ENGINEERING CHEMISTRY

Module - 4 ENVIRONMENTAL POLLUTION AND WATER CHEMISTRY

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MODULE-IV

ENVIRONMENTAL POLLUTION AND WATER CHEMISTRY

[Environmental Pollution: Air pollutants: Sources, effects and control of primary air pollutants: Carbon monoxide, Oxides of nitrogen and sulphur, hydrocarbons, Particulate matter, Carbon monoxide, Mercury and Lead. Secondary air pollutant: Ozone, Ozone depletion.

Waste Management: Solid waste, e-waste & biomedical waste: Sources, characteristics & disposal methods (Scientific land filling, composting, recycling and reuse).

Water Chemistry: Introduction, sources and impurities of water; boiler feed water, boiler troubles with disadvantages -scale and sludge formation, boiler corrosion (due to dissolved O₂, CO₂ and MgCl₂). Sources of water pollution, Sewage, Definitions of Biological oxygen demand (BOD) and Chemical Oxygen Demand (COD), determination of COD, numerical problems on COD. Chemical analysis of water: Sulphate (gravimetry) and Fluorides (colorimetry). Sewage treatment: Primary, secondary (activated sludge) and tertiary methods. Softening of water by ion exchange process. Desalination of sea water by reverse osmosis.]

ENVIRONMENTAL POLLUTION

"Pollution may be defined as the excessive discharge of undesirable substances into the environment, there by adversely affecting the natural quality of the environment and cause damage to human, plant or animal life. The term environment includes the air, water and land."

Primary Air pollutants: The pollutants that are directly emitted into the atmosphere through natural or human activities are called primary air pollutants. Ex. SO₂, NO, NO₂, CO.

Oxides of Carbon:

Carbon monoxide: carbon monoxide is one of the most serious air pollutants. It is a colorless and odorless gas, highly poisonous to living beings because of its ability to block the delivery of oxygen to the organs and tissues.

Sources: CO enters atmosphere due to the-

- Partial combustion of fuel in automobiles, industries and oil industries.
- Smoking and domestic heat appliances.
- Natural processes such as forest fires, volcanic actions, marsh gas production.

$$2C + O_2 \rightarrow 2CO$$

Effects:

▶ CO binds to the hemoglobin (Hb) to form carboxy-hemoglobin complex, which is about 300 times more stable than the oxygen-hemoglobin complex and reduces the ability of Hb to deliver oxygen to the body. This results in headache, weak eyesight, nervousness, paralysis, vomiting and cardiovascular disorder.

$$CO + Hb \rightarrow CO-Hb$$
 (complex)

Control: Release of CO into the atmosphere can be controlled by-

- developing exhaust systems which will complete the combustion process.
- developing pollution free power sources like fuel cell to replace internal combustion engines.
- modifying internal combustion engines to minimize the emission of CO.
- fixing catalytic convertor in the exhaust of automobiles.

$$CO + O \rightarrow CO_2$$

Carbon dioxide: Carbon dioxide is released into the atmosphere by respiration, burning of fossil fuels for energy, and by decomposition of limestone during the manufacturing of cement. Normally it is about 0.03% by volume of the atmosphere. Green plants need carbon dioxide for photosynthesis and they in turn, emit oxygen, thus maintaining the delicate balance. The increase in amount of carbon dioxide in the air is mainly responsible for global warming.

$$CaCO_3 \rightarrow CaO + CO_2$$

 $C + O_2 \rightarrow CO_2$

Oxides of Sulphur: SO₂ and SO₃ are common oxides of sulphur.

Sources: oxides of sulphur release to the environment by-

•Burning of sulphur containing fossil fuels.

$$S + O_2 \rightarrow SO_2$$

- Petroleum industries, oil refineries, sulphuric acid plants.
- smelting of sulphide ores.
- Sulphur dioxide oxidizes to sulphur trioxide.

$$2SO_2 + O_2 \rightarrow 2SO_3$$

Effects:

► Sulphur dioxide is poisonous to both animals and plants. It has been reported that even a low concentration (1 ppm) of sulphur dioxide causes respiratory diseases, eye irritation, damages cells and membranes, stone leprosy, acid rain, yellowing of paper, corrosion of metals etc.

$$\begin{array}{ccc} 2SO_2 &+ O_2 \rightarrow SO_3 \\ SO_3 + H_2O \rightarrow H_2SO_{4(mist)} \end{array}$$

Control: The entry of SO₂ and SO₃ into the atmosphere can be controlled by-

■ Adsorbing SO₂ on a suitable adsorbent (Na₂O.Al₂O₃) to form stable sulphates.

$$Na_2O.Al_2O_3 + SO_2 + 1/2O_2 \rightarrow Na_2SO_4 + Al_2SO_3$$

- Using natural gas instead of high sulphur fuels like coal and petroleum, emission of SOx can be reduced.
- Passing SO₂ through a slurry of CaCO₃ to form calcium sulphite. Then inject air to the reaction mixture to oxidize CaSO₃ to CaSO₄.

Oxides of Nitrogen: Nitric oxide (NO) and Nitrogen dioxide (NO₂) are the common oxides of nitrogen.

Sources: the sources of NO and NO₂ are-

- Natural processes like lightening, volcano.
- Combustion of coal, oil, natural gas and gasoline.
- Denitrifying bacteria in soil produces N₂O.

$$N_2 + O_2 \rightarrow 2NO \text{ [at 1483 K]}$$

 $2NO + O_2 \rightarrow 2NO_2$

Effects:

► High level of NO₂ in air causes eye irritation, damages lungs.

