MODELING THE SORPTION OF HYDROPHOBIC CONTAMINANTS BY AQUIFER MATERIALS—I

RATES AND EQUILIBRIA

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Abstract—This is the first of a two-part series describing experimental studies and numerical modeling of the sorption of hydrophobic contaminants by aquifer materials. The work focuses on the evaluation of predictive modeling methods for simulating sorption processes in groundwater systems. Equilibrium behavior and rates of approach to equilibrium were investigated for two hydrophobic solutes and three aquifer materials utilizing different reactor configurations. This paper discusses investigations conducted in completely mixed batch reactors. These investigations illustrate that sorption equilibria are nonlinear for the systems studied and that sorption rates involve an initial rapid step followed by a slower continuing uptake that can persist for several days. Alternative models for description of these equilibria and rate conditions are presented and compared. The second paper evaluates the use of sorption model coefficients determined from batch–reactor systems to model column–reactor systems.

Key words—sorption/desorption, groundwater modeling, pollutant transport, partitioning, aquifer materials, soils

NOMENCLATURE

$\bar{a}$ = variable grouping for analytical equilibrium/first-order solution [equation (12)]

$\bar{b}$ = variable grouping for analytical equilibrium/first-order solution [equation (13)]

b = Langmuir isotherm sorption-energy constant $(L^3 M^{-1})$

$\bar{c}$ = variable grouping for analytical equilibrium/first-order solution [equation (14)]

C = solution-phase solute concentration (ML^{-3})

C_e = equilibrium solution-phase solute concentration (ML^{-3})

C_0 = initial solution-phase solute concentration (ML^{-3})

C_s = fluid-phase equilibrium-isotherm solute concentration corresponding to the solid-phase concentration at the particle boundary (ML^{-3})

$\bar{d}$ = variable grouping for analytical second-order solution [equation (19)]

D_s = intraparticle surface-diffusion coefficient for dual-resistance model $(L^2 T^{-1})$

$\bar{e}$ = variable grouping for analytical second-order solution [equation (20)]

$\bar{f}$ = variable grouping for analytical second-order solution [equation (21)]

i = Langmuir isotherm data-point qualifier

k_f = film mass-transfer coefficient for the dual-resistance model (LT^{-1})

k_s = second-order Langmuir model rate constant $(L^3 M^{-1} T^{-1})$

K_F = Freundlich isotherm sorption-capacity constant $[(L^3 M^{-1})^n]$

$K_{F,f}$ = Freundlich isotherm sorption-capacity constant for the rapid rate component of the equilibrium/first-order rate model $[(L^3 M^{-1})^{n_f}]$

$K_{F,s}$ = Freundlich isotherm sorption-capacity constant for the slow rate component of the equilibrium/first-order rate model $[(L^3 M^{-1})^{n_s}]$

K_{ow} = octanol:water partition coefficient

K_P = linear isotherm partition coefficient $(L^3 M^{-1})$

$K_{P,f}$ = linear isotherm partition coefficient for the rapid-rate component of the equilibrium/first-order rate model $(L^3 M^{-1})$

$K_{P,s}$ = linear isotherm partition coefficient for the slow-rate component of the equilibrium/first-order rate model $(L^3 M^{-1})$

m = number of Langmuir isotherm data points

M = mass of solid phase in batch reactor (M)

n = Freundlich isotherm sorption-energy constant

n_f = Freundlich isotherm sorption-energy constant for the rapid rate component of the equilibrium/first-order rate model

n_s = Freundlich isotherm sorption-energy constant for the slow rate component of the equilibrium/first-order rate model

q = volume-averaged solid-phase solute mass normalized by the solid-phase mass (MM^{-1})

q_e = equilibrium volume-averaged solid-phase solute mass normalized by the solid-phase mass (MM^{-1})

q_f = volume-averaged solid-phase mass normalized by the solid-phase mass for the rapid sorption-rate component of the equilibrium/first-order model (MM^{-1})

q_r = solid-phase solute mass normalized by the solid-phase mass as a function of radial position (MM^{-1})

q_s = volume-averaged solid-phase mass normalized by the solid-phase mass for the slow sorption-rate component of the equilibrium/first-order model (MM^{-1})

Q^0 = Langmuir isotherm sorption-capacity constant (MM^{-1})

r = radial distance variable for dual-resistance model (L)

