Single-Pellet Technique for Irreversible and Reversible Adsorption in Soil

Timur Doğu
Dept. of Chemical Engineering, Middle East Technical University, 06531, Ankara, Turkey

Canan Cabbar and Gülşen Doğu
Dept. of Chemical Engineering, Gazi University, Ankara, Turkey

The dynamic version of the Wicke-Kallenbach diffusion cell has been used extensively for the evaluation of effective diffusion coefficients (Suzuki and Smith, 1972; Doğu and Smith, 1975; Furusawa et al., 1976; Moffatt, 1978; Baiker et al., 1982; Wang and Smith, 1983; Doğu et al., 1987). The single-pellet moment technique has also been used for the measurement of adsorption rate and equilibrium constants (Doğu and Smith, 1976; Doğu and Ercan, 1983), as well as reaction rate parameters (Doğu, 1984; Doğu et al., 1986). Recently, the technique has been modified for the measurement of thermal conductivity of a porous solid (Doğu et al., 1989a, 1991) and permeability (Doğu et al., 1989b; Lu et al., 1992). Boundary conditions used in the single-pellet moment theory were discussed by Burghardt and Smith (1979) and more recently by Lu et al. (1992). In the analysis of Lu et al., the validity region of the simplified boundary conditions used in most of the published literature of the single-pellet technique was quantified. In Lu's work, diffusion and convection were considered in a single-pellet system for a nonadsorbable tracer. In the present work, the single-pellet moment technique was modified further for the simultaneous evaluation of irreversible adsorption rate constant, adsorption equilibrium constant, and effective diffusivity of an adsorbable tracer.

Irreversible adsorption of some volatile organic compounds on porous solids is frequently encountered in soil as well as in gas purification and some catalytic processes. The contamination of the soil subsurface by volatile organic compounds has become an active area of environmental research (Smith, 1985; Steinberg et al., 1987; Calabrese and Kostechi, 1988). Benzene is one of the pollutants which is frequently found in the subsoil (Marrin and Kerfoot, 1988). Although transport and sorption studies for soil contaminants have recently increased, much remains to be done to achieve satisfactory understanding of soil pollution. In this work, sorption of benzene on soil was investigated using the single-pellet moment technique, and it was shown that irreversible and reversible adsorption parameters can be determined simultaneously from the same set of experimental moment values.

Method and Theory

In the single-pellet moment technique, carrier gas streams pass over both end faces of the porous pellet (Figure 1). A pulse, containing the diffusing or adsorbing component, is introduced into the stream flowing over one end face of the cylindrical pellet, and the response peak is measured with a detector placed in the stream leaving the other end face. Details of the cell and the method were given elsewhere (Doğu and Smith, 1975, 1976). In this work, the method was modified

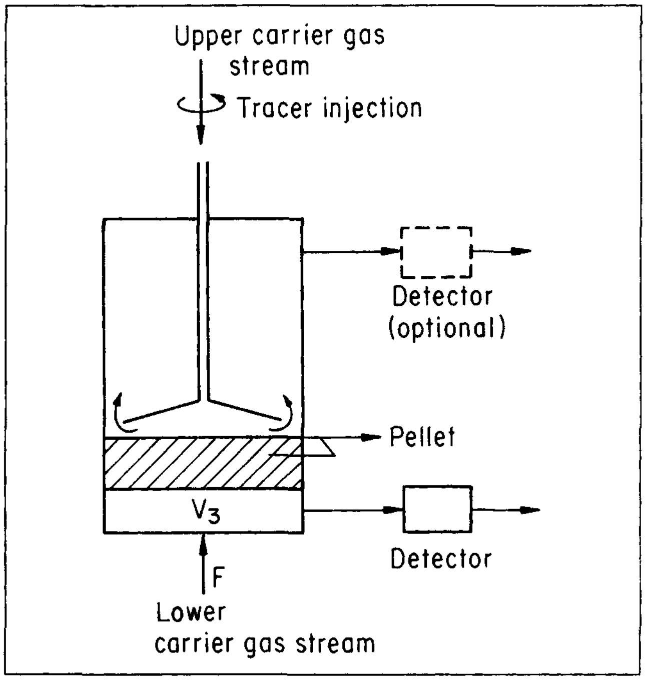

Figure 1. Single-pellet reactor.

