Module 5 - Water Technology

Water which does not produce lather with soft solution but produce white precipitate is called hard water. This is due to the presence of dissolved calcium and magnesium salts.

Soft water:- Water which produce lather with soap solution is called soft water. This is due to the absence of Ca and Mg salt.

Hardness of water;-Hardness of water can be detected in two ways

1. When the water if treated with soap solution, if it prevent lathering ,forms white precipitate the water containing hardness.

2. The water containing hardness gives black colour with EBT at Ph 9-10.

Types of hardness

It is based on the types of dissolved salt present in water .Hardness of water can be classified into two ways

I. Temporary hardness (Carbonate or alkaline hardness)

This is due to the presence of bicarbonate of Ca and Mg.

it can be removed by 1. Boiling the water 2.Adding lime to the water

1.Boiling

 $Ca(HCO_3)_2 \rightarrow CaCo_3+H_2O+Co_2$

Soluble calcium bicarbonate insoluble calcium carbonate

2. MgH (CO₃)₂ + Ca(OH)₂ \rightarrow Mg(OH)₂+CaCO₃+2H₂O

II.Permanent hardness(non carbonate)

This is due to the presence of chlorides and sulphides of Cg and Mg. It cannot be removed by boiling the water but it can be removed by lime soda process and zeolite process.

 $CaCl_2 + Na_2 CO_3 \rightarrow CaCo_3 + 2NaCl$

 $CaSO_4 \ +Na_2 Ze \quad \rightarrow \quad CaZe + Na_2 SO_4$

Total hardness: sum of temporary and permanent hardness.

Degree of hardness

The hardness of water is expressed as weight in grams of $CaCO_3$ in one million grams of water (PPM- parts per million) or lt is the number of milligrams of $CaCO_3$ present in 1 litre of water. Calcium carbonate is chosen as the standard for expressing hardness due to the following reasons:

1) CaCO₃ is found to be the most insoluble salt that can be precipitated during water treatment.

2) A standard solution of hard water can be prepared by Weighing fixed amount of CaCO₃,dissolving in dilute HCl and waking up to the known volume.

3) The molecular weight of $CaCO_3$ is 100(Equivalent weight = 50), so the calculation is easy.

Equivalent of CaCO3 = $\frac{\text{Mass of hardness producing substance } \times 2 \times \text{Eq.weight of CaCO3}}{2 \times \text{Eq.wt of hardness producing substance}}$

= Mass of hardness producing substance $\times \frac{2 \times 50}{2 \times Eq. wt of hardness producing substance}$

= Mass of hardness producing substance × Multiplication factor

SOLVED PROBLEMS

1. A water sample contains 408mg of CaSO₄ per litre.Calculate the hardness in terms of CaCO₃ equivalents.

Ans: Hardness = mass of CaSO4 in mg/L \times Multiplication factor

$$=408 \times \frac{100}{136} = 300 \text{ mg/L} = 300 \text{ ppm}$$

2. Calculate the temporary, permanent and total hardness of water (in ppm) having following composition. $Ca(HCO_3) = 4 \text{ ppm}, Mg(HCO_3)_2 = 6 \text{ ppm}, CaSO_4 = 8 \text{ ppm}, MgSO_4 = 10 \text{ ppm}.$

Ans: Temporary hardness is due to the bicarbonates of Ca and Mg

Temporary hardness =
$$4 \times \frac{100}{162} + 6 \times \frac{100}{146} = 6.58$$
 ppm

Permanent Hardness is due to CaSO₄ and MgSO₄

Permanent Hardness = $8 \times \frac{100}{136} + 10 \times \frac{100}{120} = 14.21 \text{ ppm}$

Total hardness = Temporary hardness+ Permanent hardness

= 6.58+14.21 = <u>20.79 PPM</u>

3. Calculate the temporary, permanent and total hardness of water (in ppm) having following composition. $Ca(HCO_3) = 4 \text{ ppm}, Mg(HCO_3)_2 = 6 \text{ ppm}, CaSO_4 = 8 \text{ ppm}, MgSO_4 = 10 \text{ ppm}$ and NaHCO₃ = 3 ppm

Ans: When $NaHCO_3$ is present in water temporary hardness increases at the expense of permanent harness, but the total hardness remains the same.