► NO₂ reacts with H₂O and forms acid rain.

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$$

 $HNO_2 + 1/2O_2 \rightarrow HNO_3$
(nitrous acid)

▶ Nitrogen oxides and hydrocarbons form smog, which causes asthma, bronchitis and chlorosis.

Control: release of NO and NO2 can be prevented by-

■ Treating the flue gas with ammonia in presence of vanadium catalyst. NO present in flue gas reacts with ammonia to form N₂ and H₂O

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

- Oxides of nitrogen can be removed by treating the flue gas with sorbents like powdered limestone or aluminum oxide.
- \blacksquare Oxides of nitrogen present in automobile exhaust can be reduced to N_2 and O_2 by using catalytic converters.

$$NO_x \rightarrow N_2 + O_2$$

Hydrocarbons: Hydrocarbons are composed of hydrogen and carbon only.

Sources: The sources of hydrocarbons are

- They are formed by incomplete combustion of fuels used in automobiles and industries.
- Formed by bacterial decomposition of organic matter in water and sediments.

$$2(CH_2O) \rightarrow CO_2 + CH_4$$

Effects:

- ▶ Methane is called greenhouse gas, causes global warming.
- ▶ Hydrocarbons inhalation causes irritation to mucous membrane and affect nervous system.
- ► Hydrocarbons at high concentration causes carcinogenic effects on lungs.
- ► Hydrocarbons harm plants by causing ageing, breakdown of tissues and shedding of leaves and flowers.

Control:

■ Unburnt hydrocarbons present in automobile exhaust can be converted into CO₂ and H₂O by using catalytic converter.

Hydrocarbons
$$\rightarrow$$
CO₂ + H₂O

■ The polluted air is passed through porous solid adsorbents kept in suitable containers. The hydrocarbon pollutants are adsorbed at the surface of the porous solid and clean air passes through.

Particulate matter:

Finally divided solid particles or liquid droplets suspended in air are called particulates. They include smoke, dust, fumes, mist, and spray. Particulates with less than 2.5 µm in size are called fine particulates. If their size is greater than 2.5 µm are called coarse particulates. The concentration of particulates is expressed in terms of total suspended particulate (TSP). Particulates in the atmosphere may be viable or non-viable. The viable particulates are minute living organisms that are dispersed in the atmosphere (e.g., bacteria, fungi, molds, algae, viruses etc).

Non-Viable Particulates:

Sources:

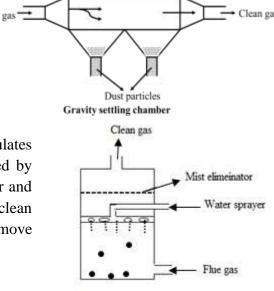
- **Smoke:** formed during the combustion of organic matter. Examples are cigarette smoke, smoke from burning of fossil fuel, garbage and dry leaves, oil smoke etc.
- **Dust:** Produced during crushing and grinding of solid materials. Sand from sand blasting, saw dust from wood works, pulverized coal, cement and fly ash from factories, dust storms etc.,
- Mist: Formed by condensation of vapour, dispersion of liquids.
- Spray: Formed during atomization of droplets.
- Fumes: Condensation of vapour by sublimation, distillation calcination etc.

Effects:

- ► They cause respiratory problems, reduction of visibility, sneezing, lung cancer, coughing, nose blocking and asthma.
- ► Causes eye, nose and throat irritation.

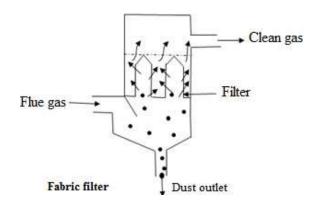
Control: There are many techniques developed for the control of particulates.

- Gravity settling chamber: It is oldest and simplest means of removing suspended particles of size greater than 50 µm from flue gas. Gas stream enters the chamber where the velocity of gas is reduced and the particle get settled at the bottom under gravitational force.
- Wet Scrubber: Pass the flue gas containing particulates and spray water over it. The particulates are captured by water droplets and collected at the bottom of chamber and clean gas moves upwards. Any mist associated with clean gas, can be removed by mist eliminator. Wet srubber remove partcles of size 0.1 to 200 µm efficiently.



Wet srubber

■ Fabric filter: Blow flue gas containing particulates into the fabric filter. It contains a porous structured fibrous material (filter) which retains the particulates and allows the gas to pass through the pores. Fabric filters can provide above 99% efficiency for particle separation.



■ Electrostatic precipitator: It has positive (collector) electrodes and negative (discharge) electrodes. The negative electrodes are in the form of rod or wire mesh. Positive electrodes are in the form of plates. Due to the high negativity of negative electrodes, the air molecules in between the electrodes undergo ionization releasing electrons, and hence there will be plenty of free electrons and ions in the space. As soon as the flue gases enter into the electrostatic precipitator, free electrons will be attached to the dust particles. As a result, the dust particles become negatively charged. Then these negatively charged particles

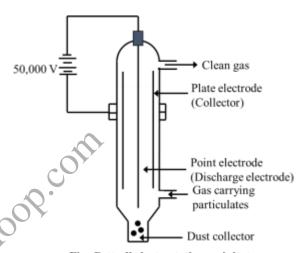


Fig. Cottrell electrostatic precipitator

will be attracted by positive plates and deposited on them. Particles then fall due to gravitational force and the flue gases become almost free from ash/dust particles and ultimately get discharged to the atmosphere through the chimney.

Chemical Pollutants: Water contains heavy metals like Hg, Pb, As, etc., as pollutants. All these metals are dangerous to humans because our body can't excrete them.

