

Analysis of Concentration Profiles for Reactive Transport in Fractured Porous Media

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ABSTRACT: Transport of reactive chemicals in a fractured porous media is affected by various factors such as sorption, degradation and physical process of advection and dispersion. In this study we investigate effect of first-order mass transfer coefficient, equilibrium sorption, first-order reverse sorption rate coefficient and matrix porosity on spatial and temporal concentration profiles of the solute in fracture. An advective-dispersive-reactive transport equation has been used for porous media, and an advective-dispersive transport equation has been used for the fracture. An implicit finite difference technique has been used for the numerical solutions of governing equations of saturated fracture-matrix system. It was found that the higher values of mass transfer coefficient, sorption coefficient, and matrix diffusion coefficient and matrix porosity decrease the solute concentration in fracture with increase in travel time. Also, large value of half fracture spacing increases the temporal and spatial solute concentration in fracture.

INTRODUCTION

The quality of subsurface water may be affected by natural processes, nonpoint agricultural and urban runoff, waste-disposal practices and industrial discharges etc. Leaching of natural chemical deposits increases the concentration of chlorides, sulphates, nitrates, iron and other inorganic chemicals in subsurface water. Other sources of subsurface contaminants are runoff from agricultural and urban water sheds. These waters contain high concentrations of nutrients, metals, pesticides, micro-organisms and other organic chemicals. Reactive chemicals may interact with porous rock and get sorbed on the fracture surfaces during transport. It may also diffuse into the stagnant water in the pores of the porous rock and get sorbed onto the pore surfaces. If a chemical does not interact with porous rock and also does not diffuse into the porous rock, it will travel at the velocity of ground water in fracture. Since the ground water moves with different velocities the contaminant velocity is dispersed around the mean due to heterogeneity of the fracture-porous matrix system. Transport of reactive chemical in porous media is thus affected by various factors such as sorption,

degradation and physical process of advection and dispersion.

During past few decades, a number of studies have been done on groundwater flow and solute transport in fractured media (Grisak and Pickens, 1981; Neretnieks *et al.*, 1982; Berkowitz and Zhou, 1996). Tang *et al.* (1981) analysed the concentration behavior in a fracture-matrix system for continuous input condition using the dual porosity approach. Sudicky and Frind (1982) developed analytical solutions for the case of radioactive contaminant transport in a system of discrete multiple parallel fractures. Kennedy and Lennox (1995) used control volume approach for modelling solute transport through fractures in a porous matrix. Durham *et al.* (2001) carried out an experimental study to examine the relationship between local rate of dissolution and local aperture during flow of acidic aqueous solution through a rough fracture in Carrara marble under a confining pressure of 0.2 MPa. West *et al.* (2004) derived transient and steady-state analytical solutions for a system of evenly spaced, parallel discrete fractures, to simulate solute transport in both the fracture and the contiguous porous matrix. Suresh

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Kumar and Sekhar (2005) presented numerical analysis of spatial moments for nonreactive solute transport through fracture-matrix system and studied the effect of fracture velocity, fracture dispersivity, fracture spacing, matrix diffusion coefficient, and matrix porosity on the spatial moments.

We use two coupled transport equations, one for the porous matrix and the other for fracture. Numerical solutions of two coupled equations have been obtained using an implicit finite difference method for the case of reactive transport through saturated fracture-porous matrix system. An attempt has been made to analyse the spatial and temporal concentration profile of solute concentration in fracture with different values of mass transfer coefficient, first order sorption coefficient, matrix diffusion coefficient, equilibrium sorption coefficient, and matrix porosity.

GOVERNING EQUATIONS

Figure 1 represents a fracture-matrix system. The transport process of reactive solute in fracture-matrix system is described by two coupled equations, one for fracture and the other for the porous matrix.

