

WATER POLLUTION

- Any contamination of water which alters the physical, chemical or biological properties of water that are detrimental to the ‘whole’ ecosystem e.g., fertilizers and pesticides from agricultural runoff; sewage and food processing waste; lead, mercury, and other heavy metals; chemical wastes from industrial discharges; and chemical contamination from hazardous waste sites.
- brought about mainly by **human activities** and **natural resources** and which cause harmful effects on terrestrial and aquatic life.

Sources of pollutants

- Natural sources:

decomposed vegetable, animal and weathered products brought into main water resources

- Anthropogenic activities:

domestic as well as industrial pollution

- Agricultural discharge:

pesticides, insecticides, plant nutrients, fertilizers etc.

- *Bacteria, algae, virus also cause water pollution.*

| Domestic | Industrial |
|--|--|
| <p>Release of huge quantities of municipal and domestic wastes through drains into the rivers and canals.</p> <p>Eg., human faeces, kitchen wastes, organic water that provide nutrition to bacteria and fungi.</p> | <p>Effluents from factories, refineries and a number of chemical industries.</p> <p>Eg., acids, alkalies, detergents, metals, pesticides etc.</p> |

Classification of Water Pollutants

1. Oxygen demanding wastes
2. Pathogens (Disease causing agents)
3. Synthetic organic compounds
4. Plant nutrients
5. Inorganic chemicals and minerals
6. Sediments
7. Radioactive substances
8. Thermal discharges
9. Oil
- 10 VOCs

1. Oxygen demanding wastes

- Organic substances formed due to death and decay of aquatic/terrestrial flora and fauna, from municipal waste water or in effluents from certain industries, like food processing, paper production
- Organic substances are oxidized by bacteria or micro organisms consuming dissolved oxygen in water. Produce **undesirable odour, tastes and reduce the acceptability** of water in domestic supply
- **Dissolved oxygen (DO) is Essential** for sustaining the plant and animal life in any aquatic system
- Amount of **DO in water is reduced** because of oxygen demanding wastes that oxidize in water, reducing the amount of DO
- Oxidation of certain inorganic compounds may also contribute to the oxygen demand

Measures of oxygen demand commonly used:

- **Biological Oxygen Demand (BOD)**: measure of biological degradation of waste; most important measure of the strength of organic pollution
- **Chemical Oxygen demand (COD)**: measure of chemical oxidation of waste

2. Pathogens (Disease causing agents)

- Grow and multiply within the host
- Carried into the water bodies by sewage and wastes from farm and various industries
- Contaminated water caused by poor sanitation can lead to both, water borne and water contact diseases.
- Examples of pathogens associated with water borne diseases include bacteria, viruses and protozoa.
- common diseases: **Cholera, Dysentery, Typhoid** etc.

Mechanism of infection:

Through ingestion or contact

- Larvae attach themselves to human skin, penetrate it and enter the blood stream, Schistosomiasis caused by free swimming larva, cercaria, in water.
- *Escherichia coli (E. coli)*, belonging to the coliform group is harmless bacteria found in large number in human faeces. A large concentration of *E. coli* in water indicates faecal contamination and evidence of the presence of pathogens.

3. Synthetic organic compounds

Pesticides, synthetic organic chemicals and detergents

- Non-biodegradable and persistent
- Accumulative toxic poisons and ultimately reach objectionable levels in water.

PESTICIDES :

- **Way to water body:** surface run off from agricultural lands, waste discharge by pesticide manufacturers and by other means.
- **Effects:** Persistent, Bio-accumulate in fatty tissues, Bio-magnifiable, Carcinogenic, Cause birth defects, Severe neurological damage etc

Detergents – “cleansing agents”

- The **basic active ingredient** in detergents is the **surfactant** or surface-active agent having hydrophobic (hydrocarbon) and hydrophilic (polar) groups.
- Surfactants decrease the surface tension of water so that they can penetrate the surface and interstices of the object being cleaned.
- Usually contain **10 – 30% surfactant** and remaining are **polysulphate salts** (the builder) and a number of other ingredients.
- Surfactant concentrations as low as **1 ppm** produce foam in rivers and in sewage treatment plants since **non-toxic to humans but imparts off-taste to drinking water**.
- It reduces the rate of oxygen absorption in water and may lead to the symptoms similar to asphyxiation in certain kind of fish (trout).
- Till the early 1960s the surfactants present in synthetic detergent was **alkylbenzene sulphonate (ABS)** which is non biodegradable. ABS have been now replaced by linear alkyl sulphonate (LAS) which is rapidly biodegradable.

4. Plant nutrients

- Chemicals such as **nitrogen, phosphorus, carbon, sulphur, calcium, potassium, iron, manganese** etc. are essential to growth of living things.
- These cause excessive growth of aquatic plants, **algal bloom**. Algae die and decompose leading to reduced DO levels.
- The gradual accumulation of silt and organic matter in the lake is known as **eutrophication**, which is serious health hazard.
- **Eutrophied lake gets shallower and warmer with further** growth and decay of algae and eventually lake turns into a marsh or bog.
- **Way to water bodies:** through municipal waste water, industrial wastes and **runoff from fertilized lands.**
- Certain bacteria in the intestines reduce nitrate in water to toxic Nitrites. Nitrites have greater affinity for haemoglobin as compared to oxygen. Thus nitrite attaches to haemoglobin forming **methaemoglobin**, producing a condition called **methaemoglobin anemia** commonly known as **blue baby syndrome**. **In young babies, it is extremely fatal.** Nitrates can be converted into **nitrosamines** in the body leading to gastric cancer.

5. Inorganic chemicals and minerals

- Includes **inorganic salts, mineral acids, finely divided metals or metal compounds, trace elements, cyanides, organometallic compounds etc.** added to the water bodies through municipal and industrial waste waters and mine runoff.
- ***Acid Mine Drainage:*** The mining of sulphur bearing ores containing lead, zinc and copper lead to acid drainage. **Coal mines** discharge containing varying amounts of **iron sulphide (pyrite)** is also a major cause of acid mine drainage. These discharges release considerable quantities of **sulphuric acid and ferric hydroxide, (which are formed as result of reactions between air, water and pyrite)** into local streams through seepage.
- ***Soluble Salts:*** Water naturally accumulates variety of dissolved salts as it passes through soils and rocks on its way to sea. These salts include cations such **sodium, calcium, magnesium and potassium** and anions such as **chloride, sulphate and bicarbonate.**
- Concentration of total dissolved solids (**TDS**) in water is less than **500 mg/L TDS - safer for drinking purpose.** WHO recommends **300 mg/L TDS, not to be less than 50 mg/L**

Heavy Metals

- The metals of particular concern in industrial waste waters are **cadmium, chromium lead, mercury, silver, arsenic, aluminium, copper, cobalt, manganese** etc. Some of these, such as chromium and iron, are extremely toxic in higher doses.
- Metals may be inhaled or may be ingested. These have a range of adverse impacts on the body, **including nervous system and kidney damage, creation of mutations and induction of tumours**. The kidneys contain millions of excretory units called nephrons and the chemicals that are toxic to kidneys are called **nephrotoxins**. Cadmium, lead and mercury are examples of **nephrotoxic metals**.

6. Sediments

- Sediments include **soil, sand and mineral particles** washed into the aquatic environment by storms and flood waters.
- These are **sources of organic and inorganic matter** in the streams, fresh water, rivers, and other water bodies.
- Soil particles **eroded** by running water ultimately find their way into water reservoirs via '**siltation**'.
- This **reduces the storage capacity** in dams, etc.
- **Blocked sunlight** and hence **decreased photosynthetic rate** of aquatic plants.
- **Evolution of oxygen is decreased.**
- **Sediments increase the cost of water treatment.**
- Sediments enter pumping equipment and power turbines and **increase the turbidity.**

7. Radioactive substances

- Enter into aquatic system through number of **human activities** involving the use of naturally occurring or artificially produced radioactive materials.
- **Activities such as mining and processing of ores** to produce radioactive ores, e.g, **uranium and thorium**. The refining of uranium ore is an important source of radioactive waste, producing radionuclides of radium, bismuth etc.
- From **nuclear power plants** and from industrial use of radioactive materials leakage from **underground nuclear detonations**.
- **Use of radio isotopes** in medicine, industry, agriculture and research operations.
- Radioactive substances can **enter living organisms** with food and water and get accumulated in blood and certain vital organs like thyroid gland, the liver, bone and muscular tissues. These may cause **cancers, leukemia and eye cataract**.

8. Thermal Discharges

- Industry and power plants (Coal fired power plants, electric powers, steel and chemical industries as well as atomic energy plants) use large quantities of **water for cooling purposes** and **discharged directly into water bodies**.
- This results in increase in temperature of the water bodies which is, in general, called as **Thermal Pollution**.
- Rise in temperature of water decreases dissolved oxygen content of water which effects the aquatic life. At 32°F the DO content of water is 12 ppm (100% Saturation) which is decreased to 6 ppm at 64° F.
- Fishes are killed due to action of heat on nervous system, inactivation of enzymes and coagulation of cell protoplasm.
- An increase in temperature also increase the toxicity of some chemical pollutants.

9. Oil

- Oil and oil wastes are added to the water bodies from industries as effluents, oil refineries, storage tanks, automobile waste oil and petrochemical plants.
- It is **insoluble in water and hence floats over it** as a thin layer.
- Oil may **penetrate the feather of the birds** and effect their **insulation and buoyancy**. Thus birds experience difficulty in floating and flying.
- The birds may ingest oil while they dive to feed. This ingestion may produce toxic effects.
- Moreover the oil slick formed on the surface prevents the diffusion of oxygen into water resulting in decreased concentration of DO.

10. Volatile Organic Compounds

- Most commonly found contaminants in water.
- Often used as **solvents in industrial processes**.
- They are volatile and hence their concentrations remain as low as few micrograms per litre in surface water.
- But in ground water their concentrations can be hundreds or thousands of times higher.
- These are toxic and carcinogenic, their presence in drinking water is cause of great concern.

Sources of water

The chief sources of water fall in two main groups:

□Surface water

Flowing

- i) Streams ii) River water iii) Sea water

Still Waters

- i) Lake water ii) Reservoirs

□Underground water: A part of the rain water, which reaches the surface of the earth, percolates into the earth. It comes in contact with a number of mineral salts present in the soil and dissolves some of them. It comes out in the form of *spring or well*. It is clear in appearance due to the filtering action of the soil, but contains more of the dissolved salts, thus more hardness.

Specification of water

The main impurities present in water are classified into three types:

Physical impurities

Physical Impurities include suspended and colloidal impurities

(a) Suspended impurities (Make the water turbid)-Clay, sand, decayed vegetable and animal matter.

(b) Colloidal impurities (Impart colour, odour and taste)-Finely divided clay and silica, colouring matter, waste products, etc.

Chemical impurities

Chemical Impurities include dissolved salts and dissolved gases.

(a) Dissolved salts (make water hard)- Chlorides, sulphates, bicarbonates, carbonates of Ca, Mg, Na, K

(b) Dissolved gases – Oxygen, carbon dioxide, hydrogen sulphide etc.(acidic and corrosive)

Bacteriological impurities

Pathogenic microorganism-Spread various diseases like typhoid, dysentery, hepatitis etc.

Various Water Quality Parameters

| Physical Parameters | Chemical Parameters | Biological Parameters |
|---|---|---------------------------|
| 1. Colour 2. Turbidity 3. Taste and odour 4. Total dissolved solids (TDS) | 1. Hardness 2. Alkalinity 3. Dissolved Oxygen (DO) 4. pH 5. Biological Oxygen demand (BOD) 6. Chemical Oxygen Demand (COD) 7. Dissolved CO ₂ 8. Trace Metals 9. Free Chlorine 10. Chlorides | Pathogenic microorganisms |

Standards for Drinking Water

| S. No | PARAMETER | NAME OF AGENCIES | | | |
|----------|---|------------------|-----------------------|-------|-----------------------|
| | | ICMR | | WHO | |
| | | A | B | A | B |
| 1. | Colour (Units) | 5 | 25 | 5 | 50 |
| 2. | Turbidity (Units) | 5 | 25 | 5 | 25 |
| 3. | Total dissolved solids | - | - | 500 | 1500 |
| 4. | pH | 7-8.5 | - | 7-8.5 | - |
| 5. | Total hardness as CaCO_3 equivalents | 125 | 350 | 125 | 350 |
| 6. | Iron | 0.3 | 1.0 | 0.3 | 1.0 |
| 7. | Manganese | 0.1 | 0.5 | 0.1 | 0.5 |
| 8. | Nitrate | 20 | 50 | - | 50-100 |
| 9. | Chloride | - | - | - | 250 |
| 10. | Fluoride | 1.0 | 2.0 | 0.5 | 1.0-1.5 |
| 11. | Sulphate | 200 | 400 | 200 | 400 |
| 12. | Pathogenic Micro Organisms (Coliform) | - | 1 coliform per 100 ml | - | 1 coliform per 100 ml |

A → Recommended concentration (mg/lit)

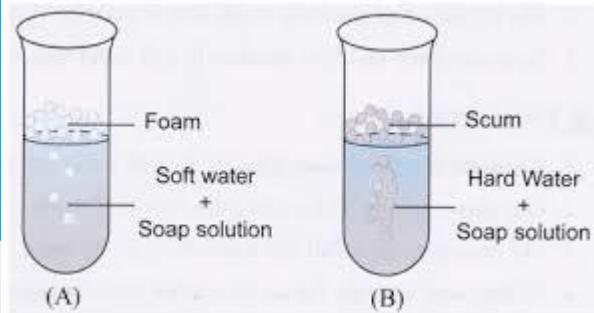
B → Maximum permissible concentration (mg/lit)

WATER QUALITY STANDARDS

- Water used for drinking purpose should meet certain quality criteria with respect to appearance (turbidity, colour) potability (taste, odour), health (bacteria, nitrates, chlorides etc.,) and toxicity (metals, organics). These criteria are established by health or other regulating agencies to ensure that the water quality in a resource is suitable for drinking purposes.

Hardness

WATER – minerals/salts dissolved in fresh water



HARDNESS MINERALS

Total hardness (TH)

All dissolved calcium and magnesium salts

CARBONATE HARDNESS (CH)

All minerals contributing to carbonate hardness

They include calcium and magnesium in the form of carbonate

NON-CARBONATE HARDNESS (NCH)

All minerals contributing to non-carbonate hardness

They include calcium and magnesium in the form of sulphate

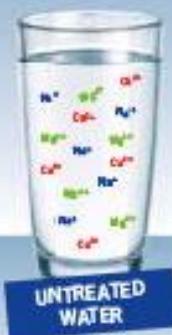
MINERALS NOT AFFECTING WATER HARDNESS

All other minerals

(other than calcium and magnesium)

e.g. sodium and potassium salts and sodium chlorite (cooking salt)

WATER IS
NOT ALWAYS
THE SAME!



UNTREATED
WATER



SOFTENED
WATER



PARTLY DESALINATED
WATER



FULLY DESALINATED
WATER / OSMOSIS
TREATED WATER

- Hardness is usually recognized in water by the increased quantity of soap or detergent required to make a permanent lather.
- As hardness increases, soap consumption rises sharply, and an objectionable scum is formed.
- Hard water forms scale in boilers, water heaters, and pipes.

Hardness

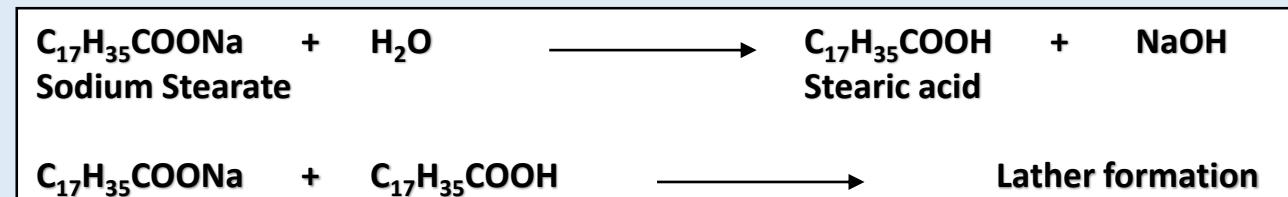
Water is defined as amount of calcium and magnesium present in water and is classified into two types based on its property to react with soap solution.

- **Soft water**

Soft water is one that gives good lather readily with soap solution.

- **Hard water**

- Water that does not produce lather with soap readily but forms an insoluble precipitate like white scum is known as hard water.
- The hardness of water is caused by the presence of dissolved salts such as bicarbonates, sulphates, chlorides and nitrates of divalent metal ions like calcium and magnesium.
- Soap is sodium or potassium salt of higher fatty acids like stearic, oleic and palmetic acids. When soap is mixed with soft water lather is produced due to stearic acid and sodium stearate.



When water with hardness is used for washing, large amount of soap is consumed. Thus hardness of water can be defined as the **soap consuming capacity of water**.

The reaction can be explained as follows,



$(\text{RCOO})_2\text{M}$ is insoluble white scum

where R = long chain fatty acid like palmitic, oleic and stearic acid.

$\text{M}^{2+} = \text{Ca}^{2+}, \text{Mg}^{2+}$

| Hardness | Name of water |
|--------------|---------------------|
| 0-70 mg/L | Soft water |
| 70-150 mg/L | Moderate hard water |
| 150-300 mg/L | Hard water |
| >300 | Very hard water |

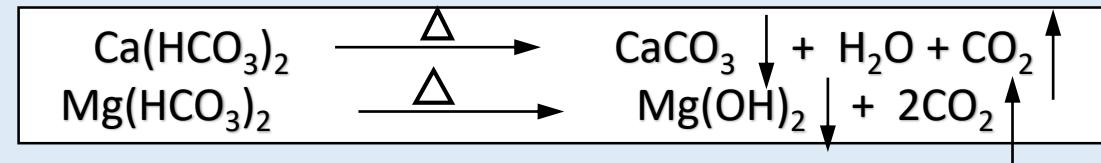
Common hardness producing salts present in water: chlorides, sulphates and bicarbonates of Calcium and Magnesium. i.e., CaCl_2 , CaSO_4 , MgCl_2 , MgSO_4 , $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$. Their quantity only decides the extent of hardness of water.

