



## CHAPTER 2

## CONCEPTS OF LIQUID ADSORPTION

Liquid-solid adsorption in a similar manner as gas-solid adsorption is a thermodynamic system consisting of a liquid phase called the adsorbate, a solid phase called the adsorbent and a liquid which has interacted with the solid phase and called the adsorbed phase.

The amount adsorbed depends on the nature of adsorbents and solutes.

### 2.1 Adsorbents

Most adsorbents are highly porous materials in which a primary adsorption takes place on the walls of the pores onto the specific sites inside the particles. Separation takes place when some molecules, of different molecular weights or polarity are held on the adsorbent longer than others. There are many types of adsorbents such as activated carbon, silica gel, zeolites, etc. For any adsorbent the most important characteristic is its high internal porosity. Thus physical characteristics such as pore volume, pore size distribution, bulk density, particle size and erosion resistance, are generally more important than chemical characteristics. This study however involves only one adsorbent namely, activated carbon.

### 2.1.1 Activated Carbon

Activated carbons were commercialized some 80 years ago and were used to purify, decolorize and upgrade the quality of liquid streams in the chemical industry. Sulfur-impregnated carbons were developed for removing mercury from hydrogen and other gas stream. Another significant environmental use is wastewater treatment to remove chemical, pesticide and other industrial impurities.

Activated carbon is a porous carbonaceous material, prepared by carbonizing and activating organic substances such as wood, peat, coal, petroleum coke, bones, fruit nuts and coconut shells with steam or carbonization at elevated temperatures (700-1100 C). Its most important property is its highly developed porous structure that is used to retain molecules on its internal surface. Pores in activated carbons similarly as in most adsorbents, exist throughout the particle in a manner as illustrated in Figure 2.1.

The areas of pores walls of activated carbons have large surface areas (between 300-2500  $\text{m}^2/\text{g}$ ). And the unique surface property of activated carbon is its nonpolar or slightly polar nature. This property makes activated carbon different from others adsorbents as follow :

- a. It does not require removing moisture before use.
- b. It adsorbs non-polar and weakly polar organic molecules to a larger extent than other adsorbents.
- c. The heat of adsorption or bond strength is generally lower on activated carbons than on other adsorbents.

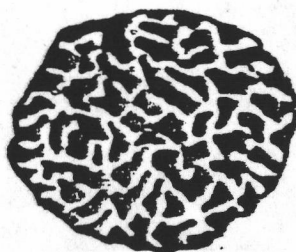


Figure 2.1 The pore structure of adsorbents.

Typical properties for activated carbons made from various materials are shown in table II and figure 2.2.(15)

Table II(15)

CHARACTERISTICS OF ACTIVATED CARBONS  
FROM VARIOUS RAW MATERIALS

Raw Material	I <sub>2</sub> No.	Mol. No.	CCl <sub>4</sub> No.	Butane Pore Vol. cc/g	Application
Lignite	550	490	34	0.23	Liquid Phase
Bituminous Coal	900/ 1000	200/ 250	60	0.45	Vapor/Liquid Phase
Petroleum Acid Sludge Coke	1150	180	59	0.46	Vapor Phase
Coconut	1350	185	63	0.49	Vapor Phase
Subbituminous Coal	1050	230	67	0.48	Vapor Phase
Wood	1230	470	76	0.57	Vapor/Liquid Phase

