Comparison of First-Order Sorption Kinetics Using Concept of Two-Site Sorption Model

Soonjae Lee,¹ Dong-Ju Kim,^{1,*} and Jae-Woo Choi²

¹Department of Earth and Environmental Sciences, Korea University, Seoul, Republic of Korea.

²Environment and Technology Research Center, Korea Institute of Science and Technology, Seoul, Republic of Korea.

Received: June 22, 2011

Accepted in revised form: June 1, 2012

Abstract

We compared two different approaches available in the literature for first-order sorption kinetics, which constitutes the slow time-dependent part of the two-site sorption model commonly used for solute transport. One approach assumes that sorbed concentrations in the Type-1 site (S_1) and the Type-2 site (S_2) are directly associated with a solute concentration (C) in liquid phase by forming two-site sorption with a parallel interface; the other assumes that S_2 is associated with only S_1 at the Type-1 site, resulting in two-site sorption with a serial interface. Application of different kinetics to a batch system where solute mass is conserved resulted in an identical type of liquid and sorbed concentration versus time equation in the form of exponential decay. However, because of the different structure and components used to define the kinetic part (S_2), some parameters estimated from observed kinetic sorption data deviated significantly from one another. For instance, the fraction (f) of the Type-1 site varied as much as twofold, which led to different transport behavior. This indicates that choice of the kinetic part in the two-site sorption model becomes important when attempting appropriate transport modeling on reactive solutes.

Key words: parallel interface; serial interface; two-site sorption; Type-1 site; Type-2 site

Introduction

ORGANIC CHEMICALS EXHIBIT various sorption processes during transport through porous medium. The sorption processes can be divided into two different patterns: one is equilibrium sorption with linear or nonlinear behavior and the other is a nonequilibrium one with the first-order reversible (Nielsen *et al.*, 1986; Nkedi-Kizza *et al.*, 2006; Lee *et al.*, 2009) and irreversible kinetics (Kim *et al.*, 2004) or second-order kinetics (Ho and McKay, 2000). Among them, either equilibrium linear or first-order kinetic sorption, and combined form of these can be conveniently accommodated into the advective-dispersive equation (ADE), which can be used to describe the fate of organic contaminants during transport in the porous medium. The combined form offers the basis of two-site sorption models, which have been often used for sorbing solutes such as organic pesticides showing a dual nature in sorption behaviors. The two-site sorption concept presumes that sorption or exchange sites in a porous medium can be classified into two fractions: one fraction (f) at the Type-1 site, on which sorption is assumed to be instantaneous,

and another fraction ($1-f$) at the Type-2, on which sorption is considered to be time-dependent. Total sorbed concentration (S) consists of concentrations at these two fractions at all times:

$$S = S_1 + S_2 \quad (1)$$

where S_1 and S_2 are sorbed concentrations at Type-1 and Type-2 sites, respectively. Introducing the distribution coefficient K (L/kg), and assuming that sorption reaches equilibrium instantaneously between sorbate and sorbent, the following equations can be obtained:

$$S = KC \quad (2)$$

$$S_1 = fKC \quad (3)$$

$$S_2 = (1-f)KC \quad (4)$$

In the literature, two different approaches are available for the construction of S_1 , S_2 depending on the way of contact with liquid concentration C . The first is a two-site sorption model with a serial interface (TSSI) (Fig. 1) and the other is a two-site sorption model with a parallel interface (TSPI) for Type-1 and Type-2 sites (Fig. 2). Each model was successfully applied to obtain sorption-related parameters of organic chemicals such as pesticides and toluene showing the dual nature of sorption behaviors in a kinetic batch system,

*Corresponding author: Department of Earth and Environmental Sciences, Korea University, Anam Dong 5-1, Sungbuk Ku, Seoul 136-701, Republic of Korea. Phone: 82-2-3290-3177; Fax: 82-2-3290-3189; E-mail: djkim@korea.ac.kr

FIG. 1. Illustration of the two-site serial interface (TSSI) model used by Nkedi-Kizza *et al.* (2006).

FIG. 2. Illustration of the two-site parallel interface (TSPI) model used by Lee *et al.* (2009).

respectively. The objective of this study was to investigate how the two different kinetics differ from each other by comparing sorption parameters of both models estimated from experimental data obtained from the kinetic sorption test and by simulating the breakthrough curves (BTCs) of a reactive chemical using a solute transport equation coupled with sorption kinetics.