Classification of Hardness of Water

Hardness of water can be classified into two categories.

1. Temporary hardness (or) Carbonate hardness

This hardness is caused by two dissolved bicarbonate salts $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$. The hardness is called temporary because, it can be removed easily by boiling. During boiling, bicarbonates are decomposed to yield insoluble carbonates or hydroxides, which are deposited as a crust at the bottom of vessel.



2. Permanent hardness (or) Non-Carbonate hardness

This hardness is due to the dissolved chlorides, sulphates and nitrates of calcium and magnesium. These salts are CaCl_2 , MgCl_2 , CaSO_4 , MgSO_4 , $\text{Ca}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$. It cannot be removed easily by boiling. Hence, it is called permanent hardness. Only chemical treatment can remove this hardness.

$$\text{Total Hardness} = \text{Temporary hardness} + \text{Permanent hardness}$$

Expression of Hardness

Hardness of water is expressed in terms of number of parts of CaCO_3 (or) its equivalent present in a particular quantity of water.

Calcium Carbonate equivalents

Hardness is expressed in terms of CaCO_3 (or) its equivalent. If water contains CaCO_3 alone the hardness is a measure of number of parts of CaCO_3 . Usually, water contains some other salts. The amount of these salts is converted in to their CaCO_3 equivalent.

CaCO_3 was selected for expression of the degree of hardness because;

1. It is an insoluble salt, and all the dissolved salts of calcium are precipitated as CaCO_3
2. The Molecular Weight of CaCO_3 is 100, and also is a primary standard.

$$\text{CaCO}_3 \text{ equivalent} = \frac{\text{Weight of hardness producing salt}}{\text{Equivalent weight of the salt}} \times \text{equivalent weight of CaCO}_3$$

CaCO₃ equivalents for various salts:

- 100g of CaCO₃ ≡ 111g of CaCl₂ ≡ 136g of CaSO₄ ≡ 95g of MgCl₂ ≡ 120g of MgSO₄ ≡ 162g of Ca(HCO₃)₂ ≡ 146g of Mg(HCO₃)₂ ≡ 164g of Ca(NO₃)₂ ≡ 44g of CO₂ ≡ 148g of Mg(NO₃)₂
- This implies that 1 mole of CaCO₃ (or 100 parts by weight) would react with the same amount of soap as 1 mole of CaCl₂ (111 parts by weight) because 1 mole of these salts will produce same number of Ca or Mg ions (Avogadro's Number)
- 1g mole of CaCl₂ ≡ 1 gm mole of CaCO₃
111g of CaCl₂ ≡ 100g of CaCO₃
55.5g of CaCl₂ ≡ 50g of CaCO₃

Thus, A gms of CaCl₂ ≡ (50/55.5) × A gms of CaCO₃

Thus, equivalents of CaCO₃ = (Eq.wt. of CaCO₃ / Eq.wt. of substance) × Mass of Substance

Units of hardness

There are four units in which the hardness of water is expressed.

1. Parts per million
2. Milligrams per litre
3. Degree Clark.
4. Degree French

1. Parts per million (ppm):

It is the parts of calcium carbonate equivalent hardness per 10^6 parts of water.

i.e. 1 ppm = 1 part of CaCO_3 eq. hardness in 10^6 parts of water.

2. Milligrams per litre (mg/L):

It is the number of milligrams of calcium carbonate equivalent hardness present per litre of water.

Thus, 1 mg/L = 1 mg of CaCO_3 eq. hardness per 1 L of water

But 1 L water = 1 kg = 1000g = 10^6 mg

1 mg/L = 1 mg of CaCO_3 eq. per 10^6 mg of water
= 1 part of CaCO_3 eq. per 10^6 parts of water = 1 ppm

3. Degree Clark (${}^{\circ}\text{Cl}$):

It is the number of grains of CaCO_3 equivalent hardness per gallon of water. (or) It is the parts CaCO_3 equivalent hardness per 70,000 parts of water.

$1{}^{\circ}\text{Cl} = 1$ grain of CaCO_3 eq. hardness per gallon of water

$1{}^{\circ}\text{Cl} = 1$ part of CaCO_3 eq. hardness per 70,000 parts of water

4. Degree French (${}^{\circ}\text{Fr}$):

It is the parts of calcium carbonate equivalent hardness per 10^5 parts of water.

i.e. $10{}^{\circ}\text{Fr} = 1$ part of CaCO_3 eq. hardness in 10^5 parts of water.

Relationship between various units of hardness:

$$1\text{ppm} = 1 \text{ mg/L} = 0.1 {}^{\circ}\text{Fr} = 0.07 {}^{\circ}\text{Cl}$$

Example 1. A water sample contains 410 mg of CaSO_4 per litre. Calculate the hardness in terms of CaCO_3 equivalents.

Solution. Hardness = (strength of CaSO_4 in mg/L) \times multiplication factor

$$= (\text{strength of } \text{CaSO}_4 \text{ in mg/L}) \times \left[\frac{\text{chemical equivalents of } \text{CaCO}_3}{\text{chemical equivalents of } \text{CaSO}_4} \right]$$

$$= (410 \text{ mg/L}) \times \left[\frac{50}{68} \right]$$

$$= 301.47 \text{ mg/L} = 301.47 \text{ ppm}$$

Example 2. How many grams of $MgCO_3$ dissolved per litre gives 84 ppm of hardness ?

Solution. Hardness

$$= (\text{strength of } \text{MgCO}_3 \text{ in mg/L}) \times \left[\frac{\text{chemical equivalent of } \text{CaCO}_3}{\text{chemical equivalent of } \text{MgCO}_3} \right]$$

$$\text{Hence, strength of } \text{MgCO}_3 = \text{Hardness} \times \frac{\text{chemical equivalents of } \text{MgCO}_3}{\text{chemical equivalents of } \text{CaCO}_3}$$
$$= (84 \text{ ppm}) \times \left(\frac{42}{50} \right) = 70.56 \text{ ppm} = 70.56 \text{ mg/L}$$

Thus, 70.56×10^{-3} gms of MgCO_3 dissolved per litre gives 84 ppm of hardness.

Example 3. A sample of water on analysis was found to contain the following impurities :

| Impurity | $\text{Ca}(\text{HCO}_3)_2$ | $\text{Mg}(\text{HCO}_3)_2$ | CaSO_4 | MgSO_4 |
|------------------------|-----------------------------|-----------------------------|-----------------|-----------------|
| Quantity (mg/L) | 4 | 6 | 8 | 10 |
| Mol. Wt. | 162 | 146 | 136 | 120 |

Calculate the temporary, permanent and total hardness of water in ppm, °Fr and °Cl.

Solution. Step (i) Conversion into CaCO_3 equivalents :

| <i>Constituent</i> | <i>Amount mg/L [A]</i> | <i>Multiplication factor [M]</i> | <i>CaCO_3 equivalent = [A] × [M]</i> |
|-----------------------------|----------------------------|--------------------------------------|--|
| $\text{Ca}(\text{HCO}_3)_2$ | 4 | 100/162 | $4 \times \frac{100}{162} = 2.47 \text{ mg/L}$ |
| $\text{Mg}(\text{HCO}_3)_2$ | 6 | 100/146 | $6 \times \frac{100}{146} = 4.11 \text{ mg/L}$ |
| CaSO_4 | 8 | 100/136 | $8 \times \frac{100}{136} = 5.88 \text{ mg/L}$ |
| MgSO_4 | 10 | 100/120 | $10 \times \frac{100}{120} = 8.33 \text{ mg/L}$ |

Step (ii) Determination of Temporary Hardness :

As Temporary hardness is due to bicarbonates of Calcium and Magnesium

$$\therefore \text{Temporary hardness} = 2.47 + 4.11 = 6.58 \text{ mg/L}$$

$$\text{As } 1 \text{ mg/L} = 1 \text{ ppm} = 0.1 \text{ }^{\circ}\text{Fr} = 0.07 \text{ }^{\circ}\text{Cl}$$

$$\begin{aligned}\text{Hence, Temporary hardness} &= 6.58 \text{ mg/L} = 6.58 \text{ ppm} \\ &= 6.58 \times 0.1 = 0.658 \text{ }^{\circ}\text{Fr} \\ &= 6.58 \times 0.07 = 0.46 \text{ }^{\circ}\text{Cl}.\end{aligned}$$

Step (iii) Determination of Permanent Hardness :

As permanent hardness in this case is due to CaSO_4 and MgSO_4

$$\begin{aligned}\therefore \text{Permanent hardness} &= 5.88 + 8.33 = 14.21 \text{ mg/L} \\ &= 14.21 \text{ ppm} \\ &= 14.21 \times 0.1 = 1.421 \text{ }^{\circ}\text{Fr} \\ &= 14.21 \times 0.07 = 0.995 \text{ }^{\circ}\text{Cl}\end{aligned}$$

Example 4. 200 mL of water sample has a hardness equivalent to 25 mL of 0.08 N $MgSO_4$. Find the hardness in ${}^{\circ}Fr$.

Solution. As Normality is number of gm. equivalents per L of solution.
Hence, number of gm. equivalents of MgSO_4

$$= \text{volume of } \text{MgSO}_4 \times \text{its normality}$$

$$= \frac{25}{1000} \times 0.08 = 2 \times 10^{-3}$$

As Number of gm. equivalents = $\frac{\text{Weight in gms.}}{\text{Eq. wt.}}$

Thus weight in gms. of MgSO_4 present in 200 mL of water sample

$$= (2 \times 10^{-3}) \times \text{Eq. wt. of } \text{MgSO}_4$$

So, wt. in gms. of MgSO_4 per L of water

$$= (2 \times 10^{-3}) \times \text{Eq. wt. of } \text{MgSO}_4 \times \frac{1000}{200} = 10^{-2} \times \text{Eq. wt.}$$

Now Hardness = (Wt. in gms. of MgSO_4 per L of water) $\times \frac{50}{\text{Eq. wt. of } \text{MgSO}_4}$

$$= (10^{-2} \times \text{Eq. wt. of } \text{MgSO}_4) \times \frac{50}{\text{Eq. wt. of } \text{MgSO}_4}$$

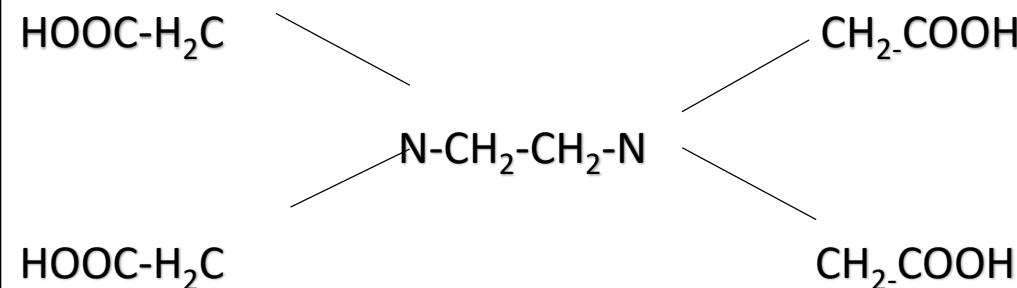
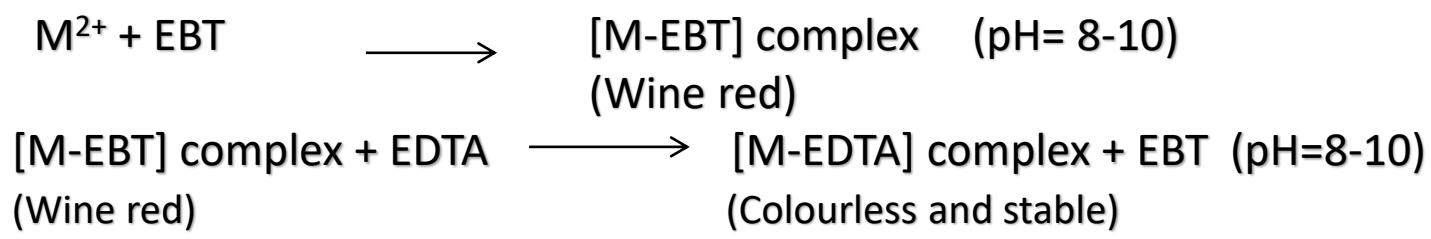
$$= 50 \times 10^{-2} \text{ gm/L} = 500 \text{ mg/L}$$

$$= 500 \text{ ppm}$$

$$= 500 \times 0.1 = 50 {}^{\circ}\text{Fr} \quad (\text{Since } 1 \text{ ppm} = 0.1 {}^{\circ}\text{Fr})$$

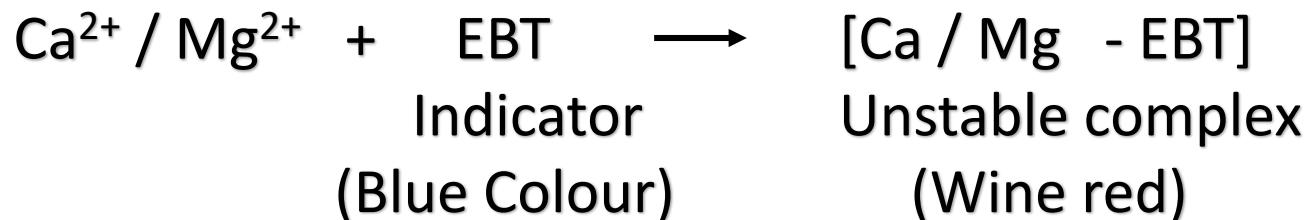
Estimation of Hardness of Water by EDTA Method

It is a complexometric titration of water sample with EDTA using EBT indicator. This is a reliable method because of its greater accuracy. EDTA (Ethylene diamine tetra acetic acid) forms a colourless stable complex with Ca^{2+} and Mg^{2+} ions in water at pH 8-10. **Ammonia buffer is used to maintain the pH.** In this method EBT (Eriochrome Black-T) is used as an indicator. Initially EBT forms an unstable complex with Ca^{2+} and Mg^{2+} ions, giving wine red colour to the solution. During the titration EDTA reacts with this complex (Ca-EBT or Mg-EBT complex), forms a stable complex (Ca-EDTA or Mg-EDTA) and releases the blue EBT into the solution. Hence the end point is **wine red to blue colour.**

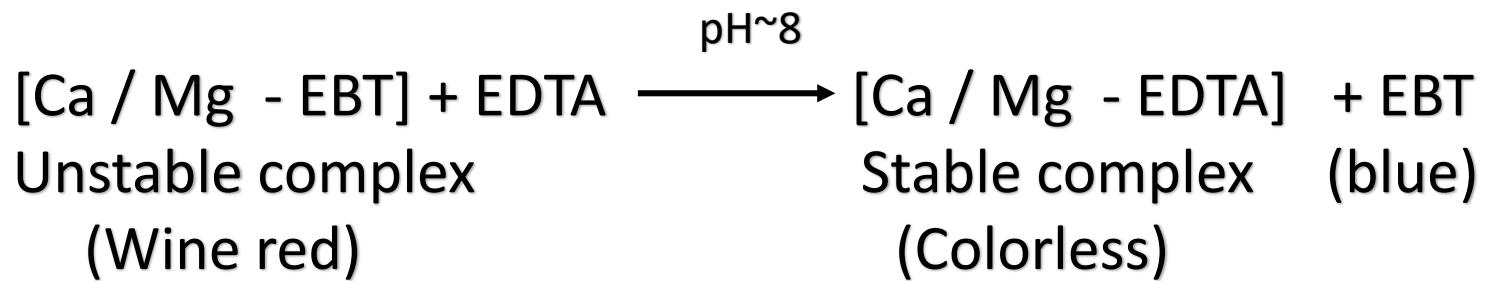


Principle of EDTA Method

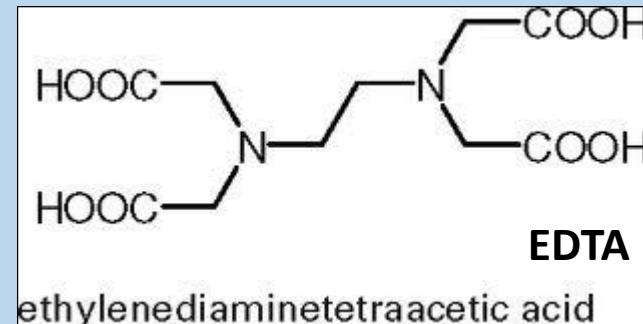
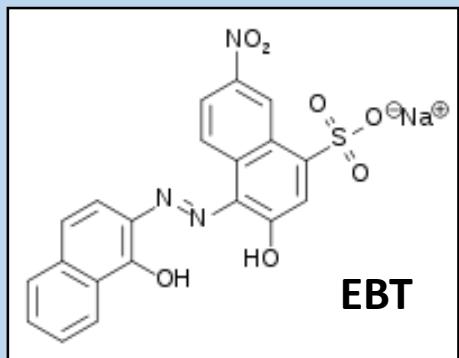
- Disodium salt of EDTA forms complex with calcium and magnesium ions present in water.
- The indicator used in this titration is Eriochrome Black-T (EBT) which also form unstable complex with calcium and magnesium ions present in water, at pH value about 8-10.
- In order to maintain the pH , buffer solution [NH₄Cl-NH₄OH] mixture is added. Only at this pH such a complexation is possible.



- This wine red colour solution is titrated against EDTA, EDTA replaces EBT indicator from [Ca / Mg - EBT] complex. The colour of the solution changes from wine red to blue at the end point.



