

# Chapter 2

## Adsorbents and Adsorption

### 2.1 Introduction

Adsorption is a phenomenon of which some materials accumulate at the interface between two phases. These phases can be any of the following combinations, i.e. liquid-liquid, liquid-solid, gas-liquid, or gas-solid. The solid is called an adsorbent, and any substances accumulating at the interface known as adsorbates. The extent of the adsorption is large or small, depending on the nature and characteristics a pair of adsorbent and adsorbete. Adsorbents are specific in their nature and properties. From the application viewpoint, adsorption processes are often subdivided into [19].

1. Separation of gases from gases, such as deodorization of air, elimination of toxic gases.
2. Separation of vapors from gases, such as recovery of solvents, drying of gases, dehumidification.
3. Separation of solutes and colloids from solutions, such as decolorizing and clarifying of liquids.
4. Separation of ions from solutions, such as concentrations of metals on adsorbents, recovery from wastes.
5. Removal of ions from solution, such as in water softening, water demineralization.

6. Separation of dissolved gases or suspended solids from liquids, as in water treatment, removal of odors and tastes.
7. Concentration of dissolved materials, often toxic in nature, to eliminate them from liquids, such as in the case of medicinal carbons, which take up poisonous chemical compounds.
8. Fractionation by selective adsorption of gases from gases, vapors from gases, vapors from vapors, liquids from liquids, dissolved materials from other solutes, and then concentrating them.
9. Continuous fractionation by differential adsorption and desorption, such as separation of mixed xylenes with simulated moving bed.

Adsorption onto solid adsorbents is of great environmental significance, since it can effectively remove pollutants from aqueous or gaseous streams. To achieve the highest degree of purification, this process is often used at the end of a treatment sequence. In discussing the fundamentals of adsorption, it is useful to distinguish between physical adsorption, involving only relatively weak intermolecular forces, and chemisorption, which involves essentially the formation of chemical bonds between the adsorbate molecules and the surface of the adsorbent. Although this distinction is conceptually useful, many cases are intermediate and it is not always possible to categorize a particular system unequivocally.

## 2.2 Industrial Adsorbents and Preparation

In principle, all microporous materials can be used as adsorbents for gas purification and separation process. Common adsorbents section with well-controlled and high microporosity, are reviewed in this section

### 2.2.1 Silica Gels

Silica gels is one of the synthetic amorphous silicas. It is a rigid, continuous network of particles of colloidal silica. Commercially, silica gel is prepared by mixing

a sodium silicate solution with a mineral acid such as sulfuric or hydrochloric acid. The reaction produces a concentrated dispersion of finely divided particles of hydrated  $\text{SiO}_2$ , known as silica hydrosol or silicic acid [20, 21]:



Various silica gels with a wide range of characteristics such as surface area, pore size distribution can be made by varying the silica concentration, temperature, pH of solution. Silica gels, along with activated alumina, is a desirable adsorbent for drying because of its hydrophilic surface. Silica gel contains 4-6% "moisture" by weight, in the form of hydroxyl groups bound to the silicon atoms on the surface, namely the silinol, Si-O-H, groups.

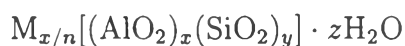
### 2.2.2 Activated Alumina

Activated alumina is one of the adsorbents having the greatest affinity for moisture. An important industrial application for activated alumina is drying of gases and liquids, because of its hydrophilic characteristics and large surface area. The surface is more strongly polar than that of silica gel. Furthermore, both acidic and basic characteristics reflects the amphoteric nature of the metal [21]. 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  $400^\circ\text{C}$  to form crystallines of mixed  $\gamma$ -alumina and  $\eta$ -alumina with a minor amount of boehmite. The surface area of obtained  $250\text{ m}^2/\text{g}$  approximately. Alternatively, the trihydrate is calcined very rapidly at  $400\text{-}800^\circ\text{C}$  to form an amorphous alumina with the specific surface area of  $300\text{-}350\text{ m}^2/\text{g}$ . A highly impure form of activated alumina can be produced by the thermal activation of bauxite, which containing alumina in the form of gibbsite.

### 2.2.3 Zeolites

Zeolites are crystalline aluminosilicates of alkaline, alkaline earth, or mixed alkaline and alkaline earth elements such as sodium, potassium, and calcium, represented

by the stoichiometry [21]:



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 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 3Å to 10Å. 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 or 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 atom ( $\frac{Si}{Al}$ ) must be greater than unity.

