

Prediction of Dispersing Coefficient in Reactive Porous Media from The Slope of An Effluent Curve

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Abstract : An excellent agreement was found between predicted and experimental results in R-value. By using this reasonable R-value, dispersing coefficient D can be calculated as $D=(1-b/R)^2(L/\eta) \cdot v$. There is no needs to find S in a nonreactive model as $D=L/(4\pi S_0^2 V_0^2) \cdot v$. These two D's may not be the same if two sets of experimental conditions are different.

I. Introduction

The coefficient of dispersion, D, is an important parameter for solving the dispersing equation. In a nonreactive porous medium, this coefficient is a function of pore velocity, \bar{v} , if the slope of effluent curve is known⁽¹⁾. In a reactive porous medium, however, D is function of \bar{v} only when the slope of a nonreactive effluent curve is available. Experimenters must seek for a solute which does not interact with the porous medium as the tracer to meet this requirement. Such an additional work usually doubles the time required for an experiment. Also, if the two effluent curves are not measured simultaneously, there might be great discrepancies in the average pore velocity and other experimental conditions. The predicted dispersing coefficient may not be correct by using the slope of a nonreactive effluent curve, which in turn is determined by pore velocity. This paper is to present a mathematical derivation of the dispersing coefficient based on the slope of an effluent curve of the tracer only.

II. Theory

For one dimensional, nonreactive system, the dispersing equation takes from

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$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \bar{v} \frac{\partial C}{\partial x} \quad (1)$$

subject to the initial and boundary conditions

$$\begin{aligned} C(0, t) &= C_0; & t \geq 0 \\ C(x, 0) &= 0; & x \geq 0 \\ C(\infty, t) &= 0; & t \geq 0 \end{aligned} \quad (2)$$

the solution will be

$$\frac{C}{C_0} = \frac{1}{2} \operatorname{erfc} \left(\frac{x - \bar{v}t}{2\sqrt{Dt}} \right) + \frac{1}{2} \exp \left(\frac{\bar{v}x}{D} \right) \operatorname{erfc} \left(\frac{x + \bar{v}t}{2\sqrt{Dt}} \right) \quad (3)$$

The second term on the right hand side was found to be very small, in order of 0.001, and can be safely neglected. Let $Q/V_0 = \bar{v}/L$ and $Qt = V$, Eq(3) can be transformed to

$$\frac{C}{C_0} = \frac{1}{2} \operatorname{erfc} \left(\frac{1 - (V/V_0)}{2\sqrt{\eta} V/V_0} \right) \quad (4)$$

where, $\eta = D/(\bar{v}L)$, L is the soil column length, Q is discharge, V and V_0 are the effluent volume and pore volume, respectively. Eq(4) shows the relation between relative concentration and number of pore volumes, i.e. $V/V_0 = 1$, $C/C_0 = 0.5$.

Rifai et al. (1956) derived the dispersing coefficient, D , from the slope of the nonreactive breakthrough curve at $C/C_0 = 0.5$. To demonstrate this relationship place $V = V_0$, by definition

$$S_0 = \left. \frac{d(C/C_0)}{dV} \right|_{V=V_0} \quad (5)$$

The solution of S_0 is

$$S_0^2 = \frac{1}{4\pi\eta V_0^2} = \frac{\bar{v}L}{4\pi V_0^2 D} \quad (6)$$

or

$$D = \frac{L}{4\pi S_0^2 V_0^2} \cdot \bar{v} \quad (7)$$

For one dimensional reactive porous media, to derive the dispersing coefficient, D , may use the same procedure as used for nonreactive system.

An adsorption term is required in Eq(1)

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \bar{v} \frac{\partial C}{\partial x} - \frac{\partial N}{\partial t} \quad (8)$$

Lapidus and Amundson (1952) developed a model of material balance equation

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \bar{v} \frac{\partial C}{\partial x} - \frac{\rho}{\alpha} \frac{\partial q}{\partial t} \quad (9)$$

where, ρ is bulk density, α is pore fraction and q is amount of cations adsorbed per unit weight of soil.

