CHAPTER I

INTRODUCTION

The environment consists of four segments, namely, atmosphere, hydrosphere, lithosphere and biosphere. The atmosphere is the protective blanket of gases surrounding the earth which sustains life on earth and saves it from the hostile environment of outer space. The hydrosphere includes all types of water resources - ocean, seas, rivers, lakes, streams, reservoirs, glaciers, polar ice caps and ground water. About 97% of the earth's water supply is in the oceans where the high salt content does not permit its use for human consumption. About 2% of the water resources is locked in the polar ice caps and glaciers while only 1% is available as fresh water which includes surface and ground water for human consumption and other uses. Lithosphere is the outer mantle of the solid earth consisting of minerals occurring in the earth's crust and the soil. Soil comprises complex mixture of minerals, organic matter, air and water. The soil is the most important part of the lithosphere. The term biosphere denotes the kingdom of living organisms and their interactions with the environment, viz., atmosphere, hydrosphere and lithosphere. Both the biosphere and environment are influenced considerably by each other.

Environmental resources may be regarded as global public goods. Their preservation not only benefits the local population but also the fauna and flora of the region. The survival and well being of a nation depend on the sustainable development. A large number of industries and other development projects have been incorrectly sited, leading on the one hand, to over-congestion and over-pollution in the urban centres and on the other hand to diversion of population and economic resources from the rural areas.
This has also resulted in low lying areas without any pre-treatment, thereby creating sewage pools, contaminating ground waters, salinising good quality lands around cities, acting as a source of foul smell and breeding grounds for mosquitoes and other pathogens. At many places this wastewater is discharged into ground, drains and rivers causing serious water pollution. Geetha Mehta et al (1995) have reviewed the various aspects of the policy statement for the abatement of pollution, documented by the Ministry of Environment and Forest, Government of India.

Environment Protection Act (1986) is a fresh enactment with a broad sweep to prevent, control and abate all types of environmental pollution and particularly lay down procedures and safeguards for manufacture and handling of hazardous substances. According to the Environment Protection Rules, all industries should obtain consent under the Air and Water Pollution Control Acts to furnish an annual environment statement covering quantities of pollutants discharged, hazardous and solid wastes generated, their characteristics and pollution abatement measurers to the State Pollution Control Boards. The pollution of most of the water bodies which are major constituents of our life support systems.

Water quality has become a major global concern due to ever increasing human developmental activities that over exploit and pollute water resources on surface and underground. Most commonly cited water quality problems are microbiological pollution, chemical pollution and high salination. Water is polluted by four kinds of substances, namely, 1. traditional organic waste, 2. waste generated from industrial processes, 3. chemical agents of fertilizers and pesticides used for crop protection and 4. slit from degraded catchments.

It is estimated that three-fourths volume of the wastewater is generated from municipal sources, and industrial wastes contribute over one-half of the total pollutant load which this is coming from large and
medium industries (The Hindu, 1993). There has been a steady increase in the amount of wastewater produced from urban communities and industries. Generally, these water are discharged into lagoons or dumped on low lying areas without any pre-treatment thereby creating sewage pools, contaminating groundwaters and salinising good quality lands around cities. At many places this wastewater is discharged into drains and rivers causing serious water pollution.

1.1 WATER POLLUTION

Water pollution may be defined as the addition of excess undesirable substances to water that make it harmful to man, animal and aquatic life. Water pollution can be classified into four categories. These are

i) Physical pollution of water
ii) Chemical pollution of water
iii) Biological pollution of water
iv) Physiological pollution of water

The physical pollution of water brings about changes in water with regard to its colour, odour, density, taste, turbidity and thermal properties. The chemical pollution of water causes changes in acidity, alkalinity or pH, dissolved oxygen (DO) and other gases in water. It may be caused either by organic pollutants or inorganic pollutants or by both. Biological pollution in water is caused by the bacteria, viruses, algae, diatoms like protozoa, ratifiers, crustaceans and plant toxins. Bacterial pollution in water is caused by the excretory products of warm blooded mammals, wild and domestic animals. Birds of various genera also degrade water. The main pollutants belong to coliform group and certain subgroups, faecal streptococci and miscellaneous organisms. Physiological pollution of water is caused by several chemical agents such as chlorine, sulphur dioxide, hydrogen sulphide, ketones, phenols, amines, mercaptans and hydroxy benzene. Based
Ground water, a gift of nature, is about 210 billion m$^3$ including recharge through infiltration, seepage and evapotranspiration. Out of this, nearly one-third is extracted for irrigation, industrial and domestic use. Over 98% of the fresh water on the earth lies below its surface. The remaining 2% is what we see in lakes, rivers, streams and reservoirs. Ground water acts as a reservoir by virtue of large pore space in earth materials. Ground water contamination is generally irreversible and it is difficult to restore the original water quality of the aquifer. Excessive mineralisation of ground water degrades water quality producing objectionable taste, odour and excessive hardness. The extent of ground water pollution depends on the following factors:

- Rain fall pattern
- Depth of water table
- Distance from the source of contamination
- Soil properties such as texture, structure and filtration rate

The common impurities present in ground water are soluble organics/inorganics, bicarbonate, calcium, chloride, magnesium, iron (III), fluoride, nitrate, potassium, sodium, silica, sulphate, suspended solids, dissolved solids and hardness causing substances. The soluble organics cause depletion of dissolved oxygen in water course. Further, it leads to septic condition and resulting odour problem. The soluble inorganics pollute the 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.

Water containing high chloride content also has a deleterious effect on metallic pipes and structures as well as on agricultural plants. Ingestion of water containing high concentration of sulphate can have a laxative effect, which is enhanced when sulphate is consumed in combination with magnesium. Sulphate causes problem of scaling in industrial water supplies, and problem of odour and corrosion in wastewater treatment due to its reduction to $\text{H}_2\text{S}$. Excessive concentration of nitrate in drinking water are considered hazardous for infants because in their intestinal track nitrates are reduced to nitrites which may cause methemoglobinæmia. The presence of iron in drinking water supplies is objectionable for a number of reasons. Under the pH condition existing in drinking water supply, ferrous sulphate is unstable and precipitate as insoluble ferric hydroxide which settles out as a rust. Such waters containing iron often tastes impalatable even at low concentration and stains laundry and plumbing fixtures. Iron also promotes the growth of iron bacteria in drinking water. Presence of heavy metals in drinking water causes acute and chronic disorders in human beings. Further, agricultural wastes like fertilizers, pesticides, insecticides, herbicides, processing wastes and animal wastes pose pollution to ground water.

Among the various contaminants in ground water fluoride is the principal and dangerous one. But the reality about fluoride is that high concentration of naturally occurring fluoride in ground water have caused wide spread fluorosis among local populations. Available information shows that endemic fluorosis exist in atleast 27 countries (Susheela, 1998). Taking into consideration the acute and chronic effects of various pollutants in ground water, each country has set a standard for drinking water based on the local geographic, socio-economic and industrial conditions. The list of
toxic substances for which limits have been set by WHO, USPHS and Indian Standards are given in Table 1.1 (WHO 1971, ISI 1991 and De 1994).

