Chapter – 1

INTRODUCTION
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Water is a primary requirement for the survival of life. It is the most precious natural resource on the Earth. Over the centuries, unfortunately, man in his capriciousness has reached a stage where the all-round development, that was said to be the reason behind the exploitation of natural resources, now looks ephemeral and not worthy it. We seem to be almost veering round to the view that perhaps our approach had been short-sighted, if not completely irresponsible. Planet Earth is heading towards becoming unlivable and its resources are nearing extinction due to over-exploitation.

Development and environment have been the issues at debate since industrialization brought in quick prosperity to the western world. In its haste to amass wealth, the natural resources were exploited blindly. The cities and towns are too crowded, too noisy and too unhygienic for healthy human living. The forests are denuded to increase disturbances in the weather and water table. Oceans are not only polluted but are getting shorn of their natural wealth through human voraciousness. Atmosphere is beset with the looming danger of depleting ozone layer. The earth through over exploitation is loosing its fertility. What a scenario which we are going to bequeath to posterity!
Development and environment need not be looked upon as contradictions but as complimentary. Both are necessary for growth of human society, and of nations. A balanced and buoyant environment is fundamental not only for continued developmental efforts, but also for ensuring quality of life. A cleaner environment means less pollution, less sickness, less misery and would result in greater productivity for development.

The environment consists of the atmosphere, the hydrosphere, and the lithosphere. The hydrosphere consists of the oceans, the lakes, streams and the shallow ground water bodies. About three-fourth of the earth's surface is covered with hydrosphere, the main components of which is water. Water is a vital element for survival of man and for this-reason human civilization. Approximately three quarter of the earth's surface is covered with water. By all accounts, total volume of global water is in the vicinity of 1400 million cubic kilometers. Of this total, 97% is saline ocean water and only 3% is fresh water. Of this 3% of global fresh water 77.2% is stored on ice caps, 22.4% is ground water, 0.35% is in lakes and swamps, 0.04% in the land and 0.01% is in the rivers us shown in the table¹ (1.1). This is the break up of the fresh water availability to meet the world wide needs, ranging 40-45 thousand cubic meters. Our fresh water resources are generally classified as surface and ground water. Through the natural processes of the hydro-biological cycle, water is exchanged between atmosphere, land, sea and all plants and animal kingdom.
Water as it is found in nature is almost pure in its evaporated state, contaminants are added as the liquid water travels through the remainder of the hydrological cycle and comes in contact with materials in the air and on or beneath the surface of the earth. Ultimately the contaminated waters will complete the hydrological cycle and return back to the atmosphere again as relatively pure water molecules. However, it is the water quality in the intermediate stage which is of greatest concern because it is the quality at this stage that will affect the human use of the water.

Table 1.1 WORLD WATER DISTRIBUTION

<table>
<thead>
<tr>
<th>Location</th>
<th>Volume $10^{12}m^3$</th>
<th>% of Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Land Areas</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i) Fresh Water Lakes</td>
<td>125</td>
<td>0.009</td>
</tr>
<tr>
<td>(ii) Saline lakes and inland seas</td>
<td>104</td>
<td>0.008</td>
</tr>
<tr>
<td>(iii) Rivers (Average instantaneous volume)</td>
<td>1.25</td>
<td>0.0001</td>
</tr>
<tr>
<td>(iv) Soil Moisture</td>
<td>67</td>
<td>0.005</td>
</tr>
<tr>
<td>(v) Ground Water (Above depth of 4000m)</td>
<td>8350</td>
<td>0.610</td>
</tr>
<tr>
<td>(vi) Ice caps and Glaciers</td>
<td>29200</td>
<td>2.140</td>
</tr>
<tr>
<td>Total Land Area (Rounded)</td>
<td>37800</td>
<td>2.800</td>
</tr>
<tr>
<td>B. Atmosphere (water vapour)</td>
<td>13</td>
<td>0.001</td>
</tr>
<tr>
<td>C. Oceans</td>
<td>1,320,000</td>
<td>97.30</td>
</tr>
<tr>
<td>Total All Locations (Rounded)</td>
<td>1,360,000</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Source:- Adopted from Todd, 1970
1.1 WATER RESOURCES OF INDIA:

For men, the major source of water is the surface water that flows in the rivers. According to the estimates made by the Central Water Commission, the total utilisable water from surface water sources is about 690 cubic Kms. Besides this, there exists a replenishable ground water potential of about 452 cubic kms., as estimated by the Central Ground Water Board, making the total water availability of 1142 cubic Kms. Of this, utilization of water for agriculture at present is estimated as 460 cubic Kms., which comprises of 300 cubic Kms. of surface water and 160 cubic Kms. of ground water. Rainfall is the only source for replenishing the water being consumed by various sectors. Taking the average annual rainfall in the country at around 112cms, the total annual precipitation works out at around 3,700,000 million cubic meters. Nearly 80% of is accounted for by the south west monsoon and falls in a short period of four months. The Central Water and Power Commission has estimated that out of the total annual precipitation, about 800,000 million cubic meters seeps into the ground; about 1,700,000 million cubic meters flow into the rivers and is available as surface water; and the rest evaporates back into the atmosphere.

In the last few decades, there has been an all-round industrialization and urbanization activity. The waste water generation from industries and cities increased gradually and in most of the cases it is being discharged to water bodies untreated. The regenerating capacity of water bodies' has also been adversely affected due to flow of waste water in greater quantities. Ultimately we are ourselves victim of such
indiscriminate disposal of waste water and other pollutants to fresh water bodies.

In the recent years, air, water and soil pollution are responsible by the rapid growth of population, industrialization, green revolution in agriculture and many other multifarious activities. Pollution is man-made problem, mainly of effluent countries. The developed countries have been in a mad race to exploit every bit of natural resource to convert them into goods for their comfort, and to export them to needy developing world. In doing so; the industrialized countries dump lot of materials in their environment which makes their environment polluted. Further the waste water from textile, carpet, pulp and paper, chemical (dye) industries, etc. have proved more hazardous due to their dual nature, firstly due to their colour which cuts the smooth penetration of sunlight in the receiving water, resulting in the decrease in the extent of dissolved oxygen (D.O.) and an increase in the extent of Biochemical oxygen demand (B.O.D.), they are displeasing on aesthetic grounds, secondly, due to the presence of certain heavy metals (e.g. Cr, Co, etc.) which were used as mordants during the dyeing processes. This adversely affects the health of all living beings. The high concentration of the said metallic species in the effluent, also decrease the soil fertility and ultimately to the plant growth and production. The major sources and pathways of pollutants entering the wastewater treatment processes and river systems are shown in Fig. 1.1. The heavy metal pollutants cause direct toxicity beyond specified limits both for humans and aquatic biota. A few of them are considered to be bio-accumulative and considered to be carcinogenic. Fig. 1.2 is a flow diagram after Nisbet showing the
heavy metal pollutants following several routes with in environment along with their pathways.

