

## CHAPTER 8 WATER TECHNOLOGY

### 8.1 INTRODUCTION

Water is the most important compound for the existence of human beings, animals and plants. Besides these, water has great applications in industries. Water is mainly used in power generation industry for the production of electric current through steam generation. Water is also used as a coolant in atomic reactors as well as chemical plants. In addition to it, water is widely used in other fields such as production of steel, rayon, paper, atomic energy, textiles, chemicals, ice and for air-conditioning, drinking, bathing, sanitary, washing, firefighting etc. It is also largely used in irrigation for agricultural purposes. Without food, human can survive for a number of days, but water is such an essential that without it one cannot survive.

### 8.2 SOURCES OF WATER

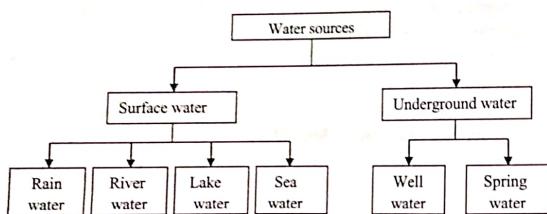


Fig. 8.1 Sources of water

Water is distributed in nature in different forms. It can be classified into surface water and underground water. The surface water can be further classified into (a) rain, (b) rivers (c) lakes and (d) sea water. Underground water can be either from springs or from wells.

**Rain water:** Rain water is probably the purest form of natural water. It is obtained as a result of evaporation from the surface water. But during its downward journey through the atmosphere it dissolves organic and inorganic suspended particles and considerable amount of industrial gases like ( $\text{CO}_2$ ,  $\text{NO}_2$ ,  $\text{SO}_2$  etc.). Rainwater is irregular in supply and generally expensive to collect.

**River water:** Rivers are fed by spring waters and rain. Water from these sources flow over the surface of land, dissolve the soluble minerals of the soil and finally falls in rivers. River water contains dissolved minerals like chlorides, sulphates, bicarbonates of sodium, magnesium, calcium and iron. It also contains suspended impurities of sand, rock dissolved impurities in it depends on its contact with soil. Greater the duration of contact, more soluble is the minerals of soil in it.

**Lake water:** Lake water has a more constant chemical composition. It, usually, contains much lesser amount of dissolved minerals than even well water, but quantity of organic matter present in it is quite high.

**Sea water:** Sea water is the most impure form of natural water. Rivers join sea and throw in, the impurities carried by them. Moreover, due to continuous evaporation of water from the surface of sea, makes the sea water continuously richer in dissolved impurities.

**Under ground water:** A part of the rain water, which reaches the surface of the earth, percolates underneath into earth. As this water moves downwards, it comes in contact with a number of mineral salts present in the soil and dissolves them. Water percolation continues till it reaches impervious strata (hard rock) which prevents further penetration. Sometimes it retards upwards and it may even come out in the form of "spring". Water from some springs contains dissolved sulphur compounds. Such water is helpful in the cure of some skin diseases. Underground water is free from organic impurities and is clearer in appearance due to the filtering action of soil. However, it contains large amounts of dissolved salts. If water from the springs contains some salts like  $\text{MgCl}_2$  and  $\text{MgSO}_4$ , it is also known as saline water.

#### Characteristics imparted by impurities in water

It is essential to understand the nature and characteristics of raw or feed water before initiating the design process of a water treatment system. The following are some of the impurities present in water which provide characteristic properties to water.

- Suspended impurities:** These impurities impart turbidity, color and odor to water.  
It can be inorganic or organic in nature.
  - Inorganic – clay and sand
  - Organic – oil globules, vegetable and animal matter.

- 2. Dissolved impurities:** It may be due to the presence of dissolved salts like carbonates, bicarbonates, chlorides and sulphates of calcium, magnesium, iron and carbonates. Hardness in water is due to the presence of these salts. Dissolved gases like CO<sub>2</sub>, O<sub>2</sub> etc. also come under this category.
- 3. Biological impurities:** These include algae, pathogenic bacteria, fungi, viruses, parasites worms etc. The source of these contamination is discharge of domestic and sewage wastes, excreta (from human, animals and birds) etc. Presence of biological impurities causes numerous health related problems.

#### Principle of water analysis

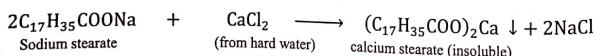
Next to oxygen, water is the most important requirement for life on earth. Only 1% of the total water on earth is fresh water and access to clean water is increasingly becoming difficult, particularly in developing countries like India. Clean water is also required in large quantities for industries like sugar, paper, beverage, textile, etc. Power plants like thermal or nuclear require large quantities of water for generating steam and cooling purposes.

The principal factors that are taken into consideration for the determination of water quality are (i) turbidity, (ii) acidity and alkalinity (pH), (iii) trace elements, (iv) dissolved oxygen content, (v) metallic ions and (vi) hardness.

#### 8.3 HARDNESS OF WATER

Water which does not produce a ready and permanent lather with soap solution is called hard water. Hardness is due to the presence of dissolved salts of calcium, magnesium and some other heavy metals. Hard water is the water that has high mineral content (in contrast with soft water). Hard water is formed when water percolates through deposits of calcium and magnesium containing minerals such as limestone, chalk and dolomite.

A sample of hard water, when treated with soap (sodium or potassium salts of higher fatty acids like palmitic, oleic or stearic acid) does not produce lather, but on the other hand forms a white scum or precipitate. This precipitate is formed due to the formation of insoluble soaps of calcium and magnesium. Typical reactions of soap (sodium stearate) with calcium chloride and magnesium sulphate are shown below.



Sodium stearate (from hard water)	Magnesium stearate (insoluble)
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Table 8.1 Comparison between hard and soft water

No.	Hard water	Soft water
1.	Hard water contains dissolved calcium and magnesium salts.	Soft water does not contain any dissolved Ca and Mg salts.
2.	Does not form lather with detergents.	Form lather with detergents.
3.	Leaves deposit called "scale"	No deposits or scale formation.
4.	Removed by Ion exchange, Zeolite processes.	None
5.	Reaction with soap produces scum or precipitate.	Forms lather no scum or precipitate.
6.	Due to the presence of dissolved hardness producing salts, the boiling point of water is elevated. Consequently more fuel and time are required for cooking.	Less time and fuel are required for cooking.

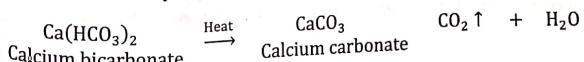
Thus, water which does not produce lather with soap solution readily, but forms a white scum, is called hard water. On the other hand, water which lathers easily with soap solution is called soft water. Soft water does not contain any dissolved calcium or magnesium salt in it. In fact, any cation which produces insoluble soap with soap solution will contribute to hardness. Thus on this basis water can be classified in to two types: viz. hard and soft water. The essential differences between the two are summarized in Table 8.1

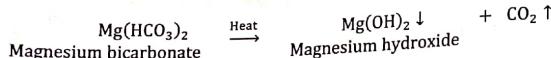
#### Types of Hardness

Hardness in water is caused by the presence of calcium ions, magnesium ions, or both. As their concentrations increase, water becomes harder. There are two types of water hardness, temporary hardness and permanent hardness.

##### 1. Temporary or Carbonate hardness or Alkaline hardness

Temporary hardness is due to the bicarbonates of calcium, magnesium and other heavy metals. This type of hardness can be removed by boiling the water to expel the CO<sub>2</sub>, as indicated by the following equations,





Presence of calcium and magnesium bicarbonates causes alkalinity to water and it can be calculated by estimating the alkalinity.

## 2. Permanent or Non-carbonate hardness or Non-alkaline hardness

It is due to the presence of dissolved chlorides and sulphates of calcium, magnesium, iron and other heavy metals. Unlike temporary hardness, permanent hardness cannot be removed by boiling. However the permanent hardness can be removed by lime soda process, zeolite process and ion exchange process. The difference between total hardness and temporary hardness is permanent hardness. The common salts responsible for permanent hardness are  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{CaSO}_4$ ,  $\text{MgSO}_4$ ,  $\text{FeSO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$  etc.

## 8.4 UNITS OF HARDNESS AND THEIR INTER- RELATIONS

Water hardness is usually expressed in several different units and it is often necessary to convert from one unit to another when making calculations. The following are the most frequently used units in hardness measurements.

- 1. Parts Per Million (ppm):** It is the number of parts of  $\text{CaCO}_3$  equivalent hardness present in  $10^6$  parts of water.  
 $1 \text{ ppm} = 1 \text{ part of } \text{CaCO}_3 \text{ equivalent hardness in } 10^6 \text{ parts of water.}$

- 2. Milligrams per liter:** It is the number of milligrams of Calcium Carbonate equivalent hardness present in 1 liter of water.  
 $1 \text{ mg/l} = 1 \text{ mg of } \text{CaCO}_3 \text{ equivalent hardness present in 1 liter of water.}$

$$1 \text{ L} = 1 \text{ Kg} = 1000 \text{ g} \approx 1000 \times 1000 \text{ mg} = 10^6 \text{ mg.}$$

$$1 \text{ mg/l} = 1 \text{ mg of } \text{CaCO}_3 \text{ equivalent per } 10^6 \text{ mg of H}_2\text{O} = 1 \text{ ppm}$$

Thus, mathematically parts per million (ppm) is same as mg/l

- 3. Clarke's Degree ( ${}^\circ\text{Cl}$ ):** It is the number of parts of  $\text{CaCO}_3$  equivalent hardness in 70,000 parts of water.  
 $1 {}^\circ\text{Cl} = 1 \text{ part of } \text{CaCO}_3 \text{ of hardness per 70,000 parts of water.}$

- 4. Degree French ( ${}^\circ\text{Fr}$ ):** It is the number of parts of  $\text{CaCO}_3$  equivalent hardness in  $10^5$  parts of water.