Table 1.1 Maximum permissible limits of contaminants in drinking water

<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>5</td>
<td>Copper</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>6</td>
<td>Zinc</td>
<td>5.0</td>
<td>5.5</td>
<td>5.0</td>
</tr>
<tr>
<td>7</td>
<td>Total hardness</td>
<td>500</td>
<td>-</td>
<td>300</td>
</tr>
<tr>
<td>8</td>
<td>Calcium (as Ca)</td>
<td>75</td>
<td>100</td>
<td>75</td>
</tr>
<tr>
<td>9</td>
<td>Magnesium (as Mg)</td>
<td>50</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>10</td>
<td>Sulphate</td>
<td>200</td>
<td>250</td>
<td>200</td>
</tr>
<tr>
<td>11</td>
<td>Chloride</td>
<td>200</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>12</td>
<td>Fluoride</td>
<td>1.5</td>
<td>1.5</td>
<td>1.0</td>
</tr>
<tr>
<td>13</td>
<td>Phenols</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>14</td>
<td>Lead (as Pb)</td>
<td>-</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>15</td>
<td>Selenium (as Se)</td>
<td>-</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>16</td>
<td>Arsenic (as As)</td>
<td>-</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>17</td>
<td>Chromium (hexavalent)</td>
<td>-</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>18</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.
1.2 INORGANIC CONTAMINATION IN GROUND WATER

The inorganic minerals present in water can be classified into three categories: (i) Minerals needed daily in large quantities like sodium, calcium, magnesium and potassium. These are present in the body as calcium in bones, magnesium in body fluids, sodium in blood and body fluids and potassium within the cells. (ii) Elements needed in smaller quantities include iron, copper, cobalt, manganese, zinc, molybdenum and fluoride. These inorganic ions are part of the enzymes and serve to catalyse biochemical reactions in addition to participation in redox reactions in biological systems (Mahler, 1970). Certain anions like chloride and fluoride have been found beneficial for skeletal system (WHO, 1970). (iii) Mineral elements which are toxic even at low concentrations include beryllium, bismuth, cadmium, lead, arsenic, mercury and silver. These heavy metals can exert toxic effects because human beings have no natural defence against them. Excessive intake of the above essential minerals causes serious health effects on the living kingdom. The occurrence of the inorganic compounds in aquatic environment is well documented in the literature (Faust and Aly, 1983). These inorganic compounds entering into the groundwater by dissolution of minerals and discharge of industrial effluents.

1.2.1 Fluoride Contamination in Groundwater

Nearly 90% of the rural population in India using groundwater from open dug wells and hand pumps for domestic purposes. Many of these sources are liable to contain fluoride in excess of the permissible limit of 1 mg/l. Fluoride is ubiquitous in the environment and is always present in plants, soils and phosphatic fertilizers (Adriano, 1986). Various rock types contain fluoride at different levels: basalt, 360 g/kg; granites, 810 g/kg; lime stone, 220 g/kg; sand stone and greywacke, 180 g/kg; shale, 800 g/kg; oceanic sediments, 730 g/kg and soils 285 g/kg (Fleischer and Robinson, 1963). The fluoride concentration in the upper continental crust is 611 mg/l
It is an essential constituent in minerals such as fluorite (fluospar), apatite, cryolite and topaz (Read, 1976). Minerals such as biotite, muscovite and hornblende may contain large percent of fluoride (Deer et al 1966) and therefore would seem to be the main source of fluoride in surface water. It appears, therefore, that the fluoride content of surface water is largely dependent on the mineralogical composition of the inorganic fraction in surface soils and sediments. Apatite may perhaps exchange some of its hydroxyl ions for fluoride via the following reaction:

$$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + 2\text{F}^- \rightarrow \text{Ca}_{10}(\text{PO}_4)_6\text{F}_2+2\text{OH}^- \tag{1.1}$$

$$K = \frac{a^2\text{OH}^-}{a^2\text{F}^-} = 10^{6.6} \tag{1.2}$$

The process converts the hydroxyl apatite of bones and calcium phosphate into fluorapatite where K is the equilibrium constant and a is the activity (Subramanian, 1980). Most of the above mentioned minerals are nearly insoluble in water and therefore it can enter ground water only when the conditions (such as high temperature) favour their dissolution. Fluoride concentrations ranging from less than 1 mg/l to hundreds of mg/l have been reported in geothermal fluids (Choi et al 1979). In surface waters, the concentration generally do not exceed 0.3 mg/l unless they are polluted from other sources (Barenett et al 1969). The use of fertilizers (Compendium of Environmental Statistics 2000) containing fluoride increases the fluoride content of water. Approximately 20-400 g of fluoride per hectare is annually leached from soils and about the same amount that is added to the soil from the atmosphere. The fluoride content of various continental precipitations shows a range of 4-89 ppb and in the vicinity of cities and industrial areas an average of 290 ppb. The order of magnitude of the normal fluoride content in the air is <0.01-0.4 µg/m³ and in industrial areas upto 5-111 µg/m³ from chemical plants producing HF, aluminium, superphosphate, brickwork and burning of low quality coal (Wedepohl, 1972).
1.2.2 Effect of Fluoride Ingestion in Human Beings and Animals

Fluoride is probably an essential ion for animals and human beings. For humans, however, the essentiality has not been demonstrated unequivocally and no data indicating the minimum nutritional requirement are available. To produce signs of acute fluoride intoxication, minimum oral doses of at least 1 mg of fluoride per kg of body weight were required (Janssen et al. 1988). Excessive intake of fluoride through water, food and air leads to various health effects. In India an estimated 62 million people including 6 million children are affected with endemic fluorosis from 20 states. The map of India showing endemic states of fluorosis is shown in Figure 1.1. The excess fluoride in ground water in the state Tamilnadu is shown in Figure 1.2. Absorbed fluoride is distributed rapidly throughout the body. It is retained mainly in the skeleton and small portions are retained by teeth, body fluids and soft tissues (Underwood, 1977). Some accumulation can also occur in the kidneys (NAS, 1977). The amount of fluoride in bone increases with age to about 55 years (Jackson and Weidmann, 1958).

