WATER

SYLLABUS

- Introduction Impurities in water, hardness of water- units (no conversions), types and numerical problems
- Determination of hardness of water by EDTA method and numerical problems
- Softening of water by Ion Exchange process and numerical problems
- BOD, COD- definition, significance and numerical problems
- Water purification-membrane technology- Electrodialysis, Reverse osmosis, and Ultra filtration

6.1 INTRODUCTION

Water is nature's most wonderful, abundant and useful compound. It is essential for the lives of all living kingdom including man, animal and plants. It has occupied a unique position in industries. It acts as a coolant in power and chemical plants. It is widely used in other fields such as rayon, paper, chemicals, ice, textiles, and production of steel. In addition to that, it is used for drinking, bathing, sanitary, washings, irrigation, fire fighting etc. It's most important use as an engineering material is in 'Steam Generation'. Thus, the science of water has become most important aspect for the mankind.

Earth, our planet on which we live is called **blue planet** because 4/5th of the earth's crust is covered with water. But the hard fact of life is that about 97% of it is locked in ocean which is too saline to drink and for direct use for agricultural and industrial purposes. Out of what is left, about 80% is trapped in polar ice caps. Another 10% of it is locked in rock crevices and minerals lying as deep as 800 meters below the Earth's crust. Only about 0.3% of the world's water resources is available for domestic, agriculture and industrial purposes. Still we do not understand the importance of water and continuously misuse it.

6.2 SOURCES OF WATER

While studying the various sources of water, our focus remains on the difference in the chemical composition of water with respect to its source.

The available water sources are:

- (i) Rain water: It is purest form of naturally occurring water since it is obtained from evaporation of surface water which is nature's own wonderful distillation unit. By the time, rain water reaches the Earth's surface, it gets contaminated due to the several gases like Carbon dioxide, Sulphur dioxide, nitrogen dioxide, ammonia etc. and also the suspended solid particles present in the atmosphere.
- (ii) River water: Rivers are fed by rain and spring waters. Water from these sources flow over the surface of land, dissolves the soluble minerals of the soil and falls into the river. River water thus contains dissolved minerals of the soil such as chlorides, sulphates, bicarbonates of sodium, calcium, magnesium and iron. It also contains organic matter derived from decomposition of plants and small particles of sand and rock in suspension.
- (iii) Lake water: It has more constant chemical composition with high amount of organic matter.
- (iv) Sea water: It is the most impure form of natural water. It contains 3.5% of dissolved salts of which sodium chloride constitutes about 2.6%. The other salts present are sulphates of sodium, bicarbonates of potassium, magnesium and calcium, bromides of potassium and magnesium etc.
- (v) Spring and well water: Rain water percolates underground to form springs and wells which contain more dissolved salts and high hardness.

6.3 HARDNESS OF WATER

Hardness in water is that characteristic which prevents the lathering of soap. Water is said to be hard when it does not produce lather readily with soap in contrast to soft water. Hardness in water is attributed to the presence of dissolved salts of calcium, magnesium and to a minor extent certain heavy metals such as iron. These metal ions form insoluble precipitate with the fatty acid components of soap.

Soap generally consists of sodium salts of long chain fatty acid such as oleic acid, palmetic acid and stearic acid. Hard water when treated with soap, sodium or potassium salt of higher fatty acid does not produce lather but forms precipitate. Thus, it does not possess any detergent value. Typical reactions of soap (sodium stearate) with calcium chloride and magnesium sulphates can be written as follows:

$$2C_{17}H_{35}COONa + CaCl_2 \longrightarrow (C_{17}H_{35}COO)_2 Ca \downarrow + 2NaCl$$

Sodium stearate Hardness Calcium stearate (Insoluble)

$$2C_{17}H_{35}COONa + MgSO_4 \longrightarrow (C_{17}H_{35}COO)_2 Mg \downarrow + Na_2SO_4$$

Sodium stearate Hardness Magnesium stearate (Insoluble)

Hard and Soft Water: Water which does not produce lather with soap solution readily but forms a white curd is called *hard water*. On the other hand, water which lathers easily on shaking with soap solution is called *soft water*. Such water does not contain dissolved calcium and magnesium salts in it. Hard water consumes much more amount of soap to produce the same amount of lather as compared to soft water because initially the soap is utilized to precipitate the hardness causing metal ions. The anions usually associated with these metal ions include chloride, sulphate, and bicarbonate but these do not contribute to the hardness of water.

6.3.1 Types of Hardness

There are two types of hardness:

(i) Temporary or Carbonate or Alkaline Hardness:

It is caused by the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals and the carbonate of iron.

The temporary hardness can be easily destroyed by mere boiling of water. On boiling, bicarbonates are decomposed, yielding insoluble carbonates or hydroxides which are deposited as a crust at the bottom of the vessel and carbon dioxide sets free.

$$\begin{array}{c} \text{Ca (HCO}_{3})_{2} & \xrightarrow{\text{heat}} & \text{CaCO}_{3} \downarrow + \text{H}_{2}\text{O} + \text{CO}_{2} \uparrow \\ & \text{Calcium} & \text{carbonate} \end{array}$$

$$\begin{array}{c} \text{Mg (HCO}_{3})_{2} & \xrightarrow{\text{heat}} & \text{Mg (OH)}_{2} \downarrow + \text{CO}_{2} \uparrow \\ & \text{Magnesium} & \text{hydroxide} \end{array}$$

(ii) Permanent or Non-carbonate or Non-alkaline Hardness:

It is caused due to the presence of chlorides, nitrates, sulphates etc. of calcium, magnesium and other metals. This type of hardness cannot be removed by adapting easy means like boiling. It requires special chemical treatment for removal of hardness causing salts, such as internal conditioning or external treatment which involves the softening methods.

Permanent hardness is obtained by subtracting the value of temporary hardness from total hardness.

Thus, Total Hardness = [Temporary Hardness + Permanent Hardness].

6.3.2 Causes of Hardness

When water flows over or percolates through the ground rocks or solids, there are various physical and chemical changes that take place. Due to these changes, it gets contaminated with dissolved salts of calcium and magnesium. We call it as hardness of water.

The various changes causing hardness of water are as follows:

- (i) **Dissolution:** Mineral constituents of rocks like sodium chloride, gypsum (CaSO₄.2H₂O) etc. dissolved in it.
- (ii) Hydration: Some minerals like anhydrite (CaSO₄), Olivine (Mg₂SiO₄) etc undergo hydration leading to the formation of products of increased volume, due to which the disintegration of mineral bearing rocks take place.

$$\begin{array}{c} \text{CaSO}_4 \ + \ 2\text{H}_2\text{O} \xrightarrow{\text{Hydration}} \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \\ \text{(Anhydrite)} \end{array} \xrightarrow{\text{(Gypsum)}} \text{CaSO}_4 \cdot x\text{H}_2\text{O} \\ \text{(Gypsum)} \\ \text{Mg}_2\text{SiO}_4 \ + \ x\text{H}_2\text{O} \xrightarrow{\text{Hydration}} \text{Mg}_2\text{SiO}_4 \cdot x\text{H}_2\text{O} \\ \text{(Olivine)} \end{array}$$

(iii) Action of dissolved oxygen: Dissolved oxygen brings about oxidation and hydration reactions.

(iv) Action of dissolved carbon dioxide:

(a) It converts insoluble carbonates of calcium, magnesium and iron into soluble bicarbonates.

For example,

$$\begin{array}{c} \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} & \longrightarrow \text{Ca}(\text{HCO}_3)_2 \\ \text{Insoluble} & \text{Soluble} \end{array}$$

$$\begin{array}{c} \text{MgCO}_3 + \text{CO}_2 + \text{H}_2\text{O} & \longrightarrow \text{Mg}(\text{HCO}_3)_2 \\ \text{Insoluble} & \text{Soluble} \end{array}$$

(b) It converts rock forming silicates and alumino silicates of sodium, potassium, calcium and iron into soluble carbonates, bicarbonates and silica.

For example,

$$K_2O.Al_2O_3.6SiO_2 + CO_2 + 2 \ H_2O \longrightarrow Al_2O_3.2Si.O_2.2H_2O + K_2CO_3 + 4SiO_2$$

(c) Rocks containing felspar disintegrate and charge nearby river water with dissolved salts, fine clay and silica in suspension.

Comparisons:

	Temporary Hardness		Permanent Hardness	
1.	It is due to bicarbonates and carbonates of Ca ²⁺ , Fe ²⁺ , Mg ²⁺ etc.	:	It is due to chlorides, sulphates, nitrates of Ca ²⁺ , Fe ²⁺ , Mg ²⁺ etc. other than carbonates and bicarbonates.	
2.	It is known as carbonate or alkaline hardness.	2. It is known as non-carbonate or non-alkaline hardness.		
3.	Temporary hardness leads to formation of loose deposits of carbonates and hydroxides of Ca ²⁺ , Mg ²⁺ respectively, if used in boilers.		Permanent hardness leads to formation of adherent scales.	
4.	Temporary hardness can be removed by simple techniques such as boiling and filtering.	:	Permanent hardness cannot be removed by simple techniques such as boiling and filtering.	

	Hard Water		Soft Water	
produ	water is one which does not ace lather with soap solution ly but forms a white curd.	l	Soft water gives lather easily on shaking it with soap solution.	
	water contains dissolved calcium nagnesium salts.		Soft water does not contain dissolved calcium and magnesium salts in it.	
and	nsing quality of soap is depressed a lot of soap is wasted during ing and bathing.		Cleansing quality of soap is not depressed and soap is not wasted during washing and bathing.	
produ eleva	to presence of dissolved hardness ucing salt, boiling point of water is ted. Consequently more fuel and are required for cooking.		Less fuel and time are required for cooking in the soft water.	

6.4 UNITS OF HARDNESS

Although hardness of water is never present in the form of calcium carbonate as it is insoluble in water, hardness of water is conveniently expressed in terms of equivalent

amount of CaCO₃. Calcium carbonate is chosen particularly for reporting the hardness of water since it simplifies the calculations as its molecular weight is 100. Moreover, it is the most insoluble salt that can be precipitated in water treatment.

The equivalents of CaCO₃

- = [Mass of hardness producing substance] × [Chemical equivalent of CaCO₃] Chemical equivalent of hardness producing substance
- = Mass of hardness producing substance × 50 Chemical equivalent of hardness producing substance

Table 6.1: Calculation of Equivalents of Calcium Carbonate

Dissolved Salt/Ion	Molar Mass	Chemical Equivalent	Multiplication Factor for converting into Equivalents of CaCO ₃
Ca(HCO ₃) ₂	162	81	100/162
Mg(HCO ₃) ₂	146	73	100/146
CaCO ₃	100	50	100/100
MgCO ₃	84	42	100/84
CaCl ₂	111	55.5	100/111
MgCl ₂	95	47.5	100/95
CaSO ₄	136	68	100/136
MgSO ₄	120	60	100/120
Mg(NO ₃) ₂	148	74	100/148
CO_2	44	22	100/44
HCO ₃ ⁻	61	61	100/61 × 2
CO ₃ ²⁻	60	30	100/60
OH ⁻	17	17	100/34
NaAlO ₂	82	82	100/82 × 2
Al ₂ (SO ₄) ₃	342	57	100/114
FeSO ₄ .7H ₂ O	278	139	100/278
\mathbf{H}^{+}	1	1	100/2
HC1	36.5	1	100/73

Following are the units for expressing hardness of water in terms of CaCO₃ equivalent:

(1) Parts per million (ppm): It is the part of calcium carbonate equivalent hardness present per 10⁶ parts of water.

1 ppm = 1 part of $CaCO_3$ equivalent hardness in 10^6 parts of water

(2) Milligrams per litre (mg/L): It is the number of milligrams of calcium carbonate equivalent hardness present per litre of water.

1 mg/L = 1 mg of $CaCO_3$ equivalent hardness of 1litre water But 1 L weighs 1 Kg.

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

$$1 \text{ mg/L} = 1 \text{ mg of CaCO}_3 \text{ equivalent per } 10^6 \text{ mg of water}$$

$$= 1 \text{ parts of CaCO}_3 \text{ equivalent per } 10^6 \text{ mg of water}$$

$$= 1 \text{ ppm}$$

(3) Clarke's Degree (°Cl): It is number of grains (1/7000 lb) of CaCO₃ equivalent hardness per gallon (10 lb) of water or it is part of CaCO₃ equivalent hardness per 70,000 parts of water.

1 °Clarke =1 grain of CaCO₃ equivalent hardness per gallon of water.

Or 1 °Clarke = 1 part of CaCO₃ equivalent hardness per 70,000 parts of water.

(4) **Degree French** (°Fr): It is the part of CaCO₃ equivalent hardness per 10⁵ parts of water.

1 °Fr = 1 part of CaCO₃ equivalent hardness per 10⁵ parts of water.

Relationship between various units:

1 ppm = 1 mg/L =
$$0.1^{\circ}$$
 Fr = 0.07° Cl
1 mg/L = 1 ppm = 0.1° Fr = 0.07° Cl
1° Cl = 1.43° Fr = 14.3 ppm = 14.3 mg/L
1° Fr = 10 ppm = 10 mg/L = 0.7° Cl

Degree of hardness is total quantity of hardness causing salts present in water and it is expressed in terms of CaCO₃ equivalent quantity. It may be called total hardness of water. The degree of hardness in a water sample can be found by methods like EDTA titration, soap solution titration. The water sample may contain temporary hardness causing salts or permanent hardness causing salts. Thus, degree of hardness or total hardness can be represented as

Degree of hardness = Permanent hardness + Temporary hardness

The degree of hardness in natural water varies from sample to sample.

NUMERICALS BASED ON HARDNESS OF WATER

Problem 1: Calculate temporary hardness and permanent hardness of water sample from the following data:

 $Mg(HCO_3)_2 = 16.8 mg/L, MgCl_2 = 19 mg/L, MgSO_4 = 24 mg/L,$

 $Mg(NO_3)_2 = 29.6 \text{ mg/L}, CaCO_3 = 4 \text{ mg/L}, MgCO_3 = 10 \text{ mg/L}$

Solution: Conversion into CaCO₃ equivalent:

Constituents	Quantity in mg/L	Multiplication factor	CaCO ₃ equivalent
Mg(HCO ₃) ₂	16.8	100/146	11.5
MgCl ₂	19	100/95	20
MgSO ₄	24	100/120	20
Mg(NO ₃) ₂	29.6	100/148	20
Ca CO ₃	04	100/100	4
MgCO ₃	10	100/84	11.9

$$Temporary \; Hardness \; = \; Hardness \; due \; to \; [Mg(HCO_3)_2 + CaCO_3 + MgCO_3]$$

$$= 11.5 + 04 + 11.9$$

Permanent Hardness = Hardness due to
$$[MgCl_2 + MgSO_4 + Mg(NO_3)_2]$$

$$= 20 + 20 + 20$$

= 60 mg CaCO₃ equivalent / litre

Thus,

Problem 2: Calculate carbonate and non-carbonate hardness of water containing following impurities in mg/L:

$$Mg(HCO_3)_2 = 7.1$$
, $Ca(HCO_3)_2 = 8.1$, $MgCO_3 = 4.2$, $CaCO_3 = 10$, $MgSO_4 = 24$.

