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Hydrosphere : Water Pollution

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INTRODUCTION

Hydrosphere constitutes all types of water resources, *viz.*, oceans, seas, rivers, streams, reservoirs and glaciers etc. Water is a vital natural resource which is essential for multiplicity of purposes, *viz.*, drinking, agriculture, power generation, transportation and waste disposal. In the chemical process industrial water is used as a reaction medium, a solvent, a scrubbing medium and a heat transfer agent. As a source of life for man, plants and animals, it cannot be replaced by any other solvent.

WATER RESOURCES

The chief sources of water are rain water, sea water, ground and surface water. The World's total quantum of water is $140 \times 10^{16} \text{ m}^3$.

Sea Water. About 97% of earth's water supply is in the ocean which is unfit for human consumption and other uses due to high salt content. Of the remaining 3%, 2.3% is locked in

the polar ice caps and hence out of bounds. The balance 0.7% is available as fresh water. If all the sea beds could be filled up and brought at the level of the earth surface, then the entire water in the seas would cover the earth's surface and make it 2.5 km deep water mass.

Ground Water.

Ground water, a gift of nature, is about $210 \times 10^9 \text{ m}^3$ (0.66%) including recharge through infiltration, seepage and evapotranspiration. Out of this nearly one-third is extracted for irrigation, industrial and domestic use, while most of the water is regenerated into rivers. Of the fresh water below the surface about 90% satisfies the description of ground water that is, water which occurs below the water table. About 2% water occurs as soil moisture in the unsaturated zone above the water table and is essential for plant growth.

The major portion of water (about $165 \times 10^{10} \text{ m}^3$) which goes to earth crust is retained as soil moisture. Only $500 \times 10^9 \text{ m}^3$ percolate down to the ground water deposits. About $120 \times 10^9 \text{ m}^3$ of water applied to agricultural fields moves down to ground water table and $50 \times 10^9 \text{ m}^3$ of surface flow also end up as ground water. Thus a total of $670 \times 10^9 \text{ m}^3$ fresh water enters the ground annually.

Surface Water.

We have a very limited stock of usable water that is, 0.03% of the mass balance. The $115 \times 10^{10} \text{ m}^3$ of surface water is enlarged by the addition of about $450 \times 10^9 \text{ m}^3$ of fresh water from ground water flow, $200 \times 10^9 \text{ m}^3$ from surface flow and $50 \times 10^9 \text{ m}^3$ as run off from irrigated areas. The surface loses almost $50 \times 10^9 \text{ m}^3$ of its water which percolates down to ground water deposits. The total surface flow per year is $185 \times 10^{10} \text{ m}^3$ which are distributed among river basins.

Rain Water.

In India, the annual rain fall is about $400 \times 10^{10} \text{ m}^2$. Out of this, $70 \times 10^{10} \text{ m}^2$ of water evaporates immediately, $115 \times 10^{10} \text{ m}^2$ runs off into surface water bodies and the remaining percolates into the soil. The hydrological cycle in nature is more or less balanced in terms of charge (cloud formation) and discharge (rain fall). Out of the 30% stream flow, water consumed by man is : 8% for irrigation, 2% for domestic use, 4% for industrial consumption, 12% for electrical utilities, 4% for transportation and waste disposal. By 2010, the total water requirement is expected to thrice as much as we had in 1974. The waste water from these is extremely polluted and on mixing with rivers is polluting the rivers also.

With the rapid growth of population, many countries in the world are now thinking of desalinated sea water as a potential source of supply of potable water in scarcity hit regions. Desalination may be accomplished by processes such as distillation, freezing, electrodialysis and reverse osmosis. World Health Organisation (WHO) has estimated that water consumption will have to be cut by 50% by 2025 if nations fail to address imbalances in global water supply and demand. Some European companies have ventured into water supply business by supplying water to water-thirsty countries across the oceans. Nordic water supply (Norwegian company) has been transporting fresh water in giant floating bags across

the oceans. In future, the company plans to build new bags of the size of supertanker. Thus the Nordic company is engaged in the business of towing fresh water from Turkey to Greek islands.

HYDROLOGICAL CYCLE

The hydrological or water cycle is the most important of all the natural cycles in the biosphere. The cycle involves a continuous natural process which helps in exchange of water between the atmosphere, the land, the sea, plants and animals. About one-third of the solar flux absorbed by the earth is used to drive the hydrological cycle. That is, solar radiation requires $8.2 \times 10^{20} \text{ kJ}^{-1}$ for massive evaporation of water which is nearly 15% of the total radiation reaching the outer atmosphere. Hydrological cycle may be having either a long or numerous short cycles.

Stages of Hydrological Cycle.

1. Evaporation, condensation and precipitation. The hydrological cycle depends on the reciprocity of evaporation and precipitation. Water on earth goes into the atmosphere as vapour by evaporation and transpiration from the plants. More than 80% of the total insolation that is not lost immediately as electromagnetic radiation evaporates the water. The vapour so produced can then condense around dust (nucleation) particles. Other nuclei may be particles of spores, pollen grains or fine mineral particles. Small droplets (0.04 mm) of condensed liquid remain as cloud in the atmosphere and finally get precipitated as rain, hail or snow under the influence of gravity (Fig. 1).

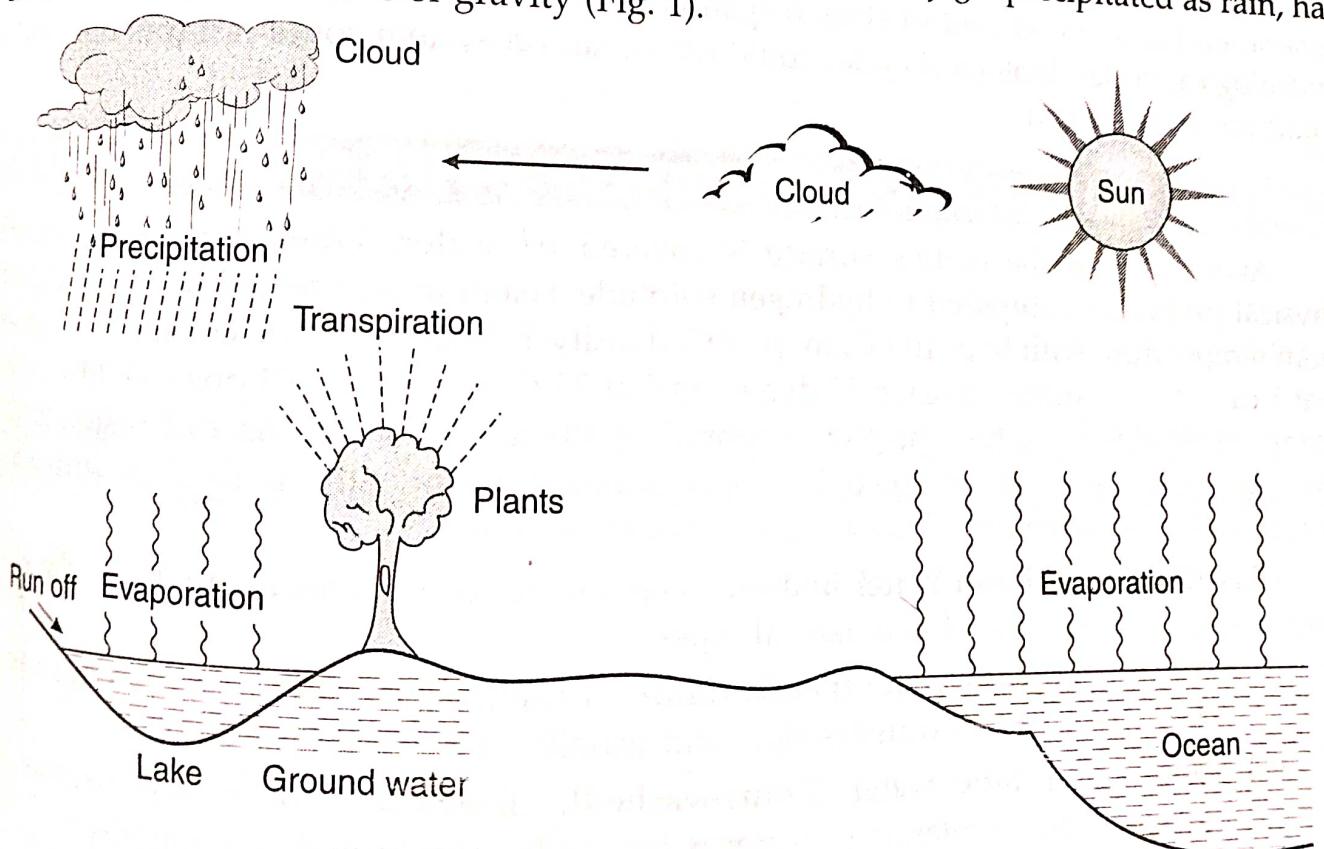


Fig. 1. The hydrological cycle.

2. Surface run-off. In the event of good rainfall, all the rain water precipitated on land does not percolate into the soil. Surface water or run-off flows into the streams, rivers, lakes and catchment areas or reservoirs.

3. Ground water movements. Water on land surface seeps into the soil as ground water. The soil below the natural water table is sustained by the underlying clay and rock strata. Ground water does not remain stationary but moves up above the water table and thereby maintains a continuous supply of water to the surface layer of soil.

