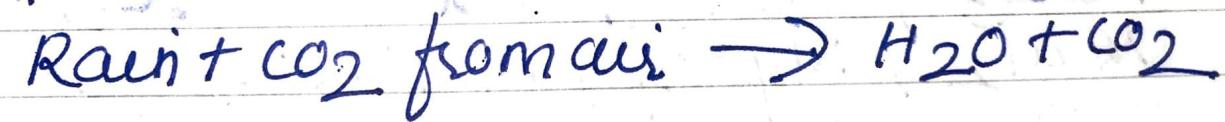


# Water

## Introduction

Water is one of the most abundant commodities in nature but is also the most misused one. Water is not only essential for the lives of animals and plants but also occupies a unique position in industries. Probably, its most important use as an engineering material is in the steam generation. Water is used as coolant in power and chemical plants. It is also used in steel, rayon, paper, atomic energy, textile, chemical, ice and for air conditioning, drinking, bathing, sanitary, washing etc.

When rain water falls to the earth's crust it solubilizes certain salts into it for eg.

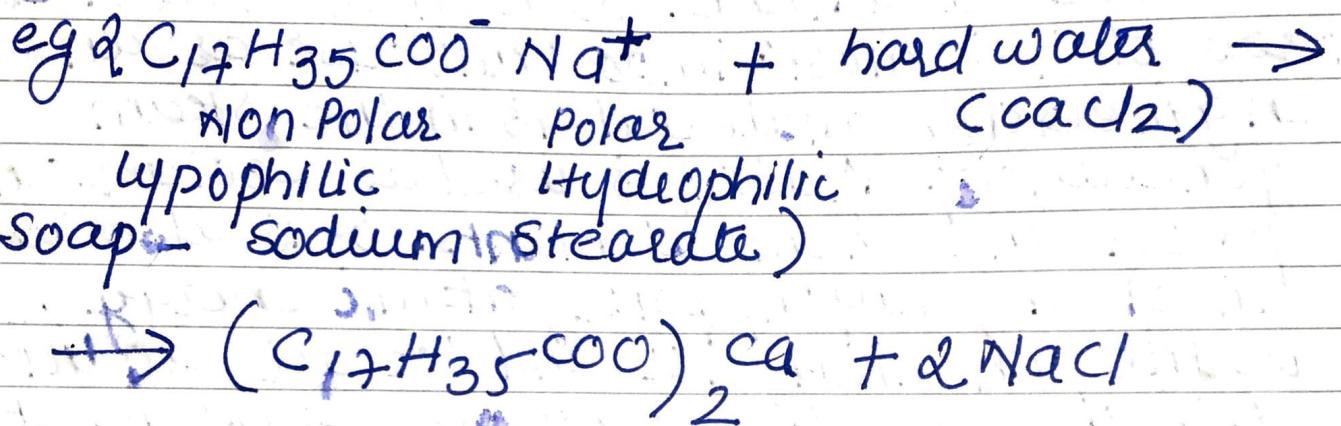


Mineral like  $\text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{Ca}(\text{HCO}_3)_2$   
 This form dissolved impurities, suspended impurities like mud, clay, Vegetable & animal matter, colloidal impurity - silica,  $\text{Fe(OH)}_2$ ,  $\text{Al(OH)}_3$  colouring matter etc.  
 Bacterial impurities, micro-organism etc.

All these impurities present in water makes it undesirable for the use in industries directly.

(2)

Hard water and soft water: The water which lathers instantly on shaking with soap  $\text{SO}_4^{2-}$  is called soft water. On the other hand, a sample of water which on shaking with soap solution does not give lather, but produce a curd like ppt is called hard water.



when certain ions like  $\text{Ca}(\text{CHCOO})_2$ ,  $\text{Mg}(\text{HCOO})_2$ ,  $\text{MgCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{CaCl}_2$ ,  $\text{CaSO}_4$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{MgCl}_2$ ,  $\text{MgSO}_4$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{FeCl}_2$ ,  $\text{FeSO}_4$ ,  $\text{AlCl}_3$ ,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{MnCl}_2$ ,  $\text{MnSO}_4$

are present in water they cause the above reaction with soap. i.e. they give hardness to water.

