

CHAPTER II

ADSORPTION THEORY

2.1 INTRODUCTION

Ever since the observation of C. W. Scheele in 1773 and Abbé F. Fontana in 1777 on the adsorption of gases by charcoal, there have been attempts to evolve a theoretical basis for the phenomena. Were adsorption to confine only to gases, the matter could be greatly simplified. In 1785, Lowitz discovered that charcoal could effectively remove coloring matters which were organic compounds. While a far greater amount of the theoretical work has been done on the adsorption of gases, the greatest volume and weight of industrial adsorbents are employed in the treatment of solutions [Mantell, 1945]. However, systems of gas adsorption are much more simpler than that of adsorption in solutions.

Jasra and Bhat, 1988 said that nearly 40% of the cost of a chemical process lies in separation processes. Consequently, development in separation technology has been almost parallel to the growth of chemical industry. Separation may be defined as a process that transforms a mixture of substances into two or more products that differs from one another in composition. The process is difficult to achieve because

it is the opposite of mixing which is a process favored by the second law of thermodynamics [Yang, 1987].

Understanding of engineering design methods of adsorption systems is an important aspect of process engineering design not only in the chemical industry but also in the field of environmental pollution control and energy utilization. Moreover, adsorption is coming to be regarded as a practical separation method for purification or bulk separation in newly developed material production processes, for example, high-technology materials and biochemical and biomedical products which can decompose to other compounds in distillation column under high temperature [Suzuki, 1990].

Adsorption is a phenomenon in which molecules in fluid phase (referred as the adsorbate) adhere to the surface of solid (referred as the adsorbent). When adsorbed, the molecules lose much of their molecular mobility, releasing heat is often in the same order of magnitude of the corresponding heat of condensation. Desorption is a reverse phenomenon, then heat must be supplied to the adsorbents. This phenomenon, usually called regeneration, is quite important in the overall process. Firstly, desorption allows recovery of adsorbates in those separations where they are valuable; and secondly, it permits reuse of the adsorbent for further cycles. In a few cases, desorption is not practical, and the adsorbate must be removed by thermal destruction or another chemical reaction, or the adsorption is simply discarded [Keller II, Anderson, and Yon, 1987].

2.2 ADSORBENTS

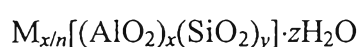
Adsorbents have been developed for a wide range of separations. Commercial materials are provided usually as pellets, granules, or beads; although powders are used occasionally. The selection of a proper adsorbent for a given separation is a complex problem. The following factors are important for adsorbent selection [Yang, 1987]:

1. Capacity of the adsorbent, within a range of operation pressure and temperature
2. A method for adsorbent regeneration such as increasing temperature or decreasing pressure
3. Separation factor

Commercial adsorbents are divided into four major classes: molecular-sieve zeolites, activated alumina, silica gel, and activated carbons. Since adsorption is a surface-related phenomenon, the useful adsorbents are usually characterized by specific surface area. The typical range of area covers from about 100 to over 3000 m²/g. However, the most common commercially useful materials exhibit surface areas ranging from about 300 to 1200 m²/g.

2.2.1 Molecular-Sieve Zeolites

Molecular-sieve zeolites are crystalline aluminosilicates of alkaline, alkaline earth or mixed alkaline and alkaline earth elements; such as sodium, potassium, magnesium, and calcium; represented by the stoichiometry [Yang, 1987]:



where x , y are integers with y/x equals to or greater than unity, n is the valence of cation M , and z is the number of water molecules in each unit cell. The cations are necessary to balance the electrical charge of aluminium atoms. The skeleton is a regular structure of cages, which is usually interconnected by six windows in each cage. The size of the window apertures which can be controlled by fixing the type and number of cations ranges from 3\AA to 10\AA . Besides surface characteristics, the sorption may occur with great selectivity because of the size of the aperture, hence the name molecular sieve. The primary structural units of zeolites are the tetrahedra of silicon SiO_4 and aluminium AlO_4 . These units are assembled into secondary polyhedral building units such as cubes, hexagonal prisms, octahedra, and truncated octahedra. The adjacent silicon-aluminium atoms and silicon-silicon atoms located at the corners of the polyhedra are jointed by a shared oxygen. The final zeolite structure consists of assemblages of the secondary units in a regular three-dimensional crystalline framework. The ratio of silicon atoms to aluminium atoms (Si/Al) must be greater than unity.

