CHAPTER 1
INTRODUCTION AND THEORETICAL FOUNDATION

1.1 Growth of Adsorption Science

1.1.1 General ideas about adsorption

For the process of separation and purification of a mixture of products, adsorption is one of the most important industrial practices today. Adsorption is regarded as a surface or interface phenomenon, which arises due to interactions between the individual atoms, ions or molecules of an adsorbate and those present in the adsorbent surface. The forces responsible for these interactions have their origin in electromagnetic interactions (Weber and van Vliet, 1980).

Depending on the nature of the interactions, four types of adsorption can be distinguished (Weber J, 1985):

(i) **Exchange adsorption.** 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.

(ii) **Physical adsorption** and Physisorption. This type of adsorption results from the action of van der Waals forces, which are comprised of both London dispersion forces and classical electrostatic forces.

(iii) **Chemical adsorption** or Chemisorption. It involves a reaction between an adsorbate and an adsorbent resulting in a change in the chemical form of the adsorbate. The resulting chemisorptive bond is usually stronger than that derived from the physical van der Walls forces.

(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, designated as "specific adsorption" 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.

1.1.2 Historical Developments

The ability of some solids to remove colour from solutions containing dyes has been known for over a century. Similarly, air contaminated with unpleasant odors could be rendered odorless by passage the air through a vessel containing charcoal. Although such phenomena were not well understood prior to the early twentieth century, they represent the dawn of adsorption technology, which has survived as a means of purifying and separating both gases and liquids to the present day. In recent years, the science and technology of adsorption has expanded tremendously as new and improved applications occur in competition with other well-established process technologies. A few early contributions towards understanding of the science of adsorption may be summarised as follows:

(i) Mantell (1945) gave a general description of the adsorption processes on fuller’s earth and activated clays, aluminium oxide base materials, bone char and related materials, decolourizing and water treatment carbons, metal and medicinal adsorbent chars, gas adsorbent carbons, silica gels, magnesia and hydrous oxides. The processes involved solvent recovery and adsorption of gases, odour removal, gas mask development, gas hydrate formation, dehydration of air and gases, use of ion exchangers and chromatographic adsorption analysis.

(ii) Davies and Rideal (1961) described the fundamental properties of various liquid interfaces including the physics of surfaces, electrostatic phenomena, properties of monolayers, diffusion through interfaces, and disperse systems and adhesion.

(iii) Gregg and Sing (1967) discussed the use of adsorption data for evaluation of the surface area and pore size distribution of finely divided and porous solids using BET methods and the use of the Kelvin equation for the calculation of pore size distribution.
(iv) Treybal (1968) described the phenomena of adsorption and ion exchange as well as single and multicomponent equilibria for both gaseous and liquid systems. The treatment included a discussion of the fixed bed absorbers and various other related phenomena such as molecular diffusion in fluids, mass transfer coefficients, diffusion in solids and interphase mass transfer.

(v) Mattson and Mark (1971) reviewed the available data on adsorption from solutions and the surface-related interactions of activated carbons for adsorption of a wide variety of solutes ranging from strong electrolytes to organic non-electrolytes.

(vi) Ponec, Knor and Cerny (1974) provided a detailed account of theoretical approaches to experimental techniques of adsorption and gave description of the adsorbent substances, surfaces and their preparation, methods for studying the texture of solids, theories of adsorption forces, adsorption kinetics and thermodynamics, theories of adsorption equilibria, the mechanisms of physical adsorption and chemisorption, adsorption from flowing gases and liquids, practical applications of adsorption, adsorption from solutions and the relationship between adsorption and catalysis, etc.

(vii) Vermeulen (1977) gave a brief introduction to the adsorption design, including equilibria, types of breakthrough and rate behaviour. Summary accounts were provided of practical design matters including choices of adsorbents, etc.

(viii) Slejko (1985) tried to give a working knowledge of the basic adsorption theory in order to design laboratory and pilot plant experiments and to help understand the results.


(x) Cheremisinoff and Cheremisinoff (1993) showed the usefulness of carbon adsorption in the specific field of pollution control.
Ruthven, Farooq and Knaebel (1994) reviewed the underlying scientific principles and the technology of pressure swing adsorption, including some important commercial processes.

Tien (1994) gave a brief description of the models and calculation procedures for the design and analysis of physical adsorption processes.

Sircar (1994) explained the development of 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 complex nature of process cycles, the fundamental understanding of multicomponent gas-solid interactions, the successful development of simplified specific models, and the understanding of heterogeneity and its effect on multicomponent gas adsorption characteristics have also been described.

The classical experiments of several scientists including Brunauer, Emmet and Teller, McBain and Bakr, Langmuir and later by Barrer, all in the early part of the twentieth century, have resulted in the emergence of quantitative theories to explain the mechanism of the adsorption processes (Thomas and Crittenden, 1998). As a result of these studies, quantitative theories emerged, which have withstood 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.

1.1.3 Adsorption Technology

In the last few years, adsorption technology has become increasingly important and has led to commercialization of the technology, which has stimulated further research into adsorbate-adsorbent interactions. Thomas and Crittenden (1998) have given an overview of the history and development of the adsorption technology, particularly with respect to how theory is put into commercial practice.

Industrial applications of adsorbents became common practice following the widespread use of charcoal for decolorizing liquids and, in particular, its use in gas
masks during the 1914-18 World War for the protection of military personnel from poisonous gases. Some examples are:

i) Alumina, bauxite and silica gel for drying of gases and vapors;
ii) Bone char and other carbons for refining of sugar and oils, fats and waxes;
iii) Activated charcoal for recovery of solvents, elimination of odors and purification of air and industrials gases;
iv) Fuller’s earth and magnesia for removing contaminants of petroleum fractions and oil, fats and waxes;
v) Base exchanging silicates for water treatment
vi) Some charcoals for recovering precious metals
vii) Some activated carbons for medical applications to eliminate bacteria and other toxins, etc.

Such adsorption processes are carried out by both batch and continuous flow equipments, the important consideration for the design of which has been to ensure adequate contact between adsorbent and fluid containing the component to be removed.

Early commercial application of adsorption included use of naturally occurring clays to refine oils and fats (Mantell, 1951). Fuller’s earth was used for removing grease from woollen materials for a very long time. Other naturally occurring clays (kaolinite and bentonite) were used for bleaching oils and petroleum spirits. Bauxite consisting of hydrated aluminium oxide was in use for decolourizing residual oil stocks. Some types of carbon were in common use for decolorizing and removing odors from wide variety of materials. The decolourization of liquids, including the refining of sugar melts, was accomplished by mixing the carbon adsorbent with the liquid to be bleached followed by filtration. In some cases, the adsorbent was regenerated for further use by passing steam through a bed of the spent adsorbent. Non-potable waters were either percolated through beds of carbonaceous adsorbent, or activated carbon for treatment. Activated carbons were in general use during the first three decades of the twentieth century for the purification of air and for recovering solvents from vapour streams.

Dehumidification of moisture-laden air and dehydration of gases were, and still are, done by using silica gel as an adsorbent. Thermal swing adsorption (TSA; raising the
temperature of the adsorbent) processes became dominant for a variety of purposes by the end of the first quarter of the twentieth century. But it was not until the advent of adsorbents possessing sieving properties when processes for the separation of gaseous mixtures developed. Naturally occurring and synthesized silica-alumina minerals have unique crystalline structures, the micro porosity being determined by configuration of silica-alumina cages linked by four or six member oxygen rings. Such structures admit and retain molecules of certain dimensions to the exclusion of others, and are therefore excellent separating agents. Barrer (1978) extensively researched and reviewed the adsorptive properties of these materials, referred to as zeolites. Walker et al. (1966a, 1966b) thoroughly investigated the adsorptive properties of microporous carbons and laid the foundation for the development of molecular sieve carbons, which are less hydrophilic than zeolites, and can therefore separate wet gaseous streams effectively.

To be technically effective in a commercial separation process, whether this be a bulk separation or purification, an adsorbent material must have high internal volume, accessible to the components being removed from the fluid phase. The internal surface areas of adsorbents should be within the range of 100 m²/g to over 3000 m²/g. Most of the adsorbents, such as carbons, silica gels and alumina, are amorphous and contain complex networks of interconnected micropores, mesopores and macrospores. However, zeolites have pores and channels of precise, uniform dimensions. The highly porous solid adsorbent may be carbonaceous or inorganic in nature, synthetic or naturally occurring, and in certain circumstances, may have true molecular sieving properties. The adsorbent must also have good mechanical properties such as strength and resistance to attrition and it must have good kinetic properties, making it capable of transferring adsorbing molecules rapidly to the adsorption sites. In most applications, the adsorbent must be regenerated after use and therefore it is desirable that regeneration can be carried out efficiently and without damage to mechanical and adsorptive properties. The methods for production of adsorbents from raw materials must be inexpensive for adsorption to compete successfully on economic grounds with alternative separation processes.

The surface area of adsorbent materials is generally obtained from BET isotherm with nitrogen adsorption measurements at liquid nitrogen temperature (77K). Pore volumes are obtained from the determination of the amount of an adsorbate, such as
nitrogen, adsorbed at a given pressure over a range of pressures up to the saturation vapour pressure. Mercury porosimetry is used to determine the pore size distribution.

1.1.4 Selectivity of an adsorbent

The ability of an adsorbent to separate molecule A from molecule B is known as its selectivity. The selectivity is given by the separation factor, which in turn is defined as (Thomas and Crittenden, 1998):

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

where $X_i$ 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. Selectivity arises in a separation process due to one or more of the following:

a) Differences may exist in the thermodynamic equilibria for each adsorbate-adsorbent interaction; this is known as the equilibrium effect,

b) Differences may exist in the rates at which different adsorbates travel into the internal structure of the adsorbent; this is known as the kinetic effect,

c) Pore openings may be too small to allow penetration by one or more of the adsorbates; this is known as the molecular sieving effect and is an extreme case of the kinetic effect,

d) Differences may exist in the rate at which different adsorbates can be desorbed from the adsorbent; this is known as the desorption effect.

The equilibrium separation factor again depends on

- The nature of the adsorbent interactions, i.e. 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 micropore diffusivities of the components being separated. For a useful separation to be based on kinetics, the size of
the adsorbent micropores must be comparable with the dimensions of the diffusing adsorbate molecules.

1.2 Types of adsorbents

A brief account of the important adsorbents, which have found wide use in practice, is given below:

a) Activated Carbon. Carbonaceous materials, in the form of activated carbon, have found the following applications in industry:

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

One of the advantages for using activated carbons is that they can be obtained in the full range of pore sizes as shown in Table 1.1.