Plants absorb capillary ground water but give off excess water through leaves by transpiration. This is an important process which ensures conduction of water and dissolved mineral salts throughout the plant. Another underground water resource is the aquifer. It exists above impermeable rock strata. Water percolates through the porous rocks and forms underground lakes or reservoirs. From these aquifers, water can be extracted by sinking wells, tube wells and pumping it to the surface.

Hence the hydrological cycle consists of a balanced continuous process of evaporation, transpiration, precipitation, surface run-off and ground water movements. Note that normal evaporation from the oceans exceeds precipitation by rain into the seas by about 10%. This excess 10% ultimately moves as water vapour over land surface and thereby balances the hydrological cycle and meets our requirements.

An approximate estimate about the quantum of annual rainfall and evaporation may be given. Each year about 50 Tm ($1 \text{ Tm} = 1 \text{ Terra cubic metre} = 10^{12}$ that is, one million cubic metre; $1 \text{ m}^3 = 1000 \text{ litres}$) water is evaporated and the same quantity of water is precipitated over the earth's surface. From the land about 44.5 Tm^3 water flows to the sea per year and this is available for man's water supplies.

Minor local modifications to the hydrological cycle are made by diverting the run-off and storage phases of fresh water for domestic (2%), industrial (4%), thermal (4%), power generation (12%), flood control (1%), irrigation (8%) and recreation. Thus without water or hydrological cycles, biological cycles could not occur, ecosystem could not function and life could not be sustained.

CHEMICAL COMPOSITION OF WATER BODIES

About 80% of the earth's surface is covered by water. Water possesses abnormal physical properties compared to hydrogen sulphide, selenide and telluride. It is a liquid at room temperature with b. p. 100°C , m. p. 0°C , density 1, high dielectric constant 82, specific heat $1 \text{ cal g}^{-1} \text{ }^\circ\text{C}^{-1}$, surface tension 73 dynes cm^{-1} at 20°C , viscosity 0.01 poise at 20°C , dipole moment $1.84 \times 10^{-3} \text{ esu}$, high heat of evaporation 540 cal g^{-1} , molar heat of fusion 6.02 kJ . These properties of water are due to hydrogen bonding. Each water molecule is surrounded by four water molecule neighbours in a tetrahedral manner.

Classification of Fresh Water Bodies. Fresh water constitutes about 3% of the global water resources. It may be of two natural types.

- Standing or lentic water (Lentis-calm).** Examples are lakes, ponds and swamps. Here circulation of water is slow and usually of vertical types.
- Running or lotic water (Lotus-washed).** Examples are rivers, streams and springs. Here circulation of water is fast and water moves horizontally.

Chemical Composition (Acid-Base Chemistry) of Lakes, Rivers and Streams

Lakes are fresh water bodies where the limnetic and profundal zones are relatively larger as compared to the littoral zone. Rivers possess a definite and continuous water

current. Stream with its load of dissolved and suspended matter flows towards a lower line following the line of least resistance.

Lakes, rivers, ponds and streams have slightly different chemical composition. Their common major anionic constituents are CO_3^{2-} , SO_4^{2-} and silicate. The dominating cation is Ca^{2+} which is present as carbonate and bicarbonate. Calcium plays an important role in controlling the pH of aquatic environment.

The average chemical composition (world mean) of river, stream and lake water is expressed in percentage weight as follows :

CO_3^{2-}	SO_4^{2-}	Cl^-	NO_3^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	$(\text{FeAl})_2\text{O}_3$	SiO_2
35.2	12.1	5.7	0.9	20.4	3.4	5.8	2.1	2.7	11.7

Some salts of Ca, P, N, Si and other minerals are present in traces. NO_3^- , NO_2^- and NH_4^+ salts are essentially the food for aquatic vegetation. The growth of phytoplankton (blue green algae) depend on N content of water. The concentration of salts in lake and river water is lower than that of seas, thus fresh water acts as hypotonic medium for aquatic organisms.

The pH of water is influenced by soluble organic and inorganic substances. It is an intensity factor that measures the concentration of alkalinity or acidity present in water. The alkalinity is a capacity factor which is a measure of the ability of a water sample to sustain reaction with added acid or base.

Lake water may be well buffered, transitional or acidic (Fig. 2) depending on their position on the titration curve. The alkalinity is then a measure of the extent of well buffered region. When a lake approaches the transitional stage, a very little acidification is needed to drive it past the end point with its drop in pH. Such lakes are highly sensitive to acid inputs from natural or anthropogenic sources. A high value of alkalinity means that an excess of acid should be added to bring the lake into transitional and acidic ranges.

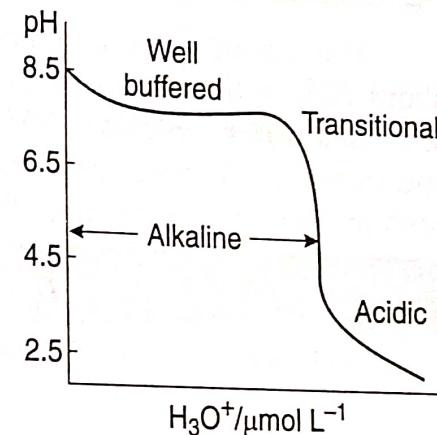


Fig. 2. Lake water status in terms of acid/base nature.

Table 1. Sensitivity of lakes in terms of alkalinity.

Sensitivity	Proton accepting capacity ($\mu\text{mol L}^{-1}$)	CaCO_3 (mg L^{-1})	Ca^{2+} (mg L^{-1})
High	< 200	< 10	< 4
Moderate	200–400	10–20	4–8
Weak	> 400	> 20	> 8

The relation between alkalinity expressed as proton accepting capacity and as CaCO_3 expressed as :

$$1 \text{ mg CaCO}_3 = 1000 \mu\text{g CaCO}_3$$

$$1000 \mu\text{g}/100 \text{ g mol}^{-1} = 10 \mu\text{mol CO}_3^{2-} \quad (100 \text{ g mol}^{-1} \text{ is molar mass of CaCO}_3)$$

Since each CO_3^{2-} ion can neutralise two H_3O^+ ions, so $10 \mu\text{mol CO}_3^{2-}$ ion is equivalent to $20 \mu\text{mol}$ proton accepting capacity. Hence alkalinity of a solution containing $20 \mu\text{mol L}^{-1}$ of proton accepting species could also be reported as $1 \text{ mg L}^{-1} \text{ CaCO}_3$.

Rivers and streams have a high percentage of O_2 than lakes. O_2 content varies with seasonal and diurnal variations. Lakes showing winter stratification exhibit depleted O_2 concentration. CH_4 and CO (toxic) gases are formed at the bottom due to decomposition of organic matter. Lakes and rivers that receive sewage and industrial effluents show an abundance of H_2S as an anaerobic decomposition product. NH_3 is formed due to discharge of industrial waste into water. It is toxic to aquatic organisms in higher concentration.

Wet Lands or Wealth Lands.

Wet lands are areas of submerged or water saturated lands, natural or artificial, static or flowing, fresh or brackish, saline including areas of marine water, the depth of which at low tide does not exceed six metres. Wet lands include ponds, lakes, rivers, streams, marshes, reservoirs, mangroves and marine water of shore lines. Chemical composition of wet lands viz., lakes, rivers and streams is described earlier.

Chemical Composition (Acid-Base Chemistry) of Sea Water.

The marine ecosystem includes seas, oceans, bays and estuaries. Seas and oceans cover about 70% of the earth's surface. They have a volume about 15 times greater than that of land. Sea water contains 0.5 M NaCl and 0.05 M MgSO_4 along with MgCl_2 , K_2SO_4 , CaCO_3 and traces of all conceivable matter in the universe. An estimate showed that the whole sea contains enough salt to cover the continents with a layer of 100 m thick.

Table 2. The elemental composition of sea water.

Element	Chemical species	Abundance mg/L (ppm)	Residence time (year)
Na	Na^+	10.5×10^3	6×10^3
K	K^+	380	1.1×10^7
Mg	Mg^{2+} , MgSO_4	1.35×10^3	4.5×10^7
Ca	Ca^{2+} , CaSO_4	400	8.0×10^6
Sr	Sr^{2+} , SrSO_4	8.0	1.1×10^7
Ba	Ba^{2+} , BaSO_4	0.03	8.4×10^4
Fe	$\text{Fe(OH)}_3(s)$	0.01	1.4×10^2
Zn	Zn^{2+} , ZnSO_4	0.01	1.8×10^5
Cu	Cu^{2+} , CuSO_4	0.01	5.0×10^4
Ni	Ni^{2+} , NiSO_4	0.02	1.8×10^4
Mn	Mn^{2+} , MnSO_4	0.02	1.4×10^4
V	$\text{VO}_2(\text{OH})$	0.02	1.0×10^4
Co	Co^{2+} , CoSO_4	0.02	1.8×10^4
Cd	Cd^{2+} , CdSO_4	5×10^{-4}	5.8×10^5

Sea water contains about 2000 times more dissolved salts than fresh water. The most abundant elements (except H and O), viz., Na, Cl, Mg constitute 90% of the matter in sea water while K, Ca, SO_4^{2-} exhibit 3% and other elements 7%. The seas and oceans are the final sinks for many substances involved in numerous geochemical processes. Ocean waters are more or less well mixed with the result that, in contrast to the variable composition of fresh water bodies, the ratios of the major constituents of sea water are almost the same all over the globe although the salinity is variable from place to place. The elemental composition of sea water with principal chemical species is illustrated in Table 2.

