CHAPTER 3

PRINCIPLES OF ADSORPTION

3.1 INTRODUCTION

In this chapter the fundamental concepts of adsorption, adsorbent, adsorbate and the factors that influence adsorption were reviewed. In addition, the experimental procedure related to the batch and columns were discussed along with the significance of isotherm and breakthrough curve.

3.2 ADSORPTION

Adsorption: “Adsorption” may be defined as the process of accumulation of any substance giving higher concentration of molecular species on the surface of another substance as compared to that in the bulk. When a solid surface is exposed to a gas or a liquid, molecules from the gas or the solution phase accumulate or concentrate at the surface. The phenomenon of concentration of molecules of a gas or liquid at a solid surface is called adsorption. “Adsorption” is a well established and powerful technique for treating domestic and industrial effluents. In water treatment, the most widely method is “adsorption” onto the surface of activated carbon.

Adsorbate: The substance that concentrates at the surface is called adsorbate.
**Adsorbent:** The material upon whose surface the adsorption takes place is called an adsorbent. Mostly activated carbon is used as an adsorbent

- Adsorbents are used usually in the form of spherical pellets, rods, moldings, or monoliths with hydrodynamic diameters between 0.5 and 10 mm.
- They must have high abrasion resistance, high thermal stability and small pore diameters, which results in higher exposed surface area and hence high surface capacity for adsorption.
- The adsorbents must also have a distinct pore structure which enables fast transport of the gaseous vapors.

Most industrial adsorbents fall into one of three classes:

- Oxygen-containing compounds are typically hydrophilic and polar, including materials such as silica gel and zeolites.
- Carbon-based compounds are typically hydrophobic and non-polar, including materials such as activated carbon and graphite.
- Polymer-based compounds are polar or non-polar functional groups in a porous polymer matrix.

Activated carbon is used for adsorption of organic substances and non-polar adsorbates and it is also usually used for waste gas (and waste water) treatment. It is the most widely used adsorbent since most of its chemical (eg. surface groups) and physical properties (eg. pore size distribution and surface area) can be tuned according to what is needed. Its usefulness also derives from its large micropore (and sometimes mesopore) volume and the resulting high surface area.
3.2.1 Mechanism of Adsorption using Adsorbent

**Figure 3.1 Mechanism of Adsorption**

**Adsorption principles:** The basic principle of operation for carbon adsorption is the mass transfer and adsorption of a molecule from a liquid or gas into solid surface. Activated carbon is manufactured in such a way as to produce extremely porous carbon particles whose internal surface area is very large. This porous structure attracts and holds organic molecules as well as certain metal and inorganic molecules. Adsorption occurs because

i) The contaminant has low solubility in the waste

ii) The contaminant has greater affinity for the carbon than for the waste

iii) A combination of two

Two most common carbon adsorption processes are the granular activated carbon (GAC) which is used in packed beds, and the powdered activated carbon. The activated carbon adsorption process is one of the most frequently applied technologies for the removal of trace organic compounds
from an aqueous solution. Adsorption is a surface phenomenon in which soluble particles from a solution are bonded onto a particular substrate. One of the most desirable properties of an adsorbent is a high surface to volume ratio. Activated carbon ratio ranging from 500 to 1000 m²/g is a good adsorbent for effective removal of organic compounds.

**Types of Adsorption:** Depending on the type of attractions between adsorbate and adsorbent, the adsorption can be divided into two types.

Forces of attraction exist between adsorbate and adsorbent. These forces of attraction can be due to Vanderwaal forces of attraction which are weak forces or due to chemical bond which are strong forces of attraction. On the basis of type of forces of attraction existing between adsorbate and adsorbent, adsorption can be classified into two types: Physical Adsorption or Chemical Adsorption.

**Physical Adsorption or Physisorption:** When the force of attraction existing between adsorbate and adsorbent are weak Vanderwaal forces of attraction, the process is called Physical Adsorption or Physisorption. Physical Adsorption takes place with formation of multilayer of adsorbate on adsorbent. It has low enthalpy of adsorption i.e. ΔH adsorption is 20-40KJ/mol. takes place at low temperature below boiling point of adsorbate. As the temperature increases in, process of Physisorption decreases.

3.2.2 **Characteristics of Physisorption**

**Energetics and kinetics:** Physisorption is an exothermic process. However it is characterized by low enthalpy values (20–40 kJ mol⁻¹), due to
weak van der Waals forces of attraction. The activation energy for physisorption is also very low and hence it is practically a reversible process.