1ppm	= 1 part per $10^6$ parts of water
${}^\circ\text{Fr}$	= 1 part per $10^5$ parts of water
${}^\circ\text{Cl}$	= 1 part per 70,000 parts of water
1ppm = $0.1 {}^\circ\text{Fr}$	$= 0.07 {}^\circ\text{Cl} = 1 \text{ mg/l}$

Table 8.2 Relationships between various units of hardness

	ppm	mg/l	${}^\circ\text{Fr}$	${}^\circ\text{Cl}$
ppm	1	1	0.1	0.07
mg/l	1	1	0.1	0.07
${}^\circ\text{Fr}$	10	10	1	0.7
${}^\circ\text{Cl}$	0.07	0.07	0.7	1

**Problem 1:** A sample of hard water has a hardness of 510 ppm. Express the hardness in terms of  ${}^\circ\text{French}$  and  ${}^\circ\text{Clark}$ .

**Solution**

$$\begin{aligned} 1 \text{ ppm} &= 0.07 {}^\circ\text{Cl} \\ 510 \text{ ppm} &= 510 \times 0.07 {}^\circ\text{Cl} = 35.7 {}^\circ\text{Cl} \\ 1 \text{ ppm} &= 0.1 {}^\circ\text{Fr} \\ 510 \text{ ppm} &= 0.1 {}^\circ\text{Fr} \times 510 = 51 {}^\circ\text{Fr} \end{aligned}$$

## Water classification

Classification of water depending on the extent of its hardness is given in Table 8.3.

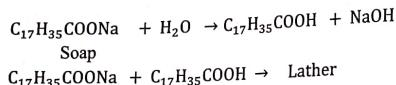
Table 8.3 Water classification

Classification	ppm
Soft	0 - 17
Slightly hard	17 - 60
Moderately hard	60 - 120
Hard	120 - 180
Very hard	Above 180

### 8.5 DISADVANTAGES OF HARD WATER

#### 1. Disadvantages in domestic use

- a) **Washing:** - Hard water does not form ready lather with soap. Instead it produces sticky scum of calcium and magnesium soaps until all the calcium and magnesium salts present in water converted to precipitate. After the completion of all calcium and magnesium salts, the soap (e.g. sodium stearate) gives lather with water.



This results in wastage of soap. Moreover, the sticky precipitate adheres on the cloth/fabric giving spots and streaks.

- b) **Bathing:** - Hard water does not lather freely with soap solution, but produces sticky scum on the bath-tub and body. Thus, the cleansing quality of soap is reduced and subsequent wastage.
- c) **Drinking:** - Hard water causes bad effect on our digestive system. Moreover, the possibility of forming calcium oxalate crystals in urinary tract is increased.
- d) **Cooking:** Due to the presence of dissolved hardness-producing salts, the boiling point of water is elevated. Hence, more time and fuel is required for cooking. The dissolved salts can deposit on the inner walls of the water heating utensils.

#### 2. Disadvantages in Industrial use

- a) **Textile industry:** - Hard water causes much of the soap to go as waste, because hard water cannot produce good quality of lather. Moreover precipitates of calcium and magnesium soaps adhere to the fabrics. These fabrics, when dyed later on, do not produce exact shades of color. Iron and manganese salt-containing water may cause coloured spots on fabrics, thereby spoiling their beauty.
- b) **Sugar industry:** - Water containing sulphates, nitrates, alkali carbonates etc., if used in sugar refining, causes difficulties in the crystallization of sugar. Moreover, the sugar so-produced may be deliquescent.
- c) **Dyeing industry:** - The dissolved calcium, magnesium and iron salts in hard water may react with costly dyes, forming undesirable precipitates, which yield impure shades and gives spots on the fabric being dyed.

- d) **Paper industry:** - Hard water causes troubles by affecting the smoothness, glossiness and color of the paper.
- e) **Concrete making:** - Water contains chlorides and sulphates, if used for concrete making, affects the hydration of cement and the final strength of the cured concrete.
- f) **Pharmaceutical industry:** - Hard water, if used for preparing pharmaceutical products (like drugs, injections, ointments etc.) may produce certain undesirable products in them.
- g) **In steam generation in boilers:** - For steam generation, boilers are almost invariably employed. Usage of hard water in boilers may cause troubles such as (1) scale and sludge formation (2) corrosion (3) priming and foaming (4) caustic embrittlement.

### 8.6 DEGREE OF HARDNESS

Hardness is usually expressed in terms of equivalent of  $\text{CaCO}_3$  in order to simplify calculations in water analysis. The choice of  $\text{CaCO}_3$  in particular is due to two reasons,

1. Its molecular weight is 100 (equivalent weight 50).
2. It is the most insoluble salt that can be precipitated in water treatment.

#### Calculation of equivalents of calcium carbonate

The following Table 8.4 can be used to get the multiplication factor for converting in to calcium carbonate equivalent hardness.

$$\frac{\text{CaCO}_3 \text{ equivalent hardness}}{\text{CaCO}_3 \text{ equivalent hardness}} = \frac{\text{Mass of hardness producing substance} \times \text{Equ. weight of calcium carbonate}}{\text{Equivalent weight of hardness producing substance}}$$

Let X be the weight of the hardness producing substance, then the above equation becomes,

$$\frac{\text{CaCO}_3 \text{ equivalent hardness}}{\text{CaCO}_3 \text{ equivalent hardness}} = \frac{X \times 50}{\text{Equivalent weight of hardness producing substance}}$$

The same formula can be modified if we change the equivalent weight of salt and equivalent weight of calcium carbonate (50) as the molecular weight of salt and molecular weight of calcium carbonate (100)

$$\frac{\text{CaCO}_3 \text{ equivalent hardness}}{\text{CaCO}_3 \text{ equivalent hardness}} = \frac{\text{Mass of hardness producing substance} \times 100}{\text{Molecular weight of hardness producing substance}}$$

Table 8.4 Calculation of equivalents of calcium carbonate

Sl. No	Dissolved salt	Molar mass	Chemical equivalent	Multiplication factor to convert to CaCO <sub>3</sub> equivalents
1	Ca(HCO <sub>3</sub> ) <sub>2</sub>	162	81	100/162
2	Mg(HCO <sub>3</sub> ) <sub>2</sub>	146	73	100/146
3	CaSO <sub>4</sub>	136	68	100/136
4	CaCl <sub>2</sub>	111	55.5	100/111
5	MgSO <sub>4</sub>	120	60	100/120
6	MgCl <sub>2</sub>	95	47.5	100/95
7	CaCO <sub>3</sub>	100	50	100/100
8	MgCO <sub>3</sub>	84	42	100/84
9	CO <sub>2</sub>	44	22	100/44
10	HCO <sub>3</sub> <sup>-</sup>	61	61	100/61
11	CO <sub>3</sub> <sup>2-</sup>	60	30	100/60
12	NaAlO <sub>2</sub>	82	82	100/82
13	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	342	57	100/114
14	FeSO <sub>4</sub> .7H <sub>2</sub> O	278	139	100/278
15.	OH <sup>-</sup>	17	17	100/34
16	H <sup>+</sup>	1	1	100/2

**Problem 2 :** A sample of water contains the following dissolved salts Mg(HCO<sub>3</sub>)<sub>2</sub> = 22mg/l, MgCl<sub>2</sub>=30mg/l, CaCl<sub>2</sub>= 85mg/l and CaSO<sub>4</sub>= 28mg/l. Calculate the temporary and permanent hardness.

**Solution:** CaCO<sub>3</sub> equivalents of the dissolved salts are given below:

Dissolved salt	Quantity	Multiplication factor	CaCO <sub>3</sub> equivalents(mg/l)
Mg(HCO <sub>3</sub> ) <sub>2</sub>	22	100 146	$\frac{22 \times 100}{146} = 15.07$
MgCl <sub>2</sub>	30	100 95	$\frac{30 \times 100}{95} = 31.58$
CaCl <sub>2</sub>	85	100 111	$\frac{85 \times 100}{111} = 76.58$
CaSO <sub>4</sub>	28	100 136	$\frac{28 \times 100}{136} = 20.58$

Temporary hardness is due to the presence of bicarbonates of Ca and Mg

Here the temporary hardness is due to Mg(HCO<sub>3</sub>)<sub>2</sub>

$$= 15.07 \text{ ppm}$$

Permanent hardness is due to [ MgCl<sub>2</sub>+CaCl<sub>2</sub>+CaSO<sub>4</sub> ]

$$= 31.58 + 76.58 + 20.58 = 128.74 \text{ ppm}$$

**Problem 3:** Calculate the carbonate and non-carbonate hardness of a sample of water containing the following dissolved salts in one liter. Ca(HCO<sub>3</sub>)<sub>2</sub>= 32.4 mg, CaSO<sub>4</sub> = 13.6 mg, MgCl<sub>2</sub> = 19 mg, Mg(HCO<sub>3</sub>)<sub>2</sub> = 14.6 mg.

**Solution:** Carbonate hardness or temporary hardness is due to the presence of bicarbonates of Ca and Mg. But permanent hardness is due to the presence of chlorides and sulphates of calcium and magnesium in water.