Other chemical species occurring in sea water constitute Pb^{2+} , PbSO_4 , Cs^+ , V^{3+} , AsCl_2 , Cl^- , SO_4^{2-} , HCO_3^- , H_2CO_3 , B(OH)_3 , HAsO_4^{2-} , H_3AsO_3 and organic compounds etc.

Physical Chemistry of Sea Water.

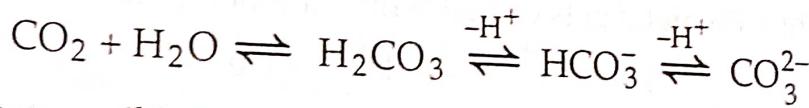
Sea water chemistry is extremely complicated since it deals with a system having un-conventional parameters such as average temperature 5°C ($0 - 30^\circ\text{C}$) and pressure 200 atm (1 atm at the surface and 1000 atm at the bottom). It is estimated that oceans have undergone about 0.5 million rotations during 500 million years assuming a rotation period of 1000 years. This indicates that the liquid phase has been thoroughly mixed. The constant interactions of sea water with atmosphere, biosphere and sediment involve unique dimensions to the equilibrium processes.

Sea Water Equilibrium.

Following parameters should be considered to understand sea water equilibrium.

1. pH. The constant pH of sea water (8.1 ± 0.2) all over the world is complicated to explain. Possible mechanisms involved are :

- (i) Buffering action of $\text{B(OH)}_3 - \text{B(OH)}_4^-$ system.
- (ii) Buffering action of $\text{H}_2\text{CO}_3 - \text{HCO}_3^- - \text{CO}_3^{2-}$ system.

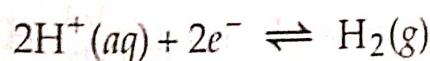


(iii) Ion-exchange equilibria of dissolved cations with silicates of the marine sediment.
 $2\text{K}^+ + 2\text{Ca}^{2+} + 3\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(s) + 4\text{SiO}_2(s) + 9\text{H}_2\text{O} \rightleftharpoons 2\text{KCaAl}_3\text{Si}_5\text{O}_{16}(\text{H}_2\text{O})_6(s) + 6\text{H}^+$

Ion-exchange equilibrium seems to be the major buffering factor in the sea water.

2. pE. Just as pH is defined as the negative log of hydrogen ion activity in aqueous solution, $\text{pH} = -\log(a_{\text{H}^+})$, similarly, pE is defined as the negative log of the electron activity in aqueous solution.

The thermodynamic definition is based on the reaction :



The free energy change for this reaction is exactly zero when all components of the reaction are at unit activity. This reaction forms the basis for the free energies of formation of ions in aqueous solution and also defines the free changes for redox processes in water.

- Addition of excess of undesirable substances to water that make it harmful to man, animal and aquatic life, or otherwise cause significant departures from the normal activities of various living communities in or around water.
- Water pollution altogether nullifies or decreases the suitability of water resources for human consumption or for the support of man's natural life process. (Felfoldy 1982)
- Foreign substances, either from natural or anthropogenic sources, contaminated with toxicant may be harmful to life because of their toxicity, reduction of normal oxygen level of water, aesthetically unsuitable and spread epidemic diseases. (WHO 1986)
- Water gets polluted when its normal functions and properties are altered. It indicates the state of deviation from the quality and purity of water sample.
- Pollution means the presence of any toxic substance in water that degrades the quality to constitute a hazard or impair its usefulness.
- Water pollution is caused due to harmful solids, liquids or gases which are non-permissible, undesirable, unpleasant and objectionable. (USPHS)
- Water pollution is a by-product of rapid and unplanned industrial progress and over population.
- Discharge of any trade effluent, sewage or solid, liquid, gaseous substances into water. This contaminant in water by foreign substances may be direct or indirect and likely to cause nuisance. It renders such water injurious to public health, domestic, commercial, industrial, agricultural and other uses.
- Water pollution is considered not only in terms of public health but also in terms of conservation, aesthetics, preservation of natural beauty and resources.
- Water pollution actually represents the state of deviation from the pure condition whereby its normal function and properties are affected. Any shift in the naturally dynamic equilibrium existing among environmental segments i.e., hydrosphere, lithosphere, atmosphere or sediments give rise to the state of water pollution.

CLASSIFICATION OF WATER POLLUTION

Water pollution can be classified into four categories viz., physical, chemical, biological and physiological pollution of water.

Physical Pollution of Water.

It brings about changes in water with regard to its colour, odour, density, taste, turbidity and thermal properties etc.

Colour. Colour change is not harmful unless it is associated with a toxic chemical, but it may affect the penetration of sunlight inhibiting plant and animal metabolism. Most of the trade wastes discharged into water systems the pronounced colours due to organic dyes and inorganic complexes. Even a micro quantity (0.002 ppm) of magenta in water imparts a distinct red colouration. Tannery wastes when discharged into iron containing water streams yield deep green or blue colouration because of the interaction of tannins with iron.

Turbidity. Turbidity in water mainly arises from colloidal matter, fine suspended particles and soil erosion. Generally greater the turbidity, stronger is the sewage and the industrial effluent concentrations and worst are the effects. Hence the degree of turbidity of

a water course may be taken as a measure of the intensity of pollution. However, non-turbidity does not mean that water is unpolluted, because clear water may also be heavily contaminated with acids, alkalies, etc., which do not cause turbidity.

Turbid water becomes unsuitable for industrial purposes and also for domestic use because Fe, Mn, Ni, Co, Pb, Sb, Bi etc. present in it may cause stains on clothes, sinks and baths etc. Turbidity measurements are useful in the evaluation of the effects of pollution by waste waters and to follow the course of self purification of rivers and streams etc. Colloidal particles, i.e., clay in natural waters and carbohydrates, proteins, fats in waste waters can be stabilized by having negative charges on their surfaces which can be neutralized by adding certain ions. Various coagulants like ferric chloride, ferric sulphate and ferric alum etc. can check turbidity of water.

Taste. Unpleasant earthy or musty taste and odour are produced by industrial effluents containing Fe, Mn, free chlorine, phenols and aquatic actinomycetes. For example, even a 0.1 ppm of Fe can produce an inky taste, while phenol produces a bitter taste at 7 ppm. Manganese, chlorophenols, petroleum products, detergents, pesticides etc. produce characteristic tastes in water. The decomposed organic matter, algae, fungi, bacteria and pathogens impart peculiar taste. However, these pollutants can be removed by conventional water purification techniques like **chlorination, chemical precipitation and using activated carbon.**

Odour. Odour pollution of water is caused both by chemical agents (like hydrogen sulphide, free chlorine, ammonia, phenols, alcohols, esters, hydrocarbons) and biological agents (such as algae, fungi, micro-organisms etc). Lower the pH, higher will be the amounts of H₂S produced and greater will be the odour nuisance. Certain organic and inorganic compounds of nitrogen, sulphur, phosphorus and putrefied organic matters present in sewage cause foul odour in polluted water.

Micro-organisms like algae, oscillatoria and rivularis cause muddy odour, whereas Anabaena produces a strong grassy odour. Protozoa Dinobryon imparts fishy odour to water.

Chemical Pollution of Water.

The chemical pollution of water causes changes in acidity, alkalinity or pH and dissolved oxygen. It may be caused either by organic pollutants or inorganic pollutants or by both. The organic pollutants can be biodegradable or non-biodegradable.

Biodegradable organic pollutants include proteins from domestic sewage, long time. Non-biodegradable organic pollutants are those which persist in the aquatic system for a protecting agricultural products also poses serious water pollution problems, because these toxic chemicals ultimately find their way into the nearby water course.

Biological Pollution of Water.

Bacterial pollution in water is caused by the excretory products of man, animals and birds. The main pollutants belong to coliform group and certain subgroups, faecal

2. By Nephelometer. Preparation of Standard Turbid Suspension. Dissolve 1 g of hydrazine sulphate in 100 mL of distilled water. Also dissolve 10 g of hexamethylene tetramine in 100 mL of water. Mix 5 mL of each solution in 100 mL volumetric flask and dilute it with distilled water to the mark. This suspension gives a turbidity of 400 NTU.

Method.

- Set the nephelometer at 100 using 40 NTU (10 mL of the above stock solution in 100 mL water) standard suspension. Every percent of the scale will be equal to 0.4 NTU.
- Shake the sample thoroughly. Take the sample in nephelometer tube and read the value on the scale. If the sample has turbidity more than 40 NTU, dilute it, so the turbidity can be read on the same scale.

Calculation.

$$\text{Turbidity (NTU)} = \text{Nephelometer reading} \times 0.4 \times \text{Dilution factor}$$

CONDUCTIVITY

Conductivity of water varies directly with the temperature and is proportional to its dissolved mineral matter content. Specific conductance can be measured by conductivity meter using dip-type cell. The instrument and cell are calibrated with 0.005 M KCl solution (conductivity = $654 \mu \text{mho cm}^{-1}$).

$$\text{Specific conductance, } \kappa = \frac{1}{R} \cdot \frac{A}{l}$$

where R is the observed resistance of a column of electrolyte, 1 cm long and cross-section area $A \text{ cm}^2$.

Electrical Conductivity (EC).

EC is a measure of water's capacity to convey electric current. EC is directly proportional to area (a) and inversely proportional to length (l).

$$\text{EC} \propto a/l \quad \text{or} \quad \text{EC} = \kappa a/l$$

where κ is proportionality constant called specific conductance.

