CHAPTER - 3

DEVELOPMENT OF MATHEMATICAL MODEL

3.1 Adsorption in a Fixed Bed

The rate of adsorption in a fixed bed or a part thereof depends upon a number of factors. There are broadly two mass transfer resistances in series: (i) the resistance to transport of solute from the bulk gas to the surface of an adsorbent particle presumably through a stagnant film of the gas, and (ii) that due to diffusion of the solute through the pores (macro-, meso- and micro-pores) of an adsorbent particle to reach the adsorption sites within the particle. Adsorption of the solute molecules at the active sites may also offer a resistance that may be called adsorption kinetic resistance. The resistance can be neglected if the intrinsic adsorption rate is fast. Thus, generally there is a concentration gradient of the solute within a particle. Figure 3.1 shows the schematic representation of the diffusion of solute into the pores of the adsorbent particle. Also, if we look at the bed as a whole, the concentration of the solute in the gas decreases along the length of the bed because the solute is removed from the flowing carrier gas by adsorption in the bed. Both these spatial changes in concentration (within a particle as well as along the bed) depend upon time. Therefore, a rigorous theoretical analysis of the adsorption rate process and the solute concentration in the bed involves two differential equations obtained by unsteady state mass balance – one for the solute concentration within a particle and another for that along the bed. Derivations of these equations will be taken up in the subsequent sections.
3.2 Derivation of Model Equations

In this section, a mathematical model is presented to predict the time-dependent (unsteady state) concentration profiles of the adsorbing species (VOCs) on a solid adsorbent under isothermal conditions. One important point that may be noted is that, in reality the steady-state condition never exists in the bed of adsorbing materials during adsorption. Hence, a finite adsorption rate always prevails in the bed. The steady-state is achieved only when the bed reaches saturation levels. The present mathematical model takes account of both external and internal mass transfer resistances as well as of non-ideal plug flow along the column. Simultaneously, instantaneous local adsorption equilibrium on the pore surface is considered.

3.2.1 Assumptions for Mathematical Model

The following assumptions are made in theoretical analysis for developing a mathematical model for the adsorption of VOCs on granular activated carbon.

(i) The system operates under isothermal conditions.
(ii) Intraparticle mass transport is due to Fickian diffusion, and is characterized by $D_e$. Mass transfer across the boundary layer surrounding the solid particles is characterized by the external-film mass transfer coefficient $k_m$.
(iii) Axial dispersion is considered to account for non-ideal flux along the longitudinal axis of the column.
(iv) The macroporous adsorbent particles are spherical and homogeneous in size and density.
The present model is based on three governing equations: (a) species balance of the adsorbing component in the bed, (b) species balance of the component inside the pores of the adsorbent, and (c) instantaneous local adsorption equilibrium at the pore surface.

3.2.2 Solute Balance in the Bulk Phase along the Length of the Bed

First, we shall derive the equation for the unsteady state concentration distribution of the solute in the gas along the bed. We consider a thin slice of the bed of thickness \( \Delta z \) at a distance \( z \) from the feed end of the bed as shown in Figure 3.2. The solute entering the slice at any time \( t \) will (i) be partly get accumulated on the solid phase in the slice (ii) partly get accumulated in the interstitial fluid in the slice (iii) partly leave the slice by bulk flow and by axial dispersion.

![Figure 3.2: Differential mass balance over a section of the bed.](image)

Rate of input of the solute to the slice by bulk flow at \( z \) is given by,

\[
\frac{(AC_b V_b \epsilon_b)}{z}
\]

Rate of input of the solute to the slice by axial dispersion at \( z \) is given by,

\[
\frac{(\epsilon_b A_f)}{z}
\]

Rate of output of the solute from the slice by bulk flow at \((z + \Delta z)\) is given by,

\[
\frac{(AC_b V_b \epsilon_b)}{z + \Delta z}
\]

Rate of output of the solute from the slice by axial dispersion at \((z + \Delta z)\) is given by,

\[
\frac{(\epsilon_b A_f)}{z + \Delta z}
\]
Rate of accumulation of the solute in the slice on the solid phase is given by,

$$(1 - \epsilon_b) A \Delta z \frac{\partial C_{ps}}{\partial t}$$

Rate of accumulation of the solute in the slice on the gas phase is given by,

$$\left( \frac{\partial C_b}{\partial t} \right) \epsilon_b A \Delta z$$

where $A$ is the cross-sectional area of the column in $m^2$.

$C_b$ is the solute concentration in the bulk gas phase in $kg/m^3$.

$V_z$ is the interstitial velocity in $m/s$.

$\epsilon_b$ is the bed porosity.

$J$ is the mass flux due to axial dispersion in $kg/m^2.s$.

