CHAPTER 3

ADSORPTION PRINCIPLES

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PRACTICES
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ADSORPTION PRINCIPLES AND PRACTICES

3.1 ADSORPTION PRINCIPLES

At the boundary between two different molecular species high surface concentration can occur locally. This trapping of molecules near a surface is termed as sorption. If the molecules trapped may be retained at the surface, then it is termed as adsorption. If the molecules diffuse through the surface into the bulk of the materials, then it is termed as absorption. So, adsorption is the concentration of a substance at the interface between two phase’s [8].

3.2 TYPES OF ADSORPTION

Adsorption occurring as a result of Vanderwaal’s forces is generally termed “physical adsorption”, a term which has come to represent cases in which the adsorbed molecules are not affixed to the specific site at the surface, but are, rather free to undergo transitional movement within the interface. Adsorption of this type is sometimes referred to as “ideal” adsorption.

If the adsorbate undergoes chemical interaction within the adsorbent, the phenomenon is referred to as “chemical adsorption”, “activated adsorption” or “chemisorption”. Chemically adsorbed molecules are considered not to be free to move on the surface or within the interface.

3.3 MECHANISM OF ADSORPTION BY CARBON

When a liquid containing impurities is brought into contact with a carbon, the attraction of the carbon for the impurities is greater than the attraction of the liquid for the impurities. The carbon, therefore, adsorbs the impurities such as colouring pigments, odour, flavour and heavy metals, until an equilibrium is reached, after which the carbon will no longer remove the substances from that particular solution. The adsorption process can be pictured as one in which molecules leave solution and are held on the solid surface by chemical and physical bonding. The fact that
activated carbon has an extremely large surface area per unit weight makes it an extremely efficient adsorptive material.

3.4 ADSORPTION EQUILIBRIUM AND THE ADSORPTION ISOTHERMS

Positive adsorption in a solid-liquid system, results in the removal of solutes from solution and their concentration at the surface of the solid to such time as the concentration of the solute remaining in solution is in dynamic equilibrium with that at the surface. At this position of equilibrium there is a defined distribution of solute between the liquid and solid phases. The plot of the amount of solute adsorbed per unit weight of solid adsorbent 'qe' and equilibrium concentration 'C' is termed as "Adsorption isotherm" (Fig 3.1).

Fig. 3.1 Graphical Representation of Adsorption Isotherm

Several types of isothermal adsorption relation have been developed. The most common relationship between qe and C obtains for systems in which adsorption from solution leads to the deposition of an apparent single layer of solute molecules on the surface of the solid. Equations that are often used to describe the experimental isotherm data were developed by:

a) Freundlich
b) Langmuir and
c) Brunauer, Emmet and Teller (BET) isotherm

The general form of FREUNDLICH ISOTHERM equation is

\[ q_e = K_F \cdot C^{1/n} \]

Where,

- \( q_e \) - Amount adsorbed per unit weight of adsorbent (carbon)
- \( C \) - Equilibrium concentration of adsorbate in solution after adsorption
- \( K_F \) & \( n \) - Empirical constants

The constants \( K_F \) and \( n \) in this equation can be evaluated by plotting \( q_e \) Versus \( C \). The amount adsorbed, \( q_e \), is equal to \((C_0 - C) / D_0\), \( C_0 \) being the initial concentration of adsorbate or other contaminant and \( D_0 \) the dosage of carbon, that is weight per unit volume. The data are usually fitted to the following logarithmic form of equation, which is illustrated in the Fig 3.2.

\[ \log q_e = \log K_F + \frac{1}{n} \log C \]

![Graphical Representation of Freundlich Isotherm](image)

**Fig. 3.2 Graphical Representation of Freundlich Isotherm**
The LANGMUIR ISOTHERM equation is derived from rational consideration and is given by:

\[
q_e = \frac{Q_0 \times b c}{1 + b c}
\]

Where

- \(q_e\) = amount adsorbed per unit weight of adsorbent (carbon)
- \(Q_0\) = the number of moles of solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface
- \(b\) = a constant related to the energy
- \(c\) = equilibrium concentration of adsorbate in solution after adsorption.

