SECOND-ORDER APPROXIMATION OF INTRAPARTICLE MASS TRANSFER RATE IN ADSORPTION PROCESSES

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Abstract. A second-order approximation of adsorbate uptake rate is presented. The derivation of this approximation is based on the methodology developed by Georgiou & Kupiec (1996). Computations have been performed for different pellet geometries and boundary conditions for which analytical solutions are available. The results obtained are of high accuracy, significantly improving on other available approximations. An illustration of the application of the new model for kinetic parameters estimation is presented.

1. INTRODUCTION

Modeling of many transient mass and/or heat transfer processes leads to coupled partial differential equations involving time and spatial variables. The unsteady-state diffusion and adsorption in particles is described by the following equation.

$$a\frac{\partial Q}{\partial t} = D\frac{1}{r^{m-1}}\frac{\partial}{\partial r}\left(r^{m-1}\frac{\partial Q}{\partial r}\right). \tag{1.1}$$

The meaning of variables and parameters in (1.1) depends on the diffusion model and is given in Table 1 below.

Table 1. Definitions of variables and parameters in diffusion model (1.1)

Variables / Parameters	Pore diffusion model	Solid diffusion model
Q	C	q
D	D_p	D_s
a	$\varepsilon_p + K$	1

Analytical solutions of equation (1.1) are available (Crank 1956) for a number of initial and boundary conditions. These solutions are often in the form of infinite series and are not easy to use. The substantial simplification of computations is achieved by the use of driving-force approximations of the form

$$\frac{d\bar{Q}}{dt} = f(Q_R, \bar{Q}) \tag{1.2}$$

and has motivated numerous studies for the development of such models.

The first and most widely used driving-force approximation is the Linear Driving-Force (LDF) approximation suggested by Glueckauf & Coates (1947) as follows.

$$\frac{dA}{d\tau} = m(m+2)(1-A). \tag{1.3}$$

Glueckauf (1955) presented a justification of the LDF model and a discussion of its applications. Liaw et al. (1979) showed that a LDF model may be derived if a parabolic intraparticle concentration profile is postulated. Yao (1991) and Yao & Tien (1992) showed that the LDF approximation is equivalent to solving the intraparticle diffusion equation by the least-squares method with a parabolic concentration profile. A detailed analysis of the applications and limitations of the LDF approximation is given (for example) in Hills (1986) and Yang (1987). Nevertheless, it is important to note that the parabolic profile leads to a physical inconsistency: for $\tau < 0.061$ a portion of the concentration profile is negative (Do & Mayfield 1987). Furthermore the results for $\tau < 0.05$ are underestimated (Do & Rice 1986).

Do & Rice (1986) suggested a quartic profile approximation. The solution in this case is valid for $\tau > 0.015$. Yao (1991) obtained the best (in least-squares sense) uptake rate expression corresponding to the quartic profile approximation. The expression was found to be accurate at large time but still underestimated the uptake rate at small times.

Tomida & McCoy (1987) considered a polynomial concentration profile of the form

$$C(r,t) = \sum_{n=0}^{N} a_{2n}(t) r^{2n} \tag{1.4}$$

and showed that as the degree of the polynomial increases indefinitely, the polynomial profile equates to the exact solution.

Buzanowski & Yang (1989) derived an extended linear driving-force approximation based on a cubic intraparticle concentration profile. The extra coefficient in this case is an adjustable parameter. This approximation is valid both for large and small times. However, Kikkinides & Yang (1993) have shown that the cubic profile is mathematically unacceptable to satisfy equation (1.1).

Vermeulen (1953) formulated the following QDF approximation.

$$\frac{d\overline{Y}}{d\tau} = \pi^2 \frac{Y_1^2 - \overline{Y}^2}{2\overline{Y}}. \tag{1.5}$$

Do & Mayfield (1987) considered the following intraparticle concentration profile.

$$Q = a_0 + a_n x^n, \tag{1.6}$$

where, a_0, a_n and n are functions of time. This profile approximation leads to a Quadratic Driving-Force (QDF) expression for the uptake rate:

$$\frac{dA}{d\tau} = 9[(1-A) + 0.533\frac{(1-A)^2}{A}], \tag{1.7}$$

resembling Vermeulen's (1953) QDF model (equation 1.5). Model (1.7) is valid for $\tau > 0.003$.

