Chapter - I

INTRODUCTION
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1.1 Environmental Pollution

The fast pace of industrialization, galloping demand for energy and reckless exploitation of natural resources during the last century have been mainly responsible for aggravating the problem of environmental pollution, which is now set to pose serious threat to biodiversity and ecosystem processes.

The environmental problems in India are growing rapidly. The increasing economic development and a rapidly growing population that has taken the country from 300 million people in 1947 to more than one billion people today is putting a strain on the environment, infrastructure, and the country’s natural resources. Industrial pollution, soil erosion, deforestation, rapid industrialization, urbanization, and land degradation are all worsening problems. Over exploitation of the country's resources either soil or water and the industrialization process has resulted in environmental degradation of resources. Environmental pollution is one of the most serious problems facing humanity and other life forms on our planet today.

Environment consists of the following important components:

(i) Abiotic or nonliving
(ii) Biotic or Living and
(iii) Energy components.

The abiotic or physical environment is subdivided into three categories, atmosphere (gaseous envelope), hydrosphere (water component) and lithosphere (solid earth). In resource management, all the factors associated with the environment have to be considered for the welfare of the present and future generations. The activities of the previous generations should not be questionable and detrimental to the current generations and those of the current to the future.
1.2 Water Pollution

The hydrosphere includes all types of water resources – oceans, seas, rivers, lakes, streams, reservoirs, glaciers, polar ice caps and ground water. Water is the elixir of life and it is known as ‘Universal solvent’ or the ‘Liquid gold’. Water is one of the materials required to sustain all forms of life. For human beings, the higher animals, its important functions depend on its unique properties as a transport medium for heat and chemical substances and its effectiveness as an evaporative coolant. The other major uses are irrigation, transportation, hydroelectric power generation, industrial manufacturing, recreation and waste disposal.

Water is an indispensable requirement of life, as well as industries, which are working for the betterment of human life and health. Industrialization made a deep impact on human health directly or indirectly creating environment (air, water, soil) pollution by releasing wastes and untreated wastewater, into the environment.

Out of the total water resources, about 97% of the earth’s water supply is from the ocean, where the high salt content does not permit its use for human consumption. Of the remaining 3% water resources, 2% is locked in the polar ice caps and glaciers, while only 1% is available as fresh water (surface water – rivers, lakes, streams and ground water) for human consumption and other uses.\(^1\,^2\)

Water pollution is a serious problem to the entire world. It threatens the health and well-being of humans, plants, and animals. Pure, unpolluted water is an essential resource to the environmental balance of the world. Water has life-giving properties, which are crucial to the world's global ecosystem.

A substantial proportion of chemical substances in drinking water is of natural origin and results from complex interactions between precipitation (rain), soil and underlying geological strata. Various biological and microbiological processes occurring in soil and water are also important. In
addition, there are anthropogenic constituents, which include agricultural chemicals and the components of urban run-off, industrial and domestic wastewater. In fact, virtually any chemical used by man could find its way into water and be detected given a sufficiently sensitive analytical technique.

Drinking water usually contains 50-500 mg/L of dissolved substances although in some arid regions water consumed contains more than 1500 mg/L of total dissolved solids. The dissolved solids consist almost entirely of bicarbonates, sulphates, chlorides and nitrates of calcium and magnesium, normally with low concentration of sodium and potassium. The trace inorganic components of drinking water include iron, manganese, aluminium, and a wide range of trace metals and metalloids including some for which limits have been prescribed on the grounds of toxicity.

Water has long been suspected of being the source of many human illnesses. It was not until approximately 150 years ago that definite proof of disease transmission through water was established. Owing to the development of urban areas, it became necessary, from public health and aesthetic considerations, to provide drainage or sewer systems to carry human wastes away from the area. The normal repository for such wastes was usually the nearest watercourse. This has led to the major epidemics of cholera and typhoid in many countries during the 19th century, which are attributable to the proliferation of public water supply and waste disposal system. It soon became apparent that rivers and other receiving bodies of water have a limited ability to handle waste materials without creating nuisance conditions. Because of the success in controlling the spread of enteric diseases through the applications of engineering principles, a new concept of the potentialities of preventive medicine was born. For many years the major consideration was to produce adequate water supplies that were hygienically safe.

As population increases, the demand for water grows accordingly and at much more rapid rate if the population growth is to be accompanied by
improved living standards. The combinations of these two factors are placing greater and greater stress upon the environment for adequate supplies. In many cases, inferior quality and often-polluted water must be utilized to meet the demand. It is to be expected that this condition will continue and grow more complications as long as population and industrial growth and increased use of agricultural chemicals occur.

To meet the demands of the growing population and the modern living standards, the existing old industries have increased their production enormously and many new industries have started coming up. There is also a dramatic increase in the production and consumption of fertilizers. For instance, the production and consumption of fertilizers (NPK) during 1960-’61 was 150 and 292 thousand tonnes of nutrients, respectively. This has increased to 11300 and 15665 thousand tonnes of nutrients during 1995-’96.

