Modeling solute transport affected by heterogeneous sorption kinetics using single-rate nonequilibrium approaches

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ABSTRACT

Single-rate transport models are commonly used for interpreting sorption-related mass transfer in porous media, often with the intention of approximating the kinetics of the sorption process. Among the most commonly used single-rate models are the two-site first-order (TSFO) and the two-site radial diffusion (TSRD) models. We fitted the parameters of the TSFO and TSRD models to simulated breakthrough data of hypothetical column experiments in which sorption rates were described by a γ-distributed sorption sites (GS) model. Our objective was to determine the conditions under which the assumption of a single-rate sorption parameter will be applicable to systems with heterogeneous sorption rates. We were further interested in knowing in what manner the fitted single-rate nonequilibrium model parameters depend upon the conditions under which the data were obtained. The considered hypothetical cases covered a range of experimental conditions and involved compounds with different sorption characteristics. The study revealed that the goodness of fit of the single rate models in simulating the transport of solutes exhibiting heterogeneous sorption rates is affected by solute residence time and pulse injection duration. Compared to the TSFO model, the TSRD model generally results in better prediction of solute transport affected kinetics. In addition, for such systems, the nonequilibrium parameters fitted using the TSFO model and their counterparts in the TSRD model are highly correlated. Moreover, an increase in the fitted mass transfer timescale of each of the single-rate models is coupled with an increase in the associated fraction of instantaneous sorption sites. A strong correlation was found between the time of the experiment and the product of the fitted characteristic time for mass transfer, pulse duration, and solute residence time. The correlation explains many of the variations in the mass transfer timescale encountered when single-rate sorption approaches were utilized to model solute transport in previous miscible displacement studies.

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1. Introduction

Sorption is an important mechanism that affects the mobility of contaminants in the subsurface environment. In many reported studies, sorption nonequilibrium was observed due to either slow chemical interaction or slow accessibility to sorption sites. For modeling purposes, sorption nonequilibrium has sometimes been characterized as a period of fast sorption kinetics followed by a period of slow kinetics (Maraqa, 2001).

However, there is growing evidence that sorption rates decrease as the length of exposure time increases (Altfelder and Streck, 2006; Altfelder et al., 2000; Connaughton et al., 1993; Johnson et al., 2009; Kempf and Brusseau, 2009; Werth and Hansen, 2002), probably due to the existence of different sorption rates created by heterogeneity in physical and chemical properties (see Haggerty and Gorelick, 1995). As indicated by Culver et al. (1997), the processes causing kinetic sorption at a particle scale are complex and remain poorly understood. In fact, a variety of processes related to the complexity and heterogeneity of natural particles may interact to give rise to the observed sorption rates (Pignatello, 2000).

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Several sorption nonequilibrium models have been formulated to better understand the transport of solutes in porous media (Culver et al., 1997). In some of these models, a single-rate mass transfer coefficient has been used to describe sorption kinetics (see Brusseau and Rao, 1989; Pignatello and Xing, 1995; Weber et al., 1991). The use of a single-rate approach to describe mass transfer limitations, however, has been only partially successful in fitting experimental data, especially when long-term desorption is encountered (Chen and Wagenet, 1997; Haggerty and Gorelick, 1998; Johnson et al., 2009; Kempf and Brusseau, 2009; Maraqa et al., 2011; Pedit and Miller, 1994; Pignatello and Xing, 1995). Among these models are the commonly used two-site equilibrium/kinetic models (Chen and Wagenet, 1997; Dousset et al., 2007; Kohne et al., 2006; Maraqa et al., 2011; Pignatello et al., 1993; Pot et al., 2005; van Genuchten and Wagenet, 1989), in which the rate of sorption is modeled either as first-order or radial diffusion.

