CHAPTER – WATER

Q1) Define Soft water and Hard water with reactions?

Ans: **Soft Water:-**

- Water which immediately (easily) produces good amount of lather (foam) with soap is called as **Soft water.**
- It is free from soluble salts of Calcium and Magnesium such as $CaCl_2$, $MgCl_2$,$MgSO_4$, $CaSO_4$,$Ca(HCO_3)_2$,and $Mg(HCO_3)_2$ etc
- Soft water does not react with soap and hence does not produce insoluble curd like precipitate of Ca and Mg stearate or palmitate.

Hard Water:-

- Water which does not immediately (easily) produces good amount of lather (foam) with soap is called as **Hard water**.
- It contains Ca and Mg soluble salts such as $CaCl_2$, $MgCl_2$,$MgSO_4$,$Ca(HCO_3)_2$, and $Mg(HCO_3)_2$.along with soluble salts of some heavy metals like Fe, Mn, Al etc.
- Hard water reacts with soap producing insoluble curd like precipitate of Ca and Mg stearate and palmitrate as shown below.
- **Reactions:**

$2C_{17}H_{35}COONa + CaCl_2 \rightarrow (C_{17}H_{35}COO)_2Ca\downarrow + 2NaCl$
Sodium stearate Hard water Calcium stearate
(White curd like ppt)

$2C_{17}H_{35}COONa + MgSO_4 \rightarrow (C_{17}H_{35}COO)_2Mg\downarrow + Na_2SO_4$
Sodium stearate Hard water Calcium stearate
(White curd like ppt)

$2C_{15}H_{31}COONa + Ca(HCO_3)_2 \rightarrow (C_{15}H_{31}COO)_2Ca\downarrow + 2NaCl$
Sodium Palmitate Hard water Calcium Palmitrate
(White curd like ppt)

Q2) What are the effects of Hard water in the manufacture sector and Domestic area?

Ans:- **a) Domestic use:i) Washing:** Hard water when used for washing, does not produce lather with soap but instead forms a white sticky precipitate of Ca, Mg soaps. This continues till all the hardness causing salts present in water are precipitated. Thereafter the soap produces lather. This causes the following disadvantages i) A lot of soap is wasted. ii) Formation of spots and streaks on the cloth. iii) Staining due to the adherence of the precipitates on the cloth.

ii) **Bathing:** Hard water does not lather freely with soap solution and instead forms a sticky precipitate on the body causing irritation to the skin.

iii)**Cooking:** Presence of dissolved salts in water causes effects such as:

Boiling point of water rises, as a result the food takes a longer time to ccok and therefore fuel is wasted. The dissolved salts are deposited as bicarbonates on the inner walls of the heating utensils.

iv) **Drinking:** Hard water gives a) Unpleasant taste to water. b) Increases the possibility of causing kidney stones.

b)<u>Industrial Use:</u>i) Textile Industry: In this industry water is used for dyeing, bleaching and washing purpose. During washing if hard water is used, a lot of soap gets wasted.

During dyeing exact shades of color are not obtained with hard water. On white clothes Fe and Mn may form colored spots.

ii) Sugar Industry: Water containing sulphates, nitrates, carbonates etc, if used in sugar refining causes difficulties in the crystallization of sugar and it may also decompose on storage.

iii) Paper Industry: Calcium and Magnesium salts tend to react with chemicals used to provide a smooth and glossy finish to the paper. Iron salts affect the color of the paper being produced.

iv) Laundry: Hard water causes wastage of soap. Iron and manganese salts causes coloration of the clothes.

v) Concrete making: Water containing chlorides and sulphates if used in concrete making, affects the hydration of cement and the final strength of the hardened concrete.

vi)Pharmaceutical Industry: Salts present in the hard water may react with the chemicals present in the pharmaceutical like drug, injections, ointments etc and produce undesirable products.

vii) Bakeries: Water should not contain any organic matter such as fungi or bacteria. These affects yeasts action and the quality of the bakery product becomes inferior.

Q3) What is hardness of water and explain it types?

Ans) Hardness of water is defined as "The soap consuming capacity of a water sample".

a) Hard water consists of Ca and Mg soluble salts such as as $CaCl_2$,, $CaSO_4$, $MgCl_2$, $MgSO_4$,$Ca(HCO_3)_2$, and $Mg(HCO_3)_2$.which are responsible for hardness in water.

b) These salts react with the soap to form white curd like precipitate and does not allow soap to produce good amount of lather. When whole of the hardness causing ions are precipitated out as shown in reaction below, further addition of soap produces lather.

$$2C_{17}H_{35}COONa + CaCl_2 \rightarrow (C_{17}H_{35}COO)_2Ca\downarrow + 2NaCl$$

Soap Hard water Ca-stearate

TYPES OF HARDNESS:

TemporaryHardness/Temporary Hard water/Carbonate Hardness/Alkaline Hardness:

i)Temporary hardness of water is caused due to the presence of bicarbonates of Ca and Mg ie $Ca(HCO_3)_2$, and $Mg(HCO_3)_2$.It is called temporary hardness because this types of hardness can be removed just by boiling, as shown :

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

$Mg(HCO_3)_2 \rightarrow MgCO_3 \downarrow + H_2O + CO_2$

On boiling soluble $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ decompose into insoluble carbonates, which is removed by filtration.

It is also called as "Alkaline hardness'.

ii) Permanent Hardness/Permanent Hard water/Non Carbonate Hardness/Non Alkaline Hardness.

Permanent hardness of water is caused due to the presence of Chlorides and sulphates of Ca , Mg and Fe ie.$CaCl_2$, $CaSO_4$,$MgCl_2$,$MgSO_4$,$FeCl_2$,$FeSO_4$,

It is called as permanent because such type of hardness cannot be removed simply by boiling.
Permanent hardness of water can be removed by adding calculated amount of Lime and Soda.
ie.$Ca(OH)_2$ and Soda (Na_2CO_3) as shown below,

$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + 2NaCl$

$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + Na_2SO_4$

$MgCl_2 + Na_2CO_3 + Ca(OH)_2 \rightarrow Mg(OH)_2 \downarrow + CaCO_3 \downarrow + 2NaCl$

$MgSO_4 + Na_2CO_3 + Ca(OH)_2 \rightarrow Mg(OH)_2 \downarrow + CaCO_3 \downarrow + Na_2SO_4$

Insoluble Ca and Mg salts are removed by filtration. Hardness caused by chlorides and sulphates of Ca and Mg is called as Non-Alkaline Hardness

Q3) What is degree of hardness in water? How is it expressed?

Ans) The net amount of hardness causing impurities present in a finite volume (usually one litre) is called **'Degree of Hardness'**

It is expressed in terms of $CaCO_3$. $CaCO_3$ is selected as standard as the molecular weight of $CaCO_3$ is 100 and Equivalent weight of $CaCO_3$ is 50.

Also it is the most insoluble salt that gets precipitated during softening of hard water.

$$\text{Degree of Hardness(H)} = \frac{\text{Mass of Hardness Producing substance} \times \text{Equivalent weight of } CaCO_3}{\text{Equivalent weight of hardness producing substance (h.p.s)}}$$

$$H = \frac{\text{(Mass of hardness producing substance)} \times 50}{\text{Equivalent weight of h.p.s}}$$

The ratio , $\frac{\text{Equivalent weight of } CaCO_3}{\text{Equivalent weight of h.p.s}}$ is referred as Multiplication factor

If the h.p.s has a bivalent cation, the ratio is expressed as $\frac{\text{Molecular weight of } CaCO_3}{\text{Molecular weight of h.p.s}}$

Q5)Define the following terms:

a) **Parts per million:** It is the number of parts of calcium carbonate equivalent hardness per 10^6 parts of water sample.

b) **Milligram per litre (mg/l) :** It is the number of milligrams of calcium carbonate equivalent hardness present per litre of water.
Thus ,1mg/lit=1mg of $CaCO_3$ equivalent in 10^6 mg of water.

