CHAPTER 1

INTRODUCTION

The quality of water is of vital concern for mankind since it is directly linked with human welfare. The problem of water pollution and its impact on environmental health is currently the focus of international attention. In the wake of rapid industrialisation, especially stimulated by the successive five year plans and recent liberalisation policy resulting in foreign investment, both new industries have been set up and existing industries expanded. Technological advancement leading to rapid industrialisation is always associated with the problem of environmental pollution. The industries consume large volumes of water and let out a major portion of them with contamination resulting in ecological imbalance which seriously interferes with the quality of environment by way of polluting water, air and land. As per Maudgal (1995), diversified industrialisation based on combination of large, medium and small scale industries has resulted in maximum exploitation of natural resources with attendant pollution of water, air and land. It is alarming that as per his report, out of the total land mass of 329 million hectares, 129 to 175 million hectares has already been degraded coupled with acute pollution in water and air. Geeta Mehta et al (1995) have reviewed the various aspects of the policy statement for abatement of pollution, documented by Ministry of Environment and Forest, Government of India in 1992, related to control of water pollution by industries with special reference to industrial wastewater treatment. She assessed the present status of implementation and identified future needs to realise in toto the objectives of the policy statement. Since industrialisation is always desirable for the advancement of a Nation, the environmental pollution has to be controlled to the maximum extent
possible. Hence industrialisation coupled with effective environmental management to control pollution is inevitable.

1.1 WASTEWATER POLLUTION

Almost all industries discharge wastewater from some stage of their manufacturing processes. The indiscriminate disposal of untreated industrial wastewater into the water courses or onto the inland invariably pollutes surface/ground water and land. Depending on the type of industry and nature of processes, the contaminants in wastewater vary. The common pollutants encountered in the industrial wastewater are soluble organics/inorganics, suspended solids, heavy metals, volatile materials, nitrogen, phosphorus, oil and grease and refractory substances.

The soluble organics cause depletion of dissolved oxygen in the receiving water course which in turn seriously affects the aquatic life. Further it leads to septic condition resulting in anaerobic decomposition and associated odour problem. Besides adversely affecting the soil characteristics, the soluble inorganics, pollute the surface and ground water by increasing dissolved solids level and make the same unfit for drinking, industrial and agricultural purposes.

The suspended solids impair the aquatic life by way of deposition in quiescent stretches of a stream. The sludge blankets containing organic solids will undergo progressive decomposition resulting in oxygen depletion and the production of noxious gases. Presence of nitrogen and phosphorous in the wastewater discharged into lakes, ponds and other recreational areas will enhance eutrophication and stimulates undesirable algal growth. The refractory substances are resistant to bio-degradation and may be undesirable for certain water-quality requirements. For example, ABS (Alkyl benzene sulphonate) is substantially non-biodegradable and frequently leads to persistence of foam in water course. Volatile materials such as hydrogen...
sulphide and other organics will create air pollution problem. Besides aesthetic value, oil and grease content in wastewater interferes with reaeration and photosynthesis and thus completely upsets the ecological balance. On the other hand, heavy metal pollution leads to various types of acute and chronic disorders in human beings through the food chain.

When industrial wastewater containing toxic organics such as phenol, even in trace quantities, is discharged into a potable water supply, the water will become unfit for drinking. Hence national and international bodies responsible for public health have become increasingly anxious about trace amount of toxic constituents like phenol in food and water and their possible harmful effects on health. Although the discussion on long term health risks associated with drinking water centers on organic micropollutants, there are certain toxic organic constituents that have been the subject of concern. Taking into consideration the acute and chronic disorders due to the various organic/inorganic pollutants in drinking water, each country has set a standard for drinking water based on the local, geographic, socio-economic and industrial conditions. The list of toxic organics and inorganics for which limits have been set by WHO, USPHS and Indian Standards are furnished in Table 1.1 (WHO 1971, ISI 1991 and De 1994).

Based on the pollutional aspects of dissolved organics/inorganics and toxicity of heavy metals, stringent discharge standards have been specified by local pollution control board authorities for their presence in the industrial effluents as per Table 1.2. (ISI 1982). Further the dissolved organics and heavy metals have been included in the 18 categories of hazardous wastes as per the gazette of India notification (Hazardous wastes management and handling rules 1989).
<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Characteristics</th>
<th>WHO</th>
<th>USPHS</th>
<th>Indian Standards</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>pH</td>
<td>7.0 - 8.5</td>
<td>6.0 - 8.5</td>
<td>6.5 - 8.5</td>
</tr>
<tr>
<td>2.</td>
<td>Total solids</td>
<td>500</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>3.</td>
<td>Iron</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>4.</td>
<td>Manganese</td>
<td>0.1</td>
<td>0.05</td>
<td>0.1</td>
</tr>
<tr>
<td>4.</td>
<td>Copper</td>
<td>1.0</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>5.</td>
<td>Zinc</td>
<td>5.0</td>
<td>5.5</td>
<td>5.0</td>
</tr>
<tr>
<td>6.</td>
<td>Total hardness</td>
<td>500</td>
<td>-</td>
<td>300</td>
</tr>
<tr>
<td>7.</td>
<td>Calcium (as Ca)</td>
<td>75</td>
<td>100</td>
<td>75</td>
</tr>
<tr>
<td>8.</td>
<td>Magnesium (as mg)</td>
<td>50</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>9.</td>
<td>Sulphate</td>
<td>200</td>
<td>250</td>
<td>200</td>
</tr>
<tr>
<td>10.</td>
<td>Chloride</td>
<td>200</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>11.</td>
<td>Fluoride</td>
<td>1.5</td>
<td>1.5</td>
<td>1.0</td>
</tr>
<tr>
<td>12.</td>
<td>Phenols</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>13.</td>
<td>Lead (as Pb)</td>
<td>-</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>14.</td>
<td>Selenium (as Se)</td>
<td>-</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>15.</td>
<td>Arsenic (as As)</td>
<td>-</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>16.</td>
<td>Chromium (hexavalent)</td>
<td>-</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>17.</td>
<td>Cyanide (as CN)</td>
<td>-</td>
<td>0.05</td>
<td>0.05</td>
</tr>
</tbody>
</table>

All values are in mg/l except pH.
Table 1.2
Tolerance limits for trade effluents

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Characteristics</th>
<th>Tolerance limits for industrial effluents discharged</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>into inland surface water</td>
</tr>
<tr>
<td>1.</td>
<td>pH</td>
<td>5.5-9.0</td>
</tr>
<tr>
<td>2.</td>
<td>Total dissolved solids (inorganic)</td>
<td>2100</td>
</tr>
<tr>
<td>3.</td>
<td>Suspended solids</td>
<td>100</td>
</tr>
<tr>
<td>4.</td>
<td>Pesticides</td>
<td>-</td>
</tr>
<tr>
<td>5.</td>
<td>Phenolic compounds</td>
<td>1</td>
</tr>
<tr>
<td>6.</td>
<td>Oil and grease</td>
<td>10</td>
</tr>
<tr>
<td>7.</td>
<td>BOD, 5 days, 20°C</td>
<td>30</td>
</tr>
<tr>
<td>8.</td>
<td>COD</td>
<td>250</td>
</tr>
<tr>
<td>9.</td>
<td>Arsenic</td>
<td>0.2</td>
</tr>
<tr>
<td>10.</td>
<td>Mercury</td>
<td>0.01</td>
</tr>
<tr>
<td>11.</td>
<td>Lead</td>
<td>0.1</td>
</tr>
<tr>
<td>12.</td>
<td>Hexavalent Chromium (as Cr⁶⁺)</td>
<td>0.1</td>
</tr>
<tr>
<td>13.</td>
<td>Total Chromium (as Cr)</td>
<td>2.0</td>
</tr>
<tr>
<td>14.</td>
<td>Cadmium</td>
<td>2.0</td>
</tr>
<tr>
<td>15.</td>
<td>Zinc</td>
<td>5</td>
</tr>
<tr>
<td>16.</td>
<td>Nickel</td>
<td>3</td>
</tr>
<tr>
<td>17.</td>
<td>Cyanides</td>
<td>0.2</td>
</tr>
<tr>
<td>18.</td>
<td>Chlorides</td>
<td>-</td>
</tr>
<tr>
<td>19.</td>
<td>Fluorides</td>
<td>2.0</td>
</tr>
<tr>
<td>20.</td>
<td>Dissolved phosphates</td>
<td>5</td>
</tr>
<tr>
<td>21.</td>
<td>Sulphates</td>
<td>-</td>
</tr>
<tr>
<td>22.</td>
<td>Sulphides</td>
<td>2</td>
</tr>
</tbody>
</table>

