

## CHAPTER II

### THEORY

#### 2.1 Fundamental of adsorption technology

Adsorption involves accumulation of a substance at an interface between two phase, which can either be liquid-liquid, gas-liquid, gas-solid or liquid-solid . Adsorption onto solid adsorbents has great environment significance, since it can effectively remove pollutants from both aqueous and gases streams. Due to the high degree of purification that can be achieved, this process is often used at the end of a treatment sequence. A solid surface in contact with a solution has the tendency to accumulate a surface layer of solute molecules, because of the imbalance of surface forces - an adsorption takes place. The adsorption results in the formation of a molecular layer of adsorbate on the surface.

The species that is adsorbed is called *adsorbate*; there may be one or more adsorbates in a given adsorption situation. The solid substance upon whose surface adsorption occurs is called *adsorbent*. Since adsorption occurs on surfaces , a substance that qualifies as a good adsorbent must have a large surface area on a per-unit-mass (or volume) basis. Inevitably, good adsorbents are microporous pellets with large internal surfaces.

Generally, adsorption is found to be useful in industry not only for purifying , but also bulk separating, The following is a partial list of adsorption application :

For liquid-phase adsorption

- Decolorizing, drying, or degumming of petroleum fractions.
- Removing dissolved organics from drinking water supplies.
- Removing odor, taste, and color from drinking water supplies.
- Decolorizing crude sugar syrup
- Decolorizing vegetable oils

- Purifying wastewater or industrial waste either as part of the physicochemical process or as a tertiary treatment step
- Bulk separating of paraffins and isoparaffins

For gas-phase adsorption

- Recovering organic solvent vapors
- Dehydrating gases
- Removing odor and toxic agents from the air
- Air separation
- Removing carbon dioxide and/or sulfur compounds from natural gas
- Separating normal paraffin from isoparaffin aromatics

In water purification, many effluent standards require tertiary or advanced wastewater treatment to remove particular contaminants or to prepare the water reuse. Adsorption technology is a separation/purifying process in this step which adsorbents are used to remove organic impurities, particularly those that are nonbiodegradable or associated with taste, odor, and color. Although adsorption is applied most often as a tertiary treatment for impurities present in low concentrations, recent physical-chemical process use adsorption as a primary technique to remove soluble organics from the wastewater. Usually the adsorbent are held in a fixed bed, and fluid is passed continuously through the bed until the solid is nearly saturated and the desired separation can no longer be achieved. The flow is then switched to a second bed until the saturated adsorbent can be replaced or regenerated.

Consider a downflow fixed-bed adsorber. Initially, the feed solution is in contact with fresh adsorbent at the top of the column. Solute is adsorbed progressively from the liquid as it flows down the column. The length of the region where most of the solute is removed is called the *adsorption zone*. The length of the adsorption zone is somewhat arbitrary since it depends upon the value of solute concentration selected for its lower boundary. Additional solute is removed as the liquid traversed the portion of the column below the adsorption zone. Because of equilibrium and kinetic factors,

however, some low concentration of solute escapes in the effluent. As more fluid enters the column, the upper portion of solid becomes saturated with solute and the adsorption zone move down the column like a slowly moving wave. Eventually, the lower edge of the adsorption zone reaches the bottom of the column and the effluent solute concentration starts to rise rapidly. When the concentration reaches some limiting permissible value, or *break point*, the flow is stopped or diverted to a fresh adsorbent bed. The break point is often taken as a relative concentration of 0.05 or 0.10, and since only the last portion of fluid processed has this high a concentration, the average fraction of solute removed from the start to the break point is often 0.99 or higher. The plot the effluent solute concentration versus time after the breakpoint is called *the breakthrough curve*. Little additional adsorption occurs after the breakpoint since the entire bed is approaching equilibrium with the feed.