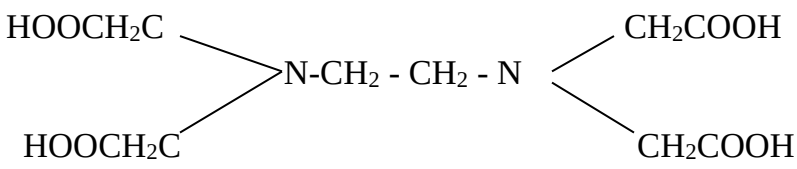
Conversion table of some impurities in water into equivalent of $CaCO_3$

Sr No	Salt	Molecular weight	Equivalent weight	Multiplication factor
1.	$Ca(HCO_3)_2$	162	81	100/162
2.	$Mg(HCO_3)_2$	146	73	100/146
3.	$CaSO_4$	136	68	100/136
4.	$CaCl_2$	111	55.5	100/111
5.	$MgSO_4$	120	60	100/120
6.	$MgCl_2$	95	47.5	100/95
7.	$Mg(NO_3)_2$	148	74	100/148
8.	$CaCO_3$	100	50	100/100
9.	$MgCO_3$	84	42	100/84
10.	HCO_3^-	61	61	100/122
11.	OH^-	17	17	100/34
12.	CO_3^-	60	30	100/60
13.	$Al_2(SO_4)_3$	342	57	100/114
14.	CO_2	44	22	100/44
15.	$FeSO_47H_2O$	278	139	100/278
16.	H^+	1	1	100/2
17.	$NaAlO_2$	82	82	100/164

Q5) Explain EDTA titration method and describe how is it use for estimation of hardness in water sample?

Ans) Ethylene Diamine tetra acetic acid (EDTA)

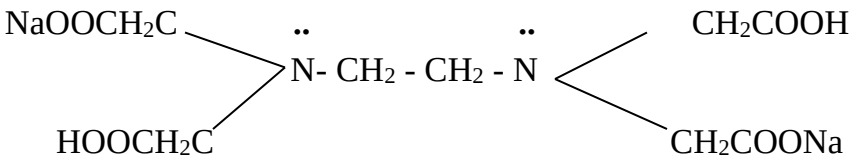
Structure:



EDTA[H4Y]

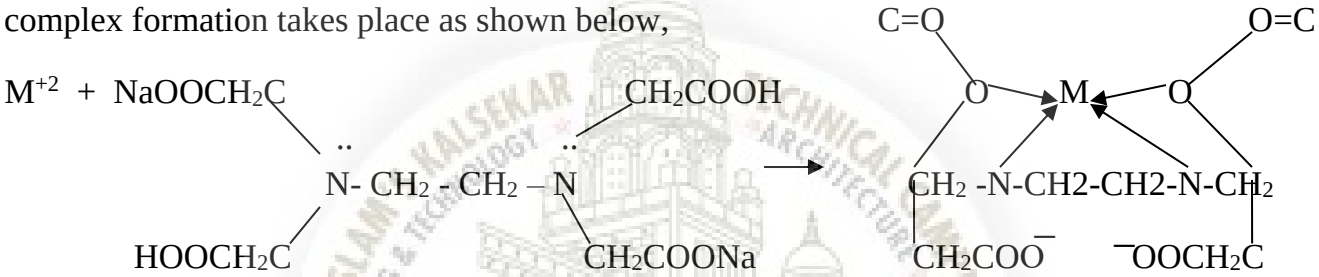
EDTA represented as H_4Y is sparingly soluble in water, hence its di-sodium salt (Na_2H_2Y) is generally used in complexometric titration.

Structure:



Disodium salt of EDTA (Na_2H_2Y)

EDTA is a hexadentate ligand. It binds the metal ions in water ie Ca^{+2} or Mg^{+2} to give highly stable chelate complex. Therefore ,this method is called as Complexometric titration. The complex formation takes place as shown below,



Principle of EDTA method:

EDTA forms a stable complexes with Ca^{+2} or Mg^{+2} and other metal cations in aqueous solution. Thus total hardness can be determined by titrating Ca^{+2} or Mg^{+2} present in an aliquot of the sample with Na-EDTA solution, using NH_4Cl, NH_4OH buffer solution of pH-10 and Eriochrome Black T (EBT) as the metal indicator.

The indicator forms a wine red colored unstable complex with Ca^{+2} or Mg^{+2} and whole solution turns wine red.

Ca^{+2} or Mg^{+2} + EBT → Ca^{+2} /Mg^{+2} -----EBT

When this wine red color solution is titrated with EDTA it first combines with free metal ions to give colourless stable metal EDTA complex.

Ca^{+2} /Mg^{+2} + EDTA → Ca^{+2} /Mg^{+2}---EDTA

Colorless and Stable

When all the free metal ions have reacted with EDTA the next drop of EDTA solution displaces the indicator (EBT) from the weak wine red colour complex and the indicator is set free giving back its original colour ie Blue. Since the stability of Ca^{+2} /Mg^{+2}EDTA is greater than Ca^{+2} /Mg^{+2}EBT

Ca^{+2}/Mg^{+2} ----EBT + EDTA → Ca^{+2} /Mg^{+2}EDTA + EBT

Wine red Colourless Blue

Thus , the end point is from wine red to blue.

Preparation and Procedure:

Standard Hard Water: Prepared by dissolving 1gm of pure ,dry $CaCO_3$ in minimum quantity of distilled water and then making the volume upto 1litre with distilled water.

EDTA solution: 4gm of pure EDTA crystals and 0.1gm of $MgCl_2$ is dissolved in 1 litre of distilled water

EBT Indicator: 0.5gm EBT indicator is dissolved in 100ml of alcohol.

Buffer solution: 67.5gm of NH_4Cl is added to 570ml of concentrated ammonia solution and then diluted with distilled water to 1 litre.

Standardisation of EDTA water:

50ml of Std hard water solution is taken in a conical flask .10-15ml of the buffer solution and 4-5 drops of the indicator solution is added to it. The solution is titrated against the EDTA solution taken in the burette. Let the volume be V1ml.

Determination of Total Hardness:

50ml of the unknown hard water solution is taken in the conical flask and titrated in a similar manner. Let the volume be V2 ml.

Determination of Permanent Hardness:

250ml of the hard water sample is boiled till its volume reduces to about $1/5^{th}$ .The solution is filtered to remove the precipitates of bicarbonates salts. The filtrate and the washings given to the precipitates are collected and the volume made back to 250ml with distilled water.

50ml of this solution is taken in a conical flask and titrated in the same manner as described earlier. Let the volume be V3ml.

Calculations:

V1ml of EDTA= 50ml of Std Hard water = 50mg of $CaCO_3$ hardness

1ml of EDTA = 50/V1 mg of $CaCO_3$ hardness

50ml of hard water = V2 ml of EDTA ……..(1)

= V2 x 50/V1 mg of $CaCO_3$ hardness …..from (1)

1000ml of hard water = 1000x V2x50 / V1x 50mg of $CaCO_3$ hardness

Total hardness = 1000 x V2/V1 mg/lit or ppm .....(2)

Now, 50ml of boiled hard water = V3ml of EDTA

From …(1), =V3 x 50/V1 mg of $CaCO_3$ hardness

1000ml of boiled hard water = (1000 x V3 x 50/V1x 50) mg of $CaCO_3$ hardness

Permanent hardness = 1000 x V3/ V1 mg/lit or ppm

From (2) and (3),

Temp Hardness = 1000[V2/V1- V3/V1] mg/lit or ppm

Q 6) Define softening of water ?

Ans)The process of removing hardness producing salts such as $CaCl_2$, $MgCl_2$, $MgSO_4$,$Ca(HCO_3)_2$, and $Mg(HCO_3)_2$ from hard water is known as softening of water. This is done by following methods:

1) Lime soda process
2) Permutit or zeolite process
3) Ion-exchange process

Q7) Explain the reaction of Lime and soda used for softening?