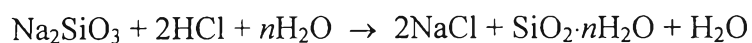
Zeolites were first recognized as a new type of mineral in 1756. Studies of the gas-adsorption properties of dehydrated natural zeolite crystals more than 60 years ago led to the discovery of their molecular-sieve behavior. As microporous solids with uniform pore sizes that range from 0.3 to 0.8 nm, these materials can selectively adsorb or reject molecules based on their molecular shape and size. This effect, with commercial overtones leading to novel processes for separation of materials, inspired attempts to duplicate the natural materials by synthesis. Many new crystalline zeolites have been synthesized. More than 150 synthetic zeolite types and 40 zeolite minerals are known. The most important molecular sieve zeolite adsorbents are the synthetic

type A, type Y, synthetic mordenite, and their ion-exchanged variations, and the mineral zeolites, chabacite, and mordenite [Keller II, Anderson, and Yon, 1987].

2.2.2 Silica Gel

Silica gel adsorbents are composed of a rigid three-dimensional network of spherical particles of amorphous colloidal silica (SiO_2). They were reported as early as 1640 and commercial production was begun around 1919. The surface area is generated by the very fine size of colloidal particles. They exhibit surface areas from as little as $100 \text{ m}^2/\text{g}$ for the “aerogels” to over $800 \text{ m}^2/\text{g}$. The product is provided both in granular and spherical forms. The silica gel surface has an affinity for water and organics, although water is preferred. The surface of the silica gel can be in a fully hydroxylated form (Si-O-H) or a dehydrated siloxane form (Si-O-Si). The former is the result of drying the gel or precipitate below 150°C , and the surface is readily wetted with water. The dehydration of the fully hydroxylated form by heating from 300 to 1000°C results in the siloxane-type surface.

The most common preparation is by mixing a sodium silicate solution with a mineral acid such as hydrochloric acid. The reaction produces a concentrated dispersion of finely divided particles of hydrated SiO_2 , known as silica hydrosol or silicic acid [Ruthven, 1984; Yang, 1987].



Various silica gels with a wide range of characteristics, such as surface area and pore-size distribution, can be made by varying the silica concentration,

temperature, and pH of solution. Silica gels is a desirable adsorbent for drying fluid stream, containing small amount of moisture, because of the hydrophilic surface.

2.2.3 Activated Alumina

Activated alumina adsorbents are amorphous or “transition aluminas” whose chemical composition is Al_2O_3 . Their surface area is generated by the removal of water constitution from hydrated aluminas. They possess reasonably large surface areas. The preferred materials have been purified during processing to high Al_2O_3 contents (about 99%), but activated bauxite has also been employed. The product is commonly as granules, and shaped forms are also available. An important industrial application for activated alumina is drying of gases and liquids because of its hydrophilic characteristics and large surface area. They can be used to produce dried gases to less than 1 ppm moisture content [Keller II, Anderson, and Yon, 1987].

Commercial activated alumina is produced exclusively by thermal dehydration of aluminium trihydrate, $\text{Al}(\text{OH})_3$ or gibbsite. The trihydrate, in the form of gibbsite, is calcined in air to about 400°C to form crystallines of γ -alumina and η -alumina with a minor amount of boehmite, and has a surface area of approximately $250 \text{ m}^2/\text{g}$. Alternatively, the trihydrate is heated very rapidly at $400\text{-}800^\circ\text{C}$ to form an amorphous alumina with a higher surface area, $300\text{-}350 \text{ m}^2/\text{g}$. A highly impure form of activated alumina is made by thermal activation of bauxite, which contains alumina in the form of gibbsite [Yang, 1987].