Estimation of Hardness of Water by EDTA Method



sodium 1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulphonate
solochrome black

1. When indicator is added to hard water it combines with free metal ions present in water.



When EDTA solution is added to the titration flask it combines with the free metal ions giving metal EDTA complex, which is stable and colorless.



When all the free metal ions are exhausted, next drop of EDTA removes the metal ion engaged with indicator and the original blue color is restored.



EDTA is tetraprotic acid, can be represented as H_4Y , where H represents the four ionizable hydrogens.

Around $\text{pH} > 12$, most of EDTA exists as Y^{4-}

At $\text{pH} \geq 8$, EDTA exists as HY^{3-}

At $\text{pH} \geq 5$, EDTA exists as H_2Y^{2-}



The protons liberated considerably alter the pH of the solution and may cause dissociation of metal-EDTA complex.

Procedure for EDTA method

Standard solution:

1 mg of CaCO_3 /ml of solution. 1g of CaCO_3 is dissolved in 100 ml of dil. HCl and then add distilled water to make 1 litre solution. Each ml of this solution contains 1 mg of CaCO_3 equivalent hardness. ($1\text{g}/1000\text{ml} = 0.01 \text{ M CaCO}_3$).

EDTA solution:

Forms 1:1 complex with metal ions, 0.01 M EDTA is prepared by dissolving 3.72 g of its disodium salt (Mol. wt. = 372.25g) in distilled water to make 1 litre solution.

Indicator solution:

0.5g of EBT (Eriochrome Black-T) in 100 ml alcohol

Buffer solution:

70 g of NH_4Cl in 570 ml of Conc. NH_3 and make upto 1000 ml with distilled water.

i) Standardisation of EDTA solution

10ml of Standard hard water is taken in a conical flask. 5 ml of buffer solution and a few drops of EBT indicator are added. The solution is titrated against EDTA taken in burette. The endpoint is the colour change from **wine red to blue colour**. Let the volume of EDTA consumed be V_1 ml.

Calculation

1ml of std. hard water = 1mg of CaCO_3

10 ml of std. hard water = 10 mgs of CaCO_3

10 ml of std. hard water consumes = V_1 ml of EDTA

V_1 ml of EDTA consumes = 10 ml of Std. hard water.

= 10×1 mg of CaCO_3 eq. hardness.

1 ml of EDTA consumes = $10/V_1$ mg of CaCO_3 eq. hardness

Or **Strength of EDTA= $10/V_1$ mg/ml of CaCO_3**

2. Estimation of Total Hardness

10ml of sample hard water is pipetted out into a conical flask and titrated against EDTA taken in burette by adding the buffer and the indicator to get the end point. Let the volume of EDTA consumed be V₂ ml.

Calculation

10 ml of sample hard water = V₂ ml of EDTA

= $V_2 \times 10/V_1$ mg of CaCO₃ equivalent hardness

In 1000 ml of water sample= $V_2 \times 10/V_1 \times 1000/10$ mg of CaCO₃ equivalent hardness

$$\text{Total Hardness} = 1000 \times \frac{V_2}{V_1} \text{ mg /litre(or) ppm of CaCO}_3 \text{ equi. hardness}$$

3. Estimation of permanent hardness

250ml of water sample is boiled off to a volume of 50 ml in a beaker to remove temporary hardness. The temporary hard salts settle down. Filter and wash thoroughly and make up the solution again to 250 ml. 10 ml of this solution which is free from carbonate hardness is titrated against the EDTA as done before. Let the volume of EDTA consumed be V₃ ml.

10 ml of boiled sample hard water consumes = V_3 ml of EDTA

= $V_3 \times 10/V_1$ mg of CaCO_3 equivalent hardness

In 1000 ml of water sample = $V_3 \times 10/V_1 \times 1000/10$ mg of CaCO_3 equivalent hardness

= $1000 \times V_3/V_1$ mg/litre (ppm)

$$\text{Permanent Hardness} = 1000 \times \frac{V_3}{V_1} \text{ mg /litre (or) ppm of } \text{CaCO}_3 \text{ equi. hardness}$$

Estimation of Temporary Hardness

This can be calculated by using the following methods.

Temporary Hardness = Total Hardness – Permanent Hardness

$$\text{Temporary Hardness} = 1000 \times \frac{V_2 - V_3}{V_1} \text{ mg /litre (or) ppm of } \text{CaCO}_3 \text{ equi. hardness}$$

Example 1. 0.28 g of CaCO_3 was dissolved in HCl and the solution was made to one litre with distilled water. 100 ml of the above solution required 28 ml of EDTA solution on titration. 100 ml of the hard water sample required 35 ml of the same EDTA solution on titration. After boiling 100 ml of this water, Cooling, Filtering and then Titration required 10 ml of EDTA solution. Calculate the temporary and permanent hardness of water.

Solution. Step (i) Standardization of EDTA solution:

Given, 1 L of standard hard water contains 0.28 gm CaCO_3 . Hence, each mL of standard hard water contains 0.28 mg CaCO_3

As, 28mL of EDTA = 100 mL of standard hard water

$$= 100 \times 0.28 = 28\text{mg CaCO}_3$$

$$\therefore 1 \text{ mL of EDTA} = \frac{28}{28} = 1 \text{ mg CaCO}_3 \quad \dots(i)$$

Step (ii) Determination of total hardness of water:

Given, 100 mL of unknown hard water sample = 35 mL of EDTA

$$= 35 \times 1 = 35 \text{ mg CaCO}_3 \quad \{\text{By using (i)}\}$$

\therefore 1,000 mL (or 1L) of unknown hard water sample

$$= \frac{35}{100} \times 1000 = 350 \text{ mg CaCO}_3 \text{ eq. hardness}$$

Hence, total hardness = 350 ppm

...(ii)

Step (iii) Determination permanent hardness

100 mL of boiled water = 10 mL of EDTA

$$= 10 \times 1 = 10 \text{ mg CaCO}_3 \text{ eq. hardness}$$

\therefore 1,000 mL (or 1L) of boiled water

$$= \frac{10}{100} \times 1000 = 100 \text{ mg CaCO}_3 \text{ eq. hardness}$$

Hence, Permanent hardness of water = 100 ppm

...(iii)

Step (iv) Determination of Temporary hardness

Temporary hardness = Total harness – Permanent hardness

$$= 350 - 100$$

\Rightarrow Temporary hardness = 250 ppm

...(iv)

Example 2. A standard hard water contain 15 g of CaCO_3 per litre. 20 ml of this required 25 ml of EDTA solution, 100 ml sample water required 18 ml of the same EDTA solution. The sample after boiling required 12 ml of EDTA solution. Calculate the temporary hardness of the given sample of water, in terms of ppm.

Solution. Step (i) Standardization of EDTA solution:

Given, 1 L of standard hard water contains 15 gm CaCO_3 .

\therefore 1 mL of standard hard water contains 15 mg CaCO_3

Now 25 mL of EDTA = 20 mL of standard hard water

$$= 20 \times 15 = 300 \text{ mg } \text{CaCO}_3$$

$$\Rightarrow 1 \text{ mL of EDTA} = \frac{300}{25}$$
$$= 12 \text{ mg of } \text{CaCO}_3 \text{ equivalent hardness}$$

Step (ii) Determination of total hardness of water:

$$\begin{aligned} 100 \text{ mL of sample water} &= 18 \text{ mL of EDTA} \\ &= 18 \times 12 = 216 \text{ mg } \text{CaCO}_3 \text{ eq. hardness} \end{aligned}$$

\therefore 1 L sample water = 2160 mg of CaCO_3 eq. hardness

Hence, total hardness of water = 2160 ppm

... (ii)

Step (iii) Determination permanent hardness

100 mL of boiled water = 12 mL of EDTA

$$= 12 \times 12 = 144 \text{ mg } \text{CaCO}_3 \text{ eq. hardness}$$

\therefore 1 L of boiled water = 1440 mg of CaCO_3 eq. hardness

Hence, Permanent hardness of water = 1440 ppm

... (iii)

Step (iv) Determination of Temporary hardness

Temporary hardness = Total harness – Permanent hardness

$$= 2160 - 1440$$

\therefore Temporary hardness = 720 ppm

... (iv)

Example 3. 50 ml of standard hard water containing 1 mg of pure CaCO_3 per ml consumed 25 ml of EDTA. 50 ml of a water sample consumed 25 ml of the same EDTA solution. Using eriochrome T as indicator, calculate the total hardness of water sample in ppm.

Solution. Step (i) Standardization of EDTA solution:

Given, 1 L of standard hard water contains 1 mg CaCO_3

$$\begin{aligned}\text{Now } 25 \text{ mL of EDTA} &= 50 \text{ mL of standard hard water} \\ &= 50 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness}\end{aligned}$$

$$\text{Hence, } 1 \text{ mL of EDTA} = \frac{50}{25} = 2 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness} \quad \dots(i)$$

Step (ii) Determination of total hardness of water sample:

$$\begin{aligned}50 \text{ mL of sample water} &= 25 \text{ mL of EDTA} \\ &= 25 \times 2 = 50 \text{ mg } \text{CaCO}_3 \text{ eq. hardness}\end{aligned}$$

$$\text{Hence, } 1 \text{ L of sample water} = \frac{50}{50} \times 1000 = 1000 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness}$$

$$\text{Thus, total hardness of water} = 1000 \text{ ppm} \quad \dots(ii)$$

Example 4. Calculate the hardness of a water sample, whose 10 ml required 10 ml of EDTA. 20 ml of CaCl_2 solution, whose strength is equivalent 1.5 g of CaCO_3 per litre, required 30 ml of EDTA solution.

Solution. Step (i) Standardization of EDTA solution:

Given, 1 L of standard hard water contains = 1.5 gm CaCO_3

\therefore 1 mL of standard hard water contains = 1.5 mg CaCO_3

Now 30 mL of EDTA = 20 mL of standard hard water (i.e CaCl_2 solution)

$$= 20 \times 1.5 \text{ mg} = 30 \text{ mg } \text{CaCO}_3$$

$$\text{So, } 1 \text{ mL of EDTA} = \frac{30}{30} = 1 \text{ mg } \text{CaCO}_3 \text{ eq. hardness} \quad \dots(i)$$

Step (ii) Determination of total hardness of water sample:

10 mL of sample water = 10 mL of EDTA

$$= 10 \times 1 = 10 \text{ mg } \text{CaCO}_3 \text{ eq. hardness}$$

$$\therefore 1 \text{ L of sample water} = \frac{10}{10} \times 1000 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness}$$

Hence, total hardness of water sample = 1000 ppm

Alkalinity

Alkalinity of water is a measure of its acid neutralizing ability or it is the tendency of water to accept H^+ ions in order to neutralize it with the supply of OH^- ions.

In water analysis, it is often desirable to know the kind and amount of various forms of alkalinity present in water.

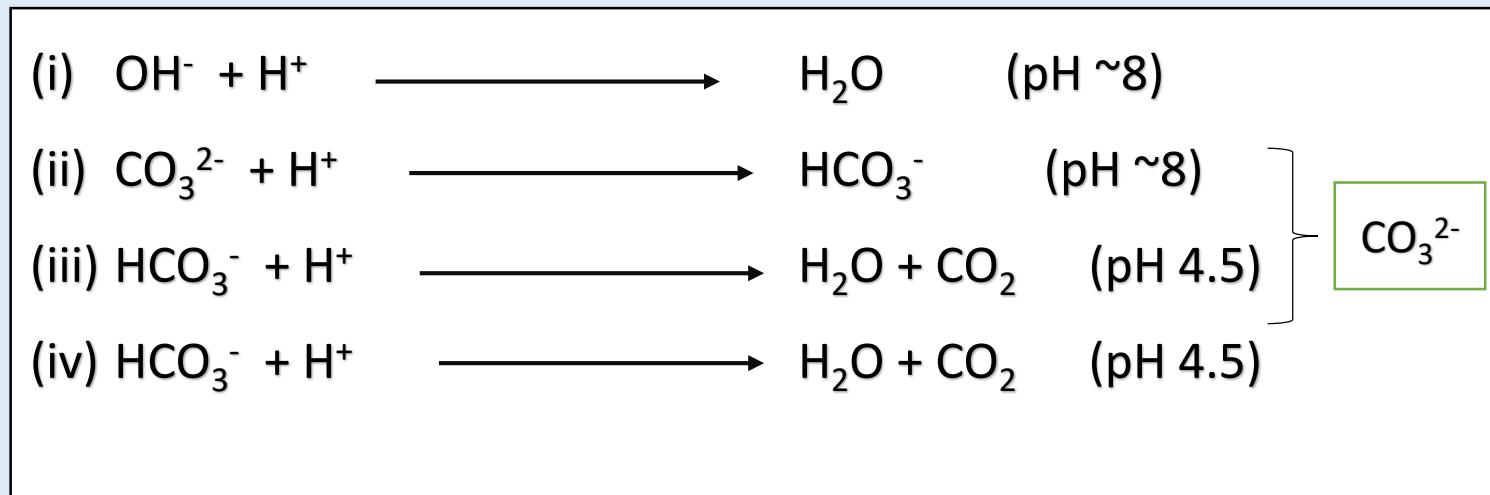
Alkalinity in water is due to the presence of **bicarbonates, carbonates and hydroxides of Ca, Mg, Na and K**.

(i) Caustic alkalinity (Due to OH^- and CO_3^{2-})

(ii) Bicarbonate alkalinity (Due to HCO_3^-)

Thus, the alkalinity of water may be due to

1. Hydroxide only
2. Carbonate only
3. Bicarbonate only
4. Both hydroxide and carbonate
5. Both carbonate and bicarbonate.
6. Hydroxide and bicarbonate
7. Hydroxide, carbonate and bicarbonate



Determination of alkalinity OH^- , CO_3^{2-} and HCO_3^- can be estimated separately by titration against standard acid using phenolphthalein and methyl orange as indicators

The possibility of hydroxide and bicarbonate existing together in water is ruled out because they combine with each other to form carbonate.



Alkalinity measurements

- Alkalinity may be determined by potentiometric method or using pH meter or titrimetry using different acid base indicators.
- Out of these methods, determination of various types and amounts of alkalinity is easily carried out by titration with standard hydrochloric acid employing phenolphthalein and methyl orange as an indicator separately or in succession.

Titrimetric method is preferred using **phenolphthalein and methyl orange as indicators**.

The titration of water sample against a standard acid upto phenolphthalein end point (P) marks the completion of reaction (i) and (ii) only. This amount of acid used thus corresponds to OH^- plus one half of the normal CO_3^{2-} present On the other hand, titration of the water sample against a standard acid to methyl orange end point (M) marks the completion of reaction (i), (ii), (iii) and (iv).

$$P = \text{OH}^- + \frac{1}{2}\text{CO}_3^{2-}$$

$$M = \text{OH}^- + \text{CO}_3^{2-} + \text{HCO}_3^-$$

Hence the total amount of acid used represents the total alkalinity.

Procedure

Part A: Phenolphthalein alkalinity

1. Pipette out 10 ml of water sample into conical flask. Add 1-2 drops of Phenolphthalein indicator.
2. Rinse and fill the burette with N/50 HCl
3. Titrate the water sample in conical flask with N/50 HCl till the pink colour just disappears.
4. Note down the reading and repeat to get concordant readings. Let V₁
5. Calculate phenolphthalein alkalinity

Part B: Total alkalinity (Methyl orange)

1. Take 10 ml of water sample in conical flask and add methyl orange indicator to it.
2. Titrate the water sample in conical flask with N/50 HCl taken in the burette till the yellow orange colour changes to orange red.
3. Note down the reading and repeat to get concordant readings. Let V₂
4. Calculate total alkalinity by using formula

Calculations:

- Phenolphthalein Alkalinity (P) in terms of CaCO_3 equivalents

Acid = Water Sample

$$N_1 V_1 = N_2 \times 10$$

$$\frac{1}{50} \times V_1 = N_2 \times 10 \text{ or } N_2 = \frac{1}{50} \times (V_1 / 10) = V_1 / 500$$

Strength in terms of CaCO_3 equivalents = $N_2 \times \text{Eq. wt of } \text{CaCO}_3$

$$= N_2 \times 50 \text{ g/l} = V_1 / 500 \times (50 \times 1000) \text{ mg/l}$$

Therefore, $P = 100V_1 \text{ mg/l} = 100V_1 \text{ ppm}$

- Methyl Orange Alkalinity (M) in terms of CaCO_3 equivalents

Acid = Water Sample

$$N_1 V_1' = N_2' \times 10$$

$$\frac{1}{50} \times V_1' = N_2' \times 10 \text{ or } N_2' = \frac{1}{50} \times V_1' / 10 = V_1' / 500$$

Strength in terms of CaCO_3 equivalents = $N_2' \times \text{Eq. wt of } \text{CaCO}_3$

$$= N_2' \times 50 \text{ g/l} = V_1' / 500 \times 50 \times 1000 \text{ mg/l}$$

Therefore, $M = 100 V_1' \text{ mg/l} = 100 V_1' \text{ ppm}$

Identification of ions present

Case 1 P = 0

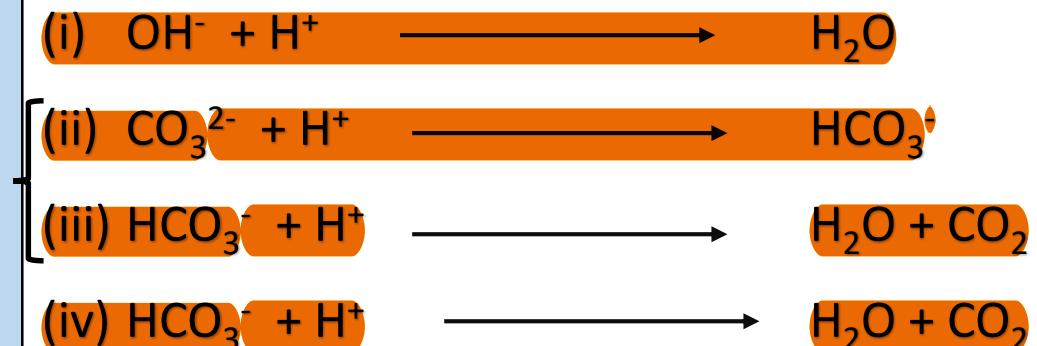
Indicates the absence of OH^- and CO_3^{2-}

