

ADSORPTION AND ION EXCHANGE

When a solid surface is exposed to a fluid phase, the molecules from the bulk of the fluid phase have tendency to accumulate or concentrate at the surface of a solid. *The phenomenon of enrichment (concentration) of a chemical substance (from a gas or a solution) at the surface of a solid is called adsorption.*

- In adsorption, a fluid phase (a gas or a liquid phase) contacts a solid phase and mass is transferred from the gas/liquid to the solid.
- Adsorption involves the transfer of a solute from either a gas or a liquid/solution (i.e., a constituent of a fluid) to the surface of a solid. The solute is held to the surface of the solid as a result of/due to intermolecular attraction with the solid molecules. In order to complete the separation, the adsorbed solute (constituent) has to be removed from the solid. By simply changing the pressure or temperature of the operation, the solute may be removed from the solid (as the adsorption process is often reversible).
- It is a fluid-solid operation that involves the selective collection and concentration of a particular type of molecules contained in a fluid on the surface of a solid. Therefore, with this operation the components of a gaseous or liquid solution can be separated from each other.
- The substance (solid) on whose surface adsorption takes place (i.e., the enrichment of a chemical substance occurs) is called the *adsorbent* and the substance which is adsorbed (or the substance that is held at the surface of the solid) is called as the *adsorbate (substrate)*. The adsorbate may be a gas or a solute from some solution while the adsorbent is a solid.
- The solid which takes up a gas or a solute from a solution is called the adsorbent whereas the gas or the solute which is held to the surface of the solid is called the adsorbate.
- In adsorption, the molecules of the substance adsorbed accumulate/concentrate at the surface of the solid and hence it is a surface phenomenon.

Applications of Adsorption :

Adsorption operation is used for :

- (i) Separation of gases from gases (gaseous separations) : Removal of toxic gases and removal of odour from waste gases for air pollution control and deodourisation of air.
- (ii) Separation of vapours from gases (gaseous separations) : Dehumidification of air and other gases, recovery of valuable solvent vapours from solvent-laden air and other gases (air leaving and evaporating process such as paint drying, news paper printing, etc.).
- (iii) Separation of solutes from solutions (liquid separations) : Removal of moisture dissolved in gasoline, decolourisation of sugar solutions (crude sugar syrups), vegetable oils and petroleum products, removal of objectionable taste, odour and colour from municipal water supplies, removal of organic components from aqueous wastes for water pollution control.

- (iv) Removal of ions from solution : Demineralisation of water by ion exchange.
- (v) Fractionation by selective adsorption of gases from gases, liquids from liquids, vapours from gases and vapours from vapours : To separate mixtures of light hydrocarbon gases (methane, ethylene, ethane, etc.), mixtures of aromatic and paraffinic hydrocarbons.
- (vi) Odour removal from municipal illuminating-gas supplies.
- (vii) Clarification of beverages.

Adsorbents :

Nature of Adsorbents (Characteristics of Adsorbent) :

1. Adsorbent solids are usually used in granular form with size ranging from 12 mm in diameter to 50 μm .
2. They must possess a large surface area per unit mass.
3. They should have preferential ability to take up the adsorbate (they should have sufficient specificity and adsorptive ability).
4. These are usually highly porous materials.
5. They should be free flowing for ease in handling.
6. They should offer a low pressure drop for flow of fluid when used in a fixed bed.
7. They should have an adequate strength and hardness.

The adsorbent should possess the above characteristics for adsorption to take place on its surface.

Adsorbents in general use :

- (i) activated carbon, (ii) activated alumina, (iii) silica gel, (iv) molecular sieves (zeolites), (v) activated clays, (vi) bone char, (vii) Fuller's earths (natural clays), (viii) charcoal and (ix) metals like Ni, Pt, etc.

1. Activated carbon - decolourising carbon is used for decolourising solutions of sugar, drugs, chemicals, water purification, etc.
2. Activated carbon - gas adsorbent carbon is used for recovery of solvent vapours from gas mixtures, gas masks, etc.
3. Silica gel is used for dehydration of air or other gases.
4. Molecular sieves are used for dehydration of gases and liquids, separation of gas and liquid hydrocarbon mixtures, etc.
5. Bone char is used for refining of sugar.
6. Activated clays are used for decolourising petroleum products.
7. Fuller's earths are useful for decolourising lubricating oils, kerosene, gasoline, and vegetable oils.
8. Charcoal is used for removal of gases like SO_2 , NH_3 , etc.
9. Nickel is used in hydrogenation of vegetable oils - H_2 adsorption.

Adsorption takes place especially on the walls of pores or at specific sites inside the particle. When the capacity of an adsorbent is exhausted, the adsorbed material can be removed by methods such as desorption of adsorbate, displacement of adsorbate and combustion of adsorbate. When we remove the adsorbate by its desorption or displacement (from an adsorbent), then the operation is called regeneration. When the method used involves combustion of the adsorbate, the operation is called reactivation.

Types of Adsorption :

Physical Adsorption : It is a result of intermolecular forces of attraction between molecules of the adsorbent and the adsorbate (substance adsorbed). In this case, the adsorbate merely condenses in a thin film on the surface of adsorbent solid. The intermolecular attractive forces that retain the adsorbent on the surface are purely physical and are called Van der Waals forces.

As these forces are very weak, the adsorbate is loosely bound to the surface of the adsorbent. For example, adsorption of O_2 on charcoal.

Chemical Adsorption/Chemisorption : In this case, molecules of the adsorbate are retained on the surface of the solid by chemical bonding, i.e., it involves chemical interaction between the adsorbent solid and the adsorbed substance (fluid). Identifiable chemical compounds may not actually result but the adhesive force is much greater than that in physical adsorption. In many cases, it is irreversible. It is of particular importance in catalysis. For example, hydrogen is chemisorbed on nickel.

Physical Adsorption	Chemisorption
1. Forces involved are weak.	1. Forces involved are stronger.
2. It is a reversible phenomenon.	2. It is an irreversible phenomenon.
3. Heat of adsorption (i.e., heat evolved) is small, of the order of the heat of condensation. (4 to 40 kJ/mol)	3. Heat of adsorption is large, of the order of the heat of reaction. (40 to 400 kJ/mol)
4. Non-specific in nature, entire surface is available for adsorption.	4. Highly specific in nature and restricted to active sites on the surface.
5. Surface coverage is complete and it may extend to multilayers.	5. Surface coverage is incomplete and it is limited to a unimolecular layer.
6. Quantity of the substance adsorbed per unit mass of adsorbent is high.	6. Quantity of the substance adsorbed per unit mass of adsorbent is low.
7. Activation energy is low, nearly negligible.	7. Activation energy is high, corresponding to chemical reaction.
8. Rate of adsorption is very rapid at low temperature and decreases with increase in temperature.	8. Rate of adsorption is negligible at low temperature and increases with increase in temperature.
9. Rate of adsorption is controlled by resistance to mass transfer.	9. Rate of adsorption is controlled by resistance to surface reaction.
10. Adsorption at low partial pressure is small, and high at high partial pressures.	10. Adsorption at low partial pressure is large, slightly increases at high partial pressures.
11. Entire surface is available for physical adsorption.	11. Chemisorption is restricted to active sites on the surface.
12. Adsorption of O_2 , H_2 gases on charcoal.	12. Adsorption of H_2 gas on nickel metal.

Characteristics of Adsorption by Solids :

- The quantity of a substance adsorbed per unit mass of the adsorbent depends on the equilibrium concentration or pressure of the adsorbate and the temperature.
- The larger the area of the surface, higher is the adsorption.
- The quantity of a substance adsorbed per unit mass of the adsorbent depends on the chemical nature of both the adsorbent and adsorbate and their physical state. In case of physical adsorption, more easily liquefiable is the gas, more readily it will be adsorbed.
- Adsorption can be highly selective, i.e., specific e.g., activated carbon will adsorb butenes (butene-1 and 2) preferentially from a mixture containing ethylene and butenes.
- Adsorption is always accompanied by decrease of enthalpy of the system, i.e., it is an exothermic process.

