**Environmental Chemistry**

**Introduction**

Environmental Chemistry deals with the origins, transport, reactions, effects and fates of chemical species in the water, air, terrestrial and living environments. It overlaps with different branches of chemistry such as organic chemistry, analytical chemistry, physical chemistry, photochemistry, geochemistry and biological chemistry and also includes many widely different fields such as physics, life sciences, agricultural sciences, medical sciences, public health and sanitary engineering.

**Environment:**

One’s surroundings including all of the living and non living factors that act on an organism, population or ecological community and influence its survival and development is called environment. Or The physical and biological habitat that surrounds us and can be felt by our physical faculties.

**Components of environment:**

1. ***Abiotic component:***

All non living components that influence us in any manner are called abiotic components. They can affect us in terms of growth, maintenance, reproduction etc. Examples are temperature, light, moisture, water levels, carbon dioxide levels, pH of water and soil, etc.

1. ***Biotic component:***

It is any living component that effects the environment of other organism and has any effect on it. All species are influenced by biotic factor in any way like increase in pathogens and disease outbreak can decrease the population number.

**Environmental Segments:**

The environment consists of various segments such as atmosphere, hydrosphere, lithosphere and biosphere. Before explaining the chemistry that is taking place in these segments one by one, a brief out line about their importance will be discussed.

***Atmosphere:***

The following points highlight the vital role played by atmosphere in the survival of life in this planet.

• The atmosphere is the protective blanket of gases which is surrounding the earth. It protects the earth from the hostile environment of outer space.

• It absorbs IR radiations emitted by the sun and reemitted from the earth and thus controls the temperature of the earth.

• It allows transmission of significant amounts of radiation only in the regions of 300 – 2500 nm (near UV, Visible, and near IR) and 0.01 – 40 meters (radio waves). i.e it filters tissue damaging UV radiation below 300 nm.

• It acts as a source for CO2 for plant photosynthesis and O2 for respiration

• It acts as a source for nitrogen for nitrogen fixing bacteria and ammonia producing plants.

• The atmosphere transports water from ocean to land.

***Hydrosphere:***

The hydrosphere is a collective term given to all different forms of water. It includes all types of water resources such as oceans, seas, rivers, lakes, streams, reservoirs, glaciers and ground waters. The distribution of earth's water supply is shown in fig 1.

***1% Fresh water, 2% Polar Ice caps, 97% Ocean high salt content Unusable for human consumption***

**(Fig 1 Distribution of earth's water supply)**

As can be seen, only 1% of the total water supply is available as fresh water in the form of rivers, lakes, streams and ground water for humanconsumption and other uses. The extent of the use of available fresh water for various purposes is shown in the following figure 2.

***50% Thermal power plants , 30% Irrigation, 13% Industrial water uses uses, 7% Domestic uses***

**Fig 2 Major use of fresh water**

The major problem with global water supply is it’s non-uniform distribution, since people in areas with low precipitation often consume more than people in regions with more rainfall.

**Lithosphere:**

• The earth is divided into layers as shown in fig3:

***Length 40 Km, Crust, Upper mantle, Lower mantle, Outer core, Inner core***

**Fig 3 Layers of eart**

• The lithosphere consists of upper mantle and the crust. The crust is the earth’s outer skin that is accessible to human. The crust consists of rocks and soil of which the latter is the important part of lithosphere.

**Biosphere:**

• The biosphere refers to the realm of living organisms and their interactions with the environment (VIZ: atmosphere, hydrosphere and lithosphere)

• The biosphere is very large and complex and is divided into smaller units called ecosystems.

• Plants, animals and microorganisms which live in a definite zone along with physical factors such as soil, water and air constitute an ecosystem.

• Within each ecosystems there are dynamic inter relationships between living forms and their physical environment These inter relationships manifest as natural cycles. (hydrologic cycle, oxygen cycle, nitrogen cycle, phosphorous cycle and sulphur cycle),

• The natural cycles operate in a balanced manner providing a continuous circulation of essential constituents necessary for life and this stabilizes and sustains the life processes on earth.

**The structure of atmosphere**

**A**tmosphere plays important life in sustaining life on earth. The oxygen is important for respiration. Nitrogen is important as plant materials are made up of nitrogen compounds. Plants can absorb carbon dioxide and release oxygen. Moreover atmosphere protects us from UV radiation. The atmosphere is broadly divided into four major zones:

1. Troposphere

* It is the region near earth surface ( 0-11 Km) and contains 70 % atmospheric mass.
* Temperature decreases with height e.g.15 to -56 oC. Decrease in tem with height is called lapse rate which is positive.
* Composition of gases is almost homogenous through out.
* 99% of water vapours of atmosphere is present in this region.
* The transition layer between troposphere and stratosphere is called tropopause.

1. Stratosphere

* It is the region above the troposphere (11-50 Km).
* It is relatively warmer region and temperature increases with height, so it has a negative lapse rate.
* Presence of Ozone layer protects from UV radiation, absorbance of which cause an increase in temperature. NO clouds can enter this layer.

1. Mesosphere:

* It is the region above stratosphere (50-85 Km).
* The temperature decreases with height so it has a positive lapse rate.
* Absence of ozone or other UV absorbing medium cause a decrease in temperature.

1. Thermosphere:

* It is the region above mesosphere (85-500 Km). The temperature increases with increase in height and reaches a maximum of 1200 degree Celsius.
* Very small molecules of any gases like oxygen or nitric oxide present in this region absorb solar radiation and ionize.

**Natural Cycles Of The Environment:**

The cyclic movement of nutrient materials between the biotic and abiotic environment is called biogeochemical cycle. Most important and common cycles are given below:

***Hydrologic cycle:***

The hydrologic cycle involves a continuous exchange of water between sea, atmosphere, land and living animals through massive evaporation of water from the ocean, cloud formation and precipitation as outlined in figure 4, and in the following paragraph.

Cloud, Transpiration, Precipitation, Plants Runoff, Lake, Ground water, Evaporation, Sun, Ocean, Evaporation, Cloud

Hydrological cycle consists of evaporation, transpiration from plants, precipitation , surface run off and ground water movements.

**Fig 4 Hydrologic cycle**

1. Evaporation:

The land surface and water surfaces on earth lose water by evaporation by solar energy. This evaporated water cools and condense to form clouds.

1. Precipitation:

* Couds on further cooling drop down in liquid form or snow or hail. This is the major source of fresh waterfor living beings.

• Normal evaporation of water from ocean exceeds precipitation by rain into seas by 10% .

• This 10% excess which precipitates on land balances the hydrological cycle.

1. Water over and through the ground:

* Some of the precipitated rain seeps into the soil as ground water.

• Ground water moves up by capillary action and there by maintains a continuous supply of water to the surface layer of soil.

1. Transpiration:

* The water from the surface layer of the soil is absorbed by plants, which in turn is returned to atmosphere through transpiration.

• Surface water or runoff flows into streams, rivers, lakes and catchment areas or reservoirs.

• Animals also take water which is also returned to the atmosphere through evaporation.

• Thus there is always a balanced continuous cycling of water between earth’s surfaces and atmosphere.

***Oxygen cycle:***

The exchange of oxygen between different segments of the environment such as atmosphere lithosphere, hydrosphere and biosphere is shown in fig 5.

**Fig 5 Oxygen cycle**

The importance of oxygen in atmospheric chemistry, geo chemical transformation and life processes is outlined in the following paragraph.

• Atmospheric oxygen contributes largely to the processes on the earth’s surface. Atmospheric oxygen participate in energy producing reactions such as burning of fossil fuels,

CH4+O2----------CO2+H2O (In natural gas) .