Equation(9) can be transformed to

$$\frac{\partial X}{\partial t} = D \frac{\partial^2 X}{\partial x^2} - \bar{v} \frac{\partial X}{\partial x} - \frac{\rho Q}{\alpha C_0} \frac{\partial Y}{\partial t} \quad (10)$$

where, Q is cation exchange capacity, $X=C/C_0$ and $Y=f(X)=q/Q$. Eq(10) becomes

$$\frac{\partial X}{\partial t} = D \frac{\partial^2 X}{\partial x^2} - \bar{v} \frac{\partial X}{\partial x} - \frac{\rho Q}{\alpha C_0} f' \frac{\partial X}{\partial t} \quad (11)$$

and

$$R \frac{\partial X}{\partial t} = D \frac{\partial^2 X}{\partial x^2} - \bar{v} \frac{\partial X}{\partial x} \quad (12)$$

in which, $\partial Y/\partial t = f' \cdot (\partial X/\partial t)$ and $R = 1 + (\rho Q/\alpha C_0) f'$

Multiply Eq(12) with C_0 , then

$$\frac{\partial C}{\partial t} = D^* \frac{\partial^2 C}{\partial x^2} - \bar{v}^* \frac{\partial C}{\partial x} \quad (13)$$

where, $D^* = D/R$ and $\bar{v}^* = \bar{v}/R$. It is same as Eq(1) with the solution

$$\frac{C}{C_0} = \frac{1}{2} \operatorname{erfc} \left(\frac{x - \bar{v}^* t}{2\sqrt{D^* t}} \right) = \frac{1}{2} \operatorname{erfc} \left(\frac{R - V/V_0}{2\sqrt{\eta R V/V_0}} \right) \quad (14)$$

we can get a breakthrough curve, in which $C/C_0=0.5$ as $V/V_0=R$.

Validation of Eq(14) needs a set of experimental data. Wann(1977) predicted solute dispersion by using 100ppm K through an Oxisol. The known parameters and variables are listed as follows:

Soil	Tracer salt	Bulk density g/cm ³	CEC me/g	Pore fraction	Tracer concnction me/ml
Molokai	KCl	1.13	0.06	0.599	0.0025

The exchange function is

$$Y = \frac{X}{X + (1-X) \exp(\ln K + c(1-2X))} \quad (15)$$

and can be simplified to⁽⁵⁾

$$Y = \frac{X}{X + (1-X) \exp(2X)} \quad (16)$$

by curve fitting, where $K=2.72$ and $c=-1.0$. Evaluate $f'(X)$ as $X=0.5$ to be 0.39.

The parameter R in Eq(12) was calculated by Wann's data⁽⁵⁾ to be 18.21. Compared with the experimental results, that is, the number of pore volumes was 17.58. The error term is less than 4% which is so small that there is a good agreement between the predicted and experimental results.

Determine the slope of the reactive breakthrough curve, S_r , at number of pore volumes, R , and place $V/V_0 = R$, by definition⁽¹⁾

$$S_r = \left. \frac{d(C/C_0)}{d(V/V_0)} \right|_{V/V_0=R} \quad (17)$$

Set $X = \frac{C}{C_0}$, $Y = \frac{R-(V/V_0)}{2\sqrt{\eta R V/V_0}}$ and $X = \frac{1}{2} \operatorname{erfc} Y$,

then,

$$\left. \frac{dX}{dY} \right|_{V/V_0=R} = \frac{-1}{\sqrt{\pi}} \quad (18)$$

and

$$\left. \frac{dY}{dV/V_0} \right|_{V/V_0=R} = \frac{-1}{2R\sqrt{\eta}} \quad (19)$$

By chain rule,

$$S_r = \frac{1}{2R\sqrt{\pi\eta}} \quad (20)$$

III. Application

By using the reactive experimental breakthrough curve to evaluate the slope at $C/C_0=0.5$ as $V/V_0=R$, we can make a tangent line at $(R, \frac{1}{2})$ and match a intercept on abscissa, b (Fig.1). The slope calculated will be $0.5/(R-b)$, substitute it to Eq(20)

$$\frac{1}{2(R-b)} = \frac{1}{2\sqrt{\pi\eta} R} \quad (21)$$

Substitute $\eta = D/(\bar{v}L)$ to Eq(21) and rearrange

$$D = \left(1 - \frac{b}{R}\right)^2 \frac{L}{\pi} \bar{v} \quad (22)$$

This D value can be used to predict other breakthrough curves with different sets of experimental conditions. Figure 2 shows the predicted breakthrough curves with different tracer conditions.

