



Simulation of nonlinear sorption of N-heterocyclic organic contaminates in soil columns

Erping Bi^{*}, Lunliang Zhang¹, Torsten C. Schmidt², Stefan B. Haderlein

Center for Applied Geoscience, University of Tuebingen, Wilhelmstr. 56, D-72074, Tuebingen, Germany

ARTICLE INFO

Article history:

Received 9 June 2008

Received in revised form 25 February 2009

Accepted 3 April 2009

Available online 6 April 2009

Keywords:

Sorption

N-heterocyclic compounds

Eurosoil

Column experiment

One-site nonlinear nonequilibrium model

AQUASIM

ABSTRACT

The transport of organic contaminants in porous media is frequently influenced by nonequilibrium sorption and/or nonlinear sorption. In this study, sorption of coal tar related contaminants with different sorption properties, i.e., toluene, quinoline, quinaldine, and benzotriazole, was studied in column experiments using a European reference soil and compared with batch sorption results in order to quantify the governing sorption features. The breakthrough curves (BTCs) were simulated with a versatile 1-D reactive transport model using a one-site first-order sorption approach. Some differences in fitted parameters from batch and column experiments were found and discussed in terms of different sorption mechanisms in different aqueous concentration ranges, effects of solution properties (e.g., pH) and differences in solid-to-solution ratio and accessible sorption sites. The modeling results show that the fitting results were not sensitive to mass transfer coefficients and that a local equilibrium assumption provides excellent agreement with BTCs in our designed column when Damkohler numbers were greater than 20. Nonequilibrium sorption resulting from intraparticle diffusion thus was negligible in the column experiments. Tailing of BTCs nevertheless occurred and was primarily attributed to nonlinear sorption due to specific interactions in the sorption processes rather than to sorption nonequilibrium. Our study demonstrates how column experiments with different concentrations and flow velocities can be designed to obtain reliable sorption parameters for polar solutes with nonlinear sorption isotherms from modeling.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Sorption plays an important role in the transport, fate and remediation of organic pollutants in the subsurface. Column experiments are widely applied to determine sorption parameters at the laboratory scale (Buergisser et al., 1993; Bayard et al., 1998; Young and Ball, 1999; Altfelder et al., 2001). In column experiments, both nonlinearity and nonequilibrium conditions for sorption can significantly influence the shape of breakthrough curves (BTCs) (Das et al., 2004). In order to address sorption

nonequilibrium, low-velocity or stop-flow experiments are commonly applied (Brusseau et al., 1989). Based on such experimental approaches, simulation of BTCs from column experiments by models considering sorption kinetics can provide information not only on sorption nonequilibrium but on sorption nonlinearity as well. In modeling, both simple one-site first-order models (Hornsby and Davidson, 1973; van Genuchten et al., 1974; Spurlock et al., 1995; Cryer, 2005) and two-region (or two-site) first-order mass transfer models (van Genuchten et al., 1977; Brusseau et al., 1991) have been used to simulate solute transport.

Although two-region/site models were used successfully in several studies, the excellent agreement between experiment and model predictions may just be a consequence of the additional adjustable parameter that can be used to “curve fit” the solution to experimental data (Cryer, 2005), and that the character of the mass transfer coefficients is more or less empirical (Worch, 2004). For example, modeling of hormone transport revealed that a two-region (dual-domain) modeling

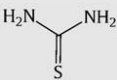



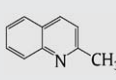
^{*} Corresponding author. Present address: School of Water Resources and Environment, China University of Geosciences (Beijing), Xueyuan Road 29, 100083, Beijing, China. Tel.: +86 10 82322311; fax: +86 10 82321081.

E-mail address: bi@cugb.edu.cn (E. Bi).

¹ Present address: College of Environmental Science & Engineering, Nankai University, Weijin Road 94, Tianjin, 300071, China.

² Present address: Instrumental Analytical Chemistry, University Duisburg-Essen, Lotharstr. 1, 47048 Duisburg, Germany.

Table 1
Some properties of the investigated solutes*.

Compound	Thiourea	Toluene	Benzotriazole	Quinoline	Quinaldine
CAS number	62-56-6	108-88-3	95-14-7	91-22-5	91-63-4
Formula	CH ₄ N ₂ S	C ₇ H ₈	C ₆ H ₅ N ₃	C ₉ H ₇ N	C ₁₀ H ₉ N
Structure					
Water Solubility (mg/L) (25 °C)	14,200	526	19,800	6110	499
Log K _{ow}	-1.08	2.73	1.44	2.03	2.59
pK _a (20 °C)	2.03 ^a	-	1.6 ^a ; 8.6 ^b	4.9 ^a	5.71 ^a

*Data from www.chemfinder.com; a) pK_a is valid for corresponding cation; b) data from Ref. (Albert et al., 1948).

approach is adequate in describing the general shape of the measured BTCs, but is physically not meaningful, and the discrepancies may have resulted from the inherent model assumptions (Das et al., 2004).