The word "pollution" has come from the Latin word POLLUTIONNEM meaning defilement (Hanney, 1966). Various authorities have given different meanings to the term pollution. Thus United States Public Health Services has stated that pollution means the presence of any foreign substance in water that degrades the quality to constitute a hazard or impair its usefulness. Baumann, 1965 has stated that pollution is caused due to solids, liquids or gases which are non permissible, undesirable or objectionable.

"Water pollution is the addition of any substance to water or changing of water's physical and chemical characteristics in any way which interferes with its use for legitimate purposes". Normally water is never pure in a chemical sense. It contains impurities of various kinds-dissolved as well as suspended. These include dissolved gases (H₂S, CO₂, NH₃, N₂), dissolved minerals (Ca, Mg, Na salts), suspended matter (clay, silt, sand) and even microbes. These are natural impurities derived from atmosphere, catchment areas and the soil. They are in very low amounts and normally do not pollute water and it is potable. Polluted waters, however, are turbid, unpleasant, bad smelling, unfit for drinking, bath, and washing or other purposes. The polluted water has now become the source of various types of waterborne diseases, such as cholera, Jaundice, typhoid, diarrhoea, dysentery, paratyphoid fever, ulceration, nausea, bone-marrow injury, dermatitis.
FIG. 1.1 SOURCES OF HEAVY METALS ENTERING WASTEWATER TREATMENT PROCESSES AND RIVER
Fig. 1.2 Routes of metal pollutants into the environment.
Water pollution can be best considered in the perspective of possible pollutants cycle throughout the environment Fig. 1.3.

The strong consciousness about Environment in India started after the International conference on Human Environment, Stockholm in 1972. Stockholm declarations are called the Magna Carta of our Environment. Late Mrs. Indira Gandhi, the then Prime Minister of India, made a historic speech in the conference. In pursuance of promise made by the Indian Prime Minister process were started to do something positive to control pollution in the Environment. The Water (Prevention and Control of Pollution) Act was passed by the Parliament in 1974. Later on, the act was adopted by various state legislatures under article 252 of the Constitution of India. According to the Act, pollution has been defined as :-

"Pollution" means such contamination of water or such alteration of the physical, chemical or biological properties of water or such discharge of any sewage or trade effluent or of any other liquid, gaseous or solid substance into water (whether directly or indirectly) as may, or is likely to create a nuisance or render such water harmful or injurious to public health or safety, or to domestic, commercial, industrial, agricultural or other legitimate uses, or to the life and health of animals and plants or of aquatic organisms.7 (Pollution Control Series: PCL/2V1992, vol.-I)

There are several laws that directly or indirectly relate to the protection of environmental resources. Among, the more recent ones are the Insecticides Act, 1968; Wild Life Protection Act, 1974; Water
pollution Cess Act, 1978; Air (Prevention and Control of Pollution) Act, 1981; Environment (Protection) Act, 1986 and The Public Liability Insurance Act, 1991. However, many of the existing environmental laws dealing with various sectors have become outdated and are not implemented properly. There is also need for new legislation to take account of the special problems arising from the objective of rapid economic development with social justice. In the first national conference for legislators on Environment held in New Delhi on April, 1982 following declarations and resolutions were taken - "While financial incentive be given to industry for installing pollution abatement equipments, it be seen that the fight against pollution and for protection of environment is not converted into another business out of which a few companies; corporations and consultants would make profit at (be cost of community and environment".

In Great Britain, the Public Health Act, 1936 started the process whereas in U.S.A. the first Act was Refuse Act, 1899 but the effective Act was Water Pollution Control Act of 1948 which gage the federal government authority for investigations, research and surveys. Japan made the basic law of Environmental Pollution Control, 1967 whereas Germany had national Environmental Law of 1979. In Germany Act, it was laid down "Local representative bodies and their executive authorities are responsible for comprehensive management of the socialist national environment in their respective regions".

Under the Water (Prevention and Control of Pollution) Act, 1974, the first case by way of Public Interest Litigation was decided in
1991 by the Hon'ble Supreme Court of India "Subhash Kumar Vs State of Bihar", concerned the discharge of coal slurry into the Bokaro River. The Apex court put environment on the highest possible legal pedestal by declaring it to be a fundamental right inherent in the fundamental right to life in Article 21 of the Constitution. The court declared : "Right to live is a fundamental right under Article 21 of the Constitution and it includes the right of enjoyment of pollution free water and air for full enjoyment of life." (Krishna Mahajan, 1997).

Having laid down three basic principles, the Apex Court went further in Indian Council for Enviro Legal Action (H acid) case, Vellore Citizens Forum (tanneries) and S Jaganathan (aqua fanning) cases and laid down three more.

1. That is the polluter who pays.
2. The precautionary principles, namely, that is the duty of all authorities to prevent pollution or hazards to health of the people.
3. The principle of the ecological restoration means that the polluter will not only pay for the damage done but also for restoration of the ecology destroyed by him in an area.

All the natural and manmade freshwater bodies are utilized as a source of water for drinking, washing, waterways, transport, boating, swimming, fishing, domestic and industrial purposes, irrigation,
hydroelectric generation, dead bodies’ cremation and for religious purposes. It is an indisputable fact that we are consuming natural water resources more and more intensively today; therefore, it is becoming more and more difficult to provide ample fresh water on account of the projected doubling and trebling of the world population, proliferation of industrial processes, greater use of energy and increased agricultural activity. They are all causing progressive and chronic deterioration of the quality of available natural water resources by the increasing use of toxic substances and other pollutants. The mutagenic and carcinogenic effect of substances like pesticides, radioactive matter and trace metals, pose a potential threat to human life.

Pure and unpolluted water is the guarantee of a bumper crop and a healthy nation. Many developed countries have taken adequate measures to bring their polluted fresh water bodies back to a reasonably attractive and clean level. In India too, consciousness arose recently in order to keep our fresh water bodies to their original clean level. In this connection, Ganga Action Plan was launched in June 1985, with the aim of immediate reduction of the pollution load of river Ganga and their tributaries. In the 2nd phase of Ganga Action Plan, other important rivers of India are proposed to be cleaned similarly.
1.2 TYPES OF POLLUTION

Different types of pollutions are:

1. Air Pollution
2. Soil Pollution
3. Radio Active Pollution
4. Noise Pollution
5. Water Pollution

Out of different types of pollutions mentioned above, water and air pollutions are most dangerous, because they occur more frequently than the rest. The ever increasing level of pollutants in air is causing unfavourable effect on growth, metabolism and productivity of plants.

Air Pollution: The problem of air pollution is not a new one. When we talk of pollution of air, we mean generally the pollution of that part of the atmosphere which is nearest to the earth’s surface extending to a height of about 80 km. This is known as homosphere since it is composed of homogeneous mixture of various constituents. The homosphere constitute about 99.99 % of the total atmosphere. The common gaseous pollutants are CO, CO$_2$, SO$_2$, H$_2$S, NO, NO$_2$ and common solid pollutants, called particulates, are carbon and dust particles, pollens, aerosols of lead etc. Air pollutants are responsible for a number of hazards like Green House
Effect, Acid Rain, Depletion of Ozone layer, climatic changes and a number of other disorders for plants and human lives. CO decreases the oxygen carrying capacity of haemoglobin thereby reducing the availability of oxygen for the body cells resulting in anoxia. Green House Effect is causing increment in the temperature of earth. It may cause rise in sea level. Acid rains are caused due to oxides of nitrogen and sulphur. Air pollution causes a number of diseases e.g. asthma, headache, etc.

