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An Orthogonal Collocation Approach to Modeling Multicomponent Adsorption in Carbon Beds

M. T. Harris
C. H. Byers

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Chemical Technology Division

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IN CARBON BEDS**

M. T. Harris
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ABSTRACT

A multicomponent, packed-bed, adsorption model which solves simultaneously for the adsorption of any number of adsorbing components in a bed or slab configuration is presented for predicting breakthrough curves of trace organics in water. Generally it may be directly applied to interacting systems in which there are two interacting adsorbed species in an inert solvent. The model assumes isothermal conditions and that axial dispersion is negligible. It is also proposed that a linear rate model can be used to describe the rate of adsorption of material on the adsorbent, although the method has been shown to apply to more complex situations. The model was tested by comparing predicted bed exit profiles with experimental data for the adsorption of trace amounts of 2-butanol and *t*-amyl alcohol on a bed of carbon. The applicability of the method to a broad range of adsorption problems in waste disposal and the process industries is discussed.

1. INTRODUCTION

The removal of persistent organic pollutants from drinking water, waste streams and hazardous wastes has assumed great importance in the past decade. In the case of waste water, some of the organic and inorganic species are not removed by normal biological treatment, at least to the extent which is required by the laws which have been enacted during this period; and therefore, carbon columns are employed as a tertiary treatment step. Carbon adsorption is also commonly used as the final stage in the treatment of drinking water. Where applicable the same techniques are used in dealing with hazardous wastes (Oswald, et. al. 1982; Brown, Harris, and Roop 1984).

Ionic and metal species are often removed by parallel ion exchange techniques (Pan and David 1978, Sherman 1978, and Helfferich 1962). While the resin beds have an entirely different chemical basis of operation, the method of mathematical analysis is almost identical to those used in dilute bed sorption.

Although the adsorption of organics on carbon and the ion exchange of ionic species are sometimes performed in slurry type reactors (EPA 1972), it is more common to adsorb these impurities by having the active granular materials arranged in filters as beds of particles. For a given set of operating conditions and a given column design, the time at which breakthrough occurs is the most important figure of merit. This can be determined by performing batch slurry tests and by conducting bench-scale and pilot-scale packed-bed studies to allow prediction of full-scale column performance. However, a full series of packed-bed studies can be quite extraordinarily time-consuming, often requiring weeks of laboratory experimentation. It has been shown to be advantageous to perform only batch tests to determine adsorption equilibria and to use correlations or mathematical models to predict the mass transfer parameters. Packed-bed behavior is subsequently modeled by computer simulations, allowing the prediction of breakthrough time for plant-scale units in a matter of minutes, or perhaps hours for the more elaborate algorithms (Raghavan and Ruthven 1984, Harwell, et al. 1980; and Spahn and Schlunder 1975).

After a satisfactory number of parameters have been examined using the computer model, a few pilot-scale runs can be used to test the computer results against experimental reality. Several advantages accrue to this procedure.

1. The parametric study can quickly identify the most relevant features of the system, allowing a design which takes advantage of the particular properties

of the species and resin.

2. Interactive systems can be studied in detail for their overall characteristics in an expeditious manner.
3. Dangerous experimentation can be minimized by the procedure, particularly where hazardous materials are the object of the design.
4. A good model can be used after construction to aid in the subsequent operation and trouble-shooting of the process.
5. In some of the better models, the effect of a changing feed material can be predicted before these cause problems.

Bearing in mind the significant number of advantages which a good model can bring to a project, it is critical that the robust, efficient algorithms be available to engineers.

The objective of this paper is to present a new model for predicting the behavior of interactive multicomponent adsorption and ion exchange systems. The model represents a significant enhancement of previous computer algorithms, particularly those developed by Carta(1986) which modeled isothermal single-component adsorption. Because this is a significant area of theoretical activity, many models have been presented in the past, and Ruthven (1984) gives a thorough review of these models. Generally they deal with adsorptively non-interactive systems or with single adsorbed components. Obviously they form a subset of the current study. Analytical solutions, while very useful for dilute, non-interactive and noncompetitive mixtures, often fail in the real situations which are the subject of this report. Therefore it was our goal to produce an efficient, accessible method of predicting these important real situations.

Generally, sorption processes are analyzed with the aid of computer algorithms. Even the analytical solutions involve series solutions which converge slowly, making computer operations necessary. In the non-linear cases considered in this study, approximate computational methods are the only way known to solve the equations.

A considerable number of finite difference solutions have been proposed (Ruthven 1984), but these are generally inefficient because of the small step sizes required to properly simulate the steep slopes in concentration profiles. A seemingly simple problem can take hours of computer time. On the other hand, within the past 10 to 15 years, interest in the methods of weighted residuals (MWR) to solve partial differential equations has increased (Finlayson, 1972). In particular, the use of orthogonal collocation in the analysis of packed-bed reactors has been studied and reported in a number of papers and texts. In this study, orthogonal collocation has been used because it offers two advantages over finite differences: relatively greater accuracy with fewer discrete points (and therefore with less computation), and a concise representation of partial derivatives as matrices, which facilitates any programming changes needed to accommodate different models.

Methods of weighted residuals (MWRs), in which the solution to one or more differential equations is expanded in a series of known functions with arbitrary coefficients, have been available since the 1940s. The use of one particular MWR, collocation, became popular in chemical engineering research after Villadsen and Stewart (1967) showed that solution accuracy can be enhanced if collocation points are chosen to be the roots of an orthogonal polynomial. Articles by Finlayson in the early 1970s discussed the use of orthogonal collocation in the analysis of reactions in packed beds (Finlayson, 1971; and Ferguson and Finlayson, 1970). Later, Michelsen and Villadsen published an important paper detailing improved algorithms for calculating collocation constants (Michelsen and Villadsen, 1972). A detailed descrip-

tion of their work is collated in their later-published text (Michelsen and Villadsen, 1980). Finlayson has published two texts on the use of MWRs. The most recent, *Non-Linear Analysis in Chemical Engineering*, contains extensive discussions on steady-state and transient modeling of reactions using orthogonal collocation (Finlayson, 1980). Recently, Raghavan and Ruthven (1983) have published results from an analysis of fixed-bed adsorption columns orthogonal collocation. Like the Carta(1986) study these were confined to single adsorbed components.

Our solution expands the orthogonal collocation approach to multicomponent mixtures. As a specific example, we studied some experimental data for the adsorption of trace amounts of *n*-butanol and *t*-amyl alcohol on a bed of carbon(Santacesaria et al 1982).

2. THEORETICAL

2.1 PACKED BED ADSORPTION THEORY.

A model which describes the behavior of packed beds is illustrated in Fig. 1. In the adsorption case, it is assumed that the fluid phase containing the components to be sorbed enters the bed and the sorbate fills the sites on the bed beginning from the entry, eventually breaking through the exit of the bed when the bed is filled. Typically one observes an 'S'-shaped curve if a single-sorbed specie is involved. In modeling a bed, it is assumed that there is homogeneity in the bed, leading to concentration variations only in the axial direction (z) and of course with time, t . Mass balances are performed on each solute in the liquid phase and the corresponding adsorbed phase leading to the following relationship (Ruthven, 1984):

$$\epsilon D_{z_i} \frac{\partial^2 c_i}{\partial z^2} = \epsilon \frac{\partial c_i}{\partial t} + (1 - \epsilon) \rho_b \frac{\partial \bar{q}_i}{\partial t} + \epsilon v \frac{\partial c_i}{\partial z} . \quad (1)$$

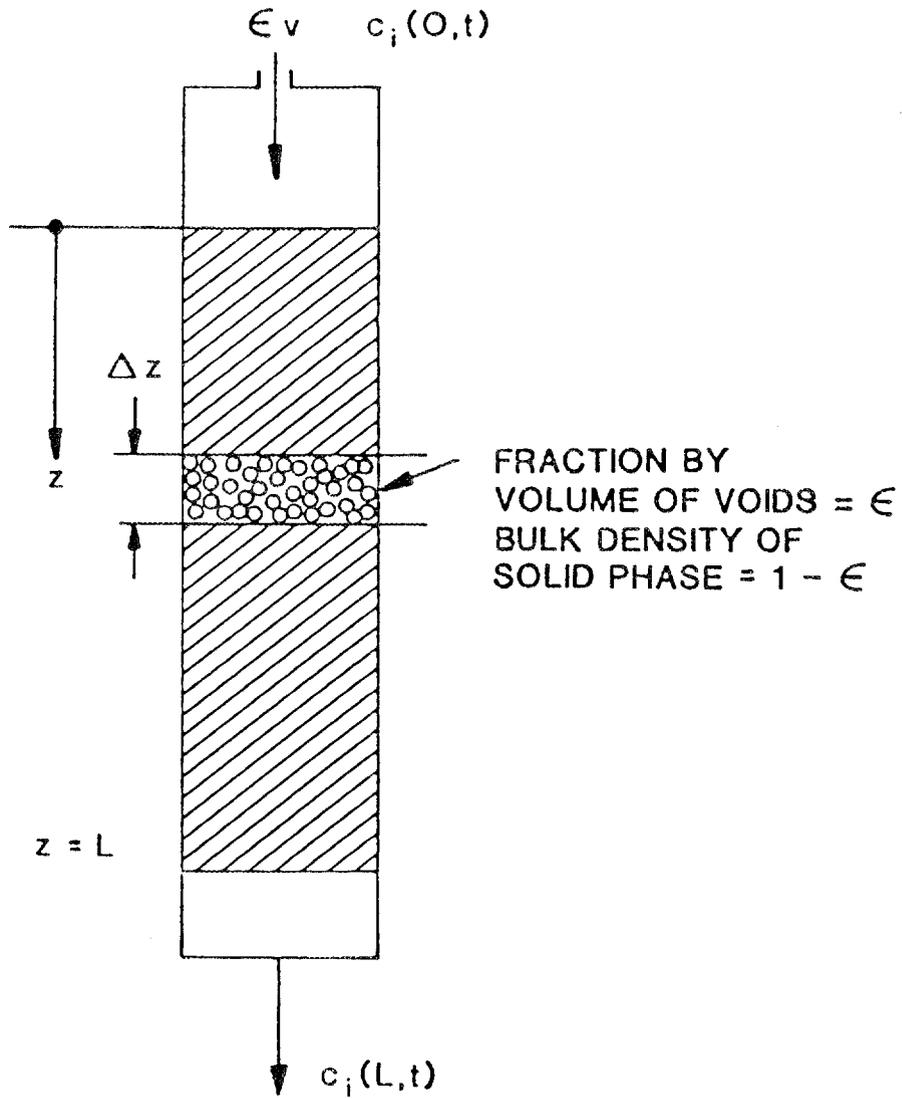


Fig. 1. Schematic diagram of a sorption bed.

with a solid or adsorbed phase balance given as

$$\frac{\partial \bar{q}_i}{\partial t} = k_{o,i} a \left(c_i - \frac{q_i}{K_i} \right) \quad (2)$$

where $k_{o,i}$ is the effective mass transfer coefficient and K_i is the equilibrium constant for component i , which may vary with concentrations of all species as well as the temperature. The axial dispersion, $D_{z,i}$, is generally negligible in usual liquid cases. In other cases where one has linear adsorption coefficients one may use the Gluekauf(1955) approximation for an overall mass transfer coefficient, which is given as follows.

$$\frac{1}{Kk_o} = \frac{D_z}{v^2} \left(\frac{1-\epsilon}{\epsilon} \right) + \frac{R_p}{3k_f} + \frac{R_p^2}{15\epsilon_p D_p} + \frac{r_c^2}{15KD_c} \quad (3)$$

where D_p and D_c are macropore and micropore diffusivity, k_f is the fluid film mass transfer resistance, R_p is the pore radius, r_c is the micropore or crystal radius, and ϵ_p is the macropore void fraction. Although component subscripts are not included, Eq. 2 must be applied to each adsorbing specie. Ruthven(1984) has shown this approach to be quite effective even with significantly nonlinear isotherms. The liquid phase mass balance then becomes

$$\epsilon v \frac{\partial c_i}{\partial z} + \epsilon \frac{\partial c_i}{\partial t} + (1-\epsilon) \rho_b \frac{\partial \bar{q}_i}{\partial t} = 0. \quad (4)$$

To simplify matters in the application of the solid phase material balance, it is often possible to replace the relationship with a linear rate expression (Carta 1986, Santacesaria et al. 1982). Then adsorbed phase mass balance for component i is:

$$\rho_b \frac{\partial \bar{q}_i}{\partial t} = k'_i (c_i - c_i^*). \quad (5)$$

This expression assumes that the mass transfer resistances in the liquid film, surface diffusion, and internal diffusion in the particle can be represented by the

linear rate expression (Eq. 2). In the model proposed by Carta (1986), it is assumed that the mass transfer in the liquid film is the controlling mechanism for adsorption. The mass transfer constant is, therefore, given by the expression

$$k'_i = \frac{3k_{fi}}{R_p}. \quad (6)$$

It should be noted in comparing Eqs. 3 and 6 that k'_i is really the product of k_{oi} and the equilibrium constant K_i . One would expect that this expression would be applicable for liquid systems containing trace impurities, since it closely follows the Gluekauf approximation (Eq. 3). It should be further noted that the application of the linear driving force expression (Eq. 6) leads to the replacement of the average solid phase species concentration \bar{q}_i with q_i^* , the local equilibrium concentration. Because of the interactive nature of the isotherms in the system which was studied here, it is possible that the Gluekauf approximation does not apply. This conservative assumption will be made throughout the remainder of the report.