Granular activated carbon (GAC is widely used in water and wastewater treatment, for example, to remove pesticides from potable water. Powdered activated carbon (PAC) can also be used directly, usually in batch applications, but the recovery of the carbon for regeneration and reuse is often very difficult.
Table 1.1. Pore sizes 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>

b) **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 resin, 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. The surface is non-polar and the main process application is the production of high purity nitrogen from air. 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). More recently there has been a resurgence of interest in the production of new CMS materials with different pore structures for specific uses.

c) **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 up to 1100 m²/g. These adsorbents tend to be more hydrophobic than granular activated carbon and therefore, one important application is the removal of organic compounds from water.
d) **Bone charcoals.** Animal bones can be carbonized to produce adsorbent materials, which have only meso and macro pores, and surface areas around 100 m$^2$/g. The surface consists of carbon and hydroxyl appetite in roughly equal proportions. Due to the dual nature of the surface, bone charcoals can be used to adsorb metals as well as organic chemicals from aqueous systems. It is also used for decolourizing sugar syrup.

e) **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 m$^2$/g. Selectivity of the adsorbents are obtained from 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.

f) **Silica Gel.** Silica gel is a partially dehydrated polymeric form of colloidal silicic acid with the formula, SiO$_2$.nH$_2$O. This amorphous material comprises spherical particles of 2 – 20 nm size, which aggregate to form an adsorbent with pore sizes between 6 – 25 nm. Surface areas are in the range of 100 – 850 m$^2$/g. The surface comprises of $\equiv$SiOH and $\equiv$Si–O–Si$\equiv$ groups and being polar, the material is effective for adsorbing water, alcohols, phenols, amines, etc., through hydrogen bonding. It is also used for commercial separation of aromatics from paraffins and the chromatographic separation of organic molecules. Typical properties of adsorbent grade silica gel are summarized in Table 1.2:
Table 1.2. Typical properties of adsorbent-grade silica gel (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$^\circ$C</td>
<td>11</td>
</tr>
<tr>
<td>Density (kg/m$^3$)</td>
<td>H$_2$O at 17.5 mm Hg, 25$^\circ$C</td>
<td>35</td>
</tr>
<tr>
<td>Reactivation temperature (°C)</td>
<td>O$_2$ at 100 mmHg, 25$^\circ$C</td>
<td>22</td>
</tr>
<tr>
<td>Pore volume (%)</td>
<td>CO$_2$ at 250 mm Hg, 25$^\circ$C</td>
<td>3</td>
</tr>
<tr>
<td>Pore size (nm)</td>
<td>n-C4 at 250 mm Hg, 25$^\circ$C</td>
<td>17</td>
</tr>
<tr>
<td>Pore volume (cm$^3$/g)</td>
<td>0.42</td>
<td></td>
</tr>
</tbody>
</table>

**g) Activated Alumina.** Activated alumina is a porous high area form of aluminium oxide with the formula Al$_2$O$_3$.nH$_2$O. Its surface is more polar than that of silica gel reflecting the amphoteric nature of aluminium. It has both acidic and basic characteristics. Surface area is in the range of 250 – 350 m$^2$/g. Activated alumina has a higher capacity for water adsorption than silica gel at elevated temperature. It is mainly used as a desiccant for warm gases including air but in many commercial applications, it has now been replaced by zeolites. Other uses for activated alumina include chromatography and drying of liquids such as kerosene, aromatics, gasoline fractions and chlorinated hydrocarbons.

**h) Clay materials.** 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 cationic forms are capable of adsorbing a range of polar molecules and non-polar molecules if some water is present. 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 polynuclear cations dehydrate on calcination to create metal oxide clusters, which act as pillars between the clay layers and create spaces of molecular dimensions. The use of
pillared clays includes the separation of oxygen and nitrogen, isomers and some metals and dyes.

i) Zeolites. Basically Zeolites are naturally occurring porous crystalline aluminosilicates, which comprise assemblies of SiO$_4$ and AlO$_4$ tetra joined together through the sharing of oxygen atoms. More than 150 synthetic zeolite types are known, the most important being the types A and X, synthetic mordenite and their ion-exchanged varieties. In crystal form, zeolites are distinct from other adsorbents. The internal porosity is high and thus, the majority of adsorption takes place internally. The process of adsorption and desorption of molecules in zeolites is based on differences in molecular size, shape and other properties such as polarity. The empirical formula of a zeolite framework is $M_{2n}.Al_{2}O_{3}.xSiO_{2}.yH_{2}O$, where $x$ is greater than or equal to 2, $n$ is the cation valency and $y$ represents the water contained in the cavities. Many zeolites are extremely polar and therefore separation may be effective using both molecular sieving and internal surface property effects. The kinetic selectivity is determined from the free diameters of the windows in the intra-crystalline channel structure. During 1970s, natural zeolites gained a significant interest among scientists due to their ion-exchange capability to preferentially remove unwanted heavy metals. This unique property makes zeolites favourable for wastewater treatment. A few important uses of zeolites as adsorbents are given in Table 1.3:

j) Some low cost adsorbents

Chitosan. Among various biosorbents, chitin is the second most abundant natural biopolymer after cellulose. However, more important than chitin is chitosan with molecular structure similar to cellulose. Presently, chitosan is attracting an increasing amount of research interest, as it is an effective scavenger for heavy metals. Chitosan is produced by alkaline N-deacetylation of chitin, which is widely found in the exoskeleton of shellfish and crustaceans. The growing need for new low-cost adsorbents undoubtedly make chitosan one of the most attractive materials for wastewater treatment. The utilization of chitosans for Cd (II), Hg (II), Cu(II), Ni(II), Cr(VI) and Zn(II) removal was intensively investigated (Babel et al., 2003). The excellent heavy metal removal by chitosans is attributed to: (i) high hydrophilicity due to large number
of hydroxyl groups, (ii) large number of primary amino groups with high activity, and (iii) flexible structure of the polymer chain of chitosans making suitable configuration for adsorption of metal ions

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Window</th>
<th>Effective channel diameter (nm)</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-A</td>
<td>8-ring</td>
<td>0.38</td>
<td>Desiccant. CO₂ removal from natural gas</td>
</tr>
<tr>
<td>Ca-A</td>
<td>8-ring</td>
<td>0.44</td>
<td>Linear paraffin separation. Air separation.</td>
</tr>
<tr>
<td>K-A</td>
<td>8-ring</td>
<td>0.29</td>
<td>Drying of cracked gas containing C₂H₄, etc.</td>
</tr>
<tr>
<td>Na-X</td>
<td>12-ring</td>
<td>0.84</td>
<td>Pressure swing H₂ purification.</td>
</tr>
<tr>
<td>Ca-X</td>
<td>12-ring</td>
<td>0.80</td>
<td>Removal of mercaptans from natural gas</td>
</tr>
<tr>
<td>Sr, Ba-X</td>
<td>12-ring</td>
<td>0.80</td>
<td>Xylene separation</td>
</tr>
<tr>
<td>Na-Y</td>
<td>12-ring</td>
<td>0.80</td>
<td>Xylene separation</td>
</tr>
<tr>
<td>K-Y</td>
<td>12-ring</td>
<td>0.80</td>
<td>Xylene separation</td>
</tr>
<tr>
<td>Ag-Mordenite</td>
<td>12-ring</td>
<td>0.70</td>
<td>I and Kr removal from nuclear off-gases.</td>
</tr>
<tr>
<td>Silicalite</td>
<td>10-ring</td>
<td>0.60</td>
<td>Removal of organics from water</td>
</tr>
<tr>
<td>Na-ZSM-5</td>
<td>10-ring</td>
<td>0.60</td>
<td>Xylene separation</td>
</tr>
</tbody>
</table>

[Na-A: Na₁₂[(AlO₂)₁₂(SiO₂)₁₂], Ca-A: Ca₂Na₂[(AlO₂)₁₂(SiO₂)₁₂], K-A: K₁₂[(AlO₂)₁₂(SiO₂)₁₂], Na-X: Na₈₆[(AlO₂)₈₆(SiO₂)₁₉₆], Ca-X: Ca₄₆Na₄[(AlO₂)₄₆(SiO₂)₁₉₆], Sr,Ba-X: Sr₂,Ba₂[(AlO₂)ₓ[(SiO₂)₁₀₆], Na-Y: Na₅₆[(AlO₂)₅₆(SiO₂)₁₉₆], K-Y: K₅₆[(AlO₂)₅₆(SiO₂)₁₉₆], Ag-Mordenite: Ag₈₆[(AlO₂)₈₆(SiO₂)₁₉₆], Silicalite: (SiO₂)₅₆, Na-ZSM-5: Na₃[(AlO₂)₃(SiO₂)₁₉₆]]
Peat moss. Peat moss, a complex soil material containing lignin and cellulose as major constituents, is a natural substance widely available and abundant. Peat moss has a large surface area (>200 m²/g) and is highly porous so that it can be used to bind heavy metals. It is also relatively inexpensive. Peat moss can remove Cu (II), Cd(II), Zn(II), Cr(VI) and Ni(II) from waste water successfully (Gosset et al., 1986; Ho and McKay, 1999, 2000; Ho et al., 2002). The most attractive advantage of this adsorbent in treatment is the simplicity of the system, low cost, and the ability to accept a wide variation of effluent composition. Peat moss exhibits a high CEC and can form complexes with metals due to the presence of carboxylic, phenolic, and hydroxylic functional groups.

Fly ash. Fly ash, an industrial solid waste of thermal power plants, is one of the cheapest adsorbents having excellent removal capabilities for heavy metals such as Cu (II), Cr (VI) and Fluoride (Panday et al., 1985; Dzombak et al., 1986; Chaturbedi et al., 1990). It is also found that the adsorption capacity increases 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.

Coal. The removal of Cd (II) using coal was intensively investigated (Bhattacharya et al., 1984). A similar study for Hg (II) sorption using bituminous coal (Babel et al., 2003) was also reported. Chemical pretreatment of the bituminous coal with nitric acid significantly enhances mercury sorption to a level higher than that exhibited by activated carbon in terms of initial rate of adsorption and adsorption capacity.

Natural oxide. Naturally occurring iron oxide and manganese oxide have 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 (Babel et al., 2003).

Industrial waste. Iron (III) waste is one of the waste materials from the fertilizer industry. It has been extensively investigated for removing Cr (VI) from wastewater (Babel et al., 2003). Waste slurry, one of the industrial by-products generated in
fertilizer plants, also 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. It was used as an adsorbent for Cu (II), Ni (II) and Zn (II) (Babel et al., 2003). The role of sawdust, collected from a timber workshop, was evaluated for copper removal (Babel et al., 2003). The use of bagasse flyash, an industrial waste generated in the sugar industry, can remove Cr (VI) for copper removal. Some commercial adsorbents and their applications for the removal of various pollutants are listed in Table 1.4.

**Low cost adsorbents.** A number of low-cost adsorbents have been studied from time to time. These include rice husk carbon (RHC) and coconut shell (Babel et al., 2003). Ajmal et al. (2000) used citrus reticulata, an agricultural waste originating from the fruit peel of orange for removal of Ni (II) from electroplating wastewater. In 2002, the potential of parthenium, an Indian agricultural waste, for removing Ni(II) from aqueous solution was also investigated (Kadiravelu et al., 2002). Most of these low cost adsorbents have been tested in the laboratory scale and would require much work for commercialization. Some of these adsorbents are listed in Table 1.5.
Table 1.4. Typical commercial adsorbents (Thomas and Crittenden, 1998).

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica Gel</td>
<td>Drying of gases, refrigerants, organic solvents, transformer oils, etc. Desiccant in packing and double-glazing. Dew point control of natural gas.</td>
</tr>
<tr>
<td>Adsorbent</td>
<td>Application</td>
</tr>
<tr>
<td>-----------</td>
<td>-------------</td>
</tr>
</tbody>
</table>
| Zeolites  | Oxygen from air.  
Drying of gases.  
Removing water from azeotrope.  
Sweetening sour gases and liquids.  
Purification of hydrogen.  
Separation of ammonia and hydrogen.  
Recovery of carbon dioxide.  
Separation of oxygen and argon.  
Removal of acetylene.  
Propane and butane from air.  
Separation of xylene and ethyl benzene.  
Separation of normal form of branched paraffins.  
Separation of olefins and aromatics from paraffin.  
Recovery of carbon monoxide from methane and hydrogen.  
Purification of nuclear off-gases.  
Separation of cresols.  
Drying of refrigerants and organic liquids.  
Separation of solvent systems.  
Purification of silanes.  
Pollution control, including removal of Hg, NOx and SOx from gases. Recovery of fructose from corn syrup. |
<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Application</th>
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</thead>
</table>
Table 1.5. Low cost adsorbents and their typical applications (plant-based adsorbents are shown in bold type) (Ho and McKay, 1999).