1.2.2.1 Skeletal fluorosis

The most important toxic effect of fluoride on human beings is skeletal fluorosis (Figures 1.3 and 1.4) which is endemic in areas with soils and water containing high fluoride concentration. The sources of fluoride that contribute to the total human intake vary geographically between endemic fluorosis areas, but the symptoms are generally similar. In adults chronic exposure of high dose of fluoride replaces bone calcium by calcium fluoride results the soft, crumbly and chalky white bone. The skeletal fluorosis is characterised by back pain in the lumber and cervical region, rigidity and fixity of spine and chest and inability to close fists. In the advanced stages, limitation of the movement of joints and spine lead to inability to walk and finally crippling occurs (Teoti and Teotia, 1988).
Fig. 1.1 Map of India showing the endemic States of fluorosis
Fig. 1.2 Fluoride concentration in ground water of Tamil Nadu State
Fig. 1.3 Skeletal deformities on children

Fig. 1.4 Chronic skeletal fluorosis on aged woman
1.2.2.2 Dental fluorosis

During the first part of 20th century, the etiology of a specific type of mottled teeth was discussed. The mottling was endemic in certain geographically well-defined areas. Eager (1901) described a "strange condition in the teeth of people living in a small village near Naples". He characterised its mildest form as "very slight", opaque, whitish areas on some posterior teeth. He identified the cause of dental defects to volcanic fumes either fouling the atmosphere or forming a solution in the drinking water. In other areas when mottled teeth occurred, the drinking water was more directly suspected (McKay, 1926) and the interest was focussed on the presence of fluoride (Churchill, 1931). Fluoride was definitely identified as the causative agent when mottled teeth developed in rats and sheep given fluoride in the food (Smith et al 1931 and Velu and Balozet, 1931). Dean et al (Dean and Elvove 1935, 1937 and Dean 1942) extensively studied the severity of dental fluorosis to different fluoride levels in the drinking water.

Intake of optimal levels of fluoride in drinking water (0.7-1.2 mg/l depending on climatic conditions) clearly demonstrated cariostatic effect (WHO, 1984). The extent of caries reduction by various methods is influenced by the initial caries prevalence and the standard of health care in the community. The factors controlling the incorporation of fluoride into dental structures have been reviewed by Weidemann and Weatherell (1970). A disfigurement in the teeth of human due to excessive intake of fluoride called as mottled enamel or dental fluorosis. The concentration above 2 mg/l gives permanent chalky white appearance or mottled brown stain coloration to children in less than 12 years of age. The teeth of the children show the following defects. i) loss of lustre and shine of the enamel of the teeth, ii) discoloration of teeth, yellow, brown and black streaks or spots, iii) pitting and chipping of teeth and iv) loss of teeth. Mottled enamel can be produced only during the period of calcification of the teeth. In other words, after
about 12 years, mottled enamel cannot be produced whatsoever the level of fluoride in the water.

Susheela et al (1988) studied the cavity formation in teeth. The studies indicated that glycosaminoglycan and its sulphated isomers are integral part of the teeth matrix and play a significant role in calcification of the teeth. It is observed that exposure to fluoride there was a reduction in the total glycosaminoglycan content whereas accumulation of dermatan sulphate on teeth and bone which is usually does not occur. Accumulation of dermatan sulphate induces loss of calcium and the teeth become soft (demineralized) and such soft areas get pitted or perforated. Fluoride induces pitting/ cavity formation on the surface of the enamel. Excessive intake of fluoride in drinking water damaging the teeth as a result of demineralisation, pitting and chipping off the teeth (Figures 1.5 and 1.6).

Fluoride ions are taken up rapidly by bone by replacing hydroxyl ions in bone apatite. It has been suggested (WHO, 1984) that fluoride ion in extracellular fluid enters the apatite crystal by a three-stage ion exchange process:

i) The hydroxy apatite of bone mineral exists as extremely small crystals surrounded by a hydration shell. Fluoride first enters the hydration shell in which the ions are in equilibrium with those of the surrounding tissue fluids and those of the apatite crystal surface.

ii) In the second stage reaction constitutes an exchange between the fluoride of the hydration shell and the hydroxyl group at the crystal surface. After entering into the surface, it firmly bound over the crystal.

iii) Some of the fluoride may migrate deeper into the crystal as a result of recrystallization.
Fig. 1.5 Mild symptoms of dental fluorosis

Fig. 1.6 Severe dental fluorosis
The consensus is that absorbed fluoride is incorporated into the hard tissues largely by a process of exchange and by incorporation into the apatite lattice during mineralisation (Neuman and Neuman 1958 and US NAS 1971).

1.2.2.3 Non-skeletal fluorosis

The fluoride enters into the body by absorption in gastro intestinal tract through water, food or even dental products. The progressive increase of fluoride in body affects the body soft tissues like ligaments, muscles, red blood cells, blood vessels, sperms and gastro-intestinal system. This type of fluorosis is known as non-skeletal fluorosis. The various symptoms related to non-skeletal fluorosis are given in the Table 1.2.

Table 1.2 Various symptoms related to non-skeletal fluorosis

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Soft tissue of organ</th>
<th>Symptoms associated with the organ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Gastro-intestine</td>
<td>Acute stomach pain, diarrhoea, constipation, bloated feeling (gas), nausea (flu-like symptoms), mouth sores and loss of appetite</td>
</tr>
<tr>
<td>2.</td>
<td>Neurological manifestations</td>
<td>Nervousness, depression, tingling sensation in fingertips and toes, excessive thirst and tendency to urinate frequently</td>
</tr>
<tr>
<td>3.</td>
<td>Muscles</td>
<td>Muscle weakness, stiffness and pain</td>
</tr>
<tr>
<td>4.</td>
<td>Allergic manifestation</td>
<td>Painful rashes on the skin, prevalent in women and children which clear up in 7-10 days</td>
</tr>
<tr>
<td>5.</td>
<td>Urinary tract</td>
<td>Urine may be much less in volume and itching in the urinary region</td>
</tr>
<tr>
<td>6.</td>
<td>Sperm</td>
<td>Sperm abnormality results in infertility</td>
</tr>
</tbody>
</table>
Upper gastrointestinal endoscopy using fibre optic endoscope and punch biopsy material examined under scanning electron microscope revealed (Susheela, 1998) (i) loss of microvilli on the cell surfaces (ii) loss of mucus in the mucosa and (iii) cracked clay appearance of the cell surfaces of the mucosa compared to normal health mucosa (Figure 1.7). The following scanning electron micrographs (Figures 1.8 and 1.9) reveal the damage caused to the human gastro-intestinal mucosa by the intake of excess fluoride.

Figure 1.7 shows the scanning electron micrograph of gastro intestinal mucosa of a normal healthy adult individual showing (i) columnar cells studded with microvilli on the cell surface. The microvilli are responsible for absorbing nutrients from the diet and (ii) the white mass spread around the mucosa is the mucus which helps in comfortable bowel movement. Figure 1.8 shows the scanning electron micrograph of gastro-intestinal mucosa of an individual consuming water contaminated with 1.2 mg/l of fluoride. The following are observed (i) microvilli are lost (ii) presence of scantly micro villi and (iii) very little mucus secretion seen on the mucosal surface. Figure 1.9 shows the scanning electron micrograph of gastro-intestinal mucosa of an individual consuming water with 3.2 mg/l of fluoride. The following are observed: (i) surfaces are cracked (ii) no microvilli and (iii) no mucus secretion.