**Pesticides Pollution**: The term pesticide is used in broad sense for a wide variety of compounds like insecticides, fungicides, herbicides, rodenticides, etc. Arsenites, arsenates, cryolite, rotenones, for example DDT (Dichloro Diphenyl Trichloroethane), DDD (Dichlorodiphenyl dichloroethane), methoxychlor (Dimethoxy diphenyl trichloroethane), BHC (Benzene hexachloride), Malathion, parathion, 2,4-D (2,4-Dichlorophenoxy acetic acid), 2,4,5-T (2,4,5-Trichlorophenoxyacetic acid), ANTU (Alpha naphthyl urea), etc. fall under the category. The pesticides have numerous harmful effects towards living beings i.e. human. These pesticides cause immense harm to trees. The pesticides cause considerable occupational illness among farm workers. Almost all the pesticides are toxic to humans. These have carcinogenic, mutagenic and teratogenic properties. Thus from their hazardous effects it is clear that the use of chemical pesticides is fraught with the danger of causing immense environmental pollution.

**Soil Pollution**: Any factor which deteriorates the quality, texture and mineral content of the soil and/or disturb the biological balance of the organisms in the soil and as a result has a lethal effect on plant growth is
called soil pollutant. There are several factors such as excessive and continuous use of fertilizers, pesticides, accumulation of excreta of grazing animals, dumping of urban, industrial and radioactive wastes, agrochemicals, etc. which cause soil pollution.

**Radioactive Pollution**: Radioactive pollution is caused due to use of radioactive materials. Radioactive isotopes are used for a number of beneficial uses such as power generation, medical uses and research. The atomic weapons, nuclear tests and accidents have brought catastrophic effect in our environment. Even the beneficial uses can not be considered free from hazards because of leaks, accidents, problems of disposal of radioactive wastes and damaging effects of long term exposure to low radioactive wastes. Besides, being carcinogenic they may also cause physical and mental imbalance for future progeny. These affect water, air, food and soil.

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Soil pollution is mainly due to excessive and continuous use of fertilizers, pesticides and agrochemicals.

1.3 WATER POLLUTION

Water is one of the most essential requirements of living beings. Life is not possible without water. Therefore the quality of water is of vital importance not only for human being but also for plants and animals. A number of water born diseases are caused due to polluted water which results in large scale death. About 90% of diseases are caused due to polluted water. Major sources of water pollution are domestic and industrial discharges.

A wide variety of both, inorganic and organic pollutants are present in effluents from breweries, tanneries, dyeing textiles, paper and pulp mills, steel industries, mining operations etc. The pollutants include oils, greases, plastics plasticizers, metallic wastes, suspended solids, phenols, toxins, acids, salts, dyes, cyanides, DDT etc., many of which are not readily susceptible to degradation and thus cause serious pollution problems.

1.3.1 CRITERIA AND INDICATORS OF WATER POLLUTION:

Water pollution essentially implies the presence of substances/impurities in water at levels undesirable or harmful for certain beneficial uses. Thus water pollution should essentially be looked upon as deterioration in water quality to levels adverse to specific uses. Central
Pollution Control Board of India proposed classification of the rivers and streams of the country based on the "BEST DESIGNATED USE" of the streams as given in the table (1.2) and laid water quality criteria for the different classes as given in the table (1.3).

Some Boards have attempted to classify roughly the different kinds of discharges in accordance with the general types of industrial activity involved. A relatively simple coding, which has been adopted in Kerala for different types of effluents, is as follows:

(A) Food And Drink Manufacturing Industries

(a) Distilleries and sugar factories
(b) Starch and food products
(c) Soap and oils

(B) Chemical Industries

(a) Fertilizers and chemicals
(b) Drug and Pharmaceuticals
(c) Insecticides and -pesticides

(C) Domestic Discharges:

Domestic discharge is also responsible for merger of heavy metals in water from residential areas and includes service industries and auto-mobile repairing shops and restaurants.
About 250 mg/kg heavy metals have been found in human faeces (September, 1956). Faeces concentration of copper is approximately 68 mg/kg followed by lead, nickel and cadmium at 11, 4.7 and 2.0 mg/kg respectively (Davis & Copper, 1980).  

Discharge of metals to sewers in residential areas is also by bathing, brushing the teeth and washing hair (Atkins & Hawley, 1978). House-hold products such as medicines, cosmetics, polishes, etc. all contain heavy metals. Fluoride and Tin (II) is a popular ingredient of tooth pastes. As reported by Crosby (1982) approximately 1,000,000 kg of Tin from these sources is released per year in USA. A few anti-dandruff shampoos may contain up to 1% Selenium Sulphide (Harr, 1978).

(D) Industrial Discharges:

A wide variety of both inorganic and organic pollutants are present in effluents from breweries, tanneries, dyeing textiles, paper and pulp mills, steel industries, mining operations, etc. the pollutants include oils, greases, plastics, plasticizers, metallic wastes, suspended solids, phenols, toxins, acids, salts, dyes, DDT, etc., many of which are not readily susceptible to degradation and thus cause serious pollution problems. Heavy metals have wide applicability in industries and it will also influence their appearance in waste waters. Metals included in W.H.O. International and European standard for drinking water quality are depicted in Table 1.2.
### Table – 1.2

Metals included in W.H.O. International and European standard for drinking water quality

<table>
<thead>
<tr>
<th>Metals</th>
<th>International</th>
<th>European</th>
<th>Guideline</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>H.D.(mg/l)</td>
<td>M.P.(mg/l)</td>
<td>M.P.(mg/l)</td>
</tr>
<tr>
<td>Cd</td>
<td>–</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Cr</td>
<td>–</td>
<td>–</td>
<td>0.05(a)</td>
</tr>
<tr>
<td>Pb</td>
<td>–</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Co</td>
<td>–</td>
<td>PC</td>
<td>–</td>
</tr>
<tr>
<td>Cu(c)</td>
<td>0.05</td>
<td>1.5</td>
<td>0.05</td>
</tr>
<tr>
<td>Mn(c)</td>
<td>0.05</td>
<td>0.5</td>
<td>0.05</td>
</tr>
<tr>
<td>Zn(c)</td>
<td>5.0</td>
<td>15.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>

**Note** -
- **HD** Highest desirable concentration
- **MP** Maximum permissible concentration
- **PC** Presence should be controlled
- **a** Cr(VI)
- **b** Total Cr
- **c** Values based on aesthetic, corrosion, deposit formation, etc.
Water pollution is a state of deviation from pure water, whereby its normal functions and properties are affected. We do not require water in its purest form for drinking purposes, because certain minerals and salts are required for taste and maintaining normal health. For boilers we require pure water. Water pollution can be best studied in perspective of possible pollutant cycle through environment.

