

CHAPTER II

ADSORPTION THEORY

Utilization of surface energy of a given solid surface to form bonds with molecules of a certain compounds in a given fluid has been known as adsorption (Mantell,1951). Therefore, 2 types of adsorption, i.e. physical adsorption and chemisorption have been classified corresponding to physical and chemical bondings, respectively (Yang,1987). The former could be either van der Waals force or electrostatic forces or both, whereas the latter related to electron transfer. In general, physical adsorption released less amount of energy than the other, hence it became an important role for separation processes, in particular gas separation.

1. ENERGIES OF ADSORPTION

An adsorption process is usually exothermic. The forces involved in physical adsorption include both van der Waals forces (dispersion - repulsion) and electrostatic interactions comprising polarization, dipole and quadrupole interactions. The van der

Waals contribution always presents while the electrostatic contributions are significant only in the case of adsorbents such as zeolites which have an ionic structure. However, for the sorption of small dipolar molecules such as H_2O and NH_3 on zeolite adsorbents the electrostatic contribution might become large, giving rise to unusually high heats of adsorption (100-125 kJ/mole)(Ruthven, 1984). Thus, although such interactions are properly regarded as physical adsorption, the heat of adsorption may well be of a magnitude generally associated with chemisorption.

2. ADSORBENTS

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 operating pressure and temperature.
- 2.) A method for adsorbent regeneration such as increasing temperature or decreasing pressure.
- 3.) Separation factor.

Commercial adsorbents might be divided into 2 groups : the first group is common porous adsorbents, e.g. silica gel, activated alumina and activated carbons.

The characteristic of these adsorbents might be distinguished by pore size distribution which are broad or multimodal and surface area. While the other is aluminosilicates crystalline of which the pore size is controlled by the crystal structure and is unique, hence named molecular sieve. Table 2-1 provides a summary of information on the most common types of adsorbents.

2.1 Silica Gel

Silica gel is a partially dehydrated form of polymeric colloidal silicic acid. The chemical composition can be expressed as $\text{SiO}_2 \cdot n\text{H}_2\text{O}$. The water content, which is present mainly in the form of hydroxyl groups does not exceed 5 wt.%. In general, silica gel can be manufactured by hydrolysis of alkali-metal silicates, ion exchange, and drying, consecutively. Both particle size and pore size can be adjusted by altering pH and other cations during precipitation.

The presence of hydroxyl groups imparts a degree of polarity to the surface so that polar molecules such as water can be adsorbed in preference to nonpolar molecules such as saturated hydrocarbons. For drying processes, it can adsorb high capacity at low temperature and moderate vapor pressures.

Table 2-1 Adsorbent summary (Keller, 1995)

Adsorbent	Characteristics	Industrial Application
Silica gel	High-capacity, hydrophilic adsorbent	Primarily, drying of gas streams
Activated alumina	High-capacity, hydrophilic adsorbent	Primarily, drying of gas streams, especially at high temperature (Ruthven, 1987)
Activated carbon	Hydrophobic surface, favors organics over air or water	Removal of organic pollutants from aqueous and gaseous effluents
Carbon molecular sieve	Separates on the basis of different intraparticle diffusivities	Production of N ₂ from air
Zeolites	polar, regular channels	Dehydration, air separation, <i>i</i> -paraffin/ <i>n</i> -paraffins separation

2.2 Activated Alumina

Activated alumina is a porous high-area form of aluminum oxide which may be prepared either directly from bauxite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$). The surface is more strongly polar than that of silica gel and has both acidic and basic characteristics, reflecting the amphoteric nature of the metal.

The capacity of activated alumina is lower than silica gel at room temperature but at elevated temperatures the capacity of activated alumina becomes relatively large. It has therefore been commonly used for drying warm air or gas streams.

2.3 Activated Carbon

Manufacturing processes for activated carbon basically consist of the following steps: raw material preparation, low-temperature carbonization, and activation. The condition for activation is controlled to achieve the desired pore structure. The special procedures are used to increase porosity, surface area and adsorptive capacity of activated carbons.

The surface of carbon is essentially nonpolar although a slight polarity may arise from surface oxidation. As a result, carbon adsorbents tend to be hydrophobic and organophilic. They are therefore widely used for the adsorption of organics in decolorizing, water purification and solvent recovery systems as well as for the

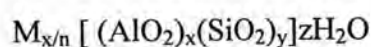
adsorption of gasoline vapors in automobiles and as a general purpose adsorption in range hoods and other air purification systems.