**Effect of temperature:** Since physical adsorption is an exothermic process, it occurs more readily at lower temperatures and decreases with increase in temperature (Le-Chatelier’s Principle).

**Effect of pressure:** In case of physisorption of gases over solids, the extent of adsorption increases with increase in pressure as the volume of the gases decrease during adsorption (Le-Chatelier’s Principle).

**Specificity:** Since the van der Waals’ forces are universal, a given surface of an adsorbent does not show any preference for an adsorbate in physisorption i.e. it is not specific with respect to adsorbent.

**Nature of adsorbate:** However, the extent of adsorption depends on the nature of gas (adsorbate). In general, easily liquefiable gases with higher critical temperatures) are readily adsorbed as the van der Waals’ forces are stronger, especially, near the critical temperatures.

**Surface area of adsorbent:** The extent of adsorption increases with the increase of surface area of the adsorbent. Hence finely powdered metals and porous substances having large surface areas perform well as adsorbents.

**Chemical Adsorption or Chemisorption:** When the force of attraction existing between adsorbate and adsorbent are chemical forces of attraction or chemical bond, the process is called Chemical Adsorption or Chemisorption. Chemisorption takes place with formation of unilayer of adsorbate on adsorbent. It has high enthalpy of adsorption. It can take place at
all temperature. With the increases in temperature, Chemisorption first increases and then decreases.

3.2.3 Characteristics of Chemisorption

Energetics and kinetics: Chemisorption is also an exothermic process and the enthalpy values are higher (80-240 kJ mol$^{-1}$) as it involves formation of chemical bonds. However, the activation energy for chemisorption is high and occurs slowly. Hence it is also called activated adsorption. It is practically irreversible.

Effect of temperature: Even though chemical adsorption is an exothermic process, it does not occur slowly at lower temperature due to high kinetic energy barrier. Hence, like most chemical changes, the extent of chemisorption increases with increase in temperature up to certain limit and then after that it starts decreasing. It is also observed that, in some cases, physisorption of a gas adsorbed at low temperature may change into chemisorption at a high temperatures.

Effect of pressure: The chemisorption is not appreciably affected by small changes in pressure. However, very high pressures are favourable for chemisorption.

High specificity: Chemisorption is highly specific and occurs only if there is some possibility of chemical bonding between adsorbent and adsorbate.

Surface area: Like physisorption, chemisorption also increases with increase of surface area of the adsorbent.
Factors influencing adsorption: Adsorption on a solid is influenced by a number of factors such as,

- Surface area
- Nature of the adsorbate
- Hydrogen ion concentration (pH) of the solution
- Temperature
- Mixed solutes and
- Nature of adsorbate

Surface Area: Adsorption is a surface phenomenon and as such the extent of adsorption is proportional to specific surface area. Specific surface area can be defined as that portion of the total surface area that is available for adsorption. Thus the amount of adsorption accomplished per unit weight of solid adsorbent is greater, if the solid is more finely divided and more porous. It was found that for porous materials like activated carbon, the breaking up of large particulars to form smaller ones can in some instances serve to open some tiny, sealed channels in the carbon with might then become available for adsorption thus possibly yielding dependence of equilibrium capacity of particular size. They also showed that both the rate and extent to adsorption by particulars of a fixed carbon size should vary approximately linearly with the dosage of adsorbent over a range of doses that do not result in great differences in the concentrations of solute remaining in bulk solution phase.

Nature of adsorbate: Adsorption increases with decrease in the solubility of the solvent. Greater the solubility, stronger the solute-solvent. The solubility of the solute is to a large extent, a controlling factor for adsorption equilibrium. The landelius rule states that an inverse relationship can be anticipated between the extent of adsorption of a solute and its
solubility in the solvent from which adsorption occurs. Adsorption increases with decrease in the solubility of the solvent. Greater the solubility, stronger the solute-solvent bond and the smaller the extent of adsorption.

**Hydrogen ion concentration:** The pH of a solution from which adsorption occurs influences the extent of adsorption. Because, hydrogen and hydroxide ions are adsorbed quite strongly, the adsorption of other ions is influenced by the pH of the solution. The majority of colored materials encountered with the industry are negatively charged and ordinarily carbons will give greater decolourisation with increase in acidity of the solution, the pH of the adsorbent itself is an important factor, as this may affect the pH of the liquid.

**Temperature:** Heavy metal removal is usually greater at higher temperature. Temperature effects on adsorption equilibria are generally not significant over the range of temperature practically encountered in water and wastewaters. Thus small variations in temperature do not alter the adsorption process to any significant extent.

