildly nonlinear transport problem, both the modified and the standard Picard methods produced very close concentration distributions (Fig. 5a) at earlier time ($t = 5$ h) with a relatively small MBE (0·7%) for the conventional method. Close results between the two methods can also be found in Fig. 5b for the BTC observed at a relatively short distance, $z = 25$ cm, from the inlet boundary. However, the mass balance error introduced by the conventional Picard method increased with time to 4·7% at $t = 40$ h. Almost zero mass balance errors were produced by the modified Picard scheme for all simulation periods. Excellent performance of the modified Picard scheme was also exhibited in the simulation for solute transport involving decay reactions. Again the standard iteration method produced relatively accurate solutions for earlier time ($t = 5$ h) but introduced considerable mass balance errors increasing with time (Fig. 6a). The increasing discrepancy between the solutions of the proposed iteration scheme and those of the standard Picard iteration method can also be seen in the BTCs (Fig. 6b). The BTCs are quite close at a relatively short distance, $z = 25$ cm, but those BTCs for $z = 100$ cm clearly deviate. It can be inferred from these two simulations that the new iteration method also bears perfect mass-conservation nature for nonlinear transport under transient flow conditions.

### Performance for different nonlinearities

Accurate solutions for the highly nonlinear transport equation are often difficult to obtain with standard numerical schemes because of the strong dependency of the solution concentration on the adsorbed concentration in solid phase and other chemical reaction characteristics.[13,30] To avoid computational errors, such problems usually require very small time increments and large numbers of iterations, hence representing a challenging computational task. We examined the performance of the proposed iteration method for solute transport involving different nonlinearities; results are summarized in Table 2. We again assumed the case of constant-flux infiltration into a dry soil. Since the nonlinear nature of the Langmuir–Freundlich isotherm is primarily represented by the exponent $\beta$, we decided to vary only the parameter (0·5, 0·8, and 1·0 corresponding to high, moderate, and mild nonlinearities, respectively) while keeping the same $k$ ($0{\cdot}12\,g\,g^{-1}$) and $Q$ ($0{\cdot}5\,g\,g^{-1}$). These three adsorption isotherms are presented in Fig. 1a to show the degree of nonlinearity related to isotherm exponent $\beta$. Values of other transport parameters were kept the same as those used in the preceding section. The solutions for transport involving mildly nonlinear adsorption ($\beta = 1{\cdot}0$), as demonstrated in Figs 5 and 6, have indicated that the proposed method (resulting in nearly zero MBE) is much more accurate than the conventional method (up to 4·7% of MBE) in terms of mass conservation. For intermediate nonlinearity of

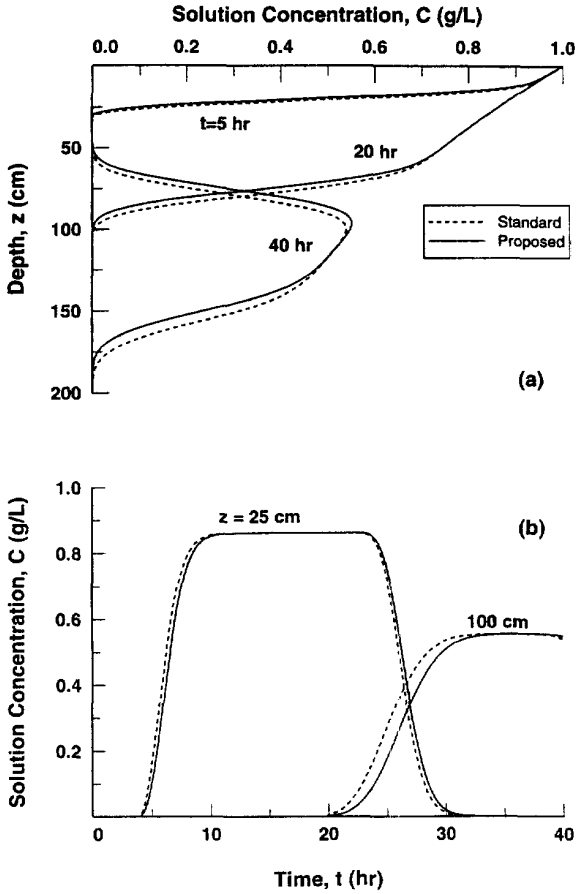


Fig. 6. Simulated concentration profiles (a), and breakthrough curves (b) by the standard and modified Picard iteration schemes for solute transport under unsaturated flow condition and subject to Langmuir–Freundlich sorption of $\beta = 1{\cdot}0$ and decay.