Hardness: is the soap consuming capacity of water. It is the property which prevents the lathering of soap. Hardness is caused by

(3)

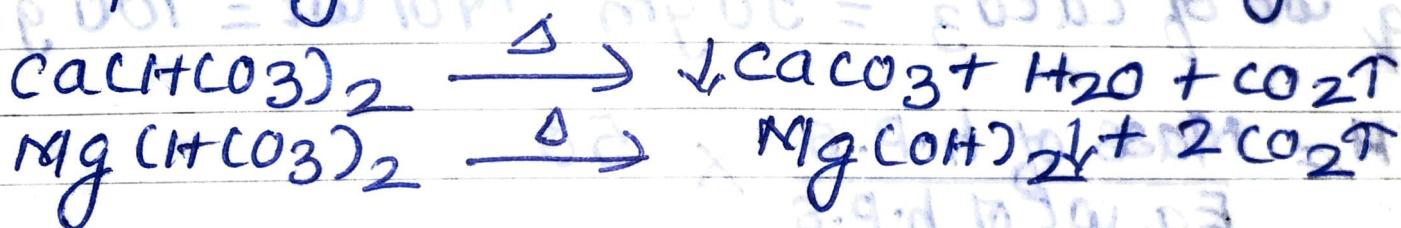
The dissolved salts of calcium and mg magnesium and also by other heavy metals like iron, aluminium, manganese.

There are two types of hardness temp orary hardness and permanent hardness.

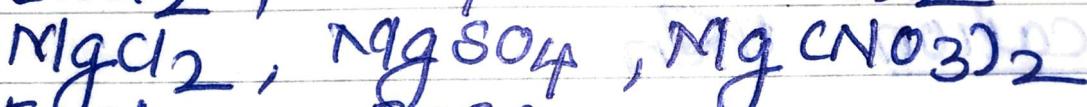
Temporary hardness is due to salts like  $\text{Ca}(\text{HCO}_3)_2$ ,  $\text{Mg}(\text{HCO}_3)_2$



This is also called carbonate hardness. Temporary hardness can be removed by boiling



Permanent hardness is due salts like



Permanent hardness can be removed to a larger extent by external methods like the lime and soda process, zeolite process and ion exchange method. By internal method by adding certain chemicals to remove the hardness.

(4)

Total hardness = temporary + permanent hardness

Degree of hardness: The degree of hardness is the net amount of hardness causing impurities present in a sample of hard water in finite volume. This is expressed in terms of equivalent of  $\text{CaCO}_3$ .

$$H = \frac{\text{Mass of hardness producing substance} \times \text{Eq. wt}}{\text{Eq. wt of hardness producing substance of } \text{CaCO}_3}$$

$$\text{Eq. wt of } \text{CaCO}_3 = 50 \text{ gm, Mol wt} = 100 \text{ gm}$$

$$H = \frac{\text{Mass of h.p.s}}{\text{Eq. wt of h.p.s}} \times 50$$

If the hardness producing substance has a bivalent cation then

$$H = \frac{\text{Mass h.p.s} \times \text{Mol wt } \text{CaCO}_3}{\text{Mol wt h.p.s}}$$

$$H = \frac{\text{Mass h.p.s} \times 100}{\text{Mol wt of h.p.s}}$$

The choice of  $\text{CaCO}_3$  is accepted since it has a mol wt = 100 gm, Eq. wt = 50 and it is the most insoluble salt that get precipitated during softening of hard water.

(5)

## Units of expressing degree of hardness.

1. Parts per million (ppm): 1 ppm of hardness is 1 part of  $\text{CaCO}_3$  equivalent hardness per million ( $10^6$ ) parts of water sample.