#### 2.2.4 Carbons Adsorbents

Activated carbon, a microcrystalline, nongraphitic form of carbon, is processed to develop internal porosity. Activated carbon are characterized by a large specific surface area of 300-2500 m<sup>2</sup>/g, and large distribution of pore sizes which allows to adsorb certain adsorbates from fluid mixtures. However, by special activation procedures it is possible to produce carbon adsorbents with a very narrow pore size distribution within the range of micropore and which behave as molecular sieves. Commercial grades of activated carbons are designed for separation processes of either gaseous mixtures or liquid mixtures. [20, 21]

Activated carbons can be produced from any carbonaceous materials, such as materials from petroleum, from some parts of animals or from agricultural products

and/or wastes, as summarized in Table 2.1. In general, manufacturing process for activated carbon can be divided into a major steps, i.e. carbonization and activation steps. However, the characteristics of the activated carbons obtained varies with based materials and conditions of carbonization and activation steps [22].

Table 2.1: Source materials that have been studied for the production of activated carbon

Sources	Example
material from petroleum	petroleum coke, coal, graphite, oil shale, lignin, lignite, lampblack
waste	pulp-mill waste, rubber waste, distillery waste, leather waste, beet-sugar sludge
parts of vegetables or animals	peat, rice hulls, fruit pits, coffee bean, saw dust, fish, bones

Carbonization step is carried out in the environment without oxygen at temperatures below 600°C [Charney and others]. However, some materials have been carbonized at the temperatures above 600°C [McBain]. After the carbonization steps, the starting materials become char which consists mainly of carbon in the graphite structure. Activation steps is carried out to alter chars, obtained from the carbonization step, into activated carbons with highly porous structure. The pore structure depends on temperature during activation steps and the methods of activation. Both carbonization and activation steps can be carried out together when both steps have to be carried out in the same range of temperature [22]. Activation step can be carried out by reacting with selected reagents, which is divided into 2 groups, as follow:

1. Mild oxidizing gas, e.g. steam, carbon dioxide etc. The reaction is usually carried out at relatively high temperatures. With steam, the temperature of activation must be high enough but below 1000°C to provide a reasonably rapid rate of oxidation. Activation with carbon dioxide is conducted at temperatures 800°C to 900 °C. Many processes involve a reaction with oxidizing gases steam, air carbon dioxide at elevated tempertures, such as.

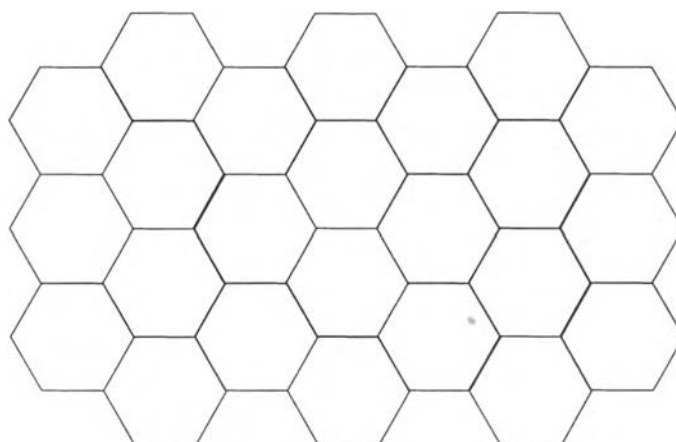
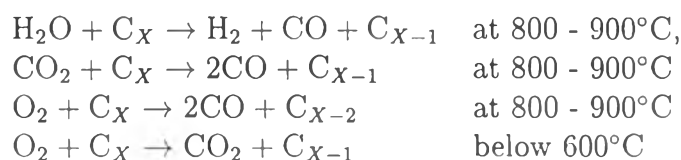


Figure 2.1: Arrangement of carbon atoms in single-layer plane of crystallines formed



2. Acid or salt solution, e.g. sulfuric acid, phosphoric acid and zinc chloride solution etc. The activation is carried out at the temperatures below  $600^\circ\text{C}$ . In the circumstance, the concentration of solution or the ratio of reagent to raw materials may affects characteristics of obtained carbon adsorbents.

The X-ray diffraction pattern has shown that amorphous carbon consists of flat plates in which the carbon atoms are arranged in a hexagonal lattice, as illustrated in Figure 2.1. The structure of activated carbon consists of 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 which illustrated in Table 2.2 [20].