With special controlled oxidation and subsequent thermal treatment, activated carbon with narrow distribution of micropore, usually less than 10 Å in diameter, can be achieved. This special type of activated carbon has been known as carbon molecular sieve (CMS) or molecular sieve carbon (MSC). Thus, the selectivity can be enhanced by the rate of diffusion into the micropores. In air separation, for instance, oxygen molecules can diffuse into the pores much more fast than nitrogen molecules do. Consequently, high purity nitrogen can be produced.

Other potential areas of application include the clean-up of the off-gases from nuclear facilities and the production of pure hydrogen from gas streams containing small amounts of hydrocarbons.

2.4 Zeolites

Zeolites are porous crystalline aluminosilicates of alkali or alkali earth elements such as sodium, potassium and calcium represented by the stoichiometry :



where x and y are integers with y/x equal to or greater than 1, n is the valence of cation M and z is the number of water molecules in each unit cell.

Each silicon atom, as well as aluminum atom, bonds with 4 oxygen atoms to form a tetrahedron. A tetrahedron is joined to 4 other tetrahedra with a shared oxygen atom for each pair of tetrahedra and then, the oxygen-ring of secondary building unit, as shown in Figure 2-1, are built up. 4R is assembled with a ring of 4 oxygen atoms and 5R, 6R, and 8R are assembled with ring of 5, 6, and 8 oxygen atoms, respectively.

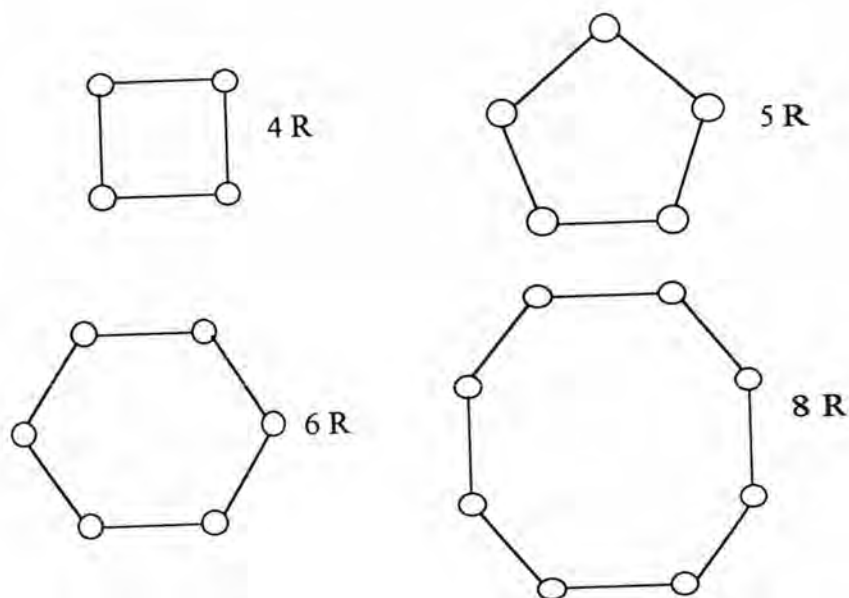


Figure 2-1 Secondary building units of zeolite

The zeolite frameworks are built up from assemblages of secondary building units. The number of oxygen-ring assembled in the frameworks becomes one of essential index for distinguishing between types of zeolites.

In addition, each aluminum atom introduces one negative charge on the framework which must be balanced by an exchangeable cation such as sodium ion, potassium ion, and calcium ion. Changing the exchangeable cation by ion exchange provides a useful and widely exploited means of modifying the adsorptive properties.

The minimum Si/Al ratio in a zeolite is 1.0 but there is no upper limit. As an increase in the Si/Al ratio, the hydrophilic properties on the zeolite surface reduces and the hydrophobic properties dominates on the surface when the Si/Al ratio becomes greater than 10. Consequently, a high silica zeolite or silicalite prefer adsorbing non-polar adsorbates to polar adsorbates.

Based on the oxygen-ring, exchangeable cations and the Si/Al ratio, zeolites can be divided into several types of zeolites as summarized in Table 2.2. Furthermore, the opening channel of zeolites depends upon the parameters mentioned above.