Comparison of C–t Relationship

TSSI Model

In the study of organic pesticide sorption (Nkedi-Kizza *et al.*, 2006), TSSI was used to characterize kinetic sorption parameters. The TSSI model is based on the following sorption kinetics between the Type-1 and Type-2 sites (Cameron and Klute, 1977; Brusseau, 1992):

$$\frac{\partial S_2}{\partial t} = k_1 S_1 - k_2 S_2 \quad (5)$$

where k_1 and k_2 are forward and backward sorption rate coefficients, respectively. In this sorption kinetics, the solute in the liquid phase instantly partitions to the Type-1 site such that

$$S_1 = fKC_{+0} \quad (t = +0) \quad (6)$$

where sorption of the solute in liquid phase onto the Type-1 site is completed at $t = +0$. Then, the time-dependent sorption (S_2) onto the Type-2 site follows the kinetics given by Equation (5) until it satisfies

$$S_2 = (1-f)KC_{\infty} \quad (t = \infty) \quad (7)$$

where C_{∞} is the solute concentration in a batch system at $t = \infty$. Assuming that the relationship given by Equations (3) and (4) is valid at $t = \infty$, then

$$S_{1,\infty} = fKC_{\infty} \quad (8)$$

$$S_{2,\infty} = (1-f)KC_{\infty} \quad (9)$$

In a batch system where the total solute mass added (A) is constant and distributed among the liquid and sorbed phases only, the following relationship can be obtained by applying the mass conservation law:

$$A = VC^0 = VC + MS_1 + MS_2 \quad (10)$$

where V , C^0 and C are volume and concentrations of solution at $t=0$ and $t=t$, respectively, and M is mass of sorbent. Introducing the relationship given by Equations (3) and (10), S_2 is related to C by

$$MS_2 = A - (V + MfK)C \quad (11)$$

In the study of Nkedi-Kizza *et al.* (2006), the time-dependent sorption at Type-2 (S_2) was assumed to obey the first-order kinetics between S_1 and S_2 given by Equation (5). When time goes to infinity, the following relationship can be obtained by introducing Equations (8) and (9) into Equation (5):

$$k_1 = k_2 \frac{(1-f)}{f} \quad (12)$$

Based on the relationships given by Equations (5), (11), and (12), the following equation can be derived:

$$(V + MfK) \frac{\partial C}{\partial t} = k_2 [A - (V + MK)C] \quad (13)$$

Using Equations (10) and (12) at $t = \infty$ the following relationship is obtained:

$$C_{\infty} = \frac{A}{(V + MK)} \quad (14)$$

Substituting Equation (14) into Equation (13) leads to the following expression:

$$\frac{\partial C}{\partial t} = -\frac{k_2}{\beta} [C - C_{\infty}] \quad (15)$$

where $\beta = (V + MfK)/(V + MK)$.

Introducing the relationships of $C_{\infty}/C^0 = 1/R$ and $C^* = C/C^0$, the following equation is obtained:

$$\frac{\partial C^*}{\partial t} = -\frac{k_2}{\beta} \left[C^* - \frac{1}{R} \right] \quad (16)$$

where $R = 1 + MK/V$, with R as the retardation factor.

TSPI Model

In another study of toluene sorption (Lee *et al.*, 2009), a TSPI for Type-1 and Type-2 sites that was given by van Genuchten

and Wagenet (1989) was used to determine both equilibrium and nonequilibrium sorption parameters.

$$\frac{\partial S_2}{\partial t} = \alpha[(1-f)KC - S_2] \quad (17)$$

where C , S_1 , and S_2 are liquid and sorbed concentrations (mg/kg) at Type-1 and Type-2 sites, f is the fraction of the Type-1 site, and α and K are the sorption rate constant (h^{-1}) and distribution coefficient (L/kg), respectively. In this sorption kinetics, the sorbed concentration (S_1) in the Type-1 site reaches equilibrium instantaneously so that it satisfies Equation (6), and the slow nonequilibrium sorption follows the kinetics given by Equation (17) until it satisfies Equation (4).

The kinetic model [Eq. (17)] was applied to a batch system where for a given initial solute concentration (C^0) and volume (V), the total solute mass ($A = VC^0$) distributed in the liquid and sorbed phase remains constant. Dividing Equations (1) and (10) by VC^0 , the following dimensionless forms are obtained:

$$S^* = S_1^* + S_2^* \quad (18)$$

$$S^* + C^* = 1 \quad (19)$$

where $C^* = C/C^0$, $S^* = MS/VC^0$, $S_1^* = MS_1/VC^0$, and $S_2^* = MS_2/VC^0$.

The relationship between S_1^* and C^* can be given from Equation (3):

$$S_1^* = (R\beta - 1)C^* \quad (20)$$

Using Equations (18–20), S_2^* can also be expressed in terms of C^* as following:

$$\frac{\partial S_2^*}{\partial t} = -R\beta \frac{\partial C^*}{\partial t} \quad (21)$$

where $R = 1 + MK/V$, $\beta = (V + MfK)/(V + MK)$, $fMK/V = R\beta - 1$, and $f = (\beta R - 1)/(R - 1)$.

