



## The Rectangular Isotherm Model for Adsorption Kinetics

DOUGLAS M. RUTHVEN

*Department of Chemical Engineering, University of Maine, Orono, ME 04469-5737, USA*

**Abstract.** The transient uptake response of an adsorbent particle, subjected to a step change in surface concentration, is considered. It is shown that, when the isotherm is highly favorable, the theoretical curves derived for a Langmuirian system reduce asymptotically to the much simpler form for a rectangular isotherm. The simple rectangular model provides a useful approximation even when the form of the actual isotherm is quite far from the rectangular limit.

**Keywords:** diffusion, shrinking core, rectangular isotherm

An understanding of the dynamic response of an adsorbent particle when subjected to a step change in sorbate concentration at the external surface is an essential requirement for modeling adsorption kinetics in both batch systems and adsorption columns. For physical adsorption the sorption kinetics are generally diffusion controlled so, if the system is isothermal and the equilibrium isotherm is linear, the dynamic response is given by familiar solutions of the Fickian diffusion equation, many of which have been summarized by Crank (1956). However, when the concentration change is large, the simplifying assumptions of a linear isotherm with a constant diffusivity are no longer valid. If the isotherm is highly favorable, so that it can be approximated as irreversible (or rectangular), an equally simple analytic solution for the uptake curve is again available (Dedrick and Beekman, 1967; Brauch and Schlunder, 1975). Under these conditions the concentration profile assumes a shock wave form and we have shrinking core behavior, in which all adsorption occurs at the adsorption front (see Fig. 1). The expressions for the uptake curve are derived by assuming that the flow of sorbate is constant in the region  $\ell > x > x_f$  (or  $R > r > r_f$ ) with all adsorption occurring at the front ( $x = x_f$  or  $r = r_f$ ):

$$\text{Slab: } \frac{t}{\tau} = \left( \frac{m_t}{m_\infty} \right)^2 \quad (1)$$

$$\tau = \frac{\lambda^2 q_s}{2D_o c_o}$$

$$\text{Sphere: } \frac{t}{\tau} = 1 + 2 \left( 1 - \frac{m_t}{m_\infty} \right) - 3 \left( 1 - \frac{m_t}{m_\infty} \right)^{2/3} \quad (2)$$

$$\tau = \frac{R^2 q_s}{6D_o c_o}$$

In these expressions  $\tau$  represents the time required for the (shock) front to penetrate to the center of the slab or sphere.

This approach has been widely used to model uptake rates for systems in which the equilibrium is highly favorable (Dedrick and Beekman, 1967; Brauch and Schlunder, 1975; Teo and Ruthven, 1986). When the curvature of the isotherm is less extreme it is more appropriate to use the Langmuir isotherm:

$$\frac{q}{q_s} = \frac{bc}{1 + bc} \quad (3)$$

$$\lambda = \frac{q_o}{q_s} = \frac{bc_o}{1 + bc_o}; \quad K = bq_s \quad (4)$$

For diffusion in a composite adsorbent in which most of the adsorptive capacity is within the micro-particles while the kinetics are controlled by pore diffusion within the gross (macro) particle the diffusion equation

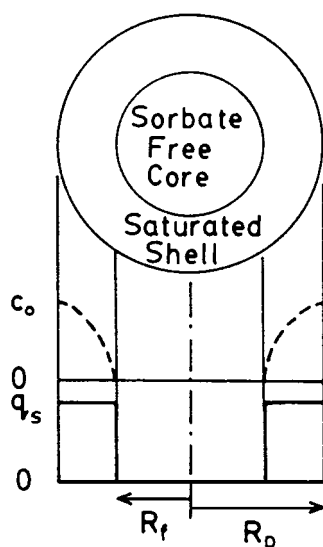


Figure 1. Schematic diagram showing the form of the concentration profiles within the fluid phase ( $c$ ) and adsorbed phase ( $q$ ) for irreversible adsorption in a spherical particle.

assumes the following form:

$$\text{Slab: } (1 - \varepsilon_p) \frac{\partial q}{\partial t} + \varepsilon_p \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (5a)$$

$$\text{Sphere: } (1 - \varepsilon_p) \frac{\partial q}{\partial t} + \varepsilon_p \frac{\partial c}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 D \frac{\partial c}{\partial r} \right] \quad (5b)$$

For a Langmuirian system these expressions are equivalent to (Ruthven and Derah, 1972; Ruthven, 1984):

$$\text{Slab: } \frac{\partial q}{\partial t} = \frac{\partial}{\partial x} \left( D_e \frac{\partial q}{\partial x} \right) \quad (6a)$$

$$\text{Sphere: } \frac{\partial q}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 D_e \frac{\partial q}{\partial r} \right] \quad (6b)$$

where  $D_e = \frac{D_0}{K(1-q/q_s)^2}$  is the effective (concentration dependent) diffusivity.