Dissolved salt	Quantity	Multiplication factor	CaCO <sub>3</sub> equivalents(mg/l)
Ca(HCO <sub>3</sub> ) <sub>2</sub>	32.4	100 162	$\frac{32.4 \times 100}{162} = 20$
CaSO <sub>4</sub>	13.6	100 136	$\frac{13.6 \times 100}{136} = 10$
MgCl <sub>2</sub>	19	100 95	$\frac{19 \times 100}{95} = 20$
Mg(HCO <sub>3</sub> ) <sub>2</sub>	14.6	100 146	$\frac{14.6 \times 100}{146} = 10$

Carbonate hardness due to Ca(HCO<sub>3</sub>)<sub>2</sub> + Mg(HCO<sub>3</sub>)<sub>2</sub> = 20+10 = 30 ppm

Non carbonate hardness due to CaSO<sub>4</sub> + MgCl<sub>2</sub> = 10+20 = 30 ppm

Total hardness = Temporary hardness + permanent hardness = 30+30 = 60 ppm

**Problem 4:** Calculate the temporary and permanent hardness of a water sample containing the following data. Ca(HCO<sub>3</sub>)<sub>2</sub>=162 mg/L, CaSO<sub>4</sub> =136 mg/L, MgCl<sub>2</sub> = 95 mg/L, Mg(HCO<sub>3</sub>)<sub>2</sub> = 73 mg/L, CaCl<sub>2</sub> = 111 mg/L

**Solution:** Temporary hardness is due to the presence of bicarbonates of Ca and Mg while permanent hardness is due to the presence of chlorides and sulphates of calcium and magnesium in water.

Dissolved salt	Quantity	Multiplication factor	CaCO <sub>3</sub> equivalents(mg/l)
Ca(HCO <sub>3</sub> ) <sub>2</sub>	162	100 162	$\frac{162 \times 100}{162} = 100$
CaSO <sub>4</sub>	136	100 136	$\frac{136 \times 100}{136} = 100$
MgCl <sub>2</sub>	95	100 95	$\frac{95 \times 100}{95} = 100$
Mg(HCO <sub>3</sub> ) <sub>2</sub>	73	100 146	$\frac{73 \times 100}{146} = 50$
CaCl <sub>2</sub>	111	100 111	$\frac{111 \times 100}{111} = 100$

Temporary hardness due to Ca(HCO<sub>3</sub>)<sub>2</sub> + Mg(HCO<sub>3</sub>)<sub>2</sub> = 100+50 = 150 ppm

Permanent hardness due to CaSO<sub>4</sub> + MgCl<sub>2</sub> + CaCl<sub>2</sub> = 100+100+100 = 300 ppm

Total hardness = Temporary + permanent hardness = 300+150 = 450 ppm

## 8.7 ESTIMATION OF WATER HARDNESS

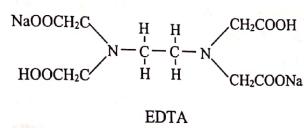
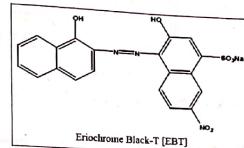
Water hardness is generally caused by the presence of Ca<sup>2+</sup> and Mg<sup>2+</sup> ions present in water. Some other polyvalent ions like strontium, iron, aluminum, zinc, manganese etc., also contribute to hardness. But because of their very low concentration in natural water, hardness is generally measured as the concentration of only calcium and magnesium ions. Estimation of hardness of water is very essential for its use in boilers for steam generation as well as for industrial uses. If dissolved salts of calcium and magnesium are relatively large, the water is hard. It is essential to determine the hardness before industrial applications. Different methods are used for the estimation of water hardness such as;

- O.Henner's method.
- Soap titration method.
- EDTA method.

## 8.8 ESTIMATION OF WATER HARDNESS BY EDTA METHOD

It is a complexometric method for the determination of the hardness of water. EDTA (Disodium salt of ethylene diamine tetraacetic acid) is used as the titrant and Eriochrome Black-T (EBT) as indicator. The titration is conducted at a pH of 10. The end point of titration is the color change from wine red to blue.

Eriochrome Black-T (EBT) as indicator. The titration is conducted at a pH of 10. The end point of titration is the color change from wine red to blue.



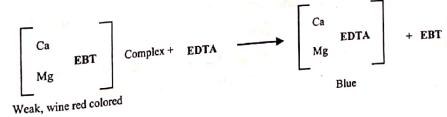
Disodium salt of ethylenediamine tetraacetic acid

### Principle of the Titration

Estimation of hardness by EDTA method is based on the principle that EDTA forms metal complexes with hardness producing metal ions in water. These complexes are stable when the pH is maintained between 8 to 10. In order to maintain the pH, buffer solution (NH<sub>4</sub>Cl and NH<sub>4</sub>OH) is added. The completion of the titration is indicated by Eriochrome Black-T (EBT) indicator. When indicator is added to the sample water, it forms indicator -metal complexes of purple red color.



When this solution is titrated against EDTA, EDTA replaces the indicator from the metal complex. When all the hardness causing ions are complexed by EDTA, the indicator is set free and the end point is the sharp change in color from purple red to blue.



**Procedure****1. Preparation of solutions and their standardization**

- a) **Standard hard water:** Dissolve one gram of pure dry calcium carbonate in the required minimum quantity of dilute HCl and evaporate to dryness. The residue obtained is dissolved in distilled water and made up to 1L. Each mL of this solution is equivalent to 1mg of CaCO<sub>3</sub> equivalent hardness.
- b) **EDTA solution:** Dissolve 4 g of pure EDTA crystals and 0.1 g of MgCl<sub>2</sub> in 1L of distilled water.
- c) **Eriochrome black-T indicator:** Dissolve 0.5g Eriochrome black-T in 100 ml alcohol.
- d) **Buffer solution:** 67.5g ammonium chloride is added to 570 ml of liquor ammonia and diluted to 1L using distilled water.

**2. Standardization of EDTA**

50 ml of the standard hard water in a 250 ml conical flask is mixed with 10-15 ml buffer solution, 2-3 drops of EBT, titrated against EDTA from the burette. At the end point, wine red color changes to blue, let V<sub>1</sub> be the volume of EDTA used.

$$V_1 \text{ ml of EDTA} = 50 \text{ ml of standard hard water.}$$

Since each ml standard hard water contains 1 mg of CaCO<sub>3</sub>,

$$V_1 \text{ ml of EDTA} = 50 \text{ mg of CaCO}_3$$

$$1 \text{ ml EDTA} = \frac{50}{V_1} \text{ mg of CaCO}_3 \text{ equivalent hardness}$$

**3. Determination of total hardness**

50 ml of unknown hard water is titrated with EDTA, let the volume of EDTA is V<sub>2</sub> ml.

$$50 \text{ ml of unknown hard water} = V_2 \text{ ml. of EDTA.}$$

$$50 \text{ ml of unknown hard water} = \frac{V_2 \times 50}{V_1} \text{ mg of CaCO}_3 \text{ equivalent hardness}$$

$$1 \text{ ml of unknown hard water} = \frac{V_2}{V_1} \text{ mg of CaCO}_3 \text{ equivalent hardness}$$

$$1000 \text{ ml of unknown hard water} = \frac{V_2 \times 1000}{V_1} \text{ mg of CaCO}_3 \text{ equivalent hardness}$$

$$\text{Total hardness} = \frac{V_2 \times 1000}{V_1} \text{ mg/L or ppm.}$$

**4. Determination of permanent hardness**

250 ml of hard water is boiled and temporary hardness is removed as CaCO<sub>3</sub> and Mg(OH)<sub>2</sub>, filtered and made up to 250ml, from that 50 ml is taken (contains only permanent hardness) and titrated with EDTA. Let V<sub>3</sub> be the volume of EDTA used,

$$50 \text{ ml of boiled water sample} = V_3 \text{ ml. of EDTA.}$$

$$50 \text{ ml of boiled water sample} = \frac{V_3}{V_1} \times 50 \text{ mg of CaCO}_3 \text{ equivalent hardness}$$

$$1000 \text{ ml (1L) of boiled water} = \frac{V_3}{V_1} \times 1000 \text{ mg of CaCO}_3 \text{ equivalent hardness}$$

$$\text{Hence permanent hardness} = \frac{V_3}{V_1} \times 1000 \text{ mg/L or ppm}$$

**5. Calculation of temporary hardness.**

Temporary hardness = Total hardness - Permanent hardness

$$= \frac{V_2}{V_1} \times 1000 - \frac{V_3}{V_1} \times 1000 \text{ CaCO}_3 \text{ equivalent hardness}$$

$$= \frac{V_2 - V_3}{V_1} \times 1000 \text{ CaCO}_3 \text{ equivalent hardness}$$

**Problem 5:** 50ml of a hard water required 15ml of EDTA solution for titration (1ml of EDTA = 1mg of CaCO<sub>3</sub>). Calculate the hardness of the sample of water.

**Solution:** 1ml of EDTA = 1mg of CaCO<sub>3</sub> equivalent

$$15 \text{ ml of EDTA} = 15 \text{ mg of CaCO}_3 \text{ equivalent}$$

This amount of hardness is present in 50ml of hard water.

$$\text{So, hardness present in one liter} = \frac{15}{50} \times 1000 = 300 \text{ ppm of CaCO}_3 \text{ equivalent}$$

**Problem 6:** 0.28 g of CaCO<sub>3</sub> was dissolved in 1 liter of water. 100 ml of this solution on titration required 28 ml of EDTA. 100 ml of unknown hard water sample required 33 ml of same EDTA. After boiling and cooling, 100 ml of this unknown sample required 10 ml EDTA. Calculate temporary and permanent hardness.