Correspondence concerning this work should be addressed to T. Doğu.

Table 1. Irreversibility of Benzene Adsorption on Soil in the Single-Pellet Cell at Different Temperatures

Temp., °C	35	50	70	90
Irreversibly adsorbed fraction of benzene tracer	0.43	0.36	0.18	0.03

and used for the measurement of sorption characteristics and effective diffusivity of benzene in soil.

To test the reversibility of benzene adsorption on the soil sample used, a set of initial experiments were carried out by placing detectors to the streams leaving both end faces of the pellet. A material balance around the diffusion cell showed that a considerable amount of benzene tracer was irreversibly adsorbed, especially at temperatures lower than 90°C. In these experiments, amount of input tracer was measured by conducting pulse-response experiments in a system where the upper face of the pellet was covered with an impermeable teflon plate and by detecting the response peak in the stream leaving the upper chamber of the cell.

Fraction of benzene tracer which is irreversibly adsorbed on soil is a function of temperature. Results of initial reversibility experiments conducted with a single-pellet cell are summarized in Table 1.

In addition to irreversible adsorption of benzene on the soil pellet, first-moment results indicated a strong reversible adsorption, as will be discussed later. Considering these results, it was concluded that both an irreversible adsorption rate term and an equilibrium adsorption term should be included in the differential mass balance for the transport of the diffusing component (benzene) within the pellet:

$$\epsilon_p \frac{\partial C_B}{\partial t} = D_e \frac{\partial^2 C_B}{\partial x^2} - \rho_p N_B \tag{1}$$

where

$$N_B = \frac{\partial n_B}{\partial t} = k_i C_B + K_B \frac{\partial C_B}{\partial t} \tag{2}$$

Here, k_i is the irreversible sorption rate constant and K_B is the equilibrium constant for reversible adsorption. The initial and boundary conditions for the system are:

$$t=0; \quad C_B=0 \quad 0<x<L \tag{3}$$

$$x=0; \quad C_B=M\delta(t) \tag{4}$$

$$x=L; \quad -AD_e\left(\frac{\partial C_B}{\partial x}\right)_L = V_3\left(\frac{\partial C_B}{\partial t}\right)_L + F(C_B)_L \tag{5}$$

where V_3 and F are the volume of the lower chamber and the flow rate through it, respectively. As discussed previously (Doğu and Smith, 1976; Burghardt and Smith, 1979), by proper design of the apparatus (keeping V_3 very small) and using sufficiently high flow rates of the carrier gas streams, complete mixing can be achieved in the lower chamber, the accumulation term in Eq. 5 can be neglected and mass-transfer resistance between pellet face and gas can be eliminated.

The moments of the response peak at $x=L$ were obtained from $C_B(L, s)$ using the following relation:

$$m_n = (-1)^n \lim_{s=0} \frac{d^n(\bar{C}_B)_{z=L}}{ds^n} \tag{6}$$

where

$$m_n = \int_0^\infty C(L, t)t^n dt. \tag{7}$$

For this system, the zeroth and first absolute moment expressions were derived.

$$m_o = \frac{M\left(\frac{A}{L}D_e\right)\alpha}{\left(\frac{A}{L}D_e\right)\alpha\cosh\alpha + F\sinh\alpha} \tag{8}$$

$$\mu_1 = \frac{m_1}{m_o} = \frac{L^2(\epsilon_p+\rho_p K_B)}{2D_e\alpha^2}\left[\frac{\left(\frac{A}{L}D_e\alpha^2 - F\right)\sinh\alpha + F\alpha\cosh\alpha}{\frac{A}{L}D_e\alpha\cosh\alpha + F\sinh\alpha}\right] \tag{9}$$

