.SIMULATION OF PACKED BED
ADSORBER   BY   ORTHOGONAL
COLLOCATION

A   Thesis

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by

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We, the undersigned, certify that Mr. ABDUL HAMID MOLLAH candidate for the degree of MASTER OF SCIENCE IN ENGINEERING (CHEMICAL) has presented his thesis on the subject SIMULATION OF PACKED BED ADSORBER BY ORTHOGONAL COLLOCATION, that the thesis is acceptable in form and content, and that the student demonstrated a satisfactory knowledge of the field covered by this thesis in an oral examination held on 28th September, 1986.

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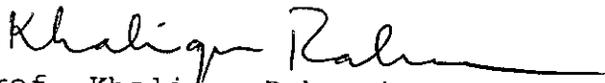
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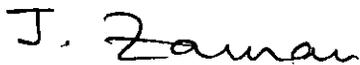
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ABSTRACT

Chromatographic technique is an important tool for the determination of equilibrium constant and diffusivity of a component. These parameters are used to design packed column for separation of trace components. In this work theoretical chromatograms are generated by orthogonal collocation technique.

A packed column subjected to pulse input at the column inlet is dynamically modelled by writting mass balance around differential section of micropore, macropore and packed bed. The model equations are reduced to ordinary differential equation by orthogonal collocation method. These equations are integrated using Runge-Kutta-Merson routine.

The effect of adsorption equilibrium constant, mass transfer resistance, pore diffusion and axial disperson on chromatograms are investigated.

It is shown that when the particles are nonporous or adsorption equilibrium constant is zero a Gaussian peak results. In this situation the peak broadening is the consequence of axial dispersion alone. When either macropore or micropore diffusion is slow, the peak assumes skewed shape.

Large particles (i.e. pellets) and high practical velocity should be used in measurement of macropore diffusion and large microparticle and high velocity should be used for measurement of micropore diffusion.

ACKNOWLEDGEMENT

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CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Adsorption in packed column is in wide industrial use
for the removal or recovery of dilute components from a fluid
stream. It is in extensive use in the chemical industry for
separating a higher boiling constituent from other components
of a system of vapors and gases (e.g., natural gasoline may
be separated from natural gas by adsorption on charcoal) and
to remove undesirable colors (e.g., from lubricating oils,
employing activated clay). The operation is gaining importance
in processes for the removal of pollutants from wastewater
and exhaust gases.

In recent years much effort has been applied to simu-
late chemical processes so as to examine at least some of
the basic phenomena occuring in the process, and hence gain
a greater understanding of the system to be developed. Mathe-
matical modelling is relatively less expensive compared to
an experimental modelling. Experimental work is time consuming
and require much effort and is usually quite costly because a
large number of experiments must be performed to extract design
data. Unfortunately in comparison with the modelling work done
on absorption and distillation systems adsorption columns have
received relatively much less attention in the literature.

Modelling of adsorption column, usually involves complex
mathematical problems to be solved and very often includes
systems of partial differential equations. Recently, aid of
highly powerful computers allows one to deal efficiently with
such problems, taking more details into considerations, in
order to achieve more accurate results. Moreover, it is possible
to perform many simulations in a relatively short time. These
benefits become increasingly apparent as the complexity of the
process increases. It is obvious that no processes can be
modelled without some experimental work. But whenever a simple
mathematical model is available it is possible to use calcula-
tions from the model to determine the best way of tackling the
experimental program so that the maximum benefit can be obtained
from the minimum amount of practical work.

A central problem in the design of these processes
is the dynamic response of the adsorption column to either a
step change or pulse input at the column input. A number of
investigators have studied the problem, and the solution
that have been obtained can be broadly classified into two
general types: the equilibrium and non equilibrium theories.
In the equilibrium theories, the local concentration of the
adsorbate in the mobile and stationary phases are assumed to
be at equilibrium. The results have been found to describe
laboratory analytical columns in which the packing particles
are small, and the fluid flow rate is low. However, the equi-
librium theories do not quantitatively apply to industrial

adsorbers owing to significant resistance to mass transfer in both the mobile and stationary phases. The non equilibrium theories takes into account the finite resistance to mass transfer in the mobile and stationary phases and are capable of giving a quantitative description of industrial columns.

Lapidus and Amundson[1] made an early theoretical contribution to the analysis of the dynamic response of an adsorption column. They obtained an analytical solution for the step response of a column subjected to a step change in sorbate concentration at the bed inlet. Their model included both finite mass transfer resistance with linear equilibrium. Kubin[2,3] and Kucera[4] made a major contribution by describing the relationship between the second moment of the pulse response and the external film mass transfer resistence and interparticle diffusion.

Thomas[5], Edeskuty and Amundson[6] presented results obtained by considering interparticle diffusion resistance but ignoring fluid to particle resistance. Masamune and Smith[7] considered the finite rates of surface adsorption in conjunction with either intraparticle diffusion or external diffusion. Rosen[8] presented an analytical solution of the combined effects of intraparticle and external diffusion for linear equilibrium systems.

In this work the model developed by Haynes[9] for bidisperse pore structure of adsorbent taking into consideration the micropore, macropore, external film resistances and axial

dispersion but with different column boundary conditions given by equation[10] in Chapter III was solved by orthogonal collocation technique. The sorbate free column was subjected to a pulse input at the column inlet and the chromatogram was generated at the column outlet for different operating conditions. Since the adsorbable component is given as a pulse in a small quantity, hence the system can be considered as isothermal. This condition is closely approximated in liquid adsorption systems in which the heat of adsorption is small. It is approximated in a gas adsorption system only when the feed gas is highly diluted in the adsorbate.

The results of this work could be useful in the design of adsorption columns as well as in the analysis and optimization of existing columns. The model is also useful in transient response studies needed in control system synthesis and analysis.

CHAPTER II

LITERATURE REVIEW

2.1 INTRODUCTION

The analysis of a packed bed system is much more complex than the analysis of kinetics of adsorption of a single particle. Because in the former case the adsorbent is contacted by a fluid flowing through a packed bed, rather than in a well mixed system of uniform composition. It is the over all dynamics of the packed bed system, rather than the adsorption kinetics for a single particle which control the design and determine the efficiency of such process.

In a plug flow system with negligible gas film, macropore and micropore resistance, the outlet concentration response would replicate the input with a time delay corresponding to hold up in the column. In actual system the outlet response is broadened as a result of combined effect of axial dispersion and mass transfer resistances. So measurement of time delay of a trace component gives information about adsorption equilibrium, while measurement of dispersion of the response (i.e. variance about the mean) gives information on adsorption kinetics and extent of axial mixing in the column. To extract these parameters, the experimental response should be matched with the theoretical response curve, calculated from a suitable dynamic model for the system. From the standpoint of design engineer the inverse problem i.e. prediction of the break through curve from basic kinetic and equilibrium data is

important because it provides, in principle, a method of predicting dynamic capacity of the column without turning to extensive and expensive experimentation.

In the study of dynamics of fixed bed adsorption column it is convenient to consider the response of an initially sorbate free column to either a step change in sorbate concentration at the column inlet (step input) or to the injection of small sample pulse of sorbate at the column inlet. The response to a step input is usually called the break through curve while the pulse response is called the chromatographic response. Since the delta function is the derivatives of the Heaviside function, for a linear system, the chromatographic response is a derivative of the breakthrough curve. Hence the same information can be obtained from responses of either input and the choice is determined by practical convenience rather than fundamental theoretical considerations.

2.2   PREVIOUS WORK

The popularity of various techniques of numerical solution of partial differential equations fluctuate among the researchers. A case to this point is the initial application of orthogonal collocation method which was overshadowed by the growing use of finite difference technique. But recently this technique was used for diverse set of problems[10-15] where simplicity and good accuracy of the method make it more preferable than other methods.

The basic method was developed by Villadsen and Stewart[16] and has been applied to non linear chemical reaction problem

by Stewart and Villadsen[17] to predict the occurance of multiple steady states in catalyst particles, Villadsen[18] to study the catalytic oxidation of SO_2, McGowin and Perlmutter[19] to study asymptotic stability as well as the plug flow models of chemical reactions, Ferguson and Finlayson[20] to study the transient heat and mass transfer in a catalyst pellet exhibiting multiple steady state solutions. Gas-solid non-catalytic reactions were solved by orthogonal collocation method on finite elements with moving boundary[11]. Orthogonal collocation method was applied to parabolic and elliptic partial differential equations, encountered in problems of viscous flow, heat transfer and diffusion with chemical reaction[16], and to the adiabatic packed bed reactors which includes all the intraparticle and interphase effects plus the additional effect of axial diffusion[21].

The equations governing a packed bed reactor with radial temperature and concentration gradients were also solved using the orthogonal collocation method[22]. This method was also applied to the dynamic model equations of a multicomponent packed separation column[23]. Recently it has been shown that this technique can be used in case of large number of equations quite easily[24].

CHAPTER III

THEORETICAL MODEL

3.1 INTRODUCTION

Models are mathematical representation of certain phenomena, of a process or a plant. Usually a process such as a reactor or an adsorption column is affected by certain physical and chemical phenomena taking place within it. A plant consists of a large number of processes. Hence an understanding of the chemical and physical phenomena and the influence on them of the different operating variables is of fundamental importance in process modelling and ultimately in the plant modelling.

In modelling of an adsorption column the accuracy and practicality of the model are important features. The model should reflect a real situation as faithfully as possible, so that reliable predictions can be obtained by minimum amount of experimental work. A model should meet the following require-ments:

a) the model should not be more detailed than it is absolutely necessary for the practical purpose.

b) in any case the models are faithful only over a certain range of the variables, and therefore, any extrapolation beyond that range is not permissible.

c) reliable correlations should exist for the parameters of the model.

d) after formulation of models, they are tested to ensure reliability.

The cost of testing a model and the time taken for such test, complexity, capacity and applicability are the other criteria) in the evaluation of models.

3.2   ADSORBER MODEL

A column packed with porous spherical particles subjected to a pulse input at the column inlet can be modelled by writing mass balance equations and appropriate boundary conditions. The assumptions of the model are,

    i)   Pressure drop across the bed is negligible;

    ii)   the operation is isothermal;

    iii)   linearity of isotherm;

    iv)   instantaneous adsorption/desorption on crystal surface;

    v)   spherical particles; and

    vi)   axially dispersed plug flow.

A mass balance for differential section of microparticle, macroparticle and column itself gives following set of partial differential equations with associated boundary and initial conditions:

Micropore Diffusion:

$$\frac{\partial^2 c_x}{\partial x^2} + \frac{2}{x} \frac{\partial c_x}{\partial x} = \frac{\theta_x}{D_x} (1 + K_a) \frac{\partial c_x}{\partial t} \tag{1}$$
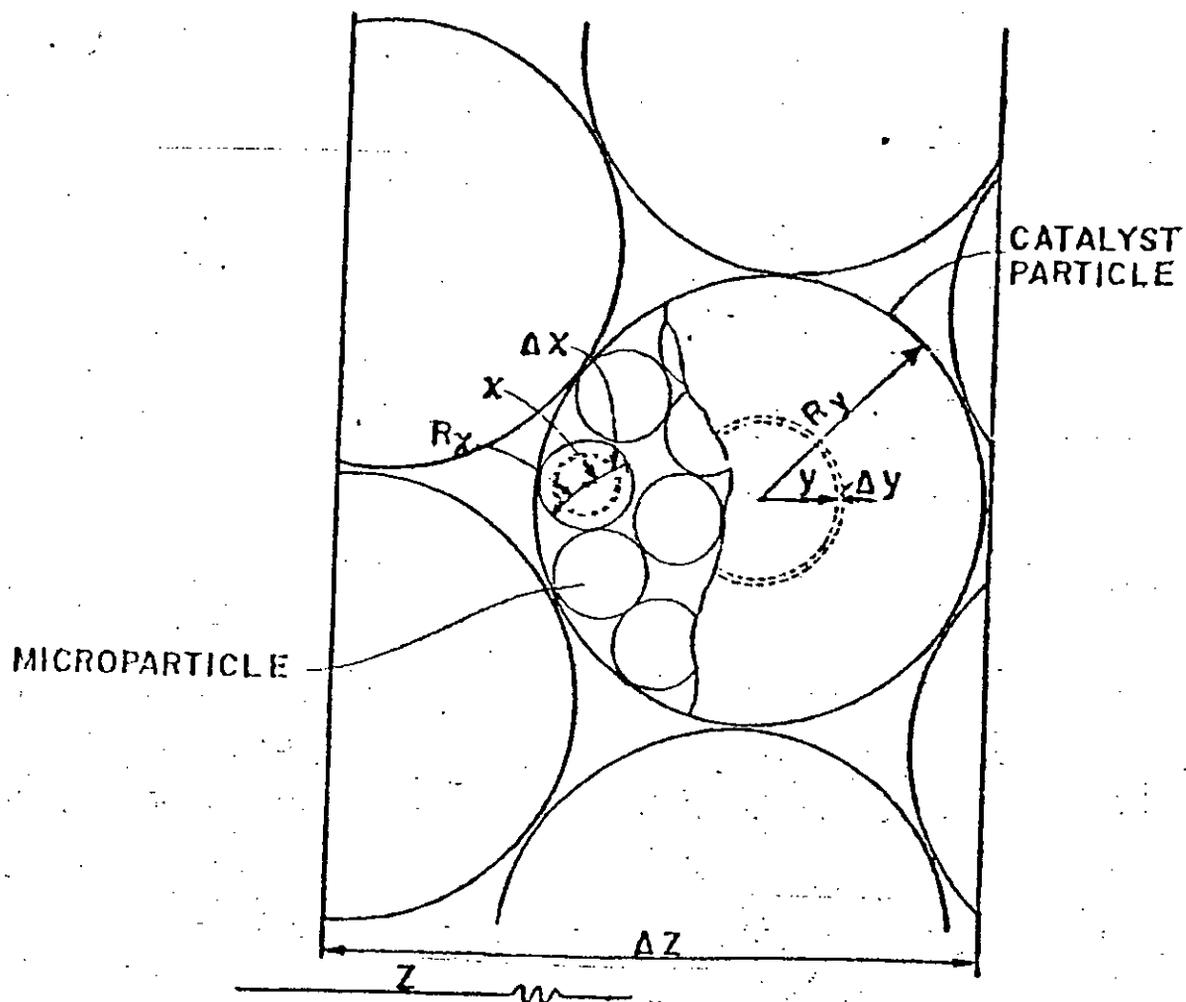
Fig. 1. Macro-micro-pore model.

Boundary conditions:

$$C_x(R_x, t) = C_y(Y, t) \tag{2}$$

$$\frac{\partial C_x}{\partial X}(0, t) = 0 \tag{3}$$

Initial conditions:

$$C_x(X, 0) = 0 \tag{4}$$

Macropore diffusion:

$$\frac{\partial^2 C_y}{\partial Y^2} + \frac{2}{Y}\frac{\partial C_y}{\partial Y} = \frac{3(1-\theta_y)}{D_y R_x} D_x \left(\frac{\partial C_x}{\partial X}\right)\Bigg|_{X=R_x} + \frac{\theta_y}{D_y}\frac{\partial C_y}{\partial t} \tag{5}$$

Boundary conditions:

$$C_y(R_y, t) = C_z(Z, t) - \frac{D_y}{K_f}\left(\frac{\partial C_y}{\partial Y}\right)\Bigg|_{Y=R_y} \tag{6}$$

$$\frac{\partial C_y}{\partial Y}(0, t) = 0 \tag{7}$$

Initial condition:

$$C_y(Y, 0) = 0 \tag{8}$$

Column:

$$\frac{\partial^2 C_z}{\partial Z^2} - \frac{V}{D_z}\frac{\partial C_z}{\partial Z} - \frac{3(1-\theta_z)D_y}{R_y D_z}\frac{\partial C_y}{\partial Y}\Bigg|_{Y=R_y} = \frac{\theta_z}{D_z}\frac{\partial C_z}{\partial t} \tag{9}$$

<u>Boundary conditions:</u>

$$D_z \left. \frac{\partial C_z}{\partial z} \right|_{z=0} = -V \left(\left. C_z \right|_{z=0^-} - \left. C_z \right|_{z=0^+} \right) \tag{10}$$

$$\left. \frac{\partial C_z}{\partial z} \right|_{z=L} = 0 \tag{11}$$

$$C_z(0,t) = C_o \delta(t), \text{ pulse input} \tag{12}$$

<u>Initial condition:</u>

$$C_z(z,0) = 0 \tag{13}$$

3.3   METHOD OF SOLUTION: ORTHOGONAL COLLOCATION

The system of equations i.e. equations (1-13) of section 3.2 can be solved by various numerical scheme. But collocation method (was) used for the solution of the model in this work. The finite difference method of solution leads to a system of algebric equation which, because it is slowly convergent, usually takes long computation times and sometimes cannot be justified. If a global equidistant approximation is employed, the problem of divergence arises[18] but the global approximation method based on orthogonal polynomials such as Galerkin, Variational methods, or Orthogonal Collocation method always

leads to a convergent solution. Orthogonal collocation method requires fewer discretization in space than finite difference method and hence requires less compution time, less storage and leads to acceptable accuracy of the solution.

Orthogonal collocation is one of the class of weighted residual methods which capitalizes on the properties of orthogonal polynomials. Orthogonal Collocation method employ zeros of the polynomial as the collocation points. If $f(x)$ be the function to be approximated for which $\int_a^b w(x) \left[f(x)\right]^2 dx$ exists and if $P_i(x)$ be a set of orthogonal functions for which

$$\int_a^b w(x)\ P_i(x)\ P_j(x)\ dx = c_i \delta_{i,j} \qquad (14)$$

$$= 0, \text{for } i = j$$

The weighting function $w(x)$ is assumed to be integreable but not necessarily continuous over the interval a to b, where $x(a,b)$. If $w(x) = x^\beta (1-x)^\alpha$ for an orthogonality interval $(0,1)$, then the set of approximation orthogonal functions $P_i(x)$ are called Jocobi polynomials $P_{n(x)}^{(\alpha,\beta)}$ and they satisfy the condition

$$\int_0^1 w(x)\ P_n^{(\alpha,\beta)}(x)\ P_J^{(\alpha,\beta)}(x)\ dx = c_n \delta_{n,J} \qquad (15)$$

$$\text{where } \delta_{n,J} = 1, \text{for } n = J$$

$$\delta_{n,J} = 0, \text{for } n \neq J$$

If $w(x) = 1$, i.e. $\alpha = 0, \beta = 0$, then the functions are Legendre polynomial.

If $w(x) = (1-x)$ i.e. $\alpha = 1, \beta = 0$, then the function are Jocobi polynomial.

If $w(x) = (1-x)^{\frac{1}{2}}$ i.e. $\alpha = \frac{1}{2}, \beta = 0$, then the functions are Chebyschef polynomial.

Three classes of collocation method are recognized. Interior collocation requires a function $f(x)$ which satisfies the boundary conditions identically, boundary collocation requires a function $f(x)$ which satisfies the differential equation identically and mixed collocation employ collocation points in both regions and is used when $f(x)$ satisfies neither of the given equation and the boundary conditions.

In orthogonal collocation the equations of the adsorber model (section 3.2) are solved by assuming a orthogonal polynomial for each of the dependent variables. The trial solution of a symmetric problem can be represented by the polynomial of the form as:

$$f(x) = \sum_{i=0}^{N+1} a_i P_i(x^2) \tag{16}$$

The above trial function can be rewritten as:

$$f(x) = \sum_{i=1}^{N+1} d_i x^{2i-2} \tag{17}$$

. Taking the first derivatives and the Laplacian of this expression and evaluating them at the collocation points one obtains;

$$y(x_j) = \sum_{i=1}^{N+1} x_j^{2i-2} \cdot d_i$$

$$\left. \frac{dy}{dx} \right|_{x_j} = \sum_{i=1}^{N+1} \left. \frac{dx^{2i-2}}{dx} \right|_{x_j} \cdot d_i, \qquad (18)$$

$$\left. \nabla^2 y \right|_{x_j} = \sum_{i=1}^{N+1} \left. \nabla^2 (x^{2i-2}) \right|_{x_j} \cdot d_i$$

These can be rewritten in matrix notation as follows:

$$\overline{y} = \overline{Q}\,\overline{d}, \qquad \overline{\frac{dy}{dx}} = \overline{C} \cdot \overline{d}$$

$$\overline{\nabla^2 y} = \overline{D} \cdot \overline{d} \qquad (19)$$

where,
$$Q_{ji} = x_j^{2i-2} \, , \quad C_{ji} = \left. \frac{dx^{2i-2}}{dx} \right|_{x_j}$$

$$D_{ji} = \left. \frac{d^2}{dx^2}(x^{2i-2}) \right|_{x_j}$$

Solving for d one can rewrite the first derivative and Laplacian as

$$\overline{\frac{dy}{dx}} = \overline{C}\,\overline{Q}^{-1}\,\overline{y} = \overline{A}\,\overline{y}, \qquad (20)$$

$$\overline{\nabla^2 y} = \overline{D}\,\overline{Q}^{-1}\,\overline{y} = \overline{B}\,\overline{y}$$

Thus the derivatives one expressed in terms of the value of the function at the collocation point. Similarly the derivatives for non symmetric function can also be expressed in terms of the value of the function at the collocation.

Therefore, partial differential equations (1-13) can be reduced to ordinary differential equation by this method as:

Micropore:

$$\frac{C_x}{dy}(1,k,j) = C_4 W_2 \left(\sum_{i=1}^{N} B_{1,i}\, C_x(i,k,j) + B_{1,N+1}\, C_y(k,j) \right)$$

$$\cdots\cdots \quad (21)$$

Macropore:

$$\frac{dC_y(k,j)}{d\tau} = C_2 W_1 \sum_{i=1}^{N} \left(B_{k,i} - \frac{B_{k,N+1}\, W_3\, A_{N+1,i}}{1+W_3\, A_{N+1,N+1}} \right) C_y(i,j) -$$

$$3C_3 W_2 \sum_{i=1}^{N} A_{N+1,i}\, C_x(i,k,j) + \frac{C_2 W_1 B_{k,N+1}}{1+W_3\, A_{N+1,N+1}}\, C_z(j) -$$

$$3C_3 W_2\, A_{N+1,N+1}\, C_y(k,j) \qquad (22)$$

Column:

$$\frac{dc_z(j)}{d\tau} = (P \sum_{i=2}^{M+1} B^x_{j,i} C_{z(i)} - F \sum_{i=2}^{M+1} A^x_{j,i} C_{z(i)}) + (PB^x_{j,1} - FA^x_{j,1})$$

$$(R_3 \sum_{i=2}^{M+1} A^x_{M+2,i} C_{z(i)} - R_4 \sum_{i=2}^{M+1} A^x_{1,i} C_{z(i)}) + (PB^x_{j,M+2} -$$

$$FA^x_{j,M+2}) \ (R_1 \sum_{i=2}^{M+1} A^x_{1,i} C_{z(i)} - R_2 \sum_{i=2}^{M+1} A^x_{M+2,i} C_{z(i)}) - (PB^x_{j,1} -$$

$$FA^x_{j,1}) \ (R_4 PEM.UZZ) + (PB^x_{j,M+2} - FA^x_{j,M+2}) \ (R_1.PEM.UZZ) - 3C_1 W_1$$

$$(ZC_{z(j)} - Z_1 \sum_{i=1}^{N} A_{N+1,i} C_{y(i,j)}) \qquad\qquad (23)$$

The ordinary-differential equations thus obtained may be solved
by standard integration routine. Derivation of the model and
their transformation into ODE by collocation method is given
in Appendix-I.

CHAPTER IV

RESULTS AND DISCUSSIONS

Difficulty encountered during the simulation of the adsorption column was the stability of the numerical integration of the resulting set of equations[21-23]. If the step size for time is slightly higher than the critical step size for the system then the system begins oscillating with ever increaning amplitude. On the other hand if the step size decreases then truncation error affects the result. Thus an efficient integration routine is required to solve the equations. Runge-Kutta method was found to fail to solve the equations due to stability problem. The integration routine Runge-Kutta-Merson, which can internally monitor the integration error and automatically adjust the step size so as to maintain the error within a specified tolerance, was used to solve the resulting set of equations[21-23]. Recently it was found that 'Gear Stiff' subroutine of integration is more efficient in the context of stability problem. Three collocation points were used in this work.

