

Chapter 2

Principles of Adsorption

A phenomenon benefited from the utilization of solid surfaces for selective removal of a certain component from a mixture is known as adsorption [18]. The mixture can be either gas or liquid and the component adsorbed is called an adsorbate, while the solid is termed as an adsorbent. The adsorbate molecules are held at the fluid-solid interface by the intermolecular forces, of which can be categorized as physical or chemical forces. The physical forces include at least van der Waals force which is relatively weak. The forces may include electrostatic forces when both adsorbent and adsorbate have polar properties. While, the chemical forces relate to electron transfer, which is usually stronger than the former [19]. However, it is difficult to distinguish the difference between physical adsorption and chemisorption, related to the physical forces and the electron transfer or chemical bonds, respectively. Therefore, only physical adsorption has been considered for separation processes [13].

2.1 Characteristics of Adsorbents

With the direct relation with the surface area of solid, the adsorbent has to be a porous material to provide a large specific surface area. Besides the specific surface area, pore size distribution, relating to accessibility of certain adsorbate molecules to the surface, becomes important as well [20].

Specific surface area of an adsorbent is usually determined from the amount of equilibrium adsorption of nitrogen gas at its normal boiling point (77 K) under vacuum condition. It is necessary to specify an additional assumption of either monolayer adsorption or multilayer adsorption. With the monolayer assumption, all nitrogen molecules are adsorbed on the adsorbent surface leading to saturation condition under which the specific surface area is determined from the maximum amount adsorbed and the molecular size. While, for the multilayer assumption, the monolayer coverage has to be determined from the BET equation, then the surface area is obtained in the same manner as the monolayer adsorption [19, 13].

With nitrogen adsorption as mentioned above, the adsorbed amount of nitrogen can usually be divided into 2 portions ; i.e. adsorption on the surface and capillary condensation in pores. For the monolayer adsorption, only adsorption on the surface is employed to determine the thickness of adsorption film on the surface with Halsey' s relation :

$$t = 4.3 \left(\frac{5}{\ln P_s/P} \right)^{1/3} \quad (2.1)$$

where t is the thickness of adsorbed layer on the surface, P is the partial pressure of nitrogen. P_s is the saturation pressure, which is the atmospheric pressure in this case [20].

While, for multilayer adsorption, the capillary condensation in pores has to be considered additionally for determination of pore radius with Kelvin equation.

$$\frac{P}{P_s} = \exp \left(\frac{-2\sigma V_m \cos\theta}{r_p RT} \right) \quad (2.2)$$

where σ is surface tension, r_p is pore radius of the adsorbent, V_m is molar volume of adsorbate, R is gas constant and T is absolute temperature [13].

However, the range of pore sizes is usually below 1,000 Å. In order to determine the distribution of large pore sizes, mercury penetration method is employed instead. Similar to the capillary condensation in pores, both pore volumes and pore radius can be determined from Kelvin equation as an increase in pressure.

2.2 Adsorption Isotherms

In gas separation processes with adsorption, adsorption equilibrium for each component in a gaseous mixture on a selected adsorbent becomes an important criteria for selection of a suitable adsorbent, in the same manner as distillation, when the rate of adsorption of each component is relatively fast. For gas adsorption,

the equilibrium for each component can be expressed as function of concentration of the corresponding component at a given temperature. Thus, the expression is named as, adsorption isotherm, which may be either linear function or nonlinear function [13].

2.2.1 Linear Adsorption Isotherm

When the amount adsorbed on the surface is sufficiently small, the molecules adsorbed hardly interact one another nor the adsorbing molecules. In addition, plenty surface is available for adsorption. Thus, the amount adsorbed depends merely on the concentration of the adsorbate [13], as follow :

$$q = K_1 c \quad (2.3)$$

Equation 2.3 is analogous Henry's law, hence the equilibrium constant, K_1 , is, sometimes, called adsorption Henry's constant. This isotherm is valid for dilute solution only.

2.2.2 Non-Linear Adsorption Isotherm

Several types of non-linearly experimental adsorption isotherms have been reported [13, 21]. However, only Langmuir isotherms and Freundlich isotherms have been employed commonly.