In Lime soda method , the soluble salts present in water is chemically converted into insoluble precipitates, on adding calculated quantities of lime $Ca(OH)_2$and Soda (Na_2CO_3) and precipitates are then filtered off

I) Reaction Of Lime:

i) Removal of Acids:- (L)

$2HCl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O$

$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2H_2O$

ii) Removal of Al and Fe salts. (L + S)

$Al_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Al(OH)_3\downarrow + 3CaSO_4$

$FeSO_4 + Ca(OH)_2 \rightarrow Fe(OH)_2 + CaSO_4$

$2Fe(OH)_2 + H_2O + 1/2\ O_2 \rightarrow 2\ Fe(OH)_3\downarrow$

iii) Removal of Dissolved CO_2&H_2S (L)

$CO_2 + Ca(OH)_2 \rightarrow CaCO_3\downarrow + H_2O$

$H_2S + Ca(OH)_2 \rightarrow CaS\downarrow + 2H_2O$

iv) Removal of Bicarbonate ions like $NaHCO_3$,$KHCO_3$ (L - S)

$2NaHCO_3 + Ca(OH)_2 \rightarrow CaCO_3\downarrow + 2HO_2 + Na_2CO_3$

v) Removal of Temporary Hardness due to Ca (L) & Mg(2L)

$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O$

$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + 2CaCO_3\downarrow + 2H_2O$

VI) Removal of permanent hardness due to Mg (L+ S)

$MgCl_2+Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow+CaCl_2$

$MgSO_4+ Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow+CaSO_4$

II) Reactions Of Soda :- (S)

Soda reacts with all Permanent Hardness Caused by Ca^{+2} Salts

$CaCl_2+ Na_2CO_3 \rightarrow CaCO_3\downarrow+2NaCl$

$CaSO_4+Na_2CO_3 \rightarrow CaCO_3\downarrow+Na_2SO_4$

Formula to calculate Lime required for softening :-

$$\text{Lime} = \frac{74}{100}(\text{TempCa}^{+2} + 2\times\text{TempMg}^{+2}) + \text{Perm}\ (Mg^{+2}+Al^{+3}+Fe^{+2})+HCl+H_2SO_4+CO_2+H_2S + NaHCO_3-NaAlO_2) \times \frac{\text{Volume in Litres}}{10^6} \times \frac{100}{\%\text{Purity}}$$

Soda required:-

$$\text{Soda} = \frac{106}{100}[\text{Perm}(Ca^{+2}+Mg^{+2}+Al^{+3}+Fe^{+2}\text{etc})+HCl+H_2SO_4-NaHCO_3-NaAlO_2) \times \frac{\text{Volm in Litres}}{10^6} \times \frac{100}{\%\text{Purity}}$$

Note:- $NaAlO_2+H_2O \rightarrow NaOH +Al(OH_3)\downarrow$

Advantages :-

1] Lime is cheap and economical

2] It removes temporary hardness without introducing soluble salts into the water

3] Addition of coagulant like alum helps in faster settling of sludge which can then be removed easily

4] $CaCO_3$ and $Mg(OH_2)$ produced in the reactions given above are insoluble and precipitate as sludge.

Disadvantages :-

Water softened by this process contains considerable quantities of soluble salts like NaCl & Na_2SO_4 and hence cannot be used in high pressure boilers.

Q8) Describe lime soda process with neat labeled diagram ? State the advantages and disadvantages of lime soda process?

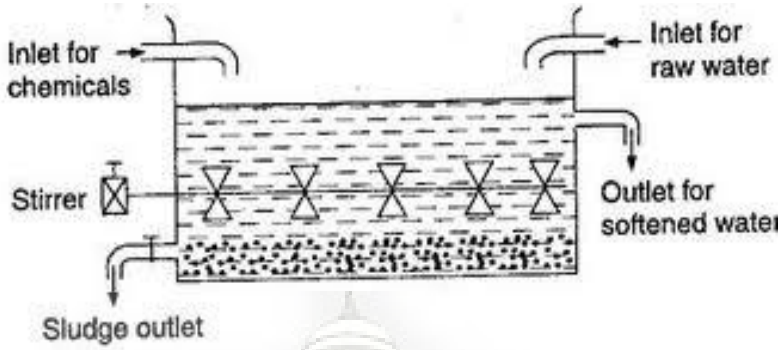
Ans]**Lime soda process :-**Principle is to convert all the soluble hardness causing constituents into insoluble precipitates by appropriate chemical treatments and then removing them by filtration. In this process calculated amounts of Lime and soda are added depending upon the concentration of impurities.

Types of Lime soda process : -

1)Cold Lime Soda process 2) Hot lime soda process .

I) Cold Lime soda process : -

A) Batch Process :



It consists of a tank provided with inlets for raw water and chemicals , outlets for softened water and sludge ,and a mechanical stirrer for thorough mixing.

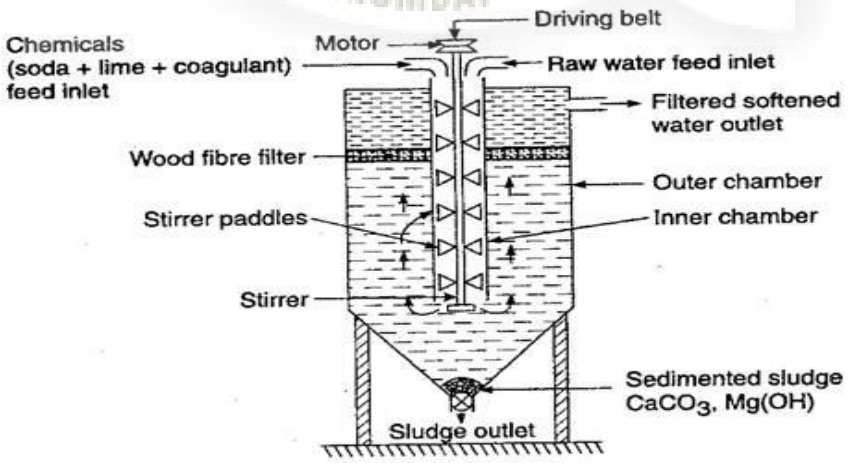
Raw water and calculated quantities of chemicals are added to the water tank and mixed thoroughly.

The precipitates formed are very fine and hence cannot be removed by filtration immediately, it takes about 24 hours for settling.

To fasten, settling coagulants like sodium aluminate, aluminium sulphate or alum has to be added .It takes about 2 hrs for the precipitate to settle down.

The softened water from the top is drawn out using pumps and passed through sand filters. The sludge formed at the bottom is removed and cleaned with water

2) Cold Lime Soda Continuous Process :



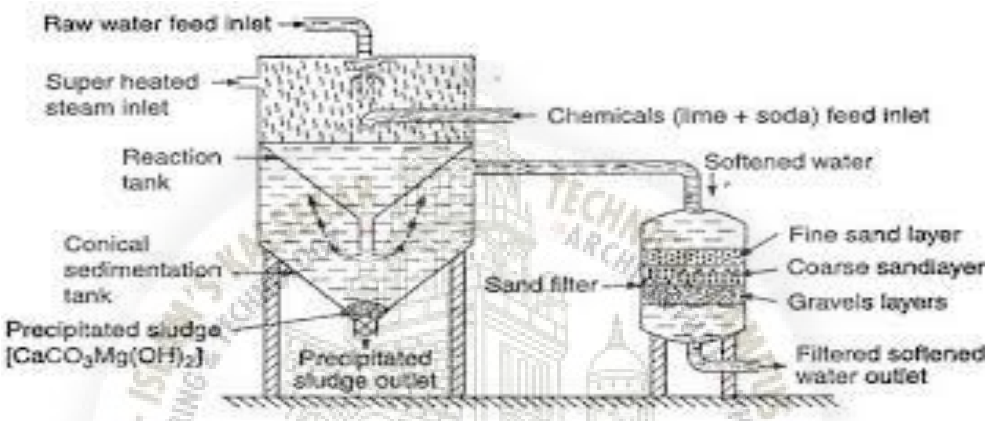
It consists of an inlet for raw water and chemicals , and outlet for softened water and sludge ; and a rotating shaft having paddles.

