Extension of Moment Analysis to Nonlinear Systems

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The moment method has been used extensively to determine the adsorption equilibrium and rate parameters (Schneider and Smith, 1968a; Suzuki and Smith, 1971; Doğu and Smith, 1976) as well as effective diffusivities in porous catalysts (Doğu and Smith, 1975; Doğu and Ercan, 1983; Schneider and Smith 1968b; Haynes and Sarma, 1973), axial dispersion in fixed beds (Hashimoto and Smith, 1973) fluidized beds (Pamuk and Doğu, 1978) and trickle beds (Eroğlu and Doğu, 1982), and reaction rate constants (Doğu, 1984). The pulse-response method also has been used to evaluate some rate parameters in slurry adsorbers and reactors (Furusawa and Smith, 1973). In such systems adsorbent particles are suspended batchwise and retained in the vessel with continuous steady liquid feed and effluent. Furusawa and Suzuki (1975) derived the moment equations for concentration decay curves of tracer in batch slurry adsorbers. In such slurry adsorbers perfect mixing, and consequently uniform concentration of adsorbate and uniform distribution of suspended particles, was assumed.

The most serious limitation of moment analysis is the application of the method to only linear processes. Many adsorption and reaction processes are not linear. In order to apply the moment technique to such systems, generally very dilute tracer concentrations are used in adsorption studies and linear adsorption isotherms are assumed. Consequently, adsorption parameters are determined for essentially zero surface coverage. The objective of the present study is to develop an iterative technique for the derivation of moment expressions for nonlinear adsorption and reaction processes. The method is illustrated for a slurry adsorber with a nonlinear adsorption process. In the derivations, the system is simplified by neglecting external mass transfer and intraparticle diffusion limitations, although the application of the technique is not limited to such idealized systems.

For a perfectly mixed slurry adsorber in which the tracer is reversibly adsorbed on the suspended particles, the species conservation equation for the tracer is

$$\tau\epsilon_b \frac{dC}{dt} = C_i - C - (1 - \epsilon_b)\,\rho_p S\tau \frac{d\theta}{dt} \tag{1}$$

In this equation, the last term on the righthand side corresponds to the rate of adsorption on the solid phase, and θ is the fraction of the surface covered by the tracer. Generally, the rate of adsorption is considered to be proportional with the concentration of adsorbate and the fraction of the surface that is not occupied. The rate of desorption is proportional to the adsorbed phase concentration. For a reversible adsorption process, the rate of change of surface coverage with respect to time can be expressed as

$$\frac{d\theta}{dt} = k_1 C(1 - \theta) - k_{-1}\theta = k_1\left[C - C\theta - \frac{1}{K}\theta\right] \tag{2}$$

In Eq. 2, the second term on the righthand side is the nonlinear term, and this term is generally neglected in the moment analysis of such systems, assuming $\theta \ll 1$ for dilute systems.

Consider a system with zero initial tracer concentration. A pulse of adsorbate is introduced to the inlet of the slurry adsorber at zero time.

$$C_i = M\delta(t) \tag{3}$$

The derivation of the moment expressions requires the simultaneous solution of Eqs. 1 and 2 in the Laplace domain.

$$(\epsilon_b s\tau + \lambda + 1)\bar{C} = M + \frac{\lambda}{K}\bar{\theta} + \lambda\,\overline{C\theta} \tag{4}$$

$$s\bar{\theta} = k_1\bar{C} - \frac{k_1}{K}\bar{\theta} - k\overline{C\theta} \tag{5}$$

Here, λ is defined as,

$$\lambda = (1 - \epsilon_b)\,\rho_p S k_1 \tau \tag{6}$$

The zeroth approximation of the solution of $\bar{C}$, $\bar{\theta}$ was derived neglecting terms containing $\overline{C\theta}$ (assuming linear adsorption).

$$\overline{C}_0 = \frac{M\left(s + \frac{k_1}{K}\right)}{(\epsilon_b s\tau + \lambda + 1)\left(s + \frac{k_1}{K}\right) - \lambda\frac{k_1}{K}} \tag{7}$$

$$\overline{\theta}_0 = \frac{k_1 M}{(\epsilon_b s\tau + \lambda + 1)\left(s + \frac{k_1}{K}\right) - \lambda\frac{k_1}{K}} \tag{8}$$