The breakpoint and breakthrough curve depend upon the nature of the adsorbate and adsorbent, the geometry of the column, and the operating conditions. If the adsorption isotherm were favorable and if the adsorption rate were infinite, the breakthrough curve would approach a straight vertical line. The breakthrough curves become less sharp as the mass transfer rates are decreased. Since mass transfer rates are always finite, the breakthrough curve are diffuse and exhibit an S-shape. The breakpoint time usually increases with increased bed height, decreased particle size and decreased flow rate. **Fig. 2-1** illustrates movement of adsorption zone for fixed-bed downflow adsorber and **Fig. 2-2** shows idealized breakthrough curve for fixed-bed adsorber (Sundstrom and Klei, 1979).

In designing a column, the length of the adsorption zone represents the minimum bed depth needed to produce a low effluent solute concentration. The actual bed depth is usually greater than this minimum to allow a reasonable operating period between regeneration of the adsorbent.

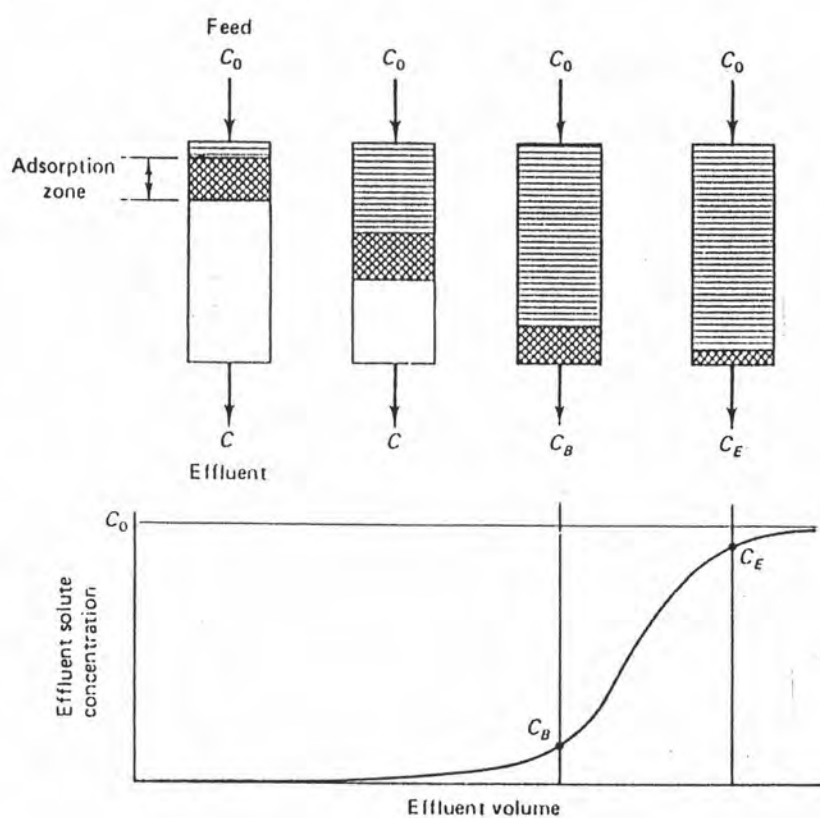


Figure 2-1 Movement of adsorption zone for fixed-bed downflow adsorber

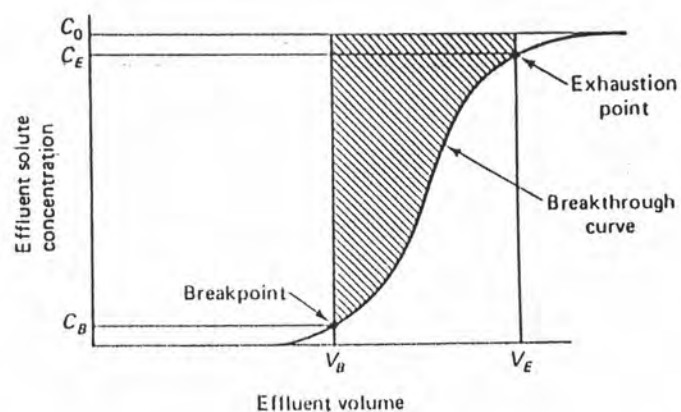


Figure 2-2 Idealized breakthrough curve for fixed-bed adsorber

especially in the areas of aeronautical and space materials technologies. Cfs are expected to be in the increasing demand for composite materials in automobile, housing, sport, and leisure industries as well as air plane and space applications. CF requires high strength and high elasticity. The high-strength type is produced from polyacrylonitrile (PAN) and the high elasticity type is manufactured from coal tar pitch.