Adsorption Isotherms :

The equilibrium data for adsorption are usually presented in the form of adsorption isotherms. The adsorption isotherm is the equilibrium relationship between the concentration of the adsorbate held on the surface of the solid (adsorbent) and the concentration (for adsorption from solutions) or partial pressure (for adsorption from gases) of the adsorbate in the fluid phase at a given temperature. The concentration of the adsorbate on the surface of the solid is expressed as the amount of the substance adsorbed per unit mass of the adsorbent. In case of gases, the concentration of the adsorbate in the fluid phase is expressed in terms of partial pressure or mole percent and in case of solutions, it is expressed in terms of mass of the adsorbate per unit volume of solution or in mass units such as ppm [parts per million (parts)].

The adsorption isotherm may be represented in the form of an equation or a curve (graphically). The equilibrium adsorption data (obtained experimentally) can be fitted to some empirical relation called the adsorption isotherm. The common types of adsorption isotherms are : Freundlich adsorption isotherm and Langmuir adsorption isotherm.

The Freundlich Equation : Data for physical adsorption can be expressed by an empirical equation. The Freundlich equation is an empirical relation that fits equilibrium adsorption data (equilibrium data for physical adsorption) in many cases.

The Freundlich adsorption isotherm is represented by the equation :

$$c^* = k (x/m)^n \text{ [for solutions]} \quad \dots (3.1)$$

$$p^* = k (x/m)^n \text{ [for gases]} \quad \dots (3.2)$$

where c^* is the equilibrium concentration of the adsorbate in the fluid phase and x/m is the mass of the substance adsorbed per unit mass of the adsorbent and p^* is the equilibrium partial pressure of the adsorbed gas (adsorbate) in the fluid phase (gas phase). x is the mass of the substance adsorbed and m is the mass of the original adsorbent. k and n are constants.

Equation (3.1) indicates that a plot of equilibrium concentration of the adsorbate against mass of the substance adsorbed per unit mass of the adsorbent, on logarithmic coordinates, is a straight line of slope n and intercept k .

Single-stage Adsorption :

This may be a batch or a continuous operation. The circle in Fig. 3.1 (a) represents all the arrangements constituting one stage.

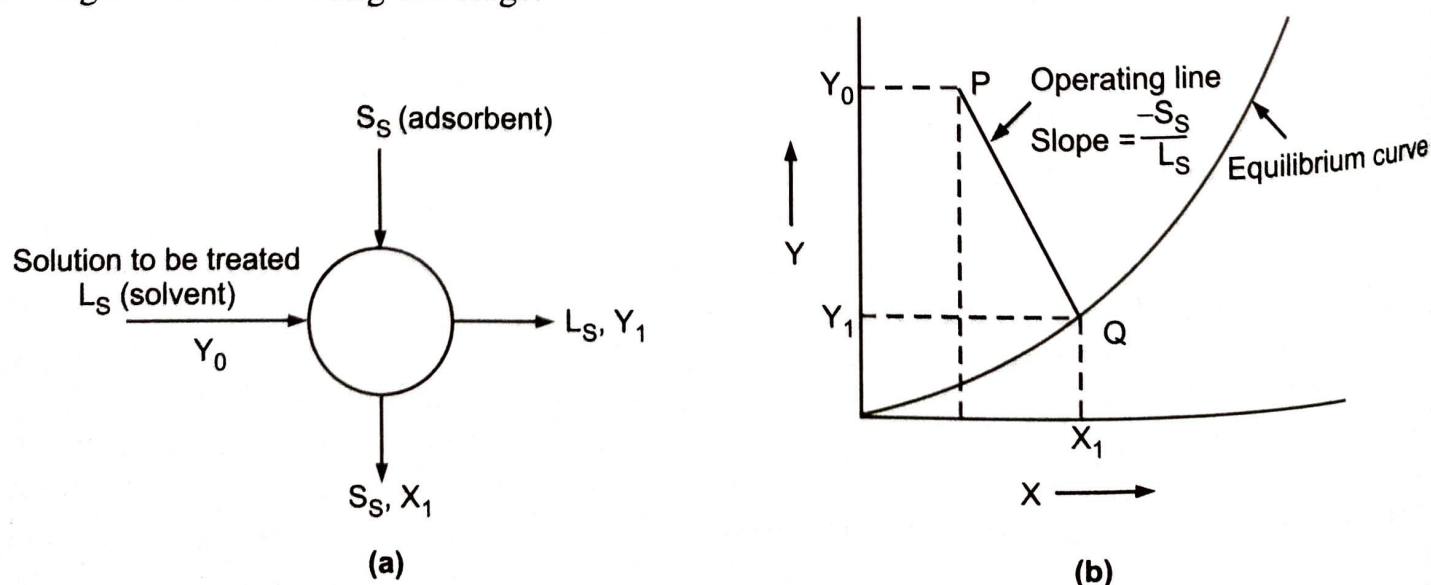


Fig. 3.1 : Single-stage adsorption

Here the solution to be treated consists of an adsorbable solute (C) in a solvent (A). It is contacted with an adsorbent (B) either in a batch or continuous manner.

The amount of the adsorbent used is very small in comparison with the solution. Only the solute (C) is adsorbed and the adsorbent is insoluble in the solution.

Let L_s be the mass of the solvent (for batch operation) or mass of solvent/time (for continuous operation) in the solution to be treated. S_s be the mass or mass/time of the adsorbent added to the stage.

Y_0 is the adsorbable solute concentration in the solution to be treated expressed as mass solute/mass solvent.

Y_1 is the adsorbable solute concentration in the solution leaving the stage expressed as mass solute/mass solvent.

X_0 is the solute concentration in the adsorbent added, in mass solute/mass adsorbent. For fresh adsorbent, $X_0 = 0$.

X_1 is the solute concentration in the adsorbent leaving the stage in mass solute/mass adsorbent.

Assume further that the amount of solution mechanically retained with the solid after phase separation (by filtration or settling) is negligible. This is quite satisfactory for most adsorption because the quantity of the adsorbent used is very small in comparison with the quantity of the solution treated.

So with this, the material balance of solute is :

Solute removed from the solution = Solute picked up by the solid

$$L_s(Y_0 - Y_1) = S_s(X_1 - X_0) \quad \dots (3.3)$$

$$\text{or} \quad \frac{Y_0 - Y_1}{X_0 - X_1} = -\frac{S_s}{L_s} \quad \dots (3.4)$$

This is the operating line equation for single stage adsorption.

On X-Y coordinates, Equation (3.4) is the equation of a straight line, of slope $-S_s/L_s$, passing through points P (X_0, Y_0) and Q (X_1, Y_1). For an equilibrium/theoretical stage, the effluent streams are in equilibrium, so X_1, Y_1 are the equilibrium concentrations of the respective streams and therefore, the point Q (X_1, Y_1) lies on the equilibrium adsorption isotherm. Fig. 3.1 (b) is a graphical representation of Equation (3.4).

If the Freundlich equation is applicable, then the Freundlich adsorption isotherm in terms of concentration units to be used here is given by

$$Y^* = m X^n \quad \dots (3.5)$$

So at the final equilibrium conditions :

$$Y_1 = m X_1^n$$

$$\therefore X_1 = [Y_1/m]^{1/n} \quad \dots (3.6)$$

Substituting X_1 from Equation (3.6) in Equation (3.4), we get

$$\frac{Y_0 - Y_1}{X_0 - (Y_1/m)^{1/n}} = -\frac{S_s}{L_s}$$

Usually, adsorbent used does not contain adsorbable solute initially, $X_0 = 0$ and with this, we get

$$\frac{Y_0 - Y_1}{[Y_1/m]^{1/n}} = \frac{S_s}{L_s} \quad \dots (3.7)$$

With the help of Equation (3.7), we can calculate the adsorbent to solution ratio for a given change in solution concentration – Y_0 to Y_1 .