Chemicals like lime soda and coagulant along with the raw water are added in the inner circular chamber and mixed thoroughly with rotating shaft .

As the water flows down in the vertical chamber there is thorough mixing & due to the various chemical reactions taking in this process , softening is achieved .The softened water rises upwards through the outer coaxial chamber.

The solid sludge formed settles at bottom, water is filtered and flows out continuously through the outlet at the top. Sludge is removed from time to time. The soft water obtained has the residual hardness of 50 to 60 ppm

2) Hot Lime soda process : -



This process is carried out at a temp 90-100^{0}c and it has the following advantages:

1) Sludge settles faster and the addition of coagulants is not required

2) The rate of reaction is increased, softening is completed in 15 min.

3) Dissolved gases like CO_2 are expelled .

4) It reduces the viscosity of water and increases the rate of filtration.

This process consists essentially of a reaction cum settling tank and a filtering setup which consists of sand , anthracite coal ,calcite or magnetite.

If a slight excess of chemicals are used, not only the process is faster but also removal of hardness is achieved , but excessive chemicals are carried through, to the softened H_2O and hence decreases its quality . The soft water obtained have relatively lower residual hardness about 15 to 30 ppm

Advantages of Lime soda process : -

1) Economical

2) Along with hardness , acids as well as CO_2 is eliminated

3) Process increases the pH value of the treated water, thereby corrosion of the distribution pipe

are reduced.

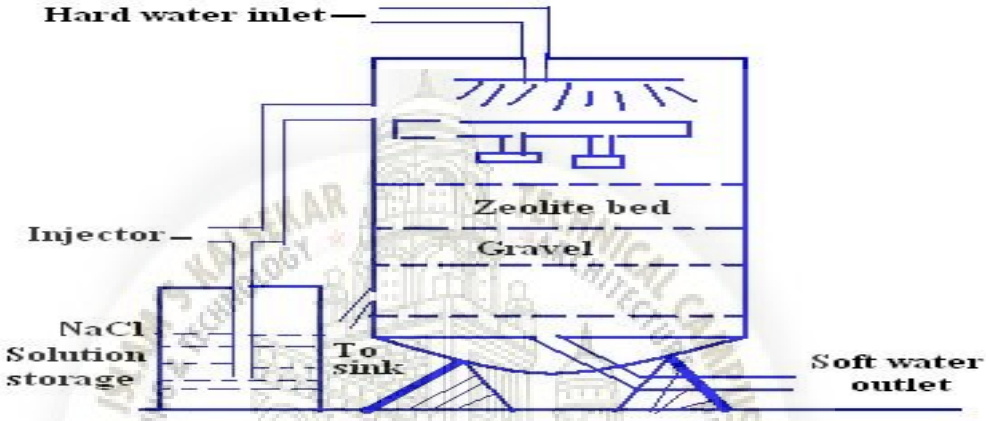
Disadvantages : -

1) Skilled persons are required for supervising the process .

2) Disposal of large amounts of sludge is an environmental problem.

3) Residual hardness is very high even 15ppm hardness is not good for boilers.

Q9) Explain the zeolite process with diagram & reactions.



Ans)" Zeolite is hydrated sodium aluminosilicate capable of exchanging reversibly their sodium ions for hardness producing ions in water." Zeolites are also known as Permutit.

They have the general formula as ,

$Na_2O .Al_2O_3 .x\ SiO_2 . y\ H_2O$ Where x =2 to 10 , y = 2 to 6

It is represented as Na_2Z where Z is Zeolite

Principle and process : -

Zeolite holds sodium ions loosely when hard water is passed through a bed of active granular Na_2Z .The hardness causing ions present in water like Ca^{+2}, Mg^{+2}etc are retained by the Zeolite bed and sodium ions are discharged by the bed and enters the water as shown in the following reactions.

$CaCl_2 + Na_2Z \rightarrow CaZ \downarrow + 2NaCl$

$CaSO_4 + Na_2Z \rightarrow CaZ.\downarrow + Na_2SO_4$

$Ca(HCO_3)_2 + Na_2Z \rightarrow CaZ\downarrow + 2NaHCO_3$

$MgCl_2 + Na_2Z \rightarrow MgZ.\downarrow + 2NaCl$

$MgSO_4 + Na_2Z \rightarrow MgZ.\downarrow + Na_2SO_4$

$Mg(HCO_3)_2 + Na_2Z \rightarrow MgZ \downarrow + 2NaHCO_3$

Thus all the hardness causing salts present in water are converted into the corresponding sodium salts, in other words the hard water becomes soft and the Na Zeolite bed gets exhausted. The regeneration is carried out by washing the bed with a concentrated solution of sodium chloride (brine solution)

Regeneration : -

$CaZ + 2NaCl \rightarrow Na_2Z + CaCl_2$

$MgZ + 2NaCl \rightarrow Na_2Z + MgCl_2$

Exhausted Zeolite Regenerated Zeolite

1) Residual hardness is 2 to 10 ppm.

2) Sludge is not produced.

3) Skilled persons are required .

4) The equipment is compact.

5) Time required for softening is very less.

Disadvantages : -

1) The treated water contains more sodium salts than in lime soda process.

2) The method only replaces Ca^{+2} and Mg^{+2} ions by Na^{+2} ions , but leaves all acidic ions

(HCO_3^- & CO_3^{-2}) in soft water .Such soft water containing ($NaHCO_3$, Na_2CO_3) etc when used in boilers $NaHCO_3$ decomposes to give CO_2 which causes boiler corrosion and Na_2CO_3 hydrolysis to NaOH , causing Caustic embrittlement.

Limitations : -

1)Turbid water cannot be used as it clogs the pores of the Zeolite bed.

2) If the water contains Fe^{+2} and Mn^{+2} they get converted to FeZ and MnZ which are difficult to regenerate because of their high stability.

3] If mineral acids are present in water they tend to destroy the Zeolite Bed hence the water has to be neutralized first before pouring down the bed.

Q10)Explain the Ion –Exchange process of softening of hard water.What are its advantages and disadvantages .

Ans) **Defination:** A process in which a reversible exchange of ions takes place between the stationary ion exchange phase and the external liquid mobile phase .

"Ion –Exchange resins are insoluble , cross – linked ,long chain, high molecular weight organic polymers which are permeable due to their microporous structure , and the functional groups attached to the chains are involved in the ion-exchanging properties."

Ion exchange resins are of two types

1)Cation Exchange resins (RH_2^+)

These resins are mainly styrene –divinyl benzene copolymers and contain acidic functional group like COOH,SO_3H,H^+etc that are capable of exchanging their H^+ ions with other cations present in water. It is represented as RH_2^+.Commercial cation exchanger is AMBERLITE IR – 120

2) Anion ExhangeResin : $(ROH)_2$

These resins are styrene – divinyl benzene or amine –formaldehyde copolymers containing amino or quaternary ammonium or tert sulphonuim hydroxyl functional group that are capable of exchanging their anions with the anions in water. Commercial anion exchange is Amberlite IR 400. It is represented as $(ROH)_2$