Langmuir Isotherms

With a monolayer assumption [13, 19], the rate of adsorption depends on the concentration of the adsorbate and free surface of the adsorbent. While the rate of desorption is a function of occupied surface (or the amount adsorbed) only. At equilibrium, the rate of adsorption must equal the rate of desorption. Therefore, the isotherm can be expressed as

$$\frac{q}{q_s} = \frac{K_L c}{1 + K_L c} \quad (2.4)$$

where the Langmuir constant, K_L , is a ratio of the adsorption rate constant to the desorption rate constant, c is the concentration of the adsorbate and q_s is the maximum amount adsorbed. Consequently, the amount adsorbed tends to saturation as an increase in the concentration of the adsorbate.

Freudlich Isotherms

Alternatively, a large number of experimental results of equilibrium adsorption can be fitted with a suitable polynomial function of degree below unity [13], as follow :

$$q = K_F c^{\frac{1}{n}} \quad (2.5)$$

where n and K_F are a constant of an adsorption system and the value of n is greater than unity. This expression has been known as a Freudlich isotherm.

Although the expressions provide adsorption equilibrium curves in similar to that of Langmuir isotherms, there is no limitation of adsorption, namely no saturation state.

2.3 Kinetics of Adsorption

To achieve high specific surface area, adsorbents ought to be porous. However, each pore may not have uniform pore diameter, and is usually not through the other side of the adsorbent. Therefore, the rate of adsorption relates to number of diffusion steps from the bulk gas to the gas-adsorbed interface, or adsorption surface. The simplest adsorption mechanism can be divided into 2 consecutive steps, see Figure 2.1.

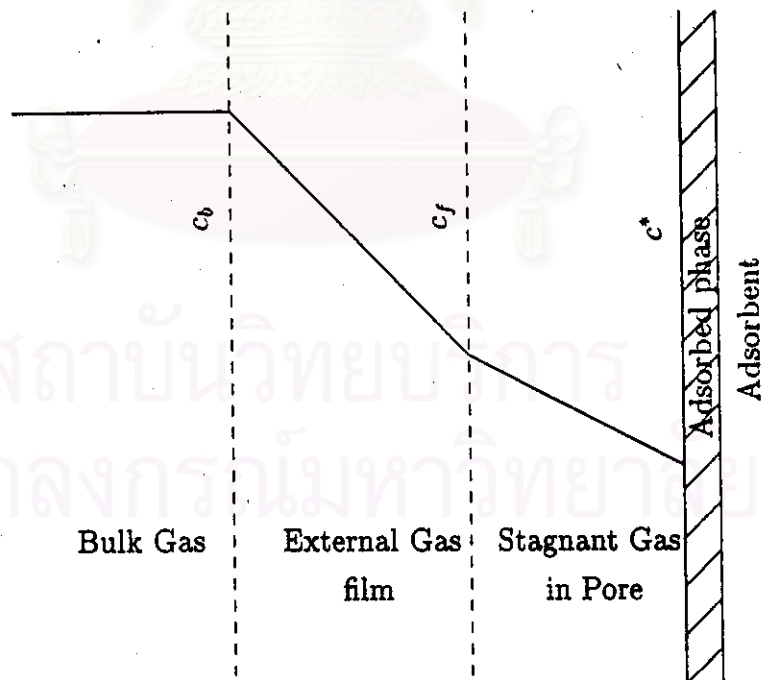


Figure 2.1: Simplified adsorption mechanism

1. External Film Diffusion : an adsorbate molecule diffuse across the external gas film to the external surface of the adsorbent, and
2. Pore Diffusion : an adsorbate molecule diffuse through stagnant gas in a pore to reach the gas-adsorbed interface.

External film diffusion

Based on the film theory, mass transfer occurs only across the thickness of the external film, as illustrated in Figure 2.1. It can be assumed that diffusion of adsorbate molecules across the film obeys Fick's law of diffusion. Therefore, the rate of diffusion can be determined from diffusion flux of the adsorbate J :

$$J = -D_{AB} \frac{dc}{dx} = -D_{AB} \frac{P}{RT} \frac{dy}{dx} \quad (2.6)$$

where $\frac{dc}{dx}$, $\frac{dy}{dx}$ represent the concentration gradient of adsorbate across the film, x is the distance in the direction of flux and D_{AB} is the molecular diffusivity of component A into the atmosphere of component B. For binary gas mixtures at pressure below 10 atm, D_{AB} is inversely proportional to the pressure, increase with increasing temperature, and is almost independent of composition. The following equation for estimation of D_{AB} at low pressure has been developed from a combination of kinetic theory and corresponding-stages arguments [22]:

$$\frac{PD_{AB}}{(P_{cA}P_{cB})^{1/3}(T_{cA}T_{cB})} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2} = a \left(\frac{T}{\sqrt{T_{cA}T_{cB}}} \right)^b \quad (2.7)$$

where T_{ci} and P_{ci} represent critical temperature and pressure of component i , respectively [22].

Analysis of experimental data gave the following values of the constants a and b :

For nonpolar gas-pair:

$$a = 2.75 \times 10^{-4}, b = 1.82 \quad (2.8)$$

For H_2O with a nonpolar gas:

$$a = 3.64 \times 10^{-4}, b = 2.33 \quad (2.9)$$

For a range of pressure above 10 atm, the diffusivity becomes function of reduced pressure, P_r , and reduced temperature, T_r , of the mixture as shown in Figure 2.2 [22].

$$D_{AB} = f(p_r, T_r) \quad (2.10)$$

where

$$p_{r,mix} = \frac{p}{p_{c,mix}} ; p_{c,mix} = y_A p_{c,A} + y_B p_{c,B} \quad (2.11)$$

and

$$T_{r,mix} = \frac{T}{T_{c,mix}} ; T_{c,mix} = y_A T_{c,A} + y_B T_{c,B} \quad (2.12)$$

The ordinate of the plot $pD_{AB}/(pD_{AB})^0$, is the ratio of the pressure-diffusivity product at pressure p and temperature T to the pressure-diffusivity product at the same temperature but at low pressure.

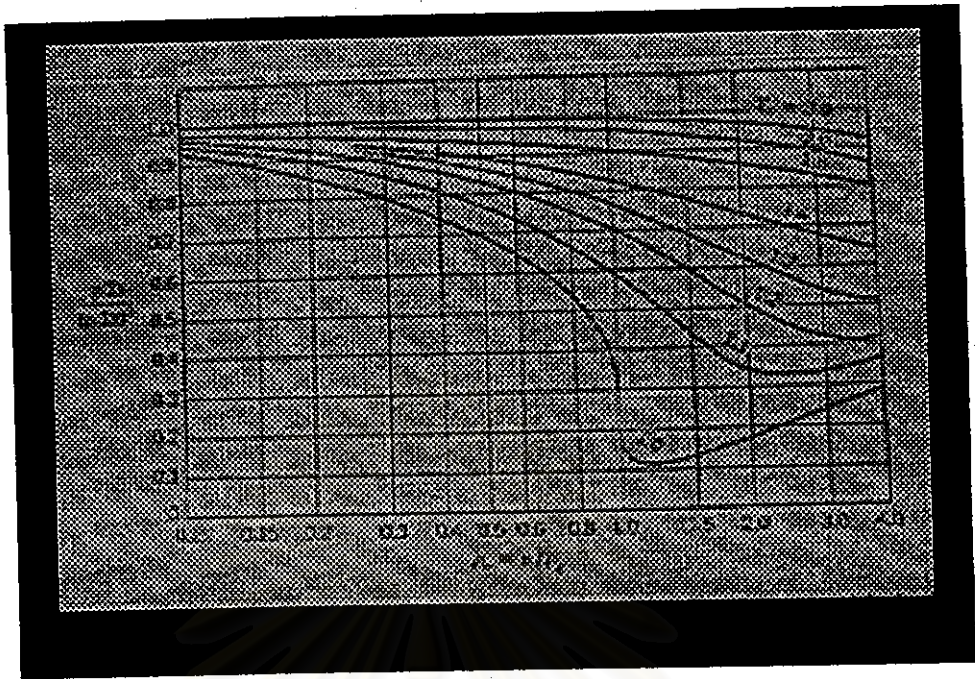


Figure 2.2: Generalized chart for diffusivities of dense gas

Alternatively, the diffusion flux may be expressed simply as

$$J_A = k_f(c_b - c_f) \quad (2.13)$$

While the film mass transfer coefficient, k_f , can be estimated from correlation of Sherwood number (Sh) as a function of Reynolds number (Re) and Schmidt number (Sc),