**Solution:** 1 liter sample hard water = 0.28 g in terms of CaCO<sub>3</sub>

$$1 \text{ ml sample hard water} = \frac{0.28}{1000} = 0.28 \text{ mg of CaCO}_3$$

$$28 \text{ ml EDTA} = 100 \text{ ml standard hard water}$$

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

$$= 28 \text{ CaCO}_3 \text{ equivalent}$$

For unknown solution, total hardness = 33 ml EDTA = 33 mg CaCO<sub>3</sub>

$$100 \text{ ml unknown water} = 33 \text{ ml EDTA}$$

$$1 \text{ ml of unknown water} = \frac{33}{100} \text{ mg CaCO}_3$$

$$1000 \text{ ml unknown water} = \frac{33}{100} \times 1000 \text{ mg CaCO}_3 = 330 \text{ mg CaCO}_3 = 330 \text{ ppm}$$

**Permanent hardness**

$$\begin{aligned}
 100 \text{ ml boiled unknown water sample} &= 10 \text{ ml EDTA} \\
 &= 10 \text{ mg CaCO}_3 \text{ equivalent} \\
 1 \text{ ml of unknown boiled water} &= \frac{10}{100} \text{ mg CaCO}_3 = 10 \text{ mg CaCO}_3 \\
 1000 \text{ ml unknown water} &= \frac{10}{100} \times 1000 = 100 \text{ mg CaCO}_3 \text{ equivalent} \\
 \text{Temporary hardness} &= \text{Total hardness} - \text{permanent hardness} \\
 &= 330 - 100 = 220 \text{ ppm CaCO}_3 \text{ equivalent}
 \end{aligned}$$

**Example 7:** 100 ml of a sample of water required 20 ml of 0.01M EDTA for the titration with Eriochrome Black-T indicator. 100ml of the same sample after boiling and filtering required, 10ml of 0.01M EDTA. Calculate the total, carbonate (temporary) and non-carbonate (permanent) hardness of the sample.

**Solution:** Total hardness

$$\begin{aligned}
 1 \text{ ml of } 0.01 \text{ M EDTA} &= 1 \text{ mg of CaCO}_3 \text{ equivalent} \\
 20 \text{ ml of } 0.01 \text{ M EDTA} &= 20 \text{ mg of CaCO}_3 \text{ equivalent} \\
 \text{This amount of hardness is present in } 100 \text{ ml of the water sample.} \\
 \text{Total hardness present in 1 liter} &= \frac{20}{100} \times 1000 = 200 \text{ ppm of CaCO}_3 \text{ equivalent}
 \end{aligned}$$

**Permanent or non-carbonate hardness**

$$\begin{aligned}
 1 \text{ ml of } 0.01 \text{ M EDTA} &= 1 \text{ mg of CaCO}_3 \text{ equivalent} \\
 10 \text{ ml of } 0.01 \text{ M EDTA} &= 10 \text{ mg of CaCO}_3 \text{ equivalent}
 \end{aligned}$$

This amount of hardness is present in 100ml of the water sample.

$$\text{So, permanent hardness in 1 liter} = \frac{10}{100} \times 100 = 100 \text{ ppm of CaCO}_3 \text{ equivalent}$$

**Carbonate or temporary hardness**

$$\begin{aligned}
 \text{Carbonate hardness} &= \text{total hardness} - \text{non carbonate hardness} \\
 &= 200 - 100 = 100 \text{ ppm of CaCO}_3 \text{ equivalent}
 \end{aligned}$$

**8.9 MUNICIPAL WATER TREATMENT**

Rivers, lakes and wells are the most common sources of water used by municipalities. The actual treatment methods depend directly on the impurities present. For removing various types of impurities (Table 8.5) the following treatment processes are employed.

**Screening:** Is the process of removing floating materials like wood pieces and leaves from water. Raw water is allowed to pass through a screen having a large number of holes which removes the small and large floating matter.

**Sedimentation:** Sedimentation is the process of removing suspended impurities by allowing water to stand undisturbed for 2-6 hours in large tanks. Due to force of gravity, most of the suspended particles settle down at the bottom and they are removed. Sedimentation removes 70-75% of the suspended matter.

**Coagulation:** Finely divided silica, clay, etc. do not settle down easily and hence cannot be removed by sedimentation. Most of these are in colloidal form and are negatively charged and hence do not coalesce due to mutual repulsion. Such impurities are removed by coagulation method. Here, certain chemicals like alum ( $\text{Al}_2(\text{SO}_4)_3$ ) are added to water. When  $\text{Al}_2(\text{SO}_4)_3$  is added to water, it hydrolyzes to form a gelatinous precipitate of  $\text{Al(OH)}_3$ . The gelatinous precipitate of  $\text{Al(OH)}_3$  entraps finely divided and colloidal impurities, settles to the bottom and can be removed easily.

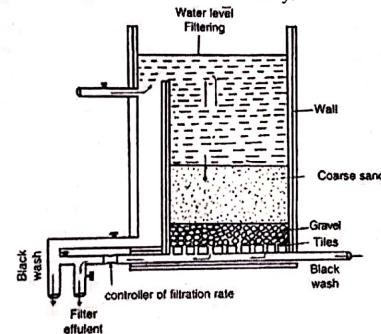


Fig. 8.2 Sand filter

**Filtration:** For removing bacteria, color, taste, odor, fine suspended particles, etc. and to produce clear water, filtration is used. In this process, water is passed through beds of fine sand, coarse sand and other granular material. The porous material used is the filtering medium and the equipment used for filtration is known as filter, e.g. Sand filter. It consists of a tank containing thick beds of fine sand (at the top), coarse sand, fine gravel and coarse gravel (at the bottom). When water passes through the filtering medium, it flows through the various beds slowly due to gravity. The rate of filtration decreases due to the clogging of impurities in the pores of the sand bed. When the rate of flow becomes very slow, filtration is stopped and the bed is cleaned by scraping off

a smaller layer of the sand bed (top layer) and replacing it with the clean sand. Bacteria are partly removed by this filtration process.

Table 8.5 Types impurities and removal processes

No	Impurity	Process used for removal
1	Floating matter such as leaves and wood pieces	Screening
2	Suspended impurities such as clay and sand	Sedimentation
3	Fine suspended matter (silt)	Coagulation
4	Microorganisms and colloidal matter	Filtration
5	Pathogenic bacteria	Disinfection (Sterilization)

## 8.10 SOFTENING METHODS

Water used for industrial purposes (for boilers and steam generation) should be sufficiently pure. It should, therefore, be freed from hardness-producing salts before applications. The process of removing hardness-producing salts from water is known as softening of water. In industry, mainly the following methods are employed to soften water.

1. Zeolite or Permutit process
2. Ion - exchange process
3. Lime-soda process

### Ion Exchange or De-Mineralization Process

Ion exchange method is an external treatment method in which temporary and permanent hardness of water can be removed. An ion exchange resin is a cross linked organic polymer network having some ionisable groups. Basically these resins are high molecular weight organic polymers with porous structure. The functional groups attached to the polymeric chains are responsible for the ion exchange properties.

#### Principle of Ion Exchange Process

Ion exchangers are materials that are capable to exchange ions (cations or anions) with ionic components in a solution. In fact ion exchange process is a reversible chemical reaction where an ion from a solution is exchanged for a similarly charged ion attached to a stationary solid phase. These solid exchangers can be either synthetic or naturally occurring inorganic zeolites. Ion exchangers can be either cation exchangers that can exchange positively charged ions (cations) or anion exchangers that can exchange

negatively charged ions (anions). Ion-exchange resins are insoluble, cross-linked, high molecular weight organic polymers with porous structure. The functional groups attached to the polymeric chains are responsible for the ion exchange properties.

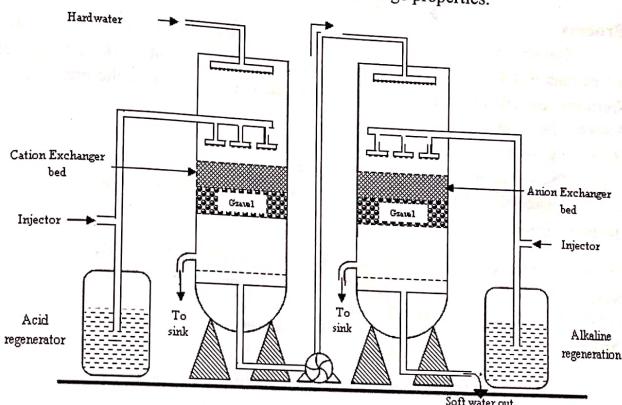
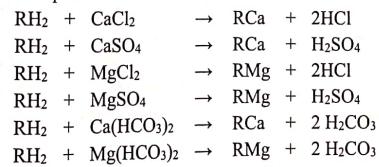
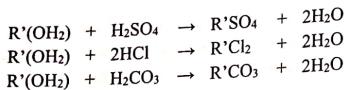


Fig.8.3 Ion Exchange Process

1. **Cation exchange resins ( $R^+H^+$ ):** These resins have acidic functional groups like  $-SO_3H$ ,  $-COOH$  or  $-OH$  (phenolic) capable of exchanging the cations of minerals by their hydrogen ions. For example, when styrene-divinyl benzene copolymers on sulphonation or carboxylation becomes capable to exchange their  $H^+$  ions with the cations in water sample.



2. **Anion exchange resin ( $R^+OH^-$ ):** When styrene-divinyl benzene or amine formaldehyde copolymers containing functional groups such as amino, quarternary ammonium, tertiary sulphonium groups, are treated with dil.  $NaOH$ , they become capable of exchanging their  $OH^-$  present in water.