Historically, the major concern with regard to pollution of surface waters was their oxygen resources. However, in the past two decades, an increasing concern is the pollution of surface waters and ground waters with other pollutants of primarily industrial or agricultural origin. The lowland rivers, which are used for water supply, are exposed to effluent disposal by a series of sources and recycling can occur with a consequent increase in the concentration of those components most resistant to biodegradation. The situation can even be worse with ground water supply as in this case the effect of pollution may be ever lasting and even irreparable.

Today, finished waters after treatment that are free of colour, turbidity, taste, odour, nitrate, harmful metal ions and a wide variety of organic chemicals such as pesticides and chlorinated solvents are required. Health problems associated with some of the chemicals include cancer, birth defects, central nervous system disorders and heart disease. In addition, the public desires water that is low in hardness and total solids, non-corrosive and non-scale forming.
1.3 Trace contaminants

The matter of trace organic and inorganic contaminants in public water supplies in relations to public health has been of concern for nearly a century. Trace contaminants are those contaminants for which drinking water standards are generally in the range of 1 mg/L or less. The literature shows that lead was the first trace contaminant to be brought under scrutiny due to the prevalent use of lead service pipes\(^4\). Then, zinc and copper were questioned in 1923 and 1926, respectively, because of the use of galvanized pipe services and the growing use of copper salts for algae control. In 1931, Churchill showed the correlation between excessive fluorides and mottling of tooth enamel\(^5\). The literature is replete with references to iron and manganese; largely because of the nuisances they produce rather than threats to the public health.

It was after 1962 that U.S. Public Health Drinking Water Standards were advanced and limits were set on the levels of trace contaminants of public health significance other than copper and zinc. The attention of public health and water supply engineers has been refocused upon trace contaminants by the following four important factors:

- The outbreak of “Itai-Itai” (Ouch-Ouch) disease\(^6\) that occurred among farmers who drank water containing cadmium from the Jintsu river in Japan during 1947;
- The discovery (during 1950\(^8\)) that metallic mercury escaping from laboratories and industry, mainly chlorine manufacture, was capable of being converted to methyl mercury, concentrated by aquatic life, and passed long through natural food chains to humans, largely through fish (Minamata disaster)\(^7\);
- The evidence that exists to indicate that certain in-organics and organics may be carcinogenic and
The realization that purposeful recycling of wastewaters for supplementation of drinking water supplies is imminent in many areas of the country.

These factors have enforced the Government agencies to bring about stringent limits for the level of trace contaminants in drinking water. Although the discussion on long-term health risks associated with drinking water centers on organic micro pollutants, several inorganic constituents have been the subject of concern. In many parts of the world, nitrate level has been increasing (due to excessive application of nitrogenous fertilizers) particularly in ground water and the possibility of carcinogenicity hazard due to indigenous synthesis of N-nitroso compounds has been referred\textsuperscript{8}. The possible relationship between fluoride levels and cancer has also been reported. There has also been evidence of a relationship between arsenic levels in water and incidence of skin cancer\textsuperscript{9}. Similarly, Chromium is reported to produce systematic toxicity and cause cancer in human\textsuperscript{10}.

1.4 Heavy Metals

The metals are abounded on earth for long time and about 75\% of the elements are classified as metals in the periodic table. Most of the contaminants listed by USEPA\textsuperscript{11} as trace inorganic contaminants are heavy metals. Metals fall into the following categories: alkali metals, alkaline earth metals, transition metals, noble metals, platinum metals, rare metals, rare earth metals, actinide metals and light metals. Heavy metals are metals that come under the group according to the following various definitions constructed:

- Metals with element densities above 7 g/cm\textsuperscript{3}.
- Metals with a specific gravity greater than 4.
- Metals with atomic weight greater than that of sodium, i.e greater than 23, thus starting with magnesium.
- Metals of atomic weights greater than 40, thus starting with scandium.
Metals with atomic number more than twenty and specific gravity at least five times greater than the specific gravity of water, excluding alkali metals, alkaline earth metals, lanthanides and actinides.

However, none of the authoritative body has defined the term “heavy metals” and is considered a non-scientific term, as there is no scientific basis and that there are lot of inconsistency in its usage.

The heavy metal pollution in the environment originates from geological weathering, industrial processing of ores and metals, use of metal and its compounds, leaching of metals from garbage and solid waste dumps, landfill waste, livestock and poultry manure, animal and human excretion, urban runoff and reuse of drainage water and sewage effluent. The principal source is the industrial wastes from manufacturing or metal finishing operations. The use of metal containing compounds as fertilizers, pesticides, etc., in agriculture is the second major source of heavy metal pollution. Due to leaching, diffusion and infiltration, these metals are transported to surface and ground waters. From the standpoint of environmental pollution, metals may be classified according to three criteria as shown in the table (Table 1.1).