Measurement of Electrical Conductivity. The instrument consists of an AC salt bridge or electrical resistance bridge and conductivity cell having electrodes coated with platinum black. Solubridge (calibrated assembly) gives conductivity of the solution in millimhos/cm or deci Siemen/m at 25°C.

Principle. A simple Wheatstone bridge circuit is used to measure EC by null method. The bridge consists of known and fixed resistances r_1, r_2 , variable standard resistance r_4 and unknown r_3 . The variable resistance r_4 is adjusted until a minimum or zero current flows through the AC galvanometer. At equilibrium,

$$\frac{r_1}{r_2} = \frac{r_3}{r_4} \quad \text{or} \quad r_3 = \frac{r_1}{r_2} \times r_4$$

Since conductivity is reciprocal of resistivity, it is measured with the help of r_3 .

Reagents, Standard KCl Solution (0.01 M). Dissolve 0.7456 g of dry KCl in double distilled water and make up the volume to one litre. It gives EC of 1.413 deci Siemen/m at 25°C.

Method.

- Take the water sample in a beaker.
- Warm up the instrument and calibrate the meter with 0.01 M KCl.
- Adjust cell constant and temperature of the conductivity meter.
- Rinse the conductivity cell with distilled water and then with the sample.
- Connect the conductivity cell to meter and dip in the sample.
- Adjust the current by rotating the dial so that maximum sensitivity is obtained.
- Read the conductivity value in dS/m . Direct reading may be obtained by digital meters.

Result. Observed values of EC are multiplied by the cell constant and a temperature factor to express results at 25°C.

pH (HYDROGEN ION CONCENTRATION)

pH, a measure of hydrogen ion activity, is used to express the intensity of acidic or alkaline condition of a solution. It is also an important factor in water analysis since it enters into the calculation of acidity, alkalinity and processes like coagulation, disinfection and corrosion control. The pH of a sample can be determined electrometrically or colorimetrically.

Electrometric Method for the Determination of pH.

Principle. Electrometric determination of pH involves the measurement of electromotive force (EMF) of a cell comprising an indicator electrode (glass electrode) responsive to hydrogen ions and a reference electrode (calomel electrode). The accurate pH meter can read to ± 0.005 pH unit.

Measurement of pH. (i) First standardize the pH meter using a standard buffer solution of pH near that of the sample to be tested. Different buffer solutions can be prepared as follows :

pH 7 buffer solution. Dissolve 1.361 g anhydrous potassium dihydrogen phosphate (KH_2PO_4) and 1.420 g disodium hydrogen phosphate Na_2HPO_4 in distilled water and make upto 1000 mL in a volumetric flask.

pH 9 buffer solution. Dissolve 3.81 g borax ($Na_2B_4O_7 \cdot 10H_2O$) in distilled water to 1000 mL.

(ii) Then check the electrode response by measuring the pH of another standard buffer solution having different pH.

Interpretation of the result. Based on pH values, following conclusions can be drawn.

- Waters having pH above 8 contain carbonates. It may be with or without bicarbonates.
- Waters with pH value in the range of 4.5 to 8 contain no carbonates but contain bicarbonates and carbonic acid. Natural waters fall under this category.

- Waters having pH value below 4.5 contain carbonic acid but not carbonates or bicarbonates.
- The desirable pH range for drinking waters is 7.0 to 8.5.
- pH in conjunction with total salinity, total alkalinity and temperature is used to determine whether a water is corrosive in nature or having scale forming tendencies.

Knowledge of pH is essential in the selection of coagulants for water purification. For instance, aluminium sulphate is effective at pH 6.7, while ferrous sulphate coagulates well at a higher pH.

ACIDITY

Acidity is a measure of the effects of combination of compounds and conditions in water. It is the power of water to neutralise hydroxyl ions and is expressed in terms of calcium carbonate. Water attain acidity from industrial effluents, acid mine drainage, pickling liquors and from humic acid.

Measurement of Acidity by Titration Method.

Principle. Acidity of water can be determined by titration with sodium hydroxide solution. The amount of sodium hydroxide required for the sample (pH below 4.5) to reach pH 4.5 (methyl orange end point) is a measure of mineral acidity while the amount of sodium hydroxide to reach pH 8.3 (phenolphthalein end point) is a measure of total acidity. Samples containing acidic wastes (pH below 4.5) correspond to both mineral and CO_2 acidity.

Procedure.

Mineral acidity. Take 50 mL or suitable dechlorinated aliquot of the sample in a 250 mL conical flask. Add 2 drops of methyl orange indicator and titrate with 0.02 N—NaOH solution till faint orange colour.

Total acidity at boiling temperature. To 50 mL of the sample, add 5 drops of phenolphthalein indicator. Heat to boil for 2 minutes. Titrate with 0.02 N NaOH solution to pink colour.

Calculations.

$$\text{Acidity as } \text{CaCO}_3 \text{ mg/L} = \frac{\text{mL titrant (NaOH)} \times 1 \times 1000}{\text{mL sample taken for titration}}$$

Result. Methyl orange acidity value shows mineral acidity. In absence of mineral acidity, total acidity is only the CO_2 acidity of the sample.

Total Acidity. Total acidity expressed as CaCO_3 , can also be determined in the following manner. Take 100 mL of a sample in a tall cylinder to decrease the surface of the sample and minimize loss of dissolved carbonic acid during titration. Now add few drops of phenolphthalein indicator and titrate the solution very rapidly against 0.02 N NaOH with constant stirring until a faint pink colour is obtained.

Calculation.

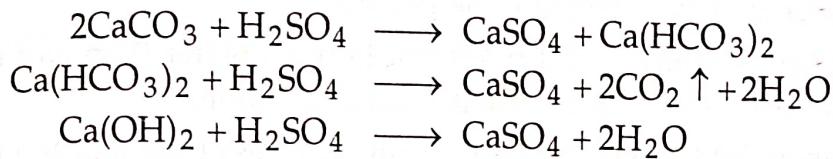
$$\text{mL alkali titration} \times \text{normality} \times 0.05 \times \frac{10^6}{\text{Vol. of sample}} = \text{ppm}$$

ALKALINITY

Alkalinity of water is due to the presence of carbonate and hydroxide ions.

Determination of Alkalinity by Titrimetric Method.

Principle. Alkalinity is determined by titration with 0.02 N H₂SO₄ using methyl orange and phenolphthalein as indicators.

Reactions.**Reagents.**

- (i) **Sulphuric acid 0.02 N.** Dilute 20 mL of 1N-H₂SO₄ to 1000 mL with distilled water.
- (ii) **Sodium carbonate solution.** Dissolve 13.25 g Na₂CO₃ in distilled water to 250 mL.
- (iii) **Phenolphthalein indicator solution.** Dissolve 500 mg phenolphthalein in 50 mL alcohol and 50 mL distilled water. Add 0.02 N NaOH solution till light pink colour appears.

Procedure. Take 50 mL of the sample in a 250 mL conical flask. Add 2 drops of phenolphthalein indicator. Titrate the pink colour with 0.02 N-H₂SO₄ till it becomes colourless. If the sample contains waste waters, then remove the suspended matter by filtration or centrifugation and then determine alkalinity.

Calculations. If H₂SO₄ used for titration is 0.02N, phenolphthalein alkalinity (as CaCO₃) mg/L

$$= \frac{\text{mL } 0.02 \text{ N H}_2\text{SO}_4 \text{ for phenolphthalein end point} \times 1 \times 1000}{\text{mL sample taken for titration}}$$

Total alkalinity (as CaCO₃) mg/L

$$= \frac{\text{mL } 0.02 \text{ N H}_2\text{SO}_4 \text{ for total alkalinity end point} \times 1 \times 1000}{\text{mL sample taken for titration}}$$

Result. Alkalinity measurements are used as the means of evaluating the buffering capacity of waste waters and sludge. It is also significant in determining the suitability of a water for irrigation, in the treatments of natural and waste waters and to calculate the Langelier Saturation Index. Alkalinity provides an idea of the nature of salts present in water. If it is equal to hardness, calcium and magnesium salts are only present in water. If alkalinity is less than hardness, sulphates of calcium and magnesium must be there. Greater alkalinity shows the presence of alkali salts of sodium and potassium in addition to those of calcium and magnesium.

Alkalinity can also be predicted in the following manner.

Take 100 mL of the filtered sample in a conical flask and add few drops of alcoholic phenolphthalein indicator to it. Now titrate the solution with 0.02N HCl until colourless. If the sample is colourless after the phenolphthalein indicator is added, add few drops of aqueous methyl orange indicator till an orange pink colour is obtained at the end point. The nature of alkalinity is then predicted from the titration as follows :

- If the titration to the phenolphthalein end point is zero, the alkalinity may be regarded as due to bicarbonate alone.
- When there is no further titration to the methyl orange end point after the phenolphthalein end point, the alkalinity is solely due to the hydroxide.
- When the phenolphthalein end point titration is half the total titration, only carbonate alkalinity is expected to be present.
- When the phenolphthalein end point titration is greater than half the total titration, the alkalinity is due to both carbonate and hydroxide.
- When the phenolphthalein end point titration is less than half the total titration, the alkalinity is due to carbonate and bicarbonate.

Those waters that have been softened with orthophosphate do not obey the above rules. All kinds of alkalinity are expressed in terms of CaCO_3 .

