Chapter 2

ADSORPTION TECHNOLOGY: THEORY AND PRACTICE

2.1 Definition
Adsorption is a surface phenomenon, which arises due to interactions between the individual atoms, ions or molecules of an adsorbate and those present in the adsorbent surface. Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). The process involves an array of phenomena that can alter the distribution of the solute among the constituent phases and in the interfaces (Weber et al., 1991). The process is accompanied by separation of the solute from one phase to another following its accumulation at the surface of the latter.

2.2 The literature on adsorption
Adsorption is operative in most natural physical, biological, and chemical systems, and is having a large number of industrial applications. The ability of some solids to remove colour from solutions containing dyes has been known for over a century, but the chemical principles underlying such phenomena were not well understood prior to the early twentieth century. Similarly, air contaminated with unpleasant odors could be rendered odorless by passing the same through a tube packed with charcoal that separates the odour components from air. Some of the earliest contributions towards understanding the process of adsorption are:

- Wolochow (1942) pointed out first the use of a solid adsorbent for dehumidifying blast furnace gases. Six silica gel units treated one million cubic metres of air per second. This is an example of one of the earliest application of adsorption in industry.

- Mantell (1945) correlated the practical, commercial and engineering aspects of adsorption on fuller’s earth and activated clays, aluminium oxide based materials, bone char and related materials, decolorizing and water treatment carbons, metal and medicinal adsorbent chars, gas adsorbent carbons, silica gel, magnesia and
hydrous oxides, etc…This is the first detailed description of early commercial practices of adsorption process. The oil industry used naturally occurring clays to refine oils and fats almost from the beginning in the first part of the twentieth century. Clay minerals were used extensively for removing grease from woolen materials. Another mineral, which was widely used as a drying agent, was refined bauxite used for decolourizing residual oil stocks. Activated carbon had wide applications for purification of air, where the multibed adsorption system was employed and the regeneration and reuse of carbon adsorbents were adopted and applied to other operations on a broader basis.

- Davies and Rideal (1961) described the fundamental properties of various liquid interfaces including the physics of surfaces, electrostatic phenomena, electro-kinetic phenomena, adsorption at liquid interface, reaction at liquid surfaces, properties of monolayer, diffusion through interfaces, and disperse systems and adhesion, etc.,

- Thorough investigations on microporous carbon were described by Walker et al. (1966a, 1966b) that included description of the development of molecular sieve carbons, used to separate wet gaseous streams effectively due to their comparatively less hydrophilic nature.

- Gregg and Sing (1967) put forward a critical description of the use of adsorption data for the evaluation of the surface area and pore size distribution of finely divided and porous solids. In addition to the BET method for determining the specific surface area and the use of Kelvin equation for estimating pore size distribution, the methods for estimating surface area based on adsorption from solution, and the application of Gibbs adsorption equation to gaseous adsorption were also described.

- Treybal (1968) gave a qualitative description of the single and multi-component equilibria for gaseous as well as liquid systems. Introduction to adsorption related phenomena such as molecular diffusion in fluids, mass transfer coefficients, diffusion in solids and interphase mass transfer had also been made.

- Mattson and Mark (1971) provided a critical review on the solution adsorption phenomena and interpreted the surface-related interactions of activated carbons for adsorption of a wide variety of solutes ranging from strong electrolytes to organic non-electrolytes. This included the activation of carbons, surface oxygen functional groups, neutralization of base by acidic surface oxides, spectroscopic methods for
molecular structure determination on surfaces, nature of the electrical double layer, adsorption of electrolytes and adsorption of weak and non-electrolytes from aqueous solution.

- Ponce et al. (1974) gave a detailed explanation of theoretical approaches and experimental techniques of adsorption. The methods of studying the texture of adsorbents, methods of studying adsorption, the surface structure of solids, theories of adsorption forces, adsorption kinetics and thermodynamics, theories of adsorption equilibria, the mechanisms of physisorption and chemisorption, adsorption from flowing gases and liquids, practical applications of adsorption, adsorption from solutions and the relationship between adsorption and catalysis, etc., were described elaborately.

- Barrer (1978) investigated the adsorptive properties of naturally occurring and synthesized alumina-silica minerals, known as zeolites.


- Holland and Liapis (1983) described the dynamic behaviour of separation processes. The physical adsorption of pure gases and mixtures, mass transfer by convective transport, the role of pore and surface diffusion in adsorption, separation of multi-component mixtures by using adsorption columns, thermodynamics of physical adsorption of pure gases and multi-component gas mixtures, etc., were analytically explained.

- Faust and Aly (1987) gave comprehensive information on carbon and resin based adsorptive process for potable water treatment. This text covers the physical and chemical properties of carbonaceous adsorbents, thermodynamic equilibria and their models, kinetics of batch and fixed bed systems. Applications included the adsorption of organic and inorganic compounds, operational, pilot plant and case studies, biological activated carbon treatment of drinking water, and adsorption by macro reticular resins.

- Yang (1987) explained all aspects of gas phase adsorption processes ranging from thermodynamics to the modeling and design of cyclic processes.
• Hutchins (1988) provided an account on the use of activated carbon systems for the separation of liquids. The design techniques were restricted to short cut methods such as residence time and service time.

• Cheremisinoff and Cheremisinoff (1993) provided in-depth description of adsorption by activated carbon. The principle of adsorption processes, treatment of liquids, gas phase adsorption, air pollution control and the treatment of hazardous wastes have been treated elaborately.

• Tien (1994) provided description of models and calculation procedures for the design and analysis of separation by physical adsorption. The biological carbon adsorption, adsorption with impregnated adsorbents, thermodynamics, adsorption equilibria, adsorption rate phenomena, theories of multi-component systems, etc. were thoroughly reviewed.

• Sircar (1994) explained the role of adsorption technology as a key separation technique for the process industries. The principles of pressure and vacuum swing adsorption are described with particular references to air separation for oxygen and nitrogen production.

• The recent theoretical and practical results achieved in gas-solid, liquid-solid and gas-liquid adsorption research has been reviewed in a volume edited by Toth (2002). The authors have given emphasis on the interpretation and application of different phenomena like adsorption on heterogeneous surfaces, adsorption from electrolyte solutions, polymer adsorption at solid surfaces, protein adsorption kinetics, principles and models of multicomponent adsorption, irreversible adsorption of particles, surface complexation models of adsorption, etc.

• Several reviews have appeared on water treatment through adsorption during the last few years. Jiuhui (2008) reviewed the use of adsorbents that specialize in their compositions, structures, functions and characteristics. An extensive list of low-cost adsorbents (prepared from waste materials) for water treatment was compiled by Bhatnagar and Sillanpää (2010) recently. Commercial waste (e.g., silica gel, zeolite, activated alumina, activated carbon), agricultural waste (e.g., rice and wheat waste, tea and coffee waste, coconut waste, peanut waste, vegetable/fruit peel, etc), industrial and municipal waste (fly ash, blast furnace slag and sludge, red mud, etc), etc., were the waste materials that were used to prepare the cheap adsorbents.
• Nitrate removal from water by carbon based adsorbents (powder activated carbon, granular activated carbon, carbon nano tubes, etc), natural adsorbents (clay, zeolite, etc.), adsorbents from agricultural waste (sugarcane bagasse, rice hull, coconut shell, wheat straw, etc.), adsorbents from industrial waste (fly ash, red mud, slag, etc.), biosorbent (bamboo powder, chitin and chitosan, etc.) has also been reviewed very recently (Bhatnagar and M. Sillanpää, 2011).

• The uses of natural and modified clays for adsorption of toxic dyes were reviewed by Liu and Zhang (2007). The modification of clays was achieved by acidification, calcination and treatment with organic molecules and the materials were effective in adsorbing a large number of dyes (e.g., rhodamine 3D, methyl green, methylene blue, basic blue 9, basic red 18, basic yellow 57, basic brown 16, victoria blue, congo red, direct orange, etc.) from aqueous solutions. The use of clay minerals, particularly kaolinite, montmorillonite and their modified forms (acid activation, intercalation and pillaring) to remove As(III)/As(V), Cd(II), Cr(III)/VI), Co(II), Cu(II), Fe(III), Pb(II), Mn(II), Ni(II), Zn(II), etc., from water under different conditions of pH, temperature, adsorbent amount and adsorbate concentration has also been described (Bhattacharyya K.G. and S. Sen Gupta, Adv. Colloid Interf. Sci., 2008, 140, 114–131).