Table 1.1 Classification of elements according to toxicity and availability

<table>
<thead>
<tr>
<th>Non-critical</th>
<th>Toxic but very insoluble or very rare</th>
<th>Very toxic and relatively accessible</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>C</td>
<td>Ti</td>
</tr>
<tr>
<td>K</td>
<td>P</td>
<td>Hf</td>
</tr>
<tr>
<td>Mg</td>
<td>Fe</td>
<td>Zr</td>
</tr>
<tr>
<td>Ca</td>
<td>S</td>
<td>W</td>
</tr>
<tr>
<td>H</td>
<td>Cl</td>
<td>Nb</td>
</tr>
<tr>
<td>N</td>
<td>Br</td>
<td>Ta</td>
</tr>
<tr>
<td>O</td>
<td></td>
<td>Re</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ga</td>
</tr>
<tr>
<td></td>
<td></td>
<td>La</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Os</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rh</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ir</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ru</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sn</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cd</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt</td>
</tr>
</tbody>
</table>

The potential toxicity of metals and their compounds depends on its bioavailability. Bioavailability depends on biological parameters and on the
physiochemical properties of metals, their ions and their compounds. These parameters in turn depend upon the atomic structure of the metals.

The toxicity of metals is well understood from their electronic configuration. Electrons are binding materials holding molecules together. Electrons are usually intended to be in pair as they whiz around the outside of atoms and give stability to the form of the atom or molecule. When, for any reason, these paired electrons become separated, the molecule is damaged. These damaged molecules are called ‘free radicals’ and are highly reactive, attacking other cellular structures to grab electron in order to become paired again. Normally, enough free electrons will be present in the vicinity, but when the level of free radicals increases beyond a certain point, the cellular protective electron-donating mechanisms, which usually keep these molecules in check, is repaired. Consequently, great numbers of these radicals are set free which eventually looks for electrons to be paired up. Therefore, when toxic metals enter the body tissues, the free radical destructive activity begins and constantly progresses resulting in rapid ageing and degeneration.13

The ability of metals to disrupt the function of essential biological molecules such as protein, enzyme and DNA is the major cause of their toxicity. Displacement of certain metals essential for cell by similar metal is another cause of toxicity. For example, cadmium can substitute zinc in certain proteins that require zinc for their structure or function. The alteration in protein can lead to toxic consequences. In the same way, lead can substitute for calcium in bone and in other sites where calcium is required.

In recent years, public awareness has increased because of the long term toxic effects of water containing dissolved metal ions. The heavy metals are not usually eliminated from the aquatic ecosystem by natural process, in contrast to most organic pollutants. Consequently, the concentration of heavy metals increases and creates biological and physiological problems. They have a unique property of accumulation along a food chain for a long period and can
cause acute or chronic toxicity to aquatic and human lives. The permissible limits of some toxic in-organics set by United States Environmental Protection Agency (USEPA) and Indian Standards Institution (ISI) for their level in drinking water is given in the table (Table 1.2).

### Table 1.2 Maximum permissible limits of some trace inorganic contaminants in drinking water

<table>
<thead>
<tr>
<th>Trace inorganic contaminants</th>
<th>USEPA (mg/L)</th>
<th>Indian Standards (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic, as As</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Barium, as Ba</td>
<td>2.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Cadmium, as Cd</td>
<td>0.005</td>
<td>0.01</td>
</tr>
<tr>
<td>Chromium, as Cr(VI)</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Copper, as Cu</td>
<td>–</td>
<td>0.05</td>
</tr>
<tr>
<td>Iron, as Fe</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Lead, as Pb</td>
<td>0.05</td>
<td>0.1</td>
</tr>
<tr>
<td>Manganese, as Mn</td>
<td>0.05</td>
<td>0.1</td>
</tr>
<tr>
<td>Mercury, as Hg</td>
<td>0.002</td>
<td>0.001</td>
</tr>
<tr>
<td>Nickel, as Ni</td>
<td>0.1</td>
<td>0.05</td>
</tr>
<tr>
<td>Selenium, as Se</td>
<td>0.05</td>
<td>0.01</td>
</tr>
<tr>
<td>Silver, as Ag</td>
<td>0.05</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Since water must be safe and acceptable to the consumer, it is subjected to treatment. In many supplies, if there is any treatment at all, it is limited to disinfection. Additional treatment, if required, concerns with the removal of colour and suspended materials by filtration often combined with coagulation and sedimentation. Occasionally, additional steps such as ozone or activated carbon treatment may be included for the control of toxic and odour causing organic contaminants. Their inclusion, however, will have a substantial effect on the treatment cost.
It has become cognizant that man and technology are inseparable parts of modern civilization. In order that public can continue to receive a safe water supply at reasonable cost and to prevent unnecessary rejection of usable water resource in those parts where water is in short supply, it has become necessary to take adequate steps to cleanse the environment and check its further pollution through various control measures. The measures include managing pollutants at the source itself, developing new technologies that would eliminate or minimize pollution and reprocessing of waste to recover useful materials. As a result, considerable growth of literature on treatment of wastes containing hazardous substances has been witnessed during the past three decades.