All values are in mg/l except pH
1.2 ORGANIC POLLUTANTS IN WATER AND WASTEWATER

There has been a great concern about the introduction and subsequent distribution of organic compounds throughout the environment, especially those from anthropogenic sources. Some insight knowledge about the occurrence and distribution of organic compounds into the natural aquatic system is essential in order to determine whether they are hazardous to the environment and need to be removed. The occurrence of organic compounds in aquatic environment is well documented in the literature (Faust and Aly 1983). These include the naturally occurring organics, polynuclear aromatic hydrocarbons, synthetic compounds such as pesticides, detergents, polychlorinated biphenyls, petrochemicals and halogenated hydrocarbons. The sources and origin of these compounds are many and diverse. The presence of low-molecular weight halogenated hydrocarbons in drinking water was noticed as early as 1974. These organic compounds are formed during the chlorination process for disinfection. Synthetic organic compounds enter natural aquatic environment concurrently with the development of different manufacturing processes in the industries.

1.2.1 Phenolic Wastes in Water and Wastewater

Hydroxy derivatives of benzene (phenol) require special attention because of their possible effects on the taste and odour quality of potable water and potential toxicity to aquatic life in natural water courses. Many phenolic compounds are derived from natural products. For example, catechol, resorcinol, vanillin, vanillic acid, syringic acid, protocatechuic acid and 3,5-dihydroxybenzoic acid were found from the degradative studies of colour macromolecules (Christman and Ghassemi 1966). These compounds may arise from the microbially catalysed degradation of colour molecules. Many of these phenols have been recovered and identified in two rivers in Japan (Faust and Aly 1983). A rather unique source of naturally occurring
Phenolic compounds such as m-hydroxybenzoic acid, m-hydroxyphenylacetic acid and m-hydroxyphenylpropionic acid were isolated from liquid manure (Rump 1974).

Phenolics are one of the most widely used organic compounds in industries. Approximately 1.25 billion Kg of phenol is being produced per annum in the global level (Chemical and Engineering news, 1980). Phenol is the raw material for a variety of synthetic organic chemicals, pharmaceutical products, dyes, perfumes, pesticides etc. The presence of phenolic compounds in wastewater arises from a number of industries including coal carbonisation, coal gasification, producer gas plants, petroleum refineries, manufacturers of synthetic organic chemicals, ammoniacal liquors from coke ovens, fibre boards, biocides, dyes, disinfectants, antioxidants, explosives, photographic chemicals, iron and steel plants, textiles, timber, mining and dressing, paper and pulp, leather and paints.

1.2.2 Environmental Hazards Caused by Phenolic Wastewater

Phenols and their derivatives represent a class of undesirable organic compounds in aquatic environment. Their effect on the organoleptic quality of potable water is reasonably well documented and discussed in the following section.

1. Phenol contributes to undesirable flavour in drinking and food processing waters. Toxic polychlorinated phenols can result when phenol containing water is chlorinated. Hence, the environmental protection agency (EPA) has set a water purification standard of less than one part per billion of phenol in surface waters (Yang and Humphrey 1975).
(2) Phenol can inhibit microbial growth at relatively low concentration of 200 mg/l. This means that surges of phenol concentrations in a waste treatment system can wash off the biomass from it. It is important, therefore, when optimising the design of these waste treatment systems for handling phenolics, that one must have an understanding of how the biosystem will respond dynamically to varying phenol concentrations (Li and Humphrey 1989).

(3) A wide range of phenolic compounds are toxic to microorganisms and inhibit nitrogen fixation (De La Rubia et al 1987).

(4) Phenols are classified as highly persistent and toxic pollutants in marine environment (Keith and Telliard 1979 and Ernst 1984). They enter coastal water through decomposition of attached algae and phytoplankton and through wastewater discharge from a variety of chemical industries (Riley and Chestar 1971, Buikema et al 1979 and Carron and Afghan 1989). Phenolic compounds have detrimental effects on water quality and they are toxic to aquatic life (McKee and Wolf 1963). According to EPA phenol at concentrations below 3.5 mg/l are not toxic to saltwater and freshwater aquatic species (EPA 1979).

(5) Phenolics are acutely toxic to fish. It has been reported that phenol in the concentration range of 0.08 to 1900 mg/l is harmful to fish (Renuka Devi and Sastry 1987). The toxicity of phenol varies with species, conditions of exposure and the duration of the tests. The effects of phenol at lethal concentrations are symptoms of agitation, difficulty in respiration, loss of pigmentation, increased secretion of mucus, clotting of blood, gastroenteritis, increased leucocytes and cyanosis of blood vessels due to phenol poisoning.
Phenols, cresols and xylols are strong skin irritants and consumption of water containing these leads to severe pain, vomiting and capillary damage. Toxic effects are felt in the brain, lungs, kidneys, liver, pancreas and spleen.

Water containing phenol when used for irrigation causes retardation of plant growth.

Consumption of phenol of concentration 240 mg/l by human beings causes mouth sore, diarrhoea, dark urine and burning mouth (Baker et al. 1978). It has been observed that phenolic compounds accelerate tumour formation and ciliostatic (Hoffmann and Wynder 1962).

As a consequence of the above mentioned problems, it is necessary to treat phenolic wastewater to bring down the phenolics to standards prescribed by pollution control authorities before discharging into water bodies.

1.3 WASTEWATER TREATMENT METHODS

From the foregoing discussions it is seen that indiscriminate disposal of untreated wastewater either into water courses or onto the inland invariably pollutes the water and/or soil. Hence it necessitates to treat the wastewater prior to disposal. A variety of methods have been developed for the removal of harmful organic and inorganic constituents from water and wastewater. The available methods to treat wastewater can be broadly divided into physico-chemical and biological treatments. The selection of wastewater treatment process or a combination of processes depends upon the characteristics of wastewater and required treated wastewater quality. A brief outline on the most common practical treatment methods are summarised below.
1.3.1 Physico-Chemical Treatment

1.3.1.1 Primary treatment

The primary treatment is performed to remove or reduce in size large suspended or floating organic solids by screening, heavy inorganic solids such as sand, gravel and cinder known as grit by settling and excessive amounts of oil and grease which exist as insoluble/free form by skimming.

1.3.1.2 Equalisation

The objective of equalisation is to minimise or control fluctuations in wastewater characteristics in order to provide optimum conditions for subsequent treatment process.

