

## CONCENTRATION DECAY IN A BATCH ADSORPTION TANK

—FREUNDLICH ISOTHERM WITH PORE DIFFUSION KINETICS—

回分吸着における液濃度変化—フロイドリッヒ平衡型における粒子内細孔拡散支配の場合

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The authors have presented the diagrams for concentration decay in a batch adsorber for non-linear isotherm system (Freundlich type) with surface diffusion kinetics in the adsorbent particles (3). Another important extreme that is met in discussing the adsorption rate is the case where pore diffusion is dominant in the particles. These cases are often met in the adsorption of high boiling point and hydrophilic organics such as DBS by activated carbons (4). This note shows the results of the computation made by a similar treatment as given in (3) for Freundlich isotherm systems, except that the modification to the basic equations was made to take into account the condition of dominant pore diffusion kinetics. The largest assumption taken here is that the isotherm was approximated with a straight line in the range  $q < 0.02 q_0$ , since Freundlich isotherm gives the infinitely large slope of isotherm at  $c = q = 0$  which is not preferable for the computation. The basic equations used for the computations are given in dimensionless forms.

$$\frac{\partial^2 X}{\partial \rho^2} + \frac{2}{\rho} \frac{\partial X}{\partial \rho} = \frac{\partial Y}{\partial \tau} \quad (1)$$

$$Y = X^{1/n} \text{ for } 0.02 < Y,$$

$$Y = 0.02^{1-n} \cdot X \text{ for } 0 \leq Y \leq 0.02 \quad (2)$$

with

$$\rho = 1 : \frac{\partial X}{\partial \rho} = -\frac{1}{3\alpha} \frac{\partial X_L}{\partial \tau} \quad (3)$$

$$\tau = 0 : Y = 0 \text{ for } 0 \leq \rho \leq 1$$

$$X_L = 1 \quad (4)$$

where  $X = C/C_0$ ,  $\tau = (De t/R^2) \cdot (C_0/\rho_p q_0)$ ,  $\alpha = W_s q_0/$

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$V_L C_0$  and the other nomenclatures are included in the previous paper (3).

Almost an identical computation procedure with the one shown before (3) was employed except only for the case of  $n=10.0$ . When  $n$  is as large as ten, strong non-linearity at the adsorption front in the particle requires the time increment of computation to be sufficiently small to give a reasonably accurate result. Hence in this case computation was started from  $\tau=10^{-4}$  and time increment ( $\Delta\tau$ ) was chosen to be  $2.5 \times 10^{-7}$  for  $10^{-4} \leq \tau < 10^{-3}$ , and then the computation was continued by changing  $\Delta\tau$  to  $2.5 \times 10^{-6}$  for  $10^{-3} \leq \tau < 10^{-2}$  and so on until  $\tau=1$  was reached. The results are shown in Figures 1-6 for  $n=1.25, 1.5, 2.0, 3.0, 5.0$  and  $10.0$ .

For a linear isotherm system ( $n=1$ ), the analytical solution has been given by Crank (1)

$$\frac{C_L}{C_0} = 1 - \frac{1}{1+\alpha} \left\{ 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha+1)e^{-q_n^2 \tau}}{9+9\alpha+q_n^2 \alpha^2} \right\} \quad (5)$$

where  $q_n$ 's are  $n$ -th non-zero positive roots of

$$\tan q_n = \frac{3q_n}{3+\alpha q_n^2} \quad (6)$$

In the case of an irreversible adsorption, the isotherm becomes rectangular ( $n=\infty$ ). The authors have presented the solution for this case (4), which is

$$\begin{aligned} \tau = \frac{(1+a^3)}{3a} \left\{ a \ln \frac{\xi^3+a^3}{1+a^3} + \ln \frac{\xi+a}{1+a} \right. \\ \left. - \frac{1}{2} \ln \frac{\xi^2-a\xi+a^2}{1-a+a^2} \right. \\ \left. + \sqrt{3} \left[ \tan^{-1} \frac{2-a}{\sqrt{3}} - \tan^{-1} \frac{2\xi-a}{\sqrt{3}} \right] \right\} \quad (7) \end{aligned}$$