1.3.2 WATER POLLUTANTS AND THEIR ILL EFFECT

Different types of water pollutants may be broadly classified under the following categories:

1. Inorganic Pollutants
2. Organic Pollutants
3. Sediments
4. Thermal Pollutants
5. Radio Active Materials

1.3.2.1 Inorganic Pollutants: This group of pollutants includes mineral acids, finally divided metals or its compounds, inorganic salts, organo-metallic compounds, trace elements and acidmine drainages.

Several trace elements are found in polluted water. The most dangerous among them are heavy metals, eg, Pd, Cd, Hg and metalloids such as As, Se and Sb. The source and pathway of heavy metals entering waste water treatment process and rivers has been represented in Fig 1.1. Heavy metals have great affinity for sulphur and attack sulphur
bonds in enzymes and immobilize the later. Heavy metals bind to cell wall. They also tend to precipitate phosphate bio-compounds and catalyze their decomposition. Metals are contributed by domestic sewage and industrial effluents. Ali Mohammed et al (1997) have studied different heavy metals in the aquatic environment and presented a general idea about the sources and ill effect of some important toxic heavy metals, which affect quality of water if present in it. Some examples of such heavy metals are as follows:

1. **Arsenic (As)**: The main sources of arsenic are pesticides, chemical waste, pharmaceuticals, mining by-product, pulp and paper industry. It is highly toxic, possibly carcinogenic. Acute poisoning results several gastro-intestinal irritation with attainments cramps, diarrhoea, nervous disorder etc.

2. **Cadmium (Cd)**: The main sources of cadmium are industrial discharges, mining wastes, metal plating, water pipes etc. It replaces zinc biochemically. It causes high blood pressure, kidney damage, destruction of testicular tissues and R.B.C.

3. **Chromium (Cr)**: The main sources of chromium are metal plating, paint industry, alloy, glass industry, electroplating effluents, tanneries wastes, etc. Chromium is carcinogenic, it is very toxic and causes ulceration and carcinoma.

4. **Copper (Cu)**: The main sources of copper are metal plating industry, domestic wastes, mining, mineral leaching, etc. It is not very toxic to animals but toxic to plants at moderate level. Excess intake causes
stomach irritation, reduction in growth, liver damage, kidney damage, brain damage, etc.

5. Cobalt (Co) : The main source of cobalt is magnet making, concerns. It is also toxic and causes coronary failure, thyroid dis-function due to impaired accumulation of iodine.

6. Iron (Fe) : The main sources of iron as effluents are industrial discharges, water flowing through basaltic rock region. It causes hemochromatosis, tension in gastro-intestinal tract, scolex and liver damage.

7. Lead (Pb) : The main sources of lead are industrial wastes such as from glass industries, paint industries, plumbing, coal, gasoline, etc. It is also very toxic and deactivates or destroys sulphur containing proteins and enzymes. It causes damaging effect on D.N.A., R.N.A., brain and central nervous system. It inhibits the formation of hemoglobin and causes suicidal tendencies over anxiety, aggression, etc. thus very harmful for living organism, especially for human beings.

8. Manganese (Mn) : The main sources of Mn are industrial wastes, acid-mine drainage, alloy industry, dry cell, battery factories, glass industry etc. It is highly toxic and causes damaging effect to central nervous system and brain.

India ranks almost the first ten heavily industrialized countries of the world. River pollution is necessary evil of essentially all the developmental activities. This has resulted heavy backlog of gaseous, liquid and solid pollution in the rivers of the country. Street dust
containing heavy metals e.g. Pb, represent an important source of metal-in-put to surface water. Metals are contributed by industrial effluents and domestic sewage. All these sources may be routed by way of sewage treatment works which reduce significantly the most of the metal discharged.

1.3.2.2 Sediments: The increase in sediments is due to natural process of soil erosion. It represents the extensive pollutants of surface water. Bottom sediments are important surfaces of inorganic and organic matter in stream, oceans and fresh water. Bottom sediments are subjected to reducing condition. Level of organic matter in sediments is higher than the soil. Sediments and suspended particles are also important repositories for trace metals, eg. Cu, Cr, Ni, Mn, Co, etc.

1.3.2.3 Thermal Pollutants: This problem originates by the use of water in many industrial processes as a coolant eg., thermal power plants. The waste hot water is returned to original water bodies where the temperature may rise to 10\(^0\) C or more. D.O. value of water is decreased and adversely affects fishes and aquatic life.

1.3.2.4 Radio Active Materials: Four activities mentioned below are responsible for radio active pollution –

(1) Mining and processing of ores to produce useable radio active substances.

(2) Use of radio active materials in nuclear weapons.

(3) Use of radio active materials in nuclear power plants.
(4) Use of radio active isotopes in medical, industrial, and research applications.

During extraction of uranium large quantities of uranium tailing are produced which pose the problem of radio active pollution.

Nuclear Power Plants generate the following types of pollutants-

(a) Low level radio active liquid wastes.

(b) Liquid and gaseous waste from fuel elements.

(c) Fission products.

(d) Heat.

The discharge of radio active wastes into air and sewer system is likely to create problems in the long run. The radio nucleoids found in water include Ra-226 and K-40 originating from leaching of minerals Sr-90, I-131, Cs-137, Kr-85, Co-60, Mn-54, Fe-55 and Pu-239 originating from reactors and uranium testing.

1.3.2.5 Organic Pollutants: This group includes disease causing agents, oxygen demonding wastes, synthetic organic compounds, pesticides, oils and detergents. In natural water, the optimum D.O. value is 4.6 ppm. Decrease in this value is due to pollution created by organic matter like industrial wastes from food processing plants, tanneries and paper mills, wastes from Slater Houses, etc. A number of health problems have been associated with the manufacturing of pesticides. Light transmission
through surface water is reduced by oil pollution and hence, photosynthesis by marine plants decreases D.O. value in water and causes damage to water birds, animals etc. Oil may cause direct lethal toxicity, destruct physiological activities or it may change the biological habitats. Dyes are also organic pollutants which affect the habit and habitat of the aquatic plants and animals, the dyes are described below-

1.4 DYE

A dye or a dyestuff is usually a coloured organic compound or mixture that may be used for imparting colour to a substrate such as cloth, paper, plastic or leather in a reasonably permanent fashion. In other words, a dyed substrate should be resistant to a normal laundry or cleansing procedures (wash fast) and stable to light (light fast).

1.4.1 REQUIREMENT OF A TRUE DYE

All coloured substances are not dyes, however the requirements of a true dye are as follows-

1. It must have a suitable colour
2. It must have an attractive colour
3. It must be able to attach itself to material from solution or to be capable of fixed on it
4. It must be soluble in water or must form a stable and good dispersion in water. Alternatively it must be soluble in the medium other than water
5. The substrate to be dyed must have a natural affinity for an appropriate dye and must be able to absorb it from solution or aqueous dispersion.

