

CHAPTER IV

MATHEMATICAL MODEL

This chapter explains the development of the mathematical model to generate the breakthrough curve of the adsorption process for removing sulfur compounds from the simulated transportation fuels. The mathematical model incorporates all resistances to mass transfer, including: diffusion in liquid film around pellets in the bed, diffusion in the binder-phase of zeolite and within crystals, and adsorption/desorption at the interface of binder-phase and crystals. In order to obtain the theoretical breakthrough curves for adsorption of sulfur compounds from simulated transportation fuels in a single layer adsorbent bed, both mass balance on pellet and on fixed bed were solved numerically by MATLAB™ program and FEMLAB™ software which is a software package for solving partial differential equations by finite element method (FEM) to validate the MATLAB™ algorithm. In case of MATLAB™ program, the method of line (MOL) combined with finite difference method (FDM) used to transform partial differential equation into a set of ordinary differential equations (ODEs). Finally, the set of ordinary differential equations (ODEs) was solved using ODE solver package available in MATLAB™ program.

4.1 Model Description

The adsorber geometry considered in the model development is schematically depicted in Figure 4.1. Transportation fuel is fed to the fixed bed adsorber packed with zeolites having a biporous structure. The void between the crystals create macropores. These pores act as conduit for transportation of sulfur compound molecules from bulk phase to the interior of the crystal. Once sulfur compound molecules are inside the particle, they are adsorbed at the pore-mouth of the micropores and hence, the adsorbed species diffuse into the interior of the crystal through micropores of the crystal. The diffusion process in the macropores and micropores follows the combination of the molecular and Knudsen diffusion

mechanisms while that inside the crystal follows an intra crystalline diffusion mechanism. Thus, in the case of former, adsorption is usually controlled by intra crystalline diffusion.

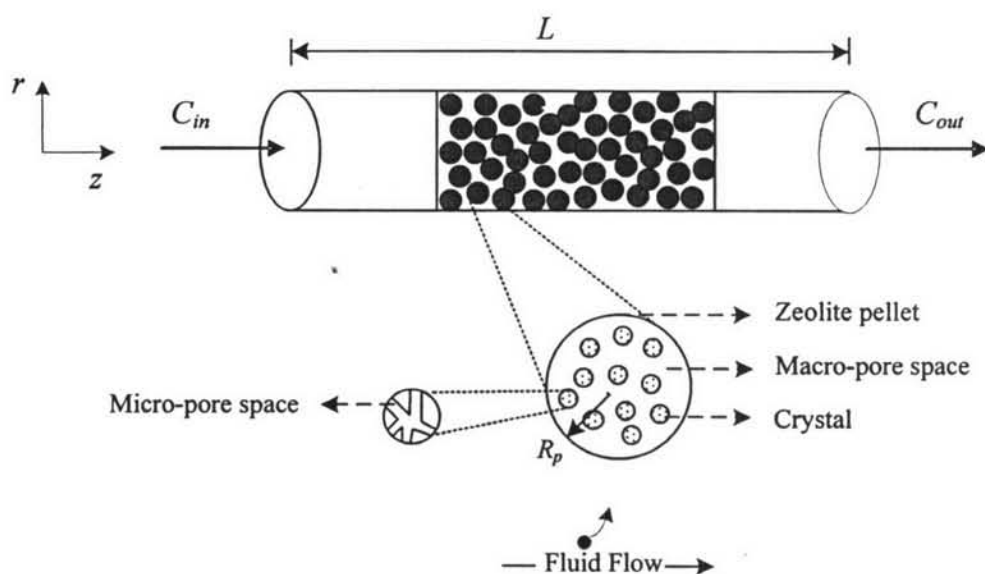


Figure 4.1 Adsorber geometry considered in the model development.