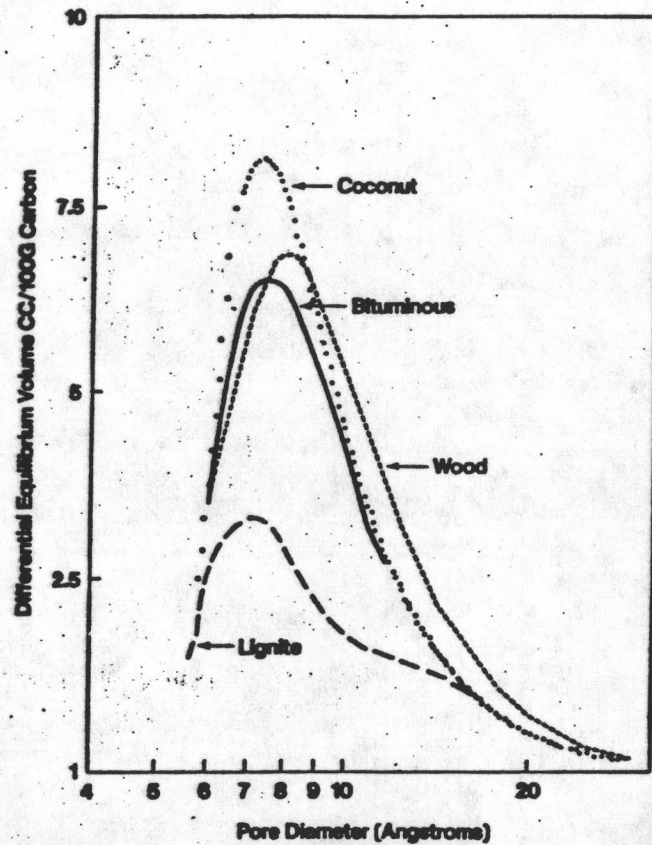


Figure 2.2 Pore size distributions of activated carbon using butane.(7)

It is to be noted that there exist molecular sieve carbons which have pore diameters of homogeneous sizes unlike carbons of naturally found raw materials which have a wide pore size distribution as shown above.

Adsorption data of liquid paraffins on activated carbon (4) from correlations based on the concept of the adsorption potential is shown in figure 2.3.

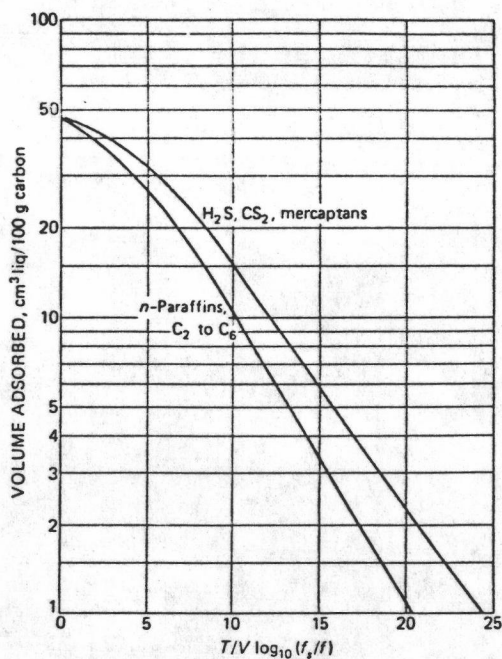


Figure 2.3 Generalized adsorption correlation for Pittsburgh Chemical Co. BPL carbon(1040 m<sup>2</sup>/g).(4)

## 2.2 Adsorption isotherms.

Adsorption can be classified as physical adsorption which involves only weak intermolecular forces, and as chemisorption which involves the formation of a chemical bond between the adsorbate molecules and the surface of the adsorbent. Almost all adsorption separation processes depend on physical adsorption rather than chemisorption. The forces involved in physical adsorption included both Van der Waals forces (dispersion-repulsion) and electrostatic interactions comprising polarization, dipole and quadrupole interactions.

The adsorption isotherm is an equilibrium relationship between the concentration of solute in the fluid phase and the amount of solute in the adsorbent particle. A general thermodynamic treatment of adsorption equilibrium was given by Gibbs(1978), who

expressed a thermodynamic equilibrium between the adsorbed phase and the bulk phase, and presented the following relationship

$$\Gamma = \frac{-1}{RT} \left( \frac{\partial \delta}{\partial \ln a_i} \right)_{T,P} \quad (2.1)$$

where  $\Gamma$  = excess number of moles of solute in solution  
 $\delta$  = surface tension of the solution  
 $a_i$  = activity of the solute  
 $T$  = temperature  
 $P$  = pressure  
 $R$  = the gas constant

For ideal solutions or dilute solutions, the activity can be replaced by the concentration and above equation can be written as :

$$\Gamma = \frac{C}{RT} \left( \frac{\partial \delta}{\partial C} \right)_{T,P} \quad (2.2)$$

The Gibbs equation is of fundamental importance for studying adsorption on any interface and determination of the amount adsorbed,  $\Gamma$ .  $\Gamma$  can be calculated graphically from plotting  $\delta$  against  $C$ . But direct experiments for the determination of the interfacial concentration is very difficult. By its means, we can directly determine the change of surface tension due to adsorption of a solute on solid adsorbent but the determination of adsorption by measuring the dependence of surface tension on concentration is not feasible because surface tension at a solid-liquid interface cannot be directly measured. However adsorption isotherms can be expressed in another manner. Kiselev (6) distinguishes three

definitions of adsorption from solutions : adsorption expressed as an excess of a given component of the solution in the volume which includes the adsorbed volume ; adsorption expressed as the total amount of a component of the solution in the adsorbed phase ; adsorption expressed as the total amount of solute contained in the pore volume.