The appropriate initial and boundary conditions are:

$$\begin{aligned} t = 0: & \quad q(x, 0) = 0 \text{ or } q(r, 0) = 0 \\ t > 0: & \quad q(\lambda, t) = q_0 \text{ or } q(R, t) = q_0 \\ & \quad \frac{\partial c}{\partial x} \Big|_{x=0} = 0 \quad \frac{\partial q}{\partial r} \Big|_{r=0} = 0 \end{aligned} \quad (7)$$

These equations are non-linear and must, in general, be solved numerically. Solutions for the uptake curve, giving the fractional approach to equilibrium ( $m_t/m_\infty$ ) as a function of the dimensionless time variable  $D_0 t/l^2$  or  $D_0 t/R^2$  and the non-linearity parameter  $\lambda$  have been presented (Garg and Ruthven, 1972; Fujita, 1952).

Since, for  $\lambda \rightarrow 1.0$  the Langmuir isotherm approaches the rectangular limit one may anticipate that the concentration profiles, and hence the uptake curves predicted from Eqs. (5–7) should converge to the limiting form predicted from the irreversible model. That this is indeed true is illustrated in Fig. 2 in which the uptake curves are plotted as  $m_t/m_\infty$  vs  $\frac{D_0 t^2}{l^2} \cdot \frac{c_0}{q_0}$  (or  $\frac{D_0 t}{R^2} \cdot \frac{c_0}{q_0}$ ), rather than against the more commonly used time parameters  $D_0 t^2/l^2$  or  $D_0 t/R^2$ . It is evident that,  $\lambda > 0.8$  the uptake curves predicted from the Langmuir model do indeed approach the rectangular limit.

For the parallel sided slab the equations are sufficiently simple to allow a direct mathematical proof. Eq. (1) may be solved explicitly for the fractional uptake to obtain:

$$\frac{m_t}{m_\infty} = \sqrt{\frac{2D_0 t}{l^2} \cdot \frac{c_0}{q_s}} \quad (8)$$

It is shown in the Appendix that, for high values of  $\lambda$  ( $\lambda \rightarrow 1.0$ ) the uptake curve for the Langmuir model reduces (approximately) to:

$$\frac{m_t}{m_\infty} = \sqrt{\left( \frac{2}{1-\lambda} \cdot \frac{D_0 t}{K l^2} \right)} \quad (9)$$

Since, for the Langmuir isotherm  $q_0/c_0 = K(1-\lambda)$ , Eq. (9) is evidently equivalent to Eq. (8), so the convergence to the rectangular limit is evident.

The form of the concentration profiles is shown in Fig. 3 at values of the dimensionless time parameter ( $\frac{D_0 t}{l^2} \cdot \frac{c_0}{q_0}$ ) corresponding to 50% fractional uptake. In the rectangular case the profile is a shock front that penetrates with a velocity that decreases inversely with the square root of time. As a result the uptake curve increases linearly with the square root of time over the entire range  $0 < t < \tau$ . In the Langmuir case the profile is of sigmoidal form but again the penetration velocity decreases inversely with the square root of time. However, except in the limit of  $\lambda = 1$  the slope of the uptake curve decreases in the final stages as the two fronts merge at the center of the slab.