2.2.4 Carbon Adsorbents

A carbon adsorbent is a microcrystalline, nongraphitic form of carbon that has been processed to develop internal porosity. This porosity yields the surface area that provides ability to adsorb gases and vapors from gases, and to adsorb dissolved or dispersed substances from liquids. The range of surface area is vast, from 300 to 2500 m²/g, although commercial adsorbents are usually limited to surface areas of less than 1200 m²/g [Keller II, Anderson, and Yon, 1987].

Carbon adsorbents can be produced from a tremendous variety of carbonaceous starting materials, such as coconut shells, peach stones, saw dust, wood char, lignin, petroleum coke, coal, rice husk, or sugarcane bagasse etc. [Girgis, Khalil, and Tawfik, 1994]. Preparation of carbon adsorbents from carbonaceous materials can be divided into 2 steps; i.e. carbonization step and activation step [Yehaskel, 1978]. For the latter, carbonized materials must be reacted with a selected reagent in 2 different approaches. One is a reaction with a mild oxidizing gas, such as steam, at high temperature above 800°C. While the other is a reaction with an acidic solution, e.g. zinc chloride solution, at relatively low temperature usually below 500°C. In practice, the carbonization step and the activation step with an acidic solution are carried out in a single step because of the same range of operating temperature [Chirasak, Deacha, and Vichitra, 1998].

Cokes, chars, and carbon adsorbents are frequently termed amorphous carbon. X-rays studies have shown that many so-called amorphous substances have crystalline characteristics, even though they may not show certain features, such as crystal angles and faces, usually associated with the crystalline state. An amorphous-

looking powder may be composed of crystals of submicroscopic dimensions, so-called crystallites [Hassler, 1974]. The X-rays diffraction pattern has shown that amorphous carbon consists of flat plates in which the carbon atoms are arranged in hexagonal lattice, as illustrated in Figure 2.1. The structure of carbon adsorbents consists of partially elementary microcrystallites of graphite, but these microcrystallites are stacked upon another layer of graphite in random orientation and the space between the adjacent layer provides micropores. The actual distribution of activated carbon may be classified by pore size as illustrated in Table 2.1 [Ruthven, 1984].

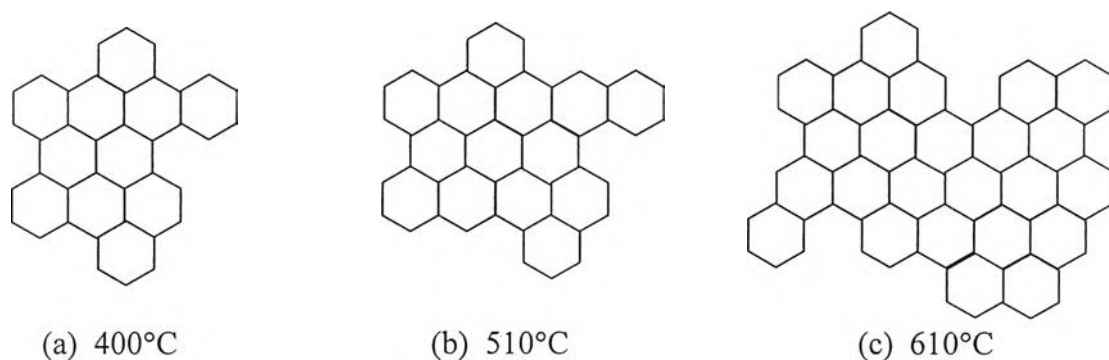


Figure 2.1 Arrangements of carbon atoms in a single-layer plane of crystallites formed at different temperature (400°C, 510°C, and 610°C)

Table 2.1 Pore sizes in typical activated carbon[†]