**Mixed solutes:** In the application of adsorption for purification of waters and wastewaters, the material to be adsorbed commonly will be mixture of many compounds rather than a single one. The compounds may mutually enhance adsorption, may act relatively a single one. The compounds may mutually enhance adsorption, may act relatively independently or may interfere with one another. In mixed solutes, each solute competes in some way with the adsorption of the other.

The degree of mutual inhibition of competing should be related to the relative size of the molecules being adsorbed, to the relative adsorptive affinities and the relative concentrations of the solutes. The presence of the
other solutes in the mixture adversely affects adsorptions of the first, leading
to much more rapid breakthrough of this material.

**Nature of adsorbent:** The physiochemical nature of the adsorbent
can have profound effects on both rate and capacity for adsorption.
Adsorption by activated carbon is a surface phenomenon and is affected by
the following parameters.

- Surface functional groups
- Structural details

Significant amount of the carbonyl and carboxyl groups are present
on activated carbon surfaces. The behaviours of activated carbon as an
adsorbent have to be related to the surface functionally of the material and the
evidence for chemical interaction at the surface between carbonyl and
carboxyl groups and organic absorbates is convincing. The adsorption
capacity of activated carbon may well be accomplished by increasing the
concentration of the appropriate functional groups.

**Adsorption of solutes from solutions:** Porus or finely divided
substances can also adsorb dissolved substances from solution. Thus activated
carbon is used to remove coloured impurities from solutions. Charcoal will
also adsorb dyestuffs. Adsorption from solution generally follows the same
principles as laid down for adsorption of gases by solids and is subject to the
same factors. Thus,

- Some adsorbents specifically adsorb certain solutes more
effectively than others.
- An increase of temperature decreases the extent of adsorption.
- An increase in surface area increases the extent of adsorption.
Adsorption of solutes also involves the establishment of equilibrium between the amount adsorbed and the concentration of the solute in solution.

The precise mechanism of adsorption from solution is not clear. However there is a limit to the adsorption by a given mass of adsorbent and hence possibly adsorption takes place unless a unimolecular layer is formed.

3.3 MODES OF OPERATION

3.3.1 Batch Flow System

In batch type contact operation, quantity of carbon is mixed continuously with a specific volume of wastewater until the pollutant in that solution has been decreased to a desired level. The carbon is then removed and either discarded or regenerated for use with another volume of solution. Batch type processes are usually limited to the treatment of small volume of effluents.

3.3.2 Column Flow System

Column type continuous flow operation appears to have distinct advantages over batch operation, because rates of adsorption depend on the concentration of the solute in solution being treated.

For Column operation, the carbon is continuously in contact with a fresh solution; consequently the concentration in the solution in contact with a given layer of carbon in a column is relatively constant. For continuous operation, solid adsorbent may be added at the top of the column and spent adsorbent withdrawn from the bottom.
Figure 3.2  Schematic diagrams of fixed bed, moving bed and fluidized bed

Figure 3.3  Fixed bed adsorption system
Three types of continuous flow systems are usually encountered namely.

- Fixed Bed Adsorption system
- Fluidized Bed Adsorption System
- Moving Beds (or) Expanded Bed Adsorption system

### 3.3.3 Fixed bed Adsorption System

This type of system is most often used to treat large quantities of wastewater in fixed bed adsorption system, the flow could be either up flow or down flow, packed bed up flow carbon columns for full counter current operation are suitable only for low turbidity water (i.e.) water having a turbidity of 2.5 JTU. Carbons finer than (8 × 30) mesh should not be used for up flow fixed beds because of clogging and high head loss problems. In liquid up flow operations, a portion of the adsorbent is usually removed periodically from the bottom and equal amount of regenerated solid is added to the top. The only reason for using a down flow bed is to make it possible to use the carbon for two purposes, adsorption of organics and removal of filtration of suspended and flocculated materials. The principal advantage of this dual use of granular carbon is that of some reduction is capital cost. The down flow bed may be fixed either in parallel or in series. Most designs consist of either two or three beds in series.

In practice, the liquid is fed continuously to either the top or bottom of a stationary bed of solid adsorbent. The solid adsorbs increasing amounts of solute with time and unsteady-state condition prevails. When the adsorptive capacity of the solid is approached, it is regenerated for reuse. In liquid down flow operation, the entire contents of the column are regenerated after exhaustion.
3.3.4 Break through Curve

Consider a down flow fixed bed adsorber. Initially the feed solution is in contact with fresh adsorbent at the top of this 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 traverses the portion of the column below the adsorption zone. Because of equilibrium and kinetic factors, however, some low concentration of solutes escapes in the effluent. As more fluids enter the column, the upper portion of the solid becomes saturated with solute and the adsorption zones moves 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. This point is called break point is called break through curve. Little additional adsorption occurs after the breakpoint since the entire bed is approaching equilibrium with the feed.

