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Numerical Simulation of a Fixed-Bed Adsorption Column by the Method of Orthogonal Collocation

(This is an R&D Note)

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The orthogonal collocation method of solving partial differential equations was developed more than a decade ago, largely by Villadsen (1970) and Finlayson (1972) The method is particularly useful for the solution of boundary value problems and, for a given accuracy of solution, has often been found to require less computer time than standard finite difference methods. Although the method has been previously applied to the simulation of fixed-bed reactors (*e.g., Hansen*, 1971; Karanth and Hughes, 1974) and recently to the simulation of an adsorption column (Liapis and Rippin, 1978; Liapis and Litchfield, 1980), it has not yet become widely adopted as a standard technique. To illustrate the application of the method to the prediction of the transient response of an adsorption column, we have solved a complicated linear problem to which an exact analytic solution has recently been derived (Rasmuson and Neretnieks, 1980). A similar nonlinear problem could be solved in exactly the same way, and the property of linearity is of no special advantage to the collocation method. However, the availability of an exact solution provides a convenient check on the accuracy of the collocation solution.

MATHEMATICAL MODEL

We consider an isothermal adsorption column, packed with porous spherical particles, which is subjected, at time zero, to a small step change in the concentration of an adsorbable species in the carrier. The flow pattern is described by the axial dispersed plug-flow model, and both external and internal diffusional resistances to mass transfer are included so that the system may be described by the following set of equations:

Particle Diffusion:

$$\frac{\partial q}{\partial t} = D\left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r}\frac{\partial q}{\partial r}\right) \tag{1}$$

Boundary Conditions:

$$q(r,t=0) = 0 \tag{2}$$

$$\left.\frac{\partial q}{\partial r}\right|_{r=0} = 0 \tag{3}$$

$$D\left.\frac{\partial q}{\partial r}\right|_{r=R} = k\left[c(z,t) - \frac{q|_{r=R}}{K}\right] \tag{4}$$

External Fluid:

$$-D_L \cdot \frac{\partial^2 c}{\partial z^2} + v\frac{\partial c}{\partial z} + \frac{\partial c}{\partial t} = -\left(\frac{1-\epsilon}{\epsilon}\right)\left\{\frac{3k}{R}\left(c(z,t) - \frac{q|_{r=R}}{K}\right)\right\} \tag{5}$$

Boundary Conditions:

$$D_L\left.\frac{\partial c}{\partial z}\right|_{z=0} = -v(c|_{z=0} - c|_{z=0+}) \tag{6}$$

$$\left.\frac{\partial c}{\partial z}\right|_{z=L} = 0 \tag{7}$$

The problem as defined in Eqs. 1–7 is identical to the problem solved analytically by Rasmuson and Neretnieks (1980) except for the column boundary conditions (Eqs. 6 and 7). These are the correct boundary conditions for a dispersed plug-flow system as discussed by Wehner and Wilhelm (1956). Rasmuson and Neretnieks employed the simpler boundary conditions $c(z=0,t) = c_o$, $c(z \rightarrow \infty,t) = 0$ used earlier by Rosen (1952). This difference in boundary conditions leads to a significant difference in the solutions only when the axial Peclet number and column length are both small.

Written in dimensionless form Eqs. 1–7 become:

$$\frac{\partial Q}{\partial \tau} = \nabla^2 Q \tag{8}$$

$$Q(\eta,\tau=0) = 0 \tag{9}$$

$$\left.\frac{\partial Q}{\partial \eta}\right|_{\eta=0} = 0 \tag{10}$$

$$\frac{1}{K}\left.\frac{\partial Q}{\partial \eta}\right|_{\eta=1} = \xi\left\{U - \frac{Q|_{\eta=1}}{K}\right\} \tag{11}$$

$$\frac{\partial U}{\partial \tau} = \frac{1}{Pe}\psi\theta\frac{\partial^2 U}{\partial x^2} - \psi\theta\frac{\partial U}{\partial x} - 3\psi\xi\left\{U - \frac{Q|_{\eta=1}}{K}\right\} \tag{12}$$

$$\left.\frac{\partial U}{\partial x}\right|_{x=0} = -Pe\{U|_{x=0-} - U|_{x=0+}\} \tag{13}$$

$$\left.\frac{\partial U}{\partial x}\right|_{x=1} = 0 \tag{14}$$

TABLE 1. DIMENSIONLESS PARAMETERS OF THIS WORK AND THOSE USED BY RASMUSON AND NERETNIEKS (1980)

