Water Treatment Methods, Treatment of Industrial Wastes and Dumping of Radioactive Waste

BSC (H) CHEMISTRY SEMESTER-VI

INDUSTRIAL CHEMICALS AND ENVIRONMENT

TREATMENT OF DOMESTIC WASTEWATER

The composition of municipal sewage depends largely on the wealth and habits of the municipal population and the amount and nature of industrial waste waters added to the domestic sewage. Sewage treatment processes are designed to remove oxygen-demanding organic wastes, suspended and dissolved solids and bacteria. The treatment processes are generally divided into three categories, *viz*.

l. Primary Treatment processes

2. Secondary Treatment processes

3. Tertiary Treatment Processes

l. Primary Treatment Processes:

Primary treatment processes involve removal of grit, screening, grinding, flocculation, sedimentation and skimming.

- Systems for **grit** removal and **screening** are designed to remove the larger suspended or floating materials such as rags, paper, twigs, wires, roots, glass and other matter. The materials removed by screening are incinerated or buried.
- **Flocculation** is carried out by agitating waste water by mechanical stirrers or air injection. This causes small-suspended solids to collide and form bigger aggregates, which settle down more rapidly.
- **Sedimentation**. i.e., removal of suspended solids by gravitational settling is carried out in large basins having a continuous flow with detention time of 4-6 hours.
- Specific wastes from industrial sources are subjected to removal of oil or grease in a skimming tank, neutralisation of excessive alkalinity or acidity and precipitation or ion-exchange treatment for heavy metals

2. **Secondary Treatment Processes**: Secondary treatment processes include the use of biological methods employing trickling filters and activated sludge plants The use of both the techniques is described below:

Use of Trickling Filters: Trickling filters comprise of beds of crushed stone imbedded with biological slimes. Waste water is allowed to percolate through these beds when the organic matter present in waste. Water gets adsorbed on slimes and undergoes decomposition by bacteria and fungi present in the slimes. When the slime layers become very thick they slough off and can be easily removed.

Activated Sludge Process: This process involves continuous circulation of biologically active growths through waste water in the presence of oxygen supplied as fine bubbles of compressed air. The suspended and dissolved organic wastes, well aerated and mixed, undergo adsorption, flocculation, oxidation and biological degradation. After a few, hours, the sludge is transferred to sedimentation tanks and allowed to settle out. A part of the sludge which is not rich in organisms, is used to seed the next batch of waste from the primary settling tanks. The activated sludge performs two functions:

l. It clarifies the water by adsorbing most of the colloidal and suspended solids on the surface of sludge particles.

2. It causes oxidative degradation of the organic matter present in waste water.

The sludge from secondary treatment plants is disposed off in several ways. A common method consists in digesting the sludge in circular digesters 6-10 metre deep which are maintained at a temperature of about 35 ºC. During digestion the organic matter is eventually reduced to gases consisting of about 70% methane and 30% CO_2 with small amounts of NH_3, H_2S, H_2 and N_2. Methane is recovered and used as fuel for heating the digester. After digestion for a few weeks, the sludge gets converted into a stable humus material which is used as a soil conditioner.

Other sludge-handling methods are: (i) Dewatering on sand beds (ii) Vacuum filtration and (iii) centrifuging.

- **Dewatering on sand beds** is carried out by filtering water through sand beds and evaporating water from the sludge surface.
- **In vacuum filtration**, a horizontal drum covered with suitable filter media is partially submerged in wet sludge. Vacuum is applied on the inside to extract water out of the wet sludge into the drum which is constantly rotated. The sludge which forms a layer on the drum is scrapped off.
- Centrifuging is generally applied for dewatering paper-mill wastes, packing-house wastes, foundry sludge's, water softening and refinery sludge's. The dewatered sludge is then disposed off in two different ways :
- A common procedure is to incinerate the dried sludge. The sludge itself furnishes sufficient heat to maintain combustion. This process, however, can lead to air pollution.
- An alternative to incinerate is composting which permit recovery of some of the organic matter and plant nutrients of the sludge.