Do & Mayfield (1987) mention that profile (1.6) leads to a physical inconsistency: for non-even values of n, the symmetry of the concentration field at the particle center is violated.

Yao & Tien (1993) presented new approximations of the uptake rate that are valid both at small and large times. These approximations were obtained by making the assumption that the significant part of the concentration profile within a pellet may be represented by a parabolic profile over a spatial domain that expands with time. This profile is given by

$$Q - Q_0 = \begin{cases} a_0 + a_1 r + a_2 r^2, & R-\delta \le r \le R \\ 0, & 0 \le r \le R-\delta \end{cases} \tag{1.8}$$

where a_0, a_1, a_2 and δ (the concentration layer thickness) are functions of time.

Georgiou & Kupiec (1995) applied an exponential approximation of the intraparticle concentration profile and developed a new driving-force model given by following equation.

$$\frac{dA}{d\tau} = (\pi^2 + \frac{18}{\pi}\frac{1-A}{A})(1-A). \tag{1.9}$$

The same authors presented a new methodology for the derivation of driving-force approximations based on an analysis of exact analytical solutions for the particular case of negligible external mass-transfer resistances. This methodology allowed for the derivation of approximate models for all basic pellet geometries (Georgiou & Kupiec 1996).

The purpose of the work presented here is to obtain a second-order driving force approximation using the methodology of Georgiou & Kupiec (1996). It is shown that the model obtained is (analytically) integrable and is applicable to all three basic pellet geometries, namely: slab, infinite cylinder and sphere. A substantial superiority on the accuracy of the new model as compared with other available approximations is demonstrated.

2. MODEL OF THE PROCESS. EXACT SOLUTIONS AND APPROXIMATIONS

We consider the case of a particle with a uniform initial concentration Q_0 subject to a unit-step change of the concentration at $r = R$. In this case, the system is described by equation (1.1) with the following initial and boundary conditions.

$$t = 0, \qquad Q = Q_0; \tag{2.1a}$$

$$r = 0, \qquad \frac{\partial Q}{\partial r} = 0; \tag{2.1b}$$

$$r = R, \qquad Q = Q_R. \tag{2.1c}$$

The following change of variables in (1.1) and (2.1):

$$Y = \frac{Q - Q_0}{Q_R - Q_0}, \qquad x = \frac{r}{R} \qquad \text{and} \qquad \tau = \frac{D}{R^2 a} t$$

leads to equation

$$\frac{\partial Y}{\partial \tau} = \frac{1}{x^{m-1}} \frac{\partial}{\partial x} \left(x^{m-1} \frac{\partial Y}{\partial x}\right), \tag{2.2}$$

with conditions

$$\tau = 0, \qquad Y = 0; \tag{2.3a}$$

$$x = 0, \qquad \frac{\partial Y}{\partial x} = 0; \tag{2.3b}$$

$$x = 1, \qquad Y = 1. \tag{2.3c}$$

The analytical solution in this case (Crank 1956) is given by

$$A = 1 - 2m\sum_{n=1}^{\infty} a_n^{-2} e^{-a_n^2 \tau}, \tag{2.4}$$

where a_n depend on the pellet geometry and A is the volume-averaged value of Y, i.e.

$$A = \frac{m_t}{m_\infty} = \frac{\iiint_V Y dV}{\iiint_V dV}. \tag{2.5}$$

At short times, upon a step change, the particle may be treated as a semi-infinite medium and this assumption leads to the following approximation (Crank 1956).

$$A = 2m\sqrt{\frac{\tau}{\pi}}, \tag{2.6}$$

applicable for $\tau < 0.01$. At large times, the series in equation (2.4) converges rapidly and, by retaining only the first term, the fractional uptake can be estimated with satisfactory accuracy.