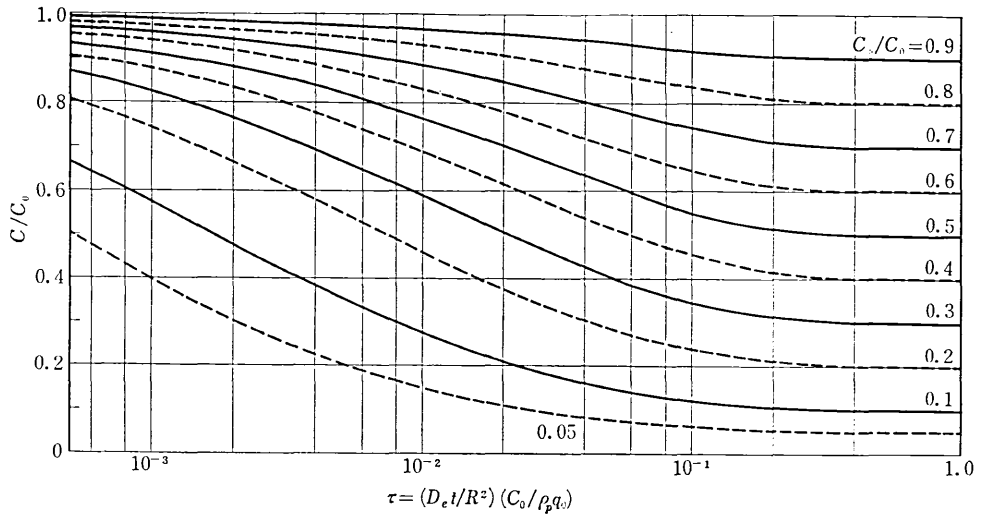


Fig. 1 Concentration decay  $C/C_0$  versus  $\tau=(D_e t/R^2)(C_0/\rho_p q_0)$  for  $n=1.25$

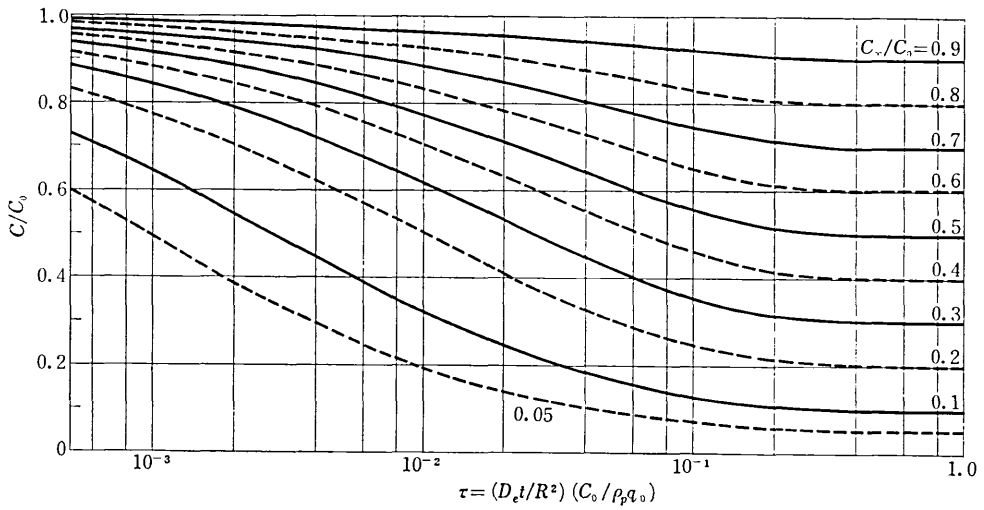


Fig. 2 Concentration decay  $C/C_0$  versus  $\tau=(D_e t/R^2)(C_0/\rho_p q_0)$  for  $n=1.5$