***Estimation of length of mass transfer zone (adsorption zone) in case of ACF packed bed column***

In a favorable isotherm system, constant pattern behavior is observed as the mass transfer zone (MTZ) progresses in the bed. The length of MTZ can be estimated from Suzuki (1991).

$$Z_a = (V/K_f a_v) N_{OF} \quad (2-1)$$

Here V is the propagation speed of MTZ , which is given by

$$V = u C_o / (\rho_b q_o + \epsilon C_o) \quad (2-2)$$

Elution time of MTZ is determined from

$$t_E - t_B = Z_a / V \quad (2-3)$$

For the Freundlich isotherm ( $y = x^{1/n}$ ) (Suzuki, 1991),

$$N_{OF} = \ln 9 + (n-1)^{-1} \ln [(1-0.1^{n-1}) / (1-0.9^{n-1})] \quad (2-4)$$

In ACF packed bed, the controlling step of adsorption kinetics is not intraparticle diffusion but axial dispersion in the bulk flow (Suzuki, 1990 and Suzuki, 1991).

Generally  $K_f a_v$  , overall mass transfer coefficient , is considered to be composed of three independent transfer resistances (Suzuki, 1991 and Suzuki, 1994) as follows

$$1/K_{fa_v} = 1/\beta k_{s,a_v} + 1/k_{fa_v} + d/(Pe.u) \quad (2-5)$$

The first and second terms on the right-hand side of equation (2-5) represent the mass transfer resistances inside the adsorbent and across the fluid film, respectively. Since the diameter of the ACF is extremely small (7~20  $\mu\text{m}$ ), the diffusion path inside the adsorbent is very short and excellent efficiency in the contact of fluid to the adsorbent is obtained owing to the large external surface area per unit volume of the adsorbent. For the above reasons, the first two terms are both expected to be negligible in the case of ACF adsorption. Then equation (2-5) may be reduced to equation (2-6)

$$1/K_{fa_v} = d/(Pe.u) \quad (2-6)$$

where  $d/Pe.u$  represents the effect of bulk fluid mixing in the adsorption column and  $Pe$  is the Peclet number on the basis of the diameter of ACF.

### 2.3 Prediction Method for Unknown Multi-solute Adsorption Systems

The adopted method was first proposed by Okazaki et. al. in 1989 for the prediction of the breakthrough curve of a packed bed adsorber used for the treatment of unknown multi-solute water without reliance on expensive time-consuming column tests. The total concentration of pollutants in the wastewater is given in terms of a comprehensive concentration index, namely, Total Organic Carbon (TOC) concentration index, and they obtained an approximate breakthrough curve using only the information from simple jar tests.

The characteristics of adsorption equilibrium for unknown multicomponent wastewater is described on the section later by using the relationship between Characteristic Distribution Curve, the Extended Langmuir equation and Adsorption equilibrium curve.

**The basic assumptions** underlying this method are following

1. The set of the coefficients, which prescribe the adsorption characteristics of individual solute, can be considered to have one-to-one correspondence to each solute in the wastewater.
2. Assume the wastewater to be a distributed system of solute on the basis of this correspondence.
3. The extended Langmuir equation is valid in describing multicomponent adsorption equilibrium.