	Micropores	Mesopores or Transitional pores	Macropores
Diameter (Å)	< 20	20 – 500	> 500
Pore volume (cm ³ /g)	0.15 – 0.5	0.02 – 0.1	0.2 – 0.5
Surface area (m ² /g)	100 – 1000	10 – 100	0.5 – 2

[†](Particle density 0.6 – 0.9 g/cm³; porosity 0.4 – 0.6)

The size of crystallites is influenced by the temperature of carbonization and, to some extent, by the composition and structure of raw material. In chars

prepared from such substances as cellulose, the *c* dimension (height of the crystal) shows little change until a temperature of 1,300°C is reached, whereas the *a* dimension (diameter of each layer) shows a continuous growth up to 700°C. This fact is of interest because many properties such as electrical conductivity and the ease of subsequent activation shows a change at this temperature.

The crystallites may be formed through several mechanisms. During pyrolysis, the original organic substances may be split into fragments which regroup to form the thermo-stable aromatic structure existing in the hexagonal. It is also possible that suitable nuclei initiate a transformation in which the hexagonal lattice grows gradually at the expense of the original substance. The transformation is seldom completed and residual hydrocarbon chain and rings are remained.

As these residual hydrocarbons cannot be extracted with solvents or removed by degassing, they are presumed to be attached by chemical bonds to the border atoms of the crystallites. A hypothetical structure is shown in Figure 2.2

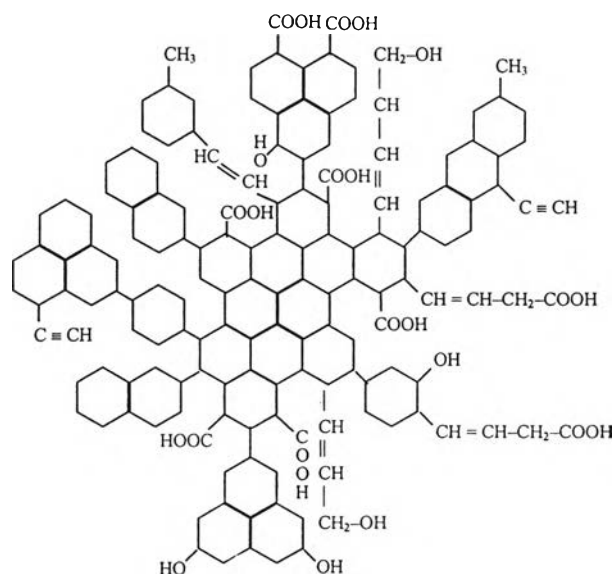


Figure 2.2 Theoretical structure of crystallites

Most carbon adsorbents contain some oxygen complexes which arise from either source materials or from chemical adsorption of air (oxidation) during the activation stage or during storage after activation. Surface oxides add a polar nature to carbon adsorbents, e.g. hydrophilicity, acidity, and negative ζ -potential [Suzuki, 1990].

The surface of carbon adsorbents might be divided into two parts. The major part, mostly of the surface, is nonpolar. Consequently, the carbon adsorbents tend to be the hydrophobic and organophilic adsorbents. So they can adsorb the organic and nonpolar strongly but adsorb polar compounds weakly. The other is slight polarity arising from surface oxidation under which some oxygen complexes are added on the surface leading to an increasing in polarity as mentioned above.

2.3 ADSORPTION EQUILIBRIUM

In practical operations, the maximum capacity of adsorbent cannot be fully utilized due to mass transfer effects involved in actual fluid-solid contacting processes. In order to estimate practical or dynamic adsorption capacity, however, it is essential, to know information on adsorption equilibrium [Suzuki, 1990]. For a given gas and amount of a given adsorbent, the amount of gas adsorbed at equilibrium is a function of the final pressure and temperature only [Mantell, 1945].

$$q = f(P, T) \quad (2.1)$$

When the pressure of a gas is varied and the temperature is kept constant, an expression of the amount adsorbed versus the pressure is called the “adsorption isotherm.”