2.2.1 Adsorption expressed as an excess of a given component of the solution in the volume which includes the adsorbed volume.

We usually start with a liquid mixture in contact with a porous adsorbent and we measure the concentration of the desired solution initially and after equilibrium is reached. The difference in concentration of the solute is expressed as the excess of the number of moles of solute in the solution volume including the adsorption phase (called adsorption volume) as compared with the number of moles in the same solution volume not including the interface . This is called the surface excess,  $n_1^s$ . So surface excess is defined as the difference between the amount adsorbed and the hypothetical amount adsorbed or

$$n_1^s = n'(x_1' - x_1) \quad (2.3)$$

An overall material balance for solute and solvent are shown as follows

$$n^t = (n_1 + n_2) + (n_1' + n_2') \quad (2.4)$$

The following development deals with binary mixtures on solids. The material balance for solute is equation 2.5.

$$n^t x_1^t = (n_1 + n_2) x_1 + n_1' \quad (2.5)$$

$x_1^t$  is defined by

$$x_1^t = \frac{n_1 + n_1'}{n_1 + n_2} \quad (2.6)$$

Substitution of  $(n_1 + n_2)$  from 2.4 and 2.5 gives

$$n^t x_1^t = n^t x_1 + n_1' - (n_1' + n_2') x_1 \quad (2.7)$$

For binary mixture equation 2.7 reduces to

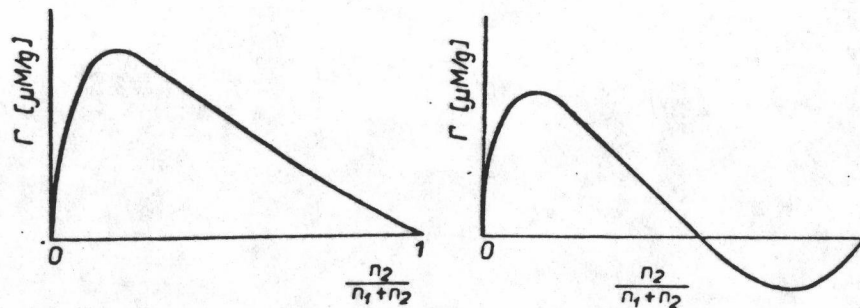
$$n_1^t = n_1' - (n_1' + n_2') x_1 \quad (2.8)$$

Combination of equation 2.7 and 2.8 gives the results.

$$n_1^t = n^0 (x_1^0 - x_1) \quad (2.9)$$

$x_1^0$  and  $x_1$  are the mole fraction of  $i^{\text{th}}$  solute before and after immersion of the adsorbent in the bulk liquid.  $n^0$  is total moles in liquid solution before immersion of the adsorbent. Thus the surface excess can be measured experimentally.





a) U-type isotherm.

b) S-type isotherm.

Figure 2.4 Adsorption isotherms expressed in terms of surface excesses,  $n_1^{\sigma}$ .

The adsorption isotherm which can be expressed as the dependence of  $n_1^{\sigma}$  on the equilibrium concentration  $C$  of the solute in the bulk phase usually follows the shapes shown in figure 2.4. In figure 2.4 a), with an increase in solute concentration the value of  $n_1^{\sigma}$  increases, however it is limited in the amount of solute that can be contained in the adsorption space, then the value of  $n_1^{\sigma}$  passes through a maximum and then decrease. In the case of figure 2.4 b) at higher concentrations of solute the competitive adsorption of the second component of the mixture (solvent) becomes predominant and leads to removal of the first component (or solute) from the adsorption space so that adsorption of solute becomes negative.

2.2.2 Adsorption expressed as the total amount of a component of the solution in the adsorbed phase.

The magnitude of adsorption can be expressed as the total amount of component in the adsorption volume when the volume of

the adsorbed phase is known by adding to the volume of  $n_1^m$  the amount of the same component present in the corresponding volume in the absence of adsorption. The adsorption isotherm as a function of the equilibrium concentration  $C$  of the solution is of a form that can often be described by the Freundlich equation ( $q = bC^p$  where  $p < 1$ ) or the Langmuir's equation ( $q = \frac{bC}{1+KC}$ ). Typical isotherm shapes of these expressions are shown in figure 2.5.