Time-dependent sorption kinetics [Eq. (17)] in the Type-2 site can be given by

$$\frac{\partial S_2^*}{\partial t} = \alpha(RC^* - 1) \quad (22)$$

From Equations (21) and (22), we obtain the following relationship:

$$\frac{\partial C^*}{\partial t} = -\frac{\alpha}{\beta} \left(C^* - \frac{1}{R} \right) \quad (23)$$

It is noted that the relationships [Eqs. (16) and (23)] between the liquid concentration (C^*) versus time (t) of the two studies result in an identical pattern, except for the difference between α in Equation (23) and k_2 in Equation (16), although each study employed different sorption kinetics in the Type-2 site (Figs. 1 and 2).

Comparison of Analytical Solutions

Solution of TSSI model

In the study of Nkedi-Kizza *et al.* (2006), the analytical solution of Equation (16) can be derived as follows:

$$C^* = \frac{1}{R} + \left(C_{+0}^* - \frac{1}{R} \right) e^{-(k_2/\beta)t} \quad (24)$$

where the liquid concentration (C_{+0}) at $t = +0$ is obtained from Equation (11) by assuming that

$$S_{1,+0} = fKC_{+0} \quad (25)$$

$$S_{2,+0} = 0 \quad (26)$$

Using Equations (11), (25), and (26), the following relationship is obtained:

$$C_{+0} = \frac{VC^0}{V + MfK} = \frac{C^0}{\beta R} \quad (27)$$

By introducing Equation (27) into Equation (24), the following analytical solution is obtained:

$$C^* = \frac{1}{R} + \left(\frac{1}{\beta R} - \frac{1}{R} \right) e^{-(k_2/\beta)t} \quad (28)$$

Graphical solution of Equation (28) is depicted in Fig. 3, where the relative concentration changes from 1.0 at $t = +0$ to

FIG. 3. Graphical presentation of liquid concentration (C) and sorbed concentrations (S) in two-sites for the TSSI model at $t = +0$ and $t = \infty$.

FIG. 5. Fit of two-site sorption models to the observed data of aqueous toluene concentrations during equilibrium and kinetic sorption. Data from two models exactly coincide with each other for $S_{1,+0}^*$ and $S_2(t)$.

$$S_2^* = 1 - \beta + \frac{1}{R} - \left[\frac{1}{R} + (1 - \beta)e^{-(\alpha/\beta)t} \right] \quad (34)$$

Graphical solutions of Equations (33–34) are depicted in Fig. 4. Details of important variables and parameters on liquid and sorbed concentrations at the completion of fast and slow sorption processes are summarized in Table 1.

Estimation of Model Parameters and Transport Modeling

To estimate parameters of two kinetic models, we fitted both analytical solutions of Equations (28) and (33) to the kinetic sorption data obtained by Lee *et al.* (2009) showing the typical two-site sorption consisting of a fast process at early time and a slow one at later times (Fig. 5). We used the following equation of exponential decay type

to fit these data, since the two equations have an identical type:

$$y = y_0 + ae^{-bt} \quad (35)$$

Application of Equation (35) to the data at $t=0$ and $t=\infty$ results in the following relationships:

$$y_0 + a = \frac{1}{R} + 1 - \beta \quad (36)$$

$$y_0 + a = \frac{1}{\beta R} \quad (37)$$

$$y_0 = \frac{1}{R} \quad (38)$$

TABLE 2. SORPTION PARAMETERS ESTIMATED USING ANALYTICAL SOLUTIONS OF C - t RELATIONSHIP DEFINED IN TWO-SITE SORPTION MODELS TSPI AND TSSI

Parameter	TSPI	TSSI
K (L/kg)	75.50	75.50
α (h^{-1})	0.13	—
k_1 (h^{-1})	—	4.06
k_2 (h^{-1})	—	0.13
f	0.07	0.03
R	2.32	2.32
$C_\infty^* = 1/R$	0.43	0.43
β	0.47	0.45
βR	1.09	1.04
$C_{+0}^* = 1/\beta R$	—	0.96
$C_{+0}^* = 1 - \beta + 1/R$	0.96	—
$S_{1,+0}^*$	0.04	0.04
$S_{2,\infty}^* = 1/\beta R - 1/R$	—	0.53
$S_{2,\infty}^* = 1 - \beta$	0.53	—

FIG. 6. Comparison of breakthrough curves simulated from sorption parameters obtained from TSPI and TSSI. Note that advection ($V=0.518$ cm/min) and dispersion ($D=0.082$ cm²/min) coefficients were assumed.