1.4.1 Need for the water treatment

Chemicals are discharged through effluents from industrial sources to surface water bodies and infiltrate into drinking water sources. The chemicals that accumulate in the sediments of water bodies are flushed out in the event of high water flow. Many industrial chemicals are toxic even at relatively low concentration and water polluted by industrial activities often contains a number of different toxic chemicals. The extent to which chemicals can be removed before the water reaches the consumer will depend on the nature of the decontamination and type of treatment processes used.

1.4.2 Treatment of heavy metals

A variety of methods has been developed for the removal of trace metals from water and wastewater. The methods include precipitation, evaporative and electrolytic recovery, solvent extraction, cementation, reverse osmosis, electrodialysis, ion exchange and adsorption.

The precipitation method is one of the oldest and most widely used methods for the removal of metals from wastewater. Many reagents have been applied for precipitation purposes and these include caustic soda, hydrated
lime, soda ash and sodium sulphide to precipitate the metal ions as insoluble hydroxides, carbonates and sulphides$^{15-20}$. Lime is generally favoured for precipitation of metals due to low cost and ease of pH control. In addition, the presence of excess of lime can serve as an adsorbent for the removal of metals ions$^{15}$. However, problems can arise due to incomplete removal of the precipitated metal from the treated effluent. As the sludge is disposed off as land fills, it could lead to contamination of ground water when conditions are favourable for their dissolution.

There are reported literature about utilizing evaporative recovery method for the removal of copper$^{21}$, cadmium$^{22}$, nickel$^{23}$ and zinc$^{24}$. However, there is a possibility of retaining all the nonvolatile constituents of the wastewater in the system itself, which is considered a major drawback. Low capital cost and low energy cost are the advantages claimed.

Solvent extraction involves equilibrium distribution of an analyst between a liquid phase and a solid phase. In this process, the operating conditions are so adjusted as to shift the equilibrium towards the benefit of the solid phase. It is considered to be an efficient alternative method to liquid-liquid extraction$^{25}$. However, this method is not commercially viable.

The cementation process involves percolation of wastewater containing copper through a bed of scrap iron and as a result copper cements onto iron$^{26,27}$. The major advantage of this process is that the metal can be obtained in the pure state.

The direct electrolytic process is successfully followed to recover copper from copper pickling and brass pickling bath$^{28}$. This process consumes high electrical power and hence cannot be adopted for the treatment of dilute wastes. In addition, a pre-concentration step, ion exchange or evaporative recovery prior to this process is needed. The use of fluidized semi conducting carbon bed increases the efficiency of metal removal$^{29}$. The major advantage of this process is the creation of a large surface area per unit volume and the
major disadvantage is the development of a low current density on the electrode surface.

**Electrodialysis** is an economically feasible treatment process for the metal recovery from rinsed waters of plating and metal finishing operations. This method can be applied even if the wastewater contains a high level of cyanide concentration. It was reported suitable for the removal of cadmium and nickel\textsuperscript{30}.

In **reverse osmosis**\textsuperscript{31}, the concentrated solution is subjected to high pressure because of which the solvent is forced out through a semipermeable membrane to the dilute solution region. The concentrated solution becomes more concentrated and can be, therefore, reused. The three membranes most commonly used are cellulose acetate, aromatic polyamide and NS-100\textsuperscript{32,33}. The recovery of copper from copper pyrophosphate and copper cyanide plating bath rinsed waters has been reported. The application of this process for the treatment of cadmium plating\textsuperscript{33} and zinc plating solutions and iron from acid mine drainage\textsuperscript{34} has been reported. The serious drawback of this method is being its high capital and operating cost.

**Ion exchange method** is a reversible process that 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 metal ions from dilute aqueous solutions\textsuperscript{35-37}. When the resin bed becomes saturated, it is regenerated using acid or alkali. The economic limitations of the process come 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 hardness of water and oxidation of resin by oxidizing agents, if present, are some frequent problems associated with ion exchange method.
Ultrafiltration is a variety of membrane filtration in which hydrostatic pressure forces a liquid against a semipermeable membrane. Suspended solids and solutes of high molecular weight are retained, while water and low molecular weight solutes pass through the membrane. This separation process is used in industry and research for purifying and concentrating macromolecular \((10^3 - 10^6 \text{ Da})\) solutions, especially protein solutions. Ultrafiltration is not fundamentally different from microfiltration or nanofiltration, except in terms of the size of the molecules it retains. Ultrafiltration is not effective in separating organic streams. It is very prone to membrane fouling caused by increased solute concentration at the membrane surface (either by macromolecular adsorption to internal pore structure of membrane, or aggregation of protein deposit on the surface of membrane), which leads to concentration polarization, which is the major culprit in decreasing, permeate flux.\(^{38}\)

Nano filtration is a relatively recent membrane filtration process used most often with water containing low total dissolved solids such as surface water and fresh groundwater, with the purpose of softening (polyvalent cation removal) and removal of disinfection by-product precursors such as natural organic matter and synthetic organic matter\(^{39,40}\). Filtration is more widely used in food processing applications. It is used in the removal of contaminants from a water source. It is also commonly used for desalination but leaves the water devoid of essential nutrients like (calcium, magnesium ions, etc.), placing the nutrient levels below that of the required WHO standards and the researchers had to go back and add nutrients to bring solute levels to the standard levels for drinking water consumption. Further, it is a very inexpensive method compared to conventional treatment systems\(^{41}\).