6. When a dye is fixed to a substrate it must be fast to washing, dry cleaning, light, heat and other agencies.

7. The shade and fastness of a given dye may vary depending on the substrate due to different interaction of the molecular orbitals of the dye with the substrate.

A few examples of dyes are as Trypan Blue, Methylene Blue, Malachite Green, Crystal Violet, Rose Bengal, Methyl Violet, Chrome Violet, Safranin T, Indigo, Bismarck Brown, etc.

1.4.2 ADVERSE EFFECTS OF DYES ON AQUATIC LIFE

In addition to natural dyes more than 7,000 synthetic dyes are used in cotton dyeing, wool dyeing and several other dyeing industries. As a result of which a large amount of effluents containing colouring materials are discharged in ambient water bodies. The dyes are highly toxic for aquatic life which has been demonstrated by damaging effect of dyes on fish tissues by Tripathi (1982)\textsuperscript{11} Shrivastwa et al (2003).\textsuperscript{12}

Some examples of dyes which cause damaging effect on aquatic life are Chrome Brilliant Blue – B, Mc. Green B.L.S., Chrome Black – T, Chrome Fast Red F, Black – T, Supra Olive Green and
Rhodamine. The dyes also change hydrochemical nature of water bodies (Tripathi, 1982).\textsuperscript{11}

In the carpet industry of carpet belt of Eastern UP huge quantities of dye supporting chemicals are being used. Shrivastwa and Tripathi (1980) indicated of their pollution potential. Shrivastwa and Ahmed and Shrivastwa et al have shown damaging effect of Methylene Blue on fish tissue.

Mrs. S. Lata and Shrivastwa studied the damaging effect of Chrome Black – T, Chrome Fast Red and Formic acid on aquatic life. They observed that these dyes induced histopathological changes in liver, intestine and kidney of \textit{P. sophare}.

1.5 POSSIBLE METHODS FOR THE WASTE WATER TREATMENT

In the past, a variety of treatment techniques have been developed for the removal of different types of pollutants from water and waste water. The treatment methods may be classified into following four groups-

a. Physical Methods

b. Biological Methods

c. Chemical Methods

d. Integrated Methods
1.5.1 PHYSICAL METHODS

Techniques generally employed to diffuse out the physical stress may be sedimentation,\textsuperscript{13,14} floatation\textsuperscript{15,16}, filtration\textsuperscript{17}, and membrane filtration etc. Sedimentation methods are employed for the removal of suspended impurities. Very fine suspended particles and some bacteria can be removed with the help of sedimentation with coagulants. Floatation method is adapted for the separation of suspended and colloidal impurities by bubbling the solution. Biological flocks and coagulates can be channalised using filtration method. A recent method is the use semi-permeable membrane\textsuperscript{18,19}; it includes ultra filtration, electrodialysis and reverse osmosis methods may also be used for water purification earlier to its disposal into water.

1.5.2 CHEMICAL METHODS

To improve the quality of water, different chemical methods such as precipitation, coagulation, adsorption and ion exchange methods may be used for the removal of various chemicals from water being poured to rivers. Reduction and Precipitation\textsuperscript{20,21} processes are generally employed for the removal of toxic metallic species from waste water. The coagulation\textsuperscript{22,23} method is used for the removal of toxicants and it consists of separation by aggregation of small particles into large ones, which settle more readily. To remove ionic species from water, ion exchange\textsuperscript{24-27} device can be used. This method is also appreciable for the removal and recovery of radio active materials from waste waters of nuclear reactors, laboratories and hospitals. Different types of inorganic and organic pollutants can be removed by adsorption technique\textsuperscript{28-36}. The used
of activated carbon as an adsorbent for the treatment of waste water has been found to be both practical and reliable, particularly where organic constituents with their organophillic\(^\text{37}\) character are involved. In addition to the methods mentioned above, evaporation, electro-deposition, cementation, freeze concentration, ion flotation, etc. are also employed for the purification of undesirable substances from the water.

1.5.3 BIOLOGICAL METHODS

These methods are used for the treatment of sewage which is highly potent in municipal wastes. Complex organic wastes may be recycled in simpler and stable and products by certain micro-organisms. These methods have ability of various micro-organisms to attract and gather trace elements\(^\text{38}\) and organic pollutants\(^\text{39}\). The end products can be safely disposed off. The most common biological methods are activated sludge process\(^\text{40,41}\), aerobic\(^\text{42}\), anaerobic\(^\text{43}\), digestions, oxidation ponds\(^\text{44,45}\), etc. Several treatment processes developed including activated sludge process and trickling filters, septic tanks, detritous tanks, oxidation ponds or aerated lagoons before adding to the river water.

1.5.4 INTEGRATED METHODS

No single method is sufficient for through treatment of water, but a series of methods are used in combination depending upon the degree of treatment required. The treatment processes can be graphed as follows-
Because of sludge free operation and easy handling of overall operation, adsorption technique was selected for the removals of toxic pollutants from water using some unconventional absorbents are frequently used.

1.6 ADSORPTION

Adsorption involves the interphase accumulation or concentration of substances at an interface. The process can occur at an interface between any two phases, such as, liquid-liquid, gas-liquid and gas-solid. The substance being adsorbed is termed as the adsorbate and the adsorbing phase as the adsorbent.

1.6.1 CHARACTERISTICS OF ADSORPTION

The various characteristics of adsorption are:

1. It is a spontaneous process and occurs in no time.

2. The phenomenon of adsorption can occur at all surfaces and there can be five interfaces \textit{viz.} gas-solid, liquid-solid, liquid-liquid, solid-solid and gas-solid.

3. It is accompanied by a decrease in the free energy of the system, i.e., \( \Delta G \). The adsorption will continue to such an extent that \( \Delta G \)
continues to be negative eventually, magnitude of $\Delta G$ decreases to zero. When $\Delta G$ for further adsorption reaches a value for zero, adsorption equilibrium is to be established.

4. As the process of adsorption involves loss of degree of freedom of the gas in passing to the adsorbed film there is a decrease in the entropy of the system (Gibbs-Helmholtz equation)-

\[ \Delta G = \Delta H - T\Delta S \]  \hspace{2cm} (i)

Or \[ \Delta H = \Delta G + T\Delta S \]  \hspace{2cm} (ii)

Where $\Delta G$ is the change in free energy, $\Delta H$ is the change in enthalpy, $\Delta S$ is the change in entropy and $T$ is the temperature of the system.

As the entropy and free energy of the system decreases in adsorption, the value of $\Delta H$ decreases. This decrease in enthalpy appears as heat. Hence the adsorption process must also be exothermic.

1.6.2 TYPES OF ADSORPTION

On the basis of the nature of the association of the adsorbate species on the surfaces of adsorbents, adsorption is of three types –

1.6.2.1 PHYSICAL ADSORPTION

Physical adsorption takes place due to non-specific Vander Waal’s forces of attraction between the solid and the adsorbate. These are
similar in nature to those acting in any condensation process. They originate due to the interaction of the entire electron shell of the adsorbate with the adsorbent. Physical adsorption is a rapid and reversible process, requiring no activation energy. In this adsorption the adsorbed molecules are not affixed to a particular site at the surface but rather are free to undergo translational movement within the interface.