• Atmospheric oxygen is utilized by aerobic organism in the degradation of organic material

[CH2O] +O2 ⎯⎯⎯⎯⎯→ CO2+ H2O

• Oxygen is consumed by some oxidative weathering processes of minerals

.........................................................................(3) FeO +O2 → 2Fe2O3

• Photosynthesis by plants return the oxygen to the atmosphere.

CO2 +H2O (plants) ⎯⎯⎯⎯→ CH2O + O2

• A form of oxygen containing species O3 occurring in the rarified region of the atmosphere (stratosphere) absorbs harmful UV radiation and serves as radiation shield.

• All the molecular oxygen now in atmosphere is thought to have originated through the action of photosynthetic organisms, which shows the importance of photosynthesis in the oxygen balance of atmosphere.

***Nitrogen cycle:***

Nitrogen cycle refers to the incorporation of N2 from the atmosphere into living matter and chemically bound nitrogen in soil, water and then back into the atmosphere again.

Atmospheric nitrogen is unable to absorb directly by living things. So the atmospheric nitrogen is converted into water soluble nitrogen compounds, called nitrates, by a process called nitrogen fixation and then absorbed by plants to form proteins.

Nitrogen fixation:

Nitrogen fixation can be of two types:

* Non biological fixation by electric sparks of thunder storms or fertilizer manufacturing.
* Biological fixation by bacteria, algae, yeast.

In this step the atmospheric nitrogen is chemically bound to form ammonia by bacteria and algae.

3(CH2 O) + 2N2 + 3H2 O + 4H+ → 3CO2 + 4NH4 +

(bacteria and algae)

These organisms are capable of catalysing the conversion of atmospheric nitrogen into forms usable by plants.

**Nitrogen back to atmosphere**

Nitrogen gets back into atmosphere by following ways:

Ammonification

Excess of the protein in the animals body is broken down to urea, uric acid or ammonia which passes out through urine. Proteins of dead anmals and plants also decompose by dcomposers into ammonia.

Nitrification:

The ammonia in the soil is oxidized by nitrosofying (nitrosomonas) nitrifying (nitrobactor) bacteria into nitrates which can be used again by plants.

It is the conversion of N(-III ) to N(V) catalysed by Nitrosomonas and Nitrobacter

2O2 + NH4+ → NO3- + 2H+ + H 2O

Ammonium ion present in water or soil is subjected to oxidation in an aerobic environment. The optimum pH for nitrification is between 6.5 and 8, and the reaction rate decreases significantly when the pH falls below 6. Nitrification is important in nature, since nitrogen is absorbed by plants primarily as nitrate. Even when nitrogen is applied in the form of ammonium salts as fertilisers, the ammonia is microbially oxidized to nitrate so that it can be assimilated by plants

Denitrification:

In this process nitrate ions are reduced into gaseous nitrogen (NO2 and N2) which returns to atmosphere. There are several types of denitrification reactions. The process involves several steps. A number of heterotrophic bacteria including species of Pseudomonas mediate these processes. In this process N2 gas is produced from chemically fixed nitrogen

4NO3- + 5{CH2 O} + 4H+ → 2N2 + 5CO2 + 7H 2O

By this natural microbial mediated process N2 gas is returned to the atmosphere. By all these processes the nitrogen cycle is balanced and thus the N2 concentration in the atmosphere is relatively kept constant.

**Phosphorous cycle:**

• For the growth and maintenance of animal bones and teeth phosphates are necessary.

• Organophosphates are essential for cell division involving the production of nuclear DNA and RNA.

• The major inorganic phosphorous includes soluble and H2 PO4- and HPO4-2 and insoluble Ca5(OH)(PO4)3, Fe3(PO4)28H2O.

• Terrestrial plants absorb inorganic phosphate salts from the soil and convert these into organic phosphate.

• Animals obtain their phosphate by eating plants.

• Plants and animals after their death return the phosphate to the soil.

• The microorganisms present in the soil convert them into soluble inorganic phosphate, a process known as mineralisation or biodegradation.

• Biodegradation also deactivates highly toxic organophosphate compounds, such as phosphate ester insecticides.

• In water phosphorous solubility is controlled by the availability of iron and aluminium under acid conditions and calcium under alkaline conditions; each of these metals form insoluble phosphates. When the pH is slightly acidic, phosphorous has its maximum solubility and under these conditions is the predominant species. H2PO4-

**Sulphur cycle:**

In the atmosphere, oxidation reactions convert lower oxidation state species into sulphate. In hydrosphere and soil, sulphur is present in many inorganic and organic forms exhibiting oxidations states from -2 to + 6. The sulphur cycle involves interconversion among a number of sulphur species. The major microbially mediated process in this cycle are the following.

Sulphate reduction to sulphide by bacteria such as desulfovibrio:

In an organic rich reducing aqueous environment, sulphate is readily reduced to species in the -2 or less commonly, zero oxidation states:

SO4-2 + 2{CH2 O} + 2H+ → H2S + 2CO2 + 2H2 O

The toxic and odiferous H2S may cause serious problem with water quality.

Sulfide oxidation by bacteria such as thiobacillus :

Sulphide is unstable under aerobic conditions and is easily oxidised via a variety of pathways. The sulphide might have been formed during the decomposition of organic matter or might have been present as sulphide mineral in the sediment or soil.

2H 2S + 4O2 → 4H+ + 2SO42-

The acid tolerant sulphur-oxidising bacteria thiobacillus produce and thrive in, environmentally damaging acidic waters, such as acid mine water. The reaction simultaneously produces hydronium ions and is thus an acidifying process.

Degradation of organic sulphur compounds:

The degradation of sulphur-containing organic compounds by bacterially mediated processes can result in the production of strong- smelling noxious H2S and other volatile organic sulphur compounds such as

methyl thiol CH3SH and dimethyl sulphide CH3SSCH3. Thus the above reactions give a brief outline of the major microbially mediated processes in the sulphur cycle.

Before going into the details of the various sections of Environmental Chemistry, it is essential to understand the following terms, which will be used often in the course of our discussions

Commonly Used Terms:-

Pollutant:

If the concentration of a substance already present in nature is increased to unrequired ratio due to human activity, which ultimately has a detrimental effect on the environment either by reducing the quality of life or affecting the health then it is known as a pollutant. For example, sulphur dioxide,

carbon monoxide, lead, mercury, excess heat, sound etc. are all called as pollutants.

Contaminant:

A contaminant is a substance that does not occur in nature, but is introduced by human activity into the environment. A contaminant is called a pollutant when it exerts detrimental effect on human health. It is also a pollutant.

Receptor:

A receptor may be any thing which is affected by the pollutant. For example,man is a receptor of contaminated water because cholera and gastroenteritis are caused by it.

Sink:

It is the medium, which interacts and retains the long lived pollutant. The oceans are the sinks for atmospheric carbon dioxide. Ground water and subsoil water act as sinks for pesticides employed in agriculture.

Dissolved Oxygen (DO):

Oxygen dissolved in water is vital for aquatic life. The optimum value for dissolved oxygen in a good quality water is 4-8mg/L. It is consumed by oxidation of organic matter/ reducing agent etc. present in water. Water which has DO value less than 4 mg/L is termed as polluted and is unfit for human or aquatic animal consumptions.

Chemical Oxygen Demand (COD):

It is an index of the organic content of water, since the most common substance oxidized by the dissolved oxygen in water is organic matter, which has a biological origin, such as dead plants etc. The COD of a water sample is determined by the chemical oxidation of the organic matter by K2Cr2O7 in 50% H2SO4. This method includes other reducible inorganic species that may be present in water such as , , etc., and hence this method does not truly reflect the organic content in water. However since this method is rapid, it is widely used. - 2NO 2- 23 SO 2- S

Biological Oxygen Demand (BOD):

The capacity of the organic matter in the sample of natural water to consume oxygen is called its BOD. It is determined experimentally by determining the dissolved oxygen (DO) at the beginning and at the end of a 5-day period in a sealed sample. The BOD gives the measure of oxygen utilized or consumed in the period as a result of oxidation of dissolved organic matter present in the water sample.