In many models, it is assumed that sorption is linear (Ball and Roberts, 1991; Brusseau et al., 1991; Culver et al., 1997; Young and Ball, 1998, 2000). Assumption of linear sorption isotherm leads to a transport equation, which can be solved analytically. However, nonlinear sorption isotherms for geosorbents have also been reported (Allen-King et al., 2002; Worch, 2004). A transport model based on linear sorption thus might not provide an accurate simulation of the transformation and transport of nonlinearly sorbing solutes (Brusseau, 1995). Compared with nonpolar compounds, a higher degree of sorption nonlinearity can be expected for polar compounds. (Chiou et al., 2000; Endo et al., 2008). Therefore, the assumption of a linear isotherm for polar organics might deduce inaccurate sorption parameters under certain conditions. Young and Ball have suggested that a wide variety of experimental conditions is needed in order to fully test the complex set of sorption equilibrium and rate mechanism (Young and Ball, 1995, 1999).

In this study, the effects of nonequilibrium sorption and nonlinear sorption on the transport of N-heterocyclic compounds (benzotriazole, quinaldine and quinoline) in soil columns were investigated using a one-site nonlinear nonequilibrium model. The reason to select these compounds is that specific interactions play an important role in their sorption and transport (Bi, 2006). The breakthrough curves were numerically simulated by fitting the sorption parameters (K_f and n in the Freundlich isotherm, and mass transfer coefficient α) using AQUASIM. Toluene was taken as a reference for non-polar compounds and Eurosoil 4 was used as a model sorbent as it exhibits average properties with regard to pH, organic carbon content, clay content, etc., compared with other Eurosoils.

2. Materials and methods

2.1. Soil and chemicals

Eurosoil 4 (IRMM, Belgium) has a pH of 6.5 in 0.01 M CaCl₂ with structure of silt 75.7%, clay 20.3%, and sand 4.1%. The organic carbon content is 1.55%. The main soil minerals are SiO₂ 68.63%, Al₂O₃ 12.07% and Fe₂O₃ 2.71%. Quartz (from Merck) was used for soil dilution in order to avoid column clogging. Both soil and

quartz were manually ground with pestle and mortar to make the packing material more homogeneous.

Thiourea and quinaldine (≥97%) were purchased from Fluka AG. Benzotriazole (99%) and quinoline (98%) were provided by Aldrich. Toluene (99%) was obtained from Acros Organics. Some properties of the investigated chemicals are summarized in Table 1. All the stock solutions were prepared in methanol and stored at 4 °C in refrigerator. The solutions were prepared from stock solutions and 0.005 M CaCl₂ in MilliQ water.

2.2. Experiments

2.2.1. Column experiments

High-performance liquid chromatography (HPLC) system (Bischoff Analysentechnik und -geräte GmbH, Germany) equipped with a soil column was used to perform column experiments. The ground soil and quartz were well mixed with a ratio of 2:1 in weight and packed into a stainless steel column (CS-Chromatography Service GmbH, Germany) with length of 60 mm and inner diameter of 3 mm. Details on packing and setup can be found elsewhere (Bi, 2006). The solid density of packing material is 2.69 g/cm³ and the porosity of the packed matrix is 0.445. The sieving results showed that the particle size is less than 0.063 mm. Therefore, the ratio of column diameter/particle diameter is higher than 47. The solution of 0.005 M CaCl₂ from reservoir was degassed online (DG1210, Dionex). Dirac (pulse) input was conducted by an injection-loop-valve (5 μL). The column oven temperature was set to 25 °C. Thiourea was used as conservative tracer to determine the hydrodynamic properties (dispersion coefficient D) of the column, due to its hydrophilic property and the possibility of convenient online UV detection (Fesch et al., 1998).

To investigate the influence of flow velocity and concentration on the sorption of compounds, the experiments were conducted under various conditions (Table 2). The pH of the

Table 2
Experimental conditions for column experiments.

Compounds	Pore water velocity (mm/s)	Injected concentrations (mg/L)
Thiourea	0.106; 0.265; 0.530; 1.06	25, 40, 100, 200, 400, 800
Toluene	0.106; 0.265; 0.530; 1.06	42.7*, 84.9, 209.3, 408.6
Benzotriazole	0.106; 0.265; 0.530; 1.06	82.6, 164.36, 404.9, 790.5
Quinoline	0.106; 0.265; 0.530; 1.06	54.4, 108.2, 520.8
Quinaldine	0.530; 1.06	103.8*, 258.3, 407.3

*BTCs not used in modeling due to high background noise in measured data.

Download English Version:

<https://daneshyari.com/en/article/4547349>

Download Persian Version:

<https://daneshyari.com/article/4547349>

[Daneshyari.com](https://daneshyari.com)