Total hardness =4 $\times \frac{100}{162}$ +6 $\times \frac{100}{146}$ +8 $\times \frac{100}{136}$ +10 $\times \frac{100}{120}$ = 20.79 ppm

Temporary hardness = $4 \times \frac{100}{162} + 6 \times \frac{100}{146} + 3 \times \frac{100}{2 \times 84} = 8.37$ ppm

Permanent hardness = Total hardness - Temporary hardness

$$= 20.79 - 8.37 = 12.42 \text{ ppm}$$

4. Calculate the temporary and permanent hardness of water which contain $Ca^+ = 200$ ppm, Mg ²⁺ =96 ppm, HCO3 ⁻ = 976 ppm, Cl⁻ = 146 ppm, SO₄ ²⁻ = 96 ppm, Na ⁺ = 112 ppm

Ans: Total hardness is due to Ca $^+$ and Mg $^{2+}$ ions

Total hardness = $200 \times \frac{100}{40} + 96 \times \frac{100}{24} = 900 \text{ ppm}$

Temporary hardness is due to bicarbonate ion

Temporary hardness = $976 \times \frac{100}{2 \times 61} = 800 \text{ ppm}$

Permanent hardness = Total hardness - Temporary hardness

= 900-800 = <u>100 ppm</u>

5. Calculate the hardness of a) 0.05 M Calcium chloride solution b) 0.08 N MgSO₄ solution

Ans: (a) Weight /litre of $CaCO_3$ = Molarity × Molecular mass of $CaCO_3$

= 0.05 × 100 = 5 g/L = 5000mg/L= 5000 ppm

Hardness = 5000 ppm

(b) Weight /litre of CaCO₃ = Normality \times Eq.wt of CaCO₃

$$= 0.08 \times 50 = 4 \text{ g/L}$$

= 4000 mg/L = 4000 ppm

Hardness = 4000

Units of hardness

There are five units, commonly used in hardness measurements.

i) Parts per million (ppm):

It is the number of parts of CaCO₃ equivalent hardness present in 10^6 parts of water .

ie, 1 ppm = 1 part of CaCO₃ equivalent hardness $/10^6$ parts of water

ii) Milligram per litre(mg/L):

It is the number of milligrams of CaCO₃ equivalent hardness present in 1 litre of water .

I.e, 1mg/L= 1 mg CaCO3 of equivalent hardness /1 L of water

But, $1L=1000mg = 10^6 mg$

Hence 1 mg/L = 1 mg CaCO3 of equivalent hardness $/10^6 \text{ mg of water}$

= 1 ppm

iii)Clarke's Degree (⁰ Cl):

It is the number of parts of CaCO3 equivalent hardness in 70,000 parts of water .

I.e, 1° Cl = 1 part of CaCO₃ equivalent hardness /70,000 parts of water

iv) Degree French (⁰ Fr):

It is the number of parts CaCO3 equivalent hardness present in 10⁵ parts of water.

ie, 1 0 Fr = 1 part of CaCO₃ equivalent hardness/ 10⁵ parts of water.

v) Milliequivalents per litre (meq/L):

It is the number of milliequivalents of CaCO₃ equivalent hardness present in 1 litre of water.

I.e, 1meq/L= 1 meq CaCO3 of equivalent hardness /1 L of water

= 50 mg/L of CaCO₃ equivalent hardness = 50 ppm

Relationship between various units of hardness is as follows.

I ppm = $1 \text{mg/L} = 0.1^{\circ} \text{ Fr} = 0.07^{\circ} \text{ Cl} = 0.02 \text{ meq/L}$

Estimation of hardness

Aim

To estimate the amount of total hardness present in the given sample of water by complexometric titration method using EDTA.

Principle

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Hardness of water is the property by which water does not give ready lather with soap. Hardness is mainly due to the presence of bicarbonates, chlorides and sulphates of calcium and magnesium (Ca(HCO₃)₂, Mg(HCO₃)₂, CaCl₂, MgCl₂, CaSO₄, MgSO₄).

EDTA (Ethylenediamine tetra acetic acid) forms colourless stable complexes with Ca^{2+} and Mg^{2+} ions present in water at pH = 9-10. EDTA is a hexadentate ligand. Disodium salt of EDTA is used in the titration due to the less solubility of EDTA in water. Eriochrome Black-T (EBT) [sodium-1-(1-hydroxy 2-naphthylato)-6-nitro-2-naphthol-4-sulphonate] is the metal ion indicator used as in this complexometric titration, which gives a colour change from wine red to blue at the end point. NH₄Cl-NH₄OH buffer is used to maintain the P^H of the solution at 9-10.