**Table 2. Cumulative mass balance errors (%) resulting from the standard iteration method***

| Time (min) | Numerical experimental scenarios | | | | | |
|---|---|---|---|---|---|---|
| | $\beta = 1{\cdot}0$ | $\beta = 1{\cdot}0$, decay | $\beta = 0{\cdot}8$ | $\beta = 0{\cdot}8$, decay | $\beta = 0{\cdot}5$ | $\beta = 0{\cdot}5$, decay |
| 5 | −4·33 | −4·34 | −6·69 | −6·07 | −8·85 | −9·07 |
| 20 | −4·11 | −4·17 | −6·63 | −5·96 | −8·24 | −9·1 |
| 40 | −4·14 | −4·31 | −7·76 | −6·95 | −9·6 | −13·07 |

*The modified Picard iteration algorithm produced almost zero ($|\delta| < 10^{-8}$%) mass balance errors for all scenarios.

adsorption ($\beta = 0{\cdot}8$), solutions obtained with the standard iteration method suffered from mass balance errors of about 7% for both transport scenarios with or without decay (see Table 2), while the proposed scheme perfectly conserved the mass, i.e. having zero mass balance errors (results are not presented further). Also note that the mass balance errors induced by the conventional method for the highly nonlinear case ($\beta = 0{\cdot}5$) are more than twice as those for the mildly nonlinear adsorption scenario ($\beta = 1{\cdot}0$).

The greatest advantage of the proposed iteration scheme over the standard method is exhibited by the simulation for a highly nonlinear adsorption with the Langmuir exponential coefficient $\beta = 0{\cdot}5$. Mass balance errors caused by the standard method are near 10% for most evaluation times. When the nonlinear decay reactions were incorporated in the transport, the mass balance error was up to 13% (see Table 2). The proposed numerical scheme again produced nearly zero mass balance errors even for this extremely nonlinear transport problem. The predicted concentration versus distance and time is presented in Fig. 7a and b, respectively. Due to the highly nonlinear favorable adsorption, the incoming concentration front remains very steep (Fig. 7a) as compared with the case of less favorable adsorption ($\beta = 1{\cdot}0$). The increased nonlinearity also resulted in much more retardation than the less nonlinear transport scenario ($\beta = 1{\cdot}0$); after the same transport time, the solute has penetrated farther for $\beta = 1{\cdot}0$ than for $\beta = 0{\cdot}5$. The calculated concentration distributions by the proposed iteration scheme and