4.2 Model Assumptions

In order to simplify the complexity of model development, the mathematical model developed to explain the breakthrough of sulfur compounds consisting of the zeolite pellets is based on the following assumptions:

- The pressure drop throughout the bed is negligible under experimental conditions studied.
- Temperature is uniform throughout the bed and pellet.
- Fluid velocity throughout the bed is constant. This assumption is valid due to the fact that change in concentration of adsorbing species is occurred at trace level which does not contribute to a significant change in local velocity inside the bed.
- There is no competitive adsorption by other components.

- The radial concentration profiles within the solid pores (macro and micro-pores) are averaged assuming parabolic concentration profiles and the average mobile phase concentration within the pores of the pellet and the average adsorbate phase concentration within the crystals are determined
- Instantaneous equilibrium exists between the mobile phase in the macro-pores of pellet and the adsorbed phase within crystal at the binder-crystal interface.

4.3 Governing Equations

4.3.1 Mass Balance in Fixed Bed Adsorber

The derivation of differential mass balance or continuity equations for the adsorbing species in the fixed bed adsorber is similar to that in the reactor. According to Bird et al. (1960), the general form of the continuity equation for a chemical species reacting in a flowing fluid is verbally expressed as,

$$\left\{ \begin{array}{l} \text{Rate of mass} \\ \text{accumulation} \end{array} \right\} = \left\{ \begin{array}{l} \text{Rate of} \\ \text{mass inlet} \end{array} \right\} - \left\{ \begin{array}{l} \text{Rate of} \\ \text{mass outlet} \end{array} \right\} + \left\{ \begin{array}{l} \text{Rate of mass} \\ \text{change by reaction} \end{array} \right\}$$

When the above verbal expression is applied to adsorption process, the mathematical formulation of differential mass balance for adsorbing species is indicated below, (Gupta *et al.*, 2004)

$$\frac{\partial c_b}{\partial t} = \frac{D_L}{\varepsilon_b} \frac{\partial^2 c_b}{\partial z^2} - \frac{1}{\varepsilon_b} \frac{\partial}{\partial z} (v_z c_b) - \frac{3(1-\varepsilon_b)}{R_p \varepsilon_b} f(z) \quad (4.1)$$

It is important to note here that, on the right hand side of Eq. (4.1), the first and second terms describe {the rate of adsorbing species inlet}-{the rate of adsorbing species outlet} while the third term represents diffusion of sulfur compound molecules from the bulk phase into the macropores of the zeolite pellets. $f(z)$ is the mass transfer rate of sulfur compound from bulk liquid to adsorbent particle and is calculated using the following equation.

$$f(z) = K_m (c_b - c_p|_{R=R_p}) \quad (4.2)$$

where c_b is the adsorbate concentration in the bulk phase, c_p the adsorbate concentration in macropores of the pellet (mole m^{-3}), D_L the axial dispersion coefficient ($\text{m}^2 \text{s}^{-1}$), v_z the interstitial fluid velocity (m s^{-1}), ε_b the voidage of adsorbent bed. Another variable used to describe mass balance through the adsorbent bed is c_p which can be determined by performing mass balance of sulfur compound molecules inside biporous structure of adsorbent pellet as explained below. (Gupta *et al.*, 2004)

4.3.2 Mass Balance at Any Radial Direction of Pellet

It is considered that crystals are uniformly distributed in the binder-phase and the adsorption of adsorbate by the binder-phase is negligible in comparison with that at interface between the binder-phase and crystal. In this case, incorporating radial diffusion within the macro-pore volume of the binder-phase and adsorption at the pore-mouth of the crystals results in obtaining the following equation.

$$\varepsilon_p \frac{\partial c_p}{\partial t} = \frac{1}{R} \frac{\partial(R^2 N_R)}{\partial R} - 3(1 - \varepsilon_p) \frac{\partial \bar{q}_c}{\partial t} \quad (4.3)$$

Where N_R is molecular diffusion flux in the radial direction of the pellet ($\text{mol m}^{-2} \text{s}^{-1}$), q_c concentration of the adsorbate inside the crystal (mol m^{-3}), \bar{q}_c average concentration of the adsorbate inside the crystal (mol m^{-3}), ε_p the voidage of pellet and R radial co-ordinate in the particle (m).