Parameter	This Work	Rasmuson and Neretnieks (1980)
Peclet Number	$P_e = Lv/D_L$	$P_e = zv/D_L$
Distribution Ratio	$\psi = K\left(\frac{1-\psi}{\psi}\right)$	$R = K/m$
Bed Length Parameter	$\theta = \frac{vR^2\epsilon}{LDK(1-\epsilon)}$	$\delta = \frac{3D_sKz}{b^2mv}$
Film Resistance parameter	$\xi = \frac{kR}{DK}$	$\nu = \frac{D_sK}{k_fb}$
Contact Time Parameter	$\tau = \frac{Dt}{R^2}$	$y = \frac{2D_st}{b^2}$

SOLUTION BY COLLOCATION

The set of Eqs. 8–14 define a linear boundary value problem involving a pair of coupled parabolic second-order partial-differential equations (Eqs. 8 and 12). These equations are first reduced to first-order ordinary-differential equations by orthogonal collocation. The ordinary-differential equations thus obtained may then be solved by any standard integration routine. Eight collocation points (M) were used for the external fluid phase while the number of interior collocation points (N) was varied from two to nine. Details are given in Appendix I.

RESULTS AND DISCUSSION

Table I shows a comparison between the dimensionless groups used in the present study and those used by Rasmuson and Neretnieks (1980). To determine the accuracy of the approximate collocation solutions, solutions were evaluated, for representative sets of parameters, from the exact analytic solution (Eq. 9 of Rasmuson and Neretnieks, 1980). This requires the evaluation of a slowly converging oscillating integral involving the product of a sine function and a decaying exponential. To accomplish this, an efficient integration routine is required. We used a slightly modified version of the routine developed by Rasmuson and Neretnieks (1980).

The comparison between the analytical and collocation solutions is shown in Table 2 and Figure 1. It is evident from Figure 1 that the agreement is excellent. The solutions show some divergence when the Peclet number is small (L small, D_L large), but this is due to the difference in the boundary conditions and not to any inaccuracy of the collocation solution. This was shown by repeating the collocation solution using the boundary conditions employed by Rasmuson and Neretnieks.

TABLE 2. COMPARISON OF COMPUTATION TIME REQUIRED BY THE PRESENT METHOD AND THE METHOD OF RASMUSON AND NERETNIEKS (1980)

		Computation Time Required in IBM 3032			
		Present Method with $M = 8, N = 4$		Method of Rasmuson and Neretnieks (1980)	
Parameter Values		min	s	min	s
$P_e = 2.0E+02$ $\psi = 1.0E+04$ $\xi = 1.0E+04$ $\theta = 3.0E+00$	Figure 1	00	23	≈10	00
$P_e = 1.93E+01$ $\psi = 6.78E+03$ $\xi = 1.00E+04$ $\theta = 3.00E+00$	Figure 1	00	26	≈18	00
$P_e = 1.93E+00$ $\psi = 6.78E+03$ $\xi = 1.00E+04$ $\theta = 3.00E+00$	Figure 1	05	00	>20	00

$\xi = 1.00E+04 \rightarrow \infty$ is assumed to be same as $\nu = 0$ of Rasmuson and Neretnieks (1980).

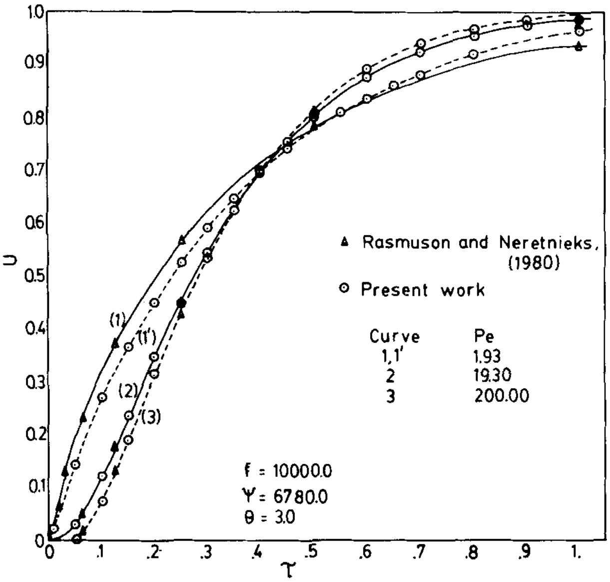

Figure 1. Comparison of numerical solution from present study with exact analytic solution of Rasmuson and Neretnieks.

