Revisiting Approximate Solutions for Batch Adsorbers: Explicit Half Time

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Modeling of adsorption in a batch adsorber involves mass balances on individual particles and on the reservoir solution. The analytical solution for this set of equations depends on whether the equations are linear or nonlinear. Nonlinear systems usually require numerical methods while sets of linear equations are readily solved by analytical methods. Engineers often look for simplified solutions, such that parametric dependence can be readily seen, by invoking approximations such as the parabolic profile (Liaw et al., 1979; Do and Rice, 1986). Such solutions are very useful for complicated situations such as solution of a fixed-bed adsorber (Cen and Yang, 1988), and cyclic operation (Nakao and Suzuki, 1983).

In this work, we modify and extend the popular parabolic profile solution. The approximate solution agrees with the exact solution for a range of capacity ratios, defined as the ratio of the mass of solute in the particle to that in the reservoir. An important feature coming out of this simple exercise is that the timescale (half time) of the system is obtained in a very compact form, which is not manifested in exact solutions. The information on time scales is a critical component of the design process.

Theory of Batch Adsorber with Linear Isotherm

Modeling of adsorption in a batch adsorber with a linear isotherm gives rise to the following nondimensional equations (Do and Rice, 1986):

$$\frac{\partial y}{\partial t}=\frac{\partial^2 y}{\partial x^2} \tag{1a}$$

and

$$\frac{dy_b}{dt}=-N\frac{\partial y}{\partial x}\bigg|_1 \tag{1b}$$

where N is the ratio of the solute which can be stored by the particles to that in the reservoir. Here we assume that the particle has a slab geometry, although it is easy to generalize these results for any particle shape (Rice and Do, 1995). The boundary conditions for the above set are:

$$x=0;\quad \frac{\partial y}{\partial x}=0 \tag{2a}$$

$$x=1;\quad y=y_b \tag{2b}$$

The initial conditions of the problem are:

$$t=0;\quad y=0\quad \text{and}\quad y_b=1$$

Integrating the particle mass balance over the whole domain of the particle yields:

$$\frac{d}{dt}\int_0^1 y\,dx=\frac{\partial y}{\partial x}\bigg|_1 \tag{3}$$

The steady-state solution can be readily obtained by combining the two mass balance equations and integrating the result with respect to time, from which we obtain:

$$y_\infty=y_{b\infty}=\frac{1}{1+N} \tag{4}$$

Approximate solutions

The intraparticle concentration profiles usually behave as shown in Figure 1. During the early stage, the profiles are rather sharp, and they become shallower as time progresses. In our approximation scheme, we will split the time domain into two time subdomains. One will be from 0 to t^*, where t^* is the time at which the intraparticle concentration profile just touches the center of the particle. The second time subdomain is (t^*, ∞). Next, we consider the approximation stage by stage.

We denote the concentration at the surface of the particle as $y_1(t)$. We then assume that the approximate solution to the concentration profile $y(x, t)$ will take a quadratic profile from the particle surface to *some position* within the particle. Let this position be $W(t)$, a function to be determined in the course of analysis.

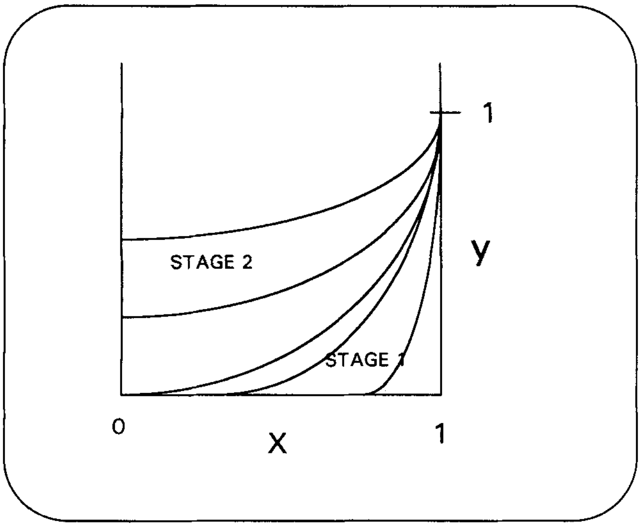

Figure 1. Intraparticle concentration profile.