3. **Tertiary Treatment Processes: Advanced Waste Water Treatment Processes:**

These processes aim at improving the waste water quality to the point at which it can be reused. The increasing costs of water supplies and the increasing emphasis on waste water quality are leading engineers to devise methods for total recycling of decontaminated water. Some common advanced waste water treatment processes are as follows:

Chemical Coagulation and Filtration:

- In this process, the waste water is treated with chemical coagulants such as alum, ferric sulphate, ferric chloride, etc., as a result of which the suspended matter gets coagulated to form flocs. In recent years, a number of-synthetic, high-molar mass water-soluble polymers have been developed as highly effective coagulants. One such coagulant is 'calgon *viz.*, polydialkyldimethyl ammoniurn chloride.
- The flocs are filtered with the help of sand, diatomaceous earth or several other multimedia filters.
- Micro screens can also be used for this purpose.

Adsorption:

- The waste water is treated with activated carbon which is a porous and highly adsorbent form of carbon with a large surface area. This treatment because of adsorption eliminates materials responsible for undesirable tastes and odours.

Chemical Oxidation:

- Waste water treatment can also be carried out by using strong oxidants such as ozone, hydrogen peroxide, chlorine and chlorine dioxide. However, oxidants do not eliminate the dissolved inorganic compounds which are present in waste water even after secondary treatment.
- These compounds are removed by ion-exchange, electrodialysis and reverse osmosis.

Ion Exchange:

- Ion exchange can be carried out by using ion exchange resins. Cation-exchange resins exchange their H^+ ions for metallic cations present in waste water whereas anion-exchange resins exchange their OH^- ions for chloride and other anions present in water. The resins are conveniently regenerated by treatment with sulphuric acid for cationic resins and sodium hydroxide for anionic resins. Ion exchange process is highly effective and produces high quality water.

