New Approach to a General Nonlinear Multicomponent Chromatography Model

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Mathematical modeling and numerical analysis of multicomponent fixed-bed adsorption/desorption operations, such as frontal, displacement and elution, have received considerable attention since the late 1960s. Various mathematical models with different complexities have been proposed and a comprehensive review was given by Ruthven (1984). Basically, they can be classified into the following three major categories: 1. staged equilibrium models, 2. interference theory (Helfferich and Klein, 1970), and 3. rate equation models. Among them, the general nonlinear multicomponent rate equation model is the most "realistic" model for all kinds of multicomponent adsorption/desorption column processes. The model is formulated according to mass balance of each species in bulk fluid and particle phases. It considers axial dispersion, external mass transfer, intraparticle diffusion and multicomponent nonlinear isotherms. *Due to the complexity and nonlinearity of the model, analytic solution is impossible and numerical computation can be very time-consuming because the system equations are stiff in many cases. Hence, an efficient algorithm is essential.*

So far three different algorithms have been proposed to solve models similar to ours. Liapis and coworkers (1978a, b, 1980) used orthogonal collocation (OC) method for the discretization of both bulk- and particle-phase equations. The resulting ordinary differential equations (ODE's) were solved using a fifth-order Runge-Kutta method. Their model was applied to frontal adsorption. Yu and Wang (1989) tried OC on finite element for bulk-phase equations and OC method for particle-phase equations. *The resulting ODE's and algebraic equations were solved using a differential algebraic equation solver.*

Recently, Mansour (1989) applied a similar model to frontal adsorption. Apparently he used finite difference method for the whole numerical procedure and iteration for nonlinear isotherms.

In this work, we present a robust and efficient approach to solve the general nonlinear, multicomponent rate equation model. It uses the finite element (FE) (with quadratic elements) method for the bulk-phase equations and the OC method for the particle-phase equations. The resulting ODE's are solved with implicit Gear's stiff method (Gear, 1972). Our code is capable of simulating the three major modes of chromatography, frontal, elution, displacement, and multistage operations accurately and efficiently.

Model

Consider a fixed-bed adsorption column packed with uniform-porous, spherical, solid adsorbents. Suppose the process is isothermal and there is no concentration gradient in the radial direction of the column. Assuming that there exists local equilibrium for each component between the pore surface and the liquid phase in the macropores inside particles, the following dimensionless governing equations for component i in the bulk fluid and particle phases can be obtained.

$$-\frac{1}{Pe_{Li}} \cdot \frac{\partial^2 c_{bi}}{\partial z^2} + \frac{\partial c_{bi}}{\partial z} + \frac{\partial c_{bi}}{\partial \tau} + \xi_i(c_{bi} - c_{pi,r=1}) = 0 \quad (1)$$

$$\frac{\partial}{\partial \tau}[(1-\epsilon_p)c'_{pi} + \epsilon_p c_{pi}] - \eta_i\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c_{pi}}{\partial r}\right)\right] = 0 \quad (2)$$

I. C.

$$\tau = 0, \quad c_{bi} = c_{bi}(o,z), c_{pi} = c_{pi}(o,r,z) \quad (3,4)$$

B. C.

$$z = 0, \quad \frac{\partial c_{bi}}{\partial z} = Pe_{Li}\left(c_{bi} - \frac{C_{fi}(\tau)}{C_{oi}}\right) \quad (5)$$

For frontal adsorption,

$$C_{fi}(\tau)/C_{oi} = 1$$

For elution process,

$$\frac{C_{fi}(\tau)}{C_{oi}} = \begin{cases} 1 & \tau \le \tau_{imp} \\ 0 & \tau > \tau_{imp} \end{cases}$$

If component i is displaced,

$$C_{fi}(\tau)/C_{oi} = 0$$

$$z = 1, \frac{\partial c_{bi}}{\partial z} = 0 \quad (6)$$

$$r = 0, \frac{\partial c_{pi}}{\partial r} = 0 \quad r = 1, \frac{\partial c_{pi}}{\partial r} = Bi_i(c_{bi} - c_{pi,r=1}) \quad (7,8)$$