- For single particle [13]:

$$Sh = 2.0 + 0.6Sc^{1/3}Re^{0.6} \quad (2.14)$$

- For packed column [13]:

$$Sh = 2.0 + 1.1Sc^{1/3}Re^{0.6} ; 3 < Re < 10^4 \quad (2.15)$$

Pore Diffusion

Gas cannot flow through any pores of adsorbents, thus gas in those pores is considered as stagnant gas. Consequently, the rate of diffusion can be expressed, in the same manner as Fick's law of diffusion, as [13] :

$$J = -D_P \frac{dc}{dx} = -D_P \frac{P}{RT} \frac{dy}{dx} \quad (2.16)$$

where D_P is pore diffusivity. If a pore diameter is greater than the mean free path of the adsorbate, the pore diffusivity can be estimated from [13]

$$D_P = \frac{D_{AB}}{\tau} \quad (2.17)$$

where τ is the tortuosity factor. It is the ratio between the actual diffusion path length and the net distance in the direction of flux.

On the other hand, when the pore diameter becomes smaller than the mean free path of the adsorbate, the pore diffusivity, D_P , is equivalent to Knudsen diffusivity which can be estimated from [20]

$$D_P = 9700 r_p \sqrt{\frac{T}{M}} \quad (2.18)$$

where r_p is the pore radius, M is the molecular weight of diffusing gas.

Alternatively, the expression of the diffusion flux in pores can be simplified as

$$J = k_p(c_f - c^*) \quad (2.19)$$

However, the pore mass transfer coefficient is difficult to measure from adsorption experiments.

Driving forces in equation 2.13 and equation 2.19 can be combined and the overall diffusion flux of adsorption can be written as

$$J = k_o(c_b - c^*) \quad (2.20)$$

Equation 2.20 is known as "Linear driving force" for rate of adsorption. The overall mass transfer coefficient, k_o , relates to both film mass transfer coefficient and pore mass transfer coefficient, as written below

$$\frac{1}{k_o a_o} = \frac{1}{k_f a_f} + \frac{1}{k_p a_p} \quad (2.21)$$

2.4 Propagation in an Adsorber

With unsteady state operation, variation of concentration profiles of an adsorbate in an adsorber provides information for design of an adsorption system. The variation of the profiles depends upon axial dispersion, adsorption equilibrium or isotherms and rate of adsorption.

2.4.1 Axial Dispersion Effects

After regeneration, the concentration profile of an adsorbate is almost uniform throughout the adsorber at extremely low level. Thus, it is usually assumed to be zero profile or clean adsorbent. During adsorption operation, axial diffusion of the adsorbate occurs because of the difference of concentration in the axial direction at a certain axial position in the adsorber. Therefore, the profile disperses as it propagate along the adsorber, as illustrated in the Figure 2.3.