Solution: Conversion into CaCO₃ equivalent:

Constituents	Quantity in mg/L	Multiplication factor	CaCO ₃ equivalent
Mg(HCO ₃) ₂	7.1	100/146	05
Ca(HCO ₃) ₂	8.1	100/162	05
MgCO ₃	4.2	100/84	05
CaCO ₃	10	100/100	10
MgSO ₄	24	100/120	20

Carbonate Hardness = Hardness due to
$$[Mg(HCO_3)_2 + Ca(HCO_3)_2 + CaCO_3 + MgCO_3]$$

$$= 05 + 05 + 05 + 10$$

$$= 25 \text{ ppm}$$
Non-carbonate Hardness = Hardness due to MgSO₄

$$= 20 \text{ ppm}$$

Thus,

Carbonate hardness = 25 ppm Non-carbonate hardness = 20 ppm

Problem 3: A sample of ground water has 150 mg/L of Ca²⁺ and 60 mg/L of Mg²⁺. Find the total hardness of water sample.

Solution: Conversion into CaCO₃ equivalent:

Constituents	Quantity in mg/L	Multiplication factor	CaCO ₃ equivalent
Ca ²⁺	150	100/40	375
Mg^{2+}	60	100/24	250

Total Hardness = Hardness due to
$$[Ca^{2+} + Mg^{2+}]$$

= 375 + 250
= 625 mg/L

Thus,

Total hardness = 625 mg/L

Problem 4: How many grams of FeSO₄ dissolved per litre gives 210.5 ppm of hardness? (Fe = 56, S = 32, O = 16, Ca = 40, C = 12).

Solution:

$$FeSO_4 = CaCO_3$$

$$136 g = 100 g$$

$$\therefore 100 \text{ ppm of hardness} = 136 \text{ ppm of FeSO}_4$$

$$\therefore 210.5 \text{ ppm of hardness} = \frac{210.5}{100} \times 136 = 286.3 \text{ ppm of FeSO}_4$$
Thus,

286.3 ppm of FeSO₄ is required

Problem 5: A water sample contains:

 $Ca(HCO_3)_2 = 32.4 \text{ mg/l}, Mg(HCO_3)_2 = 29.2 \text{ mg/l}, CaSO_4 - 13.6 \text{ mg/l}.$

Calculate temporary, permanent and total hardness.

[May 2008]

Solution: Conversion into CaCO₃ equivalent:

Constituents	Quantity in mg/l	Multiplication factor	CaCO ₃ equivalent
Ca(HCO ₃) ₂	32.4	100/162	20
$Mg(HCO_3)_2$	29.2	100/146	20
CaSO ₄	13.6	100/136	10

Temporary Hardness = Hardness due to
$$[Mg(HCO_3)_2 + Ca(HCO_3)_2]$$

= 20 + 20

=40 ppm

Permanent Hardness = Hardness due to [CaSO₄]

= 10 ppm

Total Hardness = Temporary Hardness + Permanent Hardness

= 40 + 10

= 50 ppm

Thus,

 $Temporary\ hardness = 40\ ppm,\ Permanent\ hardness = 10\ ppm,\ Total\ hardness = 50\ ppm$

Problem 6: A water sample on analysis has been found to contain following impurities in ppm:

 $Mg(HCO_3)_2 = 14.6, Mg(NO_3)_2 = 29.6, Ca(HCO_3)_2 = 8.1, MgCl_2 = 19, MgSO_4 = 24.$

Calculate the temporary and permanent hardness of water sample. [May 2009]

Solution: Conversion into CaCO₃ equivalent:

Constituents	Quantity in ppm	Multiplication factor	CaCO ₃ equivalent
Mg(HCO ₃) ₂	14.6	100/146	10
Ca(HCO ₃) ₂	8.1	100/162	05
$Mg(NO_3)_2$	29.6	100/148	20
MgCl ₂	19	100/95	20
MgSO ₄	24	100/120	20

Temporary Hardness = Hardness due to
$$[Mg (HCO_3)_2 + Ca (HCO_3)_2]$$

= 10 + 5

= 15 ppm

Permanent Hardness = Hardness due to $[Mg (NO_3)_2 + MgCl_2 + MgSO_4]$

= 20 + 20 + 20

= 60 ppm

Thus,

Problem 7: The water sample contains the following impurities in mg/L.

$$Mg(HCO_3)_2 = 7.3$$
, $MgCl_2 = 9.5$, $Ca(HCO_3)_2 = 16.2$, $CaSO_4 = 13.6$

Calculate the temporary permanent and total hardness.

[Dec 2009]

Solution: Conversion into CaCO₃ equivalent:

Constituents	Quantity in mg/L	Multiplication factor	CaCO ₃ equivalent
$Mg(HCO_3)_2$	7.3	100/146	05
MgCl ₂	9.5	100/95	10
Ca(HCO ₃) ₂	16.2	100/162	10
CaSO ₄	13.6	100/136	10

Temporary Hardness = Hardness due to
$$[Mg(HCO_3)_2 + Ca(HCO_3)_2]$$

= 5 + 10
= 15 ppm
Permanent Hardness = Hardness due to $[MgCl_2 + CaSO_4]$

$$= 10 + 10$$

Total Hardness = Temporary Hardness + Permanent Hardness

= 15 + 20= 35 ppm

Thus,

Temporary hardness = 15 ppm, Permanent hardness = 20 ppm, Total hardness = 35 ppm

Problem 8: A water sample on analysis has been found to contain

 $MgCl_2 = 19 \text{ ppm}, CaCO_3 = 5 \text{ ppm}, Ca(HCO_3)_2 = 29.5 \text{ ppm}, CaSO_4 = 13 \text{ ppm}.$

Calculate temporary, permanent and total hardness.

[May 2011]

Solution: Conversion into CaCO₃ equivalent:

Constituents	Quantity in ppm	Multiplication factor	CaCO ₃ equivalent
MgCl ₂	19	100/95	20
CaCO ₃	5	100/100	5
Ca(HCO ₃) ₂	29.5	100/162	18.21
CaSO ₄	13	100/136	9.56

Temporary Hardness = Hardness due to
$$[CaCO_3 + Ca(HCO_3)_2]$$

= 5 + 18.21
= 23.21 ppm
Permanent Hardness = Hardness due to $[MgCl_2 + CaSO_4]$
= 20 +9.56
= 29.56 ppm
Total Hardness = Temporary Hardness + Permanent Hardness
= 23.21 + 29.56
= 52.77 ppm

Thus,

 $Temporary\ hardness = 23.21ppm,\ Permanent\ hardness = 29.56ppm,\ Total\ hardness = 52.77ppm$

Problem 9: Calculate temporary, permanent and total hardness of water sample containing $Mg(HCO_3)_2 = 7.3$ ppm, $Ca(HCO_3)_2 = 16.2$ ppm, $MgCl_2 = 9.5$ ppm, $CaSO_4 = 13.6$ ppm.

[Dec 2012]

Solution: Conversion into CaCO₃ equivalent:

Constituents	Quantity in ppm	Multiplication factor	CaCO ₃ equivalent
MgCl ₂	9.5	100/95	10
Mg(HCO ₃) ₂	7.3	100/146	5
Ca(HCO ₃) ₂	16.2	100/162	10
CaSO ₄	13.6	100/136	10

Temporary Hardness = Hardness due to
$$[Mg(HCO_3)_2 + Ca(HCO_3)_2]$$

= 5 + 10
= 15 ppm
Permanent Hardness = Hardness due to $[MgCl_2 + CaSO_4]$
= 10 + 10
= 20 ppm
Total Hardness = Temporary Hardness + Permanent Hardness
= 15 + 20
= 35 ppm

Thus,

Temporary hardness = 15ppm, Permanent hardness = 20ppm, Total hardness = 35ppm

Problem 10: What is the total hardness of water sample which has following impurities in mg/l? $Ca(HCO_3)_2 = 162$, $CaCl_2 = 22.2$, $Mg Cl_2 = 95$, NaCl = 20.

[June 2013]

Solution: Conversion into CaCO₃ equivalent:

Constituents	Quantity in ppm	Multiplication factor	CaCO ₃ equivalent
MgCl ₂	95	100/95	100
CaCl ₂	22.2	100/111	20
Ca(HCO ₃) ₂	162	100/162	100
NaCl	20	-	-

Total Hardness = Hardness due to
$$[Ca(HCO_3)_2 + MgCl_2 + CaCl_2]$$

= $100 + 100 + 20 = 220 \text{ ppm}$

Thus,

Total hardness = 220ppm

Problem 11: Two samples of water A and B were analysed for their salt content:

- (i) Sample A was found to contain 168 mg MgCO₃ per litre.
- (ii) Sample B was found to contain 820 mg Ca (NO₃)₂ per litre and 2mg SiO₂ per litre.

Calculate the total hardness of each sample and state which sample is more hard.

[Dec 2013]

Solution: Hardness of sample $A = CaCO_3$ equivalent of $MgCO_3$

$$=\left(\frac{168}{84}\right) \times 100 = 200 \text{ ppm}$$

Hardness of sample $B = CaCO_3$ equivalent of $Ca(NO_3)_2$

$$=\left(\frac{820}{164}\right) \times 100 = 500 \text{ ppm}$$

Thus, the sample B is more hard than sample A.

Problem 12: Calculate all types of hardness of water sample containing:

Ca $(HCO_3)_2 - 81$ ppm, $MgSO_4 - 60$ ppm, $MgCO_3 - 42$ ppm, $Ca(NO_3)_2 - 82$ ppm.

Solution: Conversion into CaCO₃ equivalent:

[May 2015]

Constituents	Quantity in ppm	Multiplication factor	CaCO ₃ equivalent
Ca(HCO ₃) ₂	81	100/162	50
MgSO ₄	60	100/120	50
MgCO ₃	42	100/84	50
Ca(NO ₃) ₂	82	100/164	50

Temporary Hardness = Hardness due to
$$[MgCO_3 + Ca(HCO_3)_2]$$

= $50 + 50 = 100 \text{ ppm}$
Permanent Hardness = Hardness due to $[MgSO_4 + Ca(NO_3)_2]$
= $50 + 50 = 100 \text{ ppm}$
Total Hardness = Temporary Hardness + Permanent Hardness
= $100 + 100 = 200 \text{ ppm}$

Thus,

Temporary hardness = 100ppm, Permanent hardness = 100ppm, Total hardness = 200ppm

Problem 13: A hard water sample contains following impurities in ppm. $Mg(HCO_3)_2$ = 150, NaCl =77, CaCl₂ = 135, MgSO₄ = 85. Calculate temporary, permanent and total hardness of the given water sample. (May 2019)

Solution: Conversion into CaCO₃ equivalent:

Constituents	Quantity in ppm	Multiplication factor	CaCO ₃ equivalent
Mg(HCO ₃) ₂	150	100/146	102.74
MgSO ₄	85	100/120	70.83
CaCl ₂	135	100/111	121.62
NaCl	77	-	-

Temporary Hardness = Hardness due to [Mg(HCO₃)₂] = 102.74 ppm Permanent Hardness = Hardness due to [MgSO₄ + CaCl₂] = 70.83 + 121.62 = 192.45 ppm

Total Hardness = Temporary Hardness + Permanent Hardness

= 102.74 + 192.45 = 295.19 ppm

Thus,

6.5 ESTIMATION OF HARDNESS

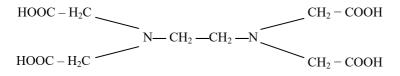
Hardness of water can be determined by two methods:

(1) Soap Solution Method: Total hardness of water can be determined by titrating a fixed volume of water sample (100 ml) against standard alcoholic soap solution. Appearance of stable lather which persists for two minutes is the end point of titration. In the beginning, sodium soap will precipitate all the hardness causing metal ions in the

form of soap and then it will form-free lather. If same water sample is boiled for 30 minutes and then titrated against same soap solution, the titration reading corresponds to permanent hardness. The difference between two measurements corresponds to the temporary hardness of water.

(2) EDTA Method: Hardness of water can be determined more accurately by EDTA method. This is a complexometric method, as EDTA forms complex ions with hardness causing Ca²⁺ and Mg²⁺ ions present in water. It is an accurate, convenient, rapid method and hence is popular.

The structure of EDTA (Ethylene diamine tetra acetic acid) is

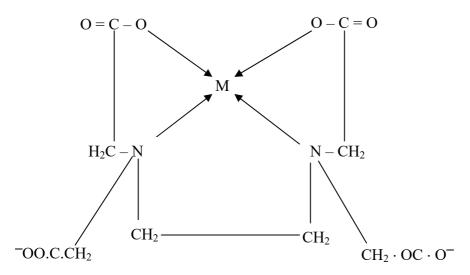


In the form of its sodium salt yields the anion

FOOC –
$$H_2C$$
 N — CH_2 — CH_2 — CH_2 — CH_2 — CH_2 — CH_2 — COO^-

EDTA is used in the form of its disodium salt. It reacts quickly with hardness causing metal ions to form cyclic coordination complex. (Chelate) Thus,

Complexation of EDTA with Ca²⁺ and Mg²⁺ ions:



Where, M = Ca or Mg

EDTA is usually employed as its disodium salt.

$$NaO.OC - H_2C \\ \hline N-CH_2 - CH_2 - N \\ \hline CH_2 - COOH \\ \hline$$

In order to determine the equivalence point, alcoholic solution of blue coloured dye Erichrome Black-T is used which forms unstable wine red complex with Ca²⁺ and Mg²⁺ ions. pH of about 10 is required for this reaction otherwise it will not go to completion.

$$\begin{array}{c} M^{2+} + EBT & \xrightarrow{\quad pH \,=\, 10 \quad} [M - EBT] \; complex \\ (Ca^{2+} \; or \; Mg^{2+} \; of \; hard \; water) & Wine \; red \end{array}$$

During the course of titration against EDTA solution, EDTA combines with M²⁺ ions to form stable complex M-EDTA releasing EBT which combines with M²⁺ ions present in the solution and wine red colour is retained.