Buffer is added to the hard water sample to adjust the P^{H} to 10. When EBT to added to this solution at P^{H} around 10, it gives unstable wine red coloured complex with Ca^{2+} and Mg^{2+} ions present in the hard water.



Structure of EDTA









Procedure

1. Preparation of standard hard water:

1 gram of pure, dry $CaCO_3$ is weighed accurately and is dissolved in minimum quantity of dilute HCl and evaporated to dryness in a China dish. The Residue is dissolved in distilled water and made up to 1000 ml in a standard flask .Then each ml of this solution will contain one milligram of CaCO₃ equivalent hardness.

2. Preparation of EDTA solution: About 4 gram of EDTA and 0.1 gram MgCl₂ crystals are dissolved in distilled water and made up to 1 L.

3. Preparation of indicator EBT: About 0.5 gram EBT is dissolved in 100 ml ethyl alcohol.

4. Preparation of buffer solution: About 67.5 gram ammonium chloride is added to 570 ml of liquor Ammonia and diluted to 1L using distilled water.

5. Standardization of EDTA solution: Burette is filled with EDTA solution. 50 ml of standard hard water is pipetted out into a conical flask .10 -15 ml of buffer solution and 4 -5 drops of EBT are added. It is then titrated against EDTA solution , till wine red colour changes to blue colour .Let the volume of EDTA consumed be V_1 mL.

6. Titration of unknown hard water: 50 mL of unknown hard water sample is titrated with EDTA solution as above and let the volume of EDTA be V_2 mL.

7 .Titration for permanent hardness: 250 ml of unknown water sample is boiled in a beaker till its volume is reduced to 50 mlL.by this process, all the bicarbonates present will be decomposed to carbonates and hydroxides of Ca²⁺ and Mg²⁺ Then the water is filtered and this filtrate is made up to 250 mL with the distilled water .50 ml of this water is titrated against EDTA solution and let the volume of EDTA be V₃ mL.

Calculations

50 mL of standard hard water \equiv V₁ ml of EDTA

 $50 \times 1 \text{ mg CaCO}_3 \equiv V_1 \text{ ml of EDTA}$

Therefore, 1 ml of EDTA $\equiv \frac{50}{V_1}$ mg of CaCO₃

Total Hardness

50 mL of unknown hard water \equiv V₂ ml of EDTA

| V ₂ ml of EDTA | $\equiv \frac{V2 \times 50}{V1} \text{ mg of CaCO}_{3}$ |
|---------------------------|---|
|---------------------------|---|

| 1L (1000 ml) of unknown hard water | ≡ | $\frac{V2 \times 1000}{V1} \text{ mg of CaCO}_3 \text{ eq.}$ | |
|------------------------------------|---|--|--|
| | | V2 ×1000 | |

Therefore, the total hardness of water $\equiv \frac{V2 \times 1000}{V1}$ mg/L Or ppm.

Permanent hardness

50 mL boiled water $\equiv V_3$ ml of EDTA $\equiv \frac{V_3 \times 50}{V_1}$ mg of CaCO₃ Therefore, permanent hardness of water $\equiv \frac{V_3 \times 1000}{V_1}$ mg/L Or ppm

Temporary hardness: Temporary Hardness = Total hardness - permanent hardness

$$=\frac{(V2-V3)\times 1000}{V1}$$
 mg/L Or ppm.

Example problem 1: Standard hard water contains 15 g of CaCO₃ per liter, 20 mL of this required 25 mL of EDTA solution, 100 mL of sample water required 18 mL of EDTA solution.100 mL sample water after boiling required 12 mL EDTA solution. Calculate the temporary hardness of the given sample of water, in terms of ppm.