The approximate solution within the subdomain (W, 1) is assumed to take the form:

$$y(x,t) = a(t) + b(t)x + c(t)x^2$$

subject to:

$$x = 1; \quad y(1,t) = y_1(t)$$

and at the position $W(t)$, we assume that the concentration and its gradient tend to zero:

$$x = W(t); \quad y = \frac{\partial y}{\partial x} = 0$$

In the domain (W, 1), the integral mass balance equation of the particle can be rewritten as:

$$\frac{d}{dt}\int_{W(t)}^{1} y\,dx = \left.\frac{\partial y}{\partial x}\right|_{1} \tag{5}$$

Note that the lower limit of the integral is replaced by $W(t)$ since the concentration within the domain (0, W) is assumed to be zero everywhere.

With these constraints, we obtain the result:

$$y(x,t) = y_1(t)\left[\frac{x - W(t)}{1 - W(t)}\right]^2 \tag{6}$$

Using this form of approximate solution, we obtain:

$$\int_{W(t)}^{1} y\,dx = \frac{y_1[1 - W(t)]}{3} \quad \text{and} \quad \left.\frac{\partial y}{\partial x}\right|_{1} = \frac{2y_1}{1 - W(t)}$$

If we substitute these two expressions into the integral mass balance equation for the particle (Eq. 5) and the mass balance in the reservoir (Eq. 1b), we obtain:

$$\frac{1}{3}\frac{d}{dt}[y_1(1 - W)] = \frac{2y_1}{1 - W} \quad \text{and} \quad \frac{1}{N}\frac{dy_b}{dt} = -\frac{2y_1}{1 - W} \tag{7}$$

The particle surface concentration y_1 is equal to the bulk concentration y_b, then Eq. 7 will become:

$$\frac{1}{3}\frac{d}{dt}[y_b(1 - W)] = \frac{2y_b}{1 - W} \quad \text{and} \quad \frac{1}{N}\frac{dy_b}{dt} = -\frac{2y_b}{1 - W} \tag{8}$$

Adding these two, we obtain the overall mass balance of the system:

$$\frac{1}{3}\frac{d}{dt}[y_b(1 - W)] + \frac{1}{N}\frac{dy_b}{dt} = 0$$

Integration of this equation with respect to time yields the following relationship between the time-dependent position $W(t)$ and the bulk concentration:

$$1 - W(t) = \frac{3(1 - y_b)}{Ny_b} \tag{9}$$

where we have used the following initial conditions:

$$t = 0; \quad y_b = 1 \quad \text{and} \quad W = 1$$

Stage 1: when $W = 0$, we have

$$y_b^* = \frac{1}{1 + N/3} \tag{10}$$

which is greater than the steady-state solution obtained earlier. This simply means that when the adsorption front $W(t)$ reaches the particle center, the particle is not yet equilibrated with the bulk concentration. This implies that the time domain of validity of this approximate solution for stage 1 will be from 0 to the time t^*.

Now, we substitute the position W of Eq. 9 into the mass balance equation for the reservoir (Eq. 8) to obtain:

$$\frac{dy_b}{dt} = -\frac{2N^2y_b^2}{3(1 - y_b)} \tag{11}$$

The integration of this gives:

$$\frac{1}{y_b} - 1 + \ln y_b = \frac{2N^2t}{3} \tag{12}$$

From this, the adsorption front is calculated to be:

$$1 - W(t) = \frac{3(1 - y_b)}{Ny_b} \tag{13}$$

and the mean particle concentration can be evaluated using:

$$\bar{y}(t) = \int_{W(t)}^{1} y\,dx = \frac{y_b[1 - W(t)]}{3} \tag{14}$$

Now, the intraparticle concentration profile is given by the following equation:

$$y(x,t) = y_b(t)\left[\frac{x-W(t)}{1-W(t)}\right]^2 \tag{15}$$

When the adsorption front reaches the particle center (that is, $W=0$), the bulk concentration is $y_b{}^* = 1/(1+N/3)$; thus, the range of time domain is $(0,t^*)$ where t^* is obtained by substituting $y_b{}^* = 1/(1+N/3)$ into Eq. 12, that is,

$$t^* = \frac{N + 3\ln\left(\dfrac{1}{1+N/3}\right)}{2N^2} \tag{16}$$

At time t^*, the adsorption front reaches the center and the bulk concentration is $y_b{}^* = 1/(1+N/3)$ and the particle mean concentration is:

$$\bar{y}(t^*) = \frac{1}{3(1+N/3)} \tag{17}$$

Thus, at $t=t^*$ the mean particle concentration is one-third of the bulk concentration. This denotes the end of Stage 1.

Now we shall investigate the behavior of t^* relative to capacity N. When N approaches zero, t^* becomes $1/12 = 0.0833$. The value $N=0$ is equivalent to saying that the reservoir is infinite, that is, $y_b = 1$ at all times.

Table 1 shows how t^* will vary with parameter N. We note that as N increases timescale t^* decreases. This is expected since N is proportional to the number of particles in the reservoir.