<table>
<thead>
<tr>
<th>Type</th>
<th>Typical application for removal of</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Giridih coal and Coconut shell</td>
<td>Cd (II)</td>
<td>Bhattacharya and Venkobachar, 1984</td>
</tr>
<tr>
<td>Fly ash/Wollastonite</td>
<td>Cr (VI)</td>
<td>Panday et al., 1984</td>
</tr>
<tr>
<td>Fly ash</td>
<td>Cu (II)</td>
<td>Panday et al., 1985</td>
</tr>
<tr>
<td>Peat</td>
<td>Cu (II), Cd (II), Ni(II), Zn(II)</td>
<td>Gosset et al., 1986</td>
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<tr>
<td>Hydrous ferric oxide</td>
<td>Cd (II),</td>
<td>Dzombak and Morel, 1986</td>
</tr>
<tr>
<td>Fly ash</td>
<td>Victoria Blue</td>
<td>Khare et al., 1987</td>
</tr>
<tr>
<td>Wollastonite</td>
<td>Fe (II)</td>
<td>Singh et al., 1998</td>
</tr>
<tr>
<td>Peat</td>
<td>Pb (II)</td>
<td>Ho and McKay, 1998</td>
</tr>
<tr>
<td>Fly ash and Impregnated fly ash</td>
<td>Phenol, o-cresol, m-cresol, p-cresol, o-nitrophenol, m-nitrophenol and p-nitro-phenol</td>
<td>Singh and Rawat, 1994</td>
</tr>
<tr>
<td>Fly ash</td>
<td>Fluoride</td>
<td>Chaturvedy et al., 1990</td>
</tr>
<tr>
<td>Peat</td>
<td>CN(^-), Cr (VI), Ni (II)</td>
<td>Ho and MacKay, 1999</td>
</tr>
<tr>
<td>Wollastonite</td>
<td>Ni (II)</td>
<td>Sharma et al., 1990</td>
</tr>
<tr>
<td>China clay</td>
<td>Ni (II)</td>
<td>Sharma et al., 1991</td>
</tr>
<tr>
<td><strong>Groundnut husk carbon</strong></td>
<td>Cr (VI)</td>
<td>Periasamy et al., 1991</td>
</tr>
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<td><strong>Banana pith</strong></td>
<td>Acid Violet</td>
<td>Namasivayam and Kanchana, 1992</td>
</tr>
<tr>
<td><strong>Beech leaves</strong></td>
<td>Cd (II)</td>
<td>Salim et al., 1992</td>
</tr>
<tr>
<td>Type</td>
<td>Typical application for removal of</td>
<td>Reference</td>
</tr>
<tr>
<td>----------------------------------------------------------------------</td>
<td>-------------------------------------------------------------</td>
<td>----------------------------</td>
</tr>
<tr>
<td>Coconut shell carbon</td>
<td>Cr(VI)</td>
<td>Rao et al., 1992</td>
</tr>
<tr>
<td>Biogas residual slurry</td>
<td>Congo red</td>
<td>Namasivayam and Yamuna, 1992</td>
</tr>
<tr>
<td>Biogas residual slurry</td>
<td>Rhoda mine-B, Acid Brilliant Blue, Direct Red 12B, Cr(VI), Pb(II)</td>
<td>Yamuna and Namasivayam, 1993</td>
</tr>
<tr>
<td>Peanut hull carbon</td>
<td>Hg(II), Cd(II), Pb(II), Ni(II), Cu(II)</td>
<td>Namasivayam and Periasamy, 1993</td>
</tr>
<tr>
<td>Waste tea, Turkish coffee, Exhausted coffee, Nut shell and Walnut shell</td>
<td>Cr(VI), Cd(II), Al(III)</td>
<td>Orhan et al., 1993</td>
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<tr>
<td>Leaf mould</td>
<td>Cr(VI)</td>
<td>Sharma and Forster, 1994</td>
</tr>
<tr>
<td>Water hyacinth roots</td>
<td>Methylene Blue</td>
<td>Low et al., 1995</td>
</tr>
<tr>
<td>Moss and Copper-coated moss</td>
<td>Cr(III), Cr(VI)</td>
<td>Lee et al, 1995</td>
</tr>
<tr>
<td>Algae</td>
<td>Lauryl benzyl sulphonate</td>
<td>Fernandez et al., 1995</td>
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<td>Orange peel</td>
<td>Congo Red, Procion Orange and RhodamineB</td>
<td>Namasivayam et al., 1996</td>
</tr>
<tr>
<td>Chrome sludge</td>
<td>Acid Blue 29, Reactive Blue2</td>
<td>Lee et al., 1996</td>
</tr>
<tr>
<td>Chitin</td>
<td>Acid Blue 193, Acid Blue 40,Direct yellow44, Direct Blue 78</td>
<td>Kim et al., 1997</td>
</tr>
<tr>
<td>Red mud</td>
<td>Congo Red</td>
<td>Namasivayam and Arasi, 1997</td>
</tr>
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<td>Fishery Wastes (chitosans)</td>
<td>Cu(II), RR222</td>
<td>Wu et al, 2000</td>
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<tr>
<td>Bagasse pith</td>
<td>Hg(II)</td>
<td>Krishnan and Anirudhan, 2002</td>
</tr>
<tr>
<td>Tree fern</td>
<td>Zn(II), Cu(II), Pb(II)</td>
<td>Ho et al., 2002</td>
</tr>
<tr>
<td>Used tea Leaves</td>
<td>Pb(II)</td>
<td>Sing et al., 1993</td>
</tr>
<tr>
<td>Type</td>
<td>Typical application for removal of</td>
<td>Reference</td>
</tr>
<tr>
<td>------------------------------------------------</td>
<td>---------------------------------------------------------------------------------------------------</td>
<td>----------------------------</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>Mn(II), Co(II), Ni(II), Cu(II)</td>
<td>Omer et al, 2003</td>
</tr>
<tr>
<td>Soya cake</td>
<td>Cr(VI)</td>
<td>Daneshvar et al, 2002</td>
</tr>
<tr>
<td>Crab shell</td>
<td>Pb(II), Cd(II), Cu(II), Cr(VI)</td>
<td>An et al, 2001</td>
</tr>
<tr>
<td>Wool, Olive Cake, sawdust, pine needles, almond shells, cactus leaves, charcoal</td>
<td>Cr(VI)</td>
<td>Dakiky et al, 2002</td>
</tr>
<tr>
<td>Fly larva shells</td>
<td>Mn(II), Zn(II), Ni(II), Cu(II), Fe(III)</td>
<td>Ona Gyiene et al, 2002</td>
</tr>
<tr>
<td>Chitosans</td>
<td>Zn(II), Ni(II), Cu(II)</td>
<td>Ruey-Shin juang et al, 2002</td>
</tr>
<tr>
<td>Chitin</td>
<td>Cd(II)</td>
<td>Benguella et al, 2002</td>
</tr>
<tr>
<td>Sepiolite</td>
<td>Co(II)</td>
<td>Kara et al, 2003</td>
</tr>
<tr>
<td>Electric Furnace slug</td>
<td>Pb(II), Cu(II)</td>
<td>Curkovic et al, 2001</td>
</tr>
<tr>
<td>Cypress, Cinchona, Pine leaves</td>
<td>Pb(II)</td>
<td>Subu, 2002</td>
</tr>
</tbody>
</table>
1.3 Basic theories of adsorption equilibrium

The preferential accumulation of a substance over a solid surface is essentially due to the attraction of adsorbate molecules to the adsorbent surface. The adsorbate-adsorbent interactions are electrostatic in nature, known as van der Waals forces, and consist of molecular forces embracing permanent dipoles, induced dipoles and quadrupoles. Physical adsorption (as distinct from chemisorption, which involves sharing or exchange of electrons between adsorbate and adsorbent) of a gas or vapour is normally characterized by the liberation of between 10 and 40 kJ mol\(^{-1}\) of heat which is close to the values associated with heats of liquefication of gases. The heat evolved on adsorption of a solute from a liquid onto a solid is strongly dependent on the source and history of the solid adsorbent.

A large number of isotherm equations have been proposed for the relation between volume of the gas or amount of the solute adsorbed per unit mass of the adsorbent and the pressure or concentration of the gas or the solute. Some of these equations have theoretical foundation while others are of a more empirical nature. Many of these equations are valid over small relative pressure ranges but do not fit experimental data when tested over the full range of relative pressures. Only those isotherms that are commonly used for the description of adsorption of gases or vapours onto the surface of porous adsorbents are outlined below. Some of these theories can also be extended to describe simultaneous adsorption of two more components.

1.3.1 Langmuir Isotherm

This isotherm describes adsorbate-adsorbent systems in which the extent of adsorbate coverage is limited to one molecular layer at or before a relative pressure of unity is reached. The isotherm was formulated on the basis of a dynamic equilibrium between the adsorbed phase and the vapor/liquid phase. Langmuir described chemisorption as the formation of an ionic or covalent bond between adsorbent and adsorbate. 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 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

\[
ka \cdot C \cdot (1-\theta) = kd \cdot \theta
\]
where $k_a$ and $k_d$ are the respective rate constants for adsorption and desorption respectively.

The above equation can be written in the form

$$\theta = \frac{q}{q_m} = b \frac{C}{(1+bC_e)}$$

(1)

where $b = k_d/k_a$ 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 ratio $q_e/q_m$ can be measured and expressed in different ways. The most widely used form, known as the two-parameter equation for a single solute system, is of the form represented by (1).

Application of the kinetic theory of gases reveals that the constant $b$ can be identified as

$$1/b = \left(\frac{v}{\sigma}\right) (2\pi mkT)^{1/2} \exp \left(-\frac{Q}{RT}\right)$$

(2)

where $Q$ is the heat of adsorption (equal to the difference $E_d - E_a$, $E_d$ and $E_a$ being the activation energies necessary for desorption and adsorption respectively. $v$ and $\sigma$ are respectively the pre-exponential factor of the desorption rate coefficient and the condensation coefficient of the adsorbate (it is defined as the fraction of those molecules that are adsorbed with an activation energy > $E_a$). $m$ and $k$ are the mass of the adsorbate molecule and the Boltzmann constant respectively.

Equation (1) can be rearranged to the form:

$$C_e/q_e = (1/bq_m) + (1/q_m) C_e$$

(3)

which shows that a plot of $(C_e/q_e)$ vs. $C_e$ should yield a straight line if the Langmuir equation is obeyed by the adsorption equilibrium. The slope and the intercept of this plot give the values of $q_m$ and $b$. These expressions have been shown to be valid in relatively higher concentration ranges (Dutta et al., 1999).

The Langmuir adsorption equilibrium constant, $b$, has the following expression in terms of statistical-mechanical thermodynamics,

$$b = \frac{Q_a}{Q_b} Q_e e^{-\Delta F_{av}/RT}$$

(4)
where \( Q_a \) is the partition function for the activated complex between the adsorbed molecule and the adsorbent, \( Q_g \) is the partition function for the adsorbate molecules, \( Q_s \) is the partition function of the solid adsorbent. \( E_o \) is the zero point activation energy of the activated complex, \( R \) is the gas constant, and \( T \) is the absolute temperature.

A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, \( R_L \) (Hall et al., 1966), also known as the separation factor, given by

\[
R_L = \frac{1}{1 + bC_e}
\]  

(5)

where \( C_e \) is any equilibrium liquid phase concentration of the solute at which adsorption is carried out. According to Hall et al. (1966), the values of \( R_L \) should lie between 0 and 1 for favorable adsorption, while \( R_L > 1 \) represents unfavorable adsorption, \( R_L = 1 \) linear adsorption and \( R_L = 0 \) irreversible adsorption.

At very low concentration/pressure, the equation (1) reduces to the linear form (Thomus and Crittenden, 1998)

\[
\theta = \frac{q}{q_m} = bp
\]  

(6)

If the adsorbate obeys the perfect gas laws, \( p \) can be replaced with \( CRT \) and the above equation becomes

\[
q_e = q_m bCRT = K(T)C
\]  

(7)

where \( K(T) \) incorporates both \( b \) and \( q_m \) and is known as the Henry’s constant, which is temperature dependent. At constant low coverage, the constant \( b \) is proportional to \( T^{-1/2} \cdot \exp (Q/RT) \). It follows then that \( K(T) \) is proportional to \( T^{1/2} \cdot \exp (Q/RT) \). Neglecting the weak component \( T^{1/2} \) of the variable, one obtains

\[
\ln K = \frac{Q}{RT}
\]  

(8)

which is identical in form to the integrated form of the classic van’t Hoff equation. Evaluation of the heat of adsorption \( Q \) may thus be obtained from the slope of a plot of \( \ln K \) against \( 1/T \).
Langmuir isotherm was originally devised to describe chemisorption processes; it is obeyed at moderately low coverages by a large number of systems and is therefore found to be of general application to describe binary adsorbate systems.