Formulation

Using Galerkin approximation (Reddy, 1984), Eq. 1 becomes

$$[DB_i][c'_{bi}] + [AKB_i][c_{bi}] = [PB_i] + [AFB_i] \quad (9)$$

where

$$(DB_i)^e_{m,n} = \int \phi_m \phi_n \, dz \quad (10)$$

$$(AKB_i)^e_{m,n} = \int \left(\frac{1}{Pe_{Li}}\frac{\partial \phi_m}{\partial z}\frac{\partial \phi_n}{\partial z} + \phi_m\frac{\partial \phi_n}{\partial z} + \xi_i \phi_m \phi_n\right) dz \quad (11)$$

$$(AFB_i)^e_m = \int \xi_i \phi_m c_{pi,r=1} \, dz \quad (12)$$

in which m, $n = 1, 2, 3$, and the superscript e indicates FE matrices and vectors evaluated over each individual element before global assembly. Four-point Gauss-Legendre quadratures (Reddy, 1984) are used for integrations. The natural boundary condition $(PB_i)|_{z=0} = -c_{bi} + C_{fi}(\tau)/C_{oi}$ is applied to $[AKB_i]$ and $[AFB_i]$ at $z = 0$.

Using the same symmetric polynomials defined by Finlayson (1980), Eq. 2 is transformed to the following equation by OC method,

$$\left(\sum_{j=1}^{Ns}\frac{\partial g_i}{\partial c_{pj}}\frac{dc_{pj}}{d\tau}\right)_1 = \eta_i \sum_{k=1}^{N+1} B_{1,k}(c_{pi})_k, 1 = 1, 2, \ldots, N \quad (13)$$

in which $g_i = (1 - \epsilon_p) c^s_{pi} + \epsilon_p c_{pi}$. The boundary condition at $r = 1$ becomes

$$\sum_{j=1}^{N+1} A_{N+1,j}(c_{pi})_j = Bi_i(c_{bi} - c_{pi,r=1}) \quad (14)$$

or

$$c_{pi,r=1} = \frac{Bi_i c_{bi} - \sum_{j=1}^{N} A_{N+1,j}(c_{pi})_j}{A_{N+1,N+1} + Bi_i} \quad (15)$$

where the matrices A and B are the same as defined by Finlayson (1980).

Algorithm

If Ne quadratic elements [i.e., $(2 Ne + 1)$ nodes] are used for z-axis in bulk-phase equations and N interior OC points are used for r-axis in particle-phase equations, the above discretization procedure gives a total of $Ns (2 Ne + 1) (N + 1)$ ODE's which are then solved simultaneously using Gear's stiff method (IMSL, 1987). Note that a function subroutine must be supplied to the ODE solver to evaluate concentration derivatives at each element node and OC point with given trial concentration values. The concentration derivatives at each element node (c'_{bi}) and OC point (c'_{pi}) are determined from Eqs. 9 and 13, respectively. At each OC point, Eq. 13 can be rewritten in the following matrix form.

$$[GP][c'_p] = [RH] \quad (16)$$

where

$$GP_{ij} = \partial g_i/\partial c_{pj}, \quad c'_{pj} = dc_{pj}/d\tau, RH_i$$

$$= \text{righthand side of Eq. 13.}$$

Since the matrices $[GP]$ and $[RH]$ are known with given species concentrations at each OC point, the vector $[c'_p]$ can be easily determined from Eq. 16. Using this approach, we can deal with complex nonlinear isotherms here without iteration. The solution of the ODE system provides the moving concentration profiles inside column and the effluent history.