• Use of natural zeolites (and those modified by treating with acids and bases or surfactants) as adsorbents for water and wastewater treatment with respect to a variety of contaminants like ammonium, heavy metals, inorganic anions, dyes and humic substances has been reviewed recently Wang and Peng, (2010).

As a consequence of all these studies and many more investigations, quantitative theories of adsorption emerged, which have endured success at the test of time. It has been found that the best results are achieved with porous solids and that adsorption occurs due to interactions between the surface atoms of the solids and the molecules being removed from the bulk phase. The adsorption could hence be described as the accumulation of concentration at a surface (Thomas and Crittenden, 1998a).

2.3 Types of Adsorption
Depending upon the nature of force existing between adsorbate molecule and adsorbent, four types of adsorption can be distinguished (Weber, 1985; Weber et al., 1991)
(i) **Physical adsorption or Physisorption**: This type of adsorption results from the action of weak van der Waals forces. These are comprised of London dispersion forces and classical electrostatic forces that are related with interactions between the dipole moments of adsorbate and adsorbent molecules. This type of adsorption is non-specific, i.e. the adsorbent does not have preference for any particular gas (Haymaker and Thompson, 1972).

(ii) **Chemical adsorption or Chemisorption**: Chemical adsorption involves strong adsorbate-adsorbent interactions resulting in a change in the chemical form of the adsorbate. Here, the gas molecules or atoms are held to the solid surface by chemical bonds. The resulting chemisorptive bond is generally stronger than that derived from the physical van der Waals forces and is very similar in strength to a covalent bond. It is highly specific and occurs only if there is some possibility of chemical bonding between adsorbent and adsorbate. The bonds that form between solute molecules and specific surface chemical groups have all the properties of true chemical bonds and are characterized by relatively large heats of adsorption.

(iii) **Exchange adsorption or ion exchange**: This involves electrostatic attachment of ionic species to sites of opposite charge at the surface of an adsorbent with subsequent displacement of these species by other ionic adsorbates of greater electrostatic affinity. In this adsorption, the characteristic interactions are ion-ion and ion-dipole type.

(iv) **Specific adsorption**: Attachment of adsorbate molecules at functional groups on an adsorbent surface can also result from specific interactions, which do not result in adsorbate transformation. These interactions exhibit a range of binding energies from values associated with physical adsorption to the higher energies involved in chemisorption. The net dispersion, electrostatic, chemisorptive, and functional-group interactions broadly define the ability of an adsorbent for a specific adsorption.

**2.4 Factors influences the extent of adsorption**

Adsorption from a solution onto a solid is dependent on a number of factors (Bernardin, 1985; Weber, 1972; 1985). Some of these are:
(i) **Characteristics of the adsorbent**

The adsorbent must have good mechanical properties such as strength and resistance to attrition and it must have good kinetic properties, that is, it must be capable of transferring adsorbing molecules rapidly to the adsorption sites. An adsorbent material must have a high internal volume, which is accessible to the components being removed from the solvent. Surface area and the distribution of area with respect to pore size are two very important factors in determining extent of adsorption. The nature of the intra-particle surface area markedly influences the types of adsorption process.

(ii) **Characteristics of the adsorbate**

The extent of adsorption relates to certain properties of the adsorbate relative to the solution phase, namely surface tension and solubility. The extent of adsorption is influenced by the solvophobicity or lyophobicity of a component in the solvent phase.

(iii) **Characteristics of the solution**

In the presence of aqueous phase, hydrogen ions and hydroxide ions often interact with adsorbents used in the system. Thus the adsorption process may be affected by solution pH (Mattson and Mark, 1971). The temperature can also remarkably influence adsorption process. The rate of adsorption usually increases with temperature (for an endothermic process) which is due primarily to the increased rate of diffusion of adsorbate molecules through the solution to the adsorbent. Temperature effects solubility which in turn affects the extent of adsorption. The presence of competing adsorbate molecules often influences the extent of adsorption. Few adsorbents demonstrate controllable selectivity for specific adsorbates and thus, all adsorbable compounds present will compete for adsorption sites.

### 2.5 Adsorption Technology

Adsorption is a process in which an adsorbate molecule is transferred from solution to the surface of an adsorbent bonded by physical/chemical forces. Any adsorbent particle has a finite capacity for adsorbate molecules and thus the interactions lead to a thermodynamic equilibrium between the adsorbent and adsorbate phases. At the equilibrium, the net loading on the adsorbent cannot increase further as the rates of
adsorption and desorption become equal. To carry out further adsorption, a fresh adsorbent surface has to be regenerated. The thermodynamics of the system ensures maximum possible interaction between the adsorbent and the adsorbate. Thermodynamic equilibrium between the adsorbate and the adsorbent is usually studied with one of the following three ways:

(i) Batch process,
(ii) Fixed bed process,
(iii) Moving bed process

(i) **Batch process**

The Batch processes are important in which the adsorbent moves relative to the walls of the containment vessel. In this process, a batch of adsorbent mixes with a batch of fluid, most commonly a liquid. After a predetermined period of time, the adsorbent and the solution are separated, either by sedimentation, filtration, decantation or centrifugation. If sufficient time is allowed for equilibrium to be reached then the loading of the adsorbent-adsorbate interactions will be related to the final concentration of the adsorbate in the solution by the thermodynamic isotherm which applies at the final temperature in the process. If the equilibrium for the adsorption is highly favorable, a single-stage batch process will reduce the concentration of solute in solution (Ruthven 1984, Ruthven and Ching 1989). When large quantities of adsorbent are to be used, a multiple batch or cross-flow system may be required. Here, the adsorbate is first contacted with a fresh batch of adsorbent. After separation of the fluid (adsorbate) from the adsorbent, the adsorbate is contacted with another fresh batch of adsorbent. Each subsequent batch of adsorbent removes less and less impurity as the concentration of the impurity in the solution decreases (Crittenden 1991).

A more competent way to perform the multiple batch-wise contacting process is to perform the adsorption steps counter-currently (Fox and Kennedy, 1985). In a counter-current process, the quantity of adsorbent required to remove a given quantity of adsorbate is substantially smaller than that required for a single stage process or a multiple-stage process utilizing fresh adsorbent in each stage.
(ii) Fixed bed process

In the fixed bed process, a degree of separation and removal is achieved that would require many steps in a batch process. The column configuration has often been modeled as a multiple-stage batch adsorption process. The uppermost portions of the bed are constantly being contacted by fresh adsorbate solution and the lower portions of the bed are contacted by solution containing adsorbate not adsorbed by the upper portion. Thus, the bed becomes fully loaded at the top of the column first and then downward. This results in the formation of an adsorption front in the column which moves downward.

The configuration of the fixed bed process is simple and relatively inexpensive to construct and the nominal attrition of adsorbent occurs when it remains fixed in position. However, the process has some disadvantages also (Thomas and Crittenden, 1998d), such as,

(i) As fluid is passed through a fixed bed of adsorbent, the transfer of adsorbate molecules from the feed to the solid initially occurs at the bed entrance. Once the adsorbent in this region becomes saturated with the adsorbate molecules, the zone in which the mass transfer occurs, moves progressively through the bed towards the exit. When breakthrough of the adsorbate begins to occur, it is necessary to take the bed off-line so that the adsorbate can be regenerated. The adsorbent particles upstream and downstream of the mass transfer zone (MTZ) don’t participate in the mass transfer processes (Lockett et al. 1992).

(ii) For any time up to breakthrough, it is practicable to take the adsorbent bed off-line. Therefore, in order to have a continuous stream of product, it is necessary to have more than one bed of adsorbent in the overall adsorption equipment. The regeneration time for the second bed must not be longer than the time to reach breakthrough of the adsorbate during adsorption in the first bed.