CHLORIDE

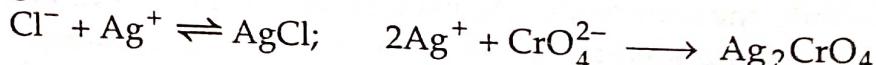
Chloride in drinking water is harmless if present below 250 ppm but its higher content harms metallic pipes and crops.

Mohr's Method.

Chloride is determined by titration with AgNO_3 solution using K_2CrO_4 as an indicator. The end point is indicated by the appearance of reddish tinge. The method is valid for 0.15 to 10 mg Cl^- and electrical conductivity of water is greater than 1 dS/m at 25°C.

Procedure.

- Take 100 mL sample in 250 mL conical flask. Adjust pH from 7 to 10 with H_2SO_4 or NaOH (0.5 g $\text{Na}_2\text{B}_4\text{O}_7$ will keep the pH at 9).
- Add 1 mL of 5% K_2CrO_4 indicator with stirring.
- Titrate with 0.0282 N AgNO_3 solution (282 mL of 0.1 N AgNO_3 diluted to 1 litre) to a reddish tinge.



Calculations. 1 mL of 0.0282 N AgNO_3 = 1 mg Cl^-

$$\text{or } \text{Cl}^- (\text{mg/L}) = \frac{\text{Normality of AgNO}_3 \times \text{Vol. of AgNO}_3 \times \text{Eq. wt. of Cl}^-}{\text{mL of Sample taken}}$$

Potentiometric titration is performed for smaller quantities of chloride with AgNO_3 using glass and $\text{Ag}-\text{AgCl}$ electrode system.

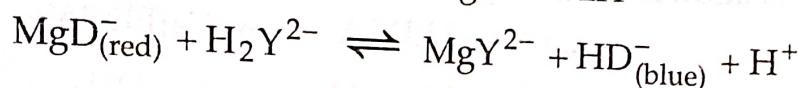
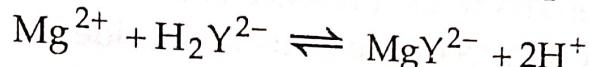
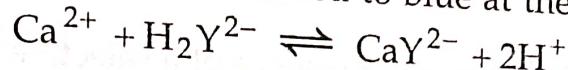
HARDNESS

Hardness indicates water quality, mainly in terms of Ca^{2+} and Mg^{2+} expressed as CaCO_3 . Temporary hardness is due to the presence of bicarbonates of Ca^{2+} and Mg^{2+} . It may be removed by boiling the water. Permanent hardness is due to the presence of sulphates and chlorides of Ca^{2+} and Mg^{2+} .

Complexometric Titration.

Principle. During titration with EDTA ($\text{Na}_2\text{H}_2\text{Y}$), Ca^{2+} first reacts to form stable CaY^{2-} followed by Mg^{2+} to give MgY^{2-} complex (indicator/ wine-red) releasing free indicator (blue). The colour changes from wine-red to blue at the end point.

Reactions.



Procedure for Ca^{2+} and Mg^{2+} Hardness.

Take 20 to 50 mL sample of hard water in a conical flask. In presence of organic matter in waste waters, add 2 to 4 drops of 30% H_2O_2 .

- Adjust the pH to 8, boil for 15 minutes and cool.
- Add 5 mL buffer of pH 10 (142 mL conc. NH_3 + 17.5 g NH_4Cl diluted to 250 mL with deionised water) and warm the solution.
- Add two drops of 1.4% Eriochrome black T in triethanolamine.

Titrate with 0.01 M EDTA solution till the colour changes from wine-red to blue.

Calculations.

$$1 \text{ mL } 0.01 \text{ M EDTA} \equiv 1.0 \text{ mg CaCO}_3$$

$$\text{Hardness (mg/L)} = \frac{\text{Vol. of EDTA used} \times 0.01 \text{ M} \times 1000}{\text{mL of Sample taken}}$$

This gives total Ca^{2+} and Mg^{2+} .

Procedure for Ca^{2+} Hardness.

- To a 100 mL sample add 20% KOH solution to bring the pH to 12 and precipitate Mg^{2+} as $\text{Mg}(\text{OH})_2$.
- Add 5 to 10 drops of calcon carboxylic acid indicator (0.4% in methanol).
- Titrate with 0.05 M EDTA under magnetic stirring till the colour changes from wine-red to pale blue.

Alternatively, add 5 drops of mureoxide indicator (0.1 g stirred with 2.5 mL deionised water and filtered). Titrate with 0.05 M EDTA solution till the colour changes from orange to violet.

Calculation. 1 mL of 0.01 M EDTA $\equiv 0.4008 \text{ mg Ca}$.

15

Treatment of Sewage and Industrial Waste Water

PROLOGUE

- INTRODUCTION
- DOMESTIC SEWAGE TREATMENT
- SEWAGE TREATMENT METHODS
- INDUSTRIAL WASTE WATER TREATMENT
- COMMONLY USED BIOLOGICAL TREATMENT PROCESSES
- AEROBIC AND ANAEROBIC TREATMENT PROCESSES
- SLUDGE TREATMENT AND DISPOSAL

INTRODUCTION

The objective of sewage and industrial waste water treatment is to extract pollutants, absorb or distil or neutralise coarse particles, perform disinfection, applying biological, chemical or membrane techniques and finally refining the effluent so as to make it fit for agricultural purposes. Since water pollution is caused by domestic sewage and industrial wastes, any abatement of water pollution depends mainly on the efficiency of waste water treatment. It is obvious that non-hazardous organic waste from domestic sewage must be treated separately from toxic industrial wastes.

DOMESTIC SEWAGE TREATMENT

The waste water from kitchens, bathrooms and lavatories is called **domestic sewage**. The wastes disposed from factories, laundries, business houses, laboratories etc. also result in sewage. The spent water from community as a whole is called **sanitary sewage**.

Table 1. Nature of domestic sewage.

Parameter	Values in mg/L	Parameter	Values in mg/L	Parameter	Values in mg/L
pH	5.5 to 9.0	BOD	500	TSS	600
Temperature	45°C	Phenolic compounds	5	Oil and grease	100
Cyanides	2.0	TDS	2100	Sulphate	1000
Cu, Cr, Pb, Ni	1-3	Zn	15	Sodium	60

Composition of Domestic Sewage. Domestic sewage contains :

- Organic impurities, urea, proteinaceous matter, fats, carbohydrates, detergents, faeces, animal wastes, pesticides such as PCB (1–10.5 ppm), DDT (0–1.0 ppm), DDD (0–0.5 ppm) and dialdrin (0–2.0 ppm).
- Inorganic impurities, e.g., nitrates, phosphates, surfactants, toxic metals like Cd (0–100 ppm), Pb (0–400 ppm), Zn (300–2000 ppm), grit, salts, Ca and C etc.
- Saprophytic bacteria which feed on organic matter.
- Pathogenic bacteria such as faecal coliform (1×10^7 /100 mL) and human viruses etc.
- Industrial wastes, wherever applicable.

Objectives of Sewage Treatment.

- To stabilise the organic content of sewage. Stabilisation is the process which involves break down of organic matter into simpler substances with the help of aerobic or anaerobic bacteria.
- To reduce toxicity and possibility of spread of diseases by pathogens.
- To render the sewage inoffensive and devoid of its nuisance value.
- To prevent contamination of water supplies, thereby protecting aquatic life.

Strength of Sewage.

Strength of sewage is usually expressed in terms of 5-day BOD and COD. On an average a sewage with 200 mg/L BOD or < 400 mg/L COD is termed as weak sewage, with 500 mg/L BOD or 1000 mg/L COD is called strong sewage and one with > 750 mg/L of BOD or > 1500 mg/L of COD is termed as extremely harmful sewage. If we consider the average composition of Indian sewage, it contains BOD 280 mg/L, chloride 200 mg/L, ammonical nitrogen 25 mg/L. With the rise in temperature, BOD value also increase.

SEWAGE TREATMENT METHODS

The extent of sewage treatment required mostly depends on the (i) content of suspended solids and (ii) BOD of the sewage. The following major treatment methods are generally employed.

1. Preliminary Treatment.

Screening. In this treatment, gross solids like large floating and suspended solid matter, grit, oil and grease are removed by passing waste water through screens, grit chambers and skimming tanks.

2. Primary Treatment.

Primary treatment of sewage removes about 60% of the suspended solids, 30% COD, 35% BOD, 10% P and 20% total N. Following processes are employed.

- (i) **Sedimentation.** The settleable solids can be efficiently removed by gravitational settling under quiescent conditions. The settled sludge is removed from horizontal flow sedimentation tanks or centre-feed circular clarifiers by mechanical scrapping into hoppers. In a well designed continuous flow sedimentation tank, about 50% of the suspended solid matter is settled out within two hours of detention time.
- (ii) **Mechanical Flocculation.** The waste water is passed through clariflocculator where by gentle stirring, the **finely divided** suspended solids coalesce into larger particles and settle out.
- (iii) **Coagulation.** Sewage or waste water is well mixed in baffled channels with certain coagulants to form a floc that absorbs and entrains suspended and colloidal particles present. Coagulants in common use are : alum, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, FeCl_3 and hydrated lime. Coagulant aids such as activated silica and poly electrolytes enhance coagulation to form quick settling flocs.

3. Secondary (Biological) Treatment.

In secondary treatment, the dissolved and colloidal organic matter in waste water/sewage is removed by aerobic or anaerobic biological processes. Micro-organisms bring about following sequential changes.