The some functional groups are observable by IR or FTIR instruments, IR (or FTIR) spectral of activated carbons provide information of surface structure, such as oxygen functional groups on the activated carbons. The oxygen surface functional groups on the surface of carbon adsorbents increase adsorption capacities for polar adsorbates as well as the contribution of chemisorption. A schematic

Table 2.2: Pore Sizes in Typical Activated Carbons<sup>†</sup>

	<i>Micropore</i>	<i>Mesopore</i>	<i>Macropore</i>
Diameter (Å)	<20	20-500	>500
Pore volume(cm <sup>3</sup> /g)	0.15-0.5	0.02-0.1	0.2-0.5
Surface area(m <sup>2</sup> /g)	100-1000	10-100	0.5-2

<sup>†</sup> Particle density 0.6-0.9 g/cm<sup>3</sup>; porosity 0.4-0.6

representation of surface oxides that are believed to present on activated carbon surface is illustrated in Figure 2.2 [23].

The surface of carbon is essentially nonpolar although a slight polarity may arise after oxidation. As a result, carbon adsorbents tend to be hydrophobic and organophilic. They are therefore used widely for the adsorption of organics in decolorizing sugar, water purification, and solvent recovery systems as well as for the adsorption of gasoline vapors in automobiles and a general purpose adsorbent and other air purification systems.

## 2.3 Adsorption Isotherms

In order to successfully represent the dynamic adsorptive behavior of any substance from the fluid to the solid phase, it is important to have a satisfactory description of the equilibrium state between the two phases composing the adsorption system. For a single adsorbate system, the adsorbed amount ( $q$ ) at equilibrium varies with the concentration of the adsorbate in the fluid, pressure and temperature of the system, besides types of adsorbents. For gas adsorption at a given temperature, the adsorbed amount ( $q$ ) depends on only the partial pressure of the adsorbate. The relationship between the adsorbed amount on the selected adsorbent and the partial pressure of the adsorbate is called “an adsorption isotherm”. Several adsorption isotherms have been modelled. Common adsorption isotherms are reviewed as follows:

### 1. Henry Isotherms

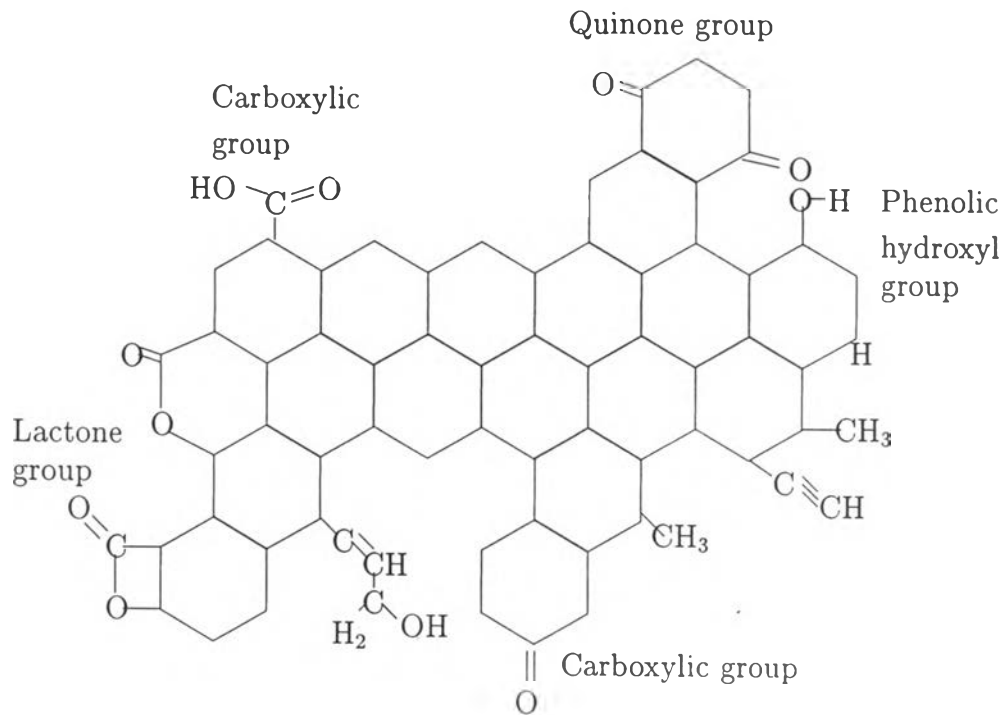


Figure 2.2: Schematic representation of the oxygen surface functional group on activated carbon

