

CONCENTRATION DECAY IN A BATCH ADSORPTION TANK

—FREUNDLICH ISOTHERM WITH SURFACE DIFFUSION KINETICS—

回分吸着における液濃度変化——フロインドリッヒ平衡型における粒子内表面拡散支配の場合

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One of the most difficult problems in the course of designing an adsorption equipment for advanced water treatment is an estimation of the adsorption rate which determines the size of the equipment. In the case of aqueous systems, diffusion of adsorbates in the adsorbent particles plays an important role in the overall adsorption kinetics. Since most of the adsorption isotherms are nonlinear and diffusion kinetics are highly dependent on the physico-chemical characteristics of both adsorbates and adsorbents, the intraparticle diffusion problem in aqueous systems has been left quite ambiguous.

The purpose of this note is to give a way to estimate the surface diffusivity for non-linear (Freundlich-type) isotherm from concentration decay in a stirred tank batch adsorber. Brief summary of algorithm for the computation is shown and diagrams are presented for an easy comparison of experimentally obtained concentration decay with the theory.

Basic concept

When surface diffusion is dominant in a particle and mass transfer between bulk liquid and external particle surface is rapid enough, the basic equations for the amount adsorbed in the particle, q , as a function of radial position r and time t and the concentration in the tank, C , during a finite batch contacting are written as

$$D_s \left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \frac{\partial q}{\partial r} \right) = \frac{\partial q}{\partial t} \quad (1)$$

with boundary conditions

$$r=R; \quad \rho_p D_s \frac{\partial q}{\partial r} = -\frac{V_L}{S} \frac{\partial C}{\partial t} \quad (2)$$

$$q = q_0 \cdot (C/C_0)^{1/n} \quad (3)$$

$$r=0: \quad \frac{\partial q}{\partial r} = 0 \quad (4)$$

and initial conditions $q=0$ for $0 \leq r \leq R$

and $C=C_0$ at $t=0$ (5)

where D_s is the effective surface diffusion coefficient based on the bulk volume of the particle (cm^2/sec), V_L is the volume of liquid in the tank (cm^3), S is the external surface area of the adsorbent particles (cm^2) and ρ_p is the particle density on the water free basis (g/cm^3). The exponent n denotes the Freundlich constant.

The set of equations (1) to (5) is expressed in a dimensionless manner.

$$\frac{\partial^2 Y}{\partial \rho^2} + \frac{2}{\rho} \frac{\partial Y}{\partial \rho} = \frac{\partial Y}{\partial \tau_s} \quad (6)$$

$$\text{with } \rho=1: \quad \frac{\partial Y}{\partial \rho} = -\frac{1}{3\alpha} \frac{\partial X_L}{\partial \tau_s} \quad (7)$$

$$Y = X_L^{1/n} \quad (8)$$

$$\rho=0: \quad \partial Y / \partial \rho = 0 \quad (9)$$

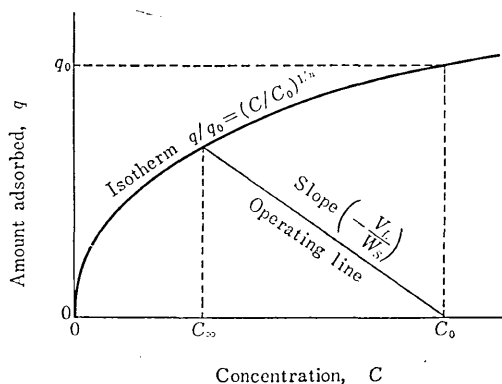


Fig. 1 Operating line in Freundlich isotherm system

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and $\tau_s=0: Y=0$ for $0 \leq \rho \leq 1$

$$X_L=1 \quad (10)$$

where $X_L=C/C_0$, $Y=q/q_0$, $\tau_s=D_s t/R^2$

$\rho=r/R$, and

$$\alpha=W_s q_0/V_L C_0=(1-C_\infty/C_0)/(C_\infty/C_0)^{1/n}.$$

In the above derivations, C_0 and q_0 represent the initial concentration in the tank and the amount adsorbed in equilibrium with C_0 , respectively. W_s is the amount of adsorbents and then the final concentration C_∞ is determined from the

total mass balance in the stirred tank as shown in Figure 1. For $n=1$ (linear isotherm) and $n=\infty$ (rectangular isotherm) the analytical solutions have been given and the diagrams have been already presented (1, 4).