The model developed by Santacesaria includes both liquid film mass transfer resistance and pore diffusion resistance. These resistances are proposed to act in parallel, following Gluekauf; therefore, the expression for the k' is given by:

$$\frac{1}{k'} = \frac{R_p}{3k_{fi}} + \frac{R_p^2}{15\epsilon_p D_{pi}}. \quad (7)$$

In Santacesaria's model the term \bar{q}_i is related to adsorbed phase concentration, q_i^* , by the expression:

$$\bar{q}_i = (1 - \epsilon_p)q_i^* + \epsilon_p c_i^*. \quad (8)$$

The adsorption equilibria, $q^* = f(c_1, c_2)$ is represented by a Freundlich-Fritz-Schluender (FFS) (Fritz and Schluender 1974 and Liapis and Rippin 1977) type

expression for n solutes. This expression has the form:

$$q_i^* = \frac{a_{i1} c_{pi}^{n+1}}{\sum_j^n b_{ij} c_{pj}^{m_{ij}}} \quad (9)$$

The initial and boundary conditions for these models are:

$$c_i(0, t) = c_{fi}, \quad t \geq 0$$

$$\bar{q}_i(x, 0) = c_i(x, 0) = 0, \quad t < 0. \quad (10)$$

The conditions in Eq. 10 are for the adsorption case in which there is a step change from a base at time zero. Our approach makes it possible to deal with virtually any boundary and initial conditions. This is important in cyclic processes and those where the feed concentration is not steady, as might be the case in wastewater adsorption simulations. However, to test the model only the conditions in Eq. 10 were explored.

2.2 SOLUTION OF MODEL EQUATIONS FOR PACKED BED ADSORPTION.

The method of orthogonal collocation (Michelsen and Villadsen 1972, Villadsen and Stewart 1967, Carta 1987) was used to simultaneously solve Eqs. 1 and 2 for each component. This method converts the system of partial differential equations into a system of algebraic expressions and ordinary differential equations by assuming that the concentration as a function of axial position in the column is represented by a polynomial. Finite difference methods have also been used to solve such equations; however, these methods usually require much longer computer time. Application of orthogonal collocation to the above equations resulted in the following set of ordinary differential equations for the collocation point x_i :

Component 1

$$\epsilon \frac{dc_{1i}}{dt} + \rho_b(1 - \epsilon) \frac{d\bar{q}_{1i}}{dt} + \frac{\epsilon v}{L} \sum_{j=1}^{NT} \left[l_k^{(1)}(x_i) c_{1j}(t, x_j) \right] = 0, \quad (11)$$

$$\rho_b \frac{d\bar{q}_{1i}}{dt} = k'_1 (c_{1i} - c_{1i}^*), \quad (12)$$

Component 2

$$\epsilon \frac{dc_{2i}}{dt} + \rho_b(1 - \epsilon) \frac{d\bar{q}_{2i}}{dt} + \frac{\epsilon v}{L} \sum_{j=1}^{NT} \left[l_k^{(1)}(x_i) c_{2j}(t, x_j) \right] = 0, \quad (13)$$

$$\rho_b \frac{d\bar{q}_{2i}}{dt} = k'_2 (c_{2i} - c_{2i}^*). \quad (14)$$

These equations were written in the following form for the purpose of computer integration:

Component 1

$$\frac{dc_{1i}}{dt} = -\frac{\rho_b(1 - \epsilon)}{\epsilon} \frac{d\bar{q}_{1i}}{dt} - \frac{v}{L} \sum_{j=1}^{NT} \left[l_k^{(1)}(x_i) c_{1j}(t, x_j) \right], \quad (15)$$

$$\frac{d\bar{q}_{1i}}{dt} = \frac{k'_1}{\rho_b} (c_{1i} - c_{1i}^*), \quad (16)$$

Component 2

$$\frac{dc_{2i}}{dt} = -\frac{\rho_b(1 - \epsilon)}{\epsilon} \frac{d\bar{q}_{2i}}{dt} - \frac{v}{L} \sum_{j=1}^{NT} \left[l_k^{(1)}(x_i) c_{2j}(t, x_j) \right], \quad (17)$$

$$\frac{d\bar{q}_{2i}}{dt} = \frac{k'_2}{\rho_b} (c_{2i} - c_{2i}^*). \quad (18)$$

In the present algorithm, it was assumed that the concentration as a function of axial position can be represented by a Jacobi orthogonal polynomial (Carta 1987).

Villadsen and Stewart (1967) established that collocation points chosen to be roots of Jacobi orthogonal polynomials are optimal in the sense that they maximize the order of the solution approximation.

3. COMPUTER SOLUTION OF A TWO-ADSORBING COMPONENT PROBLEM

A flow diagram of the computer algorithm is shown in Appendix I along with the computer programs. There are two programs; ADS3C.FOR, which uses Carta's model, and ADSSAN.FOR, which employs Santacesaria's model.

The initial function of the program is to input data from the data file "ASMC.DAT". An example of input data is given in Appendix I. The description of each data point is given for clarification and is not to be entered into the actual data set.

The constant terms (i.e. $\rho_b(1 - \epsilon)/\epsilon$, v/L , and k'/ρ_b) in Eqs. 15 through 18 are then computed from the input data. Important parameters are written to the output file, "FR.DAT".

The main program calls the subroutine JCOBI to compute the zeros of the Jacobi orthogonal polynomial. These roots are subsequently stored in "FR.DAT". The discretization matrix is computed by the subroutine DFOPR and is stored in the array EL(K,I) in the program and is represented by the term $l_k^{(1)}(x_i)$ in Eq. 19 and 20.

Initial and boundary conditions are assigned in the next portion of the main program. Before proceeding with numerical integration, a flag is set so that when the time interval, TDISP, is achieved during integration, the results are written to the output file "FR.DAT". The program then calls the subroutine RKG, which employs the Runge-Kutta method to numerically integrate Eq. 15 through 18. The

Runge-Kutta subroutine calls the subroutine DERIVS, which computes the right side of the time derivative Eqs. 15 through 18. Several other subroutines are called from DERIVS to compute the c_i^* from \bar{q}_i by applying the equilibrium relationship (Eq. 6). The list of constants, A11 through ZN21, which appears in the subroutines QEQUIL, CEQUIL, and NEWSUB, are defined in the following expanded version of Eq. 9 for each component:

$$q_1^* = \frac{A11 * c_1^{*Z N 11}}{A12 * c_1^{*Z N 12} + B11 * c_2^{*Z M 11}}, \quad (19)$$

$$q_2^* = \frac{B21 * c_2^{*Z M 21}}{B22 * c_2^{*Z M 22} + A21 * c_1^{*Z N 21}}. \quad (20)$$

An important subroutine to note is the NEWSUB subroutine, which was implemented to compute the c_i^* by simultaneously solving the two nonlinear expressions for the adsorption equilibria (Eqs. 19 and 20). The NEWSUB algorithm is based on the mathematical formulation (Appendix II) given by Scarborough (1966).

When TDISP is achieved during integration, the program exits RKG and writes the time (T in program) and c_i/c_{f_i} (i.e., XOUT in the program). The program reenters the subroutine RKG if T is less than the time (TSTEP) specified to end the program, and the process is repeated.

To test the approach against a known solution, it was decided to apply the Klinkenberg (1954) solution to two components which do not interact. The assumption in the Klinkenberg solution is the same as in our case except that the isotherm for a single adsorbing specie is linear. As in our case, trace concentration is assumed, which assures isothermal conditions. A linearized rate expression, identical to the one in Eq. 5, is assumed. The general solution is given as:

$$\frac{c_i}{c_{o,i}} = e^{-\epsilon} \int_0^\tau e_{-u} I_0 \left(2\sqrt{\xi u} \right) du + e^{-(\tau+\epsilon)} I_0 \left(2\sqrt{\tau \xi} \right), \quad (21)$$

where the nondimensional time, τ , and distance, ξ , are defined as:

$$\tau = \frac{k'_i}{\rho_b K_i} \left(t - \frac{z}{v} \right) \text{ and } \xi = \frac{k'_i z}{\rho_b v} \left(\frac{1 - \epsilon}{\epsilon} \right). \quad (22)$$

The solution can be considerably simplified for the case where ξ is > 2.0 . To within 0.6

$$\frac{c_i}{c_{o_i}} = \frac{1}{2} \left[1 + \operatorname{erf} \left(\sqrt{\xi} - \sqrt{\tau} - \frac{1}{8\sqrt{\xi}} - \frac{1}{8\sqrt{\tau}} \right) \right]. \quad (23)$$

In the limit of very large values of ξ ,

$$\frac{c_i}{c_{o_i}} = \frac{1}{2} \left[1 + \operatorname{erf} \left(\sqrt{\xi} - \sqrt{\tau} \right) \right]. \quad (24)$$

Since one may select the conditions under which to check the solution, obviously the simplicity of Eqs. 23 and 24 lead us to their application as a means of checking our numerical solution. Computation of concentration values at the exit of a bed using Eq. 23 requires a routine for calculating of erfc , the error function complement. A public domain subroutine for the calculation of error functions was used in a simple FORTRAN program to generate solutions which were used to check the orthogonal collocation program solutions.

4. RESULTS AND DISCUSSION

In checking our solution against an analytical solution, two series of tests were performed. The first, shown in Fig. 2, shows the effect of changing the number of collocation points on the fit. It would appear that five collocation points (three internal and two external collocation points) give an adequate match to the analytical data. The good agreement between the orthogonal collocation solution, even with a small number of collocation points, is strong indication that our approach is a valid one.

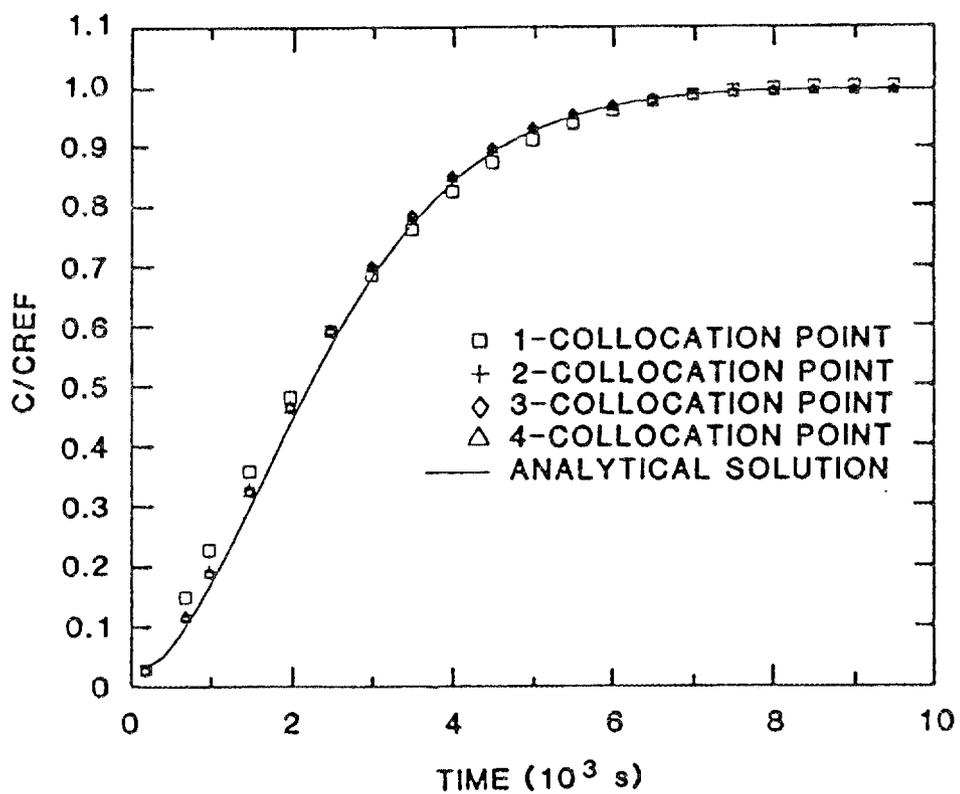


Fig. 2. A comparison of an analytical solution of a non-interacting two-component bed adsorption with the orthogonal collocation solution using different numbers of collocation points.

The second test is to increase the amount of interaction between the two adsorbing components by increasing the influence of the denominator terms in a binary, Freundlich-type isotherm, which is a reduction of Eq. 9 to the case where all the concentration exponents are as shown in the following expression:

$$q_i^* = \frac{a_i c_i^2}{b_{i1} c_j + b_{i2} c_j}, \quad (25)$$

where

$$a_1 = 6.0, a_2 = 24., b_{11} = b_{12} = b_{21} = b_{22} = 1.0$$

By increasing the c_2 from zero, interaction and non-linearity are increased. A series of four runs were made increasing the c_2 -values. Figure 3 shows the results. It is important to note that there is an orderly progression from one level of interaction to the next, and that the number of collocation points needed to arrive at a steady solution did not increase significantly with interaction. Based on these two results, it is assumed that the solutions presented in this report are valid approximations to the truth, and that the remaining solutions may be trusted.

The modified version of Carta's program for two components adsorption was tested by simulating the adsorption of 2-butanol and *t*-amyl alcohol in a carbon bed. The experimental data were extrapolated from Fig 5 in a paper by Liapis and Rippin (1978). Values of $k_{f1} = k_{f2} = 0.002 \text{ cm/s}$, $D_{p1} = 7.77 \times 10^{-6} \text{ cm}^2/\text{s}$, $D_{p2} = 13.03 \times 10^{-6} \text{ cm}^2/\text{s}$, $r_p = 0.05 \text{ cm}$, $V = 0.14 \text{ cm/s}$, $L = 41 \text{ cm}$, $\epsilon = 0.5$, and $\epsilon_p = 0.94$ were used in the column calculations. These values were taken from the paper by Liapis and Rippin (1978). The values for D_{p1} and D_{p2} were estimated by modeling the adsorption kinetics during batch studies (Liapis and Rippin 1977).