When all M²⁺ ions formed [M-EDTA] complex, the next drop of EDTA added displaces the EBT indicator from [M-EBT] complex and the wine red colour changes to blue. This is called the equivalence point. Thus, at equivalence point,

Thus, change of wine red colour to distinct blue marks the end point of titration.

Various steps involved in EDTA titration:

- (1) Preparation of standard hard water: Dissolve 1g of pure, dry CaCO₃ in minimum quantity of dilute HCl. Boil it to dryness to expel excess of acid and CO₂. Dissolve the residue in distilled water to make 1 litre solution. Each ml of the solution contains 1 mg of CaCO₃ equivalent hardness.
- (2) Preparation of EDTA solution: Dissolve 4g of pure EDTA and 0.1g MgCl₂ in 1 litre distilled water.
- (3) Preparation of indicator: Dissolve 0.5g of Eriochrome Black-T in 100 ml of alcohol.
- **(4) Preparation of Buffer solution:** Add 67.5g of NH₄Cl to 570 ml of concentrated ammonia solution and then dilute with distilled water to 1 litre.

- (5) Titration 1: Standardization of EDTA: Rinse and fill the burette with EDTA. Pipette out 50 ml of standard hard water in a conical flask. Add 10-15 ml buffer and 4-5 drops of EBT indicator. Titrate with EDTA solution till wine red colour changes to blue. Let volume used be V₁ ml.
- (6) Titration 2: Titration of unknown hard water: Titrate 50ml of hard water sample, mixed with 15 ml buffer solution and 4-5 drops of EBT with EDTA solution till wine red colour changes to blue. Let volume used be V₂ ml.
- (7) Titration 3: Titration of permanent hardness: Take 250 ml of the water sample in a large beaker. Boil it, till the volume is reduced to about 50 ml. Filter, wash the precipitate with distilled water. Collect the filtrate and washings in a 250 ml measuring flask. Make up the volume to 250 ml with distilled water. Titrate 50 ml of it with EDTA as in Titration (1). Let the volume be V₃ ml.

Calculations:

50 ml of standard hard water = V_1 ml of EDTA.

$$\therefore$$
 50 × 1 mg CaCO₃ = V₁ ml of EDTA.

$$\therefore$$
 1 ml of EDTA = 50 / V₁ mg of CaCO₃ equivalent

Now, 50 ml of given hard water = V_2 ml of EDTA

$$= \frac{V_2 \times 50}{V_1}$$
 mg of CaCO₃ equivalent

 \therefore 1 L (1000 ml) of given hard water = 1000 V₂/V₁ mg of CaCO₃ equivalent

∴ Total hardness of water =
$$1000 \text{ V}_2/\text{V}_1 \text{ mg} / \text{L}$$

= $1000 \text{ V}_2/\text{V}_1 \text{ ppm}$... (i)

Now 50 ml of boiled water = V_3 ml of EDTA

$$= \frac{V_3 \times 50}{V_1} \text{ mg of CaCO}_3 \text{ equivalent}$$

 \therefore 1000 ml of boiled water = 1000 V₃/V₁, mg of CaCO₃ equivalent

$$\therefore$$
 Permanent hardness = 1000 V₃/V₁ ppm ... (ii)

And Temporary hardness = [Total hardness – Permanent hardness]

=
$$1000 [V_2/V_2 - V_3/V_1] ppm$$

= $1000 \left[\frac{V_2 - V_3}{V_1}\right] ppm$... (iii)

Numericals Based on Calculation of Hardness by EDTA Method:

Problem 1: 50 ml of standard hard water (1.1 mg of CaCO₃ per ml) requires 38 ml of disodium EDTA. 100 ml of water sample consumes 21 ml of EDTA during titration. Find degree of hardness of the water sample.

Solution:

Strength of standard hard water = 1.1 mg CaCO_3 per ml

50 ml standard hard water = $1.1 \times 50 = 55 \text{ mg CaCO}_3$ 50 ml standard hard water = 38 ml of EDTA equivalent

= 55 mg CaCO_3 \therefore 1 ml EDTA = $55/38 \text{ mg CaCO}_3$ 100 ml of water sample = 21 ml of EDTA \therefore 1000 ml of water sample = $\frac{1000 \times 21}{100}$ = 210 ml EDTA \therefore 1 ml EDTA = $55/38 \text{ mg CaCO}_3$ \therefore 210 ml EDTA = $210 \times 55/38$ = 303.9 mg CaCO_3

Thus,

Degree of hardness of water sample = 303.9 mg/L

Problem 2: 0.28 g of CaCO₃ was dissolved in HCl and the solution made up to 1 litre with distilled water. 100 ml of the above solution required 28 ml of EDTA solution. 100 ml of hard water sample required 33 ml of EDTA solution. After boiling of this water, cooling and filtering, 100 ml of this solution on titration required 10 ml of EDTA solution. Calculate each type of hardness of water.

Solution: Step I:

1000 ml contains 0.28 g or 280 mg

$$\therefore 1 \text{ ml will contain } = \frac{280}{1000}$$

 \therefore Strength of Hard water = 0.28 mg of CaCO₃ per ml

Step II: Now, 100 ml of standard hard water = 28 ml of EDTA

And 100 ml of standard hard water = (100×0.28) mg of CaCO₃

$$\therefore 28\text{ml of EDTA} = (100 \times 0.28) \text{ mg of CaCO}_3$$

$$1 \text{ ml of EDTA} = \frac{100 \times 0.28}{28}$$

$$1 \text{ ml of EDTA} = 1\text{mg of CaCO}_3 \text{ equivalent}$$

Step III:

100 ml of unknown hard water = 33 ml of EDTA solution
=
$$33 \times 1$$
 mg of CaCO₃

∴ 1000 ml of unknown hard water =
$$\frac{1000 \times 33}{100}$$

= 330 ppm
∴ Total Hardness = 330 ppm

Step IV:

100 ml of boiled filtered water = 10 ml of EDTA
=
$$10 \times 1$$
 mg CaCO₃ equivalent / litre.
∴ 1000 ml of boiled filtered water = $\frac{1000 \times 10}{100}$
= 100 mg of CaCO₃ / litre
Permanent Hardness = 100 ppm.
Temporary Hardness = Total Hardness – Permanent Hardness
= $330 - 100$
= 230 ppm

Thus,

Total Hardness = 330 ppm, Permanent Hardness = 100 ppm, Temporary Hardness = 230 ppm

Problem 3: 50 ml of standard hard water containing 1 mg pure CaCO₃ per ml consumed 20 ml of EDTA. 50 ml of water sample consumed 25 ml of EDTA solution using Eriochrome Black-T indicator. 50 ml of water sample after boiling, filtering consumed 18 ml of EDTA. Calculate various types of hardness of sample.

Solution: Step I:

Strength of standard hard water = 1 mg/ml $50 \text{ ml of standard hard water} = 50 \text{ mg of CaCO}_3$ 50 ml of standard hard water = 20 ml of EDTA $\therefore 1 \text{ ml of EDTA} = 50/20 \text{ mg of CaCO}_3 \text{ equivalent}$ $= 2.5 \text{ mg of CaCO}_3 \text{ equivalent}$ Step II: 50 ml of water sample = 25 ml of EDTA $\therefore 1000 \text{ ml of Water Sample} = \frac{1000 \times 25}{50} \text{ ml of EDTA}$ = 500 ml of EDTA $\therefore 1 \text{ ml EDTA} = 50/20 \text{ mg of CaCO}_3 \text{ equivalent}$ $\therefore 500 \text{ ml of EDTA} = 500 \times \frac{50}{20} \text{ of CaCO}_3 \text{ equivalent}$ $\therefore 1000 \text{ ml of EDTA} = 1000 \times \frac{50}{20} \text{ of CaCO}_3 \text{ equivalent}$ $\therefore 1000 \text{ ml of EDTA} = 1000 \times \frac{50}{20} \text{ of CaCO}_3 \text{ equivalent}$ $\therefore 1000 \text{ ml of EDTA} = 1000 \times \frac{50}{20} \text{ of CaCO}_3 \text{ equivalent}$ $\therefore 1000 \text{ ml of EDTA} = 1000 \times \frac{50}{20} \text{ of CaCO}_3 \text{ equivalent}$

Step III: 50 ml of boiled water = 18 ml of EDTA
=
$$18 \times \frac{50}{20}$$
 mg of CaCO₃

$$\therefore 1000 \text{ ml of boiled water} = \frac{1000 \times 18 \times 50}{50 \times 20}$$
= 900 mg/L

- 900 mg/1

Permanent Hardness = 900 ppm

Step IV: Temporary Hardness = Total Hardness – Permanent Hardness

= 1250 - 900= 350 ppm

Thus,

 $Total\; Hardness = 1250\; ppm,\; Permanent\; Hardness = 900\; ppm,\; Temporary\; Hardness = 350\; ppm$

Problem 4: A standard hard water contains 15 g/l calcium carbonate, 20 ml of this water required 25 ml of EDTA solution. 100 ml of sample water required 18 ml of EDTA solution. The same sample after boiling required 12 ml of EDTA solution. Calculate temporary hardness of water.

[May 2008]

Solution: Step I:

Strength of standard hard water = 15 g/l

= 15000 mg / 1000 ml

= 15 mg/ml

 \therefore 20 ml standard hard water \equiv 25 ml of EDTA solution

∴ 1 ml EDTA
$$\equiv \left[\frac{20}{25} \times 15\right]$$
 mgs of CaCO₃ Equivalent hardness $\equiv \frac{300}{25}$ mgs of CaCO₃ Equivalent hardness

= 12 mgs of CaCO₃ Equivalent hardness

Step II: $100 \text{ ml water sample} \equiv 18 \text{ ml EDTA solution}$

 \equiv [18 × 12] mgs of CaCO₃ equivalent hardness

= 216 mgs of CaCO₃ equivalent hardness

 \therefore Total hardness = 2160 ppm

Step III:

100 ml water sample (after boiling)
$$\equiv 12$$
 ml EDTA solution
$$\equiv [12 \times 12] \text{ mg of CaCO}_3 \text{ equivalent}$$

$$\equiv 144 \text{ mgs of CaCO}_3 \text{ equivalent}$$

- \therefore Permanent hardness = 1440 ppm
- \therefore Temporary hardness $\equiv 2160 1440 \text{ ppm} = 720 \text{ ppm}$

Total Hardness = 2160ppm, Permanent Hardness = 720ppm, Temporary Hardness = 1440ppm

Problem 5: 0.5 gm of CaCO₃ was dissolved in HCl and the solution made up to 500 ml with distilled water. 50 ml of the solution required 48 ml of EDTA solution for titration. 50 ml of hard water sample required 15 ml of EDTA and after boiling and filtering required 10 ml of EDTA solution. Calculate temporary hardness of water.

[May 2009]

Solution: Step I:

Strength of standard hard water = 0.5 gm CaCO₃/ 500 ml of distilled water. = 500 mg in 500 ml water = 1mg/ml

Step II: 50 ml of standard hard water required \equiv 48 ml EDTA solution

i.e. 48 ml EDTA solution $\equiv 50 \text{ mg CaCO}_3$ equivalent hardness

∴ 1 ml EDTA solution $\equiv \left(\frac{50}{48}\right)$ mg CaCO₃ equivalent hardness

Now, 50 ml water sample \equiv 15 ml EDTA solution

- :. Hardness of sample $\equiv \left[15 \times \frac{50}{48}\right]$ mg CaCO₃ equivalent for 50 ml hardness
- :. Hardness per litre of sample $\equiv \left[15 \times \frac{50}{48}\right] \times \frac{1000}{50} \text{ mg/l}$
- \therefore Total hardness = 312.5 ppm

Step III: 50 ml water sample after boiling $\equiv 10$ ml EDTA solution

- ... Permanent hardness of sample $\equiv \left(10 \times \frac{50}{48}\right)$ mg CaCO₃ equivalent for 50 ml
- \therefore Permanent hardness of 1 litre sample $\equiv \left(10 \times \frac{50}{48}\right) \times \frac{1000}{50}$ mg/l
- \therefore Permanent hardness = 208.33 ppm
- \therefore Temporary hardness \equiv Total hardness Permanent hardness $\equiv 312.5 208.33$
- \therefore Temporary hardness = 104.17 ppm

 $Total\ Hardness = 312.5ppm,\ Permanent\ Hardness = 208.33ppm,\ Temporary\ Hardness = 104.17ppm$

Problem 6: 1 g of CaCO₃ was dissolved in 1 lit of distilled water. 50 ml of solution required 45 ml EDTA for titration. 50 ml of hard water required 25 ml of EDTA for titration. The same sample of water after boiling consumed 15 ml of EDTA for titration. Calculate the hardness of water.

[Dec 2010]

Solution: Step I: Strength of standard hard water = 1 mg/ml

50 ml of Standard hard water = 50 mg of $CaCO_3$

50 ml of standard hard water = 45 ml EDTA

∴ 1 ml EDTA
$$\equiv \left(\frac{50}{45}\right)$$
 mg CaCO₃ equivalent

Step II: 50 ml of hard water sample = 25 ml of EDTA

∴ 1000 ml of hard water sample =
$$\frac{1000}{50} \times 25$$
 ml EDTA
= 500 ml EDTA
500 ml EDTA = $500 \times \frac{50}{45}$ of CaCO₃ equivalent
= 555.55 ppm

 \therefore Total hardness = 555.55 ppm

Step III: 50 ml of boiled water = 15 ml EDTA

$$\therefore 1000 \text{ ml of boiled water} = \frac{1000}{50} \times 15 \times \frac{50}{45}$$
$$= 333.33 \text{ ppm}$$

Permanent hardness = 333.33 ppm

:. Temporary hardness = Total hardness - Permanent hardness

 $\therefore \qquad \text{Temporary hardness} = 555.55 \text{ ppm} - 333.33 \text{ ppm}$ = 222.22 ppm

 $Total\ Hardness = 555.55ppm,\ Permanent\ Hardness = 333.33ppm,\ Temporary\ Hardness = 222.22ppm$

Problem 7: 50 ml sample of water required 7.2 ml of N/20 disodium EDTA for titration. After boiling and filtration, the same volume required 4 ml of EDTA. Calculate both the types of hardness in it.