Osteoporosis may be defined as the loss of bone accelerated beyond the normal physiological rates (Dixon, 1983). Severe clinical manifestations of osteoporosis are the loss of bone, fracture of long bone and loss of trabecular bone. Fluorosis is accompanied by adverse effects on other systems and organs of the body, namely, liver, kidney, muscles, heart, lungs, blood and hormonal functions. Kidney is the principal organ through which maximum concentration of fluoride is excreted. High fluoride concentration causes impaired kidney functions (Whitford and Traves, 1971). Fluoride adversely affects spermatogenesis (Chinoy and Sequeria, 1989), decreases
Fig. 1.7 Scanning electron micrograph of gastro-intestinal mucosa of a normal adult

Fig. 1.8 Scanning electron micrograph of gastro-intestinal mucosa of non-ulcer dyspeptic patient consuming water with 1.2 mg/l of fluoride
Fig. 1.9 Scanning electron micrograph of gastro-intestinal mucosa of non-ulcer dyspeptic patient consuming water with 3.2 mg/l of fluoride
motility and density of sperms (Chinoy and Sequeria, 1992). Spittle (1994) also reported symptoms of impaired central nervous functioning with impaired cognition and memory after exposure of fluoride pollution.

The hazardous nature of excess fluoride in drinking water necessitated suitable treatment methods for the removal of excess fluoride. The following section deals the various techniques adopted to remove the excess fluoride in water.

1.3 TREATMENT METHODS FOR REMOVAL OF FLUORIDE

A variety of methods have been developed for the removal of fluoride from water and wastewater. Each technique provides a different and unique approach for their removal from water and perhaps provide certain advantages over others for a particular situation. However, when large volume of water containing fluoride is to be treated, it is of great advantage if the method would provide reliable results without involving much cost and working efforts. The principal methods of removal of fluoride from water are based on the principles of precipitation, adsorption, ion-exchange, adsorption and ion-exchange, reverse osmosis, electro chemically stimulated coagulation and electrodialysis. The outline of the above techniques are discussed below.

1.3.1 Precipitation Method of Fluoride Removal

Precipitation method includes the use of lime either alone or in combination with magnesium salt or aluminium salt with and without the help of coagulant aid. Boruff (1934) studied the removal of fluoride using lime and aluminium sulphate. Precipitation as calcium fluoride by addition of lime was not found to be entirely satisfactory as it was not possible to reduce the fluoride level to the permissible limit of 1.5 mg/l because the
solubility of the CaF$_2$ precipitate is about 7.7 mg/l as fluoride (Choi and Chen, 1979).

Nawlakhe et al (1975) studied removal of fluoride extensively by adding lime and alum. This process is known as "Nalgonda process". It involves direct addition of lime to maintain the pH of water and addition of known quantity of alum depending on its fluoride content. The quantity of lime and alum depends upon the quality and fluoride content of water. Therefore it is very difficult to control the alum dose. It is a cumbersome technique and hence is not suitable for use by illiterate person. Further, the process can be used only for water having a fluoride content of less than 10 mg/l. There is high free residual aluminium content available in treated water. Further, aluminium is a neurotoxin and concentration as low as 0.08 mg/l of aluminium in drinking water is reported to have caused Alzheimer's disease (Davidson et al 1982).

Precipitation method for the removal of fluoride from synthetic wastewater containing HF, NaF, NH$_4$F or Na$_2$SiF$_6$ carried out by Min Yang et al (1999) using fixed bed packed with granular calcite. The performance of the bed was affected by the existence of sulphate to some extent and significantly inhibited by phosphate. Removal of fluoride from water studied using calcined magnetite (Thergaonkar et al 1971) and magnesia. The residual concentration of fluoride in the treated water was found to be above 1 mg/l. Choi and Chen (1979) treated the wastewater from industries where CaF$_2$ and MgF$_2$ are used as raw material. This process involved the removal of fluoride by reaction with superphosphate and calcium oxide for the removal of residual fluoride.

Macintire and Hammon (1938) studied the removal of fluoride from natural waters using calcium phosphate. In this method fluoride is removed as fluorapatite. Howard Adles et al (1938) treated the potable water containing excess fluoride with tricalcium phosphate as precipitant.
Parthasarathy et al (1986) studied the combined use of calcium salt and polymeric aluminium hydroxide for the treatment of fluoridated wastewater. Calcium ions precipitated fluoride and polymeric aluminium fluoride acted as coagulant. Presence of sulphate ions reduced the precipitation efficiency.

1.3.2 Ion-Exchange Method

Ion-exchange method is one of the important methods in water and wastewater treatment. It is a reversible process which remove both cations and anions in water by exchange with the ions present in the ion-exchange material. Usually organic resins are used as ion-exchange materials. Ion-exchange resins are classified into two types: anion exchange resins and cation exchange resins.

1.3.2.1 Anion exchange resins

Polystyrene anion exchange resins in general are strongly basic quaternary ammonium type and they remove fluoride along with other anions. Sundaresan and Bulusu (1978) studied the fluoride removal capacity of 32 to 232 mg fluoride per litre resin and the resins lost their fluoride removal capacity within ten to fifteen cycles. The resin regenerated with 80g NaOH per litre of resin. Comparatively, anion exchange resins were found to exhibit low capacity for fluoride removal. Bhakani (1970) compared the fluoride removal capacity of NCL poly anion resin, Tulsion A-27, Deacidites FF-1P, Lewatit MIh-59 and Amberlite IRA-400. The removal capacity of the resin was found to be in the range of 32-500 mg fluoride per litre of the resin.

1.3.2.2 Cation exchange resins

Bhakuni and Sastry (1964) compared the performance of the cation exchange resins, waso resin 14 and a polystyrene cation exchange resin,
Lewasit S-100. The medium was regenerated with alum solution. The fluoride removal capacity reduced undesirably from the initial 262-420 mg fluoride per litre of resin within 16-65 cycles of operation. The capacity was sharply lowered with an increase in alkalinity. Removal of fluoride from industrial phosphonomethylamine group after loading with lanthanum (III) for fluoride was studied by Masatoshi et al (1988). The resin absorbed fluoride effectively in the pH range 3.0-4.0. Mohan Rao and Bhaskaran (1988) studied the removal of fluoride using aluminium impregnated cation exchange resins. Ion exchange resin was regenerated with 2-4% aluminium sulphate solution. In this study, it was observed that the material can be regenerated 20 times without loss of defluoridation efficiency.

Castel et al (2000) used two anion exchange columns pre-equilibrated with hydrogen carbonate anion for the removal of fluoride ion in water. This process is based on the chromatographic separation of fluoride ion from other anions of the feed solution on an anion-exchange resin. This process achieved the removal of fluoride ion from a carbonated water containing chloride and sulphate ions as major anions. The process achieved removal rate of 95-99% at its initial level.

Haron et al (1994) studied the removal of fluoride using yttrium-loaded poly (hydroxamic acid) ion exchange resin from aqueous solution. The sorption selectivity showed that the fluoride removal may be interfered by the presence of phosphate and sulphate but not affected by chloride, bromide, iodide and nitrate ions. Sorption capacity for fluoride increased with decrease in pH and reached maximum in the pH range of 3-4. It was reported that the fluoride is exchanged with hydroxide ions on the yttrium loaded resin.