1.3.2 Freundlich Isotherm

There is abundant evidence to show that, for many systems, the heat of adsorption decreases in magnitude with increasing extent of adsorption. This has been well taken care of by the Freundlich isotherm, initially proposed only as an empirical isotherm. This isotherm was later derived by Laidler (Thomas and Crittenden, 1998) who showed that for small values of \( \theta \), the following equation can be obtained:

\[
\ln \theta = \frac{(RT)}{Q_0} \ln p + \text{constant} \tag{9}
\]

\( Q_0 \) is a constant related to the energy distribution of the adsorption sites. The above equation may be recast into the familiar Freundlich isotherm

\[
\theta = K_f p^n \tag{10}
\]

which is valid for \( n < 1 \). \( K_f \) and \( n \) are known as Freundlich coefficients. For adsorption from solution, equation (10) takes up the form:

\[
q_e = K_f C_e^n \tag{11}
\]

The Freundlich coefficients can be determined from the plots of \( \log q_e \) versus \( \log C_e \) on the basis of the linear form of the equation –

\[
\log q_e = \log K_f + n \log C_e \tag{12}
\]

The Freundlich isotherm is regarded as a special case of the Langmuir isotherm at intermediate coverage (\( 0 < \theta < 1 \)) and in contrast to the Langmuir isotherm, it does not provide an adsorption limit when coverage is sufficient to fill a monolayer (\( \theta = 1 \)).
1.3.3 Brunauer – Emmett – Teller (BET) isotherm

The formation of multiple layers of an adsorbate on the adsorbent surface could be interpreted with a theory proposed by Brunauer, Emmet and Teller (1938) who argued that the rate of condensation (adsorption) onto the bare surface equals the rate of evaporation from the first layer of adsorbate. If \( \theta \) denotes the fraction of the surface which is bare and \( z_m \theta_1 \), the number of occupied sites in the first layer (\( z_m \) is the number of molecules necessary to complete a monolayer and \( \theta_1 \) is the corresponding fraction of sites) then, the expression

\[
a_1 p \theta_0 - b_1 z_m \theta_1 e^{-E_1/RT} \tag{13}
\]

describes the dynamic equilibrium between the gas phase at pressure \( p \) and the first layer of the adsorbate. Here, \( a_1 \) is the number molecules which would successfully condense onto the bare surface per unit time per unit pressure and \( b_1 \) is the frequency with which molecules possessing sufficient energy \( E_1 \) leave the surface (desorption); the exponential term \( e^{-E_1/RT} \) in the expression is the probability that molecules have an energy greater than \( E_1 \) to escape from the first layer. The BET theory presumes that the probability of molecules evaporating from the layers is equal and is given by \( \exp (-E_i/RT) \) where \( E_i \) is the heat of liquefaction. The general expression for equation (13), when the interactions between the layers (i-1) and i are considered, is

\[
a_i p \theta_{i-1} - b_i z_m e^{-E_i/RT} \quad i = 2, 3, \ldots, n \tag{14}
\]

It is further assumed in the BET theory that \( a_i/b_i = c \) (a constant) at a given temperature. The sum \( \Sigma_i (i \theta_i) \) from \( i = 1 \) to \( i = n \) is the fractional extent of adsorption (\( \theta_i \) is the fraction of occupied sites corresponding to the ith layer having i molecules stacked one upon the other). The actual number of molecules adsorbed is \( z_m \Sigma_i (i \theta_i) \). The ratio, \( q_e/q_m \), of the quantity of the adsorbate adsorbed (expressed either in mass or volume at standard temperature and pressure) to the total adsorption capacity of the adsorbent is equivalent to \( z_e/z_m \). When the saturated vapour pressure \( p_o \) is reached, the adsorbate molecules totally condense on the adsorbent surface and \( \theta_1 = \theta_2 \) when \( p = p_o \). Thus,

\[
A_2 p_o = b_2 z_m e^{-E_1/RT} \tag{15}
\]

Proceeding similarly, the most useful form of the BET equation is derived as
\[
\frac{p}{[q_e(p_0 - p)]} = \left[\frac{1}{(q_mC)}\right] + \left[\frac{(C - 1)}{q_mC}\right] \cdot \left(\frac{p}{p_0}\right) \tag{16}
\]

At a fixed temperature, the plot of \(p/[q_e(p_0 - p)]\) against \((p/p_0)\) yields a slope of \((C - 1)/(q_mC)\) and an intercept of \((1/q_mC)\) enabling both \(q_m\) and \(C\) to be determined. The BET equation is extensively applied to the determination of the surface area of porous adsorbents. It is implicit in the BET theory that (i) there is no interaction between neighboring adsorbed molecules and (ii) the heat evolved during the formation of the second and subsequent layers of molecules on the surface equals the heat of liquefaction. At relatively small values of the relative pressure \((p/p_0)\), the BET equation reduces to the Langmuir equation.

1.3.4 Polanyi’s Potential Theory

This theory was first conceived by Polanyi and was well documented in the classic text by Brunauer (1943). Polanyi based his considerations on the adsorption potential, \(\varepsilon\), of the adsorbent surface, which was according to him independent of temperature so that \(\varepsilon = f(\Phi)\) is essentially an isotherm equation (\(\Phi_i\) is the volume space between the \(i\)th equipotential surface of energy, \(\varepsilon\) and the adsorbent surface). The adsorption potential is defined as the work of compression of the gas from a pressure \(p\) to the saturation pressure \(p_0\). For one mole of a perfect gas of volume \(v\) in an open thermodynamic system the adsorption potential is given by

\[
\varepsilon = \int v \, dp = RT \ln \left(\frac{p_0}{p}\right) \tag{17}
\]

where the integration is carried out from \(p\) to \(p_0\). It is assumed that the work of creating a liquid surface is small in comparison to the magnitude of \(\varepsilon\). The volume in the adsorption space is \(\Phi = nV_m\), where \(n\) is the number of moles adsorbed per unit mass of adsorbent and \(V_m\) is the molar volume. By plotting \(\varepsilon\) as a function of \(\Phi\), a characteristic curve \(\Phi(\varepsilon)\) is obtained which represents the extent of adsorption at any relative pressure and temperature below the critical temperature of the gas for a given adsorbate – adsorbent system.

Polanyi’s Potential Theory has found applications for both microporous solids and large pore adsorbents. For large pore adsorbents, Dubinin and Radushkevich (1947) had found a direct correlation between the molar volume in the liquid state and affinity coefficient \(\beta\) characterizing the polarizibility of the adsorbate and assumed that \(\varepsilon_i/\varepsilon_j = \beta_i/\beta_j = v_{mi}/v_{mj}\). For
non-polar and weakly polar adsorbates, such a correlation is not always obeyed, but this relationship continues to be utilized in order to force the characteristic curves of all gases on the same adsorbent to be coincident so that \( \varepsilon = \beta \cdot f(0) \). Spontaneous filling of large pores resulting in capillary condensation occurs if the adsorption potential is high and the repulsive forces are low. This gives rise to strong adsorbate-adsorbent affinity and weak interaction between successive adlayers.

Dubinin (1960) related the volume \( v \) adsorbed in micropores to the adsorption potential. The semi-empirical equation obtained by Dubinin, relating adsorbed volume \( v \) to the adsorption potential \( \varepsilon \) is

\[
v/v_0 = \exp(- \kappa \varepsilon^2/\beta^2) \tag{18}
\]

where \( v_0 \) is the total adsorption capacity of the adsorbent. The logarithmic form of the above equation in combination with the equation (17) is

\[
\ln \left( \frac{v}{v_0} \right) = -\kappa \left( \frac{RT}{P} \right)^2 \ln \left( \frac{P}{P_0} \right)^2 \tag{19}
\]

The volume \( v_0 \), according to Dubinin, represents the micropore volume and can be evaluated by plotting \( \ln \left( \frac{v}{v_0} \right) \) against \( \ln \left( \frac{P}{P_0} \right)^2 \).

### 1.3.5 Gibbs adsorption isotherm

The Gibbs function for a mobile adsorbate (an adsorbate which is not localized at particular adsorption sites) is represented as \( G(p, T, A, n) \) where \( A \) is the area over which the adsorbate has distributed itself and \( n \) is the number of moles of adsorbate on the adsorbent surface. At constant temperature \( T \) and pressure \( p \), a change in \( G \) can be written as

\[
dG = (\partial G/\partial A)_{p, T, n} dA + (\partial G/\partial n)_{p, T, A} dn \tag{20}
\]

the change depends on the initial and final states only, and any change in \( G \) can take place along any desired path. The negative value of the partial differential \( (\partial G/\partial A)_{p, T, n} \) is termed the spreading pressure \( \pi \), while the positive value of \( (\partial G/\partial A)_{p, T, A} \) is the chemical potential \( \mu \) of the adsorbate in the potential field of the adsorbent. The integrated form of (20) is:

\[
G = -\pi A + \mu n \tag{21}
\]
On general differentiation, it yields

\[ dG = - \pi dA + A d\pi + \mu dn + n d\mu \]  

(22)

which shows how all the variables A, \( \pi \), n and \( \mu \) contribute to a change in G. Subtracting (20) from (22),

\[ - A d\pi + n d\pi = 0 \]  

(23)

Using the thermodynamic relation \( d\mu = RT d\ln p \) (p is the partial pressure of the adsorbate), one obtains

\[ A d\pi = n RT d\ln p \]  

(24)

which is the differential form of the Gibbs adsorption isotherm. The integrated form is

\[ \pi = RT \int \frac{dn}{A} d\ln p = \frac{RT}{MS_g} \int q(p) d\ln p \]  

(25)

(Integration limits are from 0 to \( p_0 \))

in which \( q(p) \) is the mass of gas adsorbed per unit mass of the adsorbent, M the molecular mass of adsorbate and \( S_g \) the surface area per unit mass of the adsorbent. The simplest equation of state is \( \pi A = nRT \), analogous to the perfect gas law, and it is a simple matter to show that this equation of state substituted into the differential form of the Gibbs isotherm leads to Henry's law. If, on the other hand, \( (A - \alpha) \) replaces A in the equation of state (therefore allowing for the total extent, \( \alpha \), of area which the adsorbate molecules occupy), the results of substitution in the differential form of the Gibbs isotherm is Volmer's isotherm

\[ bp = \frac{\theta}{1 - \theta} [\exp(\theta/(1 - \theta))] \]  

(26)

provided the integration constant is defined in a way that Henry's law (\( \theta = bp \)) is obeyed when the pressure tends to zero and \( \theta \) is equal to \( \alpha/A \).

1.3.6 Redlich - Peterson Isotherm

Since Langmuir and Freundlich isotherms give poor performance in a large number of adsorption systems, isotherms with three adjustable parameters were developed. One of the
three-parameter isotherms proposed was by Redlich and Peterson (Ho et al, 2002), which has the form:

\[ \frac{C_c}{q_e} = \left(\frac{1}{K_R}\right) + \left(\frac{a_R}{K_R}\right) (C_e)^\beta \]  

(27)

where \( C_c \) is the equilibrium liquid phase concentration of the adsorbate (mmol/L), \( q_e \) is the equilibrium solid phase concentration of the adsorbate (mmol/g), \( K_R \) (L/g), \( a_R \) (L/mg) and \( \beta \) (exponent such that \( 0 < \beta < 1 \)) are adjustable Redlich-Paterson coefficients. This isotherm gave good fits in a large number of cases such as adsorption of phenol on various resins (Dutta, 1999). The Redlich-Paterson isotherm was subsequently modified by Jossens and co-workers (Ho et al., 2002) to the following form:

\[ q_e = \frac{(K_R C_e)}{[1+a_R(C_e)^\beta]} \]  

(28)

This equation has two limiting cases: at \( \beta = 0 \), it reduces to Henry's law equation, i.e.

\[ q_e = \frac{(K_R C_e)}{[1+a_R]} \]  

(29)

and at \( \beta = 1 \), it gives the Langmuir isotherm, i.e.

\[ q_e = \frac{(K_R C_e)}{[1+a_R C_e]} \]  

(30)

Rearranging equation (28) to the form

\[ K_R \left(\frac{C_c}{q_e}\right) - 1 = a_R (C_e)^\beta \]  

(31)

Which can be converted to a linear form by taking logarithm (McKay et al., 1984; Allen et al., 2003; Wang et al., 2003):

\[ \ln \left[K_R \left(\frac{C_c}{q_e}\right) - 1\right] = \ln a_R + \beta \ln C_e \]  

(32)
A minimisation procedure is adopted to solve equation (32) by maximizing the correlation coefficient between the theoretical data for $q_e$ predicted from the above equation and the experimental $q_e$ values.