(iii) Adsorption is mostly an exothermic process and desorption can therefore be affected by raising the temperature of the adsorbent. In thermal swing processes it is
difficult to heat and cool large beds of highly porous adsorbent materials. Poor heat transfer leads to long heating and cooling times creates the need for large beds. Since the loading of an adsorbate is reduced by increasing the temperature of the adsorbent (Ruthven 1984).

(iv) Despite the apparent simplicity of fixed beds, they are difficult to design accurately because the progress of the mass transfer zone introduces time into the design equations. In most practical applications, sets of partial differential equations which describe the mass and heat transfer phenomenon are required to be solved (Ruthven and Ching 1989).

(iii) **Moving bed process**
Two general possibilities exist for having the adsorbent in motion. In the first, the adsorbent particles move relative to the walls of the containing vessel such that adsorption, regeneration and back-washing can take place simultaneously, though in different locations. In the second, the particles remain in a fixed position relative to the walls of the vessel. Typically, in the operating mode, all contact of adsorbent with fluid takes place for a precise period of time.

Moving bed process has several advantages. Holding tanks and adsorber duplication are not required as the process is truly continuous. Moreover, the process will achieve a steady-state of operation resulting in an effluent constant quality rather than the changing effluent concentration resulting from adsorption from the fixed bed. The continuous counter-current mode is more efficient in regeneration than fixed bed mode. But these processes also have some disadvantages as the capital costs are higher than the fixed bed systems. The operation of the process is complex and requires automatic controls and extensive process instrumentation. Attrition of the adsorbent occurs during the movement of the bed, leading to adsorbent loss and significant makeup requirements (Avery and Tracey 1968, Rowson 1963).
2.6 Selectivity of an Adsorbent

To be technically effective in a bulk separation or a purification, an adsorbent material must possess some unique characters such as high internal volume, high surface area, porosity, appropriate pore structure and suitable adsorbing surfaces, etc. The selectivity of the adsorbent is defined in terms of its ability to separate two components from each other in a mixture (Thomas and Crittenden, 1998b). The separation factor, $\alpha$, is given as:

$$\alpha_a = \frac{X_i / Y_i}{X_j / Y_j}$$

Here, $X_i$ and $Y_i$ are the equilibrium mole fractions of component i and $X_j$ and $Y_j$ are the equilibrium mole fractions of component j, in the adsorbed and fluid phases, respectively. In a particular separation process, the selectivity of an adsorbent becomes noticeable in one or more ways of the following:

(i) **Equilibrium effect**: Differences may exist in the thermodynamic equilibria for each adsorbate-adsorbent interaction which is known as the equilibrium effect.

(ii) **Kinetic effect**: Differences may exist in the rates at which different adsorbates travel into the internal structure of the adsorbent and is known as the kinetic effect.

(iii) **Molecular sieving effect**: Sometimes pore openings of the adsorbent may be too small to allow penetration by one or more of the adsorbates; this is known as the molecular sieving effect. The molecular sieving effect is an extreme case of the kinetic effect.

(iv) **Desorption effect**: When there exists some differences in the rate at which different adsorbates can be desorbed from the adsorbent, the desorption effect takes place.

The equilibrium separation factor depends on

- The nature of the adsorbent, that is, whether the surface is polar, non polar, hydrophilic, hydrophobic, etc., and
- The process conditions such as temperature, pressure and concentration.
Kinetic separation is possible only with molecular sieve adsorbents such as zeolites and carbon sieves and it is largely determined by the ratio of micro pore diffusivities of the components being separated. For a useful separation to be based on kinetics, the size of the adsorbent micro pores must be comparable with the dimensions of the diffusing adsorbate molecules.

2.7 Types of Adsorbents

Different types of conventional and non-conventional adsorbents have been used in the laboratory as well as for industrial purposes. Some of these are:

**Conventional Adsorbents**

a) Activated carbon  
b) Carbon molecular sieves (CMS)  
c) Carbonized polymers and Resins  
d) Bone charcoal  
e) Polymeric Adsorbents  
f) Silica gel  
g) Activated alumina  
h) Clay minerals  
i) Zeolites

**Non-conventional adsorbents**

a) Adsorbent from industrial wastes  
b) Adsorbent from coal  
c) Adsorbent from agricultural wastes and agricultural byproducts  
d) Peat  
e) Oxides and related materials as adsorbents  
f) River sediments as adsorbent  
g) Adsorbent from bio-resources  
h) Adsorbent made from biopolymers such as chitosan  
i) Adsorbents form various other materials
Activated carbon. Activated carbons are unique adsorbents because of their extended surface area, microporous structure, high adsorption capacity and high degree of surface reactivity (McKay, 1979; Ozcan and Ozcan, 2004; Sarma and Bhattacharyya, 2004, 2005; Ozcan et al., 2006). Mainly, the presence or absence of different surface functional groups, especially oxygen groups, causes the phenomenon of ion adsorption on activated carbons. The raw materials for activated carbons are wood, rice husk, peat, lignin, coal tar, coconut shells, etc. These are activated either by gas activation or chemical activation process. Activated carbons contain a full range of pore sizes as micro pores is shown in Table 2.1.

Table 2.1. Characteristics of typical activated carbons (Ruthven, 1984)

<table>
<thead>
<tr>
<th>Characteristics of carbons</th>
<th>Micro pores</th>
<th>Meso pores</th>
<th>Macro pores</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (nm)</td>
<td>&lt; 2</td>
<td>2 – 50</td>
<td>&gt; 50</td>
</tr>
<tr>
<td>Pore volume (cm³/g)</td>
<td>0.15 – 0.5</td>
<td>0.02 – 0.1</td>
<td>0.2 – 0.5</td>
</tr>
<tr>
<td>Surface area (m²/g)</td>
<td>100 – 1000</td>
<td>10 – 100</td>
<td>0.5 – 2</td>
</tr>
<tr>
<td>Particle density</td>
<td>(0.6 – 0.9 g/cm³)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porosity</td>
<td>(0.4 – 0.6)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Activated carbons are widely used in industrial applications like

i) Decolourization of sugar solutions,

ii) Personal protection against obnoxious and toxic gases,

iii) Solvent recovery,

iv) Volatile organic compound control,

v) Hydrogen purification, and

vi) Water treatment

Generally, activated carbons are hydrophobic and organophilic, and therefore, are extensively used for adsorbing compounds of low polarity in water treatment, decolourizing, solvent recovery and air purification, etc. The adsorption of 2, 4-dichlorophenoxyacetic acid by two powdered coal activated carbons was studied in aqueous solution (Belmouden et al., 2000). The removal of Congo red (CR) by
adsorption on various activated carbons (commercial activated carbon (CAC) and indigenously prepared activated carbons (IPAC) from raw materials like rice husk and straw bamboo dust, groundnut shell, coconut shell has yielded good results (Kannan and Meenakshisundaram, 2002). Granular activated carbon (GAC) is widely used as an adsorbent and is favorite for removal of dyes and many other pollutants from water, (Sarma and Bhattacharyya, 2004; 2005; Ozcan et al., 2006) Normally, the activated carbon is used to reduce and recover organic compounds in effluent streams (Srinivasan et al., 1990; Kikic et al., 1996). Activated carbon adsorption is a well-known method for the removal of heavy metals (Cheremisinoff and Ellerbush, 1979; Pollard et al., 1992; Lalvani et al., 1998; Gupta et al., 2003) but the high cost of activated carbon restricts its large-scale use for the abatement of heavy metal pollution in developing countries. Powdered activated carbon (PAC) can also be used directly, because it is easier to handle and is widely used in water treatment, usually in batch applications. Kadirvelu and Namasivayam, (2003) investigated the feasibility of using carbonized coir pith for removal of Cd(II) from water. The adsorption of Zn(II) onto different commercial activated carbons has been done by Ramos et al. (2002).