Lead: Lead is a major air pollutant emitted by vehicles.

Sources:

- Produced from metal smelting, lead-acid batteries, automobile exhaust and other factories that use lead.
- Lead enters water through lead based pipes or solder.

Effects: If the concentration of lead exceeds permissible limit-,

- ▶ it affects the nervous system, kidney function, immune system, and cardiovascular systems.
- ▶ it affects the oxygen carrying capacity of blood.
- ▶ it inhibits production of hemoglobin and causes anemia.
- it decreases the growth and reproductive rates of plants and animals.

Control:

- Use unleaded petrol in automobiles.
- Eliminate lead contaminant in drinking water by processes such as reverse osmosis, distillation and filtration using carbon filters.
- Minimize plant absorption of lead from soil by maintaining soil pH level at 6.5 and adding organic matter like composted leaves and manure.

Mercury: Mercury affects human health and ecosystem and is a global pollutant.

Sources:

- Natural sources include volcanic emissions and vegetation.
- Thermometers, Mercury Vapour Lamp, Batteries, Electric switches, Dental amalgam, Pharmaceuticals etc.

Effects:

- ▶ Elemental and methyl mercury are toxic to the central and peripheral nervous system.
- ▶ It affects nervous, digestive and immune systems, lungs and kidneys.
- ▶ Inorganic salts of mercury are corrosive to skin, eyes and gastrointestinal tract.
- ▶ It results in complex neurological problems, especially in young children and babies.

Control:

- Avoid mercury mining and use of mercury in gold extraction.
- Discontinue the usage of non-essential mercury containing products, such as batteries, thermometers, lamps, skin lightening products etc.
- Use fabric filters, wet scrubbers or electrostatic precipitators at the source to control the mercury emission.

Secondary Air Pollutants: Secondary air pollutants are those they are not directly released into the atmosphere but forms when primary pollutants react in the atmosphere. Ex. Ozone, nitric acid, sulphuric acids.

Ozone: Ozone in the stratosphere formed by the photo dissociation of oxygen molecules by absorbing UV radiations of 240 nm wavelength. The UV radiations split apart molecular oxygen into free oxygen atoms. These oxygen atoms combine with the molecular oxygen to form ozone.

$$O + O \rightarrow O_2$$

 $O_2 + O \rightarrow O_3$

For ecosystem, the ozone layer is more significant since it absorbs harmful UV radiations of sun and protects the life of plants and animals.

Depletion of Ozone Layer: Ozone depleting substances like Chlorofluoro carbons (CFCs) dissociate ozone into oxygen. CFCs are used as coolants in refrigerators and air conditioners.

i) CFCs on decomposition gives Chlorine free radical

$$CF_2Cl_2 \rightarrow Cl + F_2CCl$$

ii) The chlorine radical then reacts with stratospheric ozone to form chlorine monoxide radicals and molecular oxygen.

$$Cl^{\bullet} + O_3 \rightarrow ClO^{\bullet} + O_2$$

iii) Reaction of chlorine monoxide radical with atomic oxygen produces more chlorine radicals.

$$ClO^{\bullet} + O \rightarrow Cl^{\bullet} + O_2$$

iv) The chlorine radicals are continuously regenerated and cause the breakdown of ozone. Thus, CFC^s are transporting agents for continuously generating chlorine radicals into the stratosphere and damaging the ozone layer.

Effects of Depletion of Ozone Layer:

As ozone depletes in the stratosphere, more UV radiation enters into the troposphere. UV radiations lead to ageing of skin, cataract, sunburn, skin cancer, damage to fish productivity etc.

Control:

- Encourage growth of plants and discourage deforestation.
- Instead of CFCs, use hydro chlorofluoro carbons (HCFC) and hydrofluoro alkanes (HFA). These compounds undergo degradation before reaching stratosphere.

Waste Management:

Waste management is the collection, transport, treatment and disposal of waste together with monitoring and regulating. The term usually relates to the materials produced by human activity, and is generally undertaken to reduce their effect on health and the environment.

Solid Waste: It refers to all non-liquid garbage arising from animal and human activities that are discarded as unwanted and useless. It can be categorized based on materials such as plastic, paper, glass, metal, demolition materials, wood, pesticides, insecticides and organic waste.

Solid Waste Management is a planned process of collection, transport and disposal of solid waste materials in safe and economic manner.

Everyday tons of waste is disposing off at various landfill sites and recycling units. This landfill sites produce foul smell if the waste is not stored and treated properly.

Sources: The major sources of solid waste are Residential areas, Industries, Commercial establishments, Institutions, Municipal services, Manufacturing units, and Construction and demolition sites.

Characteristics: Information and data on characteristics of solid waste are important for selecting a suitable disposal technique.

i) Physical characteristics:

Density: It is a crucial factor to design a solid waste management system, Ex. design of sanitary landfills, storage and type of collection.

Moisture content: It is ratio of weight of water to the total weight of wet waste. As the moisture content in waste increases, the cost of collection and transportation also increases. A typical range of moisture content is 20% to 40%.

Size distribution: It is also important factor for separation and transportation purpose.

ii) Chemical characteristics: If the solid wastes are to be used as fuel or any other purpose, one must know the chemical properties.

Lipids: have high heating values of about 38000 kJ/kg.

Carbohydrates: are readily biodegradable to CO₂ and H₂O.

Proteins: the partial decomposition of these compounds yield amines that have unpleasant odour.

Natural fibers: contain high proportion of paper and wood products, having high heating value. They are suitable for incineration.

Synthetic organic material: now a days plastics become the major component of solid waste. They are highly resistant to biodegradation. Have high heating value of about 32000 kJ/kg.