Hence only HCO_3^- is present

Alkalinity due to OH^- = 0 ppm

Alkalinity due to CO_3^{2-} = 0 ppm

Alkalinity due to HCO_3^- = M ppm



$$P = \text{OH}^- \text{ & } \frac{1}{2}\text{CO}_3^{2-}$$

$$M = \text{OH}^- \text{ & } \text{CO}_3^{2-} \text{ & } \text{HCO}_3^-$$

$$M-P = \frac{1}{2}\text{CO}_3^{2-} \text{ & } \text{HCO}_3^-$$

Identification of ions present

Case 2 $P = M$

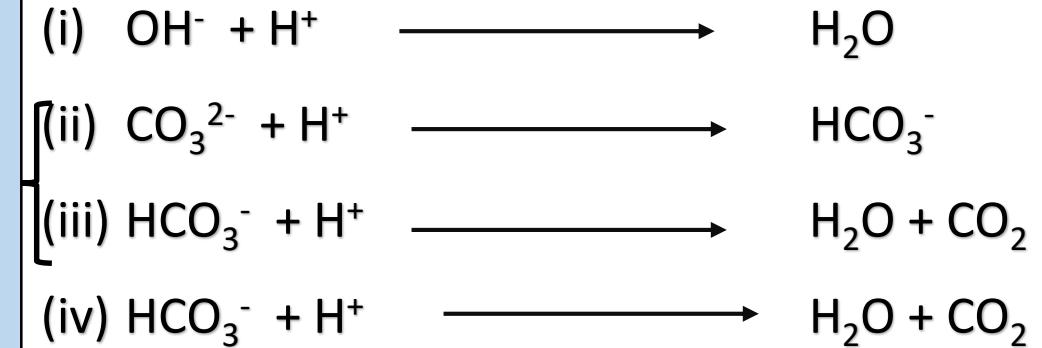
Indicates the absence of CO_3^{2-} and HCO_3^-

Hence only OH^- is present

Alkalinity due to $\text{OH}^- = P=M$ ppm

Alkalinity due to $\text{CO}_3^{2-} = 0$ ppm

Alkalinity due to $\text{HCO}_3^- = 0$ ppm



$$P = \text{OH}^- \text{ & } \frac{1}{2}\text{CO}_3^{2-}$$

$$M = \text{OH}^- \text{ & } \text{CO}_3^{2-} \text{ & } \text{HCO}_3^-$$

$$M-P = \frac{1}{2}\text{CO}_3^{2-} \text{ & } \text{HCO}_3^-$$

Identification of ions present

Case 3 **P = 1/2M**

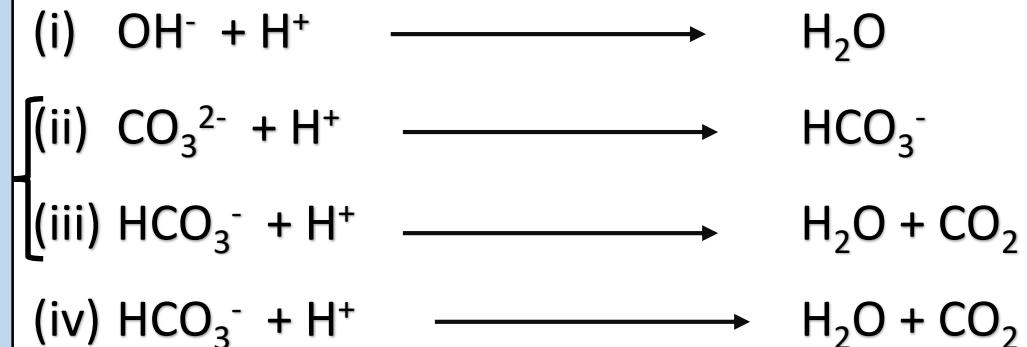
Indicates the absence of OH^- and HCO_3^-

Hence only CO_3^{2-} is present

Alkalinity due to OH^- = 0 ppm

Alkalinity due to CO_3^{2-} = M=2P ppm

Alkalinity due to HCO_3^- = 0 ppm



$$P = \text{OH}^- \& \frac{1}{2}\text{CO}_3^{2-}$$

$$M = \text{OH}^- \& \text{CO}_3^{2-} \& \text{HCO}_3^-$$

$$M-P = \frac{1}{2}\text{CO}_3^{2-} \& \text{HCO}_3^-$$

Identification of ions present

Case 4 $P < 1/2M$

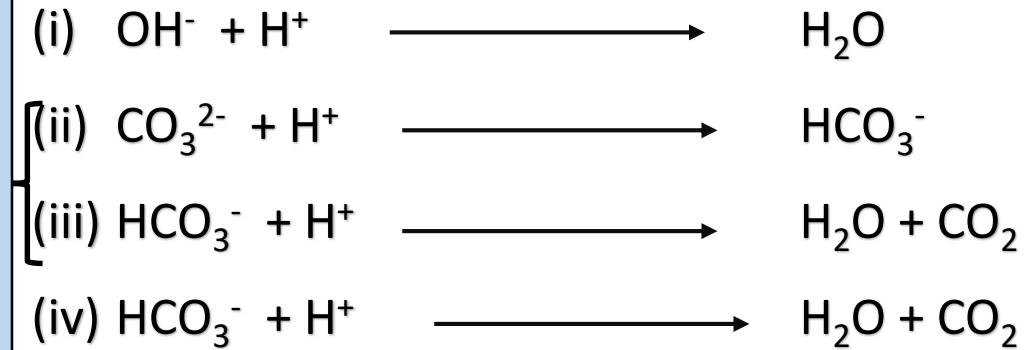
Indicates the absence of OH^-

Hence CO_3^{2-} and HCO_3^- are present

Alkalinity due to $\text{CO}_3^{2-} = 2P$ ppm

Alkalinity due to $\text{OH}^- = 0$ ppm

Alkalinity due to $\text{HCO}_3^- = (M-2P)$ ppm



$$P = \text{OH}^- \text{ & } 1/2\text{CO}_3^{2-}$$

$$M = \text{OH}^- \text{ & } \text{CO}_3^{2-} \text{ & } \text{HCO}_3^-$$

$$M-P = 1/2\text{CO}_3^{2-} \text{ & } \text{HCO}_3^-$$

Identification of ions present

Case 5 $P > 1/2M$

Indicates the absence of HCO_3^-

Hence OH^- and CO_3^{2-} are present

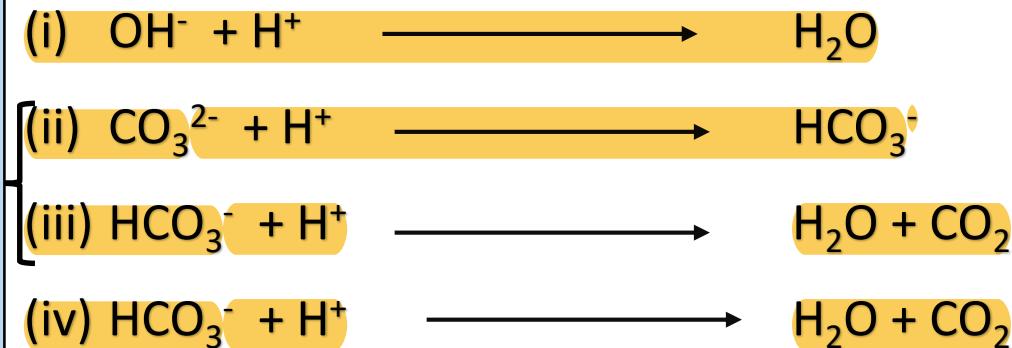
Alkalinity due to $\text{CO}_3^{2-} = 2(M - P)$ ppm

Alkalinity due to $\text{OH}^- = M - 2(M - P)$

$$= M - 2M + 2P = (2P - M) \text{ ppm}$$

Alkalinity due to $\text{HCO}_3^- = 0$ ppm

- <https://www.youtube.com/watch?v=zXvEmIFqicw>



$$P = \text{OH}^- \text{ & } 1/2\text{CO}_3^{2-}$$

$$M = \text{OH}^- \text{ & } \text{CO}_3^{2-} \text{ & } \text{HCO}_3^-$$

$$M - P = 1/2\text{CO}_3^{2-} \text{ & } \text{HCO}_3^-$$

From the above, following conclusions may be drawn

1. When $P=0$, both OH^- & CO_3^{2-} are absent
2. When $P=M$, the sample consists of only OH^- ions.
3. When $P= (1/2)M$, the sample consists of only CO_3^{2-}
4. When $P>(1/2)M$, the sample consists of OH^- and CO_3^{2-}
5. When $P<(1/2)M$, the sample consists of HCO_3^- and CO_3^{2-}

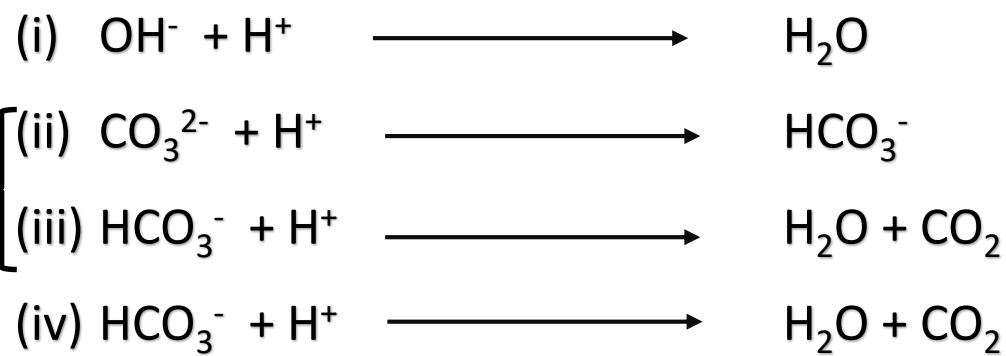
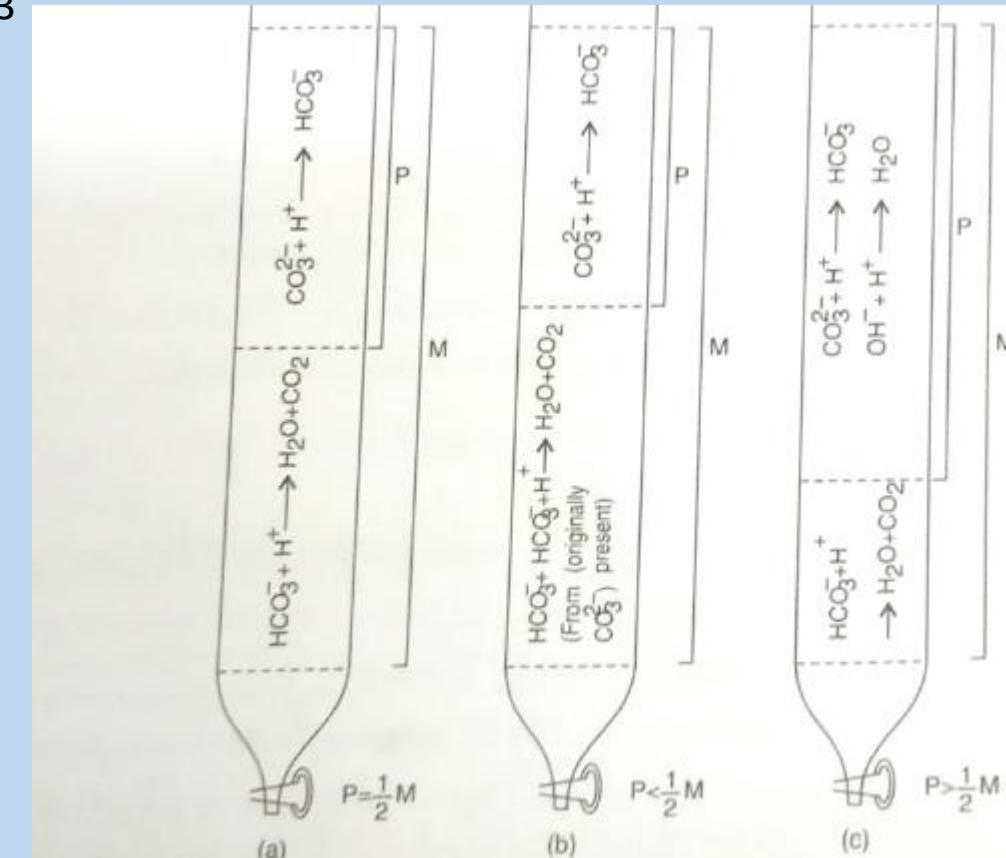


Table 4.6: Computing the alkalinity due to different ions

| Alkalinity | OH (ppm) | CO_3^{2-} (ppm) | HCO_3^- (ppm) |
|-------------------|-------------------|--------------------------|------------------------|
| $P=0$ | NIL | NIL | M |
| $P= \frac{1}{2}M$ | NIL | 2P | NIL |
| $P< \frac{1}{2}M$ | NIL | 2P | $(M-2P)$ |
| $P> \frac{1}{2}M$ | $(2P-M)^*$ | $2(M-P)$ | NIL |
| $P=M$ | $P=M$ | NIL | NIL |

$$*M - 2(M-P) = M-2M + 2P = 2P-M$$



Problems on Alkalinity

Example 1: 100ml of a water sample required 30ml of N/50 H_2SO_4 for neutralization to phenolphthalein end point. After this, methyl orange indicator was added to this and further acid required was again 30ml. Calculate the alkalinity of water as CaCO_3 in ppm.

Solution: (i) 100ml of water upto phenolphthalein end point

$$= 30\text{ml of N/50 H}_2\text{SO}_4$$

$$100\text{ml} \times N_p = 30\text{mL} \times N/50$$

$$\text{Normality, } N_p = \frac{30}{100} \times \frac{1}{2} = \frac{3}{500} N$$

Strength of alkalinity upto phenolphthalein point (in terms of CaCO_3 equiv.)

$$(P) = \frac{3}{500} \times 50 \text{ g/L} = 0.3\text{g/L} = 300\text{mg/L}$$

(ii) 100ml of water upto methyl orange end point = 30mL + 30mL of N/50 H_2SO_4

$$\text{Normality, } N_m = \frac{60}{100} \times \frac{1}{50} = \frac{6}{500} N$$

Strength in terms of CaCO_3 equivalents)

$$(M) = \frac{6}{500} \times 50 \text{ g/L} = 0.6\text{g/L}$$
$$= 600\text{mg/L}$$

From (i) and (ii) $P = \frac{1}{2} M$, so alkalinity is due to CO_3^{2-} ions only.

Hence total alkalinity = $2P = M = 600\text{mg/L}$

Example 2: A water sample is alkaline to both phenolphthalein as well as methyl orange. 100ml of water sample on titration with N/50 HCl required 6.8mL of the acid up to phenolphthalein end point. When a few drops of methyl orange are added to the same solution and the titration further continued, the yellow colour of the solution just turned red after the addition of another 12.6mL of the acid solution. Elucidate the type and extent of alkalinity present in water sample.

Solution: (i) 100ml of water upto phenolphthalein end point = 6.8mL of N/50 HCl

$$\text{Normality, } N_P = \frac{6.8}{100} \times \frac{1}{50} = .00136\text{N}$$

Strength in terms of CaCO_3 eq.

$$(P) = 0.00136 \times 50 \text{ g/L} = 0.068\text{g/L} = 68\text{mg/L} = 68\text{ppm}$$

(ii) 100ml of water upto methyl orange end point = 6.8mL + 13.6mL of N/50 HCl

$$\text{Normality, } N_M = \frac{19.4}{100} \times \frac{1}{50} = 0.0039 \text{ N}$$

Strength in terms of CaCO_3 eq.

$$(M) = 0.0039 \times 50 \text{ g/L} = 0.195\text{g/L} = 195\text{mg/L} = 195\text{ppm}$$

From (i) and (ii), $P < \frac{1}{2} M$, therefore the alkalinity is due to CO_3^{2-} and HCO_3^-

$$\text{Alkalinity due to } \text{CO}_3^{2-} = 2P = 2 \times 68\text{ppm} = 136\text{ppm}$$

$$\text{Alkalinity due to } \text{HCO}_3^- = (M - 2P) = 195 - 136\text{ppm} = 59\text{ppm}$$

Example 3: A sample of water was alkaline both to phenolphthalein and methyl orange. 100ml of water sample required 20mL of N/50 H₂SO₄ for phenolphthalein end point and another 15mL for complete neutralization. Calculate the of alkalinity in ppm.