Threshold limit value (TLV):

This value indicates the permissible level of a toxic pollutant in atmosphere to which a healthy industrial worker can be exposed during an eight hour day without any adverse effect. TLV of a pollutant is found by experimentation on animals, medical knowledge and experience and environmental studies.

Now let us discuss the various segments of our environment in detail one by one. In the first instance let us discuss about the atmosphere and atmospheric

chemistry.

**Water Pollution**

The quality of drinking water is an important factor in determining human welfare. It has been noted that polluted drinking water is the cause for waterborne diseases which wiped out the entire populations of cities. The major sources of water pollution are domestic waste from urban and rural areas, and industrial wastes which are discharged into natural water bodies. The rivers and lakes near urban centres emit disgusting odours and fish are being killed in millions along the sea coasts. The meat of some of them is tainted and unsafe to eat because of excessive levels of mercury and pesticides in their bodies. The origin of these problems must be attributed to many sources and types of pollutants. To aid in a systematic discussion of water pollutants they are classified into fourteen categories as described below. In this chapter the different types of water pollutants are discussed in the following sequence, concluding with an outline of prescription of water quality for drinking.

• Synthetic organic pollutants such as detergents, pesticides,

polychlorinated biphenyls and other synthetic organic chemicals.

• Inorganic pollutants which include heavy metals, metalloids, speciation,

anionic pollutants and ammonia.

• Eutrophication and algal nutrients. • Acid mine drainage. • Oxygen sag curve.

• Regulation of water quality.

**Synthetic Organic pollutants:**

These include ***detergents, pesticides, polychlorinated biphenyls and other synthetic organic chemicals***. These compounds in contrast to the organic wastes, are not biodegradable and may persist for long periods. These are of great concern to environmentalists because most of the synthetic organic compounds are accumulative toxic poisons and ultimately may reach objectionable levels in water or in aquatic life. Analysis of polluted waters show the presence of a wide variety of these compounds and many others are probably not being detected. Of these, detergents, pesticides, polychlorinated biphenyls have been subjected to intensive study since these degradation resistant organics are not efficiently removed from the treatment processes and disposal of inadequately treated sewage can cause severe problems.

**Soaps and Detergents**:

Soaps are salts of long chain fatty acids such as sodium stearate . The cleaning action of soap results largely from its emulsifying power caused by the dual nature of the soap anion. In the presence of oils, fats, and other water insoluble organic materials, the “tail” of the anion tends to dissolve in the organic

matter, whereas the carboxyl "head" remains in aqueous solution. Thus the soap emulsifies, or suspends, organic material in water. All sodium and potassium salts of soap are soluble in water. If the water is hard, the calcium, magnesium and any other ions causing hardness precipitate the soap as shown by the following equation.

C17 H35 COO- Na+ + Ca+2 → Ca(C17 H35 COO)2(s)+ 2Na+ ........(1)

These insoluble products are not at all effective as cleaning agents. In addition, the insoluble "curds" form dirty deposits on clothing and in washing machines.

However soap has a distinctive advantage from the environmental stand point. As soon as soap gets into sewage or an aquatic system, it generally precipitates as calcium and magnesium salts. Hence any effects that soap might have in solution are eliminated. As it is eventually biodegrades, the soap is

completely eliminated from the environment. Thus soap does not cause any substantial pollution problems.

A wide variety of synthetic **detergent**s, commonly called syndets have been accepted as a substitute for soap. Their major advantage is that they do not form insoluble precipitates with the ions causing hardness. As marketed most of them contain from 20 to 30 percent surfactant, and 70 to 80 percent builders. The builders are usually sodium sulphate, sodium tripolyphosphate, sodium silicate and other materials that enhance the detergent properties of the active ingredient. Of these polyphosphates undergo fast biodegradation by hydrolysis giving HPO4-2 and H2PO4-  .Eventhough these hydrolysis products do not pose any threat to aquatic animal life, they act as nutrients for plants and thus cause

eutrophication by excessive growth of plants. The synthetic surfactants are of three major types: anionic, nonionic and cationic of which anionic surfactants are widely used.

The anionic surfactants are all sodium salts and ionise to yield Na+ plus a negatively charged, surface active ion. The common ones are all sulphates and sulphonates.

Long chain alcohols when treated with sulphuric acid produces sulphates (inorganic esters) with surface-active properties. Dodecylalcohol or Lauryl alcohol is commonly used. The sulphated alcohol is neutralised with sodium hydroxide to produce the surfactant. (e.g: C12H25OSO3Na, sodium lauryl sulphate).

The principal sulphonates of importance are derived from esters, amides and alkyl benzenes. The esters and amides are of organic acids with 16 to 18 carbon atoms. In the past the **alkyl benzene sulphonates** **(ABS)** were derived largely from polymers of propylene, and the alkyl group, which averaged 12 carbon atoms, was highly branched.

**Structure of ABS**

The environmental problem associated with ABS was that it had the disadvantage of being only very slowly biodegradable because of the branched chain structure of the alkyl groups and because the benzene rings are attached principally to tertiary carbon of the branched chain groups. Because of this resistance, these detergents persisted even after biological treatment of the effluent and have contaminated both surface water and ground water with objectionable foaming properties.

It is because of this problem these detergents are now made from normal (straight chain) paraffins, and thus the alkane chain is not branched and the benzene ring is attached primarily to secondary carbon atoms. These latter materials have been labelled as **LAS (linear alkyl sulphonate)**

**Structure of LAS**

**Pesticides**

Eventhough the following paragraphs give a brief account of the toxicity of different pesticides, more detailed account of some of the important pesticides are given under chapter "toxicological chemistry".

The term pesticide is used to cover a wide range of chemicals that kill organisms that human consider undesirable and includes the more specific categories of insecticides, herbicides, rodenticides, and fungicides. There are three main groups of synthetic organic insecticides: **organochlorines** (also known

as chlorinated hydrocarbons), **organo phosphates**, and **carbamates**. In addition a number of herbicides, including the chlorophenoxy compounds 2,4,5-T (trichlorophenoxy acetic acid, which contains the impurity dioxin, which is one of the most potent toxins known) and 2,4-D (dichlorophenoxyaceticacid) are common water pollutants.

The most well known **Organo Chlorine pesticide is DDT** (dichlorodiphenyltrichloroethane) which has been widely used to control insects that carry such diseases such as malaria, typhus, and plague. By contributing to the control of these diseases, DDT is credited with saving literally millions of lives worldwide. In spite of its more recent reputation as a dangerous pesticide, in terms of human toxicity, DDT is considered to be relatively safe. It was its impact on food chains, rather than human toxicity, that led to its ban. Organochlorine pesticides, such as DDT, have two properties that cause them to be particularly disruptive to food chains. **They are persistent**, which means they last a long time in the environment before being broken down into other substances and they are **quite soluble in lipids**, which means they easily accumulate in fatty tissue.

The accumulation of organochlorine pesticides in fatty tissue means that organisms at successfully higher trophic levels in a food chain are consuming food that has successively higher concentrations of pesticide. At the top of food chain body concentrations of these pesticides are the highest, and it is there that organochlorine toxicity has been most recognisable. Birds, for example , are high on the food chain and it was the adverse effect of DDT on their reproductive calcium metabolism in birds, resulting in **eggs with shells that are too thin to support the weight of the parent**. The resulting difficulty to reproduce has been shown to affect a number of species, including falcons, bald eagles, ospreys, and

brown pelicans.

Other widely used organochlorines included methoxychlor, chlordane, heptachlor, aldrin, dieldrin, and chlordane produce liver cancers, and aldrin, dieldrin, and endrin have shown to cause birth defects in mice and hamsters.