Disposal: This involve the safe disposal of waste to minimize pollution. The following are the methods.

Landfill: It is the oldest waste disposal method where waste is directly disposed into a large pit or trench and is covered with a thin layer of soil.

- Ordinary landfills are associated with the problems like i) seepage of waste into soil and water and ii) emission of methane from waste into atmosphere. These problems can be eliminated by scientific landfills.
- Scientific landfills are constructed with a base layer of 90 meters of clay to prevent any seepage or leakage within the landfill. They also reduce the speed of methane production. Scientific landfills generate methane slowly which can be used as alternative fuel for electricity and heat generation purpose. Narela-Bawana in New Delhi is the only scientific landfill in India. It has the capacity to treat 2000 tons of waste every day, generating 24 megawatts of electricity.

Composting: It involves the biodegradation of organic waste. The organic waste is mixed with water, oxygen, carbon and nitrogen, the micro-organisms are able to break down organic matter to produce compost, which can be used as organic fertilizer.

Incineration: It involves the burning of solid waste at high temperature until the wastes are turned into ashes. It reduces the volume and weight of waste for safe disposal in outer land fields.

Recycling: It is a process of taking use full things from discarded items for next use.

- Primary recycling involves processing of waste/scrap into a product with characteristics similar to those of original material. Remolding of plastics is an example.
- Secondary recycling involves processing of waste/scrap plastics into materials that have characteristics different from those of original plastics.
- Tertiary recycling involves the production of basic chemicals and fuels from plastic wastes using a suitable chemical process such as pyrolysis. This method is suitable for all types of plastic wastes including multi-layered plastics.

Reuse: ■ The organic waste generated from household can be used for making compost, which can be used as manure.

- Waste papers of old books and newspapers can be reused for making paper bags.
- Old electrical appliances and furniture can be reused as far as possible rather than dumping them.

E-Waste:

E-waste can be defined as electronic and electrical equipments/products which have become obsolete due change in fashion, style, status and attaining the end of their useful life.

"E-wastes are considered dangerous, as certain components of some electronic products contain materials like mercury, lead, antimony, phosphorus etc., which are hazardous, depending on their condition and density. The hazardous content of these materials poses a threat to human health and environment.

Sources: Discarded computers, televisions. VCRs. stereos, copiers, fax machines, electric lamps, cell phones, audio equipments, DVDs, CDs, washing machines, microwave ovens, mother boards. PCBs, batteries, etc., if improperly disposed can penetrates into soil and groundwater.

Biomedical waste is any kind of waste containing infectious materials. It includes waste of medical or laboratory origin (e.g., packaging, unused bandages, infusion kits, etc.), as well as research laboratory waste containing biomolecules or organisms.

Biomedical waste must be properly managed and disposed off to protect the environment, general public and workers, especially healthcare and sanitation workers who are at risk of exposure to biomedical waste.

Steps in the management of biomedical waste include generation, accumulation, handling, storage, treatment, transport and disposal.

WATER CHEMISTRY

Sources of water: The sources of water classified as follows **Surface water**: Rain water, River water, Lake Water, Sea water

- 1) Rain water: Purest form of water contains dissolved gases and suspended solid particles.
- 2) River water: Contains dissolved minerals of soil such as chlorides, sulphates, bicarbonates of sodium, calcium, Mg, Fe etc. It also contains the organic matter, small particles of soil and sand in suspension.
- 3) Lake water: It contains less dissolved minerals but high quantity of organic matters.
- 4) Sea water: It is the most impure form of natural water. It contains dissolved salts such as NaCl, sulphates of Na and K, bicarbonates of Mg & Ca.

Impurities in water: The water found in nature is never pure which contains large number of impurities in varying amount. These impurities mainly depend upon its source and are classified into four different types.

- 1) **Dissolved gases**: these includes dissolved oxygen, CO₂, SO₂, NH₃, (NO)x, all of which derived from atmosphere.
- 2) **Dissolved solids:** these includes salts like bicarbonates, Chlorides and Sulphates of Ca, Mg, & Na in addition to that small amount of nitrates, nitrites, silicates, ammonia and ferrous salt etc.

- 3) **Suspended impurities:** Suspended impurities are the dispersed solids which can be removed by filtration or settling. Suspended impurities are of two types.
 - i) Inorganic Impurities: clay, silica, oxides of Fe & Mg etc
 - ii) **Organic Matter**: organic compounds derived from the decay of vegetable and animal matter including bacteria may be present in water. Water also gets contaminated with sewage and excretal matter. Consequently, the pathogenic bacteria and microorganism are the main causes for water borne diseases.

Boiler feed water: The water fed into the boiler for the production of steam is called boiler feed water. If the boiler feed water is impure, it leads to boiler troubles. Boiler troubles are due to

- 1. Scale & sludge formation
- 2. Priming& foaming
- 3. Boiler corrosion

1. Scale & sludge formation:

Scale: The thick and hard precipitate of salts deposited on the inner wall of the boiler is called as scale. Ex.-CaSO₄, MgCl₂, MgSO₄, Ca(OH)₂, Ca₃(PO₄)₂ etc.,

Sludge: If the precipitate formed is loose, non-adherent and suspended in the boiler feed water, it is called sludge. Sludge is formed due to Ca(HCO₃)₂, Mg(HCO₃)₂,

Disadvantages:

- Sludge are poor conductors of heat and causes wastage of fuel.
- Danger of explosion due to excess pressure inside the boiler.
- Excess of sludge formation decreases the efficiency of boiler.
- Scales act as a thermal insulators, it decreases the efficiency of the boiler.