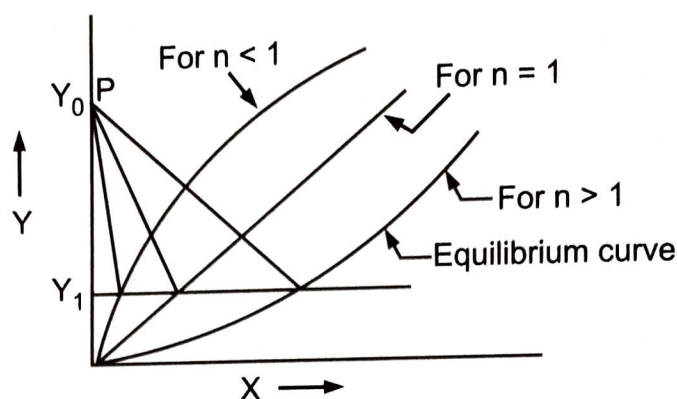


Fig. 3.2 : Freundlich adsorption isotherms – single-stage adsorption, different 'n' values

The Freundlich adsorption isotherm is a straight line for $n = 1$, concave down for $n < 1$ and concave upward for $n > 1$. If in each case, the solution concentration is to be reduced from Y_0 to Y_1 in a single-stage operation, then the three operating lines will radiate from point P with a slope proportional to the adsorbent to solution weight ratio. Generally, values of n in the range 2 to 10 represent good, 1 to 2 moderately difficult, and less than 1, poor adsorption characteristics.

Multistage Crosscurrent Adsorption Operation :

In this case, the solution is successively contacted with separate batches of adsorbent so that the effluent from any stage will be the feed to the next stage where it is contacted with a fresh batch of adsorbent.

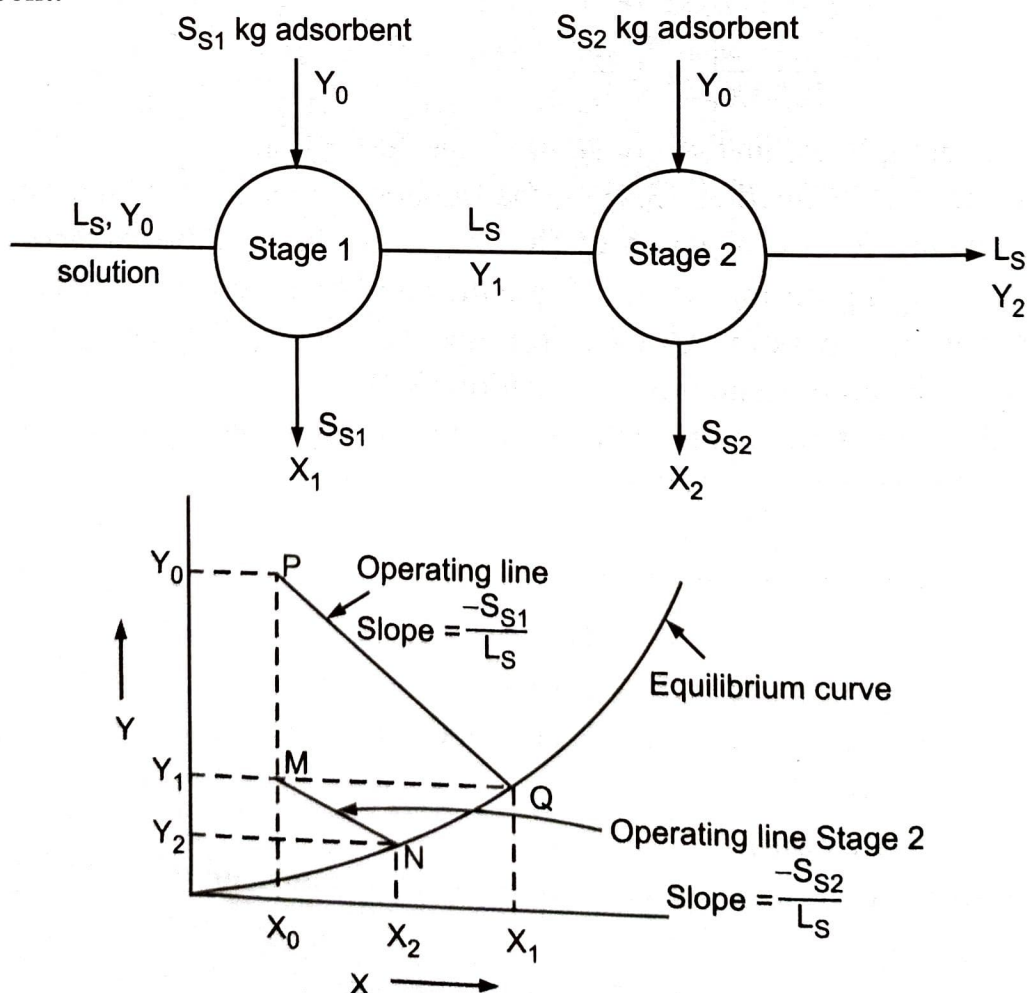


Fig. 3.3 : Two-stage crosscurrent adsorption (different amount of adsorbent in each stage)

With this arrangement, the removal of solute is achieved with a greater economy of adsorbent than that with a single stage but at the same time the operating cost (on filtration) increases with the number of stages and considering this it is seldom economical to use more than two stages.

Consider that a feed solution containing an adsorbable solute at concentration Y_0 and L_S mass of a solvent is treated with S_{S1} and S_{S2} amounts of adsorbent in the two successive stages respectively. [Refer Fig. 3.3]. The adsorbent to each stage contains X_0 mass adsorbate solute per mass adsorbent and it is required to reduce the solute concentration of the solution from Y_0 to Y_2 mass solute/mass solvent.

The material balance of the solute [considering - only solute is adsorbed, negligible amount of solution with adsorbent and adsorbent is insoluble in the solution] is :

$$\text{For stage - 1 : } L_S (Y_0 - Y_1) = S_{S1} (X_1 - X_0) \quad \dots (3.8)$$

$$\text{For stage - 2 : } L_S (Y_1 - Y_2) = S_{S2} (X_2 - X_0) \quad \dots (3.9)$$

Equation (3.8) is an equation of the operating line for stage-1 and Equation (3.9) is an equation of the operating line for stage-2.

The operating line for stage-1, having a slope of $-S_{S1}/L_S$, passes through points P (X_0, Y_0) and Q (X_1, Y_1) on X - Y coordinates [Refer Fig. 3.3].

The operating line for stage-2, having a slope of $-S_{S2}/L_S$, passes through points M (X_0, Y_1) and N (X_2, Y_2) on X - Y coordinates.

As the effluent streams leaving both the stages are in equilibrium, the points Q and N lie on the equilibrium curve.

As different amounts of adsorbent are used each time, the slope of the operating line is different and so the operating lines are not parallel.

If the amounts of adsorbent used in each stage are equal, then the operating lines will be parallel to each other.

For fresh adsorbent used in each stage : $X_0 = 0$.

When fresh adsorbent is used in each stage, $X_0 = 0$ and with this Equations (3.8) and (3.9) reduce to

$$L_S (Y_0 - Y_1) = S_{S1} (X_1)$$

$$\text{and } L_S (Y_1 - Y_2) = S_{S2} (X_2)$$

Rearranging, we get

$$\frac{S_{S1}}{L_S} = \frac{Y_0 - Y_1}{X_1} \quad \dots (3.10)$$

$$\text{and } \frac{S_{S2}}{L_S} = \frac{Y_1 - Y_2}{X_2} \quad \dots (3.11)$$

If the Freundlich equation describes the adsorption isotherm satisfactorily, then the minimum amount of adsorbent required for a two-stage crosscurrent adsorption operation can be calculated directly.