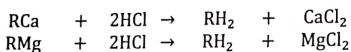
**Process**

The hard water is passed first through a cation exchange column, which removes all cations like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  etc. from it, and equivalent amount of  $\text{H}^+$  ions are released from this column to water. The outgoing water is acidic due to the presence of  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{CO}_3$  etc.

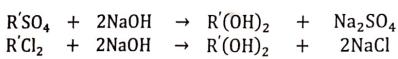
After this, water is passed through anion exchange bed where acids are converted to water. The water flowing out of the anion exchange column is free from all cations and anions. Hence, the water is called deionized water or demineralized water.

**Regeneration**

When capacities of cation and anion exchangers to exchange  $\text{H}^+$  and  $\text{OH}^-$  are lost, they are said to be exhausted. The exhausted cation exchange resin is regenerated by passing a solution of dilute  $\text{HCl}$  or dilute  $\text{H}_2\text{SO}_4$  (after stopping the water supply). The regeneration can be represented as



Similarly, the exhausted anion exchange resin is regenerated by passing dilute  $\text{NaOH}$  through the solution. The regeneration can be represented as

**Mixed Bed deionizer**

The mixed bed deionizer consists of a single cylinder containing an intimate mixture of strongly acidic cation exchanger and a strongly basic anion exchanger. When water is passed through this mixed bed, it comes in contact, a number of times, with the two kinds of exchangers alternatively. This is equivalent to passing hard water through a series of anion and cation exchangers. This method is very effective and the residual hardness of treated water is 0-10 ppm.

**Advantages of Ion exchange process**

1. Highly acidic or alkaline water can be treated by this process.
2. This produces water of very low hardness (nearly 2 ppm).
3. More efficient removal of salts.

**Disadvantages of Ion exchange process**

1. The equipment is costly and more expensive chemicals are required.
2. If water contains turbidity, then the output is reduced.

**8.11 DESALINATION / DESALTING**

The process of removing common salt (sodium chloride) from water is known as desalination. Water containing high concentrations of dissolved salts with a peculiar salty taste is known as brackish water. Sea water is an example of brackish water and it contains about 3.5% dissolved salts. Brackish water is totally unfit for drinking purpose, domestic and industrial applications. Commonly used techniques for the desalination of brackish water are

1. Reverse osmosis.
2. Electro dialysis
3. Freezing
4. Distillation

**8.12 REVERSE OSMOSIS**

Reverse osmosis is one of the most promising methods for desalting the brackish water.

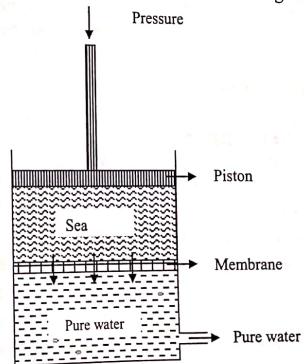


Fig.8.4 Reverse osmosis

**Principle of Reverse Osmosis**

Osmosis is the flow of solvent molecules from a region of low concentration to a region of higher concentration through a semi-permeable membrane (Note: a semi-

permeable membrane is a selective membrane which does not permit the flow of dissolved solute particles). The flow continues till the concentration is equal on both sides. The driving force for osmosis is the osmotic pressure. When a pressure higher than the osmotic pressure is applied externally, osmosis takes place in the opposite direction which is known as reverse osmosis. In reverse osmosis, pure solvent is separated from its contaminants rather than removing contaminants from water.

#### Reverse Osmosis Process

In actual process, the sea water, which is to be purified, is taken in a chamber separated by semi-permeable membrane (films of cellulose acetate, polyamide polymers, poly methacrylate etc.) from the other chamber containing pure water. A pressure of about 15-40 kg/m<sup>2</sup> is applied on the sea water side, to force its pure water out through the semi-permeable membrane, leaving behind the dissolved solids (ionic and no-ionic).

#### Advantages

1. It removes ionic, non-ionic, colloidal and high molecular weight organic impurities.
2. The life time of semi permeable membrane is high.
3. Low capital, operation and maintenance cost.
4. It removes colloidal silica which is not removed by demineralization.
5. The membrane can be replaced within few minutes, thereby ensuring uninterrupted water supply.
6. Simple and reliable process.

#### 8.13 STERILIZATION / DISINFECTION

Disinfection is normally the last step in purifying drinking water. Even after filtration, water still contains a small percentage of disease producing (pathogenic) bacteria which must be removed or destroyed if the water has to be used for drinking or municipal purposes. The process of destroying/killing the pathogenic bacteria, micro-organisms etc. from water to make it safe for use is known as disinfection. It does not ensure total destruction of all living organisms. On the other hand, sterilization means complete destruction of all living organisms. The following methods are generally used for the sterilization of water.

#### Characteristics of an ideal disinfectant

1. It should kill the disease producing micro-organisms quickly at room temperature.
2. It should be inexpensive.
3. It should not be toxic to humans.

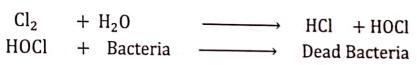
4. It should provide protection against any contamination in water during transportation or storage.

Table 8.6 Various disinfection methods

Chemical Methods	Physical methods
Addition of potassium permanganate	By simple boiling
Addition of bleaching powder	By sunlight
Using chloramine	By UV light
Addition of Ozone	
Chlorination process	

#### Chlorination

Sterilization by chlorine is the most common sterilizing method in water treatment. Chlorine may be added directly as a gas or in the form of concentrated solution in water. When Chlorine is added to water, HOCl which acts as a powerful germicide is produced. It is believed that HOCl reacts with bacteria and inactivate the enzymes present in the cells of bacteria. These enzymes are responsible for the metabolic activities of microorganisms. Since these enzymes are inactivated, microorganisms become dead.



#### Advantages

1. It is effective and economical
2. Requires less space for storage
3. It is stable and does not deteriorate on keeping
4. It introduces no salt impurities in water
5. Most ideal disinfection

#### Disadvantages

1. Excess of chlorine if added produces characteristic unpleasant taste and odor.
2. Excess chlorine causes irritation to mucous membrane.
3. Excess of chlorine precipitates other ingredients present in it.

#### 8.14 BREAK POINT OF CHLORINATION

Break point of chlorination means the chlorination of water to such an extent that living organisms as well as other organic impurities in water are destroyed. It involves the addition of sufficient amount of chlorine to oxidize organic matter, reducing substances,

and free ammonia in raw water, leaving behind mainly free chlorine which possesses disinfecting action against pathogenic bacteria. It is also known as Free-residual chlorination. The typical relationship between the amount of chlorine added to water and the experimentally determined free residual chlorine is shown in the graph (Fig.8.6).

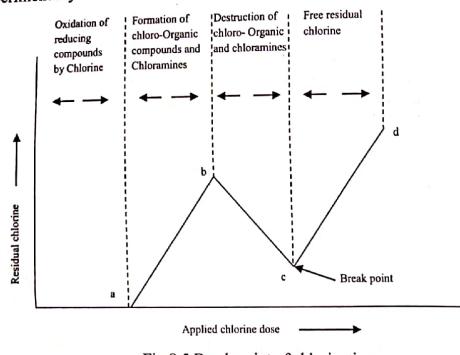


Fig.8.5 Break point of chlorination

- Initially for lower doses of chlorine, there is no residual chlorine since all the added chlorine gets consumed for the complete oxidation of reducing substances present in water.
- As the amount of chlorine dosage increases, the residual chlorine also increases due to the formation of chloro-organic compounds and chloramines.
- At still higher dosage of chlorine, oxidation of organic compounds and microorganisms takes place. When the oxidative destruction is complete it reaches minima.
- After minima, the added chlorine is not used for any action. Thus, the residual chlorine increases in proportion to added chlorine.

Hence, for effectively killing the microorganisms, sufficient chlorine (corresponding to the minima in the curve) has to be added. Addition of chlorine in such dosages is known as **break-point** or free-residual chlorination.

#### Advantages of Break Point of Chlorination

- It ensures complete destruction of organic compound which imparts color, bad odor and unpleasant taste to water.

- It completely destroys all disease causing bacteria.
- It prevents the growth of any weeds in water.

#### 8.15 STERILIZATION BY UV LIGHT

Ultraviolet (UV) light is electromagnetic radiation traveling in wavelengths in all directions from its emitting source (bulb). Sterilization by UV rays is carried out by exposing water to ultraviolet rays.

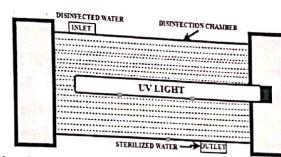


Fig. 8.6 Basic schematic of UV unit with bulb

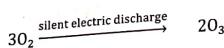
This is the latest method for the sterilization of drinking water and is preferred over all the chemical methods. UV light penetrates an organism's cell walls and disrupts the cells' genetic activities, making reproduction impossible. The absorption of UV energy by microbes results in photochemical damage to nucleic acids (RNA and DNA). The high energy associated with UV radiation ranging from 200-300 nm forms new bonds between adjacent nucleotides, creating dimmers and killing the pathogens instantly. UV light kills bacteria and virus very quickly. Since the process does not introduce any chemicals, it is widely used in domestic and commercial water purification systems. Water free from suspended impurities is fed in to the sterilization unit through an inlet. And inside the chamber sterilization takes place. Pure water can be collected through the outlet. In practice, all the suspended particles are removed before sterilization and UV rays from a mercury lamp enclosed in quartz container is used as the source. The process is quite expensive and can't be used for the sterilization of municipal water supply.