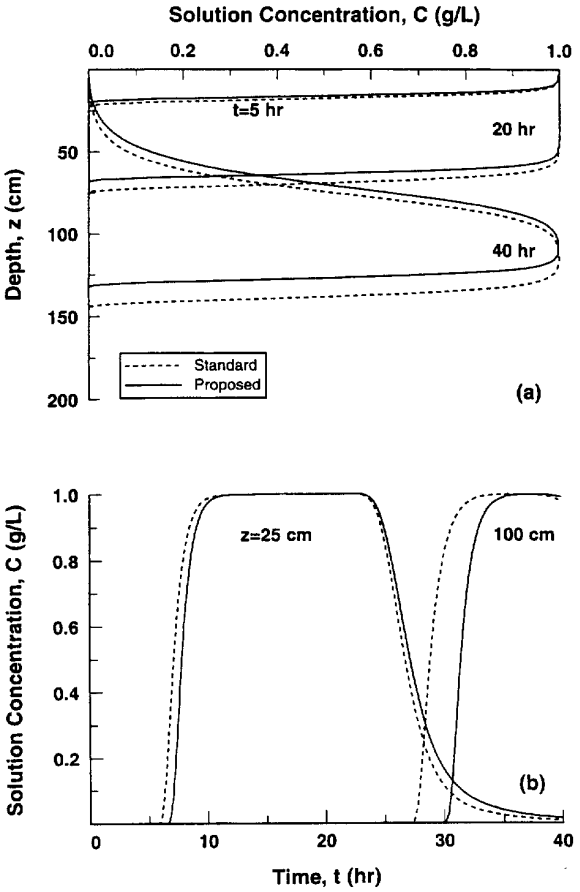


**Fig. 7.** Predicted concentration profiles (a), and breakthrough curves (b) by the standard and modified iteration schemes for solute transport under unsaturated flow condition and subject to highly nonlinear Langmuir–Freundlich sorption ($\beta = 0{\cdot}5$).

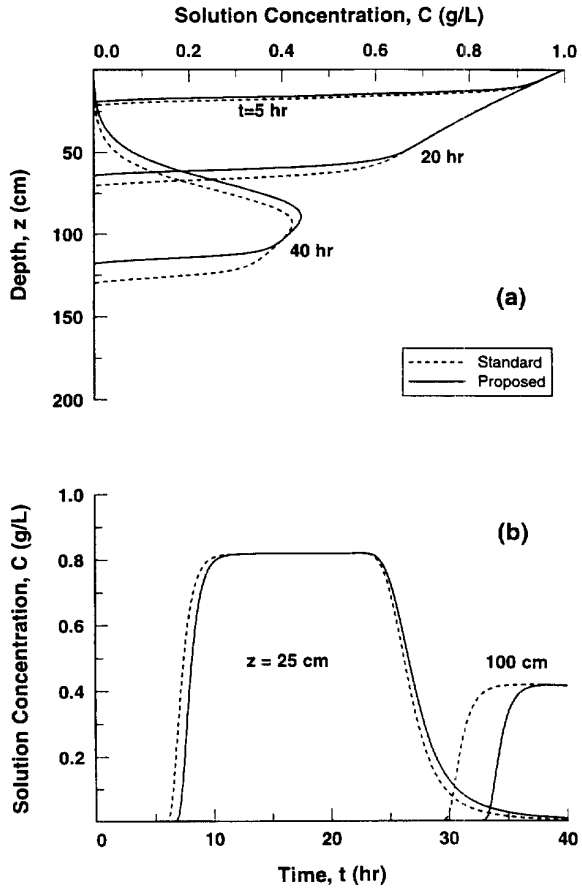


**Fig. 8.** Concentration profiles (a), and breakthrough curves (b) predicted by the standard and modified Picard iteration methods for solute transport during infiltration into a dry soil having highly nonlinear Langmuir–Freundlich sorption ($\beta = 0{\cdot}5$) and decay.

**Table 3. Total number of iterations used by the modified Picard iteration algorithm and the standard iteration method for each simulation**

| Isotherm: | Langmuir–Freundlich | | | | | | | | | | | | Freundlich | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Test: | $\beta = 1{\cdot}0$ | | $\beta = 1{\cdot}0$, decay | | $\beta = 0{\cdot}8$ | | $\beta = 0{\cdot}8$, decay | | $\beta = 0{\cdot}5$ | | $\beta = 0{\cdot}5$, decay | | $\beta = 0{\cdot}5$ | |
| Method: | P | S | P | S | P | S | P | S | P | S | P | S | P | S |
| Average number | 2·65 | 2·54 | 2·56 | 2·34 | 2·55 | 3·17 | 2·49 | 3·16 | 2·96 | 5·96 | 2·96 | 5·9 | 2·12 | 4·6 |
| Total number | 2620 | 2508 | 2528 | 2311 | 2519 | 3124 | 2454 | 3115 | 2917 | 5878 | 2917 | 5824 | 1697 | 3685 |

P: the modified Picard iteration method.
S: the standard Picard iteration method.

the standard method are fairly close at early time ($t = 5$ h), but the discrepancy between the two solutions increases with the transport time. A similar performance of the proposed method can be observed in Fig. 8 for transport involving decay. The standard iteration scheme gave rise to even larger mass balance errors (as high as 12%), while the new method maintained very precise mass balance.