Solution: (i) 100ml of water upto phenolphthalein end point = 20mL of N/50 H₂SO₄

$$\text{Normality, } N_P = \frac{20}{100} \times \frac{1}{50} = .004N$$

Strength in terms of CaCO₃ eq.

$$(P) = 0.004 \times 50 \text{ g/L}$$

(ii) 100ml of water upto methyl orange end point

$$\text{Normality, } N_M = 20\text{ml} + 15\text{ml of N/50 H}_2\text{SO}_4$$

$$\text{Normality, } N_M = \frac{35}{100} \times \frac{1}{50} = .007N$$

Strength in terms of CaCO₃ eq.

$$(M) = 0.007 \times 50 \text{ g/L} = 0.35\text{g/L} = 350\text{mg/L}$$

From (i) and (ii), P > $\frac{1}{2} M$, therefore the alkalinity is due to OH and CO₃²⁻ ions.

$$\text{Alkalinity due to CO}_3^{2-} \text{ ions} = 2(M-P) = 2(350-200)\text{mg/L}$$

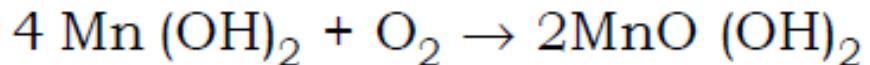
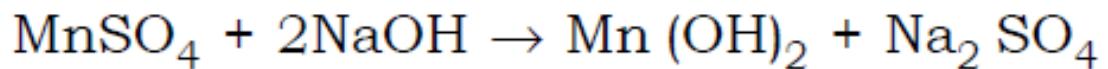
$$= 300\text{mg/L} = 300\text{ppm}$$

$$\text{Alkalinity due to OH ions} = (2P-M) = [2(200)-350]\text{mg/L}$$

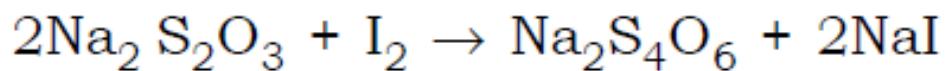
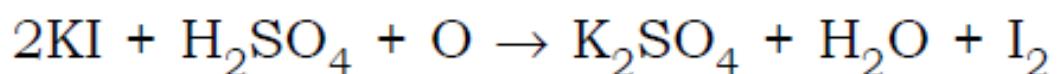
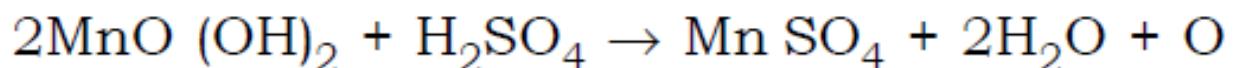
$$= 50\text{mg/L} = 50\text{ppm}$$

DISSOLVED OXYGEN

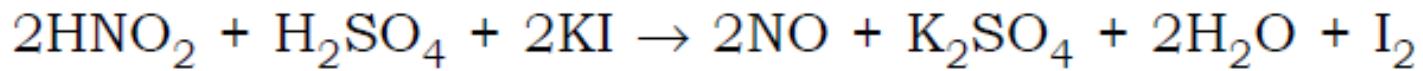
- Oxygen is poorly soluble in water. The amount of oxygen in water depends on physical, chemical and biological activities taking place in water. The solubility of dissolved oxygen (DO) in water at saturation at any temperature and pressure is given by Henry's law.
- Oxygen itself is not a pollutant in water but its deficiency is an indicator of several types of pollution in water.
- DO is determined by Winkler's method or iodometric titration. The DO in water oxidizes KI and an equivalent amount of iodine is liberated.
- This iodine is titrated against a standard hypo solution. However, since DO in water is in molecular state and is not capable of reacting with KI, therefore an oxygen carrier such as manganese hydroxide is used.
- The method involves introducing a conc. solution of MnSO_4 , NaOH and potassium iodide-sodium azide reagent, into the water sample. The white precipitate of $\text{Mn}(\text{OH})_2$ which is formed, is oxidized by oxygen in water sample to give a brown precipitate of basic manganic oxide $\text{MnO}(\text{OH})_2$.
- This $\text{MnO}(\text{OH})_2$ in acidic medium dissolves and liberates free iodine from the added KI in a equivalent amount of DO in water sample. This liberated I_2 is then titrated against $\text{Na}_2\text{S}_2\text{O}_3$ solution using starch as indicator.



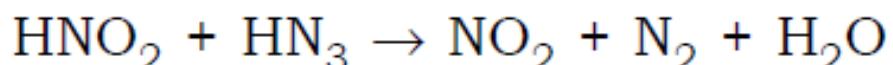
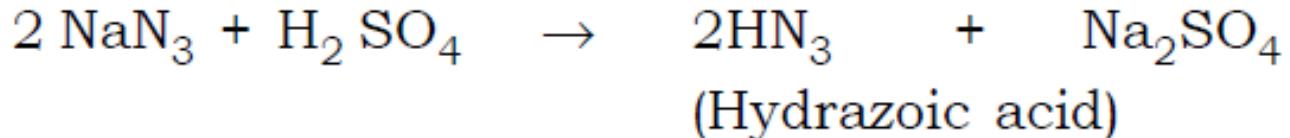
Basic Manganic oxide



The nitrites present in water, interfere with the titration as these can also liberate I_2 from KI



Thus to destroy nitrite, sodium azide is used.



PROCEDURE

- Take a known amount of sample water in a stoppered bottle avoiding contact with air.
- Add 2 mL of $MnSO_4$ solution by pipette (dip the end well below the surface of water). Also add 2 mL of alkaline iodide-azide solution to it.
- Stopper the bottle and shake thoroughly. Allow the brown precipitates of $MnO(OH)_2$ formed, to settle down.
- When some portion of the liquid below the stopper is clear, add 2 mL of conc. H_2SO_4 with the help of pipette. Stopper and mix till the precipitate is completely dissolved. The characteristic brown colour of iodine is produced.
- Transfer 100 ml of the above solution in a 250 ml flask with a pipette. Titrate the liberated I_2 with standardized sodium thiosulphate solution until the sample becomes pale yellow.
- Add 2 ml of starch solution, the solution will turn blue.
- Continue titration till blue colour disappears.



OBSERVATIONS

Volume of the water sample taken for titration = 100 ml

Observation Table:

| S. No. | Volume of the solution taken in the titration flask (ml) | Burette Readings | | Volume of the titrant used (Final-Initial reading) (ml) |
|--------|--|------------------|---------------|---|
| | | Initial Reading | Final Reading | |
| 1. | | | | |
| 2. | | | | |
| 3. | | | | |

CALCULATIONS

Hypo O₂ in water

$$N_1 V_1 = N_2 V_2$$

$$\frac{1}{100} \times V_1 = N_2 \times 100$$

$$N_2 = \frac{V_1}{10000}$$

Strength of dissolved oxygen = N₂ × Eq. wt

$$= \frac{V_1}{10000} \times 8 \text{ g/L}$$

$$= \frac{V_1}{10000} \times 8 \times 1000 \text{ mg/L}$$

$$= 0.8 V_1 \text{ ppm.}$$

PRECAUTIONS

1. The water should be taken in the stoppered bottle very carefully without trapping air bubbles which could raise oxygen level by aerating the sample.
2. MnSO_4 and alkaline iodine -azide solutions are added to the water sample just below the surface of water.
3. Whole of the precipitate of MnO(OH)_2 should be dissolved in H_2SO_4 .

BIOCHEMICAL OXYGEN DEMAND

- When biodegradable organic matter is released into water, the microorganisms feed on the wastes and break it down into simpler organic or inorganic substances. If the decomposition takes place in the presence of oxygen i.e aerobically, the non objectionable, stable end products are formed.



- On the other hand if insufficient oxygen is available, the decomposition takes place anaerobically.
- The micro organisms causing the decomposition of the organic matter without the presence of oxygen are entirely different from aerobic bacteria and produce highly objectionable end products including H_2S , NH_3 and CH_4 .



- The amount of oxygen required by micro-organisms to oxidize organic water aerobically is called **Biochemical oxygen demand(BOD)**. The BOD of raw water will indicate the extent of organic matter present, thus indicating the extent of treatment required to make it safe for use.
- The BOD of treated water should be nil, so as to make it free from any organic matter. If BOD is high, the dissolved oxygen becomes low and this results in greater pollution.

- ❑ Polluted waters will continue to absorb oxygen for many months, till the oxidation gets completed and hence it is not practical to determine this ultimate oxygen demand which would require an extended period of time.
- ❑ As a result, it has become standard practice simply to measure the oxygen over a shorter period of 5 days. This is known as 5 day BOD test. **BOD₅ is the total amount of oxygen consumed by microorganisms during the first five days of biodegradation.**
- ❑ In its simplest form BOD₅ would involve diluting a known volume of sample water with a known volume of pure water, whose oxygen content is already known.
- ❑ This is kept for 5 days at 20°C in a stoppered bottle, away from light. The dissolved oxygen is measured after period of incubation.
- ❑ The difference between the original oxygen content and residual oxygen will indicate the oxygen consumed by the water sample in five days in oxidizing the organic matter present in water sample. Thus BOD₅ is given by :

$$\text{BOD}_5 = \text{Loss of oxygen in mg/L} * \text{Dilution factor}$$

$$\text{BOD}_5 = D_1 - D_2 \times \frac{\text{Volume of sample after dilution}}{\text{Volume of sample before dilution}}$$

D_1 = D.O of the sample in mg/L at the start of the experiment

D_2 = D.O of the sample in mg/L after 5 days.

= Loss of oxygen in mg/L \times Dilution Factor.

The dilution of the waste water sample with pure water is necessary because waste water contains more of oxygen demanding material and hence the dissolved oxygen may not be sufficient to decompose it aerobically.

Preparation of dilution water:

1. Take 1000 ml of distilled water in a bottle. Add 1 ml each of phosphate buffer (pH = 7.2), CaCl_2 (27.5g/L), MgSO_4 (22.5g/L) and FeCl_3 (0.25g/L)
2. Water is aerated by passing compressed air through a diffusion tube until it is completely saturated.

Determination.

1. Take about 5ml of the sample and dilute it to 300 ml with dilution water prepared above. (or any appropriate dilution)
2. The diluted sample is taken in two bottles filled upto the neck.
3. The dissolved oxygen in one bottle is determined immediately and in the other bottle after five days of incubation

OBSERVATION

(i) Determination of DO in bottle No - 1

| S. No. | Volume of the solution taken in the titration flask (ml) | Burette Readings | | Volume of the titrant used (Final-Initial reading) (ml) |
|--------|--|------------------|---------------|---|
| | | Initial Reading | Final Reading | |
| 1. | | | | |
| 2. | | | | |
| 3. | | | | |

(ii) Determination of DO in bottle No-2 (after incubation for 5 days

| S. No. | Volume of the solution taken in the titration flask (ml) | Burette Readings | | Volume of the titrant used (Final-Initial reading) (ml) |
|--------|--|------------------|---------------|---|
| | | Initial Reading | Final Reading | |
| 1. | | | | |
| 2. | | | | |
| 3. | | | | |

Volume of sample taken for each titration = 100 ml

Normality of $\text{Na}_2\text{S}_2\text{O}_3$ used = N/100

CALCULATIONS

Volume of the sample before dilution = 5 ml.

Volume of the sample after dilution = 300 ml.

* (i) D.O in bottle no.- 1.

(Hypo) (O₂ in sample)

$$N_1 V_1 = N_2 V_2$$

$$\frac{1}{100} \times V_1 = N_2 \times 100$$

$$N_2 = \frac{V_1}{10000}$$

Strength of dissolved oxygen = N₂ × Eq. wt

$$(D_1) = \frac{V_1}{10,000} \times 0.8 \text{ g/L} = 0.8 V_1 \text{ ppm.}$$

** (ii) D.O in bottle- 2.

Similarly find D.O in bottle-No-2

Let it be D₂

$$(iii) \text{BOD} = D_1 - D_2 \times \frac{\text{Volume of sample after dilution}}{\text{Volume of sample before dilution}} \text{ mg/L}$$

RESULT BOD of the given water sample = ...ppm

CHEMICAL OXYGEN DEMAND

- Although BOD test is applicable to organic wastes, there are many drawbacks. Certain organic materials are not biodegradable and hence can give wrong conclusions that less organic matter is present because BOD of such water samples will be low.
- In this case **COD, chemical oxygen demand** reveals the real organic content present. Here the oxidation of organic substances present in water is done chemically.
- **COD, is the amount of oxygen required by organic matter in a sample of water for its oxidation by a strong chemical oxidizing agent such as $K_2Cr_2O_7$.**

DETERMINATION:

- A known amount of $K_2Cr_2O_7$ is added to a measured amount of the sample and the mixture is boiled with concentrated H_2SO_4 . After boiling , the amount of unreacted $K_2Cr_2O_7$ is determined by titrating against a standard Mohr' salt solution using ferroin as indicator.
- The difference between the dichromate originally present and the dichromate remaining unreacted gives the amount of dichromate used for oxidation of organic matter.

- A known amount of $K_2Cr_2O_7$ is added to the measured amount of the sample and mixture is boiled with conc. H_2SO_4 . The organic matter gets completely oxidized to produce CO_2 and H_2O
- **$K_2Cr_2O_7$ acts as oxidizing agent in the presence of acid.**

- $K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$
- The excess of $K_2Cr_2O_7$ remained after the reaction is titrated against standard Mohr's salt solution using Diphenylamine as indicator. **The dichromate consumed is calculated which gives the oxygen required for the oxidation of organic matter.**
- **INDICATOR** - Diphenylamine
- **END POINT** - violet to green

PROCEDURE

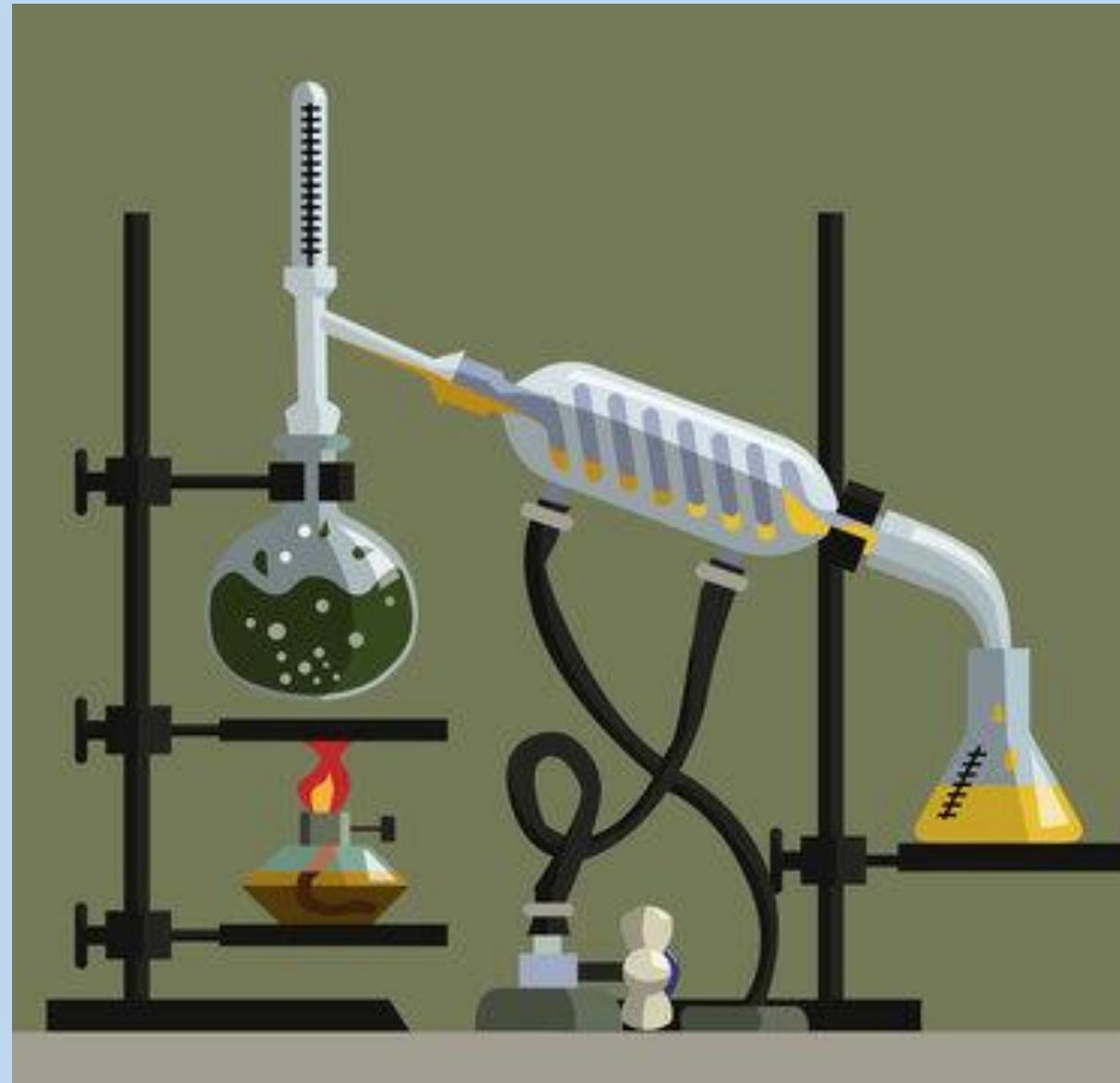
- 1.** Take 50 ml of the sample in a round bottomed flask and add **1 g of HgSO₄** and some broken porcelain pieces.
- 2.** Immerse the flask in cold water and slowly add **7.5 ml silver sulphate** with continuous shaking. (As this is an exothermic process that is why the flask is immersed in cold water)
- 3.** Now add **25ml of K₂Cr₂O₇ (0.25N)** to this solution and mix the contents of the flask.
- 4.** Attach the reflux condenser and reflux for 2 hours.
- 5.** Wash the condenser with distilled water into the flask. Cool and dilute to about 200ml by distilled water.
- 6.** Take 10 ml of sample, add 2-3 drops of **Diphenylamine** as indicator and titrate against 0.25N Mohr's salt solution till the end point i.e. **violet to green.**

7. Record the volume of Mohr's salt solution used. Let it be X ml.
8. Perform a blank titration using distilled water in place of sample solution. For this, take 50ml of distilled water in a round bottomed flask, add the same amounts of reagents and reflux for two hours. Titrate it the same way as is done with the sample water.
9. Record the volume of Mohr's salt solution used. Let it be Y ml.

HgSO₄ is used to remove the chloride ions which may interfere because of their oxidation under the experimental conditions.