The chromatogram of figure-2 is the response of an adsorption column to a pulse input at the bed inlet calculated from present adsorption model. The various parameters on which the response is based is shown in figure-2. The value of the external film mass transfer coefficient was assumed to be high so that the value of W_3 becomes low and as a consequence film

resistance to mass transfer could be neglected. Moreover

the micropore diffusion parameter W_2 was small in relation to

macropore diffusion parameter W_1. Thus the dominant mass

transfer resistance in this case is due to micropore diffu-

sion. It can be shown by moment analysis that the combination

of mass transfer resistances and axial dispersion to the

variance of the chromatogram is additive. Hence the variance

of the chromatogram of figure-2 shows the effect of micropore

diffusion alone. It has been experimentally observed by various

authors[9,14] that when the mass transfer resistance is impor-

tant, one obtains peaks which are skewed to the right, as in

the case of this work.

Figure 3 shows the effect of adsorption equilibrium

constant on the break time of the curve. As the equilibrium

constant increases the mean of the curve increases. This is

evident from the increases in the break time of the peaks.

For curve with $K_a=0$, the variance is due to axial dispersion

alone and hence a Gaussian curve results. For curves with

$K_a=29.43$ and $K_a=100$ it is evident that value of equilibrium

constants significantly alters the variance of the peaks which

is in accord with moment analysis of the model but with diffe-

rent boundary condition for the column equation.

Figure 4 shows the effect of external mass transfer

resistance on the chromatogram. The effect seems to be important

only when the value of external mass transfer parameter W_3 is

higher i.e. around 1, or higher.

The effect of axial peclet number is shown in figure 5. It seems that at higher peclet number for mass transfer does not have any effect on break time and variance of the peak. But when the peclet number is small the break time falls off and the contribution of the axial dispersion to the peak width increases. For commercial adsorber operating under ordinary conditions the $PEM \approx L/R_y$ it is clear that the effect of peclet number becomes insignificant except when the bed is very short. This is the rational for using plug flow assumption in most practical fixed bed adsorption column simulation problems. But if the peclet number is small as in laboratory column, then it may have significant effect. Another point is that as the peclet number decreases the axial dispersion contribute to the broadening of the peak. Hence at low peclet number contribution from the axial dispersion may become important.

If both macropore and micropore mass transfer resistance is important they will contribute to the variance of the peak. This is shown in figure 6. The peak broadening occur when W_2 decreases from 100 to 2.07, since the resistance to micropore diffusion is higher at 2.07 than 100. Another point is that when W_2 is 100 then both macro and micropore diffusion become important. Hence the variance of the curve at $W_2=100$ is higher than that of at $W_2=2.07$. One would expect to get the behaviour of a non-porous particle if the macropore and micropore diffusivity approaches to zero or infinity.
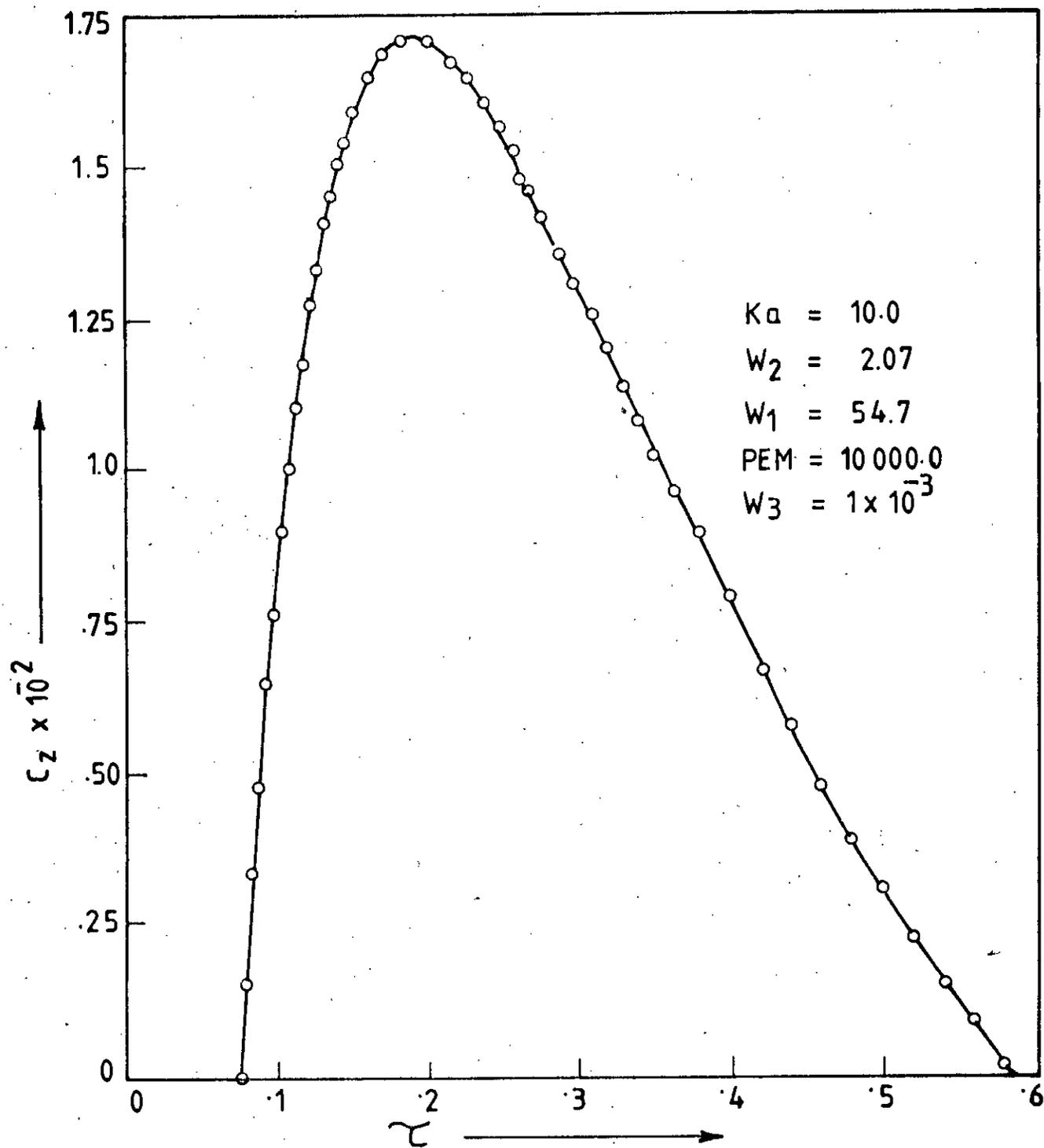
Fig. 2 Theoretical chromatogram calculated by collocation method.
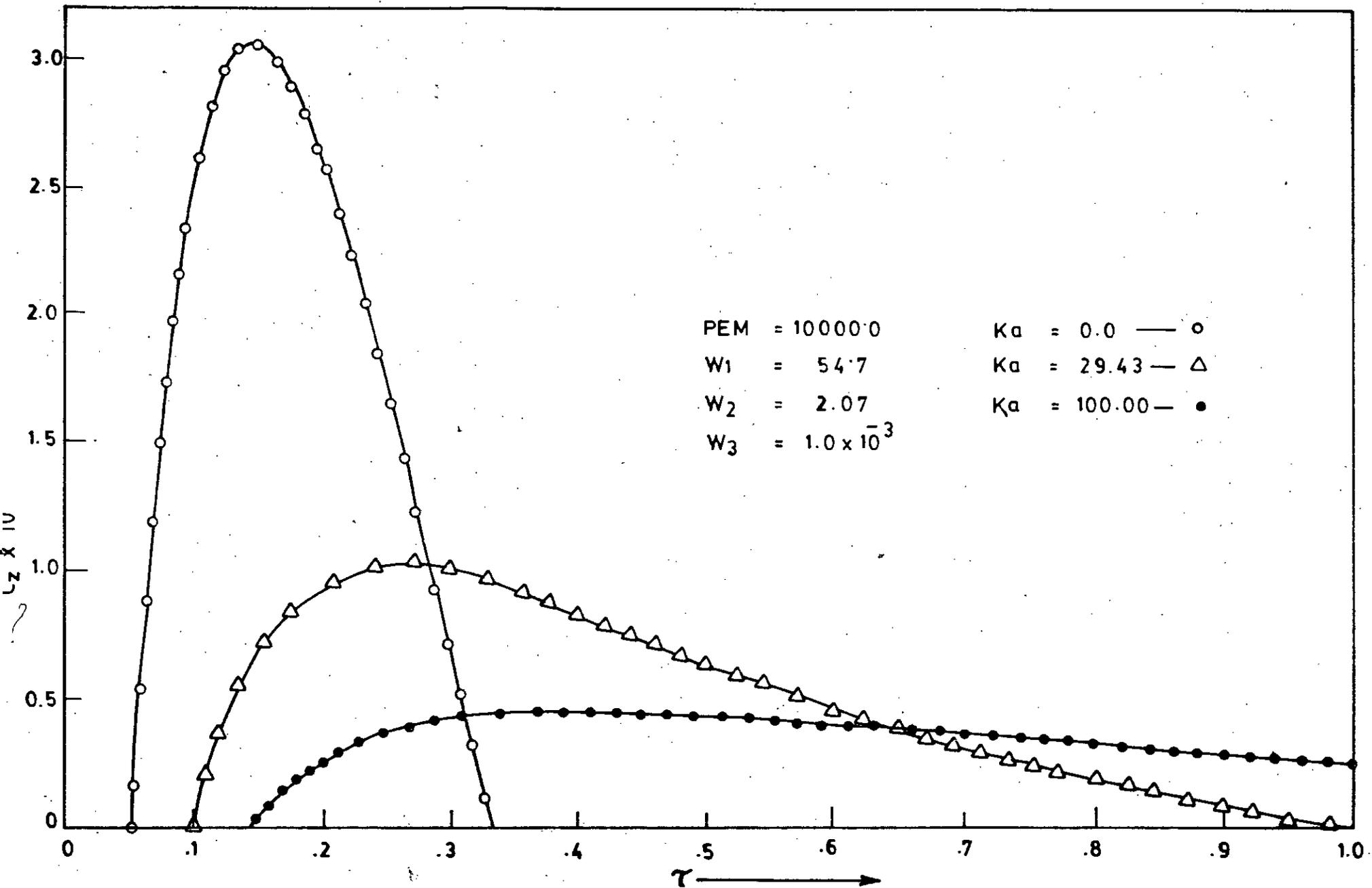
Fig. 3 Theoretical chromatograms calculated by collocation method showing the effect of adsorption equilibrium constant.

Legend in figure:

$PEM = 10000.0$

$W_1 = 54.7$

$W_2 = 2.07$

$W_3 = 1.0 \times 10^{-3}$

$Ka = 0.0$ —— o

$Ka = 29.43$ — △

$Ka = 100.00$ — ●
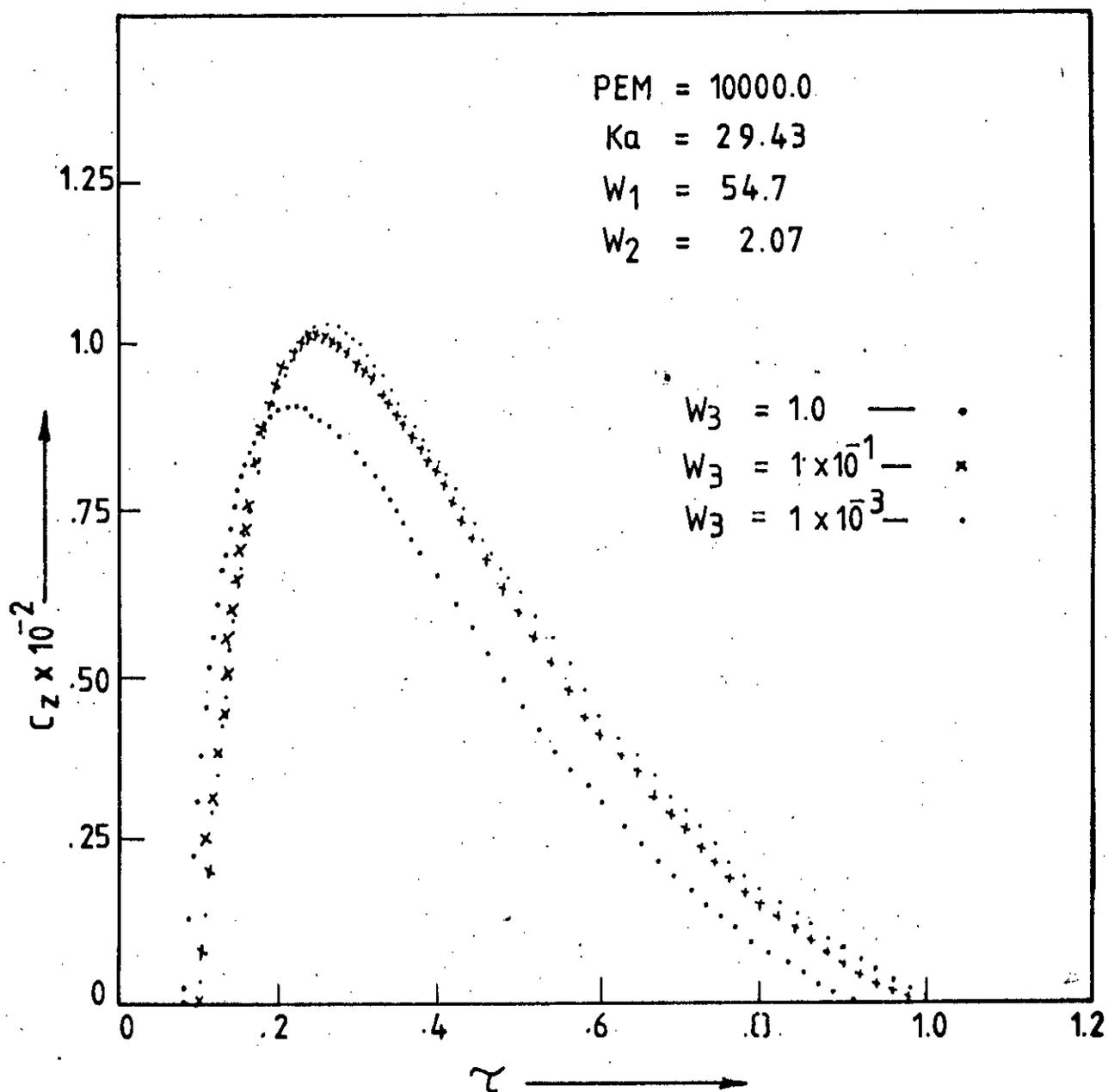
Fig. 4 Theoretical chromatograms calculated by collocation method showing the effect of external film resistance.
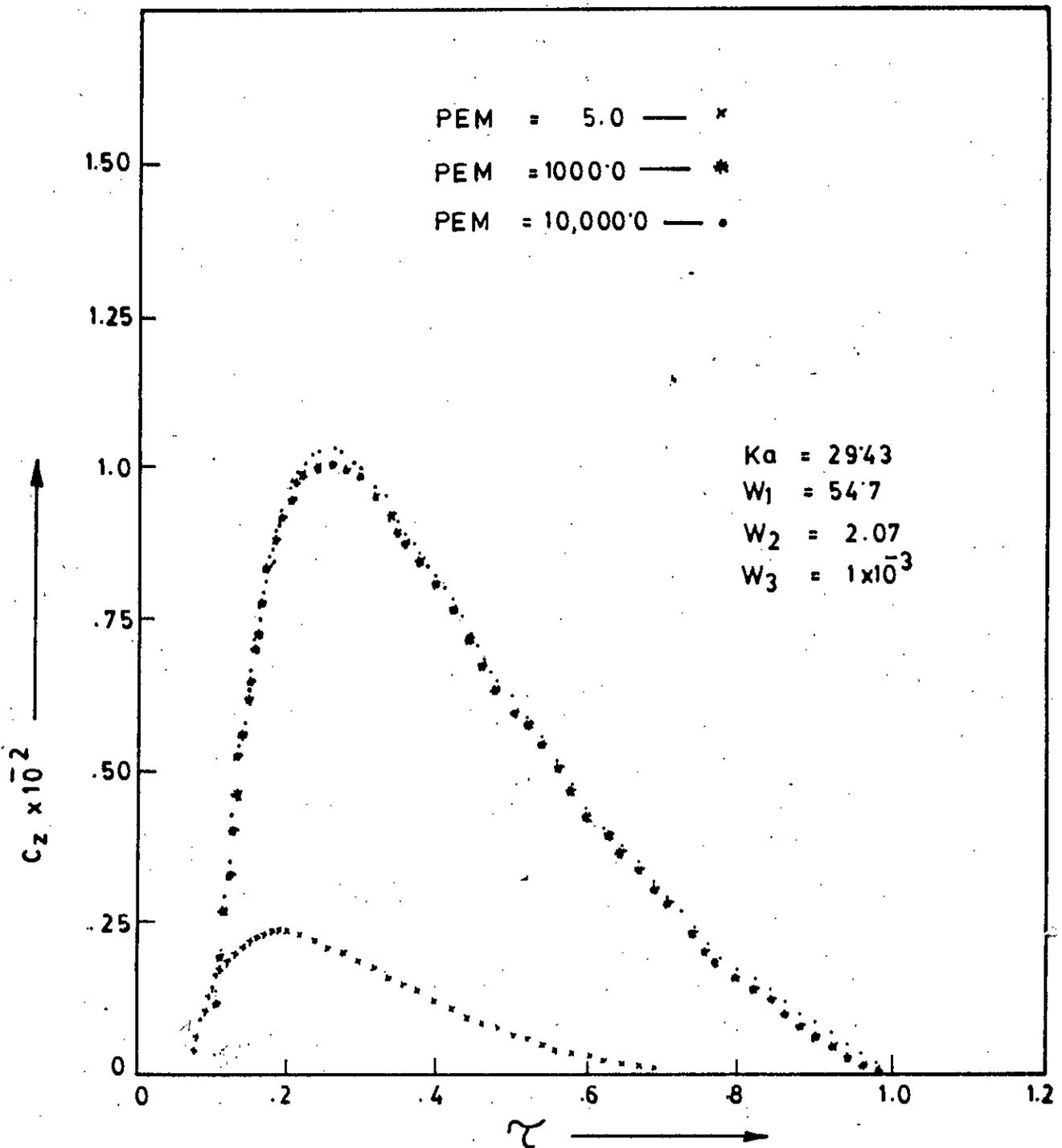
Fig. 5 Theoretical chromatograms calculated by collocation
method showing the effect of peclet number
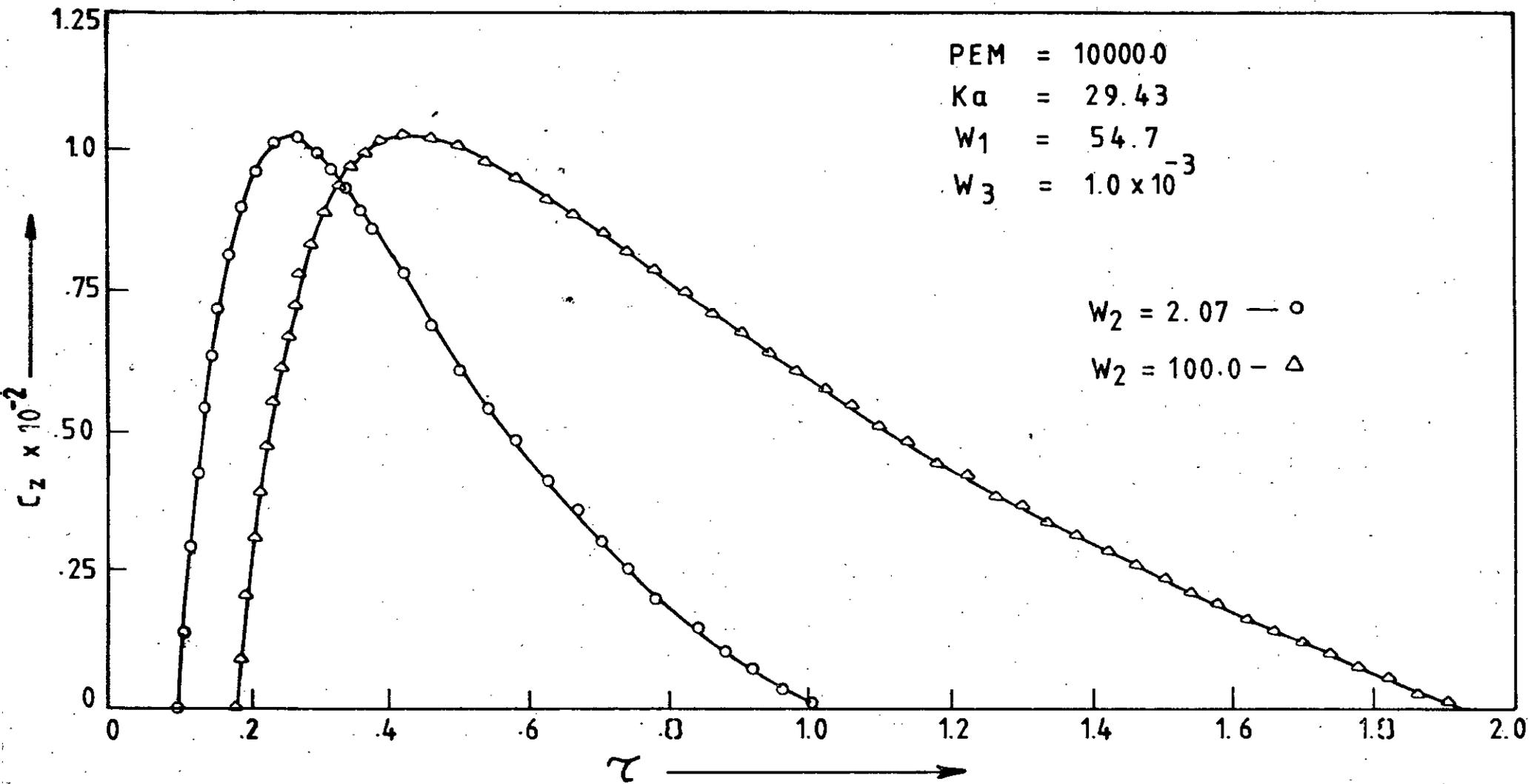
Fig. 6   Theoretical chromatograms calculated by collocation method showing the effect of pore diffusion.

CHAPTER V

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

Three interior collocation points were used to simulate the sorbate free packed column subjected to pulse input at the column inlet. The effect of axial dispersion, the adsorption equilibrium constant, macropore and micropore diffusivity on the break through curve/chromatogram was studied. The results are consistent with the approximate time domain solution for column dynamics with slightly different boundary conditions for column equation.

The response of an adsorption column to pulse input at the bed inlet calculated from present adsorption model by collocation method is shown in figure-2. The dominant mass transfer resistance in this case is the micropore diffusion.

It is noted from the result that approximately Gaussian curve is obtained when equilibrium constant is zero. Break through time and the variance of the chromatogram increases with the increasing adsorption equilibrium constant as stipulated by the approximate time domain solution by the method of moments. This is shown in figure 3.

The effect of external film mass transfer resistance is shown in figure 4. The effect seems to be important at low value of mass transfer coefficient. At high value the effect is minimal.

The effect of axial dispersion coefficient is shown in figure 5. The break time falls off as the Peclet number for mass transfer is decreased i.e. axial dispersion becomes significant. At higher Peclet number it seems that the Peclet member does not have any influence on break time.

The situation when micro and macropore resistance is both important is shown in figure 6. In this case both these resistances contribute additively in broadening the chromatogram. So if any one wanting to extract either of the transport properties he should choose experimental conditions in such a way that either micropore or macropore resistance is dominating.

5.2 RECOMMENDATION

The dynamics of the packed column is given by three coupled parabolic second order partial differential equation having a slowly converging oscillating integral involving the product of a sine function and decaying exponential function. So more effecient integration routine should be used (such as GEAR, PDECOL, LSODE, EPISODE, which can handle stiff equations) to cut down the excessive, expensive computer time as in the present case.

To determine the accuracy of the collocation solution, it should be compared with analytic solution if it is at all available.

The chromatogram generated by orthogonal collocation method should be compared with experimental chromatogram for a given system.

NOMENCLATURE

$A_{j,i}$ collocation coefficients for the macro & micro particle (internal) phase gradient.

$A^x_{j,i}$ collocation coefficients for the external fluid phase gradient.

A_c cross-section area of the column, cm^2.

$B_{j,i}$ collocation coefficients for the macro & micro particle (internal) phase Laplacian.