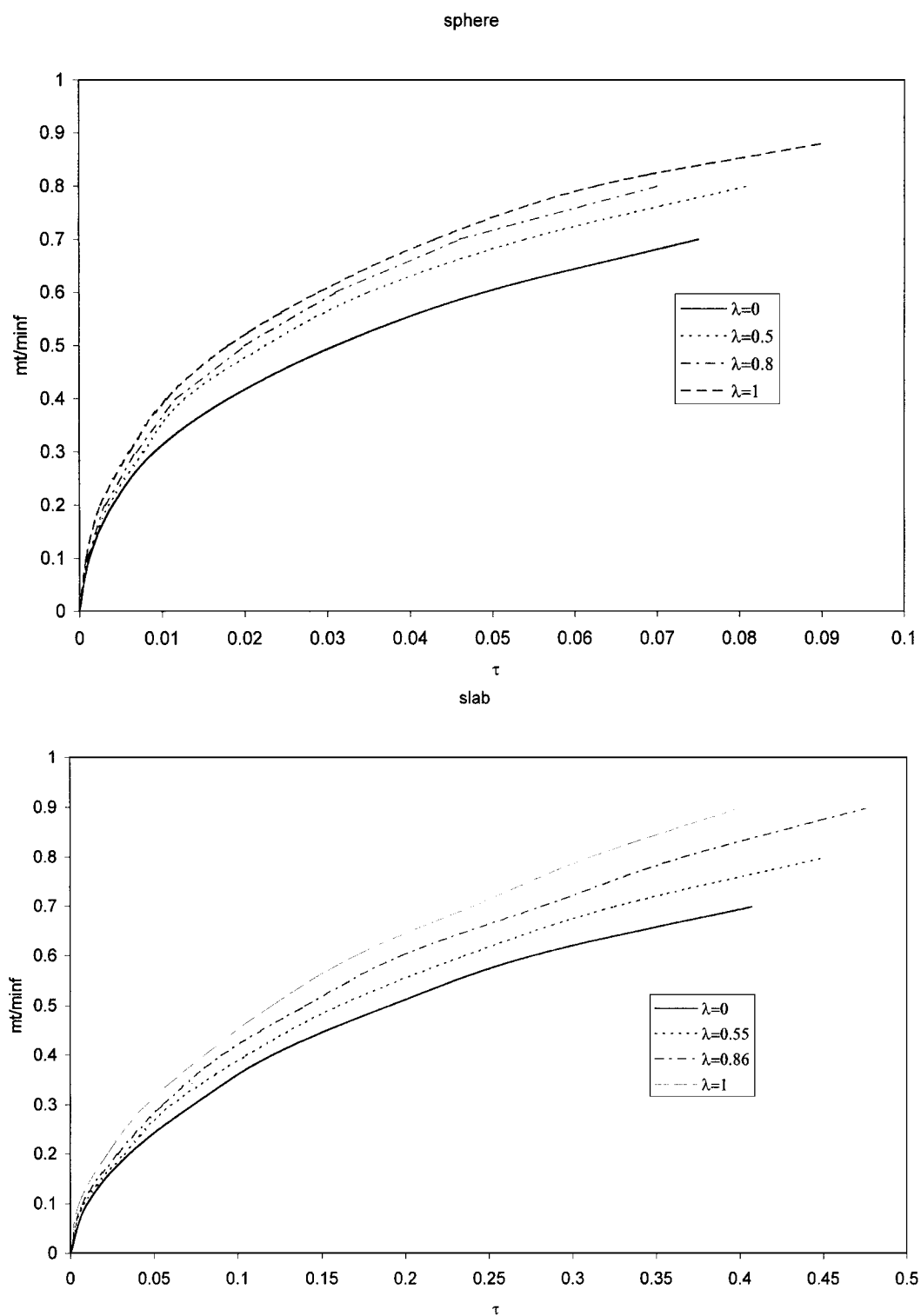


Figure 2. Theoretical uptake curves showing fractional approach to equilibrium as a function of the dimensionless time variable for (a) spherical particles and (b) a parallel sided slab of thickness  $2\ell$ . The curves for the linear system ( $q_0/c_0 = K$ ) are calculated from the expression given by Crank (1956). The curves for the rectangular model are from Eqs. (1) and (2) while the curves for the Langmuir model are from Garg and Ruthven (1972) and Fujita (1952).