Ans: (i) Standardization of EDTA solution:

Given 1L of standard hard water contains 15 g, or 15000 mg CaCO₃

Therefore 1 mL of standard hard water contains 15 mg CaCO₃

25 mL of EDTA \equiv 20 mL of the standard hard water

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

Therefore, 1 mL of EDTA $\equiv \frac{300}{25} = 12$ mg of CaCO₃ equivalent

(ii) Determination of total hardness of water:

100 mL of sample water $\equiv 18$ mL of EDTA

 $= 18 \times 12 = 216$ mg of CaCO₃ eq.hardness

Therefore

1 L of sample water = $216 \times 1000/100 = 2160$ mg of CaCO₃ eq.hardness

Hence, total hardness of water = 2160 ppm

(iii) Determination of permanent hardness:

100 mL of boiled water \equiv 12 mL of EDTA

 $= 12 \times 12 = 144$ mg of CaCO₃ eq.hardness

Therefore

1L of boiled water $= 1440 \text{ mg of } CaCO_3 \text{ eq.hardness}$

(iv) Determination of temporary hardness:

Temporary hardness = Total hardness - Permanent hardness

= 2160- 1440 = <u>720 ppm</u>

Disadvantages of hard water

1. It interferes with cleansing action of soap which leads to wastage of soap.

2 Water containing chlorides and sulphates if used for concrete mixing, affects the curing and the final strength of the concrete.

3. Boilling point of the hard water being high, due to the presence of dissolved salts, leads to the consumption of more fuel if it is used for cooking.

4. Hard water cannot be used in dyeing industry as it changes the exact shades of colour due to adherence of Ca and Mg soaps

5. In sugar industry hard water causes difficulties during crystallization of sugar.

6. In paper industry hard water causes troubles by affecting the smoothness, colour etc. of the paper.

7. Hard water if used in boilers cause many troubles such as

i) Scale and sludge formation: If these precipitates are in the form of loose and slimy deposits on the walls of the boiler they are called **sludge** and if the precipitates are hard and adhering coating on the inner walls of the boiler, they are called **scales.** Scale and sludge formation leads to decrease of heat transfer efficiency which results in wastage of fuel. It also affects the bolier safety and may lead to explosion of boiler.

ii) Priming and Foaming in boilers: When a boiler produces steam rapidly, some particles of liquid water wil also be carried along with the steam. This wet steam formation is called **priming.Foaming** is the process of formation of foams or bubbles at the surface of water in boilers, which do not break easily. Foaming is caused by the presence of oils, alkalis etc.

iii) It causes Boiler corrosion.

Softening of water : The process of removal of the hardness producing salts, which are present in the water, is known as softening of water.

Methods of water softening

The most common method for water softening are ion-exchange polymers and reverse osmosis.

Ion – Exchange method (Demineralisation)

The process in which the dissolved ions present in water are completely separated by the help of some complex organic compounds is known as ion exchange method.

In this method ion exchange resins are used for the removal ions from the water. Ion exchange resins are long chain, cross linked, insoluble organic polymers with a microporous structure. The functional groups attached to the chains are responsible for the ion exchanging properties. These resins act as ion exchangers and remove all minerals from the hard water. They remove all cations and anions from hard water and make it completely free from ions, so it is called demineralization.

Principle

The resins (polymer) are very complex organic compounds capable of exchanging all the ions present in hard water. They are of following two types:

 Cation Exchange Resins: The cation exchange resins are mainly carboxylated or sulphonated styrene-divinylbenzene copolymers .These resins process acidic groups such as -COOH or - SO₃H groups and may be represented as R⁻ H⁺.The structure of cation exchange resin containing $-SO_2H$ groups can be represented as shown in figure. These types of resins exchange only the cations present in hard water with H^+ ions.

2) Anion Exchange Resins: The anion exchange resins are mainly styrene-divinyl benzene or amine formaldehyde copolymers containing amino or quaternary ammonium groups. They possess basic groups such as OH- or NH2; group and may be represented as R-OH. The structure of an anion exchange resin may be represented as shown in figure. They after treatment with dilute NaOH solutions become capable of exchanging their OH- ions with anions present in hard water.



WORKING



The arrangement of the apparatus is in such a manner than it consists of two chambers. One containing cation exchange resin and the other anion exchange resin .

Hard water is first allowed to pass through the cation exchange resin. The cations present in hard water get exchanged with H⁺ ions of the resin as shown by the following reactions;

The water coming out of the first chamber thus contains free H+ ions and is acidic in nature. It is now passed through the anion exchange resin. Resin present in the next chamber exchanges the anions (Cl^{-} , SO_4^{2-}) with OH ⁻ ions.