Using the definition of moments,

$$m_n = \int_0^\infty C(t)t^n\,dt = (-1)^n \lim_{s\to 0}\frac{d^n\overline{C}(s)}{ds^n} \tag{9}$$

$$\mu_1 = \frac{m_1}{m_0}, \tag{10}$$

the zeroth approximation of the first moment expression for this system was found to be

$$\mu_{1,0} = \psi_1\tau \tag{11}$$

where

$$\psi_1 = (\epsilon_b + (1 - \epsilon_b)\rho_p SK) \tag{12}$$

The zeroth approximations of $\overline{C}$, $\overline{\theta}$ and the first moment were then corrected, evaluating the $\overline{C\theta}$ term using the zeroth solutions (Eqs. 7 and 8) and substituting this into Eqs. 4 and 5. Simultaneous solution of Eqs. 4 and 5 gives the corrected solution (first correction). The procedure can be repeated a number of times and the solutions might be further improved.

In this procedure, the following property of the Laplace transformation is used. The Laplacian of the product of two functions can be evaluated from

$$L[f_1(t)f_2(t)] = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} F_1(p)F_2(s-p)\,dp \tag{13}$$

$$= \sum_{k=1}^{q} (\mathrm{Res}\,[F_1(p)F_2(s-p)])_{p=s_k}\ [\text{at poles of } F_1(p)] \tag{14}$$

where $F_i(s)$ is the Laplacian of $f_i(t)$, c is a line parallel to the imaginary axis and to the right of all the singularities of the integrand, and q is the number of poles (Robert and Kaufman, 1966; McCollum, 1965). If $F(p)$ is not finite at $p = s_k$ but if for some integer m the product $(p - s_k)^m F(p)$ is analytic at $p = s_k$, then $p = s_k$ is called a pole of $F(p)$. The integer m is called the order of the pole. The residual of a function $(F_1(p)F_2(s - p)$ in our case) at a given pole $p = s_k$ can be evaluated from (Hildebrand, 1962):

$$\mathrm{Res}\,[F_1(p)F_2(s-p)]_{p=s_k} = \frac{1}{(m-1)!}\left\{\frac{d^{m-1}}{dp^{m-1}}[(p-s_k)^m F_1(p)F_2(s-p)]\right\}_{p=s_k} \tag{15}$$

For a first-order pole ($m = 1$), Eq. 15 reduces to

$$\mathrm{Res}\,[F_1(p)F_2(s-p)]_{p=s_k} = \lim_{p\to s_k}(p-s_k)F_1(p)F_2(s-p) \tag{16}$$

If $F_1(p)$ is a rational function,

$$F_1(p) = \frac{T_1(p)}{G_1(p)} \tag{17}$$

and has only q first-order poles, then Eq. 14 reduces to

$$L[f_1(t)f_2(t)] = \sum_{k=1}^{q}\frac{T_1(s_k)}{G_1'(s_k)}F_2(s-s_k) \tag{18}$$

where G_1' is the derivative of $G_1(p)$ with respect to p.

Using Eqs. 14–18, the zeroth approximation of $L(C\theta) = \overline{C\theta}$ was then evaluated from

$$L(C\theta) = \sum_{k=1}^{q}\{\mathrm{Res}\,[\overline{C}_0(p)\,\overline{\theta}_0(s-p)]\}_{p=s_k} \tag{19}$$

The poles of $\overline{C}_0(p)$ are

$$s_1 = -A + B \tag{20}$$

$$s_2 = -A - B \tag{21}$$

where

$$A = \frac{\left(\frac{k_1}{K}\epsilon_b\tau + \lambda + 1\right)}{2\epsilon_b\tau} \tag{22}$$

$$B = \frac{\left[\left(\frac{k_1}{K}\epsilon_b\tau + \lambda + 1\right)^2 - 4\epsilon_b\tau\frac{k_1}{K}\right]^{1/2}}{2\epsilon_b\tau} \tag{23}$$