The reasons that the extended Langmuir equation are as follows

- the number of solutes in equation can be increased easily to infinity
- the equation has no parameter which represents interactions among the solutes
- the consequent calculation is simple

### ***2.3.1 Approximate method representing the characteristics of adsorption equilibrium of unknown multi-component solution (M.Okazaki et.al., 1981)***

The characteristics of adsorption equilibrium for unknown multicomponent wastewater is described by using the relationship between Characteristic Distribution Curve, the Extended Langmuir equation and Integral Adsorption equilibrium curve as follows:

#### **1. Characteristic Distribution curve (CDC)**

A comprehensive index for representation of concentration is necessary to describe the characteristics of adsorption equilibrium of wastewater in which many unknown solutes are contained. The concentration of pollutants in wastewater is usually given in terms of TOC, BOD or COD, so the approximate description is proposed by the use of these comprehensive indexes.

The correlation formulas for multi-solute adsorption equilibrium usually have several kinds of coefficients which prescribe the adsorption characteristics of individual solute. The set of these coefficients can be considered to have one-to-one correspondence to each solute in the wastewater (assumption 1).

Using a correlation formula which represents its multi-solute adsorption behavior, we can define a topological space composed of the coefficients and the probability density of the concentration as its coordinates. We can define a plan prescribing the distribution of coefficients of concentrations formula in this space, and can predict the adsorption equilibria at any conditions using the distribution.

Furthermore, if there are numerous solutes, it is reasonable to assume the wastewater is a distribution curve of the concentration probability density relative to the axis of this, the most predominant, coefficient may be defined (assumption 2). The distribution curve is then called the Characteristic Distribution Curve (CDC) of the wastewater.

## 2. The Extended Langmuir equation

Being the most simple equation for multi-solute adsorption equilibrium, the Extended Langmuir Equation is adopted here (assumption 3).

$$Q_i = \frac{Q_{\infty i} k_i C_i}{1 + \sum_j k_j C_j} \quad (2-7)$$

The equation includes two kinds of parameters,  $Q_{\infty}$  and  $k$ . The adsorption characteristics of the  $i^{\text{th}}$  component can be specified by the values of these two parameters. Taking account of the fact that  $Q_{\infty}$ , rather than  $k$ , shows monotonic differences between the various solutes over the whole concentration range, Okazaki et. al. choose  $Q_{\infty}$  as the dominant parameter. Furthermore,  $k_i$  is assumed constant for all the solutes.

When  $Q_{\infty i}$  is represented as  $x$ , the distributed form of equation (2-7) becomes

$$q(x) = \frac{kxc(x)}{1 + k \int_{x_{\min}}^{x_{\max}} c(x) dx} \quad (2-8)$$

Here  $c(x)$  is a probability density function of the concentration of the  $x^{\text{th}}$  component. The TOC concentration of the wastewater,  $C_T$ , is then given by



$$C_T = \int_{x_{\min}}^{x_{\max}} c(x) dx \quad (2-9)$$

When  $c(x)$  is known, the adsorption equilibrium under any conditions can be calculated readily from the  $c(x)$  function of the wastewater and eqn.(2-8), thus the problem essentially becomes the determination of  $c(x)$ .