Results and Discussion

The proposed numerical approach was demonstrated using the following Langmuir isotherm in different column operations.

$$C^s_{pi} = \frac{a_i C_{pi}}{1 + \sum_{j=1}^{Ns} b_j C_{pj}}$$

That is,

$$c^s_{pi} = \frac{a_i c_{pi}}{1 + \sum_{j=1}^{Ns} (b_j C_{oj}) c_{pj}} \quad \text{(dimensionless)}$$

where $a_i = C_i^{-} b_i$. Figure 1 shows a three-component breakthrough analysis, which is compared to the corresponding single-component systems. The dotted dashed lines were obtained with $N = 1$ compared to solid lines with $N = 2$. Figure 2 shows a two-component displacement anlaysis with near shock wave stiffness in concentration profiles. Figure 3 shows a
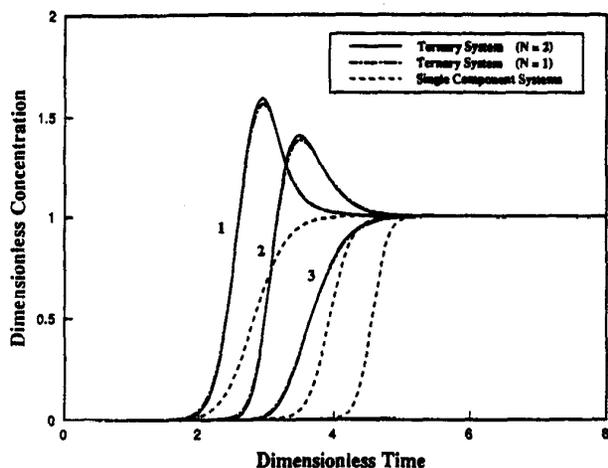
Figure 1. Three-component breakthrough analysis.

Figure 3. Two-stage operation.

comparison of reverse flow displacement and forward flow displacement after an incomplete frontal adsorption which lasted $\tau = 2$. Such multistage operations can be simulated using our code with a single execution. In Figure 4, a four-component elution was shown ($\tau_{imp} = 0.1$). Its CPU time on SUN 4/280 computer (15.10 min) further proves the ability and efficiency of our code in simulating complicated systems. Other operations such as nonlinear gradient elution can also be accommodated using our code. The comparison of multicomponent system with corresponding single-component systems in Figures 1 and 4 shows that the general rate equation model is a powerful tool for the study of interference in multicomponent adsorption and chromatography.