As can be seen from the above examples, computational mass balance error increases with the degree of the nonlinearity, corresponding to the decrease of $\beta$ from 1·0 (mildly nonlinear) to 0·5 (extremely nonlinear), when the nonlinear transport equation is solved by the standard iteration method. In contrast, induced mass balance errors by the modified iteration scheme are almost zero even when highly nonlinear problem is solved. These findings indicate a significant advantage of the proposed iteration method over the traditional method for transport problems involving high nonlinearity.

**Computational efficiency**

Accurate yet computationally efficient numerical algorithm is a prerequisite for any numerical model of flow and transport in porous media. Accurate solutions may be obtained by using very small discretizations and strict tolerance in the numerical model, as long as the numerical scheme used is stable and convergent. However, tremendous computational efforts required to obtain a meaningful and accurate prediction of the flow and transport processes may make the numerical model impractical. Consequently, computational efficiency becomes even more desirable for long-term simulations of large-scale, multi-dimensional, heterogeneous, and, especially, nonlinear flow and transport problems. This section compares the computational requirements by the proposed iteration method with those by the standard scheme for the numerical tests presented before. Summarized in Table 3 are the total numbers of iterations used for each simulation by the modified and the standard iteration algorithms as well as the average number of iterations required for each step for various simulations. Two simulation scenarios were included in this table: solute transport under unsteady flow condition and subject to the Langmuir–Freundlich type adsorption with different exponent coefficient $\beta$ (examples illustrated in the section Performance for Different Nonlinearities); and the other transport scenario involved steady-state flow condition and Freundlich type adsorption (example of the section Verification of the Proposed Method). As is shown in Table 3, the number of iterations for both the proposed method and the standard scheme generally increases with the degree of nonlinearity, as manifested primarily by the exponent $\beta$. However, the rate of increase with the standard method was much faster in comparison with the modified iteration scheme. For the proposed method, the average number of iterations for each time step varied from 2·5 to 3·0, while the standard method required 3·0 to 6·0 of iterations for each time step. As a result, the total number of iterations for the proposed modified Picard iteration scheme was much smaller than that of the standard method. The proposed scheme required only half as much the computational efforts as the standard method for the highly nonlinear transport cases ($\beta = 0{\cdot}5$): 0·15 min of CPU time (the proposed) versus 0·30 min (the standard) for the transport involving Freundlich type adsorption isotherm, and 1·3 min (the proposed) versus 2·7 min (the standard) for the Langmuir–Freundlich type adsorption scenario. Table 3 also shows that the number of iterations for the proposed method is comparable to or slightly greater than that for the standard method for the transport with $\beta = 1$ (an essentially linear adsorption scenario). These findings point out an additional advantage of using the proposed iteration algorithm instead of traditional scheme to enhance the computational efficiency for highly nonlinear transport problems.

## SUMMARY AND CONCLUSIONS

The modified Picard iteration algorithm of Celia *et al.*[5] was generalized to solve the solute transport problem involving nonlinear adsorption and decay. Instead of solving the concentration-based transport equation as widely used in the conventional numerical schemes, the proposed method solved a mixed-form formulation of the transport eqn (12). The core of the proposed iteration scheme was given by eqn (15), the first-order Taylor series expansion of the discrete total concentration $M^{n+1,m+1}$ with respect to the liquid concentration $c$ around $c^{n+1,m}$, calculated at previous iteration level $m$. The modified Picard iteration method was successfully applied to a large number of one dimensional transport problems involving a variety of adsorption isotherms with different degrees of nonlinearity, and transient or steady-state flow conditions. The performance of the proposed method was evaluated against the commonly used standard Picard iteration algorithm. The following conclusions could be drawn from our numerical experiments:

1. The new method assured a perfect mass balance, the calculated concentration distributions for all numerical experiments were essentially free of mass balance error (MBE). As a result, the proposed method produced very close results as the 'exact' solutions obtained by the method of characteristics (MOC). In contrast, the standard iteration method always resulted in mass balance errors ranging from 5 to 15%, depending on the degree of nonlinearity inherent in the transport problem.