Stage 2: To find solution valid beyond t^* we resort to the parabolic profile approximation, which is applied *only for* $t>t^*$. The initial condition for the parabolic profile approximation of stage 2 will be:

$$t=t^*;\quad y_b = \frac{1}{(1+N/3)};\quad \bar{y} = \frac{1}{3(1+N/3)} \tag{18}$$

For time $t>t^*$, we assume that the profile to follow the parabolic concentration profile:

$$y(x,t) = a_0(t) + a_2(t)x^2 \tag{19}$$

where $a_0(t)$ and $a_2(t)$ are unknown coefficients. From this, we obtain:

$$\bar{y} = a_0 + \frac{a_2}{3} \quad \text{and} \quad \left.\frac{\partial y}{\partial x}\right|_1 = 2a_2$$

Since $y_b = y(1,\ t) = a_0 + a_2$, this together with the above two gives the linear driving force (LDF) formula:

$$\left.\frac{\partial y}{\partial x}\right|_1 = 3(y_b - \bar{y}) \tag{20}$$

Table 1. Capacity N vs. Timescale t

N	0	0.2	0.5	1	2	5
t^*	0.0833	0.0798	0.0751	0.0685	0.0584	0.0412

From this, the mean intraparticle concentration and the bulk concentration become:

$$\frac{d\bar{y}}{dt} = 3(y_b - \bar{y}) \quad \text{and} \quad \frac{1}{N}\frac{dy_b}{dt} = -3(y_b - \bar{y}) \tag{21}$$

The initial conditions for these two equations are given in Eq. 18.

Combining the two mass balance equations and integrating the result from t^* to t yields:

$$\bar{y} = \frac{1-y_b}{N} \tag{22}$$

At steady state, $\bar{y}_\infty = y_{b\infty}$, and the above equation then produces the correct SS solution. Substituting the equation for $\bar{y}$ (Eq. 22) into the mass balance equation for y_b (Eq. 21b) and integrating the result, we have the final solution for y_b:

$$y_b = \frac{1}{1+N} + \frac{2N}{3(1+N)(1+N/3)}\exp[-3(N+1)(t-t^*)];\quad t>t^* \tag{23}$$

And the solution for $\bar{y}$ is obtained from Eq. 22:

$$\bar{y} = \frac{1}{1+N} - \frac{2}{3(1+N)(1+N/3)}\exp[-3(N+1)(t-t^*)] \tag{24}$$

Knowing $\bar{y}$ and y_b, the coefficients a_0 and a_2 are given by:

$$a_0 = \frac{3}{2}\bar{y} - \frac{1}{2}y_b;\quad a_2 = \frac{3}{2}(y_b - \bar{y}) \tag{25}$$

Thus, the intraparticle concentration profile can now be evaluated over the whole time. Continuity of the concentration between the two stages is obtained, since we see at $t=t^*$:

$$\left(\left.\frac{dy_b}{dt}\right|_{t=t^*}\right)_{\text{STAGE 1}} = \left(\left.\frac{dy_b}{dt}\right|_{t=t^*}\right)_{\text{STAGE 2}} = -\frac{6N}{N+3} \tag{26}$$

Figure 2 shows a typical curve for the complete approximate solution.

Conventional parabolic profile approximation

If we use the parabolic approximation for the whole time domain from time $t=0$, the mass balance equations will be:

$$\frac{d\bar{y}}{dt} = 3(y_b - \bar{y}) \tag{27a}$$

$$\frac{1}{N}\frac{dy_b}{dt} = -3(y_b - \bar{y}) \tag{27b}$$

with the following initial conditions:

$$t=0;\quad \bar{y}=0 \quad \text{and} \quad y_b = 1$$

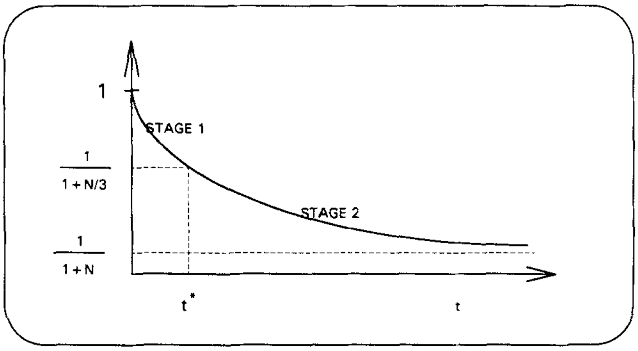

Figure 2. Typical response of the bulk concentration.