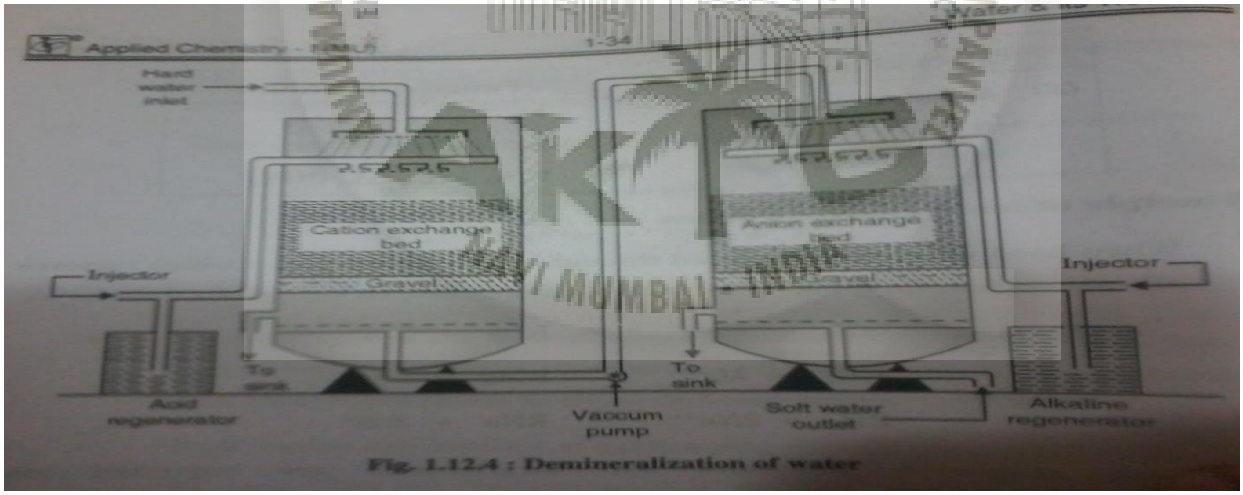


Fig. 1.12.4 : Demineralization of water

Hard water is first pass through cation exchange column. All the cations like Ca^{+2}, Mg^{+2} etc. present in water are removed and an equivalent amount of H^+ are discharged from the column into water as shown in the following reactions.

$$R - H_2 + Ca(HCO_3)_2 \rightarrow R - Ca \downarrow + 2H_2CO_3$$

$$R - H_2 + Mg(HCO_3)_2 \rightarrow R - Mg \downarrow + 2H_2CO_3$$

$$R - H_2 + CaCl_2 \rightarrow R - Ca \downarrow + 2HCl$$

$$R - H_2 + MgCl_2 \rightarrow R - Mg \downarrow + 2HCl$$

$$R - H_2 + CaSO_4 \rightarrow R - Ca \downarrow + H_2SO_4$$
$$R - H_2 + MgSO_4 \rightarrow R - Mg \downarrow + H_2SO_4$$

Thus, all the salts are converted into the corresponding acids in the cation exchange column. The water is next pumped into the anion exchange column. All the anion present in the column get absorbed into the bed and an equivalent amount of $\overline{OH}$ ions discharged from the bed enters the water as shown in the following reactions;

$R - (OH)_2 + H_2CO_3 \rightarrow R - CO_3\downarrow + 2H_2O$

$R - (OH)_2 + 2HCl \rightarrow R - Cl_2\downarrow + 2H_2O$

$R - (OH)_2 + H_2SO_4 \rightarrow R - SO_4\downarrow + 2H_2O$

H^+ and OH^- ,released from cation and anion exchange columns respectively get combines to from water molecule.

Thus, the water coming out of exchange is free from cations as well as anions. Ion free water, is known as deionised or demineralised water.

Regeneration

When capacities of cation and anion exchangers to exchange H^+ , and OH^- ions respectively are lost, they are said to be exhausted. These columns are regenerated by acid and alkali solutions respectively as given below.

The cation exchange column is regenerated using dil. HCl.

$$R - Ca + 2HCl \rightarrow R - H_2 \downarrow + CaCl_2$$
$$R - Mg + 2HCl \rightarrow R - H_2\downarrow + MgCl_2$$

While in order to regenerate anion exchange resins, diluted NaOH is passed through it.

$$R - CO_3 + 2NaOH \rightarrow R - (OH)_2\downarrow + Na_2CO_3$$
$$R - Cl_2 + 2NaOH \rightarrow R - (OH)_2 \downarrow + 2NaCl$$
$$R - SO_4 + 2NaOH \rightarrow R - (OH)_2 \downarrow + Na_2SO_4$$

The columns are then washed with deionised water and the washing is passed into the drain. The regenerated column is used again.

Advantages:-

1)The residual hardness is only around 0-2 ppm.

2)The process can be used to treat both acidic as well as alkaline water.

3) The equipment is compact.

4)The process is suitable even for removing colored metal ions like Mn^{+2} , Fe^{+2}

5) No sludge is produced.

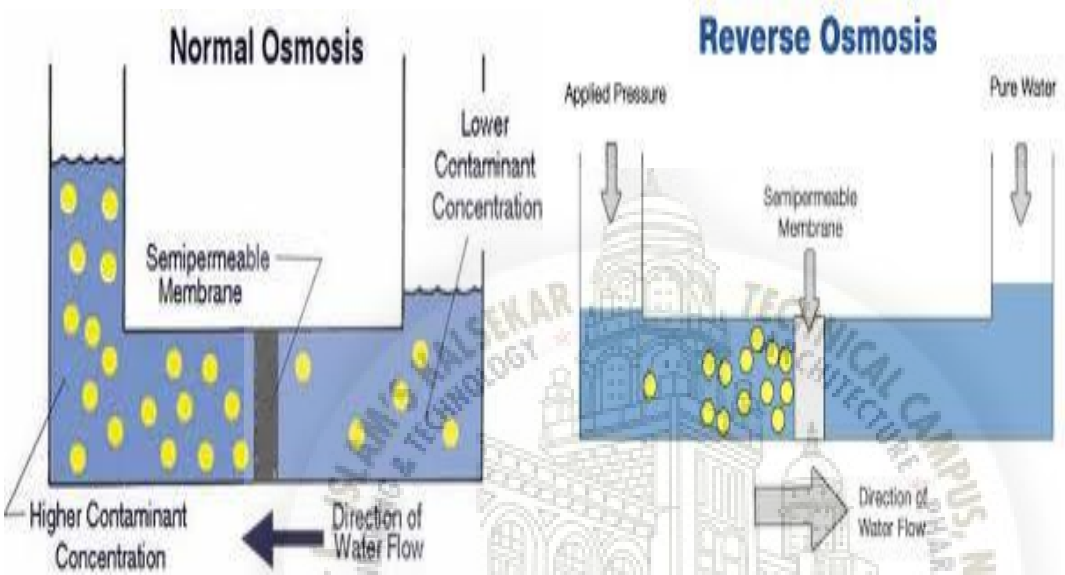
Disadvantges:

1) The equipment is costly.

2) Turbid water blocks the pores of the exchangers, hence turbidity has to be removed before pouring the water in the exchanger. Turbidity must be less than 10ppm.

Q11] Give a brief account of Reverse Osmosis.

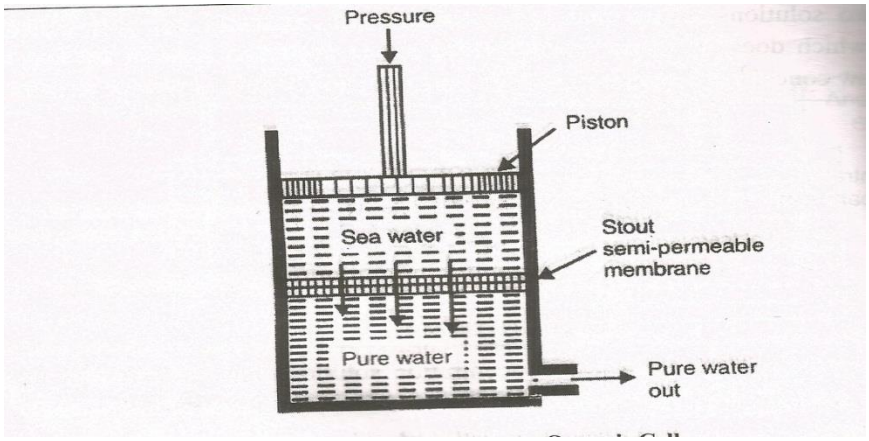
Ans



Definitions:-Osmosis: When two solutions of unequal concentration are separated by a semi-permeable membrane the solvent flows from the dilute solution to the concentrated solution.

Reverse Osmosis: When a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side, the solvent flow is reversed i.e. The solvent is forced to move from the concentrated solution to the dilute solution. Thus in reverse osmosis, pure solvent is separated from its salts and other impurities, rather than removing impurities from water. This membrane filtration is sometimes also called as **' Super filtration'** or ' **Hyper filtration'**

Desalination:-



Process:- Pressure of the order of 15 to 40kg/cm^2 is applied to the sea water to be treated.