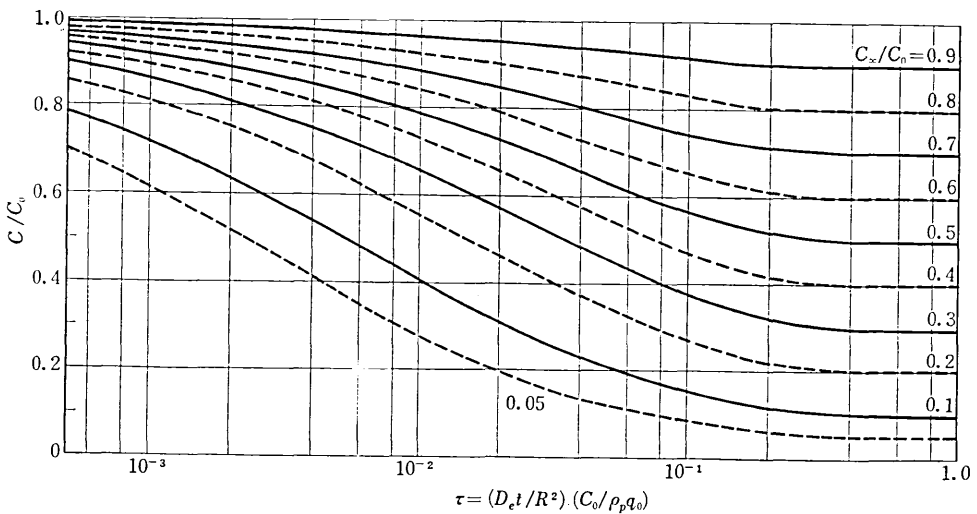


Fig. 3 Concentration decay  $C/C_0$  versus  $\tau=(D_e t/R^2)(C_0/\rho_p q_0)$  for  $n=2$

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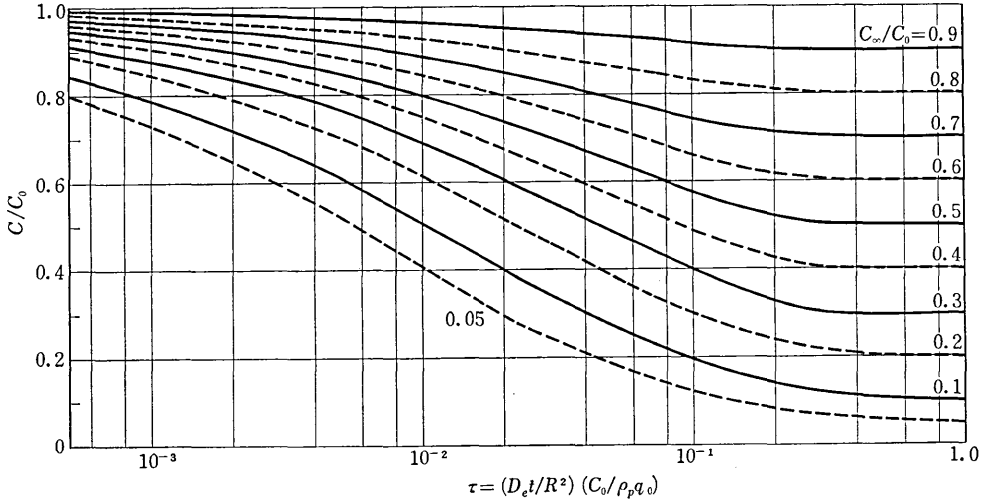


Fig. 4 Concentration decay  $C/C_0$  versus  $\tau = (D_e t / R^2) (C_0 / \rho_p q_0)$  for  $n=3$