The Freundlich equation is

$$Y^* = m X^n$$

For stage-1, at the final equilibrium conditions, it becomes :

$$Y_1 = m X_1^n$$

$$X_1 = [Y_1/m]^{1/n}$$

Similarly, for stage-2 :

$$X_2 = [Y_2/m]^{1/n}$$

Substituting values of X_1 and X_2 obtained above in terms of Y in Equations (3.10) and (3.11) respectively, we get

$$\text{For stage-1 : } \frac{S_{S1}}{L_S} = \frac{Y_0 - Y_1}{(Y_1/m)^{1/n}} \quad \dots (3.12)$$

$$\text{For stage-2 : } \frac{S_{S2}}{L_S} = \frac{Y_1 - Y_2}{(Y_2/m)^{1/n}} \quad \dots (3.13)$$

The total amount of adsorbent used is

$$\begin{aligned} \frac{S_{S1} + S_{S2}}{L_S} &= \frac{Y_0 - Y_1}{(Y_1/m)^{1/n}} + \frac{Y_1 - Y_2}{(Y_2/m)^{1/n}} \\ \frac{S_{S1} + S_{S2}}{L_S} &= m^{1/n} \left[\frac{Y_0 - Y_1}{Y_1^{1/n}} + \frac{Y_1 - Y_2}{Y_2^{1/n}} \right] \quad \dots (3.14) \end{aligned}$$

For minimum total adsorbent required we have to set :

$$\frac{d[(S_{S1} + S_{S2})/L_S]}{dY_1} = 0$$

$$\text{We have : } \frac{S_{S1} + S_{S2}}{L_S} = m^{1/n} \left[\frac{Y_0 - Y_1}{Y_1^{1/n}} + \frac{Y_1 - Y_2}{Y_2^{1/n}} \right]$$

Note that for a given case m , n , Y_0 and Y_2 are constants.

Differentiating the above equation with respect to Y_1 , we get

$$\begin{aligned} \frac{d[(S_{S1} + S_{S2})/L_S]}{dY_1} &= m^{1/n} \left[Y_0 \cdot \left(-\frac{1}{n}\right) \cdot Y_1^{-\frac{1}{n}-1} - \left(1 - \frac{1}{n}\right) Y_1^{1-\frac{1}{n}-1} + \frac{1}{(Y_2)^{1/n}} \right] \\ \therefore 0 &= m^{1/n} \left[Y_0 \left(-\frac{1}{n}\right) Y_1^{-\frac{1}{n}-1} - \left(1 - \frac{1}{n}\right) Y_1^{-\frac{1}{n}} + \frac{1}{(Y_2)^{1/n}} \right] \\ -\frac{1}{n} \left(\frac{Y_0}{Y_1}\right) Y_1^{-1/n} - \left(1 - \frac{1}{n}\right) Y_1^{-1/n} + \frac{1}{(Y_2)^{1/n}} &= 0 \end{aligned}$$

Multiplying each term by $Y_1^{1/n}$ gives

$$\begin{aligned} -\frac{1}{n} \left(\frac{Y_0}{Y_1}\right) - \left(1 - \frac{1}{n}\right) + \left(\frac{Y_1}{Y_2}\right)^{1/n} &= 0 \\ \left(\frac{Y_1}{Y_2}\right)^{1/n} - \frac{1}{n} \left(\frac{Y_0}{Y_1}\right) &= 1 - \frac{1}{n} \quad \dots (3.15) \end{aligned}$$

With the help of Equation (3.15), we can obtain the intermediate concentration Y_1 and using this value of Y_1 in Equation (3.14) or Equations (3.12) and (3.13), we can calculate the minimum total adsorbent required.

Multistage Countercurrent Operation :

Here the solution to be treated and the adsorbent to be used, flow in opposite directions through a cascade of stages as shown in Fig. 3.4.

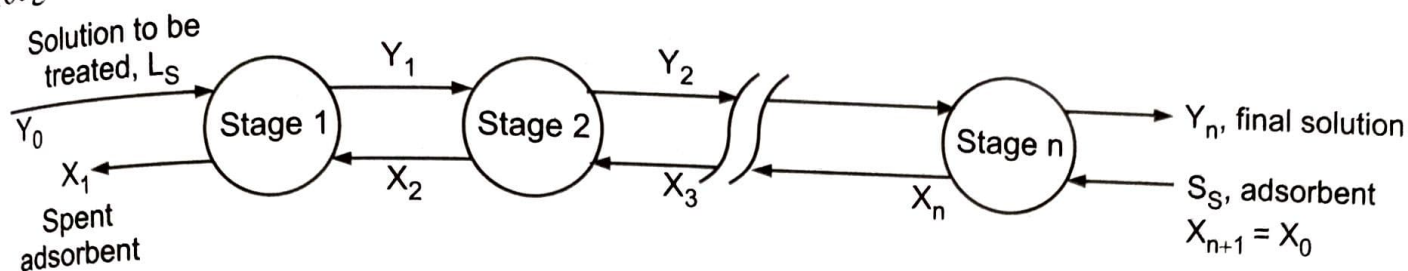


Fig. 3.4 : Multistage countercurrent adsorption

Overall material balance of the solute about the entire cascade :

$$L_S (Y_0 - Y_n) = S_S (X_1 - X_{n+1}) \quad \dots (3.16)$$

$$\text{or} \quad \frac{Y_0 - Y_n}{X_1 - X_{n+1}} = \frac{S_S}{L_S} \quad \dots (3.17)$$

This is the operating line equation for a countercurrent multistage adsorption. On X-Y coordinates, it is a straight line of slope S_S/L_S passing through points of coordinates of the terminal conditions (X_{n+1}, Y_n) and (X_1, Y_0) .

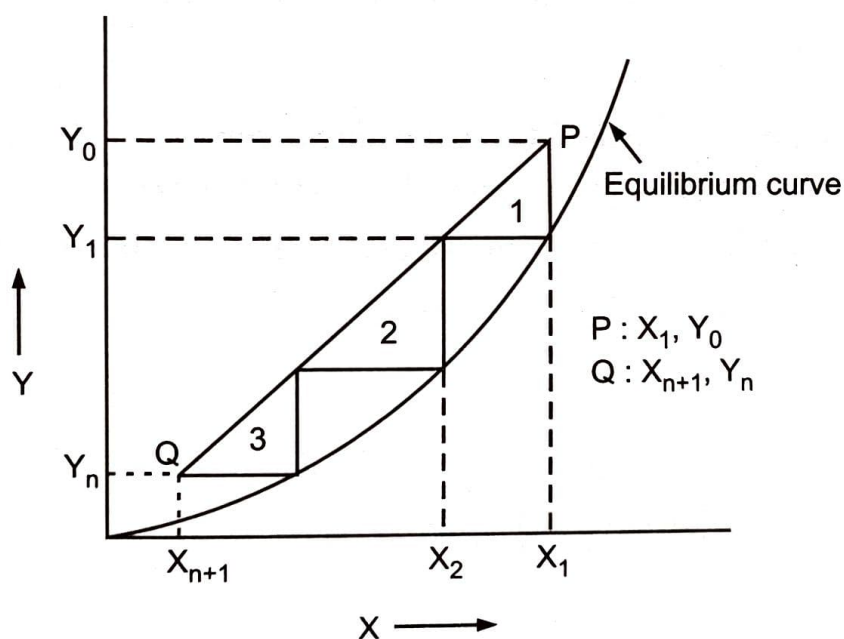


Fig. 3.5 : Graphical construction for number of stages (countercurrent adsorption)

On X-Y plot, locate P (X_1, Y_0) and Q (Y_n, X_{n+1}) and draw the operating line and construct the number of stages between the equilibrium curve and the operating line starting from the point P and ending exactly or crossing the point Q.