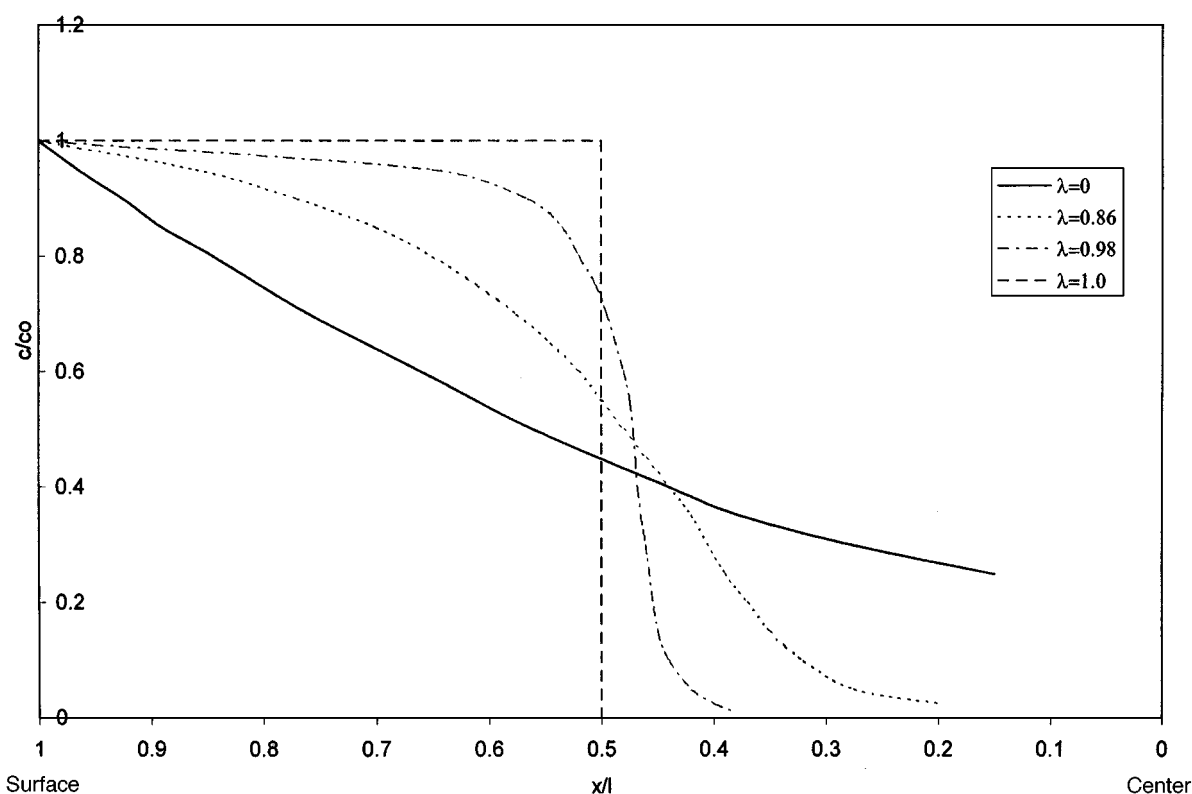


Figure 3. Theoretical concentration profiles at 50% fractional uptake for a parallel sided slab showing the difference in the shape of the profiles for linear, Langmuir and irreversible adsorption isotherms. The curves are calculated at the following values of the dimensionless time parameter corresponding to 50% uptake:

$\lambda$	$D_0 t c_0 / \ell^2 q_0$
0 (linear)	0.2
0.86	0.135
0.98	0.128
1.0	0.125

The assumption of isothermal behavior is implicit in this model but it is clear that, in practice, a large step change in adsorbed phase concentration will induce a significant temperature excursion, especially for vapor phase systems. However, when the equilibrium isotherm is highly favorable the effect of a temperature change on the uptake kinetics is minor since it depends only on the temperature dependence of the saturation limit ( $q_s$ ) and the *limiting* diffusivity ( $D_0$ ), both of which are modest. The rectangular model thus remains a valid approximation even under non-isothermal conditions.

The practically important conclusion from this analysis is that when the isotherm is strongly favorable, even if it is not really irreversible, the simple rectangular model provides a useful approximation to the uptake curve.

## Appendix

Diffusion in a semi-infinite medium in which the diffusivity varies with concentration in accordance with Eq. (6) has been studied by Fujita (1952). His solution

for a step change in concentration (0 to  $c_o$ ) at the external surface has been summarized by Crank (1956):

$$C = \frac{c}{c_o} = \frac{f(\theta)}{\lambda[1 - \lambda + f(\theta)]}$$

$$f(\theta) = \sqrt{\pi} \beta e^{\beta^2} \operatorname{erfc}(\theta \beta)$$

$$\lambda = \sqrt{\pi} \beta e^{\beta^2} \operatorname{erfc} \beta$$

$$y = \frac{x}{2\sqrt{D_o t/K}}$$

$$= \frac{\beta}{1 - \lambda} [\{1 - \lambda + f(\theta)\} \theta - \exp[\beta^2(1 - \theta^2)]]$$

The concentration is a function only of the single variable  $y$  and the parameter  $\lambda$ . The profile  $C(\lambda, y)$  is given by the above equation with  $\beta$  and  $\theta$  as intermediate parameters.