For a numerical calculation, Saul'yev's two-point average method is known to be effective (2, 3). Then, for a given set of n and C_∞/C_0 , Eqs. (6) ~ (10) were solved to give the relations between $X_L=C/C_0$ and τ_s . Radial increment in a particle was chosen to be $1/40$. Computation was started from $\tau_s=10^{-5}$ and the time increment ($\Delta\tau_s$) is set to be 2×10^{-7} which is changed to 2×10^{-6} at $\tau_s=10^{-4}$ and so on. In this way, computation was continued till τ_s became unity.

C_∞/C_0 was set to be 0.9, 0.8, ..., 0.1 and 0.05. In order to avoid the final offset due to the accumulation of truncation error during computation, concentration in a bath, C was compensated at a certain interval (every 25 to 50 steps) by means of the total mass balance equation

$$X_L \equiv \frac{C}{C_0} = 1 - \alpha \left[\frac{1}{3} \int_0^1 Y \rho^2 d\rho \right]^n$$

This integration was made by

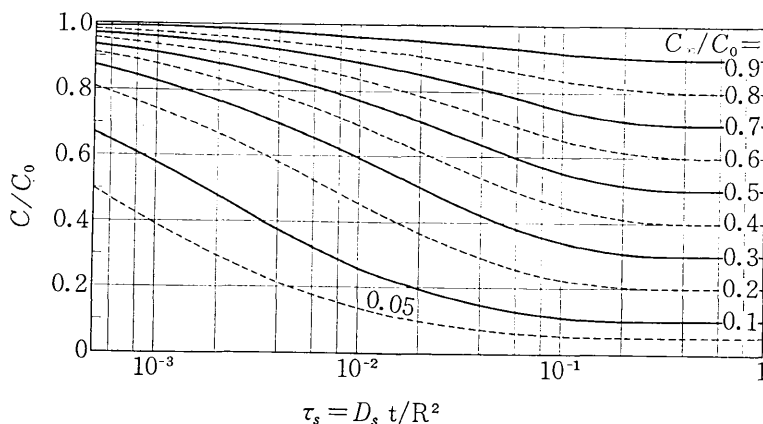


Fig. 2 C/C_0 versus $\tau_s=D_s t/R^2$ for $n=1.25$

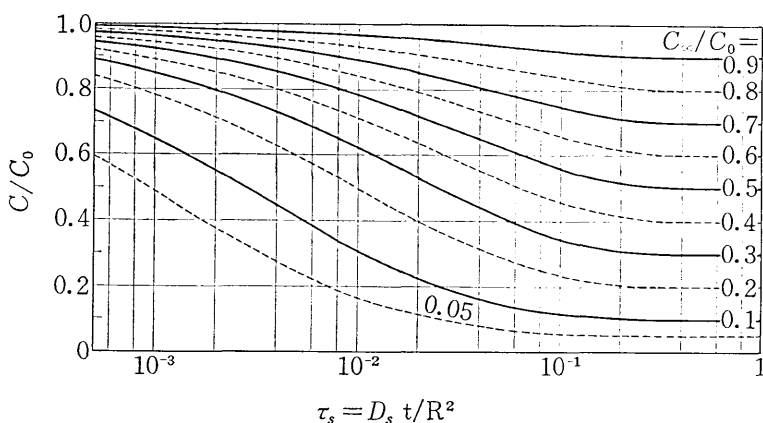


Fig. 3 C/C_0 versus $\tau_s=D_s t/R^2$ for $n=1.5$

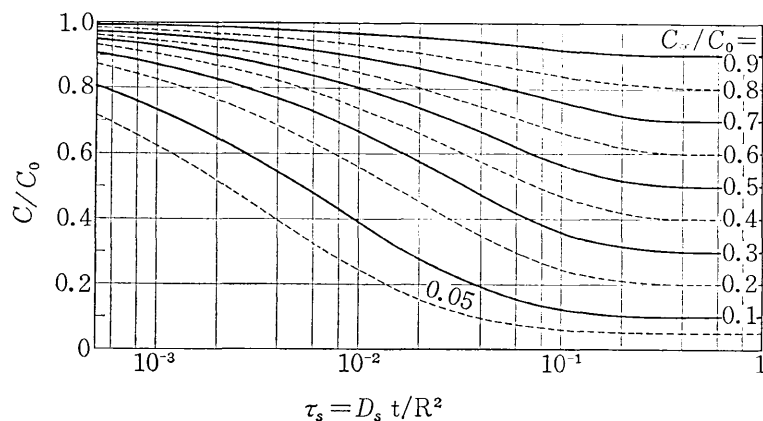
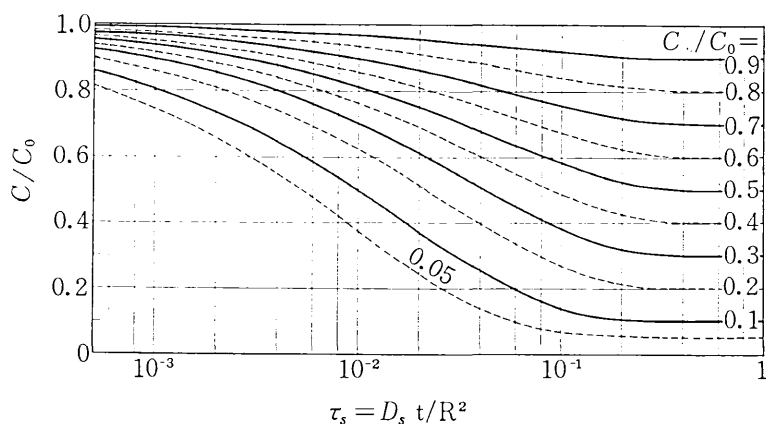