The OH – ions liberated from the chamber now react free H+ ions (coming from the first chamber) to form H_2O molecules.

$$H^+ + OH^- \rightarrow H_2O$$

Thus, the water coming out from the second chamber is free from all cations and anions that were present in hard water. Hence, it is generally known as deionised or demineralised water. As the continuous use of the process of demineralization makes the resins exhausted (exchange sites are block), therefore for further use, resins must be regenerated.

Regeneration of Resins

The exhausted resin in the first chamber is regenerated by passing a dilute HCl or sulphuric acid solution through chamber. It again makes the site of ion exchange active.

 R_2Ca + $2H^+ \rightarrow 2R^-H^+ + Ca^{2+}$

This column is washed with de ionized water to take away the Cl^{-} and SO_4^{2-} - etc.

The exhausted resin in the second chamber is regenerated by passing a dilute NaOH solution through it. The regenerated resins are ready for reuse.

 $RCl + OH^{-} \rightarrow R^{+}OH^{-} + Cl^{-}$

The chamber is also washed in de ionized water to remove Na+. Thus regenerated ion exchanger can be used again

Advantages

- 1. By this process it is possible to highly acidic or alkaline waters.
- 2. The water obtained by this process will have very low hardness (Nearly 2 ppm)

- 3. The resins can be regenerated and reuse.
- 4. There is no scale or sludge is formation.
- 5. There will not be priming and forming.

Disadvantages

- 1. The resins used in the process are quite costly, Hence, the process becomes expensive.
- 2. The resins needs to be regenerated again and again, thus making the process inconvenient and complex.
- 3. If the water contains turbidity, it decreases the efficiency of the process.

Desalination

The process of removal of dissolved salts such as NaCl, KCl, MgCl₂ etc from water is known as desalination. The common method for desalination of brackish water is reverse osmosis

The spontaneous process, which involves the flow of the solvent from a dilute solution to a more concentrated solution through a semi-permeable memberane, is called osmosis. In this natural process, only solvent can flow and not the solute, which develops pressure, known as osmotic pressure. But, when applying a greater pressure than the osmotic pressure on side of more concentrated solution reverses this process is called reverse osmosis. The flow of solvent under pressure from more concentrated solution to solvent or less concentrated solution through semi-permeable membrane is called the **reverse osmosis**.





Process of Reverse Osmosis

The desalination of saline water is carried-out in a reverse osmosis cell, which is shown diagrammatically in figure. Saline water is added to the cell through the water inlets. The

chamber is separated from other chamber having some fresh water by a semi-permeable membrane made of very thin films of cellulose acetate. More recently, superior membrane made of poly methacrylate and polyamide polymers have been introduced. A pressure of 15-40 kg/cm² is applied to the sea water gently. The solvent or water starts flowing from saline water to side of fresh water through semi-permeable membrane.Hence,the reverse osmosis takes place.Fresh water obtained is taken out through an outlet.

Reverse Osmosis



Advantages

- 1. This process is economical and convenient. It can be used at room temperature.
- 2. The process can remove ionic as well as non-ionic dissolved salts easily.
- 3. It is also effective in removing colloidal impurities present in the water.
- 4. It is suitable for converting sea water into drinking water.

Disadvantages

1. High usage of electricity

<u>Municipal water Treatment</u>

Water from rivers and canals contain a lot of impurities. The domestic water should be free from suspended impurities, pathogenic organisms, unpleasant taste, odour, colour etc.It should also have a p H around 8. Purification of Municipal water for domestic purpose involves two major purposes.

Removal of suspended impurities and Removal of micro - organisms

I. Removal of suspended impurities

The various steps involved are,

- i) Screening: Large, floating impurities are removed, when raw water is passed through screens with large number of holes.
- ii) Sedimentation: Water is allowed to stand undisturbed in big tanks for 2-6 hours so that most of the suspended particles settle down at the bottom, due to gravitational force.
- iii) Filtration: Water is passed through a bed of fine sand and some other granular materials, so that colloidal matter bacteria, micro- organisms etc are removed. Sand filter is used for this process.

II. Removal of micro – organisms: Disinfection Methods

Disinfection is the process, which involves the elimination of disease causing (pathogenic) microorganism from water. Chemicals used in disinfection are called disinfectants. Common methods of disinfection include use of ozone, chlorine, or UV light.