1.5 Adsorption methods

Among other processes for removal of metal ions/dyes from industrial/mining wastewater, adsorption process is an economically feasible
alternative. Adsorption is a process in which a single or a group of ions/compounds get accumulated on the surface of another solid or liquid. The substance on which the adsorption takes place is known as adsorbent and the substance, which is adsorbed, is called adsorbate. Based on the extent of attraction between the adsorbent and adsorbate, the adsorption process can be classified into two types:

- Physical adsorption or van der Waal’s adsorption and
- Chemisorption.

Adsorption, which can result from the van der Waal’s force of interaction, is known as physical adsorption or van der Wall’s adsorption. In this type of adsorption, the process in which the heat change is in the order of 20-40 kJ/mol. Physical adsorption process is reversible and established rapidly. Physical adsorption can be of two types, i.e., monolayer adsorption and multilayer adsorption.

In chemisorption, the chemical interaction/electrostatic force of attraction occur between the adsorbent surface and adsorbate molecules. In this process, the heat of adsorption usually varies from 40 to 400kJ/mol. It is associated with appreciably high activation energy and therefore termed as activated adsorption. It is a relatively slow process. Physical adsorption is a reversible process that occurs at a temperature lower or close to the critical temperature of an adsorbed substance. On the other hand, chemisorption in general, is an irreversible process because of strong electrostatic force of interaction between the adsorbent and adsorbate molecules. Physical adsorption is very effective, particularly at a temperature close to the critical temperature of a given fluid. Chemisorption occurs usually at temperatures much higher than the critical temperature and by contrast to physical adsorption, is a specific process, which can only take place on some solid surface for a given fluid. Contrary to physical adsorption, chemisorption leads to monolayer adsorption. Under favorable conditions, both the processes can occur simultaneously or
alternately. Physical adsorption is accompanied by a decrease in free energy and entropy of the adsorption system and, there by, this process is exothermic in nature.

Among the various cleaning methods, adsorption using activated carbon appears to have the least adverse effects. It includes a broad range of carbonaceous materials that exhibit a high degree of porosity, large surface area\textsuperscript{42} and good mechanical properties and finds use in the removal of toxic biodegradable and non-biodegradable substances from wastewaters. It is attractive as it can treat wastewater to acceptable quality suitable for reuse. In addition, the process is insensitive to temperature and intermittent discharge.

1.6 Applications of activated carbon

Activated carbon is used in gas purification, gold purification, metal extraction, water purification, medicine, sewage treatment, air filters in gas masks and filter masks, filters in compressed air and many other applications.

One major industrial application involves the use of activated carbon in metal finishing field. It is very widely employed for the purification of electroplating solutions. For example, it is a main purification technique for removing organic impurities from bright nickel plating solutions.

1.6.1 Environmental applications

Carbon as adsorbent has numerous applications in removing pollutants from air or water streams both in the field and in industrial processes such as: Spill cleanup, Groundwater remediation, Drinking water filtration, Air purification, Volatile organic compounds capture from painting, dry cleaning, gasoline dispensing operations, and other processes. Activated charcoal is also used for the measurement of radon concentration in air.
1.6.2 Medical applications

Activated carbon is used to treat poisonings and overdoses following oral administration\(^43\).

1.6.3 Fuel Storage

Research is being done in testing the ability of various activated carbons to store natural gas and hydrogen gas.

1.6.4 Gas purification

Filters with activated carbon are usually used in compressed air and gas purification to remove oil vapours, odours, and other hydrocarbons from the air.

1.6.5 Distilled alcoholic beverage purification

Activated carbon filters can be used to filter vodka and whisky of organic impurities, which can affect colour, taste, and odour.

Early applications of activated carbon were associated mainly with material production such as sugar refining, oil and drug purification\(^44\). Lowitz\(^45\) was the first to observe the decolourizing effects of charcoal on coloured solution. A few years later, wood charcoal employed to purify cane sugar in 1808 was applied by the beet sugar industry. Fuguier discovery\(^46\) in 1811 of greater decolourizing power of bone char led to its immediate adoption by sugar industries. The use of activated carbon for water treatment was first reported in 1930 for the removal of organics\(^47\). Activated carbons are generally derived from a wide variety of feedstocks.

Many methods have been reported for the carbonization of waste organic materials and are adequately covered in the textbook by Hassler\(^44\). Carbonization methods include carbonization using chloride and sulphate salts and sulphuric acid. Carbonization or pyrolysis consists of slowly heating the material in the absence of air at temperatures below 600°C. During
carbonization, dehydration takes place followed by pyrolytic decomposition of the precursor with concurrent elimination of many noncarbon elemental species. The release of low molecular weight volatiles followed by lighter aromatics, results in a product called char rich in fixed carbon\textsuperscript{48}.