[May 2011]

Solution: N/20 EDTA = 0.05 N EDTA.Step I: $1000 \text{ ml 1N EDTA} = 50 \text{ g of CaCO}_3$ $1 \text{ ml of 1N EDTA} = 50 \text{ mg of CaCO}_3$ 50 ml water sample = 7.2 ml of 0.05 N EDTA

$$\therefore 1000 \text{ ml of water sample} = \frac{1000}{50} \times 7.2 \text{ ml of } 0.05 \text{ N EDTA}$$
$$= 144 \text{ ml of } 0.05 \text{ N EDTA}$$

As $1 \text{ml} \text{ of } 1 \text{N EDTA} = 50 \text{ mg of } \text{CaCO}_3$

∴ 144 ml of 0.05 N EDTA =
$$144 \times 0.05 \times 50$$
 mg of CaCO₃ = 360 ppm

Total Hardness of water = 360 ppm

$$\therefore 1000 \text{ ml of boiled water} = \frac{1000}{50} \times 4 \text{ ml of } 0.05 \text{ N EDTA}$$

= 80 ml of 0.05 N EDTA

As, 1 ml of 1 N EDTA = 50 mg of CaCO₃

 \therefore 80 ml of 0.05 N EDTA = $80 \times 0.05 \times 50$

= 200 mg of CaCO₃ equivalent

Permanent Hardness = 200 ppm

Step III: Temporary Hardness = Total Hardness – Permanent Hardness

=360 ppm - 200 ppm

= 160 ppm

Thus,

Total Hardness = 360 ppm, Permanent Hardness = 200 ppm, Temporary Hardness = 160 ppm

Problem 8: 20 ml of standard hard water (containing 1.2 g CaCO₃ per litre) required 35 ml of EDTA. 50 ml of hard water sample required 30 ml of same EDTA. 100 ml of hard water sample after boiling required 25 ml of same EDTA. Calculate various hardnesses.

Solution: Step I:

Strength of hard water = 1200/1000 mg of CaCO₃ per ml

= 1.2 mg of CaCO₃ per ml

Step II: 20 ml of standard hard water = 35 ml of EDTA

20 ml of standard hard water = (20×1.2) mg of CaCO₃

1 ml of EDTA =
$$\frac{(20 \times 1.2)}{35}$$
 = 0.685 mg of CaCO₃ equivalent

Step III: 50 ml of hard water sample = 30 ml of EDTA

$$\therefore 1000 \text{ ml of hard water sample} = \left(\frac{1000}{50} \times 30\right) \times 0.685$$

= 411 ppm

 \therefore Total hardness = 411 ppm

Step IV: 100 ml boiled hard water = 25 ml of EDTA

$$\therefore 1000 \text{ ml of boiled hard water} = \frac{1000 \times 25}{100} \times 0.685$$

= 171.25 ppm

∴ Permanent hardness = 171.25 ppm

Thus,

Problem 9: 0.5 gm of CaCO₃ was dissolved in HCl and the solution made up to 500 ml with distilled water. 50 ml of the solution required 45 ml of EDTA solution for titration. 50 ml of hard water sample required 15 ml of EDTA and after boiling and filtering required 10 ml of EDTA solution. Calculate temporary hardness and total hardness of water.

[June 2013]

Solution: Step I:

Strength of standard hard water = 0.5 gm CaCO₃/ 500 ml of distilled water. = 500 mg in 500 ml water = 1mg/ml

Step II: 50 ml of standard hard water required \equiv 45 ml EDTA solution

i.e. 45 ml EDTA solution $\equiv 50$ mg CaCO₃ equivalent hardness

∴ 1 ml EDTA solution $\equiv \frac{50}{45}$ mg CaCO₃ equivalent hardness

Now, 50 ml water sample $\equiv 15$ ml EDTA solution

- :. Hardness of sample $\equiv \left[15 \times \frac{50}{45}\right]$ mg CaCO₃ equivalent for 50 ml hardness
- $\therefore \text{ Hardness per litre of sample} \equiv \left[15 \times \frac{50}{45}\right] \times \frac{1000}{50} \text{ mg/l}$
- \therefore Total hardness = 333.33 ppm

Step III: 50 ml water sample after boiling $\equiv 10$ ml EDTA solution

- ∴ Permanent hardness of sample $\equiv \left[10 \times \frac{50}{45}\right]$ mg CaCO₃ equivalent for 50 ml
- \therefore Permanent hardness of 1 litre sample $= \left[10 \times \frac{50}{45}\right] \times \frac{1000}{50} \text{ mg/l}$
- \therefore Permanent hardness $\equiv 222.22$ ppm
- ∴ Temporary hardness \equiv Total hardness Permanent hardness \equiv 333.33 222.22
- ∴ Temporary hardness = 111.11 ppm

Total Hardness = 333.33ppm, Permanent Hardness = 222.22ppm, Temporary Hardness = 111.11ppm Problem 10: 50ml of standard hard water containing 1 mg of pure CaCO₃ per ml consumed 20 ml of EDTA. 50 ml of the water sample consumed 30 ml of same EDTA solution. After boiling and filtering, 50 ml of the water sample required 10 ml of the same EDTA for titration. Calculate the total and permanent hardness of water sample.

[Dec 2013]

Solution: Step I:

Thus,

Total Hardness = 1500 ppm, Permanent Hardness = 500 ppm, Temporary Hardness = 1000 ppm

Problem 11: Calculate total hardness in ppm in given water sample. (i) 50ml standard hard water containing 1 mg pure CaCO₃ per ml, consumed 20ml EDTA solution (ii) 50ml water sample consumed 30ml EDTA solution using Erio-Black T indicator.

[Dec. 2017, May 2018]

Solution: Step I:

Strength of standard hard water = 1 mg/ml

50 ml of standard hard water = 50 mg of $CaCO_3$

50 ml of standard hard water = 20 ml of EDTA

 \therefore 1 ml of EDTA = 50/20 mg of CaCO₃ equivalent

= 2.5 mg of CaCO₃ equivalent

Step II: 50 ml of water sample = 30 ml of EDTA

$$\therefore 1000 \text{ ml of Water Sample} = \frac{1000 \times 30}{50} \text{ ml of EDTA}$$

= 600 ml of EDTA

 \therefore 1 ml EDTA = 50/20 mg of CaCO₃ equivalent

$$\therefore 600 \text{ ml of EDTA} = 600 \times \frac{50}{20} \text{ of CaCO}_3 \text{ equivalent}$$

Total Hardness = 1500 mg/L

Thus,

Hardness of water = 1500 ppm

Problem 12: In the process of determination of hardness, standard hard water sample was prepared by dissolving 2.5g CaCO3 and making solution up to 1 liter. 50ml of above hard water required 45ml of EDTA. 50ml of unknown hard water sample consumed 30ml EDTA solution using Erio-Black T indicator. The unknown hard water sample was boiled and filtered. 50ml of this boiled solution required 20ml of EDTA. Calculate hardness of all types of unknown hard water sample.

[May 2019]

Solution: Step I:

Step II: 50 ml of standard hard water = 45 ml of EDTA

50 ml of standard hard water = (50×2.5) mg of CaCO₃

1 ml of EDTA =
$$\frac{(50 \times 2.5)}{45}$$

= 2.777 mg of CaCO₃ equivalent

Step III: 50 ml of hard water sample = 30 ml of EDTA

$$\therefore 1000 \text{ ml of hard water sample} = \left(\frac{1000}{50} \times 30\right) \times 2.777$$

$$= 1666.2 \text{ ppm}$$

$$\therefore 1000 \text{ ml of boiled hard water} = \frac{1000}{50} \times 20 \times 2.777$$

= 1110.8 ppm

∴ Permanent hardness = 1110.8 ppm

Temporary hardness = Total hardness - Permanent hardness = 1666.2 - 1110.8

= 555.4 ppm

Thus,

Total Hardness = 1666.2 ppm, Permanent Hardness = 1110.8 ppm, Temporary Hardness = 555.4 ppm

6.6 UNDESIRABLE EFFECT OF HARD WATER

The use of hard water is not possible for domestic purpose, industrial purpose or even in steam generation in boilers as it has a lot of disadvantages for various purposes.

In Domestic Use:

- (1) Washing: Hard water does not lather freely with soap. It produces sticky precipitates of calcium and magnesium soaps which adhere on the fabric giving spots and streaks. This causes wastage of soap. Iron salts present in the water cause staining of cloth.
- (2) Bathing: Hard water does not lather freely decreasing cleansing quality of soap and wastages of soap.
- (3) **Drinking:** Hard water has adverse effect on our digestive system. There is an increased possibility of forming calcium oxalate crystals in urinary tracks.
- (4) Cooking: Because of the presence of dissolved salts, the boiling point of water is increased. It causes wastage of fuel and time. It also gives unpleasant taste to tea and coffee. The dissolved salts are deposited as carbonates on the inner walls of the water heating utensils.

In Industrial Use:

- (1) Sugar industry: Water containing sulphates, nitrates, alkali, carbonates etc. if used in sugar refining causes difficulties in the crystallization of sugar. The sugar so produced may be deliquescent.
- (2) Textile industry: Hard water causes soap to go waste as it cannot produce good quality of lather. Precipitates of calcium and magnesium soaps adhere to the fabric giving improper shades on dyeing. Iron and manganese cause coloured spots on fabric.

- (3) Paper industry: Calcium and Magnesium salts tend to react with chemicals to provide a smooth and glossy finish to paper. Iron salts affect the colour of the paper.
 - (4) Laundry: There is wastage of soap and colouration of the clothes due to iron.
- (5) Concrete making: Water containing chlorides and sulphates affect the hydration of cement and final strength of hardened concrete.
- (6) Pharmaceutical industry: Hard water, if used for preparing pharmaceutical products like drugs, injection, ointments etc., may produce certain undesirable products in them.
- (7) **Dyeing industry:** The dissolved calcium, magnesium and iron salts react with costly dyes forming undesirable precipitates which give impure shades and spots on the fabric.

6.7 WATER TREATMENT (SOFTENING)

The process whereby the hardness of water can be reduced or removed irrespective of whether it is temporary or permanent is called 'softening' of water. It is very essential process since hard water is unsuitable for domestic as well as industrial use. The hardness causing salts can be removed from water by following two types:

(1) External treatment

(2) Internal treatment.

External Treatment:

The external treatment of water is carried out before its entry into the boiler.

In industry, the important methods generally employed for softening are :

- (A) Lime-Soda Process,
- (B) Zeolite Permutit Process,
- (C) Ion exchange Process.

6.7.1 Ion Exchange or Deionization or Demineralization Process

Now-a-days synthetic ion exchange resins are used in the industry. Ion exchange resins are insoluble, cross-linked; long chain organic polymers with a microporous structure and the functional groups attached to the chains which are responsible for the ion exchanging properties. They may be classified as follows.

(i) Cation Exchange Resins (RH⁺): Resins containing acidic functional groups (-COOH, -SO₃H etc) are capable of exchanging their H⁺ ions with other cations. They are mainly styrene divinyl benzene copolymers, which on sulphonation or carboxylation

acquire capability to exchange their hydrogen ions with the cations in the water. They can be simply represented as RH⁺ where R represents the insoluble polymeric matrix. Their exchange reaction with other cation is shown below.

$$2RH^{\scriptscriptstyle +} + M^{\scriptscriptstyle +2} \, \longrightarrow \, R_2M + 2H^{\scriptscriptstyle +}$$

Amberlite IR -120 and Dowex -50 are some of the examples of commercially available cation excahnge resins.

For example,

....-CH₂-CH-CH₂-CH-CH₂-CH-CH₂-....

$$SO_3^-H^+$$
 $SO_3^-H^+$
 $SO_3^-H^+$
 $SO_3^-H^+$
 $SO_3^-H^+$
 $SO_3^-H^+$
Fig. 6.1 : Cation Exchange Resin

(ii) Anion Exchange Resins (R'OH⁻): Resins containing basic functional groups -NH₂, = NH etc. as hydrochloride are capable of exchanging their anions with other anions. They are styrene divinyl benzene or amine formaldehyde copolymers, which contain amino or quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups as an integral part of resin matrix. This after treatment with dilute NaOH solution becomes capable to exchange their OH⁻ ions with anions of water.

They can be represented as R'OH⁻ where R' represents insoluble organic matrix. Their exchange reaction with other anions is shown below.

$$R'OH^- + X^- \longrightarrow R'X^- + OH^-$$

Amberlite -400 & Dowex -3 are some of the examples of commercially available anion exchange resins.

For example,

Principle:

When raw water passes through cation exchanger resin, all cations from water are absorbed in exchange of H⁺ and when it passes through anion exchanger resins, all anions are absorbed in exchange of OH⁻. Thus, the water obtained is of distilled quality.

Process:

The hard water is passed first through cation exchange column, which removes all the cations like Ca²⁺, Mg²⁺ etc. from it and equivalent amount of H⁺ ions are released from this column to water.

Reaction:

$$2RH^{+} + Ca^{2+} \longrightarrow R_{2}Ca^{2+} + 2H^{+}$$

$$2RH^{+} + Mg^{2+} \longrightarrow R_{2}Mg^{2+} + 2H^{+}$$

Then the hard water is passed through anion exchange column, which removes all the anions like SO_4^{2-} , Cl^- etc. present in the water and equivalent amount of OH^- ions are released from this column to water.

Reaction:

$$R'OH^{-} + CI^{-} \longrightarrow R'CI^{-} + OH^{-}$$

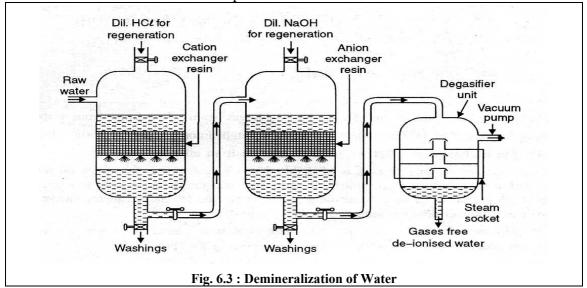
$$2R'OH^{-} + SO_{4}^{2-} \longrightarrow R_{2}^{'}SO_{4}^{2-} + 2OH^{-}$$

$$2R'OH^{-} + CO_{3}^{2-} \longrightarrow R_{2}^{'}CO_{3}^{2-} + 2OH^{-}$$

H⁺ ions released from cation exchange and OH⁻ ions released from anion exchange columns combine to produce water molecule.

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

As the water coming out is free from all ions (deionised water), the process is called as deionisation or demineralisation process.



Regeneration:

When cation exchangers and anion exchangers are exhausted completely (i.e. they lose their capacity to exchange H^+ and OH^- ions), regeneration process is carried out. The exhausted cation exchangers is regenerated by passing a solution of dilute HCl or dilute H_2SO_4 . The regeneration can be represented as:

$$R_2Ca^{2+} + 2H^+ \longrightarrow 2RH^+ + Ca^{2+}$$

The column is washed with deionised water and washings are sent to sink. The exhausted anion exchanger is regenerated by passing a solution of dilute NaOH. The regeneration can be represented as

$$R'_{2}SO_{4}^{2-} + 2OH^{-} \longrightarrow 2R'OH + SO_{4}^{2-}$$

Then the column is washed with deionised water and washings are passed to sink.