Determination of minimum adsorbent requirement :

The minimum adsorbent/solvent ratio requiring an infinite number of stages for the desired change in concentration of the solute in the solution corresponds to the operating line of the largest slope that touches the equilibrium curve.

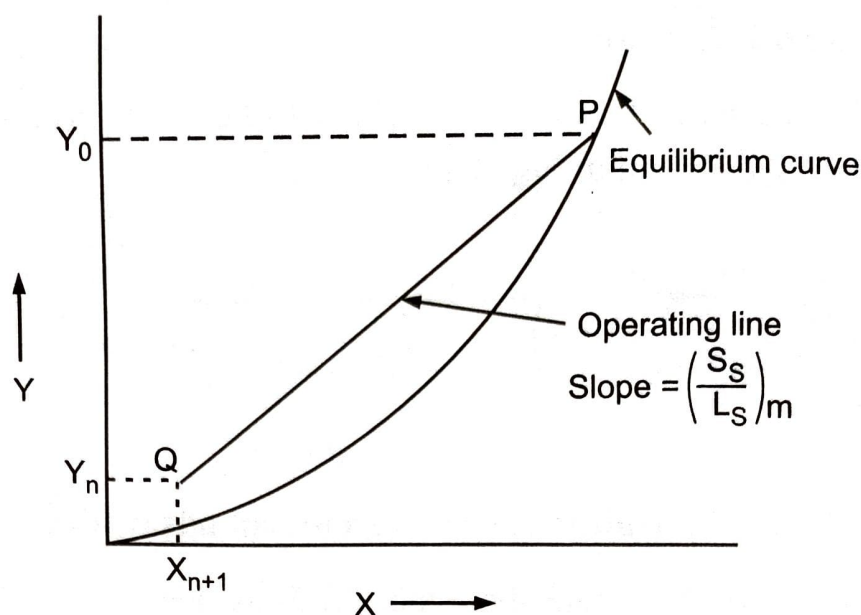
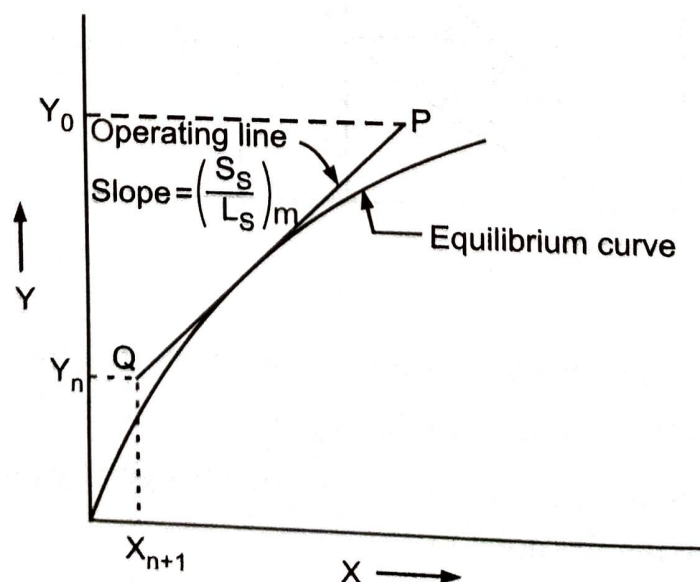


Fig. 3.6 : Minimum adsorbent requirement for infinite stages (X-Y plot concave upward)

(i) **For the equilibrium curve/equilibrium isotherm - Straight or Concave upward :** On X-Y plot, locate the point Q (X_{n+1} , Y_n) and through Y_0 draw a line parallel to X-axis which will cut the equilibrium curve at P (the coordinates of P are X_1 , Y_0). Join PQ, which is the operating line for the minimum adsorbent to solvent ratio. The slope of this operating line gives the value of $(S_s/L_s)_m$, so measure the slope and then calculate the minimum amount of adsorbent required (as L_s is known).

(ii) **For the equilibrium curve - Concave downward :** In this case, locate the point Q (X_{n+1} , Y_n). Through the point Q, draw a line which will be a tangent to the curve and measure the slope of this line to get $(S_s/L_s)_m$ and then calculate the minimum adsorbent required from the value of slope and a known value of L_s .



**Fig. 3.7 : Minimum adsorbent to solvent ratio for infinite stages
(Y v/s X plot, concave downward)**

Consider a two-stage cascade as shown in Fig. 3.8.

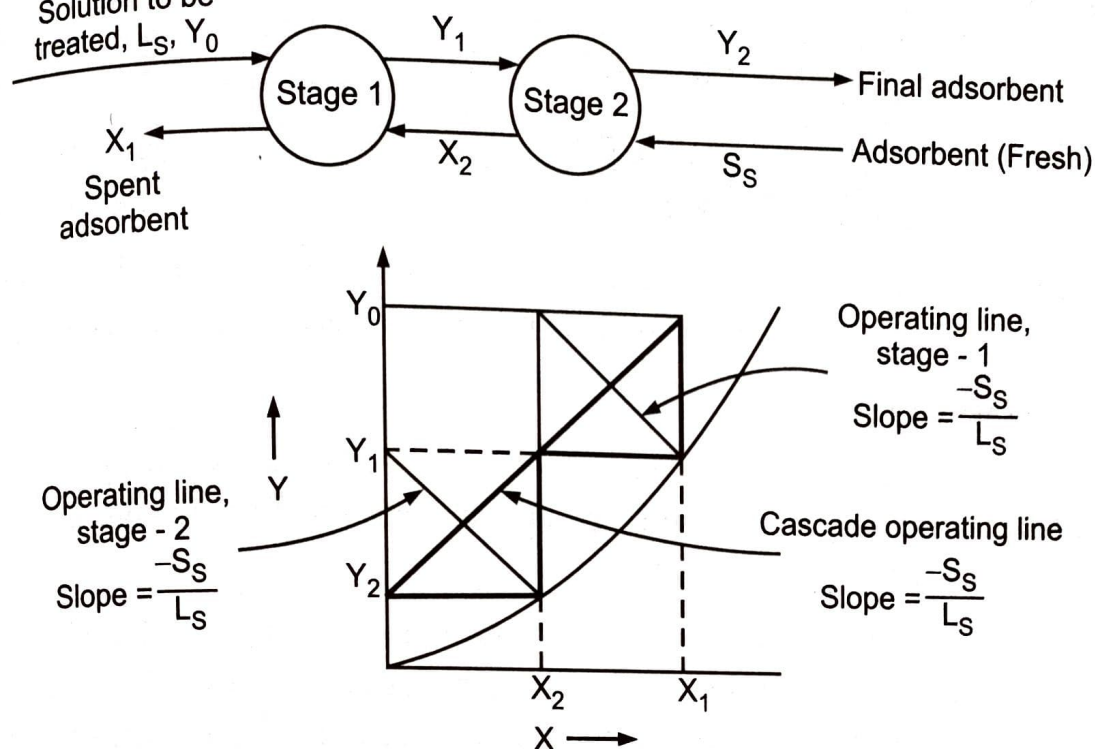


Fig. 3.8 : Two-stage countercurrent adsorption

For fresh adsorbent, $X_{n+1} = X_0 = 0$

Overall material balance of solute :

$$S_S (X_1 - 0) = L_S (Y_0 - Y_2) \quad \dots (3.18)$$

The Freundlich equation is

$$Y^* = m X^n$$

Applying the above Freundlich relation to the effluents from the first equilibrium stage, gives