During pyrolysis, it is believed that the original substance splits into fragments, which regroup to form thermo stable 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\textsuperscript{49,50}. The formation of crystallite is influenced by the carbonization temperature and to some extent by the composition and structure of the raw material\textsuperscript{51}.

Activation is carried out followed by carbonization to remove the tarry residues and volatile impurities present in the pores\textsuperscript{52}. Activation is a process of subjecting the chars to controlled oxidation with oxidizing gases (physical activation) or oxidizing chemicals (chemical activation). The adsorption capacity of activated carbon is determined by its physical structure (porosity) as well as chemical structure.

\section*{1.7 Physical structure of activated carbon}

The pores in activated carbon can be divided into three basic classes:

\begin{itemize}
\item Macropores (d>50 nm),
\item Transitional pores (meso pore ) (2<d<50 nm)
\item Micropores (diameter, d<2 nm).
\end{itemize}

Macropores were first formed by the burnoff of the edge group of microcrystallites. The micropores were formed mainly by the branch off of the microcrystallite planes. The porous structure of an activated carbon is predominantly arranged in the following pattern: the macropores open out directly to the external surface of the particle, transitional pores branch off
from macropores and micropores, in turn, branch off from the transitional pores\(^{53}\). Pores of effective radius greater than about 500-1000 Å were classified as macropores by Dubinin. In activated carbon, the effective radius of macropores frequently lies in the range of 5000-20000 Å having surface area ranging between 0.5 and 2 m\(^2\)/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, the transport arteries and make the internal parts of carbon accessible to the molecules adsorbed.

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 20-70 m\(^2\)/g\(^{53}\). Micropores, which have radius less than 20 Å, usually amount to at least 95% of total surface area. Micropores are of greatest significance for adsorption due to their very large surface area\(^{54}\). Commercial activated carbons have a typical surface area in the range of 400-1500 m\(^2\)/g.

### 1.8 Chemical structure of activated carbon

The adsorptive properties of activated carbon are determined not only by its porous structure but also 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 because of imperfect carbonization or they can become chemically bonded to surface during activation. The presence of oxygen has been found to have a great effect on the adsorptive properties of activated carbon.

In 1863, Smith was probably the first worker to suggest that, unlike nitrogen and other gases, when oxygen is chemisorbed on a carbon it undergoes a chemical change\(^{55}\). The oxygen could only be removed as CO\(_2\) or CO by strongly heating the carbon. Hart \textit{et al.}\(^{56}\), studied the 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.\textsuperscript{57} 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.

Rhead and Wheeler\textsuperscript{58} reported that oxygen combines with the carbon to form a physico-chemical complex, $C_xO_y$, of variable composition, indicating that it remains as oxide. 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 feedstock was exposed to oxygen at temperatures between 200-400°C. Apart from lowering the pH value of neutral or basic solutions, they possessed negative surface charge. Such carbons, referred to as L-type carbons, were capable of adsorbing cations from the solution.

Huang and Ostovic\textsuperscript{59} reported that the surface oxides (-CO$_x$) undergo hydration forming surface hydroxo groups (-COH). Depending on pH, therefore, L-carbon can have negative and/or neutral functional groups.

$$\text{COH} \xleftrightarrow{} \text{CO}^- + \text{H}^+$$

The nature of the functional groups in L-carbons was investigated by many workers based on reactions with bases of different strengths\textsuperscript{59-63}. 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 has also been confirmed by IR spectral studies.

Basic surface oxides, on the other hand, referred to as H-carbons formed when the carbon feedstock were exposed to temperature between 800-1000°C. The resulting material was found to raise the pH of neutral or acidic solutions. As they possessed positive surface charge, they readily adsorbed anions from the solution. Depending on pH, H-carbons can have positive and or neutral functional groups. The basic surface oxides of H-carbons were not as
thoroughly investigated as acidic surface oxides. Garten and Weiss\textsuperscript{64} proposed a chromene structure. Chromene groups, which contain active methylene group $>\text{CH}_2$ or $>\text{CHR}$, can react

$$\text{COH}^+ \rightleftharpoons \text{COH} + H^+$$

with strong acids in the presence of oxygen to form carbonium ions and hydrogen peroxide\textsuperscript{65}. The resulting carbonium ion tends to associate with anions. The charge carried by the carbon surface; therefore, depend on the nature of surface oxide groups that result by chemisorption of oxygen.