The pure water is forced out through the semi- permeable membrane, leaving behind the dissolved salts and other impurities. The membrane usually consists of very thin films of cellulose acetate, affixed on either side of a perforated tube.

Nowadays, membranes made of polymethylmethacrylate and polymide polymers are being used.

Advantages of Reverse Osmosis Over Conventional Processes

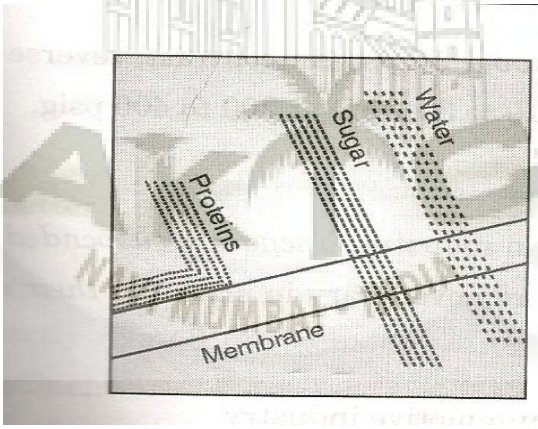
1) Compared with other conventional water treatment process, reverse osmosis has proven to be the most efficient means of removing salts, chemical contaminants and heavy metals, such as lead from drinking water.

2) For waters with total dissolved solids of 200 or more, reverse osmosis is less expensive than ion exchange.

3) Compared with distillation, reverse osmosis use only a fraction of the total energy and does not have high temperature problems or scaling and corrosion.

4) Simple to operate and maintain.

Q12) Write a short note on 'Ultrafiltration'



Ans)Ultrafiltration, like reverse osmosis is a cross flow separation process. It consists of membranes with pore size in the range of 0.1 to 0.001 micron.

When pressure is applied on the feed, the feed water flows through the semi – permeable membrane depending upon their MWCO.[MWCO is the smallest molecular weight species for which membrane has more than 90% rejection].

The stream of liquid that comes through the membrane is called as **Permeate.** The other liquid stream is called as **' Concentrate'** and gets progressively concentrated in those species removed by the membrane.

In cross flow separation , therefore the membrane itself does not act as a collector of molecules but merely as a barrier to these species.

Ultrafiltration membranes will remove high molecular weight substances, colloidal materials, and organic and inorganic polymeric molecules.

Low molecular – weight organics and ion such as sodium, calcium , magnesium , chloride, and sulfate are not removed by UF membranes,

Because only high molecular weight species are removed , the osmotic pressure differential across the UF Membrane surface is negligible.

Low applied pressure are therefore sufficient to achieve high flux rates from an ultra -filtration membrane.

Flux is defined as ' The amount of permeate produced per unit area of membrane surface per unit time.

Generally flux is expressed as gallons per square foot per day (GFD) or as cubic meters per square meters per day (M^3/M^2/Day).

UF membranes can have extremely high fluxes but in most practical application the flux varies between 50 and 200 GED at an operating pressure of about 50 psi in contrast, reverse osmosis membranes only produce between 10 to 30 GFD at 200 to 400 psi.

Q13) Define Water Pollution.

Ans:- Any alteration in the physical, chemical and biological properties of water as well as contamination with any foreign substances which would constitute a health hazard or otherwise decrease the utility of water is called as Water Pollution.

Q14) Explain the BOD and COD . What is their significance.

Ans:- Biochemical Oxygen Demand (BOD): The amount of free oxygen required for the biological oxidation of the organic matter under aerobic condition at 20°C and for a period of 5 days. Unit = mg/lit or ppm

Determination of BOD:- A known volume of sample of sewage is diluted with a known volume of diluted water, whose dissolved oxygen content is predetermined. The whole solution is incubated in a closed bottle at 20°C for 5days. After this unused O_2 is determined. The difference in the diluted water and unused oxygen of solution after 5 days gives BOD.

Significance:- It indicates the amount of decomposable organic matter in the sewage. Larger the concentration of decomposable organic matter, greater is the BOD.

It enables us to determine the degree of pollution at any time in the sewage stream.

Chemical Oxygen Demand(COD):- It is the amount of oxygen consumed under specified conditions in the oxidation of organic and oxidizable inorganic matter.

Determination of COD:A known volume of sample is refluxed with a known excess of standard potassium dichromate ($K_2Cr_2O_7$) and dil. H_2SO_4 in presence of a little Ag_2SO_4 catalyst and $HgSO_4$ for 1 ½ hours. The unreacted $K_2Cr_2O_7$ is then titrated against standard Mohr's salt solution [$FeSO_4(NH_4)_2, SO_4 6H_2O$] .The O_2 equivalent of $K_2Cr_2O_7$ consumed is taken as a measure of COD.

The COD is calculated as follows: $$COD = \frac{(V_1 - V_2) \times N \times 8 \times 1000}{X}$$

where V_1 and V_2 = Volume of FAS, N = Normality of FAS, X = The volume of sample taken for test.

Significance :-COD measures the biological oxidisable and biologically inert organic matter such as cellulose.COD values can be employed to estimate BOD values.

Determination of COD takes just 3 hours. Since in the COD test both biologically oxidisable and the biologically inert matter are oxidized, the COD value for a sample is always higher than BOD value.

Q 15] What are the methods to control Water Pollution.

Ans:-1) **Stabilisation of Ecosystem:** This involves reduction of the waste at the source, harvesting and removal of bio mass, trapping of nutrient fish management and aeration.

2**] Recycling of waste water by suitable treatment :-** Before discharging the waste water into the water bodies, methods like aeration and use of trickling filters or activated sludge treatment can be used for treating the waste water or sewage.

3] Waste Water Reclamation:- For example, sewage water can be directly used for irrigation, for fish farming, since it already contains dissolved nutrients such as Nitrogen, Phosphorus,

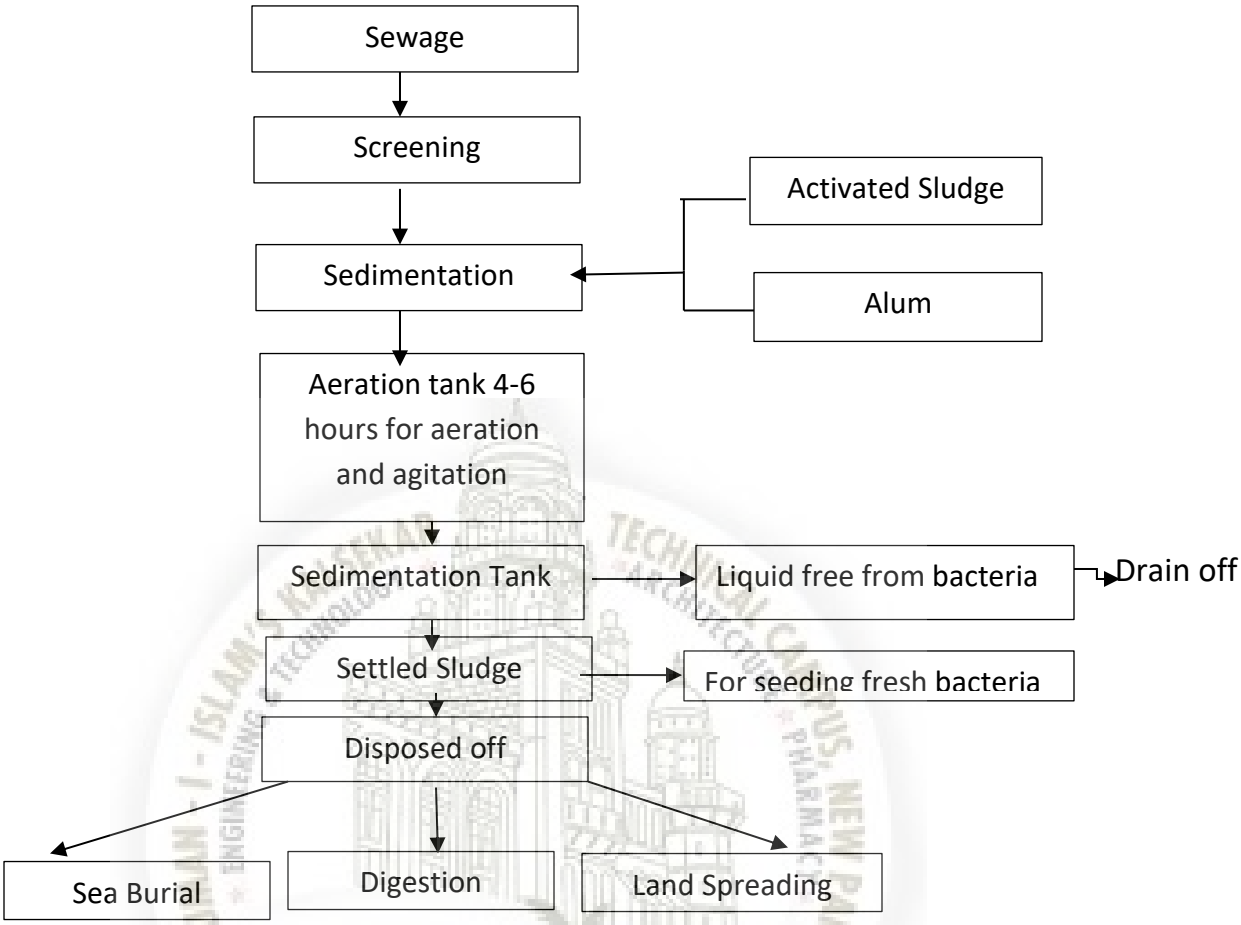
Potassium etc.