Following the methodology of Georgiou & Kupiec (1996), we define the following function.

$$F(\tau) = \frac{dA / d\tau}{1 - A} \tag{2.7}$$

or, equivalently (using 2.4)

$$F(\tau) = \frac{\sum_{n=1}^{\infty} e^{-a_n^2 \tau}}{\sum_{n=1}^{\infty} a_n^{-2} e^{-a_n^2 \tau}}. \tag{2.8}$$

Then, it is not difficult to show that

$$\lim_{\tau \to \infty} F(\tau) = a_1^2. \tag{2.9}$$

(Note that since $F = F(\tau)$ and $A = A(\tau)$, we can obtain dependency $F = F(A)$).

We next define another function as follows.

$$G(\tau) = (\frac{dA/d\tau}{1-A} - a_1^2)\frac{A}{1-A}. \tag{2.10}$$

It follows (using 2.6) that

$$G_0 = \lim_{\tau\to 0} G(\tau) = \frac{2m^2}{\pi} \tag{2.11}$$

and (using 2.10)

$$\lim_{\tau\to\infty} G(\tau) = 0. \tag{2.12}$$

In figure 1 below is shown the dependency $G = G(A)$ for the three basic pellet geometries.

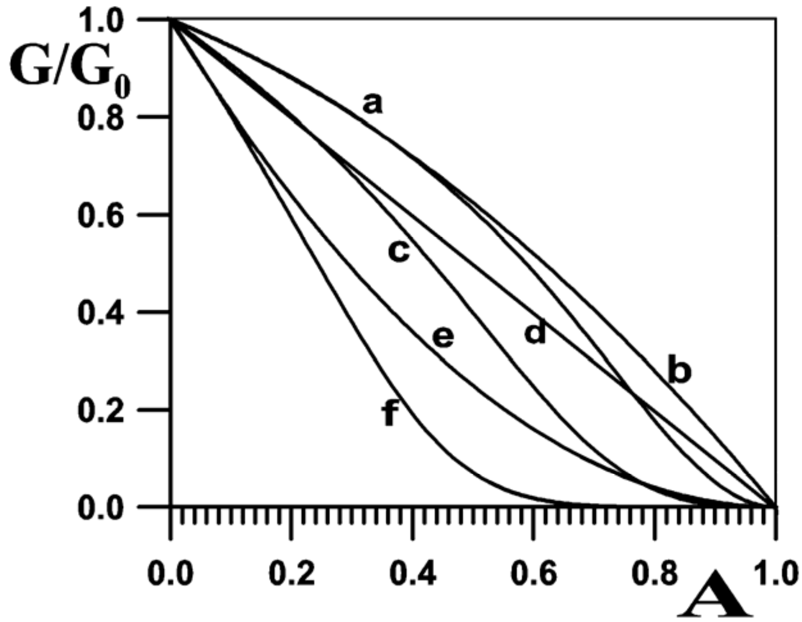

Fig. 1: Comparison of exact and approximate G(A) functions.
(a) Exact - sphere, (b) approximate - sphere, (c) exact - cylinder, (d) approximate - cylinder,
(e) exact - slab, (f) approximate - slab.

Some earlier published approximations along with a proposed second-order approximation may be considered as resulting from suitable approximations of function $G(A)$.

A. Zeroth-order approximations

I. Linear driving-force approximation

The LDF model is equivalent to the approximation

$$G(A) \approx 0. \tag{2.13}$$

II. Vermeulen's QDF approximation

The QDF model (equation 1.7) is applicable only to spherical particles and it is equivalent to the approximation

$$G(A) \approx \frac{\pi^2}{2} \approx 4.934. \tag{2.14}$$

III. Do and Mayfield approximation

The DM model (equation 1.5) is applicable only to spherical particles and it is equivalent to the approximation

$$G(A) \approx 4.797. \tag{2.15}$$

IV. Georgiou and Kupiec approximation

The GK model (equation 1.8) is also applicable only to spherical particles and it is equivalent to the approximation

$$G(A) = \frac{18}{\pi}. \tag{2.16}$$

B. First-order approximation

Georgiou & Kupiec (1996) developed the following first-order approximation (see figure 1).

$$\frac{dA}{d\tau} = \{\alpha_1^2 + \frac{2m^2}{\pi}\frac{(1-A)^{2,}}{A}\}(1-A). \tag{2.17}$$

This is equivalent to

$$G(A) = \frac{2m^2}{\pi}(1 - A). \tag{2.18}$$

C. Second-order approximation

A second-order approximation of function $G(A)$ is now proposed as follows.

$$G(A) \approx \frac{2m^2}{\pi}[1 + \frac{2(m-2)}{m+1}A](1 - A). \tag{2.19}$$

A comparison of this second-order approximation with the exact function (2.10) is shown in figure 1.