$B^x_{j,i}$ collocation coefficients for the external fluid phase Laplacian.

C_a concentration of adsorbed species, $gmole/cm^2$.

C_x, C_y, C_z gas phase concentration of diffusing species in micropore, macropore & bed, gmole/cc.

C^*_x, C^*_y, C^*_z dimensionless concentrations.

C_1 dimensionless quantity, $\dfrac{1-\theta_z}{z}$

C_2 dimensionless quantity, $1/\theta_y$

C_3 dimensionless quantity, $\dfrac{1-\theta_y}{\theta_y}$

C_4 dimensionless quantity $\dfrac{1}{\theta_x(1+K_a)}$

D_x, D_y diffusion coefficient based on total area in micropore and macropore, cm^2/sec

D_z — axial dispersion coefficient based on total area, cm^2/sec

F — dimensionless parameter, $1/\theta_z$

k_f — external film mass transfer coefficient, cm/sec

K_a — adsorption equilibrium constant, dimensionless

L — length of column, cm

M — number of collocation points in the external fluid phase

N — number of collocation points in the macro & microparticle (internal phase)

N_x, N_y, N_z — diffusion flux in micropore, macropore and bed, $gmole/cm^2$-s

P — dimensionless parameter, $\dfrac{1}{\theta_z \cdot PEM}$

PEM — Peclet number

R_x, R_y — particle padius, microparticle and macroparticle, cm

S_x — surface area in micropores, cm^2/g

t — time, s

UZZ — dimensionless pulse input

V — superficial velocity, cm/s

W_1 — macropore diffusion parameter, $\dfrac{D_y L}{R_y^2 V}$

W_2 micropore diffusion parameter, $\dfrac{D_x L}{R_x^2 V}$

W_3 film resistance parameter, $\dfrac{D_y}{k_f R_y}$

X   radial distance from center of microparticle, cm

X*   dimensionless distance, X/R_x

Y   radial distance from center of Pellet, cm

Y*   dimensionless distance, Y/R_y

Z   axial distance from column entrance, cm

Z*   dimensionless distance, Z/L

Greek letters

η dimensionless radial distance in macro & micro particle

θ_x micropore porosity, cc micropores/cc microparticle

θ_y macropore porosity, cc macropore/cc pellet

θ_z column porosity, cc bed voids/cc bed

ρ catalyst particle density, g/cc

τ dimensionless time parameter, $\dfrac{Vt}{L}$

Subscripts

x   microparticle quantity

y   macroparticle quantity

z   column quantity

R_x quantity evaluated at surface of microparticle

R_y quantity evaluated at surface of pellet

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APPENDIX - 1

ADSORBER   MODEL

The dynamic model of packed bed system can be developed by writing mass balance equation for differential section of microparticle, macroparticle and column itself.

The basic mass balance equation is:

$$\text{Mass in} \pm \begin{array}{c} \nearrow \; 0 \\ \text{Generation} \\ \diagdown \\ \text{Disappearance} \\ \diagup \end{array} = \begin{array}{l} \text{Mass} + \text{Accumulation} \\ \text{out} \end{array}$$

Micropore:

A mass balance around the differential element of micropore or microparticle as shown in figure-I.1(a) gives:

Mass in - Mass Out = Accumulation + Accumulation in adsorbed
in gaseous   phase
phase

$$\left[N_x 4\pi X^2 \Big|_X - N_x 4\pi X^2 \Big|_{X+\Delta X} \right] \Delta t = \theta_x C_x 4\pi X^2 \Delta X \Big|_{t+\Delta t} - \theta_x C_x 4\pi X^2 \Delta X \Big|_t$$

$$+ C_a S_x \rho \frac{1}{1-\theta_y} 4\pi X^2 \Delta X \Big|_{t+\Delta t} - C_a S_x \rho \frac{1}{1-\theta_y} 4\pi X^2 \Delta X \Big|_t$$

Dividing all through by $4\pi X^2 \Delta X \Delta t$ and taking the limit as

$$\Delta X \longrightarrow 0$$
$$\Delta t \longrightarrow 0$$, we get

$$- \frac{1}{x^2} \frac{\partial}{\partial x} (N_x x^2) = \theta_x \frac{\partial C_x}{\partial t} + \frac{\rho S_x}{1-\theta_y} \frac{\partial C_a}{\partial t} \tag{I-1}$$

$$\text{where} \quad N_x = - D_x \frac{\partial C_x}{\partial X} \tag{I-2}$$

The dimensionless adsorption constant K_a is defined by

$$K_a = \frac{\rho S_x}{\theta_x (1-\theta_y)} \frac{C_a}{C_x} \tag{I-3}$$

Putting (2) & (3) in (1), we get

$$\frac{1}{x^2} \frac{\partial}{\partial X} (D_x \frac{\partial C_x}{\partial X} x^2) = \theta_x \frac{\partial C_x}{\partial t} + \frac{S_x \rho}{1-\theta_y} \frac{K_a \theta_x (1-\theta_y)}{S_x \rho} \frac{\partial C_x}{\partial t}$$

For constant Diffusivity, D_x

$$\frac{D_x}{x^2} (x^2 \frac{\partial C_x}{\partial x^2} + 2X \frac{\partial C_x}{\partial X}) = \theta_x \frac{\partial C_x}{\partial t} + K_a \theta_x \frac{\partial C_x}{\partial t}$$

$$\text{or,} \quad (\frac{\partial^2 C_x}{\partial x^2} + \frac{2}{X} \frac{\partial C_x}{\partial X}) = \frac{\theta_x}{D_x} (1+K_a) \frac{\partial C_x}{\partial t} \tag{I-4}$$

Equation (4) is the basic equation for micropore diffusion. The boundary and initial conditions are

$$C_x (R_x, t) = C_y (Y, t) \tag{I-5}$$

$$\frac{\partial C_x}{\partial X} (0, t) = 0 \tag{I-6}$$

$$C_x (X, 0) = 0 \tag{I-7}$$

Macropore:

A mass balance on differential element of catalyst particle or macropore as shown in figure- I.1(b) gives:

Mass in - Mass out + Mass in from = Accumulation in
by con-   by con-   micropore by   macropore
vection   vection   diffusion

$$\left[N_y 4\pi Y^2 \Big|_Y - N_y 4\pi Y^2 \Big|_{Y+\Delta Y} \right] \Delta t + N_{R_x} \left(\frac{4\pi R_x^2}{4/3\pi R_x^3} \right) (1-\theta_y)(4\pi y^2 \Delta y)\, \Delta t$$

$$= C_y \theta_y 4\pi Y^2 \Delta Y \Big|_{t+\Delta t} - C_y \theta_y 4\pi Y^2 \Delta Y \Big|_t$$

Dividing all through by $4\pi Y^2 \Delta Y \Delta t$ and taking the limit as

$$\Delta Y \longrightarrow 0$$
$$\Delta t \longrightarrow 0, \quad \text{we get}$$

$$- \frac{1}{Y^2} \frac{\partial}{\partial Y}(Y^2 N_y) + N_{R_x} \left(\frac{3}{R_x} \right)(1-\theta_y) = \frac{\partial}{\partial t}(C_y \theta_y) \qquad (I\text{-}8)$$

where
$$N_y = -D_y \frac{\partial C_y}{\partial Y} \qquad (I\text{-}9)$$

Assuming macropore diffusivity D_y to be constant, One obtains

$$\frac{D_y}{Y^2} \frac{\partial}{\partial Y}\left(Y^2 \frac{\partial C_y}{\partial Y}\right) + \frac{3}{R_x} N_{R_x} (1-\theta_y) = \theta_y \frac{\partial C_y}{\partial t}$$

or,
$$\frac{\partial C_y^2}{\partial Y^2} + \frac{2}{y} \frac{\partial C_y}{\partial Y} + \frac{3(1-\theta_y)}{D_y R_x} N_{R_x} = \frac{\theta_y}{D_y} \frac{\partial C_y}{\partial t} \qquad (1\text{-}10)$$

$$\text{where } N_{R_x} = -D_x \left.\frac{\partial C_x}{\partial x}\right|_{X=R_x} \tag{I-11}$$

$$\therefore \quad \frac{\partial^2 C_y}{\partial y^2} + \frac{2}{Y} \frac{\partial C_y}{\partial Y} = \frac{3(1-\theta_y)}{D_y R_x} D_x \left.\frac{\partial C_x}{\partial x}\right|_{X=R_x} + \frac{\theta_y}{D_y} \frac{\partial C_y}{\partial t} \tag{I-12}$$

The boundary and initial conditions are given by

$$C_y(R_y, t) = C_z(Z, t) - \frac{D_y}{k_f} \left.\left(\frac{\partial C_y}{\partial Y}\right)\right|_{Y=R_y} \tag{I-13}$$

$$\frac{\partial C_y}{\partial Y}(0, t) = 0 \tag{I-14}$$

$$C_y(Y, 0) = 0 \tag{I-15}$$

Column:

A mass balance on the differential element of the column as shown in Figure-I.2 gives:

(Mass in due   − Mass out due) + (Mass in by − Mass out by) +
to convection   to convection   diffusion   diffusion

Mass in from Micropore by diffusion = Accumulation

$$\left[\left(VA_c C_z\Big|_Z - VA_c Z\Big|_{Z+\Delta Z} \right) + \left(N_z A_c\Big|_Z - N_z A_c\Big|_{Z+\Delta Z} \right) + N_{R_y} \left(\frac{4\pi R_y^2}{4/3\pi R_y^3}\right) \right.$$

$$\left. (1-\theta_z)A_c\Delta Z \right]\Delta t = C_z\theta_z A_c\Delta Z\Big|_{t+\Delta t} - C_z\theta_z A_c\Delta Z\Big|_t$$

Dividing throughout by $A_c \Delta Z \Delta t$ and taking the limit as

$$\Delta Z \longrightarrow 0$$
$$\Delta t \longrightarrow 0 \quad , \text{ we get}$$

$$-\frac{\partial}{\partial Z}(VC_z) - \frac{\partial}{\partial Z}(N_z) + \frac{3}{R_y}(1-\theta_z)N_{R_y} = \theta_z \frac{\partial C_z}{\partial t} \qquad (I-16)$$

$$\text{where} \quad N_z = -D_z \frac{\partial C_z}{\partial Z} \qquad (I-17)$$

If the axial dispersion, D_z, is constant then

$$-V\frac{\partial C_z}{\partial Z} + D_z \frac{\partial^2 C_z}{\partial Z^2} + \frac{3}{R_y}(1-\theta_z)N_{R_y} = \theta_z \frac{\partial C_z}{\partial t} \qquad (I-18)$$

$$\text{where} \quad N_{R_y} = -D_y \left.\frac{\partial C_y}{\partial Y}\right|_{Y=R_y}$$

$$\therefore \frac{\partial^2 C_z}{\partial Z^2} - \frac{V}{D_z}\frac{\partial C_z}{\partial Z} - \frac{3D_y}{R_y D_z}(1-\theta_z)\left.\frac{\partial C_y}{\partial Y}\right|_{Y=R_y} = \frac{\theta_z}{D_z}\frac{\partial C_z}{\partial t} \qquad (I-19)$$

The boundary and initial conditions are given by

$$D_z \left.\frac{\partial C_z}{\partial Z}\right|_{Z=0} = -V\left(\left.C_z\right|_{Z=0^-} - \left.C_z\right|_{Z=0^+}\right) \qquad (I-20)$$

$$C_z(0,t) = C_o \delta(t), \quad \text{Pulse input} \qquad (I-21)$$

$$\left.\frac{\partial C_z}{\partial z}\right|_{z=L} = 0 \tag{I-22}$$

$$C_z(Z,0) = 0 \tag{I-23}$$

Normalizing equations (4-7, 12-15, 19-23) by using following dimensionless variables

$$Y^* = \frac{Y}{R_y} \quad , \quad C_y^* = \frac{C_y}{C_o} \quad , \quad \mathcal{T} = \frac{Vt}{L} \quad , \quad C_x^* = \frac{C_x}{X} \quad , \quad C_z^* = \frac{C_z}{Z}$$

$$X^* = \frac{X}{R_x} \quad , \quad Z^* = Z/L$$

For the shake of conciseness let us write the set of equations in the dimensionless form, dropping the primes as:

Micropore Diffusion:

$$\frac{1}{R_x^2} \frac{\partial C_x}{\partial x^2} = \frac{\theta_x}{D_x} (1+K_a) \frac{V}{L} \frac{\partial C_x}{\partial \mathcal{T}}$$

or, $$\frac{\partial C_x}{\partial \mathcal{T}} = \frac{D_x L}{R_x^2 V} \frac{1}{\theta_x (1+K_a)} \frac{\partial^2 C_x}{\partial x^2}$$

or, $$\frac{\partial C_x}{\partial \mathcal{T}} = W_2 \, C_4 \cdot \frac{\partial^2 C_x}{\partial x^2} \tag{I-24}$$

where $$W_2 = \frac{D_x L}{R_x^2 V}$$

$$C_4 = \frac{1}{\theta_x (1+K_a)}$$

Boundary conditions:

$$C_x(X=1,\tau) = C_y(Y,\tau) \qquad (I-25)$$

$$\frac{\partial C_x}{\partial X}(0,\tau) = 0 \qquad (I-26)$$

Initial condition:

$$C_x(X,0) = 0 \qquad (I-27)$$

Macropore Diffusion:

$$\frac{1}{R_y^2}\frac{\partial^2 C_y}{\partial Y^2} - \frac{3(1-\theta_y)}{R_x^2 D_y}D_x\left.\frac{\partial C_x}{\partial X}\right|_{X=1} = \frac{\theta_y}{D_y}\frac{V}{L}\frac{\partial C_y}{\partial \tau}$$

$$\text{or,}\quad \frac{\partial C_y}{\partial \tau} = \frac{D_y}{R_y^2 V}\frac{L}{\theta_y}\frac{\partial C_y}{\partial Y^2} - \frac{3(1-\theta_y)}{\theta_y}\frac{D_x L}{R_x^2 V}\left.\frac{\partial C_x}{\partial X}\right|_{X=1}$$

$$\text{or,}\quad \frac{\partial C_y}{\partial \tau} = \frac{1}{\theta_y}\frac{D_y L}{R_y^2 V}\frac{\partial C_y^2}{\partial Y^2} - \frac{3(1-\theta_y)}{\theta_y}\frac{D_x L}{R_x^2 V}\left.\frac{\partial C_x}{\partial X}\right|_{X=1}$$

$$\text{or,}\quad \frac{\partial C_y}{\partial \tau} = C_2 W_1\frac{\partial^2 C_y}{\partial Y^2} - 3.0\,C_3 W_2\left.\frac{\partial C_x}{\partial X}\right|_{X=1} \qquad (I-28)$$

where $\quad C_2 = 1/\theta_y$

$$W_1 = \frac{D_y L}{R_y^2 V}$$

$$C_3 = (1-\theta_y)/\theta_y$$

Boundary conditions:

$$C_y(Y=1,\tau) = C_z(Z,\tau) - \frac{D_y}{k_f R_y} \left.\frac{\partial C_y}{\partial y}\right|_{Y=1}$$

or,
$$C_y(1,\tau) = C_z(Z,\tau) - W_3 \left.\frac{\partial C_y}{\partial Y}\right|_{Y=1} \tag{I-29}$$

$$\frac{\partial C_y}{\partial Y}(0,\tau) = 0 \tag{I-30}$$

Initial condition: $C_y(Y,0) = 0$ (I-31)

where $W_3 = \dfrac{D_y}{k_f R_y}$

Column:

$$\frac{1}{L^2}\frac{\partial^2 C_z}{\partial z^2} - \frac{V}{D_z L}\frac{\partial C_z}{\partial z} = \frac{3(1-\theta_z)}{R_y^2 D_z} D_y \left.\frac{\partial C_y}{\partial Y}\right|_{Y=1} + \frac{\theta_z}{D_z}\frac{V}{L}\frac{\partial C_z}{\partial \tau}$$

or,
$$\frac{\partial C_z}{\partial \tau} = \frac{1}{\theta_z}\frac{D_z}{LV}\frac{\partial^2 C_z}{\partial z^2} - \frac{1}{\theta_z}\frac{\partial C_z}{\partial z} - 3\left(\frac{1-\theta_z}{\theta_z}\right)\frac{D_y L}{R_y^2 V}\left.\frac{\partial C_y}{\partial Y}\right|_{Y=1}$$

or,
$$\frac{\partial C_z}{\partial \tau} = F\frac{1}{PEM}\frac{\partial^2 C_z}{\partial z^2} - F\frac{\partial C_z}{\partial z} - 3C_1 W_1 \left.\frac{\partial C_y}{\partial Y}\right|_{Y=1}$$

or,
$$\frac{\partial C_z}{\partial \tau} = P\frac{\partial^2 C_z}{\partial z^2} - F\frac{\partial C_z}{\partial z} - 3C_1 W_1 \left.\frac{\partial C_y}{\partial Y}\right|_{Y=1} \tag{I-32}$$

$$\text{where} \quad F = 1/\theta_z$$

$$PEM = \frac{LV}{D_z}$$

$$C_1 = (1-\theta_z)/\theta_z$$

$$P = F/PEM$$

Boundary conditions:

$$\frac{\partial C_z}{\partial z}\bigg|_{z=1} = -\frac{VL}{D_z}\left(C_z\bigg|_{z=0^-} - C_z\bigg|_{z=0^+}\right)$$

$$\text{or,} \quad \frac{\partial C_z}{\partial z}\bigg|_{z=1} = -PEM\left(C_z\bigg|_{z=0^-} - C_z\bigg|_{z=0^+}\right) \tag{I-33}$$

$$\frac{\partial C_z}{\partial z}\bigg|_{z=1} = 0 \tag{I-34}$$

$$C_z(0,\mathcal{T}) = \delta(\mathcal{T}), \text{ pulse input} \tag{I-35}$$

Initial condition: $\quad C_z(Z,0) = 0$ $\hfill$ (I-36)

The dimensionless partial differential equations (24-36) can be reduced to ordinary differential equations by the method of Orthogonal Collocation.

In the present collocation method, the concentration profile in the microparticle and macroparticle is approximated by the symmetric trial function:

$$Q(\eta, \mathcal{T}) = Q(1, \mathcal{T}) + (1-\eta^2) \sum_{i=1}^{N} a_i(\mathcal{T}) \, P_{i-1}(\eta^2) \qquad \text{(I-37)}$$

where Q refers to the dimentionless concentration C_x, C_y; $a_i(\mathcal{T})$ are function of time (or constants) and P_i are the orthogonal polynomials defined by:

$$\int_0^1 w(\eta^2) \, P_j(\eta^2) \, P_i(\eta^2) \, \eta^{a-1} \, d\eta = C_i \delta_{ij} \qquad \text{(I-38)}$$

$$\text{where} \quad w(\eta^2) = 1 - \eta^2$$

$$j = 1, 2, \ldots\ldots\ldots i-1$$

a=1,2,3, for planer, cylindrical and spherical geometry.

The constant C_i in equation (38) is as defined in eqn. (9) of Villadsen and Steward (21) and δ_{ij} is unity if i=j and zero otherwise. Using eqns. (37) and (38), equations for micropore and macropore diffusion may be written in collocation form as follows:

Equations (24) & (25) can be written in collocation form as:

$$\frac{dC_{x(1,k,j)}}{d\mathcal{T}} = C_4 W_2 \sum_{i=1}^{N+1} B_{1,i} \, C_{x(i,k,j)} \qquad \text{(I-39)}$$

and $\quad C_{x(N+1,k,j)} = C_{y(k,j)}$ (I-40)

$$\text{where} \quad i = 1,2, \ldots\ldots\ldots N$$

$$k = 1,2, \ldots\ldots\ldots N$$

$$j = 2,3, \ldots\ldots\ldots M+1$$

N and M are the number of collocation points for the particle (macro & micro) and column respectively.

Substituting equation (40) in (39), we get

$$\frac{dC_{x(1,k,j)}}{d\tau} = C_4 W_2 \left(\sum_{i=1}^{N} B_{1,i} C_{x(i,k,j)} + B_{1,N+1} C_{y(k,j)} \right) \quad \text{(I-41)}$$

Equations (28) & (29) in collocation form is written as:

$$\frac{dC_{y(k,j)}}{d\tau} = C_2 W_1 \sum_{i=1}^{N+1} B_{k,i} C_{y(i,j)} - 3C_3 W_2 \sum_{i=1}^{N+1} A_{N+1,i} C_{x(i,k,j)}$$

$$\ldots\ldots\ldots \quad \text{(I-42)}$$

and $\quad C_{y(N+1,j)} = C_{z(j)} - W_3 \sum_{i=1}^{N+1} A_{N+1,i} C_{y(i,j)}$ (I-43)

$$\text{where} \quad k = 1,2, \ldots\ldots\ldots N$$

$$j = 2,3, \ldots\ldots\ldots M+1$$

Putting value of $C_{x(N+1,k,j)}$ & $C_{y(N+1,j)}$ from equation (40) & (43) in equation (42), we get

$$\frac{dC_{y(k,j)}}{d\mathcal{T}} = C_2 W_1 \sum_{i=1}^{N} (B_{k,i} - \frac{B_{k,N+1} \, W_3 \, A_{N+1,i}}{1+W_3 \, A_{N+1,N+1}}) \, C_{y(i,j)} -$$

$$3C_3 W_2 \sum_{i=1}^{N} A_{N+1,i} \, C_{x(i,k,j)} + \frac{C_2 W_1 B_{k,N+1}}{1+W_3 \cdot A_{N+1,N+1}} \, C_{z(j)} -$$

$$3C_3 W_2 \, A_{N+1,N+1} \, C_{y(k,j)} \qquad\qquad (I-44)$$

The concentration profile in the external fluid phase is similarly approximated by the following trial function based on non symmetrical polynomials:

$$C_z(Z,\mathcal{T}) = (1-Z)C_z(0,\mathcal{T}) + XC_z(1,\mathcal{T}) + Z(1-Z) \sum_{i=1}^{M} a_i(\mathcal{T}) \, P_{i-1}(Z)$$

$$\cdots \qquad \cdots \qquad (I-45)$$

where $a_i(\mathcal{T})$ are, as before, functions of time or constants and P_i are the non symmetrical polynomials defined by the condition

$$\int_0^1 w(Z) \, P_n(Z) \, P_m(Z) \, dZ = 0 \; , \; n = 0,1 \ldots\ldots \; , \; m-1 \qquad (I-46)$$

where $w(Z) = 1$ in this work

Based on equations (45) and (46), the dimensionless external fluid phase equations, equations (32-34), can be

written in collocation form as:

$$\frac{dC_{z(j)}}{d\tau} = P \sum_{i=1}^{M+2} B_{j,i}\, C_{z(i)} - F \sum_{i=1}^{M+2} A_{j,i}\, C_{z(i)} - 3C_1 W_1 \sum_{i=1}^{N+1} A_{N+1,i} C_{y(i,j)}$$

$$\cdots\cdots\cdots \quad (I\text{-}47)$$

$$\sum_{i=1}^{M+2} A_{1,i}\, C_{z(i)} = - PEM(UZZ - C_{z(1)}) \qquad (I\text{-}48)$$

$$\sum_{i=1}^{M+2} A_{M+2,i}\, C_{z(i)} = 0 \qquad (I\text{-}49)$$

Equations (45) & (46) can be used to eliminate $C_{z(1)}$ and $C_{z(M+2)}$ from equation (47) which can then be written, after proper substitution from equation (43), in the form as:

$$\frac{dC_{z(j)}}{d\tau} = (P \sum_{i=2}^{M+1} B_{j,i}^{x}\, C_{z(i)} - F \sum_{i=2}^{M+1} A_{j,i}^{x}\, C_{z(i)}) + (PB_{j,1}^{x} - FA_{j,1}^{x})$$

$$(R_3 \sum_{i=2}^{M+1} A_{M+2,i}\, C_{z(i)} - R_4 \sum_{i=2}^{M+1} A_{1,i}^{x}\, C_{z(i)}) + (PB_{j,M+2}^{x} -$$

$$FA_{j,M+2}^{x}) (R_1 \sum_{i=2}^{M+1} A_{1,i}^{x}\, C_{z(i)} - R_2 \sum_{i=2}^{M+1} A_{M+2,i}\, C_{z(i)}) - (PB_{j,1}^{x} -$$

$$FA_{j,1}^{x}) (R_4 PEM \cdot UZZ) + (PB_{j,M+2}^{x} - FA_{j,M+2}^{x}) (R_1 \cdot PEM \cdot UZZ) - 3C_1 W_1$$

$$(ZC_{z(j)} - Z_1 \sum_{i=1}^{N} A_{N+1,1}\, C_{y(i,j)}) \qquad (I\text{-}50)$$

where

$$R = - \frac{A^x_{1,M+2} - \frac{A^x_{11} - PEM}{A^x_{M+2,1}} A^x_{M+2,M+2}}{A^x_{11} - PEM}$$

$$R_1 = \frac{1}{R(A^x_{11} - PEM)}$$

$$R_2 = \frac{1}{RA^x_{M+2,1}}$$

$$R_3 = R_2 A^x_{M+2,M+2} - \frac{1}{A^x_{M+2,1}}$$

$$R_4 = R_1 \frac{A^x_{M+2,M+2}}{A^x_{M+2,1}}$$

$$Z = \frac{A_{N+1,N+1}}{1 + W_3 A_{N+1,N+1}}$$

$$Z_1 = \frac{-1}{1 + W_3 A_{N+1,N+1}}$$

The procedures for generating the A,B and A^x, B^x matrices of equations (39)-(50) are described by Finlayson (25) and are easy to follow.