4) Dilution of waste water before their discharge into water bodies.

5)Removal of pollutants like phosphorus compounds mercury, ammonia, sodium salts, phenolic compounds etc. using special techniques like adsorption, ion - exchange, reverse osmosis etc.

Q16] Write a short note on 'Activated Sludge' process.

Ans:-**Activated Sludge Process:-**



Waste water treatment consists of following stages:-

1) Preliminary treatment:- This treatment is done to remove large suspended solids, grit, oil, grease. The different methods used are screening i.e passing through bar screens or mesh screens.

2) Primary treatment:- It consists of sedimentation process to remove suspended organic solids. Chemicals are sometimes added in primary clarifies to assist in the removal of finely divided and colloidal solids or to precipitate phosphorus.

3] Secondary or Biological Treatment:-In this category, process such as filtrate or activated sludge process are included.

The process consists of the mixing off sedimented sewage with proper quantity of activated sludge. The mixture is then sent to the aeration tank, in which the mixed liquor is simultaneously aerated and agitated for 4 – 6 hours.

During this aeration process, oxidation of the organic suspended matter takes place, followed by nitrogen to nitrites and nitrates.

After aeration, the effluent is sent to setting or sedimentation tank, where sludge is deposited and clean liquid free from bacteria is drawn off.

A part of settled sludge is sent back for seeding fresh batch of sewage, while the remaining is disposed off either by sea burial, digestion or by land spreading.

Overall, the activated sludge process plants involve following parts for carrying out the above mentioned process.

1] Setting tanks 2] Aerators 3] Clarifiers 4] Dilution tank.

Q17) Explain the treatment methods for removal of micro-organisms from Drinking water or Municipal Water.

Ans) The process of destroying the disease producing bacteria, micro – organism etc. from the water and making it safe for use is called **Desinfection** and the chemicals or substances which are added to water for killing the bacteria etc are known as **Desinfection.**

The disinfection of water can be carried out by following methods:-

1] <u>By Adding Bleaching powder:-</u>

After removing organic matter, suspended impurities etc, water is mixed with required amount of bleaching powder (about 1kg per 1000 kiloliters of water) and is allowed to stand undisturbed for several hours. The chemical action produces hypochlorous acid which is a powerful germicide.

$$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

$$Cl_2 + H_2O \longrightarrow HCl + HOCl \text{ (Hypochlorous acid)}$$

$$\text{Germs} + HOCl \longrightarrow \text{Germs are killed.}$$

1] The disadvantages of using bleaching powder are:-

i] It introduces calcium in water and makes it more hard.

ii] It deteriorates, due to its continuous decomposition during storage and therefore it has to be analyzed for its effective chlorine content before treatment.

iii] It is very important to use calculated amount of bleaching powder because excess of it gives bad color and disagreeable taste to treated water.

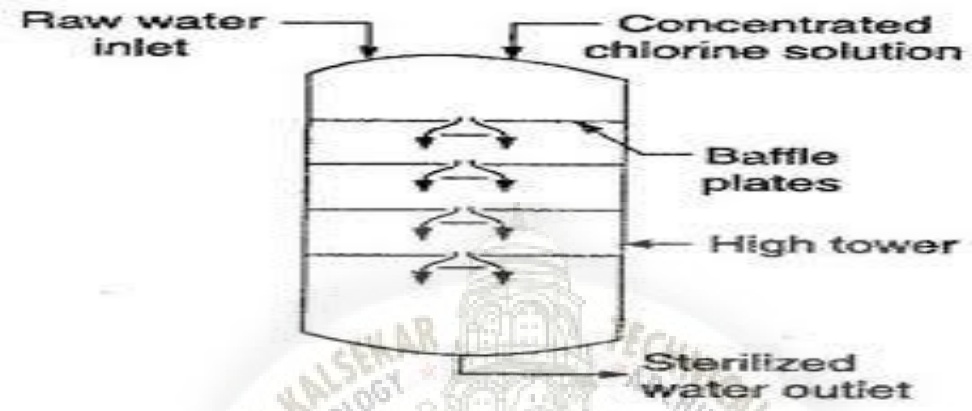
2] By Chlorination :- Chlorination produces hypochlorous acid which is a powerful germicide as follows.

$$Cl_2 + H2O \longrightarrow HOCl + HCl \text{ (Hypochlorous acid)}$$

The micro-organisms are killed due to the chemical reaction of hypochlorous acid with the enzymes in the cells of the organisms.

Since, enzymes is essential for the metabolic growth of the micro-organisms, so death of micro-organisms results due to inactivation of enzyme (in the cells of organisms) by hypochlorous acid,

The apparatus used for chlorination is called as Chlorinator. It is a high tower, having a number of baffle plates. Chlorine either in the form of gas or concentrated solution is introduced from the top along with the water. The mixture is mixed thoroughly due to baffle plates and sterilized water is collected using outlet. For filtered water, about 0.3 to 0.5 ppm of chlorine is sufficient.



Factors affecting efficiency of Chlorine:-

i] Time of Contact:- With time the efficiency goes on decreasing.

ii] Temperature of water:-As the temperature increases, the rate of reaction with enzyme increases and therefore efficiency increases.

iii] pH value of water:- At lower pH values (between 5 – 6.5) the efficiency is higher.

Advantages of Chlorine:-

i] It is effective , economical, stable and does not deteriorate on keeping.

ii] Requires less space for storage and can be used for low, as well as high temperatures.

iii] Does not introduces any impurities in treated water and therefore it is the most ideal disinfectant.

Disadvantages :-

i] If used in excess leads to.

a] Bad taste and odour

b]i) Irritation on mucus membrane.

ii] Free Chlorine in treated water should not exceed 0-1 to 0-2 ppm.

iii] It is more effective below 6.5pH and less effective at higher pH values.

3] Disinfectant by Ozone:- Ozone is an excellent disinfectant, which is produced by passing silent electric discharge through cold and dry oxygen.

$$O_2 \longrightarrow 2O_3$$

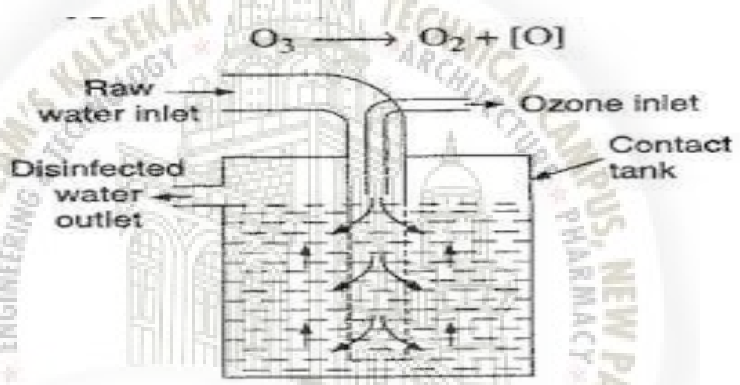
(Oxygen)Discharge (Ozone)

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

$$2O_3 \longrightarrow O_2 + [O]$$

Ozone Nascent oxygen.