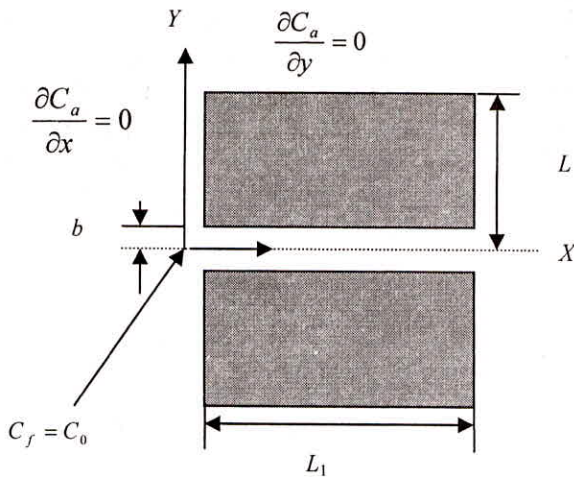


Fig. 1: Fracture porous matrix system

The groundwater velocity in fracture is assumed constant, and a solute source of constant strength is assumed to exist at the inlet of the fracture. The width of fracture is much smaller than its length. The transport along fracture is much faster than transport within the matrix. Tang *et al.* (1981) showed that the coupling between the fracture and porous matrix is represented by the continuity of fluxes and concentration along the interface. It is assumed that diffusive flux from fracture to porous matrix takes place perpendicular to the fracture. It is also assumed

that complete mixing across the fracture width takes place at all times.

For porous matrix Brusseau *et al.* (1992) developed general transport equations that account for both the physical and chemical nonequilibrium. This advective-dispersive-reactive transport equation for transport through the advective region of a porous matrix can be written as,

$$\begin{aligned} & (\theta_a + f\rho F_a K_a) \frac{\partial C_a}{\partial t} + f\rho \frac{\partial S_{a2}}{\partial t} \\ & = \theta_a D_L \frac{\partial^2 C_a}{\partial x^2} + \theta_a D_m \frac{\partial^2 C_a}{\partial y^2} - q \frac{\partial C_a}{\partial x} - \alpha (C_a - C_n) \\ & - [\mu_a \theta_a + \mu_{a1} f \rho F_a K_a] C_a - \mu_{a2} f \rho S_{a2} \quad \dots (1) \end{aligned}$$

The mass balance for the nonadvective region can be described by the following equation,

$$\begin{aligned} & [\theta_n + (1-f)\rho F_n K_n] \frac{\partial C_n}{\partial t} + (1-f)\rho \frac{\partial S_{n2}}{\partial t} \\ & = \alpha (C_a - C_n) - [\mu_n \theta_n + \mu_{n1} (1-f)\rho F_n K_n] \\ & C_n - \mu_{n2} (1-f)\rho S_{n2} \quad \dots (2) \end{aligned}$$

where, θ_a is the fractional volumetric water content of the advective region (L^0), θ_n is the fractional volumetric water content of the nonadvective region (L^0), f is the mass fraction of sorbent constituting the advective region (M^0), ρ is the bulk density of the porous medium (ML^{-3}), F_a, F_n are the mass fraction of sorbent for which sorption is essentially instantaneous, K_a, K_n are the equilibrium sorption coefficient for advective and nonadvective region (L^3M^{-1}), C_a is the concentration of solute in solution phase for advective region (ML^{-3}), C_n is the concentration of solute in solution phase for nonadvective region (ML^{-3}), S_{a2} and S_{n2} are the rate-limited sorbed-phase concentration in advective and nonadvective regions (MM^{-1}), D_L is the longitudinal hydrodynamic dispersion coefficient (L^2T^{-1}), q is the specific discharge (LT^{-1}), α is the first-order coefficient for mass transfer between the advective and nonadvective regions (T^{-1}), μ_a and μ_n are the first-order transformation coefficient for the solution phase in advective and nonadvective regions, μ_{a1} and μ_{n1} are the transformation coefficients (T^{-1}) for the instantaneous sorbed-phase of advective and nonadvective regions, respectively, and μ_{a2} and μ_{n2} are the transformation coefficients for rate-limited sorbed-phase domains of advective and nonadvective

regions, respectively. Subscript *a* refers to the advective region and *n* to the nonadvective region.