Figure 4 shows the results of a simulation where Carta's model was used, where k' was computed using Eq. 6, where $\bar{q}_i = q_i^*$ and where six collocations points (four

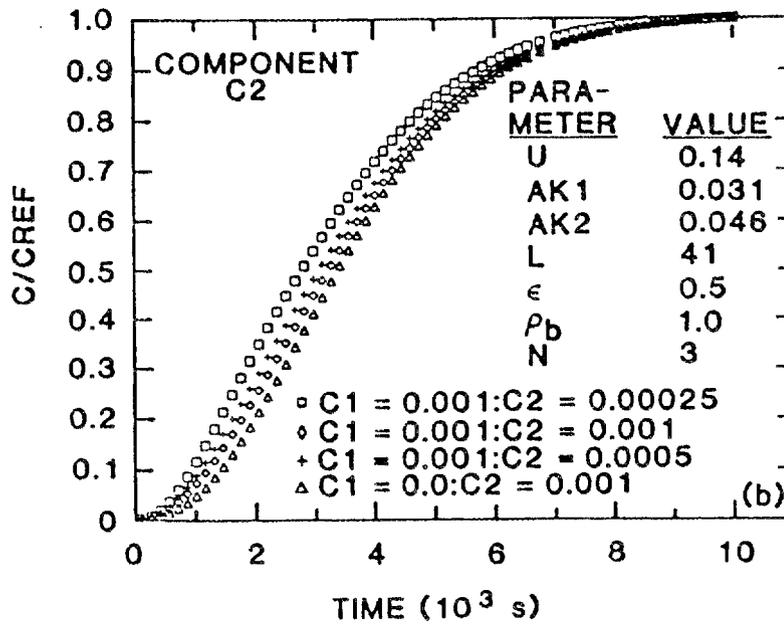
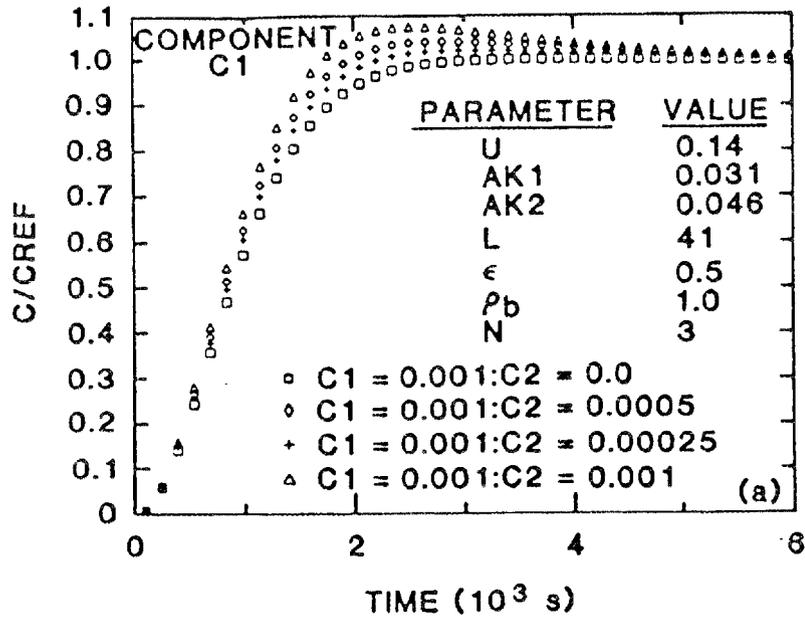


Fig. 3. Theoretical results using orthogonal collocation for four situations with increasing competition for sites between the adsorbing components.

internal and two external) were used. The model is qualitatively correct in that it predicts correctly that the 2-butanol begins to exit the column before *t*-amyl alcohol. The experimental data confirms this behavior. Furthermore, the model predicts that a maximum appears in the 2-butanol breakthrough curve. The model predicts a maximum value for $c_i/c_{f,i}$ (where $i=2$ -butanol) of 1.5. An experimental value of 1.1 is observed. The model does predict that the time at which this maximum occurs is approximately 8000 s, which agrees very well with experimental data. The experimental *t*-amyl alcohol data does not show a maximum value, which is also predicted by the model. Thus the disagreements are probably caused by incorrect values of the constants rather than a completely inapplicable model.

The initial breakthrough of each component as predicted by Carta's method of predicting k' , tends to lag the experimental data. This would indicate that adsorption of these components on the carbon particles is not controlled by mass transfer in the liquid film, thus suggesting that internal pore diffusion in the particles is the controlling parameter. Internal pore diffusion has been found to be the most important resistance in the adsorption of trace organics from liquids and especially wastewater (Westermarck 1975). To correct for internal pore diffusion resistance, Carta's assumption concerning the model was slightly modified by replacing the constant, k'_i , derived from the fluid film model (Eq. 3) with one predicted by Eq. 7. The latter prediction includes the effect of macropore diffusion as well as the fluid film resistance. In this case, $k'_1 = 0.031s^{-1}$ and $k'_2 = 0.046s^{-1}$. The result of this change is illustrated in Fig. 5 where 6 collocation points were also used. There is a significant improvement in agreement between the predicted and experimental breakthrough curves for both 2-butanol and *t*-amyl alcohol. Another area of considerable improvement is in the comparison between the predicted and experimental maximum point for the 2-butanol breakthrough curve. This model indicates that

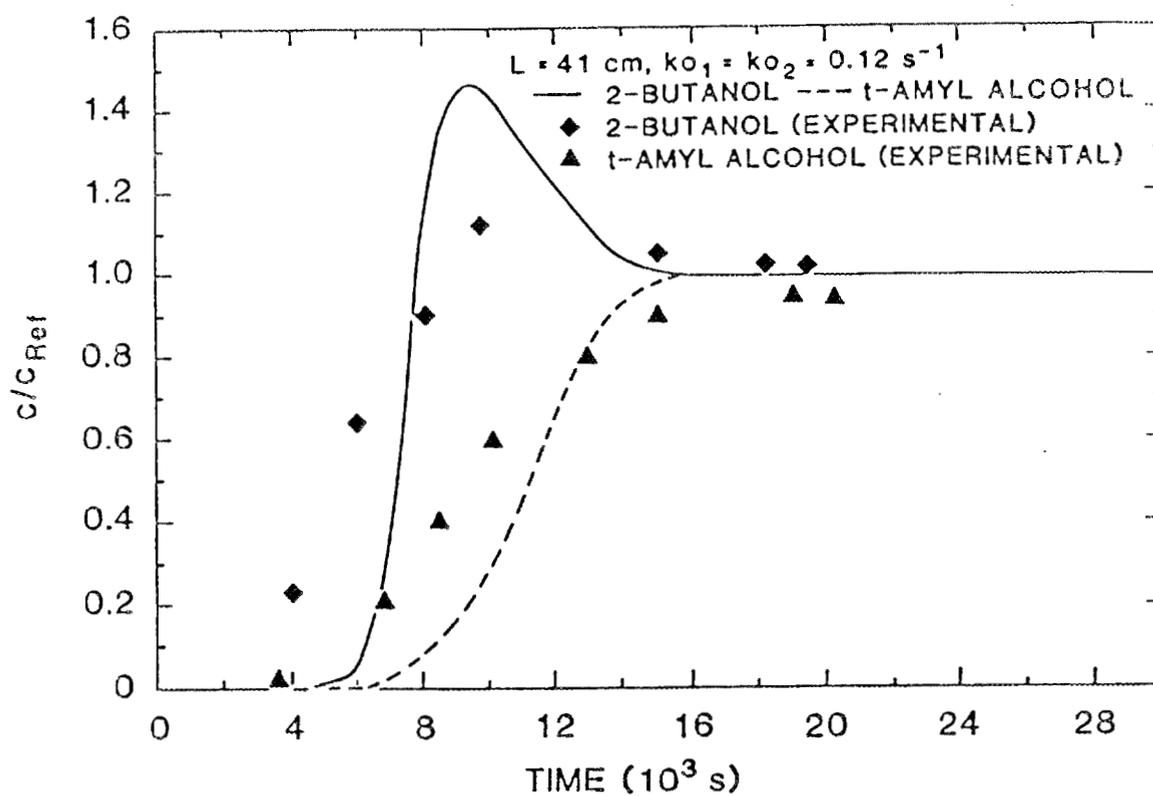


Fig. 4. Carbon Adsorption of Two Components (Film Model).

they are within 10% of each other.

The question of the proper number of collocation points was resolved in Fig. 6. It shows that when eight collocation points are used, the results are substantially unchanged from the six-point solution. Therefore, six collocation points are sufficient for convergence. It is possible that fewer points may be sufficient, but areas of large change in slope would show oscillatory behavior, and further testing would be required in that area. Typical run time on a Definicon 780+ Board operating at 20MHz is approximately 45 minutes. It is about 2.5 times faster on a VAX 8600. It is possible that considerable reductions in run time could be gained by improving the algorithms for solving the ODEs.

Figure 7 shows the result of using Santacesaria's model. There are no significant improvements by applying Santacesaria's model over the result in using the model which was employed in Fig. 5. The computational time is about the same (~ 45 min for six collocation points).

It is evident that a large number of runs are possible which would improve the prediction. However, empiricism was not our objective so we did not attempt a "best fit" of the data. Rather, the objective was to establish an efficient multicomponent adsorption program which could be used in a number of applications. Extensions to this work might include the introduction of dispersion, and micropore diffusion. These changes would be relatively easy and could give a considerably improved simulation of the data. Of course, the extension of the program to n components is feasible. Times associated with solution would increase proportionately; but, with the accelerating pace of speed increases in computation that will not pose a significant problem in the near future.

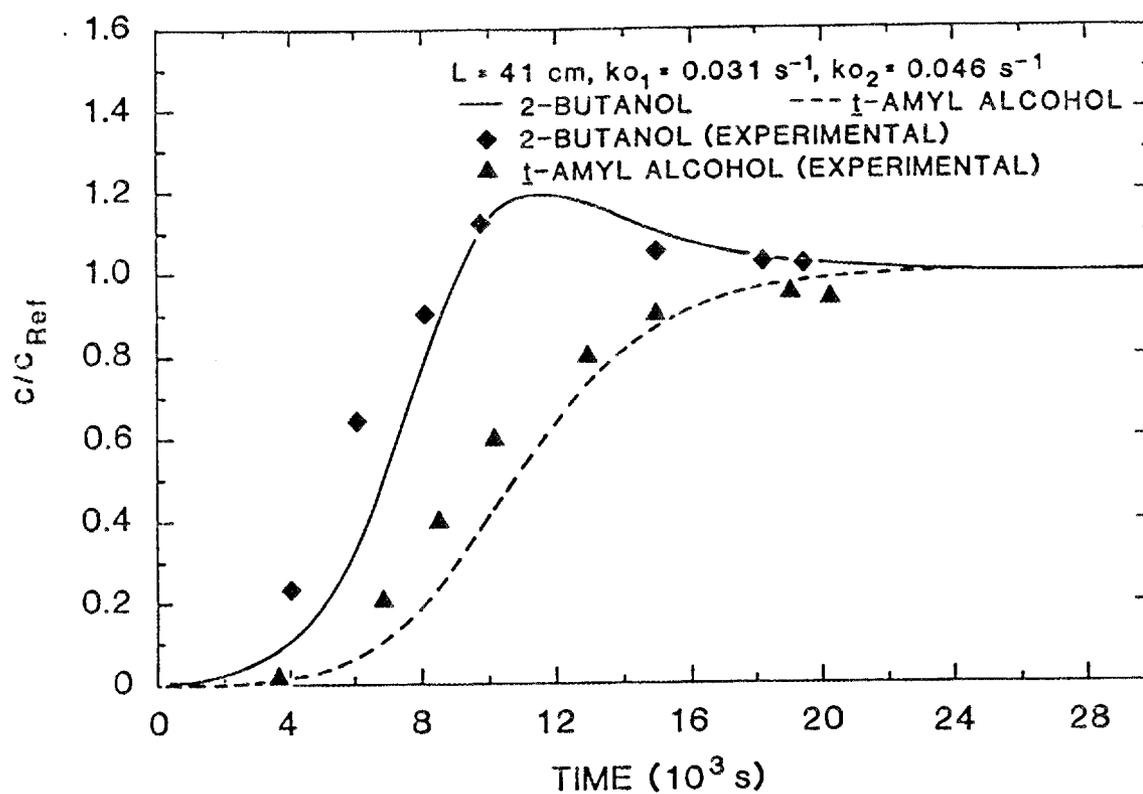


Fig. 5. Carbon Adsorption of Two Components (Film and Pore Diffusion Model-Six Collocation Points).

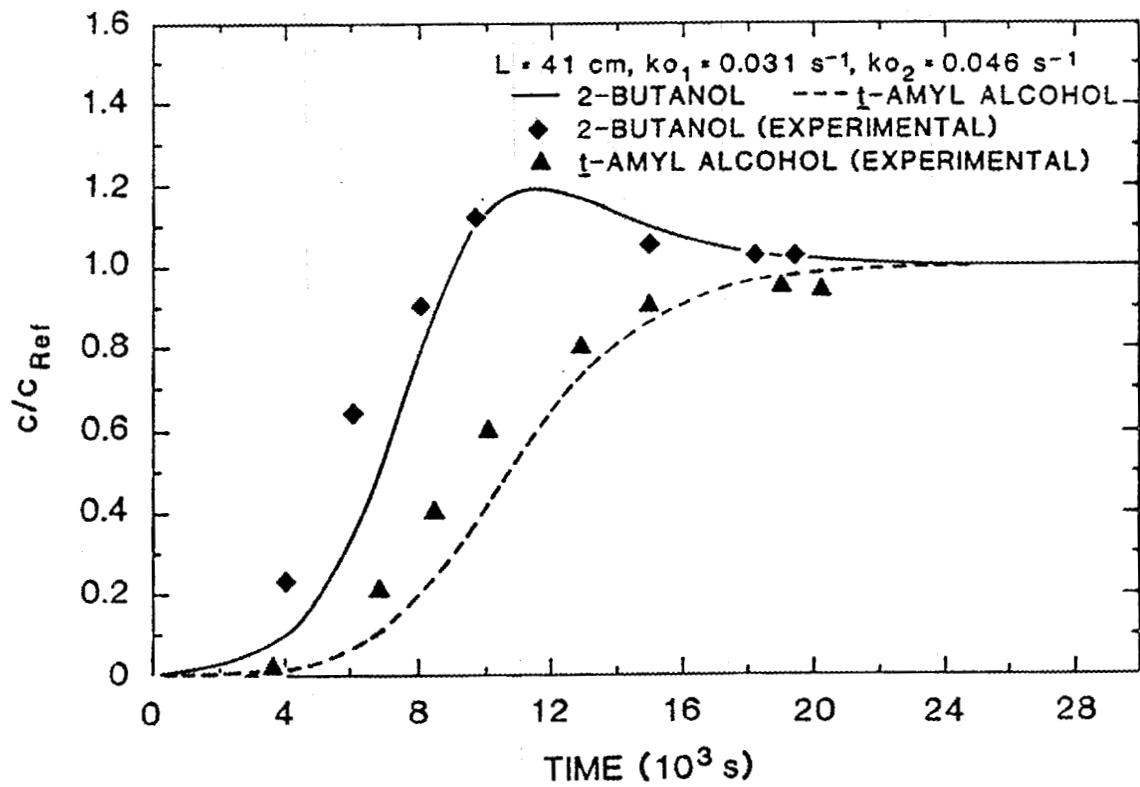


Fig. 6. Carbon Adsorption of Two Components (Film and Pore Diffusion Model-Eight Collocation Points).