1.3.7 Temkin Isotherm

The derivation of the Temkin isotherm is based on the assumption that the adsorption heat decreases linearly with coverage (instead of a logarithmic decrease as implied in the Freundlich isotherm). The isotherm has the form (Aharoni and Ungarish, 1977; Aharoni and Sparks, 1991):

$$q_e = \frac{RT}{b_T} \ln (A_T C_e) \quad (33)$$

where $b_T$ and $A_T$ (L/mmol) are Temkin isotherm coefficients.

1.3.8 Toth Isotherm

Derived from the potential theory, Toth isotherm (Toth, 1962) has proved useful in describing sorption in heterogeneous systems. In deriving this equation, an asymmetrical quasi-Gaussian energy distribution was assumed such that most of the adsorption sites have sorption energy less than the mean value. This equation has the following form:

$$q_e = \frac{K_t C_e}{(a_t + C_e)^{1/t}} \quad (34)$$

where $K_t$ and $a_t$ are Toth coefficients, and $t$ is Toth exponent.

1.3.9 Multi Component Adsorption Isotherm

The techniques used to obtain single-component experimental isotherm may also be employed to gather data for multicomponent isotherms with the additional premise that for every quantity of adsorbate mixture adsorbed by the adsorbent of the gas or liquid phase must be determined. Correlations based upon the Langmuir, Polanyi and Gibbs theories for the adsorption of gases have emerged and the statistical thermodynamic approach outline by Ruthven has also been extended to incorporate the adsorption of gaseous mixture.

Langmuir isotherm can be extended to gaseous or liquid mixture (Thomus and Crittenden, 1998) by assuming that for each component, equilibrium exists between the amount adsorbed at the surface and the partial pressure/concentration of that component in the mixture.
Fractional coverage \( \theta_i \) and partial pressure \( P_i \) are ascribed to each of the components, the total surface coverage being the sum of the coverages of the individual components. The resulting isotherm for component \( i \) is

\[
\theta_i = \frac{q_i}{q_{mi}} = \frac{b_i p_i}{(1 + \Sigma b_i p_i)}
\]

(Summation is from \( n = 1 \) to \( n = n \))

where \( q_{mi} \) is the quantity of component \( i \) in a monolayer of mixed adsorbates. It has been seen from thermodynamic principles that for consistency, the monolayer quantity or volume for each of the adsorbed components must be identical. This is demonstrated by defining a separation factor

\[
K_{12} = \frac{q_2}{c_2} / \frac{q_1}{c_1}
\]

by analogy with the definition for vapour-liquid mixtures in which a comparison is made of the relative volatilities of each component. If \( Q_T \) and \( C_T \) represent total concentrations of adsorbed and gas phases respectively, then the above equation may be written in the form

\[
q_i/Q_T = \frac{(c_i C_T)}{[K_{12} + (1 - K_{12})(c_i/C_T)]}
\]

A plot of \( (c_i Q_T / q_i C_T) \) as a function of \( (c_i C_T) \) should yield a straight line if \( K_{12} \) is constant (or \( b_1 = b_2 \) for equal \( q_m \) values).

If for a binary mixture, \( a_1 = a_2 \), and the extended Langmuir equation is obeyed and if \( q^0_1 \) and \( q^0_2 \) are the adsorbed phase concentrations for the pure components at pressure \( P^0_1 \) and \( P^0_2 \) while \( q_1 \) and \( q_2 \) are the corresponding quantities for the mixture at partial pressure \( P_1 \) and \( P_2 \), then

\[
q_1/q^0_1 + q_2/q^0_2 = 1
\]

provided \( P^0_1 = P^0_2 = (P_1 + P_2) \). This correlation was first proposed by Lewis et al. (1950) and is of general applicability as an empirical relation. If the maximum capacity for micropore filling of the adsorbent is \( m_0 \) and \( v_m \) is the molar volume of the adsorbate mixture then the total number, \( n_T \), of moles of mixture adsorbed is \( m_0 / v_m \). The number of moles \( n_i \) of a component \( i \) is \( (x_i n_T) \) where \( x_i \) is the mole fraction of component \( i \). Provided there is no volume change in mixing, the partial molar volumes are additive and \( v_m = \Sigma x_i v^0_i \) where \( v^0_i \)
is the molar volume of component 1 for the pure gas at the temperature and total pressure of adsorption. Hence, it follows that

\[ \sum n_i/n_0^i = 1 \]  \hspace{1cm} (39)

where \( n_0^i \) is written for \( m_0/v_m \). This relation has the advantage of having both pure component and mixture data.

Grant and Manes (1966) have suggested a model for mixed adsorption – based on the Polanyi potential theory with the assumption of equal potential energy of all the components in the mixture. The equipotential energy concept for the two-component system is thus \((c_i/\beta_i) = (e_j/\beta_j)\), where represent affinity coefficient of a component. Hence using equation (17) for each of the components,

\[ \frac{(RT/v_m)}{ln \left( \frac{p_0^i}{p_i} \right)} = \frac{(RT/v_m)}{ln \left( \frac{p_0^j}{p_j} \right)} \]  \hspace{1cm} (40)

1.3.10 Thermodynamics of Adsorption

The phenomenon of adsorption is essentially an attraction of adsorbate molecules to an adsorbent surface. There are many reasons why it should be possible 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). In general, the interaction potential may be written as

\[ U = U_d + U_r + U_p + U_{fd} + U_{fq} + U_{sp} \]  \hspace{1cm} (41)

where \( U_d \) is the attractive (dispersion) potential, \( U_r \) the close-range repulsion term, \( U_p \) the polarization energy, \( U_{fd} \) the field-dipole interaction, \( U_{fq} \) the field-gradient–quadrupole interaction, and \( U_{sp} \) a self-potential, which take into account adsorbate-adsorbent interactions. The first three terms on the right hand side of the above equation are always present, irrespective of the nature of the adsorbate and adsorbent. The next two, \( U_{fd} \) and \( U_{fq} \), depend upon the presence or absence of permanent dipoles or quadrupoles respectively in the adsorbate; and \( U_{sp} \) vanishes for small uptakes.
Interaction between adsorbate and adsorbent consist of molecular forces embracing permanent dipole, induced dipole and quadrupole electrostatic effects, otherwise known as van der Waals forces. Both short range (repulsive) and long range (attractive) forces between adsorbate and adsorbent become balanced when adsorption occurs. The adsorption is nearly always an exothermic process. Physical adsorption (as distinct from chemisorption involving the sharing or exchange of electrons between adsorbate and adsorbent) of a gas or vapour is normally characterized by the liberation of between 10 and 40 kJ mol\(^{-1}\) of heat which is close to values associated with heats of liquefaction of gases.

The important thermodynamic parameters, entropy (S), enthalpy (H) and Gibbs energy (G) for the adsorption process can be obtained from the following two fundamental relationships:

\[
\Delta G^0 = \Delta H^0 - T \Delta S^0 \tag{42}
\]
\[
\Delta G^0 = -2.303 \, RT \log K \tag{43}
\]

where \(\Delta G^0\), \(\Delta H^0\) and \(\Delta S^0\) respectively represent standard Gibbs energy change, standard enthalpy change and standard entropy change for the adsorption process, and \(K\) is the equilibrium constant for the adsorbate-adsorbent equilibrium. Equation (43) is the classic van't Hoff equation.

The equations (42) and (43) can be used to find the thermodynamic parameters utilizing the Langmuir isotherm equation

\[
\theta = \frac{q_e}{q_m} = \frac{bC_e}{(1+bC_e)} \tag{1}
\]

which at low concentrations reduces to the linear form

\[
\theta = \frac{q_e}{q_m} = bC_e \tag{44}
\]

The equation (44) can be written in the form (Thomas and Crittenden, 1998):

\[
q_e = q_m bRT C_e = K(T) C_e \tag{45}
\]

where \(K(T)\) incorporating both \(b\) and \(q_m\) is dependent on temperature and is known as Henry's Constant. The equation (45) in combination with equation (2) i.e.
\[ \frac{1}{b} = \left( \frac{v}{\sigma} \right) (2\pi mkT)^{1/2} \exp \left( -\frac{\Delta H^0}{RT} \right) \]  

(2)

may be written as

\[ K(T) = \frac{q_e}{C_e} - q_m bRT = q_m \left( \frac{\sigma}{\nu} \right) (2\pi mkT)^{1/2} \exp\left( -\frac{\Delta H^0}{RT} \right) \]

\[ \log K = \log \left( \frac{q_e}{C_e} \right) = -\frac{\Delta H^0}{2.303RT} + \text{constant} \]  

(46)

Comparing the equation (46) with the classic van’t Hoff equation (43) and also using equation (42), one gets

\[ \log K = -\frac{(\Delta G^0/2.303 RT)}{2.303 RT} = -\frac{\Delta H^0}{2.303RT} + \Delta S^0/2.303 R \]  

(47)

From equation (47), it is seen that the 'constant' in equation (46) is given by \((\Delta S^0/2.303 R)\) which is true when the weak component \(T^{1/2}\) is neglected as was done by Thomas and Crittenden (1998). Plotting \(\log K\) against \(1/T\), \(\Delta H^0\) and \(\Delta S^0\) could be determined along with \(\Delta G^0\).

1.4 Adsorption Kinetics

In the ideal case, when a clean non-porous adsorbent surface is exposed to a gaseous adsorbate and the fluid boundary layer between the two offers no resistance to the transport of the gas molecules to the solid surface, the rate of adsorption will be extremely rapid. In case of physical adsorption, adsorbate molecules are bound to the surface by weak van der Waals forces and the energy barrier that the molecules have to overcome for undergoing adsorption is very small. Consequently, the energy released in physical adsorption is close to the heat of liquefaction of the adsorbate gas and desorption takes place with equal ease with approximately similar quantity of heat of desorption. The two processes are reversible and non-activated. Chemisorption involves moderately strong chemical bonds between adsorbate and adsorbent.

The mass of a gas striking unit area of the adsorbent surface in unit time could be obtained from the kinetic theory of gases as

\[ R_m = p \left( \frac{M}{2\pi RT} \right)^{1/2} \]  

(48)
where $R_m$ is the rate (kg m$^{-2}$ s$^{-1}$) at which gas molecules of molecular mass, $M$, at a pressure, $p$ and temperature, $T$, strike the surface. Equation (36) actually gives the upper limit of the rate. In actual case, there are many factors, which resist transport of fluid molecules to the solid surface (Thomas and Crittenden, 1998), viz.,

i) Mass and heat transfer of adsorbate to and from the exterior surface of the adsorbent (inter particle transport),

ii) Maxwellian diffusion (bulk molecular diffusion) in moderately large pores (macropores) or Knudsen diffusion in micropores (which have a diameter smaller than the mean free path of the adsorbate molecules),

iii) Intra-crystalline diffusion within the channel and cage-like structure of molecular sieve materials such as zeloîtes and silicates,

iv) Surface diffusion when adsorbate molecules move freely over the internal surface of adsorbents in parallel with intraparticle diffusion, and

v) Heat transfer within the interior of particles due to the exothermic nature of adsorption.