Zeolite A with equi-fraction of silicon and aluminum atoms is assembled with double 4R and sodalite cages (composed with 4R and 6R), as shown in Figure 2.2, in order to form the eight-oxygen ring which becomes an effective opening channel or micropore. The effective pore size can be altered by types of cations. When the Na^+ cations, for instance, are exchanged for Ca^{2+} or Mg^{2+} cations, which are smaller than Na^+ ion, the pore size becomes larger than the size before exchanging ion. With the replacement of a cation of larger size than the existing one, such as exchanging Na^+ ion with K^+ ion, the effective pore size is reduced.

Table 2-2 Characteristics of major synthetic zeolite

Zeolite Type	Cation	Si/Al	Number of Oxygen Ring
3A	K	1	8
4A	Na	1	8
5A	Ca, Mg	1	8
10X	Ca	1 - 1.5	12
13X	Na	1 - 1.5	12
Y	Na	1.5 - 3	12
ZSM-5	Na, NH_4 , H	≥ 30	10

Zeolites X and Y with the Si/Al ratio of 1-1.5 and 1.5-3, respectively, are composed of double 6R and sodalite cages to assemble the effective micropore of twelve-oxygen ring, as shown in Figure 2.2.

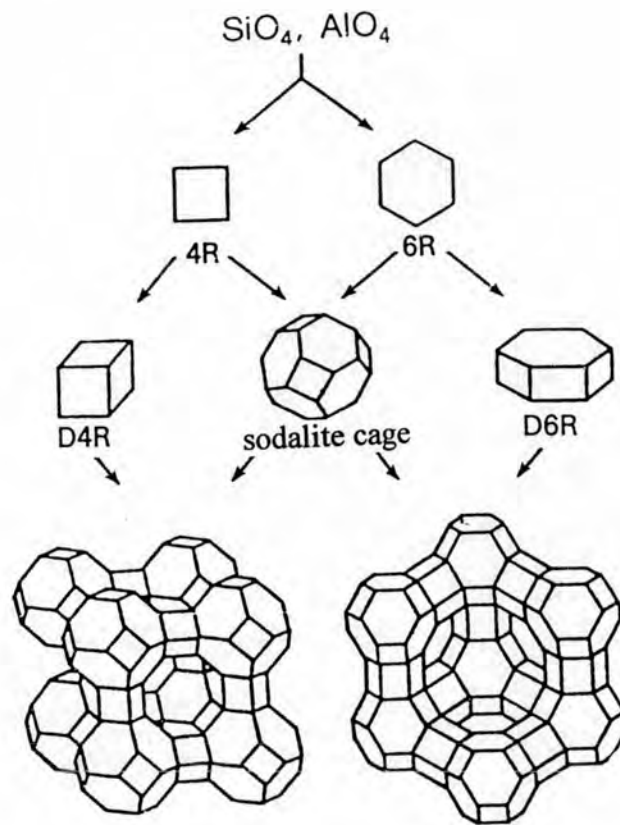


Figure 2-2 Structure of zeolite A, X and zeolite Y

Similarly, the effective pore size can be altered by the change in types of cations.

Only the double 5R units are joined together to form the effective micropores of the ten-oxygen ring for ZSM-5 zeolites with relatively small fraction of aluminum atoms, as illustrated in Figure 2-3.