1.6.2.2 CHEMICAL ADSORPTION

It is due to the action of specific ‘chemical’ forces i.e. transfer or sharing of electrons between an adsorbent and adsorbate. Energies associated with this type of adsorption are usually much higher than those associated with physical adsorption and may approach to the energy of chemical bond formation. Chemical adsorption may be irreversible and slow, with a temperature dependence showing the presence of activation energy. In this process the adsorbate forms localized bonds at the active centers on the adsorbent.

1.6.2.3 ACTIVATED ADSORPTION

In this type of adsorption, with the increase in temperature the physisorption gradually changes to chemisorption and the activation energy for this adsorption is of the order 5-20K Cal/mole.

1.6.3 THEORIES OF ADSORPTION

Various theories of adsorption have been proposed from time to time to explain the phenomenon of transfer of adsorbate species from
the bulk of the solid surface. Some of the important theories are described here in brief. These are as –

1.6.3.1 CHEMICAL BOND THEORY

According to chemical bond theory\textsuperscript{46}, during the process of adsorption there are surface interactions of chemical nature between the adsorbent and the adsorbate species. Thus there is the formation of a bond between the adsorbed atom and single atom of adsorbent as a result of a chemical reaction. Pauling developed an empirical relation for bonds between single atoms and extended that to adsorption bonds in the case of covalent bonding.

1.6.3.2 CAPILLARY METHOD

The adsorption of adsorbate species which condense into the pores of the adsorbent to form a thin layer of molecules inside the walls has been explained with the help of the capillary theory. Zsigmondy\textsuperscript{47} proposed a similar theory to elucidate the uptake of water vapour by silica gel, and Foster\textsuperscript{48} extended it to make clear the adsorption behaviour of Ferric Oxide gel. The work of Patrick and Long\textsuperscript{49} represents an extension of the theory into a general theory of adsorption in order to illuminate a physical adsorption on the basis of capillary condensation.

1.6.3.3 RESIDUAL VALENCE THEORY

In 1914, Hober\textsuperscript{50} suggested that the outer surface of an adsorbent is unsaturated and exhibits residual valences, which can adjust atoms, molecules or ions. The bonds thus formed are weaker in
comparison to the common chemical bonds. Langmuir adsorption isotherm was predicted on the basis of this theory in which only monolayer of adsorbate molecules is formed.

1.6.3.4 POLARIZATION THEORY

In order to explain the adsorption of non-polar molecules on ionic adsorbents de Boer and Zwikker\textsuperscript{51}, Bradley\textsuperscript{52} and others\textsuperscript{53,54}, on the basis of their exhaustive study, have implies that the outermost layer of the adsorbent includes dipole in the first layer of the adsorbed molecules which further polarizes the neighbouring layers. As a result of this induced dipole interaction, the formation of multilayer of adsorbate species on the surface of adsorbent takes place.

1.6.3.5 THERMODYNAMICS POTENTIAL THEORY

It was developed by Polanyi\textsuperscript{55} and was further tested by several workers. According to this theory the adsorbent exerts a strong attractive force within a short range from the surface. The region of operation of the attractive force is called the “Field of adsorption potential”, which brings about the mono or multilayer adsorption. The potential energy of interaction of a gas molecule with the particles of the lattice is the sum of all the individual interactions,

\[ U = \sum_{i} U(r_{i}) \] \hspace{1cm} (iii)
Where \( U(r_i) \) is the potential energy of the interaction of the gas molecule with the \( i^{th} \) particle of the lattice at a distance \( r_i \), \( U \) is a function of coordinates \( X, Y \) and \( Z \) of adsorbed molecule in the plane of the surface parallel to the rows and columns respectively of the solid particles and \( Z \) is the coordinate perpendicular to the surface. If \( X \) and \( Y \) are kept constant while \( Z \) varies, \( U(Z) \) has a shape of the potential energy curve such as that given by Lennard-Jones intermolecular pair potential, \( i.e. \)

\[
U(r) = \frac{A}{r^{12}} - \frac{C}{r^6} \quad \text{(iv)}
\]

Where \( A \) and \( C \) are constants and \( r \) is the distance perpendicular to the surface. The value of \( U(Z) \) above a particle of solid will be different from \( U(Z) \) between two particles and, therefore, \( U_m \), the potential maximum of \( U(Z) \), will vary periodically in both the \( X \) and \( Y \) directions. Thus a plot of \( U_m \) against \( X \) or \( Y \) will give a curve with maxima and minima. In the simplest case of localized adsorption, an adsorbed molecule is considered to be held at the bottom of a potential well whose depth is much greater than the thermal energy of the molecule, \( KT \). When the adsorbate species are free to migrate along the surface, the adsorption is generally classified as non-localized.
1.6.3.6 B.E.T. THEORY (MULTIMOLECULAR THEORY)

This theory was developed by Brunauer, Emmett and Teller\textsuperscript{56} in 1938 for the multilayer adsorption of gases. Later on it has also been employed to explain the adsorption of solutes from solutions on the solid surfaces. They derived the following equation:

\[
\frac{C}{(Cs - C) q_e} = \frac{1}{BQ^0} + \left(\frac{B - 1}{BQ^0}\right) \frac{C}{Cs} \quad \text{...................(V)}
\]

Where, $Cs$ is the saturation concentration of the solute, $C$ is the measured concentration in solution at equilibrium, $Q^0$ is the number of moles of solute adsorbed per unit weight of the adsorbent in forming a complete monolayer on the surface, $q_e$ is the number of moles of the solute adsorbed per unit weight of the adsorbent at concentration $C$ and $B$ is a constant showing the energy of interaction with the surface of the adsorbent. This equation is helpful in determining the nature of the adsorption isotherm, heat of adsorption and the amount of adsorbate required to provide a monolayer. This theory has been generally employed for the determination of surface area. The following types of isotherms are expected:
Type I represents the formation of monolayer coverage, type II and III stands for multilayer formation. The isotherms IV and V are supposed to be the result of condensation of adsorbed species in the pores and capillaries of the adsorbent.
1.6.3.7 BOUNDARY LAYER THEORY

This theory is based on the donor or accepter properties of the adsorbate molecules. According to this theory the adsorption occurs as a result of electron transfer\textsuperscript{57-59} between the adsorbate and the adsorbent. The direction of electron transfer depends upon the relative positions of the two electron levels \textit{i.e.} Fermi level of the adsorbent and the ionization potential of the adsorbate. The adsorbent surface, thus, acquires positive or negative charge altering with the adsorption and affects conductivity of the system. The decrease or increase in the conductivity of the system is due to the fact that adsorption provides "cumulative" or "depletive" chemisorption, respectively. This theory fails to explain the cases where there is no conductivity change.