The first order ordinary differential equations (41), (44) & (50) must be solved in order to simulate the adsorber column. In the present work number of collocation points for both particle (micro & macro) and column i.e. N and M are taken as 3. The integration routine used to solve the resulting ordinary differential equations was Runge - Kutta - Merson method.

(a)

(b)
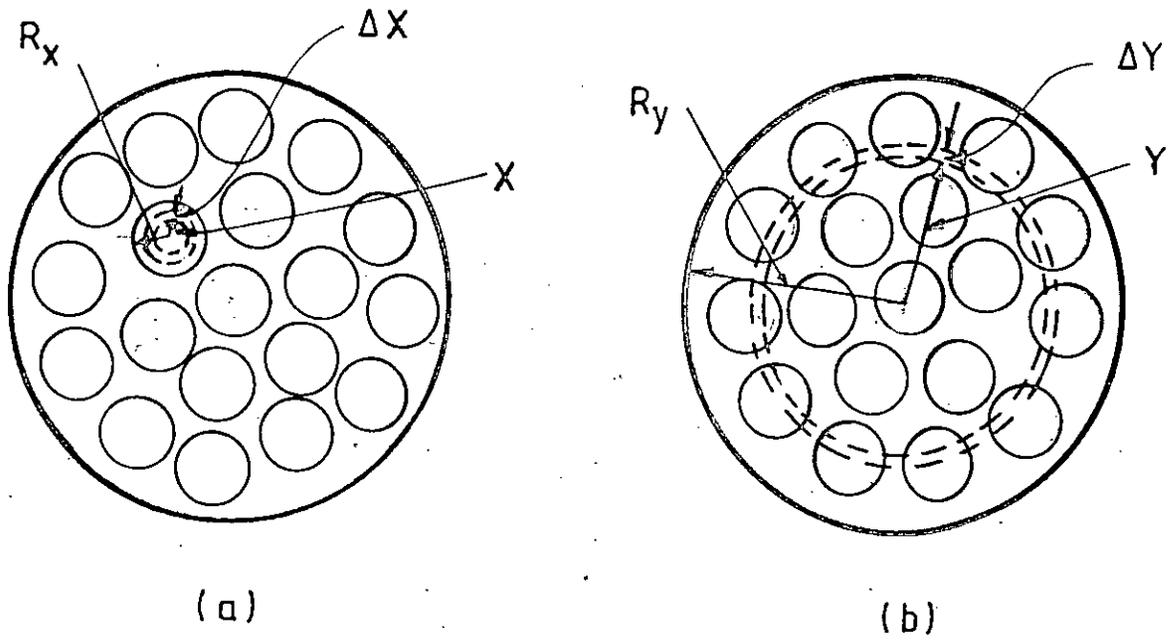
Figure I.1   Idealized Representation of a
Macroparticle containing Microparticle.
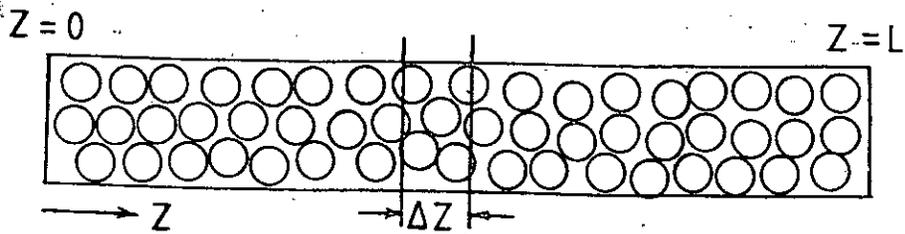
Figure I.2   Schematic Diagram of a Packed
Column.

```fortran
C     *********************************************
C     *********************************************
C     SIMULATION OF PACKED BED ADSORBER
C         BY ORTHOGONAL COLLOCATION
C     *********************************************
C
C     MAIN PROGRAM
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(6,6),B(6,6),AX(6,6),BX(6,6),UXO(6,6,6),UYO(6,6),UZO(6)
     *,XB(6),XP(6),UX(6,6,6),UY(6,6),UZ(6),UZT(6)
      DIMENSION UXT(6,6,6)    ,UYT(6,6)   ,AKZ(6,6) ,AKY(6,6,6)
      DIMENSION AKX(6,6,6),DELX(6,6,6),DELY(6,6),DELZ(6)
      DIMENSION EPX(6,6,6),EPY(6,6),EPZ(6)
      M=3
      M2=M+2
      M1=M+1
C     ** INITIALIZATION **
      DO 4 J=1,M2
      UZO(J)=0.0
      DO 4 K=1,M2
      UYO(K,J)=0.0
      DO 4 L=1,M2
      UXO(L,K,J)=0.0
4     CONTINUE
      CALL VALMAT(M,XP,XB,A,B,AX,BX)
C     WRITE(3,998)(XP(I),I=1,M1)
C     WRITE(3,999)(XB(I),I=1,M2)
C     WRITE(3,998) ((A(J,I),I=1,M1),J=1,M1)
C     WRITE(3,998) ((B(J,I),I=1,M1),J=1,M1)
C     WRITE(3,999) ((AX(J,I),I=1,M2),J=1,M2)
C     WRITE(3,999) ((BX(J,I),I=1,M2),J=1,M2)
C999  FORMAT(5X,E20.7)
C998  FORMAT(5X,E20.7)
      TO=0.0
      CALL RUNGE(M,UXO,UYO,UZO,TO,A,B,AX,BX)
      STOP
      END
```

```fortran
C     ***********************************
C     INTEGRATION SUBROUTINE
C     RUNGE-KUTTA-MERSON
C     ***********************************
      SUBROUTINE RUNGE(M,UXO,UYO,UZO,TO,A,B,AX,BX)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION UXO(6,6,6)    ,UYO(6,6)   ,UZO(6)      ,UX(6,6,6)
      DIMENSION    A(6,6)    ,B(6,6)   ,AX(6,6)   ,BX(6,6)   ,UXT(6,6,6)
      DIMENSION AKX(6,6,5,5)    ,AKY(6,6,6)   ,AKZ(6,6)  ,DELX(6,6,6)
      DIMENSION   DELY(6,6)   ,DELZ(6)   ,UY(6,6)   ,UYT(6,6),EPZ(6)
      DIMENSION UZ(6)   ,UZT(6),EPY(6,6),EPX(6,6,6)
      HX=0.0001
      TOL=0.001
      TK=0.0
      M1=M+1
      M2=M+2
      WRITE(3,43)
      WRITE(3,44)
      WRITE(3,48)
499   ITN=0
500   ITN=ITN+1
498   DO 100 JZ=1,5
      GO TO (31,32,33,34,35),JZ
31    DO 26 J=2,M1
      UZ(J)=UZO(J)
      DO 26 K=1,M
      UY(K,J)=UYO(K,J)
      DO 26 L=1,M
26    UX(L,K,J)=UXO(L,K,J)
      T=TO
      GO TO 10
32    DO 27 J=2,M1
      UZ(J)=UZO(J)+AKZ(JZ-1,J)
      DO 27 K=1,M
      UY(K,J)=UYO(K,J)+AKY(JZ-1,K,J)
      DO 27 L=1,M
27    UX(L,K,J)=UXO(L,K,J)+AKX(JZ-1,L,K,J)
      T=TO+HX/3.0
      GO TO 10
33    DO 28 J=2,M1
      UZ(J)=UZO(J)+AKZ(JZ-1,J)/2.0+AKZ(JZ-2,J)/2.0
      DO 28 K=1,M
      UY(K,J)=UYO(K,J)+AKY(JZ-1,K,J)/2.0+AKY(JZ-2,K,J)/2.0
      DO 28 L=1,M
28    UX(L,K,J)=UXO(L,K,J)+AKX(JZ-1,L,K,J)/2.0+AKX(JZ-2,L,K,J)/2.0
      T=TO+HX/3.0
      GO TO 10
34    DO 29 J=2,M1
      UZ(J)=UZO(J)+3.0*AKZ(JZ-3,J)/8.0+9.0*AKZ(JZ-1,J)/8.0
      DO 29 K=1,M
      UY(K,J)=UYO(K,J)+3.0*AKY(JZ-3,K,J)/8.0+9.0*AKY(JZ-1,K,J)/8.0
      DO 29 L=1,M
29    UX(L,K,J)=UXO(L,K,J)+3.0*AKX(JZ-3,L,K,J)/8.0+9.0*AKX(JZ-1,L,K,J)/8
     ..0
      T=TO+HX/2.0
      GO TO 10
35    DO 30 J=2,M1
      UZ(J)=UZO(J)+3.0*AKZ(JZ-4,J)/2.0-9.0*AKZ(JZ-2,J)/2.0+6.0*AKZ(JZ-1,
     .J)
      DO 30 K=1,M
      UY(K,J)=UYO(K,J)+3.0*AKY(JZ-4,K,J)/2.0-9.0*AKY(JZ-2,K,J)/2.0+6.0*A
     .KY(JZ-1,K,J)
      DO 30 L=1,M
30    UX(L,K,J)=UXO(L,K,J)+3.0*AKX(JZ-4,L,K,J)/2.0-9.0*AKX(JZ-2,L,K,J)/2
     ..0+6.0*AKX(JZ-1,L,K,J)
      T=TO+HX
C     -------------------------------------
10    UZZ=1.00/DEXP(T/0.1)
      CALL DIFFEQ(M,UX,UY,UZ,A,B,AX,BX,UZZ,UXT,UYT,UZT)
      DO 200 J=2,M1
C     -------------------------------------
      AKZ(JZ,J)=UZT(J)*HX/3.0
      DO 200 K=1,M
      AKY(JZ,K,J)=UYT(K,J)*HX/3.0
      DO 200 L=1,M
      AKX(JZ,L,K,J)=UXT(L,K,J)*HX/3.0
200   CONTINUE
C     -------------------------------------
```

```
100     CONTINUE
        DO 201 J=2,M1
        EPZ(J)=(AKZ(1,J)-4.5*AKZ(3,J)+4.0*AKZ(4,J)-0.5*AKZ(5,J))/5.0
        IF(DABS(EPZ(J)) .GT. TOL) GO TO 203
        DO 201 K=1,M
        EPY(K,J)=(AKY(1,K,J)-4.5*AKY(3,K,J)+4.0*AKY(4,K,J)-0.5*AKY(5,K,J))
       */5.0
        IF(DABS(EPY(K,J)) .GT. TOL) GO TO 203
        DO 201 L=1,M
        EPX(L,K,J)=(AKX(1,L,K,J)-4.5*AKX(3,L,K,J)+4.0*AKX(4,L,K,J)-5.0*AKX
       *(5,L,K,J))/5.0
        IF(DABS(EPX(L,K,J)) .GT. TOL) GO TO 203
201     CONTINUE
        TO=TO+HX
        TK=TK+HX
        DO 202 J=2,M1
        DELZ(J)=(AKZ(1,J)+4.*AKZ(4,J)+AKZ(5,J))/5.0
        UZO(J)=UZO(J)+DELZ(J)
        DO 202 K=1,M
        DELY(K,J)=(AKY(1,K,J)+4.*AKY(4,K,J)+AKY(5,K,J))/5.0
        UYO(K,J)=UYO(K,J)+DELY(K,J)
        DO 202 L=1,M
        DELX(L,K,J)=(AKX(1,L,K,J)+4.*AKX(4,L,K,J)+AKX(5,L,K,J))/5.0
C
202     UXO(L,K,J)=UXO(L,K,J)+DELX(L,K,J)
        PEM=10000.0
C       CALL VALMAT(M,XP,XB,A,B,AX,BX)
        SUMC=0.0
        DO 1100 I=2,M1
        SUMC=SUMC+((AX(M2,I)*(AX(1,1)-PEM)/AX(M2,1))-AX(1,I))*UZO(I)
1100    CONTINUE
        UZO(M2)=(SUMC/(AX(1,M2)-(AX(M2,M2)*(AX(1,1)-PEM)/AX(M2,1))))-(PEM*
       *UZZ/(AX(1,M2)-(AX(M2,M2)*(AX(1,1)-PEM)/AX(M2,1))))
        IF(TK. GE. 0.01) GO TO 501
        HX=2.0*HX
        GO TO 498
203     HX=HX/2.0
204     GO TO 500
501     IF(UZO(M2) .LT. 0.0) GO TO 61
        WRITE(3,2000) TO ,UZO(M2)
C       DO 2004 J=2,M2
C       WRITE(3,2001) J,UZO(J)
C        DO 2004 K=1,M
C       WRITE(3,2002) K,J,UYO(K,J)
C        DO 2004 L=1,M
C2004    WRITE(3,2003) L,K,J,UXO(L,K,J)
61      IF(TO .LE. 1.0) GO TO 2055
        IF(UZO(5) .LE. 0.0) GO TO 205
2055    HX=2.0*HX
        TK=0.0
        GO TO 499
205     CONTINUE
2000    FORMAT(20X,F8.5,5X,F10.6/)
2001    FORMAT(10X,'CZ=',I6,F13.10)
C2002   FORMAT(10X,'CY=',2I6,F13.10)
C2003   FORMAT(10X,'CX=',3I6,F13.10)
43      FORMAT(25X,'SAMPLE OUTPUT',/,26X,'******************',//)
44      FORMAT(20X,'TIME',10X,'BED OUTLET CONCENTRATION')
48      FORMAT(20X,'____',10X,'_____')
        RETURN
        END
```

```fortran
C'
C     ********************************************************************
C     CALCULATION OF DERIVATIV. OF DIFFERENTIAL EQUATION
C     ********************************************************************
C     SUBROUTINE DIFFEQ(M,UX,UY,JZ,A,B,AX,BX,UZZ,UXT,UYT,UZT)
      IMPLICIT REAL*8(A-H,.-Z)
      DIMENSION A(6,6)   ,B(6,6)   ,AX(6,6)   ,BX(6,6)   ,UX(6,6,6)
      DIMENSION UZ(6)  ,UXT(6,6,6)   ,UYT(6,6)  ,UZT(6)  ,UY(6,6)
      DIMENSION UXO(6,6,6)   ,UY0(6,6)  ,UZO(6)  ,AKX(6,6,6,6)    ,AKY(5,5
     .,6)   ,AKZ(6,6)  ,DELX(6,6,6)   ,DELY(6,6)  ,DELZ(6)
      M1=M+1
      M2=M+2
C     ** INPUT PARAMETERS **
      PEM=10000.0
      EB=0.410
      F=1.0/EB
      CON1=(1.0-EB)/EB
      EMAP=0.320
      CON3=(1.0-EMAP)/EMAP
      CON2=1.0/EMAP
      EMP=0.420
      EQB=29.43
      CDN4=1.0/(EMP*(1.0+FQB))
      P=1.0/(PEM*EB)
      BIGSI=1.00D-03
      W1=5.470D01
      W2=2.07
C
      R=(AX(M2,M2)/AX(M2,1))-(AX(1,M2)/(AX(1,1)-PEM))
      R1=1.0/(R*(AX(1,1)-PEM))
      R2=1.0/(R*AX(M2,1))
      R3=((R2*AX(M2,M2))-1.0)/AX(M2,1)
      R4=(R1*AX(M2,M2))/AX(M2,1)
      Z=A(M1,M1)/(1.0+BIGSI*A(M1,M1))
      Z1=((A(M1,M1)*BIGSI)/(1.0+BIGSI*A(M1,M1)))-1.0
      DO 101 J=2,M1
      SUM1=0.0
      DO 102 I=2,M1
      SUM1=SUM1+((P*BX(J,1)-F*AX(J,I))+(P*BX(J,1)-F*AX(J,1))*(R3*AX(M2,
     .I)-R4*AX(1,I))+(P*BX(J,M2)-F*AX(J,M2))*(R1*AX(1,I)-R2*AX(M2,I)))*
     .UZ(I)
  102 CONTINUE
      SUM2=0.0
      DO 103 I=1,M
      SUM2=SUM2+3.0*CON1*W1*71*A(M1,I)*UY(I,J)
  103 CONTINUE
      UZT(J)=SUM1+SUM2-P*M*UZZ*R4*(P*BX(J,1)-F*AX(J,1))+PEM*UZZ*R1*(P*B
     .X(J,M2)-F*AX(J,M2))-3.0*CON1*W1*Z*UZ(J)
      DO 101 K=1,M
      SUM3=0.0
      DO 104 I=1,M
      SUM3=SUM3+CON2*W1*(B(K,I)*UY(I,J)-(B(K,M1)*BIGSI*A(M1,I)*UY(I,J))/
     .(1.+BIGSI*A(M1,M1)))-3.0*CON3*W2*A(M1,I)*UX(I,K,J)
  104 CONTINUE
      UYT(K,J)=SUM3+CON2*W1*B(K,M1)*UZ(J)/(1.0+BIGSI*A(M1,M1))-3.0*CON3*
     .W2*A(M1,M1)*UY(K,J)
      DO 101 L=1,M
      SUM4=0.0
      DO 106 I=1,M
      SUM4=SUM4+CON4*W2*B(L,I)*UX(I,K,J)
      UXT(L,K,J)=SUM4+CON4*W2*B(L,M1)*UY(K,J)
  101 CONTINUE
      RETURN
      END
```

```
C     ****************************************
C     COLLOCATION COEFFICIENTS
C     ****************************************
C
      SUBROUTINE VALMAT(M,XP,XB,A,B,AX,BX)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(6,6)    ,B(6,6)   ,AX(6,6)    ,BX(6,6)   ,XB(6)  ,XP(6)
      DIMENSION UXO(6,6,6)    ,JYO(6,6)  ,UZO(6) ,UX(6,6,6)    ,UY(6,6)
      DIMENSION UZ(6) ,AKX(6,6,6,6)   ,AKY(6,6,6) ,AKZ(6,6) ,UYT(6,6)
      DIMENSION UXT(6,6,6)    ,UZT(6) ,DFLUX(6,6,6)    ,DELUY(6,6)
      DIMENSION DELUZ(6)
      XP(1)=0.3631175D+00
      XP(2)=0.6771863D+00
      XP(3)=0.8997580D+00
      XP(4)=0.1000000D+01
      A(1,1)=-0.4130895D+01
      A(1,2)=0.6881913D+01
      A(1,3)=-0.4547539D+01
      A(1,4)=0.1796520D+01
      A(2,1)=-0.1338863D+01
      A(2,2)=-0.2215048D+01
      A(2,3)=0.5289055D+01
      A(2,4)=-0.1735144D+01
      A(3,1)=0.6257033D+00
      A(3,2)=-0.3740616D+01
      A(3,3)=-0.1667115D+01
      A(3,4)=0.4782028D+01
      A(4,1)=-0.1072725D+01
      A(4,2)=0.5325570D+01
      A(4,3)=-0.2075254D+02
      A(4,4)=0.1650000D+02
      B(1,1)=-0.2385300D+02
      B(1,2)=0.3059365D+02
      B(1,3)=-0.7412940D+01
      B(1,4)=0.3005707D+01
      B(2,1)=0.1109991D+02
      B(2,2)=-0.4323766D+02
      B(2,3)=0.4081877D+02
      B(2,4)=-0.8681012D+01
      B(3,1)=-0.3322846D+01
      B(3,2)=0.3835681D+02
      B(3,3)=-0.1254073D+03
      B(3,4)=0.9037530D+02
      B(4,1)=-0.3367560D+02
      B(4,2)=0.1523752D+03
      B(4,3)=-0.3111996D+03
      B(4,4)=0.1925000D+03
      XB(1)=0.0000000D+00
      XB(2)=0.1127017D+00
      XB(3)=0.5000000D+00
      XB(4)=0.8872983D+00
      XB(5)=0.1000000D+01
      AX(1,1)=-0.1300000D+02
      AX(1,2)=0.1478831D+02
      AX(1,3)=-0.2666667D+01
      AX(1,4)=0.1873361D+01
      AX(1,5)=-0.1000000D+01
      AX(2,1)=-0.5323790D+01
      AX(2,2)=0.3872983D+01
      AX(2,3)=0.2065591D+01
      AX(2,4)=-0.1290990D+01
      AX(2,5)=0.6762100D+00
      AX(3,1)=0.1500000D+01
      AX(3,2)=-0.3227486D+01
      AX(3,3)=0.1017704D-13
      AX(3,4)=0.3227486D+01
      AX(3,5)=-0.1500000D+01
      AX(4,1)=-0.6762100D+00
      AX(4,2)=0.1290994D+01
      AX(4,3)=-0.2065591D+01
      AX(4,4)=-0.3872983D+01
      AX(4,5)=0.5323790D+01
      AX(5,1)=0.1000000D+01
      AX(5,2)=-0.1873361D+01
      AX(5,3)=0.2666667D+01
      AX(5,4)=-0.1478831D+02
      AX(5,5)=0.1300000D+02
      BX(1,1)=0.8400000D+02
      BX(1,2)=-0.1220632D+03
```

```
BX(1,3)=0.5866667D+02
BX(1,4)=-0.4460350D+02
BX(1,5)=0.2400000D+02
BX(2,1)=0.5323790D+02
BX(2,2)=-0.7333333D+02
BX(2,3)=0.2666667D+02
BX(2,4)=-0.1333333D+02
BX(2,5)=0.6762100D+01
BX(3,1)=-0.6000000D+01
BX(3,2)=0.1666667D+02
BX(3,3)=-0.2133333D+02
BX(3,4)=0.1666667D+02
BX(3,5)=-0.6000000D+01
BX(4,1)=0.6762100D+01
BX(4,2)=-0.1333333D+02
BX(4,3)=0.2666667D+02
BX(4,4)=-0.7333333D+02
BX(4,5)=0.5323790D+02
BX(5,1)=0.2400000D+02
BX(5,2)=-0.4460350D+02
BX(5,3)=0.5866567D+02
BX(5,4)=-0.1220632D+03
BX(5,5)=0.8400000D+02
RETURN
END
```