Table 1 lists the parameters we used (in the input data file) to obtain fully-converged concentration profiles (solid lines in Figures 1 to 4). CPU times are also listed. In addition, we also tried Figure 1 (solid lines) case on a low-end personal computer (IBM PS/2 30 286), with a running time of 162 min. Excellent mass balances (numerical area integration vs. theoretical calculation) were obtained. The difference in all cases is below 0.1%!
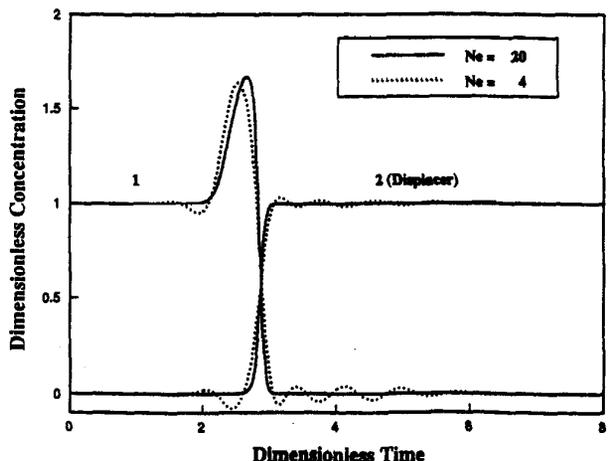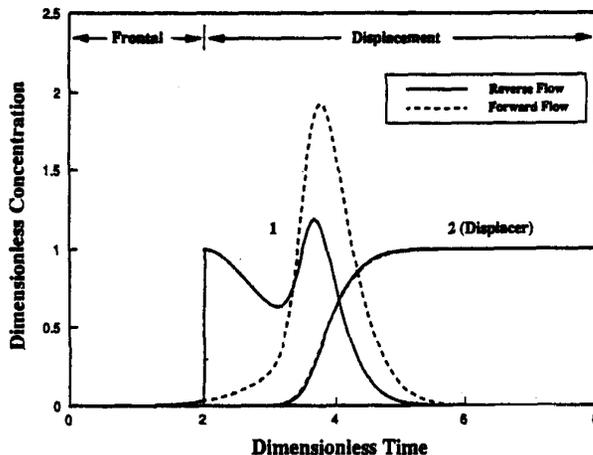
It is found that in some cases, especially in cases with small Bi_i values (no larger than 1.0, say), one interior OC point ($N = 1$) is enough, because quadratic curves are quite sufficient to describe concentration profiles inside the particle in such cases. Often, $N = 2$ is needed, which is sufficient. This reveals the weak point in lumped particle models which fail even to consider the internal gradient inside the particle. Sometimes $N = 1$ causes only minor error, but gives large saving in CPU time. For example, in Figure 4, if $N = 1$ is used instead of $N = 2$, it will only slightly reduce peak heights (by less than 1.5%), while CPU time (on SUN 4/280) drops to 5.91 min compared to 15.10 min for $N = 2$. If bulk concentration profiles are not stiff, $Ne = 1$ to 6 is usually sufficient. Stiff cases need more elements to overcome oscillation. For near shock wave stiffness in concentration profiles, $Ne = 20$ to 30 usually is enough. From our extensive computer simulations of various studies, including cases with isotherms other than Langmuir type such as constant separation factor type in ion exchange (Helfferich, 1970), Langmuir-Freundlich type (Ruthven, 1984), and even some unfavorable types, we found that the CPU time depends on total number of ODE in the system, stiffness of concentration profiles,
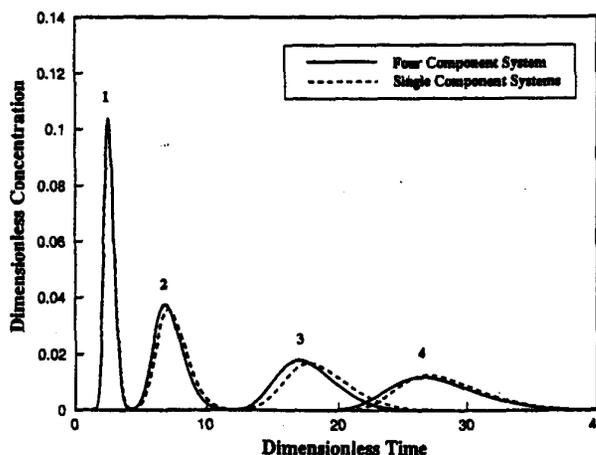

Figure 2. Two-component displacement analysis.

Figure 4. Four-component elution.

Table 1. Parameters and CPU Times*

Fig.	Species	Physical Parameters					Numerical Parameters			CPU Time (min)		
		Pe_{Li}	η_i	Bi_i	a_i	$b_i \times C_{oi}$	Ne	N	Total ODE's	VAX 11/780	Gould NP-1	SUN 4/280
	1	100	6	4	2	4 × 0.1						
1	2	100	6	4	7	14 × 0.1	7	2	135	51.81	6.79	5.45
	3	100	6	4	15	30 × 0.1						
2	1	600	60	0.5	3	6 × 0.1	20	1	164	123.13	15.29	14.94
	2	600	30	0.6	12	24 × 0.3						
3	1	100	1	3	6	12 × 0.1	7	2	90	46.45	6.49	4.94
	2	200	2	1	8	16 × 2.0						
	1	100	40	2	1.2	1.5 × 0.1						
4	2	120	42	1.7	8	10 × 0.1	7	2	180	141.86	16.16	15.10
	3	200	55	1.6	24	30 × 0.1						
	4	300	70	1.5	38.4	48 × 0.1						