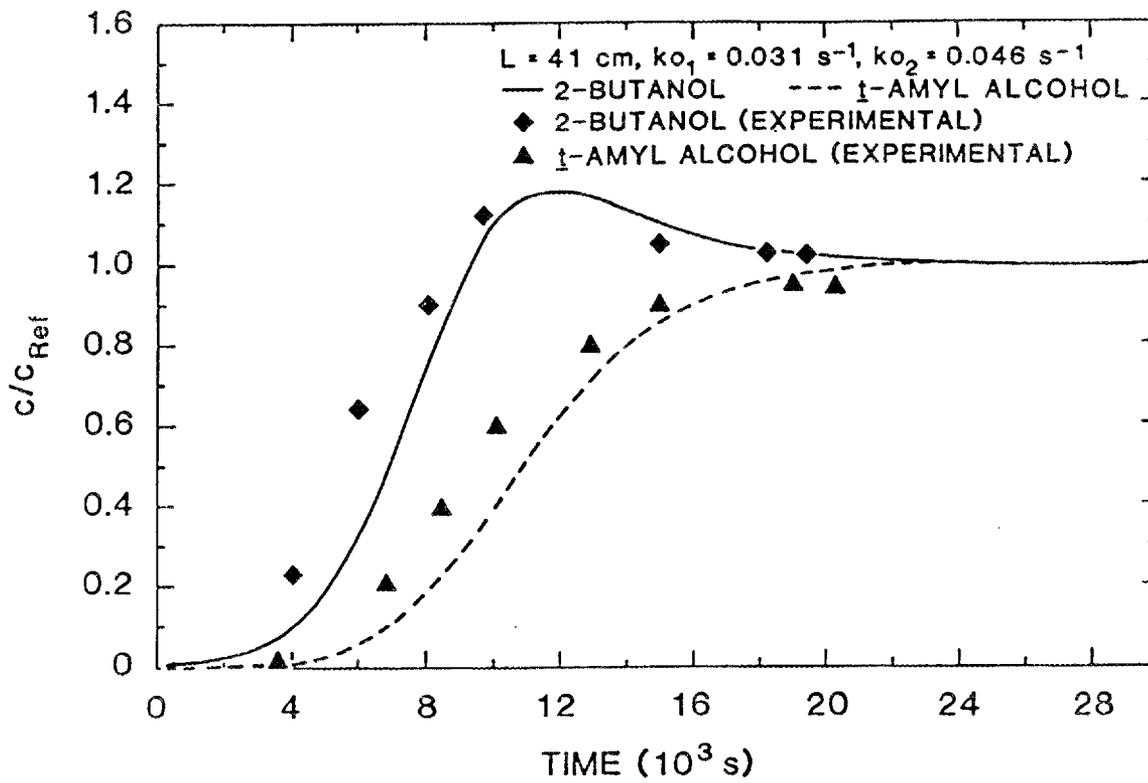


Fig. 7. Carbon Adsorption of 2-butanol and t-amyl alcohol as predicted by the Santacesaria (1982) model. Comparison is with the experimental data of Liapis and Rippin (1978).

5. CONCLUSIONS

The multicomponent bed adsorption model has been formulated to account for the interactions between components. The current application was to three-components systems, of which one is an inert carrier. A linear adsorption rate equation was used to model the dynamic characteristics of the adsorbed phase material. The orthogonal collocation routine, based on a single component program by Carta, simulated the behavior of the species in the bed with six collocation points.

The model was tested on experimental data for the adsorption of trace amounts of *2*-butanol and *t*-amyl alcohol in water on a bed of carbon. A simple film resistance controlled model does not adequately model the adsorption of these organics from water. Previous investigators determined that internal pore diffusion was the most significant resistance in this system; hence, this effect was incorporated into the model. This approach gave a significantly improved rendition of the data. The model proposed by Santacesaria was tested and was not significantly different from the model proposed in this study. There was some indication that our solution converged much more quickly.

Future work should include the development of an algorithm which incorporates a detailed model of the internal pore diffusion resistance as described by Liapis and Rippin (1978). Improvements may also be realized if the concentration driving force, $(c_i - c_i^*)$, in the linear rate model proposed by Carta and Santacesaria were replaced by $(q_i^* - \bar{q}_i)$. The numerical integration routines should also be upgraded to more efficient algorithms (i.e. fourth- or fifth- order Runge-Kutta method or DGEAR). Streamlining of the code for easier user access to variables such as the constants in Eqs. 19 and 20 and the plotting of the exit concentration profiles are needed.

6. ACKNOWLEDGEMENT

The authors are indebted to Dr. Giorgio Carta of the Department of Chemical Engineering, University of Virginia, for the permission to adapt his program and for the hours of consultation which he so freely gave.

7. NOTATION

$a_{i,1}$	constants (Eq. 9)
$b_{i,j}$	constants (Eq. 9)
c_i	liquid-phase concentration of component i, g/cm ³ .
c_{fi}	liquid-phase feed concentration of component i, g/cm ³ .
c_i^*	equilibrium concentration of component i, g/cm ³ .
c_{pi}	equilibrium concentration of component i, g/cm ³ .
$c_{i,j}$	concentration of component i at collocation point j, g/cm ³ .
$c_{i,j}^*$	equilibrium concentration of component i at collocation point j, g/cm ³ .
D_{pi}	pore diffusion coefficient of component i, cm ² /s.
k'_i	mass transfer constant of component i, s ⁻¹ .
k_{fi}	film mass transfer coefficient of component i, cm/s.
$l_k^{(1)}(x_i)$	discretization matrix.
L	total length of packed column, cm.
$m_{i,j}$	constants (Eq. 9).
$n_{i,1}$	constants (Eq. 9).
q_i^*	equilibrium sorbate concentration, g /cm ³ .
\bar{q}_i	average sorbate concentration, g /cm ³ .
r_p	radius of particles, cm.
t	time, s.
v	velocity of bulk fluid, cm/s.
x_i	dimensionless axial position in column, z/L , at collocation point i.
z	axial position in column, cm.
ϵ	bed porosity.
ϵ	particle porosity.
ρ_b	density of sorbent, g/cm ³ .

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APPENDIXES

APPENDIX 1: COMPUTER PROGRAM LISTINGS

This appendix lists the two main computer programs which are used to solve the system of equations described in Sect. 3 of the main body of this report. All of the programs are written in FORTRAN 77 and have been shown to operate on a wide variety of computers, including a VAX 8600, a SUN Model 3, and a Definicon 780+ plug-in board for an IBM PC-AT. A flowsheet of the two main programs is given in Fig. 6. The first FORTRAN program is for the solution of the two-component problem with interactive multicomponent Freundlich isotherms. The resistance to mass transport is assumed to be in the form of an effective fluid film which is modeled by a single constant for each component. The program was originally written by Giorgio Carta, University of Virginia, and was substantially modified by Michael Harris.

```

C*****
C TWO-COMPONENT ADSORPTION
C MICHAEL T. HARRIS - MODIFICATION IN NOVEMBER '87
C GIORGIO CARTA - ORIGINAL PROGRAM 8/14/86
C*****
C ADS3C.FOR - EFFECTIVE FLUID FILM RESISTANCE - 2 COMPONENT
C*****
C PROGRAM SOLVES FIRST ORDER PDE'S FOR WAVE PROPAGATION IN
C *
C FIXED BED ADSORPTION
C *
C CONSTANT FLUID VELOCITY
C *
C FLUID FILM MASS TRANSFER RESISTANCE
C *
C SOLUTION BY ORTHOGONAL COLLOCATION
C *
C RKG USED TO SOLVE RESULTING ODE'S
c *
C FREUNDLICH ADSORPTION ISOTHERM
c *
C*****
C*****
C*
C EPSI=VOIDAGE FRACTION ROB=BED SORBENT DENSITY
c *
C Z=BED LENGTH U=SUPERFICIAL VELOCITY
C *
C AK=MASS TRANSFER PARAMETER CF=FEED CONCENTRATION
C *
C C0=INITIAL CONCENTRATION CREF=REFERENCE CONC.
C *
C DTP=FEED PULSE DURATION X=COUT/CREF
C *
C TSTEP=STEP DURATION
C *

```

BLOCK FLOW DIAGRAM FOR ADS3C. FOR AND ADSSAN. FOR

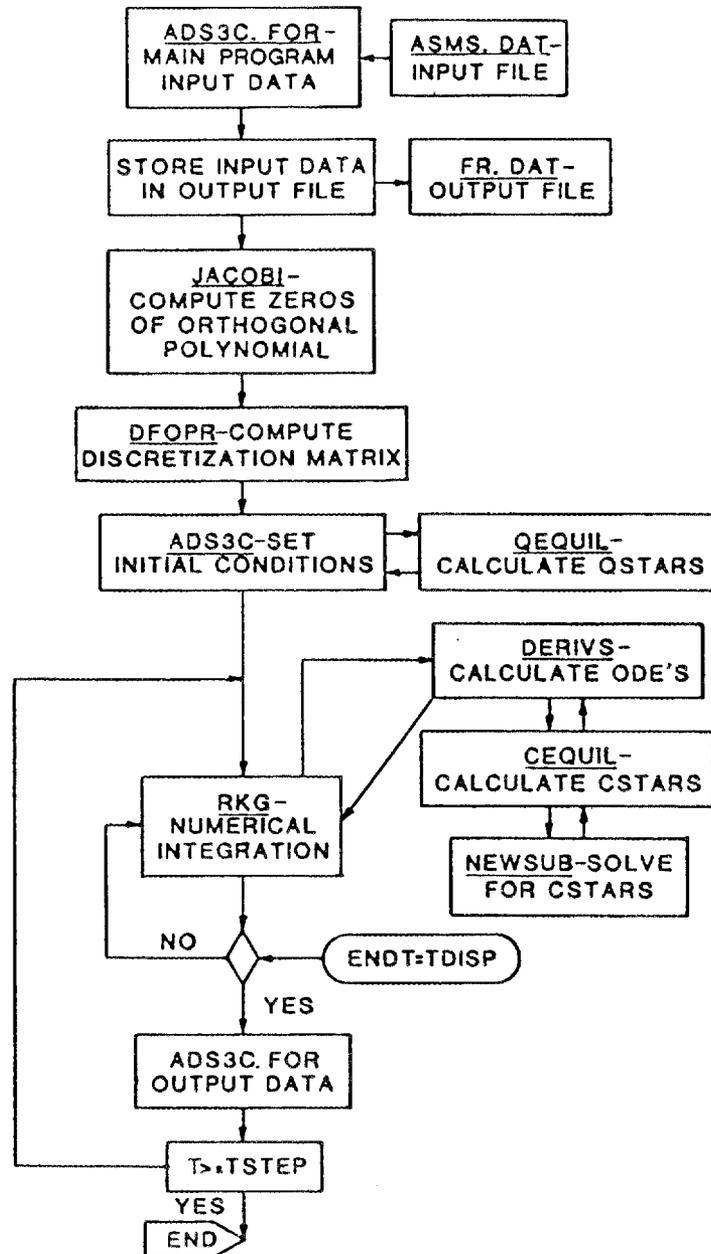


Fig. 8. Block Diagram for the orthogonal collocation solution of the adsorption of two components on a resin bed.

```

C*****
C
IMPLICIT REAL*8 (A-H,O-Z)
COMMON/LAGR/EL(40,40),NT,AKE1,AKE2,AKRB1,AKRB2,VZ,AM,Y01,
1Y02
COMMON/QE1/QM,QK,CREF
COMMON/ULK/CF1,CF2
DIMENSION Y(80)
DIMENSION DIF1(40),DIF2(40),DIF3(40),ROOT(40),VECT(40)
C
C
C INPUT COLUMN PARAMETERS
C
OPEN(UNIT=5,FILE='ASMC.DAT', STATUS='OLD')
REWIND 5

READ(5,*) U,AK1,AK2,Z
READ(5,*) EPSI,ROB
V=U/EPSI
C
C ASSIGN EQUILIBRIUM PARAMETERS QM AND QK
C FOR FREUNDLICH ISOTHERM: Q=QK*(C**QM)
C
QM=0.5
QK=0.6
C
READ(5,*) CF1,CF2,C01,C02,CREF1,CREF2
READ(5,*) TSTEP
C
C
AKE1=AK1/EPSI*(1-EPSI)
AKE2=AK2/EPSI*(1-EPSI)
AKRB1=AK1/ROB
AKRB2=AK2/ROB
VZ=V/Z
READ(5,*) N
READ(5,*) H
READ(5,*) TDISP
OPEN(UNIT=6,FILE='FR.DAT', STATUS='NEW')
WRITE(6,500)
500 FORMAT(' *** ESEB PROGRAM TO COMPUTE OUTPUT
1 PROFILE ***')
WRITE(6,501)
501 FORMAT(' ***** >> INPUT INFORMATION << *****')
WRITE(6,502) Z,AK1,AK2,U
502 FORMAT(' BED DEPTH =', F10.4, ' CM — BED
1AREA = ',F10.4,' CM — BED AREA = ',F10.4,