Advantages of Ion Exchange Process:

- (1) It produces water of very low hardness (2 ppm).
- (2) Treated water contains negligible amount of total dissolved solids.
- (3) Water obtained can be used for high pressure boilers.
- (4) Highly acidic and alkaline water can be softened.

Disadvantages of Ion Exchange Process:

- (1) The equipment is costly.
- (2) More costly chemicals are needed.
- (3) The turbidity of water should be below 10 ppm as efficiency of the process gets affected.

Numerical Based on Ion Exchange Process

Problem 1: After treating 10⁴ Litre of water by ion exchanger, the cationic resin required 200 Litre of 0.1 N HCL and anionic resin required 200 Litre of 0.1 N NaOH solutions. Find the hardness of the above sample of water.

Solution: In an ion exchanger all hardness causing cations are removed by cation exchanger. Hence the amount of acid used for regeneration of cation resin refers to hardness.

```
Hardness in 10^4 litres of water ≡ 200 L of 0.1 N HCl

= 200 L of 0.1 N CaCO<sub>3</sub> eq

= 200 × 0.1 L of 1 N CaCO<sub>3</sub> eq

= 20 L of 1N CaCO<sub>3</sub> eq

= 20 × 50 g of CaCO<sub>3</sub> eq

= 1000 g of CaCO<sub>3</sub> eq

= 1000 g of CaCO<sub>3</sub> eq

= 0.1 × 1000 mg of CaCO<sub>3</sub> eq

= 100 mg of CaCO<sub>3</sub> eq

= 100 mg of CaCO<sub>3</sub> eq
```

Thus,

Hardness of water sample = 100 mg/L

6.8 DESALINATION OF BRACKISH WATER

Water containing high concentration of dissolved solids with a peculiar salty taste is called brackish water. Sea water is a good example of brackish water as it contains 3.5% of dissolved salts. It is totally unfit for most of the domestic and industrial applications. The process of removing common salt (NaCl) from such water is known as desalination.

Commonly used techniques for the desalination of brackish water are as follows.

1. Electrodialysis:

Electrodialysis (ED) is an electro membrane process in which ions are transported through ion permeable membranes from one solution to another under the influence of potential gradient. It depends on the following general principles.

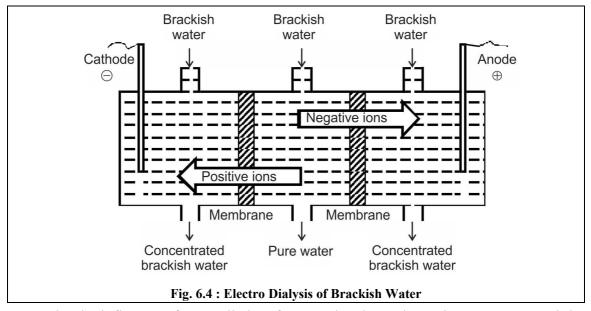
Most salts dissolved in water are ionic, being positively (cationic) or negatively (anionic) charged. These ions are attracted to electrodes with an opposite charge.

Membranes can be constructed to permit selective passage of either anions or cations.

It is an electrically driven membrane separation process that is capable of separating, concentrating, and purifying selected ions from aqueous solutions. The process is based on the property of ion exchange membranes to selectively reject anions or cations.

Electrodialysis is based on the fact that the ions present in the saline water migrate towards respective electrodes through ion-selective membranes under the influence of applied emf.

Fig. 6.4 illustrates the method of electro dialysis. The unit consists of electrodes and ion selective membranes. These membranes are thin and rigid, which are also permeable to either cation or anion. The anode is placed near anion selective membrane while the cathode is placed near the cation selective membrane.



Under the influence of an applied emf across the electrodes cations move toward the cathode and anions move towards the anode through respective membranes. There is depletion of ions in the central compartment while it increases in the two side compartments. Desalinated water is taken out from the central compartment and brackish water is replaced by fresh samples.

An electro dialysis cell based on the same principle is used for practical purposes. It consists of a large number of paired sets of rigid plastic membranes. Under the pressure of about 5-6 kg/m² saline water is passed between membrane pairs. An electric field is applied perpendicular to the direction of water flow. Fixed positive charges inside the membrane repel positively charged ions (Na⁺) and permit negatively charged ions (Cl¹) to pass through. Similarly, the fixed negative charges inside the membrane repel chloride ions but permit sodium ions. Thus water in one compartment is deprived of salts while the salt concentration in the adjacent compartment is increased. Thus alternate streams of pure water and brackish water are obtained.

Advantages:

- (1) Easy operation and variability of ED equipment.
- (2) The unit is compact.
- (3) Demineralization of biological solutions without affecting the quality.
- (4) Separation of salts and ions without changing phase and adding chemicals.
- (5) Higher feed recovery in many applications.
- (6) The process is economical as the cost of installation of the plant and its operational expenses are less.

Disadvantages:

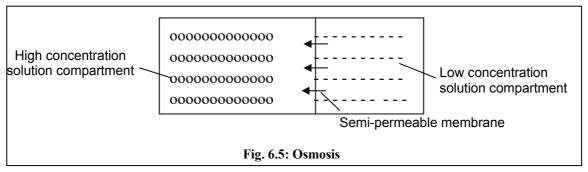
- (1) Sometimes pretreatment is necessary before the electrodialysis.
- (2) Suspended solids with a diameter that exceeds $10 \mu m$ need to be removes else they may plug the membrane pours.
- (3) Substances such as large organic anions, colloids, ion oxides and manganese oxide can disturb the selective effect of the membrane.

2. Reverse Osmosis:

There are various membrane techniques available for the separation of solutes on the basis of pore size which include reverse osmosis, ultra filtration etc.

Osmosis:

When two solutions of unequal concentrations are separated by semi-permeable membrane (which does not allow movement of solute particles) flow of solvent takes place from low concentration solution to high concentration solution side due to osmosis.



This passage of solvent from low concentration solution side compartment to high concentration solution side compartment is due to difference in vapour pressure of the two compartments. The flow continues till the concentration is equal on both the sides. The driving force for osmosis is called osmotic pressure.

Reverse Osmosis:

If a hydrostatic pressure in excess of osmotic pressure is applied on higher concentration solution side, solvent starts moving from higher concentration to lower concentration side compartment through semi-permeable membrane; this is the principle of reverse osmosis.

Thus, in the process of reverse osmosis pure solvent is separated from its contaminants, rather than removing contaminants from water. This membrane filtration is also called 'super filtration' or 'hyper filtration'.

Advantages:

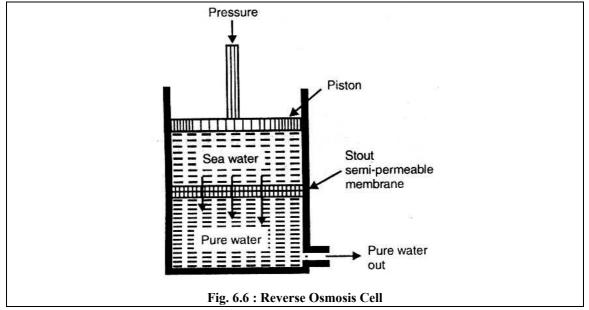
- (1) Reverse osmosis can be used to remove ionic as well as non-ionic, colloidal and high molecular weight organic matter.
- (2) It removes colloidal silica which is not removed by deminerization.
- (3) The process is economical, simple, highly reliable and has low capital and operating cost.
- (4) The life of the semipermeable membrane is about two years and can be replaced with in few minutes there by nearly uninterrupted water supply can be provided.

Disadvantages:

- (1) RO units use a lot of water but have production efficiency close to 48% (for large scale industrial and municipal system).
- (2) It is not practical for household systems to have low back pressure as it recovers only 5-15% of water that enters the system. This adds to the load on the household septic system.

Industrial Applications:

(i) Due to low capital cost, simplicity, low operating cost and high reliability, reverse osmosis is used for desalination and purification of brackish and sea water for drinking and industrial use (for high pressure boilers).



The process of removing common salt from sea water is known as desalination. The principle of reverse osmosis is applied to treat sea water. The membrane consists of thin films of cellulose acetate. Recently membranes made of polymethacrylate and polyamide polymers are used. In this process, pressure (15 to 40 kg cm⁻²) is applied to sea water and pure water is forced through semi-permeable membrane. [Ionic and non-ionic, dissolved salts are left behind].

(ii) Water recycle and recovery system: Reverse osmosis can be used for a variety of specialized membrane application for chemical recovery and waste water reclamation. For example, Recovery of Nickel and Chromium solutions, purification of pickling acids, water from recycle in textile, electroplating, paper and pulp industries.

3. Ultrafilteration:

Ultra filtration is a separation process using membranes with pore sizes in the range of 0.1 to 0.001 micron. It is membrane filtration in which hydrostatic pressure forces a liquid against a semi-permeable membrane. Suspended solids and solute of high molecule weight are retained, while water and low molecular weight solutes pass through the membrane. Ultra filtration does this by pressuring the solution flow, which is tangential to the surface of supported membrane. The solvent and other dissolved components that pass through the membrane are known as **permeate** and the components that do not pass through membrane are known as **retenate**. It is fundamentally not different from reverse osmosis. Generally low applied pressures are sufficient to achieve high flux rates from an ultra filtration membrane. Flux of a membrane is defined as the amount of permeate produced per unit area of membrane surface per unit time which is expressed as gallons per square foot per day or as cubic meters per square meters per day.

Advantages:

- (1) It removes high molecular weight substances, colloidal materials, organic and inorganic polymeric molecules.
- (2) As only high molecular weight species are removed, the osmotic pressure differential across the membrane surface is negligible.
- (3) Low applied pressures are sufficient to achieve high flux rates from an ultrafiltration membrane.

Disadvantages:

(1) Low molecular weight organics and ions such as sodium, calcium, magnesium, chloride and sulfate are not removed.

Applications:

(1) This separation is used in industry and research for purifying and concentrating macromolecular solution especially protein solutions.

- (2) It is used in industry to separate suspended solids from solution.
- (3) It is used in paint recovery in automotive industry.
- (4) It is used in the fractionation of milk and whey.
- (5) It is used in removal of colloids.

6.9 WATER POLLUTION

Water pollution is contamination of water by foreign matter that deteriorates the quality of the water. Water pollution covers pollutions in liquid forms like ocean pollution and river pollution. As the term applies, liquid pollution occurs in the oceans, lakes, streams, rivers, underground water and bays, in short liquid-containing areas. It involves the release of toxic substances, pathogenic germs, substances that require much oxygen to decompose, easy soluble substances, radioactivity, etc. that becomes deposited upon the bottom and their accumulations will interfere with the condition of aquatic ecosystems. For example, the eutrophication: lack of oxygen in a water body caused by excessive algae growths because of enrichment of pollutants. Polluted water means water that does not meet even the minimum standards for any function and purposes for which it would be suitable in its natural state. The water pollution may be defined as any alteration in the physical, chemical and biological properties of water, as well as contamination with any foreign substance which would constitute a health hazard or decrease the utility of water.

Sewage:

Sewage is the liquid wastes which includes human and household waste waters, industrial waste, ground waste, and street and storm waters.

Constituents of Sewage:

- (1) Domestic sewage (human excreta, discharges from bath, kitchen, lavatories etc.) from public and private buildings.
- (2) Industrial and trade wastes from manufacturing processes (tanneries, slaughter houses, distilleries, textile mills, chemical plants etc.)
- (3) Ground water entering through severs.
- (4) Storm water i.e. rain water from houses and roads.

If the water polluted by domestic effluent, industrial effluent and agricultural waste is consumed by human beings, it causes various types of diseases. 5-7 ppm of dissolved oxygen is present in unpolluted water and is essential for supporting aquatic life. In presence of good amount of dissolved oxygen (> 8 ppm) aerobic bacteria lead to oxidation of organic compound present in water (which is called aerobic oxidation). Oxidation products are inoffensive smelling, non putrefying nitrites, nitrates, sulphates,

phosphates etc. But if the dissolved oxygen is less (< 5 ppm) the sewage is called stale and anaerobic bacteria bring about putrefaction producing methane, hydrogen sulphide and phosphine which give offensive odour (which called anaerobic oxidation). In an anaerobic oxidation the bacteria extract combined oxygen contain inorganic matter, nitrates, nitrites and sulphates of sewage. When the anaerobic decomposition is continuing the sewage is known as septic sewage.

6.9.1 BOD - Biological Oxygen Demand

The water when gets polluted with large amount of organic matter, a lot of dissolved oxygen is consumed in the biological aerobic decay. The decreased DO affects the aquatic lives. The biological oxygen demand (BOD) is an index of water pollution. It is used in water quality management and assessment, Ecology and environmental science. BOD is not an accurate quantitative test, although it could be considered as an indication of the quality of a water source. BOD indicates amount of decomposable organic matter in the sewage. It enables us to determine the degree of pollution at any time in the sewage stream. Thus it is very essential in sewage treatment.

Biological oxygen demand (BOD) of sewage is defined as amount of free oxygen required for the biological oxidation of the organic matter under aerobic conditions at 20°C and for a period of 5 days. The unit of BOD is mg/L or ppm.

An average sewage has BOD of 100-150 mg/L

Reaction:

Organic matter +
$$O_2$$
 \longrightarrow $CO_2 + H_2O$

The demand for oxygen is proportional to the amount of organic waste to be degraded aerobically. Thus BOD approximates the amount of oxidizable organic matter present in the solution.

The higher the BOD of a sample the higher will be pollution caused by it.

Source of effluents Degree of Pollution BOD (mg/liter) 320 Low Domestic sewage Community Kitchen Sewage 2170 Medium Cow Shed Sewage 3010 Medium Paper Mill Effluent 8190 High Very High 12360 Tannery Effluent

Table 6.2: BOD values of some effluents

Drinking water should have BOD preferably less than 1 ppm.

Determination of BOD:

A known volume of effluent sample is diluted with a known volume of dilution water. The diluted sample is taken in two stoppered bottles. The dissolved oxygen content of one of the bottles is immediately determined (blank). Another bottle is incubated at 20°C for 5days, after which unused oxygen is determined. The difference between original oxygen content in the blank and unused oxygen of effluent water after five days gives the BOD. Thus BOD is equal to $(DO_b - DO_i) \times Dilution$ Factor.

Where, BOD = Biological oxygen demand.

DO_b = Dissolved oxygen present in the effluent sample before incubation.