AgSO₄ is used as a catalyst to achieve oxidation of straight-chain aliphatic hydrocarbons and low molecular weight fatty acids

Reflux Condenser



Observation Table

(a) For sample solution

| S. No. | Volume of the solution taken in the titration flask (ml) | Burette Readings | | Volume of the titrant used (Final-Initial reading) (ml) |
|--------|--|------------------|---------------|---|
| | | Initial Reading | Final Reading | |
| 1. | | | | |
| 2. | | | | |
| 3. | | | | |

For distilled water (blank titration)

| S. No. | Volume of the solution taken in the titration flask (ml) | Burette Readings | | Volume of the titrant used (Final-Initial reading) (ml) |
|--------|--|------------------|---------------|---|
| | | Initial Reading | Final Reading | |
| 1. | | | | |
| 2. | | | | |
| 3. | | | | |

Volume of Mohr's salt solution used in case of sample solution = X ml (say)

Volume of Mohr's salt solution used in case of distilled water = Y ml (say)

$$\left[\begin{array}{l} \text{Volume of } K_2Cr_2O_7 \text{ used} \\ \text{to oxidize the organic} \\ \text{matter present in water sample} \end{array} \right] = \left[\begin{array}{l} \text{Volume of Mohr's salt} \\ \text{solution equivalent to} \\ K_2Cr_2O_7 \text{ used} \end{array} \right] = [Y - X] \text{ ml}$$

$$\frac{N_1 V_1}{(\text{sample})} = \frac{N_2 V_2}{(\text{Mohr's salt solution})}$$

$$N_1 \times 50 = \frac{1}{4} (Y - X)$$

$$N_1 = \frac{1}{4 \times 50} (Y - X)$$

Therefore COD = $N_1 \times \text{Eq.wt of oxygen} = N_1 \times 8 \text{ g/L} \times \text{DF/volume of sample}^*$

RESULT: COD of given water sample (mg/l) = $(N_1 \times 8 \times 1000 \times \text{DF}) / \text{volume of sample (in ml)}$

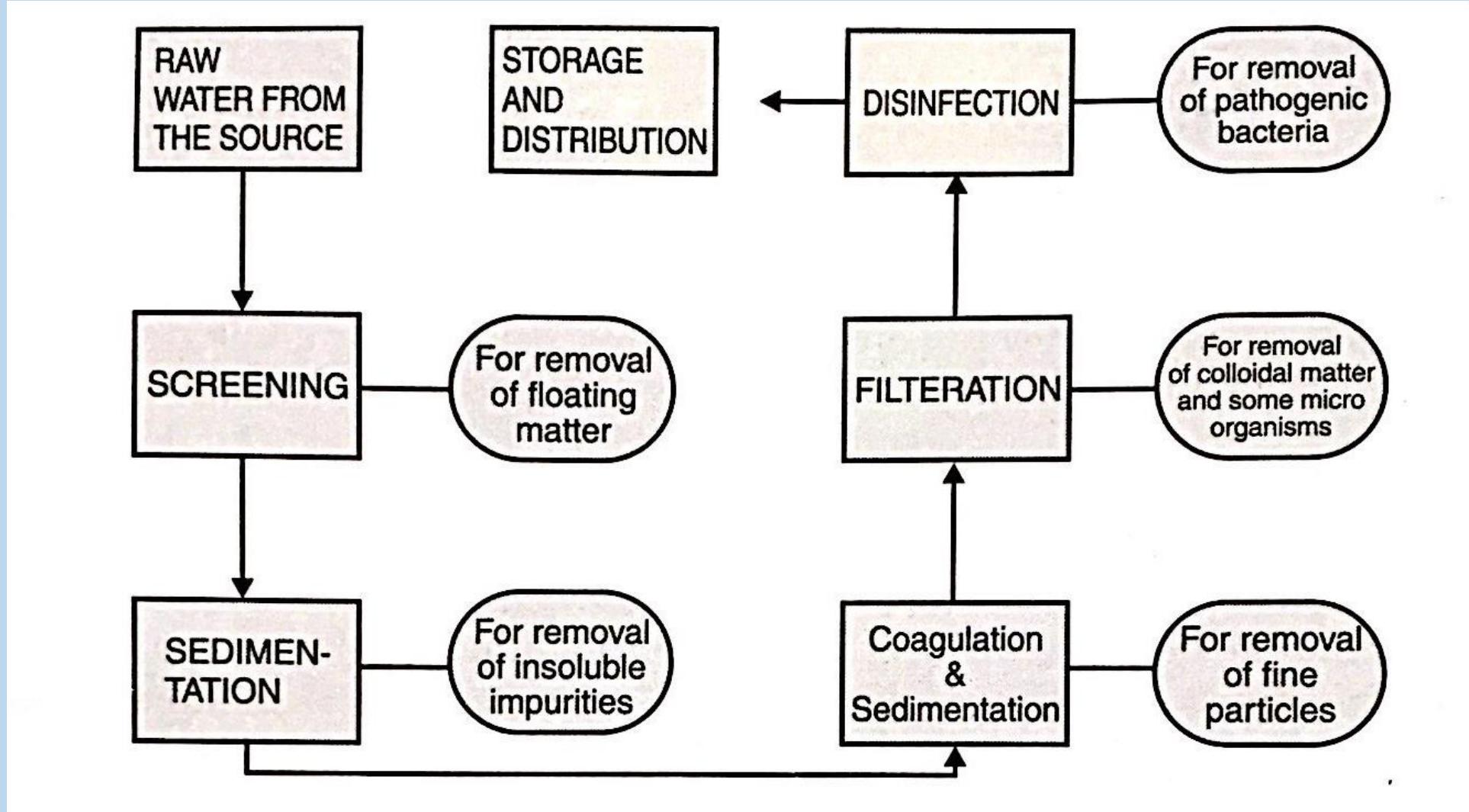
* DF-Dilution factor to be considered, if applicable

PRECAUTIONS

1. The addition of $\text{Ag}_2\text{SO}_4 - \text{H}_2\text{SO}_4$ to the sample should be done slowly with shaking and cooling during mixing.
2. It should always be added through the open end of the condenser.
3. Smaller volume of the sample should be taken.

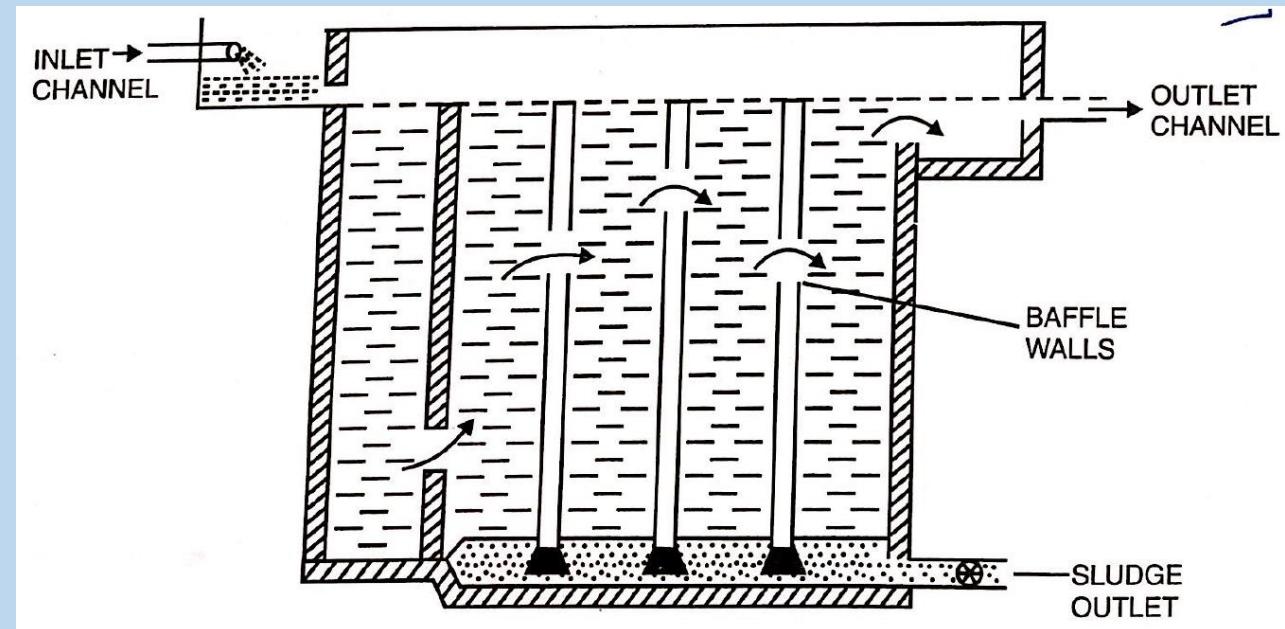
WATER TREATMENT FOR DOMESTIC PURPOSE

Schematic representation of Water Treatment Plant



Screening: Screening is the process by which the floating material like wood pieces, leaves etc are removed. Raw water is made to pass through large screens having number of holes which hold back the **floating matter** and allow the water to pass.

Sedimentation: Water is made to stand undisturbed in big tanks for sufficient period of time (2 to 8 hours), so that the suspended particles settle down at the bottom. In sedimentation tank, flow of water is reduced and water is not brought to complete rest. It consists of a rectangular tank. It is provided with baffle walls to reduce the velocity of the incoming water. Settled sludge is taken out from bottom.



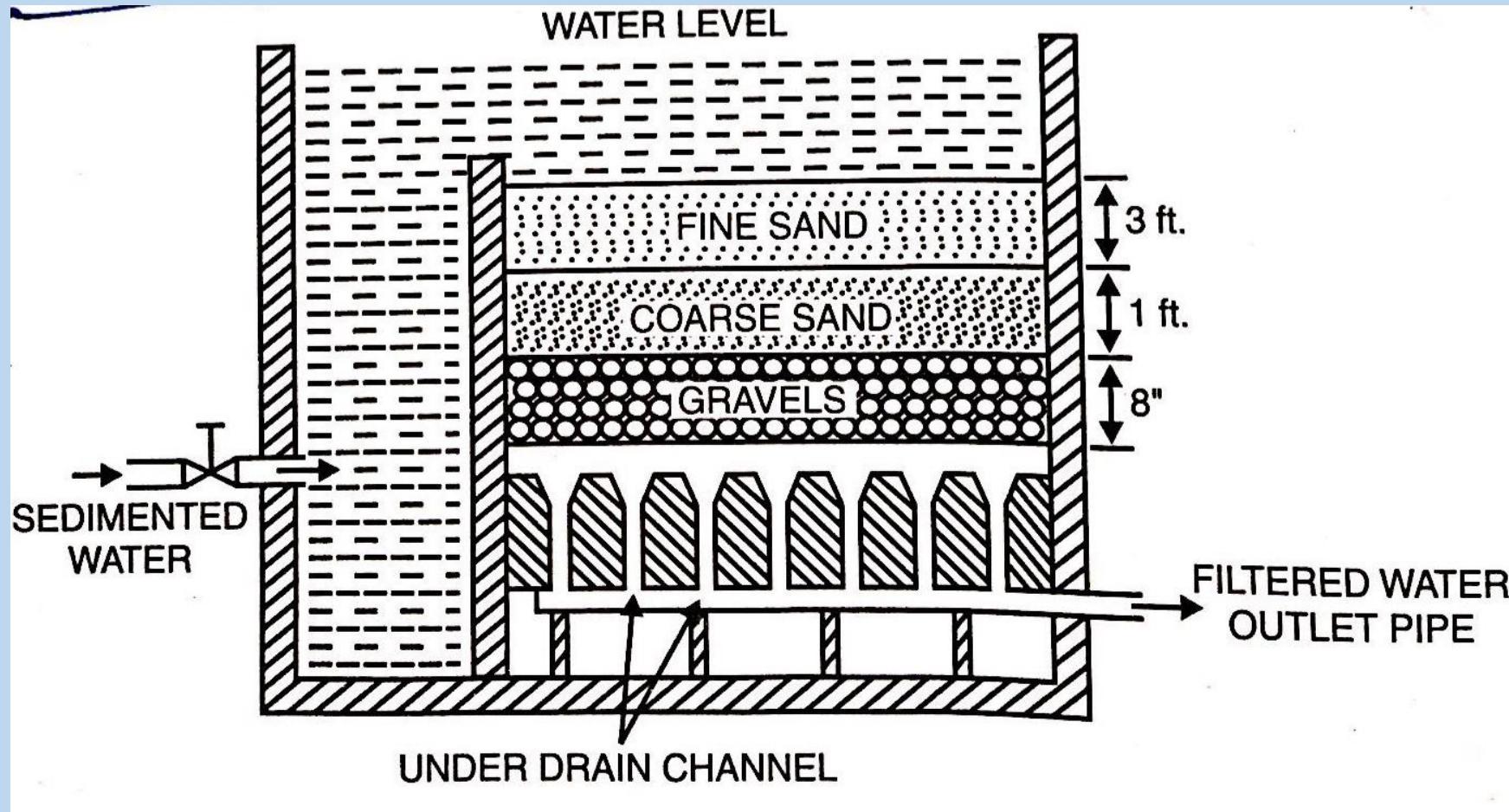
Horizontal flow Sedimentation

Sedimentation Aided with Coagulation: Finely divided silica, clay and organic matter does not settle down easily. These are in the form of colloids and are generally negatively charged. Because of their same charge, these particles do not coalesce together to form larger particles and hence do not settle down easily. They can be removed easily by adding coagulants. Coagulants when added to water, form insoluble gelatinous precipitates which entrap very fine suspended particles, forming bigger sized agglomerates which settle down easily. Cationic coagulants are generally added to bring about coagulation in water. These cationic coagulants neutralize the negative charge on the colloids which thereby come together and coalesce to form bigger particles and hence settle down. The most commonly used coagulants in water treatment plants are Alum, sodium aluminate and ferrous sulphate.

Filtration: Rapid Sand filters are most widely used and are of two types-

- (a) Rapid Gravity filters
- (b) Rapid pressure filters,

Rapid Gravity filters: Consist of a large rectangular concrete tank. The filtering medium is a layer of coarser sand which is supported by a bed of graded gravel. A layer of fine sand is carefully sieved at the top of coarser sand. Sedimented water entering the sand filter is uniformly distributed over the entire fine sand bed. After passing through the filter beds, the filtered water is taken out from the drain system provided at the bottom. When the filter bed is clogged by the particles removed from the water, it has to be cleaned. When the rate of filtration becomes slow, the working of the filter is stopped. The filter bed is cleaned by backwashing i.e by reversing the flow of water through the filter. The top most layer of sand is scrapped off and replaced with clean sand. The rapid gravity filters get clogged very frequently and have to be washed every 24 to 48 hours.



Rapid Gravity filters

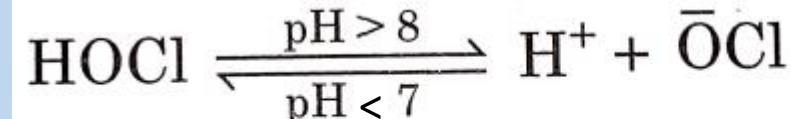
Rapid Pressure Filters: Water is passed through pressure filters at a pressure greater than the atmospheric pressure in airtight containers. The raw water is pumped into these vessels by means of pumps.

Disinfection of water by chlorination

- It means the chlorination of water to such an extent that living organisms as well as other organic impurities in water are destroyed.
- Chlorine is cheap, reliable and easy to handle. Moreover it is capable of providing residual disinfecting effects for long periods and thus prevent future recontamination of water.
- It involves addition of sufficient amount of chlorine to oxidise organic matter, reducing substances, and free ammonia in raw water, leaving behind mainly free chlorine, which possesses disinfecting properties against pathogenic bacteria.
- It is also known as free residual chlorine.
- When chlorine is added to water, it forms hypochlorous acid or hypochlorite ions which have immediate disastrous effect on most forms of microscopic organisms.

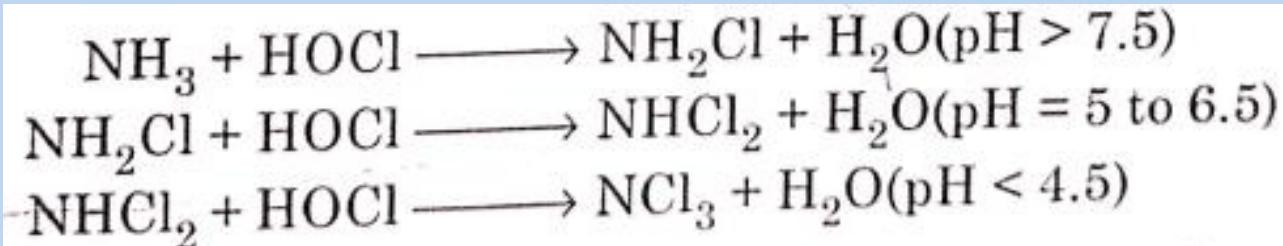


- The hypochlorous acid is unstable and dissociates as



Hypochlorite ions

- All the three forms HOCl, $\cdot\text{OCl}$, Cl_2 existing in a sample of water are termed as **free chlorine**. HOCl is found to be most destructive according to enzymatic hypothesis given by Gleen and Stumpt. For this reason the pH value of water during chlorination is generally maintained slightly less than 7 so as to prevent the dissociation of HOCl. The HOCl also reacts with ammonia likely to be present in water to form various chloramines as



- In the usual chlorination process, the pH is kept slightly less than 7 around 6.5 and hence dichloramine is the predominant species.
- These chloramines so formed are stable and are found to possess disinfecting properties. They act as chlorine reserves. The chlorine in this form is called **combined chlorine**. As compared to the free chlorine, combined chlorine is less effective.

Break point chlorination

- The amount of chlorine required for disinfecting water depends upon the inorganic and organic impurities present in water.
- When chlorine is added to water and its amount is estimated after a few minutes, it is found that the available chlorine is not equal to the amount of chlorine added.
- A relationship between the amount of chlorine added to water and the free residual chlorine is shown in figure. The curve shown in figure can be divided into four stages.