```

```

2'CM**2 — SUPERFICIAL VELOCITY = ', F10.4,' CM/SEC')
C WRITE(6,503) EPSI, ROB
C 503 FORMAT( ' BED VOID FRACTION =',F6.4,
C 1' BED DENSITY = ',F10.4,' GRAM/LITER')
C WRITE(6,504) CF1,CF2,C01,CO2,CREF1,CREF2
C 504 FORMAT(' CONCENTRATIONS - FEED1 = ',E10.4,'MOLES/L
C 1-FEED2 = ',E10.4,'MOLES/L-INITIAL2 = ',E10.4,'MOLES/L
C 1-INITIAL1 = ',E10.4, 'MOLES/L — REF1=',E10.4,' MOL/L'
C 1,'MOLES/L — REF2 =',E10.4,' MOL/L')
C WRITE(6,505) QM,QK
C 505 FORMAT(' FREUNDLICH CONSTANTS — PRE = ',F10.7,
c 1'EXPONENT = ',F10.7)
WRITE(6,506) TSTEP, H,TDISP,N
506 FORMAT(' TIMES =',3E10.4,
1' # OF COLLOCATION PT =',I2)
N0=1
N1=1
AL=0.
BE=0.
NT=N+N0+N1
NEQ=2*(NT+NT-1)
CALL JCOBI (N,N0,N1,AL,BE,DIF1,DIF2,DIF3,ROOT)
WRITE(6,114)
114 FORMAT(/,'COLLOCATION POINTS',/, '*****',/)
DO 200 I=1,NT
WRITE(6,115)I,ROOT(I)
115 FORMAT('X( ',I2,' ) = ',F7.4)
200 CONTINUE
WRITE(6,120)
120 FORMAT(/,'*****')
ID=1
DO 10 I=1,NT
C WRITE(6,125) I
CALL DFOPR (N,N0,N1,I,ID,DIF1,DIF2,DIF3,ROOT,VECT)
DO 5 K=1,NT
EL(K,I)= VECT(K)
C WRITE(6,130)K,EL(K,I)
5 CONTINUE
10 CONTINUE
125 FORMAT(/,'COLLOCATION POINT I = ',I2)
130 FORMAT(' L[1]( ',I2,' ) = ',E12.6)
C
C ASSIGN INITIAL CONDITIONS
C
T=0.0
CALL QEQUIL (C01,C02,QSTAR1,QSTAR2)
DO 20 I=1,NT-1

```

```

Y(I)=C01
Y(2*NT-1+I)=C02
Y(NT+I)=QSTAR1
Y(3*NT-1+I)=QSTAR2
20 CONTINUE
Y(NT)=QSTAR1
Y(3*NT-1)=QSTAR2
C
C ASSIGN BOUNDARY CONDITION
Y01=CF1
Y02=CF2
C
WRITE(6,123)
123 FORMAT(/,' RESULTS OF NUMERICAL INTEGRATION',/)
C
ENDT=TDISP
IFLAG=0
30 CONTINUE
IF(ENDT.LT.TSTEP.OR.IFLAG.EQ.1) GOTO 35
ENDT=TSTEP
IFLAG=1
35 CONTINUE
C
CALL RKG (NEQ,H,T,ENDT,Y)
C
IF(IFLAG.EQ.1) Y01=C01
IF(IFLAG.EQ.1) Y02=C02
XOUT1=Y(NT-1)/CREF1
XOUT2=Y(3*NT-2)/CREF2
c print *,t,xout
WRITE(6,40)T,XOUT1,XOUT2
40 FORMAT(F12.4,' ',F10.7,' ',F10.7)

C WRITE(6,45)Y01,Y(NT),Y02,Y(3*NT-1)
C45 FORMAT(/,'ENTRANCE CONCENTRATION = ',E12.6,' Y(NT) = ',
C > E12.6)
C
IF(IOUTF.EQ.1) WRITE(5,*)T,XOUT1,XOUT2
ENDT=ENDT+TDISP
IF(T.GE.TSTEP) GOTO 510
IF(IFLAG.EQ.1) GOTO 510
GOTO 30
510 CONTINUE
END
C
C

```

```

C
C SUBROUTINE TO CALCULATE DERIVATIVES OF ODE'S
C
SUBROUTINE DERIVS (NEQ,X,V,YP)
IMPLICIT REAL*8 (A-H,O-Z)
COMMON/LAGR/EL(40,40),NT,AKE1,AKE2,AKRB1,AKRB2,VZ,
1AM,Y01,Y02
DIMENSION V(80),YP(80)
CALL CEQUIL (V(NT),V(3*NT-1),CSTAR1,CSTAR2)
YP(NT)=AKRB1*(Y01 -CSTAR1)
YP(3*NT-1)=AKRB2*(Y02 - CSTAR2)
DO 10 I=1,NT-1
YSUM1=Y01*EL(1,I+1)
YSUM2=Y02*EL(1,I+1)
DO 15 K=1,NT-1
YSUM1=YSUM1+EL(K+1,I+1)*V(K)
YSUM2=YSUM2+EL(K+1,I+1)*V(2*NT-1+K)
15 CONTINUE
CALL CEQUIL (V(NT+I),V(3*NT-1+I),CSTAR1,CSTAR2)
YP(I)=-ake1*(v(i)-cstar1)-vz*ysum1
YP(2*NT-1+I)=-ake2*(v(2*nt-1+i)-cstar2)-vz*ysum2
YP(NT+I)=AKRB1*(V(I)-CSTAR1)
YP(3*NT-1+I)=AKRB2*(V(2*NT-1+I)-CSTAR2)
10 continue
RETURN
END
C
C
SUBROUTINE QEQUIL (X,Y,Q1,Q2)
IMPLICIT REAL*8 (A-H,O-Z)
COMMON/QE1/QM,QK,CREF
C
C SUBROUTINE CALCULATES QSTAR GIVEN C FROM THE
C EQUILIBRIUM ISOTHERM: Q=f(C)
C

A11=1.6
ZN11=1.27
A12=1.0
ZN12=0.812
B11=0.626
ZM11=0.76
B21=1.07
ZM21=1.254
B22=1.0
ZM22=0.906
A21=0.045

```

```

ZN21=0.634

IF(X.LT.1.0E-12) X=DABS(X)
IF(Y.LT.1.0E-12) Y=DABS(Y)
IF(Y.EQ.0.AND.X.EQ.0) GOTO 2111
Q1 = A11*X**ZN11/(A12*X**ZN12 + B11*Y**ZM11)
Q2 = B21*Y**ZM21/(B22*Y**ZM22 + A21*X**ZN21)
GOTO 2112
2111 Q1 = 0
Q2 = 0
2112 CONTINUE
C
RETURN
END
C
SUBROUTINE CEQUIL (Q1,Q2,C1,C2)
IMPLICIT REAL*8 (A-H,O-Z)
COMMON/QE1/QM,QK,CREF
C
C SUBROUTINE CALCULATES CSTAR GIVEN Q FROM THE
C EQUILIBRIUM ISOTHERM: C=f(Q)
C
A11=1.6
ZN11=1.27
A12=1.0
ZN12=0.812
B11=0.626
ZM11=0.76
B21=1.07
ZM21=1.254
B22=1.0
ZM22=0.906
A21=.045
ZN21=.634
IF(Q1.LT.1.0E-12) Q1=DABS(Q1)
IF(Q2.LT.1.0E-12) Q2=DABS(Q2)
CALL NEWSUB (Q1,Q2,C1,C2)
C C=(Q/QK)**(1.0/QM)
C
RETURN
END
C
C
C SUBROUTINE JCOBI
C
C EVALUATION OF ROOTS AND DERIVATIVES OF JACOBI POLYNOMIALS
C P(N) (AL,BE)

```

```

C
C FIRST EVALUATION OF COEFFICIENTS IN RECURSION FORMULAE
C RECURSION COEFFICIENTS ARE STORED IN DIF1 AND DIF2
C
C SUBROUTINE FROM MICHELSEN AND VILLADSEN, P. 418
C
SUBROUTINE JCOBI(N,N0,N1,AL,BE,DIF1,DIF2,DIF3,ROOT)
IMPLICIT REAL*8(A-H,O-Z)
DIMENSION DIF1(40),DIF2(40),DIF3(40),ROOT(40)
C
AB=AL+BE
AD=BE-AL
AP=BE*AL
DIF1(1)=(AD/(AB+2.)+1.)/2.
DIF2(1)=0.0
IF(N.LT.2) GO TO 15
DO 10 I=2,N
Z1=I-1.
Z=AB+2.*Z1
DIF1(I)=(AB*AD/Z/(Z+2.)+1.)/2.
IF (I.NE.2) GO TO 11
DIF2(I)=(AB+AP+Z1)/Z/Z/(Z+1.)
11 Z=Z*Z
Y=Z1*(AB+Z1)
Y=Y*(AP+Y)
DIF2(I)=Y/Z/(Z-1.)
10 CONTINUE
15 X=0.
DO 20 I=1,N
25 XD=0.0
XN=1.0
XD1=0.0
XN1=0.0
DO 30 J=1,N
XP=(DIF1(J)-X)*XN-DIF2(J)*XD
XP1=(DIF1(J)-X)*XN1-DIF2(J)*XD1-XN
XD=XN
XD1=XN1
XN=XP
30 XN1=XP1
ZC=1.0
Z=XN/XN1
IF(I.EQ.1) GO TO 21
DO 22 J=2,I
22 ZC=ZC-Z/(X-ROOT(J-1))
21 Z=Z/ZC
X=X-Z

```

```

IF(DABS(Z).GT.1.0D-12) GO TO 25
ROOT(I)=X
X=X+.0001
20 CONTINUE
C
C ADD INTERPOLATION POINTS AT X=0 AND X=1 IF REQUIRED
C
NT=N+N0+N1
IF(N0.EQ.0) GO TO 35
DO 31 I=1,N
J=N+1-I
31 ROOT(J+1)=ROOT(J)
ROOT(1)=0.
35 IF(N1.EQ.1) ROOT(NT)=1.0
C
C EVALUATE DERIVATIVES OF NODAL POLYNOMIAL
C
DO 40 I=1,NT
X=ROOT(I)
DIF1(I)=1.
DIF2(I)=0.
DIF3(I)=0.
DO 40 J=1,NT
IF(J.EQ.I) GO TO 40
Y=X-ROOT(J)
DIF3(I)=Y*DIF3(I)+3.*DIF2(I)
DIF2(I)=Y*DIF2(I)+2.*DIF1(I)
DIF1(I)=Y*DIF1(I)
40 CONTINUE
RETURN
END
C
C
C SUBROUTINE DFOPR
C FINDS DISCRETIZATION MATRICES AND GAUSSIAN QUADRATURE
C WEIGHTS FOR GENERAL COLLOCATION APPROXIMATION
C SUBROUTINE JCOBI MUST BE EXECUTED FIRST TO FIND ZEROS AND
C DERIVATIVED OF NODAL POLYNOMIAL
C
SUBROUTINE DFOPR (N,N0,N1,I,ID,DIF1,DIF2,DIF3,ROOT,VECT)
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION DIF1(40),DIF2(40),DIF3(40),ROOT(40),VECT(40)
C
C GAUSSIAN WEIGHTS NORMALIZED TO SUM 1
C ID=1 : DISCRETIZATION MATRIX FOR Y'(X)
C ID=2 : DISCRETIZATION MATRIX FOR Y''(X)
C ID=3 : GAUSSIAN QUADRATURE WEIGHTS

```

C VECT:= COMPUTED DIFFERENTIATION WEIGHTS

C

```
NT=N+N0+N1
IF(ID.EQ.3) GOTO 10
DO 20 J=1,NT
IF(J.NE.1) GOTO 21
IF(ID.NE.1) GOTO 5
VECT(I)=DIF2(I)/DIF1(I)/2
GOTO 20
5 VECT(I)=DIF3(I)/DIF1(I)/3
GOTO 20
21 Y=ROOT(I)-ROOT(J)
VECT(J)=DIF1(I)/DIF1(J)/Y
IF(ID.EQ.2) VECT(J)=VECT(J)*(DIF2(I)/DIF1(I)-2/Y)
20 CONTINUE
GOTO 50
10 Y=0.
DO 25 J=1,NT
X=ROOT(J)
AX=X*(1-X)
IF (N0.EQ.0) AX=AX/X/X
IF (N1.EQ.0) AX=AX/(1-X)/(1-X)
VECT(J)=AX/DIF1(J)**2
25 Y=Y+VECT(J)
DO 60 J=1,NT
60 VECT(J)=VECT(J)/Y
50 RETURN
END
```

C

C

```
SUBROUTINE RKG (N,H,T,ENDT,Y)
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION YP(80),V(80),Y(80),C(80),W(80),Q(80)
```

C

```
C ..SOLVES SYSTEMS OF N ODE'S
C ...REQUIRES AS INPUT:
C .....N = NO. OF EQUATIONS
C .....H = DELTA-T
C .....ENDT = FINAL T-VALUE
C .....T = INDEPENDENT VARIABLE
C .....Y(J) = DEPENDENT VARIABLES
C ...REQUIRES AS SUBROUTINE "DERIVS"
C .....dY(1)/dT = YP(1)
C .....dY(2)/dT = YP(2)
C .....
C .....dY(N)/dT = YP(N)
C ..VARIABLES Y(J) IN SUBROUTINE DERIVS ARE:
```

```

C .....V(1) = Y(1)
C .....V(2) = Y(2)
C .....
C
C
K=3
20 CONTINUE
U=T
DO 30 J=1,N
V(J)=Y(J)
30 CONTINUE
CALL DERIVS (N,T,V,YP)
DO 40 J=1,N
C(J)=H*YP(J)
W(J)=Y(J) + .5*C(J)
Q(J)=C(J)
V(J)=W(J)
40 CONTINUE
U=T+H/2
CALL DERIVS (N,T,V,YP)
DO 50 J=1,N
C(J)=H*YP(J)
W(J)=W(J) + .2928932*(C(J)-Q(J))
Q(J)=.5857864*C(J) + .1213024*Q(J)
V(J)=W(J)
50 CONTINUE
CALL DERIVS (N,T,V,YP)
DO 60 J=1,N
C(J)=H*YP(J)
W(J)=W(J) + 1.707107*(C(J)-Q(J))
Q(J)=3.414214*C(J) - 4.12132*Q(J)
V(J)=W(J)
60 CONTINUE
U=T+H
CALL DERIVS (N,T,V,YP)
DO 70 J=1,N
C(J)=H*YP(J)
Y(J)=W(J) + C(J)/6. - Q(J)/3.

70 CONTINUE
T=T+H

IF (T.LT.ENDT) GOTO 20
RETURN
END

SUBROUTINE NEWSUB (Q1,Q2,XO,YO)