Puri and Balani (2000) reported lanthanum hydroxide supported on alumina to sorb fluoride from aqueous solution in batch and column methods. The sorption capacity was 0.82 mM fluoride per g of the adsorbent.
The removal of fluoride was affected by the presence of phosphate and sulphate but not by chloride, bromide, iodide and nitrate ions. Mechanism of fluoride removal was reported by ion exchange process between fluoride and hydroxide group of alumina. Sorption capacity of fluoride increased in the acidic pH range and attained maximum at pH 5.7.

1.3.3 Reverse Osmosis

Reverse osmosis is effected by forcing the water alone through a semi permeable membrane by exerting hydraulic pressure on one side. This process separates water by leaving salts at another end. The membrane used for this purpose should possess high permeability for water over a wide pH range even at moderate pressure. Kumar and Gopal (1999) reported the fluoride removal efficiency by reverse osmosis technique.

1.3.4 Electrodialysis

Electrodialysis is a physical method of separation. In this method, the driving force for separation is the electrical field which carries the ions through the membrane but does not carry the water molecules. The method is extensively tested in the laboratory by Licheng (1985) for the removal of fluoride from drinking water. Gavach et al (2000) reported defluoridation of water by donnan dialysis and electrodialysis. It is reported that fluoride concentration is reduced to permissible level and also reduce the concentration of sulphate and hydrocarbonates, but did not affect the cationic concentrations except sodium. Both the technique were applied for model water containing excess fluoride.

Donnan dialysis is a potentially attractive membrane separation process for concentrating valuable materials in the ionic form from dilute solutions. This process involves the exchange of ions between two solutions

Srinivasan et al (1988) reviewed various methods available for fluoride removal. The study described the various removal methods under three categories: precipitation, adsorption and ion exchange. The authors concluded that application of activated alumina is attractive but the material is costly. Further, the study showed various waste organic materials after carbonisation followed by aluminium sulphate impregnation are found to remove fluoride but showed poor mechanical strength.

1.4 ADSORPTION

Adsorption is an unit operation in which matter is attracted from one phase and concentrated at the surface of a second phase. Adsorption is a surface phenomenon. The surface which adsorbs is known as adsorbent and the substance which is adsorbed is referred to as adsorbate. Adsorption is quite distinct from absorption. Absorption implies that a substance is uniformly distributed throughout the body of a solid or a liquid. The general term which includes both adsorption and absorption is simply sorption. The adsorption process occurs at solid-solid, gas-solid, gas-liquid, liquid-liquid and liquid-solid interfaces (Hassler, 1963). Adsorption with a solid adsorbent like activated carbon is dependent on the surface area of the solid.
1.4.1 Types of Adsorption

There are two types of adsorption: physisorption and chemisorption. Both types take place when the molecules in the liquid phase become attached to the surface of the solid as a result of the attractive forces at the solid surface overcoming the kinetic energy of the liquid molecules.

1.4.1.1 Physisorption

Molecules in the interior of any solid are subjected to equal forces in all direction whereas molecules on the surface of the solid are subjected to unbalanced forces. These forces can be balanced by other molecules becoming attached to the surface. The attractive forces are relatively weak and are of the Van der Waals type. Physisorption is usually explained in terms of the energy per unit area of the solid. This type of adsorption is multilayered and more molecular layers form with higher concentration of adsorbate solution. The adsorbed molecules are not affixed to specific site at the surface. Adsorption of this type is sometimes referred to as ideal adsorption.

1.4.1.2 Chemisorption

A process involving chemical interaction between the surface atoms of the adsorbent and the atoms of the adsorbate is known as chemisorption. Here the forces arise from the formation of chemical bonds between the adsorbed molecules and the particles at the surface of the adsorbent. Chemisorption involves the transfer of electrons and the formation of true chemical bonding between the adsorbate and solid surface (Young and Crowell, 1962).
1.4.2 Adsorbents

Adsorption technique is undoubtedly attractive because it can render the water free from both inorganics and organics particularly toxic compounds like fluoride. Many adsorbents other than activated carbon such as alumina, flyash, clay minerals, red mud, rare earth oxides, polymeric resins and carbonaceous adsorbents have been evaluated for the removal of fluoride in water. The following section explains the detailed literature survey of different sorbents and their efficiency in the removal of inorganics.

Adsorption of Cd, Zn, Ni and Pb 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. Teles de Vasconceios and Gonzalez Becac (1997) conducted continuous flow tests in fixed bed columns packed with natural and ammonia activated pine bark in order to remove Pb(II) ions from aqueous solution. The adsorption capacity was more for ammonia activated bark than natural bark.

Reed and Arunachalam (1994) studied the removal of lead and cadmium from aqueous waste streams using granular activated carbon. Removal of chromium (VI) from aqueous solution was investigated using adsorbents based on bagasse and coconut jute (Shrichand et al 1994). The removal was most effective at low pH. Activated coconut jute carbon was the most active material for the removal of four contaminants studied. It was fairly stable even at higher pH and the removal of about 97% Cr (VI) was observed at neutral pH. Palanivelu and Elangovan (1996) studied the removal of phosphate using aluminium impregnated coconut shell carbon by batch experiments. The study was extended to municipal sewage and fertilizer industrial wastewater. The phosphate removal efficiency was found to be 65% for the fertilizer industrial waste.
The use of activated alumina for the removal of fluoride has been examined by a number of workers. Bishop and Sansoucy (1978) studied fluoride removal using fluidized activated alumina adsorption from water supplies. The study revealed that continuous flow fluidized system is an economical and efficient method for defluoridation. This mode showed high defluoridation capacity due to large surface area available for adsorption than a down-flow reactor. The capacity of medium decreased with increase in the pH and alkalinity of the water.

Wu (1978) removed fluoride ions with activated alumina. Wu and Itemakin (1979) derived mathematical basis for the determination of activated alumina for fluoride removal. They reported few formal constants for adsorption of fluoride on activated alumina experiments. Wu and Anan Nitya (1979) successfully removed fluoride ion from water by the use of untreated activated alumina. The optimum pH for the removal was found to be 5. The study showed higher fluoride uptake capacity of 12 mg of fluoride per gram of activated alumina and the rate of adsorption was influenced by the ratio of the initial fluoride ion concentration to the activated alumina. Rubel and Woosley (1979) developed cost effective water treatment plant for removing excess fluoride from drinking water by activated alumina. It was reported that low operating cost for fluoride removal from potable water was achieved with activated alumina system. Further, they documented the reliability of plant equipment, materials and operational costs.

Hao and Huang (1986) studied the adsorption characteristics of fluoride onto hydrous alumina. The study showed that the adsorption purely depended on the pH and surface loading. Activated alumina rendered soluble by forming alumina-fluoro complexes which were stable in the acidic pH region and became unstable as pH increase. It was suggested that alumina adsorption system for fluoride removal should be operated at pH
values where alumina-fluoro complexes are unstable, which prevent the dissolution of alumina.

Bulusu and Nawlakhe (1983, 1988 & 1990) studied defluoridation of drinking water in batch and continuous flow operations employing activated alumina. They found a distinct advantage with continuous flow over batch type operation. The defluoridation capacity decreases with increase in basicity of water. Hydrochloric acid of 0.1 M was identified as a better regenerant for the desorption of fluoride from activated alumina.