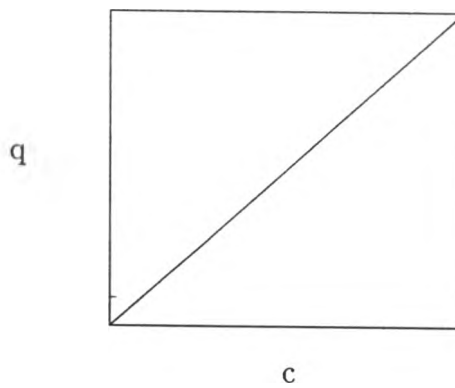


Figure 2.3: Henry Equilibrium



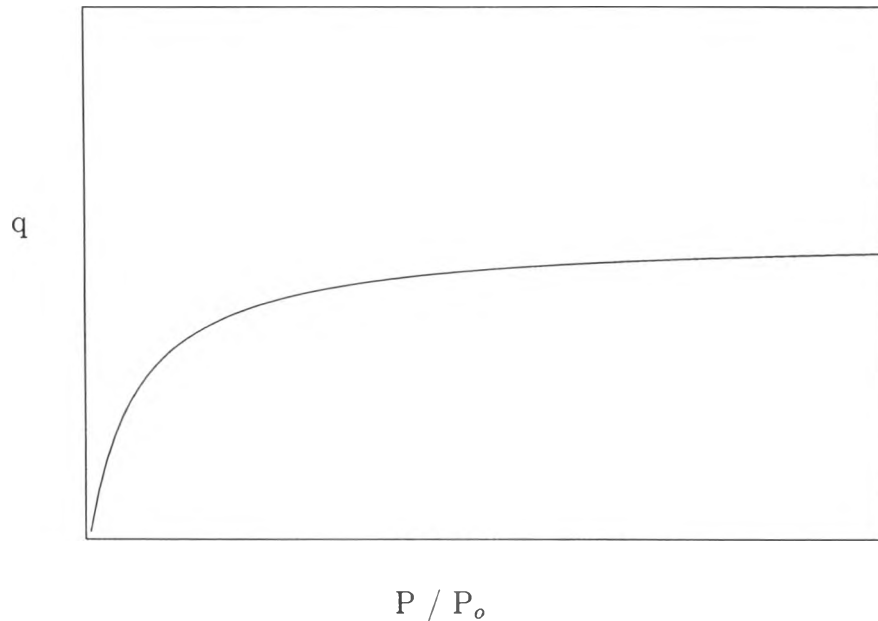


Figure 2.4: Langmuir Equilibrium

For dilute solutions, the equilibrium adsorbed amount has been found to be proportional to the partial pressure of the adsorbate, written as

$$q = K_{HC} \quad (2.1)$$

Equation 2.1, which corresponds to Henry's law, is known as "Henry's isotherm" or "Linear isotherm". In these systems the adsorbed layer is extremely dilute, the amount adsorbed corresponding to a fraction of one percent of the monolayer capacity.

## 2. Langmuir Isotherms

Langmuir isotherms have been developed by the analogy between adsorption and reversible reaction [20]. With power law kinetics, the rate of adsorption is proportional to the partial pressure of the adsorbate and the empty adsorption sites, while the rate of desorption depends on only the adsorbed amount or the occupied adsorption sites. The resulted expression can be written as

$$\frac{q}{q_0} = \frac{K_L c}{1 + K_L c} \quad (2.2)$$

where  $q_0$  is the maximum adsorbed amount on the selected adsorbent and  $K_L$  is the adsorption equilibrium constant. The limitation of adsorbed amount corresponds to monolayer adsorption. For dilute solution, equation 2.2. In the circumstances the equilibrium constant of the Henry's isotherm,  $K_H$  is equal to the product of the maximum adsorbed amount and the equilibrium constant of Langmuir isotherm ( $q_0 K_L$ ).

### 3. Freundlich Isotherm

Freundlich isotherms are empirical equilibrium models for adsorption without theoretical supports, written as

$$q = K c^{1/n} \quad (2.3)$$

Although several researchers have suggested that  $n$  might represent the number of adsorption sites occupied by each adsorbate molecule, where  $n$  is a constant, which is greater than unity, for a system of adsorption. There is no upper limit of the adsorbed amount. Equation 2.3 can represent multilayer adsorption.