1.6.3.8 ELECTRON THEORY

Wolkenstein\textsuperscript{60} proposed a theory to explain the chemisorption and catalysis on semiconductors. This theory is successful in explaining the process of adsorption. This theory is quite pertinent to adsorption in which charge transfer occurs accompanied by a change in conduction and also refers to adsorption in which no charge transfer takes place. This theory comprises the probability of simultaneous existence of two or more types of adsorption and it enables the calculation of equilibrium constant between them. For example, hydrogen may be adsorbed on ZnO and ZnO.Cr\textsubscript{2}O\textsubscript{3} by two mechanisms, one of which, predominates at high temperature and other at low temperature. From the comparison of the conductivity curves, it is concluded that the chemisorption of the high temperature type is entirely responsible for
observed increase in conductivity. Hence, chemisorption at low temperature does not imply the conduction band. According to Wolkenstein\textsuperscript{60} both weak and strong chemisorptions take place and are distinguished as follows:

(a) There is no change in the number of electrons in the conduction band or positive hole in the valence band of the crystal in case of "weak chemisorption". The chemisorbed particles with their adsorption centers remain electrically neutral.

(b) The chemisorbed particles either donate or capture electrons in the case of "strong chemisorption". Thus, the number of electrons in the conduction band or positive holes in the valence band of the crystal changes.

Weak and strong chemisorptions are not essentially equivalent to reversible and irreversible chemisorptions. Reversible adsorption though weak in comparison to irreversible, may sometimes involve changes in conduction.

1.6.3.9 MODERN CONCEPT

Based on quantum and statistical mechanics\textsuperscript{61-63}, a modern theory of adsorption has been developed to explain the chemisorption of gases on solids. The molecular orbital model for surface adsorbed species has been proposed and further extended by several workers\textsuperscript{64,65}. Fava and Eyring\textsuperscript{66} have developed the following model for the adsorption and desorption of dodecyl benzene on cotton:
\[
\frac{d\phi}{dt} = 2K_1(1 - \phi) \sin hb(1 - \phi) \quad \text{(vi)}
\]

Where \( \phi \) denotes the fraction adsorbed, \( K_1 \) is the rate constant for adsorption and \( b \) is a constant. Another equation due to Langmuir which has successfully explained the adsorption of polyvinyl acetate on chrome plate\(^{67} \) is:

\[
\frac{d\theta}{dt} = K_1(1 - \theta)C - K_{-1}\theta \quad \text{............... (vii)}
\]

Where \( K_1 \) and \( K_{-1} \) are the rate constants of adsorption and desorption respectively, \( C \) is the solution concentration and \( \theta \) is the fraction of the surface covered by the adsorbate.

Relying on the Langmuir interpretations, Lindstorm and coworkers\(^{68} \) were able to propose the following rate expression:

\[
\frac{d\phi}{dt} = K'_1(1 - \phi)(1 - \phi/2)e^{-b\phi} + K'_2(1 - \phi/2)e^{b(2-\phi)} - \frac{\phi^2}{2} e^{b\phi} \quad \text{...(viii)}
\]

Where \( \phi \) is the fraction of amount adsorbed and \( K'_1, K'_2 \) and \( b \) are real non-negative constants.
1.6.4 FACTORS AFFECTING ADSORPTION:

The following types of parameters affect the rate and extent of adsorption:

1.6.4.1 NATURE OF ADSORBENT

The extent of adsorption depends on the physico-chemical nature of adsorbent such as particle size\(^{69-72}\), surface area and residual charge\(^{73-77}\) on the surface of adsorbent. The adsorption on metallic oxides is dependent on their residual valencies owing to the edge, cracks and corners present on their surface. Further, the adsorptive sites of clays have different adsorptive potential due to irregular faces, edges and interlaminar regions. The pretreatment of the surface by etching, grinding, cleaning, etc. also influences the adsorption.

1.6.4.2 NATURE OF ADSORBATE

The solubility of the adsorbate (solute) is a controlling factor, to a large extent, for adsorption equilibria describing adsorption from solutions. The degree of solubility is determined by the strength of the bonds between solute and the solvent. According to the Lundelius rule, in general, an inverse relationship exists between the extent of the adsorption of a solute and its solubility in the solvent from which adsorption occurs. The relative polarity of the adsorbent and adsorbate also influences the adsorption equilibria. A solute molecule prefers that phase which is closest to it in polarity.
1.6.4.3 NATURE OF SOLVENT

In the adsorption process, a significant role is played by the polarity and dielectric constant of the solvent. Freundlich and Heller\textsuperscript{78} have investigated the effect of solvent on adsorption. The results indicate that the addition of non-aqueous solvent to aqueous solutions increases the adsorption of Sr(II) and cations on different oxides.

1.6.4.4 CONCENTRATION

The extent of adsorption of ionic species is highly affected by the concentration of the adsorbate species in the system. For a particular system, at a constant temperature the relationship between the solution concentration and amount adsorbed sometimes becomes complicated owing to the formation and overlapping of mono- and multi-layered adsorption as well as capillary condensation. Giles and coworkers\textsuperscript{79} classified the various types of adsorption isotherms into five groups. It has been reported that the adsorption of some ions follows the Langmuir isotherm, given below:

\[
q_e = \frac{Q^0bC}{(1 + bC)} \quad \text{........................................ (ix)}
\]

Where \( q_e \) is the amount adsorbed per gram of adsorbent at equilibrium, \( C \) is the equilibrium concentration of ions in solution and \( Q^0 \) and \( b \) are the Langmuir constants, related to the capacity and energy of
adsorption. For a limited concentration range at constant temperature, the variation of adsorption with concentration can also be depicted by the Freundlich equation:

$$q_e = K_f C^{1/n}$$ ...........................................(x)

Where, $K_f$ and $1/n$ are the Freundlich constants. However, at micro and tracer concentrations, the equilibrium data obey the Henry's law:

$$q_e = K C$$ ............................................. (xi)

In some cases, adsorption data do not agree with the Langmuir or Freundlich isotherms. For these cases, Sips proposed the following isotherm:

$$q_e = \frac{Q^0 C^{1/n}}{b + C^{1/n}}$$ ........................................... (xii)

1.6.4.5 TEMPERATURE

Temperature can influence both kinetics and the final values of adsorption. As adsorption reactions are usually exothermic, the
adsorption, in principle, decreases with increasing temperature. This can be shown by the following relationship:

\[ K = \text{const.} \, e^{Q/RT} \]  

(xiii)

Where, \( K \) is the adsorption coefficient in Langmuir relationship and \( Q \) is the heat of adsorption. The heat of adsorption can be calculated from the temperature dependence of the sorption by the differential form of the above equation\(^{80,81}\).

\[
\left( \frac{\partial (\ln C)}{\partial T} \right)_{q_e} = \frac{Q}{RT^2} \quad \text{.................. (xiv)}
\]

The calculation of heat of adsorption helps in the elucidation of sorption mechanism. It was Traverse\(^82\) who for the first time observed the effect of temperature on adsorption. The nature of adsorption and its thermodynamics were further studied by Hill\(^83\) and Everett\(^84\).
1.6.4.6 EFFECT OF pH

pH affects the extent, rate and mechanism of adsorption because of the following reasons\textsuperscript{72,85-91}:

(i) The pH can substantially affect the surface electric charge of the adsorbent, which is important for the electrostatic adsorption of ions. For instance paper\textsuperscript{92-94}, organic polymers\textsuperscript{95,98} and glass\textsuperscript{95-99} are negatively charged due dissociation of their surface groups or due to adsorption of hydroxide ions.