$$Y_1 = m X_1^n$$

$$\therefore X_1 = (Y_1/m)^{1/n} \quad \dots (3.19)$$

Combining Equations (3.18) and (3.19), we get

$$\frac{S_S}{L_S} = \frac{Y_0 - Y_2}{(Y_1/m)^{1/n}} \quad \dots (3.20)$$

Material balance of the solute over the second equilibrium stage :

$$L_S (Y_1 - Y_2) = S_S (X_2 - 0)$$

$$X_2 = (Y_2/m)^{1/n}$$

$$L_S (Y_1 - Y_2) = S_S X_2 = S_S (Y_2/m)^{1/n} \quad \dots (3.21)$$

$$\frac{S_S}{L_S} = \frac{Y_1 - Y_2}{(Y_2/m)^{1/n}} \quad \dots (3.22)$$

Therefore, from Equations (3.20) and (3.22), we have

$$\frac{Y_0 - Y_2}{(Y_1/m)^{1/n}} = \frac{Y_1 - Y_2}{(Y_2/m)^{1/n}}$$

$$\frac{Y_0 - Y_2}{Y_1^{1/n}} = \frac{Y_1 - Y_2}{Y_2^{1/n}}$$

$$Y_0 Y_2^{1/n} - Y_2 Y_2^{1/n} = Y_1 Y_1^{1/n} - Y_2 Y_1^{1/n}$$

Dividing both the sides of the above equation by $Y_2 Y_2^{1/n}$, we get

$$\left(\frac{Y_0}{Y_2}\right) - 1 = \left(\frac{Y_1}{Y_2}\right) \left(\frac{Y_1}{Y_2}\right)^{1/n} - \left(\frac{Y_1}{Y_2}\right)^{1/n}$$

$$\frac{Y_0}{Y_2} - 1 = \left(\frac{Y_1}{Y_2}\right)^{1/n} \left[\frac{Y_1}{Y_2} - 1\right] \quad \dots (3.23)$$

From Equation (3.23), we can obtain the intermediate concentration Y_1 for given terminal compositions Y_0 and Y_2 . Using this value of Y_1 and Equation (3.20), we can get S_s/L_s .

Continuous Contact Operations :

These operations can be carried out either in (i) continuous steady state fashion or (ii) semicontinuous fashion. The fluid to be treated and adsorbent are in contact throughout the unit without periodic separation of the phases.

In a continuous adsorber used for adsorption from gases or liquids, the solid and the fluid move through the bed countercurrently. The solid particles are fed from the top and flow down by gravity through the adsorption and regeneration sections and are returned to the top of the column by means of either an air lift or a mechanical conveyor.

Continuous countercurrent adsorption (one component adsorbed) :

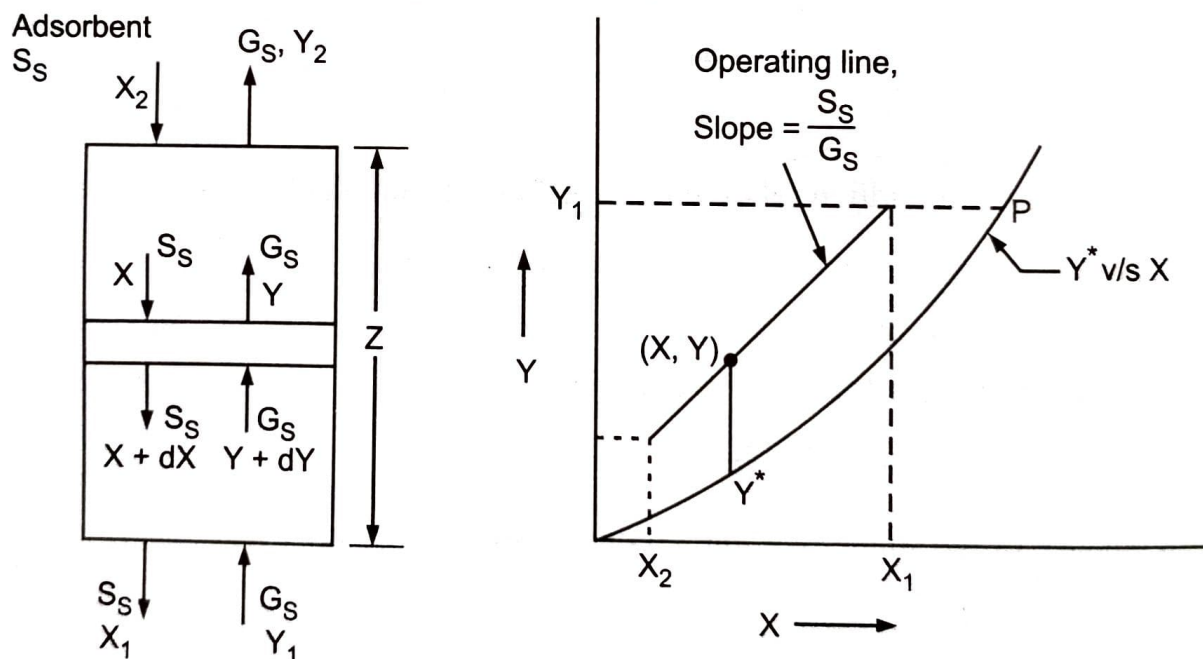


Fig. 3.9 : Continuous countercurrent adsorption of one component

G_s – flow rate of gas on a solute-free basis or mass velocity of solvent gas, mass/(area) · (time).

S_s – flow rate of adsorbent solid on a solute-free basis or mass velocity of adsorbate-free adsorbent solid, mass/(area)·(time). Solute concentrations in the various streams are expressed in terms of mass ratio – mass solute/mass solute-free substance.

Y_1 – mass solute/mass solute-free gas, i.e., mass solute/mass solvent gas at the entrance.

Y_2 – mass solute/mass solvent gas at the exit.

X_1 – mass solute/mass adsorbent at exit.

X_2 – mass solute/mass adsorbent at entrance.

We have considered here the case for treating of a gas, but the treatment can be equally applicable for treating a liquid by replacing G_s by L_s .

Overall material balance of solute over the entire column :

$$G_s (Y_1 - Y_2) = S_s (X_1 - X_2) \quad \dots (3.24)$$

Material balance of solute in the upper part of the column :

$$G_s (Y - Y_2) = S_s (X - X_2) \quad \dots (3.25)$$

On X, Y coordinates, Equation (3.24) is the equation of a straight line having a slope equal to S_s/G_s joining the terminal conditions (X_1, Y_1) and (X_2, Y_2) . This operating line is plotted with the equilibrium curve in Fig. 3.9. The solute concentrations X and Y at any horizontal plane/height in the column lie on this line. The minimum solid/fluid ratio is given by the operating line of maximum slope which anywhere touches the equilibrium curve - which is tangent to the equilibrium curve. [The point (X_2, Y_2) in this case is fixed and a line is to be drawn through this point. In the present case of plot, draw a horizontal line through Y_1 to cut the equilibrium curve say at point P and the line joining this cutting point P and the point with coordinates (X_2, Y_2) is the line corresponding to the minimum solid/fluid ratio.]

The rate of solute transfer over the differential height dZ of adsorber is :

$$S_s dX = G_s dY = K_Y a_p (Y - Y^*) dZ \quad \dots (3.26)$$

where $K_Y a_p$ is the overall gas phase mass-transfer coefficient based on a_p , the outside surface of the solid particles (surface of solids/volume of solid fluid mixture).