Dynamics of sorption and transformation for the rate-limited domains are described by,

$$\frac{\partial S_{a2}}{\partial t} = k_{a2}[(1 - F_a)K_a C_a - S_{a2}] - \mu_{a2} S_{a2} \quad \dots (3)$$

$$\frac{\partial S_{n2}}{\partial t} = k_{n2}[(1 - F_n)K_n C_n - S_{n2}] - \mu_{n2} S_{n2} \quad \dots (4)$$

where, k_{a2} and k_{n2} are the first-order reverse sorption rate coefficients (T^{-1}) for the advective and nonadvective region, respectively.

The transport equation for the fracture can be written as,

$$\frac{\partial C_f}{\partial t} + V_0 \frac{\partial C_f}{\partial x} = D_0 \frac{\partial^2 C_f}{\partial x^2} + \frac{\theta_a D_m}{b} \frac{\partial C_a}{\partial y} \quad \dots (5)$$

where V_0 is the ground water velocity in fracture (L/T); b is half fracture aperture (L); D_0 is hydrodynamic dispersion coefficient (L^2/T); D_m effective molecular diffusion coefficient (L^2/T); α_0 is local longitudinal dispersivity in the fracture (L); x and y are the spatial coordinates (L); and t is time (T).

MODEL DEVELOPMENT AND VALIDATION

In this investigation, an implicit finite-difference technique has been used to get the numerical solution of one-dimensional advective-dispersive transport equation for fracture and two-dimensional advective dispersive reactive equations for porous matrix (Equation 1-5). The following initial and boundary conditions for the fracture and porous matrix have been used,

$$C_f(x, 0) = 0; \quad C_f(0, t) = C_0; \quad \left. \frac{\partial C_f}{\partial x} \right|_{(\infty, t)} = 0 \quad \dots (6)$$

$$C_a(x, y, 0) = 0; \quad C_a(x, b, t) = C_f(x, t); \quad \left. \frac{\partial C_a}{\partial y} \right|_{(x, L, t)} = 0 \quad \dots (7)$$

$$C_n(x, y, 0) = 0; \quad S_{a2}(x, y, 0) = 0; \quad S_{n2}(x, y, 0) = 0 \quad \dots (8)$$

where, C_0 is initial injected concentration of solute source at the inlet of the fracture (M/L^3).

Both direct and Gauss-Seidel iteration methods have been used to get the solution of a set of finite difference formulated equations for governing equations of fracture-porous matrix. The numerical model for reactive solute has been validated for the case of one-dimensional nonreactive solute transport through fracture-matrix system (Suresh Kumar and Sekhar, 2005). The input parameters listed in Table 1 were used to obtain the first spatial moment of the solute in the fracture.

Table 1: Input Parameters for Fracture

Parameter	Value
Injected fracture velocity, V_0	1.0 m/d
Local fracture dispersivity, α_0	0.5 m
Half-fracture aperture, b	50 micron
Half-fracture spacing, L	0.01 m
Porosity of porous matrix	0.01

Figure 2 shows the temporal variation of first moment of nonreactive solute in fracture with different values of matrix diffusion coefficient. It is observed that the first moment varies nonlinearly during early time of transport and increases linearly with increasing time at later times. At large times, the behavior of first moment in fracture is similar for conservative solute in homogeneous porous media. It is also observed that first moment decreases with increasing value of matrix diffusion coefficient. As expected, higher value of matrix diffusion coefficient enhances the mass flux from the fracture into the porous matrix.