2. Computational efforts (the average number of iterations for each time step and the total number of iterations) using the proposed method were usually considerably less than the standard method. Computational efficiency for the modified Picard method is particularly remarkable when the transport problem involved highly nonlinear adsorption.
3. The modified Picard iteration scheme was found to be more robust than the standard method for transport associated with highly nonlinear adsorption and decay ($\beta = 0{\cdot}5$, for example). Numerical solutions for these extreme conditions using the standard method suffered from serious mass balance errors that increase with the simulation time.

Although the proposed iteration method is primarily tested for one-dimensional transport problems, generalization of the proposed scheme to two- or three-dimensional nonlinear transport scenarios should be straightforward since our modification mainly involves the discretization of the partial derivatives related to time. We believe that in addition to ensuring excellent mass conservation property, the modified Picard iteration algorithm may also effectively improve the computational efficiency.

## REFERENCES


1. Boris, J. P. & Book, D. L., Flux-corrected transport, I, SHAST, A fluid transport algorithm that works. *J. Comput. Phys.*, **11** (1973) 38–54.
2. Boris, J. P. & Book, D. L., Flux-corrected transport, III, Minimal-error FCT. *J. Comput. Phys.*, **20** (1976) 397–431.
3. Celia, M. A. & Binning, P., A mass-conservative numerical solution for two-phase flow in porous media with application to unsaturated flow. *Water Resour. Res.*, **28** (1992) 2819–28.
4. Celia, M. A., Kindred, J. S. & Hererra, I., Contaminant transport and biodegradation: 1. A numerical model for reactive transport in porous media. *Water Resour. Res.*, **25(6)** (1989) 1141–48.
5. Celia, M. A., Bouloutas, E. T. & Zarba, R. L., A general mass-conservative numerical solution for the unsaturated flow equation. *Water Resour. Res.*, **26** (1990) 1483–96.
6. Chiang, C. Y., Wheeler, M. F. & Bedient, P. B., A modified method of characteristics technique and mixed finite elements method for simulation of groundwater solute transport. *Water Resour. Res.*, **25(7)** (1989) 1541–49.
7. Fabriol, R., Sauty, J.-P. & Ouzounian, G., Coupling geochemistry with a particle tracking transport model, *J. Contaminant Hydrol.*, **13** (1993) 117–29.
8. Gamliel, A. & Abriola, L. M., A one-dimensional moving grid solution for the coupled non-linear equations governing multiphase flow in porous media. 1: Algorithm, *Int. J. Numer. Meth. in Fluids*, **14** (1992) 47–69.
9. Goode, D. J. & Konikow, L. F., Modification of a method-of-characteristics solute-transport model to incorporate decay and equilibrium-controlled sorption or ion exchange. *Water-Resources Investigation Report 89-4030*, U.S. Geological Survey, Reston, Virginia, 1989.
10. Hills, R. G., Fisher, K. A., Kirkland, M. R. & Wierenga, P. J., Application of flux-corrected transport to the Las Cruces Trench. *Water Resour. Res.*, **30(8)** (1994) 2377–85.
11. Hinz, C., Gaston, L. A. & Selim, H. M., Effect of sorption isotherm type on predictions of solute mobility in soil. *Water Resour. Res.*, **30(11)** (1994) 3013–21.
12. Huang, K., Mohanty, B. P. & van Genuchten, M. Th., A new convergence criterion for the modified Picard iteration method to solve the variably-saturated flow equation. *J. Hydrol.*, **178** (1996) 69–91.
13. Junchu, G. H. & Iliuta, I., Preconditioned CG-like methods for solving non-linear convection-diffusion equations. *Int. J. Num. Meth. Heat Fluid Flow*, **5** (1995) 239–50.
14. Kaluarachchi, J. J. & Morshed, J., Critical assessment of the operator-splitting technique in solving the advection-dispersion-reaction equation: 1. First-order reaction. *Adv. Water Resour.*, **18(2)** (1995) 89–100.
15. Kinzelbach, W., Schäfer, W. & Herzer, J., Numerical modeling of natural and enhanced denitirification processes in aquifers. *Water Resour. Res.*, **27(6)** (1991) 1123–35.
16. Kuiper, L. K., A comparison of iterative methods as applied to the solution of nonlinear three-dimensional groundwater flow equation. *SIAM J. Scientific and Statistical Computing*, **8(4)** (1987) 521–28.
17. Lacroix, M. & Garon, A., Numerical solution of phase change problems: An Eulerian-Lagrangian approach. *Numer. Heat Transfer*, **19** (1992) 57–78.
18. Mayer, A., Mitchell, R. J., Carriere, P. P. E., Hein, G. L., Rabideau, A. J. & Wojick, C. L., Groundwater quality. *Water Environ. Res.*, **67(4)** (1995) 629–85.
19. Millington, R. J. & Quirk, J. M., Permeability of porous solids. *Trans. Faraday Soc.*, **57** (1961) 1200–07.
20. Neuman, S. P., Adaptive Eulerian–Lagrangian finite element method for advection-dispersion. *Int. J. Numer. Meth. Eng.*, **20** (1984) 321–37.
21. Paniconi, C., Aldama, A. A. & Wood, E. F., Numerical evaluation of iterative and noniterative methods for the solution of the nonlinear Richards equation. *Water Resour. Res.*, **27(6)** (1991) 1147–63.
22. Rathfelder, K. & Abriola, L. M., Mass conservative numerical solutions of the head-based Richards equation. *Water Resour. Res.*, **30(9)** (1994) 2579–86.
23. Rifai, H. S. & Bedient, P. B., Comparison of biodegradation kinetics with an instantaneous reaction model for groundwater. *Water Resour. Res.*, **26(4)** (1990) 637–45.
24. Spurlock, F. C., Huang, K. & van Genuchten, M. Th., Isotherm nonlinearity and non-equilibrium sorption effects on transport of fenuron and monuron in soil columns. *Environ. Sci. Technol.*, **29** (1995) 1000–07.
25. Valocchi, A. J. & Malmstead, M., Accuracy of the operator splitting for advection-dispersion-reaction problems. *Water Resour. Res.*, **28(5)** (1992) 1471–76.
26. van Genuchten, M. Th., A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Sci. Soc. Am. J.*, **44** (1980) 892–8.
27. van Genuchten, M. Th. & Parker, J. C., Boundary conditions for displacement experiments through short laboratory soil columns. *Soil Sci. Soc. Am. J.*, **48(4)** (1984) 703–08.
28. Van Der Zee, S. E. A. T. M. & Riemsdijk, W. H., Transport of reactive solutes in soils. In *Advances in Porous Media*, ed. M. Y. Corapcioglu. Elsevier, New York, pp. 1–150, 1994.
29. Vogel, T., Huang, K., Zhang, R. & van Genuchten, M. Th.,