(ii) H\textsubscript{3}O\textsuperscript{+} or OH\textsuperscript{-} ions can compete with the adsorbate ions in ion exchange. The extent of competition depends on the activity of the hydrogen and the hydroxyl ions,

(iii) The acidity or basicity of the solution can influence the composition and properties of the adsorbent surface,

(iv) Anions of acids or cations of hydroxides used for adjustment of pH can compete with the adsorbate ions.

(v) The state of most of the ionic adsorbents in solution strongly depends on the pH and adsorbability of different forms usually differs.

1.6.4.7 EFFECT OF TIME AND AGITATION

The adsorption process can be broken down into at least three consecutive steps:
(a) Transport of the adsorbate to the adsorbent surface,

(b) The adsorption process i.e., the formation of adsorption bond, and

(c) The transport (diffusion) of the adsorbed particles to deeper layers of the adsorbent and/or a change in the state (bond) of the adsorbate on the surface of the adsorbent.

The transport of the adsorbate to the surface of the adsorbent is strongly dependent upon agitation of the solution. In many cases there exists a layer of solution on the surface of the adsorbent depending on the wettability of the adsorbent surface. The adsorbate molecule has to reach the adsorbent surface through this adhering layer. It has been observed that stirring intensity accelerates transport to the surface to a certain limit.

The factors to be considered relevant for the time dependence of adsorption are: the contact time of the solution, the age of the adsorbent (i.e., time interval between its preparation and the beginning of the adsorption) and the age of the solution. If there is a change in the state of the adsorbate molecule with the age of the solution or a change in some other properties of the solution important for adsorption, the adsorption kinetics and the final (equilibrium) adsorption values may be influenced\textsuperscript{100-103}. The age of the adsorbent may bring changes in the surface area, composition or structure of the adsorbent with time, thus influencing the adsorption.
1.6.4.8 PRESENCE OF FOREIGN IONS

Foreign ions if present in the solution may compete with the species being adsorbed\textsuperscript{104,105}. The effect of such impurities is much more pronounced when the concentration of the solution is low.

1.6.4.9 RATE OF ADSORPTION

One of the important aspects of applying adsorption for waste water treatment is to study the rate of adsorption. The process of adsorption in case of a solid-solution system involves three steps:

(i) Transfer of adsorbate species from bulk to solid surface through the aqueous film that surrounds the adsorbent

(ii) Diffusion through the pores, if adsorbent is porous, and

(iii) The uptake of the adsorbate species by the active surfaces, including formation of bonds between the adsorbate and adsorbent.

The last step is comparatively rapid as compared to others, because in case of non-porous adsorbent the equilibrium is attained within few minutes. Thus, the first and second steps are commonly considered as rate limiting steps. However, in rapidly stirred batch reactors, pore diffusion is often the rate limiting step\textsuperscript{69,70,106-109} and in case of continuous flow systems, the rate determining step is film diffusion\textsuperscript{110-116}.
1.6.5 ADSORPTION MODELS

An understanding of the mechanism of metal ions interaction with hydrous solid surface is essential for the control of heavy metals in the aquatic systems. Many adsorption models have been developed from time to time to describe the adsorption behaviour and to predict the extent of adsorptions in a certain system. The following are the common adsorption models employed:

1.6.5.1 THE ION-EXCHANGE MODEL

According to this model the trace metal ions are adsorbed when surface protons are displaced\textsuperscript{117,118}.

1.6.5.2 THE GONY-CHAPMAN-STERN-GRAHAME MODEL

This account for electrostatic and specific chemical reaction as major adsorption energies\textsuperscript{119-121}.

1.6.5.3 IONS-SOLVENT INTERACTION MODEL

This states that the adsorption energy includes electrostatic specific chemical reaction and solvation\textsuperscript{122}.

1.6.5.4 THE SURFACE COMPLEX FORMATION MODEL

According to this model, the specific chemical adsorption energy plays a more important role\textsuperscript{123-126} than the electrostatic energy and solvation energy.
1.6.6 CONTACTING SYSTEM AND MODES OF OPERATION

In order to provide an intimate contact between adsorbate and adsorbent for the effective removal of pollutants from wastewater, various experimental techniques have been employed by several coworkers. The contacting system may be mainly divided into two groups:

1. Batch adsorption
2. Continuous flow adsorption

1.6.6.1 BATCH ADSORPTION

In a batch adsorption operation the adsorbent is contacted with the liquid in a tank or vessel, provided with an agitation device, for a period of time. For most of the cases in batch type of system the rate has been found to be controlled by the pore diffusion i.e. the rate at which adsorbate is transported from the exterior to the interior sides of the adsorbents.

The time required to reach the equilibrium condition depends upon the particle size of the adsorbent, concentration of the solute, degree of agitation and amount of the adsorbent. To reduce the diffusional resistance inside the pores, the adsorbent is taken usually in powdered form giving increased surface area. After treatment for a fixed time, the adsorbent is separated from the fluid by setting, filtration or centrifugation and is then regenerated or discarded. It has been observed...
by Weber and Morris\textsuperscript{136} that the pore diffusion derives from the net action of several molecular forces such as adsorption, two dimensional micelle formation, three dimensional micelle formation, electrokinetic interactions and molecular diffusion.

1.6.6.2 CONTINUOUS FLOW ADSORPTION

In this type of operation the adsorbent is always in the contact of a fresh solution. The fresh adsorbent is added from the top and the spent adsorbent is withdrawn from the bottom. The wastewater is made to flow upwards through the vertical column containing the adsorbent. The continuous flow system can be steady state moving adsorber, unsteady state fixed bed adsorber or fluidized bed adsorber type. These have been shown in the Fig. 1.4.

1.7 AIM OF THE PRESENT WORK:

In the present investigations, the author has studied the removal of Methylene blue, Trypan blue, Crystal violet and Met omega chrome orange G.L. (M.C.O.) by adsorption technique with the help of suitable and easily available adsorbents such as Koalinite, coal, tobacco dust and treated rice husk ash due to the following reasons :-

(1) The selected dyes are commercial dyes, which are frequently used in woolen carpet industries. In the course of dying and washing processes reasonable amount of the dyes come into contact with water and soil, where may cause adverse effects on the living beings.
FIG. 1.4 ADSORBER CONFIGURATION
(2) These dyes are non-oxidizable by conventional biological waste water treatment processes, owing to their complex structure and larger molecular size.

(3) The adsorbents used in this work are koalinite, coal, tobacco dust and treated rice husk ash, which are cheap and easily available.

(4) The technique adopted here is simple and easy to handle.

(5) The removal of dyes by adsorption technique does not involve extra expenditure on sludge removal.

(6) A batch mode of operation has been employed here which helps the technologists in the design and fabrication of a treatment plant wherein the continuous removal of the pollutants could be possible.

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