The dimensionless group α which appear in the moment expressions is similar to Thiele modulus:

$$\alpha = L\left(\frac{\rho_p k_i}{D_e}\right)^{1/2} \tag{10}$$

By rearranging Eq. 8, the following linear relation was obtained between M/m_o and F:

$$\frac{M}{m_o} = \cosh\alpha + \left(\frac{\sinh\alpha}{\frac{A}{L}D_e\alpha}\right)F \tag{11}$$

The slope and intercept of this linear relation contain the two unknown parameters D_e and α. On the other hand, the first absolute moment expression contains the adsorption equilibrium constant $\rho_p K_B$ in addition to D_e and α. In principle, α and D_e can be evaluated from the zeroth-moment data and $\rho_p K_B$ from the first-moment data.

Characterization of irreversible and reversible adsorption by the moment technique was considered first by Galan et al. (1975). In Galan's work, moment expressions were derived for a packed-bed system, in which all the parameters, such as irreversible rate constant, adsorption equilibrium constant, effective diffusivity in the pores, axial dispersion coefficient in the column, and external film mass-transfer coefficient, appear in the first-moment expression. Difficulty of obtaining irreversible adsorption rate constant from this moment expression was mentioned by Galan (1975). In a packed-bed system, simultaneous evaluation of all these five parameters from a single-moment expression is very difficult. The major advantage of the single-pellet technique is the elimination of axial dispersion and film mass-transfer effects. Consequently, intraparticle rate and equilibrium parameters can, in principle, be studied more effectively. In fact, in this work irreversible adsorption rate and reversible adsorption equilibrium constants were evaluated from two equations (Eqs. 9 and 11) very easily and accurately.

For low values of F, mass-transfer resistance between the lower face of the pellet and the lower carrier gas stream might become significant. To eliminate this, all the experiments were conducted at sufficiently high flow rates. As a result, precise evaluation of the intercept from the experimental data becomes difficult. Considering this and failure of the derived moment expressions at low flow rates, we used only the slope of M/m_o vs. F curve in the analysis. Since the slope of Eq. 11 contains both α and D_e, effective diffusivity was determined from another set of experiments conducted with an inert tracer.

Before conducting experiments with benzene tracer, pulse response experiments were carried out using helium tracer and effective diffusivity of helium was determined from the first-moment data. In this analysis, the moment expression derived by Doğu and Smith (1975) was used:

$$\mu_1 = \frac{L^2\epsilon}{6D_e}\left(\frac{3\frac{A}{L}D_e+F}{\frac{A}{L}D_e+F}\right) \tag{12}$$

Then, tortuosity factor based on macroporosity of the pellet was evaluated using the following relation:

$$D_e = \left(\frac{1}{\frac{1}{D_{AB}}+\frac{1}{D_{KA}}}\right)\frac{\epsilon_a}{\tau_a} \tag{13}$$

Using this tortuosity factor, effective diffusivity of benzene was calculated from Eq. 13 and then α was evaluated from the slope of Eq. 11.

Experimental Results

The experimental setup used is similar to the one used by Doğu et al. (1986). A soil pellet containing simetite-, illite-, and kaolin-type clays is used in the experiments. Chemical composition of the soil used is given in Table 2. Dried and sieved soil was pressed into a cylindrical pellet holder, and a pellet with a porosity of 0.49 was prepared. The length and the diameter of the pellet are 0.29 cm and 1.35, respectively. Soil sample was characterized by X-ray diffraction analysis and porosity was determined using a Quantachrome 60 Mercury Intrusion Porosimeter.

Nitrogen was used as the carrier gas flowing past both upper and lower faces of the pellet. The benzene pulse (0.5 μL) was introduced into the upper carrier gas (nitrogen) stream by a syringe. The whole unit is placed into a constant temperature oven, and the response peak was detected using a gas chromatograph. Pulse response experiments were carried out at different lower stream flow rates ranging from 0.8 to 2.0 cm^3/s. These experiments were repeated at different temperatures in the range of 35-90°C. Experimental moments of the response peak were evaluated by numerical integration of Eq. 7.