The use of models with a single-rate coefficient has been questioned due to soil heterogeneity and the complex structure of natural particles (Haggerty and Gorelick, 1995; Haws et al., 2007). To address these factors, models that incorporate multiple kinetic compartments with different mass-transfer rates have been suggested or used (Ahn et al., 1996; Carrera et al., 1998; Chen and Wagenet, 1995, 1997; Connaughton et al., 1993; Culver et al., 1997; Cunningham and Roberts, 1998; Cunningham et al., 1997; Deitsch et al., 1998; Haggerty and Gorelick, 1995, 1998; Haggerty et al., 2000; Hollenbeck et al., 1999; Johnson et al., 2003a,b; Kauffman et al., 1998; Li and Brusseau, 2000; Liu et al., 2009; Lorden et al., 1998; Pedit and Miller, 1994, 1995; Sahoo and Smith, 1997; Saiers and Tao, 2000; Shang et al., 2011; Werth et al., 1997, among others). However, the approach used to describe the distribution of mass transfer rates in the multirate models varies. Haggerty and Gorelick (1995), for example, used a series of first-order equations to characterize various mass transfer processes. Johnson et al. (2003a) assumed a dual-rate behavior to describe local-scale physical and chemical nonequilibrium processes. Carrera et al. (1998) developed a transport model in which mass transfer rates are described by a convolution product of concentrations in the mobile domain and a memory function. Other investigators assumed that variations in the mass-transfer rates follow a probability density function, such as a γ-distribution (Chen and Wagenet, 1997; Connaughton et al., 1993; Culver et al., 1997; Cunningham et al., 1997; Deitsch et al., 1998; Kauffman et al., 1998; Lorden et al., 1998; Pedit and Miller, 1994; Sahoo and Smith, 1997; Saiers and Tao, 2000; Werth et at., 1997) or a lognormal distribution (Culver et al., 1997; Haggerty and Gorelick, 1998; Johnson et al., 2003b; Pedit and Miller, 1994, 1995; Shang et al., 2011). Additional approaches that have been utilized to characterize solute transport with mass transfer limitations include the use of temporal moments (Cunningham and Roberts, 1998; Harvey and Gorelick, 1995; Luo et al., 2008; Valocchi, 1985), the use of continuous time random walk (Berkowitz and Scher, 1998; Berkowitz et al., 2006; Dentz and Berkowitz, 2003; Dentz et al., 2004), and the use of fractional derivative (Benson et al., 2000; Schumer et al., 2003, 2009).

Comparison between the performance of single-rate and multirate models in predicting solute transport reveals that multirate models generally produce more accurate simulations of mass transfer and transport. Pedit and Miller (1994, 1995), for example, modeled mass transfer in a batch reactor using a model that incorporates a probability distribution of rate coefficients. The model significantly improved the prediction of mass transfer compared to that achieved by single-rate sorption models. Haggerty and Gorelick (1995) concluded that, in a heterogeneous aquifer, a model that assumes a homogeneous diffusion-limited mass transfer rate may greatly under-predict the long-term rate-limited behavior. Culver et al. (1997), modeled desorption of trichloroethene for batch and column experiments using multirate models that incorporate a first-order lognormal and a first-order γ-distributed mass transfer rates. They found that the multirate models provided similar fitting ability, but significantly outperformed the single-rate model. Chen and Wagenet (1997) successfully predicted atrazine transport using a model with γ-distributed mass transfer rates and parameter values from an independent experiment, but could not adequately predict atrazine transport using single-rate models. Moreover, Haggerty and Gorelick (1998) modeled the desorption of trichloroethene and tetrachloroethene from packed soil columns and concluded that extreme variability in diffusion rate coefficients is necessary to reflect mass transfer in the considered experiments. These authors also found that models with a lognormal distribution of diffusion rate coefficients generally represent mass transfer much better than those that employ a single-rate coefficient or even those with two-rate coefficients.

A major limitation of using single-rate sorption models is the dependence of the mass transfer timescale on the employed experimental conditions (see for example, Brusseau, 1992; Haggerty et al., 2004; Maraqa, 2001; Maraqa et al., 2011). This suggests that the representation of the sorption mechanisms by the single-rate models are either "overly simplified or incorrectly specified" (Saiers and Tao, 2000). We hypothesize that such variability in the mass transfer timescale is due to the deficiency of the used modeling approach in accounting for multirate sorption behavior. To test this hypothesis, we explored the effects of experimental conditions on fitting single-rate sorption models to the results of miscible transport experiments that are affected by heterogeneous sorption kinetics. A γ-distributed sorption-site (GS) model for the transport of contaminants with heterogeneous sorption rates was utilized to generate breakthrough data for cases under various experimental conditions. The breakthrough data of each case were then fitted to each of the single-rate sorption models. The fitted parameters were then correlated to the conditions under which the data were obtained. We then utilized the correlations obtained to explain the observed variations in the characteristic mass transfer timescale of the single-rate models as reported in the literature.

2. Transport models

The general equation describing transport of dissolved non-degradable chemicals under one-dimensional, steady-state water flow in porous media is as follows:

$$\frac{\partial C}{\partial t} + \frac{\rho}{\theta}\frac{\partial S}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v_o\frac{\partial C}{\partial x} \tag{1}$$

where C is the concentration in the liquid phase, S is the concentration on the solid phase, D is the dispersion coefficient, v_o is average pore-water velocity, ρ is soil bulk density, θ is volumetric water content, t is time, and x is distance. Because