The relative importance of these processes depends on the nature of the adsorbent and the adsorbate, and the adsorption conditions, i.e. pressure, temperature, etc.

The rate law describing a sorption system should address the requirements of the knowledge of all the molecular details of the reaction including the energetics and the stereochemistry, interatomic distances and angles throughout the course of the reaction, and the individual molecular steps involved in the mechanism. Several kinetic models are in use to explain the mechanism of the adsorption processes.

1.4.1 Simple Pseudo-First order Kinetics

The mechanism of adsorption often involves chemical reaction between the functional groups present on the adsorbent surface and the adsorbate molecules, ions or atoms. This involves, in most cases, formation of metal-organic complexes or cation exchange reactions due to high cation exchange capacity of the adsorbents. Other possible mechanisms involve mass-transport processes, bulk transport in the liquid phase, diffusion across the liquid film surrounding the solid particles, and diffusion into micro pores and macro pores.
The net dispersion, electrostatic, chemisorptive and functional group interactions broadly define the affinity of an adsorbent for a specific adsorbate. The factors, which affect adsorption with respect to a particular adsorbate, are

i) Concentration,
ii) Molecular mass,
iii) Molecular size,
iv) Molecular structure,
v) Molecular polarity,
vi) Steric form or configuration,
vii) Competitive adsorption with other adsorbates, and
viii) The nature of the background.

The important characteristics of the adsorbent that determine equilibrium capacity and rate, are

i) The surface area,
ii) The physico-chemical nature of the surface,
iii) The availability of that surface to adsorbate molecules or ions,
iv) The physical size and form of the adsorbent particles.

System parameters such as temperature and pH can also markedly influence adsorption as they affect one or more of the above parameters.

The order of adsorbate-adsorbent interactions has been described by using various kinetic models. Traditionally, the pseudo first order model derived by Lagergren (1898) has found wide applications. In the case of adsorption preceded by diffusion through a boundary, the kinetics in most cases follows the pseudo first order rate equation of Lagergren.

\[
dq_t / dt = k_1 (q_e - q_t)
\]  

(49)
where \( q_t \) and \( q_e \) are the amount adsorbed at time \( t \) and at equilibrium, \( k_1 \) is the rate constant of the pseudo first order adsorption process. The integrated rate law, after applying the initial condition of \( q_t = 0 \) at \( t = 0 \), is

\[
\log (q_e - q_t) = \log q_e - \left( \frac{k_1}{2.303} \right) t
\]  

(50)

Plot of \( \log (q_e - q_t) \) vs. \( t \) gives a straight line for first order kinetics, which allows computation of the adsorption rate constant, \( k_1 \). If the experimental results do not follow equations (49) and (50), they differ in two important aspects:

(i) \( k_1 (q_e - q_t) \) then does not represent the number of available sites, and

(ii) \( \log (q_e) \) (obtained from the experimental values of \( q_e \)) is not equal to the intercept of the plot of \( \log (q_e - q_t) \) against \( t \).

1.4.2 Simple Pseudo-second Order Kinetics

If the above two conditions are not satisfied by the Lagergren plots, pseudo second order kinetics (Ho and McKay, 1998b; 1998d) have to be applied to the results. The second order kinetic equation is given by

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

(51)

where \( k_2 \) is the second order rate constant. For the boundary conditions \( t = 0 \) to \( t = t \) and \( q_t = 0 \) to \( q_t = q_t \), the integrated form of the equation is:

\[
\frac{1}{(q_e - q_t)} = \frac{1}{(q_e)} + k_2 t
\]  

(52)

which can also be written as

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

(53)

or, in the linear form,

\[
\frac{t}{q_t} = \frac{1}{h} + \left( \frac{1}{q_e} \right) t
\]  

(54)
where \( h = k_2 q_b^2 \) can be regarded as the initial sorption rate as \( t \to 0 \). If the pseudo second order kinetics is applicable, the plot of \( t/q_t \) vs. \( t \) gives a linear relationship, which allows computation of \( q_e \), \( k_2 \) and \( h \) without having to know any other parameter.

1.4.3 Elovich Equation

The Elovich Equation (Thomas and Thomas, 1997) represents adsorption kinetics by the following equation,

\[
dq_t/dt = \alpha \exp(-\beta q_t)
\]  

(55)

where \( q_t \) is the amount adsorbed at time \( t \), \( \alpha \) and \( \beta \) are known as the Elovich coefficients. This equation was first formulated to describe the kinetics of oxidation reactions, but it has been found to be equally useful in the description of the adsorption processes. The constant, \( \beta \) is independent of pressure and temperature while the constant, \( \alpha \) is related to

i) The rate at which molecules strike the surface,

ii) The number \( N_s \) of active adsorption sites per unit area available initially and

iii) The probability of molecules possessing sufficient activation energy to form chemical bonds at the surface.

Thus, \( \alpha \) in its full form is given by

\[
\alpha = \left[ s' p N_s / (2 \pi m k T)^{1/2} \right] \exp \left( - E_a / RT \right)
\]  

(56)

where \( s' \) is the condensation coefficient and \( E_a \) is the activation energy for adsorption. For a linear dependence of the activation energy on the amount adsorbed, \( E_a \) is given by

\[
E_a = E_0 + mq
\]  

(57)

where \( E_0 \) is independent of the amount adsorbed. Substitution of (56) and (57) in (55) gives:

\[
dq/dt = \left[ s' p N_s / (2 \pi m k T)^{1/2} \right] \exp \left( - E_0 / RT \right)
\]  

(58)
which is another form of the Elovich equation. $N_s$ is sometimes expressed as the fraction $(1-\theta)$ of free surface related to the amount adsorbed by the expression:

$$N_s = N_s^0 \exp(-\beta q)$$

Chien and Clayton (1980) simplified the Elovich equation (55) by assuming $\alpha \beta t >> 1$ and by applying the boundary conditions, $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ to obtain the following equation by integration (Spades, 1986; Ho and McKay, 2002):

$$q_t = \beta \ln (\alpha \beta) + \beta \ln t$$

A plot of $q_t$ against $\ln t$ is linear when the Elovich equation is obeyed. Discontinuity in these plots is indicative of the presence of contaminants vitiating the single rate process. Slow chemisorption processes, sometimes preceded by an initial rapid uptake of the adsorbate, can often be described by the Elovich equation.

The basis of most models to explain the Elovich equation is the concept that the rate of adsorption is a function of the partial pressure $p$ of the gaseous adsorbate and the concentration $N_s$ of available adsorption sites at a given moment. This is the starting point leading to a variety of interpretations. At constant temperature and partial pressure the equation becomes

$$\frac{dq}{dt} = k N_s$$

but to obtain the Elovich equation from the above, further assumptions are necessary. Two types of models, one based on a variation in the number of adsorption sites, and the other based on an activation energy which varies with coverage, are successful in explaining the experimentally observed adsorption kinetics. A theoretical interpretation of the linear portion of a plot of $q_t$ against $\ln t$ thus rests on assumptions concerning the constancy, or otherwise, of the number of adsorption sites.

The Elovich equation is also valid for a situation in which there is (i) an exponential variation of the number of ensembles of molecules requiring a given activation energy for adsorption and (ii) a linear dependence of activation energy on the number of ensembles present. The Elovich equation is a most convenient way of representing the relatively slow chemisorption processes typical of a wide variety of gas-solid interactions.
1.4.4 Intra particle Diffusion

Evaluating the role of diffusion in the adsorption process can explain the variation in the amount of adsorption with time at different initial metal ion concentrations. Adsorption is a multi-step process involving transport of the solute molecules from the aqueous phase to the surface of the solid particulates and then, diffusion of the solute molecules into the interior of the pores – which is likely to be a slow process and is therefore, rate determining. When the intra particle diffusion process controls the rate of a reaction, the uptake curve for the solution is represented by the following familiar expression (Ruthven 1984; Banerjee et al., 1997):

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

(62a)

where \(X_A/X_{Ae}\) = fractional approach to equilibrium, \(D_c\) = intracrystalline diffusivity, \(r\) = particle radius, and \(t\) = reaction time. The summation is carried out from \(n = 1\) to \(n = \alpha\).

The lines representing the above expression converge asymptotically over time since the higher terms of the summation become small and are negligible. Therefore, the equation above can be rewritten in the following simplified form:

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

(62b)

A 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:

\[
k = \frac{\pi^2 D_c}{r^2}
\]  

(63)

where \(k\), the overall rate constant is inversely proportional to the square of the particle radius. The intra-particle diffusion rate constant (\(k_i\)) is given by the equation (Weber and Morris, 1963):

\[
q_t = k_i t^{0.5}
\]  

(64)

If a linear relation is observed between \(q_t\) and \(t^{0.5}\) (McKay and Allen, 1980), \(k_i\) can be obtained from the slope.
Adsorption of ions is normally controlled by an ion exchange mechanism consisting of three diffusion steps:

(i) Transport of the ions from the bulk solution to the film surrounding the adsorbent,
(ii) Transfer from the film to the adsorbent surface leading to surface adsorption, and
(iii) Diffusion from the surface to the internal sites, followed by binding of the ions on the active sites (Boyd et al., 1949; Cortina and Miralles, 1997; Yu et al., 2004).

The kinetics of the exchange adsorption of ions from aqueous solution may be governed either by a diffusion mechanism or by a mass action mechanism depending on which of the above steps is slowest. Boyd et al. (1949) suggested the following equation to describe the kinetics of exchange adsorption of ions from solution:

\[
\ln(1 - F) = -kt
\]

where \( F \) is the fractional attainment of equilibrium (\( = q_t/q_e \), \( q_t \) and \( q_e \) are the amount of solute adsorbed at any time and at equilibrium per unit mass of the adsorbent), \( k \) is the adsorption rate constant. A linear plot of \( -\ln(1 - F) \) vs. \( t \) with zero intercept is a clear indication that the adsorption process is controlled by liquid film diffusion. This is also known as the Liquid film Diffusion Model.

### 1.5 The Adsorption Process

The interactions between adsorbate and adsorbent ultimately lead to a thermodynamic equilibrium between the solid and the fluid phases. Under equilibrium conditions, the rates of adsorption and desorption are equal and the net loading on the solid cannot increase further. It may be necessary for regenerating the adsorbent to carry out further adsorption. The adsorption system is devised in a way to ensure maximum contact between the fluid (adsorbate) and the solid (adsorbent). The adsorption processes are carried out in any of the following three ways:

a) Batch process,

b) Fixed bed process, or

c) Moving bed process.
Batch process. In a batch process (Thomas and Crittenden, 1998), the adsorbent moves relative to the walls of the containing vessel. The simplest process involves mixing a batch of adsorbent with a batch of fluid, most commonly a liquid. After a predetermined time, the adsorbent can be separated from the fluid by sedimentation, filtration, etc. Powdered activated carbon (PAC) is often used in this way to remove tastes and odor from waters. If sufficient time is allowed for equilibrium to be reached then the loading of the adsorbate on the adsorbent will be related to the final concentration of the adsorbate in the solution through an isotherm equation. Powdered or granular adsorbents are usually added to the equipment in slurry form in such a way as to allow adequate dispersion and mixing. The adsorbent can be removed as a settled sludge. When large quantities of adsorbent are to be used, a multiple batch or cross-flow system may be designed. After separation of the fluid from the adsorbent, the fluid 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 fluid decreases.

Fixed and moving bed processes. Vessels and columns, which hold the adsorbent in a fixed position, appear initially to provide distinct advantages over their counterparts in which the adsorbent is allowed to move. First, such equipment is simple and relatively inexpensive to fabricate. Secondly, minimal attrition of adsorbent occurs when it remains fixed in position. However, despite their simplicity, the fixed bed processes have the following disadvantages (Thomas and Crittenden, 1998):

(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. At any instant in time, the adsorbent particles upstream and downstream of the mass transfer zone (MTZ) do not participate in the mass transfer processes. Upstream of the MTZ, the adsorbent will be in equilibrium with the feed and unable to adsorb further adsorbate molecules. Downstream of the MTZ, the adsorbent will not have been in contact with any adsorbate molecules and therefore,
despite having the capability of doing so, will also be unable to adsorb adsorbate molecules. In addition, the pressure drop will be proportionately large.