4.3.3 Mass Balance at Any Radial Direction of Crystal

Mass balance in the crystal is given by the following solid diffusion equation:

$$\frac{\partial q_c}{\partial t} = \frac{D_c}{r} \frac{\partial(r^2 \partial q_c / \partial r)}{\partial r} \quad (4.4)$$

Where D_c is the diffusivity of the adsorbate within the crystal and r radial co-ordinate in the crystal (m).

4.3.4 Adsorption Isotherm

The adsorption isotherm is normally described by Langmuir or Freundlich isotherm. However, in this particular model formulation, a linear isotherm is assumed in order to reduce the complexity of numerical computation. This isotherm correlates the adsorbate concentration in the crystal with the mobile phase concentration in macro-pore volume of the binder phase at the crystal-binder-phase interface.

$$q_c = Kc_p \quad (4.5)$$

Where K is the equilibrium or partition coefficient between macro and micro-pores volume. The isotherm can also be seen as an equilibrium condition obtained by equating first order adsorption and desorption rates.

$$\frac{dq_c}{dt} = k_a c_p - k_d q_c \quad (4.6)$$

$$K = k_a / k_d = q_c / c_p \quad (4.7)$$

Where k_a and k_d are adsorption and desorption rate constant (s^{-1}). Eqs. (4.1), (4.3) and (4.4) coupling with Eq. (4.5) are solved simultaneously to predict the adsorbent performance, especially breakthrough characteristics in the bed. As these equations are coupling partial differential equations, independent variables being time (t), axial (z) and radial (both in r and R). Essentially, in this approach radial concentration profiles within the solid pores (macropores and micropores) are averaged assuming

parabolic concentration profiles and the average bulk phase concentration within the pores of the pellet and the average adsorbate phase concentration within the crystals are determined. This mathematical approximation is the reduction of second order PDEs to first order PDE with variation only in z direction. Moreover, the number of the governing equations to be solved is also reduced to two. As a consequence of this approximation, the simplified governing equations which are the bulk phase in the bed and the adsorbate in the pellet are obtained as follows (Gupta *et al.*, 2004):

$$\frac{\partial c_b}{\partial t} = \frac{D_L}{\varepsilon_b} \frac{\partial^2 c_b}{\partial z^2} - \frac{v_z}{\varepsilon_b} \frac{\partial c_b}{\partial z} - \frac{15(1-\varepsilon_b)K_m D_p (c_b - \bar{c}_p)}{\varepsilon_b R_p^2 (K_m + 5D_p / R_p)} \quad (4.8)$$

$$\frac{\partial \bar{c}_p}{\partial t} = -\frac{(c_b - \bar{c}_p)K_m}{(K_m + 5D_p / R_p)\varepsilon_p} \left[\frac{27D_c K(1-\varepsilon_p)}{R_c^2} - \frac{15D_p}{R_p^2} \right] \quad (4.9)$$

Where D_p is effective diffusivity inside the pores ($\text{m}^2 \text{s}^{-1}$), D_c diffusivity of the adsorbate within the crystal ($\text{m}^2 \text{s}^{-1}$), K equilibrium or partition coefficient between macro and micro-pores volume, R_p pellet radius (m) and R_c crystal radius (m). The calculation of these parameters can be found in Appendix D.