The simplified form of the BET ISOTHERM equation is

\[
q_e = \frac{Q_0 \times B \times C}{(C_s - C) \left[ 1 + (B - 1) \left( \frac{C}{C_s} \right) \right]}
\]

in which ‘\(C_s\)’ is the saturation concentration of the solute, ‘\(C\)’ is the measured concentration in solution at equilibrium, ‘\(Q_0\)’ is the number of the moles of solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface, ‘\(q_e\)’ is the number of moles of solute adsorbed per unit weight at concentration ‘\(C\)’ and ‘\(B\)’ is a constant expressive of the energy of interaction with the surface.

### 3.5 SIGNIFICANCE OF ISOTHERMS

The adsorption isotherm would consist of a curve, plotted with residual adsorbate in the sample as the abscissa and the adsorbate adsorbed per gram of carbon as the ordinate. A reading taken at any point on the isotherm gives the amount of
adsorbate adsorbed per unit weight of carbon, which is the carbon adsorptive capacity at a particular adsorbate concentration and at the sample temperature.

From an isotherm test, it can be determined, whether or not a particular degree of heavy metal removal can be effected by adsorption alone. It will show the approximate adsorptive capacity of the carbon for the application and provide a rough estimate of the carbon dosage required. Isotherm tests also afford a convenient means of studying the effects of pH and temperature on adsorption.

3.6 FACTORS INFLUENCING ADSORPTION

Adsorption on a solid is influenced by a number of factors such as
i Surface area
ii Nature of the adsorbate
iii Hydrogen ion concentration (pH) of the solution
iv Temperature
v Mixed solutes and
vi Nature of adsorbent

3.7 MODES OF OPERATION

3.7.1 BATCH FLOW SYSTEM

In batch type contact operation, a known 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.

3.7.2 CONTINUOUS FLOW SYSTEM

In 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. Three types of continuous flow systems are usually encountered. Namely,
1. Fixed-bed adsorption system.
2. Fluidized-bed adsorption system.
3. Moving bed or expanded bed adsorption system

Among the three, conventional fixed bed (fig.3.3) adsorption techniques are widely used for water and wastewater treatment.

![Schematic Diagrams of Fixed, Moving and Fluidized beds.](image)

**3.8 THE BREAK THROUGH CURVE**

Considering a down flow fixed-bed adsorbent column, initially the feed solution is in contact with fresh adsorbent at the top of this column. Solute is adsorbed progressively from the liquid as it flows down the column. 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 solute escapes in the effluent. As more fluid enters the column, the upper portion of the solid becomes saturated with solute and adsorption zone moves down the column like a slowly moving wave. (Fig. 3.3). 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 and a plot of effluent solute concentration versus time, after the break point is called, break through curve (Fig. 3.4).

Break-through curve exhibits a characteristic S – shape, but with varying degrees of steepness and deposition of break point. At a general rate, the time to break point is decreased by
1. increased particle size of carbon  
2. increased concentration of the solute in the effluent  
3. pH of water  
4. increased flow rate  
5. 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.

Fig. 3.4 Movement of Adsorption Zone for Fixed Bed, Down Flow Adsorber.

3.8.1 PILOT CARBON TEST

Although the treatability of a particular wastewater by activated carbon and the relative capacity of different types of carbon for treatment may be estimated from adsorption isotherm, 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. Pieces of information which can be obtained from pilot tests include,
I. Type of carbon

II. Contact time

III. Depth

IV. Pre-treatment requirement

V. Carbon dosage in terms of kilogram per million litres of wastewater or kilogram organic material removed per kilogram of carbon.

VI. Break-through characteristics

VII. Backwash flow rates

VIII. Effect of biological activity including possible extension of the carbon capacity as well as potential deleterious effect such as generation of hydrogen sulfide.

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Co = Initial Concentration of Solute

Vb = Total Mass Quantity of Effluent Passed per unit cross section to the Break Point

Cb = Break Point chosen at some Low Arbitrary Value

Vx = Effluent Concentration chosen Arbitrarily

Ms = Adsorption Zone from the Break Point to Exhausion

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Fig. 3.5 Ideal Break through Curve
3.9 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 for reactivating granular carbons - Solvent wash, acid or caustic soda wash, steam reactivation and thermal regeneration.