1.3.1.3 Neutralisation

Industrial wastewater containing acidic or alkaline materials requires neutralisation prior to discharge to receiving water course or prior to chemical or biological treatment. The common acids used in treatment process to neutralise alkaline wastewater are hydrochloric and sulphuric acids. Hydrated lime, caustic soda and soda ash are employed to neutralise acidic wastewater.

1.3.1.4 Sedimentation

Sedimentation is employed for the removal of suspended solids from wastewater. There are three basic classifications in sedimentation, namely, discrete, flocculent and zone settling. In discrete settling, the particle maintains its individuality and does not change in size, shape, or density during the settling process. Flocculent settling occurs when the particles agglomerate during the settling period with a resulting change in
size and settling rate. Zone settling involves a flocculated suspension which forms a lattice structure and settles as mass, exhibiting a distinct interface during the settling process.

1.3.1.5 De-emulsification

Emulsified oily materials require special treatment to break the emulsion so that the oily materials will be free and can be separated. The breaking of emulsions is a complex art requiring laboratory or pilot-scale investigations prior to developing a final process design.

1.3.1.6 Floatation

Floatation is used for the removal of suspended solids and oil and grease from wastewater. When the pressurised air-liquid mixture is released to atmospheric pressure in the flotation unit, minute air bubbles are released from solution. The suspended solids or oil globules are floated by these air bubbles and raise to the surface, from where it is skimmed off. The clarified wastewater is removed from the bottom of the flotation unit.

1.3.1.7 Coagulation

Coagulation is employed for the removal of waste materials in suspended or colloidal form. The colloids do not settle out on standing and cannot be removed by conventional physical treatment process. The stability of colloid is primarily due to electrostatic forces and neutralisation of this charge is necessary to induce flocculation and precipitation. Since the vast majority of colloids in industrial wastewater possess a negative charge, the coagulation is induced by the addition of high valence cations. The most common coagulants used are alum, ferrous sulphate, ferric chloride and lime. Polyelectrolytes act as coagulant aids enhancing coagulation by promoting the growth of large and rapid settling flocs.
1.3.1.8 Chemical oxidation

Chemical oxidation of wastewater is employed to oxidise pollutants to terminal end products or to intermediate products that are more readily biodegradable or more readily removable by adsorption. Common oxidants are chlorine, ozone, hydrogen peroxide and potassium permanganate.

1.3.1.9 Chemical reduction

Chemical reduction is employed for the reduction of heavy metals which cannot be precipitated in their high valence state (hexavalent chromium to trivalent chromium by sodium sulphite), de-chelation of metal complexes (cuprammonium complex by ferrous sulphate) and removal of colour (reactive dye colour by sodium hydrosulphide).

1.3.1.10 Precipitation

Precipitation method is used for the removal of inorganics from wastewater. Caustic soda, hydrated lime, soda ash and sodium sulphide are being used to precipitate the metal ions as insoluble hydroxides, carbonates and sulphides (Sorg 1978, Kakabadse 1979 and Patterson et al 1977). Lime is generally favoured for the precipitation of heavy metals due to low cost and ease of pH control. In addition, the presence of excess lime can serve as an adsorbent for the removal of metal ions (Kakabadse 1979). However, problems can arise due to incomplete removal of the precipitated metal from the treated effluent. The sludge, disposed off as land fill, can lead to contamination of ground water when conditions are favourable for their dissolution.
1.3.1.11 Ion exchange

Ion exchange is a reversible process which facilitates the removal of anionic and cationic constituents present in water by exchange with the ions of the resin. A variety of synthetic organic resins, inorganic gels and liquid ion exchangers have been examined for the removal of heavy metal ions from dilute aqueous solutions (Gupta et al 1984). When the resin bed becomes saturated, it is regenerated using acid or alkali. The economic limitations of the process comes from the initial investment cost. The presence of complex forming species, however, can interfere with the exchange process. In addition, fouling of resin bed with wetting agents and organic brighteners used in plating, clogging due to precipitated water hardness and oxidation of resin by oxidising agents, if present, are the frequent problems associated with ion exchange method.

1.3.1.12 Solvent extraction

Liquid extraction is the most economic alternative for the treatment of highly concentrated phenolic wastewater (Patterson 1975). Most of the liquid extraction techniques use benzene as a solvent to extract phenol. The extracted phenol could be recovered by washing with sodium hydroxide solution. The reported efficiency of this method is extremely high in the order of 98-99%. Other solvents like light oil, petroleum oil, creosote oil etc were also tried. Yasuda Sinichi et al (1982) treated wastewater containing phenol by liquid extraction method using benzene and 4-benzylpyridine with a removal efficiency of 98%. The main disadvantages in this method are the solvent loss due to solubility in wastewater and increase in organic load of wastewater.
1.3.2 Biological Treatment

The bio-degradable soluble/suspended organics in wastewater can be effectively removed by biological treatments process.

1.3.2.1 Aerobic treatment

In the aerobic treatment, microorganisms consume oxygen and degrade organic matter to carbon dioxide and water with the synthesis of new cell mass. The main aerobic biological waste treatment includes high-rate processes such as activated sludge and its modifications including extended aeration, trickling filter and rotating biological treatment and low-rate processes such as aerated lagoon, facultative lagoon and oxidation pond.

1.3.2.2 Anaerobic treatment

The anaerobic treatment involves the breakdown of organic matter to methane and carbon dioxide in the absence of oxygen. The yield of new cell mass by synthesis is less in this case compared to aerobic degradation. The septic tank is a common example for anaerobic treatment. Many improvements have been made in both fundamental and practical aspects. High rate digester, anaerobic filter, suspended growth and fixed film reactors, upflow anaerobic sludge blanket reactor (UASB) and fluidised bed reactor have also been developed.

1.4 ADSORPTION

Adsorption is an unique process for the removal of both organics and inorganics from water and wastewater. It is a process by which the concentration of solute is enriched at the surface or interface between two phases. It provides reliable results without much cost and working efforts. Adsorption partially restores the balance of forces and is accompanied by a
decrease in free energy. Adsorption may be classified as physical or chemical, depending on the nature of the forces involved.

1.4.1 Physical Adsorption

Physical adsorption on solids is attributed to forces of interactions between the solid surface and adsorbate molecules that are similar to the van der Walls forces between the molecules. These forces that involve the electrons and nuclei are electrostatic in origin and are called dispersing forces. This dispersing forces exist in all types of matter and always act as an attractive force between the adjacent atoms and molecules. Molecules in the interior of any solid are subjected to equal force in all directions whereas molecules on the surface of the solids are subjected to unbalanced forces. These forces can be balanced by other molecules becoming attached to the surface. The attractive forces are relatively weak. In addition to dipole-dipole interactions, other possible dispersion interactions contributing to physical adsorption include dipole-quadrapole and quadrapole-quadrapole interactions.