R = solid-phase particle radius (L)
t = time (T)
V = volume of solution in batch reactor (L^3)
α = equilibrium/first-order model rate constant (T^{-1})
ϵ = residual square error for Langmuir isotherm
ρ = solid particle density (ML^{-3})

INTRODUCTION

The transport and ultimate disposition of hydrophobic organic pollutants in groundwater systems can be affected importantly by sorption/desorption or partitioning reactions between aqueous (groundwater) and solid (aquifer material) phases. The modeling of such systems for assessment of risk or for evaluation of decontamination alternatives must include quantification of these sorption/desorption processes. There are two aspects of sorption/desorption (herein referred to simply as "sorption") reactions that must be quantified and modeled in this context; first, the form or character of the equilibrium distribution between the aqueous and solid phases toward which a particular solute of concern in the system is thermodynamically driven and, second, the rate at which this distribution is approached. This paper examines the nature of equilibrium distributions obtained for a matrix of two compounds, lindane and nitrobenzene, and three aquifer materials. Rates of approach to these distributions are characterized and several models evaluated for description and simulation of the rate data.

BACKGROUND

A variety of physical and chemical factors operative in environmental systems influences the extent to which forces underlying sorption phenomena in those systems are affected. Thorough attention to all of these factors is beyond the scope and intent of this discussion; detailed reviews are readily available in the literature (Bailey and White, 1970; Pierce et al., 1971; Hamaker and Thompson, 1972; Weber, 1972; Browman and Chesters, 1975; Morrill et al., 1982; Voice and Weber, 1983). In the specific context of hydrophobic pollutant sorption by natural soils and sediments, recent work (Karickhoff et al., 1979; Kenaga and Goring, 1980; Roberts et al., 1982; Voice, 1982) suggests that for many systems reasonable estimates of assumed linear equilibrium sorption behavior may be made from discrete measurements of the constitutive properties of the solute and the solid in question—specifically, the octanol:water partition coefficient (K_{ow}) of the former and the organic-carbon content of the latter.

Several investigators (O'Connor and Connolly, 1980; Voice, 1982; Weber et al., 1983) have noted that hydrophobic systems do not generally partition in a linear fashion over large ranges of equilibrium concentration, and that at low solids concentration the actual partition coefficient may be a function of the solids:solvent ratio. Second, nonlinear sorption behavior and desorption hysteresis have been reported for a large number of solid/contaminant systems (Bailey and White, 1970; Hamaker and Thompson, 1972; Van Genuchten et al., 1974; Davidson et al., 1980; Miller, 1984). Such behavior significantly affects solute profiles in groundwater, even if assumptions regarding local equilibrium are reasonable. The literature also substantiates that rates of sorption may be important for many organic–solute solid systems (Kay and Elrick, 1967; Leenheer and Ahlrichs, 1971; Boucher and Lee, 1972; Karickhoff, 1980, 1984; Hutzler et al., 1984; Miller, 1984; Miller and Weber, 1984b, 1986).

MATERIALS

The aquifer materials used for this investigation included three relatively uniform sands of glacially deposited origin. The most important characteristic of these aquifer materials—for the solutes studied—was the total organic-carbon content, which ranged from 0.12 to 1.14% (as determined by the ampule persulfate oxidation technique, Oceanography International Corporation). Miller and Weber (1986) give a detailed description of the physical and chemical characteristics of these materials.

Lindane (γ-1,2,3,4,5,6-hexachlorocyclohexane) and nitrobenzene were selected as solutes representative of moderately to slightly hydrophobic contaminants. Lindane is a slightly polar, chlorinated insecticide with low volatility and solubility, and moderate hydrophobicity—a log K_{ow} of 3.72 (Hansch and Leo, 1979). Nitrobenzene is a substituted benzene compound used in the production of dyes, solvents, and a variety of other products. Nitrobenzene is more soluble and volatile than lindane and partitions less extensively to organic phases—a log K_{ow} of 1.89 (Hansch and Leo, 1979). Additional properties of these compounds are summarized elsewhere (Miller and Weber, 1986).