Y^* is the equilibrium composition of the solute in the gas corresponding to the adsorbate concentration X . The overall gas phase driving force $Y - Y^*$ is denoted by the vertical distance between the operating line and equilibrium curve.

$$G_s dY = K_Y a_p (Y - Y^*) dZ \quad \dots (3.27)$$

Rearranging and integrating Equation (3.27), we get the number of transfer units as

$$dZ = \frac{G_s}{K_Y a_p} \cdot \frac{dY}{Y - Y^*}$$

$$\int_0^Z dZ = \frac{G_s}{K_Y a_p} \int_{Y_2}^{Y_1} \frac{dY}{Y - Y^*}$$

$$Z = \frac{G_s}{K_Y a_p} \int_{Y_2}^{Y_1} \frac{dY}{Y - Y^*} \quad \dots (3.28)$$

$$Z = H_{\text{TOG}} \cdot N_{\text{TOG}} \quad \dots (3.29)$$

The number of overall gas transfer units are :

$$N_{\text{TOG}} = \int_{Y_2}^{Y_1} \frac{dY}{Y^* - Y} \quad \dots (3.30)$$

The height of an overall gas transfer unit is

$$H_{\text{tOG}} = \frac{G_s}{K_Y a_p} \quad \dots(3.31)$$

$$N_{\text{tOG}} = \int_{Y_2}^{Y_1} \frac{dY}{Y - Y^*} = \frac{Z}{H_{\text{tOG}}} \quad \dots(3.32)$$

The value of the integral of Equation (3.30) is evaluated graphically and the active height Z is then determined using a known value of the height of a transfer unit H_{tOG} .

The relationship between the overall mass-transfer coefficient and the mass-transfer coefficients of the phases involved is

$$\begin{aligned} \frac{1}{K_Y a_p} &= \frac{1}{k_Y a_p} + \frac{m}{k_s a_p} \\ \therefore \frac{G_s}{K_Y a_p} &= \frac{G_s}{k_Y a_p} + \frac{m G_s}{k_s a_p} \\ \frac{G_s}{K_Y a_p} &= \frac{G_s}{k_Y a_p} + \frac{m G_s}{S_s} \cdot \frac{S_s}{k_s a_p} \\ \therefore H_{\text{tOG}} &= H_{\text{tG}} + \frac{m G_s}{S_s} H_{\text{ts}} \quad \dots(3.33) \end{aligned}$$

where $m = dY^*/dX = \text{slope of the equilibrium curve.}$

$H_{\text{tG}} = \text{height of a gas transfer unit}$

$H_{\text{ts}} = \text{height of a solid transfer unit}$

$k_s = \text{solid phase mass transfer coefficient}$

$k_Y = \text{gas phase mass transfer coefficient.}$

Fixed-Bed Adsorbers :

A fixed-bed adsorber is a continuous contact apparatus, which may superficially resemble a packed column. But there is a fundamental difference between these two units. The packing in a packed column provides a large interfacial area between the fluid phases involved in the mass transfer, while the solid particles in a fixed bed adsorber are in fact one of the phases involved in the mass transfer. It is operated in semicontinuous fashion-the fluid to be treated is passed continuously through a stationary bed of adsorbent. In such units, continuous flow of fluid phase through a stationary adsorbent results in unsteady state conditions, where compositions in the fluid phase and solid phase change with time as well as with position in the bed. Fixed-bed adsorbers are used for recovery of solvent vapours from gases, dehydration of gases and liquids, and decolourising lubricating oils, vegetable oils and sugar solutions.

A typical system used for adsorption of solvent vapours is shown in Fig. 3.10. Generally two beds are used; when one is in operation, the other is regenerated. In order to operate the adsorber with a small pressure drop, adsorbents in granular form are used. The diameter of the adsorber is much greater than the bed depth. The bed length usually varies from 0.3 to 1.3 m and the bed of the adsorbent particles is supported by a screen or perforated plate. The feed gas is fed downward through the bed at a superficial gas velocity of order of 0.25 to 0.6 m/s. Upflow of feed is usually avoided because at high gas flow rates there is a tendency of fluidisation of adsorbent particles which results in attrition and loss of fines. When the concentration of the

solute in the effluent gas reaches a certain value or at a schedule time, valves are automatically switched so that the feed is diverted to the second bed and regeneration of the first bed starts.

Regeneration can be carried out using either a hot inert gas or low pressure steam. The low pressure steam is usually used for regeneration purpose, if the solvent is not miscible with water. Steam condenses in the bed and provides the necessary heat of desorption (the hot inert gas or steam provides the necessary heat of desorption) and consequently the desorption process starts. The steam-vapour effluent from the bed is condensed in a condenser, the solvent is separated from water by decantation and dried before reuse. The bed may then be cooled and dried with the inert gas if the moisture interferes with vapour adsorption. If some water vapour is tolerated in the clean gas then the moisture is removed by the vapours during an adsorption cycle in which case the heat released in adsorption of vapour is used to desorb water.

For very large gas flow rates, a rectangular bed of certain depth may be installed in a horizontal cylinder.

The size of the bed depends upon the gas flow rate and the desired cycle time. The adsorption cycle is usually of 2 to 24 h. With a longer bed, the adsorption cycle could be extended to several days but it results in a large pressure drop and requires high capital cost. With small bed depth, the pressure drop is small but separation with a shallow bed is incomplete and it also requires more energy for regeneration.

In fixed-beds, an alternative procedure to provide the energy for regeneration is to heat the bed electrically (embedded electric heaters) or with embedded steam coils. The procedures which utilise heat as a regenerative means are called as thermal swing procedures.

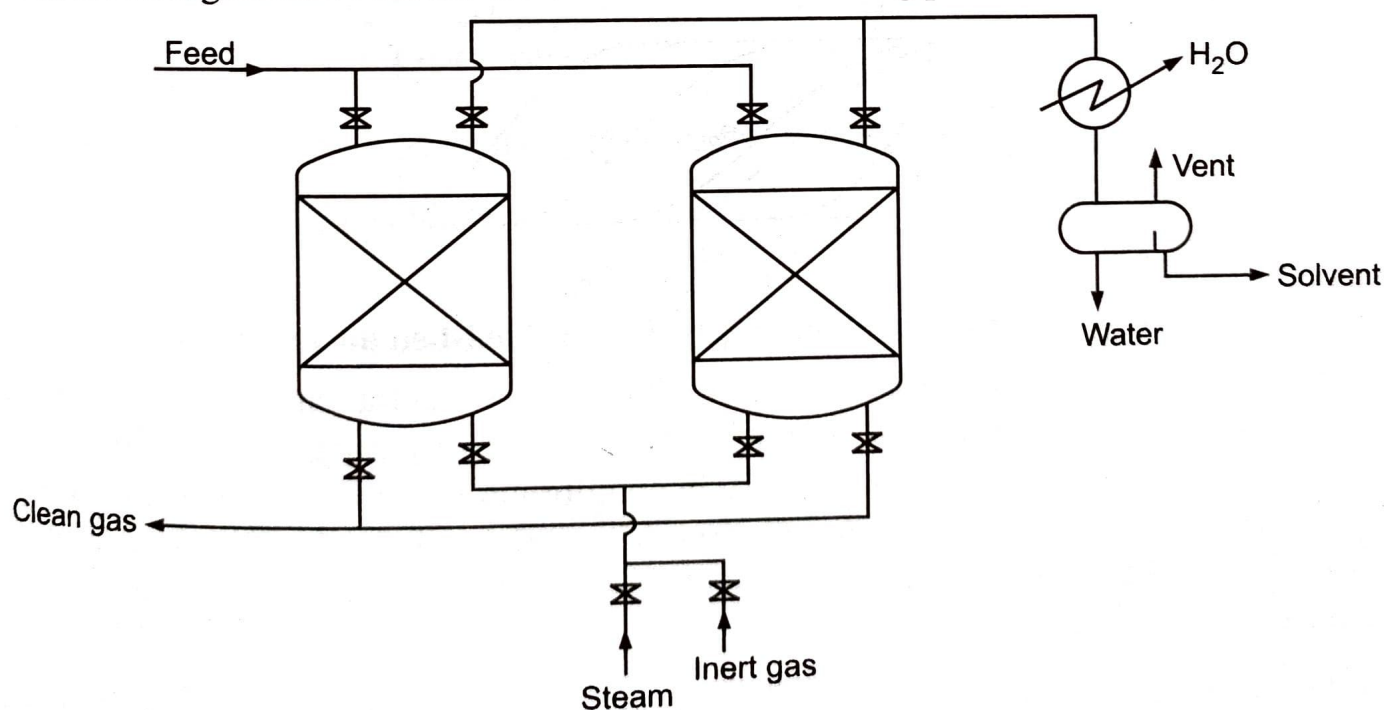


Fig. 3.10 : Vapour adsorption system

For adsorption from liquids, the bed of adsorbent may be tall upto 10 m and tall beds are needed because the rate of adsorption from liquids is much slower than from gases. (e.g., the removal of trace organics from municipal water supplies using carbon - that improves taste and a chance of forming toxic compounds in the chlorination step.)