1.4.2 Chemisorption

This is characterised mainly by large interaction potentials that lead to high heat of adsorption approaching the value of chemical bonds. Chemisorption involves the transfer of electrons and the formation of true chemical bonding between the adsorbate and solid surface (Young and Crowell 1962). Since chemisorption involves chemical bonding, it occurs at high temperature and is usually associated with activation energy.
1.4.3 Factors Affecting Adsorption

1.4.3.1 Nature of the adsorbent

Since the adsorption results in the concentration of solutes at the surface it is obvious that the surface area is one of the principle factors affecting the adsorptive capacity of an adsorbent. The adsorptive capacity of solid adsorbents is generally proportional to the specific surface area. The surface area of non porous adsorbents increases considerably with decrease in particle size. Consequently, the adsorptive capacity should increase with reduction in particle size. However, for highly porous adsorbents such as activated carbon most of the surface area resides in the internal pore structure and the adsorptive capacity is expected to be independent of the particle size. The presence of specific functional groups on the surface of the adsorbent imparts certain characteristics that affect the adsorption process. For example surface oxides consisting of acidic functional groups reduce the capacity of carbon for adsorption of many organic compounds. On the other hand surface oxides consisting of carbonyl groups enhance the adsorption of aromatic compounds such as phenol, p-nitrophenol and naphthalene. This enhanced adsorption has been attributed to the interaction of aromatic ring π electrons with the carbonyl groups by a donar-acceptor mechanism involving the carbonyl oxygen as the electron donor and the aromatic ring as the acceptor (Mattson and Mark 1971).

1.4.3.2 Nature of adsorbate

Adsorption by activated carbon in aqueous solution is influenced by several physicochemical properties of the organic compounds. Solubility is the most significant property affecting the adsorptive capacity. In general, a higher solubility indicates a strong solute-solvent interaction and the extent of adsorption is expected to be low because of the necessity of breaking the solute-solvent bond before adsorption can occur. A general rule for adsorption of organic compounds, known as Trauber's rule
(Adamson 1967), states that the adsorption of organic compounds from aqueous solution increases strongly and regularly as the homologous series is ascended. Thus the adsorption of a series of aliphatic acids, from formic acid to butyric acid, on activated carbon increases with an increase in the chain length. The increase in adsorption is due to the increase in hydrophobicity and the decrease in solubility with the increase in chain length. The reverse order of adsorption of these series is observed for their adsorption from nonpolar solvents. The molecular weight and size of the adsorbate molecule also affects the adsorptive capacity. Weber (1972) showed that the adsorptive capacity of activated carbon increases with an increase in molecular weight of a series of sulphonated alkylbenzenes. The increase in the side chain length increases the hydrophobicity of the molecule, which results in greater adsorption. In aqueous systems, nonpolar solutes are more strongly adsorbed on activated carbon than polar solutes. Several investigators evaluated the effects of functionality, molecular weight, solubility and polarity of solutes on carbon adsorption. Giusti et al (1974) reported that functionality has a substantial effect on adsorption which is interrelated with solubility and polarity. The adsorptive capacity of carbon for aromatic compounds is influenced by substitution in the ring.

### 1.4.3.3 Effect of pH

The adsorption of nonelectrolytes by activated carbon from aqueous solution is generally not affected by the solution pH, although some exceptions can occur. However, the effect of pH on the adsorption of weak electrolytes, both acids and bases, is quite pronounced. Extensive studies have been reported for the adsorption of organic compounds at different pH values (Mattson and Mark 1971).
1.4.4 Adsorbents

Adsorption techniques have been applied for the removal of trace inorganics and organics from water and wastewater. Many adsorbents other than activated carbon such as yellow ochre, clay minerals, acidic and basic fly ashes, vermiculite, polymeric adsorbents, carbonaceous adsorbents and ion-exchange resins have been evaluated for the removal of contaminants in water and wastewater. The following sections describe the detailed literature survey of different sorbents and their efficiency in the removal of organics/inorganics.

Adsorbents such as fly ash and clay minerals have been found useful to remove organic and inorganic constituents from contaminated water. Fly ash which contains 12-30% carbon is apparently responsible for its adsorption property (Ferrailo et al 1990). Several reports have appeared for the effective removal of phenol, dyes and metal ions from wastewater (Boyd 1982, Kumar et al 1987, Gupta et al 1990 and Sen and De 1987a and 1987b). Naturally occurring minerals like fuller’s earth and kaolinite have also been examined for the treatment of wastewater containing organic and inorganic pollutants (Korczak and Kubiel 1987 and 1989 and Pollard et al 1991). There are, however, no reports on the regeneration of these materials after use or on the recovery of the adsorbed constituents.

Among the various adsorbents, adsorption using activated carbon appears to have the least adverse effects. Activated carbon includes a broad range of carbonaceous materials that exhibit a high degree of porosity and large surface area (Bansal et al 1988). It has been found suitable for the removal of both toxic biodegradable and non-biodegradable substances from wastewater thus making the wastewater suitable for reuse. The use of activated carbon for water treatment was first reported in 1930 for the removal of organics (Mantell 1968).
Activated carbons are generally derived from a wide variety of feed stocks. Currently, the most common feed stocks for the production of commercial activated carbon are wood, peat, lignite and bitumin (Bansal 1988). Production of activated carbon is a two stage process and involves carbonisation of the raw material below 600°C in the absence of oxygen followed by activation at elevated temperature using an oxidant such as steam, carbon dioxide or air. The heating rate, the dwell time for carbonisation and the activation atmosphere are the parameters which affect the final pore structure and surface area of the carbon produced.

Diamadopoulos et al (1993) studied the removal of As(V) using fly ash from aqueous solution. The studies indicated that the degree of removal of arsenic depend markedly on the pH. Ho et al (1995) investigated the removal of nickel from aqueous solution by Shpagnnum moss peat. Its removal is poor compared with other metals and the best results were obtained in the pH range 4-7. Percent nickel removal at equilibrium increased with increasing adsorption dose.

Gaikwad and Vipin Bhardwaj (1995) studied the removal of zinc from industrial effluents by fly ash in glass column and in a clarifier model. The performance of fly ash was better in the clarifier than in the glass column. Tiwari et al (1995) investigated the adsorption of Hg (II) on rice husk ash and found it to be a suitable adsorbent for the removal of Hg(II) from effluent solution in the pH range 4-6.

Pradhan et al (1997) studied the removal of selenite from aqueous solution by adsorption on activated red mud. Red mud, a waste material from aluminum industry was converted into an adsorbent which exhibited good adsorption properties for selenite in aqueous solution at low pH.

Jesuja et al (1997) studied the removal of Cr (VI) from wastewater by ablesmoschus esculentus (lady finger plant). The effects of
pH, Cr (VI) concentration, adsorbent dose and contact time were studied in batch experiments. The removal was in general most effective at low pH values.

Adsorption of cadmium, zinc, nickel and lead from aqueous solution by mangifera indica seed shell was investigated by Mohammed Ajmal et al (1998). The shell was used successfully for the removal of Cd, Zn, Ni and Pb from water. The degree of removal was found to be dependent on initial pH of the solution and the adsorption increased as the pH increased.

Gopalakrishnamoorthy and Shanmugam (1987) studied the removal of phenol from effluent of low temperature carbonisation of lignite plant by resins. It was found that by percolating industrial effluents containing phenol through a filter packed with anionic exchange resins, the effluent is free from phenol.

Reddy et al (1989a) studied the sorption of phenolic compounds on porous polymeric adsorbents based on acrylic matrix and they showed quite a good sorption of phenolic compounds. Kennedy (1973) has reported a series of macroreticular adsorbents such as amberlite XAD-2, XAD-4 for removing chlorinated phenols from pesticide industrial wastewater. Crook et al (1975) reported the removal of phenols from industrial waste effluents using amberlite XAD - 7 porous polymeric adsorbent. Farrier et al (1979) reported the uptake of phenol and benzoic acid by macroreticular adsorbent, amberlite XAD-8. Wojaczynska et al (1984) studied the sorption of various aromatic compounds on porous polymeric adsorbents based on styrene-divinylbenzene and acrylonitrile-divinylbenzene matrices.