**Carbon molecular sieves (CMS).** Special manufacturing process is used for obtaining amorphous carbons in the form of Carbon Molecular Sieves (CMS), which have a very narrow distribution of pore sizes with effective diameters ranging from 0.4 – 0.9 nm. Raw materials can be chemicals such as polyvinylidene dichloride and phenolic resins, or naturally occurring materials such as anthracite or hard coals. The pore structure of activated carbons can be modified to produce a molecular sieve carbon by coating the pore mouths with a carbonized or coked thermosetting polymer giving good kinetic properties with desired selectivity. The surface is essentially non-polar type. The main application of CMS is in the production of high purity nitrogen from air by pressure swing adsorption (Cabrera et al. 1993). Carbon molecular sieves in the 1970s was obtained from a coal-based material with modification of the underlying carbon pore structure by depositing carbon in the pore mouths through the cracking of an organic material (Thomas and Crittenden, 1998).
Carbonized polymers and Resins. Resins such as phenol formaldehyde and highly sulphonated styrene/divinyl benzene macroporous ion exchange resins can be pyrolysed to produce carbonaceous adsorbents, which have macro-, meso-, and micro-porosity. Surface areas may be as high as 1100 m²/g. These adsorbents are usually more hydrophobic than granular activated carbon and therefore, one important application is the removal of organic compounds from water.

Bone charcoal. These are produced by carbonizing the animal bones. They have only meso- and macro-pores with surface area of ~ 100 m²/g. The surface has carbon and hydroxyl apatite in roughly equal proportions. This dual nature makes the bone charcoal a useful adsorbent for metals as well as organic chemicals from aqueous solutions. The adsorption of Cu(II), Zn(II) and Cd(II) on bone char has been reported by Ko et al, (2004).

Polymeric Adsorbents. A broad range of synthetic, non-ionic polymers is available for analytical chromatography separations. For industrial applications, commercially available resins in bead form (typically 0.5 mm diameter) are based on co-polymers of styrene/divinyl benzene and acrylic acid esters/divinyl benzene and have a range of surface polarities. The monomer emulsions polymerize into polymer matrix with surface areas up to 750 m²/g. Selectivity of the adsorbents is determined by the structure-controlled distribution of pore sizes, high surface areas and chemical nature of the matrix. These materials are used for the recovery of a wide range of solutes from the aqueous phase, including phenol, benzene, toluene, chlorinated organics, PCBs, pesticides, antibiotics, acetone, ethanol, detergents, emulsifiers, dyes, steroids, amino acids, etc. Regeneration may be effected by steam desorption, solvent elution, pH change and chemical extraction. Polyacrylamidoxime fiber, a fibrous sorbent containing chelating amidoxime groups –C(NH₂)=NOH prepared from the Romanian commercial polyacrylonitrile-based fiber Melana has been found to be a good adsorbent for the removal of Hg²⁺ from aqueous solutions (Bilba et al., 2007).

Silica gel. These are partially dehydrated polymeric form of colloidal silicic acid. These adsorbents have pore size and surface area in the range 6–25 nm and 100–850 m²/g.
respectively. The surface comprises mainly Si-OH and Si-O-Si groups, and, being polar, these are mainly used in separation of aromatics from paraffins and chromatographic separation of organic molecules. However, the use of chromatography and desiccant silica gel for Pb(II), Cu(II), Ni(II), Zn(II), Cd(II) (Tran et al, 1999), poly(ethyleneimine) silica gel for Pb(II), Zn(II), Cd(II), Ni(II) (Ghoul et al., 2003), grafted silica for Cu(II) and Pb(II) (Chiron et al., 2003) has been reported. A microporous organosilica incorporating various amounts of sulphonyl groups (MS-SO$_3$H) and having a regular porous structure has proved as a successful adsorbent for ammonia. (Matsumoto et al., 2006). Typical properties of adsorbent grade silica gel are presented in Table 2.2 (Keller et al., 1987)

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Adsorption properties</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area (m$^2$/g)</td>
<td>H$_2$O at 4.6 mm Hg, 25$^0$C</td>
<td>11</td>
</tr>
<tr>
<td>Density (kg/m$^3$)</td>
<td>H$_2$O at 17.5 mm Hg, 25$^0$C</td>
<td>35</td>
</tr>
<tr>
<td>Reactivation temperature ($^0$C)</td>
<td>O$_2$ at 100 mmHg, 25$^0$C</td>
<td>22</td>
</tr>
<tr>
<td>Pore volume (%)</td>
<td>CO$_2$ at 250 mm Hg, 25$^0$C</td>
<td>3</td>
</tr>
<tr>
<td>Pore size (nm)</td>
<td>n-C4 at 250 mm Hg, 25$^0$C</td>
<td>17</td>
</tr>
<tr>
<td>Pore volume (cm$^3$/g)</td>
<td>0.42</td>
<td></td>
</tr>
</tbody>
</table>

**Activated alumina.** These are the porous, high surface area forms of aluminium oxide. Their surfaces are amphoteric in nature, having both acidic and basic characteristics. The surface area is in the range of 250 to 350 m$^2$/g. Activated alumina has been used earlier as a desiccant for warm gases including air but nowadays, it is replaced by zeolites. Alumina is also used in chromatography and drying of liquids, like gasoline fractions and chlorinated hydrocarbons. The use of activated alumina to remove arsenite and arsenate for ground water has also been discussed (Babel et al., 2003).

**Clay minerals.** The use of clay minerals as adsorbents is of particular interest because of their large specific surface areas (Carnerio et al., 2004). An alternative adsorbent is
the modified clay proposed by Coelho et al. (2001). Clays are found in natural deposits, but also can be synthesized. They comprise of layered silicates, which imbibe guest molecules between their siliceous layers causing their crystals to swell. Fuller’s earth is an activated natural montmorillonite. Its pore size is altered and its surface area is increased by acid treatment to 150 – 250 m$^2$/g. It is relatively inexpensive and can be used for re-refining edible and mineral oils, adsorbing toxic chemicals, removing pigments, etc. The space between the natural layers in clays can be enlarged to form pillared clays by introducing cations with polynuclear metal ion hydro-complexes, such as those of polyvalent metal ions such as Al (III) or Zr (IV). The use of pillared clays includes the separation of oxygen and nitrogen, isomers and some metals and dyes. Commercially available clay, kaolin is an effective adsorbent for the removal of Cr(III) from chromium bearing liquid waste (Bandyopadhyay et al., 2005). Two organoclays, hexadecyltrimeylanmonium bentonite clay (HDTMA-clay) and benzyltriethylammonium bentonite clay (BTEA-clay) are capable of simultaneously removing benzene and either Zn, Cd, Hg, or Pb from aqueous solution (Fullar et al., 2006).

**Zeolites.** Zeolites are intrinsically microporous aluminosilicates of the general formula [(AlO$_2$)$_x$ (SiO$_2$)$_y$].mH$_2$O and can be considered as open structures of silica in which aluminium has been substituted in a fraction $x / (x + y)$ of the tetrahedral sites. Cavities or cages are contained within the framework of zeolites and are connected by pores. These pores are of molecular dimensions and the adsorbate molecules can infiltrate into these pores. The process of adsorption and desorption of molecules in zeolites are based on differences in molecular size, shape and other properties such as polarity. Some typical applications of zeolites in pollution control, including removal of Hg, NO$_x$ and SO$_x$ from gases, purification of silanes, drying of refrigerants and organic liquids, separation of solvent systems, etc. Different types of natural and modified zeolites are well known due to their metal adsorptive properties. Some of them are: natural zeolites for Zn(II), Cu(II) and Pb(II) (Peric et al., 2004), natural and cysteamine hydrochloride- and cystamine dihydrochloride-zeolite for Hg(II) (Gebremedhin-Haile et al., 2003), amine-modified zeolites for Pb(II)and Cd(II) (Wingenfelder et al., 2005), etc.
Non-conventional adsorbents. Various non-conventional and low cost adsorbents have been tried for removal of pollutants from water. Some of these are:

(a) Adsorbents from industrial wastes

Fly Ash. A considerable amount of research has been devoted to the search of inexpensive adsorbents especially developed from various industrial waste materials. Fly ash, a coal combustion residue of thermal power plants is one of the cheapest adsorbents having excellent removal capabilities for heavy metals, Fluoride (Panday et al., 1985; Dzombak et al., 1986; Chaturbedi et al., 1990; Bayat, 2002a; 2002b) and phenol and substituted phenols (Singh et al., 1994) from wastewater. Adsorption capacity of fly ash has been found to increase with increase in temperature. The fly ash could be easily solidified after the heavy metals are adsorbed. However, since it also contains heavy metals, the possibility of leaching should be considered and evaluated. Bagasse fly ash, a waste material from sugar industry, has been tried for removal of pesticides, lindane and malathion (Gupta et al., 2002) and heavy metals, Cu(II) and Zn(II) (Gupta and Ali, 2000), Pb(II) and Cr(VI) (Gupta and Ali, 2004). The removal of Pb(II) (Mathur & Rupainwar, 1988), bottom ash from thermal power plants (Kaur et al., 1991), steel-plant granulated slag (Loomba & Panday, 1993), oil-palm fibre and coconut husk (Latif & Jaafar, 1989), coconut-shell carbon (Arulanathan et al., 1989), peanut-hull carbon (Periasamy & Namasivayam, 1996), waste Fe(III)/Cr(III) hydroxide (Namasivayam & Ranganathan, 1995) have also been tried for the removal of lead from wastewaters. The utility of bagasse pith for removing Hg(II) has been explored (Anoop Krishnan and Anirudhan, 2002). Pith has also been used for the removal of dyes, namely, basic red 22 and acid red 114 (Ho and McKay, 1999b). The adsorption capacity of blast furnace sludge (which is a by-product of steel-making industry), was studied with the adsorption of heavy metals namely, Cu(II), Ni(II) and Zn(II) (Dimitrova, 1996), Pb(II), Zn(II), Cd(II), Cu(II) and Cr(III) (Lopez-Delgado et al., 1998) and Pb(II) and Cu(II) (Curkovic et al., 2001). Red mud is a waste material formed in the Bayer process of alumina production in the aluminium industries, which has been used for the adsorption of Cu(II), Zn(II), Ni(II) and Cd(II) (Lopez et al., 1998) as well as for Pb(II) and Cr(VI) (Gupta et al., 2001a).
(b) Adsorbents from coal
Coal and coal based adsorbents have played an important role in pollution control due to their availability and cost effectiveness. The removal of Cd (II) using coal was intensively investigated (Bhattacharya et al., 1984). Exploration of lignite coal for Cr(VI) (Kannan and Vanangamudi, 1991) and Pb(II) (Balasubramanian and Jafar Ahamed, 1998) and bituminous coal for Pb(II) (Rawat et al., 1993) and Hg(II) (Babel et al., 2003) was also reported. Waste slurry, one of the industrial by-products generated in fertilizer plants shows good sorptive property for removal of Cu(II), Cr(VI), Hg(II) and Pb(II) from aqueous solution (Babel et al., 2003). Similarly lignin was used to adsorb Pb (II) and Zn (II) from black liquor (Babel et al., 2003) from paper industry. Another low-cost adsorbent showing capability to adsorb heavy metals is blast-furnace slag, generated in steel plants.

(c) Adsorbents from agricultural wastes and by-products
Various adsorbents prepared from agricultural wastes are well known for their economic, abundant and eco-friendly nature. Rice husks have been used for adsorption of Ni(II) (Dadhich et al., 2004), and Cd(II) and Pb(II) (Tarley and Arruda, 2004). Sawdust has been utilised for adsorption of Cu(II) (Yu et al., 2000), Pb(II) and Cu(II) (Yu et al., 2001) and Cd(II) and Pb(II) (Taty-Costodes et al, 2003). Similarly, the adsorption of Cu(II) by tree fern (Ho, 2003) and wheat bran (Singh et al., 2004) has also been reported.

Peat moss. Peat moss, a complex soil material containing lignin and cellulose as major constituents, is a natural substance, widely available and abundant. The functional groups present in cellulose and lignin (e.g. OH) may be involved in chemical bonding and are responsible for the cation exchange capacity of peat. Peat moss has a large surface area (>200 m²/g) and is highly porous so that it can be used to bind heavy metals. Use of peat for removal of Cu(II) (Ho and McKay, 2002), and Cu(II), Ni(II), Pb(II) (Ho et al., 2002) has been known. Peat has also been used for adsorption of dyes, namely, basic blue 69 and acid blue 25 (Ho and McKay, 1998a).
(d) Oxides
The application of various natural and modified oxides has received importance as adsorbents. Naturally occurring iron oxide and manganese oxide have been used for the removal of heavy metals like Cr (VI), As (III), As(V), Ni(II), Co(II), Mg(II) in ground water and waste water (Benjamin et al., 1996; Babel et al., 2003). Fe-Al oxides have been used for the adsorption of Cu(II), Co(II), Pb(II) and Zn(II) (Violante et al., 2003) and Fe(III)/Cr(III) hydroxide for removal of Pb(II), Ni(II) and Cd(II) (Namasivayam and Ranganathan, 1998). Adsorption of As(III) and As(V) on polymetallic sea nodules (major elemental constituents of sea nodules as oxides are MnO$_2$, 31.8%, Fe$_2$O$_3$, 21.2%, and SiO$_2$, 14.2%, with traces of Cu, Ni, Co, Ca, K, Na and Mg) has been investigated (Maity et al., 2005). Lai et al. (2002) studied the adsorption of Cd(II) on goethite-coated sand. Iron oxide-coated sand (IOCS) was used for removal of both As(III) and As(V) (Thirunavukkarasu et al. 2003). Hydrous titanium oxide (HTO) has been exploited for treatment of industrial effluents contaminated with Cr(VI) (Ghosh et al., 2003).

(e) River sediments
River water (natural conditions), suspended and bed sediments play an important role in buffering higher metal concentrations of water particularly by adsorption. Generally, the adsorptive qualities of sediments of size < 50 µm has received more attention since fractions of size > 75 µm show little adsorption. Usually clay and silt fractions adsorb metal ions much better than the coarser fractions of sediment. Therefore, in river systems with high sand percentage and low clay and silt content, the overall contribution of sand to the adsorption of metal ions could be comparable to or even higher than that of the clay and silt fractions (Jain and Ali, 2000). Adsorption of Pb(II) and Zn(II) on bed sediments of the river Kali (India) (Jain and Ram, 1997) and adsorption of Cd(II) on bed sediments of the river Hindon (India) has been reported (Jain and Sharma, 2002).

(f) Adsorbents from bio-resources
Newly developed bio-adsorbent materials are known for their high versatility, metal selectivity, high tolerance for organics and ease of regeneration (Volesky, 1990). Biosorption can be defined as the ability of biological materials to accumulate heavy
metals, dyes or other pollutants from wastewater through metabolically mediated or physico-chemical pathways of uptake. Algae, bacteria and fungi and yeasts have proved to be potential metal biosorbents (Volesky, 1986). The ability of raw crab shell of *Chinonecetes opilio* to remove Pb(II), Cd(II), Cu(II), Cr(III) from aqueous solution was investigated by An et al. (2001). The adsorption of Cd(II) and Zn(II) onto dried *Fontinalis antipyretica*, a widely spread aquatic moss has also received attention (Martins et al., 2004). The use of *Tephrosia purpurea* (Wild indigo) leaf powder for uptake of Ni(II) (Murali and Suseela, 2001) and *Azadirachta indica* (Neem) leaf powder for elimination of Pb(II), Cr(VI) and Cd(II) (Bhattacharyya and Sharma, 2004; Sharma and Bhattacharyya, 2004; 2005) have also been demonstrated. Pre-treated biomass of marine algae *Durvillaea potatorum* for Cd(II) (Matheickel et al., 1999), green algae *Spirogyra* for Cr(VI) (Gupta et al., 2001b), hazelnut shell for Cd(II), Zn(II), Cr(III) and Cr(VI) (Cimino et al., 2000) and *Sphaerotilus natans* biomass for Pb(II), Cu(II), Zn(II) and Cd(II) (Pagnanelli et al. 2003) have shown potential as adsorbents.