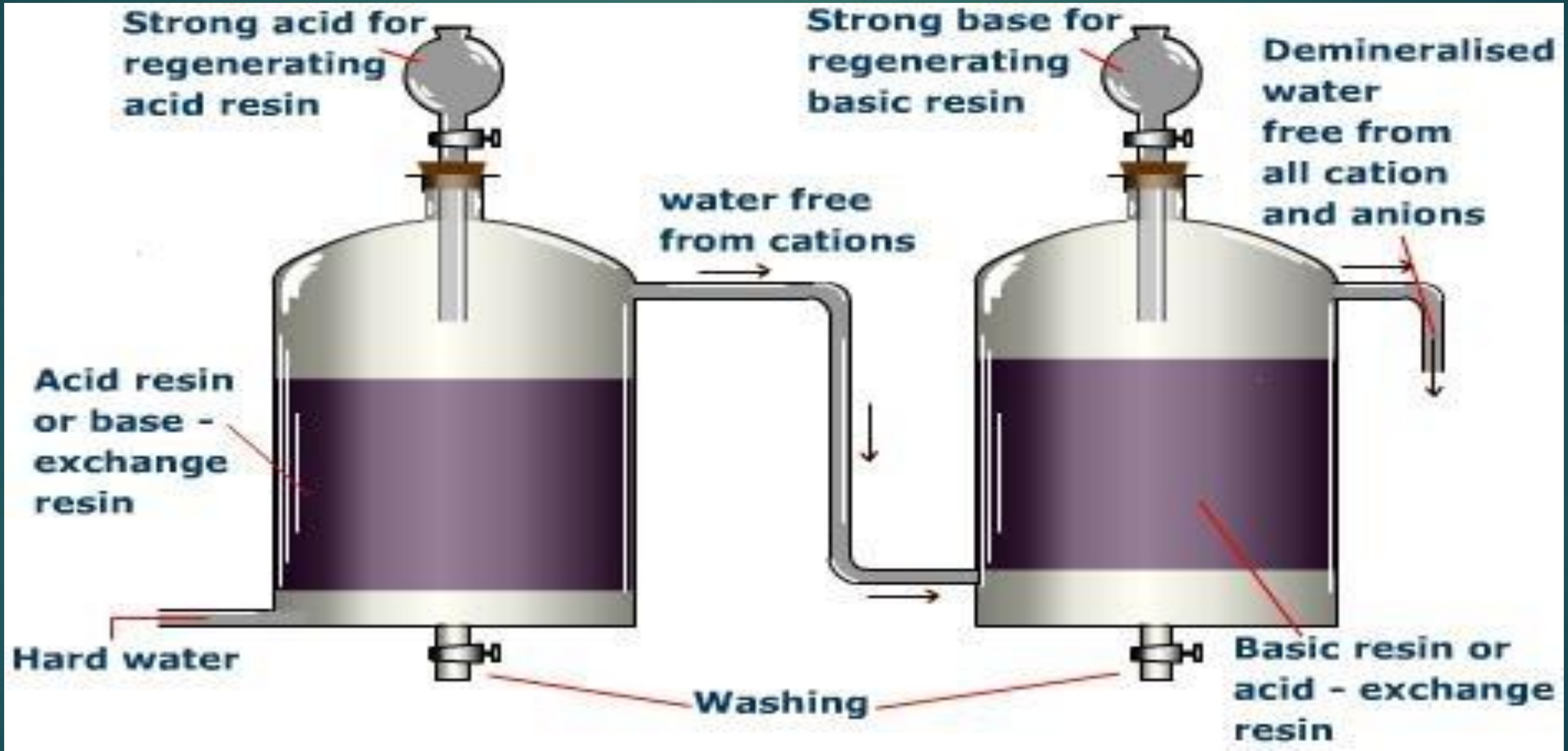


Fig: Diagrammatic representation of Ion-exchange purification of water.

Electrodialysis:

In this process, the waste water is exposed to an electrical potential difference in big tanks which are fitted with membranes consisting of sheets of ion-exchange resins. These sheets are permeable to only cations or only anions. The anions and cations present in waste water thus migrate through the membranes towards the anode and the cathode, respectively. Electrodialysis does not eliminate the organic matter from the waste water.

Reverse Osmosis: In this process, waste water is separated from fresh water by a semipermeable membrane (SPM) which is permeable to water but not to the dissolved materials. Pressure considerably higher than the osmotic pressure of waste water is applied on the waste water as a result of which pure water is forced to the other side of the membrane (Fig. 4). This process is known as reverse osmosis (RO). It eliminates organic as well as inorganic matter from the waste water.