The zeroth approximation of $L(C\theta)$ is

$$\overline{(C\theta)}_0 = \frac{M^2\left(-A + B + \frac{k_1}{K}\right)k_1}{(X+Y)(Z-F)} + \frac{M^2\left(-A - B + \frac{k_1}{K}\right)k_1}{(X-Y)(Z+F)} \tag{24}$$

where

$$X = -2\,\epsilon_b\tau A + \frac{k_1}{K}\epsilon_b\tau + \lambda + 1 \tag{25}$$

$$Y = 2\,\epsilon_b\tau B \tag{26}$$

$$Z = \epsilon_b\tau(s^2 + A^2 + B^2 + 2sA) + \left(\frac{k_1}{K}\epsilon_b\tau + \lambda + 1\right)(s + A) + \frac{k_1}{K} \tag{27}$$

$$F = \epsilon_b\tau(2AB + 2Bs) + \left(\frac{k_1}{K}\epsilon_b\tau + \lambda + 1\right)B \tag{28}$$

By substituting $(\overline{C\theta})_0$ from Eq. 24 into Eqs. 4 and 5, corrected solutions for $\overline{C}$ and $\overline{\theta}$ were evaluated.

$$\overline{C}_1 = \frac{M\left(s + \frac{k_1}{K}\right) + s\lambda\left[\frac{M^2\left(-A + B + \frac{k_1}{K}\right)k_1}{(X+Y)(Z-F)} + \frac{M^2\left(-A - B + \frac{k_1}{K}\right)k_1}{(X-Y)(Z+F)}\right]}{(\epsilon_b \tau s + \lambda + 1)\left(s + \frac{k_1}{K}\right) - \frac{k_1}{K}\lambda} \qquad (29)$$

The corrected first and second absolute moment expressions were then evaluated as

$$\mu_{1,1} = \frac{m_1}{m_0} = \psi_1\tau - \frac{1}{2}(MK)\frac{\frac{k_1}{K}\psi_2\tau}{\left(\frac{k_1}{K}\psi_1\tau + 1\right)} \qquad (30)$$

$$\mu_{2,1} = \frac{m_2}{m_0} = 2\left[(\psi_1\tau)^2 + \psi_2\tau\frac{K}{k_1}\right] - \frac{1}{2}(MK)\frac{\psi_2\tau\left[3\left(\frac{k_1}{K}\psi_1\tau + 1\right)^2 - \left(\frac{k_1}{K}\psi_1\tau + 1\right) + 2\left(\frac{k_1}{K}\psi_1\tau - \frac{k_1}{K}\psi_2\tau\right)\right]}{\left(\frac{k_1}{K}\psi_1\tau + 1\right)^2} \qquad (31)$$

where

$$\psi_2 = (1 - \epsilon_b)\rho_p SK \qquad (32)$$

Comparison of Eq. 11 with Eq. 30 shows that the correction term corresponding to the nonlinearity (the second term in the first moment expression in Eq. 30) contains the adsorption rate constant in addition to the adsorption equilibrium constant.

If the adsorption rate is very fast, the adsorbed phase concentration of the adsorbent can be assumed to be in equilibrium with the fluid phase concentration at any instant. Considering a Langmuir-type adsorption isoterm, the fraction of the surface covered by the adsorbent can then be expressed as

$$\theta = \frac{KC}{1 + KC} \qquad (33)$$

By making a Taylor expression, this Langmuir isotherm can be approximated as

$$\theta = KC - K^2C^2 \qquad (34)$$

for not very large deviations from linearity. This assumption requires that KC be small. Using this expression in Eq. 1, a nonlinear equation is obtained for $\overline{C}$. Using the same procedure as outlined for the reversible adsorption process, the first and second moment expressions were derived considering the nonlinear term. Zeroth, first, and second approximations for the moment expressions were derived. The second approximation of the first and second absolute moment expressions are