The best fit of Equation (35) to the data using the nonlinear least-squares method resulted in $y_0 + a = 0.9609$ and $y_0 = 0.4302$. Parameters of two kinetic models could be obtained by substituting these values into Equations (36–38). Based on the model parameters, BTCs of a reactive chemical were simulated using the following one-dimensional ADE coupled with each sorption kinetics:

$$\beta R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \frac{\rho}{\theta} (k_1 S_1 - k_2 S) \quad (39)$$

$$\beta R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \frac{\rho}{\theta} (k_1 f K C - k_2 S) \quad (40)$$

Comparison of Model Parameters and BTCs

Results of estimated parameters are shown in Table 2. It is noted that K (distribution coefficient), R (retardation factor), and values of C_{+0}^* , C_{∞}^* , $S_{1,+0}^*$, and $S_{2,\infty}^*$ are identical for two models. However, values of β are slightly different, since they are defined with constants a and R in a different mathematical form for each model. Accordingly, values of f for two models varied, and rate constants controlling slow sorption α and k_2 also appeared to be different. It is remarkable that the fraction of the Type-1 site ($f = 0.0686$) of the TSPI model was two times greater than that of the Type-2 site ($f = 0.0307$) of the TSSI model, although the sorbed concentration ($S_{1,+0}^*$) at the Type-1 site was identical. The simulated BTCs of a reactive chemical obeying two different sorption kinetics (TPSI and TSSI) with a certain advection (V) and dispersive property (D) for a pulse type injection are shown in Fig. 6. It is evident that the two BTCs showed different peak travel time and thus caused more retardation for BTC of TPSI. The retardation of BTC simulated from parameters of TPSI is attributed to the higher value of βR by 5%, which was originated from the different f value.

Conclusion

In this study, we compared two different two-site sorption models, which rely on different first-order sorption kinetics; one [TSSI model by Nkedi-Kizza *et al.* (2006)] is based on slow sorption between the sorbed concentration (S_1) at the Type-1 site and the sorbed concentration (S_2) at the Type-2 site, and the other [TSPI model by Lee *et al.* (2009)] based on slow sorption between the liquid concentration (C) and the sorbed concentration (S_2) at the Type-2 site. Application of these two models to a batch system resulted in an identical type of C - t relationship. Model parameters such as distribution coefficient and retardation factor estimated by fitting

the analytical solutions of the C - t relationship to the kinetic sorption data well coincided. However, due to differences in the definition of liquid concentration (C_{+0}^*) at $t = +0$, some of the parameters deviated from each other. For instance, the fraction of the Type-1 site (f) differed by two-fold, which led to different BTCs in terms of retardation. Therefore, care should be taken in the selection of the first-order sorption kinetics of the two-site model when modeling reactive solute transport in a porous medium, since the fraction is closely related to βR , which is responsible for the retardation phenomenon.

Acknowledgment

Authors acknowledge that this study was supported by KOSEF (Grant 2009-0060679).

Disclosure Statement

The authors declare that no competing financial interests exist.

References

- Brusseau, M.L. (1992). Nonequilibrium transport of organic chemicals: The impact of pore-water velocity. *J. Contam. Hydrol.* 9, 353.
- Cameron, D.R., and Klute, A. (1977). Convective-dispersive transport with a combined equilibrium and kinetic adsorption model. *Water Resour. Res.* 13, 183.
- Ho, Y.S., and McKay, G. (2000). The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Water Res.* 34, 735.
- Kim, D.J., Choi, N.-C., and Kim, S.-B. (2004). Quantification of irreversible benzene sorption in sandy materials. *Hydrol. Process.* 18, 3229.
- Lee, S.J., Chung, S.G., Kim, D.J., Lee, C.E., and Choi, J.W. (2009). New method for determination of equilibrium/kinetic sorption parameters. *Curr. Appl. Phys.* 9, 1323.
- Nielsen, D.R., van Genuchten, M. Th., and Biggar, J.W. (1986). Water flow and solute transport in the unsaturated zone. *Water Resour. Res.* 22, 89S.
- Nkedi-Kizza, P., Shinde, D., Savabi, M.R., Ouyang, Y., and Nieves, L. (2006). Sorption kinetics and equilibria of organic pesticides in carbonatic soils from South Florida. *J. Environ. Qual.* 35, 268.
- van Genuchten, M. Th., and Wagenet, R.J. (1989). Two-site/two-region models for pesticide transport and degradation: Theoretical development and analytical solutions. *Soil Sci. Soc. Am. J.* 53, 1303.