## 2.4 Adsorption Kinetics

Adsorption mechanism can be divided into 3 steps as [24]:

- External diffusion step: adsorbate molecules diffuse across the stagnant film around adsorbent particles to reach the external surface of adsorbent particles.
- Pore diffusion step: adsorbate molecules diffuse further into the pore volume in which fluid can not flow.

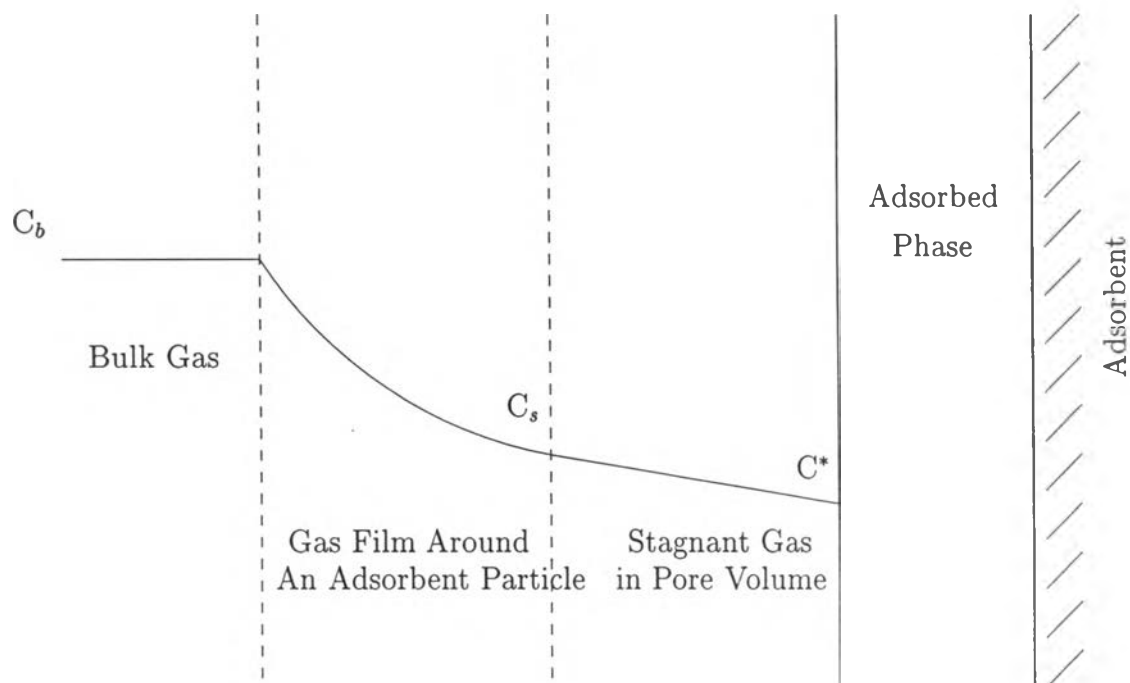


Figure 2.5: Adsorption mechanisms

- Adsorption step: adsorbate molecules are adsorbed on the surface of adsorbent as diffusing in the pore volume. Usually adsorption occurs so rapidly that local adsorption equilibrium can be achieved instantly.

#### 2.4.1 Mass transfer Coefficients for External Diffusion

Based on the adsorption mechanism, the rate of adsorption is controlled by the diffusivity of the external diffusion or one of the pore diffusion. The former can be estimated from an approximate expression for molecular diffusion. While the latter can be estimated from either molecular diffusion or the Knudsen diffusivity, the concentration profile of the adsorbate is essential for determination the rate of adsorption. In practice, the rate of adsorption can be determined in terms of mass transfer coefficient instead, as illustrated in Figure 2.5

##### External Mass Transfer Coefficient

If the external diffusion is a controlling step, the rate of adsorption can be written as

$$\frac{\partial \bar{q}}{\partial t} = k_{ext} a (c_b - c_s) \quad (2.4)$$

where  $k_{ext}$  is an external mass transfer coefficient, and  $a$  is specific external surface of the pellet. The coefficient can be estimated from an appropriate correlation of sherwood number [8] written as

$$Sh = 1.15 Sc^{1/3} Re^{1/2} \quad (2.5)$$

### Pore Mass Transfer Coefficient

For the pore diffusion control, the rate of adsorption may be expressed in term of pore mass transfer coefficient, as follow:

$$\frac{\partial \bar{q}}{\partial t} = k_{pore} a_p (c_s - c_*) \quad (2.6)$$

However, this coefficient must be determined from experimental results. Instead of measuring the rate of mass transfer in the pore volume directly, the effective rate can be measured conveniently by combining the external film and the pore volume as a whole. Subsequently, the effective rate can be written as

$$\frac{\partial \bar{q}}{\partial t} = k_{eff} (c_b - c_*) \quad (2.7)$$

Although the effective mass transfer coefficient ( $k_{eff}$ ) must be determined from experimental results, it can be obtained much more easily than the pore mass transfer coefficient. And the relationship among  $k_{eff}$ ,  $k_{ext}$  and  $k_{pore}$  is

$$\frac{1}{k_{eff}} = \left[ \frac{1}{k_{ext} a} + \frac{1}{k_{pore} a_p} \right] \quad (2.8)$$