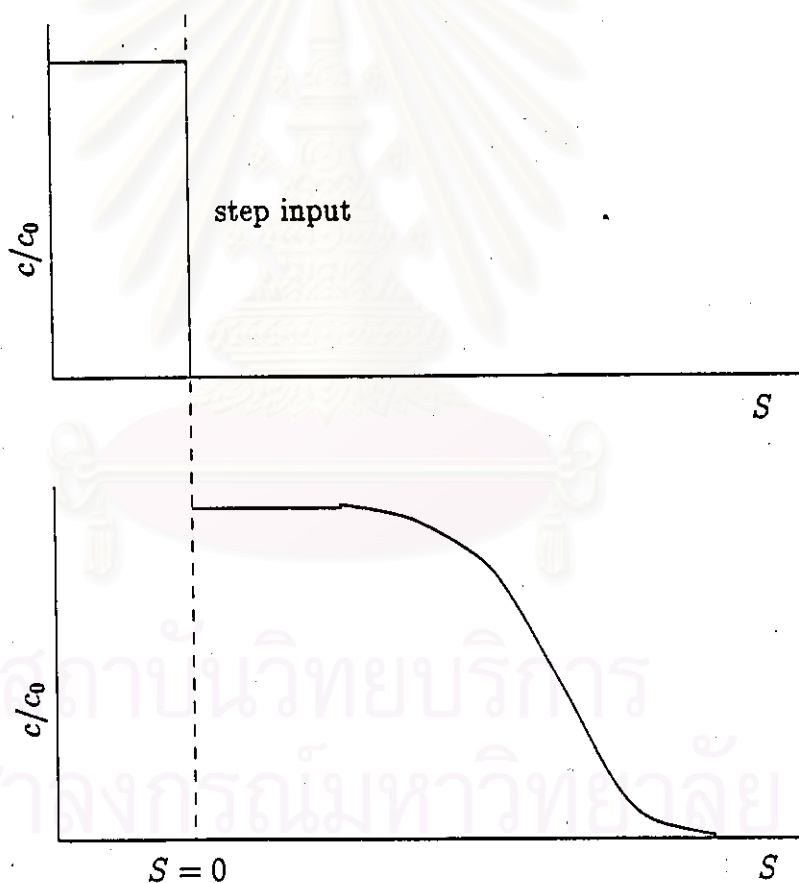


Figure 2.3: Axial dispersion effects

Since axial mass transfer consists of convection in the same direction of fluid/gas

velocity and axial diffusion. The relative importance between the axial mass convection and the axial mass diffusion is indicated by the Peclet number, Pe , i.e. the convection is important at high Pe , otherwise the axial diffusion becomes major role of mass transfer.

2.4.2 Adsorption Isotherm Effects

For high rate of adsorption of non-dilute gaseous mixture, the propagation rate of the adsorbate alters as flowing through a bed of adsorbents because of mass transfer from the gas phase to the adsorbed phase. Variations of the propagation rate depends upon an adsorption isotherm of an adsorbate. In other words, variation of amount adsorbed of an adsorbate with respect to the concentration in gas phase affects the propagation rate of the adsorbate. The effects of adsorption isotherm of an adsorbate can be analysed qualitatively from a simplified equilibrium adsorption model. The adsorption process for a single adsorbate in an inert can be assumed that

1. isothermal process
2. no axial dispersion
3. concentrate solution
4. instantaneous local equilibrium

Thus, the equation of continuity for the adsorbate can be expressed as

$$\left(1 + \left(\frac{1-\epsilon}{\epsilon}\right) (1-y) \frac{dq_1}{dc_1}\right) \frac{\partial c_1}{\partial t} + v \frac{\partial c_1}{\partial z} = 0 \quad (2.22)$$

With the method of characteristic, the propagation velocity, w , of the adsorbate can be yielded

$$w = \left(\frac{\partial z}{\partial t}\right)_{c_1} = -\frac{\left(\frac{\partial c_1}{\partial t}\right)_z}{\left(\frac{\partial c_1}{\partial z}\right)_t} = \frac{v_i}{1 + \left(\frac{1-\epsilon}{\epsilon}\right) (1-y) \left(\frac{\partial q_1}{\partial c_1}\right)} \quad (2.23)$$

Thus, the adsorbate always moves behind and inert throughout the bed of adsorbents. For a linear isotherm, the propagation velocity does not alter with concentrations since the slope of the isotherm is constant at any concentrations. On the contrary, the propagation velocity alters with concentrations for non-linear isotherm. Alteration of the slope of a non-linear isotherm can be divided into 2 cases, as illustrated in Figure 2.4. One is that the slope decrease with an increase in concentration, namely a favorable isotherm. The other is an increase in the slope as increasing concentration, called an unfavorable isotherm. For the former, the propagation velocity increases as an increase in concentrations, and, consequently, a high concentration region tends toward a low concentration region which is the lead yielding a compressive concentration profile. While, for the latter, the propagation velocity of a high concentration region becomes less than the velocity of a low one, resulting a dispersive concentration profile.