Figure 3.4 is an idealized breakthrough curve expressed in terms of the mass concentration of the solute free in effluent, $C$ and the total mass quantity of solute free water $V_e$ which has passed a unit cross sectional area of the adsorber. The breakthrough curve is idealized in one sense by the assumption that removal of solute is complete over the initial stages of operation. In practice, the break point is chosen arbitrarily at some low value $C_x$, closely approaching $C_o$, the sorbent is considered to be essentially exhausted. Mass units for $C$ and $V_c$ are used to illustrate the concept of mass balance in the adsorption system.

- The mass quantity of the effluent, $V_b$ passed per unit cross section to the break point. The nature of the break through curve between the values $V_b$ and $V_x$. 
Figure 3.4 Ideal break through curve

where, $C_0$ - Initial concentration of solute

$V_b$ - Total mass quantity of effluent passed per unit cross section to the breakpoint.

$C_b$ - Breakpoint chosen at some low arbitrary value

$V_x$ - Adsorption zone from the break point to exhaustion

$M_s$ - Adsorption zone from the break point to exhaustion

For most adsorption operation in water and wastewater treatments, breakthrough curve exhibit a characteristics S - shape. As a general rule, the time to break point is decreased by

- Increased particle size of carbon
- Increased concentration of the solute in the effluent
- Increased pH of the wastewater
- Increased flow rate
- Decreased bed depth
The break through curve is more advantageously used to note the stages at which the regeneration is to be done or fresh carbon is to be added.

3.3.5 **Pilot Carbon Test**

Although the treat ability of a particular wastewater by activated carbon and the relative capacity of different types of carbon for treatment may be estimated from adsorption isotherms, carbon performance and design criteria are best done by pilot tests. Pilot tests provide much more accurate estimates of the performance that can be expected in a full-scale unit.

Information which can be obtained from pilot test includes,

- Type of carbon
- Contact time
- Bed depth
- Pre-treatment requirement
- Carbon dosage in terms of kilogram per million liters of wastewater
- Break through characteristics
- Back wash flow rates

3.3.6 **Carbon Regeneration System**

To make activated carbon economically feasible for wastewater treatment in most applications, the exhaust carbon must be regenerated and reused. When the plant effluent quality reaches the minimum effluent quality standards or when a predetermined carbon dosage is achieved, spent carbon is removed from the column and regenerated. There are four general methods
namely solvent wash, acid or caustic wash, stream activation and thermal regeneration for reactivating granular carbon.

3.3.7 Adsorption Isotherm

Adsorption process is usually studied through graphs known as adsorption isotherm. Adsorption is the amount of adsorbate on the adsorbent as a function of its pressure or concentration at constant temperature. The quantity adsorbed is nearly always normalized by the mass of the adsorbent to allow comparison of different materials. From the above we can predict that after saturation pressure $P_s$, adsorption does not occur anymore, that is there are limited numbers of vacancies on the surface of the adsorbent. At high pressure a stage is reached when all the sites are occupied and further increase in pressure does not cause any difference in adsorption process. At high pressure, adsorption is independent of pressure.

![Figure 3.5 Adsorption Isotherm](image)
3.3.8 Types of Adsorption Isotherm

3.3.8.1 Type I adsorption isotherm

The above graph depicts Monolayer adsorption. This graph can be easily explained using Langmuir Adsorption Isotherm. Examples of Type-I adsorption are Adsorption of Nitrogen ($\text{N}_2$) or Hydrogen (H) on charcoal at temperature near to -1800°C.

![Type I Adsorption Isotherm](image)

Figure 3.6 Type I Adsorption Isotherm

3.3.8.2 Type II adsorption isotherm

Type II Adsorption Isotherm shows large deviation from Langmuir model of adsorption. The intermediate flat region in the isotherm corresponds to monolayer formation. Examples of Type-II adsorption are Nitrogen ($\text{N}_2$ (g)) adsorbed at -1950°C on Iron (Fe) catalyst and Nitrogen (N2 (g)) adsorbed at -1950°C on silica gel.
3.3.8.3 Type III adsorption isotherm