The resulting driving-force model is therefore given by equation

$$\frac{dA}{d\tau} = \{\alpha_1^2 + \frac{2m^2}{\pi}[1 + \frac{2(m-2)}{m+1}A]\frac{(1-A)^{2,}}{A}\}(1 - A) \tag{2.20}$$

with initial condition $A(0) = 0$.

3. ANALYTICAL SOLUTION

The proposed model (2.20) may be solved analytically as follows.

Introducing $z = 1 - A$, (2.20) yields

$$(1 - z)\frac{dz}{d\tau} = MzP(z) \quad \text{(with } z(0) = 1\text{)}, \tag{3.1}$$

where

$$M = \frac{4m^2(m-2)}{\pi(m+1)}, \quad \mu = \frac{3(m-1)}{2(m-2)}$$

and

$$P(z) = z^3 - \mu z^2 + \frac{\alpha_1^2}{M}z - \frac{\alpha_1^2}{M}, \tag{3.2}$$

on condition

$$m \neq 2. \tag{3.3}$$

The first root of cubic polynomial $P(z)$ is given by

$$z_1 = S + T + \frac{1}{3}\mu,$$

where

$$S = \sqrt[3]{V + \sqrt{U^3 + V^2}}, \quad T = \sqrt[3]{V - \sqrt{U^3 + V^2}},$$

$$U = \frac{\alpha_1^2}{3M} - \frac{1}{9}\mu^2 \quad \text{and} \quad V = -\frac{\mu\alpha_1^2}{6M} + \frac{\alpha_1^2}{2M} + \frac{1}{27}\mu^3.$$

It follows polynomial (3.2) may be factorized as

$$P(z) = (z - z_1)[z^2 + (z_1 - \mu)z + \frac{\alpha_1^2}{M} + W],$$

where

$$W = (S + T)^2 - \frac{1}{3}(S + T)\mu - \frac{2}{9}\mu^2.$$

Now, separation of variables in (3.1) yields

$$\int d\tau = \int \frac{M^{-1}(1-z)}{zP(z)}dz = \int \frac{M^{-1}(1-z)}{z(z-z_1)[z^2 + (z_1 - \mu)z + \alpha_1^2 / M + W]}dz. \tag{3.4}$$

Decomposing the integrand in right-hand side of (3.4) into partial fractions yields

$$\frac{M^{-1}(1-z)}{z(z-z_1)[z^2 + (z_1 - \mu)z + \alpha_1^2 / M + W]} = \frac{B_1}{z} + \frac{B_2}{z - z_1} + \frac{B_3 z + B_4}{z^2 + (z_1 - \mu)z + \alpha_1^2 / M + W},$$

where

$$B_1 = -\frac{1}{M(\alpha_1^2/M+W)z_1},$$

$$B_2 = \frac{1-z_1}{Mz_1(z_1^2+(z_1-\mu)z_1+\alpha_1^2/M+W},$$

$$B_3 = -\frac{1}{M(1+z_1)} - B_1(1+\alpha_1^2/M+W) + \frac{1}{1-z_1^2}B_2[1+(z_1-\mu)z_1+\alpha_1^2/M+W],$$

and

$$B_4 = \frac{1}{M(1+z_1)} - B_1(z_1-\mu) - \frac{1}{1-z_1^2}B_2[z_1+(z_1-\mu)+(\alpha_1^2/M+W)z_1].$$