Reddy et al (1989b) studied the sorption of phenol and substituted phenols from aqueous solution using porous weak base anion exchangers based on acrylonitrile. The sorption performance is governed by the sorbate,
sorbent and solution characteristics. The sorption of phenolic compounds has been observed to be fast and reversible under dynamic conditions.

Singh and Mishra (1990) studied the removal of phenolic compounds from water using chemically treated saw dust. Three kinds of impregnated saw dust were prepared. Impregnated saw dust in Fe$^{3+}$ form behaves as a chelating material by forming iron (III) - phenol complex and may be used in the recovery of phenolic compounds from water. Saw dust being a waste material of saw mills, impregnated saw dust can be utilised as a low cost adsorbent for the removal of phenols from waste effluents.

Adsorption characteristics of some phenol and phenolic effluents on sodium and TEBA - montmorillonite was studied by Sarkar et al (1990). It was observed that polar substituted phenols are better adsorbed than others. Synthetic phenol plant effluent could be dephenolised using this clay to some extent.

Davis and Huang (1990) studied the adsorption of some substituted phenols onto hydrous CdS(s). It has been shown that the process is a partitioning of the hydrophobic organic from the aqueous phase onto the solid surface. Cadmium sulfide demonstrates characteristics of a hydrophilic surface and has an adsorption capacity for phenols near that of activated carbon on a per unit surface area basis. The hydrophobicity differences between solids may explain some of the inconsistencies noted with phenol adsorption onto various surfaces.

Reed and Arunachalam (1994) studied the removal of lead and cadmium from aqueous waste stream using granular activated carbon. Significant quantities of metal - bearing wastewater were treated using granular activated carbon columns. Column pH and influent characteristics appear to be the critical parameters influencing GAC column performance. GAC columns were successfully regenerated using 0.1 N HNO$_3$ and NaOH.
Column performance was not adversely affected by the regeneration procedure. When the regeneration step was used on virgin carbon, a dramatic improvement in column performance was observed. This was attributed to an increase in -OH available for surface and pore liquid precipitation as well as an increase in the number of surface sites available for adsorption.

Budinova et al (1994) studied the removal of metal ions from aqueous solution using activated carbon obtained from different raw materials. They were found to adsorb metal ions from aqueous solution with the capacity increasing in the order \( \text{Cd}^{2+} < \text{Zn}^{2+} < \text{Cu}^{2+} < \text{Pb}^{2+} \). The adsorption of metallic ions is negligible at very low pH values and increases considerably in the pH range of 3-4. The presence of other ions in the solution decrease the adsorption of each of them.

Removal of chromium (VI) from aqueous waste was investigated using adsorbents based on bagasse and coconut jute (Shri Chand et al 1994). The removal was in general most effective at low pH values and low chromium (VI) concentrations. Activated coconut jute carbon was the most active among the four adsorbates studied. It was fairly stable even at higher pH. Removal of about 97% Cr (VI) was observed at natural pH.

Khalfaoni et al (1995) studied the adsorption of copper from industrial wastewater and aqueous solution by activated carbon obtained from reeds. The presence of other metal ions in the solution decrease the adsorption capacity for copper.

Sujatha and Surendra Kumar (1995) studied the removal of chromium (VI) by activated carbon. Effective removal of chromium at low pH value was found to be due to simultaneous adsorption and reduction. Removal of lead (II) ions from aqueous solutions using particles of lignite as adsorbent was studied by Balasubramanian and Jafar Ahamed (1997).
(protonated) species was predominant. In the case of trichlorophenol, sorption could be quantitatively attributed to the neutral species.

Srivastava and Renu Tyagi (1995) studied the competitive adsorption of substituted phenols by activated carbon developed from the fertilizer waste slurry. Studies on competitive adsorption was performed to give insight into some of the factors affecting selective uptake of organic compounds on activated carbon from bisolute aqueous solutions. Srivastava et al (1995) studied the removal of 2,4,6-trinitrophenol using bagasse fly ash. The effect of particle size was more predominant at smaller dose of the adsorbent.

Gupta et al (1998) studied the utilisation of bagasse fly ash generated in the sugar industry for the removal and recovery of phenol and p-nitrophenol from wastewater. It was found that the uptake of p-nitrophenol is more than that of phenol. The removal of phenols by this adsorbent takes place via particle diffusion mechanism. Phenols adsorbed on the columns of this material can be eluted quantitatively with 8% aqueous NaOH. Exhausted columns can be chemically regenerated by treating with 1 M HNO₃ without dismantling.

Streat et al (1995) investigated the sorption of phenol and p-chlorophenol from water using carbonised and subsequently activated straw, carbon from used rubber tyres as well as conventional activated carbon. Experimentally determined k and n values indicated the sorption of phenol and p-chlorophenol on activated carbon derived from straw and used rubber tyres to be almost identical to that of conventional activated carbon.

Mollah and Robinson (1996) studied the pentachlorophenol adsorption and desorption characteristics with granular activated carbon and the kinetics was successfully modelled for both batch process in a stirred flask and continuous liquid flow process in a column containing a
packed bed of granular activated carbon. Sorption capacity of hydrotalcite for trinitrophenol was studied by Hermosin et al (1996). It was found that adsorption of trinitrophenol on hydrotalcite and its calcined product (HT 500) is a chemisorption process, showing a high irreversibility. In both cases trinitrophenol was adsorbed as an anion in the interlayer spaces.

Sachan et al (1996) studied the removal of phenol from wastewater by activated carbon. The study shows that the equilibrium time is independent of the initial phenol concentration and amount of adsorbent dose. The adsorption equilibrium data for different phenol concentrations are found to fit well with the models proposed by Freundlich and Langmuir for individual doses. The adsorption of phenol on activated carbon has the first order kinetics proposed by Lagergren.

Adsorption of phenol, p-chlorophenol and p-nitrophenol onto granular activated carbon in a liquid-solid fluidised-bed was studied by Wang et al (1997). The effect of particle size of activated carbon, liquid flow rate, initial phenol concentration and activated carbon mass were investigated. The isotherm data were analysed by using the well-known isotherm equations to realise the adsorption characteristics of granular activated carbon. The model which takes into account the external mass transfer with film-surface diffusion, surface adsorption equilibrium and internal mass transfer was employed to fit the experimental data of the break through curve. The model agreed with the experimental results very well when the Langmuir isotherm was employed.

Impact of pH on the adsorption and desorption kinetics of 2-nitrophenol on activated carbons was studied by Karimi and Narbaitz (1997). The differences in the adsorption and desorption kinetics are primarily attributable to the differences in the equilibrium loadings at various pH values.
Adsorption characteristics of carbonised bark for phenol and pentachlorophenol was studied by Edgelhill and Lu (1998). The use of less expensive, single use adsorbents to replace activated carbon is of significant interest. Adsorption isotherm tests with carbonised bark was done with phenol and pentachlorophenol. Pentachlorophenol is weakly adsorbed. Non-linear regression of the data showed that the Langmuir equation best represents both sets of phenol adsorption data, whereas the protonated pentachlorophenol adsorption data fitted best with the BET equation. The non-linear regression method provided more accurate adsorption constants for the three adsorption models tested.

Mahadeva Swamy et al (1998) studied the sorption characteristics of o-cresol on bagasse fly ash and activated carbon. It was found that o-cresol removal efficiency is enhanced by decreasing the concentration and pH of the solution. Equilibrium data were well represented by both Freundlich and Langmuir models. Results of column study have shown that the break through time increases with increasing bed height and decreasing flow rates.