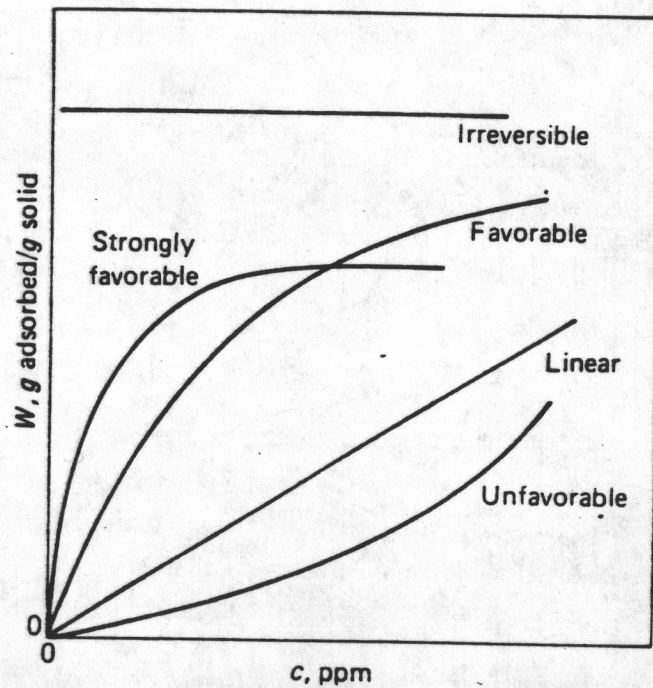


Figure 2.5 Typical adsorption isotherm expressed in term of total amount in adsorbed phase.

Linear isotherms pass through the origin and the amount of adsorbed phase is proportional to the concentration in the fluid. Isotherms that are convex upward are called favorable because solid adsorbents can contain large amounts of solute at low concentration solution. The Langmuir and Freundlich isotherms are of the favorable types. And the Freundlich equation often gives a better

fit for liquid phase adsorption data. An adsorption isotherm that is concave upward is called unfavorable because it leads to long mass transfer zones in the bed.

2.2.3 Adsorption expressed as the total amount of solute contained in the pore volume .

This expression is obtained in the same manner as the above when we take the total volume of the pores of the adsorbent instead of the adsorbed phase.

In figure 2.6 the same adsorption isotherm is plotted for all three expressions of adsorption.

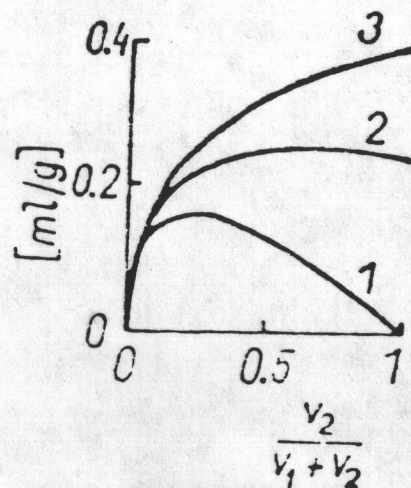


Figure 2.6 The adsorption isotherms as difference expressions.

In liquid phase adsorption concentration is often expressed in terms of mass unit and the concentration in the adsorbed phase is given as mass per unit mass of adsorbent.

### 2.3 Adsorption kinetics of a single solute (10).

In adsorption on an adsorbent such as an activated carbon, it is assumed that the rate of deposition onto the surface is larger than the rate of diffusion from the surface, which means that there is adsorption equilibrium at every point on the surface of the carbon. Mass transfer from the solution to the internal surface of the adsorbent can be divided into two steps.

1. Diffusion of the dissolved molecules through the boundary layer of the surrounding liquid to the surface of the adsorbent (film diffusion).

2. Diffusion from the outer surface into the inside of the particle (intraparticle diffusion).

#### Basic equations

For design of fixed-bed adsorbers, breakthrough curves (or concentration-time curves of the effluent stream) have to be determined beforehand. Basic equations for breakthrough curves involve equilibrium isotherm, mass transfer coefficients in the fluid film surrounding the adsorbent particle, intraparticle diffusion coefficients and axial dispersion in the fixed bed. The mechanisms of liquid adsorption in fixed beds may be described as follows.

- a. Transport of the solute in the bed to the vicinity of the adsorbent particles.

- b. Fluid phase mass transfer around an adsorbent particle

(external diffusion) to the particle external surface.

c. Diffusion within the porous network within the particle (intraparticle diffusion).