It then follows that (3.4) yields,

$$\tau = \Phi(z) \tag{3.5}$$
$$\equiv B_1 \ln|z| + B_2 \ln|z-z_1| + \frac{1}{2}B_3 \ln|z^2+(z_1-\mu)z+\frac{\alpha_1^2}{M}+W| + \frac{B_5}{B_6}\tan^{-1}\frac{2z-(z_1-\mu)}{2B_6} + \kappa,$$

where

$$B_5 = B_4 - \frac{1}{2}(z_1-\mu)$$

and

$$B_6^2 = \alpha_1^2/M+W-\frac{1}{4}(z_1-\mu)^2 \quad \text{(with condition } B_6^2>0).$$

4. SPECIAL CASES

We now consider the second-order model (2.20) for the three basic pellet geometries.

4.1. Slab

A slab corresponds to parameter values $m = 1$ and $\alpha_1 = 0.5\pi$ in equation (2.20). As result, we obtain the following table of values for each of the coefficients that arose in the analysis of section 3.

It follows that (3.5) (with substitution $A = 1 - z$ and initial condition $A(0) = 0$) becomes

$$\tau = -0.405 \ln|1-A| + 0.176 \ln|3.350-A| + 0.114 \ln|A^2 - 4.350A + 4.999|$$

$$+ 0.281 \tan^{-1} \frac{-0.175-A}{0.517} - 5.181. \qquad (4.1)$$

Table 2. Coefficient values for slab (m = 1 and α_1 = 0.5π)

Coefficient	Numerical value
M	–0.5π = –0.636620
U	–1.291928
V	–1.937892
S	–0.876485
T	–1.473988
μ	0
z_1	–2.350473
W	$(S+T)^2 = z_1^2 = 5.524723$
B_1	–0.405284
B_2	0.176328
B_3	0.228955
B_4	–0.123698
B_5	0.145378
B_6	$\sqrt{0.517455} = 0.267759$

4.2. Sphere

A sphere corresponds to parameter values m = 3 and $\alpha_1 = \pi$ in equation (2.20). As result, we obtain the following table of values for each of the coefficients that arose in the analysis of section 3.

Table 3. Coefficient values for sphere (m = 3 and α_1 = π)

Coefficient	Numerical value
M	9/π = 2.864789
U	0.148381
V	1
S	1.260264
T	–0.117738
μ	1
z_1	2.142526

W	$(S+T)^2-(S+T)-2=-1.837160$
B_1	–0.101321
B_2	–0.091446
B_3	0.267066
B_4	–0.192555
B_5	–0.078054
B_6	$\sqrt{1.424167}=1.193385$

It follows that (3.5) (with substitution $A = 1 - z$ and initial condition $A(0) = 0$) becomes

$$\tau = -0.101\ln|1-A| - 0.091\ln|-1.143-A| + 0.134\ln|A^2-1.143A+1.751|$$

$$+\,0.065\tan^{-1}\frac{1.429-A}{1.193} - 3.216. \tag{4.2}$$

4.3. Cylinder

A cylinder corresponds to parameter values $m = 2$ and $\alpha_1 = 2.4048$ in equation (2.20). This is a degenerate case (see condition 3.3) for the analysis of section 3, as parameter $\mu \to \infty$. Hence, a separate analysis must be followed.

The model equation (2.20) becomes

$$\frac{dA}{d\tau} = \{\alpha_1^2 + \frac{8}{\pi}\frac{(1-A)^2}{A}\}(1-A), \tag{4.3}$$

with initial condition $A(0) = 0$, or ($z = 1 - A$)

$$-(1-z)\frac{dz}{d\tau} = zP_c(z) \quad \text{(with } z(0) = 1\text{)}, \tag{4.4}$$

where

$$P_c(z) = \frac{8}{\pi}z^2 - \alpha_1^2 z + \alpha_1^2. \tag{4.5}$$

Note that $P_c(z)$ may have real roots for $\alpha_1^2 \geq \frac{32}{\pi}$. Hence, for the cylinder case (α_1 = 2.4048) $P_c(z)$ has no real root.