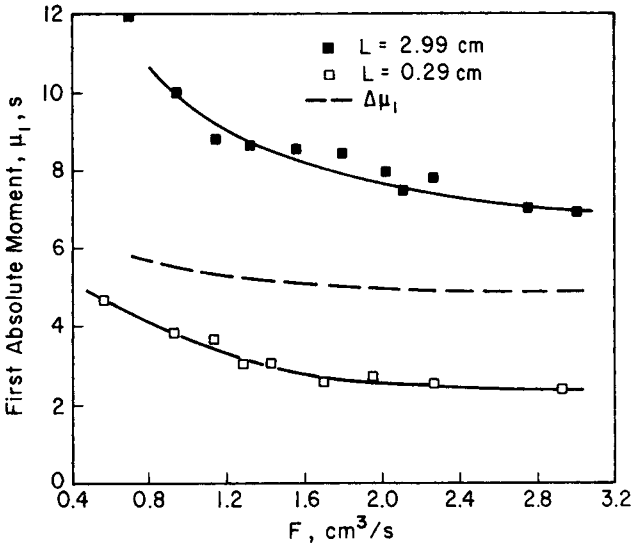

Figure 2. First absolute-moment data obtained with an inert tracer (He) at 70°C.

Experiments conducted with helium tracer were repeated with two pellets of identical physical and chemical properties, but of different lengths (2.99 and 0.29 cm) (Figure 2). Then, the differences between the first moments obtained with these two pellets ($\Delta\mu_1$) were used in the evaluation of effective diffusivity. By taking differences, the correction terms, for example, for dead volumes cancel. For large values of the lower stream flow rate, F, $\Delta\mu_1$ becomes:

$$\lim_{F\to\infty}\Delta\mu_1 = \frac{\epsilon}{6D_e}(L_1^2-L_2^2) \tag{14}$$

Using the data in Figure 2, effective diffusivity of helium was determined as 0.148 cm^2/s at 70°C. The tortuosity factor was then calculated using Eq. 13 as 1.8.

Similar results were obtained for tortuosity at different temperatures conducted between 35 and 90°C, and an average value of 1.8 was used to calculate the effective diffusivity of benzene at different temperatures. Results are reported in Table 3.

Zeroth-moment results obtained with benzene tracer are shown in Figure 3, where experimental M/m_o values were plot-

Table 2. Chemical Composition of the Soil Pellet (wt.%)

SiO_2	65.73	CaO	6.35
TiO_2	1.52	Na_2O	0.41
Al_2O_3	13.40	C	2.02
Fe_2O_3	5.23	H	0.68
FeO	1.85	N	0.34
MgO	2.20	S	0.09
MnO	0.09		

Table 3. Effective Diffusivities and Adsorption Parameters of Benzene in Soil

T, °C	D_e, cm^2/s	α	$\rho_p k$, s^{-1}	$\rho_p K_B \times 10^{-4}$
35	0.0177	4.95	5.16	1.56
50	0.0188	4.60	4.73	0.97
70	0.0208	4.15	4.26	0.75
90	0.0226	3.33	2.98	0.49