EXPERIMENTAL METHODS

Measurement of lindane and nitrobenzene was performed by electron capture gas chromatography employing a Hewlett Packard 5880A gas chromatograph, a 6-ft long 2-mm dia stainless-steel column packed with 3% OV-1 on 80/100 Gas Chrom Q^0, and an argon (95%)–methane (5%) carrier gas. Analyses were performed at column temperatures of 190°C for lindane and 130°C for nitrobenzene. The above conditions yielded original solution-phase detection limits of about 1 μg l^{-1} for lindane and 10 μg l^{-1} for nitrobenzene—exact limits being a function of solvent extraction ratio.

The laboratory investigations were conducted in completely mixed batch reactors (CMBRs). CMBR isotherm experiments employing individual reactors for each data point (bottle-point technique) were performed by placing a known and equal amount of solid in each of 20–40 borosilicate centrifuge bottles, adding constant volumes of solution of known concentration of solute to each, and tumbling all bottles long enough to ensure that sorption equilibrium was attained (approx. 200 h). The reactors and their contents were centrifuged at the end of an equilibration period to separate solid and aqueous phases, solution phase concentrations were measured, and solid-phase concentrations were calculated by difference. Overall recoveries, determined by extracting the solute mass from the solid phase with hexane and adding to the solute mass in solution, were typically greater than 95%.

CMBR bottle-point rate investigations were performed by preparing a number of identical 50-ml glass bottle reactors, each containing an equal volume and concen-

tration of solute solution and identical amounts of solid. Reactors were tumbled to maintain completely mixed conditions. Replicate reactors and a solution blank were removed from the tumbler at times ranging from 1 to 196 h. The reactors and their contents were then centrifuged and solution phase concentrations measured—giving serial rate data for sorption as a function of time.

Additional sorption rate experiments were carried out in a 3-l. stirred CMBR comprised of a glass beaker fitted with a plexiglass top and 1.27-cm dia glass baffles. Agitation was accomplished using a 1/4-h.p., rheostat-controlled motor driving a glass stirring rod fitted with a Teflon® paddle. Experiments were conducted at a stirring speed of 1000 rpm to maintain well-mixed conditions. In these experiments, the solute solution to be studied was first equilibrated with the reactor, after which a predetermined quantity of aquifer material was added and samples of solution withdrawn at predetermined intervals for analysis. Initial sampling of the reactor was done at frequent intervals (several min), and then continued at increasingly longer intervals for total experimental times of 5–10 d. Separation of solids from sample solutions was accomplished by filtration through a 0.1-μm pore-size glass filter. All solute solutions were buffered to a pH of 8 with a boric acid–sodium borate hydrate–acid conjugate-base solution having a 0.01 N calcium (chloride or sulfate) background to maintain a constant calcium level in the solid phase.

SORPTION EQUILIBRIA

Three common sorption equilibrium isotherm models were evaluated for description of experimental data, specifically:
the linear model,

$$q_e = K_P C_e \tag{1}$$

the Freundlich model,

$$q_e = K_F C_e^n \tag{2}$$

and the Langmuir model,

$$q_e = \frac{Q^0 b C_e}{1 + b C_e}. \tag{3}$$

The terms C_e and q_e in each of these models represent the solution-phase and solid-phase concentrations of solute, respectively. K_P, K_F and Q^0 are sorption-capacity coefficients and n and b are characteristic coefficients relating to sorption energy or intensity. The properties of these isotherm models and their respective thermodynamic bases have been summarized by Voice and Weber (1983).

Parameter estimates were derived in each case by solving for the isotherm model parameter(s) that minimized the variance between experimental and model concentration values. For the Freundlich model the minimization was performed on the logarithmically-linearized form. For the Langmuir model a nonlinear method was developed by defining the objective function as the minimization of

$$\epsilon(Q^0, b) = \sum_{i=1}^{m} \left(\frac{Q^0 b C_{e,i}}{1 + b C_{e,i}} - q_{e,i} \right)^2. \tag{4}$$