$C_{ps}$ is the solute concentration at the external surface of the adsorbent particle in $kg/m^3$.

An unsteady state mass balance of solute over the slice yields:

Input – Output = Accumulation

$$(AC_b V_z \epsilon_b) / z - (AC_b V_z \epsilon_b) / z + \Delta z = (1 - \epsilon_b) A \Delta z \frac{\partial C_{ps}}{\partial t} + \left( \frac{\partial C_b}{\partial t} \right) \epsilon_b A \Delta z$$

$$= (1 - \epsilon_b) A \Delta z \frac{\partial C_{ps}}{\partial t} + \left( \frac{\partial C_b}{\partial t} \right) \epsilon_b A \Delta z$$

Divide eq. (3.1) by $A \Delta z$, and take the limit $\Delta z \to 0$, we get

$$-V_z \epsilon_b \left( \frac{\partial C_b}{\partial z} \right) - \epsilon_b \left( \frac{\partial J}{\partial z} \right) = (1 - \epsilon_b) \left( \frac{\partial C_{ps}}{\partial t} \right) + \epsilon_b \left( \frac{\partial C_b}{\partial t} \right)$$

In terms of external mass transfer coefficient, $k_m \frac{\partial C_{ps}}{\partial t}$ can be expressed as

$$\frac{\partial C_{ps}}{\partial t} = k_m \alpha (C_b - C_{ps})$$

where $\alpha$ is external surface area per unit volume of the pellet and its value is $3/R_p$ for spherical pellet where $R_p$ is the radius of the adsorbent particle in $m$.

$k_m$ is the external-film mass-transfer coefficient in $m/s$.

Now mass flux due to axial dispersion can be expressed in terms of Fick’s law and is given by

$$J = -D_L \left( \frac{\partial C_b}{\partial z} \right)$$
where $D_L$ is the axial dispersion coefficient in m$^2$/s.

Substitute the value of eq. (3.3) and eq. (3.4) in eq. (3.2), we get
\begin{equation}
-\varepsilon_b V_z \frac{\partial C_b}{\partial z} - \varepsilon_b \frac{\partial}{\partial z} \left(-D_L \frac{\partial C_b}{\partial z}\right) = (1 - \varepsilon_b) \frac{k_m}{R_p} \left(C_b - C_{ps}\right) + \varepsilon_b \frac{\partial C_b}{\partial t}
\end{equation}
\begin{equation}
\varepsilon_b \left(\frac{\partial C_b}{\partial t}\right) + \varepsilon_b V_z \left(\frac{\partial C_b}{\partial z}\right) - D_L \varepsilon_b \left(\frac{\partial^2 C_b}{\partial z^2}\right) = -\frac{3(1 - \varepsilon_b)}{R_p} k_m (C_b - C_{ps})
\end{equation}

Initial and boundary conditions for eq. (3.6) are as follows:

at $t = 0$, $C_b = 0$ for all $z$

at $t > 0$ and at $z = 0$, $C_b = C_{b0}$

at $z = L$, $\frac{\partial C_b}{\partial z} = 0$

where $C_{b0}$ is the initial concentration of solute in the gas phase in kg/m$^3$ and $L$ is the length of the fixed bed in m.

3.2.3 Solute Balance inside the Pores of the Adsorbent

Secondly, we shall derive the equation for the unsteady state concentration distribution of the solute inside the pores of the adsorbent particle. We consider a thin slice of thickness $\Delta r$ at a distance $r$ from the center of the particle as shown in Figure 3.3. The solute entering the slice at any time $t$ will (i) be partly get accumulated inside the pores in the slice (ii) partly get accumulated on the surface of the pores in the slice (iii) partly leave the slice by pore diffusion.

![Figure 3.3: Differential mass balance over a section of the spherical adsorbent particle.](image)
Rate of input of the solute to the slice by diffusion at \( r + \Delta r \) is given by,
\[
(\alpha 4\pi r^2 N) / (r + \Delta r)
\]
Rate of output of the solute to the slice by diffusion at \( r \) is given by,
\[
(\alpha 4\pi r^2 N) / r
\]
Rate of accumulation of solute on the surface of the pores is given by,
\[
(1 - \alpha) \rho \left( \frac{\partial q}{\partial t} \right) (4\pi r^2) \Delta r
\]
Rate of accumulation of solute inside the pores is given by,
\[
\alpha \left( \frac{\partial C_p}{\partial t} \right) (4\pi r^2) \Delta r
\]

where \( \alpha \) is the particle porosity.

\( N \) is the mass flux due to pore diffusion in kg/m².s.

\( q \) is the solute concentration on the adsorbed phase in kg/kg.