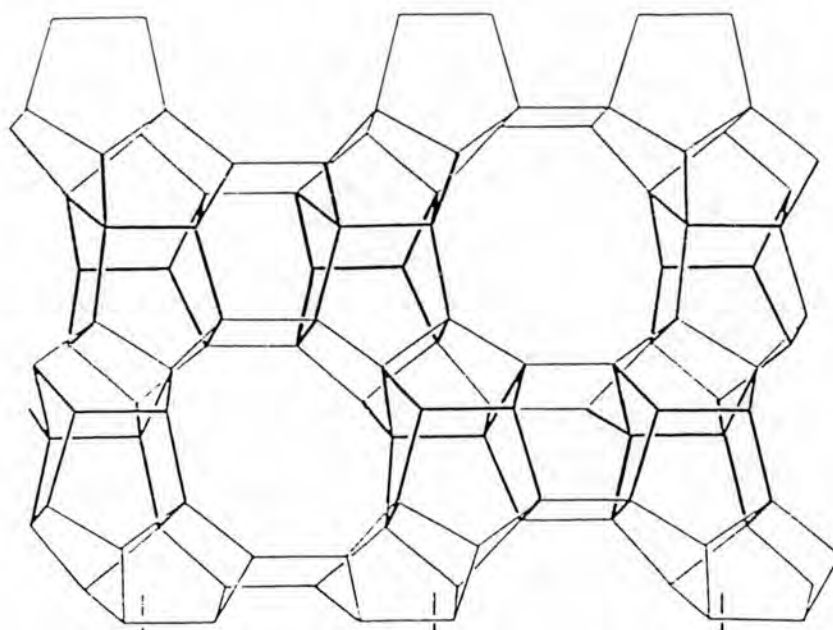


Figure 2-3 Structure of ZSM-5 zeolite

Furthermore, the channel system of ZSM-5 consists of a three direction intersection of a straight channel with elliptical cross-section $5.1 \times 5.7 \text{ \AA}$ along the orthorhombic b-axis and a zigzag channel along the a- and c-axis, as illustrated in Figure 2-4 (Clifton, 1987). Four channels meet at each intersection.

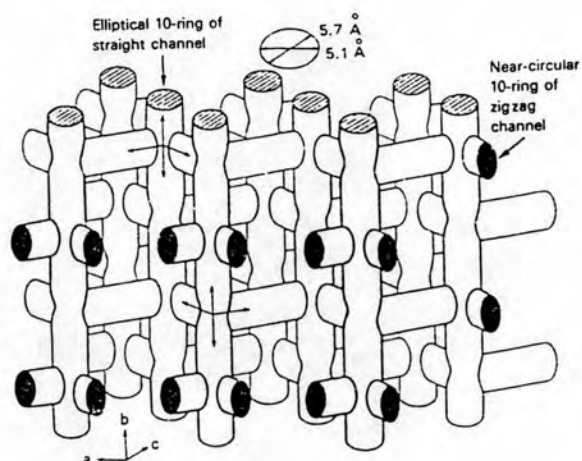


Figure 2-4 Channel system of ZSM-5 zeolite

3. EQUILIBRIUM ADSORPTION

For a given pair of adsorbate-adsorbent, the amount of gas adsorbed at equilibrium is described phenomenologically by :

$$q = f(P, T) \quad \text{----- (2-1)}$$

At a given temperature, q is only a function of P , which is called an adsorption isotherm.

3.1 Linear Isotherm

When the amount adsorbed is sufficiently small, 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.

$$q = Kc \quad \text{or} \quad q = K' P \quad \text{----- (2-2)}$$

Equation (2-2) represents the linear isotherm which analogy the Henry's law of dilute solution. Hence K or K' is call adsorption Henry constant.

The temperature dependence of the Henry constant obeys the van't Hoff equation :

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \quad \text{----- (2-3)}$$

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

3.2 Nonlinear Isotherm

When the amount adsorbed is large, the relationship between the amount adsorbed and the concentration of adsorbate in the fluid or the partial pressure of the

adsorbate in the gas phase will be nonlinear. The simplest and still the most useful isotherm, for both physical and chemical adsorption, is the Langmuir isotherm.

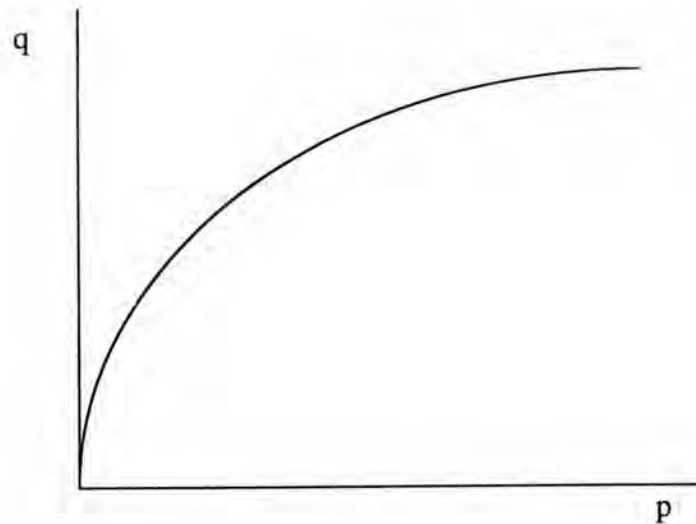


Figure 2-5 Langmuir isotherm

The basic assumptions on which the 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 one adsorbate molecule.
3. All sites are energetically equivalent.
4. There is no interaction between molecules adsorbed on neighboring sites.

The Langmuir model is
$$\frac{q}{q_s} = \frac{K_L p}{1 + K_L p} \quad \text{----- (2-4)}$$

4. ADSORPTION KINETICS

Mass transfer kinetics between fluid and adsorbed phases can also be the foundation of adsorption-based separation processes. The difference between the rates of diffusion through the solid results in separation; the slowly diffusing component remains primarily in the gas, while the quickly diffusing adsorbate is held up in the adsorbent phase.