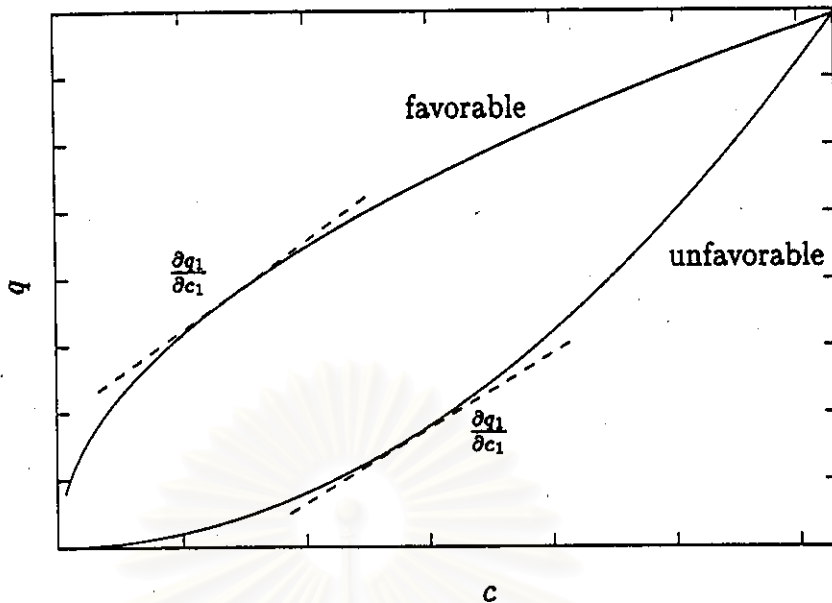


Figure 2.4: Non-linear adsorption isotherms

2.4.3 Adsorption Rate Effects

When the rate of adsorption is limited with either the external film diffusion or the (stagnant) pore diffusion, the concentration in the gas phase within the packed bed becomes higher than the equilibrium concentration (at the same position). It requires a certain period to achieve the adsorption equilibrium. Therefore, the leading region of the concentration profile hardly reaches the equilibrium as propagating through the bed. The concentration profile tends to spread out, as illustrated in Figure 2.5. With low rate of adsorption, the profile tends to dispers more than that of the high rate of adsorption. As the lead of the profile just breakthroughs the bed, a certain amount of adsorbent in the bed is not utilized for adsorption. The information of the unused amount of adsorbents is essential

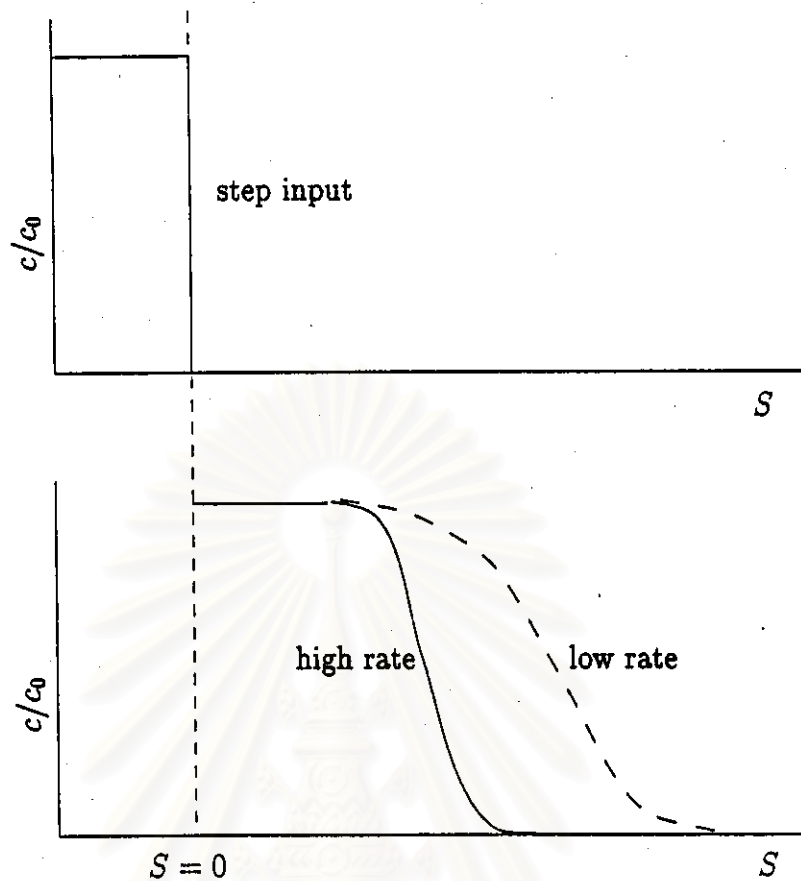


Figure 2.5: Adsorption rate effects

for determination of the length of the packed bed and/or the service period of an adsorber.