The HYDRUS (version 5.0) code for simulating one-dimensional water flow, solute transport, and heat movement in variably-saturated media, *Research Report No. 140*, U.S. Salinity Laboratory, USDA, ARS, Riverside, California, 1995.

30. Wang, C. Y., Beckermann, C. & Fan, C., Numerical study of boiling and natural convection in capillary porous media using the two-phase mixture model. *Numer. Heat Transfer*, **26** (1994) 375–98.
31. Wheeler, M. F. & Dawson, C. N., An operator-splitting method for advection–diffusion-reaction problems, *Technical Report 87-9*, Department of Mathematical Science, Rice University, Houston, Texas, 1987.
32. Yeh, G. T., A Lagrangian–Eulerian method with zoomable hidden fine-mesh approach to solving advection–dispersion equations. *Water Resour. Res.*, **26(6)** (1990) 1133–44.
33. Yeh, G. T. & Tripathi, V. S., A critical evaluation of recent developments of hydrogeochemical transport models of reactive multichemical components. *Water Resour. Res.*, **25(1)** (1989) 93–108.
34. Yeh, G. T., Chang, J. R. & Short, T. E., An exact peak capturing and oscillation-free scheme to solve advection-dispersion transport equations. *Water Resour. Res.*, **28(11)** (1992) 2937–51.
35. Yu, T. S. & Li, C. W., Efficient higher-order backward characteristics schemes for transient advection. *Int. J. Numer. Meth. in Fluids*, **19** (1994) 997–1012.