One of the great environmental disasters that had resulted from pesticide manufacture users in the production of **kepone** at virginia, USA. This pesticide was used for the control of banana-root borer, tobacco wire-worm, ants and cockroaches during mid 1970's. However the plant was ultimately closed since worker's exposure to kepone in the manufacturing unit showed severe neurological damage. Given the ecosystem disruption, the toxicity, and the biological resistance to these pesticides that many insect species have developed, organochlorines have largely been replaced with organophosphates and carbamates.

The organophosphates, such as parathion, malathion, diazinon, TEPP (tetraethylpyrophosphate), and dimethoate, are effective against a wide range of insects and they are not persistent. However, they are much more toxic than the organochlorines that they have replaced. They are rapidly absorbed through the skin, lungs, and gastrointestinal tract and, hence, unless proper precautions are taken they are very hazardous to those who use them. Humans exposed to excessive amounts have shown a range of symptoms including tremor, confusion, sturred speech, muscle twitching, and convulsions.

Propoxur, carbaryl, and aldicarb are some of the popular carbamate pesticides. Acute human exposure to carbamates has led to a range of symptoms, such as nausea, vomiting, blurred vision, and in extreme cases convulsions.

**Polychlorinated Dibenzodioxins (PCDDs) And Polychlorinated Dibenzofurans (PCDFs):**

Polychlorinated dibenzodioxins are highly toxic and are the by-products in the manufacture of chlorophenoxy herbicides and hexachlorophene. The chlorophenoxy herbicides including 2,4,5-trichlorophenoxyacetic acid, were manufactured on a large scale for weed and brush control and as military defoliants. The best known member of the PCDDs group is 2,3,7,8-tetrachlorodibenzo-p-dioxin (often referred to simply as dioxin) which shows very acute toxicity for some species in laboratory tests. Also of concern is the related polychlorinated dibenzofuran group of compounds (PCDFs), the most toxic member once again being 2,3,7,8 tetrachlorinated compound. These compounds are found in the environment in complex mixtures containing PCDDs and PCDFs with all possible substitution patterns. The two group of compounds are formed during the combustion of organic material containing chlorine such as chemical and municipal incinerators, coal-fired power stations and domestic coal fires. They are also found as contaminants in some chlorinated chemical products as described previously.

The solubility of 2,3,7,8-tetrachlorodibenzopdioxin(molecular mass=322) is 5.9x10-5 µ mol l-1 at 25oC. It is a solid with a vapour pressure of 6.2x10-7 pa at normal temperature. The bioconcentration factor for this pollutant is extremely high. In addition the compound is also likely to accumulate in sediments. There are few investigations of dioxin concentrations in natural water samples (concentrations would be at or below lower detection limits), but many in sediments and living organisms.

**Polychlorinated Biphenyls:**

Polychlorinated biphenyls, PCBs, are among the most hazardous human made substances. PCBs are extremely stable to heat, chemical, and biological decomposition. They are excellent insulating and cooling fluids, extensively used for many years in manufacture of transformers and capacitors. PCBs are also used in hydraulic fluids, lubricating oils, paints, adhesive resins, inks, fire retardants, wax extenders, and numerous other products. The chemical and physical properties of PCBs make the remediation of the pollution sites difficult.

They resist the degradation and adsorb into soils and colloidal materials in water. Some persist with half-lives of 8-15 years in the environmental compartments. This stability contributes to their dispersion in the environment and long-range air pollution. Because they are lipophilic, these species are stored in fatty tissues and accumulate in food webs.

The physical and toxicological properties and molecular structures of PCBs are related to their degree of chlorination. Substitution of electronegative chlorines at one or more ortho--positions lead to rotation about the bond between phenyl rings. The three most toxic congeners are 3,4,3,'4'- tetrachlorobiphenyl,

3,4,3,'4',5' - pentachlorobiphenyl and 3,4,5,3,'4',5' -hexachlorobiphenyl. Because these have no chlorines at the ortho-positions, the biphenyl rings can be coplanar and structurally resumble dioxin, which is the most toxic organic compound.

**Elemental Pollutants:**

Trace elements are those that occur at very low levels of a few parts per million or less in the environment. Some of these trace elements are recognized as nutrients required for animal and plant life. There are some elements which are essential at low levels but toxic at higher levels. The most harmful of these elements have been found to be heavy elements. These elements include essential elements like iron as well as toxic elements like lead, cadmium and mercury. Most of these have tremendous affinity for sulfur and sulfur bonds in enzymes, thus immobilizing the enzymes. The carboxylic acid and amino groups from protein are also chemically bound by heavy metals. Cadmium, copper, lead and mercury ions bind to cell membranes, hindering transport processes through the cell wall. Heavy metals may also precipitate phosphate biocompounds or catalyze their decomposition. Most of these substances produce physiological poisoning by becoming attached to the tissues of aquatic organisms and accumulate. Consequently, their increasing concentrations can build up in food

chains. The metals of particular concern in industrial waste waters are cadmium, chromium, lead and mercury. The following paragraph give an account of the toxicity of these heavy metals. More details however are given under chapter "Toxicological chemistry".

**Heavy metals**

***Cadmium***

Cadmium is generated in waste streams from pigment works, textiles, electroplating chemical plants etc. In rivers polluted by cadmium, the metal may be undetectable in filtered water, although it is present in high concentration in particulate fraction. The **itai-itai** disease in Japan was probably due to the transport of cadmium containing particulates in water to the irrigation fields. Chemically cadmium is very similar to zinc and both are found in water in +2 oxidation state. Cadmium causes acute poisoning in humans resulting in kidney damage, destruction of testicular tissue and distruction of red blood cells.

Because of its chemical similarity to zinc, cadmium replace zinc in some enzymes, thus altering the stereo structure of the enzyme and impairing its catalytic activity. It has been found that 0.1 mg per liter cadmium can be lethal to both oysters and aquatic plants.

***Lead:***

Of all the toxic metals in the environment lead is the most pervasive; it poisons many thousands of people yearly especially children in urban areas. Unlike cadmium, lead is not taken up actively by plants; nevertheless it contaminates the food supply because it is abundant in dust and is deposited on food crops or on food as it is being processed. Food and direct ingestion of the dust account for most of the average lead intake by humans. The sources for lead pollution are industry and mining in which lead is present in +2 oxidation state.

Lead pollution from leaded gasoline which used to be a major source of atmospheric and terrestrial lead has been stopped because of the use of other environmental friendly antiknock agents. Acute lead poisoning in human causes malfunctioning of kidneys, reproductive system, liver, and the brain and central nervous systems.

***Chromium***

Chromium is found in two forms in waste waters - hexavalent and trivalent. Hexavalent is present in waste waters of plating operations, aluminium anodising, paint and dye operations, and leather industries. Trivalent chromium is present in waste waters from textile dyeing, the ceramic and glass industry, and photography. As the effluent flows downstream, the dissolved oxygen can oxidise

Cr3+ to Cr2O7. Cr(III) has low toxicity, but in the hexavalent form it is both toxic and carcinogenic to humans.

***Mercury***

Mercury is discharged into natural waterways from various industrial effluents such as those of manufacture of paint, paper, chlorine and caustic soda, fertilisers and pesticides. Among the more severe toxicological effects of mercury is neurological damage, chromosome breakage; and birth defects. The toxicity of mercury was tragically illustrated in the minamata bay area of Japan during the

period 1953-1960. The level of metal in the contaminated sea food was 5-20 ppm. Unexpectedly high concentrations of mercury was found in water and fish tissues in the US and Canada around 1970. They were attributed to the formation of soluble monomethyl mercury ion CH3Hg+, and volatile dimethyl

mercury, (CH3)2Hg by anaerobic bacteria in sediments. Mercury from these compounds becomes concentrated in fish lipid tissue and the concentration factor from water to fish may exceed 103. The methylating agent by which inorganic mercury is converted to methyl mercury compound is methylcobal

amine, a vitamin B12 analog.