Tutem et al (1998) studied the adsorptive removal of chlorophenols from water by bituminous shale. Acid activated bituminous shale was used as adsorbent for the removal of 2-chlorophenol and 2,4-dichlorophenol from water and the related process parameters were investigated. Kinetic analysis showed that the adsorption reaction could be approximated by a first order rate equation for which pore-diffusion was the essential rate-controlling step. Adsorption was endothermic and basically of a physical character. Equilibrium modelling by linearised adsorption isotherms revealed that Langmuir equation could well represent the observed data.

Removal of some substituted phenols by activated carbon obtained from agricultural waste was studied by Daifullah and Girgis (1998). The adsorption was found to be a direct function of the molecular dimensions of
the sorbates and inversely proportional to the solubility and $pK_a$ of the phenols. Only 2,4-dinitrophenol showed deviation from this trend.

1.5 ACTIVATED CARBON

Activated carbon has long been recognised as one of the most versatile adsorbents to be used for the effective removal of low concentrations of organic compounds from aqueous solution. Charcoal, the forerunner of modern activated carbon whose ability to purify water dates back to 2000 B.C. Its adsorptive properties for gases were first reported by Scheele and later by Fontanna. Louitz observed the ability of charcoal to decolourise many liquids (Faust and Aly 1983). This led to the widespread application of wood and bone chars in the refinery of cane and beet sugars (Hassler 1974). Several attempts were made to prepare activated carbons from other sources such as blood, coconut, flour and paper mill wastes. The development of modern commercial activated carbon is attributed to Ostrejka, who described a basic process for producing activated charcoal from vegetable materials (Hassler 1974). This led to the manufacture of powdered activated carbon as a substitute for bone char. The real development of activated carbon began during World War I when hard granular activated carbon was developed for use in gas masks. These earlier carbons had relatively less adsorptive capacity than modern carbons. The developments in the manufacture of activated carbon with sufficient hardness to resist abrasion and the ability to be regenerated for reuse paved the way for utilisation of activated carbon in many industrial applications (Hassler 1974). During the last two decades, increased awareness of the occurrence of organics in water and wastewater and the need for their control led to the emergence of activated carbon adsorption as one of the most effective methods for removing these organics from water and wastewater.
1.5.1 Carbon Structure
1.5.1.1 Physical structure

The properties of activated carbon are attributed to its highly porous structure and relatively large surface area. The uptake of organics depends on the distribution of pores in the carbon structure. A particle of activated carbon is composed of a complex network of pores that can be divided into three basic classes: (1) macropores, (2) transitional pores and (3) micropores. Macropores were first formed by the burn off the edge group of microcrystallites. The micropores were formed mainly by the branch off of the microcrystallite planes. The macropores open out directly to the external surface of the particle, transitional pores branch off from macropores and micropores, intum, branch off from the transitional pores (Dubinin 1966).

Pores of effective radius greater than about 500-1000 Å were classified as macropores. In activated carbon, the effective radius of macropores frequently lie in the range of 5,000-20,000 Å with surface area between 0.5 mm and 2 m²/g. These negligible values of the specific areas indicate that the macropores of activated carbon do not play any appreciable role in adsorption process. They are, however, serve as conduits for transport of the adsorbate from the outer particle surface to the interior micropore surface where most of the adsorption occurs.

Transitional pores are those in which capillary condensation with the formation of meniscus of the liquified adsorbate can take place. The effective radius of transitional pores usually falls within 40-200Å and their surface area lies between 20 and 70 m²/g. Micropores, which have radius less than 20 Å, usually amount to atleast 95% of total surface area (Dubinin 1966). Micropores are of greatest significance for adsorption due to their very large surface area (Wolf 1958 and Smisek and Cerrny 1970). Commercial activated carbons have a typical surface area in the range of
400-1500 m$^2$/g. This large surface area is one of the main reasons for the high adsorptive capacity of activated carbon. The pore size distribution depends on the type of starting material and the method of preparation of the activated carbon.

1.5.2 Chemical Structure

The adsorptive properties of activated carbon are also determined by its chemical composition. Activated carbon contains chemically bonded elements such as oxygen and hydrogen. These elements are derived from the starting material and remain as a result of imperfect carbonisation or they can become chemically bonded to the surface during activation. The presence of oxygen has been found to have a good effect on the adsorptive properties of activated carbon.

Unlike nitrogen and other gases when oxygen is chemisorbed on carbon it undergoes a chemical change. Oxygen could only be removed as CO$_2$ or CO by strongly heating the carbon. Smisek and Cerrny (1970) reported that chemisorption of oxygen at a pressure of 500 millitorr at various temperatures and concluded that the oxygen adsorbed at temperatures up to 250°C are primarily involved in the formation of lactone groups and above 300°C leads to the formation of carbonyl groups. Smith et al (1960) also studied the reaction of oxygen with carbon between 25 and 450°C and from IR spectral measurement confirmed the presence of the carbonyl and lactone structures on the surface.

Smisek and Cerrny (1970) reported that oxygen combines with carbon to form a physico-chemical oxide complex, C$_x$O$_y$, of variable composition. The oxides are commonly classified as acidic or basic and the temperature was found to have a pronounced effect on the nature of the oxide. Acidic surface oxides were formed when the carbon feedstock was exposed to oxygen in the temperature range 200-400°C. Apart from lowering
the pH value of neutral or basic solutions, they possess negative surface charge. Such carbons, referred to as L carbons, are capable of adsorbing cations from the solution.

Smisek and Cerny (1970) reported that the surface oxides (-CO\textsubscript{x}) undergo hydration forming surface hydroxo groups (-COH). Depending on pH, therefore, L-carbon can have negative and/or neutral functional groups.

\[
\begin{align*}
- \text{C-OH} & \Rightarrow -\text{CO}^- + H^+ \\
\end{align*}
\]

... 1.1

The nature of functional groups in L-carbons was investigated by Coughlin and Ezra (1968) based on reaction with bases of different strength. The acidic functional groups were found to be similar to carboxylic acid, phenolic hydroxyl and quinone-type carbonyl group of organic compounds. The presence of these groupings have also been confirmed by IR spectral studies (Mattson and Mark 1971).

Basic surface oxides, on the other hand, referred to as H-carbons were formed when the carbon feed stock was exposed to temperature between 800 and 1000°C. The resulting material was found to raise the pH of neutral or acidic solutions. As they possess positive surface charge they readily adsorb anions from the solution. H-carbons can have positive and/or neutral functional groups depending on the pH.

\[
\begin{align*}
- \text{COH}_2^+ & \Rightarrow -\text{COH} + H^+ \\
\end{align*}
\]

... 1.2

The basic surface oxides on H-carbons that sorb acids from aqueous solution were not as thoroughly investigated as acidic surface oxides. Garten and Weiss (1957) proposed a chromene structure responsible for chemisorption of acids. Chromene groups contain active methylene groups,
- CH₂ or > CHR, that can react with strong acids in presence of oxygen to form carbonium ions and hydrogen peroxide. The resulting carbonium ions tend to associate with anions which accounts for the fact that adsorbed acids are very difficult to wash from activated carbon.

\[
\text{Cyclic Dimer} \quad \text{UVB} \quad \text{UVB} \\
\text{Carbonium ion}
\]

The charge carried by the carbon surface, therefore, depends on the nature of surface oxide groups formed by chemisorption of oxygen.