### 3. Integral Adsorption Equilibrium Curve (IAEC)

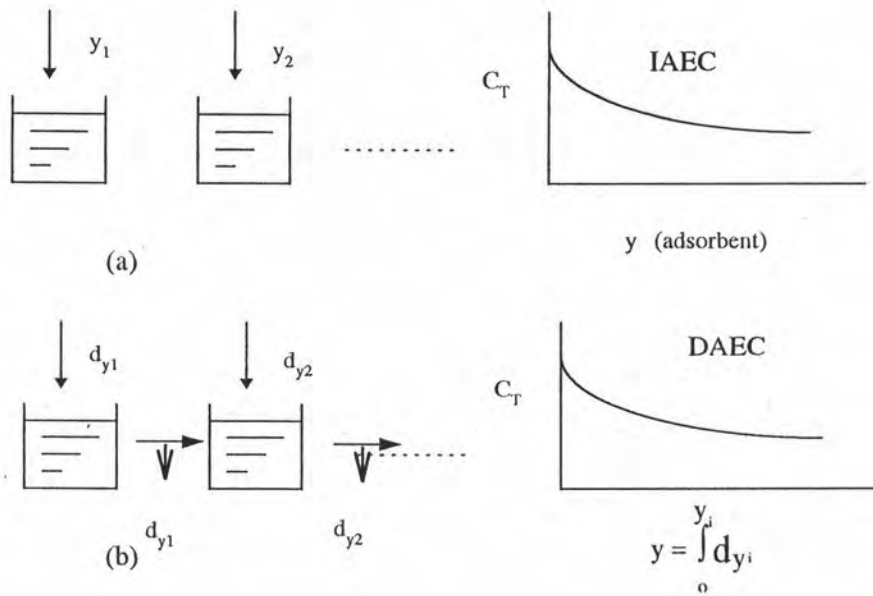
To describe the adsorption equilibrium, we can use either the adsorption isotherm or the curve relating the amount of adsorbent used to the concentration in the liquid. The two relations are interchangeable. As far as the latter relationship, which is used in the present work for the identification of the characteristic distribution curve (CDC) is concerned. Two different types exist.

The first is the integral adsorption equilibrium curve (IAEC), which is the relationship between the amount of adsorbent and the equilibrium concentration in solution experiments where different quantities of adsorbent,  $y_i$ , are in contact with the same amount of wastewater.

The second type is the differential adsorption equilibrium curve (DAEC). In this case, a small amount of adsorbent,  $dy_D$ , is added to the wastewater. After equilibrium has been achieved, the wastewater is separated from the adsorbent by filtration and the TOC concentration of the solution phase measured. Successive repetition of this operation gives the DAEC as the relationship between the accumulated amount of adsorbent,  $y_D$ , and the concentration of the solution phase. Fig. 2-3 illustrate Integral (a) and differential (b) adsorption equilibrium curve.

#### *Determination of the Characteristic Distribution Curve*

Although the DAEC describes the multi-solute adsorption behaviour of the wastewater more explicitly than the IAEC, IAEC have also adopted as a mean of identifying the CDC, taking into account the simplicity of the experimental procedure and, in comparison with the DAEC, the small accumulation of experimental errors.



**Figure 2.3** Integral (a) and differential (b) adsorption equilibrium curves

The next step is to determine the CDC from the IAEC. The material balance between before and after an integral adsorption operation gives

$$c(x,0) - c(x,y) = yq(x,y) \quad (2-10)$$

by substituting eqn.(2-10) into eqn.(2-8) we get

$$c(x,0) - c(x,y) = \frac{kxyc(x,y)}{1 + k \int_{x_{\min}}^{x_{\max}} c(x,y) dx} \quad (2-11)$$

Here

$$\int_{x_{\min}}^{x_{\max}} c(x, y) dx = C_T(y) \quad (2-12)$$

From eqn.(2-11) and (2-12) we obtain

$$c(x, y) = c(x, 0) \frac{1 + k C_T(y)}{1 + k C_T(y) + kxy} \quad (2-13)$$

By substituting the above equation into (2-12) we can determine the IAEC from

$$C_T(y) = \int_{x_{\min}}^{x_{\max}} \frac{[1 + k C_T(y)]c(x, 0)}{1 + k C_T(y) + kxy} \quad (2-14)$$

where  $c(x, 0)$ , the initial concentration distribution of the solute, is the CDC of the wastewater. The CDC can then be determined from the observed IAEC,  $C_T(y)$ , using eqn.(2-14). Although there are various methods to solve eqn.(2-14) for a given  $C_T(y)$ , we apply a parameter fitting method.