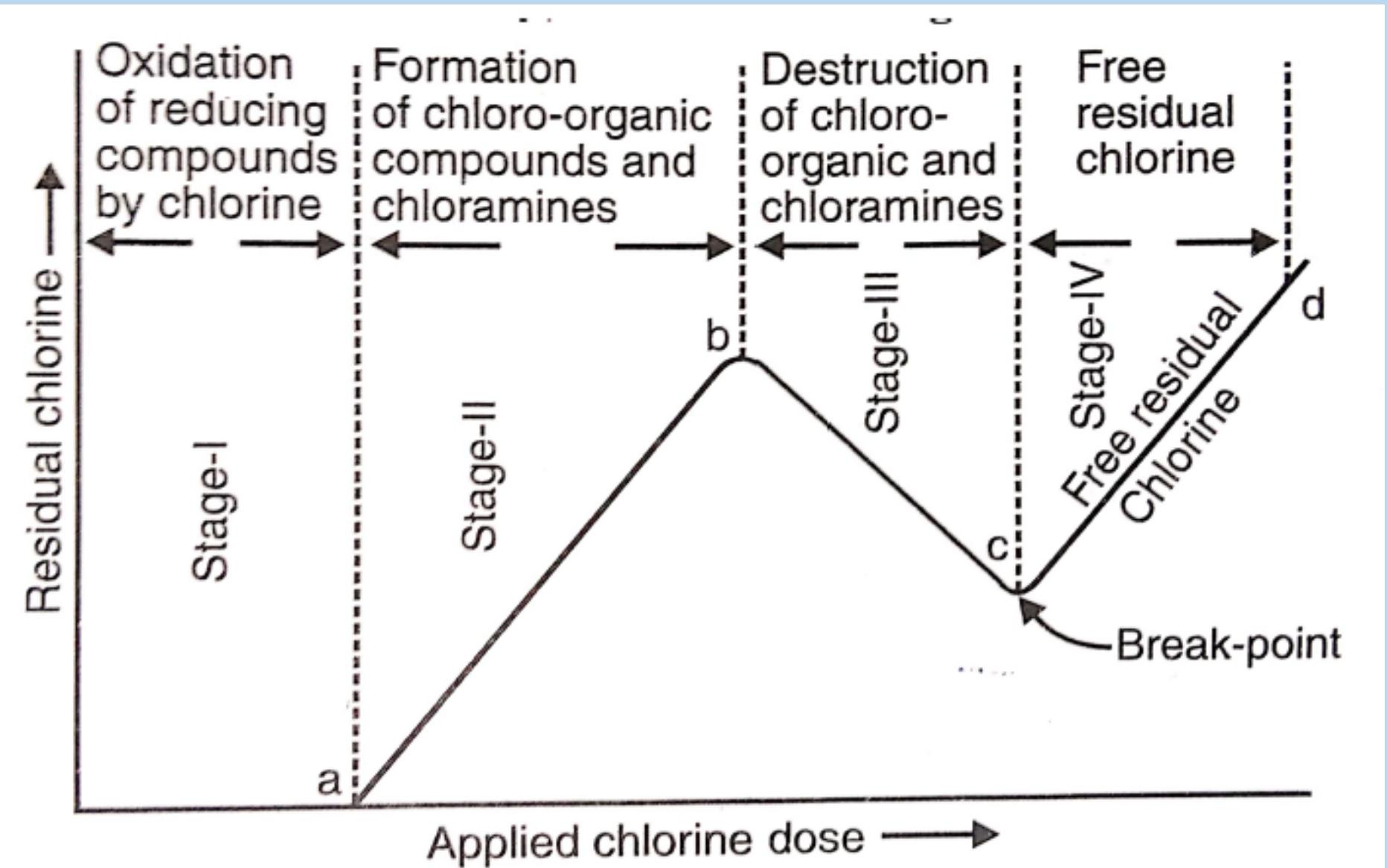


Fig. 4.20 Break-point chlorination curve

Stage I: Initially for lower doses of chlorine, there is no free residual chlorine since all the added chlorine gets consumed for complete oxidation of reducing substances present in water. This is due to the fact that initially Cl_2 reacts with the inorganic impurities present in water forming chlorides. These chlorides do not have any residual oxidizing power.

Stage II: As the amount of chlorine dosage is increased, amount of residual chlorine also show steady increase. This stage corresponds to the formation of chloramines. But chloramines respond to the test for estimation of chlorine in the same way as free chlorine and hence curve represents the chlorine available from combined residuals. Chloramines remain in water body for longer periods which help to kill the micro organisms even in a distribution system. Simultaneously this stage also corresponds to the formation of chloro-organic compounds without oxidizing them. These are responsible for bad odour and unpleasant taste in water.

Stage III: At still higher dose of applied chlorine, the complete oxidation of chloro-organic compounds and partial oxidation of chloramines takes place and accordingly free residual chlorine also decreases and reaches a dip when the oxidative destruction is complete. This dip is known as break point. The chlorination upto breakpoint ensures complete destruction of organic compounds which give unpleasant taste and bad odour.

Stage IV: After break point, the added chlorine is not used in any reaction and the residual chlorine agrees fairly well with the quantity of chlorine added. Thus free chlorine is available only if the demand for chlorine by other reacting substances present in water is met with.

Hence, for effectively killing the micro organisms as well as bad tastes and odours, sufficient chlorine has to be added. Addition of chlorine in such doses is known as break point chlorination.

- Chlorination after break point increases the free residual chlorine (Cl_2 , HOCl , -OCl).
- The free chlorine as well as the combined chlorine will cause germicidal action on micro organisms.
- Free chlorine will instantaneously kill the pathogens, while the combined chlorine will provide long term germicidal effect.
- Hence to use chlorine as an effective disinfectant, the chlorine dosage has to be slightly more than the break point.
- In general, water is satisfactorily disinfected if the free chlorine residual is about 0.2 ppm i.e. the chlorine added in the dosage upto break point + 0.2 ppm.
- Amount greater than 0.2 ppm of free residual chlorine causes bad taste in water and its harmful as it irritates the membrane of intestine.

WASTE WATER TREATMENT

The purpose of waste water treatment is to remove the contaminants from water so that the treated water can meet the acceptable quality standards. The quality standards usually depend upon whether water will be reused or discharged in to a receiving stream..

Available waste water treatment processes can be broadly classified as

- Physical processes
- Chemical processes
- Biological processes

These processes consists of a series of unit operations. These are applied in different combinations composition and specifications of the waste water.

Waste water treatment process

Primary treatment -- Removes suspended solids and floating matter using screens, a grit chamber and sedimentation tank, from which the sludge goes to a **digester**.

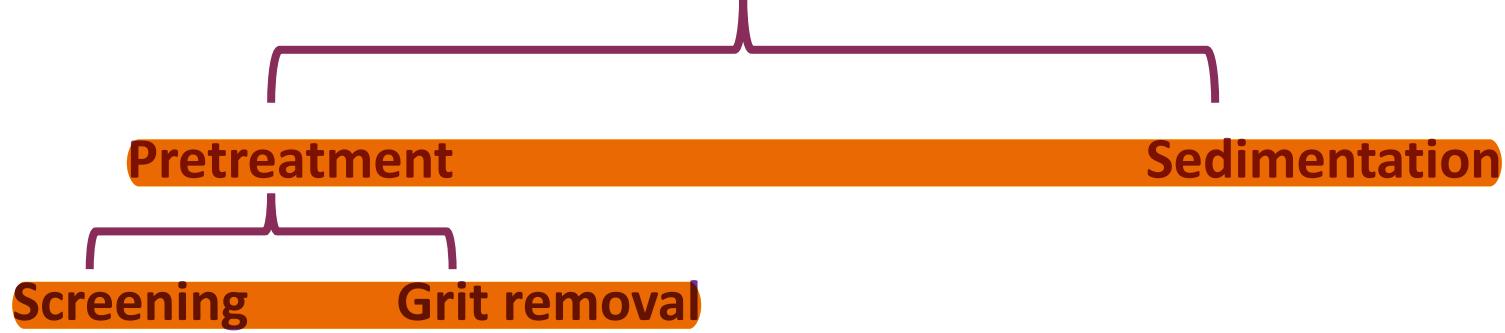
Secondary treatment -- Wastewater moves into the **aeration tank** where air is pumped in and **aerobic bacteria** break down organic material. The water goes to a final **sedimentation tank** which allows more sludge to settle out.

➤ **Digester** uses **anaerobic bacteria** to digest organic compounds left in the sedimentation tanks and produces **methane** in the process. The methane can be used to run equipment or to cool/heat the processing plant.

Tertiary treatment: *Physical, chemical or biological* processes depending upon the impurities to be removed.

Disinfecting the water, usually with chlorine, is the final step in the tertiary process.

I. Primary Treatment



One way to deal with coarse material in waste water is to use a device called **comminuter**, which grinds the coarse material in to small pieces which flow along with water and handled in Sedimentation tank.

Screening

Grit removal

Removes large floating objects

Such as rags, sticks, wood and other large floating and suspended solids

A typical screen consists of a parallel steel bars

Bars spaced anywhere from 2 to 7 cm apart.

Followed by a wire mesh screen

After screening, the waste water passes into a grit chamber

Velocity of water is reduced or it is detained for a few minutes

Grit settling chambers are periodically disconnected from the main system to remove grit manually

For possible use in landfilling, road making and on sludge drying beds.

Grit also is a food manure for growing crops

Sedimentation

- From the grit chamber, the sewage passes to a primary settling tank known as sedimentation basin.
- Here the velocity of the water is reduced considerably to allow most of the suspended solids to **settle out by gravity**.
- The most common equipment used include **horizontal flow sedimentation tanks**.
- The water is detained in the horizontal flow tanks for **2-3 hours** resulting in **removal of 50% of the suspended solid matter**.
- An efficient sedimentation tank or clarifier **removes** about **80-90% of the suspended solids and 40% of organic matter**. The solids that settle are called **primary sludge or raw sludge**.

Sedimentation aids

For the removal of finely divided solids **mechanical flocculation** or **chemical coagulation** is employed.

Mechanical Flocculation

Waste water is passed through a sedimentation tank which is **fitted with rotating paddles** moving slowly at a speed of 0.4-0.5 m/s.

This slow mechanical stirring allows the **finely divided solid particles to coalesce into larger particles** and settle out.

Chemical Coagulation

The coagulants react with colloidal matter in the sewage to form Floc. The floc entraps the smaller particles and eventually **settles down as sludge**.

Common coagulants used in sewage treatment are: **alum, copperas, hydrated lime, ferric chloride, and chlorinated copperas**.

In industrial waste water, sometimes the primary treatment also includes equalization and neutralization:

| Equalization | Neutralization |
|---|---|
| <p>Sometimes different types of wastes are produced by some industries. To apply uniform treatment, different effluents are held in big tanks for certain periods and are mixed thoroughly to produce homogeneous equalized effluent.</p> | <p>Acidic wastes are neutralized with lime stone and alkaline wastes are neutralized by treatment with sulphuric acid or CO_2 or waste boiler flue gas.</p> |

If both acid and alkaline wastes are produced in the nearby plants then mutual neutralization by mixing them is the cheapest method of neutralization.

II. Secondary Treatment

In waste water much of the **organic material is dissolved or in colloidal form** which is not removed by primary treatment. Thus removed by secondary treatment.

secondary treatment is achieved through biological processes:

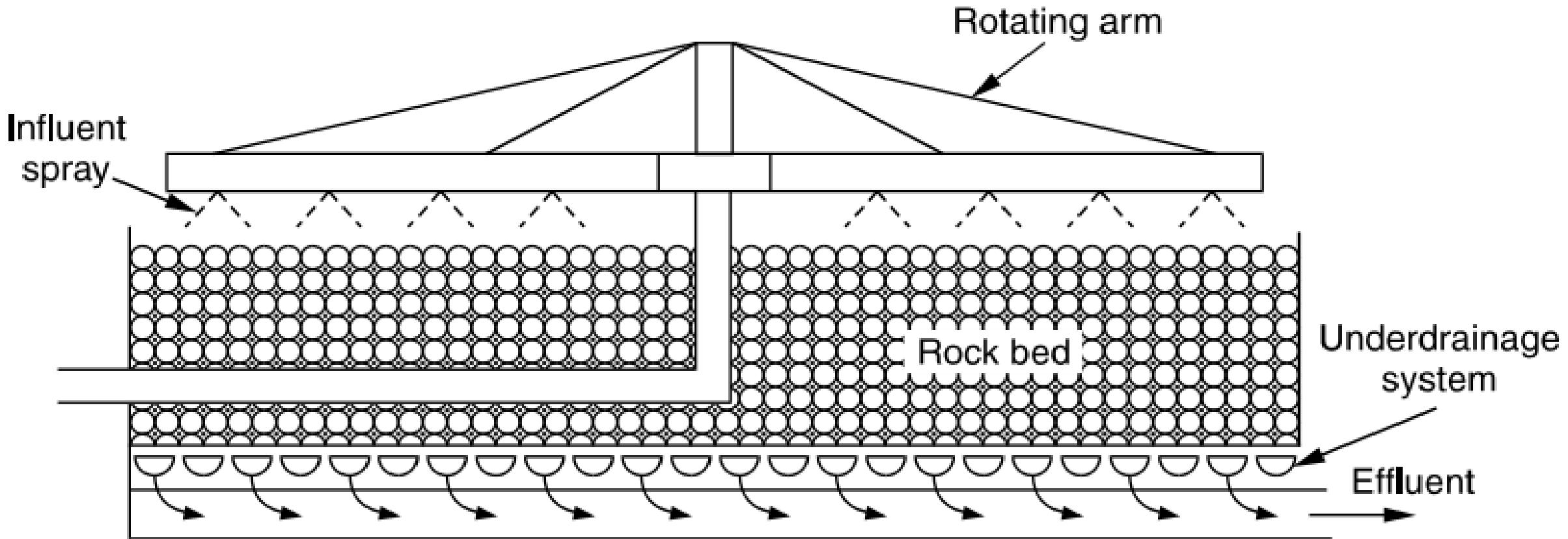
- Coagulation of the finely divided or colloidal matter.
- Oxidation of organic matter to CO_2
- Conversion of nitrogenous organic matter to ammonia, which is eventually converted into nitrite and nitrate.
- Anaerobic digestion of the sludge so obtained.

Three commonly used approaches are:

- (i) Trickling filters
- (ii) Activated Sludge Process
- (iii) Oxidation Ponds (Lagoons)

(i) Trickling Filters (Aerobic filtration)

A trickling filter consists of a rotating distribution arm that sprays the liquid over a circular bed of rocks or other coarse material. Individual rocks get coated with layer of biological slime (aerobic microorganisms, zoogaea-bacteria, algae, protozoa etc.) that absorbs and consumes wastes through the bed. **Biological towers** made with plastic media are prevalent.



Advantages

1. Simple to operate and can produce BOD removal to the extent of 65 to 85%.
2. Constant monitoring is not required.
3. Effluents so produced are of better quality.

Limitations

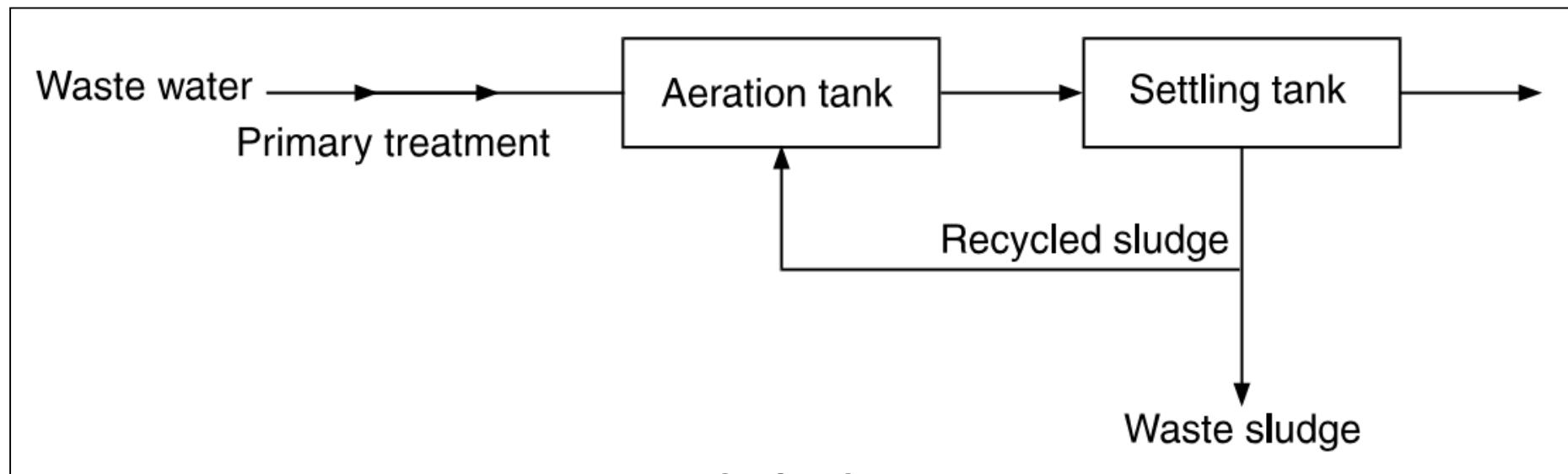
1. Microbial film formed is sensitive to temperature changes.
2. Efficiency of the filter is dependent upon the composition of waste, pH, size uniformity of the filtering medium & supply of air.
3. Cost of construction is high.
4. Trickling filters are used for treating industrial waste water from dairy, brewery, food processing, pulp and paper mills, pharmaceuticals, petrochemicals etc.

(ii) Activated Sludge Process

Most versatile biological oxidation method, employed for the treatment of waste water containing organic matter. Mixture of waste water and activated sludge is agitated and aerated.

The activated sludge is the sludge obtained by settling the sewage in presence of excess of oxygen.