- Coagulation and flocculation of colloidal matter.
- Oxidation of dissolved organic matter to CO_2 .
- Degradation of nitrogenous organic matter to NH_3 which is then converted into NO_2^- and NO_3^- .
- Reduction of BOD and removal of oil, phenol, grit, grease and scum.

The effluent from primary sedimentation tank is first subjected to **aerobic oxidation** in systems such as aerated lagoons, activated sludge units, trickling filters, oxidation ditches, ponds etc. Then the sludge obtained in these aerobic processes, together with that obtained in the primary sedimentation tank, is subjected to **anaerobic digestion** in the sludge digesters.

Almost all organic substances, except a few hydrocarbons and ether can be oxidised by aerobic biological treatment. Complex cell tissues and protein materials are also synthesized during the process, which are then agglomerated and removed from the waste by settling. Resistant organics like cyanides and phenols can also be destroyed by special type of

microbes, after prolonged acclimatization periods. Under anaerobic conditions, certain group of micro-organisms carry out the digestion of complex organic wastes.

After secondary treatment, about 80% reduction in COD, 90% reduction in BOD, 30% reduction in P, 50% reduction in total N, could be achieved.

4. Tertiary Treatment.

Tertiary treatment is the final treatment, meant for polishing the effluents from the secondary treatment processes.

Main objectives of tertiary treatment are :

- Removal of fine suspended and dissolved inorganic solids with the help of micro-strainers and sand filters.
- Removal of final traces of organics.
- Reducing the load of N and P in the effluents.
- Removal of bacteria, particularly of faecal origin by retaining the waste water from secondary biological treatment plants in maturation ponds or lagoons for specified period of time. Three lagoons arranged in series give an excellent final effluents with very low BOD and suspended solids.

Processes Employed in Tertiary Treatment.

(i) **Coagulation.** The residual solids in waste water are coagulated and removed by filtration.

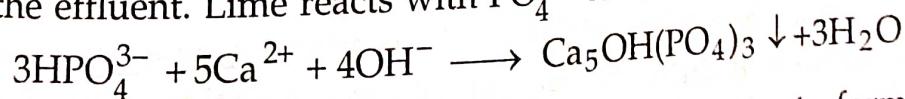
(ii) **Precipitation.** Lime is added to precipitate calcium salts as calcium phosphate.

(iii) **Adsorption.** The undesirable tastes and odours are removed by adsorption on activated charcoal.

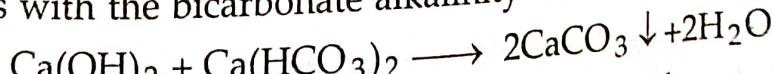
(iv) **Chlorination.** The residual micro-organisms in the effluent are removed by chlorination before it is discharged.

(v) **Nitrogen stripping.** Nitrogen is present in the effluent in the form of NH_3 , NO_2^- and NO_3^- which enhance eutrophication. NH_3 in the effluent is removed by trickling the effluent from the top of a baffle tower while it meets the air coming upwards.

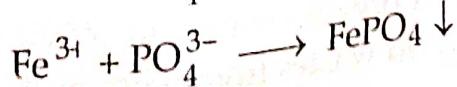
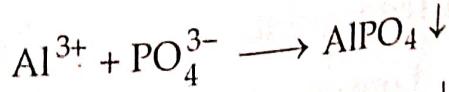
(vi) **Phosphorus removal.** A number of chemicals such as lime, ferric chloride, ferric sulphate, aluminium sulphate and sodium aluminate are effective for the removal of phosphorus from the effluent. Lime reacts with PO_4^{3-} to form insoluble hydroxypatite.



Lime also reacts with the bicarbonate alkalinity of waste water to form CaCO_3 .



Fe and Al salts may be used to precipitate soluble phosphorus as ferric or aluminium phosphate.



The hydroxides of Fe and Al are also formed which aid in coagulation of the phosphate precipitate. Biological Bardenpho and Phostrip processes are also used to remove phosphorus. Some bacteria can accumulate phosphorus within their bacterial cells in the form of polyphosphates which can be eliminated from the system.

(vii) **Oxidation** ponds, oxidation ditches, lagoons or sewage stabilisation ponds can remove microbes by 99% and BOD by 90%.

(viii) **Desalination.** The residual dissolved inorganic impurities may be removed by ion-exchange, reverse osmosis or electrodialysis.

(ix) **Anaerobic digestion.** It is carried out using digesters, septic tanks and imhoff tanks. The process removes about 90% BOD and 60% settleable solids. The biogas so produced can be used as domestic fuel.

INDUSTRIAL WASTE WATER TREATMENT

1. Preliminary Treatment.

The principal objectives of preliminary treatment are the removal of gross and suspended solids. Removal of **gross solids** is accomplished by passing waste water through mixed or moving screens. The modern mechanical screens cum filters include rotary, self cleaning, gravity type and circular over head fed vibratory units. These screens are very effective in reducing **suspended solids and BOD**. The emulsified oil and grease from wool-scouring wastes can only be removed by chemical reagents instead of skimming methods.

2. Primary Treatment.

- (i) **Sedimentation.** Sedimentation is particularly useful for treatment of waste water containing high percentage of settleable solids or when the waste is subjected to combined treatment with sewage. For larger proportion of industrial wastes, a long detention time helps in mixing and balancing the various wastes and safe guards against unduly heavy loads being passed on to the biological purification plants.
- (ii) **Mechanical Flocculation and Coagulation.** These processes are used to remove fine suspended solids and colloidal particles using coagulants.
- (iii) **Equalisation.** Some industries produce different types of wastes having different characteristics at different intervals of time. **Aeration** or mechanical agitation give better mixing of the different unit volumes of effluents.
- (iv) **Neutralisation.** Highly acidic wastes are neutralised by lime-slurry or NaOH while alkaline wastes are neutralised by H_2SO_4 or CO_2 or waste boiler flue gas.

3. Secondary (Biological) Treatment.

The dissolved and colloidal organic matter in waste water is removed by aerobic or anaerobic processes. Organic liquid wastes from dairy and slaughter house etc. were treated

by anaerobic method more economically. The efficiency of this process depends upon pH, temperature, waste loading, absence of O₂ and toxic materials.

[For details—Refer to commonly used Biological treatment processes for sewage and industrial waste water.]

4. Tertiary Treatment.

Tertiary treatment is the final treatment meant for polishing the secondary effluents and removal of fine suspended solids, traces of organics and bacteria. Removal of dissolved inorganic solids is a major problem with waste waters from industries such as fertilizers, textile processing, tannery and electroplating. Depending upon the required quality of the final effluent and the cost of treatment, any of the following treatment methods can be employed.

(i) Adsorption. Activated charcoal, an effective microporous adsorbent, is particularly useful for the removal and retrieval of toxic heavy metals from waste water. Also 99% reduction in the concentration of several chlorinated hydrocarbons can be achieved in the effluent stream.

Table 2. Removal of some toxic chlorinated organics.

Compound ($\mu\text{g/L}$)	Aldrin	Dieldrin	Endrin	DDT	PCB
Initial concentration	48	19	62	42	45
Concentration after treatment	0.1	0.05	0.05	0.1	0.5

Special adsorbents (peat moss, brown coal) are available for the removal of refractory organics, toxic metals and colour from industrial waste water. The ALM series of adsorbents can reduce metal levels up to 1 ppb from mining waste water.

(ii) Ion Exchange. Special ion-exchangers are now available for the retrieval of toxic metals from the industrial waste water. Styrene-divinyl benzene co-polymer can remove chlorinated pesticides by adsorption at the surface, while cationic and anionic ion-exchange resins can eliminate ionic dyes from textile mill waste water.

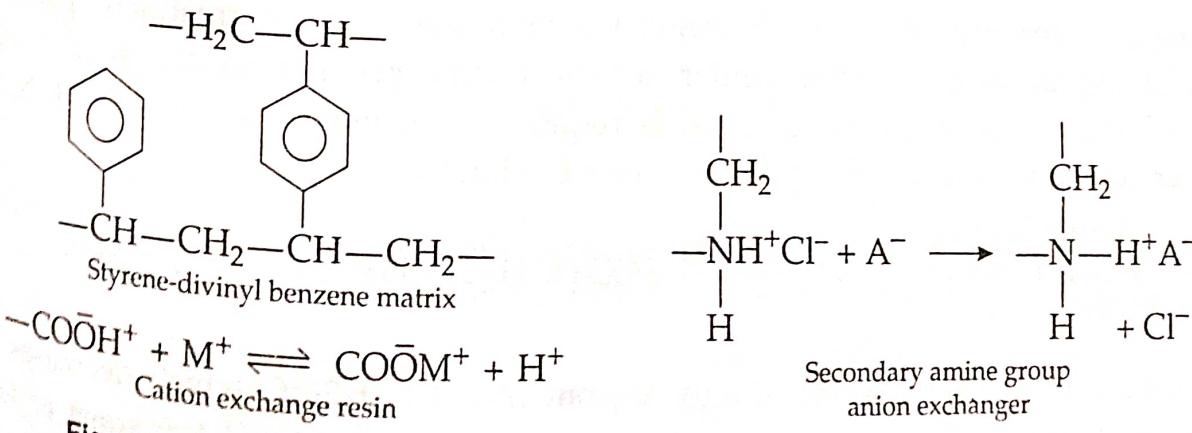


Fig. 1. Filtering industrial waste water by synthetic ion-exchange resin.