The partial derivatives of the residual equation with respect to the model coefficients Q^0 and b must

be zero for the optimum solution. These partial derivatives are

$$\frac{\partial \epsilon}{\partial b} = \sum_{i=1}^{m} 2 \left(\frac{Q^0 C_{e,i}(1 + b C_{e,i}) - Q^0 b C_{e,i}^2}{(1 + b C_{e,i})^2} \right) \times \left(\frac{Q^0 b C_{e,i}}{1 + b C_{e,i}} - q_{e,i} \right) = 0 \tag{5}$$

$$\frac{\partial \epsilon}{\partial Q^0} = \sum_{i=1}^{m} 2 \left(\frac{b C_{e,i}}{1 + b C_{e,i}} \right) \left(\frac{Q^0 b C_{e,i}}{1 + b C_{e,i}} - q_{e,i} \right) = 0 \tag{6}$$

Simultaneous solution of equations (5) and (6) yields the best estimate of the parameters for the Langmuir isotherm model. Alternatively, a single parameter search can be performed on one coefficient and the remaining coefficient calculated for the given value of the searched parameter. This technique was used to evaluate the Langmuir sorption isotherm coefficients by searching for a range of b and calculating Q^0 for each search iteration using a simplified version of equation (6)

$$Q^0 = \frac{\sum_{i=1}^{m} (q_{e,i} b C_{e,i})/(1 + b C_{e,i})}{\sum_{i=1}^{m} (b C_{e,i})^2/(1 + b C_{e,i})^2}. \tag{7}$$

SORPTION RATES

A series of bottle-point CMBR rate studies was performed initially to elucidate the time-dependent nature of sorption processes in the systems under investigation. These studies indicated that the sorption process exhibited a phased or bifurcated behavior, proceeding at a rapid initial rate that was followed by a slower sustained rate, which required as long as several days to approach equilibrium.

Primary objectives for the investigation were to mathematically model the sorption process and to evaluate the system dependence of model parameters. Based on the observed nonlinear behavior of sorption equilibria and bifurcated rate characteristics, three models were postulated for evaluation and comparison: (1) an equilibrium/first-order rate model incorporating a Freundlich isotherm relationship; (2) a second-order Langmuir rate and equilibrium model; and (3) a dual-resistance diffusion model with equilibrium conditions characterized by the Freundlich equation.

The equilibrium/first-order model

Several investigators have approximated rates of sorption of organic contaminants on natural solid phases with simple first-order rate models (Lapidus and Amundson, 1952; Lindstrom et al., 1970; Oddson et al., 1970; Van Genuchten et al., 1974; Selim et al., 1977; Bencala et al., 1983). In attempts to improve on this approach, a modified equilibrium/first-order model has been suggested and investigated in different forms to accommodate the two-step behavior commonly observed (Selim et al., 1976;
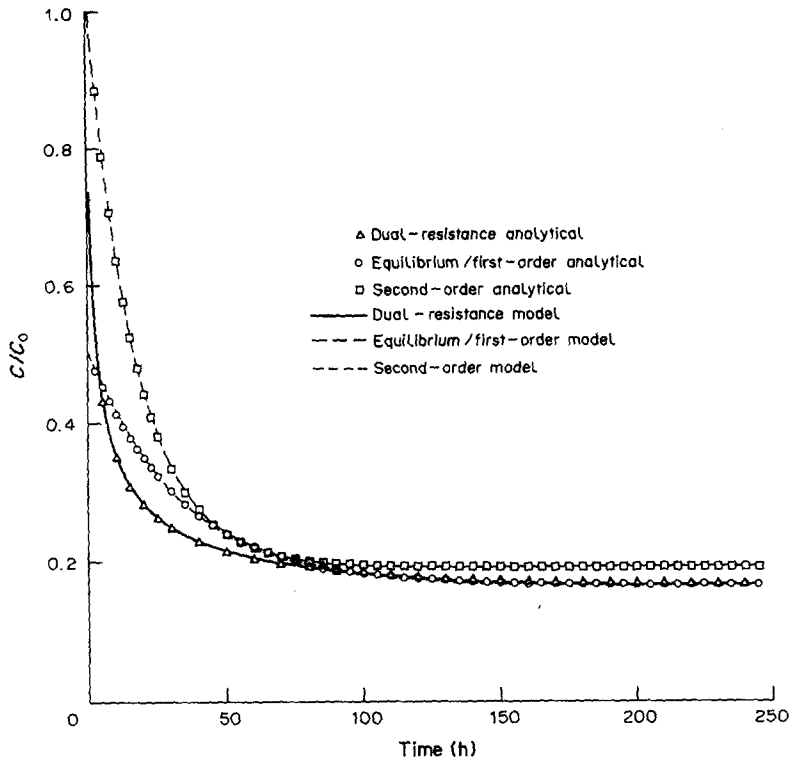
Fig. 1. Comparison of analytical and numerical solutions for CMBR rate models.