DO_i = Dissolved oxygen present in the effluent sample after incubation.

While carrying out the BOD test, water is always diluted to ensure that sufficient oxygen is available for the complete oxidation of organic matter. BOD is the requirement of oxygen due to biodegradable organic matter only, and is biological phenomenon carried out more or less under natural conditions existing in water. BOD test is usually influenced by type of micro organism, presence of toxins, pH, some reduced mineral matters etc.

Significance of BOD:

The BOD values are useful in designing of treatment plants and calculations of waste load. It is a measure of efficiency of operation in treatment plant. It is important in sewage treatment as it indicates the amount of decomposable organic matter in sewage. It is the best test in assessing the organic pollution. From the BOD value, self purifying capacity of streams can be determined. This serves as a measure to assess the quantity of waste which can be safely discharged into the stream. Thus its significance in pollution control is unique since it provides the degree of pollution at any time in the sewage stream. BOD test is the best test for assessing the organic pollution which serves as a guideline for Regulatory Authorities to check the quality of effluents discharged into water bodies.

Limitations of BOD:

BOD values of effluents of rayon, paper and chemical industries are much less although they contain enough organic matter. The conclusion of presence of less organic matter in these effluents should not be drawn from their low BOD values. Thus Bod values should not be used as equivalent to organic load because of presence of other non-degradable organic matter.

6.9.2 COD - Chemical Oxygen Demand

Chemical Oxygen Demand is the amount of oxygen consumed under specified conditions in the oxidation of organic and oxidisable inorganic matter. Most applications of COD determine the amount of organic pollutants found in surface water (e.g. lakes and rivers), making COD a useful measure of water quality. It is a measure of oxidisable impurities present in the sewage. In COD test, the sample is subjected to chemical oxidation with potassium dichromate ($K_2Cr_2O_7$) which is a strong oxidizing agent. It oxidizes both biologically oxidisable and biologically inert material in the effluent water sample. Thus COD values are higher than BOD values as BOD measures only the oxygen consumed by living organisms while assimilating organic matter present in the water. COD may be defined as the amount of oxygen required for oxidation of chemically degradable organic matter in the hot conditions with use of oxidant like acidified potassium dichromate ($K_2Cr_2O_7$) in $1\frac{1}{2}$ hours. It is expressed in milligrams per litre (mg/L) or ppm which indicates the mass of oxygen consumed per litre of solution.

Determination of COD:

A known volume (25 ml) of waste water sample is refluxed with a known excess of standard potassium dichromate ($K_2Cr_2O_7$) (1N) and dilute sulphuric acid (H_2SO_4) in presence of silver sulphate (Ag_2SO_4) for $1\frac{1}{2}$ hours. Silver sulphate is used as a catalyst to promote oxidation of straight chain aliphatic compounds, aromatic compounds and pyridine. The organic matter of the sample is oxidized to ammonia, carbon dioxide and water. The unreacted potassium dichromate ($K_2Cr_2O_7$) is titrated against Ferrous Amonium Sulphate (FeSO₄.(NH₄)₂SO₄.6H₂O) i.e. Mohr's salt solution. This experimentally measured amount of potassium dichromate (consumed) is used to calculate the equivalent oxygen required by the waste water for degradation of the pollutants.

Reaction:

$$C_XH_YO_Z + (X + Y/4 - Z/2) O_2 \longrightarrow X CO_2 + Y/2 H_2O$$

The unreacted dichromate solution is titrated against (FeSO₄.(NH₄)₂.6H₂O) using ferroin as indicator. At end point, blue colour changes to wine red.

$$Cr_2O_7^{-2} + 14 \text{ H}^+ + 6e^- \longrightarrow 2 \text{ Cr}^{+3} + 7 \text{ H}_2O$$

 $[Fe^{+2} \longrightarrow Fe^{+3} + e^-] \times 6$
 $Cr_2O_7^{-2} + 14 \text{ H}^+ + 6 \text{ Fe}^{2+} \longrightarrow 2 \text{ Cr}^{+3} + 6Fe^{3+} + 7\text{H}_2O$

The COD of the sample can be calculated as follows:

$$COD = \frac{(V_1 - V_2) N \times 8000}{Y} mg/L$$

Where, Y is the volume of effluent water sample taken for test. V_1 and V_2 are volume of ferrous ammonium sulphate consumed in blank and test experiments respectively.

N is the normality of Ferrous Ammonium Sulphate.

Significance of COD:

The COD value is not affected by the presence of toxins and other unfavourable conditions for the growth of micro organisms. It measures the effect of pollutants on dissolved oxygen. It is taken as basis for calculation of efficiency of treatment plant. It is important in proposing standards for discharging domestic and industrial effluents in various kinds of water. Due to its rapid determination over BOD, it has become important in the management and design of treatment plants.

Limitations of COD:

COD is a poor measure of strength of organic matter as oxygen gets consumed in oxidation of some of the inorganic matter. Some organic matter like benzene does not get oxidized by the test. COD test fails to differentiate between bio-inert and bid-degradable materials.

Comparison:

BOD	COD
BOD of water is a measure of amount of oxygen required for biological oxidation of organic matter under aerobic condition at 20 °C for a period of 5 days.	COD of water is a measure of amount of oxygen required by organic matter in a water sample for its oxidation by strong oxidizing agent.
It measures the oxygen demand of bio degradable pollutants only.	It measures the oxygen demand for biodegradable pollutants along with non-biodegradable pollutants.
Less stable measurement method as it uses micro organisms which are susceptible to pH, temperature and other variables in the water.	More stable measurement method as it uses potassium dichromate which oxidises regardless of water conditions.
Slow process. It takes five days.	Fast process. It takes 2-3 hours.
BOD values are generally less than COD values.	COD values are generally greater than BOD values.

Numericals Based on BOD

Problem 1: A 50 ml of sample contains 840 ppm of dissolved oxygen. After 5 days the dissolved oxygen value becomes 230 ppm after the sample has been diluted to 80 ml. Calculate the BOD of the sample.

Solution: BOD =
$$(DO_b - DO_i) \times Dilution Factor$$

= $(DO_b - DO_i) \times \frac{ml. \text{ of sample after dilution}}{ml. \text{ of sample before dilution}}$
= $(840 - 230) \times \frac{80}{50}$
= 976 ppm

Problem 2: A 50 ml of water sample contains 500 ppm of dissolved oxygen. The water sample is diluted to 100 ml. After 5 days of incubation the DO value of water sample reduces to 400 ppm. Calculate BOD of water sample.

Solution: BOD =
$$(DO_b - DO_i) \times Dilution Factor$$

= $(DO_b - DO_i) \times \frac{ml. \text{ of sample after dilution}}{ml. \text{ of sample before dilution}}$
= $(500 - 400) \times \frac{100}{50}$
= 200 ppm

Problem 3: A 100 ml of water sample contains 600 ppm of dissolved oxygen. The water sample is diluted to 200 ml. After 5 days of incubation the DO value of water sample reduces to 300 ppm. Calculate BOD of water sample.

Solution: BOD =
$$(DO_b - DO_i) \times Dilution Factor$$

= $(DO_b - DO_i) \times \frac{ml. \text{ of sample after dilution}}{ml. \text{ of sample before dilution}}$
= $(600 - 300) \times \frac{200}{100}$
= 600 ppm

Numericals Based on COD

Problem 1: A 25 ml of a sewage water sample was refluxed with 10 ml of 0.25 N $K_2Cr_2O_7$ solution in presence of dil. H_2SO_4 , Ag_2SO_4 and $HgSO_4$. The unreacted dichromate required 6.5 ml of 0.1 N ferrous ammonium sulphate. 10 ml of the same $K_2Cr_2O_7$ solution and 25 ml of distilled water, under the same conditions as the sample, required 27 ml of 0.1 N ferrous ammonium sulphate. Calculate the COD of the sewage water sample.

Solution: Given Vb = 27 ml
Vt = 6.5 ml
N = 0.1 Normal
Ve = 25 ml
∴ COD =
$$\frac{(27 - 6.5 \times 0.1 \times 8)}{25} \times 1000 = 0.656 \text{ ppm}$$

Problem 2: A 25 ml of a sewage water sample was refluxed with 10 ml of 0.25 N $K_2Cr_2O_7$ solution in presence of dil. H_2SO_4 , Ag_2SO_4 and $HgSO_4$. The unreacted dichromate required 5.5 ml of 0.1 N ferrous ammonium sulphate. 10 ml of the same $K_2Cr_2O_7$ solution and 25 ml of distilled water, under the same conditions as the sample, required 15 ml of 0.1 N ferrous ammonium sulphate. Calculate the COD of the sewage water sample.

Solution: Given
$$Vb = 15 \text{ ml}$$

$$Vt = 5.5 \text{ ml}$$

$$N = 0.1 \text{ Normal}$$

$$Ve = 25 \text{ ml}$$

$$COD = \frac{(15 - 5.5) \times 0.1 \times 8 \times 1000}{25} = 304 \text{ ppm}$$

Problem 3: A 5ml sample of waste water was refluxed with 30ml of potassium dichromate solution and after refluxing the excess unreacted dichromate required 23ml of 0.1M FAS solution. A blank of distilled water on refluxing with 30ml of dichromate solution required 36ml of 0.1M FAS solution. Calculate the COD value of the waste water.

[Dec 2015]

Solution: Given
$$Vb = 36 \text{ ml}$$

$$Vt = 23 \text{ ml}$$

$$N = 0.1 \text{ Normal}$$

$$Ve = 5 \text{ ml}$$

$$COD = \frac{(36-23) \times 0.1 \times 8 \times 1000}{5} = 2080 \text{ ppm}$$

Problem 4: Calculate the COD of an effluent sample if 25cc of the effluent sample required 8.3cc of 0.001M K₂Cr₂O₇ for oxidation.

[May 2016]

Solution: Given Vb - Vt = 8.3 ml
N = 0.001 Normal
Ve = 25 ml
∴ COD =
$$\frac{8.3 \times 0.001 \times 8 \times 1000}{25}$$
 = 2.656 ppm

Problem 5: 6ml of waste water was refluxed with 25ml of $K_2Cr_2O_7$ and after refluxing the excess unreacted dichromate required 20ml of 0.1N FAS solution. A blank of distilled water on refluxing with 25ml of $K_2Cr_2O_7$ solution required 35ml of 0.1N FAS solution. Calculate the COD of waste water sample.

Solution: Given
$$Vb = 35 \text{ ml}$$

$$Vt = 20 \text{ ml}$$

$$N = 0.1 \text{ Normal}$$

$$Ve = 6 \text{ ml}$$

$$COD = \frac{(35-20) \times 0.1 \times 8 \times 1000}{6} = 2000 \text{ ppm}$$

Problem 6: 10ml of waste water was refluxed with 20ml of $K_2Cr_2O_7$ and after refluxing the excess unreacted dichromate required 36.2ml of 0.1N FAS solution. A blank of 10ml of distilled water on refluxing with 20ml of $K_2Cr_2O_7$ solution required 46ml of 0.1N FAS solution. Calculate the COD of waste water sample. [May 2017]

Solution: Given
$$Vb = 46 \text{ ml}$$
 $Vt = 36.2 \text{ ml}$ $N = 0.1 \text{ Normal}$ $Ve = 10 \text{ ml}$ ∴ $COD = \frac{(46 - 36.2) \times 0.1 \times 8 \times 1000}{10} = 784 \text{ ppm}$

Problem 7: 10ml of waste water was refluxed with 20ml of $K_2Cr_2O_7$ and after refluxing the excess unreacted dichromate required 26.2ml of 0.1N FAS solution. A blank of 10ml of distilled water on refluxing with 20ml of $K_2Cr_2O_7$ solution required 36ml of 0.1N FAS solution. Calculate the COD of waste water sample. May 2018,19

Solution: Given
$$Vb = 36 \text{ ml}$$
 $Vt = 26.2 \text{ ml}$ $N = 0.1 \text{ Normal}$ $Ve = 10 \text{ ml}$ ∴ $COD = \frac{(36 - 26.2) \times 0.1 \times 8 \times 1000}{10} = 784 \text{ ppm}$

Problem 8: 20ml of waste water was refluxed with 30ml of $K_2Cr_2O_7$ and after refluxing the excess unreacted dichromate required 11ml of 0.1N FAS solution. A blank of 20ml of distilled water on refluxing with 30ml of $K_2Cr_2O_7$ solution required 14ml of 0.1N FAS solution. Calculate the COD of waste water sample.

Dec 2018

Solution: Given
$$Vb = 14 \text{ ml}$$

 $Vt = 11 \text{ ml}$

$$N = 0.1 \text{ Normal}$$

$$Ve = 20 \text{ ml}$$
∴
$$COD = \frac{(14 - 11) \times 0.1 \times 8 \times 1000}{20} = 120 \text{ ppm}$$

6.10 SEWAGE TREATMENT BY ACTIVATED SLUDGE PROCESS

Sewage contains minerals and inorganic matter in suspension and in solution. It contains sometimes harmful living organisms. Hence it is better to treat sewage before releasing into the river, lake and sea. The treatment processes are as follows:

(1) Preliminary Treatment:

The principal objective of preliminary treatment is the removal of gross solids i.e. large floating and suspended solid matter, grit, oil and greases if present in considerable quantities. For removing inorganic matter, sewage is allowed to pass through bar screen and mesh screens.

(2) Primary Treatment:

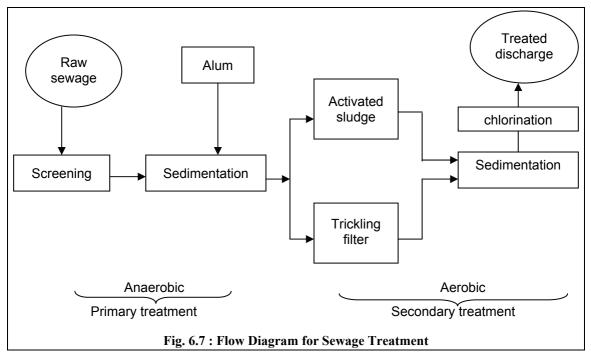
For removing suspended matter efficiently and economically, sedimentation process is carried out. The sewage is treated with certain chemicals (like alum, hydrated lime etc.) which form a floc that absorbs and entrains the suspended and colloidal particles present.

(3) Secondary or Biological Treatment:

It is essentially an aerobic chemical oxidation which includes filtartion and activated sludge process. In this process, sewage water is filtered through specially designed sprinkling filters so that aerobic conditions are maintained all the times. During this process, carbon of the organic matter is converted into CO₂; the nitrogen into NH₃ and finally into nitrites and nitrates.