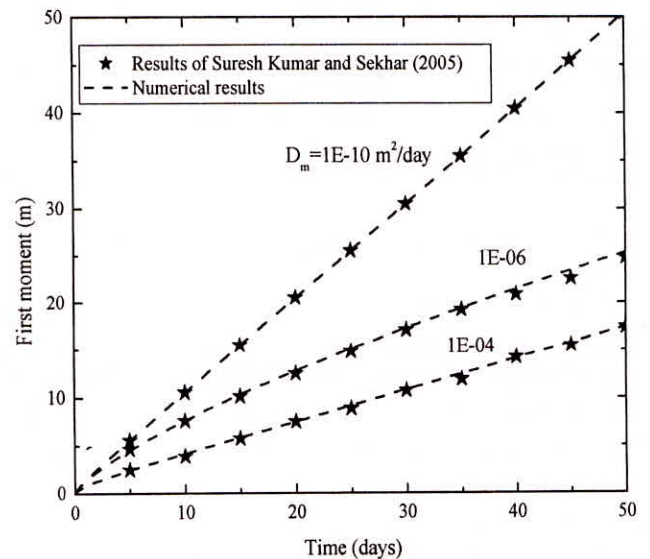


Fig. 2: First spatial moment in fracture with different values of matrix diffusion coefficients

APPLICATIONS

Numerical results of various temporal and spatial concentration profiles are discussed for the case of reactive solute in fracture-porous matrix system. The physical and chemical input parameters used for this simulation are shown in Table 2. The temporal concentration profiles have been computed at a distance of 10 m down gradient of contaminant source along the fracture. Spatial concentration profiles have been predicted at 400 days for all cases.

Table 2: Input Parameters for Porous Matrix

Parameter	ρ	θ_a	θ_n	f	$F_a (= F_n)$	$K_a (= K_n)$
Value	2.0 g/mL	0.01	0.01	0.5	0.5	0.15 mL/g
Parameter	$k_{a2} (= k_{n2})$	V	α_L	α	μ	
Value	0.3 d ⁻¹	0.1 m/d	0.5 m	0.01 d ⁻¹	0.0 d ⁻¹	

The temporal relative concentration profile for solute in fracture with different values of mass transfer coefficient is shown in Figure 3a. During early stage of reactive transport, the concentration profile is identical for both values of mass transfer coefficient. However, a higher peak is obtained for the lower value of mass transfer coefficient during large travel time. It indicates that large value of mass transfer coefficient causes more mass to be transferred from fracture to porous matrix. Figure 3b shows the spatial concentration profile with different values of mass

transfer coefficient after a time of 400 days. It is observed that spatial concentration profile at this time is similar for both values of mass transfer coefficient.

The temporal relative concentration profile for solute in fracture with different value of first-order sorption coefficient is shown in Figure 4a. During early stage of transport, solute concentration in fracture is identical for both values of sorption rate coefficient. For large travel time, concentration in fracture is higher for low value of sorption coefficient. It indicates that the large value of sorption coefficient reduces the solute concentration in fracture. Figure 4b shows the spatial concentration profile for solute in fracture with different values of sorption rate coefficient, which is identical for both values.

Figure 5a represents temporal relative concentration profile with different values of the equilibrium sorption coefficient. Higher value of the equilibrium sorption coefficient reduces the solute concentration in fracture during large travel time. It implies that more solute mass is transferred from fracture to porous matrix. The spatial concentration profiles, with different values of equilibrium sorption coefficient, are shown in Figure 5b. Again, higher value of equilibrium sorption coefficient reduces the solute concentration in fracture.

Figure 6a shows the temporal relative concentration profile with different values of matrix porosity for solute in fracture. Higher value of matrix porosity reduces the solute concentration in fracture.