Now, separation of variables in (4.4) yields

$$\int d\tau = \int \frac{-(1-z)}{zP(z)}dz = \int \frac{-0.393(1-z)}{z(z^2-2.271z+2.271)}dz. \tag{4.6}$$

Decomposing the integrand in right-hand side of (4.6) into partial fractions yields

$$\frac{-0.393(1-z)}{z(z^2-2.271z+2.271)} = \frac{-0.173}{z} + \frac{0.173z}{z^2-2.271z+2.271}.$$

It then follows that (4.6) (with substitution $A = 1 - z$ and initial condition $A(0) = 0$) yields,

$$\tau = -0.173\ln|1-A| + 0.086\ln|A^2+0.271A+1| + 0.198\tan^{-1}\frac{-0.136-A}{0.991} - 1.543. \tag{4.7}$$

5. COMPARISON BETWEEN THE EXACT AND THE APPROXIMATE MODELS

The validation of approximate models is based on their comparison with the exact solution (equation 2.4). In figure 2 is shown a comparison of the uptake curves for each of the pellet geometries presented in section 4 resulting from the exact and approximate model (2.20). It is evident that the agreement between the two models is very good.

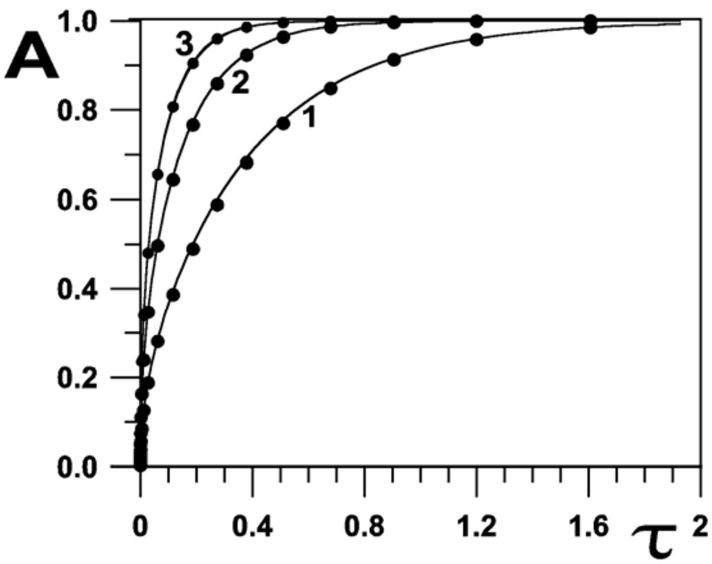

Fig. 2: Comparison of exact and approximate uptake curves.
(• - exact, lines - approximate; 1 - slab, 2 - cylinder, 3 - sphere)

The percent relative errors resulting from the application of model (2.20) are shown in figure 3 for each of the above-mentioned geometries. Note that the maximum error does not exceed 2.5%.

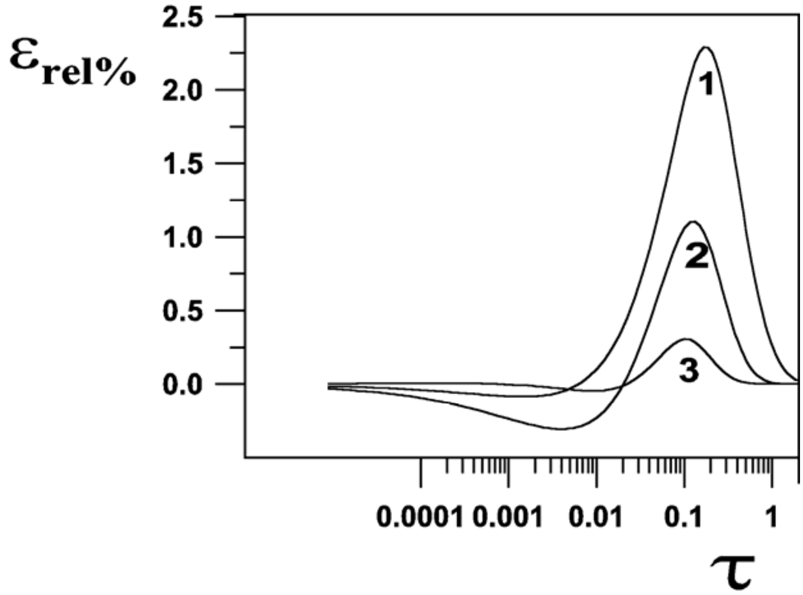

Fig. 3: Percent relative errors resulting from the application of the approximate model.
(1 - slab, 2 - cylinder, 3 - sphere)