\( \rho \) is the particle density in kg/m³.

\( C_p \) is the solute concentration in the gaseous phase inside the pores in kg/m³.

An unsteady state mass balance over the slice yields:

Input – Output = Accumulation

\[
(\alpha 4\pi r^2 N) / (r + \Delta r) = (\alpha 4\pi r^2 N) / r
\]

\[
= (1 - \alpha) \rho \left( \frac{\partial q}{\partial t} \right) (4\pi r^2) \Delta r + \alpha \left( \frac{\partial C_p}{\partial t} \right) (4\pi r^2) \Delta r
\]

(3.7)

Divide the eq. (3.7) by \( (4\pi \Delta r) \) and taking limit \( \Delta r \rightarrow 0 \).

\[
\alpha \frac{\partial}{\partial r} (r^2 N) = (1 - \alpha) \rho \left( \frac{\partial q}{\partial t} \right) r^2 + \alpha \left( \frac{\partial C_p}{\partial t} \right) r^2
\]

(3.8)

Mass flux due to pore diffusion can be written as,

\[ N = D_e \left( \frac{\partial C_p}{\partial r} \right) \]  

(3.9)

where, \( D_e \) is the effective diffusivity in m²/s.

Substitute the value of \( N \) from eq. (3.9) in eq. (3.8), we get

\[
\alpha \frac{\partial}{\partial r} \left( r^2 D_e \frac{\partial C_p}{\partial r} \right) = (1 - \alpha) \rho \left( \frac{\partial q}{\partial t} \right) r^2 + \alpha \left( \frac{\partial C_p}{\partial t} \right) r^2
\]

(3.10)
\[ \alpha D_e \left[ r^2 \frac{\partial^2 C_p}{\partial r^2} + 2r \frac{\partial C_p}{\partial r} \right] = (1 - \alpha) \rho \left( \frac{\partial q}{\partial t} \right) r^2 + \alpha \left( \frac{\partial C_p}{\partial t} \right) r^2 \]  

(3.11)

Divide eq. (3.11) by \( r^2 \), we get

\[ \alpha D_e \left[ \frac{\partial^2 C_p}{\partial r^2} + \frac{2}{r} \frac{\partial C_p}{\partial r} \right] = (1 - \alpha) \rho \left( \frac{\partial q}{\partial t} \right) + \alpha \left( \frac{\partial C_p}{\partial t} \right) \]  

(3.12)

\[ \left( \frac{\partial C_p}{\partial t} \right) + \left( \frac{1 - \alpha}{\alpha} \right) \rho \left( \frac{\partial q}{\partial t} \right) = D_e \left[ \frac{\partial^2 C_p}{\partial r^2} + \frac{2}{r} \frac{\partial C_p}{\partial r} \right] \]

(3.13)

Assuming instantaneous equilibrium

\[ \frac{\partial q}{\partial t} = \frac{\partial C_p}{\partial t} \frac{\partial q}{\partial C_p} \]  

(3.14)

Here Langmuir isotherm is assumed to describe the equilibrium relationship between amount adsorbed and concentration of solute in the pores and is given by the following equation.

\[ q = \frac{q_m K C_p}{1 + K C_p} \]  

(3.15)

where \( q_m \) is the maximum adsorption capacity of the adsorbent in kg/kg and \( K \) is the langmuir isotherm constant in m³/kg.

Differentiating eq. (3.15) w.r.t \( C_p \), we get

\[ \frac{\partial q}{\partial C_p} = \frac{q_m K}{(1 + K C_p)^2} \]  

(3.16)

From equations (3.16), (3.14) and (3.13), we get

\[ \left( \frac{\partial C_p}{\partial t} \right) = \left[ \frac{1}{1 + \rho \left( \frac{1 - \alpha}{\alpha} \right) \frac{q_m K}{(1 + K C_p)^2}} \right] D_e \left[ \frac{\partial^2 C_p}{\partial r^2} + \frac{2}{r} \frac{\partial C_p}{\partial r} \right] \]  

(3.17)

Initial and boundary conditions for eq. (3.17) are as follows:

at \( t = 0, C_p = 0 \)

The symmetry condition at the center of the particles is expressed as:

at \( r = 0, \frac{\partial C_p}{\partial r} = 0 \)
The continuity condition on the external surface of the adsorbent particle is as follows:

\[ a t \ r = R_p, \quad D_e \frac{\partial C_b}{\partial r} = k_m (C_b - C_{ps}) \]

### 3.3 Non-Dimensionalisation of the Governing Equations

In this section, the governing equations (3.6) and (3.17) have been written in non-dimensionalised form by introducing non-dimensional variables.