In practice, all effects occurs simultaneously. Consequently, the concentration profile alters as propagating through the bed of adsorbents. Initially, the profile tends to disperse longitudinally according to effects of the axial dispersion or that of the finite rate of adsorption or both. After a certain distance of propagation, the profile may propagate through the bed further without alteration of the shape of the profile, namely constant pattern [13]. Under the circumstance, the mass transfer zone or the length of unused bed can be determined conveniently.

2.5 Breakthrough Curve

In practice, it is difficult to obtain the concentration profile within the adsorber at a given time. While the variation of the concentration at the column exit, namely breakthrough concentration, can be measured conveniently. The breakthrough curve is equivalent to the concentration profile as illustrated in Figure 2.6. Therefore, the breakthrough concentration of column with various length provide approximated profile at the exit of each column.

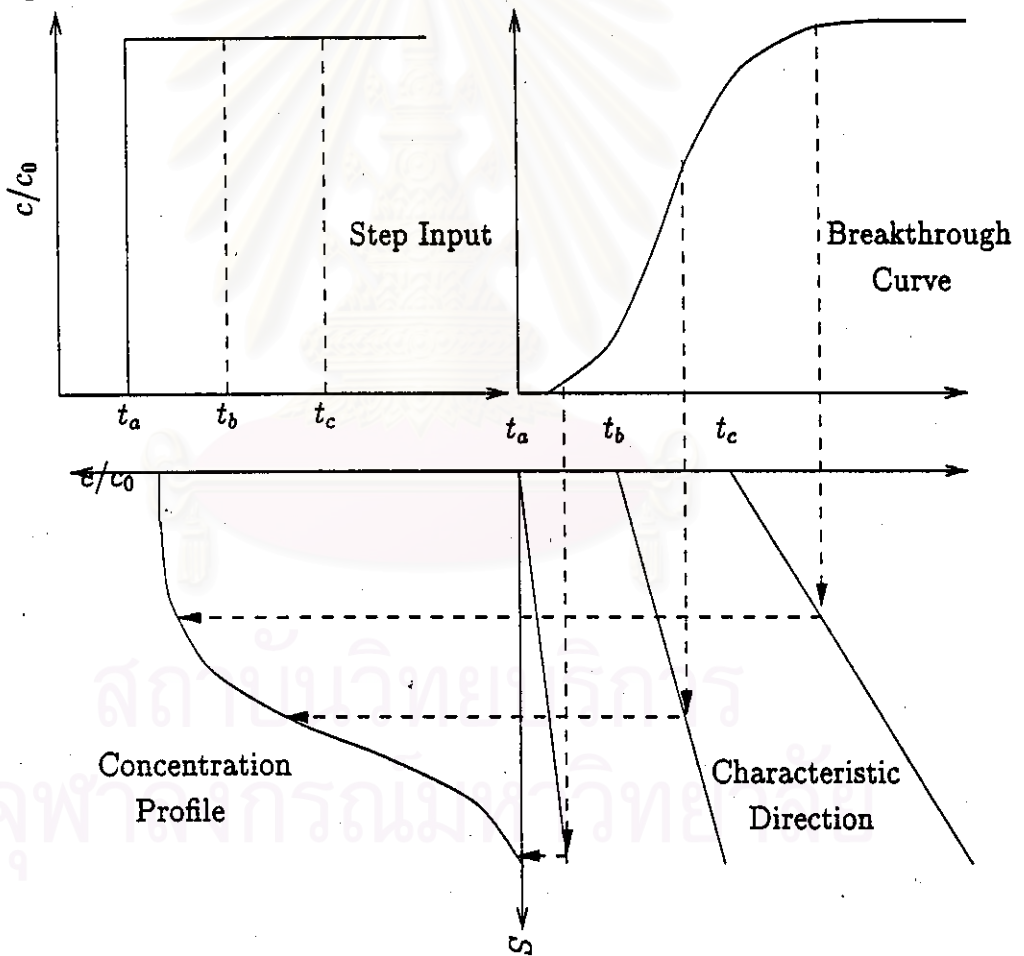


Figure 2.6: Relation between the concentration profiles and breakthrough curve.