### 2.4.2 Determination of Adsorption Parameters

Adsorption parameters can divided into 2 groups, i.e. equilibrium and kinetics parameters. The former usually consists of adsorption equilibrium constant and

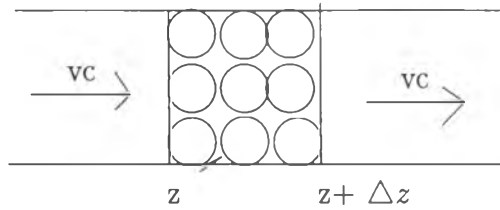


Figure 2.6: Material balance in chromatographic column

others, such as the saturation adsorbed amount for Langmuir isotherm. The latter is composed of mass transfer coefficients.

### 2.4.3 Equilibrium Parameters

The equilibrium parameters can be determined directly from adsorption equilibrium results, which are able to be obtained by volumetric or gravimetric method [25, 26]. Another approach, which is limited to linear isotherm, is chromatographic method, under which the equilibrium constant can be obtained without equilibrium results. This method can be applied appropriately with a system of dilute solution.

Consider material balance for adsorbate species in chromatographic column as illustrated in Figure 2.6 with assumptions:

1. Isothermal
2. Neglect axial dispersion
3. Instantaneous local equilibrium
4. Complete radial mixing
5. Ideal gas in gas phase
6. Constant gas velocity

$$W = \int_0^t (c - c(t)) dt \quad (2.9)$$

Material balance around the adsorber at  $t_r$

$$W = Svt_r c = SL(\varepsilon c + (1 - \varepsilon)\bar{q}) \quad (2.10)$$

So, we obtain

$$t_r = \frac{\varepsilon L}{v} \left\{ 1 + \left( \frac{1 - \varepsilon}{\varepsilon} \right) \frac{\bar{q}}{c} \right\} \quad (2.11)$$

With chromatographic conditions, the first absolute moment of pulse chromatogram is defined as weighted mean residence time of adsorbate, written as

$$t_r \equiv \frac{\int_0^\infty ct dt}{\int_0^\infty c dt} \quad (2.12)$$

For linear isotherm

$$\frac{\bar{q}}{c} = K \quad (2.13)$$

The mean residence time relates to the equilibrium constant

$$t_r = \frac{L}{v} \left[ 1 + \frac{1 - \varepsilon}{\varepsilon} K \right] \quad (2.14)$$

In order to obtain reliable adsorption equilibrium constant, several pulses of adsorbate have to be injected into the column of a selected adsorbent at various flow rates of carrier. Subsequently, the equilibrium constant is determined from the slope of the linear plot between the mean residence time and the reciprocal velocity as given in equation 2.14.

### Kinetic Parameters

For a system of dilute solution, the effective mass transfer coefficient can also be obtained by the chromatographic method. With the chromatographic conditions, the resulted pulse chromatogram provides information of the effective coefficient, besides the equilibrium constant. Since the finite rate of adsorption causes spreading the injected pulse longitudinally, the variance of the resulted chromatogram includes the coefficient of mass transfer. The variance is the second central moment of the chromatogram, defined as

$$\sigma^2 = \frac{\int_0^\infty (t - t_r)^2 c dt}{\int_0^\infty c dt} \quad (2.15)$$

The relationship between the variance and the mass transfer coefficient [20] is written as

$$\frac{\sigma^2 L}{2t_r^2 v} = \frac{D_L}{v^2} + \frac{\epsilon}{1 - \epsilon} \frac{1}{kK} \left[ 1 + \frac{\epsilon}{(1 - \epsilon)K} \right]^{-2} \quad (2.16)$$

With the results of the first absolute moment of the source chromatogram, as well as the corresponding equilibrium constant, the effective mass transfer coefficient is determined from the intercept of the linear plot, as expressed in equation 2.16.