At lower pressure region of graph is quite similar to Type II. This explains formation of monolayer followed by multilayer. The intermediate flat region in the isotherm corresponds to monolayer formation. The saturation level reaches at a pressure below the saturation vapor pressure. This can be explained on the basis of a possibility of gases getting condensed in the tiny capillary pores of adsorbent at pressure below the saturation pressure (PS) of the gas. Examples of Type IV Adsorption Isotherm are of adsorption of Benzene on Iron Oxide (Fe₂O₃) at 500°C and adsorption of Benzene on silica gel at 500°C.
3.3.8.4 Type IV adsorption isotherm

At lower pressure region of graph is quite similar to Type II. This explains formation of monolayer followed by multilayer. The intermediate flat region in the isotherm corresponds to monolayer formation. The saturation level reaches at a pressure below the saturation pressure ($P_s$) of the gas. Example of Type IV adsorption isotherm is adsorption of Benzene on Iron oxide at 500°C and adsorption of Benzene on Silica gel at 500°C.
3.3.8.5 Type V adsorption isotherm

Explanation of Type V graph is similar to Type IV. Example of Type V Adsorption Isotherm is adsorption of Water (vapors) at 1000°C on charcoal. Type IV and V shows phenomenon of capillary condensation of gas.

Figure 3.10 Type V Adsorption Isotherm
3.3.8.6 Freundlich adsorption isotherm

In 1909, Freundlich expressed an empirical equation for representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. This equation is known as Freundlich Adsorption Isotherm or Freundlich Adsorption equation or simply Freundlich Isotherm.

\[
\frac{x}{m} = kP^n
\]  

(3.1)

where \( \frac{x}{m} \) - adsorption per gram of adsorbent which is obtained by dividing the amount of adsorbate (x) by the weight of the adsorbent (m).

\( P \) - Pressure, \( k \) and \( n \) are constants whose values depend upon adsorbent and gas at particular temperature.

Though Freundlich Isotherm correctly established the relationship of adsorption with pressure at lower values, it failed to predict value of adsorption at higher pressure. This relation is called as the Freundlich adsorption isotherm. As see the following diagram. The value of \( \frac{x}{m} \) is increasing with increase in \( p \) but as \( n>1 \) it does not increase suddenly. This curve is also called the Freundlich isotherm curve.
Taking the logarithms of a first equation

\[
\frac{\log(x)}{m} = \log k + \frac{1}{n} \log P
\]  

(3.2)

Hence, if a graph of log \( x/m \) is plotted against log \( p \), it will be a straight line in the following diagram.
From this the value of slope equal to \( 1/n \) and the value of intercept equal to \( \log k \) can be obtained. Over and above, it the graph of \( \log x/m \) against \( \log p \) comes out to be a straight line, it can be assured that the Freundlich adsorption isotherm is satisfied for this system.

### 3.3.8.7 Langmuir adsorption isotherm

In 1916, Irving Langmuir published a new model isotherm for gases adsorbed to solids, which retained his name. It is a semi-empirical isotherm derived from a proposed kinetic mechanism. This isotherm was based on different assumptions one of which is that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.

It is based on four assumptions:

i) The surface of the adsorbent is uniform, that is, all the adsorption sites are equivalent.

ii) Adsorbed molecules do not interact.

iii) All adsorption occurs through the same mechanism.

iv) At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

Langmuir suggested that adsorption takes place through this mechanism:

\[
A(g) + B(s) \xrightarrow{\text{Adsorption}} AB \xleftarrow{\text{Desorption}}
\]

where, \( A(g) \) - Unadsorbed gaseous molecule
B(s) - Unoccupied metal surface
AB - Adsorbed gaseous molecule.

The direct and inverse rate constants are \( k \) and \( k^{-1} \)

Based on his theory, Langmuir derived an equation which explained the relationship between the number of active sites of the surface undergoing adsorption and pressure. This equation is called Langmuir equation.

\[
\theta = \frac{KP}{1 + KP}
\]

where, \( \theta \) - the number of sites of the surface which are covered with gaseous molecule,

\( P \) - pressure

\( K \) - is the equilibrium constant for distribution of adsorbate between the surface and the gas phase.

The basic limitation of Langmuir adsorption equation is that it is valid at low pressure only. At lower pressure, \( KP \) is so small, that factor \((1+KP)\) in denominator can almost be ignored. So Langmuir equation reduces to denominator is nearly equal to \( KP \). So Langmuir equation reduces to

\[
\theta = KP
\]
3.4 SUMMARY

In this chapter, the fundamental concepts of adsorption, adsorbent and adsorbate have been discussed along with the adsorption principles and adsorption isotherms. In the next chapter, the methods of preparation of sludge powder and the proposed activated carbon from seeds of gooseberries and shells of almond and wood apple will be discussed.