![Chemical structure of Chromene and Carbonium ion]

Literature survey on the inexpensive alternative materials reported include clay minerals\textsuperscript{66}, metal oxides\textsuperscript{67}, serpentine mineral\textsuperscript{68}, peat\textsuperscript{69}, peat moss\textsuperscript{70} (a complex material of lignin and cellulose), feldspar\textsuperscript{71}, flax shive\textsuperscript{72}, synthetic pumice\textsuperscript{73} saw dust\textsuperscript{74}, coconut shell\textsuperscript{76,77}, crop residues\textsuperscript{78}, waste rubber\textsuperscript{79}, lignin\textsuperscript{80} (a paper industry waste), activated sludge\textsuperscript{81}, steel plant granulated slag\textsuperscript{82}, paddy straw\textsuperscript{83}, rice husk\textsuperscript{84}, rice straw\textsuperscript{85}, Indian medicinal plants\textsuperscript{86}, dried plant material of \textit{Ipomea aquatice} Forsk\textsuperscript{87} and garden herbs and vegetables\textsuperscript{88}. These materials either as such or in modified forms or after converting into carbon were tried as adsorbents for the removal of heavy metals from water/wastewater.

Babel and Kurniawan\textsuperscript{89} have reviewed the technical feasibility of various low cost adsorbents for heavy metal removal from contaminated water. The removal performance of various adsorbents, compiled from 100 reported articles, was compared to that of activated carbon. Johns \textit{et al.}\textsuperscript{90} studied the granular activated carbons derived from surplus, low value agricultural
byproducts like rice straw, soybean hull, sugarcane bagasse, peanut shell and harder materials such as pecan and walnut shells as effective removers of organics and metals from water. The CO$_2$ or steam activated precursors after oxidation using O$_2$-N$_2$ gas showed increased metal adsorption.

Ferro-Garcia et al.$^{91}$ have investigated three activated carbons obtained by activation of almond shells, olive stones and peach stones by heating in CO$_2$ at 1123 K for the removal of Zn(II), Cd(II) and Cu(II) from aqueous solution. Their adsorption capacities at 293 and 313 K, according to Langmuir isotherm, were reported to be 131.0 and 141.6, 145.1 and 134.0, 113.5 and 133.9 µmol/g, respectively.

Rajeshwarisivaraj et al.$^{92}$ used carbon derived from an agricultural waste, cassava peel (Manihot esculenta) for the removal of dyes and metal ions and concluded that H$_3$PO$_4$ impregnated peel showed relatively higher efficiency than the heat treated peel. Biogas residual slurry (BRS), a lignocellulosic waste which is a byproduct of biogas plants was applied by Namasivayam and Yamuna$^{93}$ for the removal of Pb(II). The process of Pb(II) uptake conformed to Langmuir isotherm and the adsorption capacity was 28.0 mg/g. An almost quantitative removal from 50 mL of 100 mg/L Pb(II) solution was achieved by using 5.0 g/L of BRS at an initial pH of 2.5. Fe(III)/Cr(III) hydroxide, a waste byproduct produced in the treatment of wastewaters containing Cr(VI) was investigated by Namasivayam and Ranganathan$^{94}$ for its removal of Fe(II) and found that the adsorption capacity to be 27.78, 34.48 and 38.46 mg/g, respectively, at 20 , 30 and 40°C at pH 4.5.

The rate of removal of Cu (II) ions from aqueous solution by mercaptoacetic acid modified cassava wastes (0.5MCF and 1.0MCF) was studied by Augustine et al.$^{95}$ in batch conditions. The rate of sorption of copper ion was rapid initially within 5-15 minutes and reached a maximum in 30 minutes. Kinetic modelling analysis showed that the pseudo-second order
equation was the most appropriate model for the description of Cu (II) transport with chemical sorption as its rate-limiting step.

Chun Yang Yin et al.\textsuperscript{96} reviewed a comprehensive list of literatures on chemical, physical and biological modification techniques of activated carbon pertaining to enhancement of contaminant removal from aqueous solutions.

1.9 Dyes

Dyes or dyestuffs are coloured substances capable of imparting their colour, fast to light, water, soap, etc., to the fibres. The first synthetic dyestuff was prepared in 1856 by W.H. Perkin called Perkin’s violet dye, commonly known as mauve\textsuperscript{97}. This discovery stimulated the study and research on the synthetic dyes and the progress was very rapid. Through hundreds of years, the scale of production and nature of dyes changed drastically and now it has been estimated that there are more than 3000 dyes in use worldwide\textsuperscript{98}. Dyes are widely used in textile, paper, carpet, printing, leather, food and cosmetic industries. Some dyes are also used in medicine and biological stains and for colouring plastics, gasoline, varnish, fats, oils and waxes. Textile mills engaged in dyeing nylon, polyacrylonitrile modified nylon, wool, silk and cotton is the main consumer of dyes.

The dye-bearing wastewaters are disposed in two ways: (i) into the sewer and (ii) into a nearby river/stream. In many cases, the effluent is discharged into a sewer to be treated with other domestic and industrial wastes. In the absence of any sewer passing sufficiently nearby the effluent is discharged to a river or a stream. In either case, restrictions are likely to be applied limiting the concentration or load of contaminants that may be discharged.