The rate of flow of water Q_w through the SPM is given by

$$Q_w = \{(\Delta P - \Delta \Pi)\, \chi_w A/\delta$$

where

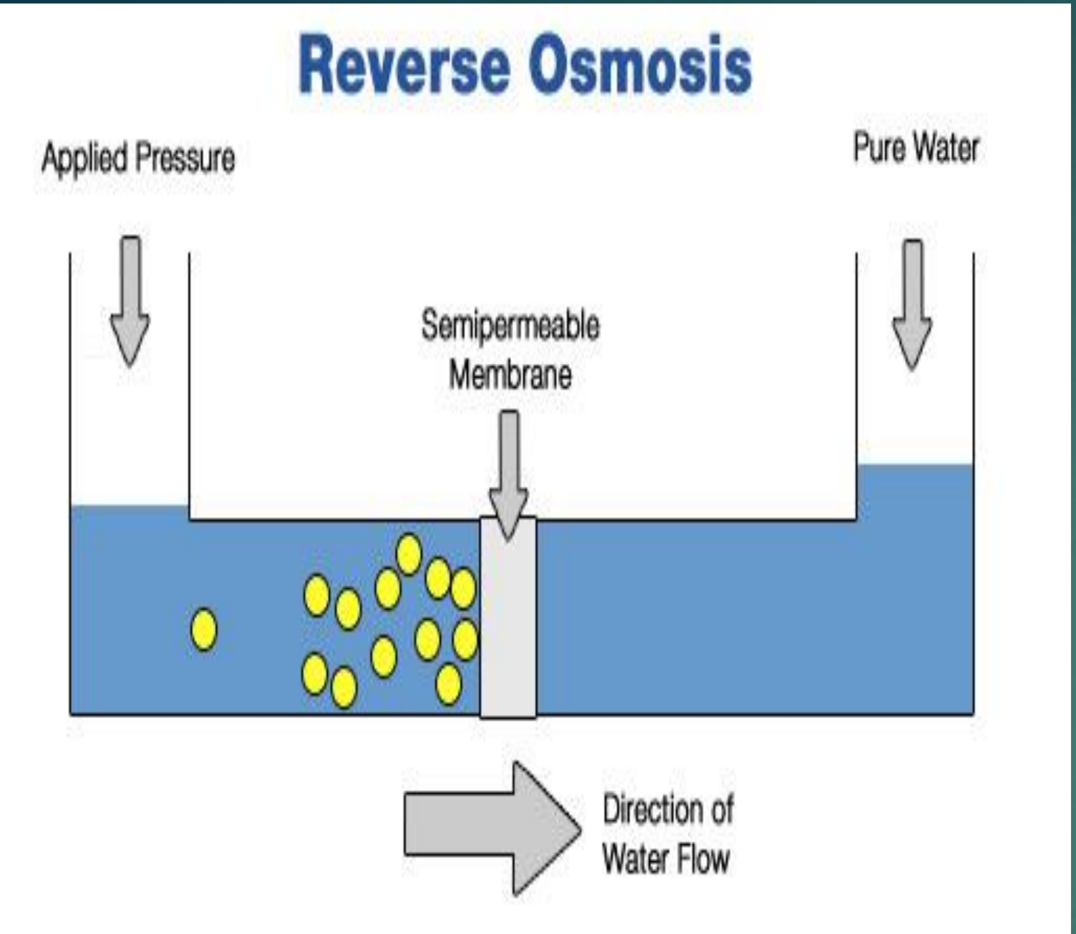
ΔP = Hydraulic pressure differential across the membrane

$\Delta \Pi$ = Osmotic pressure differential across the membrane

χ_w = Membrane permeability coefficient for water

IA= Membrane area

δ = Membrane thickness



Depending upon the salt concentrations, the osmotic pressures of domestic waste waters are considerably high. This implies that for effective treatment of the waste waters, the pressures to be applied for reverse-osmosis are considerably high. For quite some time, it was a problem to have commercial semipermeable membranes which could withstand such high pressures. These days, however, the problem of this availability of such SPMs has been completely solved. SPMs for RO were first obtained in later 1950s from cellulose acetate. But their use in RO was impractical since, being dense, they permitted very low flow rates. A few years later, techniques were developed for the fabrication of cellulose acetate membranes with asymmetric density. By using proper casting-solution composition and proper casting and quenching conditions, it has been now possible to prepare cellulose acetate membranes with thin 0.l-1.0 µm surfaces (termed as 'skin' of the membranes) supported by porous cellulose structures.

These membranes permit high water flow rates since the rate-determining factor for water transport is only the thickness of the skin of the membrane which is now evidently very small. Still better semipermeable membranes have recently been obtained from aromatic polyamides.

Industrial Waste Water: Its Contamination and Treatment

Industrial waste water is invariably contaminated, the nature of contaminants depending upon industries from which the waste water is obtained.

Waste Water from Food Processing Industry

- Food processing units such as beat sugar refining, brewing, distilling and canning, etc., dealing with meat and dairy products, yield waste water which contains high content of decomposable organic matter which leads to heavy oxygen depletion.
- The dairy industry produces organic wastes high in protein, fat and lactose. The beet sugar refining industry produces wastes which have a high biochemical oxygen demand (BOD).
- Breweries and distilleries produce organic solids including fermented starches.
- The processing of to produce canned or frozen products leads to large amounts of wet solids.
- The wastes from meat processing industry are associated with blood proteins, feathers and other organic wastes and so on.

Waste Water from Textile Industries

- The waste water from textile mills is generally alkaline and has a high biochemical oxygen demand. The textile wastes arise from impurities in the fibres and from the chemicals used in processing, *viz.*, cooking the fibres, desizing the fabrics, etc.