It is believed that the bacteria that synthesise methane, produce methyl cobal amine as an intermediate in the synthesis. In neutral of alkaline waters, the formation of dimethyl mercury, (CH3)2Hg is favoured. This volatile compound can escape to the atmosphere. One aspect of mercury poisoning that is causing

concern is its effect on the rate of photosynthesis of phytoplanktons. There is some evidence that the oxygen producing activities of phytoplankton can be inhibited at mercury levels as low as 0.001 mg l-1.

***Metalloids:***

Among the metalloids arsenic is the most significant water pollutant. Although arsenic is in the same column of periodic table as phosphorous, and has similar chemistry, it is more easily reduced from V to III oxidation state. As (III) (arsenite, AsO33-) is more toxic than As(V) (arsenate, AsO43-), probably because

it binds more readily to sulfhydryl groups on proteins. Toxicity of As(V) probably results from its reduction to As(III) in the body. Arsenic occurs with phosphate minerals and enters into the environment along with some phosphorous compounds. Arsenic produced as a by-product of copper, gold and lead refining, greatly exceeds the commercial demand for arsenic, and it accumulates as waste material. Like mercury, arsenic may be converted to more mobile and toxic methyl derivatives by bacteria such as methyl arsenic acid (CH3As O(OH)2) and dimethyl arsenic acid {(CH3)2 As O (OH)} which are highly reactive and damage DNA at least in cultured human cells. In another recent discovery low levels of arsenic were found to inhibit activation receptors of glucocorticoid hormone, receptors that turn on many genes that suppress cancer and regulate blood sugar.

**Chemical speciation of metal pollutants:**

Natural waters are extremely complex chemical environments. Not only do they contain almost every element in the periodic table, but also dissolved organic matter of largely unknown composition (fulvic acid and humic acid) and colloidal and particulate material, both inanimate and living. The range of chemical process affecting pollutant metals can be illustrated by the case of copper in natural waters. Copper dissolved at trace levels in distilled water is present as hydrated Cu2+ ion. In natural water this cation is subjected to range of interactions as shown in fig 1.

The distribution of copper between the different chemical species and forms shown in fig.1 is termed chemical speciation, and it is chemical speciation which holds key to understanding the geochemical and biological reactivity of trace metals. Metal organic interaction may increase or decrease the toxicity of metals in aquatic ecosystems, and they have strong influence on the growth of algae in water.

**Other inorganic pollutants:**

***Cyanide***

Cyanide is a deadly poisonous substance, that exists in water as HCN; It is a very weak acid. Cyanide ion forms stable complexes with metal ions and these complexes are relatively less toxic. The cyanide ion has a strong affinity for many metal ions forming relatively less toxic complexes. For example with iron (II) it forms less toxic [Fe (CN)6 ] 4 - where as volatile HCN is toxic. Especially metal cleaning and electroplating industry use large quantities of cyanides. The presence of cyanide in water is indicative of a serious pollution problem.

**Ammonia :**

Ammonia is formed during the microbial degradation of decaying biomass and organic matter in soil and water. Nitrogenous compounds like proteins are ammonified to release ammonia into the surroundings. Sometimes it is added to drinking water during chlorination where it reacts to provide residual disinfectant **chlorine.**

**Hydrogen sulfide:**

The anaerobic decay of organic matter containing sulphur leads to the production of H2S. Anaerobic reduction of sulphate in water by microorganisms is also a natural source for hydrogen sulphide H2S is evolved as a gaseous pollutant from geothermal waters. Wastes from chemical plants, paper mills, textile mills, and tanneries may also contain H2S. It is a weak diprotic acid and S-2 is not present in normal natural waters. The sulphide ion has tremendous affinity for many heavy metals and precipitation of metallic sulphides often accompanies production of H2S.

**Nitrite nitrogen:**

Nitrite nitrogen seldom appears in concentrations greater than 1mg l-1, even in waste treatment plant effluents. Its concentration in surface and ground waters is normally much below 0.1 mg l-1. Nitrite is added to some industrial process water to inhibit corrosion; it is rarely found in drinking water at levels over 0.1 mg l-1.

**Sulfite ion**

Some industrial wastes contain sulphite ions where sodium sulphite is added to boiler feed waters as an oxygen scavenger: −

SO3-2+ O2 →2SO4− 2 ............................................................................. (3)

Since pKa, of sulfurous acid is 1.76 and pKa2 is 7.20, sulfite exists as either or in natural waters, depending upon its pH. - 3HSO 2- 3SO

**Eutrophication And Algal Nutrients:**

Eutrophication is a process of providing a water body with nutrients for the aquatic life it, supports. A lake starts its life as a clean body of water. Small amounts of nitrates and phosphates occur in all aquatic systems and these are sufficient to maintain a balanced biological growth (a balance between the production of aquatic life and its destruction by bacterial decomposition). With the introduction of nutrients through land run off and growth and decay of aquatic life, the lake collects good amount of organic substances. Thus when unusually large concentrations of nutrients are present in water bodies, there is an excess of growth of algae known as algal bloom. This produces an unsightly green slime layer over the surface of water body. This slime layer reduces the penetration of light and restricts atmospheric reoxygenation of the water. The dense algal growth eventually dies and the subsequent biodegradation produces oxygen deficit which can result in foul smelling anaerobic conditions. The anaerobic conditions created by rotting algae can present health hazard to aquatic systems.

Thus with large inputs of nutrients from human sources, the bacterial decomposition cannot keep pace with the productivity and sedimentation is accelerated, whereby eutrophication only is favoured. Lakes can be protected from eutrophication only by providing measures for sewage treatment and preventing the sewage from entering the water bodies.

**Acid Mine drainage:**

Coal mines, especially those that have been abandoned, are known to release substantial quantities of sulphuric acid and iron hydroxide into local streams. The first step in the process is the oxidation of pyrire (FeS2 ), which is common in underground coal streams.

FeS2 + O2 + H2 O−⎯⎯→ Fe+2 + 2HSO4-2 .......................... (4)

This step is mediated under aerobic conditions by the bacterium thiobacillus ferro oxidans, which oxidises FeS2 as an energy source much the same way that other aerobic bacteria oxidise organic carbon (CH2O) in respiration reactions. The oxidation step occurs spontaneously at ambient temperatures once iron sulphide , which is stable in the absence of air is exposed to atmosphere.

Thus one mole of pyrite produces 2 moles of sulphuric acid and one mole of ferric hydroxide , which is removed from the solution as a brown precipitate. The pH of the streams receiving this drainage can be as low as 3.0 Environmental chemists have a tough challenge in the prevention of water pollution from acid mines. Even though at the first instance, it may appear that this problem can be remedied by using carbonate rocks to neutralise the acid as per the following equation.

222 34 42CaCO 2H SO Ca SO H O CO +− +− ++ → + ++2 ↑ ………………………..(8)

this reaction is inhibited after sometime since the formed ferric hydroxide form an impermeable layer with the calcium carbonate particles.

**Accumulation of Salts in water:**

Water naturally accumulates a variety of dissolved solids, or salts as it passes through the soils and rocks on its way to the sea. A more commonly used measure of salinity is to determine the concentration of total dissolved solids in the water sample. All naturally occuring water has some amount of salt in it. While human activities may increase salinity by adding salts to a given volume of water, it is more often the opposite process, the removal of fresh water by evaporation, that causes salinity problems. When water evaporates, the salts are left behind, and since there is less remaining fresh water to dilute them, their concentration increases.