As a simulating formula for  $c(x, 0)$ , we adopt

$$c(x, 0) = \frac{1}{2} \sum_{i=1}^n [f_i(x) + |f_i(x)|] \quad (2-15)$$

where

$$f_i(x) = A_i (x - B_i)(x - D_i); \quad B_i < D_i, \quad A_i < 0 \quad (2-16)$$

An adjunct condition should be satisfied :

$$\min(B_1, B_2, \dots, B_n) \leq x_{\min} < x_{\max} \quad (2-17)$$

$$\leq \max(D_1, D_2, \dots, D_n) \quad (2-18)$$

Because the value of  $C_T$  of the initial wastewater is given,  $A_i$ , among the  $2n+3$  parameters  $A_i, B_i, D_i, x_{\min}, x_{\max}$  and  $k$ , depends on the other parameters through eqn.(2-9). The number of unknown parameter is thus  $2n+2$ . The fitting of these parameters is performed by the simplex method.

### 2.3.2 Breakthrough Curve Prediction

The conventional method to calculate the breakthrough curve of an isothermal packed bed adsorber is to simultaneously solve the mass balance equations and the mass transfer rate equations. However, for an unknown multi-solute wastewater, a rigorous solution of these equations would seem somewhat futile. When a nearly instantaneous equilibrium exists between the liquid phase and the adsorbent phase, it is possible to calculate an approximate breakthrough curve using only the information from the jar test results, i.e., the Characteristic Distribution Curve (CDC).

If the flow velocity of liquid in the column is low, then equilibrium may be assumed and the experimental results may be compared with those predicted by a method where the mass transfer rate is neglected. Dividing the range of "Component" into  $N$  intervals, they approximated the wastewater to a water containing  $N$  kinds of solute. When the initial concentrations of these solute in the water are  $c_{1,1}$ ,  $c_{2,1}$ ,  $c_{3,1}$ , ...,  $c_{N,1}$ , the longitudinal change in the concentration distribution is stepwise as shown in Fig. From the mass balance to the  $j$ th step

$$uC_{j,j} = v[\varepsilon C_{j,j} + (1-\varepsilon)Q_{j,j}] \quad (2-19)$$

$$u(C_{j+1,j} - C_{j+1,j+1}) = v[\varepsilon(C_{j+1,j} - C_{j+1,j+1}) + (1-\varepsilon)(Q_{j+1,j} - Q_{j+1,j+1})] \quad (2-20)$$

$$u(C_{N,j} - C_{N,j+1}) = v[\varepsilon(C_{N,j} - C_{N,j+1}) + (1-\varepsilon)(Q_{N,j} - Q_{N,j+1})] \quad (2-21)$$

The moving velocity of the  $j^{\text{th}}$  step is given from eqn (2-19)

$$v_j = \frac{uC_{j,j}}{\varepsilon C_{j,j} + (1-\varepsilon)Q_{j,j}} \quad (2-22)$$

Dividing eqn. (2-20) by (2-19),

$$Q_{j+1,j+1} = Q_{j+1,j} - Q_{j,j}(C_{j+1,j} - C_{j+1,j+1}) \quad (2-23)$$

From eqn. (2-7)

$$Q_{j+1,j+1} = \frac{k X_{j+1} C_{j+1,j+1}}{1+k \sum_{l=j+1}^N C_{l,j+1}} \quad (2-24)$$

From eqns. (2-23) and (2-24)

$$C_{j+1,j+1} = \frac{W_j C_{j+1,j} - Q_{j+1,j}}{W_j - k X_{j+1} / Y_{j+1}} \quad (2-25)$$

where

$$Y_{j+1} = 1+k \sum_{l=j+1}^N C_{l,j+1} \quad (2-26)$$

$$W_j = Q_{j,j} / C_{j,j} \quad (2-27)$$

Similar to the above calculation,

$$C_{l,j+1} = \frac{W_j C_{l,j} - Q_{l,j}}{W_j - k X_l / Y_{j+1}} \quad (2-28)$$

Where  $l = j+2, j+3, \dots, N$

Consequently, when all concentrations in the  $j^{\text{th}}$  step are known, the concentrations in the  $(j+1)^{\text{th}}$  step can be obtained as the solution of the next  $N-j+1$  simultaneous equations :