Prevention:

- **External treatment:** This treatment is given before the feed water enters the boiler. It involves the removal of salts responsible for scale formation by sedimentation, coagulation and filtration techniques.
- ii) **Internal treatment:** This involves addition of chemicals directly into the boiler to remove the impurities, which were not removed during external treatment.
- iii) **Blow-down operation:** It involves the periodical removal of a portion of the concentrated boiler water and its replacement by fresh water.

Removal of Scales:

- i) Scales can be removed with the help of scraper or wire brush.
- ii) Brittle scales can be removed by giving thermal shocks i.e, heating the boiler and suddenly cooling with cold water.
- iii) Scales can be removed by treating them with chemicals. For Ex., Ca(CO₃)₂ scales are removed by treating with 5-10% HCl. Ca(SO₄)₂ scale can be removed by using EDTA.

Boiler corrosion: Degradation of boiler due to the presence of impurities in boiler feed water is called boiler corrosion. Corrosion of boiler due to—

- 1. Dissolved O₂ 2. Dissolved CO₂ 3. Dissolved MgCl₂
- 1. Corrosion due to dissolved oxygen: Dissolved oxygen in presence of water, causes corrosion.

$$2Fe + 2H2O + O2 \rightarrow 2Fe(OH)2$$
$$2Fe(OH)2 + O2 \rightarrow 2[Fe2O3.2H2O] + 2H2O$$
(Rust)

Prevention:

i. By adding Sodium Sulphite: $2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$

This method is less preferred as it leads to the formation of other precipitates.

ii. By adding Hydrazine: $N_2H_4+O_2 \rightarrow N_2+2H_2O$

This method results in the formation of pure water, and has no side effects. So it is preferred.

2. Corrosion due to dissolved CO₂

Salts like Calcium bicarbonate on heating produces CO₂. CO₂ dissolves in water to form carbonic acid which corrodes the boiler metal.

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2$$

$$H_2O + CO_2 \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^-$$

$$Fe^{2+} + HCO_3^- \rightarrow Fe(HCO_3) \rightarrow Fe(OH)_2 \downarrow + 2CO_2$$

$$2Fe(OH)_2 + O_2 \rightarrow 2[Fe_2O_3.2H_2O] + 2H_2O$$
(Rust)

Prevention:

- i. By treating with lime: $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$
- ii. By adding ammonium hydroxide: $2NH_4OH + CO_2 \rightarrow (NH_4)_2CO_3 + H_2O$
- **3.** Corrosion due to MgCl₂: Dissolved salt like MgCl₂ causes acid formation.

$$MgCl_2+ 2H_2O \rightarrow Mg(OH)_2+ 2HCl$$
 (Corrosive acid)
 $Fe^{2+} + 2HCl \rightarrow FeCl_2 + 2H^+$
 $FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2HCl$
 $2Fe(OH)_2 + O_2 \rightarrow 2[Fe_2O_3.2H_2O] + 2H_2O$
(Rust)

Prevention:

This can be prevented by alkali neutralization. Excess acidic nature is neutralized by adding alkalis and vice versa.

$$HCl + NaOH \rightarrow NaCl + H_2O$$

Water Pollution:

Discharge of certain foreign substances into water that affects the physical, biological and chemical properties of water which in turn decreases the utility of water is known as water pollution. The matter which is responsible for these unhealthy changes in water is known as water pollutants. Eg. Pd, Hg, CN, As, Cu, acids, alkalis, pesticides, insecticides, fungicides, animal matter, human excreta, radioactive wastes etc. The contaminated water is called sewage water or effluent.

Depending on the sources of water pollutants, sewage water is classified into two types:

1.Domestic Sewage 2. Industrial sewage

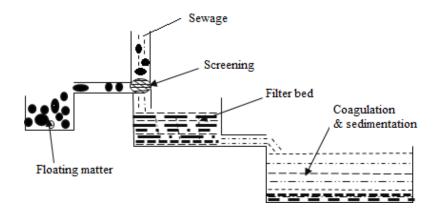
Domestic sewage: It is the waste discharging away from residences, institutes, hospitals etc. These include certain organic wastes, pathogenic bacteria, plant materials, pesticides, detergents and other materials. Domestic sewage causes water borne diseases like dysentery, cholera, typhoid, and hookworm infection.

Industrial sewage: It is the waste released by industries. It contains Pd, Hg, CN, As, Cu, acids, alkalis, pesticides, detergents, insecticides, fungicides, soap, phenol etc. It can be render harmless by suitable treatments. The organic waste present in water undergoes degradation and breakdown into simple molecules by bacteria. The bacterial degradation is of two types:

- 1. Aerobic degradation or oxidation: Brought about by bacteria in presence of air and dissolved oxygen of water. Aerobic oxidation produces harmless compounds like water and CO₂.
- 2. Anaerobic degradation or oxidation: Brought about by bacteria in absence of air and produces harmful products such as NH₃, H₂S, CH₄ etc.

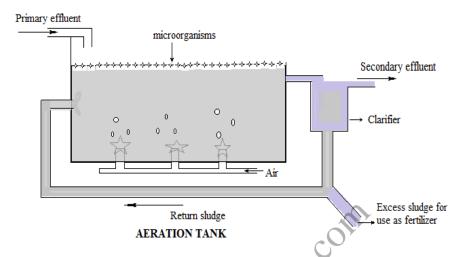
Sewage treatment: The process of removal of contaminants present in the sewage is called sewage treatment. It involves three stages. i). Primary, ii). Secondary and iii). Tertiary treatment.