Most commercial activated carbons derived from coal based materials are mostly of H-type carbons. The use of such carbon for the removal of a broad spectrum of organic compounds is well documented (Borneff 1980, Wood and De Marco 1979 and USEPA 1978). The removal of polynuclear aromatic hydrocarbons (PAH) to an extent of 99% and nitrosoamines, which are carcinogenic, to an extent of 99% has been reported (Borneff 1980). They also showed high removal efficiencies for pesticides, chlorinated hydrocarbons and total organic carbon (TOC) (USEPA 1978).
1.6 PREPARATION OF ACTIVATED CARBON FROM CARBONACEOUS PRECURSORS

Despite the prolific use of the commercial activated carbon for water and wastewater treatment carbon, adsorption remains an expensive treatment process. This has prompted a growing interest for the production of low cost activated carbon from other carbonaceous precursors. Much emphasis has been focussed in recent years on agricultural wastes as source of carbon with a view to bring a significant cost reduction in the treatment of water and wastewater.

Bansal et al (1988) reviewed the criteria to be considered while selecting a potential carbonaceous precursor for the preparation of activated carbon. They include (i) storage life of the material (ii) volume and cost of the material (iii) workability of the material and (iv) minimum presence of inorganics. Other desirable characteristics include density, carbon content, porosity and availability of the raw material. Although a few materials satisfy all these requirements selection are often made primarily on the basis of the availability of the raw material.

The various feedstock proposed for the preparation of activated carbon are listed below.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Feedstock</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bagasse</td>
<td>Sugar-beet sludge</td>
</tr>
<tr>
<td>Molasses</td>
<td>Leather waste</td>
</tr>
<tr>
<td>Coffee beans</td>
<td>Jute stick</td>
</tr>
<tr>
<td>Palm tree cobs</td>
<td>Cotton seed hulls</td>
</tr>
<tr>
<td>Corn cobs</td>
<td>Kelp and sea weed</td>
</tr>
<tr>
<td>Coconut coir</td>
<td>Oil shale</td>
</tr>
<tr>
<td>Nut shells</td>
<td>Wheat straw</td>
</tr>
<tr>
<td>Rice hulls</td>
<td>Olive stone</td>
</tr>
<tr>
<td>Petroleum acid sludge</td>
<td>Almond shells</td>
</tr>
</tbody>
</table>
The preparation of activated carbon from these precursors involve two steps (i) carbonisation and (ii) activation

1.6.1 Carbonisation

Carbonisation or pyrolysis consists of slowly heating the material in the absence of air at temperatures below 600°C. During carbonisation, dehydration takes place followed by pyrolytic decomposition of the precursor with concurrent elimination of many non-carbon elemental species (Fitzer et al 1971). The release of low molecular weight volatiles followed by lighter aromatics results in a product called char rich in fixed carbon (Hucknall 1985). The pores formed during carbonisation usually remain filled with tarry residues.

During pyrolysis, it is believed that the original substance splits into fragments which regroup to form thermostable aromatic structure resembling that of graphite. As the transformation is seldom complete, some residual hydrocarbon chains and rings remain in the burnt material. X-ray studies have shown that the chars have crystalline characteristics and amorphous carbon powder may be composed of crystals of submicroscopic dimensions called crystallites (Wolf 1959). The formation of crystallite is influenced by the temperature of carbonisation and to some extent by the composition and structure of the raw material (Juntgen 1975). Many methods have been reported for the carbonisation of waste organic materials (Hassler 1974).
1.6.1.1 Carbonisation with chloride salts

In this method, the effectiveness of carbonisation is controlled by the use of metal chlorides such as CaCl₂, ZnCl₂, NH₄Cl and MnCl₂ and their presence minimise the formation of objectionable tarry products. Thus the presence of metal chloride was reported to facilitate hydrogen and oxygen atoms in the source materials to be stripped away as water rather than as hydrocarbons. During carbonisation, the metal chloride perhaps provides a skeleton on which carbon is deposited, which becomes bonded to mineral elements by adsorption process. When the mineral ingredients are subsequently dissolved in acid or water, the exposed carbon surfaces become free for adsorption purposes.

The material to be carbonised is impregnated with the solutions of chloride salts for varying periods of time. After decanting off the liquid, they are dried and subjected to pyrolysis at 600°C. The charred material is then washed with acid to remove the metal oxides formed and dried.

1.6.1.2 Carbonisation with sulphate salt

Incorporation of sulphate salts on the source materials was found to enhance the carbonisation process (Hassler 1974), possibly due to the oxidation of carbon by sulphate and erosive action of the resulting hydrogen sulphide on the carbon. In this method, materials to be carbonised are soaked in a solution of sodium, potassium or ammonium sulphate for varying periods of time. The liquid portion is then decanted off and the material, after drying is subjected to carbonisation at 600°C. Finally the charred material is washed with water and dried.
1.6.1.3 Carbonisation with sulphuric acid

Carbon has also been prepared by reacting organic wastes with concentrated sulphuric acid in the temperature range 120-300°C. The organic wastes used are lignin rich cellulosic materials (phenyl propane derivative) containing (-COOH) and phenolic (-OH) functional groups (Cullen and Siviour 1982). When these materials are carbonised using sulphuric acid, sulphonic acid groups (-SO₃H) are introduced through sulphonation of phenyl propane derivative which are capable of exchanging cations present in the solution. The carbon, therefore, show both adsorptive and ion exchange properties (Govinda Rao 1980). In this method, the waste organic material was treated with large excess of concentrated sulphuric acid and left in an air oven maintained at 120-300°C. The carbon formed is washed thoroughly with water to remove the free acid and dried.

1.6.1.4 Carbonisation with carbonate salts

Potassium carbonate has been used since very early days for the production of blood char by igniting a mixture of 8 parts of dried blood with 1 part of potassium carbonate at 800°C in the absence of air. The product, after washing and drying, was applied for decolourisation purposes.

1.6.1.5 Dolomite process

A process that provides a uniform distribution of oxidising gases throughout the entire mass involves incorporation of substances such as dolomite which release carbon dioxide at the activating temperature. Generally pulverised dolomite and the material to be carbonised are mixed in 1:1 ratio with sufficient milk of starch to form a paste. After drying, the mixture is carbonised and then heated at 600-900°C, when carbon dioxide is released uniformly throughout the mass. The resulting char was washed with acid and water to remove magnesium oxide and dried.
is maintained. A basic surface oxide is reported to form upon cooling the carbon to room temperature.

\[
\text{CO}_2 + C_x \rightarrow 2\text{CO} + C_{x-1} \quad (800-900^\circ\text{C})
\]

Activation with air involves an exothermic reaction and hence measures must be taken to control the temperature. Since there is always some local over heating the product obtained is not uniform. Thus the method is rarely used.

\[
\text{O}_2 + C_x \rightarrow 2\text{CO} + C_{x-2} \quad (800-900^\circ\text{C})
\]

\[
\text{O}_2 + C_x \rightarrow \text{CO}_2 + C_{x-1} \quad \text{(below 600}^\circ\text{C)}
\]

Irrespective of the method of activation it has been found that the adsorptive capacity of the finished product depends primarily on (i) the oxidising gas and its concentration (ii) the temperature during oxidation and (iii) the period to which the activation is carried.

### 1.6.2.2 Chemical activation

The use of oxidising chemicals has also been examined for activation purpose. Although not much information is available, carbons activated by treatment with aqueous solution of oxidising agents such as aqueous chlorine, permanganate, persulphate, hydrogen peroxide and nitric acid were reported to produce the materials with characteristics similar to L-carbons (Faust and Aly 1983 and Puri 1970). Thus the treatment of coconut shell with nitric acid, potassium persulphate or hydrogen peroxide was found to adsorb ammonium ions from wastewater due to the formation of acidic CO₂ complex on the surface.
1.7 SOURCES OF LOW COST ACTIVATED CARBONS

Both industrial and agricultural wastes have been examined as sources for the preparation of low cost activated carbons.