Types of disinfection methods

a) Chlorination

When chlorine is added to water .It become soluble and form HCl and HOCl. It reduces the alkalinity of water. HOCl being highly unstable readily decomposes into HCl and nascent oxygen [O]. The nascent oxygen oxidizes the micro organisms present in water by destroying their enzymes.

 $H_2O + Cl_2 \rightarrow HCl + HOCl$

HOC1 \rightarrow HCl + [O]

Factors affecting efficiency of chlorine

- 1. Time of contact: The rate of killing of microorganism is maximum at the beginnings.
- 2. Temperature: As temperature increase death rate also increase.
- 3. p H of water:- At lower p H, only a small contact period is required to kill a major percentage of organisms.

Advantages

- 1. It is economical and effective
- 2. Storage is easy
- 3. Can be used at low and high temperature

4. Salty impurities are not introduced to water.

Disadvantages

1. Chlorine, when added is excess, produces an unpleasant taste and odour.

2. More effective below p H = 6.5 and less effective at higher p H values.

Break point chlorination: It refers to the addition of chlorine in amounts sufficient to oxdise all the microorganisms present in water. Impurities like organic matter, reducing substances, colouring matter, freeammonia etc.also get oxidized and destroyed.

The typical relationship between amounts of chlorine added to water is experimentally detected.



Break Point Chlorination Curve

Hence for effectively killing the microorganism, sufficient Cl (corresponding to minima in the curve) added. Addition Cl in such dosage is known as breakpoint or free residual chlorination. OR

Break point of chlorination indicates that the point of which residual chlorine begin to appearance.

Stage I: - Oxidation of reducing compounds

Stage II: - Formation of chloro-organic compounds and chloramines

Stage III: - Destruction of chloro-organic and chloramines

Stage IV: - Free residual chlorine

Advantages

- 1. It completely oxidizes the organic compounds, ammonia and other reducing compounds.
- 2. It removes colour, odour and taste from water.
- 3. It destroys all the disease- producing bacteria.
- 4. It prevents the growth of any weeds in water.

b) Using chloramines(ClNH₂)

Chloramine is a mixture of chlorine and ammonia in the ratio 2:1

 $Cl_2 + NH_3 \rightarrow ClNH_2 + HCl$

Chloramine is soluble in water and form HCl,which further decomposes into nascent oxygen [O] which oxidizes the organic matter.

 $CINH_2 + H_2O \rightarrow HOCl + NH_2$ $HOCl \rightarrow HCl + [O]$

The effect of chloramines in water is long lasting compared to chlorine. There will not be unpleasant smell .it has a good taste.

c) Using UV radiation

When electric current is passed through mercury vapour lamp enclosed in quartz container, it produces ultraviolet radiations (200- 400 nm). There radiations are absorbed by the microorganisms present in water which initiates photochemical reactions at their DNA bases. Thus, the micro organisms are destroyed by UV radiation. The effectiveness of this method depends on the intensity of radiation and extend of irradiation.

Advantages

- 1. There will not be any unpleasant taste or smell in water as no chemicals are used.
- 2. Quick process.

- 3. All the pathogenic organisms are killed.
- 4. Complete sterilization.

Disadvantages

- 1. Equipments are costly.
- 2. Applicable only for small quantity of water.

d) Using Ozone

Ozone is used in gaseous form. Ozone is a powerful disinfectant agent and readily absorbed by water .Ozone is highly unstable and breakdown to nascent oxygen.

 $O_3 \rightarrow O_2 + [O]$

It is a powerful oxidizing agent and kills the bacteria and oxidized the organic matter present in water.

Advantages

- 1. No smell or unpleasant taste.
- 2. Complete sterilization.

Disadvantages

- 1. Expensive.
- 2. Applicable only for small quantity of water.

DISSOLVED OXYGEN

It is the amount of free, dissolved oxygen present in a sample of water. Oxygen enters in to water through air or aeration of water by wind. It can also be due to photosynthesis of aquatic plants.

- DO levels fluctuate seasonally and over a 24 hour period.
- They vary with water temperature and altitude.Pure water at 30^oCcan holdonly 7.8ppm dissolved oxygen at saturated condition.
- At 20^oC it can hold up to 9.2ppm.
- This is according to Henry's law which states that dissolution of a gas in a liquid is directly proportional to pressure and inversely proportional to absolute temperature.
- That is solubility of oxygen decreases with rise in temperature and increases with pressure.
- Cold water holds more dissolved oxygen than warm water.water hold less dissolved oxygen at higher altitude due to lowering of atmospheric pressure.