Chitin is the second most abundant natural biopolymer after cellulose. Chitosan is produced by alkaline N-deacetylation of chitin, which is widely found in the exoskeleton of shellfish and crustaceans. Chitosan is a hydrophilic, natural cationic polymer, which is present in fungi, insects, and crustaceans. It is an effective ion-exchanger with a large number of amino groups (Evans et al., 2002). The binding ability of chitosan for metal cations is mainly due to the amine groups on the chitosan chain which can serve as coordination sites for many metals. The utilization of chitosan for Cd(II), Hg(II), Cu(II), Ni(II), Cr(VI) and Zn(II) removal was intensively investigated (Babel et al., 2003). Juang and Shao (2002) studied the adsorption of Cu(II), Ni(II) and Zn(II) on cross-linked chitosan and Chu (2002) used prawn shell chitosan for Cu(II) removal. Recently aminated chitosan beads have been used for removal of Hg(II) (Jeon and Park, 2005).

**(g) Adsorbents from various other materials**

Different low cost adsorbents from a variety of sources have been explored in recent times. Examples are:

- Wood (Asfour et al. 1985)
• Chemically treated tea leaves to remove Pb(II) (Singh et al., 1993) and polyacrylamide grafted tea leaves to remove Cd(II) (Singh et al., 2001).
• Biogas waste slurry, waste orange peel, banana pith, coir pith, (Namasivayam et al., 1995, 1996)
• Palm-fruit bunch for dyeing wastewater treatment (Nassar et al. 1995, 1997)
• Sugar industry mud (Magdy et al 1998)
• Plum kernels (Juang et al. 2000)
• Different types of ion-exchange resins for metal ion removal, viz., Duolite GT-73 ion-exchange resins for Hg(II) (Chiarle et al., 2000), Amberlite IRC-718 for Cu(II) and Zn(II) (Lin et al., 2000), and IRN77 cation-exchange resin for Co(II), Cr(III) and Ni(II) (Rengaraj et al, 2002)
• Low-grade phosphate for removal of Zn(II) and Cd(II) from aqueous solution (Kandah, 2004).

2.8 Fundamentals of Adsorption equilibria

Adsorption involves different types of attractive forces between adsorbate, adsorbent and solvent molecules. Such forces usually act in concert, but one particular type may be more predominant than the others in any particular situation (Ho and McKay, 1999a).

Adsorption interactions generally lead to the accumulation of concentration at a surface and may be essentially represented as arising from attraction of adsorbate molecules (gaseous or liquid components) to an adsorbent surface (a solid). It is one of the fascinating phenomena connected with the behaviour of fluids in a force field extorted by the solid surface (Borowko, 2002). The adsorption of a substance from one phase to the surface of another in a particular system leads to a thermodynamically defined distribution of that substance between the phases when the system reaches equilibrium. A variety of different isotherm equations have been proposed, some with firm theoretical foundation and others of empirical nature. Experimental isotherms are useful for describing adsorption capacity of a variety of solids and to find out the viability for the process for a given application such that the most appropriate adsorbent may be chosen. Adsorption equilibrium is established when the concentration of
adsorbate in the bulk solution is in dynamic balance with that of the interface. The two most well known isotherms are described below:

### 2.8.1 The Langmuir isotherm

The Langmuir model (Langmuir, 1918) is the most straightforward non-linear isotherm model which is based on the assumption that adsorption energy is constant and independent of surface coverage. The adsorption takes place on localized sites with no lateral adsorbate-adsorbate interactions. Langmuir model can be derived variously by mass action, kinetic, or statistical thermodynamic approaches. The rate at which adsorbate molecules strike a surface of an adsorbent is proportional to the product of the concentration of the solute (C) and the fraction \((1 - \theta)\) of the surface remaining uncovered by adsorbate and therefore available as adsorption sites. The rate of desorption from the surface is directly proportional to the fractional surface coverage, \(\theta\), and the rates of adsorption and desorption are equal at equilibrium. Thus,

\[
k_a \cdot C \cdot (1 - \theta) = k_d \cdot \theta
\]

(2)

where \(k_a\) and \(k_d\) are the rate coefficients for adsorption and desorption respectively. The fractional surface coverage, \(\theta\), is then,

\[
\theta = \frac{q_d}{q_m} = bC_e/(1+bC_e)
\]

(3)

where \(b = k_a/k_d\) and \(q_m\) is the quantity of adsorbate required to form a single monolayer on unit mass of the solid and \(q_e\) is the amount adsorbed on unit mass of the solid when the equilibrium concentration is \(C_e\).

The simple derivation assumes that a single molecule occupies a single surface site and that there are no interactions between adjacent adsorbed molecules. Application of the kinetic theory of gases reveals that the constant \(b\) can be identified as

\[
1/b = (v/\sigma) \cdot (2\pi mkT)^{1/2} \exp (-Q/RT)
\]

(4)

where, \(Q = \) the heat of adsorption,

\(v = \) the pre-exponential factor of the desorption rate coefficient,

\(\sigma = \) the condensation coefficient of the adsorbate,
\[ m = \text{the mass of the adsorbate molecule, and} \]
\[ k = \text{the Boltzmann constant.} \]

Equation (2) can be rearranged to the form:
\[ q_e = \frac{q_m b C_e}{1 + b C_e} \quad (5) \]
or in the linear form as:
\[ \frac{C_e}{q_e} = \left( \frac{1}{b q_m} \right) + \left( \frac{1}{q_m} \right) C_e \quad (6) \]

The linear Langmuir plots are obtained by plotting \( \frac{C_e}{q_e} \) vs. \( C_e \). The slope and the intercept of this plot give the values of \( q_m \) and \( b \). The Langmuir equation is also used to obtain \( R_L \), a dimensionless equilibrium parameter or the separation factor (Hall et al. 1966), from the expression:
\[ R_L = \frac{1}{1 + b C_e} \quad (7) \]
where \( C_e \) is any equilibrium liquid phase concentration of the solute at which adsorption is carried out. The nature of the isotherms is indicated by the \( R_L \) value as follows (Ho, 2003):

<table>
<thead>
<tr>
<th>( R_L ) value</th>
<th>Type of isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 &lt; ( R_L &lt; 1 )</td>
<td>Favourable</td>
</tr>
<tr>
<td>( R_L &gt; 1 )</td>
<td>Unfavourable</td>
</tr>
<tr>
<td>( R_L = 1 )</td>
<td>Linear</td>
</tr>
<tr>
<td>( R_L = 0 )</td>
<td>Irreversible</td>
</tr>
</tbody>
</table>

### 2.8.2 The Freundlich isotherm

The Freundlich model (Freundlich, 1906) is perhaps the most widely used non-linear adsorption equilibrium model, which can be shown to be thermodynamically rigorous for adsorption on heterogeneous surfaces (Weber et al., 1991). The isotherm has the expression:
\[ q_e = K_f C_e^n \quad (8) \]
where $C_e$ and $q_e$ are the equilibrium concentrations of the solute in the liquid phase and in the solid phase respectively, $K_f$ and $n$ being Freundlich coefficients, representing adsorption capacity and adsorption intensity respectively. For favorable adsorption, $n$ is generally $< 1$. The logarithmic form of the equation (8) is more useful for fitting data from batch equilibrium studies, and is given by

$$\log q_e = \log K_f + n \log C_e$$  \hspace{1cm} (9)

The values of $K_f$ and $n$ are obtained from intercept and slope of the plots of $\log q_e$ vs. $\log C_e$, respectively.

### 2.8.3 Utility of an adsorption isotherm

The adsorption isotherm provides a number of valuable information (Bernardin, 1985). Some of them are:

- The absorbability of an adsorbent,
- The amount adsorbed per unit mass or the concentration of the adsorbate on the adsorbent,
- The equilibrium adsorbate concentration indicates the maximum amount that can be removed from solution. This quantity remains unchanged with increasing adsorbent amounts,
- The relative steepness of the isotherm can be equated to the sensitivity of the adsorbent to changes in adsorbate concentration.

On the other hand, the adsorption isotherm has some limitations as given below:

- Isotherms are strictly applicable to equilibrium conditions without any time restriction, and hence if true equilibrium is difficult to ascertain, the applicability of the isotherm will be very much hampered,
- Long-term chemical and biological effects are not accounted for by the isotherm.