Waste Water from Paper and Pulp Industries

- The effluents from paper and pulp industry contain chemicals used in the craft process, bits of barks, wood chips, cellulose fibres and dissolved lignin. About 50 % of the wood used as input is eventually discharged as waste material. The effluents contain materials which are toxic to fish and shell fish.

Waste Water from Chemical Industries: The waste water from chemical industries is very heavily contaminated. Chemical plants manufacturing acids, bases, pesticides, synthetic fibres, detergents and many other organic and inorganic compounds produce wastes which are associated with wide variety of contaminants numbering into thousands many of which are highly toxic.

Waste Water from Petroleum Industry: Waste water from oil drilling includes drilling muds brine pumped out of the well along with crude oil and some oil as well. Oil refineries and petrochemical plants yield a large number of contaminants such as hydrocarbons, alkalies, cyanides, numerous sodium salts, phenolic compounds, inorganic and organic sulphur compounds and halogenated hydrocarbons. Many of these compounds generate undesirable odours and tastes and many of cause fish flesh to acquire adverse taste.

Waste Water from Metal Industries: Steel mills produce waste water blast furnace flue gases and pickling of the steel. These wastes contain phenol, cyanogen, coke, lime stone, mill scale and fine suspended solids. The waste water may also contain metals such as Cr, Pb, Ni, Cd, Zn, Cu, and Ag as well acids, alkaline cleaners, grease and oil. Waste water from metal-plating industry is highly toxic on account of the presence of metal cyanides.

Waste Water from Other Industries:

Waste water from other industries is associated with a wide variety of contaminants. For instance leather tannery wastes contain high content of solids, salts causing hardness, sulphides, chromium salts and lime. These wastes have high biochemical oxygen demand (BOD). Radioactive wastes originate from nuclear power plants and research laboratories using radio isotopes. Soft drinks bottling plants produce highly alkaline wastes with high BOD from the washing of bottles, which involves removal of cigarrete butts, paper and other debris left in bottles by previous users. Laundries have turbid wastes that are alkaline and contain organic solids, and so on.

Treatment of Industrial Waste Water:

It is evident from the above discussion drat if industrial waste water is discharged into lakes, rivers or oceans as such, it would cause severe pollution. The waste water thus has to be treated properly before it can be disposed off. Most of the water treatment methods used by industries are in general the same as used for the treatment of municipal waste water. However, some specific treatments have been used with advantage in specific cases. For example, while biological treatments are more suited for wastes and food industries, chemical treatments have worked for wastes ir.om metal-plating industries.

Since large amounts of water are required by many large industries, there is great emphasis on subjecting industrial waste waster to advanced treatments, *viz*., tertiary treatments, to render the water suitable for reuse. These treatments are essentially the same as carried out in the case of municipal waste water.

Dumping of Urban Solid Waste: The urban solid waste contains domestic waste, garbage, plastics, glasses, metallic cans, rubble, burnt up fuels, discharged articles of domestic use, etc. In cities like Delhi, Mumbai, Calcutta, Kanpur, etc., 3000 to 4000 tons of solid refuse is collected from houses, streets and roads and dumped into landfills every day which causes pollution of land. The problem is even more acute in big cities of developed countries. New York alone throws around 30,000 tonnes of solid urban waste into its already choked landfills. Urban domestic wastes are not biodegraded easily. In addition, the slimy water oozing out of the dumping sites of urban waste is extremely toxic as it emits poisonous gases due to anaerobic decomposition of organic matter. Apart from this, the water harbours many disease-causing bacteria. The excreta of dairy animals harbour extremely harmful bacteria and viruses, which ultimately enter the soil from where they infect animals and human beings.

In view of the above hazardous effects, several measures are taken to dispose off the urban solid waste and thus avoid its dumping into the landfills. Some of these measures are discussed below:

(i) **Recycling of Reusable Waste**: Waste-paper rags and cotton waste are separated and converted into card-board and low-grade paper. In recent years. New techniques have been developed to convert the above wastes into document paper, album paper and even high-grade stationary. Japan recycles about 40% of its waste-paper to obtain new high-grade paper. It has been estimated that recycling of one tonne of waste-paper saves 16-17 trees from the axe.