For a parallel sided slab the solution for a semi-infinite medium applies until the point at which the concentration waves penetrating from the two surfaces meet at the center. In the limit  $\lambda \rightarrow 1$  these profiles approach the limiting form of a shock front so this solution applies over the entire range from zero to saturation.

The fractional uptake is given by:

$$\frac{m_t}{m_\infty} = 2\sqrt{\frac{D_o t}{K \lambda^2}} \int_{y=0}^{\infty} \frac{c}{c_o} \cdot dy = 2\sqrt{\frac{D_o t}{K \lambda^2}} \int_{\theta=1}^{\infty} C \cdot \frac{dy}{d\theta} \cdot d\theta$$

Substituting for  $C$  and  $dy/d\theta$  and integrating yields for  $\lambda \rightarrow 1$ :

$$\int C \frac{dy}{d\theta} d\theta = \frac{\beta e^{\beta^2}}{\lambda(1 - \lambda)} [\theta \sqrt{\pi} \operatorname{erfc}(\theta \beta) - e^{-(\beta \theta)^2}]_1^{\infty}$$

$$= \frac{\beta}{\lambda}$$

$$\frac{\lambda}{\beta} = \sqrt{\pi} \beta e^{\beta^2} \operatorname{erfc} \beta$$

For larger values of  $\beta$  (corresponding to  $\lambda \rightarrow 1.0$ ) we may use the series approximation:

$$\frac{\lambda}{\beta} = \sqrt{\pi} \beta e^{\beta^2} \operatorname{erfc} \beta = 1 - \frac{1}{2\beta^2}$$

$$\beta = \frac{1}{\sqrt{2(1 - \lambda)}}$$

so  $\frac{m_t}{m_\infty} = \sqrt{\frac{2}{1 - \lambda}} \cdot \sqrt{\frac{D_o t}{K \lambda^2}}$  the same as for the irreversible model.

## Notation

$b$	Langmuir equilibrium constant
$c$	fluid phase concentration
$c_o$	fluid phase concentration in feed
$D$	diffusivity
$D_o$	limiting diffusivity at low sorbate concentration
$D_e$	effective (concentration dependent) diffusivity
$K$	Henry constant ( $= bq_s$ ) based on particle volume
$\ell$	half thickness of slab
$m_t$	mass adsorbed at time $t$
$m_\infty$	mass adsorbed at equilibrium ( $t \rightarrow \infty$ )
$q$	adsorbed phase concentration
$q_o$	adsorbed phase concentration at equilibrium with $c_o$
$q_s$	saturation limit (Langmuir model)
$r$	radial coordinate
$R$	particle radius
$t$	time
$x$	distance (measured from center of slab)
$y$	$x/2\sqrt{D_o t/K}$ dimensionless distance parameter
$\varepsilon_p$	porosity of particle
$\tau$	dimensionless time to saturate slab or particle
$\lambda$	non-linearity parameter ( $= q_o/q_s$ )

## References

- Brauch, V. and E.U. Schlunder, *Chem. Eng. Sci.*, **30**, 540 (1975).  
 Crank, J., *The Mathematics of Diffusion*, Oxford Press, London 1956.  
 Dedrick, R.L. and R.B. Beekman, *Chem. Eng. Prog. Symp. Ser.*, **63**(74), 68 (1967).  
 Fujita, H. *Textile Research Journal*, **22**, 757 (1952).  
 Garg, D.R. and D.M. Ruthven, *Chem. Eng. Sci.*, **27**, 417–423 (1972).  
 Ruthven, D.M. *Principles of Adsorption and Adsorption Processes*, p. 175, John Wiley, New York, 1984.  
 Ruthven, D.M. and R.I. Derrah, *Can. J. Chem. Eng.*, **50**, 743 (1972).  
 Teo, W.K. and D.M. Ruthven, *I and EC Research*, **25**, 17 (1986).