The basic assumptions used in this study are as follows :

1. The adsorbent particles are spherical.
2. The pore structure inside the particle is uniform.
3. The intraparticle diffusion coefficient is constant.
4. The superficial velocity is constant along the column length.

With these assumptions the solute concentration  $C(z,t)$  is determined as follows ( derivation of the following equations are shown in appendix C).

The driving force for surface diffusion is the gradient of the concentration of the adsorbate on the pore walls. The diffusion flux can be written as follows.

$$N_s = -D_s \rho_p \left( \frac{\partial q}{\partial r} \right) \quad (2.10)$$

where  $\rho_p$  = particle density

$D_s$  = surface diffusion coefficient

$N_s$  = diffusion flux

For microporous adsorbent particle mass transfer may be described by a diffusion equation, written in spherical coordinates:

$$\frac{\partial q}{\partial r} = \frac{1}{r} \frac{\partial}{\partial r} (r^2 D_e \frac{\partial q}{\partial r}) \quad (2.11)$$

If the diffusivity is constant this equation simplifies to

$$\frac{\partial q}{\partial t} = D_e \left( \frac{\partial^2 q}{\partial r^2} + 2 \frac{\partial q}{\partial r} \right) \quad (2.12)$$

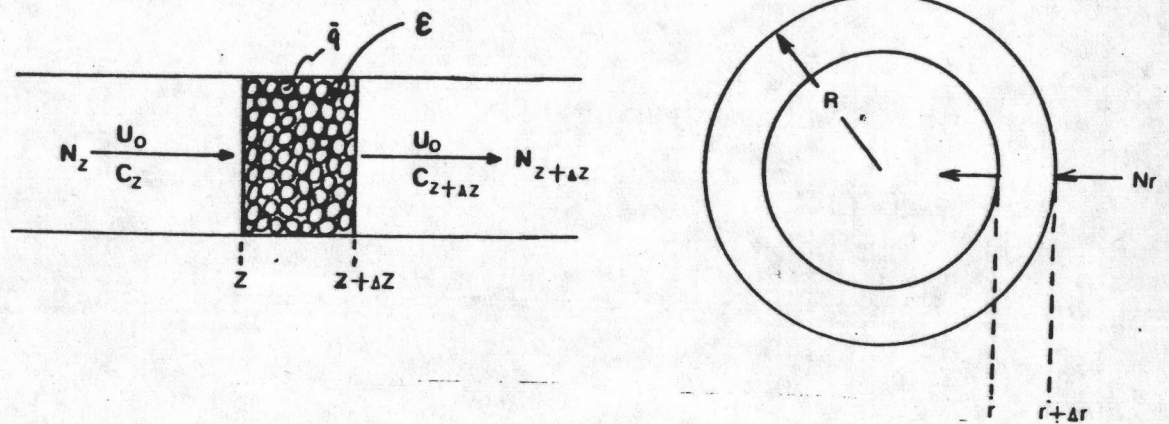


Figure 2.7 Component balance in liquid phase in column and in particle

The equations for mass transfer for fixed-bed adsorption obtained from a material balance in the bed as shown in figure 2.7. The adsorbent particles are assumed to be spherical with a radius  $R$ , and the pore structure inside the particle is assumed uniform. The superficial velocity and diffusion rate are assumed constant. The following equation is then obtained.

$$-D_L \frac{\partial^2 \bar{C}}{\partial z^2} + \epsilon \frac{\partial \bar{C}}{\partial t} + (1-\epsilon) \rho_s \frac{\partial \bar{q}}{\partial t} + U_0 \frac{\partial \bar{C}}{\partial z} = 0 \quad (2.13)$$

where  $\epsilon$  = the void fraction of the bed

$D_L$  = Axial dispersion coefficient ( $\text{cm}^2/\text{min}$ )

$\rho_s$  = adsorbent density in bed ( $\text{g}/\text{cm}^3$ )

$U_0$  = superficial velocity (cm/min)

The transfer process is approximated using an overall volumetric coefficient and overall driving force.

$$\rho_s (1-\epsilon) \frac{\partial q}{\partial t} = K_a (C - C^*) \quad (2.14)$$

the external diffusion boundary conditions is given as

$$D_s \left. \frac{\partial q}{\partial r} \right|_{r=R} = k_f (C - C_s) \quad (2.15)$$

the boundary and initial condition for the equation are as follow:

$$\bar{C} = 0 \quad \text{for } t = 0 \quad z \geq 0 \quad (2.16)$$

$$\bar{q} = 0 \quad \text{for } t = 0 \quad z \geq 0 \quad (2.17)$$

$$\bar{C} = C_0 \quad \text{for } t \geq 0 \quad z = 0 \quad (2.18)$$

The average solid phase concentration  $\bar{q}$  is calculated by the following equation.