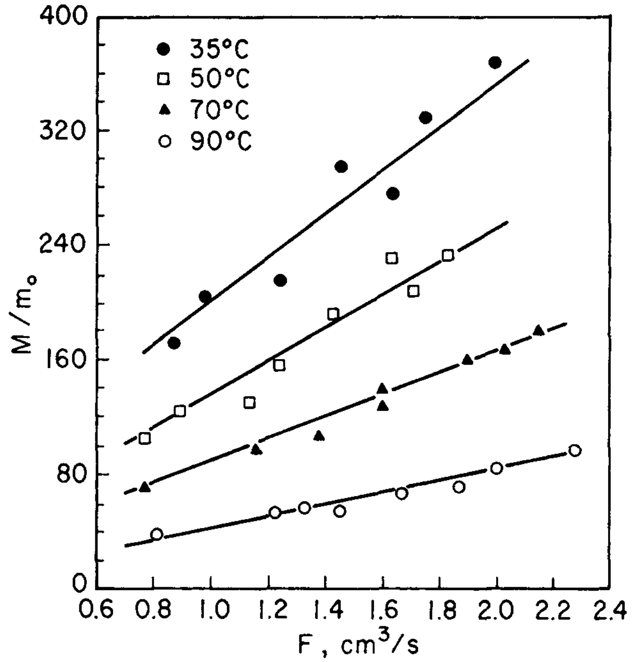

Figure 3. Variation of M/m_o with respect to lower stream flow rate (benzene tracer).

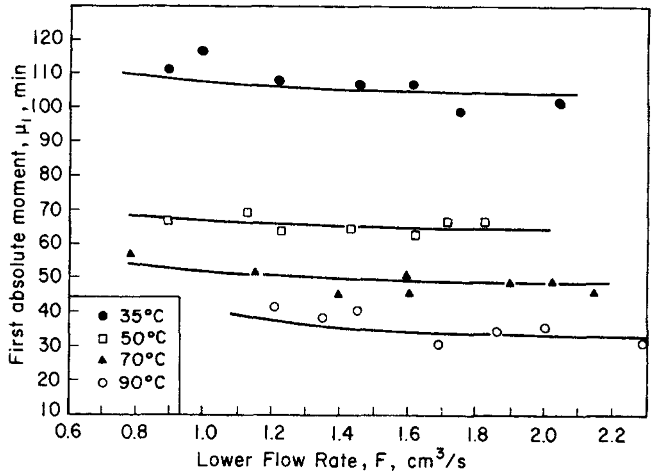

Figure 4. First absolute-moment data obtained with benzene tracer at different temperatures.

ted as a function of the lower stream flow rate (F). To find the numerical value of M (strength of the input pulse), a pulse response experiment was made by placing an impermeable teflon plate over the pellet and by detecting the response peak leaving the top chamber of the single-pellet cell. The area under the curve of this peak corresponds to M. These experiments were repeated at four different temperatures (35°C, 50°C, 70°C, and 90°C), as shown in Figure 3. The values of the dimensionless parameter α were then determined from the slopes of the curves in Figure 3. Results are summarized in Table 3.

In all the pulse response experiments, sufficient amount of time was waited until the concentration of benzene tracer leaving the cell became zero (below the detection limits). This period was about 6 h at low temperatures. The experimental first absolute moment values calculated from these response curves are shown in Figure 4. As expected, flow rate dependence of μ_1 values are small, and $\rho_p K_B$ values were determined from the high flow rate values of μ_1 vs. F curves (Table 3).

Discussion

The soil sample used in this study is composed of a number of clay minerals and some organic matter. As a result, its surface characteristics for the adsorption are expected to be highly heterogeneous. A distribution of activation energies for desorption and heat of adsorption are the natural consequences of this surface heterogeneity. Experimental results of this work showed that sorption on some of the sites of the soil is irreversible within the time scale of experiments conducted in this work. From these sites, desorption ceased leaving an appreciable amount of adsorbate still on the surface. On the other hand, adsorption on the remaining sites of the soil is reversible. The reversible adsorption process is also quite strong, especially at low temperatures. At 35°C, the first absolute-moment values of benzene were found to be over 100 min for a pellet of 0.29 cm in length. On the other hand, the first absolute-moment values for an inert tracer (He) are only a couple of seconds for the same pellet.

The irreversibly adsorbed fraction of the tracer was found to decrease with an increase in temperature. This indicated that the number of sites which participated in this irreversible adsorption decreased with an increase in temperature. In this work, the total number of adsorption sites (S_o) of the soil was considered to be the summation of sites which participated in irreversible adsorption, S_i, and reversible adsorption, S_r. At higher temperatures, the desorption rate increases and thus some of the irreversibly adsorbed species also desorp within the time scale of the experiments. This indicates that the number of sites which participate in irreversible adsorption (S_i) decreases with an increase in temperature.