Waste plastic articles are extremely stable and do not biodegrade. Polythene, polyethene tetraphthalate (PET) and PVC, etc., are recycled to yield low quality plastics which are used in making plastic toys, hard low-grade slippers, buckets, cans, etc.

Tin cans, scrap iron, etc. picked up from urban wastes are recycled to get iron.

Similarly, glass and glass articles picked up from urban waste are recycled to manufacture low grade glass for bottles.

Urban authorities in developed countries have started putting separate garbage bins for collecting different types of wastes. These are, thus, separate bins for papers, plastics, metals, glass, etc.

(i) **Bioremediation of Waste**: The solid municipal waste which is rich in organic matter is subjected to biodegradation with the help of genetically engineered bacterial strains resulting in useful manure. Effects are being made to synthesise plastics which can be degraded common microbes. The farm waste consisting of cattle dung is converted into biogas with the help of a variety of bio- organisms. The main constituents of biogas are methane, CO_2. The residual slurry from biogas plants is a very good manure.

In small towns and villages, the human waste is disposed off in pour flush toilets which are linked to biogas plants. About a lakh of such toilets are linked with biogas units in several states in the country such as Maharashtra, West Bengal and Gujrat. The biogas produced is utilized for cooking purposes and residue is used as manure.

(iii) Incineration: The technique involves burning of solid waste at high temperature (>2000 ºC) in incinerators. The bulk of the solid waste is reduced to a small volume of ash and the heat generated is utilised for raising steam for turbines. For incineration to be successful it is essential that the waste contains enough burnable material so that the smoke produced is minimum. Incineration is, of course, a costly process and requires high technical know-how to burn almost the entire waste without causing air pollution. If the solid waste contains materials such as plastics, papers, synthetic polymers, etc., their combustion produces toxic vapours. Therefore, as for as possible such materials should be sorted out of the solid waste.

Dumping of Urban Waste in Landfills: The low lying untilled and uninhabited land can be used for dumping urban waste however, the most commonly anticipated danger in unscientific dumping of urban waste in landfills is the contamination of the soil of the landfills with toxic constituents of the waste. Also the dumping sites becomes the breeding grounds for several disease-spreading microbes.

Now-a-days, the urban waste is dumped in landfills by controlled tipping process. In this process, the waste is spread on the ground and is compactly pressed by bulldozers into a layer about l0 cm thick over which a layer of soil is laid. Piling of many such compressed layers of waste and soil can slowly convert a low lying patch of land or a dried unusable lake into a park, play ground or an area for raising buildings. The compact clay layer spread over the compressed urban waste checks the escape of gases which result from the decomposition of the waste. The unwanted gases are removed from the landfills with the help of special techniques.

Dumping of Industrial Waste: A large number of industries generate huge quantities of industrial wastes which pollute the soil. In some industries, as much as half of the raw material becomes a waste. Many industrial effluents are dumped into the surroundings which in the long run pollute the soil because the chemicals present in the waste are absorbed by the soil. This alters the chemical and biological properties of the soil. The toxic chemicals absorbed by the soil enter the animal food chain through paints grown on the polluted soil which may cause serious biological disorder in animals and human beings.

It is to be noted that both biodegradable and non-biodegradable parts of industrial wastes pollute the soil. For instance, the biodegradable wastes from food processing units contain nitrogen, phosphorus and other micronutrients. The dumping of such wastes may increase the nitrate concentration in the soil which, as already mentioned, it as an adverse effect on the fertility of soil. The high nitrogen and phosphorus

content causes excessive growth of weeds growing under water which leads to choking of aquatic life.

A number of industries such as textile, pesticides, paints, dyes, soaps, detergents, tanneries, drugs, rubber, petroleum, paper, sugar, steel, glass, electroplating and chemical industries pour their hazardous effluents containing a variety of harmful chemicals into the soil, creating disastrous effects on biological systems. Some industries discharge their effluents containing inorganic salts such as $CaSO_4$, $CaCO_3$, $Ca(HCO_3)_2$, etc., on the soil. This makes the soil unproductive. The metallic contaminants in industrial wastes (such as Hg^{2+}, Pb^{2+}, Zn^{2+}, Al^{3+}, Cd^{2+}, Cr^{3+}, Na^{+}, Cu^{2+} etc.) destroy useful bacteria present in the. soil. The wastes from chemical industries also change the pH of the soil which affects the productivity of the soil.