Solution for the bulk concentration can be obtained as:

$$y_b=\frac{1}{1+N}+\frac{N}{1+N}\exp\left[-3(1+N)t\right] \tag{28}$$

Exact solution

The exact solution to this problem can be solved by applying the Laplace transform to the mass balance equations (Rice and Do, 1995):

$$y_b=\frac{1}{1+N}+\sum_{n=1}^{\infty}\frac{\exp(-\beta_n^2 t)}{1+\frac{\beta_n}{2N}\left[\beta_n\cot^2(\beta_n)+\beta_n+\cot(\beta_n)\right]} \tag{29}$$

where β_n are positive roots of the following transcendental equation:

$$\beta_n\cot(\beta_n)-1=-(1+N)+\frac{\beta^2}{Bi} \tag{30}$$

We evaluate the applicability of the new approximate solutions in Figure 3 which shows the exact solution as well as the approximate solution for the case of $N=1$. The parabolic profile solution (Eq. 28) is also shown.

Figure 4 shows the comparison between the approximate solutions and the exact solution for the case of higher particle concentration inside the reservoir ($N=5$). Again, the new solution is a far superior approximation to the exact solution.

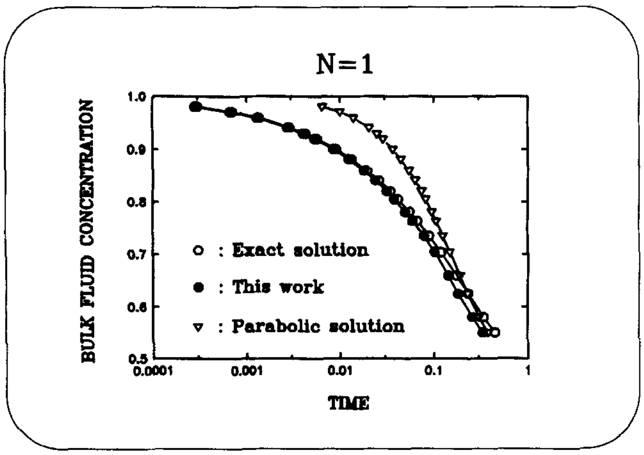

Figure 3. Log scale of time vs. bulk concentration for $N=1$.

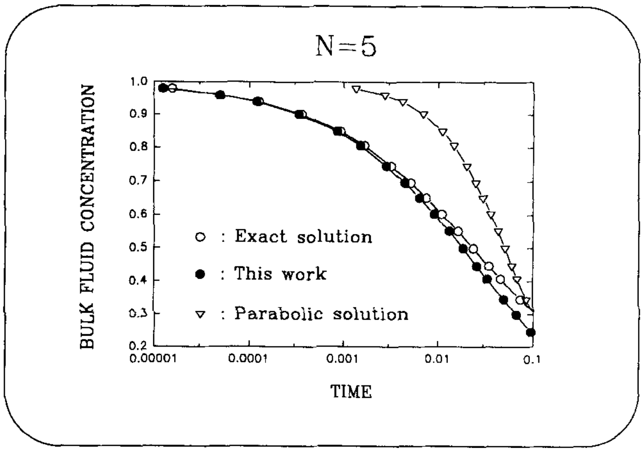

Figure 4. Log scale of time vs. bulk concentration for $N=5$.

Half time

In the new approximate solutions, there are two stages. In stage 1 ($t<t^*$), the solution is given in Eq. 12 and the solution for stage 2 ($t>t^*$) is given in Eq. 23. The bulk concentration at this demarcation time t^* is $y_b^*=1/(1+N/3)$.

As the bulk concentration decreases from unity to a steady-state concentration of $1/(1+N)$, the half time can be defined as the time when the bulk concentration is:

$$y_b(t_{0.5})=\frac{1+\left(\frac{1}{1+N}\right)}{2}=\frac{2+N}{2+2N}$$

When $N>1$, this half time concentration is less than the demarcation concentration $y_b(t^*)$; thus, the stage 1 approximation solution (Eq. 12) can be used to determine the half time. When $N<1$, the stage 2 approximate solution (Eq. 23) is used to calculate the half time. Therefore, the half time is:

$$t_{0.5}=\frac{3}{2N^2}\left[\frac{N}{2+N}+\ln\left(\frac{2+N}{2+2N}\right)\right]\quad \text{for}\quad N\geq 1$$

$$t_{0.5}=\frac{N+3\ln\left(\frac{1}{1+N/3}\right)}{2N^2}+\frac{1}{3(1+N)}\ln\left(\frac{4}{3+N}\right)\quad \text{for}\quad N<1$$

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