Cameron and Klute, 1977; Karickhoff, 1980; Miller, 1984). The model describes sorption in terms of two components, one of which achieves essentially instantaneous equilibrium while the other proceeds at a first-order rate. The general differential form of the model is

$$\frac{dq}{dt} = \frac{dq_f}{dt} + \frac{dq_s}{dt} \qquad (8)$$

where q_f is the solid-phase volume-averaged solute concentration associated with that component of sorption that attains equilibrium rapidly, and q_s is the solid-phase volume-averaged solute concentration associated with the slower rate component. The most simple form of the model is obtained when both components of sorption can be described by linear isotherms (Cameron and Klute, 1977). Miller (1984) derived an analytical soluton to this model for a CMBR system, which may be summarized as

$$q = \bar{b} + \bar{c} \exp(-\alpha \bar{a} t) \qquad (9)$$

$$\frac{dq}{dt} = \frac{-V}{M} \frac{dC}{dt} \qquad (10)$$

$$K_P = K_{P,f} + K_{P,s} \qquad (11)$$

$$\bar{a} = \frac{1 + MK_P/V}{1 + MK_{P,f}/V} \qquad (12)$$

$$\bar{b} = \frac{VC_0(1 + K_{P,f}/K_{P,s})}{M\{1 + (V/MK_{P,s}) + (K_{P,f}/K_{P,s})\}} \qquad (13)$$

$$\bar{c} = \frac{C_0 V}{M} \left(1 - \frac{V}{MK_{P,f} + V}\right) - \bar{b} \qquad (14)$$

where V is the volume of solution in the CMBR, M is the mass of the solid, and $K_{P,f}$ and $K_{P,s}$ are linear partition coefficients for the rapid (assumed instantaneous) and slower rate components of sorption.

When the equilibria associated with the rapid and rate-controlled components of sorption are nonlinear, as for the systems described here, equation (8) may be written in terms of the Freundlich isotherm to give

$$\frac{dq}{dt} = n_f K_{F,f} C^{n_f - 1} \frac{dC}{dt} + \alpha(K_{F,s} C^{n_s} - q_s) \qquad (15)$$

where $K_{F,f}$ and n_f are the isotherm parameters corresponding to the rapidly attained equilibrium component of sorption and $K_{F,s}$ and n_s are the parameters for the slower rate sorption component.

Equations (9)–(14) were used to validate a specific case of a finite-difference model solution to the more general form of the equilibrium/first-order rate model given by equation (15) for a CMBR. Figure 1 illustrates good agreement between the analytical and the numerical solutions for the model validation parameters detailed in Table 1.

The second-order model

The second-order Langmuir rate model describes sorption and desorption respectively as second-order and first-order processes. The model is written in

general differential form as

$$\frac{dq}{dt} = k_s \left[C(Q^0 - q) - \frac{q}{b} \right] \qquad (16)$$

where k_s is a second-order rate constant. The model has received only minor attention for characterization of sorption data in natural–solid systems (Lindstrom et al., 1970; Griffin and Jurinak, 1973; Miller, 1984) but has been treated extensively in other sorption applications (Keinath and Weber, 1968; Weber, 1972; Weber and Crittenden, 1975). At large values of time (i.e. at equilibrium) the derivative dq/dt, approaches zero and equation (16) reduces to the Langmuir isotherm model [equation (3)].

Equation (16) may be written in terms of one dependent variable for the case where only sorption and desorption are occurring; i.e. when no other solute reaction mechanisms are operative

$$\frac{dq}{dt} = k_s \left[\frac{M}{V} q^2 - \left(\frac{MQ^0}{V} + C_0 + \frac{1}{b} \right) q + Q^0 C_0 \right] \qquad (17)$$

Equation (17) may be integrated to yield an analytical solution

$$q = \frac{1}{d} \left(\frac{-\bar{f}}{\tanh[(\bar{f}k_s t/2) + \tanh^{-1}(-\bar{f}/\bar{e})]} - \bar{e} \right) \qquad (18)$$

where

$$\bar{d} = \frac{2M}{V} \qquad (19)$$

$$\bar{e} = \frac{-MQ^0}{V} - C_0 - \frac{1}{b} \qquad (20)$$

$$\bar{f} = (\bar{e}^2 - 2\bar{d}Q^0 C_0)^{1/2} \qquad (21)$$

Equation (17) was used as the basis for a Crank–Nicolson finite-difference solution for the Langmuir second-order sorption rate model for a CMBR system. Figure 1 illustrates good agreement between the analytical and the numerical solutions for the model validation parameters detailed in Table 1.