The activated sludge is biologically active because it is heavily laden with microorganisms which are in active state of growth.



Activated sludge process

Advantages

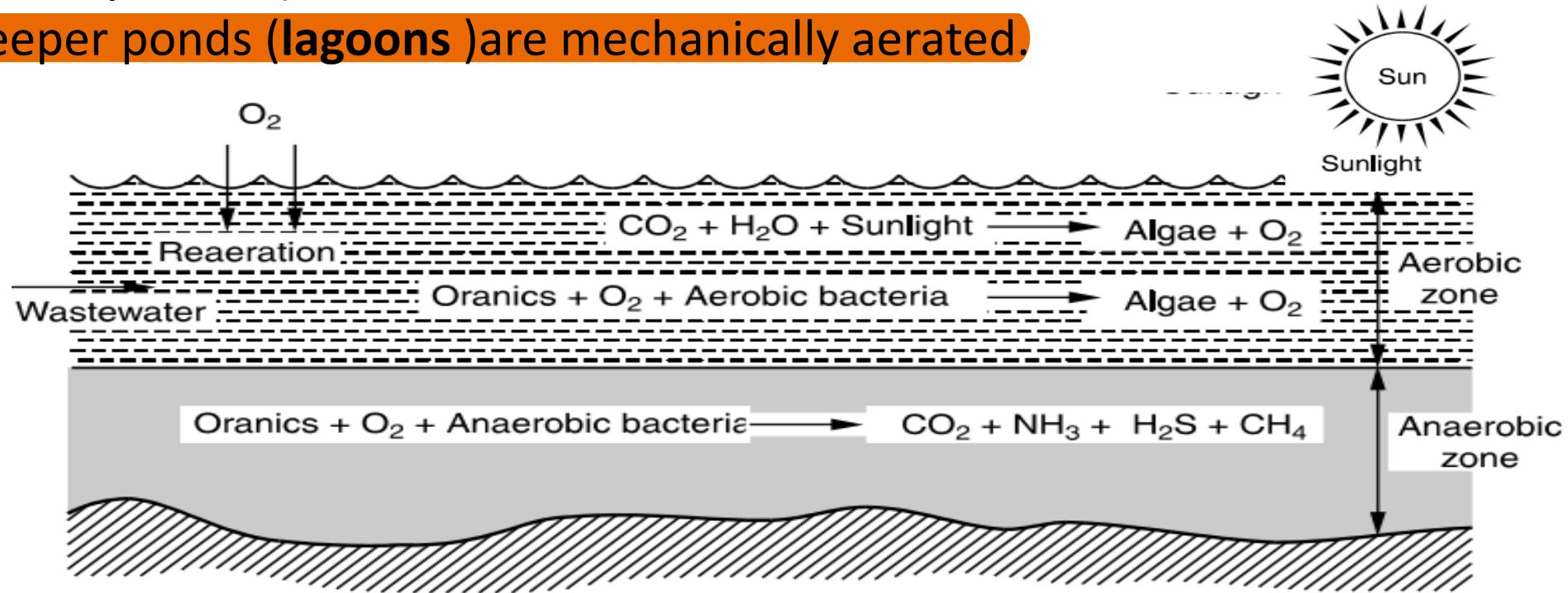
1. The primary advantage is good effluent quality. The effluent after going through activated sludge has little BOD (< 20mg/L)
2. It takes less area as compared to trickling water filters.
3. The activated sludge process equipment is less expensive.

Limitations

1. For the process to be efficient, at least 0.5ppm oxygen must be present.
2. The optimum pH 6.5 to 9.0 has to be maintained throughout.
3. The presence of detergents (which are not biodegradable) lead to the formation of foam, making the process difficult.
4. The disadvantage of this process is production of a huge amount of sludge, which should be digested and disposed off.

(iii) Oxidation Ponds

- Shallow ponds, typically **1-2 m deep**
- Organic matter is oxidized by microorganisms present in the pond
- **Waste water enter the pond at one end and treated waste water is collected at the other end**
- Decomposition of the organic matter near the surface is aerobic (algal photosynthesis), anaerobic near the bottom, hence, called **facultative ponds**
- deeper ponds (**lagoons**) are mechanically aerated.



Advantages

1. The process is simple and cheap.
2. Can be used for all types of waste waters
3. Due to the high pH of waste water in the pond, the heavy metal ions present in waste water are precipitated as hydroxides which settle as sludge.

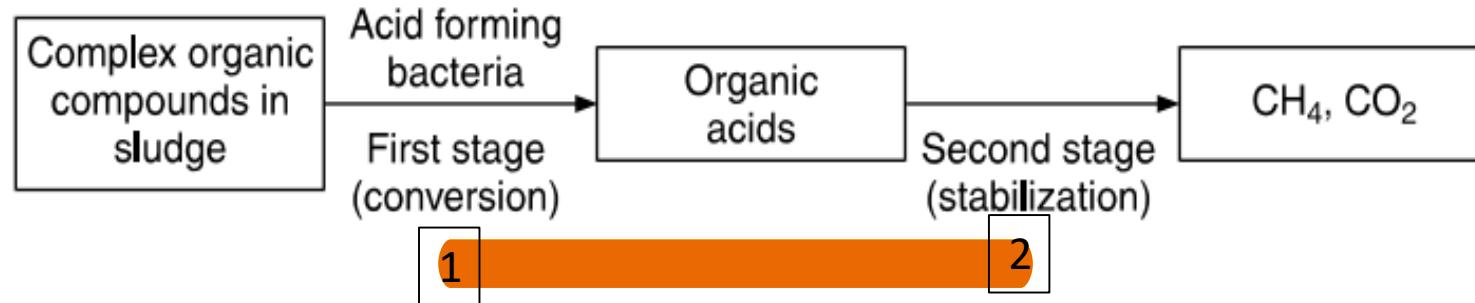
Limitations

1. The oxidation ponds require larger space.
2. Anaerobic conditions may lead to release of bad odours.
3. The main drawback of the above secondary treatment processes is the formation of sludge.
4. The collection, processing and disposal of sludge can be the most costly and complex aspect of waste water treatment.

Sludge Treatment and Disposal

- Sludge is the **watery residue from the primary sedimentation tank** and humus tank from secondary treatment. **Quantity of sludge produced** may be as high as 2% of the original volume of waste water, depending upon the treatment process used.
- The traditional method of sludge digestion is **anaerobic digestion**.
- It involves the microorganisms that thrive in absence of oxygen. The organic material in sludge is digested by these microorganisms under Anaerobic conditions to give **carbon dioxide and methane gas**. The components of the sewage which can be converted into gases are called **volatile solids**.

Sludge digestion in digester:



Sludge is maintained at 35°C for 30 days at pH 7.0 to 8.0.

CH_4 , CO_2 and NH_3 are liberated as the end products. Digested sludge is removed from the anaerobic digester. This sludge contains 90 to 93% water and is **dewatered**.

- **Dewatering is accomplished by** mechanical methods, the most common being **centrifugation and filtration**, which includes *pressure filtration* and *vacuum filtration*. **Drying beds** are also commonly used.
 - The dewatered sludge is sent for ultimate disposal. Wet sludge is sprayed on to crop land where it functions as fertilizer.
 - Dried sludge may be used as a landfill or a soil conditioner.

III. Tertiary Treatment

- The emphasis on recovery of valuables from industrial wastewaters have created the need for tertiary treatment.
- Tertiary treatment improves the quality of the effluent further.
- The effluent after secondary treatment plant **still contains suspended solids (20-40mg/L)** which may settle on the stream or river bed and inhibit certain forms of aquatic life.
- Some amount of **BOD**, significant amount of **nutrients, dissolved solids, traces of organic chemicals** and other contaminants are also present.

Type of tertiary treatment depends upon the specific goal which include removal of:

1. suspended solids
2. bacteria
3. dissolved organic solids
4. toxic substances
5. nutrients (phosphorus and nitrogen)

(i) Removal of suspended solids (Micro-straining):

- This can be achieved by **micro-straining**.
- The filter media consists of **finely woven** stainless steel fabric.
- The treated waste is allowed to pass through it.
- The solids retained on the fabric are washed into a trough, which recycles the solids to the sedimentation tank.

(ii) Removal of dissolved solids

a) **Adsorption:** Dissolved solids can be organics or inorganics which are removed by **adsorption on activated carbon**. Special adsorbents are commercially available for the removal of toxic heavy metals from industrial waste water.

b) Solvent Extraction: Used to recover phenolic materials from waste waters of refineries and coke plants. waste water is intimately brought in contact with a solvent having high affinity for the solute.

c) Ion Exchange: Used to remove hardness and iron and manganese salts from drinking water. This technique has been extended to waste water treatment for the removal and recovery of waste during water treatment.

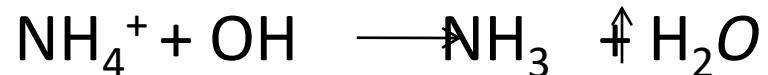
d) Reverse Osmosis: When waste water containing dissolved solids is allowed to pass through a semi-permeable membrane at a pressure, which is more than osmotic pressure, the water from the waste passes through the membrane. Hence a highly concentrated solution containing dissolved salts is left behind.

e) Chemical precipitation: The precipitating agents like lime etc. remove heavy metal ions by precipitating these as hydroxides. Precipitating agents include FeSO_4 , alum and ferric chloride.

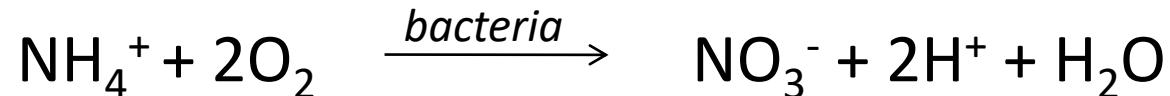
(iii) Removal of Nutrients

(a) Nitrogen Removal: All forms of nitrogen in wastewater are harmful because plants can utilize the inorganic forms as nutrients, NH_3 can be utilized by bacteria resulting in reduced oxygen in water.

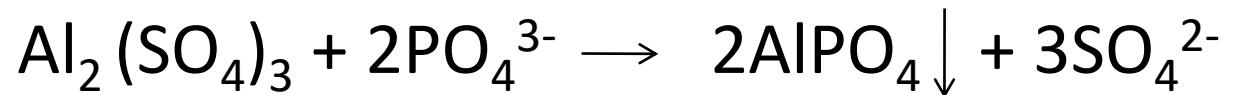
- **Ammonia stripping:** Ammonia is present in natural water as ammonium ion. This NH_4^+ is changed to ammonia gas by raising the pH (the OH^- concentration) of the waste water by adding quick lime. The ammonia gas is liberated.



- Another approach of nitrogen removal is **nitrification** i.e. to convert NH_4^+ to NO_3^- , followed by anaerobic stage in which microorganisms convert nitrates to nitrogen gas (N_2).

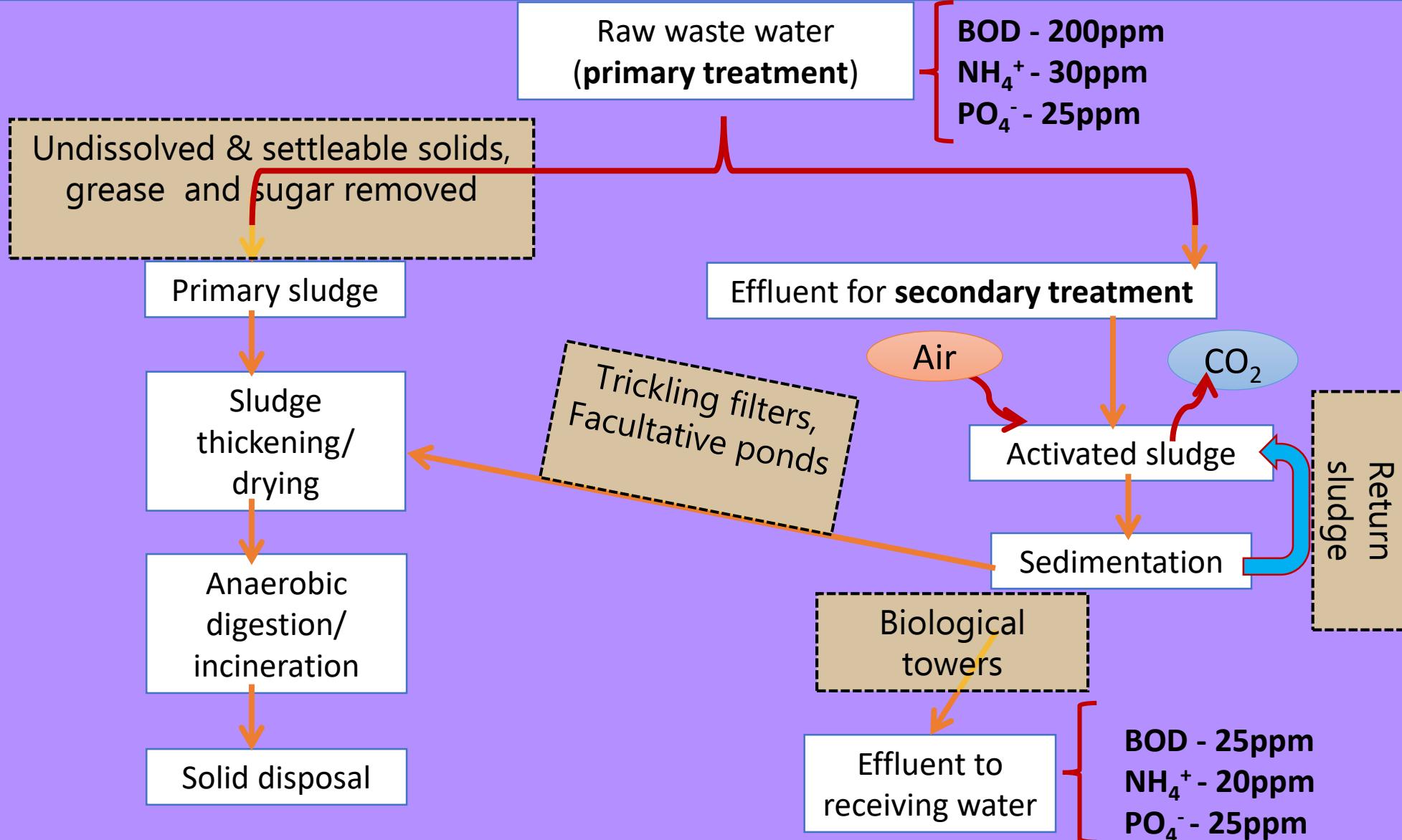


(b) Phosphorus Removal (Chemical precipitation): Phosphorus is present in the form of orthophosphates (H_2PO_4^- , HPO_4^{2-} and PO_4^{3-}). Phosphates are removed by adding coagulants usually alum [$\text{Al}_2(\text{SO}_4)_3$] or lime [$\text{Ca}(\text{OH})_2$].



(iv) Removal of bacteria

- Chlorination (already discussed in 1st Semester)
- Bacteria are removed by retaining the effluents in maturation ponds or lagoons for specified period of times.



Primary & secondary treatment of municipal waste water

Conservation of water:

- A step to conserve water is the step to secure the future. The most essential among all the natural resources on earth is water. A drop of water is worth more than a sack of gold for the thirsty man. Water conservation is what that can reduce the scarcity of water. It aims to improve the efficiency of use of water, and reduce losses and waste.
 - **Tips to save water :**
Avoid leakage of water from the taps.
 - **Turn the tap off when not in use especially when you brush your teeth or wash clothes.**
 - **Rainwater harvesting is the another method to conserve water.**
 - **The water supply should be limited in those areas which enjoys the unlimited water supplies.**

Technical methods to conserve water :

- 1.Rainwater Harvesting
- 2.Historical Water Bodies
- 3.Ponds

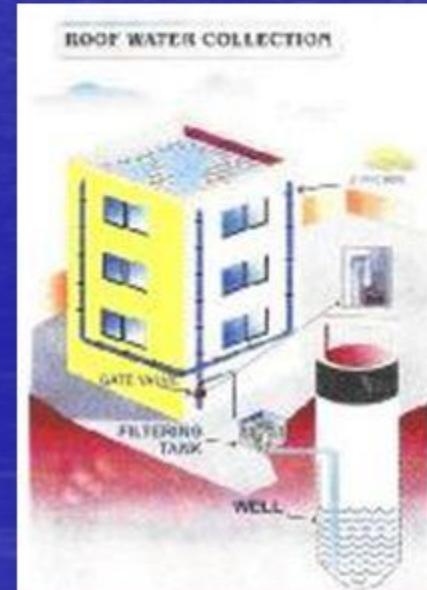
Water Harvesting

What is Water Harvesting?

- The collection of rain and ground water into storage receptacles and using it for municipal purposes.

Examples of Water Harvesting:

- On a small scale you could collect rain water in a container or bucket and use it to water your household plants.
- Recycle used waste water, treat it, and put it back into the water system into the aquifers and rivers.



Traditional Types of Water Harvesting.

→ The type used depends on conditions including both physical and human:-

□ **KULS-**

- Water channels found in precipitous mountain areas.
E.g.: - Himachal Pradesh, Jammu.



□ **VIRDAS-**



- Shallow wells dug in low depressions called *jheels* (tanks).
E.g.: - Great Rann of Kutch in Gujarat



Bamboo drip irrigation in Meghalaya



- 200-year-old system
- Used by tribal farmers of Khasi and Jaintia hills
- Bamboos divert water from perennial springs on hilltops to the lower reaches by gravity
- Used to irrigate the betel leaf or black pepper crops
- 18-20 litres of water entering the bamboo pipe system per minute gets transported over several hundred meters and finally gets reduced to 20-80 drops per minute at the site of the plant.
- Attempts made to introduce modern pipe systems but farmers prefer to use their indigenous form of irrigation.

Any questions?