#### 3.3.1 Non-Dimensionalisation of the Governing Equation (3.6) and Initial and Boundary Conditions

The following dimensionless variables are introduced to render the governing eq. (3.6) dimensionless:

- Solute concentration in the bulk phase
  \[ C_b^* = \frac{C_b}{C_{b0}} \]
- Length of the fixed bed column
  \[ z^* = \frac{z}{L} \]
- Solute concentration at the external surface of the adsorbent particle
  \[ C_{ps}^* = \frac{C_{ps}}{C_{b0}} \]

Introducing the dimensionless variables \((C_b^*, z^*\) and \(C_{ps}^*\)) in governing eq. (3.6), we get

\[
C_{b0} \left( \frac{\partial C_b^*}{\partial t} \right) + \frac{V_z C_{b0}}{L} \left( \frac{\partial C_b^*}{\partial z^*} \right) - \frac{D_l C_{b0}}{L^2} \left( \frac{\partial^2 C_b^*}{\partial z^{*2}} \right) = -\frac{3(1 - \epsilon_b)}{\epsilon_b R_p} k_m C_{b0} (C_b^* - C_{ps}^*)
\]

\[
\left( \frac{\partial C_b^*}{\partial t} \right) = -\frac{V_z}{L} \left( \frac{\partial C_b^*}{\partial z^*} \right) + \frac{D_l}{L^2} \left( \frac{\partial^2 C_b^*}{\partial z^{*2}} \right) - \frac{3k_m (1 - \epsilon_b)}{\epsilon_b R_p} (C_b^* - C_{ps}^*)
\]

\[
\left( \frac{\partial C_b^*}{\partial t} \right) = -\frac{1}{t_{res}} \left( \frac{\partial C_b^*}{\partial z^*} \right) + P \left( \frac{\partial^2 C_b^*}{\partial z^{*2}} \right) - Q (C_b^* - C_{ps}^*)
\]

where \( t_{res} = \frac{L}{V_z}, P = \frac{D_l}{L^2} \) and \( Q = \frac{3k_m (1 - \epsilon_b)}{\epsilon_b R_p} \)

The dimensionless initial and boundary conditions for eq. (3.20) are as follows:

- at \( t = 0 \) and at all \( z^* \), \( C_b^* = 0 \)
- at \( t > 0 \) and at \( z^* = 0 \), \( C_b^* = 1 \)
\[ at\ z^* = 1, \quad \frac{\partial C^*_b}{\partial z^*} = 0 \]

### 3.3.2 Non-Dimensionalisation of the Governing Equation (3.17) and Initial and Boundary Conditions

The following dimensionless variables are introduced to render the governing eq. (3.17) dimensionless:

- **Solute Concentration inside the pores of the adsorbent particle**
  \[ C^*_p = \frac{C_p}{C_{b0}} \]

- **Radius of the adsorbent particle**
  \[ r^* = \frac{r}{R_p} \]

Introducing the dimensionless variables \((C^*_p \text{ and } r^*)\) in governing eq. (3.17), we get

\[
\frac{\partial C^*_p}{\partial t} = \frac{\alpha \left( 1 + KC_{b0}C^*_p \right)^2}{\alpha \left( 1 + KC_{b0}C^*_p \right)^2 + \rho(1 - \alpha)q_mK} \left[ \frac{D_e}{R_p^2} \frac{\partial^2 C^*_p}{\partial r^*^2} + \frac{2C_{b0}}{r^*} \frac{\partial C^*_p}{\partial r^*} \right] \tag{3.21}
\]

\[
\frac{\partial C^*_p}{\partial t} = \frac{T \alpha \left( 1 + KC_{b0}C^*_p \right)^2}{\alpha \left( 1 + KC_{b0}C^*_p \right)^2 + \rho(1 - \alpha)q_mK} \left[ \frac{\partial^2 C^*_p}{\partial r^*^2} + \frac{2}{r^*} \frac{\partial C^*_p}{\partial r^*} \right] \tag{3.22}
\]

**Where** \( T = \frac{D_e}{R_p^2} \)

The dimensionless initial and boundary conditions for eq. (3.22) are as follows:

- **at** \( t = 0, \quad C^*_p = 0 \)

- **at** \( r^* = 0, \quad \frac{\partial C^*_p}{\partial r^*} = 0 \)

- **at** \( r^* = 1, \quad \frac{\partial C^*_p}{\partial r^*} = R\left( C^*_b - C^*_p^1 \right) \) \text{ where } R = \frac{k_mR_p}{D_e} \]

The governing equations (3.20) and (3.22) are non-linear coupled partial differential equations whose solution technique is given in the next chapter. The validity of these equations will be checked based on experimental results. Then the equations will be used to predict bed performance for which experiments are not conducted.