For comparison purposes, the percent relative errors resulting from the application of the widely applied LDF model (recall equation 1.3) that yields

$$A_{\mathrm{LDF}} = 1 - e^{-m(m+2)\tau}, \tag{5.1}$$

are shown in figure 4. Observe that the LDF model at small times underestimates the fractional uptakes by more than 80%. This, clearly, indicates that the proposed approximation (2.20) is more suitable than the LDF approximation for the modeling of kinetic separations.

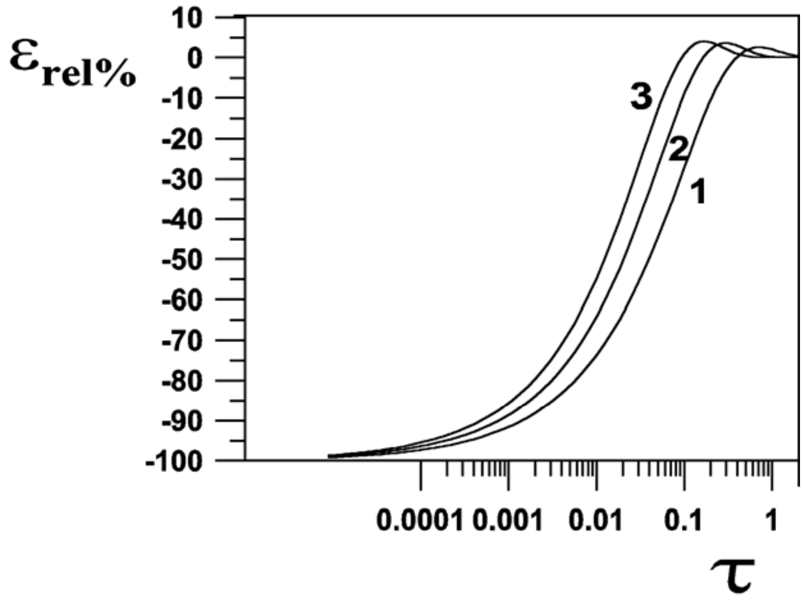

Fig. 4: Percent relative errors resulting from the application of the LDF model. (1 - slab, 2 - cylinder, 3 - sphere)

6. THE APPLICATION OF THE SECOND-ORDER APPROXIMATION IN KINETIC PARAMETER ESTIMATION

An important application of the proposed model is the estimation of kinetic parameters. The resulting analytical solution of the approximate model (see equation 3.5) may be written as

$$\Phi(A) = \frac{D}{R^2 a} t. \tag{6.1}$$

The equation above shows a linear relation between function $\Phi = \Phi(A(\tau))$ and time t, with gradient $\frac{D}{R^2 a}$. The experimental results by Yucel & Ruthren (1980) and Prinz & Riekert (1986) give estimates of this gradient, as shown in figure 5. Based on linear regression, diffusion times $t_d = \frac{R^2 a}{D}$ were found to be t_d = 7037 [s] for nitrogen on zeolite 4A spherical pellets (line 1) and t_d = 604 [s] for benzene on zeolite slab pellets (line 2).