In order to determine concentration profile along the fixed bed adsorber, Eqs. (4.8) and (4.9) are solved simultaneously subject to the following initial and boundary conditions:

Table 4.1 Initial and Boundary Conditions for solving

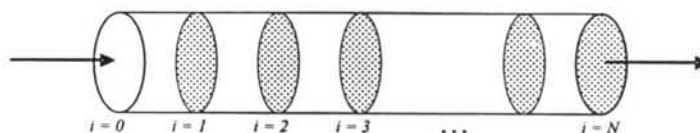
Equation	Initial Conditions	Boundary Conditions
Eq. (4.1)	$c_b = 0$ at $z > 0, t = 0$ $c_b = c_{inlet}$ at $z = 0, t > 0$	$c = c_{inlet}$ at $z = 0, t > 0$ $\frac{\partial c}{\partial z} = 0$ at $z = L, t > 0$
Eq. (4.2)	$\bar{c}_p = 0$ at $R > 0, t = 0$	$\frac{\partial \bar{c}_p}{\partial R} = 0$ at $R = 0, t > 0$

4.4 Numerical Implementation

4.4.1 Discretization Technique

Method of line (MOL) combined with Finite Difference Method (FDM) is used to discretize the governing equations (Eqs. (4.8) and (4.9)) and transform a partial differential equations (PDEs) into a set of ordinary differential equations (ODEs) for solving in MATLAB™ program. The mass balance equation is discretized by:

(1) replacing the continuous domain of fixed bed adsorber by a finite number of regular-spaced mesh- or grid-points.

**Figure 4.2** Discretization of fixed bed adsorber.

(2) approximating the derivatives of the PDE for each of these points using central finite differences method with the error of $O(\Delta z^2)$ as indicated below;

For the 1st order derivative term,

$$\frac{dc_i}{dz} = \frac{1}{2\Delta z} (c_{i+1} - c_{i-1}) + O(\Delta z^2) \quad (4.10)$$

For the 2nd order derivative term,

$$\frac{d^2c_i}{dz^2} = \frac{1}{\Delta z^2} (c_{i+1} - 2c_i + c_{i-1}) + O(\Delta z^2) \quad (4.11)$$

where i is step size number of axial direction (z).

Therefore, Eqs. (4.8) and (4.9) in the discretized forms are written as:

$$\frac{dc_{bi}}{dt} = \frac{D_L}{\varepsilon_b} \left[\frac{1}{\Delta z^2} (c_{b,i+1} - 2c_{b,i} + c_{b,i-1}) \right] - \frac{v_z}{\varepsilon_b} \left[\frac{1}{2\Delta z} (c_{b,i+1} - c_{b,i-1}) \right] - \frac{15(1-\varepsilon_b)K_m D_p (c_{bi} - \bar{c}_{pi})}{\varepsilon_b R_p^2 (K_m + 5D_p / R_p)} \quad (4.12)$$

$$\frac{\partial \bar{c}_{pi}}{\partial t} = - \frac{(c_{bi} - \bar{c}_{pi})K_m}{(K_m + 5D_p / R_p)\varepsilon_p} \left[\frac{27D_c K(1-\varepsilon_p)}{R_c^2} - \frac{15D_p}{R_p^2} \right] \quad (4.13)$$

Finally, the system of ordinary differential equations based on Eqs. (4.12) to (4.13) is solved simultaneously to determine the concentration profile of adsorbing species along the bed.

4.4.2 Programming Algorithm for MATLAB™

A programming algorithm used to develop the breakthrough curve is illustrated in Figure 4.3. Initially, the input parameters are specified including operating conditions, physical properties of adsorbent and the fitting parameter in the calculation. Mass balance in the fixed bed and in pellet as previously indicated in

Eqs. (4.12) and (4.13) are solved simultaneously using the ODE solver provided by the MATLAB™ program to determine the concentration profiles along the bed length for various times. Thereafter, the exit concentration of the adsorbing species is plotted against time to develop the mathematical breakthrough curve and it is compared to experimental data. Finally, the “fitting parameter”, a , is iteratively adjusted until the breakthrough curves obtained from the program and experiment agree well each other.