(ii) 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 process. 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 an exothermic process and desorption can therefore be effected by raising the temperature of the adsorbent. In thermal regeneration, or thermal swing, processes it is difficult to heat and cool large beds of highly porous adsorbent materials quickly because the heat transfer processes are not good. Poor heat transfer leads to long heating and cooling times, which thereby creates the need for large beds. A further disadvantage of poor heat transfer can manifest itself in a rise in the temperature of the bed in or near to the MTZ due to the exothermic nature of the adsorption process.

(iv) Despite the apparent simplicity of fixed beds, they are difficult to design accurately because the progress of the MTZ introduces time into the design equations. Several short-cut design techniques exist but they can vary considerably in their accuracy. The uncertainties, which arise, and the simplifications which are often required, inevitably introduce complications in the design.

The main advantage of moving bed processes is that the adsorbent can be regenerated as soon as its role in the adsorption process has been completed. Additionally, heat transfer in moving bed and fluidized bed systems is better than in fixed beds. Thus, if the technical challenges of designing adsorbents, which are sufficiently rugged for moving bed and fluidized processes, can be overcome, then not only will less amount of adsorbent be required but also the processes will be easier to design. In order to gain the best advantages of both the fixed bed and the moving bed techniques, it is technically and economically feasible to operate a single fixed bed in such a way that a continuous steady state process can be simulated.

A fixed bed adsorber consists of vertical and cylindrical vessels. While horizontal vessels are occasionally used, vertical orientation is preferred to avoid the creation of flow misdistribution when settling of a bed or movement of particles within it occurs.
Five categories of data are required in any adsorption process (Thomas and Crittenden, 1998), viz.,

a) Adsorbate-adsorbent thermodynamic equilibrium relationships, including appropriate interaction data for multicomponent system. It is necessary initially to identify an adsorbent, which is capable of effecting the required separation. Then it is necessary to consider the effect that the other adsorbates in a multicomponent feedstock may have on equilibrium of each component, and the method by which the adsorbent is to be regenerated if it is going to be discarded after the adsorption step.

b) Adsorbate-adsorbent kinetic relationships, again including appropriate interaction data for multicomponent systems. Separations are rarely controlled by equilibrium considerations alone and therefore it is necessary to determine whether or not the selected adsorbent has the requisite kinetic properties. The rate of adsorption will determine the size of the equipment for those separations, which do not have extremely, fast kinetics, i.e. those that cannot be described as being equilibrium controlled.

c) Heat of adsorption as a function of the operating conditions including the composition. The process can be considered isothermal or not depending on the magnitude of the heat of adsorption per mol and the concentration(s) of the adsorbate(s) in the feedstock. The design process using rigorous methods is simplified considerably if the heat released on adsorption is low. Even so, energy balance calculations may still be required if desorption, or regeneration of the adsorbent is to be carried out at elevated temperature.

d) Hydrodynamic data. These are required to determine pressure gradients and to evaluate the importance of dispersion in the design process.

e) Physical property data. Basic information required over the ranges of temperature, pressure and composition to be encountered in the process includes the density, viscosity, thermal conductivity, specific heat and molecular diffusivities of fluids together with the specific heat of the adsorbent and bulk voidage and bulk density of the adsorbent bed.

It is fortunate that for many fixed bed adsorption processes of commercial interest, the shape of the mass transfer zone remains unaltered as it progresses through the bed. This allows substantial simplification in design.
Procedures for the treatment of water/wastewater were first developed in response to the concern for public health and the adverse conditions caused by the discharge of wastewater to the environment. Biological degradation, although very common in treating organic wastes, requires large land area and is constrained by sensitivity towards diurnal variation as well as toxicity of some chemicals and less flexibility in design and operation. Limited availability of land due to rapid expansion of urbanization is another reason for this. In general, early treatment objectives were concerned with

a) The removal of suspended and floatable material,
b) The treatment of biodegradable organics, and
c) The elimination of pathogenic organisms.

A significant event in the field of wastewater management was the enactment of a large number of statutes and rules by various countries starting from the early seventies. These also prescribed the treatment methods. The contaminants in wastewater are removed by physical, chemical, and biological means (Metcalf and Eddy, 1989).

**Physical unit operations.** Treatment methods in which the application of physical forces predominates are known as physical unit operations. Because most of these methods evolved directly from man's observations of nature, they were the first to be used for wastewater treatment. Screening, mixing, flocculation, sedimentation, floatation, and filtration are typical unit operations.

**Chemical unit processes.** Treatment methods in which the removal or conversion of contaminants is brought about by the addition of chemicals or by other chemical reactions are known as chemical unit processes. Precipitation, gas transfer, adsorption, and disinfection are the most common examples of chemical unit processes used in wastewater treatment. In chemical precipitation, treatment is accomplished by producing a chemical precipitate that will settle. In most cases, the settled precipitate will contain both the constituents that may have reacted with the added chemicals and the constituents that were swept out of the wastewater as the precipitate settled. Adsorption involves the removal of specific components from the wastewater on solid surfaces using the forces of attraction between bodies.
Advantages with adsorption. Adsorption has remained one of the most used techniques for removal of toxic trace metals and persistent organic micro pollutants from water. Adsorption is a superior technique in terms of initial cost, simplicity of design, ease of operation and insensitivity towards toxic substances (Meshko et al., 2001). However, it is to be noted that many adsorbents have poor removal efficiency, high cost of production and regeneration. Some adsorbents also generate secondary pollution and are ineffective at low pollutant load. The choice of an adsorbent is to be based on these considerations.

Application of the adsorption process for water treatment is usually through application of a fixed bed. Operational factors such as input liquid concentration, particle size, and flow rate are important in column design (Noll et al., 1992). Adsorption onto solid adsorbents has great environmental significance, since it can effectively remove pollutants from both aqueous and gaseous streams. Due to the high degree of purification that can be achieved, this process is often used at the end of a treatment sequence. In many of the industrial applications, recovery and reuse of the removed pollutants have become possible, since under certain conditions, the adsorption process is reversible.

Desorption and Regeneration of the adsorbent.

The success of an economical adsorption system usually depends on the regenerability of the adsorbent. The exception is where there are very long adsorption or loading cycles due to very low concentration of solute in the inlet feed; this type of system usually uses the adsorbent only once on a "through-way" basis and safe disposal is a key problem. Clearly the nature and concentration of the adsorbates will dictate the disposal route to be followed. Disposal would be favoured when the adsorbent is of low cost, is very difficult to regenerate (perhaps because the adsorbates are held by strong chemical forces) and the non-adsorbed products of the adsorptive separation are of very high value. In the majority of process applications, disposal of the adsorbent as a waste is not an economic option and therefore regeneration is carried out either in situ or external to the adsorption vessel to an extent that the adsorbent can be reused. Practical methods of desorption regeneration include one, or more, usually a combination, of the following:

- Increase in temperature,
- Reduction in partial pressure,
- Reduction in concentration,
- Purging with an inert fluid,
• Displacement with a more strongly adsorbing species,
• Change of chemical condition such as pH.

As a variable for changing thermodynamic potential, a change in temperature is much more effective than a change in pressure. However, the final choice of regeneration methods depends upon technical and economical considerations. The most common methods are changes in temperature (thermal swing adsorption) and changes in pressure (pressure swing adsorption). The general advantages of each method together with some process examples are presented in Table 1.6.

Temperature, pH, and solvent play important role on desorption of the adsorbate from the adsorbent and its regeneration. Chern and Wu (2001) have demonstrated the effect of temperature, pH, and alcohol on desorption of dyes from activated carbon beds. Kadiravelu et al. (2003) have reported that a cadmium-loaded adsorbent could be regenerated by first washing with distilled water and then agitating with hydrochloric acid.

1.6 Literature Review on removal of pollutants by adsorption

The literature is full of references on use of various materials as adsorbents for removal of a large number of pollutants from water. A large number of published works with treatment of various aspects of the adsorption process have been studied during this work and these have been very useful in understanding the complex process of adsorption and in the use of various computational and other techniques in the present work. It is almost impossible to list all these references. An attempt only is made to include a cross-section of the references consulted during the present work, which have been useful in some way or other. Most of the references included are from published works of last few years. A list of such references is given in Table 1.7.
Table 1.6. Methods of regeneration with process examples

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Process</th>
<th>Adsorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal swing</td>
<td>Good for strongly adsorbed species.</td>
<td>Thermal ageing of sorbent.</td>
<td>Drying of gases.</td>
<td>3A, 4A, 13X</td>
</tr>
<tr>
<td></td>
<td>Desorbate recovered at high concentrations.</td>
<td>Heat loss leads to thermal inefficiency.</td>
<td>Drying of solvents.</td>
<td>4A</td>
</tr>
<tr>
<td></td>
<td>For gases and liquids</td>
<td>Long cycle times mean inefficient use of sorbent.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>High latent heat for liquids.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressure swing</td>
<td>Good for weakly adsorbed species required in high purity</td>
<td>Very low pressure may be required</td>
<td>Drying of gases.</td>
<td>3A, 4A, 13X</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mechanical energy more expensive than heat</td>
<td>Hydrogen recovery</td>
<td>Molecular sieve</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Air separation</td>
<td>Carbon molecular sieve</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Zeolite</td>
</tr>
<tr>
<td>Vacuum (Special case of pressure Swing)</td>
<td>Rapid cycling gives efficient use of sorbent</td>
<td>Desorbate recovered at low purity</td>
<td>Separation of linear paraffin</td>
<td>5A mol sieve</td>
</tr>
<tr>
<td>Displacement</td>
<td>Good for strongly held species.</td>
<td>Product separation and recovery needed. (Choice of desorbent fluid is crucial)</td>
<td>Separation of linear from branched and cyclic paraffins</td>
<td>5A molecular sieve</td>
</tr>
<tr>
<td>Purge gas stripping</td>
<td>Essentially at constant T and P</td>
<td>Only for weakly sorbed species, purge flow is high.</td>
<td>Relatively uncommon without thermal swing since purging alone is suitable for weakly adsorbed species.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Not normally used when desorbate needs to be recovered.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stream Stripping (combination of thermal swing and displacement)</td>
<td>As for thermal swing and displacement above</td>
<td></td>
<td>Waste water purification</td>
<td>Activated carbon</td>
</tr>
</tbody>
</table>

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Table 1.7: A selection of recently published works on removal of pollutants by the adsorption technique.