The computing times required for evaluation of the breakthrough curves of Figure 1 from the exact analytic solution and by the collocation method are compared in Table 2. Since both calculations were carried out on the same machine (IBM 3032), the ratio of times provides a valid comparison although the absolute times would be different for a different machine. It is evident that in all cases the time required to solve the problem by the collocation method is very much shorter than the time required to evaluate the breakthrough curve from the exact analytic solution. At large values of P_e the problem reduces to an initial value problem and this is reflected in a significant reduction in the computing time requirement.

Effects of Axial Dispersion and External Mass Transfer Resistance

Figure 2 shows the influence of axial Peclet number on adsorber performance. It is evident that for axial Peclet numbers of less than

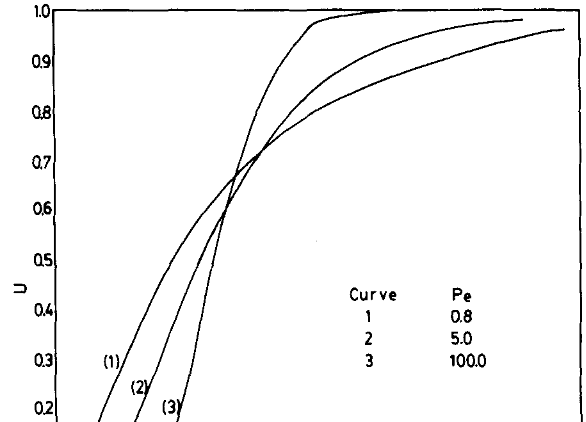

Figure 2. Theoretical breakthrough curves calculated by collocation method showing the effect of Peclet Number.

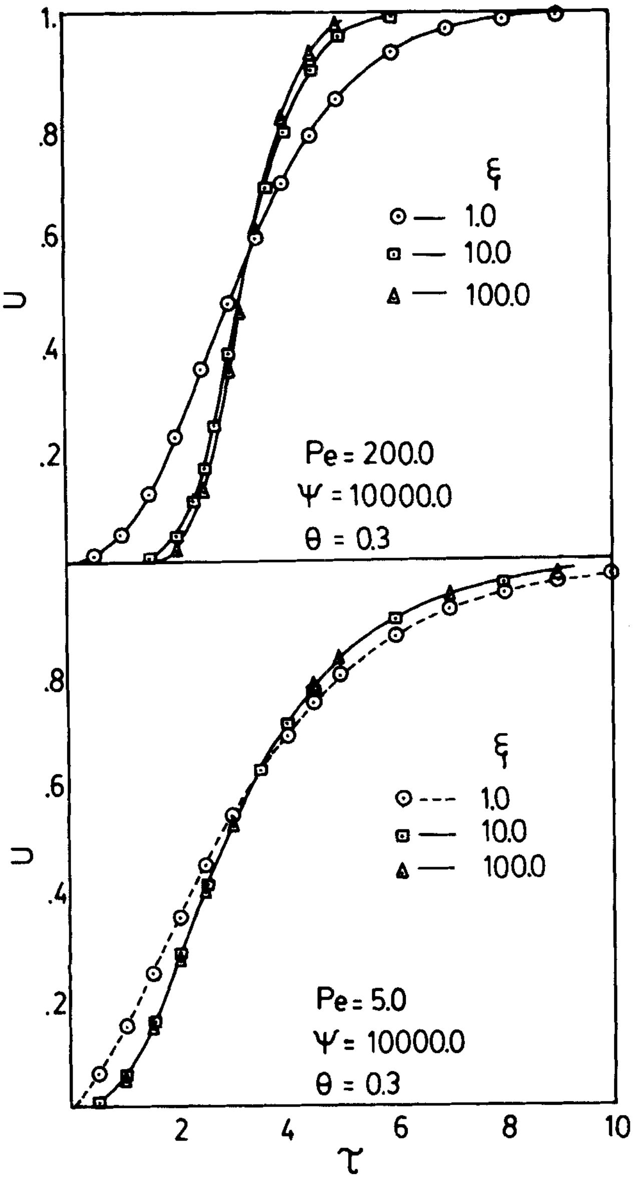

Figure 3. Theoretical breakthrough curves calculated by collocation method showing the effect of external film resistance.