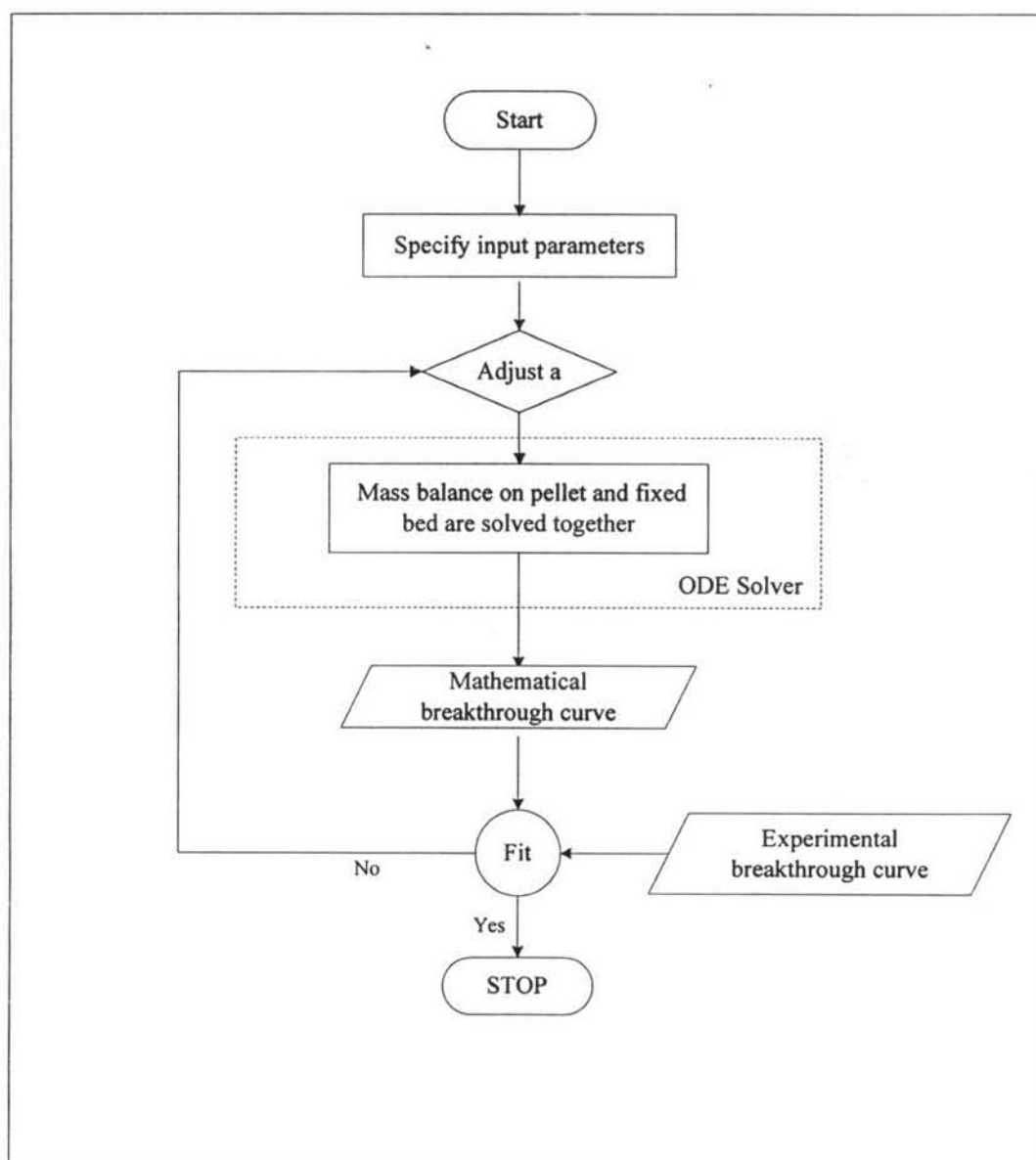


Figure 4.3 Programming algorithm for the model development.