- 1. Primary treatment: It is the process of removal of course, suspended and floating solids.
 - Screening: It removes large suspended or floating matter in the sewage.
- **Filtration:** The water is passed through conventional sand filter beds to remove the last trace of suspended matter.
- **Sedimentation:** Sedimentation is a process of removing suspended impurities by allowing the water to stay undisturbed for some time in a larger tank. Due to gravitation force almost all the suspended particles settle down.
- Coagulation: It is a process of removing colloidal particles from water by the addition of coagulating agents. Potash alum [K₂SO₄, Al₂(SO₄)₃.24H₂O] and ferrous sulphate (FeSO₄.7H₂O) are commonly used coagulants.



2. Secondary treatment (Activated sludge process): It involves the removal of organic matter. The waste water after primary treatment is allowed to flow to large tanks where biological treatment is carried out.

Activated sludge containing microorganisms is sprayed over the water and oxygen is passed vigorously from the bottom of tank. Under these conditions, aerobic oxidation of organic matter takes place.



The sludge formed is removed and the residual water (secondary effluent) is treated with chlorine or UV radiations to remove bacteria and finally discharged into running water or reused for watering plants.

(**Sludge**: The matter which settles down at the bottom after treatment is called sludge and the liquid is called effluent).

- **3. Tertiary treatment**: If the residual water contains high concentration of phosphates, heavy metal ions, colloidal impurities and non-degradable organic matter, the water is taken to tertiary treatment. It involves-
 - i) The removal of phosphate as insoluble calcium phosphate by treating with lime.
 - ii) The removal of heavy metal ions as insoluble sulphide by treating with sulphide ions.
 - iii) The removal of remaining organic matter by adding activated charcoal.
 - iv) The removal of remaining colloidal impurities by adding alum.

Biological Oxygen Demand (BOD):

The amount of oxygen required in milligrams by microorganisms to oxidize the biologically oxidizable impurities present in 1 dm³ of waste water over a period of five days at 20°C.

Importance of BOD: BOD is most important in sewage treatment, as it indicates the amount of decomposable organic matter in the sewage or extent of pollution or amount of dissolved oxygen.

"Greater the concentration of organic matter in the sewage, greater is the BOD".

Example: calculate the BOD of an effluent sample containing 9 mg dm⁻³ of impurities denoted by the formula CH₂O.

Solution: Write the equation for the oxidation of impurities

$$CH2O + O2 \rightarrow CO2 + H2O$$
30 32 44 18

According the equation, 30 mg of CH₂O requires 32 mg of O₂ for complete oxidation

Therefore, 9 mg of CH₂O requires =
$$\frac{32x9}{30}$$
 mg of O₂
= 9.6 mg of O₂
:. BOD of effluent sample is 9.6 mg of O₂

Chemical oxygen demand (COD):

It is the amount of oxygen in milligrams required to oxidize organic and inorganic impurities present in one dm³ of waste water using strong oxidizing agent like acidified K₂Cr₂O₇.

Procedure: Pipette out 25cm^3 waste water into a conical flask, add 1 test tube of 1:1 sulphuric acid containing mercuric sulphate and silver sulphate and a known amount potassium dichromate. The above mixture is refluxed for two hours and cool to room temperature. Then the mixture is titrated against standard FAS solution, using ferroin as indicator, till the colour changes from greenish yellow to reddish brown. Let the volume of FAS consumed be $V_1 \text{ cm}^3$.

Blank: The same procedure is repeated for 25 cm 3 of distilled water. Let the volume of FAS required be V_2 cm 3 .

Observation and calculation

Then, COD of the sample =
$$\frac{N \times (V_2 - V_1)}{V} \times 8 \text{ g.dm}^{-3}$$
$$= \frac{N \times (V_2 - V_1)}{V} \times 8 \times 1000 \text{ mg.dm}^{-3}$$

Where, N= Normality of FAS solution

V= Volume of waste water titrated

Importance:

- 1) The COD test is widely used for measuring the pollution strength of domestic and industrial wastes.
- 2) Management and designing of treatment plant.
- 3) The major advantages of COD test are that the determination is completed in three hours as compared to the 5 days required for BOD determination.

Problem 1

In a COD test, 25 ml of sewage sample as made to react with 25 ml of K₂Cr₂O₇ solution and the unreacted K₂Cr₂O₇ required 9.0 ml and 16 ml of 0.002N FAS solution for back and blank titrations respectively. Calculate COD of the sample.

Solution:

Volume of sample taken=V= 25 ml

Volume of 0.05 N FAS required to react with unconsumed K₂Cr₂O₇=V₁= 9.0 ml

Volume of FAS consumed in blank titration =V₂= 16 ml

Then, COD of the sample =
$$\frac{N \times (V_2 - V_1)}{V} \times 8 \ g.dm^{-3}$$

COD of the sample = $\frac{0.05 \times (16 - 9)}{25} \times 8 \times 1000 = 112 \ mg / dm^3$

Problem 2: 25 ml of an effluent requires 9.5 ml of $0.001M \text{ K}_2\text{Cr}_2\text{O}_7$ for oxidation. Calculate the COD of the effluent sample. [Given molecular mass of $\text{K}_2\text{Cr}_2\text{O}_7 = 294$).