#### Advantages of UV Sterilization

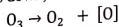
- No odor or taste is imparted to water.
- No toxic byproducts.
- No danger of overdosing.
- Requires very little contact time.
- Removes organic contaminants.
- Simple to install, operate, and maintain.
- Inline process requiring no contact tanks.

### 8.16 DISINFECTION BY OZONE /OZONATION

Ozone is an excellent disinfectant, which is produced by passing silent electric discharge through cold and dry oxygen.



Ozone is highly unstable and breaks down, liberating nascent oxygen.



The nascent oxygen is a very powerful oxidizing agent and kills almost all the bacteria as well as oxidizes the organic matter present in water. For carrying out the disinfection by ozone, ozone is released/injected to the water and the two are allowed to come in contact in a sterilization tank. The disinfected water is removed from the top. The contact period is about 10-15 minutes and the usual dose strength is 2-3 ppm.

#### Advantages of Ozone sterilization

1. The process is not harmful, since it is unstable and decomposes to oxygen.
  2. The taste of water is improved with ozone.
  3. It removes color, odor etc. without any residue.
- But ozone sterilization is an expensive process.

### 8.17 DISSOLVED OXYGEN (D.O)

Free oxygen is necessary for organisms to live in sewage water. Dissolved oxygen is the amount of free, non-compound oxygen present in water or other liquids. The measurement of dissolved oxygen gives a ready assessment of the purity of water. The determination of DO is the basis for B.O.D (Biochemical Oxygen Demand) test, which is commonly used to evaluate the pollution level of waste water. The determination of DO is also essential for maintaining aerobic conditions in water and waste water treatment.

#### Winkler's Method

The dissolved oxygen in water can be determined by Winkler's method. This method for measuring dissolved oxygen was introduced in 1888 by L.W.Winkler of Budapest. In fact this is one of the most useful titrations for the determination of the amount of dissolved oxygen in water.

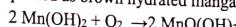
**Principle:** This method is based on the fact that in alkaline medium, dissolved oxygen oxidizes  $\text{Mn}^{2+}$  to  $\text{Mn}^{4+}$ , which in turn, in acidic medium oxidizes  $\text{I}^-$  to free iodine. The

amount of liberated iodine can be estimated by titrating with a standard solution of sodium thiosulphate using starch as indicator. The end point is indicated by the disappearance of blue color. The amount of iodine is indirectly equivalent to the DO amount. The following reactions take place:

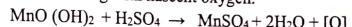
1. When  $\text{MnSO}_4$  and alkaline KI are added, a white precipitate of  $\text{Mn}(\text{OH})_2$  is formed.



2. The dissolved oxygen (DO) present in the sample oxidizes some of the  $\text{Mn}^{2+}$  to  $\text{Mn}^{4+}$ , which is precipitated as brown hydrated manganese dioxide.



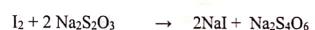
3. When  $\text{H}_2\text{SO}_4$  is added, after sometime, hydrated manganese dioxide reacts with the acid to give  $\text{MnSO}_4$  along with nascent oxygen.



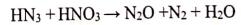
4. Nascent oxygen reacts with KI in the solution in presence of  $\text{H}_2\text{SO}_4$  to liberate iodine.



5. The liberated iodine is estimated by titrating it with standard  $\text{Na}_2\text{S}_2\text{O}_3$  solution using freshly prepared starch as indicator.



**Alsterberg's modification:** The oxidizing agents present in water such as nitrate and ferric ions oxidize  $\text{I}^-$  to  $\text{I}_2$  and give positive error. To overcome this problem, sodium azide is used in alkaline iodide solution to decompose the nitrite or sulphite. This is known as Alsterberg's modification.



**Rideal –Stewart modification:** The reducing agents like  $\text{Fe}^{2+}$ ;  $\text{SO}_3^{2-}$  or  $\text{S}^{2-}$  can reduce  $\text{I}_2$  to  $\text{I}^-$  and produce negative error. To overcome this problem,  $\text{KMnO}_4$  is used for pretreatment. Excess  $\text{KMnO}_4$  is removed by reaction with potassium oxalate. This is known as Ideal –Stewart modification.

**Procedure:** The water sample is collected in specially designed bottles having a stopper, known as DO bottles. Carefully fill a 250 ml DO bottle with the water sample eliminating any further dissolution of atmospheric oxygen. Add 2 ml of manganous sulphate solution and 2 ml of alkaline KI solution. Stopper the bottle and shaken thoroughly. Allow the precipitate to settle completely for 15 minutes and then add 2 ml of conc.  $\text{H}_2\text{SO}_4$ . Shake

the bottle until the precipitate dissolves completely and release free iodine. Pipette 100ml of the solution and titrate against N/100 standard  $\text{Na}_2\text{S}_2\text{O}_3$  (hypo) using starch as indicator. End point is the disappearance of blue color. From the titre value, the strength of dissolved oxygen is calculated and hence, the amount of dissolved oxygen in water sample is calculated. To standardize  $\text{Na}_2\text{S}_2\text{O}_3$  solution, a standard solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  can be used. 1 ml of 0.01N  $\text{Na}_2\text{S}_2\text{O}_3$  solution  $\equiv$  0.1 mg of D.O

### 8.18 SEWAGE

Sewage is commonly a cloudy, dilute aqueous solution containing minerals and organic matter. Sewage is the liquid waste, which includes human and house-hold waste water, street washings, storm waters and ground wastes. About 75% water pollution is caused by sewage, domestic wastes and food processing units. Sewage contains about 99.9 percent water and the rest organic and inorganic matters in dissolved, suspended and colloidal state. It also includes human excreta, soap, detergent, metals, glass, etc. The indiscriminate method of handling the domestic sewage may cause pollution of underground water sources. If sewage or partially treated sewage is discharged in to water bodies, such as river, there are higher chances of water pollution. Fresh domestic sewage is, usually, grey-green to grey-yellow in color. It darkens rapidly with time due to decomposition and an offensive smell is produced (due to the evolution of hydrogen sulphide, phosphine, ammonium sulphide etc.)

**Constituents of sewage:** Sewage contains

1. Domestic sewage contains human excreta as well as discharges from kitchen, baths and lavatories.
2. Industrial and trade wastes, tanneries, slaughter houses oil refineries etc.
3. Storm water, which is rain water from houses and streets.
4. Ground water entering through severs.

Sewage consists of bacteria and other microorganisms. Bacteria are more active and it is of two types.

1. Aerobic bacteria.
2. Anaerobic bacteria

### Aerobic Oxidation Process

Organic compounds present in sewage undergo oxidation in presence of excess of oxygen and aerobic bacteria are called aerobic oxidation. Aerobic oxidation products are inoffensive smelling, non-putrefying nitrates, sulphates, phosphates etc. Aerobic

oxidation produces large quantity of bio mass and  $\text{CO}_2$ . About 50 % of the biodegradable carbon present in sewage is converted to bio mass and rest in to  $\text{CO}_2$ .

Table 8.7 Difference between Aerobic oxidation and anaerobic oxidation

No	Aerobic oxidation	Anaerobic oxidation
1	Oxidation of organic compounds present in the sewage occurs in presence of aerobic bacteria.	Oxidation of organic compounds present in the sewage occurs in presence of anaerobic bacteria.
2.	Takes place in presence of excess of oxygen.	Takes place in the absence or insufficient quantity of oxygen.
3.	Is a rapid process.	Is a slow process.
4.	No fuels produced during aerobic oxidation (except $\text{CO}_2$ )	Biogas fuels are produced during anaerobic oxidation.
5.	About 50% of the organic matter is converted to biomass and rest into $\text{CO}_2$	About 90-95% of organic matter present in the waste water is converted to bio gas and remaining into biomass.
6.	Produces inoffensive salts like nitrates, phosphates, sulphates etc.	Anaerobic oxidation produces offensive smelling gases like hydrogen sulphide, methane, etc.
7.	Utilized in trickling filter process.	Used in UASB process.
8.	There is no putrefaction.	Results in putrefaction of sewage.
9.	Biodegradation of organic wastes.	Fermentation of yeast.

### Anaerobic Oxidation Process

The oxidation of organic compounds in sewage by anaerobic bacteria in the absence of or insufficient quantity of oxygen is called anaerobic oxidation. This results in putrefaction of the sewage, producing methane, hydrogen sulphide, phosphine, etc with offensive smell. When the anaerobic decomposition is continuing, the sewage is known as "septic sewage". Anaerobic oxidation is a slow process. The digested sludge is safer to be used as manure than undigested sludge.

### Biochemical Oxygen Demand (B.O.D)

Biochemical oxygen demand (B.O.D) represents the quantity of oxygen required by aerobic bacteria and other microorganisms during the biochemical degradation and transformation of organic matter present in waste water under aerobic conditions at 20°C

for five days. BOD test is a very valuable test in the analysis of sewage, industrial effluents and waste waters. It gives information regarding the purification capacity of streams and serves as a guide line for Regulatory Authorities to check the quality of effluents discharged in to water bodies. BOD is expressed in mg/liter or ppm. Sewage sample usually gives a BOD value in between 100 to 150 mg/liter. Higher the BOD greater the pollution.

**Limitations of BOD:** 1) High concentration of active bacteria is necessary in the sample. 2) Pre-treatment of sewage necessary if it also contains toxic wastes. 3) Before the test, the effects of nitrifying organisms are to be reduced. 4) Time for the test is too long. 5) Test is applicable only for bio-degradable organic matter.