2. Milligram per litre (mg/lit): 1 mg/lit of hardness is 1 mg of  $\text{CaCO}_3$  equivalent hardness per litre of water sample.

$$1 \text{ mg/lit} = 1 \text{ mg of } \text{CaCO}_3 \text{ equivalent hardness in } 10^6 \text{ mg of water.}$$

Degree Clarke (°Cl) is 1 grain ( $1/7000 \text{ lb}$ ) of  $\text{CaCO}_3$  equivalent hardness present in 1 gallon ( $10 \text{ lb}$ ) of water.

$1^{\circ}\text{Cl} \equiv 1 \text{ grain of } \text{CaCO}_3 \text{ equivalent in 1 gallon}$

$\equiv 1/7000 \text{ lb of } \text{CaCO}_3 \text{ equivalent in 10 lb}$

$1^{\circ}\text{Cl} \equiv ? \text{ of } \text{CaCO}_3 \text{ equivalent in } 10^6 \text{ lb}$

$$1^{\circ}\text{Cl} \equiv \frac{10^6}{7000 \times 10} = \frac{100}{7} = 14.3 \text{ ppm}$$

(6)

4. French Degree ( ${}^{\circ}\text{F}_2$ ): 1 part of  $\text{CaCO}_3$  equivalent hardness per 105 parts of hard water.

$$10^{\circ}\text{F}_2 \equiv 10 \text{ ppm}$$

$$1 \text{ ppm} = 1 \text{ mg/liter} \quad 10^{\circ}\text{Cl} = 14.3 \text{ ppm} \quad 10^{\circ}\text{F}_2 = 10 \text{ ppm}$$

$$1 \text{ ppm} = 0.07^{\circ}\text{Cl} \quad 1 \text{ ppm} = 0.1^{\circ}\text{F}_2$$

### Numericals

1. A natural water sample has temporary hardness of  $3.8^{\circ}\text{Cl}$  and permanent hardness of  $12.3^{\circ}\text{F}_2$ . Find the total hardness as ppm in  $\text{CaCO}_3$  equivalent

$$1 \text{ ppm} = 0.07^{\circ}\text{Cl}$$

$$= 3.8 \times 0.07 = 12.3 \text{ ppm}$$

$$54.28 \text{ ppm}$$

$$1 \text{ ppm} = 0.1^{\circ}\text{F}_2$$

$$123 \text{ ppm}$$

$$\text{Total hardness} = \text{temp} + \text{permanent}$$

$$= 54.28 + 123 = 177.34 \text{ ppm}$$

2. Calculate in ppm, total hardness, permanent hardness and magnesium permanent hardness of a sample of water which has following analysis.

$$\text{Total hardness} = 20^{\circ}\text{Cl} \times 14.3 = 286 \text{ ppm}$$

$$\text{Carbonate hardness} = 10^{\circ}\text{Cl} \times 14.3 = 143 \text{ ppm}$$

$$\text{Magnesium permanent hardness} = 5^{\circ}\text{Cl} \times 14.3 = 71.5 \text{ ppm}$$

(7)

Total = temporary + permanent

$$286 = 143 + ?$$

Permanent =  $143 \text{ ppm}$

Permanent =  $\text{Mg} + \text{Ca}$

$$143 = 71.5 + ?$$

$$\text{Ca perm} = 71.5 \text{ ppm}$$

3. Find the carbonate and non carbonate hardness of a water sample which contains

$$\text{Ca}(\text{HCO}_3)_2 = 35.64 \text{ ppm}, \text{MgCl}_2 = 19 \text{ mg/lit}$$

$$\text{MgCO}_3 = 3.36 \text{ mg/lit} \quad \text{SiO}_2 = 5 \text{ ppm}$$

$$\text{CaCl}_2 = 22.2 \text{ ppm} \quad \text{CO}_2 = 2 \text{ ppm}$$

$\text{Al}^{+3} = 6 \text{ ppm}$ . Also find total hardness of water

( $\text{SiO}_2, \text{CO}_2$  do not render hardness  $\therefore$  should not be considered)