The dual-resistance diffusion model

The dual-resistance diffusion model describes sorption as a process of coupled mass transfer through a boundary film external to the solid particle followed by diffusion within a representative portion of the particle itself. Diffusion formulations have been used to describe transport in fractured rock systems (Neretnieks, 1980; Rasmuson and Neretnieks, 1981), in solid particle clusters (Hutzler et al., 1984, 1986; Crittenden et al., 1986) and in groundwater systems for nonlinear and hysteretic sorption equilibria (Miller, 1984; Miller and Weber, 1984a,b, 1986).

For spherical solid particles the intraparticle–diffusion process can be described by the relationship

$$\frac{\partial q_r}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q_r}{\partial r} \right) \qquad (22)$$

where q_r is the solid-phase concentration of solute as a function of the radial dimension, r and D_s is the intraparticle surface-diffusion coefficient. The volume-averaged solid-phase concentration of solute, q, is given by

$$q = \frac{3}{R^3} \int_0^R q_r r^2 \, dr \qquad (23)$$

where R is the solid particle radius.

The solid-phase equation is coupled to the fluid phase by assuming that solute mass transfer across the phase boundary is controlled by a flux through a "film" at the solid-phase boundary

$$\left. \frac{\partial q_r}{\partial r} \right|_{r=R} = \frac{k_f}{\rho D_s} (C - C_s) \qquad (24)$$

C_s is the solution-phase equivalent to the solid-phase concentration at the exterior of a solid particle of radius R; ρ is the solid-particle density; and k_f is the boundary-layer film mass-transfer coefficient. The concentration C_s is related to q_r by the Freundlich equation

$$C_s = \left(\frac{q_r}{K_F} \right)^{1/n} \quad \text{at } r = R \qquad (25)$$

The analytical solution for the linear-isotherm, intraparticle-diffusion case given by Crank (1975)

Table 1. Summary of model validation parameters

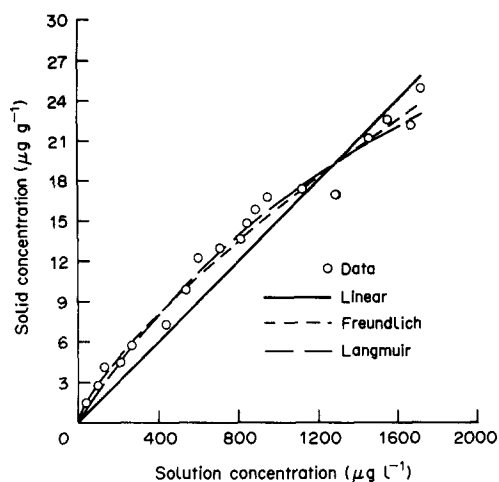| Variable	Value			Dimensions
	Equilibrium/ first-order	Second-order	Dual-resistance	
C_0	1.00	1.00	1.00	ML^{-3}
K_P	10.00		10.00	L^3M^{-1}
$K_{P,f}$	2.00			L^3M^{-1}
$K_{P,s}$	8.00			L^3M^{-1}
M	1.00	1.00	1.00	M
V	2.00	2.00	2.00	L^3
α	0.01			T^{-1}
b		1.00		L^3M^{-1}
k_s		0.01		$L^3M^{-1}T^{-1}$
Q^0		10.00		MM^{-1}
D_s			0.10	L^2T^{-1}
k_f			∞	LT^{-1}
R			10.00	L

Fig. 2. Isotherm model comparison for sorption of lindane on Ann Arbor aquifer material.

was used to validate a Crank–Nicolson finite-difference solution model employed for the more general problem involving nonlinear equilibrium and film mass-transfer resistance. Figure 1 illustrates good agreement between the analytical and the numerical solutions for the model validation parameters detailed in Table 1.