$$\bar{q} = \frac{3}{R^3} \int_0^R q r^2 dr \quad (2.19)$$

The isotherm which relates  $C$  to  $q$  is assumed to be expressed by the following Freundlich equation.

$$\bar{q} = x \bar{C}^B \quad (2.20)$$

The basic equations were solved numerically using a Crank-Nicolson implicit method and an explicit method for the intraparticle and bed equations (as shown in appendix E). The

external resistance at the external surface of the adsorbent may be easily calculated by using known correlation for the mass transfer coefficients in fixed beds (4). The intraparticle diffusion coefficients in liquid phase adsorption with nonlinear isotherms can be determined from the data presented by K. Hashimoto and K. Miura (3).

In fixed-bed adsorption, the concentration in the fluid phase and solid phase change with time and position in the bed. Concentration profiles are shown in figure 2.8. At first, the mass transfer zone takes place near the inlet of the bed, if the adsorbent contains no adsorbate initially, the concentration in the liquid will drop exponentially with distance essentially to zero before the end of the column.

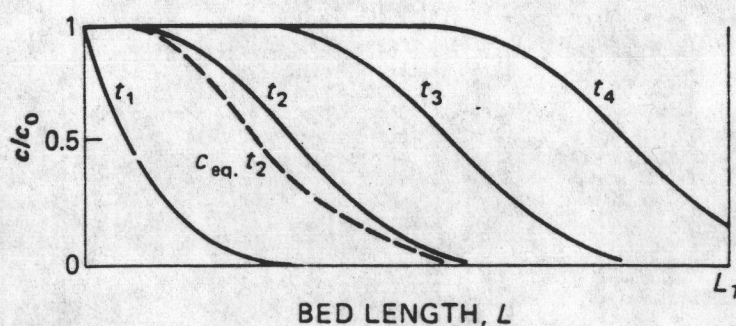


Figure 2.8 The concentration profiles in the liquid phase of the adsorption column.

The region where most of the change in concentration



occurs is called the mass transfer zone. The breakthrough curve is the curve of concentration at the end of column as a function of time as shown in figure 2.9.

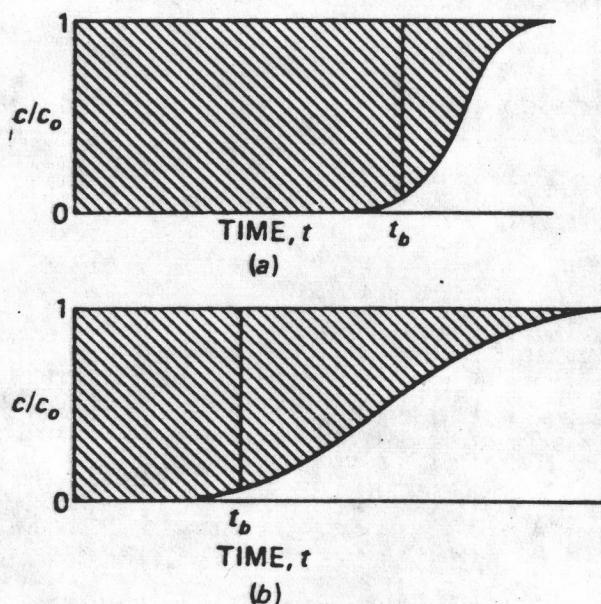


Figure 2.9 The breakthrough curves

A relative concentration of 0.05 or 0.10 is called the the break point. From analysis of the breakthrough curve we can see the mass transfer zone, if the curve is steep it means that the mass-transfer zone is narrow relative to the bed length as shown in figure 2.9(a) and most of the capacity of the solid will be utilized at the break point. If the breakthrough curve is greatly extended as shown in figure 2.9(b) the mass transfer zone will be compared to bed length. A narrow mass transfer zone is preferable for high efficiency and to reduce energy costs in regeneration. For the ideal case of no mass transfer zone length and no axial dispersion, the mass transfer zone should be very narrow and the

breakthrough curve would be a vertical line from 0 to 1 when all the solid adsorbent is saturated. The width of the mass transfer zone depends on the mass transfer rate, the flow rate and the shape of the equilibrium curve.