• DO can be measured using titration or by dissolved oxygen meter.

Estimation of DO in water(wrinkle's method)

- A Known amount of given water sample is taken in a stoppered bottle.
- 1ml MnSO4 and 1ml alkaline potassium iodide are added.
- The bottle is stoppered and shaken welland allowed to stand for about 15 minutes.
- When the precipitate is settled,add 2ml conc.H2SO4 and shake the bottle until the precipitate is completely dissolved.
- 100ml of this solution is taken into a conical flask,2ml starch solution is added and titrated against standard sodium thiosulphate solution.
- At the end point blue colour changes to light green colour.
- The value of DO is calculated using volume of thiosulphate used for titration.

Calculation

$$V_1x N_1 \!\!=\!\! V_2x N_2$$

Vol.of oxygen solution (V_1) x Normality $(N_1) =$ Vol.of thiosulphate (V_2) xNormality (N_2)

Normality of oxygen solution(N_1) = ($V_2 x N_2$)/ 100 =X N

Weight of DO per litre= x X 8 X1000ppm.

Significance

- DO is important for aquatic life, and in the quality of water.
- When it is too high or too low it affects aquatic life.
- DO help corrosion.

BIOLOGICAL OXYGEN DEMAND (BOD)

BOD can be defined as the amount of oxygen required by aerobic bacteria for oxidation of all biologically oxidisable matter present in 1L of sewage water for a period of five days at 20° C.

BOD is proportional to the amount of organic waste in water.As BOD increases,DO decreases.So BOD is an indication of the extent of pollution.

Determination

- A known volume of the given sewage sample is diluted with a known volume of dilution water.(Dilution water is organic free distilled water-that is water having no BOD containing 9.2ppm dissolved oxygen.)
- Known volume of diluted sample is in two stoppered bottles(I &II).
- The DO content of bottle (I) is determined immediately(blank).
- The bottle (II) is incubated at 20^oC for 5 days.

• After which the unused DO is determined.

Calculation

BOD=(DO b-DO i) X Dilution factor.

DO b=DO present in the blank, bottle I

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DO i= DO present after incubation, bottle II
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Dilution factor = volume of sewage sample in ml after dilution

volume of sewage sample in ml before dilution

Significance of BOD

- Shows the amount of decomposable organic matter in the sewage.
- Helps to determine the degree of pollution at any time in sewage.
- Lesser the BOD better is the quality of water.
- Pure water has BOD less than 3ppm.

CHEMICAL OXYGEN DEMAND [COD]

Defined as the amount of oxygen present in ppm, needed for the chemical oxidation of all oxidisable impurities present in the sewage using an oxidising agent like K₂Cr₂O₇.Dicromate is strong oxidizing agent than oxygen. Hence oxidations of all biologically oxidisable and biologically inert matters in the sample take place. So COD value will be higher than BOD value.COD test needs only three hours, while BOD needs five days.

Determination

A known volume, 25ml,of the waste water sample is refluxed(boil without allowing the vapours to escape ,but condense back in to the liquid stock).For 11/2 hours with known excess $K_2Cr_2O_7$ in dil H_2SO_4 in presence of AgSO₄ catalyst and HgSO₄.The organic matters are oxidized to H_2O ,CO₂ and NH₃

The uncreated K₂Cr₂O₇ is titrated against standard FeSO₄ (FAS).

Let the volume of $FAS=V_1$ ml

A blank experiment is also carried out using the same volume of distilled water.