Irrigated agriculture, especially in acid areas, is always vulnerable to an accumulation of salts due to this evaporation on the cropland itself. The salinity is enhanced by the increased evaporation in storage reservoirs that typically accompany irrigation projects. In addition irrigation drainage water may dissolve

more salt from soils with which it comes in contact further increasing its salinity. As a result, irrigation water is always higher in salinity than the supply water and with every reuse, its salt concentration increases even more. In rivers that are heavily used for irrigation, the salt concentration progressively increases downstream as the volume of water available to dilute salts decreases due to evaporation and diversions.

**Oxygen sag curve**:

Oxygen which is present in water is vitally important. If the water contains organic matter (CH2O), the oxidation of this compound is mediated by microorganisms as shown below.

+ ⎯⎯⎯⎯⎯⎯⎯→+ Microorganisms 22 22{CH O} O CO H O.............................................(9)

When the river water is turbulant, it gets reaerated quickly. With the introduction of organic loaded polluted water into the river, the dissolved oxygen content in the water body rapidly gets depleted and it cannot support higher forms of aquatic life. In addition to microorganism mediated oxidation of organic matter, oxygen may be consumed by the oxidation of nitrogenous material,

++− +→+ + 42 32NH 2O 2H NO H O......................................................(10)

Or by chemical reducing agents present in water may consume oxygen for their chemical or biochemical oxidation as shown below:

++ ++ → +2 22 34Fe O 10H O 4Fe(OH) (s) 8H .......................................(11)

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+→ 2 32 42SO O 2SO − 2 .................................................................(12)

All these processes involve the removal of dissolved oxygen in water. The measure of oxygen utilised by microorganisms during the oxidation of organic materials is called the biochemical oxygen demand or the biological oxygen demand (BOD). This parameter is commonly measured by determining the quantity of oxygen utilized by suitable aquatic micro organisms during a five-day period. The five day BOD test is empirical and semiquantitative. But it still remains a respectable measure of the short-term oxygen demand exerted by a pollutant.

The discharge of wastes into a body of river stream results in the depletion of dissolved oxygen level as the wastes are oxidised by the bacteria. Opposing this drop in dissolved oxygen is reaeration which replaces oxygen through the surface, at the rate which is proportional to the depletion of oxygen below the saturation value. The simultaneous action of deoxygenation and reaeration produces a typical pattern in the dissolved-oxygen concentration of the aquatic system. **This pattern is known as the oxygen sag curve which is shown in fig 2.**

To begin with a well – aerated unpolluted stream is relatively free from oxidisable material; the oxygen level is high; and the bacterial population is relatively low.

Fig. 2 Oxygen sag curve resulting from the addition of oxidisable pollutant to a stream

However with the addition of oxidisable pollutant, the oxygen level drops because reaeration cannot keep up with oxygen consumption. In the decomposition zone, the bacterial population rises. The bacterial population is very high and the dissolved oxygen levels are very low in the septic zone. When

the oxidisable pollutant is exhausted, the septic zone terminates and then the recovery zone begins. The bacterial population decreases in the recovery zone and the dissolved oxygen level increases until the water regains its original conditions.

**Regulation of water quality:**

Governments around the world try to regulate water quality in the interest of public health and environmental protection. In the U.S. the legal instruments for regulation are two basic laws, the Clean Water Act (CWA), of 1972 and Safe Drinking Water Act (SDWA) of 1974, both of which have been amended several times. Under this act, the Environmental Protection Agency (EPA) is required to set standards that protect from harmful effects of contaminants. Similar initatives have been undertaken in most of the industrially advanced countries. These measures have helped to produce marked reductions in pollutant discharges to water bodies.

With regard to the drinking water standards, it falls into two categories:

primary standards which specify maximum contamination Levels (MCLs) based on health related criteria and secondary standards, which are unenforceable guidelines based on both asthetic such as taste, odour and colour of drinking water, as well as non aesthetic characteristics such as corrosivity and hardness.

In setting MCLs , the EPA is required to balance the public health benefits of the standard against what is technologically and economically feasible.

**Primary standards:** Contaminants for which MCLs are established are classified as being inorganic chemicals, organic chemicals, radionuclides, or microbiological contaminants. A list of standards for inorganic chemicals have been prescribed which included many metallic cations and anions with their permissible levels.

Organic chemical contaminants for which MCLs are being promolgated are classified conveniently using the following three groupings.

Synthetic organic chemicals :These are used in the manufacture of a wide variety of agricultural and industrial products. They include primarily pesticides and herbicides.

Trihalomethanes: These are the products of water chlorination. They include chloroform (CHCl3), bromodichloromethane (CHBrCl2), dibromochloromethane (CHBr2Cl) , and bromoform (CHBr3).

Volatile organic chemicals (VOCs) : These are synthetic chemicals that readily vaporise at room temperature. These include degreasing agents, paint thinners, glues, dyes, and some pesticides. Representative chemicals include benzene, carbontetrachloride, 1,1,1-trichloro ethane (TCA), trichloroethylene (TCE), and vinyl chloride.

Radioactivity in public drinking water supplies is the third category of contaminants regulated by safe water drinking act. Some radioactive compounds, or radionuclides, are naturally occuring substances such as radon and radium-226 (which are often found in ground water) while others such as strontium-90 and tritium are surface water contaminants resulting from atmospheric nuclear weapons testing fall out. The most significant radionuclide associated with drinking water is dissolved radon gas. It is an unusual contaminant because the danger arises not by drinking radon contaminated water, but from breathing the gas which is believed to be the cause for lung cancer.

The fourth category of primary MCLs is microbiological contaminants. While it would be desirable to evaluate the safety of a given water supply by individually testing for specific pathogenic microorganisms, such tests are too difficult to perform on a routine basis. Instead a much simpler technique is used, based on testing water for evidence of any fecal contamination. In this test coliform bacteria are used as indicator organisms whose presence suggests that the water is contaminated.

**Secondary standards:**

Secondary standards are non enforceable, maximum contaminant levels based on aesthetic factors such as taste, colour, and odour, rather than on health effects. The limits suggested for chloride, copper, total dissolved solids and zinc are in large part based on taste. Excessive sulphate is undesirable because of its

laxative effect; iron and manganese are objectionable because of taste and their ability to stain laundry and fixtures. Foaming and colour are visually upsetting and odour from various dissolved gases may make water unacceptable for drinking.

**MODULE 1.5 Advanced Waste Water Treatment**

The effluent from a typical secondary treatment plant still contains 20-40 mg/L BOD which may be objectionable in some streams. Suspended solids, in addition to contributing to BOD, may settle on the stream bed and inhibit certain forms of aquatic life. The BOD if discharged into a stream with low flow, can cause damage to aquatic life by reducing the dissolved oxygen content.

In addition the secondary effluent contains significant amounts of plant nutrients and dissolved solids. If the waste water is of industrial origin, it may also contain traces of organic chemicals, heavy metals and other contaminants.

Different methods are used in advanced waste treatment to satisfy any of the several specific goals, which include the removal of (1) suspended solids (2) BOD (3) plant nutrients (4) dissolved solids and (5) toxic substances. These methods may be introduced at any stage of the total treatment process as in the case of industrial waterways or may be used for complete removal of pollutants after secondary treatment.

**Removal Of Suspended Solids:**

This treatment implies the removal of those materials that have been carried over from a secondary treatment settler. Many methods were proposed of which two methods were commonly used. The two methods are **microstaining and chemical coagulation** followed by settling and mixed media filtration.

**Microstraining:**

It is a special type of filtration procedure which makes use of filters oven from stainless steel wires with opening only 60-70 µm across to remove very small particles. High flow rates and low back pressures are normally achieved.