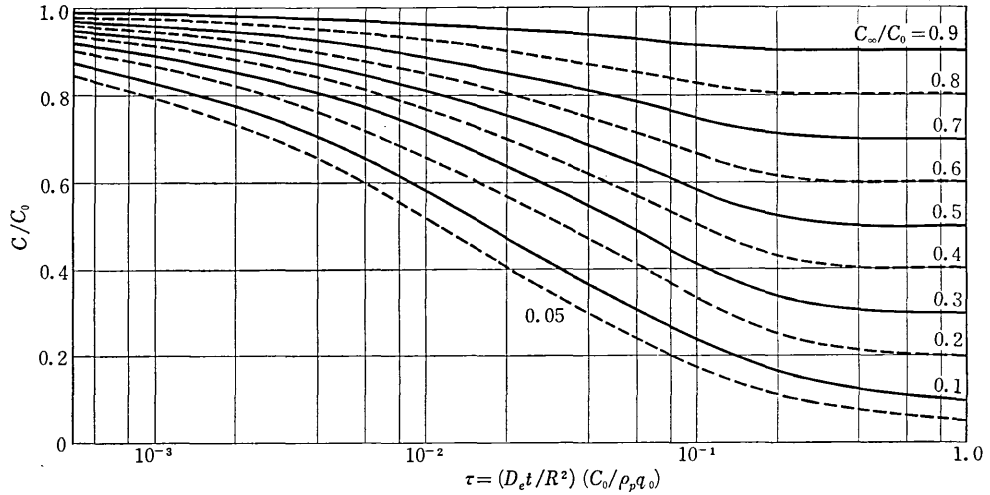


Fig. 5 Concentration decay  $C/C_0$  versus  $\tau = (D_e t / R^2) (C_0 / \rho_p q_0)$  for  $n=5$

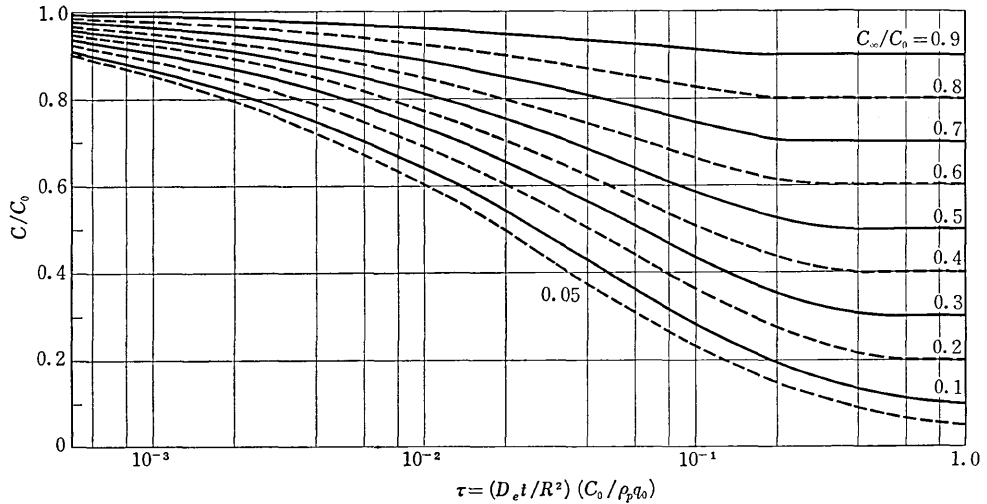


Fig. 6 Concentration decay  $C/C_0$  versus  $\tau = (D_e t / R^2) (C_0 / \rho_p q_0)$  for  $n=10$

where  $a = \{C_\infty / (C_0 - C_\infty)\}^{1/3}$  and  $\xi = \{(C_L - C_\infty) / (C_0 - C_\infty)\}^{1/3}$ . The similar diagrams derived from Eqs. (5) and (7) have been given by the authors (4).

### Discussion

The assumption of an isotherm of the type shown by Eq. (2) is partly justified by the work Radke and Pransnitz (2).

They showed that the adsorption isotherms for organic adsorbates by activated carbons in aqueous systems are generalized by the equation

$$q = \frac{1}{\frac{1}{Ac} + \frac{1}{Bc^{1/n}}} \quad (8)$$

which means that the isotherm reduces to Henry's relation (linear) at low concentrations while at high concentrations the Freundlich relation is valid.

For the comparison with experiment, the same procedure given before (3) is recommended and it must be added here that the discrimination between pore diffusion kinetics and surface diffusion kinetics is possible for a strongly non-linear isotherm system by comparing the data ( $C/C_0$  vs.  $\log t$ ) obtained for several runs with different carbon loading ( $V_L/W_s$ ) and the same initial concentration, with the diagrams obtained for the both cases.

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### Literature Cited

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