$$q = f(P) \quad (\text{constant } T) \quad (2.2)$$

When pressure is constant and temperature is varied, such the relationship is called the “adsorption isobar.”

$$q = f(T) \quad (\text{constant } P) \quad (2.3)$$

The relationship of the variation of equilibrium pressure with respect to temperature at a certain amount of the amount adsorbed is called the “adsorption isostere.”

$$P = f(T) \quad (\text{constant } q) \quad (2.4)$$

2.3.1 Types of Adsorption Isotherms

The adsorption isotherm is the initial experimental test step in an evaluation to determine feasibility of adsorption treatment and whether further test work should be conducted. The adsorption isotherm is a batch equilibrium test which provides data relating adsorbate adsorbed per unit mass of adsorbent to the amount of adsorbate in the fluid [Bernardin, Jr., 1985].

2.3.1.1 Linear Isotherms

For adsorption on an uniform surface with relatively small amount adsorbed, each adsorbate molecule adsorbed hardly interferes neither adsorption nor desorption of other molecules. Then at equilibrium, the amount adsorbed becomes proportion to the concentration of adsorbate in the fluid or the partial pressure of the adsorbate in the gas phase

$$q = KC \quad (2.5)$$

Equation 2.5 represents the linear isotherm which is analogous to the Henry's law of dilute solution. Hence K is called adsorption Henry constant. The temperature dependence of the Henry constant obeys van't Hoff equation:

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \quad (2.6)$$

where ΔH represents the difference in enthalpy between adsorbed phase and the gas phase or the heat of adsorption.

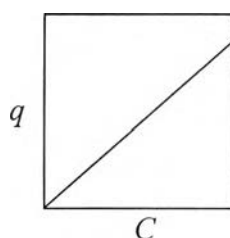


Figure 2.3 Linear Isotherm

2.3.1.2 Nonlinear Isotherms

When a large number of adsorbate molecules are adsorbed on the adsorbent surface, the isotherm tends to be nonlinear. With an increase in the partial pressure of the adsorbate, the amount adsorbed usually approaches a certain value which represents the maximum amount adsorbed on the surface or the monolayer adsorbed amount. Under circumstances, the amount adsorbed is limited of this value which is known as the saturated value. Otherwise, the adsorbate can be adsorbed without upperbound or saturation. This type of adsorption may be called multilayer adsorption.

The simplest and still the most useful isotherm, for both physical and chemical adsorption, is Langmuir isotherm.

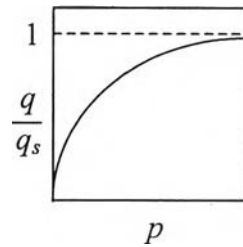


Figure 2.4 Langmuir isotherm

For a gas-solid system, the pressure of the system is limited to the dew point of a given adsorbate since beyond this point, condensed vapour can be obtained leading to wrong information of adsorption equilibria.

The basic assumptions on which Langmuir model was based are [Ruthven, 1984]:

1. Molecules are adsorbed at a certain number of well-defined localized sites.
2. Each site can hold only an adsorbate molecule.
3. All sites are energetically equivalent.
4. There is no interaction between molecules adsorbed at neighboring sites.

Therefore, the amount adsorbed also depends upon the fraction of empty adsorption surface. According to the same rate of adsorption and that of desorption, Langmuir model can be written as:

$$\frac{q}{q_s} = \frac{K_L P}{1 + K_L P} \quad (2.7)$$

where q_s is the maximum adsorbed amount on the selected adsorbent and K_L is Langmuir adsorption equilibrium constant. The limitation of adsorbed amount corresponds to monolayer. For dilute solution, equation 2.7 becomes linear isotherm, the Henry adsorption equilibrium constant, K , is equal to the product of the maximum adsorbed amount and the equilibrium constant of Langmuir isotherm ($q_s \cdot K_L$).