1.7.1 Industrial Wastes

Many industrial wastes which are rich in carbon content such as oil wastes and scrap tyres, after controlled pyrolysis, yield porous products that were found useful to treat wastewater. Crude oil residue, after initial sulphonation at 100°C, was carbonised at 400°C. The material after activation with steam at 900°C was examined for the removal of methylene blue. The capacity of the carbon was found to be 160 mg/g.

1.7.2 Agricultural Wastes

Cellulosic and lignocellulosic wastes have long been recognised as starting materials for the preparation of activated carbon and many materials such as olive stones (Linares-Solaro *et al* 1980 and Caturla *et al* 1988) have been evaluated for the preparation of activated carbon. Bhattacharya and Venkobachor (1984) prepared rice husk carbon by carbonising the material at 600°C and then activating with steam at 700°C. It could remove 94% of Cd(II) from a solution containing 0.5 mg/l of Cd(II). This carbon was found to be very effective in the removal of phenol to an extent of 99% (Caturla *et al* 1988).

Srinivasan *et al* (1988a) prepared activated carbon from tamarind nut and examined its suitability for phenol removal. The carbon derived from the material after charring with sulphuric acid and carbon dioxide activation at 850°C exhibited phenol uptake of 0.3-2.0 mg/g. Rice husk has been evaluated by Srinivasan *et al* (1988b) for the preparation of carbon by treating the material with sulphuric acid followed by carbon dioxide activation. The resulting carbon was found useful to remove 88% and 99% total chromium and Cr(VI) respectively from plating wastewater.

Coconut shell has long been known as a precursor of high quality activated carbon and 9% of total commercial activated carbon production is currently from coconut shell (Bansal *et al* 1988). It possesses high bulk density, hardness and low ash content. Banerjee *et al* (1976) prepared a carbon by heating ZnCl$_2$ impregnated coconut shells at 600°C and then activating the char with steam at 900°C. The carbon exhibited a capacity of 130 mg/g for the removal of methylene blue. Arulanantham *et al* (1989) prepared a carbon from coconut shell by charring the pieces with concentrated sulphuric acid followed by steam activation and examined it for the removal of Pb(II) and Cd(II) from wastewater. The removal efficiencies were found to be more than 99% in both cases. The material
after alum impregnation was found to be effective for the removal of fluoride to an extent of 85% (Arulanantham 1992).

Periasamy et al (1991) prepared activated carbon from peanut shell and evaluated the removal of Cd(II), Hg(II) and Cr(VI). Peanut shell was carbonised in the presence of sulphuric acid. After neutralisation with sodium bicarbonate solution the material was evaluated for the removal of Cd(II) and Hg(II). The removal efficiencies were found to be 99% in both cases. In another study peanut shell after carbonisation with sulphuric acid was activated using carbon dioxide at 850°C. The prepared carbon was found to remove 80% Cr(VI) from wastewater in the pH range 2-3.

Balci et al (1994) prepared activated carbon from almond shell and hazelnut shell by treatment with NH$_4$Cl. The surface area of the products obtained from NH$_4$Cl impregnated samples was above 700 m$^2$/g when the carbonisation temperature was increased to 700°C.

Khalfaoni et al (1995) obtained activated carbon from reeds by pyrolysis method. The carbon thus obtained was used for the removal of copper from industrial wastewater. The surface area of the carbon was about 400 m$^2$/g at a carbonisation temperature of 700°C. Kannan and Srinivasan (1998) prepared low cost activated carbon from rice husk and wood shavings by treating with sulphuric acid. The carbon thus prepared was used for the adsorption of copper from aqueous solution.

Johns et al (1998) prepared activated carbon from different raw materials like rice straw, soyabean hull, sugarcane bagasse, peanut shell, pecan shell and walnut shell. The carbon thus prepared was used for the removal of Pb(II), Cu(II), Ni(II), Cd(II) and Zn(II) from aqueous solution.
Edgelhill and Lu (1998) prepared activated carbon from carbonised slash pine bark and used for the removal of phenol and pentachlorophenol. The surface area of the carbon was about 332 m²/g at a carbonisation temperature of 672°C.

Daifullah and Girgis (1998) prepared the activated carbon from apricot stone and examined its suitability for phenol removal. The apricot stone was treated with 50% phosphoric acid and activated at 500°C. The uptake of phenol increases in the order phenol < 2-chlorophenol < 4-nitrophenol < 2,4-dinitrophenol < 2,4-dichlorophenol which correlates well with respective increase in molecular dimensions and acidity and decrease in solubility of the sorbates.

From the foregoing discussion it is clear that adsorption using activated carbon is an effective process to treat water and wastewater as it can render the water free from both organic and inorganic constituents. However, the commercial activated carbon has the disadvantage of being relatively expensive and therefore find only limited use. The carbon derived from industrial wastes and agricultural wastes are no doubt inexpensive but they are mostly H-carbons which are more suited for the removal of organic and inorganic anionic constituents from water. In addition, most of the carbons, excepting those derived from coconut shell, have low bulk density and show poor mechanical strength and abrasion resistance. In any case, no comprehensive study has been undertaken to regenerate the spent carbon to find use for repeated application.
1.8 SCOPE OF THE PRESENT WORK

Of the presently used clean up methods, adsorption using activated carbon appears to have the least adverse effects. It is attractive as it can treat wastewater to quality suitable for use. Other advantages offered by adsorption process include flexibility and dependability together with good performance for wastewater treatment.

Though activated carbon has proven history of performance for wastewater treatment, the technique does not find widespread application due to lack of suitable alternative for the expensive commercial variety. This has necessitated the development of alternative materials which are cheaper and possess properties comparable to those of commercially available varieties of carbon. In view of this and as a consequence of increased interest in the removal of toxic organics from water and wastewater, it was felt that attention should be directed to the preparation of activated carbon from organic waste materials which are readily available in India.

In the present investigation, an attempt has been made to prepare activated carbon from readily and cheaply available agricultural waste materials, namely, rubber seed coat, palm seed coat, palm tree flower, myrobalan waste, cashewnut sheath and pongam seed coat.

The study comprises the following:

1. Preparation of activated carbon from rubber seed coat, palm seed coat, palm tree flower, cashewnut sheath, myrobalan waste and pongam seed coat by acid, sulphate, dolomite, chloride, carbonate and pyrolysis processes.

2. Characterisation of the carbons thus prepared by determining the parameters like bulk density, moisture content, ash content, matter soluble in water, matter soluble in acid, decolourising
power, phenol number, ion exchange capacity, surface area and iron content, and to compare with that of commercial activated carbon.

3. Identification of the suitable carbon for the adsorption studies to remove phenolics in wastewater.

4. Evaluation of the performance of the carbon selected for the removal of phenolics from wastewater.

5. Optimisation of the conditions like pH, carbon dosage and contact time for maximum removal of phenolics.

6. Kinetic studies to evaluate the nature of the diffusion process.

7. Desorption studies for the regeneration of carbon and recovery of phenolics.

8. Column studies to assess the suitability of carbon in field studies. The study includes

   (i) optimisation of carbon dosage and flow rate.
   (ii) desorption of the phenol from the adsorbent.
   (iii) reuse of the carbon after desorption of phenol to assess the economic viability of the process.


10. Evaluation of the suitability of the prepared carbons for the removal of phenol from the effluent collected from phenol-based resin manufacturing industry.