Industrial sludges cause much greater soil pollution than the solid industrial waste because the hazardous chemicals in the sludges seep into the soil more easily. The composition of an industrial sludge varies with the type of industry which produces the sludge. For example, in the, coal fired power plants, a stirred slurry of lime stone is used for trapping SO_2 from the escaping flue gases. Apart from SO_2 the slurry also absorbs harmful and toxic volatile elements thrown out by the burning coal. Thus, when flue gases are passed through the lime slurry, As, Se, Hg, Cd, etc.- also get trapped.in the slurry. Such a slurry which is known as FGDS (Flue Gas Desulphurisation Sludge) pollutes the soil immensely. The toxic metals of the waste sludge get absorbed by the soil and from the soil they enter plants and from plants they enter animals and human beings. It is thus very essential that the industrial waste be treated to make it free from the hazardous chemicals. Since each industry produces it own typical industrial waste, each type of industrial waste has to be treated separately.

Dumping of Radioactive Waste:

The radioactive fallout from nuclear explosions consists of radioactive particles which fly into the atmosphere during explosion and the dust of the crater. All these particles eventually settle down on earth's surface. They comprise of both the longer-lived radio elements such as ^{137}Cs, ^{141}Ce, 90Sr, ^{147}Pm, ^{151}Sm, etc. and the shorter lived elements such as ^{131}I, ^{132}I, etc. The shorter-lived radio-elements deposited on the soil are comparatively less harmful since they decay to normal isotopes of the elements within a short duration. The longer-lived radio-elements, on the other hand, are very harmful since they retain their identity for a long time and emit alpha-particles as well as gamma radiations. The gamma radiations are highly penetrating-and cause mutation of biological cells by disrupting the molecule which come in their path. Thus, water molecules of the cells get dissociated into ions (H^+ and Cl^-) and free radicals (such as H and OH radicals). The ionic species deactivate the enzymes as a result of which the cell growth and cell multiplication may stop. Similarly, the free radicals being highly reactive, react with protein molecules in the living cell setting a chain of events which destroys the living cells or makes them function abnormally. The alpha particles emitted from the radioactive fallout may damage or break DNA molecules. The broken parts of DNA of molecules recombine producing modified DNA molecules which have scrambled genetic code. The modified DNA molecules generate cancerous cells.

The radioactive ^{90}Sr and ^{137}Cs enter plants through soil. From plants they enter grazing animals and from to man through animal milk or meat. ^{90}Sr replaces Ca from bones once it enters the body through food. Similarly, ^{137}Cs replaces K from the living cells. These replacements produce highly damaging effects.

It would be very hazardous if the radioactive waste recovered from nuclear power plants and nuclear reactors is dumped as such into the soil. The waste is, therefore, subjected to specialised chemical and electrochemical treatments to eliminate the unreacted ^{235}U and the nuclear by-product ^{239}Pu so as to bring down the radioactivity to as a low level as possible and the residual waste is then stored in underground thick steel containers which are further protected by a thick covering of concrete. The method, however, is not completely safe because even the strongest steel tanks may get corroded with the passage of time.

An alternative technique for disposing off the nuclear waste obtained from nuclear power plants and nuclear reactors with high and intermediate levels of activity is in the offing. In this technique, the radioactive waste is “imprisoned” in crystalline structures of some special types of synthesised materials which are practically insoluble in water. These crystalline materials are capable of imprisoning the radioactive waste are enclosed in nickel-iron alloy containers which are inserted into holes made in granite rocks. These rocks are then dumped deep into the earth.

It was previously thought that low activity (0.01µCi litre) radioactive aqueous solution resulting from radio therapeutic treatments being given in hospitals were reasonably safe and thus could be discharged into surface water. However, recent studies have shown that the radio isotopes eventually get concentrated and contaminate-sea weeds, oysters and fish.

References
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