```

IMPLICIT REAL*8 (A-H,O-Z)

C REM NEWTON-RAPHSON METHOD FOR SOLVING SIMULTANEOUS
C NONLINEAR EQUATIONS

COMMON/ULK/CF1,CF2

i=0

A11=1.6

ZN11=1.27

A12=1.0

ZN12=0.812

B11=0.626

ZM11=0.76

B21=1.07

ZM21=1.254

B22=1.0

ZM22=0.906

A21=.045

ZN21=.634

X=(Q1*A12/A11)**(1/(ZN11-ZN12))

Y=(Q2*B22/B21)**(1/(ZM21-ZM22))

IF(CF2.EQ.0.OR.Q2.EQ.0) GOTO 2241

IF(CF1.EQ.0.OR.Q1.EQ.0) GOTO 2242

IF(Q1.EQ.0.and.q2.eq.0) goto 2240

2100 PHI = A11*X**ZN11/(A12*X**ZN12 + B11*Y**ZM11) - Q1

XI = B21*Y**ZM21/(B22*Y**ZM22 + A21*X**ZN21) - Q2

BB1 = (A12*X**ZN12 + B11*Y**ZM11)

BB2 = (B22*Y**ZM22 + A21*X**ZN21)

DPHX1=A11*ZN11*X**(ZN11-1)/BB1

DPHX2=-A12*A11*ZN12*X**(ZN11-ZN12+1)/BB1**2

DPHX=DPHX1+DPHX2

DPHY = -A11*B11*ZM11*X**ZN11*Y**(ZM11-1)/BB1**2

DXIY1 = B21*ZM21*Y**(ZM21-1)/BB2

DXIY2= - B22*B21*ZM22*Y**(ZM21-ZM22+1)/BB2**2

DXIY = DXIY1 + DXIY2

DXIX = -B21*A21*ZN21*X**(ZN21-1)*Y**ZM21/BB2**2

DDD = DPHX*DXIY-DXIX*DPHY

ZH11= (-PHI*DXIY+XI*DPHY)/DDD

ZK11 = (-XI*DPHX+PHI*DXIX)/DDD

X = X + ZH11

Y = Y + ZK11

IF(X.LT.0) GOTO 2240

IF(Y.LT.0) GOTO 2240

XO=X

YO=Y

```
RPXS = ZH11/X  
RPYS=ZK11/Y  
IF(RPXS.LE. 0.01.AND.RPYS.LE.0.01) GOTO 2250
```

```
GOTO 2100  
2240 X=0  
Y=0  
YO=0  
XO=0  
GOTO 2250  
2241 XO=(Q1*A12/A11)**(1/(ZN11-ZN12))  
YO=0.  
GOTO 2250  
2242 YO=(Q2*B22/B21)**(1/(ZM21-ZM22))  
XO=0.  
2250 CONTINUE
```

```
RETURN  
END
```

This appendix lists the second of the main computer programs which are used to solve the system of equations described in Sect. 3 of the main body of this report. The routine is written in FORTRAN 77 and have been shown to operate on a wide variety of computers, including a VAX 8600, a SUN Model 3, and a Definicon 780+ plug-in board for an IBM PC-AT. A flowsheet of this program is given in Fig. 6. Like the first FORTRAN program, this is for the solution of the two- component problem with interactive multicomponent Freundlich isotherms. The resistance to mass transport is assumed to be in the form assumed by Santacesaria et al. (1982) of an effective fluid film plus macropore diffusion is modeled by a two constants for each component. The program was originally written by Giorgio Carta, University of Virginia, and was substantially modified by Michael Harris.

```

C*****
C TWO-COMPONENT ADSORPTION -SANTACESARIA MODEL
C MICHAEL T. HARRIS - MODIFICATION IN NOVEMBER '87
C GIORGIO CARTA - ORIGINAL PROGRAM 8/14/86
C*****
C ADSSAN.FOR - FILM AND MACROPORE RESISTANCE - 2 COMPONENT
C *
C*****
C PROGRAM SOLVES FIRST ORDER PDE'S FOR WAVE PROPAGATION IN
C *
C FIXED BED ADSORPTION
C *
C CONSTANT FLUID VELOCITY
C *
C SANTACESARIA'S MODEL (EXCLUDING AXIAL DISPERSION EFFECTS)

C *
C SOLUTION BY ORTHOGONAL COLLOCATION
C *
C RKG USED TO SOLVE RESULTING ODE'S
c *
C FREUNDLICH ADSORPTION ISOTHERM
c *
C*****_
c*
C*****_
C*
C EPSI=VOIDAGE FRACTION ROB=BED SORBENT DENSITY
c *
C Z=BED LENGTH U=SUPERFICIAL VELOCITY
C *
C AK=MASS TRANSFER PARAMETER CF=FEED CONCENTRATION
C *
C CO=INITIAL CONCENTRATION CREF=REFERENCE CONC.
C *
C DTP=FEED PULSE DURATION X=COU/CREF
C *

```

```

C TSTEP=STEP DURATION
C *
C*****
c *
C
IMPLICIT REAL*8 (A-H,O-Z)
COMMON/LAGR/EL(40,40),NT,AKE1,AKE2,AKRB1,AKRB2,VZ,AM,Y01,
1y02
COMMON/QE1/QM,QK,CREF
COMMON/ULK/CF1,CF2,ESP
DIMENSION Y(80)
DIMENSION DIF1(40),DIF2(40),DIF3(40),ROOT(40),VECT(40)
C
C
C INPUT COLUMN PARAMETERS
C
OPEN(UNIT=5,FILE='ASMC.DAT', STATUS='OLD')
REWIND 5

READ(5,*) U,AK1,AK2,Z
READ(5,*) EPSI,ROB
V=U/EPSI
C
C ASSIGN EQUILIBRIUM PARAMETERS QM AND QK
C FOR FREUNDLICH ISOTHERM: Q=QK*(C**QM)
C
QM=0.5
QK=0.6
C
READ(5,*) CF1,CF2,C01,C02,CREF1,CREF2
READ(5,*) TSTEP
C
C
AKE1=AK1/EPSI*(1-EPSI)
AKE2=AK2/EPSI*(1-EPSI)
AKRB1=AK1/ROB
AKRB2=AK2/ROB
VZ=V/Z
READ(5,*) N
READ(5,*) H
READ(5,*) TDISP,ESP
OPEN(UNIT=6,FILE='FR.DAT', STATUS='NEW')
WRITE(6,500)
500 FORMAT(' *** ESEB PROGRAM TO COMPUTE OUTPUT
1 PROFILE ***')
WRITE(6,501)
501 FORMAT(' ***** >> INPUT INFORMATION << *****')
WRITE(6,502) Z,AK1,AK2,U
502 FORMAT(' BED DEPTH =', F10.4, ' CM — BED

```

```

1AREA = ,F10.4, ' CM — BED AREA = ,F10.4,
2'CM**2 — SUPERFICIAL VELOCITY = , F10.4, ' CM/SEC'
C WRITE(6,503) EPSI, ROB
C 503 FORMAT( ' BED VOID FRACTION =',F6.4,
C 1' BED DENSITY = ,F10.4, ' GRAM/LITER')
C WRITE(6,504) CF1,CF2,C01,CO2,CREF1,CREF2
C 504 FORMAT(' CONCENTRATIONS - FEED1 = ',E10.4,'MOLES/L
C 1-FEED2 = ',E10.4,'MOLES/L-INITIAL2 = ',E10.4,'MOLES/L
C 1-INITIAL1 = ',E10.4, 'MOLES/L — REF1=',E10.4, ' MOL/L'
C 1,'MOLES/L — REF2 =',E10.4, ' MOL/L')
C WRITE(6,505) QM,QK
C 505 FORMAT(' FREUNDLICH CONSTANTS — PRE = ,F10.7,
c 1'EXPONENT = ,F10.7)
WRITE(6,506) TSTEP, H,TDISP,N
506 FORMAT(' TIMES =',3E10.4,
1' # OF COLLOCATION PT =',I2)
N0=1
N1=1
AL=0.
BE=0.
NT=N+N0+N1
NEQ=2*(NT+NT-1)
CALL JCOBI (N,N0,N1,AL,BE,DIF1,DIF2,DIF3,ROOT)
WRITE(6,114)
114 FORMAT(/,'COLLOCATION POINTS',/, '*****',/)
DO 200 I=1,NT
WRITE(6,115)I,ROOT(I)
115 FORMAT('X( ',I2, ' ) = ',F7.4)
200 CONTINUE
WRITE(6,120)
120 FORMAT(/, '*****')
ID=1
DO 10 I=1,NT
C WRITE(6,125) I
CALL DFOPR (N,N0,N1,I,ID,DIF1,DIF2,DIF3,ROOT,VECT)
DO 5 K=1,NT
EL(K,I)= VECT(K)
C WRITE(6,130)K,EL(K,I)
5 CONTINUE
10 CONTINUE
125 FORMAT(/,'COLLOCATION POINT I = ',I2)
130 FORMAT(' L[1]( ',I2, ' ) = ',E12.6)
C
C ASSIGN INITIAL CONDITIONS
C
T=0.0
CALL QEQUIL (C01,C02,QSTAR1,QSTAR2)
DO 20 I=1,NT-1
Y(I)=C01

```

```

Y(2*NT-1+I)=C02
Y(NT+I)=QSTAR1
Y(3*NT-1+I)=QSTAR2
20 CONTINUE
Y(NT)=QSTAR1
Y(3*NT-1)=QSTAR2
C
C ASSIGN BOUNDARY CONDITION
Y01=CF1
Y02=CF2
C
WRITE(6,123)
123 FORMAT(/,' RESULTS OF NUMERICAL INTEGRATION',/)
C
ENDT=TDISP
IFLAG=0
30 CONTINUE
IF(ENDT.LT.TSTEP.OR.IFLAG.EQ.1) GOTO 35
ENDT=TSTEP
IFLAG=1
35 CONTINUE
C
CALL RKG (NEQ,H,T,ENDT,Y)
C
IF(IFLAG.EQ.1) Y01=C01
IF(IFLAG.EQ.1) Y02=C02
XOUT1=Y(NT-1)/CREF1
XOUT2=Y(3*NT-2)/CREF2
c print *,t,xout
WRITE(6,40)T,XOUT1,XOUT2
40 FORMAT(F12.4,' ',F10.7,' ',F10.7)

C WRITE(6,45)Y01,Y(NT),Y02,Y(3*NT-1)
C45 FORMAT(/,'ENTRANCE CONCENTRATION = ',E12.6,' Y(NT) = ',
C > E12.6)
C
IF(1OUTF.EQ.1) WRITE(5,*)T,XOUT1,XOUT2
ENDT=ENDT+TDISP
IF(T.GE.TSTEP) GOTO 510
IF(IFLAG.EQ.1) GOTO 510
GOTO 30
510 CONTINUE
END
C
C
C
C SUBROUTINE TO CALCULATE DERIVATIVES OF ODE'S
C

```

```

SUBROUTINE DERIVS (NEQ,X,V,YP)
IMPLICIT REAL*8 (A-H,O-Z)
COMMON/LAGR/EL(40,40),NT,AKE1,AKE2,AKRB1,AKRB2,VZ,
1AM,Y01,Y02
DIMENSION V(80),YP(80)
CALL CEQUIL (V(NT),V(3*NT-1),CSTAR1,CSTAR2)
YP(NT)=AKRB1*(Y01 -CSTAR1)
YP(3*NT-1)=AKRB2*(Y02 - CSTAR2)
DO 10 I=1,NT-1
YSUM1=Y01*EL(1,I+1)
YSUM2=Y02*EL(1,I+1)
DO 15 K=1,NT-1
YSUM1=YSUM1+EL(K+1,I+1)*V(K)
YSUM2=YSUM2+EL(K+1,I+1)*V(2*NT-1+K)
15 CONTINUE
CALL CEQUIL (V(NT+I),V(3*NT-1+I),CSTAR1,CSTAR2)
YP(I)=-ake1*(v(i)-cstar1)-vz*ysum1
YP(2*NT-1+I)=-ake2*(v(2*nt-1+i)-cstar2)-vz*ysum2
YP(NT+I)=AKRB1*(V(I)-CSTAR1)
YP(3*NT-1+I)=AKRB2*(V(2*NT-1+I)-CSTAR2)
10 continue
RETURN
END
C
C
SUBROUTINE QEQUIL (X,Y,Q1,Q2)
IMPLICIT REAL*8 (A-H,O-Z)
COMMON/QE1/QM,QK,CREF
C
C SUBROUTINE CALCULATES QSTAR GIVEN C FROM THE
C EQUILIBRIUM ISOTHERM: Q=f(C)
C

A11=1.6
ZN11=1.27
A12=1.0
ZN12=0.812
B11=0.626
ZM11=0.76
B21=1.07
ZM21=1.254
B22=1.0
ZM22=0.906
A21=0.045
ZN21=0.634

IF(X.LT.1.0E-12) X=DABS(X)
IF(Y.LT.1.0E-12) Y=DABS(Y)
IF(Y.EQ.0.AND.X.EQ.0) GOTO 2111