#### Determination of Biochemical oxygen demand (B.O.D)

The BOD test essentially consists of the measurement of dissolved oxygen content of the sample, before and after incubation at 20°C for 5 days. While carrying out the BOD test, microbial organism (called seed) may have to be provided if necessary. A known volume of sample of sewage is diluted with a known volume of dilution water (containing nutrients for bacterial growth), its dissolved oxygen content is determined using a dissolved oxygen meter. The whole solution is incubated in a closed bottle at 20°C for 5 days. After this, the unused oxygen is determined. The difference between the initial and final oxygen content will give BOD.

$$\text{Thus, BOD } 5 = \frac{(D_1 - D_2) \times \text{Volume of sample after dilution}}{\text{Volume of sample before dilution}}$$

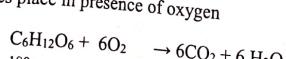
Where  $D_1$  = D.O of sample in mg/l at the beginning of the experiment

$D_2$  = D.O of sample in mg/l after 5 days

The dilution of 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.

**Example 8:** Calculate the BOD value of a sewage sample containing 9.2 mg/l of organic matter with the formula  $C_6H_{12}O_6$ .

**Solution:** Gram molecular weight of  $C_6H_{12}O_6$  =  $[6 \times 12 + 12 \times 1 + 6 \times 16] = 180$  g  
Oxidation of  $C_6H_{12}O_6$  takes place in presence of oxygen



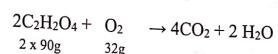
From the above equation it is clear that 180 mg/l of  $C_6H_{12}O_6$  requires 192 mg/l of oxygen for the complete oxidation of sewage water.

Therefore, 1 mg/l of  $C_6H_{12}O_6$  requires  $\frac{192}{180}$  mg/l of oxygen for oxidation.

Required oxygen for 9.2 mg/l of sewage water =  $9.2 \times \frac{192}{180} = 9.813$  mg/l of oxygen.  
Hence BOD of given sewage water = 9.813 mg/l

**Example 9:** An effluent water sample emerging out from a chemical factory is found to contain only an organic compound of molecular formula  $C_2H_2O_4$ . If the waste water required to oxidize by micro organisms under experimental conditions of BOD estimation. [ C=12, H=1, and O=16].

**Solution:** Gram molecular weight of  $C_2H_2O_4$  =  $[2 \times 12 + 2 \times 1 + 4 \times 16] = 90$  g  
Oxidation of  $C_2H_2O_4$  takes place in presence of oxygen



Therefore, 1 mg/l of  $C_2H_2O_4$  requires  $\frac{32}{180}$  mg/l of oxygen for oxidation

Required oxygen for 60 mg/l of sewage water =  $60 \times \frac{32}{180} = 10.67$  mg/l  
Hence BOD of given sewage water = 10.67 mg/l

**Example 10:** 100 ml sewage water is diluted to 1000 ml with dilution water; the initial dissolved oxygen was 7.6 ppm, dissolved oxygen level after five days of incubation was 3.2 ppm. Find the BOD of the sewage water. (KTU June 2019)

**Solution:**

$$\text{BOD} = \frac{(D_1 - D_2) \times \text{Volume of sample after dilution}}{\text{Volume of sample before dilution}} = \frac{(7.6 - 3.2) \times 1000}{100} = 4.4 \times 10 = 44 \text{ mg/l}$$

**Example 11:** 6 ml of waste water is diluted to 300 ml distilled water in standard BOD bottle. Initial D.O in the bottle is determined as 8.5 mg/l. DO after 5 days at 20°C is found to be 5 mg/l. Determine the BOD of waste water.

**Solution:**

$$\text{BOD} = \frac{(D_1 - D_2) \times \text{Volume of sample after dilution}}{\text{Volume of sample before dilution}} = \frac{(8.5 - 5) \times 300}{6} = 3.5 \times 50 = 175 \text{ mg/l}$$



### 8.19 SEWAGE TREATMENT

From public health point of view, sewage needs proper treatment, before its disposal in to rivers, lakes or land. The major objectives behind sewage water treatment are.

1. To make it inoffensive so that it causes no odor or nuisance.
2. To eliminate possible contamination of water bodies and bathing areas.
3. To prevent the destruction of fish and aquatic life in rivers, canals etc.

Sewage treatment involves the following steps.

1. **Screening or preliminary process:** It involves the removal of large and coarse solids, inorganic materials, suspended and floating materials in sewage. This involves in passing the sewage through bar screens and mesh screens.

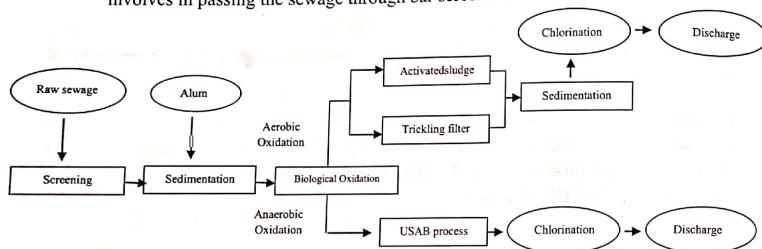


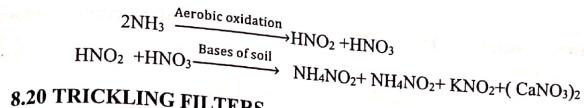
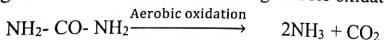
Fig.8.7 Sewage Treatment

2. **Sedimentation or Settling process:** The suspended organic and inorganic matter is removed by this process. Sedimentation is done in large sedimentation tanks. The suspended particles settle down due to gravity. Sedimentation is accelerated by coagulants like alum,  $\text{FeSO}_4$  etc. The settled solids called 'raw sludge' are removed mechanically. This process helps to reduce about 50% of the whole BOD.

3. **Secondary (Biological) treatment process:** The secondary treatment process involves the biological oxidation of organic compounds at aerobic or anaerobic conditions.

1. **Aerobic treatment process:** During aerobic oxidation process, the carbon of the organic matter is converted in to  $\text{CO}_2$ , nitrogen in to  $\text{NH}_3$  and finally in to nitrates and nitrates.

The following chemical reactions occur during aerobic oxidation treatment of sewage.



### 8.20 TRICKLING FILTERS

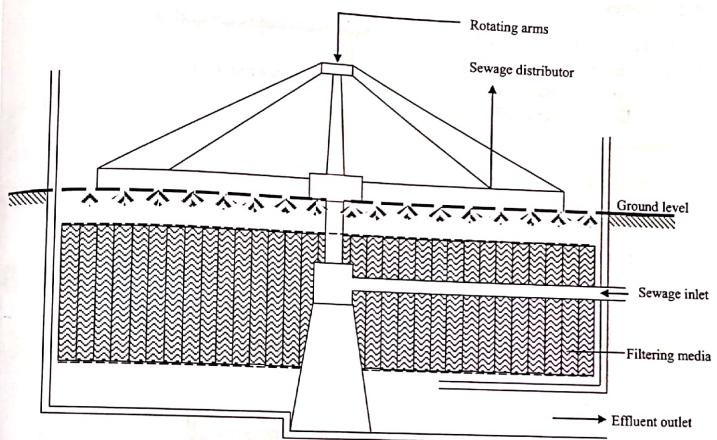


Fig.8.8 Trickling Filter treatment

Trickling filters are the most widely used secondary aerobic treatment process. Trickling filter consists of a rectangular or circular tank of about 2 m depth. The tank is filled with either coarse, crushed rock or large anthracite coal or graded clinkers. There is a drain at the bottom to collect the treated effluent. Sewage is delivered to the filters by means of a rotating distributor.

#### Working of trickling filters

Sewage is delivered to the filters by means of a rotating distributor. As the trickled sewage starts percolating downwards, through the filtering media, microorganisms (present in sewage) grow on the surface, aerobic oxidation takes place and the sewage gets purified. The treated sewage (effluent) can be collected through the bottom drain. The spraying mechanism helps to saturate the waste water with oxygen and supports to

maintain aerobic conditions. This can help to the development of a gelatinous film containing microorganisms.

#### Advantages

1. Trickling filter can produce effluents of consistent and better quality.
2. It can bring down the BOD level to 60-65%.
3. Simple to operate and constant manual attention is not required.
4. Low manpower requirement

#### Disadvantages

1. High capital investment
2. Efficiency decreases with increase in load.

#### 8.21 UP FLOW ANAEROBIC SLUDGE BED UASB PROCESS

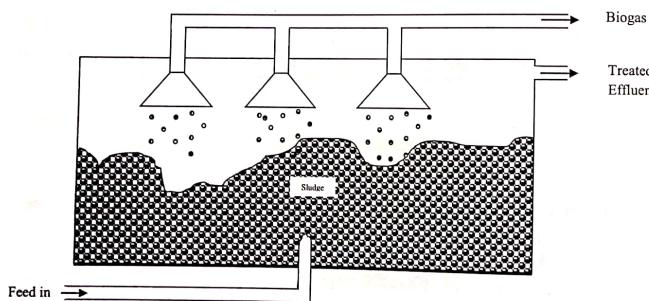


Fig.8.9 UASB Process

USAB process is a secondary anaerobic oxidation treatment method, based on the settle ability of microbial flocs. UASB reactor consists of a rectangular tank with proper inlet and outlet for feeding and collecting the effluent. There is mechanism for the collection of fuels formed. In this process, the effluent is fed from the bottom of the reactor, so that it moves upward through the sludge blanket. The sludge blanket is basically biologically formed granules of diameter 1 to 1.5 mm. As the waste water comes in contact with the granules, anaerobic oxidation takes place and gases like

methane are formed. The temperature is maintained around 35°C and the gases are collected through the gas collector domes fitted to the top of the reactor. USAB process is the most preferred method of sewage treatment in developing countries, due to its low capital cost and integrated pollution control mechanism.