about 40 the break time falls rapidly with decreasing Peclet number, but if the Peclet number is greater than 40 the effect of this parameter is minimal. For a commercial packed bed operating within the practical Reynolds number range $P_e \approx L/R$ it is evident that the effect of axial dispersion will be minimal except when the bed is very short (less than 20 particle diameters). This justifies the use of the plug-flow assumption in most practical fixed-bed adsorber simulation problems. In laboratory scale columns, however, it has been shown that the Peclet number may be very much smaller (Langer et al., 1978) so that axial dispersion may be important.

The effect of external film resistance is illustrated in Figure 3 from which it is evident that the effect is important only when ξ is less than about 10. For systems in which the main mechanism of intraparticle diffusion is molecular diffusion within the macropores, $D \approx \epsilon_p D_m/\chi$ and

$$\xi = \frac{Sh}{2}\left(\frac{\psi}{\epsilon_p}\right)\cdot\frac{1}{K}.$$

Under practical operating conditions for a fixed-bed adsorber the Sherwood number is generally in the range 2–50 and $\chi/\epsilon_p \sim 10$. It is evident that when K is large, the value of ξ may be considerably smaller than 10 and under these conditions external film resistance may be practically important.

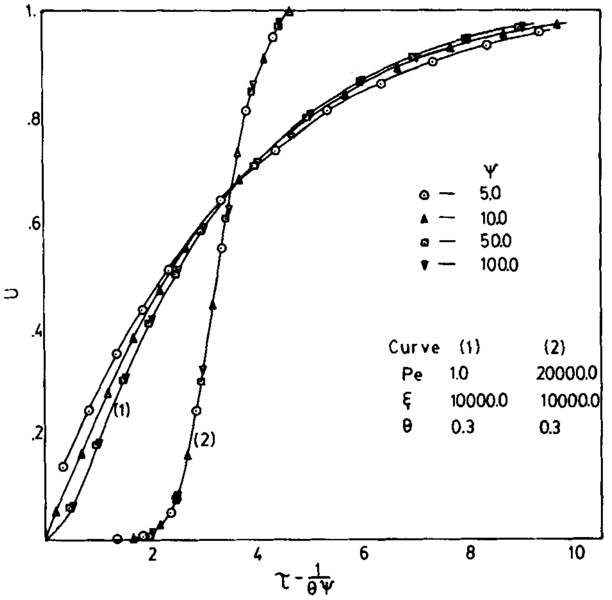

Figure 4. Theoretical breakthrough curves calculated by collocation method showing the effect of distribution ratio.

It may be shown by moments analysis that the contribution of mass transfer resistance and axial dispersion to the second moment of the frequency response are linearly additive. This implies that in a sufficiently long column in which the adsorbate concentration front approaches a symmetric form the entire breakthrough curve may be calculated with good accuracy from the plug-flow solution by using a modified mass transfer resistance parameter α, defined by

$$\alpha \equiv \left(\frac{\theta}{3\xi}\right) = \frac{1}{P_e} + \frac{\theta}{3\xi}.$$

However, this principle cannot be expected to apply rigorously for short columns and small P_e. The results of calculations carried out with a series of different values of P_e and ξ selected to give the same value of the linear combination are summarized in Table 3. It is evident that in the case of the "short" column, there is some deviation between the different curves in the short time region. However, for the longer column the agreement is seen to be good over the entire range.

Effect of Distribution Ratio ψ

If axial dispersion effects are negligible ($P_e \rightarrow \infty$) the present problem reduces to the Rosen problem. Under these conditions the breakthrough curve when plotted against the modified time variable $D/R^2(t - L/v) \equiv (\tau - 1/\theta\psi)$ depends only on the bed length and film resistance parameters and is independent of the distribution ratio. Thus, one may expect the effect of the distribution ratio to be significant only when the effect of axial dispersion is also important. This is confirmed by the results shown in Figure 4 in which the breakthrough curves are plotted against this modified time variable. When P_e is large (negligible axial dispersion) it is evident that the breakthrough curve is independent of the distribution parameter. For small P_e the distribution parameter is seen to have a small effect. However, under most practically important conditions the effect of the distribution parameter is minimal and the breakthrough curve can be considered to depend only on P_e, ξ and θ.