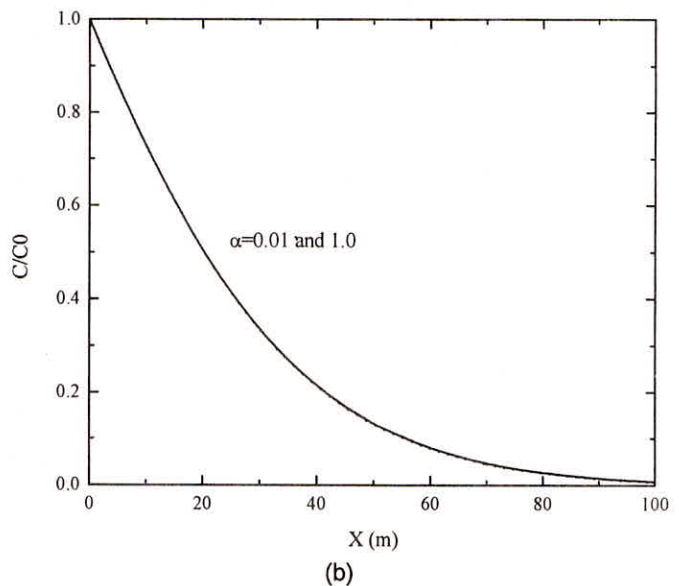
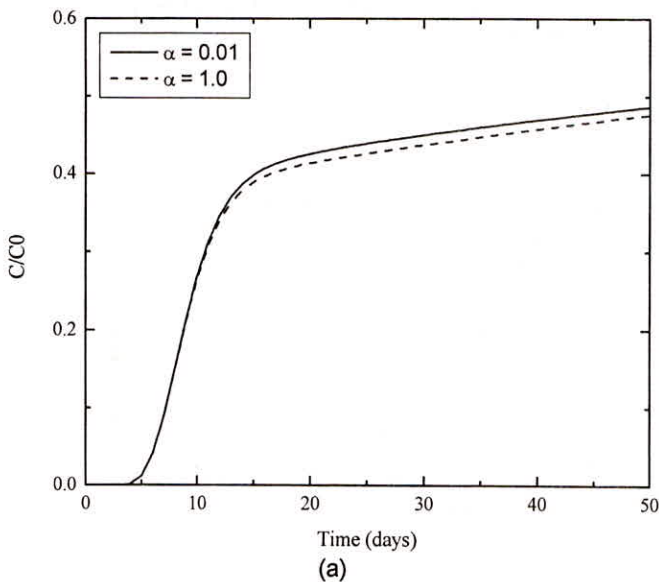


Fig. 3: Concentration profile for solute in fracture with different values of mass transfer coefficients: (a) Temporal profile (b) Spatial profile

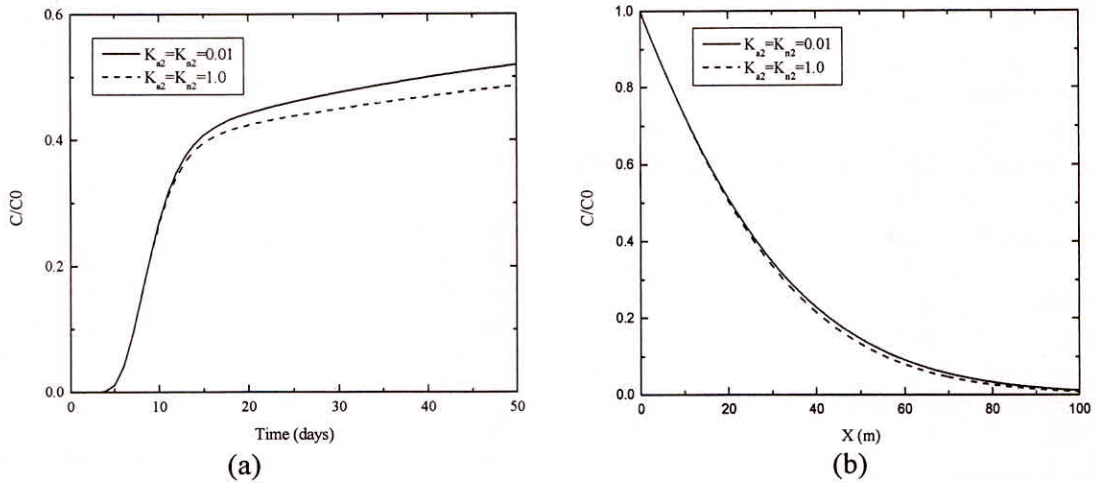


Fig. 4: Concentration profile for solute in fracture with different values of first order sorption coefficients: (a) Temporal profile (b) Spatial profile