Karthikeyan et al (1994) developed a defluoridation unit using activated alumina for 3 mg/l level water. They reported the defluoridation capacity increases with decrease in particle size. Rongshu et al (1995) developed a new adsorbent by loading activated alumina on the surface of silica gel which is used as a carrier for the removal of fluoride from water. The absorbent was characterised as having high selectivity for fluoride, large adsorption capacity, applicability to neutral medium and much better adsorption at high temperature. The fluoride removal mechanism was a typical chemisorption which is different from the one used for activated alumina.

Azbar and Turkman (2000) evaluated various chemical agents like powdered activated carbon, activated alumina, locally prepared alumina, anionic exchange resins, processed bone and tricalcium phosphate for the removal of fluoride from drinking water. Among the methods, adsorption was reported the most suitable method for fluoride removal. Mohan Rao and Bhaskaran (1988) studied the removal of fluoride by aluminium impregnated cation exchange resins and sulphated carbonaceous materials prepared from coconut shell and paddy husk. Cation exchange resins showed high fluoride removal capacity. Raichur and Jyoti Basu (2001) studied the removal of fluoride using mixed rare earth oxides. The mixture is composed of oxides of La, Ce, Pr, Nd, Sm and Y. Desorption study showed that the
fluoride was easily desorbed at pH 12. The capacity was reported as high as 12.5 mg of fluoride per gram of absorbent.

Lai and Liu (1996) studied the fluoride removal by spent catalyst from water. The adsorption density decreases with increase in pH. The adsorption reaction is endothermic and the activation energy is very low. It is proposed that a fluoro-alumino complex and fluoride ion are involved in the adsorption reaction. Removal of fluoride from aqueous solution was studied by Sujana et al (1998) using alum sludge. Adsorption experiments were conducted with raw and treated alum sludge for fluoride removal. The removal efficiency was maximum at pH 6. The adsorption process followed first order kinetics.

Fly ash packed column experiments were conducted for the removal of fluoride from aqueous solution by Piekos and Paslawska (1999). The studies indicated that the retention capacity of fly ash increases with increasing initial fluoride ion concentration. It is reported that double mechanism, namely, chemical binding by calcium hydroxide and physical sorption by residual carbon particles in fly ash are operating for the removal of fluoride by fly ash.

Meenakshi Maruthamuthu and Sivasamy (1994, 1996) studied defluoridation of water using zeolites, apophyllite and clay minerals. Laboratory samples and potable water samples were tested for fluoride removal using zeolite and apophyllite. Greater defluoridation was found in the pH range 3-4. Ca type zeolite was more effective than Na type zeolite for defluoridation. In the case of clay minerals fluoride removal efficiency was more at low pH value and the efficiency decreased with increasing concentration of chloride in the fluoride solution. Mayadevi (1996) also investigated removal of fluoride from water using adsorbents like zeolites and clays. The adsorbents were used for fluoride removal as such and activated by treating them at 60°C with 0.5 and 1N hydrochloric acid
solution. From the studies it was observed that the removal capacity of acid treated materials were high compared to the untreated materials. The adsorption capacity of sodium and calcium exchanged zeolite materials were comparatively high than H and K exchanged forms for fluoride.

Padmasiri and Fonseka (1994) designed domestic defluoridation filter using burnt clay as the adsorbing material. It was reported that the silicates, aluminates and hematite present in burnt clay were responsible for the removal of fluoride and a reasonable removal was found within 4-5 h contact time in the filter. A simple and new defluoridation method was reported by Zevenbergen et al (1996) using local Kenyan soil derived from volcanic ash as a fluoride sorbent. Kenyan Ando soil showed high defluoridation capacity which is due to the high active aluminium content and acidic character of the soil. Further it is also reported that the Ando soil showed high water permeability and abundance in regions with high fluoride concentrations in the ground water. Hence they suggested that adsorption of fluoride with Ando soil is an economically efficient method and it may be used for rural defluoridation in Kenya.

Killedar and Bhargava (1994) tried low cost adsorbents like blast furnace slag, natural dolomite, tamarind seed shell carbon and fish bone charcoal for the removal of fluoride from water by batch and jar test experiments. From the results it was observed that fish bone charcoal adsorbs fluoride instantaneously within 5 minutes of contact time. Serpentine, a mineral was used as a defluoridating medium from waters by Kulkarni and Nawlakhe (1974). The experiment was conducted in jar test, bottle and column adsorption experiments using different sizes of the mineral. The results indicated that serpentine is a weak defluoridating medium and it is influenced by particle size, flow rate, fluoride and alkalinity of test water sample.
Thergaonkar et al (1969) prepared a new medium Defluoron-2 for the removal of fluoride from water supplies. Alum solution of 5 percent was used as regenerant. A higher concentration of alum solution showed decrease in adsorption capacity due to its high acidity. There was no notable difference in the pH, alkalinity and hardness of the effluents.

Okopnaya et al (1982) studied defluoridation of water using a mixture of a coagulant and bentonite. The study concluded that adsorption with the simultaneous use of bentonitic clays and aluminium sulphate permitted the fluorine ions well below the permissible level. Shablovskaya et al (1988) studied the removal of manganese, phosphates and fluorides from water by passing through filter packed with crushed semi calcined dolomite. The fluoride removal capacity was reported as 400 g/m³ which is about 2 times less than the capacity of granular activated alumina.

Bhargava and Killedar (1991 and 1995) studied the adsorption of fluoride on fish-bone and animal bone charcoal in batch type contact experiments. The fluoride removal was found to be a function of time and dose of adsorbent at a given initial fluoride concentration. The time required to reach the equilibrium was found to be independent of the type of charcoal. It was reported that fish bone charcoal showed comparatively higher fluoride removal than animal bone charcoal. Killedar and Bhargava (1990 and 1993) varied the contact time, stirring rate and temperature on fluoride removal using fish bone charcoal. The fluoride removal increased with increase in time and stirring rate. Further, the study showed that the initial rate of adsorption increases with temperature whereas the overall fluoride removal at equilibrium decreases with increasing temperature.

Bhakuni and Sharma (1962) studied defluoridation with 2% aluminium sulphate solution quenched saw dust from water in batch adsorption studies. The exhausted carbon bed was regenerated with 1% alum solution. The observation showed that smaller the particle size better
the fluoride removal and thus proved that it is a surface phenomenon. Continuous flow column experiments were conducted with 2 percent alum solution impregnated saw dust for the removal of fluoride in water. The influence of factors like flow rate, bed height and common ions were studied. Common ions like chloride and sulphate influenced fluoride removal efficiency.

Several workers (Seethapathi Rao 1964, Arulanantham et al 1997 and Muthukumar et al 1995) studied the removal of fluoride using coconut shell carbon. The coconut shell carbon was used as adsorbent for fluoride removal after impregnation with aluminium sulphate solution. The exhausted carbon bed was regenerated with 0.2% aluminium sulphate solution. The study revealed that the removal was maximum in the pH range of 5.0 - 8.0.