The problems of discharging these wastewaters are compounded by the concentration of dyestuff industries/dyeing units in small areas. For example, in India the dyestuff industries are concentrated in the western states of Maharashtra and Gujarat, accounting for over 90 percent of the dyestuffs
production in the country. Similarly, most of the dyeing units are concentrated in cities like Coimbatore, Tirupur, Erode and Karur, situated in southern part of India. In Tirupur alone, there are around 500 dyeing industries and the effluent from those industries has already started polluting the ground waters making them unfit for any use.

Recent estimates indicate that, approximately, 12% of synthetic textile dyes used each year is lost during manufacture and processing operations and that 20% of these lost dyes enter the environment through effluents that result from the treatment of residual industrial waters. Though the dye bearing wastewaters contain various pollutants, the most obvious impact is the high degree of colour that the residual dye often imparts. Dyes being one of the important recalcitrants, colour persists for long distances in flowing waters, retards photosynthetic activity in streams, inhibits the growth of aquatic biota, decreases recreational value of the streams and has a tendency to sequester metal ions producing microtoxicity to fish and other organisms.

1.9.1 Treatment of dyes

Among various treatment methods, coagulation, oxidation, biological method and adsorption are the widely used methods. Coagulation results from a lowering of the zeta potential at the surface of particles and the association of those particles to form flocculated agglomerates. Lime is used as a main inorganic coagulant. Other coagulants commonly used are calcium hydroxide, calcium sulphate, magnesium hydroxide, magnesium sulphate, ferric chloride, ferrous sulphate, alum and a combination of these salts. Synthetic cationic, anionic or nonionic polymer has been shown to remove dyes.

Oxidation is one of the principal chemical methods for decomposing dyes in wastewater. The oxidizing agents include chlorine, sodium hypochlorite, ozone, hydrogen peroxide, Fenton’s reagent, UV irradiation and potassium permanganate. Though chlorination is the most effective method for
removing colour from dyeing wastewater, the formation of chlorinated compounds, such as dioxin and their environmental impact cannot be overlooked\textsuperscript{101}. The hydroxyl radicals produced from hydrogen peroxide by adding a soluble iron salt or passing UV light are capable of degrading the organic pollutants. Interestingly, the UV catalyzed oxidation by hydrogen peroxide is not effective in treating dye wastewater because of UV absorption by coloured effluent. In ozonization, the decomposition products of ozone, the free radicals and ions formed by ozone degradation are the chief species that react with organic pollutants. Removal of various dyes by ozonation was reported\textsuperscript{102}. But this method has less commercial application due to its high capital cost, high ozone dose required and the toxicity of final ozonation products\textsuperscript{103}.

**Electrolytic methods** to treat industrial wastewater were first developed to remove heavy metals. The first patent on the application of the process to the treatment of textile wastewater was issued to Andco Environmental Processes and after that, numerous methods for electrolytic treatment have been developed. Electrochemical ion generation is one among the effective methods for the removal of colour, BOD, COD, TOC, suspended solids and heavy metals from textile mill wastewater\textsuperscript{101}. This method has to be coupled with conventional processes such as clarification and filtration to produce clean water for reuse. Because, this method leaves a precipitate of hydrous iron oxide when iron electrode is used and if aluminium electrodes are used, it leaves a combination of aluminium hydroxide and aluminium oxyhydroxide as end products.

**Biological treatment**, whether by the activated sludge process, trickling filters or other process, is the standard method for treating dilute wastewaters in both municipalities and industries. Although biological treatment can treat many of the solvents or contaminants in a dye manufacturing or dye use operation, most dyes are made to be nonbiodegradable and are, not well treated
by conventional biological treatment processes\textsuperscript{101}. This is evident from the reports that a high COD/BOD ratio was obtained after subjecting the textile wastewater to biological treatment. Hence, technology improvement was made to achieve decolourization by combining biological treatment with activated carbon adsorption.

\textbf{Adsorption} is an effective method for lowering the concentration of dissolved organics in an effluent. One of the main aims of dye research is to increase the adsorption onto the fabrics being dyed. Consequently, adsorption of dyes onto suitable materials offers a means of removing them from effluents. In this regard, activated carbon has been evaluated extensively for the treatment of different classes of dyes, that is, acid, direct, basic, reactive, disperse and so forth and is now the most widely used adsorbent for dyes.

The alternatives reported include peat\textsuperscript{104}, maize cob\textsuperscript{105}, coconut husk\textsuperscript{106}, jute fibres\textsuperscript{107}, paddy straw\textsuperscript{108}, groundnut shell\textsuperscript{109}, rice hulls\textsuperscript{110}, chitosan\textsuperscript{111}, orange peel\textsuperscript{112}, bentonite\textsuperscript{113}, silica\textsuperscript{115}, red mud\textsuperscript{116}, freshly precipitated Mg(OH)\textsubscript{2}\textsuperscript{117}, chrome slugde\textsuperscript{118}, \textit{hydrilla verticillata}\textsuperscript{119}, and water hyacinth root\textsuperscript{120}. 