*In all runs, $\epsilon_p = 0.5$, $\epsilon_b = 0.4$. The ODE solver's tolerance is tol $= 10^{-5}$. Double precision is used in the Fortran code.

and the type of operation being simulated. Frontal adsorption takes less time to simulate than the displacement and elution. Generally speaking, with medium stiffness which typically requires $Ne = 7$, CPU time on SUN 4/280 for binary systems is less than 1 min for frontal adsorption, and 5 min for displacement and elution. In a stiff case, we may use a small Ne to have a quick look at the crude solution. For example, in Figure 2, the unconverged solution which gives a general shape similar to the converged concentration profiles can be obtained with $Ne = 4$ and a CPU time of only 0.43 min on SUN 4/280. It is interesting to note that oscillation *does not* destroy mass balance of capacity area. In Figure 2, for component 1, the theoretical dimensionless capacity area ($[[(1 - \epsilon_b)(1 - \epsilon_p) \ a_1/(1 + b_1 C_{o1}) + (1 - \epsilon_b)\epsilon_p + \epsilon_b]/\epsilon_b$) is 3.15625, and numerical integrations for the areas under component 1 concentration profiles (converged and unconverged) are 3.15630 and 3.15626, respectively.

Table 1 clearly shows that the numerical approach presented in this work is indeed very efficient and robust under various operation conditions. This is mostly due to the following facts:

• The use of FE method for bulk-phase equations enables us to deal with stiff systems with high efficiency and accuracy. Note that, OC method is not suitable for stiff cases (Finlayson, 1980).

• The use of OC method for particle-phase equations is very efficient.

• Our final ODE system contains no algebraic equations and thus enables us to use the highly-efficient Gear's stiff method.

• No iteration is used to take care of nonlinear isotherms.

Other noticeable features of our approach are: 1. axial dispersion is considered in the model with almost no added complexity, as shown in Eq. 11; and 2. finite element has a renowned feature of being able to deal with variable physical properties, which is very useful because in many cases physical property parameters are variables.

Acknowledgment

Notation

a_i, b_i = constants in Langmuir isotherm for component i
Bi_i = Biot number of mass transfer for component i, $(k_i R_p/\epsilon_p D_{pi})$

C_{bi} = bulk-phase concentration of component i
C_{fi} = feed concentration of component i
C_{oi} = concentration used for nondimensionalization for component i, $(\max \{C_{fi}(t)\})$
$c_{bi} = C_{bi}/C_{oi}$
C_{pi} = concentration of component i in the fluid phase within particle
$c_{pi} = C_{pi}/C_{oi}$
C_{pi}^s = concentration of component i in the solid phase within particle (based on unit volume of particle solid, excluding pores)
C_i^* = adsorption capacity for component i
$c_{pi}^* = C_{pi}^*/C_{oi}$
D_{bi} = axial dispersion coefficient of component i
D_{pi} = effective diffusivity of component i
k_i = film mass transfer coefficient of component i
L = column length
N = number of collocation points
Ne = number of quadratic elements
Ns = number of components
Pe_{Li} = Peclet number in bulk fluid phase for component i, (vL/D_{bi})
R = radial coordinate for particle
R_p = particle radius
$r = R/R_p$
t = time
v = interstitial velocity
Z = axial coordinate variable
$z = Z/L$

Greek letters

ϵ_b = bed void volume fraction
ϵ_p = particle porosity
η_i = dimensionless constant for component i, $(\epsilon_p D_{pi}L/R_p^2 v)$
ξ_i = dimensionless constant for component i, $(3Bi_i\eta_i(1 - \epsilon_b)/\epsilon_b)$
τ = dimensionless time, $[t/(L/v)]$
τ_{imp} = dimensionless impulse time duration
ϕ = Lagrangian interpolation function

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