Applications. Ion-exchange process in waste water treatment is used for the recovery of phosphate, Cr, Ni and H₂SO₄ from anodising baths, recovery of Cr from cooling tower and removal of cyanides from waste streams.

(iii) Ultra Filtration and Microfiltration. (Membrane Technique). The waste water is pushed under pressure through an ion-exchange membrane which contains pores of size 2 to 10,000 nm whereby large molecules (0.001 microns) are retained and the effluent that passes off is free of toxic molecules.

(iv) Reverse Osmosis for Desalting Water. Reverse osmosis is based on pushing salt contaminated water through a semipermeable membrane (pore size 0.04 to 600 nm) made of cellulose acetate or polyamide by applying high pressure to overcome the osmotic pressure. The membrane permits passage of demineralised water but not of solute (impurity) through it (Fig. 2). High pressures of the order of 500 psi are required to obtain adequate water flux and recovery can be achieved by back flushing.

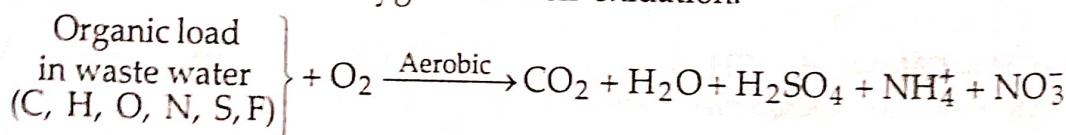
Applications of reverse osmosis include (a) purification and recycling of waste water from textile, metal, electroplating, food, pulp and paper industries, (b) recovery of valuable components from effluents, pollution control and reuse of water.

(v) Electrodialysis. Refer to Chapter-Purification of water.

(vi) Electrolytic Recovery. In this process, electrochemical reduction of metal ions to elemental metal takes place at cathode. Process efficiency is increased by using eco-cell involving rotating electrodes (for concentrated wastes) and extended surface electrolysis (for dilute wastes). This process is used to recover Cu, Sn, Ag and other metals from plating, etching or pickling baths.

Commonly Used Biological Treatment Processes for Sewage and Industrial Waste Water.

Biological Decomposition of Sewage. Conventional sewage treatment plants are based on biological decomposition under aerobic conditions. For oxidation of 1 mg of carbon, 2.67 mg of dissolved oxygen, DO is required. The major elements C, H, N, S in waste water consume additional oxygen for their oxidation.



The solubility of O₂ in water is only 9 ppm (mg/L) at 20°C which decreases with increasing temperature. The purity of water depends on the rate of transport of O₂ by aeration and on the total organic load which requires oxidation. The organic load is expressed in terms of BOD which means quantity of O₂ in mg needed to decompose the organic material in 1 L waste water. As a rough estimate, the BOD values (mg O₂/L waste

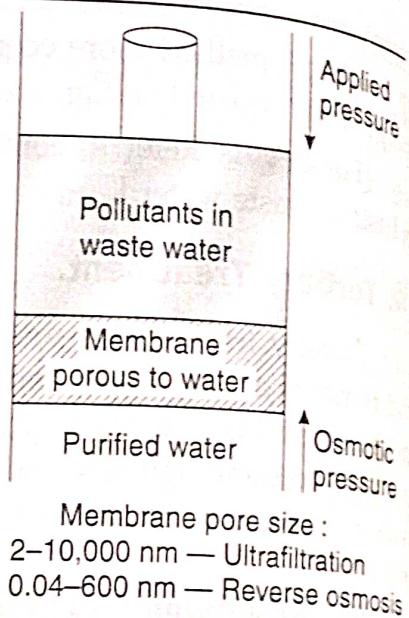


Fig. 2. Industrial waste water purification by membrane technique of ultrafiltration or reverse osmosis.

water) are : Domestic sewage 165, industrial waste water 200, food industry 747, paper industry 372. Such a heavy load is likely to disrupt the natural water bodies so that sewage treatment is essential for maintaining the water quality.

Aerobic Treatment Processes.

Aerobic digestion is the most widely used sludge stabilization process in waste water treatment plants that treat less than $20,000 \text{ m}^3/\text{d}$ (5 mg d). It is a process of oxidation and decomposition of organic part of the sludge by micro-organisms in special tanks in presence of oxygen. Aerobic processes are listed below.

1. Lagooning Processes.

Lagoons may be defined as natural or artificial earth basins used to receive sludge. Lagooning processes include (a) aerobic lagooning, (b) anaerobic lagooning, and (c) aerobic-anaerobic lagooning. The waste waters from primary treatment processes are collected in tanks and aerated. A healthy flocculent sludge is formed which brings about oxidation of organic matter. About 90% BOD can be removed. But the bacterial contamination in the lagoon effluent necessitates further purification in maturation pond.

2. Trickling Filters.

Conventional trickling filters normally consist of a rock bed, 1 to 3 metres in depth, with enough openings between rocks to allow air to circulate easily. The influent is sprinkled over the bed packing (Fig. 3) which is coated with a biological slime. As the liquid trickles over the packing, oxygen and the dissolved organic matter diffuse into the film to be metabolized by the micro-organisms in the slime layer. End products such as CO_2 , NO_3^- , etc., diffuse back out of the film and appear in the filter effluent.

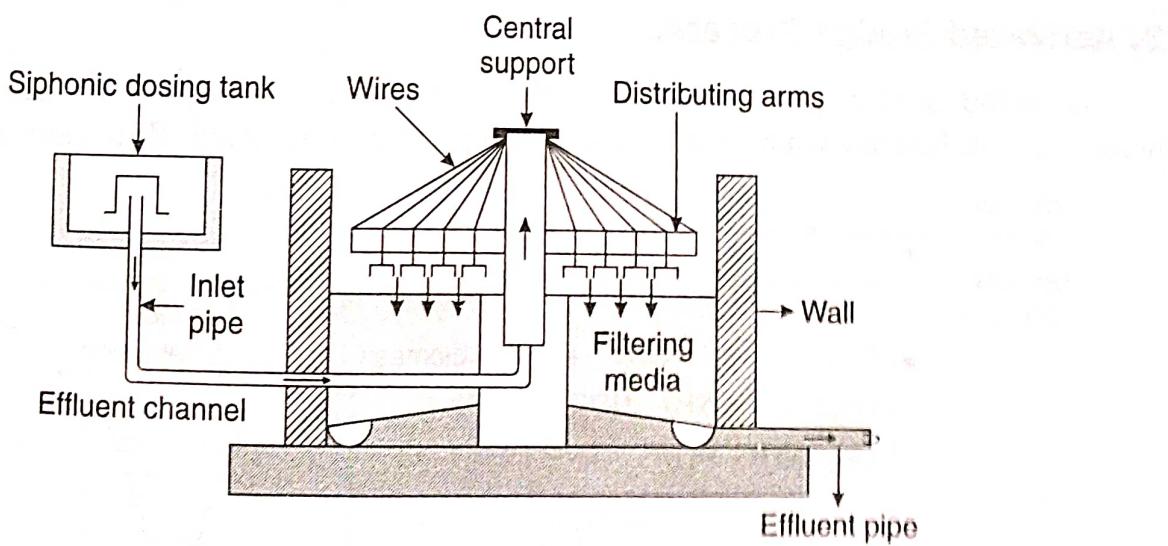


Fig. 3. Circular trickling filter.

As the micro-organisms utilise the organic matter, the thickness of the slime film increases to a point where it can no longer be supported on the solid media and gets detached from the surface. This process is known as sloughing. A settling tank following the trickling filter removes the detached bacterial film and some suspended matter.

Although trickling filtration is an aerobic process, it is indeed a facultative system. Aerobic bacterial species and bacillus are present in the upper layer of the filter while anaerobic species (*Desulphovibrio*) are present in the interfaces of the rocks media. Facultative bacteria such as *Pseudomonas*, Flavo bacterium, *Alcaligenes*, *Micrococcus* etc. are also present in trickling filters.

Smaller media give better results but they tend to choke easily. Plastic filters, particularly useful for industrial wastes of higher loading, can afford maximum surface area for the growth of microbial film and their light weight is more economical. The microbial activity is proportional to the temperature of the waste water passing through the filter. Thus efficiency of microbes in the filter decreases in winter.

The efficiency of the filter depends upon the composition of the waste, temperature, pH, depth of filter, strength of hydraulic loading, air supply, uniformity of the filter medium and waste water distribution over the filter. Trickling filter has greater resistance to toxic waste as compared to the Activated sludge process and can recuperate more promptly from the overdose of toxicants. However, shock loads or sudden surges should be avoided to protect the filter.

Advantages. Trickling filters are :

- Safer to operate with no potential for gas explosion.
- BOD removal is 85%. Lower TSS and ammonia nitrogen in supernatant liquor.
- Constant manual attention is not needed.
- Used for the treatment of industrial wastes from dairy, distillery, food processing, pulp and paper mills, pharmaceuticals, petrochemicals etc.

Disadvantages. Trickling filters are expensive. Their efficiency decreases with increased loading of the waste water (Fig. 4). However, the waste water may be diluted with the effluent from the previous treatment.