Moist gases can be dried of their water content in a equipment similar to that shown in Fig. 3.10. In this case, a moist gas is passed through the bed of activated silica gel, alumina, or molecular sieves. The hot gas is used for regeneration. The moist gas leaving the bed being regenerated may be vented or much of the water may be removed in a condenser and the gas is recirculated through a heater to the bed.

Concentration profiles in fixed beds :

In two-component fixed-bed operation, the solute from the fluid phase is removed continuously and accumulated on the solid phase as the fluid phase moves through a stationary solid phase, and as a result the concentrations in the fluid phase and the solid phase change with time as well as with position in the bed. At first, most of the mass transfer takes place near the inlet of the bed where the fluid first comes in contact with the adsorbent. If the adsorbent solid is free of adsorbate initially, the concentration in the fluid drops exponentially with the bed length essentially to zero-before the end of the bed is reached. This concentration profile is shown by curve θ_1 in Fig. 3.11, where Y/Y_0 is the concentration in the fluid relative to that in the fluid entering the fixed-bed. After a few minutes of operation, the solid near the inlet becomes nearly saturated, and most of the mass transfer takes place further from the inlet. The concentration profile then becomes S shaped, as shown by curve θ_2 . The region in which most of the change in concentration takes place is called the mass-transfer zone (adsorption zone) and the limits of which are often taken as Y/Y_0 values of 0.95 to 0.05. With passage of time, the adsorption zone moves down the bed, as shown by profiles θ_3 and θ_4 . Similar profiles could also be drawn for the average concentration of adsorbate retained on the solid, indicating nearly saturated solid at the inlet, a large change in the adsorbate concentration in the mass transfer zone and zero at the end of the adsorbent bed.

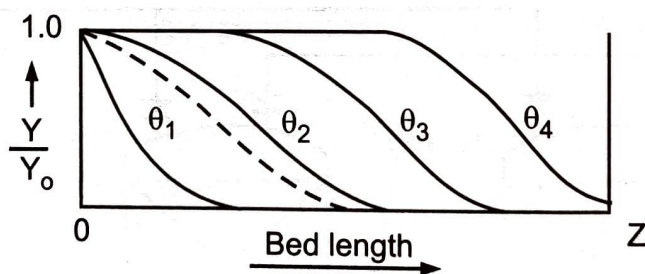


Fig. 3.11 : Concentration profiles in fixed-bed adsorber

Instead of plotting the adsorbate concentration, the concentration in the fluid phase in equilibrium with the adsorbent solid is plotted and indicated by a dashed line for time θ_2 in Fig. 3.11. The concentration in the fluid phase in equilibrium with the adsorbent solid has to be always less than the actual fluid concentration. The difference in these two concentrations (driving force) is large where the concentration profile is steep (mass transfer is rapid).

Breakthrough Curves :

When a binary solution (either gas or liquid) containing strongly adsorbed solute at concentration Y_0 mass solute/mass solvent flows continuously downward through a relatively deep bed of adsorbent initially free from adsorbate. The topmost layer of adsorbent which first comes in contact with the strong solution fed, at first adsorbs solute rapidly and effectively, and whatever a little amount of it left in the solution unadsorbed is then removed by the layers of adsorbent in the lower part of the bed. The effluent leaving the adsorbent bed from the bottom is

practically a solute-free carrier fluid (i.e., concentration of solute in the effluent is zero). The topmost layer of the bed gets saturated with adsorbed solute (thus exhausted) and the bulk of the adsorption takes place over a relatively narrow adsorption zone in which the concentration changes very rapidly. If solution continues to flow, the adsorption zone moves gradually through the bed as a wave, with a rate ordinarily very much slower than the linear velocity of the solution in the bed. At the leading boundary of the adsorption zone, the advance solute is being adsorbed, while at the back of the zone the bed is just reaching saturation. As the zone moves downward, more and more portion of the bed gets saturated with the solute. The effluent leaving the bed is solute-free during the progress of the zone until the lower boundary of the adsorption zone coincides with the bottom of the adsorbent bed. At the moment of coincidence, the solute breaks through the bed, i.e., the solute appears in the effluent-for the first time the concentration of solute suddenly rises to an appreciable value Y_B (breakpoint/breakthrough point). Afterwards, the concentration of solute in the effluent rises rapidly as the adsorption zone passes through the bottom of the bed and reaches to Y_E (substantially close to Y_0) at which time the entire bed is practically saturated (the entire adsorption zone leaves the bed).

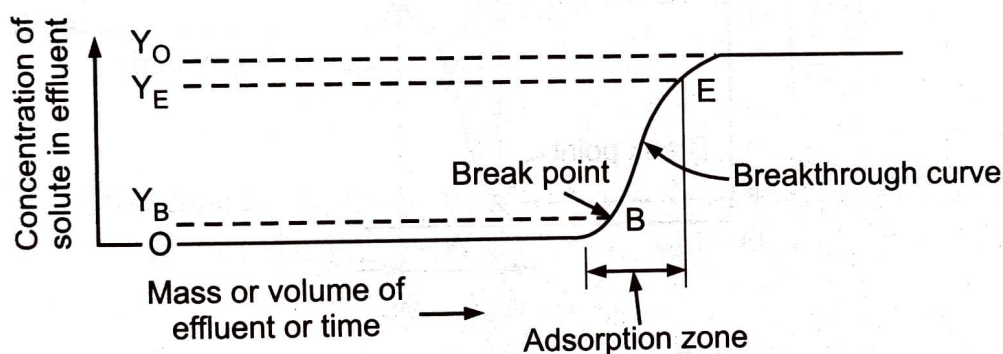


Fig. 3.12 : Adsorption breakthrough curve for adsorption at finite mass transfer rate

The portion/part of the effluent concentration curve between points B and E is termed as the breakthrough curve.

The portion of a plot of effluent concentration as a function of time between the breakpoint and time corresponding to practical saturation of the bed is termed as the breakthrough curve.

Generally, the breakthrough curve is S-shaped and it is often nearly symmetrical. The slope of the breakthrough curve is a function of the rate of adsorption. The higher the rate of adsorption, the steeper the breakthrough curve. If the adsorption process were instantaneous, i.e., infinitely rapid mass transfer rate (of adsorption) (ideal case), the adsorption zone would be of an infinitesimal width, and the breakthrough curve would be a straight vertical line from 0 to Y_0 when all the adsorbent solid was saturated.

The breakpoint - the point in time at which solute is first noticed in the effluent is often taken as a solute concentration of $Y_B = 0.05 Y_0$. Similarly, the point at which the bed is practically saturated is often taken as a solute concentration of $Y_E = 0.95 Y_0$. For the symmetrical curve, the ideal adsorption time (for the vertical breakthrough curve) is the time when $Y = 0.5 Y_0$.