Tricking Filters: Tricking filters are commonly used for the biological oxidation of sewage. It is rectangular or circular in shape and about 2 meters deep. They are filled with coarse, crushed rock or anthracite coal or broken bricks.

Sewage is delivered to the filters by means of rotating distributor. As the trickled sewage starts percolating downwards, through the filtering medium, the aerobic bacteria grow on the surface of aggregates by using organic matter in sewage as food. Highly aerobic condition is maintained constantly in this design. The bacteria bring about the biological oxidation of organic matter of sewage. The treated water comes out from bottom. A normal trickling filter removes about 90% BOD within few hours.



Activated Sludge Process: This is the much faster oxidation of organic matter in sewage by aerobes, under highly aerobic conditions, in the presence of a part of sludge from previous oxidation process. The sludge from the previous oxidation process is known as activated sludge, since it contains organic matter inhabited by numerous aerobes.

This process consists of mixing the sedimented sewage from step (2) with proper quantity of activated sludge and the mixture is sent to the aeration tank in which agitation is carried out for 4-6 hours by blowing air in it. Here suspended and dissolved organic matter is oxidised efficiently by the aerobic bacteria. After aeration, the affluent is sent to sedimentation tank, where sludge is deposited and clean water is drawn off. A part of the sludge deposited is used for next oxidation batch and the remainder is either spread on land as fertile matter or used for biogas or dumped in sea.

(4) Tertiary Treatment:

It is applied to decrease the load of nitrogen and phosphorous compounds present in the effluents.

- (i) Precipitation: It involves treatment of effluent with lime which reacts with phosphorus to form calcium phosphate.
- (ii) Nitrogen Stripping: It is carried out to remove ammonia gas.
- (iii)Chlorination: It involves treating the water from nitrogen stripping with chlorine so as to kill the disease causing micro-organisms present in sewage waste water. The so treated water is finally discharged into rivers or lakes.

6.11 REVIEW QUESTIONS

1. What causes soft water to form lather with soap?

Ans. Refer Section 6.3.

2. Explain hardness of water?

Ans. Refer Section 6.3.

3. Differentiate between temporary hardness and permanent hardness.

Ans. Refer Section 6.3.1.

4. Why temporary hardness is called carbonate hardness?

Ans. Refer Section 6.3.1.

5. Differentiate between hard water and soft water.

Ans. Refer Section 6.3.2.

6. Explain how you would determine hardness of water using EDTA method.

Ans. Refer Section 6.5.

7. What are the problems caused by hard water in different industries?

Ans. Refer Section 6.6.

8. How the regeneration of ion exchange resin is done?

Ans. Refer Section 6.7.1.

9. What is deminiralisation? Explain its merits and demerits.

Ans. Refer Section 6.7.1.

10. What is brackish water?

Ans. Refer Section 6.8.

11. What is desalination?

Ans. Refer Section 6.8.

12. Explain reverse osmosis. Give its industrial application.

Ans. Refer Section 6.8.

13. Define BOD and COD. What is the difference between them?

Ans. Refer Section 6.9.1 and 6.9.2.

14. What is COD of waste water? How its numerical value is important?

Ans. Refer Section 6.9.2.

15. Write a note on ultrafilteration.

Ans. Refer Section 6.8.

16. Explain with the help of neat and labeled diagram the method of electro dialysis.

Ans. Refer Section 6.8.

17. With the help of diagram explain the activated sludge method to control water pollution.

Ans. Refer Section 6.10.

6.12 UNSOLVED PROBLEMS

1. A water sample on analysis has been found to contain following impurities in ppm: $Mg(HCO_3)_2 = 5.84$, $Ca(HCO_3)_2 = 4.86$, $MgSO_4 = 16.8$, $CaSO_4 = 13.6$.

Ans. [Temporary hardness = 7ppm, Permanent hardness = 24ppm,

Calculate the temporary, permanent and total hardness of water.

Total hardness = 31ppm]

2. A water sample contains the following impurities in ppm:

 $Mg(HCO_3)_2 = 73$, $Ca(HCO_3)_2 = 81$, $MgSO_4 = 120$, $CaSO_4 = 136$.

Calculate the temporary and permanent hardness of water.

Ans. [Temporary hardness = 100 ppm, Permanent hardness = 200 ppm]

3. Find out temporary, permanent and total hardness in a sample of water with following impurities: $Ca(HCO_3)_2 = 81$ ppm, $MgSO_4 = 60$ ppm, $MgCO_3 = 84$ ppm, KCl = 30 ppm, $CaCl_2 = 22.2$ ppm.

Ans. [Total hardness = 220 ppm, Permanent hardness = 70 ppm,

Temporary hardness = 150 ppm]

4. Calculate carbonate and non-carbonate hardness of water containing following impurities in mg/L:

 $Mg(HCO_3)_2 = 14.6$, $Ca(HCO_3)_2 = 8.1$, $MgCl_2 = 19$, $Mg(NO_3)_2 = 29.6$.

Ans. [Carbonate hardness = 15 ppm, Non-carbonate hardness = 40 ppm]

5. Calculate total hardness of water sample containing the following impurities:

 $Mg(HCO_3)_2 = 146 \text{ mg/L}, Ca(HCO_3)_2 = 81 \text{ mg/L}, MgCl_2 = 95 \text{ mg/L},$

NaCl = 10 mg/L Express the result in °Cl and °Fr.

Ans. [Total hardness = $250 \text{ mg/L} = 25 \text{ }^{\circ}\text{Fr} = 17.5 \text{ }^{\circ}\text{Cl}$]

6. What is the total hardness of a sample of water which has the following impurities in mg/L: $Ca(HCO_3)_2 = 162$, $CaCl_2 = 22.2$, $MgCl_2 = 95$, NaCl = 20.

Express the result as °Cl and °Fr.

Ans. [Total hardness = $220 \text{ mg/L} = 22 \text{ }^{\circ}\text{Fr} = 15.4 \text{ }^{\circ}\text{Cl}$]

7. Three water samples A, B and C were analyzed for their salt content. Sample A was found to contain 168 mg magnesium carbonate per litre. Sample B was found to contain 82 mg of calcium nitrate and 2 mg of silica per litre. Sample C was found to contain 20 mg of potassium nitrate and 20 mg of calcium carbonate per 500 ml. Determine the hardness in all the above three water samples A, B and C.

Ans. [Sample A = 200 ppm, Sample B = 50 ppm, Sample C = 40 ppm]

8. A water sample contains 16.8 mg of MgCO₃ and 6.0 mg of SiO₂ per litre. Find its temporary and permanent hardness.

Ans. [Temporary hardness = 20 ppm]

9. 50 ml of standard hard water (1.2 g of CaCO₃/l) requires 30 ml of EDTA solution. 100 ml of water sample consumes 14 ml of EDTA solution. 100 ml of boiled filtered water takes 7.0 ml of EDTA. Find temporary and permanent hardness of water sample.

Ans. [Permanent hardness = 140 ppm, Temporary hardness = 140 ppm]

10. 0.5 g of CaCO₃ was dissolved in dilute HCl and diluted to 500 ml. 50 ml of this solution required 45 ml of EDTA solution for titration. 50 ml of hard water sample required 15 ml of EDTA solution for titration. 50 ml of same water sample on boiling, filtering requires 10 ml of EDTA solution. Calculate the temporary, permanent and total hardness in ppm.

Ans. [Total hardness = 333.34 ppm, Permanent hardness = 222.23 ppm Temporary hardness = 111.11 ppm]

11. 0.2 gm of CaCO₃ is dissolved in dilute HCl and diluted to 250 ml. 25 ml of this solution required 24.0 ml of EDTA using Eriochrome Black-T indicator. 50 ml of a hard water sample requires 20 ml of the same EDTA. 100 ml of the water after boiling and filtering requires 24 ml of the same EDTA. Calculate the hardness in the water sample.

Ans. [Total hardness = 336 ppm, Permanent hardness = 201.6 ppm, Temporary hardness = 134.4 ppm]

12. 50 ml of standard hard water containing 1 mg pure CaCO₃ per ml consumed 30 ml of EDTA, 50 ml of water sample consumed 35 ml of EDTA solution using Eriochrome Black-T indicator, 50 ml of water sample requires 21 ml of EDTA using the same indicator. Calculate the temporary and permanent hardness.

Ans. [Temporary hardness = 466.67 ppm, Permanent hardness = 700 ppm]

13. Calculate the hardness of water sample whose 20 ml requires 30 ml of EDTA. 10 ml of calcium chloride solution, whose strength is equivalent to 300 mg of calcium carbonate per 200 ml required 20 ml of EDTA solution.

Ans. [Hardness = 1013.25 ppm]

14. A 50 ml of sample contains 840 ppm of dissolved oxygen. After 5 days the dissolved oxygen value becomes 230 ppm after the sample has been diluted to 80 ml. Calculate the BOD of the sample.

Ans. [BOD = 976 ppm]

15. A 50 ml of water sample contains 500 ppm of dissolved oxygen. The water sample is diluted to 100 ml. After 5 days of incubation the DO value of water sample reduces to 400 ppm. Calculate BOD of water sample.

Ans. [BOD = 200 ppm]

16. A 40 ml of sample contains 700 ppm of dissolved oxygen. After 5 days the dissolved oxygen value becomes 200 ppm after the sample has been diluted to 80 ml. Calculate the BOD of the sample.

Ans. [BOD = 1000 ppm]

17. A 25 ml of a sewage water sample was refluxed with 10 ml of 0.25 N K₂Cr₂O₇ solution in presence of dil. H₂SO₄, Ag₂SO₄ and HgSO₄. The unreacted dichromate required 6.5 ml of 0.1 N ferrous ammonium sulphate. 10 ml of the same K₂Cr₂O₇ solution and 25 ml of distilled water, under the same conditions as the sample, required 27 ml of 0.1 N ferrous ammonium sulphate. Calculate the COD of the sewage water sample.

Ans. [COD = 0.656 ppm]

18. A 25 ml of a sewage water sample was refluxed with 10 ml of 0.25 N K₂Cr₂O₇ solution in presence of dil. H₂SO₄, Ag₂SO₄ and HgSO₄. The unreacted dichromate required 5.5 ml of 0.1 N ferrous ammonium sulphate. 10 ml of the same K₂Cr₂O₇ solution and 25 ml of distilled water, under the same conditions as the sample, required 15 ml of 0.1 N ferrous ammonium sulphate. Calculate the COD of the sewage water sample.

Ans. [COD = 304 ppm]

19. A 20 ml of a sewage water sample was refluxed with 10 ml of 0.1 N K₂Cr₂O₇ solution in presence of dil. H₂SO₄, Ag₂SO₄ and HgSO₄. The unreacted dichromate required 10 ml of 0.1 N ferrous ammonium sulphate. 10 ml of the same K₂Cr₂O₇ solution and 20 ml of distilled water, under the same conditions as the sample, required 20 ml of 0.1 N ferrous ammonium sulphate. Calculate the COD of the sewage water sample.

Ans. [COD = 400 ppm]

6.13 UNIVERSITY QUESTIONS

December 2007

1. What do you mean by hardness of water? Distinguish between alkaline and non-alkaline hardness of water. (3 M)

6.51

Ans. Refer Section 6.3 and 6.3.1.

2. Explain the terms : (i) BOD, (ii) COD.

What is their significance?

(3 M)

Ans. Refer Section 6.9.1 and 6.9.2.

May 2008

1. A water sample contains:

 $Ca(HCO_3)_2 = 32.4 \text{ mg/L}, Mg(HCO_3)_2 = 29.2 \text{ mg/L}, CaSO_4 = 13.5 \text{ mg/L}.$

Calculate temporary, permanent and total hardness.

(At. Wt. Ca =
$$40$$
, Mg = 24 , H = 1 , C = 12 , O = 16 , S = 32).

(3 M)

Ans. Temporary Hardness = 40 ppm. Perm. Hardness = 10 ppm, Total Hardness = 50 ppm.

2. What are carbonate and non carbonate hardness?

A standard hard water contains 15gm/litre calcium carbonate. 20 ml of this water required 25 ml of EDTA solution. 100 ml of sample water required 18 ml of EDTA solution. The same sample, after boiling required 12 ml of EDTA solution. Calculate temporary hardness of water.

Ans. Refer Section 4.3.1 and Total Hardness = 2160 ppm,

Temporary Hardness = 1440 ppm, Perm. Hardness = 720 ppm.

3. Give brief account of reverse osmosis.

(3 M)

Ans. Refer Section 6.8.

4. Write a note on activated sludge method.

(5 M)

Ans. Refer Section 6.10.

December 2008

1. Explain the principle of EDTA method.

(3 M)

Ans. Refer Section 6.5.

2. Define the terms : (i) BOD, (ii) COD. What is their significance?

(5 M)

Ans. Refer Section 6.9.1 and 6.9.2.

3. Explain Reverse Osmosis and Ultra filtration.

(5 M)

Ans. Refer Section 6.8.

4. Write a note on activated sludge method.

(5 M)

Ans. Refer Section 6.10.

May 2009

1. A water sample contains:

 $Mg(HCO_3)_2 = 14.6 \text{ ppm}, Mg(NO_3)_2 = 29.6 \text{ ppm}, Ca(HCO_3)_2 = 8.1 \text{ ppm},$

 $MgCl_2 = 19 \text{ ppm}, MgSO_4 = 24 \text{ ppm}.$

Calculate the temporary and permanent hardness of water sample.

(At. Wt. Ca =
$$40$$
, Mg = 24 , H = 1 , C = 12 , O = 16 , S = 32)

(3 M)

Ans. Temporary Hardness = 15 ppm, Perm. Hardness = 60 ppm.

2. How demineralization of water is carried out?

(6 M)

Ans. Refer Section 6.7.1.

3. 0.5 gm CaCO₃ was dissolved in HCl and the solution made up to 500 ml with distilled water. 50 ml of the solution required 48 ml of EDTA solution for titration. 50 ml of hard water sample required 15 ml of EDTA and after boiling and filtering required 10 ml of EDTA solution. Calculate temporary hardness of water. (5 M)

Ans. Temporary Hardness = 104.17 ppm.

4. Give brief account of Ultra filtration.

(3 M)

Ans. Refer Section 6.8.

5. Write a note on activated sludge method.

(5 M)

Ans. Refer Section 6.10.

December 2009

1. Calculate temporary and total hardness of a water sample containing,

$$Mg(HCO_3)_2 = 7.3 \text{ mg/L}, Ca(HCO_3)_2 = 16.2 \text{ mg/L}, MgCl_2 = 9.5 \text{ mg/L}, CaSO_4 = 13.6 \text{ mg/L}.$$

(3 M)

Ans. Temporary Hardness = 15 ppm, Total Hardness = 35 ppm.