Choi and Chen (1979) studied the removal of fluoride employing activated carbon, activated bauxite and activated alumina. It was noted that the sites on the activated carbon have less affinity for fluoride in comparison with the surfaces of activated bauxite and activated alumina. No salinity effect on fluoride removal by activated bauxite and alumina was noticed while it was phenemological in the activated carbon. It was concluded that the activated carbon is not suitable for the removal of fluoride because of the narrow optimal pH, low removal capacity and the effects of salinity, competition of common ions and the initial fluoride concentration.

Slipchenko et al (1984 and 1987) studied the removal of fluoride from potable water and ground water by activated carbon treated with aluminium sulphate solution. Experiments were conducted by filtering the test water through a layer of sorbent treated with 2.5% aluminium sulphate solution. Fluoro-aluminium complexes were formed and there was sorption of free and bound fluorine by products of hydrolysis of aluminium sulphate. The exhausted bed regenerated with aluminium sulphate solution. The
investigation showed that this method of removal of fluoride is not practically inferior to the treatment method using alumina. The advantage of this method is the low cost of the treatment.

Low cost materials like kaolinite, bentonite, charfines, lignite and nirmali seeds were investigated for the removal of fluoride from drinking water by Srimurali et al (1998) in batch adsorption experiments. The study revealed that at optimum system conditions charfines and bentonite exhibited highest fluoride removal capacity whereas lignite and nirmali seed showed poor uptake capacity. Sreenivasulu et al (1999) prepared activated carbon from umbels of prangos pabularia by carbonisation method. The adsorption of fluoride was examined with this activated carbon and it was observed that the rate of adsorption is fast, irreversible and the time required for equilibrium was independent of initial fluoride concentration. The adsorption process followed first order kinetics and obeyed Langmuir adsorption isotherm.

Agarwal et al (1999) developed a new low cost defluoridation technology using a low cost support material in column study named as KRASS technology. The columns after exhaustion were regenerated with 10% alum solution. The fluoride removal capacity of recharged material increased with increasing influent fluoride concentration. It was reported that the operation of the domestic filter is very easy and cost effective. Cost of treated water is equivalent to that of the Nalgonda process and less than that of activated alumina method. Gupta et al (1999) installed a concrete tank packed with 55 kg of support material for defluoridation of water named as KRASS process. It was reported that the defluoridation filter based on KRASS process brought down the fluoride and aluminium level well below the permissible limit. It also maintained the pH, colour, total dissolved solids and turbidity levels to the input levels well below the permissible limits.
Sivasamy et al (2001) studied defluoridation of water by three varieties of coal-based sorbents in batch adsorption studies. The studies concluded that the adsorption process followed first order kinetics and obeyed Freundlich and Langmuir adsorption isotherms. Fine coke and bituminous coal showed higher defluoridation efficiency at acidic pH, and lignite at pH range 6-12. It was reported that the capacities of the three coal-based sorbents were 6.9, 7.44 and 7.09 mg/g respectively.

1.5 ACTIVATED CARBON

The term activated carbon comprises a family of substances. Among the various clean up methods discussed above, adsorption using activated carbon appears to have the least adverse effects. Activated carbon has long been recognised as one of the most versatile adsorbents to be used for the effective removal of low concentrations of inorganics from aqueous solution. Charcoal, the forerunner of modern activated carbon whose ability to purify water dates back to 2000BC. 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 carbon 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. 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). The presence of fluoride in ground and surface water in India has been known for six decades and the need for its control led to the
emergence of activated carbon adsorption as one of the most effective methods.

1.5.1 Carbon Structure

The adsorption capacity of activated carbon is determined by their physical structure as well as chemical structure. The uptake of organics depends on the distribution of pores in the carbon structure.

1.5.1.1 Physical 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 microcrystalite planes. The macropores open out directly to the external surface of the particle, transitional pores branch off from macropores and micropores, inturn, branch off from the transitional pores (Dubinin 1966). Pores of effective radius greater than about 5000-1000 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 liquefied adsorbate can take place. The effective radius of transitional pores usually falls within 40-200 Å and their surface area lies between 20 and 70 m²/g. Micropores, which have radius less than 20 Å, usually amount to at least 95% of total surface area (Dubinin
Micropores are of greatest significance for adsorption due to their very large surface area (Wolf 1958 and Smisek and Cerny 1970). Commercial activated carbons have a typical surface area in the range of 400-1500 m²/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 not only 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 CO₂ or CO by strongly heating the carbon. Smisek and Cerny (1970) reported that chemisorption of oxygen at a pressure of 500 millitorr at various temperatures and concluded that the oxygen adsorbed at temperatures upto 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 Cerny (1970) reported that oxygen combines with carbon to form a physico-chemical oxide complex 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 feed stock 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 Cerrny (1970) reported that the surface oxides (-CO\textsubscript{x}) undergo hydration forming surface hydroxo groups (-COH). Depending on pH, L-carbon can have negative and/or neutral functional groups.

\[ \text{C-OH} \xleftrightarrow{} \text{CO}^- + \text{H}^+ \]

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 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 group depending on the pH.
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, $>\text{CH}_2$ or $>\text{CHR}$, 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.

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 (Bornoff, 1980, Wood and De Macro 1979 and USEPA 1978). Despite the prolific use of the commercial activated carbon for water and wastewater treatment, 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 waste as source of carbon with a view to bring a significant cost reduction in the treatment of water and wastewater.

1.6 PREPARATION OF ACTIVATED CARBON FROM CARBONACEOUS PRECURSORS

In recent years much attention has been devoted on agricultural wastes as source material for preparation of activated carbon with a view to bring down the cost 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 is often made primarily on the basis of the availability of the raw material.

The various feed stock proposed for the preparation of activated carbon are listed below:

<table>
<thead>
<tr>
<th>Bagasse</th>
<th>Suga-beet sludge</th>
</tr>
</thead>
<tbody>
<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>Cron 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 sluge</td>
<td>Almond shells</td>
</tr>
<tr>
<td>Distillery waste</td>
<td>Fruit stone</td>
</tr>
<tr>
<td>Pulp-mill waste</td>
<td>Rubber waste</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).

1.6.2 Activation

The chars obtained by carbonisation of organic wastes, however, do not show adequate adsorptive capacity as the pores formed during carbonisation remain filled with tarry residues and volatile impurities. In order to remove these impurities, activation treatment is required.
Activation is a process of subjecting the chars to controlled oxidation and may be accomplished with oxidising gases (physical activation) or oxidising chemicals (chemical activation). During activation, tarry residues from the interstitial layers are removed by oxidation leading to systematic development and enlargement of micropores resulting an increase in surface area.

1.6.2.1 Physical activation

In physical activation the chars are heated at elevated temperature in the presence of oxidising gases such as steam, carbon dioxide or air. The oxidising gases selectively attack the impurities in the char and transform them into gaseous products. This results in the development of pores and hence an increase in the surface area. Although several investigators have studied the reaction of carbon with steam at different temperatures, the mechanism of the reaction is not fully understood. However, the existence of two intermediate surface complexes such as "CO-complex" (CO) and "CO₂-complex" (CO₂) have been postulated where (CO) and (CO₂) represent oxygen surface complexes. All these reactions are considered important in the temperature range 600-1000°C.