```

```

Q1 = A11*X**ZN11/(A12*X**ZN12 + B11*Y**ZM11)
Q2 = B21*Y**ZM21/(B22*Y**ZM22 + A21*X**ZN21)
GOTO 2112
2111 Q1 = 0
Q2 = 0
2112 CONTINUE
C
RETURN
END
C
SUBROUTINE CEQUIL (Q1,Q2,C1,C2)
IMPLICIT REAL*8 (A-H,O-Z)
COMMON/QE1/QM,QK,CREF
C
C SUBROUTINE CALCULATES CSTAR GIVEN Q FROM THE
C EQUILIBRIUM ISOTHERM: C=f(Q)
C
A11=1.6
ZN11=1.27
A12=1.0
ZN12=0.812
B11=0.626
ZM11=0.76
B21=1.07
ZM21=1.254
B22=1.0
ZM22=0.906
A21=.045
ZN21=.634
IF(Q1.LT.1.0E-12) Q1=DABS(Q1)
IF(Q2.LT.1.0E-12) Q2=DABS(Q2)
CALL NEWSUB (Q1,Q2,C1,C2)
C C=(Q/QK)**(1.0/QM)
C
RETURN
END
C
C
C SUBROUTINE JCOBI
C
C EVALUATION OF ROOTS AND DERIVATIVES OF JACOBI POLYNOMIALS
C P(N) (AL,BE)
C
C FIRST EVALUATION OF COEFFICIENTS IN RECURSION FORMULAE
C RECURSION COEFFICIENTS ARE STORED IN DIF1 AND DIF2
C
C SUBROUTINE FROM MICHELSEN AND VILLADSEN, P. 418
C
SUBROUTINE JCOBI(N,N0,N1,AL,BE,DIF1,DIF2,DIF3,ROOT)

```

```

IMPLICIT REAL*8(A-H,O-Z)
DIMENSION DIF1(40),DIF2(40),DIF3(40),ROOT(40)
C
AB=AL+BE
AD=BE-AL
AP=BE*AL
DIF1(1)=(AD/(AB+2.)+1.)/2.
DIF2(1)=0.0
IF(N.LT.2) GO TO 15
DO 10 I=2,N
Z1=I-1.
Z=AB+2.*Z1
DIF1(I)=(AB*AD/Z/(Z+2.)+1.)/2.
IF (I.NE.2) GO TO 11
DIF2(I)=(AB+AP+Z1)/Z/Z/(Z+1.)
11 Z=Z*Z
Y=Z1*(AB+Z1)
Y=Y*(AP+Y)
DIF2(I)=Y/Z/(Z-1.)
10 CONTINUE
15 X=0.
DO 20 I=1,N
25 XD=0.0
XN=1.0
XD1=0.0
XN1=0.0
DO 30 J=1,N
XP=(DIF1(J)-X)*XN-DIF2(J)*XD
XP1=(DIF1(J)-X)*XN1-DIF2(J)*XD1-XN
XD=XN
XD1=XN1
XN=XP
30 XN1=XP1
ZC=1.0
Z=XN/XN1
IF(I.EQ.1) GO TO 21
DO 22 J=2,I
22 ZC=ZC-Z/(X-ROOT(J-1))
21 Z=Z/ZC
X=X-Z
IF(DABS(Z).GT.1.0D-12) GO TO 25
ROOT(I)=X
X=X+.0001
20 CONTINUE
C
C ADD INTERPOLATION POINTS AT X=0 AND X=1 IF REQUIRED
C
NT=N+N0+N1
IF(N0.EQ.0) GO TO 35

```

```

DO 31 I=1,N
J=N+1-I
31 ROOT(J+1)=ROOT(J)
ROOT(1)=0.
35 IF(N1.EQ.1) ROOT(NT)=1.0
C
C EVALUATE DERIVATIVES OF NODAL POLYNOMIAL
C
DO 40 I=1,NT
X=ROOT(I)
DIF1(I)=1.
DIF2(I)=0.
DIF3(I)=0.
DO 40 J=1,NT
IF(J.EQ.I) GO TO 40
Y=X-ROOT(J)
DIF3(I)=Y*DIF3(I)+3.*DIF2(I)
DIF2(I)=Y*DIF2(I)+2.*DIF1(I)
DIF1(I)=Y*DIF1(I)
40 CONTINUE
RETURN
END
C
C
C SUBROUTINE DFOPR
C FINDS DISCRETIZATION MATRICES AND GAUSSIAN QUADRATURE
C WEIGHTS FOR GENERAL COLLOCATION APPROXIMATION
C SUBROUTINE JCOBI MUST BE EXECUTED FIRST TO FIND ZEROS AND
C DERIVATIVED OF NODAL POLYNOMIAL
C
SUBROUTINE DFOPR (N,N0,N1,I,ID,DIF1,DIF2,DIF3,ROOT,VECT)
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION DIF1(40),DIF2(40),DIF3(40),ROOT(40),VECT(40)
C
C GAUSSIAN WEIGHTS NORMALIZED TO SUM 1
C ID=1 : DISCRETIZATION MATRIX FOR Y'(X)
C ID=2 : DISCRETIZATION MATRIX FOR Y''(X)
C ID=3 : GAUSSIAN QUADRATURE WEIGHTS
C VECT= COMPUTED DIFFERENTIATION WEIGHTS
C
NT=N+N0+N1
IF(ID.EQ.3) GOTO 10
DO 20 J=1,NT
IF(J.NE.I) GOTO 21
IF(ID.NE.1) GOTO 5
VECT(I)=DIF2(I)/DIF1(I)/2
GOTO 20
5 VECT(I)=DIF3(I)/DIF1(I)/3
GOTO 20

```

```

21 Y=ROOT(I)-ROOT(J)
VECT(J)=DIF1(I)/DIF1(J)/Y
IF(ID.EQ.2) VECT(J)=VECT(J)*(DIF2(I)/DIF1(I)-2/Y)
20 CONTINUE
GOTO 50
10 Y=0.
DO 25 J=1,NT
X=ROOT(J)
AX=X*(1-X)
IF (N0.EQ.0) AX=AX/X/X
IF (N1.EQ.0) AX=AX/(1-X)/(1-X)
VECT(J)=AX/DIF1(J)**2
25 Y=Y+VECT(J)
DO 60 J=1,NT
60 VECT(J)=VECT(J)/Y
50 RETURN
END
C
C
SUBROUTINE RKG (N,H,T,ENDT,Y)
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION YP(80),V(80),Y(80),C(80),W(80),Q(80)
C
C ..SOLVES SYSTEMS OF N ODE'S
C ...REQUIRES AS INPUT:
C .....N = NO. OF EQUATIONS
C .....H = DELTA-T
C .....ENDT = FINAL T-VALUE
C .....T = INDEPENDENT VARIABLE
C .....Y(J) = DEPENDENT VARIABLES
C ...REQUIRES AS SUBROUTINE "DERIVS"
C .....dY(1)/dT = YP(1)
C .....dY(2)/dT = YP(2)
C .....
C .....dY(N)/dT = YP(N)
C ...VARIABLES Y(J) IN SUBROUTINE DERIVS ARE:
C .....V(1) = Y(1)
C .....V(2) = Y(2)
C .....
C
C
K=3
20 CONTINUE
U=T
DO 30 J=1,N
V(J)=Y(J)
30 CONTINUE
CALL DERIVS (N,T,V,YP)
DO 40 J=1,N

```

```

C(J)=H*YP(J)
W(J)=Y(J) + .5*C(J)
Q(J)=C(J)
V(J)=W(J)
40 CONTINUE
U=T+H/2
CALL DERIVS (N,T,V,YP)
DO 50 J=1,N
C(J)=H*YP(J)
W(J)=W(J) + .2928932*(C(J)-Q(J))
Q(J)=.5857864*C(J) + .1213024*Q(J)
V(J)=W(J)
50 CONTINUE
CALL DERIVS (N,T,V,YP)
DO 60 J=1,N
C(J)=H*YP(J)
W(J)=W(J) + 1.707107*(C(J)-Q(J))
Q(J)=3.414214*C(J) - 4.12132*Q(J)
V(J)=W(J)
60 CONTINUE
U=T+H
CALL DERIVS (N,T,V,YP)
DO 70 J=1,N
C(J)=H*YP(J)
Y(J)=W(J) + C(J)/6. - Q(J)/3.

70 CONTINUE
T=T+H

IF (T.LT.ENDT) GOTO 20
RETURN
END

```

```

SUBROUTINE NEWSUB (Q1,Q2,XO,YO)
IMPLICIT REAL*8 (A-H,O-Z)

```

```

C REM NEWTON-RAPHSON METHOD FOR SOLVING SIMULTANEOUS
C NONLINEAR EQUATIONS
COMMON/ULK/CF1,CF2,ESP
i=0
A11=1.6
ZN11=1.27
A12=1.0
ZN12=0.812
B11=0.626
ZM11=0.76
B21=1.07
ZM21=1.254
B22=1.0

```

```

ZM22=0.906
A21=.045
ZN21=.634
X=(Q1*A12/A11)**(1/(ZN11-ZN12))
Y=(Q2*B22/B21)**(1/(ZM21-ZM22))

IF(CF2.EQ.0.OR.Q2.EQ.0) GOTO 2241
IF(CF1.EQ.0.OR.Q1.EQ.0) GOTO 2242
IF(Q1.EQ.0.and.q2.eq.0) goto 2240
Z100 PHI = (1-0.0)*A11*X**ZN11/(A12*X**ZN12 + B11*Y**ZM11)+
1ESP*X-Q1
XI = (1-0.0)*B21*Y**ZM21/(B22*Y**ZM22 + A21*X**ZN21)
1+ESP*Y - Q2

BB1 = (A12*X**ZN12 + B11*Y**ZM11)
BB2 = (B22*Y**ZM22 + A21*X**ZN21)
DPHX1=A11*ZN11*X**(ZN11-1)/BB1
DPHX2=-A12*A11*ZN12*X**(ZN11-ZN12+1)/BB1**2
DPHX=DPHX1+DPHX2 + ESP
DPHY = -A11*B11*ZM11*X**ZN11*Y**(ZM11-1)/BB1**2
DXIY1 = B21*ZM21*Y**(ZM21-1)/BB2
DXIY2= - B22*B21*ZM22*Y**(ZM21-ZM22+1)/BB2**2
DXIY = DXIY1 + DXIY2 + ESP
DXIX = -B21*A21*ZN21*X**(ZN21-1)*Y**ZM21/BB2**2
DDD = DPHX*DXIY-DXIX*DPHY
ZH11= (-PHI*DXIY+XI*DPHY)/DDD
ZK11 = (-XI*DPHX+PHI*DXIX)/DDD
X = X + ZH11
Y = Y +ZK11
IF(X.LT.0) GOTO 2240
IF(Y.LT.0) GOTO 2240
XO=X
YO=Y

RPXS = ZH11/X
RPYS=ZK11/Y
IF(RPXS.LE. 0.01.AND.RPYS.LE.0.01) GOTO 2250

GOTO 2100
2240 X=0
Y=0
YO=0
XO=0
GOTO 2250
2241 ALP = A11/A12
ZNP = ZN11 - ZN12
CALL NEWP (Q1,XO,ALP,ZNP,ESP)
YO = 0.
GOTO 2250

```

```
2242 ALP = B21/B22
ZNP = ZM21 - ZM22
CALL NEWP (Q1,YO,ALP,ZNP,ESP)
XO=0.
2250 CONTINUE
```

```
RETURN
END
```

```
SUBROUTINE NEWP (QA1,XO1,A1,ZNU,EP)
IMPLICIT REAL*8 (A-H,O-Z)
write(*,*)'enter newsub'
i=0
IF(QA1.EQ.0.)GOTO 203
201 ZH=(1-EP)*A1*XO1**(ZNU-1.0)+EP
i=i+1
XO1 = XO1 + ZH
RZH = ZH/XO1
write(*,*)i,rzh
IF(RZH.LE.0.0001) GOTO 202
GOTO 201
203 XO1=0.0
202 CONTINUE
RETURN
END
```

A1.1 Program input information

The two programs we have listed operate in precisely the same way. One must create a data input file, (ASMC.DAT), which is used to provide parameters and other input information for the operation of the program. The file is open format with one input per line as follows:

TYPICAL INPUT INFORMATION[†]

Input	Description
0.11	Superficial Velocity, U
0.05	Mass Transfer Coefficient, AK1
0.05	Mass Transfer Coefficient, AK2
438.5	Length of Column, L
0.35	Density of Particles, ROB
0.5	Porosity of Bed, EPSI
0.0502	Feed Concentration, CF1
0.0502	Feed Concentration, CF2
0.000	Initial Concentration, CO1
0.000	Initial Concentration, CO2
0.0502	Reference Concentration, CREF1
0.0502	Reference Concentration, CREF2
200000	TSTEP
4	No. of Internal Collocation Points
2.00	Numerical Integration Step
1000	TDISP
0.94	Particle Porosity (ADSSAN.FOR only)

[†] In the data file only the numerical values appear.