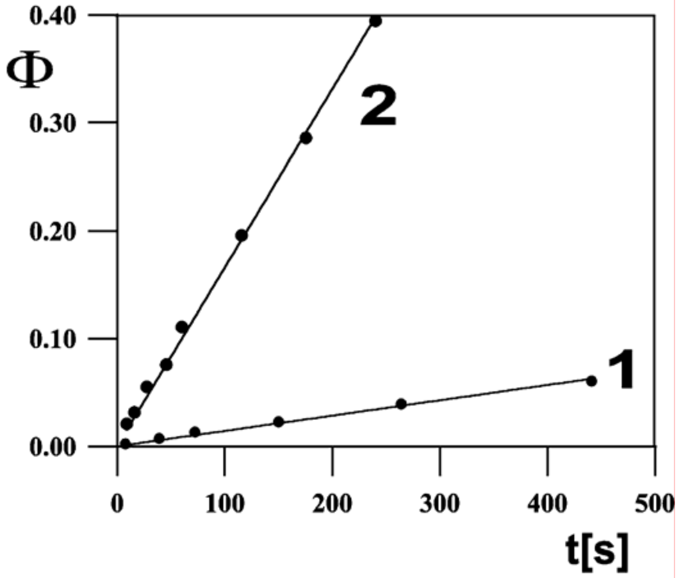

Fig. 5: Estimation of kinetic parameters. (• - experimental, lines - linear regression)
(1 - Yucel & Ruthren (1980), 2 - Prinz & Riekert (1986))

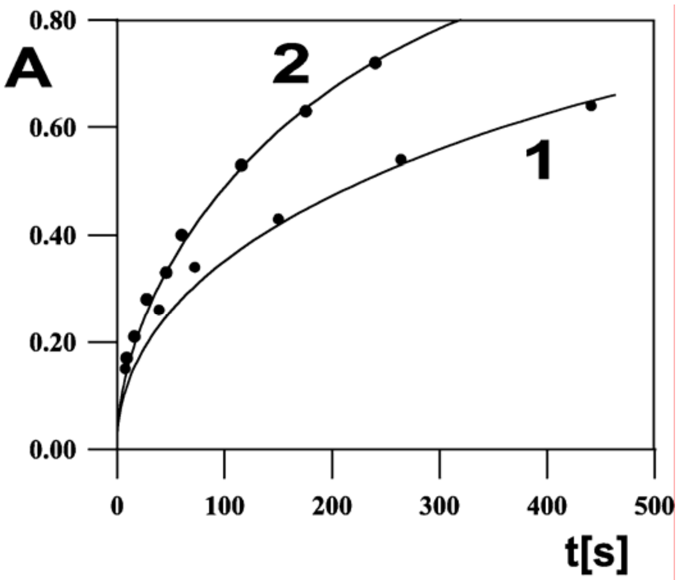

Fig. 6: Comparison of the experimental data with the predictions of the approximate model.(• - experimental, lines – approximate model)
(1 - Yucel & Ruthren (1980), 2 - Prinz & Riekert (1986))

Finally, using the estimated t_d values, the fractional uptake curves were computed for sphere (using equation 4.1) and slab (using equation 4.2). A comparison of the experimental data and the computed fractional uptake curves is shown in figure 6.

7. CONCLUSIONS

In this paper a second-order driving-force approximation of intraparticle mass transfer in adsorption processes with a linear isotherm and negligible external mass transfer resistances has been presented. The derivation of this approximation is based on an analysis of the available analytical solution of the problem, thus resigning from the widely exploited methodology based on intraparticle concentration profile approximations. The obtained approximate expression has been applied to batch adsorption systems for various pellet geometries. The obtained results have been compared with the exact analytical solution of each problem. It has been shown that the maximum errors do not exceed 2.5%, with the accuracy being even better in the small-time region. Furthermore, the proposed model has been applied to kinetic parameters estimation using experimental data from literature. It has been shown that the estimated kinetic parameters may be used for the accurate prediction of the fractional uptake curves.

NOTATION

a defined in Table 1
A fractional uptake
C gas-phase concentration
D defined in table 1
D_p effective pore diffusion coefficient
D_s effective surface diffusion coefficient
K linear equilibrium adsorption constant
m geometry factor
q solid-phase concentration
Q defined in table 1
r radial coordinate
R particle radius
t time
t_d diffusion time
x dimensionless spatial variable
Y dimensionless solid phase concentration

Greek letters

ε percent-relative error
ε_p porosity of particle
τ dimensionless time

Subscripts

0 value at $\tau = 0$
1 value at surface
∞ value at $\tau \to \infty$
R value at $r = R$

Superscripts

$-$ volume-averaged quantity

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