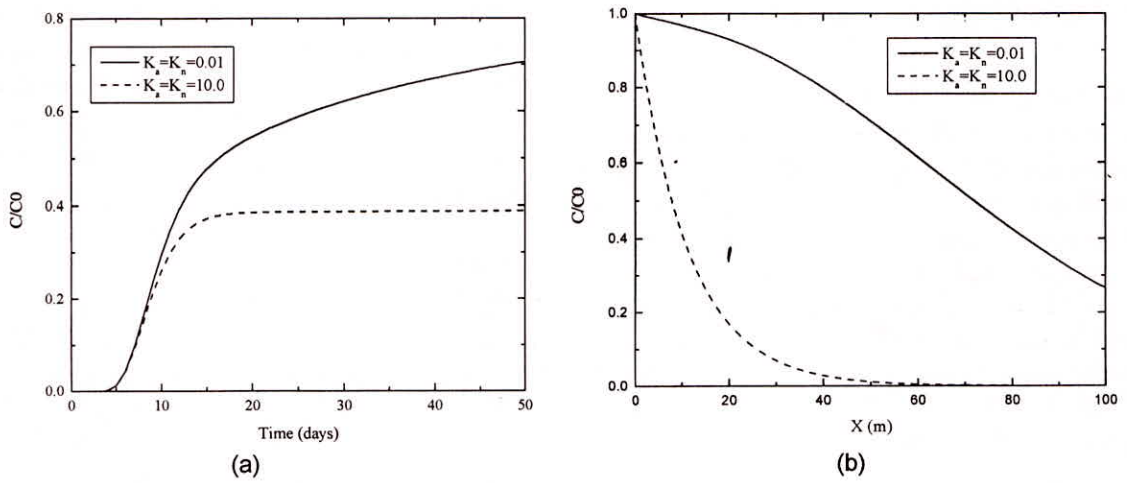


Fig. 5: Concentration profile for solute in fracture with different values of equilibrium sorption coefficients: (a) Temporal profile (b) Spatial profile