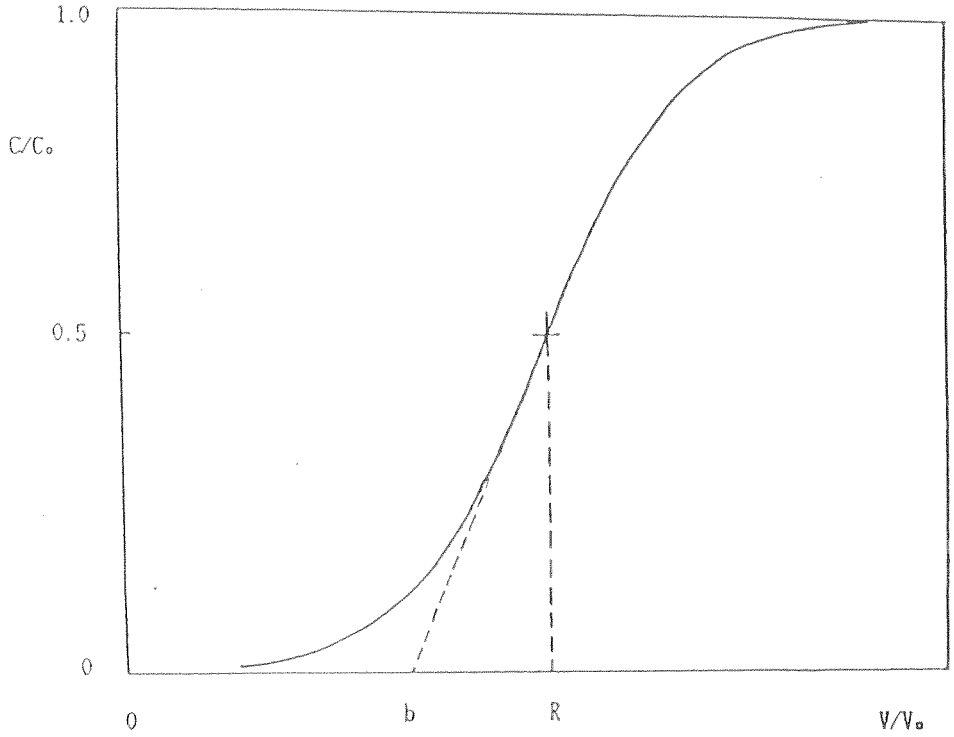


Fig.1 The schematic drawing of BTC and tangent line at $(R,0.5)$.