2. Explain the ion exchange process of softening of hard water. What are its advantages and disadvantages? (7 M)

Ans. Refer Section 6.7.1.

3. Write a note on activated sludge method.

(5 M)

Ans. Refer Section 6.10.

May 2010

1. Write a short note on reverse osmosis.

(3 M)

Ans. Refer Section 6.8.

2. Describe the Demineralisation process. State its advantages and disadvantages.

Ans. Refer Section 6.7.1.

(5 M)

December 2010

1. Explain the principle of EDTA method.

(3 M)

Ans. Refer Section 6.5.

2. Explain the terms : (i) BOD, (ii) COD. What is their significance?

(3 M)

Ans. Refer Section 6.9.1 and 6.9.2.

3. Write a note on reverse osmosis.

(3 M)

Ans. Refer Section 6.8.

4. 1 gm of CaCO₃ was dissolved in 1 litre of distilled water. 50 ml of this solution required 45 ml of EDTA solution for titration. 50 ml of hard water required 25 ml of EDTA for titration. The same sample of water after boiling consumed 15 ml of EDTA for titration. Calculate the hardness of water.

Ans. Total Hardness = 555.55 ppm, Perm. Hardness = 333.33 ppm,

Temporary Hardness = 222.22 ppm.

5. Write a note on activated sludge method.

(5 M)

Ans. Refer Section 6.10.

May 2011

A water sample on analysis has been found to contain MgCl₂ = 19 ppm,
 CaCO₃ = 5 ppm, Ca(HCO₃)₂ = 29.5 ppm, CaSO₄ = 13 ppm. Calculate temporary, permanent and total hardness.

Ans. Total hardness = 52.77 ppm, Perm hardness = 29.56 ppm,

Temp hardness = 23.21 ppm.

2. 50 ml water sample required 7.2 ml of N/20 disodium EDTA for titration. After boiling and filtration the same volume required 4 ml of EDTA. Calculate each type of hardness. (5 M)

Ans. Total hardness = 360 ppm, Perm hardness = 200 ppm,

Temp hardness = 160 ppm.

3. Explain the reverse osmosis and ultrafiltration.

(5 M)

Ans. Refer Section 6.8.

December 2011

1. Classify the following impurities into temporary, permanent and non hardness causing impurities. Ca(HCO₃)₂, MgSO₄, CaCl₂, Mg(HCO₃)₂, CaSO₄, NaCl. How many grams of CaCl₂ dissolved per litre gives 150 ppm of hardness? (3 M)

Ans. Temp hardness = $Ca(HCO_3)_2$, $Mg(HCO_3)_2$, Perm hardness = $MgSO_4$, $CaCl_2$, $CaSO_4$, Non hardness = NaCl.

2. Define BOD and COD. Give its significance.

(3 M)

Ans. Refer Section 6.9.1 and 6.9.2.

3. What is reverse osmosis? Give its applications.

(3 M)

Ans. Refer Section 6.8.

4. 20 ml of standard hard water containing 1.2 gm CaCO3 per litre required 35 ml of EDTA. 50 ml of hard water sample required 30 ml of the same EDTA. 100 ml of hard water sample after boiling required 25 ml of same EDTA. Calculate the various hardnesses. (5 M)

Ans. Total hardness = 411 ppm, Perm hardness = 342.5 ppm,

Temp hardness = 68.5 ppm.

5. Write a note on activated sludge method.

(5 M)

Ans. Refer Section 6.10.

December 2012

1. Distinguish between BOD and COD.

(3 M)

Ans. Refer Section 6.9.1 and 6.9.2.

2. Calculate temporary, permanent and total hardness of water sample containing Mg(HCO₃)₂ = 7.3 ppm, Ca(HCO₃)₂ = 16.2 ppm, MgCl₂ = 9.5 ppm, CaSO₄ = 13.6 ppm. (3 M)

Ans. Temp hardness = 15 ppm, Perm hardness = 20 ppm, Total hardness = 35 ppm.

3. Write a note on activated sludge method.

(5 M)

Ans. Refer Section 6.10.

June 2013

1. Differentiate between BOD and COD.

(3 M)

Ans. Refer Section 6.9.1 and 6.9.2.

2. What is the total hardness of water sample which has following impurities in mg/l? $Ca(HCO_3)_2 = 162$, $CaCl_2 = 22.2$, $Mg Cl_2 = 95$, NaCl = 20. (3 M)

Ans. Total hardness = 220 ppm.

3. 0.5 g of CaCO₃ was dissolved in dil HCl and diluted to 500 ml. 50 ml of this solution required 45 ml of EDTA solution for titration. 50 ml of hard water sample required 15 ml of EDTA solution for titration. 50 ml of same water sample on boiling & filtering reqires 10 ml EDTA solution. Calculate temporary hardness and total hardness.

Ans. Temp hardness = 111.11 ppm, Total hardness = 333.33 ppm.

4. Explain demineralization of water by ion exchange method.

(5 M)

Ans. Refer Section 6.7.1.

December 2013

1. What Happens when temporary hard water is boiled? Give equation to explain.

Ans. Refer Section 6.3.1.

(3 M)

- 2. Two samples of water A and B were analysed for their salt content:
- $(\mathbf{J}|\mathbf{N})$
- (i) Sample A was found to contain 168 mg MgCO₃ per litre.
- (ii) Sample B was found to contain 820 mg Ca (NO₃)₂ per litre and 2 mg SiO₂ per litre.

Calculate the total hardness of each sample and state which sample is more hard.

Ans. Total Hardness of A = 200 ppm, Total Hardness of B = 500 ppm. Sample B is more hard.

3. 50 ml of standard hard water containing 1 mg of pure CaCO₃ per ml consumed 20 ml of EDTA. 50 ml of the water sample consumed 30 ml of same EDTA solution. After boiling and filtering, 50 ml of the water sample required 10 ml of the same EDTA for titration. Calculate the total and permanent hardness of water sample.

Ans. Perm hardness = 500 ppm, Total hardness = 1500 ppm.

4. Write short notes of any two:

(6 M)

(a) Reverse Osmosis, (b) Electro dialysis, (c) Ultra filtration.

Ans. Refer Section 6.8.

May 2014

1. Give the principle of estimation of hardness of water using EDTA method (Only Equations). (3 M)

Ans. Refer Section 6.5.

- 2. Classify the following salts into temporary and permanent hardness causing salts and also calculate their hardness:

 (3 M)
 - $\mbox{(a)} \ \ Ca \ (HCO_3)_2 16.2 \ mg/L, \quad \mbox{(b)} \ \ MgSO_4 1.2 \ mg/L, \quad \mbox{(c)} \ \ FeCl_2 12.7 \ mg/L.$

Ans. Ca $(HCO_3)_2$ Temporary hardness = 10 ppm and

 $MgSO_4$ Permanent hardness = 1 ppm.

3. With a neat diagram explain the principle and reaction of Ion-Exchange method of softening of water. (5 M)

Ans. Refer Section 6.7.1.

4. (a) Define the significance of BOD and COD.

(6 M)

(b) Discuss Reverse Osmosis.

Ans. Refer Section 6.9.1 and 6.9.2, and 6.8.

December 2014

1. Explain the principle of EDTA method.

(3 M)

Ans. Refer Section 6.5.

2. 25 ml of sewage water is refluxed with 0.1N K₂Cr₂O₇ solution in presence of H₂SO₄ and Ag₂SO₄. The unreacted dichromate required 5.5ml of 0.1N FAS solution. Blank titration consumed 15 ml of 0.1N FAS solution. Calculate COD of the effluent.

Ans. COD = 304 ppm.

May 2015

1. Differentiate between temporary and permanent hardness.

(3 M)

Ans. Refer Section 6.3.2.

2. Calculate all types of hardness of water sample containing:

(3 M)

 $Ca (HCO_3)_2 - 81 ppm$

 $MgSO_4-60\;ppm$

 $Mg CO_3 - 42 ppm$

 $Ca(NO_3)_2 - 82 \text{ ppm}.$

Ans. Temporary hardness = 100 ppm and Permanent hardness = 100 ppm.

3. Write note on Ultra filtration and Reverse osmosis.

(5 M)

Ans. Refer Section 6.8.

December 2015

1. A 5ml sample of waste water was refluxed with 30ml of potassium dichromate solution and after refluxing the excess unreacted dichromate required 23ml of 0.1M FAS solution. A blank of distilled water on refluxing with 30ml of dichromate solution required 36ml of 0.1M FAS solution. Calculate the COD value of the waste water.

Ans. COD = 2080 ppm.

2. Write a note on activated sludge method.

(5 M)

Ans. Refer Section 6.10.

May 2016

1. Write two balanced equations to describe the changes that occur when hard water is boiled. (3 M)

Ans. Refer Section 6.3.1.

2. Calculate the COD of an effluent sample if 25cc of the effluent sample required 8.3cc of 0.001M K₂Cr₂O₇ for oxidation. (3 M)

Ans. COD = 2.656 ppm.

3. (a) Discuss the softening and regeneration reactions in the ion exchange process.

(b) Discuss the reverse osmosis method of purification of water.

(6 M)

Ans. (a) Refer Section 6.7.1.

(b) Refer Section 6.8.

December 2016

1. Distinguish between alkaline and non-alkaline hardness.

(3 M)

Ans. Refer Section 6.3.2.

2. 6ml of waste water was refluxed with 25ml of K₂Cr₂O₇ and after refluxing the excess unreacted dichromate required 20ml of 0.1N FAS solution. A blank of distilled water on refluxing with 25ml of K₂Cr₂O₇ solution required 35ml of 0.1N FAS solution. Calculate the COD of waste water sample.

Ans. COD = 2000 ppm.

3. What are the advantages of ion exchange process?

(3 M)

Ans. Refer Section 6.7.1.

4. What are the industrial applications of ultrafiltration?

(2 M)

Ans. Refer Section 6.8.

<u>June 2017</u>

1. What are cation and anion exchangers?

(3 M)

Ans. Refer Section 6.7.1.

2. 10ml of waste water was refluxed with 20ml of K₂Cr₂O₇ and after refluxing the excess unreacted dichromate required 36.2ml of 0.1N FAS solution. A blank of 10ml of distilled water on refluxing with 20ml of K₂Cr₂O₇ solution required 46ml of 0.1N FAS solution. Calculate the COD of waste water sample. (3 M)

Ans. COD = 784 ppm.

3. Explain ion exchange process for softening of hard water. It's advantages and disadvantages. (6 M)

Ans. Refer Section 6.7.1.

4. Write a note on ultrafiltration.

(3 M)

Ans. Refer Section 6.8.

5. Distinguish between temporary and permanent hardness of water.

(2 M)

Ans. Refer Section 6.3.2.

December 2017

1. Distinguish between BOD and COD.

(3 M)

Ans. Refer Section 6.9.1 and 6.9.2.

2. Calculate total hardness in ppm in given water sample.

 $3 \, \mathrm{M}$

- (i) 50ml standard hard water containing 1 mg pure CaCO₃ per ml, consumed 20ml EDTA solution.
- (ii) 50ml water sample consumed 30ml EDTA solution using Erio-Black T indicator.

Ans. Hardness of water = 1500 ppm.

3. Explain Reverse Osmosis.

(2 M)

Ans. Refer Section 6.8.

4. Write a note on activated sludge method.

 $\overline{(6 \mathrm{M})}$

Ans. Refer Section 6.10.

<u>May 2018</u>

1. 10ml of waste water was refluxed with 20ml of K₂Cr₂O₇ and after refluxing the excess unreacted dichromate required 26.2ml of 0.1N FAS solution. A blank of 10ml of distilled water on refluxing with 20ml of K₂Cr₂O₇ solution required 36ml of 0.1N FAS solution. Calculate the COD of waste water sample. (3 M)

Ans. COD = 784 ppm.

2. Calculate total hardness in ppm in given water sample.

(4 M)

- (i) 50ml standard hard water containing 1 mg pure CaCO₃ per ml, consumed 20ml EDTA solution.
- (ii) 50ml water sample consumed 30ml EDTA solution using Erio-Black T indicator.

Ans. Hardness of water = 1500 ppm.

3. Distinguish between BOD and COD.

(3 M)

Ans. Refer Section 6.9.1 and 6.9.2.

4. Discuss reverse osmosis.

(2 M)

Ans. Refer Section 6.8.

December 2018

1. Write a short note on reverse osmosis.

(2 M)

Ans. Refer Section 6.8.

2. 20ml of waste water was refluxed with 30ml of K₂Cr₂O₇ and after refluxing the excess unreacted dichromate required 11ml of 0.1N FAS solution. A blank of 20ml of distilled water on refluxing with 30ml of K₂Cr₂O₇ solution required 14ml of 0.1N FAS solution. Calculate the COD of waste water sample. (3 M)

Ans. COD = 120 ppm.

3. Draw the diagram for demineralization process and write suitable reactions involved in the process. What are the advantages and disadvantages of the method?

(6 M)

Ans. Refer Section 6.7.1.

4. Explain the principle of EDTA method.

(3 M)

Ans. Refer Section 6.5.

5. Write a note on activated sludge method.

(3 M)

Ans. Refer Section 6.10.

May 2019

1. 10ml of waste water was refluxed with 20ml of K₂Cr₂O₇ and after refluxing the excess unreacted dichromate required 26.2ml of 0.1N FAS solution. A blank of 10ml of distilled water on refluxing with 20ml of K₂Cr₂O₇ solution required 36ml of 0.1N FAS solution. Calculate the COD of waste water sample. (3 M)

Ans. COD = 784 ppm.

2. In the process of determination of hardness, standard hard water sample was prepared by dissolving 2.5g CaCO3 and making solution up to 1 liter. 50ml of above hard water required 45ml of EDTA. 50ml of unknown hard water sample consumed 30ml EDTA solution using Erio-Black T indicator. The unknown hard water sample was boiled and filtered. 50ml of this boiled solution required 20ml of EDTA. Calculate hardness of all types of unknown hard water sample.

Ans. Total Hardness = 1666.2 ppm

Permanent Hardness = 1110.8 ppm

Temporary Hardness = 555.4 ppm.

3. A hard water sample contains following impurities in ppm. $Mg(HCO_3)_2 = 150$, NaCl =77, CaCl₂ = 135, MgSO₄ = 85. Calculate temporary, permanent and total hardness of the given water sample. (3 M)

Ans. Temporary hardness = 102.74ppm Permanent hardness= 192.45ppm Total hardness = 295.19 ppm.

4. Write a short note on reverse osmosis.

(3 M)

Ans. Refer Section 6.8.

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