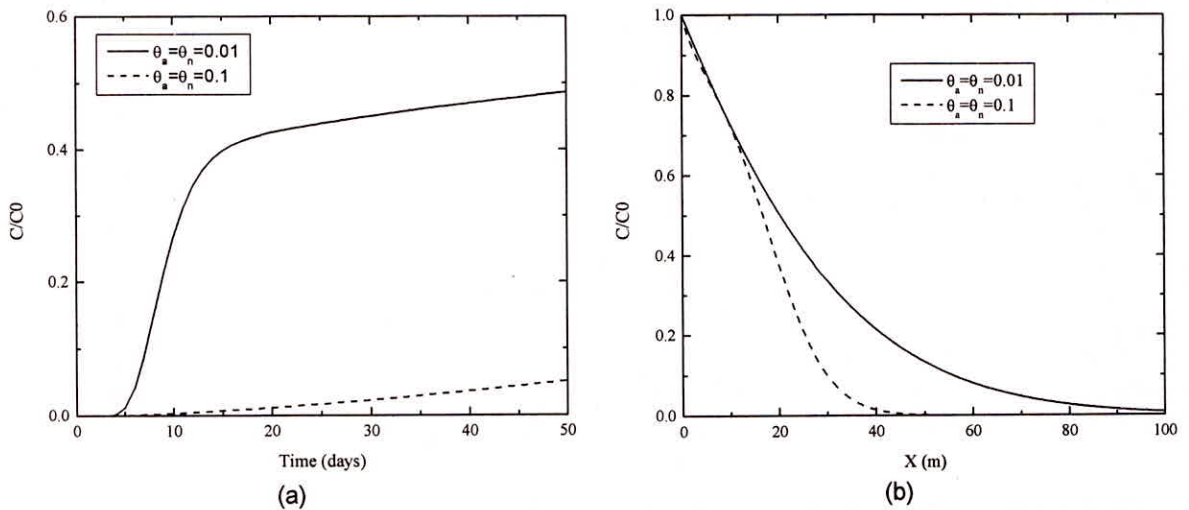


Fig. 6: Concentration profile for solute in fracture with different values of matrix porosity: (a) Temporal profile (b) Spatial profile

It indicates that higher value of matrix porosity causes a transfer of larger mass of solute from fracture to matrix system. The spatial relative concentration profile with different values of matrix porosity is shown in Figure 6b. For small travel distance, spatial concentration profile is similar for both values of matrix porosity. But due to large value of matrix porosity, the concentration in fracture decreases with increase in travel distance.

Figure 7a shows the temporal relative concentration profile for solute in fracture with different values of half-fracture spacing. It is observed that higher value of fracture spacing increases the solute concentration

in fracture. It means that transfer of solute mass flux from fracture to porous matrix reduces due to higher value of fracture spacing. Figure 7b shows a similar trend for the spatial relative concentration profile.

Finally, the temporal relative concentration profile for solute in fracture with different values of matrix diffusion coefficient is shown in Figure 8a. Higher value of matrix diffusion coefficient reduces the solute concentration in fracture. It means that the mass of solute transferred from fracture to porous matrix increases due to higher value of matrix diffusion coefficient. Similar behavior is seen for the spatial concentration profile (Figure 8b).

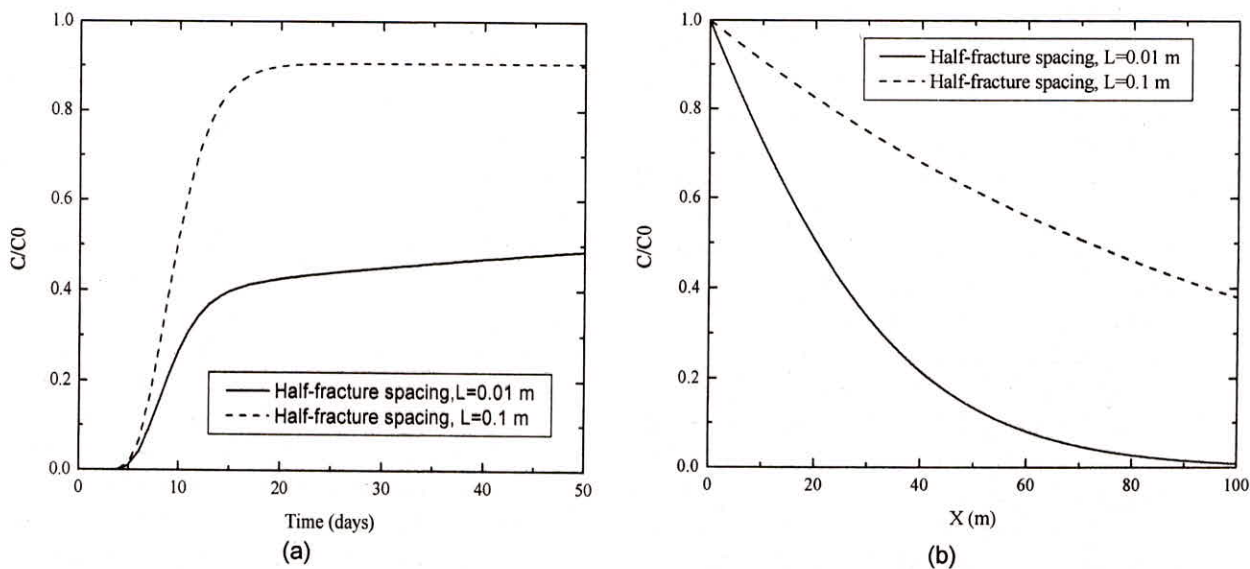


Fig. 7: Concentration profile for solute in fracture with different values of fracture spacing: (a) Temporal profile (b) Spatial profile