$$\mu_{1,2} = \psi_1\tau - (MK) \cdot \left[\frac{1}{2}\frac{\psi_2}{\psi_1} + \frac{1}{3}\left(\frac{\psi_2}{\psi_1}\right)^2\left(\frac{MK}{\psi_1\tau}\right) + \frac{1}{6}\left(\frac{\psi_2}{\psi_1}\right)^3\left(\frac{MK}{\psi_1\tau}\right)^2\right] \qquad (35)$$

$$\mu_{2,2} = 2(\psi_1\tau)^2 - (MK)(\psi_1\tau) \cdot \left[\frac{3}{2}\left(\frac{\psi_2}{\psi_1}\right) + \frac{5}{9}\left(\frac{\psi_2}{\psi_1}\right)^2\left(\frac{MK}{\psi_1\tau}\right) + \frac{4}{9}\left(\frac{\psi_2}{\psi_1}\right)^3\left(\frac{MK}{\psi_1\tau}\right)^2\right] \qquad (36)$$

These equations are very similar to the moment expressions derived by the perturbation method suggested by McCoy and coworkers (Allal et al., 1985).

The first terms of Eq. 35 and the first moment expression for reversible adsorption (Eq. 30) correspond to a linear adsorption process. For linear adsorption, the first moment expressions for reversible and equilibrium adsorption are identical.

The second term of Eq. 35 corresponds to the second term of Eq. 30, and as expected for a fast adsorption process these terms take the same form [for $(k_1/K)\ \psi_1\tau > 1$]. The third and fourth terms in the moment expressions given in Eqs. 35 and 36 correspond to the second-order corrections of the first and second absolute moments for nonlinearity. An examination of first moment expressions for nonlinear adsorption processes reveals that overestimated values of the adsorption equilibrium constants would be obtained if a nonlinear adsorption process were approximated by a linear adsorption isotherm. The error introduced to the first moment analysis by this assumption can be predicted from.

$$\frac{(\mu_1)_{\text{linear}} - (\mu_1)_{\text{nonlinear}}}{(\mu_1)_{\text{linear}}} = \frac{1}{2}\left(\frac{MK}{\psi_1\tau}\right)\left(\frac{\psi_2}{\psi_1}\right) + \frac{1}{3}\left(\frac{MK}{\psi_1\tau}\right)^2\left(\frac{\psi_2}{\psi_1}\right)^2 + \frac{1}{6}\left(\frac{MK}{\psi_1\tau}\right)^3\left(\frac{\psi_2}{\psi_1}\right)^3 \qquad (35)$$

The procedure outlined here can be applied to the analysis of many nonlinear processes. For instance, moment expressions for systems with significant external and intraparticle diffusion limitations might also be derived considering nonlinear adsorption or reaction terms.

Notation

A = defined by Eq. 22
B = defined by Eq. 23
C = concentration of tracer, mol/cm^3
C_i = concentration of tracer at adsorber inlet, mol/cm^3
$\overline{C}$ = Laplace transform of function $C(t)$
$f(t)$ = a time-dependent function
$F(s)$ = Laplace transform of function $f(t)$
F = defined by Eq. 28
K = adsorption equilibrium constant, (mol/cm^3)$^{-1}$
k_1 = adsorption rate constant, (mol/cm^3)$^{-1}$ · s^{-1}
k_{-1} = desorption rate constant, s^{-1}
M = strength of input pulse, mol · s/cm^3
m_n = nth moment about origin, Eq. 9
s = Laplace variable, s^{-1}
s_k = kth pole of function $F(s)$, s^{-1}
S = adsorbed concentration at complete coverage of surface, mol/g

t = time, s
x = defined by Eq. 25
Y = defined by Eq. 26
Z = defined by Eq. 27

Greek letters

$\delta(t)$ = Dirac delta pulse, s^{-1}
ϵ_b = fraction of adsorber occupied by liquid phase
ψ_1 = defined by Eq. 12
ψ_2 = defined by Eq. 32, $(mol/cm^3)^{-1}$
λ = defined by Eq. 6
μ_1 = first absolute moment, m_1/m_0, s
$\mu_{1,i}$ = ith approximation of first absolute moment, s
ρ = density of the solid particles, g/cm^3
τ = space time, s
θ = fraction of surface covered by tracer molecules

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