3. Activated Sludge Process.

Activated sludge process (ASP) is the most versatile method for the treatment of sewage and industrial waste water (Fig. 4). ASP is a continuous flow flocculated growth

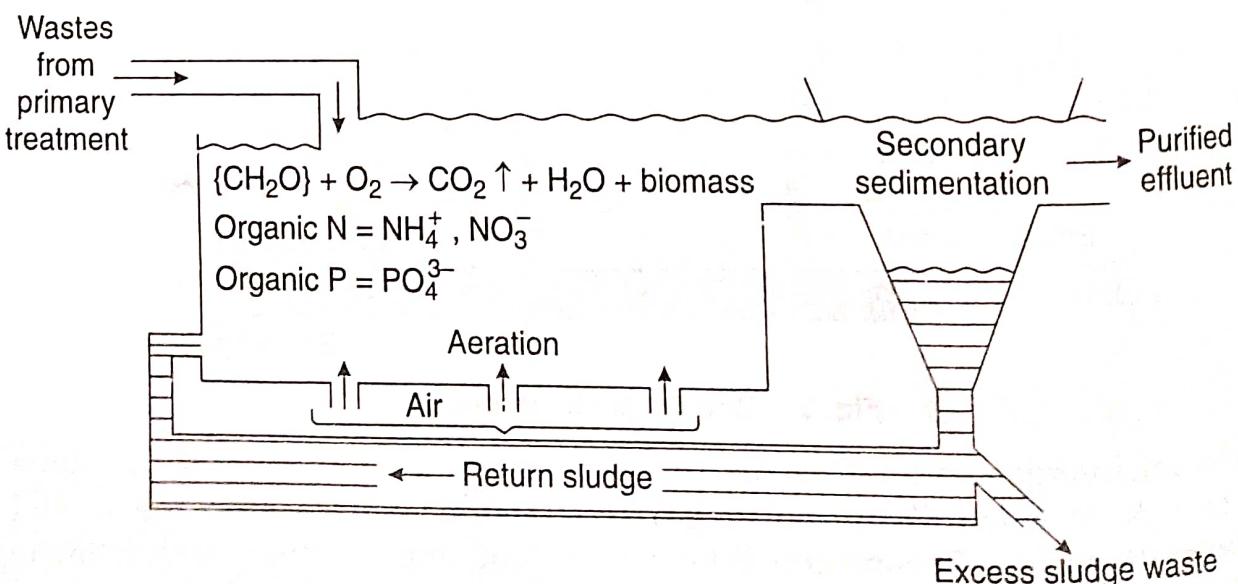
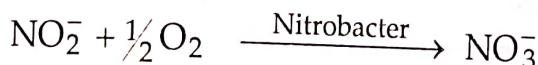
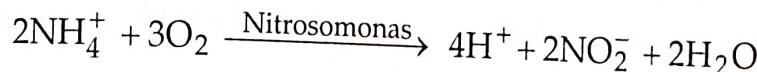


Fig. 4. Activated sludge system for secondary (biological) waste water treatment.

process in which bacterial flocs (active centres forming activated sludge) are separated from treated effluent by a clarifier and recycled to the aeration tank to maintain a high degree of process intensity. The process involves an aeration stage, solid-liquid separation following aeration and a sludge recycle system. Waste water enters in the aeration tank where the organic matter is brought into intimate contact with the sludge from the secondary clarifier. The sludge is heavily laden with chemoheterotrophic bacteria and ciliated protozoa.

The microbial cell matter is generally kept in the aeration tank till the micro-organisms reach their saturation point of growth when the cells flocculate well to form settleable solids. These solids settle out in a settler and part of it is discarded. The bulk of the solids, return sludge, is recycled to the bottom of the aeration tank and encounters the fresh sewage. The return sludge and the influent sludge provide optimum conditions for rapid degradation of organic matter.

Effective oxidative degradation is caused by *Pseudomonas*, *Zoogloea*, *Flavobacterium*, *Alcaligenes* etc. Nitrification in the activated sludge process (ASP) proceeds by the action of *Nitrosomonas*, *Nitrospira* etc. in the first step and by *Nitrobacter*, *Nitrococcus* etc., in the second step. Denitrification takes place by the action of *Pseudomonas* *micrococcus* etc.



This process of nitrification and denitrification is specially geared to the removal of N_2 (Fig. 5).

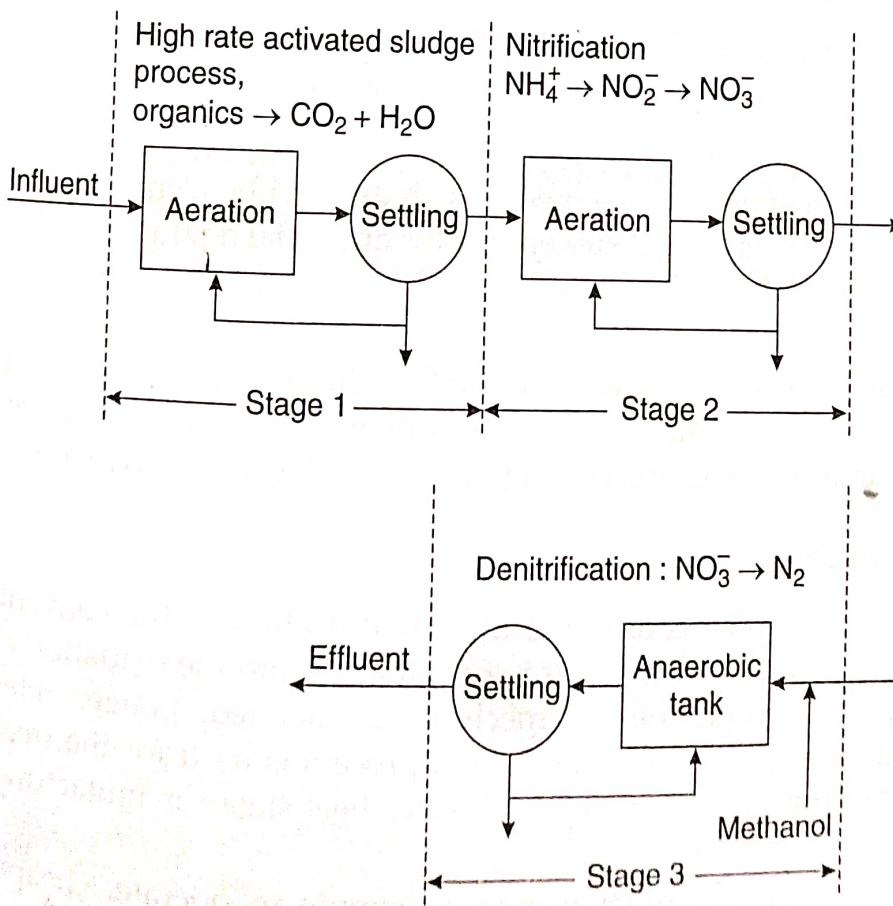


Fig. 5. Three stage nitrification-denitrification process.

Thus the micro-organisms utilise the oxygen and convert the organic matter into stabilized, low-energy compounds such as NO_3^- , SO_4^{2-} , CO_2 and synthesize new bacterial cells. Important factors which determine the efficiency of the activated sludge are pH, temperature, aeration and oxidation-reduction potential.

Air may be replaced by pure oxygen which promotes increased bacterial activity, decreased sludge volume and improved sludge settleability. Oxygen requirement for an activated sludge system can be obtained from the following equation.

$$\left[\frac{\text{Mass of O}_2 \text{ required}}{\text{per day}} \right] = \left[\frac{\text{Mass of ultimate BOD}}{\text{removed per day}} \right] - 1.42 \left[\frac{\text{Total active mass of organisms wasted per day}}{} \right]$$

Sludge Volume Index (SVI). A conventional measure of the settling ability of the sludge is the sludge volume index, defined as the volume in millilitres occupied by one gram of sludge after it has settled in one litre cylinder for 30 minutes.

$$\text{SVI (mL/g)} = \frac{\text{Sludge volume after settling for 30 min., mL/L}}{\text{MLSS concentration, mg/L}} \times 1000$$

SVI varies from 40 to 100 for a good sludge, but may exceed 200 for a poor sludge having a tendency towards bulking. The poor settling (high SVI) may be due to variable F/M ratios, high concentration of heavy metals and temperature variations.

Merits of Activated Sludge Process. (ASP).

- Low retention time and BOD removal upto 95%.
- ASP is used satisfactorily for the treatment of effluent from food processing, sugar, textile mills, antibiotic manufacturing industries.

Demerits of ASP.

- Low strength waste, BOD 1500 to 2500 mg/L.
- High sludge production and its disposal problem.
- High cost of operation and maintenance.
- The presence of synthetic detergents, such as alkyl benzene sulphonates (ABS) and polyethylene glycols are not susceptible for microbial degradation. They lead to foam formation and make the process difficult. Antifoaming compounds are used in such situations.

Recent modifications of conventional ASP include compressed aeration, tapered or dispersed or extended aeration, contact stabilization, high rate aerobic treatment process, simplex process, aeration rotor process, lagooning and Swedish INKA process.

4. Oxidation Ditch.

Oxidation ditch may be considered as a modification of the conventional Activated Sludge Process. Waste water after screening is allowed into the oxidation ditch. The mixed liquor containing the sludge solid is mechanically aerated. Longer retention times are needed to separate the sludge. Oxidation ditch process is used for the treatment of wastes having low BOD from fruit canning industry, beet-sugar manufacture, meat packing industry and edible oil refineries.

Advantages. Oxidation ditch process is simple to operate, cheaper, efficient and flexible.