ACKNOWLEDGMENT

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TABLE 3. TEST OF LINEAR ADDITION OF RESISTANCES

Time	Short Column $\theta = 3.0, \psi = 10^4, \alpha = 0.2$ Concentration at Bed Outlet			Time	Long Column $\theta = 0.03, \psi = 10^4, \alpha = 0.3$ Concentration at Bed Outlet		
τ	$P_e = 5.0$ $\xi = 10^3$	$P_e = 10$ $\xi = 9.9$	$P_e = 200$ $\xi = 5.1$	τ	$P_e = 10$ $\xi = 0.05$	$P_e = 20$ $\xi = 0.04$	$P_e = 200$ $\xi = 0.0339$
0.0625	0.115	0.155	0.169	1.0	0.036	0.045	0.049
0.125	0.263	0.287	0.296	2.5	0.055	0.066	0.070
0.20	0.416	0.424	0.427	5.0	0.092	0.103	0.107
0.25	0.502	0.504	0.504	10	0.177	0.187	0.191
0.30	0.579	0.575	0.573	16	0.290	0.297	0.299
0.35	0.645	0.638	0.635	20	0.366	0.37	0.372
0.40	0.702	0.693	0.689	25	0.458	0.459	0.459
0.50	0.792	0.782	0.778	30	0.543	0.541	0.541
0.60	0.857	0.847	0.844	40	0.686	0.682	0.680
0.70	0.902		0.891	50	0.792	0.787	0.785
0.80	0.933		0.925	60	0.865	0.862	0.861
0.90	0.955		0.950	70	0.914	0.912	0.911
1.0	0.969		0.966	80	0.946	0.945	0.944
				90	0.965	0.965	0.965

APPENDIX I

Appendix I, which contains details of the collocation method, may be obtained by writing to the authors.

NOTATION

b = particle radius of Rasmuson and Neretnieks (1980), m
c = fluid phase-concentration, mol/m^3
c_o = fluid-phase inlet concentration, mol/m^3
D = solid-phase diffusivity, m^2/s
D_L = axial dispersion coefficient, m^2/s
D_m = molecular diffusivity, m^2/s
D_s = solid-phase diffusivity of Rasmuson and Neretnieks (1980), m^2/s
d_p = diameter of particle, m
K = volume equilibrium constant, m^3/m^3
k = mass transfer coefficient, m/s
k_f = mass transfer coefficient of Rasmuson and Neretnieks (1980), m/s
L = length of adsorber, m
M = number of collocation points in the external fluid phase
m = $\epsilon/(1 - \epsilon)$ in Rasmuson and Neretnieks (1980)
N = number of collocation points in the particulate (internal) phase
P_e = vL/D_L, Peclet number
Q = q/c_o, dimensionless internal concentration in particles
q = internal concentration in particles, mol/m^3
R = particle radius, m; also refers to the distribution parameter in Rasmuson and Neretnieks (1980)
r = radial distance from center of spherical particle, m
Sh = kd_p/D_m, Sherwood Number
t = time, s
U = c/c_o, dimensionless fluid-phase concentration
v = average linear pore velocity, m/s
x = z/L, dimensionless axial distance
y = $2D_st/b^2$, contact time parameter of Rasmuson and Neretnieks (1980)
z = axial distance coordinate, m; also refers to the distance in flow direction in Rasmuson and Neretnieks (1980), m

Greek Letters

α = $(1/P_e + \theta/3\xi)$, modified mass transfer parameter
θ = $vR^2\epsilon/LDK(1 - \epsilon)$, bed length parameter
ϵ = bed porosity, m^3/m^3
ϵ_p = macropore porosity, m^3/m^3
η = r/R, dimensionless radial distance in particle
δ = $3D_sKz/b^2mv$, bed length parameter of Rasmuson and Neretnieks (1980)
∇^2 = Laplacian operator
ξ = kR/DK, film resistance parameter
ψ = $K(1 - \epsilon/\epsilon)$, distribution ratio
τ = Dt/R^2, contact time parameter
ν = D_sK/k_fb, film resistance parameter of Rasmuson and Neretnieks (1980)
χ = tortuosity factor

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