### 2.9 Adsorption Kinetics

The adsorption kinetics normally includes two phases: a rapid removal stage followed by a much slower stage before the equilibrium is established (Ho and McKay, 1999c).
To arrive at an unambiguous rate law, it is necessary that (i) all the molecular details of the reaction, including the energetics and stereo chemistry, should be known and (ii) the mechanism of the reaction including all the elementary steps should be fairly understood (Ho and McKay, 1999d).

The rates at which metal ions are taken up by the adsorbent determine the adsorption kinetics and it directly controls the efficiency of the adsorption process. The transfer of metal ions from the liquid phase to the solid phase can be considered as a reversible reaction with an equilibrium being established between the two phases. A batch adsorption kinetic model was used to analyze the batch adsorption data in order to obtain estimates for the rate constants. The simple way to describe the metal removal by adsorbent is (Banerjee et al., 1997):

\[ \begin{align*}
A & \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \\
\end{align*} \]

The rate equation for the above reaction is expressed as:

\[ \frac{dC_B}{dt} = -\frac{dC_A}{dt} = k_1(C_{A0} - C_{A0}X_A) - k_2(C_{B0} + C_{A0}X_A) \]  (10)

where \( C_A \) and \( C_B \) are the concentrations of the metal ions in solution and on adsorbent, respectively, at any time; \( C_{A0} \) and \( C_{B0} \) are the initial concentrations of metal ions in solution and in adsorbent, respectively (at \( t = 0 \)); \( X_A \) is the fraction of metal adsorbed onto the adsorbent; \( k_1 \) and \( k_2 \) are the first-order adsorption and desorption rate coefficients, respectively. At equilibrium:

\[ \frac{dC_B}{dt} = -\frac{dC_A}{dt} = 0 \]  (11)

and,

\[ X_{Ae} = \frac{[k_c - (C_{B0}/C_{A0})]}{(1 + k_c)} \]  (12)

where \( X_{Ae} \) is the fraction of the metal ions adsorbed at equilibrium, and \( k_c \) is the equilibrium constant.

The equilibrium constant, \( K_c \) is represented as:

\[ K_c = \frac{k_1}{k_2} = \frac{(C_{B0} + C_{A0}X_{Ae})}{(C_{A0} - C_{A0}X_{Ae})} \]  (13)
The equation (10) can be written as:

$$\frac{dX_A}{dt} = (k_1 + k_2) (X_{Ae} - X_A)$$  \hspace{1cm} (14)

Substituting \((k_1/K_c)\) for \(k_2\), the integrated form of the equation (14) can be written as:

$$-\ln \left(1 - \frac{X_A}{X_{Ae}}\right) = \left(k_1 + \frac{k_1}{K_c}\right) t$$ \hspace{1cm} (15)

or,

$$-\ln \left(1 - \frac{X_A}{X_{Ae}}\right) = -k' t$$ \hspace{1cm} (16)

where, \(k'\) is the overall rate coefficient and is given by,

$$k' = k_1 + k_1/K_c = k_1 + k_2$$ \hspace{1cm} (17)

In most cases, however, the adsorption kinetics can be best described by adopting well known simple models and by trying to fit the experimental data into them. A few established models for adsorption kinetics are:

**(i) Lagergren pseudo first order kinetics.** The Lagergren equation (Lagergren, 1898; Ho, 2004) has been one of the most used equations particularly for pseudo first order kinetics:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t)$$ \hspace{1cm} (18)

where \(k_1 (\text{min}^{-1})\) is the pseudo first order adsorption rate coefficient. The integrated form of the equation (18) for the boundary conditions of \(t = 0, q_t = 0\) and \(t = t, q_t = q_e\), is

$$\ln (q_e - q_t) = \ln q_e - k_1 t$$ \hspace{1cm} (19)

where \(q_e\) and \(q_t\) are the values of the amount adsorbed per unit mass at equilibrium and at any time \(t\). The values of \(k_1\) can be obtained from the slope of the linear plot of \(\ln (q_e - q_t)\) vs. \(t\).

An important test for the validity of the pseudo-first order kinetics is to compare \(q_e\) obtained from the intercept (\(\ln q_e\)) of the plots of \(\ln (q_e - q_t)\) vs. \(t\) with the value obtained experimentally when the adsorption reaches equilibrium. In most cases, the Lagergren equation does not fit well in the whole range of interaction time (Ho and McKay, 1999c) and then, another suitable model will have to be looked for.
(ii) **Pseudo-second order equation.** When the applicability of the first order kinetics becomes untenable (for example, if \( q_e \) obtained on the basis of equation (19) is not the same as the one obtained experimentally), the adsorption may follow second order kinetics on the basis of the equation (Ho and McKay, 1999e)

\[
\frac{dq_t}{dt} = k_2 (q_e - q_t)^2
\]  

(20)

where \( k_2 \) is the second order rate coefficient. The integrated form of the equation (20) under the boundary conditions of \( q_t = 0 \) at \( t = 0 \) and \( q_t = q_e \) at \( t = t \) is given by,

\[
q_t = t\left[\frac{1}{k_2 q_e^2} + \frac{1}{q_e}\right]
\]

(21)

The linear form of this equation

\[
\frac{t}{q_t} = 1/(k_2 q_e^2) + (1/q_e)\cdot t
\]

(22)

makes it possible to obtain \( q_e \) and \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) from the plots of \( t/q_t \) vs. \( t \).

(iii) **Elovich equation.** The Elovich equation assumes that the actual solid surfaces are energetically heterogeneous. Such assumption seems obvious because neither desorption nor interactions between the adsorbed molecules could substantially affect the kinetics of adsorption at low surface coverage. The crucial effect of the surface energetic heterogeneity on the equilibria of adsorption in the gas/solid systems has been demonstrated by Rudzinski and Everett (1992). The Elovich Equation (Ho and McKay, 1998b; Rudzinski and Panczyk, 2002) has been used in the form:

\[
\frac{dq_t}{dt} = \alpha \exp(-\beta q_t)
\]  

(23)

Assuming \( \alpha\beta t >>1 \), and \( q_t = 0 \) at \( t = 0 \) and \( q_t = q_e \) at \( t = t \), the linear form of the equation (23) is given by (Chien and Clayton, 1980):

\[
q_t = \beta \ln (\alpha\beta) + \beta \ln t
\]

(24)

where \( \alpha \) and \( \beta \), known as the Elovich coefficients, represent the initial adsorption rate (g mg\(^{-1}\)min\(^{-2}\)) and the desorption coefficient (mg g\(^{-1}\)min\(^{-1}\)) respectively. The Elovich coefficients could be computed from the plots of \( q_t \) vs. \( \ln t \).
(iv) **Intra particle diffusion.** For porous adsorbents, the diffusion of the adsorbate molecules or ions into the pores has also to be taken into account in finding a suitable kinetic model for the process. In many cases, the intra particle diffusion may control the rate of uptake of an adsorbate, which is represented by the following familiar expression (Ruthven 1984; Banerjee et al., 1997, Manju et al., 2002):

\[
\frac{X_A}{X_{Ae}} = 1 - \left(\frac{6}{\pi^2}\right) \sum \left(\frac{1}{n^2}\right) \exp \left(-\frac{n^2 \pi^2 D_c t}{r^2}\right)
\] (25)

where \(X_A\) is the amount of the adsorbate (A) adsorbed at any time and \(X_{Ae}\) the amount adsorbed at equilibrium, their ratio giving the fractional approach to equilibrium, \(D_c\) = intra-crystalline diffusivity, \(r\) = particle radius, \(t\) = reaction time, and the summation is carried out from \(n = 1\) to \(n = \alpha\).

The equation (25) can be rewritten in the following simplified form:

\[
1 - \frac{X_A}{X_{Ae}} = \left(\frac{6}{\pi^2}\right) \exp \left(-\frac{\pi^2 D_c}{r^2}\right) t
\] (26)

Or, \[\ln \left(1 - \frac{X_A}{X_{Ae}}\right) = \left(-\frac{\pi^2 D_c}{r^2}\right) t + \ln \left(\frac{6}{\pi^2}\right)\] (27)

Therefore, the plot of \(\ln \left(1 - \frac{X_A}{X_{Ae}}\right)\) versus \(t\) should be linear with a slope of \(-\frac{\pi^2 D_c}{r^2}\), which is known as the reaction rate constant or diffusion time constant. The slope can be expressed as:

\[k' = \frac{\pi^2 D_c}{r^2}\] (28)

where \(k'\) is the overall rate constant, inversely proportional to the square of the particle radius.