$$C_{l,j+1} = \frac{W_j C_{l,j} - Q_{l,j}}{W_j - k X_l / Y_{j+1}} \quad (2-29)$$

Where  $l = j+1, j+2, \dots, N$ , and

$$Y_{j+1} = 1+k \sum_{i=j+1}^N C_{i,j+1} \quad (2-30)$$

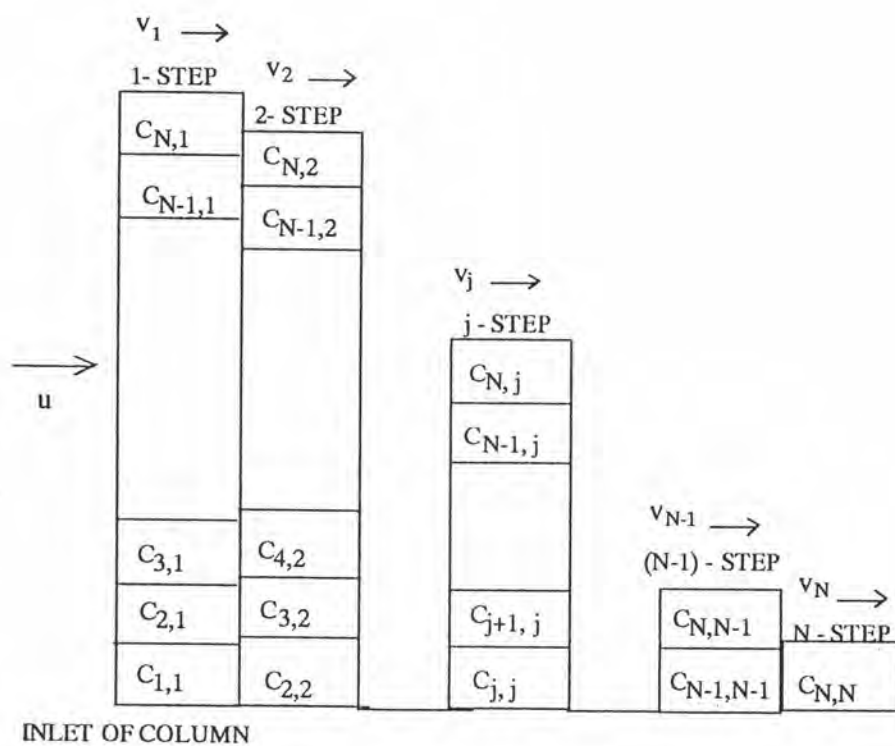
The moving velocity of the  $(j+1)^{\text{th}}$  step is given by

$$v_{j+1} = \frac{u C_{j+1,j+1}}{\varepsilon C_{j+1,j+1} + (1-\varepsilon) Q_{j+1,j+1}} \quad (2-31)$$

The concentrations in the first step are given by the CDC. Then the breakthrough curve can be calculated successively from the second step to the final  $N^{\text{th}}$  step by solving the set of eqns.(2-29) and (2-30), and by calculating the moving velocities of each step.

The concentrations in the  $N$ -step are given by the Characteristic Distribution Curve (CDC). The breakthrough curve can then be calculated successively from the 2-step to the  $N$ -step by solving the terms  $c_{j+1,j+1}$  and  $q_{j+1,j+1}$  simultaneously by an iterative method and by calculating the moving velocities from each step.

In this principle, the concentration of the components at the exit end of the column changes suddenly (similarly as for a single component) there being as many steps as there are substance present.



**Figure 2-4** Distribution of water-phase concentration in bed of adsorbent

Each step, however, represents not a pure substance, but a mixture. Only the first zone contains the least adsorbable component without any admixture (Smisek and Cerny, 1970). The second zone contains in addition to the second least adsorbable component also some of the first one. And the last, nth zone, contains all the components originally present in the mixture, its composition is the same as that of the mixture fed to the column. **Fig. 2-4** shows distribution of water-phase concentration in bed of adsorbent