<table>
<thead>
<tr>
<th>Author</th>
<th>Adsorbent</th>
<th>Pollutants</th>
<th>Study parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Singh et al, 1988</td>
<td>Haematite</td>
<td>As (III)</td>
<td>Kinetics, Thermodynamics</td>
</tr>
<tr>
<td>Khan et al., 1995</td>
<td>Bentonite</td>
<td>Cr (VI), Cr (III), Ag (I)</td>
<td>Adsorption equilibrium, Thermodynamics</td>
</tr>
<tr>
<td>Ho et al., 1995</td>
<td>Sphagnum Moss peat</td>
<td>Ni (II)</td>
<td>Adsorption equilibrium, Thermodynamics</td>
</tr>
<tr>
<td>Jain et al., 1997</td>
<td>Bed Sediments</td>
<td>Pb (II), Zn (II)</td>
<td>Adsorption equilibrium</td>
</tr>
<tr>
<td>Ho and McKay, 1998b</td>
<td>Wood</td>
<td>Basic Blue 69, Acid Blue 25</td>
<td>Kinetics, adsorption capacity</td>
</tr>
<tr>
<td>Ho and McKay, 1998a</td>
<td>Peat</td>
<td>Basic Blue 69, Acid Blue 25,</td>
<td>Kinetics, adsorption capacity</td>
</tr>
<tr>
<td>Ho and McKay, 1998c</td>
<td>Wood and peat</td>
<td>Basic Blue 69, Acid Blue 25,</td>
<td>Optimization model</td>
</tr>
<tr>
<td>Tran et al., 1999</td>
<td>Silica Gel</td>
<td>Pb(II), Cu(II), Ni(II), Zn(II), Cd(II),</td>
<td>Adsorption capacity, Kinetics</td>
</tr>
<tr>
<td>Ho and McKay, 1999a, 1999e</td>
<td>Peat</td>
<td>Pb (II)</td>
<td>Kinetics, Adsorption capacity</td>
</tr>
<tr>
<td>Ho and McKay, 1999b</td>
<td>Peat</td>
<td>Cu (II), Ni(II)</td>
<td>Competitive adsorption, Isotherm</td>
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<tr>
<td>Ho and McKay, 1999c, 1999f</td>
<td>Pith</td>
<td>Basic Red 22, Acid Red 114</td>
<td>Kinetics, Adsorption capacity</td>
</tr>
<tr>
<td>Ho and McKay, 2000</td>
<td>Sphagnum Moss peat</td>
<td>Pb (II)</td>
<td>Isotherm, Kinetics</td>
</tr>
<tr>
<td>Wu et al., 2000</td>
<td>Chitosans</td>
<td>Cu (II), Reactive dye RR222</td>
<td>Adsorption capacity</td>
</tr>
<tr>
<td>Al-Qodah, 2000</td>
<td>Shale oil ash</td>
<td>Drim yellow-K4G, Drim blue-KBL, Drim yellow-K4BL</td>
<td>Adsorption capacity, Isotherm, Kinetics</td>
</tr>
<tr>
<td>Ho and Chiang, 2001c</td>
<td>Mixture of activated carbon and activated clay</td>
<td>Acid Blue 9</td>
<td>Isotherm, Kinetics</td>
</tr>
<tr>
<td>Ko et al., 2001</td>
<td>Bone Char</td>
<td>Cu (II), Cd (II)</td>
<td>Fixed Bed Study with Film pore Diffusion model</td>
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<tr>
<td>Author</td>
<td>Adsorbent</td>
<td>Pollutants</td>
<td>Study parameter</td>
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<td>De Castro Dantas et al., 2001</td>
<td>Diatomite</td>
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<td>Adsorption capacity, Desorption study</td>
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<td>Gupta et al., 2001</td>
<td>Red Mud–Aluminium industry waste</td>
<td>Pb (II), Cr (VI)</td>
<td>Adsorption capacity, Isotherm</td>
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<tr>
<td>An et al., 2001</td>
<td>Crab Shell</td>
<td>Pb (II), Cd (II), Cu (II), Cr (VI)</td>
<td>Adsorption capacity, Isotherm</td>
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<tr>
<td>Curkovic et al., 2001</td>
<td>Electric Furnace sludge</td>
<td>Pb (II), Cu (II)</td>
<td>Adsorption capacity, Thermodynamics</td>
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<td>Sotelo et al., 2001</td>
<td>GAC</td>
<td>Lindane</td>
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<td>Meshko et al., 2001</td>
<td>GAC &amp; Natural Zeolite</td>
<td>MS-300</td>
<td>Adsorption capacity, Isotherm, Kinetics</td>
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<td></td>
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<td>MG-400</td>
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<td>Sivraj et al., 2001</td>
<td>Orange peel</td>
<td>Acid violet 17</td>
<td>Adsorption capacity, Isotherm, Desorption</td>
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<tr>
<td>Dukiky et al., 2002</td>
<td>Wool, Olive cake, Sawdust, Pine needles, Almond shells, Cactus leaves, Charcoal</td>
<td>Cr (VI)</td>
<td>Adsorption Isotherm, Thermodynamic</td>
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<tr>
<td>Ho et al., 2002</td>
<td>Peat</td>
<td>Cu (II), Ni (II), Pb (II)</td>
<td>Isotherm, Kinetics</td>
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<tr>
<td>Mathialagan and Viraraghaban, 2002</td>
<td>Perlite</td>
<td>Cd (II)</td>
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<td>Benguella and Benaisa, 2002</td>
<td>Chitin</td>
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<td>Lai et al., 2002</td>
<td>Goethite -- coated sand</td>
<td>Cd (II)</td>
<td>Adsorption capacity</td>
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<tr>
<td>Gyliene et al., 2002</td>
<td>Fly (Musca domestica) larva shells</td>
<td>Pb (II), Cu (II), Ni (II), Zn (II), Mn (II), Fe (III)</td>
<td>Adsorption capacity, Adsorption Equilibrium</td>
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<td>Juang &amp; Shao. 2002</td>
<td>Chitosan</td>
<td>Zn (II), Cu (II), Ni (II)</td>
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<td>Chu, 2002</td>
<td>Prawn shell</td>
<td>Cu (II)</td>
<td>Kinetics, Adsorption capacity</td>
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<td>Evans et al., 2002</td>
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<td>Krishnan and Anirudhan, 2002</td>
<td>Bagasse pith</td>
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<tr>
<td>Sotelo et al., 2002</td>
<td>GAC</td>
<td>Pesticides (lindane, alachlor)</td>
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<td>Adsorbent</td>
<td>Pollutants</td>
<td>Study parameter</td>
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<td>Al–Subu, 2002</td>
<td>Cypress (Cupressus semperviresis) leaves, chinchona (Eucalyptus longifolia), Pine (Pinus halepensis) leaves</td>
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<td>Lyocell fibres</td>
<td>Direct Blue 1</td>
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<td>Delval et al., 2002</td>
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<td>Acid green 27, Basic Blue 1, Acid Black 48, Acid Red 1, Acid Red 40, Basic blue 3, Basic blue 3, Disperse Blue 3</td>
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<td>Annadurai et al., 2002</td>
<td>Cellulose-based waste (Banana and orange peels)</td>
<td>Methyle orange, Methylene blue, Congo Red, Methyl violet, Amido black</td>
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<td>Kaolinite</td>
<td>Methylene blue</td>
<td>Adsorption affinity, Kinetics, thermodynamics</td>
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<td>Namasivayam &amp; Kavitha, 2002</td>
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<td>Congo Red</td>
<td>Adsorption affinity, Kinetics, Isotherm</td>
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<td>Fu &amp; Viraraghavan, 2002</td>
<td>Fungus Aspergillus niger</td>
<td>Congo Red</td>
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<td>Ho, 2003</td>
<td>Tree fern</td>
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<td>Kinetics, Thermodynamics</td>
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<td>Study parameter</td>
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<td>Bayramoglu et al., 2003</td>
<td>White-rot fungus (Trametes versicolor)</td>
<td>Cu (II), Pb (II), Zn (II)</td>
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<td>Kara et al., 2003</td>
<td>Sepiolite</td>
<td>Co (II)</td>
<td>Adsorption capacity, Thermodynamics</td>
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<td>Veglio et al., 2003</td>
<td>Olive mill residues</td>
<td>Cu (II)</td>
<td>Kinetics, Equilibrium, Regeneration</td>
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<td>Feng &amp; Aldrich, 2003</td>
<td>Marine alga (Ecklonia maxima)</td>
<td>Cu (II), Pb (II), Cd (II)</td>
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<td>Matthew et al., 2003</td>
<td>Polymeric/inorganic hybrid sorbent</td>
<td>V (V), Re (VII), Mo (VI), Ge (IV), As (V), Cd (II), Hg (II), Al (III), Pb (II), Fe (II), Fe (III), Cu (II)</td>
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<td>Palma et al., 2003</td>
<td>Pinus radiata bark and tannins</td>
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<td>Yavur et al., 2003</td>
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<td>Taty-Costodes et al, 2003</td>
<td>Sawdust of Pinus sylvestris</td>
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<td>Adsorption affinity, Kinetics</td>
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<td>Abou-Mesalam, 2003</td>
<td>Silico-antimonate ion exchanger</td>
<td>Cu (II), Ni (II), Zn (II), Cd (II)</td>
<td>Kinetics, Thermodynamics</td>
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<td>Abia et al., 2003</td>
<td>Cassava waste</td>
<td>Cu (II), Zn (II), Cd (II)</td>
<td>Adsorption capacity</td>
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<tr>
<td>Ghoul et al., 2003</td>
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<tr>
<td>Othman &amp; Amin, 2003</td>
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<td>Chern &amp; Chien, 2003</td>
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<td>Benzoic acid, p-nitrophenol</td>
<td>Isotherm and Column study</td>
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<td>Meunier et al., 2003</td>
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<td>Martyniuk &amp; Wieckowska, 2003</td>
<td>Brown coals</td>
<td>Pb (II), Cu (II), Hg (II), Cd (II), Ba (II)</td>
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<tr>
<td>Zeroual et al., 2003</td>
<td>Ulva Lactuca biomass</td>
<td>Hg (II)</td>
<td>Adsorption efficiency</td>
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<td>Author</td>
<td>Adsorbent</td>
<td>Pollutants</td>
<td>Study parameter</td>
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<td>Kadirvelu et al., 2003</td>
<td>Silk cotton hull, coconut tree sawdust, sago waste, maize cob, banana pith</td>
<td>Hg (II), Ni(II), Methyl violet, Malachite green, Methylene blue, Congo Red, Rhodamine-B</td>
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<td>Allen et al., 2003</td>
<td>Kudzu</td>
<td>Basic yellow 21, Basic Red 22</td>
<td>Adsorption efficiency, isotherms</td>
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<td>Walker et al., 2003</td>
<td>Dolomite</td>
<td>Brilliant Red</td>
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<td>Jain et al., 2003</td>
<td>Steel and fertilizer industries waste</td>
<td>Ethyl orange, metanil yellow, acid blue 113</td>
<td>Adsorption efficiency, Kinetics</td>
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<td>Wange et al., 2003</td>
<td>Steel wool, Mg pellets, Zn pellets, coal, GAC, Fe$_3$O$_4$, Fe$_2$O$_3$</td>
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<td>Adsorption efficiency</td>
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<td>Ozacar &amp; Sengil, 2003</td>
<td>Calcined alunite</td>
<td>Reactive Blue 114, Reactive yellow 64, Reactive Red 124</td>
<td>Adsorption capacity, Kinetics</td>
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<td>Atun &amp; Hisarli, 2003</td>
<td>Glass powder</td>
<td>Ceramic acid (dye)</td>
<td>Adsorption capacity, Kinetics, isotherm</td>
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<td>Hydrotalcite</td>
<td>Cibacron Yellow LS-R</td>
<td>Adsorption capacity, Kinetics</td>
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<tr>
<td>Malik, 2003</td>
<td>Sawdust, rice-husk</td>
<td>Acid yellow 36</td>
<td>Adsorption capacity, Kinetics, isotherm</td>
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<tr>
<td>Wong et al., 2003</td>
<td>Chitosan</td>
<td>Acid orange 12, Acid Red 18, Acid Red 73, Acid Green 25</td>
<td>Adsorption capacity, Kinetics, isotherm</td>
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<tr>
<td>Chiou &amp; Li, 2003</td>
<td>Chitosan beads</td>
<td>Reactive Red 189</td>
<td>Adsorption capacity, Kinetics, isotherm, Thermodynamic</td>
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<td>Bouzaida &amp; Rammah, 2003</td>
<td>Treated cotton</td>
<td>Acid dyes</td>
<td>Adsorption capacity</td>
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<tr>
<td>Metivier-Pignon et al., 2003</td>
<td>Activated carbon cloth</td>
<td>Acid green, Acid orange, Acid red, Basic blue, Basic green 1, Basic orange, Basic violet, Direct red, Direct yellow 4, Mordant orange 1</td>
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<td>Author</td>
<td>Adsorbent</td>
<td>Pollutants</td>
<td>Study parameter</td>
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<td>Pereira et al., 2003</td>
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<td>Solophenyl red 3BL, Solophenyl yellow ARL, Sirius supra</td>
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<td>Blue G, Erionyl red B, Telon light yellow FG, Erionyl</td>
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