#### Advantages of USAB process

1. Low capital investment than trickling filters.
2. Biogas produced as additional resource.

#### SOLVED PROBLEMS

**Example 1:** 0.5 g of  $\text{CaCO}_3$  was dissolved in dil. HCl and diluted to 500ml with distilled water. 50ml of this solution required 48ml of EDTA solution for titration. 50ml of a hard water sample required 15ml of the same EDTA solution for titration. Calculate the total hardness of water.

**Solution:** 500ml of standard hard water  $\approx$  0.5g of  $\text{CaCO}_3$

1 ml of Standard hard water	$= 0.5 \times 1000 = 500 \text{ mg of } \text{CaCO}_3$
50ml of Standard hard water	$\approx 1 \text{ mg of } \text{CaCO}_3$
48ml of EDTA solution	$= 50 \text{ mg of } \text{CaCO}_3$
1ml of EDTA solution	$= 50 \text{ mg of } \text{CaCO}_3$
	$= \frac{50}{48} \times 1 = 1.04 \text{ mg of } \text{CaCO}_3$

#### Total hardness

1ml of EDTA solution	$= 1.04 \text{ mg of } \text{CaCO}_3$
15ml of EDTA solution	$= 1.04 \times 15 = 15.6 \text{ mg of } \text{CaCO}_3$

This amount of hardness is present in 50ml of the water sample.

∴ Total hardness present in 1 liter	$= \frac{15.6}{50} \times 1000$
	$= 312 \text{ ppm of } \text{CaCO}_3 \text{ equivalent}$

**Example 2:** 0.25g of  $\text{CaCO}_3$  was dissolved in dil. HCl and diluted to 250 ml. 100 ml of this solution required 20 ml of EDTA solution for titration. 100ml of a hard water sample required 30ml of the same EDTA solution for titration. 100ml of the same water sample on boiling, filtering required 10ml of EDTA. Calculate the total, permanent and temporary hardness.

**Solution:** 250 ml of standard hard water  $= 0.25 \text{ g of } \text{CaCO}_3$

$$= 0.25 \times 1000 = 250 \text{ mg of } \text{CaCO}_3$$

1 ml of standard hard water = 1 mg of  $\text{CaCO}_3$

#### Standardization of EDTA

100 ml of standard hard water = 100 mg of  $\text{CaCO}_3$

20ml of EDTA solution = 100 mg of  $\text{CaCO}_3$

1ml of EDTA solution =  $\frac{100}{20} \times 1 = 5 \text{ mg of } \text{CaCO}_3$

#### Total hardness

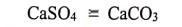
30ml of EDTA solution =  $30 \times 5 = 150 \text{ mg of } \text{CaCO}_3$

This amount of hardness is present in 100ml of the hard water.

$$\therefore \text{Total hardness present in 1 liter} = \frac{150}{100} \times 1000 \\ = 1500 \text{ ppm of } \text{CaCO}_3 \text{ equivalent}$$

**Example 3:** A water sample contains 204 mg of  $\text{CaSO}_4/\text{L}$ . Calculate the hardness in terms of  $\text{CaCO}_3$  equivalent.

**Solution:**



$$136 \text{ g mol}^{-1} \equiv 100 \text{ g mol}^{-1}$$

$$\therefore 136 \text{ mg/L of } \text{CaSO}_4 \equiv 100 \text{ mg/L } \text{CaCO}_3 \text{ equivalent}$$

$$1 \text{ mg/L of } \text{CaSO}_4 \equiv 100/136$$

$$204 \text{ mg/L of } \text{CaSO}_4 \equiv \frac{100}{136} \times 204 \text{ mg/L } \text{CaCO}_3 \text{ equivalent}$$

$$\text{Hardness of } \text{CaSO}_4 = 150 \text{ mg/L } \text{CaCO}_3 \text{ equivalent}$$

**Example 4:** How many grams of  $\text{FeSO}_4$  dissolved per litre gives 210.5 ppm of hardness? ( Fe = 56, S = 32, O = 16, Ca = 40, C = 12)

**Solution:**  $\text{FeSO}_4 \equiv \text{CaCO}_3$

$$\text{i.e } 56 + 32 + 4 \times 16 \equiv 152 \text{ mg } \text{FeSO}_4 \equiv 100 \text{ mg } \text{CaCO}_3$$

$$\text{Therefore, } 100 \text{ ppm of hardness} \equiv 152 \text{ mg } \text{FeSO}_4$$

$$210.5 \text{ ppm of hardness} = \frac{152}{100} \times 210.5 = 319.96 \text{ mg/L of } \text{FeSO}_4$$

**Example 5:** How many grams of  $\text{MgCO}_3$  dissolved per litre gives 84 ppm of hardness?

**Solution:** Hardness =  $\frac{\text{Mass of } \text{MgCO}_3 \text{ in mg/L} \times 100}{\text{Molecular weight of hardness producing substance}}$

$$\text{Mass of } \text{MgCO}_3 \text{ for producing } 84 \text{ mg/L hardness} = 84 \times 84 / 100 = 70.56 \text{ mg/L}$$

**Example 6:** Calculate the temporary, permanent and total hardness of water (in ppm) having the following composition.  $\text{Ca}(\text{HCO}_3)_2 = 4 \text{ ppm}$ ,  $\text{Mg}(\text{HCO}_3)_2 = 6 \text{ ppm}$ ,  $\text{CaSO}_4 = 8 \text{ ppm}$ ,  $\text{MgSO}_4 = 10 \text{ ppm}$ ,  $\text{NaHCO}_3 = 3 \text{ ppm}$ .

**Solution:**  $\text{NaHCO}_3$  removes permanent hardness causing ions. Hence its presence will increase the temporary hardness while the total hardness remains same.

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

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

$$\text{Permanent hardness} = \text{Total hardness} - \text{Temporary hardness} = 20.79 - 8.37 = 12.42 \text{ ppm}$$

#### IMPORTANT QUESTIONS

- Describe the estimation of hardness of a sample of water by EDTA method.
- Describe how water is softened by ion exchange process
- Describe the various steps of purification of drinking water
- Give the principle of EDTA titration. Briefly describe the estimation of permanent hardness of water by EDTA method. (K.U.2009, 2008 Jun)
- Write the notes on the following:
  - Write the structure of EDTA
  - What is the principle of EDTA titration? Briefly describe the estimation of hardness of water by EDTA method. OR. Write short note of complexometric titration
  - What is the role of buffer in EDTA solution? (SK, Jun 01; GGSIP, Mar 2000)
  - In the determination of hardness of water by EDTA method,  $\text{NH}_4\text{OH-NH}_4\text{Cl}$  buffer is used. Why? (RGPV, May 01)
- Describe one method used for the desalination of water. (2008, Jun)
- Write notes on the following:
  - What is the principle of EDTA titration? Briefly describe the estimation of hardness of water by EDTA method. OR. Write short note of complexometric titration
  - What is the role of buffer in EDTA solution? (SK, Jun 01; GGSIP, Mar 2000)
  - In the determination of hardness of water by EDTA method,  $\text{NH}_4\text{OH-NH}_4\text{Cl}$  buffer is used. Why? (RGPV, May 01)
- Write notes on the following:
  - Describe in detail the ion exchange process for softening demineralization of water. (Anna, Jul 2000; GGSIP, Mar 2000; MK, Apr 01., K.U.April 2014)
  - What is demineralized water how is it different from soft water? ( Tripura, 2000; Anna, Nov2000, Jan 01; KU, Dec 97, May 99, Jan 01; PT, Dec 97; SK, Jun 01)

10. Distinguish between temporary and permanent hardness. What are the different units of hardness? (Anna 2006, Jun K.U. April 2014)
11. In hardness estimation by EDTA method 50ml of a sample of hard water required 30ml of a standard solution of EDTA. Calculate the hardness of a sample of water (1ml of EDTA solution is equivalent to 1.8 mg of  $\text{CaCO}_3$ )
12. A sample of water contains 0.02%  $\text{CaSO}_4$  and 0.1%  $\text{MgCl}_2$ . Calculate the degree of hardness in ppm and degree Clark. (K.U. 2009, Jun)
13. Calculate the hardness of a water sample containing the following (a) Calcium chloride = 20mg (b) Magnesium sulphate = 48mg (c) Magnesium chloride = 52.5mg (Molecular mass of calcium chloride, Magnesium sulphate and magnesium chloride are 111, 120 and 95 respectively. (K.U. 1999)
14. If a water sample has hardness 210.5 ppm, find its hardness in Clarke's degree. (KU 2002) [Answer: 14.73 C]
15. Explain the different steps involved in the sewage treatment. (KU.2009, June)
16. What is the significance of BOD and COD in the sewage treatment?
17. How is BOD determined? Explain the USAB process. (KU.2009, June)
18. Describe the working of Trickling Filter with a neat labeled sketch. (KTU 2019 June)
19. Discuss the steps involved in sewage water treatment. (KTU 2019 June)
20. Compare aerobic and anaerobic oxidation of sewage water. (KTU 2019 June)
21. Define reverse osmosis (KTU 2019 June)
22. How is exhausted resin regenerated from an Ion-exchange process? (KTU 2019 June)
23. Water sample contains 204 mg of  $\text{CaSO}_4$  per litre. Calculate its hardness in terms of  $\text{CaCO}_3$  equivalents. (KTU 2019 June)