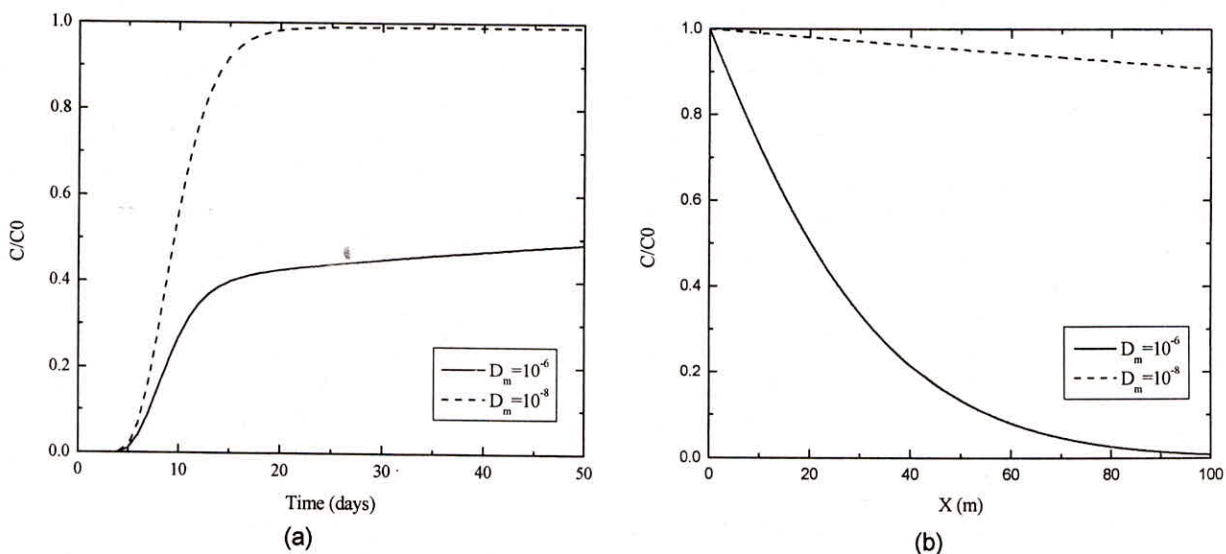


Fig. 8: Concentration profile for solute in fracture with different values of matrix diffusion coefficient: (a) Temporal profile (b) Spatial profile

CONCLUDING REMARKS

In this study, the two-dimensional advective dispersive reactive transport equation for reactive solute in homogeneous porous media, and one-dimensional advective dispersive transport equation for conservative solute in fracture have been used. An implicit finite difference technique has been used to get the numerical solution of governing equations to obtain the solute concentration in one-dimensional fracture. Since the transport of reactive chemicals in porous matrix is affected by sorption and degradation in addition to the physical process of advection and dispersion, an attempt has been made to investigate the effect of first-order reverse sorption, first-order mass transfer coefficient, equilibrium sorption and porosity of matrix on spatial and temporal concentration profiles of solute transport through one-dimensional homogeneous fracture. Higher values of mass transfer coefficient, first order sorption coefficient, equilibrium sorption coefficient, and matrix diffusion coefficient and matrix porosity decrease the solute concentration in fracture with increase in travel time. It indicates that transfer of solute mass flux from fracture to porous matrix increases due to higher values of mass transfer coefficient, sorption coefficient, and matrix diffusion coefficient and matrix porosity. However, large value of half fracture spacing increases the temporal and spatial solute concentration in fracture. This model can be used for numerical simulations of reactive and non-reactive solute transport through fracture porous matrix system.

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