Let the volume of $FAS=V_2$ ml

 $COD = \frac{(V2 - V1) * N * 8 * 1000}{X}$

 V_1 = volume of FAS Consumed by sewage sample

 V_1 = volume of FAS Consumed by blank

N=Normality of FAS

X=Volume of sewage sample

| BOD | COD |
|--|---|
| 1. it is the amount of oxygen required for biological oxidation of organic matter under aerobic condition at 20 ⁰ C for 5 days | 1. it is the amount of oxygen required for the complete oxidation of organic matter present in sewage by means of a chemical |
| 2.Average BOD in sewage is 100-15-mg/L | 2. Average value is > 150mg/L |
| 3. It enables one to determine the degree of pollution | 3. it gives information about the total amount of oxygen required for complete oxidation of sewage |
| 4. BOD determination takes 5 days | COD determination takes 3 hours |
| 5. a constant tem of 20 [°] C is essential | 5. high temp., above 100 ⁰ C is essential |
| 6. value of BOD <cod< th=""><th>6. Value of COD>BOD</th></cod<> | 6. Value of COD>BOD |
| 7. Aerobic bacteria is essential | 7. Anaerobic bacteria is essential |
| 8. Unit-mg/L or ppm | Unit-mg/L or ppm |

SEWAGE TRATMENT

Sewage water has to be treated before sending it into running streams.Presence of biologically oxidisable matter(carbohydrates, proteins etc)in water increases the BOD of thewater.The sewage treatment is carried out to reduce BOD of water.If high BOD water is sent to running streams,due to lack of dissolved oxygen aquatic life get extinct.sewage treatment iscarried out using an artificial process.The various steps involved are,

- 1. Primary treatment
- 2. Secondary treatment
- 3. Tertiary treatment.



Figure 5.10: Flow diagram sewage treatment

<u>1. Primary treatment</u>

a) **Screening**: In this process, large solids and inorganic matter, which are suspended in the sewage, are removed. Sewage is passed in upward direction through bar and mesh screens to remove suspended and coarse solids.

b) **Sedimentation or settling process**: Continuous flow type sedimentation tanks are employed for this purpose. Most of the suspended solids are removed by this process. Sometimes, chemical coagulant is added to sewage, before sedimentation. Coagulant forms gelatinous precipitate, which can entrap small sized organic matter, making them settle down easily. Aluminium sulphate, alum etc are the commonly used coagulants.

 $Al_2(SO_4)_3+6H_2O \longrightarrow 2Al(OH)_3(Gelatinous precipitate)+3H_2SO_4$

2.Secondary treatment(biological)

It involves the biological decomposition of organic matters percent in sewage water. The carbon is converted into carbon dioxide while Nitrogen is converted into nitrates and nitrites.

 NH_2 -CO- NH_2 [O] \rightarrow CO₂ + 2 NH_3

 $NH_3 - O \rightarrow HNO_2 + HNO_3$

HNO₂ + HNO₃ Base present in soil NH₄NO₂+NH₄NO₃

There are two types,

Trickling filter method and UASB process.

a)Trickling filter method(Aerobic filtration method)

Biological treatment is carried out with the help of trickling filters. The filter is in rectangular shape. It is filled with material like broken bricks, crushed rocks etc. and fitted with a rotating distributer.

The sewage trickles over the filter with the help of a rotating distributer then it moves down through the filtering medium and aerobic micro organism start consuming the organic matter in the sewage. They grow over the surface of the rock particles and more or less clear effluent is collected using under drive system.

Advantages

- 1. Highly effective
- 2. BOD is reduced by 60-80%
- 3. Low maintenance cost

Disadvantages

1. The equipments are costly



b)Upflow Anaerobic Sludge Bed Reactor (UASB)Process.

This is an anaerobic methane producing process. A blanket of granular sludge is suspended in the UASB reactor. It is a rectangular tank made of concrete. In this process, the effluent is fed from the bottom of the reactor so that it moves upward through a sludge blanket. The suspended sludge filters and treats the waste water. The anaerobic microorganism living in the sludge breakdown the organic matter producing Bio-gas. The rising gas bubbles mix the sludge and waste water. Bio-gas is collected at the top of the reactor. The treated water and sludge can be used as manure in agriculture.



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Advantages:-

- High BOD reduction
- Low sludge production
- No need of aeration system
- Little CO₂ emission.

Disadvantages:-

- Needs skilled operations
- Long startup time
- Constant power supply
- Difficult to set up

3.Tertiary Treatment

This is the most advanced stage of sewage treatment. By this process, the amount of nitrogen and phosphorous compounds present in the effluent can be reduced. The three steps involved are

a) Precipitation: Effluent from the secondary process is treated with CaO so that calicium phosphate will be precipitated.

b) Nitrogen stripping: Ammonia gas is removed by passing the effluent through a series of baffle plates.

c) **Chlorination**: Disinfection of sewage is done by treating with chlorine, when pathogenic bacteria are killed.