When an adsorbate molecule can be adsorbed either on an adsorbent surface or on the adsorbed molecules upon the surface, saturation of adsorption never occurs with an increase in the partial pressure of the adsorbate. An expression of this isotherm can be written as

$$q = K_F C^{1/n} \quad (2.8)$$

Parameter n is a constant which is not unity. If the parameter n is greater than unity, equation 2.8 is known as Freundlich isotherm which is an empirical expression. Although the expression provides similar results of Langmuir's model, the amount adsorbed is not limited. Equation 2.8 can represent multilayer adsorption.

When adsorption takes place in multilayers, adsorption on the adsorbent surface and above the adsorbed molecules is considered to be based on different attractive forces. Monolayer adsorption is formed by the same concept as the Langmuir type adsorption while adsorption above monolayers is considered as the adsorption on the actual surface, the expression, namely BET equation [Brunauer, Emmett, and Teller, 1938] can be written as

$$\frac{q}{q_s} = \frac{K_{\text{BET}} P_r}{[(1 - P_r)(1 - P_r + K_{\text{BET}} P_r)]} ; P_r \equiv P/P_s \quad (2.9)$$

The expression is commonly used to determine the surface area of a selected adsorbent instead of determination of adsorption equilibria as other expressions, mentioned above. For instance, gaseous nitrogen adsorption at liquid nitrogen temperature, the surface area of the adsorbent is determined by converting q_s to the surface area. In most cases, q_s is obtained from the BET plot of the adsorption data. It gives a straight line in the range of $0.05 < P_r < 0.35$ and q_s is readily determined. Then by multiplying nitrogen surface area ($3,480 \text{ m}^2/\text{g}$) with q_s , specific surface area of the adsorbent based on nitrogen adsorption is calculated [Suzuki, 1990].

2.4 ADSORPTION EQUILIBRIUM MEASUREMENT

There are three types of experimental techniques used for measuring gas-solid equilibrium data: gravimetric, volumetric, and dynamic. The volumetric and gravimetric apparatus are static types, that is, the adsorbate equilibrates with the adsorbent in a closed apparatus. The number of moles adsorbed is found either by weight (gravimetric) measurements or by pressure and volume (volumetric) measurements. In the dynamic type of experiment, a gas chromatograph is used for measuring equilibrium data either by frontal analysis or by perturbation analysis [Kaul, 1987].

2.4.1 Volumetric Method

In determining the amount of gas adsorbed, volumetric method is the oldest and probably still most widely used [Mantell, 1945]. The volumetric method is the commonest method which a certain amount of adsorbents has to be placed under vacuum and let adsorbate gas into the system of which the volume and temperature are controlled. The adsorbed amounts of adsorbate is the difference of the amount of

adsorbate between the amount fed into system and the amount remained in the system. The remaining amounts of the adsorbate can be determined from an incremental pressure of the system. This concept is similar to BET adsorption measurement.

2.4.2 Gravimetric Method

In view of the dead-space difficulty of the volume method, attempts have been made to obtain the amount adsorbed by direct weighing. The success of the gravimetric method is largely due to McBain and Baker's sorption balance [Mantell, 1945]. In this method, a change in grained weight of the adsorbent is measured. Thus, the unadsorbed amount is a different amounts of the adsorbed amounts from the fed amounts. Alternatively, the unadsorbed amount can be represented by the pressure of the system. In order to obtain the equilibrium rapidly, the measurement has to be carried under the vacuum condition.

2.4.3 Chromatographic Method

In a chromatographic method, a small packed adsorption column is subjected to a perturbation in the inlet concentration of an adsorbable species and the dynamic response at the column inlet is measured. Such measurements provide, in principle, a simple and rapid means of studying adsorption kinetics and equilibria. In practice, it is usual to employ either a pulse or a step input although other types of perturbation may also be used [Ruthven, 1984].

The chromatogram obtained provides information of the equilibrium constant, which has to be estimated from the first moment of the chromatogram given as equation 2.10.