Solution:

1M K₂Cr₂O₇ = 294g of K₂Cr₂O₇ in 1 liter of solution ≡ 48 g of oxygen i.e., 1000 ml of 1M K₂Cr₂O₇ solution ≡ 48 g of oxygen
∴ 9.5 ml of 0.001M K₂Cr₂O₇ solution =
$$\frac{48 \times 0.001 \times 9.5}{1000} = 0.000456 \text{ g or } 0.456 \text{ mg of oxygen}$$
It means 25 ml of effluent sample ≡ 0.456 mg of oxygen
∴ 1000 ml of effluent sample ≡
$$\frac{0.456 \times 1000}{25} = 18.24 \text{ mg of oxygen}$$
∴ COD of water =18.24 mg/dm³

Problem 3: 30 ml of waste water sample required 10 ml of 0.02N K₂Cr₂O₇ for oxidation. Calculate the COD of the effluent sample. [Given equivalent mass of K₂Cr₂O₇=49).

Solution:

1N K₂Cr₂O₇ = 49g of K₂Cr₂O₇ in 1 liter of solution ≡ 8 g of oxygen i.e., 1000 ml of 1N K₂Cr₂O₇ solution ≡ 8 g of oxygen
∴ 10 ml of 0.02N K₂Cr₂O₇ solution
$$\equiv \frac{8 \times 0.02 \times 10}{1000} = 0.0016$$
 g or 1.6 mg of oxygen
It means, 30 ml of effluent sample ≡ 1.6 mg of oxygen
∴ 1000 ml of effluent sample $\equiv \frac{1.6 \times 1000}{30} = 53.3$ mg of oxygen
∴ COD of water =53.3 mg/dm³

Determination of sulphate ions by gravimetry method

Sulphate concentration should be less than 200 mg/L. Sulphate ions in water sample reacts with BaCl₂ under acidic conditions to give BaSO₄ ppt. By knowing the weight of BaSO₄ ppt. formed, the amount of sulphate in the sample can be determined.

Procedure:

- i. Take 200 ml water in a beaker and heat it.
- ii. Add 1 tt dil. HCl and 5% BaCl₂ solution slowly with constant stirring till the precipitation completes.
- iii. Filter the BaSO₄ ppt using Whatman filter paper.
- iv. Transfer the filter paper containing BaSO₄ into a dried, previously weighed (W₁g) crucible.
- v. Place the crucible in an electric burner and ignite the precipitate.
- vi. Cool the crucible to lab temperature and note down its weight (W₂ g).

vii. Calculate the weight of BaSO₄ formed $(W_2 - W_1 = W g)$.

Calculations:

233.4 g of BaSO₄ contains 96.06g of sulphate
$$W \text{ g of BaSO}_4 \text{ contains} = \frac{96.06 \times W}{233.4} \text{g of sulphate}$$

i.e., 200ml of water sample contains =
$$\frac{96.06 \times W}{233.4}$$
 g of sulphate

$$\therefore 1000 \text{ml of water sample contains} = \frac{96.06 \times W \times 1000}{233.4 \times 200} = \text{`a' g of sulphate}$$

 \therefore The amount sulphate in the water sample = 'a' g of sulphate

Determination of fluoride by SPADNS Method

Fluoride ion severely affects the qualities of drinking water. If its concentration exceeds 1 mg/L, causes dental fluorosis. Its concentration can be estimated colorimetrically by using Zirconyl-SPADNS [sodium 2-(p-sulphophenylazo)-1,8-dihydroxy-3,6 naphthalene disulphonate] reagent.

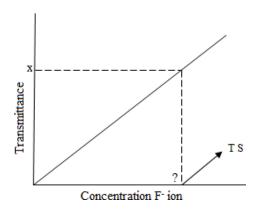
Principle: Under Acidic conditions, fluoride ion reacts with Zr-SPADNS reagent and Color of this reagent gets bleached. The extent of bleaching depends on the concentration of F ion.

$$Zr\text{-SPADNS} + F^- \rightarrow (ZrF_6)^{2-} + SPADNS$$

Procedure:

- i. Prepare a reference solution by adding 10 ml of SPADNS in HCl and dilute to 50 ml and use this solution to set the colorimeter to zero at 570 nm.
- ii. Prepare Zr-SPADNS reagent by dissolving ZrCl₂. 8H₂O and SPADNS in HCl and dilute to 500 ml.
- iii. Prepare a stock solution of NaF by dissolving 0.022 g in 1000 ml.
- iv. Prepare a series of standard solutions by adding 2,4,6,8 ml of NaF Solution in 50 ml standard flasks.
- v. To each flask, 1 drop of sodium arsenite (NaAsO₂) and 10ml of Zr-SPADANS reagent are added. Dilute up to the mark using distilled water. Mix well and measure transmittance at 570 nm.
- vi. Draw a calibration curve by plotting transmittance versus concentration of fluoride ion.
- vii. Take a known volume of water sample in which fluoride concentration has to be determined, add NaAsO₂ and 10ml of Zr-SPADANS and measure transmittance at 570 nm.
- viii. Calculate the F-ion concentration using calibration curve.

Conc.	Zr-SPADNS	Conc. of F	Transmi
NaF		in (mg/L)	ttance
2	10	0.398	
4	10	0.796	
6	10	1.194	
8	10	1.592	
10	10	1.989	
TS	10	?	X

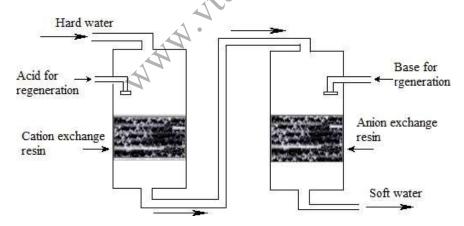


Softening of water by Ion exchange process

The process of removing hardness causing ions such as calcium and magnesium ions from hard water is called softening of water. Water softening process involves cation and anion exchange resins which are made of cross linked polymers with porous structure and desirable functional groups.