The output information is given in a file called FR.DAT which is created by the program. The results appear as follows:

Typical Output File

TIME	XOUT1	XOUT2
100.0	-.0166266	-.0041621
200.0	.0539132	.0056909
300.0	.0536714	.0057257
400.0	.0540616	.0058031
500.0	.0546014	.0059109
600.0	.0553202	.0060504
700.0	.0562222	.0062226
800.0	.0573093	.0064278
900.0	.0585764	.0066659
1000.0	.0600262	.0069374
1100.0	.0616591	.0072429
1200.0	.0634749	.0075825
1300.0	.0654777	.0079567
1400.0	.0676783	.0083677
1500.0	.0700456	.0088120
1600.0	.0725943	.0092917
1700.0	.0753236	.0098068
1800.0	.0782330	.0103579
1900.0	.0813222	.0109453
2000.0	.0845912	.0115695
2100.0	.0880403	.0122310
2200.0	.0916699	.0129307
2300.0	.0954808	.0136693
2400.0	.0994741	.0144477
2500.0	.1036511	.0152672
2600.0	.1080133	.0161290
2700.0	.1125625	.0170345
2800.0	.1173007	.0179852
2900.0	.1222297	.0189829

Typical Output File
CONTINUED

TIME	XOUT1	XOUT2
3000.0	.1273512	.0200295
3100.0	.1327631	.0211239
3200.0	.1384219	.0222938
3300.0	.1442828	.0235212
3400.0	.1503633	.0248116
3500.0	.1567755	.0261790
3600.0	.1633354	.0276053
3700.0	.1701359	.0291039
3800.0	.1771796	.0306781
3900.0	.1845563	.0323452
4000.0	.1922083	.0340947
4100.0	.2000405	.0359239
4200.0	.2081361	.0378450
4300.0	.2164984	.0398622
4400.0	.2251307	.0419797
4500.0	.2340361	.0442018
4600.0	.2432174	.0465329
4700.0	.2526766	.0489775
4800.0	.2624157	.0515401
4900.0	.2724359	.0542250
5000.0	.2828898	.0570659
5100.0	.2937639	.0600490
5200.0	.3046674	.0631360
5300.0	.3158547	.0663637
5400.0	.3273207	.0697362
5500.0	.3390619	.0732575
5600.0	.3510739	.0769315
5700.0	.3635181	.0806343
5800.0	.3761890	.0846618
5900.0	.3893704	.0888618

Typical Output File
CONTINUED

TIME	XOUT1	XOUT2
6000.0	.4026807	.0932403
6100.0	.4162485	.0977965
6200.0	.4303758	.1025778
6300.0	.4444953	.1075133
6400.0	.4588580	.1126368
6500.0	.4734456	.1179454
6600.0	.4882394	.1234559
6700.0	.5032174	.1291637
6800.0	.5189223	.1351517
6900.0	.5342569	.1412626
7000.0	.5497749	.1475793
7100.0	.5654656	.1540971
7200.0	.5812423	.1608141
7300.0	.5971108	.1677314
7400.0	.6130499	.1748479
7500.0	.6290383	.1821624
7600.0	.6450374	.1896762
7700.0	.6610842	.1973825
7800.0	.6770891	.2052782
7900.0	.6930541	.2133616
8000.0	.7089560	.2216291
8100.0	.7258146	.2302875
8200.0	.7414635	.2389162
8300.0	.7570825	.2477231
8400.0	.7725392	.2566952
8500.0	.7878178	.2658268
8600.0	.8028963	.2751117
8700.0	.8177531	.2845431
8800.0	.8323675	.2941140
8900.0	.8468658	.3038560

Typical Output File
CONTINUED

TIME	XOUT1	XOUT2
9000.0	.8608105	.3136562
9100.0	.8745708	.3235997
9200.0	.8880240	.3336514
9300.0	.9011441	.3438026
9400.0	.9139167	.3540444
9500.0	.9263284	.3643679
9600.0	.9383670	.3747639
9700.0	.9500218	.3852232
9800.0	.9612832	.3957365
9900.0	.9721432	.4062942
10000.0	.9825953	.4168868
10100.0	.9926341	.4275050
10200.0	1.0022557	.4381391
10300.0	1.0114577	.4487799
10400.0	1.0202387	.4594179
10500.0	1.0285989	.4700439
10600.0	1.0365395	.4806489
10700.0	1.0440629	.4912239
10800.0	1.0511728	.5017601
10900.0	1.0578736	.5122490
11000.0	1.0641709	.5226824
11100.0	1.0700713	.5330521
11200.0	1.0755821	.5433504
11300.0	1.0807113	.5535697
11400.0	1.0854676	.5637030
11500.0	1.0898606	.5737432
11600.0	1.0939001	.5836839
11700.0	1.0975964	.5935189
11800.0	1.1009605	.6032422
11900.0	1.1040033	.6128483

Typical Output File
CONTINUED

TIME	XOUT1	XOUT2
12000.0	1.1067363	.6223322
12100.0	1.1091711	.6316889
12200.0	1.1113194	.6409141
12300.0	1.1131930	.6500036
12400.0	1.1148039	.6589538
12500.0	1.1161638	.6677612
12600.0	1.1172846	.6764229
12700.0	1.1181781	.6849362
12800.0	1.1188557	.6932987
12900.0	1.1193290	.7015085
13000.0	1.1196091	.7095638
13100.0	1.1197070	.7174634
13200.0	1.1196336	.7252061
13300.0	1.1193994	.7327912
13400.0	1.1190144	.7402183
13500.0	1.1184888	.7474870
13600.0	1.1178320	.7545975
13700.0	1.1170534	.7615500
13800.0	1.1161619	.7683451
13900.0	1.1151661	.7749835
14000.0	1.1140745	.7814661
14100.0	1.1128948	.7877941
14200.0	1.1116348	.7939688
14300.0	1.1103017	.7999917
14400.0	1.1089025	.8058644
14500.0	1.1074438	.8115887
14600.0	1.1059319	.8171665
14700.0	1.1043727	.8225998
14800.0	1.1027720	.8278908
14900.0	1.1011351	.8330416

Typical Output File
CONTINUED

TIME	XOUT1	XOUT2
15000.0	1.0994670	.8380546
15100.0	1.0977725	.8429322
15200.0	1.0960561	.8476768
15300.0	1.0943221	.8522909
15400.0	1.0925743	.8567770
15500.0	1.0908165	.8611377
15600.0	1.0890522	.8653756
15700.0	1.0872846	.8694933
15800.0	1.0855166	.8734935
15900.0	1.0837510	.8773789
16000.0	1.0819905	.8811519
16100.0	1.0802375	.8848154
16200.0	1.0784941	.8883719
16300.0	1.0767623	.8918241
16400.0	1.0750440	.8951744
16500.0	1.0733410	.8984256
16600.0	1.0716546	.9015801
16700.0	1.0699865	.9046405
16800.0	1.0683377	.9076093
16900.0	1.0667095	.9104888
17000.0	1.0651028	.9132815
17100.0	1.0635186	.9159898
17200.0	1.0619577	.9186160
17300.0	1.0604208	.9211624
17400.0	1.0589084	.9236312
17500.0	1.0574211	.9260246
17600.0	1.0559593	.9283448
17700.0	1.0545234	.9305938
17800.0	1.0531136	.9327738
17900.0	1.0517303	.9348867

Typical Output File
CONTINUED

TIME	XOUT1	XOUT2
18000.0	1.0503734	.9369345
18100.0	1.0490433	.9389191
18200.0	1.0477398	.9408424
18300.0	1.0464630	.9427061
18400.0	1.0452129	.9445122
18500.0	1.0439894	.9462622
18600.0	1.0427923	.9479579
18700.0	1.0416216	.9496009
18800.0	1.0404769	.9511928
18900.0	1.0393581	.9527352
19000.0	1.0382650	.9542295
19100.0	1.0371973	.9556773
19200.0	1.0361546	.9570799
19300.0	1.0351368	.9584387
19400.0	1.0341435	.9597551
19500.0	1.0331742	.9610304
19600.0	1.0322288	.9622658
19700.0	1.0313068	.9634625
19800.0	1.0304078	.9646218
19900.0	1.0295315	.9657448
20000.0	1.0286775	.9668327
20100.0	1.0278454	.9678865
20200.0	1.0270347	.9689072
20300.0	1.0262452	.9698959
20400.0	1.0254763	.9708536
20500.0	1.0247277	.9717813
20600.0	1.0239990	.9726799
20700.0	1.0232898	.9735502
20800.0	1.0225996	.9743932
20900.0	1.0219280	.9752097

Typical Output File
CONTINUED

TIME	XOUT1	XOUT2
21000.0	1.0212747	.9760006
21100.0	1.0206393	.9767666
21200.0	1.0200213	.9775085
21300.0	1.0194203	.9782270
21400.0	1.0188360	.9789230
21500.0	1.0182680	.9795970
21600.0	1.0177159	.9802498
21700.0	1.0171793	.9808820
21800.0	1.0166578	.9814943
21900.0	1.0161511	.9820873
22000.0	1.0156588	.9826616
22100.0	1.0151805	.9832178
22200.0	1.0147160	.9837565
22300.0	1.0142648	.9842781
22400.0	1.0138266	.9847832
22500.0	1.0134011	.9852724
22600.0	1.0129880	.9857461
22700.0	1.0125869	.9862048
22800.0	1.0121975	.9866491
22900.0	1.0118195	.9870792
23000.0	1.0114526	.9874957
23100.0	1.0110966	.9878991
23200.0	1.0107510	.9882896
23300.0	1.0104158	.9886678
23400.0	1.0100904	.9890340
23500.0	1.0097748	.9893885
23600.0	1.0094685	.9897318
23700.0	1.0091715	.9900642
23800.0	1.0088833	.9903860
23900.0	1.0086038	.9906976

Typical Output File
CONTINUED

TIME	XOUT1	XOUT2
24000.0	1.0083328	.9909992
24100.0	1.0080699	.9912913
24200.0	1.0078149	.9915740
24300.0	1.0075677	.9918478
24400.0	1.0073280	.9921128
24500.0	1.0070956	.9923694
24600.0	1.0068703	.9926177
24700.0	1.0066519	.9928581
24800.0	1.0064402	.9930909
24900.0	1.0062349	.9933162
25000.0	1.0060360	.9935343
25100.0	1.0058432	.9937454
25200.0	1.0056563	.9939497
25300.0	1.0054752	.9941475
25400.0	1.0052997	.9943390
25500.0	1.0051297	.9945243
25600.0	1.0049649	.9947037
25700.0	1.0048052	.9948773
25800.0	1.0046505	.9950453
25900.0	1.0045006	.9952079
26000.0	1.0043555	.9953652
26100.0	1.0042148	.9955175
26200.0	1.0040786	.9956649
26300.0	1.0039466	.9958076
26400.0	1.0038187	.9959456
26500.0	1.0036949	.9960792
26600.0	1.0035750	.9962084
26700.0	1.0034589	.9963335
26800.0	1.0033464	.9964546
26900.0	1.0032375	.9965717

Typical Output File
CONTINUED

TIME	XOUT1	XOUT2
27000.0	1.0031320	.9966850
27100.0	1.0030299	.9967946
27200.0	1.0029310	.9969007
27300.0	1.0028352	.9970034
27400.0	1.0027425	.9971027
27500.0	1.0026528	.9971988
27600.0	1.0025659	.9972917
27700.0	1.0024818	.9973816
27800.0	1.0024003	.9974686
27900.0	1.0023215	.9975528
28000.0	1.0022452	.9976342
28100.0	1.0021713	.9977130
28200.0	1.0020998	.9977892
28300.0	1.0020306	.9978629
28400.0	1.0019636	.9979342
28500.0	1.0018988	.9980031
28600.0	1.0018361	.9980698
28700.0	1.0017754	.9981343
28800.0	1.0017166	.9981967
28900.0	1.0016598	.9982571
29000.0	1.0016048	.9983154
29100.0	1.0015516	.9983719
29200.0	1.0015001	.9984265
29300.0	1.0014502	.9984793
29400.0	1.0014020	.9985303
29500.0	1.0013554	.9985797
29600.0	1.0013102	.9986275
29700.0	1.0012666	.9986736
29800.0	1.0012243	.9987183
29900.0	1.0011835	.9987615
30000.0	1.0011439	.9988032

APPENDIX 2. NEWTON-RAPHSON METHOD FOR SOLVING SIMULTANEOUS EQUATIONS

The following is an example of the Newton-Raphson method for solving two simultaneous equations. First, define two functions as follows:

$$\phi(x, y) = 0, \quad (\text{A1})$$

$$\psi(x, y) = 0. \quad (\text{A2})$$

If x_o and y_o are approximate values of a pair of roots and h and k are corrections, so that

$$x = x_o + h,$$

$$y = y_o + k,$$

then (A1) and (A2) becomes

$$\phi(x_o + h, y_o + k) = 0, \quad (\text{A3})$$

$$\psi(x_o + h, y_o + k) = 0. \quad (\text{A4})$$

Expanding (A3) and (A4) by Taylor's theorem for a function of two variables, the following expression is derived:

$$\phi(x_o, y_o) + h \left(\frac{\partial \phi}{\partial x} \right)_o + k \left(\frac{\partial \phi}{\partial y} \right)_o = 0 \quad (\text{A5})$$

$$\psi(x_o, y_o) + h \left(\frac{\partial \psi}{\partial x} \right)_o + k \left(\frac{\partial \psi}{\partial y} \right)_o = 0 \quad (\text{A6.})$$

Equations A5 and A6 are solved simultaneously to determine values of h and k . New values of x_o and y_o are computed by calculating x and y , and substituting these values into Eqs. A5 and A6. This procedure is repeated until h and k approach zero or some predetermined quantity.

In the present algorithm (Carta's Model), the functions ϕ and ψ are defined as follows:

$$\phi(c_1^*, c_2^*) = \frac{A11 * c_1^{*Z N 11}}{A12 * c_1^{*Z N 12} + B11 * c_2^{*Z M 11}} - \bar{q}_1 \quad (A7)$$

$$\psi(c_1^*, c_2^*) = \frac{B21 * c_2^{*Z M 21}}{B22 * c_2^{*Z M 22} + A21 * c_1^{*Z N 21}} - \bar{q}_2 \quad (A8)$$

Santacesaria's model requires that ϕ and ψ are to be defined as:

$$\phi(c_1^*, c_2^*) = \frac{A11 * c_1^{*Z N 11}}{A12 * c_1^{*Z N 12} + B11 * c_2^{*Z M 11}} - \bar{q}_1 + \epsilon_p c_1^* \quad (A7)$$

$$\psi(c_1^*, c_2^*) = \frac{B21 * c_2^{*Z M 21}}{B22 * c_2^{*Z M 22} + A21 * c_1^{*Z N 21}} - \bar{q}_2 + \epsilon_p c_2^* \quad (A8)$$

The term $(1 - \epsilon_p)$ has been deleted because q_i^* , as is given by Liapis and Rippin (1978), is in terms of grams of sorbent per unit total particle volume; therefore, a volume correction is not necessary.

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