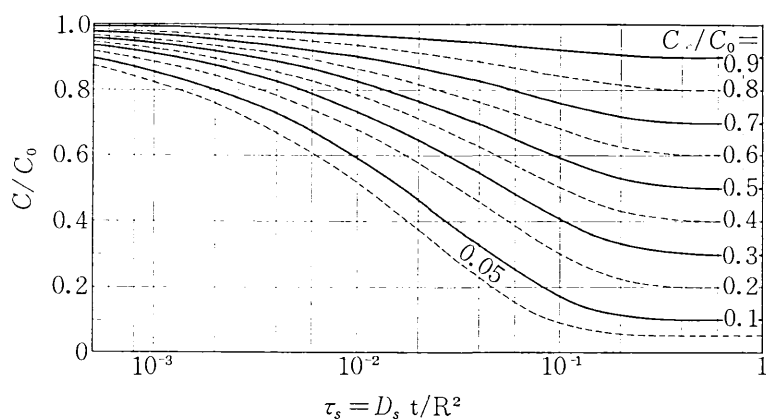
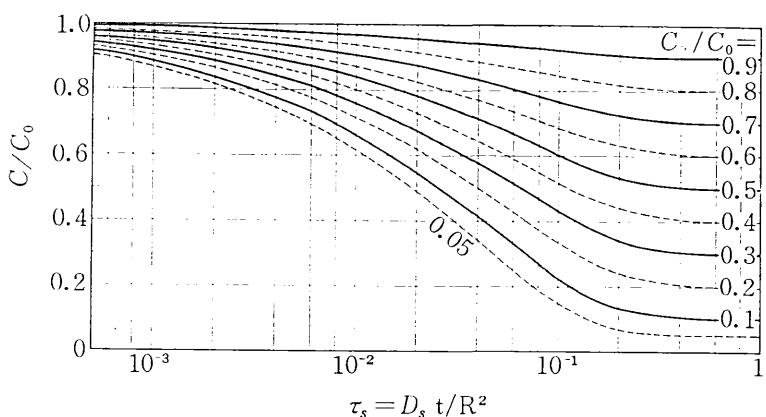


Fig. 4 C/C_0 versus $\tau_s=D_s t/R^2$ for $n=2.0$

Fig. 5 C/C_0 versus $\tau = D_s t / R^2$ for $n=3.0$ Fig. 6 C/C_0 versus $\tau = D_s t / R^2$ for $n=5.0$ Fig. 7 C/C_0 versus $\tau = D_s t / R^2$ for $n=10.0$

Simpson's three-point rule. Computed results for $n=1.25, 1.5, 2, 3, 5$ and 10 are shown in Figures 2~7. Results for $n=1$ and $n=10^3$ agreed reasonably well with the previously shown analytical results for $n=1$ and $n=\infty$, respectively and then

are not shown here.

Application of the figures

For each solute-adsorbent combination, at least two different adsorbent loading ratio (W_s/V_L) must be employed. From the final concentrations of the runs, an isotherm is determined and Freundlich constant n can be obtained. Then the figure for the nearest n can be used for curve fitting to determine τ_s-t relation, which gives the value of D_s . By employing the experimental curves for $C_\infty/C_0 > 0.5$, it is possible to determine, in this way, the magnitude of D_s within 10 percent error, which can be improved by using a proper interpolation regarding n .

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