Adsorption mechanism can be divided into two consecutive steps, i.e. external film diffusion and pore diffusion. External film diffusion characterizes the transport of adsorbate from the bulk gas to the adsorbent surface. Pore diffusion refers to transport through the narrow channels of the adsorbent crystals or micropore diffusion and the interstitial passages between these crystals or macropore diffusion.

4.1 External film diffusion

External film mass transfer characterizes the transport of adsorbate from the bulk gas through the fluid film surrounding the adsorbents to the external surface of the adsorbents. The appropriate dimensionless group characterizing film mass transfer is the Sherwood number, defined by $Sh \equiv 2R_p k_f / D_m$, when k_f is the external film mass transfer coefficient. Sherwood number have a correlation of the form $Sh = f(Sc, Re)$.

For mass transfer in packed bed, Sherwood number is (McCabe, 1985) :

$$\text{Sh} = 1.17 \text{Re}^{0.585} \text{Sc}^{1/3} \quad \text{----- (2.5)}$$

This equation is recommended for spheres or roughly spherical solid particles packed in a bed with porosity of 0.40 - 0.45.

4.2 Pore diffusion

When the molecular size of an adsorbate is smaller than the pore diameter, types of diffusion in the pores of an adsorbent relates to the ratio of the channel diameter of porous media to molecular diameter, and with the ratio of molecular mean free path to molecular diameter.

When the molecular mean free path is small relatively to the pore diameter, molecular diffusion will be the dominant transport mechanism. The resistance to flow arises from collisions between diffusing molecules. In small pores and at low pressure the mean free path is greater than the pore diameter and collisions of molecules with the pore walls occur more frequently than that between diffusing molecules. Under these circumstances, the collisions between molecule and pore wall, known as Knudsen diffusion, provide the main diffusional resistance.

When a fluid flows through a packed bed, axial mixing or dispersion can occur due to the difference in concentration. Any such mixing is undesirable since it reduces the efficiency of separation. The minimization of axial dispersion is therefore a major design objective, particularly when the separation factor is small.

Flow through a packed bed may generally be adequately represented by the axial dispersed plug flow model:

$$-D_L \frac{\partial^2 c}{\partial z^2} + \frac{\partial}{\partial z}(vc) + \frac{\partial c}{\partial t} + \left(\frac{1-\epsilon}{\epsilon}\right) \frac{\partial \bar{q}}{\partial t} = 0 \quad \text{----- (2-6)}$$

In this model the effects of all mechanisms which contribute to axial mixing are lumped together into a single effective axial dispersion coefficient.

There are 2 mechanisms which contribute to axial dispersion in gaseous systems: molecular diffusion, which is dominant at low velocities, and turbulent mixing, which is dominant at high velocities. The axial dispersion coefficient are represented by (Ruthven, 1984) :

$$D_L = \gamma_1 D_m + \gamma_2 2R_p v \quad \text{----- (2-7)}$$

where γ_1 and γ_2 are constants and l/γ_1 is the bed tortuosity.

The binary molecular diffusivity of gas mixtures at low pressure could be estimated from the equation below (Bird, 1960) :

$$\frac{pD_{AB}}{(P_{cA}P_{cB})^{1/3}(T_{cA}T_{cB})^{5/12}\left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{1/2}} = 2.745 \times 10^{-4} \left(\frac{T}{\sqrt{T_{cA}T_{cB}}}\right)^{1.823} \quad \text{---(2-8)}$$

5. EXPERIMENTAL MEASUREMENT OF ADSORPTION EQUILIBRIUM AND RATE OF ADSORPTION

5.1 Volumetric Method

The volumetric method requires the simplest, less expensive apparatus but the determination of the amount adsorbed at a specific equilibrium pressure requires the determination of the amount of adsorbate in the gas phase before and after exposure to the adsorbent sample (Rees, 1992). The errors of this method are at least $\pm 1\%$ in the amount adsorbed. To achieve this accuracy the adsorption apparatus has to be maintained in an environment thermostated to ± 0.1 °C and the gas phase volumes of the vacuum system have to be determined by Boyle's Law expansions from calibrated volumes using helium as the calibrating gas.