**Coagulation and flocculation:**

The object of coagulation is to alter these particles in such a way as to allow them to adhere to each other. Most colloids of interest in water treatment remain suspended in solution because they have a net negative surface charge that causes the particles to repel each other. The intended action of the coagulant is to neutralise that charge, allowing the particles to come together to form larger particles that can be more easily removed from the raw water. The usual coagulant is alum [Al2(SO4)2• 18H2O ], though FeCl3, FeSO4 and other coagulants, such as polyelectrolytes, can be used. Alum when added to water, the aluminium in this salt hydrolyses by reactions that consume alkalinity in the water such as:

+− +→ ++326 3 3 2 2[Al(H O) ] 3HCO Al(OH) (s) 3CO 6H O..............(1)

The gelatinous hydroxide thus formed carries suspended material with it as it settles. In addition, however, it is likely that positively charged hydroxyl-bridged dimers such as

(H2O)4 Al

H O

O H

Al(H2O)4

4+

and higher polymers are formed which interact specifically with colloidal

particles, bringing about coagulation. Metal ions in coagulants also react with

virus proteins and destroy upto 99% of the virus in water.

Anhydrous ion (III) sulphate can also act as effective coagulant similar to

aluminium sulfate. An advantage with iron (III) sulfate it that it works over a wide

range of pH.

Filtration:

If properly formed, the addition of chemicals for promoting coagulation and

flocculation can remove both suspended and colloidal solids. After the flocs are

formed, the solution is led to a settling tank where the flocs are allowed to settle.

While most of the flocculated material is removed in the settling tank, some floc

do not settle. These flocs are removed by the filtration process, which is usually

carried out using beds of porous media such as sand or coal. The current trend is

to use a mixed -media filter which consists of fine garnet in the bottom layer,

silica sand in the middle layer and coarse coal in the top layer which reduces

clogging.

Removal of dissolved solids:

The dissolved solids are of both organic and inorganic types. A number of

methods have been investigated for the removal of inorganic constituents from

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waste water. Three methods which are finding wide application in advanced

waste treatment are ion-exchange, electrodialysis and reverse osmosis. For the

removal of soluble organics from waste water the most commonly used method

is adsorption on activated carbon. Solvent extraction is also used to recover

certain organic chemicals like phenol an d amines from industrial waste waters.

Ion exchange:

This technique has been used extensively to remove hardness, and iron

and manganese salts in drinking water supplies. It has also been used selectively

to remove specific impurities and to recover valuable trace metals like chromium,

nickel, copper, lead and cadmium from industrial waste discharges. The process

takes advantage of the ability of certain natural and synthetic materials to

exchange one of their ions.

A number of naturally occuring minerals have ion exchange properties.

Among them the notable ones are aluminium silicate minerals, which are called

zeolites. Synthetic zeolites have been prepared using solutions of sodium silicate

and sodium aluminate. Alternatively synthetic ion-exchange resins composed of

organic polymer with attached functional groups such as (strongly

acidic cation exchange resins), or - COO

3-SO H+ - H+ (weakly acidic cation exchange resins or -N+(CH3)3OH- (strongly basic anion exchange resins) can be used.

In the water softening process, the hardness producing elements such as

calcium and magnesium are replaced by sodium ions. A cation exchange resin in

sodium form is normally used. The water-softening capability of cation exchange

can be seen when sodium ion in the resin is exchanged for calcium ion in

solution.

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2 3322ResSO Na Ca (ResSO ) Ca 2Na −+ + − + +→ +2 + − ………………….….(2)

(where “Res” represents resin phase)

The product water thus has high sodium content, which is not likely to be

troublesome unless the original water is very hard. When the exchanger is

saturated, it has to be regenerated to allow reuse of expensive resin. Regeneration can be achieved by sodium chloride solution which removes Ca2+ and Mg2+ ions from the resin.

22 32 3(Res SO ) Ca 2Na 2Cl 2Na (Res SO ) Ca 2Cl − + +− + − + ++→ ++…….(3)

Since for regeneration large amounts of NaCl has to be used, appreciable

amounts of sodium chloride can be introduced into sewage by this route. This

problem can be overcome by using weakly acidic cation exchange resin such ResCOO-H+. These cation exchangers having -COOH as functional group are

useful for removing alkalinity along with hardness. Alkalinity is generally

manifested by bicarbonate ion. This ion is sufficiently basic to neutralise the acid

of weak cation exchange. Another advantage with these resins is that these can

be regenerated almost stoichiometrically with dilute strong acid, thus avoiding

pollution problem caused by excess NaCl. This technique has also been

successfully applied to the recovery of chromate from waste water in pigment

manufacturing.

The removal of inorganic solute is essential for complete water recycling.

The effluent from secondary waste treatment contains 300-400 mg/L more

dissolved inorganic material than does municipal water. The removal of these

bulk inorganics can be efficiently done by reverse osmosis and electrodialysis .

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Reverse osmosis:

In the reverse osmosis process, demineralisation water is produced by

forcing water through semipermeable membranes at high pressure. In ordinary

osmosis, if a vessel is divided by a semipermeable membrane (one that is

permeable to water but not the dissolved material), and one compartment is filled

with water and other with concentrated salt solution, water diffused through the

membrane towards the compartment containing salt solution until the difference

in water levels on the two sides of the membrane creates a sufficient pressure to

counteract the original water flow. The difference in levels represents the osmotic

pressure of the solution (fig.1a).

Pure water

Salt solution

Fig 1a Osmosis

membrane

The process can be reversed by applying sufficient pressure to the

concentrated solution to overcome the osmotic pressure force the net flow of

water through the membrane towards the dilute phase. The solute concentration

(impurity) builds up on one side of the membrane while relatively pure water

passes through the membrane . In order to obtain adequate solvent (water) flux through the membrane, pressures of the order of 4000 to 7000 kN/m2 are

required. Fig.1b represents the principle of operation of the reverse osmosis unit.

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Pressure

membrane

Pure Salt water solution

Fig 1b Reverse Osmosis

Electrodialysis:

Electrodialysis uses ion-selective membranes and an electrical potential

difference to separate anions and cations in solution.

+ ++ - - - -

+ + +

+

Electrode

membrane passes only ions

membrane passes only ions +

Electrode

deionised water

salt solution

Fig.2 Electrodialysis cell

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In the past electrodialysis was most often used for purifying brackish

water, but it is now finding a role in hazardous waste treatment. Metal salts from

plating rinses are sometimes removed in this way.

Fig.2 shows a simple dialysis cell in which waste water may be deionised.

As shown in the figure two types of membranes (anionic and cationic) are

arranged alternatively to form many compartments between the electrodes

placed at the two ends. When the voltage is applied across the cell containing

mineralised water, the anions migrate to the positive electrode and the cations

migrate to the negative electrode. This causes solution in alternate

compartments to become more concentrated while that in the remaining

becomes more dilute. The electric power requirement is proportional to the

number of ions removed from the water.

In the electrodialysis process, organic molecules are not removed and

they can collect on and clog the membranes. Another disadvantage of this

method is that it still leaves concentrated waste water to be disposed of by some

appropriate scheme. The process does not require any chemical additives and

has low energy requirements and as such it can be an economically feasible

means of demineralisation.

Removal of nitrogen:

Nitrogen compounds may be removed in waste water in two ways. Even after

secondary treatment, most of nitrogen exists as ammonia. Increasing the pH

produces the reaction,

43NH OH NH H O +− +→↑+2...............................................................(4)

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Much of the dissolved ammonia gas may then be expelled from the water

into the atmosphere. The ammonium ion in the waste water may also be oxidised

to nitrate by bacteria like nitrobacter and nitrosomonas, in a process called

nitrification.

nitrosomonas 42 222NH 3O 2NO 2H O 4H +− + ⎯⎯⎯⎯⎯⎯→+++

3 −

2

............................(5)

nitrobacter 222NO O 2NO − + ⎯⎯⎯⎯⎯→ .......................................... ....... .....(6)

These reactions are slow and require long retention times in the aeration

tank as well as sufficient DO. If the flow rate is too high, the slow-growing

microorganisms are washed out of the aeration tank.