First absolute moment:

$$t_R = \frac{\int_0^{\infty} ct \cdot dt}{\int_0^{\infty} c \cdot dt} \quad (2.10)$$

The mean residence time relates to the adsorption equilibrium constant, configuration of the packed bed, and the operating conditions as follows [Schneider and Smith, 1968].

$$t_R = \frac{L}{v} \left(1 + \left(\frac{1-\varepsilon}{\varepsilon} \right) K \right) \quad (2.11)$$

In order to obtain reliable equilibrium constant, several small pulses of adsorbate have to be injected into the column at various flow of carrier gas. Then the equilibrium constant can be estimated from the slope of the linear plot of the first absolute moment with the reciprocal velocity.

2.5 ADSORPTION KINETICS

For adsorption on a single adsorbent, an adsorbate molecule in bulk gas has to travel across gas film surrounding the adsorbent particle and subsequently travel through stagnant gas containing in pore volume of the adsorbent in order to reach gas-adsorbed phase interface, as illustrated in Figure 2.5. When the bulk gas is set in motion, the gas film can move slowly corresponding to laminar flow. Thus, the adsorbate molecule can be assumed to transfer across the film with molecular diffusion only, namely film diffusion. In the pore volume, since gas cannot flow, the adsorbate has to diffuse through the stagnant gas within the restricted space. This phenomenon is called pore diffusion. At the gas-adsorbed phase interface, the adsorbate is

adsorbed and is considered as adsorption equilibrium. In the adsorbed phase, the adsorbed molecule does not move further because of pure adsorbate on the surface. Consequently, the mechanism of adsorption can be divided into 2 consecutive steps, i.e. the film diffusion and the pore diffusion, of which the slower diffusion becomes the rate of adsorption.

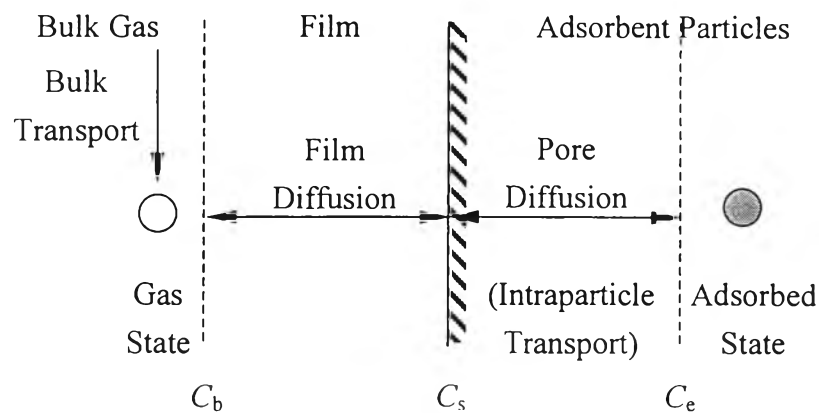


Figure 2.5 Mass-transport steps in adsorption by porous adsorbents

2.5.1 External Film Diffusion

In practice, the rate of adsorption, which is the rate of mass transfer across the film, can be expressed in term of a film mass-transfer coefficient, k_f , as follows:

$$R_{\text{ads}} = (k_f a) \left(\frac{\varepsilon}{1 - \varepsilon} \right) \frac{(C_b - C_s)}{\rho_s} \quad (2.12)$$

For spherical adsorbents, the interfacial area per unit volume, a , equals to $6/D_p$ or $3/R_p$. The film mass-transfer coefficient can be determined from an appropriate correlation of Sherwood number (Sh) with Reynolds number (Re) and Schmidt number (Sc) such as

Ranz and Marshall equation for a single adsorbent [Ruthven, 1984; and Yang, 1987] is written as

$$\text{Sh} = k_f \frac{2R_p}{D_m} = 2.0 + 0.6\text{Sc}^{1/3}\text{Re}^{1/2} \quad (2.13)$$

For a packed bed of uniform size of adsorbent particles with radius, R_p , an appropriate correlation for determination of the external mass-transfer coefficient was developed by Wakes and Funazki [Ruthven, 1984; Yang, 1987] written as

$$\text{Sh} = k_f \frac{2R_p}{D_m} = 2.0 + 1.1\text{Sc}^{1/3}\text{Re}^{0.6} \quad (2.14)$$

The estimated mass-transfer coefficient is satisfied as the Reynolds number is in the range of 3–10,000.