5.2 Gravimetric Method

The gravimetric method is conceptually simpler as one weighs the amount of adsorbate adsorbed by the adsorbent under equilibrium conditions. Known amount of adsorbent is placed in a closed system and is exposed to the desired sorbate vapor. After a small step change in the sorbate pressure, the adsorbent weight gain history is followed while keeping total pressure constant. Micro-vacuum balances (e.g. CAHN 2000) are simple to use and can measure relatively small amounts adsorbed down to 0.1 μg .

5.3 Sorption Uptake (SU) method (Hufton, 1993)

In this technique, the adsorbed-phase weight, gas phase pressure at constant volume, or gas phase volume at constant pressure is measured as a function of time after a step change in the gas phase composition has been made. Comparison of the shape of this response with a suitable mathematical model allows determination of the micropore diffusion coefficient. This technique may not be appropriate in practice because the rate of heat transfer resulting from the exothermic adsorption process frequently influences the system kinetics.

5.4 Chromatographic Method (Hufton, 1993)

The general method of perturbation chromatography is to introduce some type of pulse to a previously equilibrated chromatographic system and measure the response. The evolution of the pulse can be described mathematically, and various mass transfer parameters contained therein can be determined by comparison with the experiments. Various versions of this method have been used. The most common one is concentration pulse chromatography (CPC). In this technique, a pulse of adsorbate is injected into an inert carrier gas which passes through a packed column and, eventually, the detectors.

The response of an adsorption column of length L , subjected to a pulse injection of adsorbate at the inlet at time zero, is measured isothermally. For a system containing only a single adsorbate at low concentration, $c(z,t)$, the flow pattern can be represented as axial disperse plug flow. Without taking account the pressure drop across the packed bed, the differential fluid phase mass balance is

$$-D_L \frac{\partial^2 c}{\partial z^2} + v \frac{\partial c}{\partial z} + \frac{\partial c}{\partial t} + \left(\frac{1-\epsilon}{\epsilon} \right) \frac{\partial \bar{q}}{\partial t} = 0 \quad \text{----- (2-9)}$$

where

$$\bar{q} = \left(\frac{3}{R_p^3} \right) \int_0^{R_p} R^2 q dR \quad \text{----- (2-10)}$$

The net rate of adsorption is written as :

$$\frac{\partial \bar{q}}{\partial t} = k(q^* - q) \quad \text{----- (2-11)}$$

so that the equilibrium constant for the adsorption , K, is given as

$$K = q^*/c \quad \text{----- (2-12)}$$

The initial and boundary conditions are

$$c(z, 0) = 0 \quad \text{----- (2-13)}$$

$$q(z, 0) = 0 \quad \text{----- (2-14)}$$

$$c(0, t) = c_0\delta(t) \quad \text{----- (2-15)}$$

$$c(\infty, t) = 0 \quad \text{----- (2-16)}$$

The above set of equations can be solved by Laplace transformation. To obtain the solution of the model equations in the Laplace domain is straightforward but inversion of the transform to obtain an analytic expression for the pulse response can be derived from the solution in Laplace form directly by the application of the method of moments (Ruthven, 1984).

$$\text{First absolute moment} \quad t_R = \frac{\int_0^\infty c t dt}{\int_0^\infty c dt} \quad \text{----- (2-17)}$$

$$\text{Second central moment} \quad \sigma^2 = \frac{\int_0^\infty (t - t_R)^2 dt}{\int_0^\infty c dt} \quad \text{----- (2-18)}$$

The first absolute moment, t_R , characterizes the position of the center of gravity of the chromatogram, whereas the second central moment, σ^2 , represents the variance of the peak. By this method, the expressions for the relationship between the first and second moments of the pulse and some adsorption parameters, i.e. adsorption equilibrium constant and adsorption rate constant can be written, respectively, as :

$$t_R = \frac{L}{v} \left(1 + \left(\frac{1 - \varepsilon}{\varepsilon} \right) K \right) \quad \text{----- (2-19)}$$

$$\frac{\sigma^2}{2t_R^2} = \frac{D_L}{vL} + \frac{v}{L} \left(\frac{\varepsilon}{1 - \varepsilon} \right) \frac{1}{kK} \left(1 + \frac{\varepsilon}{(1 - \varepsilon)K} \right)^{-2} \quad \text{----- (2-20)}$$

Since experimental values of the first absolute and second central moments for the bed can be evaluated from the observed effluent chromatograms. Equation of the first absolute moment is used to calculate the adsorption equilibrium constant directly while the rate parameters are determined from the second central moment.