RESULTS

Typical results of sorption-isotherm parameter determinations and model fits for lindane and the Ann Arbor aquifer material are shown in Fig. 2. This figure illustrates the nonlinear nature of the equilibrium and the better fit afforded by the Freundlich and Langmuir models. Table 2 summarizes the best-fit model parameters for each of the four solid-solute combinations.

The stirred CMBR experimental apparatus was used to obtain rate data for sorption of lindane on all three aquifer materials. The method allows for fre-

quent sampling from a single system, thus providing a valuable data set for comparison of rate models. Data from these studies were used to evaluate the performance of each of the three models described above.

The fluid-phase sorption equilibrium levels observed in stirred CMBR systems were lower than those obtained in the bottle-point CMBR isotherm studies for comparable solids ratios and initial solute solution-phase concentrations. This may be attributable to particle or aggregate breakup due to the more vigorous agitation. It was necessary to adjust the sorption equilibrium capacity parameters K_F and Q^0 to reflect the observed conditions while holding the intensity parameters (n and b) equal to those measured in the bottle-point isotherms.

The instantaneous component of sorption for the equilibrium/first-order model was calculated in each case from the observed response for times < 10 min. For the dual-resistance mass-transfer model it was found that film resistance was small for the vigorous conditions of agitation in the stirred CMBRs and the model was treated as insensitive to this parameter.

Each model therefore required calibration for only one parameter, all other variables being either calculated or independently measured. The remaining fit parameters were α, k_s and D_s—the rate parameters of the equilibrium/first-order, second-order, and dual-resistance models. These parameters were fit with an objective function defined to minimize the variance between measured and observed fluid-phase concentrations.

The results of the fitting procedures are summarized in Table 3. Figure 3 illustrates typical model fits to experimental data for the Ann Arbor aquifer materials and lindane. This figure and the errors tabulated in Table 3 show that the equilibrium/first-order model and the dual-resistance model provided good fits of the observed data, while the second-order model was a poor predictor of observed trends.

Table 2. Sorption isotherm constants

Aquifer material	Solute	Linear		Freundlich			Langmuir		
		K_P $(cm^3 g^{-1})$	Variance	K_F $(cm^3 g^{-1})^n$	n	Variance	Q^0 $(g\,g^{-1})$	b $(cm^3 g^{-1})$	Variance
Ann Arbor	Lindane	15.0	3.7×10^{-12}	0.46	0.74	1.1×10^{-12}	5.3×10^{-5}	4.4×10^5	1.2×10^{-12}
Ann Arbor	Nitrobenzene	6.7	8.4×10^{-12}	0.22	0.73	2.6×10^{-12}	4.4×10^{-5}	2.9×10^5	1.4×10^{-12}
Delta	Lindane	1.7	1.2×10^{-13}	0.94	0.95	1.1×10^{-13}	1.0×10^{-5}	2.5×10^5	6.9×10^{-14}
Michaywe	Lindane	3.4	2.0×10^{-14}	0.48	0.86	1.7×10^{-14}	3.9×10^{-5}	9.7×10^4	1.3×10^{-14}

Table 3. Stirred CMBR rate-model parameter summary for lindane

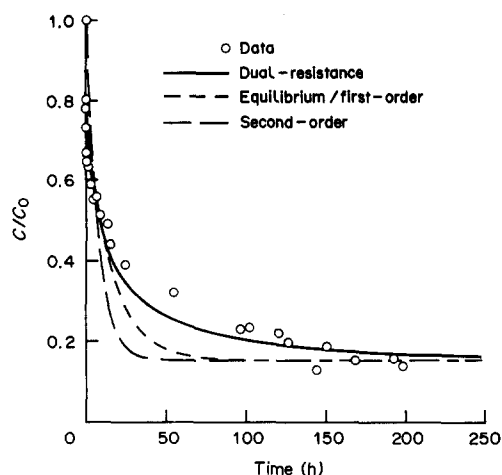| Aquifer material	Equilibrium/first-order		Second-order		Dual-resistance	
	α (h^{-1})	Variance	k_s $(cm^3 g^{-1} h^{-1})$	Variance	D_s $(cm^2 h^{-1})$	Variance
Ann Arbor	1.8×10^{-2}	8.3×10^{-3}	8.8×10^3	2.4×10^{-2}	8.2×10^{-8}	4.8×10^{-3}
Delta	4.4×10^{-2}	1.9×10^{-3}	3.3×10^5	1.4×10^{-2}	1.9×10^{-6}	6.6×10^{-3}
Michaywe	1.9×10^{-2}	2.5×10^{-3}	2.4×10^3	1.1×10^{-2}	3.2×10^{-7}	1.5×10^{-3}