Once the ammonia has been oxidised to nitrate, it may be reduced by

anaerobic bacteria like pseudomonas. This denitrification requires a source of

carbon and methanol is often used for that purpose.

33 22 6NO2CHOH 6NO2CO 4HO −− +→+↑+..................................(7)

.......................(8) 23 2 226NO 3CH OH 3N 3CO 3H O 6OH −− + → ↑+ ↑+ +

Phosphate removal (chemical treatment):

Phosphate may be removed chemically or biologically. The most popular

chemical methods use lime, Ca(OH)2 and alum, Al2(SO4)3.Under alkaline

conditions, the calcium will combine with phosphate to form calcium

hydroxyapatite, a white insoluble precipitate that is settled out and removed from

waste water. Insoluble calcium carbonate is also formed and removed.

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2 2454325Ca(OH) 3HPO CaOH(PO ) 3HO 6OH −− +→ ↓++.................(9)

The aluminium ion from alum precipitates as very slightly soluble

aluminium phosphate,

33 4Al PO AlPO +− +→4 ↓ ..................................................................(10)

and also forms aluminium hydroxide.

3 3A l3OHAl(OH) +− +→ ↓ ................................................................(11)

which forms sticky flocs that help to settle out phosphates.

Phosphate removal (biological treatment)

Biological phosphorous removal does not require the addition of

chemicals. In this process, the aeration tank in the activated sludge system is

subdivided into zones, some of which are not aerated. In these zones, the

aerobic microorganisms become solely stressed because of the lack of oxygen. If

these microorganisms are then transferred to an aerated zone, they try to make

up for lost time and assimilate organic matter (as well as phosphorous) at a rate

much higher than they ordinarily would. Once the microorganisms have adsorbed

the phosphorous, they are removed as waste activated sludge, thus carrying with

them high concentrations of phosphorous. Using such sequencing of nonaerated

and aerated zones, it is possible to remove as much as 90% of the phosphorous.

Removal of dissolved organic compounds:

Adsorption:

One of the most commonly used techniques for removing organics involves

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the process of adsorption, which is the physical adhesion of chemicals on to the

surface of the solid. The effectiveness of the adsorbent is directly related to the

amount of surface area available to attract the particles of contaminant. The most

commonly used adsorbent is a very porous matrix of granular activated carbon, which has an enormous surface area (~ 1000 m2/g). Adsorption on activated

carbon is perhaps the most economical and technically attractive method

available for removing soluble organics such as phenols, chlorinated

hydrocarbons, surfactants, and colour and odour producing substances from

waste water.

Granular activated carbon treatment systems consist of a series of large

vessels partially filled with adsorbent. Contaminated water enters the top of each

vessel, trickles down through granulated activated carbon, and is released at the

bottom. After a period of time, the carbon filter becomes clogged with adsorbed

contaminants and must be either replaced or regenerated. Regeneration of the carbon is accomplished by heating it to 950oC in a steam air atmosphere. This

process oxidises surface, with an approximately 10% loss of carbon.

Synthetic organic polymers such as Amberlite XAD-4 have hydrophobic

surfaces and are quite useful in removing relatively insoluble organic compounds

such as chlorinated pesticides. These absorbents are readily regenerated by

solvents such as isopropanol and acetone.

Sludge treatment and disposal:

Both primary and secondary sewage treatments involve settling of

particulate matter, and thus produce sludge. The concentration of solids in the

primary sewage sludge is about 5%; the activated sludge contains about 1%; and

the sludge from trickling filters has about 2% solids. Thus the sludge is

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composed of almost entirely of water and volume reduction is the key to

economic disposal. In addition to reducing its high water content, the sludge must

be stabilised so that its biological activity and tendency towards putrefaction are

reduced drastically.

The sludge is concentrated by gravity settling and floatation. After

concentration the sludge is subjected to anaerobic digestion in a digester in

which the organic content of the sludge decomposes to give mainly methane and

carbondioxide and at the same time the bound water is released from the sludge.

The sludge is then conditioned to improve its dewatering characteristics by

adding chemicals like iron salts and polyelectrolytes. These chemicals bind the

sludge particles together and encourage the release of water. The sludge is then

heated under pressure and after a period of time the gel structure of the sludge

breaks down so that the water is released. The thickened sludge is then

dewatered for efficient handling and disposal. The dewatering is accomplished by

mechanical methods, the most common being centrifugation and filtration. The

dewatered sludge is then subjected to oxidation to reduce the organic content,

with the consequent destruction of bacteria and a significant reduction in their

volumes. Incineration and wet oxidation are the two common methods employed

for oxidation.

Several methods are employed for the ultimate disposal of sludge. The

wet digested sludge may be sprayed on to a cropland where it functions as

fertiliser. Dried sludge may be used a land fill or soil conditioner. Wet or partially

dewatered sludge or ash from incineration may be transported from the shore to

dumping grounds at sea. The potential drawback to the use of sewage sludge as

fertiliser in agricultural fields is the presence of both organic and inorganic toxic

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compounds. The former compounds are oxidation-resistant organic substances,

such as organochlorine species which become bound in the organic matrix of the

sludge. The inorganic toxicants are represented by heavy metals, mainly arsenic,

cadmium , lead, mercury and zinc. These metals can be taken up by crops and

introduced into the food chains or leached to the ground water.

Disinfection:

Disinfection, using chemical and physical methods is the final step in

drinking water purification. The finished water is disinfected often with chlorine. It

kills the remaining microorganisms in the water, some of which will be

pathogenic. It is a very efficient oxidising, bleaching and disinfecting agent. In

water chlorine reacts as follows:

22Cl H O H Cl HOCl +−⎯⎯→ +++ ←⎯⎯ …………………………………………...(12)

The hypochlorous acid (HOCl) is the prime disinfecting agent. Its dissociation in pH dependent yielding less effective hypochlorite ions (OCl-) at

higher pH values:

HOCl H OCl +⎯⎯→ +←⎯⎯ −…………………………………………………….…(13)

Together, HOCl and OCl- are called the free available chlorine.

A principal advantage of chlorination over other forms of disinfection is

that a chlorine residual is created that can protect the treated water after leaving

the treatment plant. This guards against possible contamination that might occur

in water distribution system. To increase the lifetime of the residual, some

systems add ammonia to the treated water, forming chloramines.

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42NH HOCl NH Cl(monochloramine) H O H ++ +⎯⎯→ 2 ++

2 +

2 +

………………………..(14)

………………………...………(15)

………………………..............(16)

22NH Cl HOCl NHCl (dichloramine) H O +⎯⎯→

23NHCl HOCl NCl (trichloramine) H O +⎯⎯→

Chloramines, although they are less effective as oxidants than HOCl, are

more persistent. Residual chlorine that exists as chloramine is referred to as

combined available chlorine.

Chlorine may have adverse secondary effects. It has the potential to

combine with trace amounts of organic substances to form trihalomethanes

(THMs) such as the carcinogen chloroform. Some studies have shown an

association between bladder and rectal cancer and consumption of chlorinated

drinking water. One approach to reducing THMs is to remove more of the

organics before any chlorination takes place, which can be accomplished by

adsorption on activated carbon.

The problem faced with the formation of THMs has spurred interest in

alternatives to chlorination as the preferred method of disinfection. Alternative

disinfectants include chlorine dioxide and ozone. Chlorine dioxide (ClO2) is a

potent bactericide and viricide and it does not form a residual capable of

protecting water in the distribution system. However, there is concern for certain

toxic chlorate and chlorite substances that it may create, and it is a very costly

method of disinfection. Ozonation involves the passage of ozone (O3) through

water.

Ozone is a very powerful disinfectant that is even more effective against

cysts and viruses than chlorine, and it has the added advantage of having no

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taste or odour problems. Unfortunately, the disinfective power of ozone is limited

by its relatively low solubility in water.

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