The rate of irreversible sorption should actually be written as $\rho_p k S_i (1-\theta) C_B$. By carrying out experiments with very small amounts of tracer, θ term was neglected and linear adsorption assumption was made in writing Eq. 2. The adsorption rate constant, k_i, in Eq. 2 is the product of actual adsorption rate constant and the number of sites which participate in irreversible adsorption, kS_i. Some increase of k with temperatures was expected. On the other hand, S_i decreases with temperature. The product of $\rho_p k$ and S_i, (which is $\rho_p k_i$) showed a decreasing trend with temperature (Table 3) essentially due to the decrease in the number of sites which participated in irreversible adsorption. To test the linear adsorption assumption made for both irreversible and reversible adsorption processes, a set of experiments were carried out with different tracer amounts. No significant effect of tracer concentration on the M/m_o and μ_1 values were observed in these experiments.

Figure 5 shows the temperature dependence of adsorption equilibrium constant. Heat of adsorption evaluated from the slope of this curve was found to be −4,560 cal/mol. This value indicated that the reversible adsorption process is physical adsorption. On the other hand, the irreversible adsorption process is either chemisorption or can be considered as an entrapment is soil micropores. In the work of Steinberg et al. (1987), the residual sorption of 1,2-dibromoethane in soil was explained by entrapment in the intraparticle micropores.

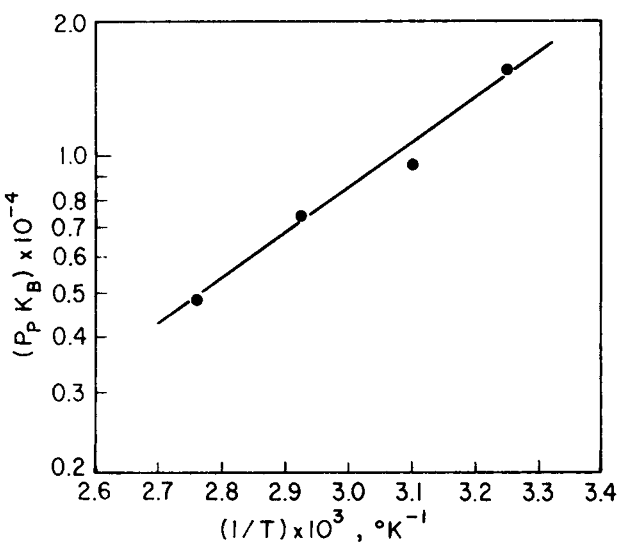

Figure 5. Variation in adsorption equilibrium constant of benzene on soil with temperature.

The results of this work showed that the modified single-pellet moment technique proposed here can be used successfully for the investigation of both irreversible and reversible adsorption processes.

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Notation

A = area of end face of pellet
C_B = concentration of benzene tracer
D_{AB} = molecular diffusivity of A in B
D_{K_A} = Knudsen diffusivity of A
D_e = effective diffusivity
F = lower stream volumetric
k = adsorption rate constant
k_i = kS_i, apparent adsorption rate constant
K_B = adsorption equilibrium constant
L = length of the pellet
m_n = nth moment defined in Eq. 7
M = strength of the input pulse
s = Laplace variable
S_i = number of sites which contribute to irreversible adsorption
S_o = total number of sites
S_r = number of sites which contribute to reversible adsorption

Greek letters

α = dimensionless group defined by Eq. 10
ϵ_a = macroporosity of the pellet
ϵ_p = porosity of the pellet
μ_1 = first absolute moment
$\Delta\mu_1$ = difference of first absolute moments
ρ_p = pellet density
θ = fraction of the sites covered by adsorbed species
τ_a = tortuosity based on macroporosity

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