2.5.2 Pore Diffusion

Pore diffusion may occur by several different mechanisms depending on the pore size, the adsorbate concentration, and other conditions [Ruthven, 1984], such as mean free path of adsorbate molecules. Thus, the diffusion in the pore volume of the selected adsorbent also depends on the collision frequency among adsorbate molecules and that between adsorbate molecules and the pore area. If the collision frequency among adsorbate molecules is higher than the other, the pore diffusion can be represented by the molecular diffusion in open space. Otherwise, the pore diffusion has been known as Knudsen diffusion [Ruthven, 1984]. A common criteria for identification of diffusion in pore volume is the ratio of the average pore diameter of the selected adsorbent to the mean free path of the adsorbate. If the ratio is greater

than unity, the pore diffusion is equivalent to the molecular diffusion. Otherwise, it becomes Knudsen diffusion. In order to increase the specific area, the average pore diameter tends to be relatively small so that the diffusion in the pore volume should be Knudsen type. In the circumstances, the rate of adsorption relates to Knudsen diffusivity which can be estimated from the following expression:

$$D_k = \frac{2\sqrt{8RT}r_p}{3\sqrt{\pi}M} = 9700r_p\left(\frac{T}{M}\right)^{1/2} \quad (2.15)$$

Alternatively, the rate of adsorption, which is controlled by the pore diffusion, may be expressed in term of pore mass-transfer coefficient (k_p), defined as

$$R_{\text{ads}} = k_p a_s \frac{1}{\rho_s} \left(\frac{\varepsilon}{1-\varepsilon}\right)(C_s - C_e) \quad (2.16)$$

The mass-transfer coefficient can be obtained from experimental results only. Instead of determination of the rate of pore diffusion, the effective rate of adsorption is determined practically in term of overall mass-transfer coefficient (k_0) which is defined as:

$$R_{\text{ads}} = k(C_b - C_e) \quad (2.17)$$

where

$$k = \rho_s \left(\frac{1-\varepsilon}{\varepsilon}\right) \left(\frac{1}{k_f a} + \frac{1}{k_p a_s}\right)^{-1} \quad (2.18)$$

The overall mass-transfer coefficient is a combined mass-transfer coefficient of the external film and the pore mass-transfer coefficient. Equation 2.17 has been known as “linear driving force rate of adsorption.”

The overall mass-transfer coefficient has to be determined from experimental results. One of the simple methods is the chromatographic method as mentioned previously. According to moment analysis of pulse chromatograms, the second central moment of the chromatogram which is defined as equation 2.19

$$\sigma^2 = \frac{\int_0^{\infty} (t - t_R)^2 \cdot c \, dt}{\int_0^{\infty} c \cdot dt} \quad (2.19)$$

The relationship between the second central moment (variance) and the overall mass-transfer coefficient [Ruthven, 1984] is written as

$$\frac{\sigma^2 L}{2t_R^2 v} = \frac{D_L}{v^2} + \left(\frac{\varepsilon}{1-\varepsilon} \right) \left(\frac{1}{kK} \right) \left(1 + \frac{\varepsilon}{(1-\varepsilon)K} \right)^{-2} \quad (2.20)$$

However, the determination of the overall mass-transfer coefficient requires the equilibrium constant, which can be determined from the first absolute moment of such chromatograms, as described previously. The overall mass-transfer coefficient is determined from the intercept of the linear plot, as expressed in equation 2.20. In addition, the axial dispersion coefficient can be evaluated by the slope of the plot between the left term of equation 2.20 versus $1/v^2$.