Cation exchange resin is made of **Styrene-divinyl benzene** copolymer with SO₃H functional groups containing replaceable H⁺ ions and is represented as RH⁺. It exchanges H⁺ ions with cations like Ca²⁺ and Mg²⁺ present in hard water.

Anion exchange resin is made of **Styrene-divinyl benzene** copolymer with basic quaternary ammonium functional groups containing replaceable OH⁻ ions and is represented as ROH⁻. It exchanges OH⁻ ions with anions like SO₄²⁻ and Cl present in hard water.



Process: Cation and anion exchange resins are packed in separate columns as shown in the diagram. Hard water is first passed through the cation exchange resin where Ca²⁺ and Mg²⁺ are exchanged with H+ ions.

$$RH^{+} + M^{+} \rightarrow RM^{+} + H^{+}$$

 $2RH^{+} + M^{2+} \rightarrow R_{2}M^{2+} + 2H^{+}$

Where M⁺ is monovalent like Na⁺ and M²⁺ is divalent like Ca²⁺.

The water is then passed through anion exchange resin where anions like SO ²⁻ and Cl⁻ are exchanged for OH⁻.

$$ROH^{-} + X^{-} \rightarrow RX^{-} + OH^{-}$$

 $2ROH^{-} + X^{2-} \rightarrow R_{2}X^{2-} + 2OH^{-+}$

Where X^{-} and X^{2-} represents the anions like Cl^{-} and $SO_4{}^{2-}$

Regeneration: On prolonged use, resins become deactivated, they need to be regenerated. Cation exchange resin is regenerated by HCl.

$$R_2M^{2+} + 2H^+ \rightarrow 2RH^+ + M^{2+}$$

Anion exchange resin is regenerated by NaOH.

$$R_2X^{2-} + 2OH^- \rightarrow 2ROH^- + X^{2-}$$

The columns finally washed with distilled water before use.

Advantages of Ion exchange method:

- i) It can be used for high pressure boilers also.
- ii) Water of 1 to 2 ppm purity can be obtained from this process.
- iii) It can be regenerated and used for long period of time.

Drawbacks of Ion exchange method:

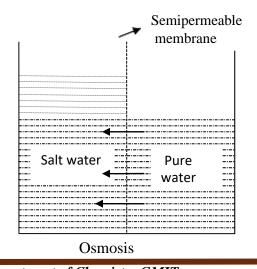
- i) Expensive
- ii) Fe, Mn cannot be removed as they form complexes with resins
- iii) Cannot be used for turbid water as they clog the resins.

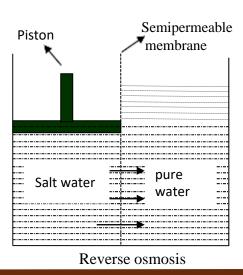
Potable water:

Water which meets all the parameters of pure water and fit for drinking called potable water. It should be clear, colorless, odorless and free from pathogenic bacteria with agreeable taste.

Desalination or Desalting: Desalination is a process of removal of dissolved salts from saline water (sea water) and water become potable. It can be achieved by Reverse Osmosis.

Reverse osmosis:





When pure water and salt water are separated by a semipermeable membrane, due to the difference in chemical potential, water molecules move from pure water to salt water until the chemical potential become equal in both the sides. This movement is called osmosis. The water molecules can be made to move in reverse direction that is from salt water to pure water by applying pressure on salt water, it is called reverse osmosis.

The process of movement of water through a semi permeable membrane from salt water to pure water by the application of pressure greater than osmotic pressure on salt water is called as reverse osmosis.

A reverse osmosis unit consists of a vessel, high pressure pump and a semi permeable membrane made up of cellulose acetate. When pressure in the range 410-540 psi is applied on the salt water (sea water), water molecules flow from salt water to fresh water which can be used for domestic applications.

Advantages:

- 1) It is economical, simple, continuous and compact.
- 2) The process needs extremely low energy.
- 3) It has long life and membrane is easily replaceable.
- 4) It is possible to connect number of tubes in parallel, to get more fresh water.
- 5) Ionic, non-ionic, colloidal and high molecular weight organic matters are easily removed.

Disadvantage:

1) Colloidal silica is not removed by this process.



Question Bank

- 1. What is meant by primary pollutant and secondary pollutant?
- 2. What are viable particulates and non-viable particulates?
- 3. Explain the Sources, Ill effects and control of CO, NO and SO₂.
- 4. Explain E-waste, Biomedical waste and Solid waste.
- 5. Explain the ozone formation, depletion and its consequences.
- 6. Explain the determination of concentration of fluoride ion in water by colorimetry.
- 7. Describe the estimation of concentration of sulphite by Gravimetry.
- 8. What is boiler feed water? What is sludge and scale? What are the reasons for sludge and scale formation? Mention the disadvantages and preventive measures.
- 9. Explain boiler corrosion due to dissolved oxygen/CO₂/MgCl₂ with reactions and mention the preventive measures for the same.
- 10. Define BOD and COD. Explain method of determination of COD of a waste water sample.
- 11. Discuss the primary, secondary and tertiary treatment steps of sewage water treatment with neat diagram.
- 12. What is desalination? Discuss desalination of water by reverse osmosis process.
- 13. Explain purification of water by ion exchange resin method.
- 14. 25 cm 3 of sewage sample reacted with 10cm^3 of $K_2\text{Cr}_2\text{O}_7$ solution and unreacted sample requires 8.5cm^3 of .025 N FAS solution. Under similar conditions in blank titration 15cm^3 of same FAS is used up. Calculate the COD of the sewage sample.