Fig. 3. Experimental data and model fits for rate of lindane sorption on Ann Arbor aquifer material in a stirred CMBR.

The stirred CMBR reactor was deemed not suitable for rate studies with nitrobenzene because of potential volatilization losses. The bottle-point rate data for this solute were therefore used for model parameter estimation. To provide a basis for comparison of model parameter estimates from the bottle-point and stirred CMBRs the bottle-point data for lindane were also used to estimate rate parameters. Estimated parameter values and associated errors for the bottle-point studies are summarized in Table 4. Resulting model traces for the Ann Arbor aquifer material and nitrobenzene solute are depicted
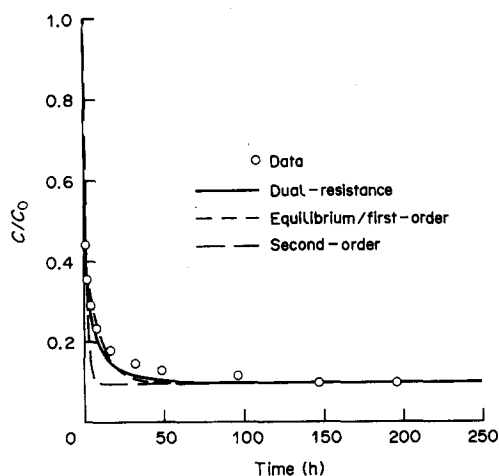

Fig. 4. Experimental data and model fits for rate of nitrobenzene sorption on Ann Arbor aquifer material in a bottle-point CMBR.

graphically in Fig. 4. The results of the bottle-point CMBR model analyses are generally consistent with those for the stirred reactor. In both cases the equilibrium/first-order model and dual-resistance diffusion model provide better characterization of the observed sorption rate patterns than does the second-order model. Further, there is agreement (usually within a factor of 3–4) between the rate parameters determined for lindane from the bottle-point and stirred-reactor rate data for the equilibrium/first-order, and dual-resistance rate models.

CONCLUSIONS

The sorption of two hydrophobic compounds, lindane and nitrobenzene, on three aquifer materials in CMBR systems was found to exhibit nonlinear equilibrium behavior that can be characterized reasonably well by either the Freundlich or Langmuir isotherm model.

Rates of sorption were observed to be initially rapid, but quickly declined to a lower sustained level resulting in a gradual approach to equilibrium conditions. Several days were required to obtain equilibrium in the systems studied.

Three models were investigated with respect to their suitability for describing the observed rate phenomena. A two-step equilibrium/first-order rate model and a dual-resistance mass-transfer model each provided good characterization of the experimental data. A second-order model was found to be less suitable for simulation of the observed rate patterns.

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Table 4. Bottle-point CMBR rate-model parameter summary

Aquifer material	Solute	Equilibrium/first-order		Second-order		Dual-resistance	
		α (h^{-1})	Variance	k_s (cm^3 g^{-1} h^{-1})	Variance	D_s (cm^2 h^{-1})	Variance
Ann Arbor	Lindane	1.5×10^{-2}	3.6×10^{-3}	1.9×10^4	7.3×10^{-3}	1.7×10^{-7}	9.8×10^{-3}
Ann Arbor	Nitrobenzene	3.3×10^{-2}	6.0×10^{-3}	1.9×10^4	5.9×10^{-3}	3.4×10^{-7}	4.4×10^{-3}
Delta	Lindane	1.3×10^{-2}	3.5×10^{-4}	1.1×10^5	7.2×10^{-3}	1.6×10^{-6}	4.7×10^{-3}
Michaywe	Lindane	1.6×10^{-2}	1.4×10^{-3}	1.5×10^4	1.2×10^{-2}	1.8×10^{-6}	5.3×10^{-3}

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