SAMPLE OUTPUT
****

TIME	BED OUTLET CONCENTRATION
0.10090	0.000281
0.11100	0.002045
0.12110	0.003528
0.13120	0.004780
0.14130	0.005838
0.15140	0.006731
0.16150	0.007481
0.17160	0.008108
0.18170	0.008627
0.19180	0.009052
0.20190	0.009393
0.21200	0.009661
0.22210	0.009864
0.23220	0.010009
0.24230	0.010104
0.25240	0.010155
0.26250	0.010166
0.27260	0.010143
0.28270	0.010090
0.29280	0.010011
0.30290	0.009908
0.31300	0.009786
0.32310	0.009647
0.33320	0.009493
0.34330	0.009327
0.35340	0.009150
0.36350	0.008964
0.37360	0.008772
0.38370	0.008573
0.39380	0.008370
0.40390	0.008164
0.41400	0.007955
0.42410	0.007744
0.43420	0.007532
0.44430	0.007321
0.45440	0.007109
0.46450	0.006898
0.47460	0.006689

	0.000511
0.94890	0.000437
0.95900	0.000365
0.96910	0.000295
0.97920	0.000225
0.98930	0.000160
0.99940	0.000095
1.00950	0.000031

APPENDI^X - III

ALGORITHM FOR ADSORBER MODEL

1. Choose values of N and M

2. Read the initial values and input parameters

3. Determine the roots of the polynomial for particle and column

4. Generate the matrices A, B, A^X and B^X

5. Calculate the constant terms in the model equations

6. Solve the differential equations by Runge-Kutta-Merson method.