Nascent oxygen being a powerful oxidizing agent kills the bacteria as well as oxidizes the organic matter present in water.



In this process, the ozone is injected into the water and the two are allowed to come in contact in a sterilizing tank. The contact period is about 10-15 min and the usual dose strength is 2-3 ppm. The disinfectant water is removed from top.

Advantages:-

It removes color, odour and taste without giving any residue.

It added in excess, is not harmful, since it is unstable and decompose into oxygen.

Disadvantages:-

i] It is very expensive and hence not employed for disinfectant of municipal water supply.

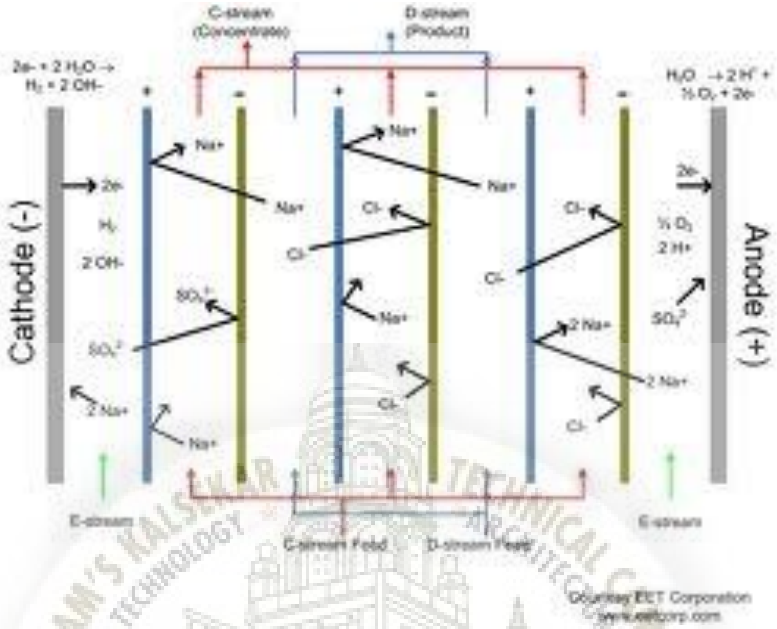
4] Electrodiaysis:- It is a method in which the ions are pulled out of the salt water by passing direct current, using electrodes and thin rigid plastic membrane pair (natural or synthetic).

Working:-

When direct electric current is passed through saline water, the sodium ions (Na^+) start moving towards negative pole (cathode) while the chloride ion ($C\bar{l}$) start moving towards the positive

pole cathode, through the membrane. As a result the concentration of brine decreases in the central compartment while it increases in the two side compartments.

Desalinated brine (or pure water) is removed from the central compartment from time to time , while concentrated brine is replaced by fresh sea water.



For more efficient separation, ion selective membranes, which are permeable to only one kind of ions with specific charge, have been used in recent years.

Cation selective membranes are permeable to only cations and anion selective membranes are permeable to only anions.

The ion selective membrane pores are designed with fixed charge while exclusively allows one type of charged ions to pass through its pores and does not allow oppositely charged.

Q18) What are the BIS specifications for potable water.

Ans)

Sr No	Test	Acceptable Limit	Permissible Limit	Method of test IS:3025
1.	Odour	Agreeable	Agreeable	IS:3025 –Part 5
2.	Taste	Agreeable	Agreeable	IS:3025 –Part 8
3.	pH	6.5 – 8.5	No relaxation	IS:3025 –Part 11
4.	Total Dissolved Solids (TDS mg/l)	500mg/l	2000mg/l	IS:3025 –Part 16
5.	Total Alkalinity as CaCO3 mg/l	200mg/l	600mg/l	IS:3025 –Part 23
6.	Total Hardness as CaCO3 mg/l	200mg/l	600mg/l	IS:3025 –Part 21

Water is potable and safe for drinking if the parameters are within the permissible limits .

The purification of water is maintained by Municipal Corporations/municipalities/Gram Panchayat and ensure that the various parameters are maintained within their permissible limits.

Q19)Distinguish between Hard water and soft water

Hard water	**Soft water**
1) Water which does not immediately produces good amount of lather with soap is called as Hard water.	1)) Water which immediately produces good amount of lather with soap is called as Soft water.
2) It contains dissolved salts of calcium , magnesium and heavy metals. Eg. $CaCl_2$, $CaSO_4$, $MgCl_2$,$MgSO_4$, $Ca(HCO_3)_2$, $Mg(HCO_3)_2$,$FeSO_4$ etc	2) It does not contains dissolved salts of calcium, magnesium and other heavy metals. Eg. $CaCl_2$, $CaSO_4$, $MgCl_2$,$MgSO_4$, $Ca(HCO_3)_2$, $Mg(HCO_3)_2$,$FeSO_4$ etc
3) It forms a curd like insoluble milky white precipitate.	3) It does not forms a curd like insoluble milky white precipitate.
4) It is not suitable for both industrial and domestic use.	4) It is suitable for both industrial and domestic use.

Distinguish between Temporary Hardness and Permanent Hardness.

Temporary Hardness	**Permanent Hardness**
1)It is due to bicarbonates and carbonates of Ca^{2+},Mg^{2+}etc	1)It is due to chlorides, sulphates ,nitrates of Ca^{2+},Mg^{2+}, Fe^{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)It leads to formation of loose deposits of carbonates and hydroxides of Ca^{2+},Mg^{2+} respectively if used in boilers.	3) It leads to formation of adherent scales.
4) It can be removed by simple techniques such as boiling and filtering	4) It cannot be removed by simple techniques such as boiling and filtering.

Comparison of water Softening Processes

Sr.no	**Lime-soda Process**	**Permutit/Zeolite Process**	**Ion-Exchange Process**
1	Chemical process involved in removal of hardness causing cations is precipitation	Chemical process involved in removal of cations is exchange of cations with sodium ions	Chemical process involves removal of all ions cations with protons and anions with hydroxide ions.
2	Residual hardness is 15-50ppm	Residual hardness is 0-15ppm	Residual hardness is 0-2ppm

3	It removes Fe^{2+} and Mn^{2+}	Small quantity of $Fe^{2+}$and Mn^{2+}can be removed	It removes all cations
4	It removes mineral acids from water	It does not remove mineral acids from water	It removes mineral acids from water
5	It can be used for turbid water	It cannot be used for turbid water	It cannot be used for turbid water
6	It removes CO_2 from hard water	It does not removes CO_2 from hard water.	It removes all dissolved gases from hard water
7	It involves many steps like coagulations settling of precipitate filtration , removal and disposal of sludge etc.	No such steps are involved	No such steps are involved
8	Reagent cannot be regenerated	The exchange medium can be regenerated	The exchange medium can be regenerated
9	Capital cost is low.	Cost of plant and material is high.	Capital cost is higher.
10	Operating expenses high.	Operating expenses are low.	Operating expenses are low.

Comparison BOD &COD

SR NO	BOD	COD
1)	It measures the oxygen demand of biodegradable pollutants only.	It measures the oxygen demand for biodegradable pollutants along with non – biodegradable pollutants
2)	Less stable measurement method as it uses microorganisms which are susceptible to pH, temperature and other variables in the water.	More stable measurement method as it uses potassium dichromate which oxidizes regardless of water conditions.
3)	Slow process. It takes five days.	Fast process. It takes 2-3 hours.
4)	BOD values are generally less than COD values.	COD values are generally greater than BOD values.

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