Weber and Morris (1963) introduced a simpler expression to obtain the diffusion rate coefficient, \(k_i\):

\[q_t = k_i \cdot t^{0.5}\] (29)

The significant feature of this expression is that the linear plots of \(q_t\) vs. \(t^{0.5}\) should pass through the origin (zero intercept). Thus the intra-particle diffusion model can be easily tested through the above plots provided they have zero intercept, which indicates a controlling influence for the diffusion process on the kinetics. The rate coefficient, \(k_i\) (mg g\(^{-1}\) min\(^{-0.5}\)) could be obtained from the slope of the plots.
(v) **Liquid film diffusion.** When the flow of the reactant from the bulk liquid to the surface of the adsorbent is the slowest process determining kinetics of the rate processes, the liquid film diffusion model (Boyd et al., 1947) given by the simple relation

\[
\ln (1 - F) = - k_{fd} t
\]  

(30)

could be the appropriate way to characterize the kinetics. F is the fractional attainment of equilibrium (\(= q_t/q_e\)) and \(k_{fd}\) (min\(^{-1}\)) is the adsorption rate coefficient. A linear plot of \(- \ln (1 - F)\) vs. t with zero intercept suggests that the kinetics of the adsorption process is controlled by diffusion through the liquid film surrounding the solid adsorbent.

### 2.10 Thermodynamics of adsorption

The phenomenon of adsorption is essentially an attraction of adsorbate molecules to an adsorbent surface. It is important to estimate the strength of binding of species to a surface. When an isolated species approaches the surface of a solid, several interactions come into play, each of which contributes to the heat or energy of physical adsorption (Thomas and Thomas, 1997). Physical adsorption has always been found to be an exothermic process accompanied by release of heat as the adsorbate molecules accumulate on the adsorbent surface due to weak binding forces such as van der Waals forces. The exothermic nature of the process is supported by the facts that (i) physical adsorption is a spontaneous process accompanied by a decrease in Gibbs energy (\(\Delta G < 0\)), and (ii) since the adsorbate molecule lose at least one degree of freedom, the process is also accompanied by a decrease in entropy (\(\Delta S < 0\)). Therefore, it follows from the basic thermodynamic relation, \(\Delta G = \Delta H - T \Delta S\), that with both \(\Delta G, \Delta S < 0\), the enthalpy change, \(\Delta H\) also decreases, i.e. \(\Delta H < 0\). The Gibbs free energy, enthalpy and entropy (\(\Delta G, \Delta H, \Delta S\)), for the adsorption process are obtained from the experiments carried out at different temperatures using this equation:

In physical adsorption, weak forces are involved. These may be van der Waals type, dipole-dipole interactions, hydrogen bonding, etc. With chemisorption, the forces involved are strong and chemical in nature leading to formation of surface compounds and the mechanism of adsorption will be vastly different from that of physical
adsorption. While the heat measured for physical adsorption corresponds to the normal crystallization enthalpies, the chemisorption heat is at least an order of magnitude higher (Fox, 1985). It is also possible that both physical and chemical adsorption take place simultaneously and in such cases, the actual mechanism will be a combination of both the processes. The thermodynamics of an adsorbate-adsorbent system therefore depends on various factors, viz., (i) chemical nature of the adsorbate and the adsorbent, (ii) the environmental conditions such as pH in case of adsorption from solution, and (iii) the type of forces interacting. Physical adsorption is normally characterized by enthalpy change of 10 to 40 kJ mol\(^{-1}\).

The thermodynamic parameters for the adsorption process, \(\Delta H\) (kJ mol\(^{-1}\)), \(\Delta S\) (J K\(^{-1}\) mol\(^{-1}\)) and \(\Delta G\) (kJ mol\(^{-1}\)), are evaluated using the equations (31), (32) and (33) (Thomas and Crittenden, 1998c):

\[
\Delta G = -RT \ln K_d \tag{31}
\]

\[
\ln K_d = -\Delta G / RT = \Delta S / R - \Delta H / RT \tag{32}
\]

where, \(K_d = \) the distribution coefficient of the adsorbate, (= \(q_e / C_e \) in L g\(^{-1}\)),

\(T = \) the temperature (K),

\(R = \) universal gas constant (8.314 \times 10\(^{-3}\) kJ K\(^{-1}\) mol\(^{-1}\)).

The plot of \(\ln K_d\) vs. \(1/T\) should be linear with the slope (\(- \Delta H / R\)) and the intercept (\(\Delta S / R\)) giving the values of \(\Delta H\) and \(\Delta S\). The Gibbs energy change, \(\Delta G\), is the fundamental criterion of spontaneity. Processes occur spontaneously at a given temperature if \(\Delta G\) is a negative quantity. All these relations are valid when the enthalpy change remains constant in the range of temperatures considered.

2.11 Desorption and Regeneration of the Adsorbent

In certain applications it may be economic to discard the adsorbent after use in which case it may be necessary to describe it as a waste. Disposal would be favoured when the adsorbent is of low cost, is very difficult to regenerate (due to chemical forces) and the non-adsorbed products of the adsorptive separation are of very high value.
However, the disposal of the adsorbent as a waste is not considered as an economic option, and regeneration should be considered as an option. For this, desorption and regeneration is to be carried out with one or more of the following:

(i) Increase in temperature;
(ii) Reduction in partial pressure;
(iii) Reduction in concentration;
(iv) Removal with an inert fluid;
(v) Displacement with a more strongly adsorbing species;
(vi) Change of chemical condition such as pH.

2.12 Conclusion

A number of technologies exist for the removal of metal pollutants from waste water. Some of these are reverse osmosis, chemical precipitation, electroplating, ion exchange, solvent extraction, and membrane separation, etc.

Traditionally, the most widely applied methods for heavy metal removal from wastewaters are chemical and electrochemical precipitation (Ayyappan et al. 2005, Li et al. 2007) cationic and anionic ion-exchange resins, membrane filtration, and sorption (Shukla et al., 2002). Chemical precipitation is one of the most common conventional treatment methods to effectively decrease metal concentration to acceptable levels. It requires large excess of chemicals and generates volumetric sludge and increases the cost. Other available treatment methods, such as electrolysis and reverse osmosis require high capital investment and running cost (Kumar et al. 2008, Singh et al. 2009). Ion exchange has the advantage of allowing the recovery of metallic ions, but it is expensive and sophisticated. Moreover, selective recovery of one or more metals from a multi component mixture using common organic cation exchange resins is generally not feasible, especially for those metals having the same valence (Juang and Wang, 2003). These processes have several disadvantages such as incomplete metal removal, high reagent and energy requirement and generation of toxic sludge/waste products that require disposal and further treatment. This led to the need to develop an effective, low cost and environment friendly process for wastewater treatment.
Adsorption is one of the techniques that would be comparatively more useful and economical for the above purpose (Rodrigues et al. 2009). Metal adsorption and removal efficiency may be influenced by a number of factors, such as pH, adsorbent dose, contact time, and initial metal concentration. A further increase in the contact time has a negligible effect on the rate of metal adsorption. Also, it is apparent that the percent removal of metal ions increases with increasing amount due to the greater availability of surface area and thus exchangeable sites.

The process of adsorption has become one of the preferred methods for removal of toxic contaminants from water as it has been found to be very effective, versatile and simple with much less sludge disposal problems (Tran et al., 1999). It is a better technique due to its ease of operation and insensitivity towards toxic substances (Meshko et al., 2001). However, some adsorbents have poor removal efficiency, high cost of production and regeneration can generate secondary pollution and are ineffective at low pollutant load.

In general, it is recognized that a great need exists for new and cost-effective materials and processes for metal removal from wastewaters and storm waters.