Smisek and Cerrny (1970) reported that reaction of carbon dioxide with carbon around 1000°C and concluded that the resulting product has essentially no oxygen present on the surface provided an inert atmosphere is maintained. A basic surface oxide is reported to form upon cooling the carbon to room temperature.

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

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.

\[
O_2 + C_x \rightarrow 2CO + C_{x-2} \ (800-900^\circ C) \\
O_2 + C_x \rightarrow CO_2 + C_{x-1} \ (below \ 600^\circ C)
\]

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 of activation.

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, permanganage, persulphate, hydrogen peroxide and nitric acid were reported to produce materials with characteristics similar to L-carbons (Faust and Aly 1983). 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 CO\(_2\) complex on the surface.

1.7 AGRICULTURAL WASTES AS SOURCE MATERIAL FOR ACTIVATED CARBONS

Agricultural wastes have long been identified as source material for the preparation of activated carbon. Lopez-Gonzalez et al (1980) prepared successfully activated carbon from olive stones. Bhattacharya and Venkobachar (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).
Ferro-Garcia et al (1988) prepared three activated carbons from almond shells, olive stones and peach stones by carbonising and activating in CO₂ at 1123 K. The adsorption study was carried out for the removal of zinc, cadmium and copper. The extent of adsorption in the presence of Cl⁻, CN⁻, SCN⁻ or EDTA has been investigated. The adsorptive behaviour of these activated carbons was explained on the basis of their chemical nature and porous texture. The prepared carbon possessed good surface area.

Srinivasan et al (1988) prepared activated carbon from rice husk by treating the material with sulphuric acid followed by carbon dioxide activation. Bansal et al (1988) reported that coconut shell was a best source material for the preparation of activated carbon. He reported that 9% of total commercial activated carbon production was from coconut shell.

Arulanantham et al (1992) prepared activated carbon from coconut shell by carbonising with sulphuric acid and examined for the removal of fluoride from water after impregnating with aluminium sulphate. The fluoride removal capacity was reported as 2.96 mg per g of the carbon. Muthukumaran et al (1995) prepared activated carbon by charring coconut shell with sulphuric acid in the presence of potassium per sulphate. It was examined for fluoride removal after impregnation with aluminium sulphate. Column study showed that the fluoride removal capacity of the carbon was reported as 4.05 mg per g of carbon. In addition, the carbon possessed good bulk density and good attritional characteristics.

Peanut shell was identified as a source material for the preparation of activated carbon by Periasamy and Namasivayam (1991). They used as sorbent for the removal of Cu(II) from copper plating industry wastewater. Activated carbon with surface area of above 700 m²/g was prepared from almond shell and hazelnut shell with ammonium chloride by Balci et al (1994).
Palanivelu and Elangovan (1995) prepared activated carbon from coconut shell with sulphuric acid. The prepared activated carbon was impregnated with aluminium sulphate and tried for phosphate removal. 80% removal of phosphate from sewage water was reported. Kannan and Srinivasan (1997) prepared activated carbons from rice husk and wood shaving by treating with sulphuric acid. The low cost carbonaceous adsorbents prepared were examined for the removal of copper from aqueous solution. Rice straw, soyabean hull, sugarcane bagasse, peanut shell, pecan shell and walnut shell were identified as source material for the preparation of activated carbon by Johns et al (1998). The carbons thus prepared were examined for the removal of Pb(II), Cu(II), Ni(II), Cd(II) and Zn(II) from aqueous solution.

Sreenivasulu et al (1999) prepared activated carbon from umbels of prangos pabularice Lin by carbonising at 563 K for 3 h in an inert atmosphere. The carbonised material was used for the defluoridation of water. The study showed that the rate of adsorption was fast and irreversible. The rate of adsorption followed first order kinetics and obeyed Langmuir adsorption isotherm. Lua and Guo (1999) identified oil palm fibre as starting material for the preparation of activated carbon by carbonisation in an inert atmosphere at 700-900°C and activated at above 900°C with carbon dioxide.

Singh and Bhavana Srivastava (2001) prepared activated carbon from rice husk. Rice husk was impregnated with 50% orthophosphoric acid, carbonised at 300°C and finally washed well with water. The prepared carbon was used for the removal of basic dyes from wastewater by adsorption.

From the above discussion it is obvious that adsorption using activated carbon is an efficient method to treat water and wastewater to remove inorganic and organic constituents. However, the commercial
activated carbon have the disadvantage of being relatively expensive and therefore find use only when the contaminant concentration is very low. The carbons prepared from agricultural wastes are mostly H-carbons which are most suited for the removal of inorganic anions and organic constituents from water.

1.8 OBJECTIVES OF THE RESEARCH WORK

The discussion in the previous sections briefly reveals the risks associated with excessive fluoride in drinking water. The fluoride related health hazards have received a great deal of attention from researchers in the recent years. Keeping in view of the problem it is necessary to remove excess fluoride from water before its usage. Of the presently available removal methods, adsorption using activated carbon appears to be the least adverse effects and economically viable process. But the technique does not find widespread application due to lack of suitable alternative for the expensive commercial activated carbon. India is an agricultural based country and every year millions of tonnes of agricultural waste materials are discarded. Hence it was decided to make use these waste materials for the preparation of useful by products like activated carbon.

The present study aimed at the preparation of activated carbon from readily and cheaply available agricultural waste materials like palm seed coat, rubber seed coat, cashewnet sheath, pinnaie seed coat and casuarina seed. The main objectives of the proposed work are:

1. Identification of various agricultural wastes like palm seed coat, rubber coat, cashewnet sheath, palm tree flower, myrobalam waste, pongam seed coat, pinnaie seed coat and casuarina seed for the preparation of activated carbon.
2. Preparation of activated carbon from the above agricultural wastes by acid, carbonate, chloride, dolomite, pyrolysis and sulphate processes in two step carbonisation and activation methods.

3. Physico-chemical characterisation of the prepared activated carbons for various parameters such as 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 coal based commercial activated carbon.

4. Preliminary screening of the prepared carbon for the removal of fluoride from water by treating the carbon with suitable reagent.

5. Evaluation of the performance of the carbon selected for the adsorption of fluoride by varying pH, amount of adsorbent and contact time in batch experiments.

6. Regeneration of the carbon using suitable regenerant for reuse of the carbon.


8. Revaluation of the nature and rate of adsorption of fluoride by kinetic studies.

9. Assess the suitability of the carbon for field application by column type continuous flow experiments by varying flow rate of influent, particle size of the adsorbent, bed height of the adsorbent, initial concentration of fluoride and quantity of regenerant.
10. Evaluation of the effect of common anions like chloride, sulphate, bicarbonate and hardness causing ions on the defluoridation capacity of the carbon.


12. Evaluation of the suitability of the prepared carbons for the removal of fluoride from fluoride added ground water.


14. Evaluation of the domestic defluoridation filter for the removal of fluoride from ground water.