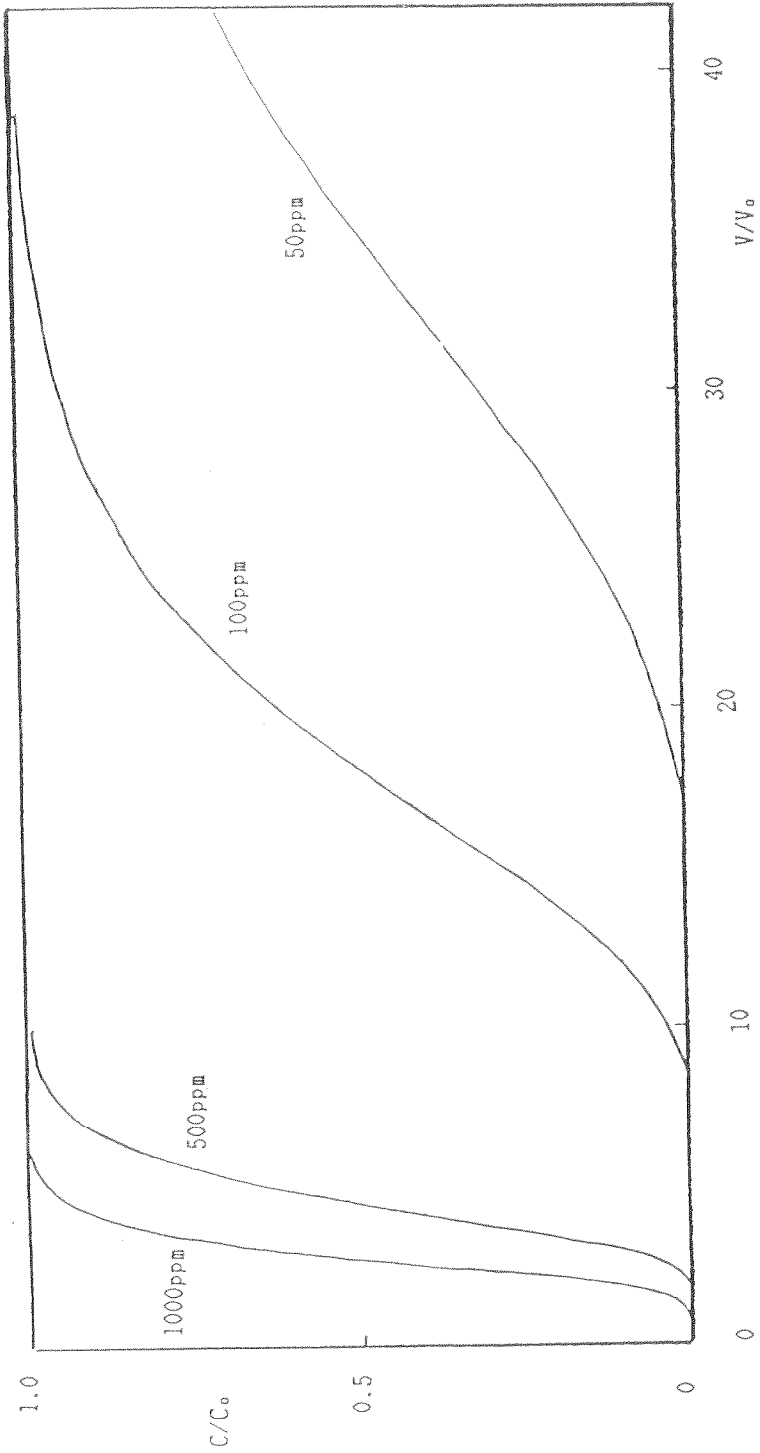


Fig.2 Predicted breakthrough curves by using the calculated D value.

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V. Notation

- C : effluent concentration (me/ml)
C₀: influent concentration (me/ml)
V : volume of the effluent solution at time t (ml)
V₀: pore volume (ml)
 \bar{v} : average pore velocity (cm/hr)
D : fluid dispersion coefficient (cm²/hr)
 ρ : bulk density (g/cm³)
 α : pore fraction
q : cations adsorbed of soil
Q : cation exchange capacity (me/g)
c : a constant in exchange function
K : equilibrium constant
 η : constant in complimentary error function
X : relative concentration of cation in solution
Y : relative concentration of cation in exchange phase
L : column length (cm)
x : distance (cm)
t : time (hr)
S₀: slope of the breakthrough curve at C/C₀=0.5
S_r: slope of the reactive breakthrough curve at C/C₀=0.5
N : concentration of soluble matter adsorbed
f' : derivative of function f
R : retardation factor

由突破曲線推估溶質在多孔體中之流散係數

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摘要：溶質在多孔體中之傳輸，其流散係數之求法多仰賴以無反應氫離子或重氫水分子為追蹤劑之突破曲線，當流出濃度為二分之一時之斜率，代入既有公式求解。惟該試驗與以其它陽離子當追蹤劑時，有時無法同時進行，所求得之平均孔隙流速及其它試驗情況必然不盡相同，致所得結果能否直接應用，不無存疑。本研究係以數學模式推導，直接以溶質在反應多孔體中傳輸所得之突破曲線，俟流出濃度達二分之一時，以其流出孔隙體積數及切線斜率計算流散係數，可節省試驗時間，減少試驗誤差。

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