Calculate the mol wt of all hardness causing salt

(AT.wt Ca = 40, Mg = 24, Fe = 55.8, Al = 27  
 Mn = 54.9, C = 12, H = 1, N = 14, S = 32, O = 16,  
 Cl = 35.5)

$$\text{Ca}(\text{HCO}_3)_2 = 40 + (1 + 12 + 16 \times 3) \times 2 = 162$$

$$\text{MgCl}_2 = 24 + (35.5 \times 2) = 95$$

$$\text{MgCO}_3 = 24 + 12 + 16 \times 3 = 84$$

$$\text{Fe}(\text{HCO}_3)_2 = 55.8 + (1 + 12 + 16 \times 3) \times 2 = 177.8$$

$$\text{CaCl}_2 = 40 + (35.5) \times 2 = 111$$

(8)

carbonate hardness i.e temporary hardness

$$\text{Ca}(\text{HCO}_3)_2 \text{ H} = \frac{35.64}{76.2} \times 100 = 22 \text{ mg}$$

$$\text{MgCO}_3 \text{ H} = \frac{3.36}{84} \times 100 = 4 \text{ mg}$$

~~and 22 + 4 = 26 mg CaCO<sub>3</sub> equivalent~~

Non carbonate hardness i.e. Permanent hardness

$$\text{MgCl}_2 = \frac{19}{95} \times 100 = 20 \text{ mg}$$

$$\text{CaCl}_2 = \frac{22.2}{111} \times 100 = 20 \text{ mg}$$

since Al<sup>3+</sup> is trivalent we use the formula

$$\text{H} = \frac{\text{Mass h.c.s}}{\text{Eq.wt h.c.s}} \times \text{Eq wt of CaCO}_3$$

$$\text{Eq.wt} = \frac{\text{Molar wt / At wt}}{\text{Valency of cation}} = \frac{27}{3} = 9$$

$$\text{H Al}^{3+} = \frac{(8 \times 6) + 50}{9} = 33.3 \text{ mg}$$

$$20 + 20 + 33.3 = 73.33 \text{ mg}$$

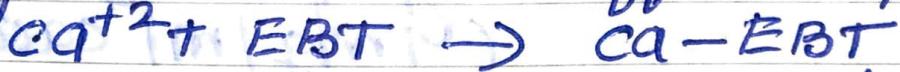
Total = carbonate + non carbonate

$$26 + 73.33 = 99.33 \text{ mg/litre}$$

Estimation of hardness: EDTA (ethylene diamine tetra acetic acid) is most accurate method for the estimation of hardness of water.

Principle: This is a very convenient method for rapid estimation of hardness of water. Sample. It involves complexometric titration of water sample buffered at pH 10, against a std solution of EDTA. EDTA forms a stable complex with metal ion like  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$  and other heavy metal ion.

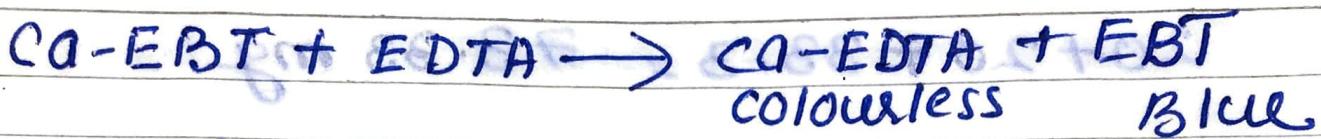
For the detection of end pt of alcoholic solution of a blue coloured dye, EBT (Eriochrome black T) is added to the water sample. Initially  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$  etc form wine red unstable complex with dye at pH -10 (Buffer  $\text{NH}_4\text{Cl} + \text{NH}_3\text{OH}$ )



wine red unstable complex

Now EDTA is added from the burette. It displaces EBT and itself form a stable complex with  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  ion which is colourless and release the indicator therefore the original blue colour of the dye appears.

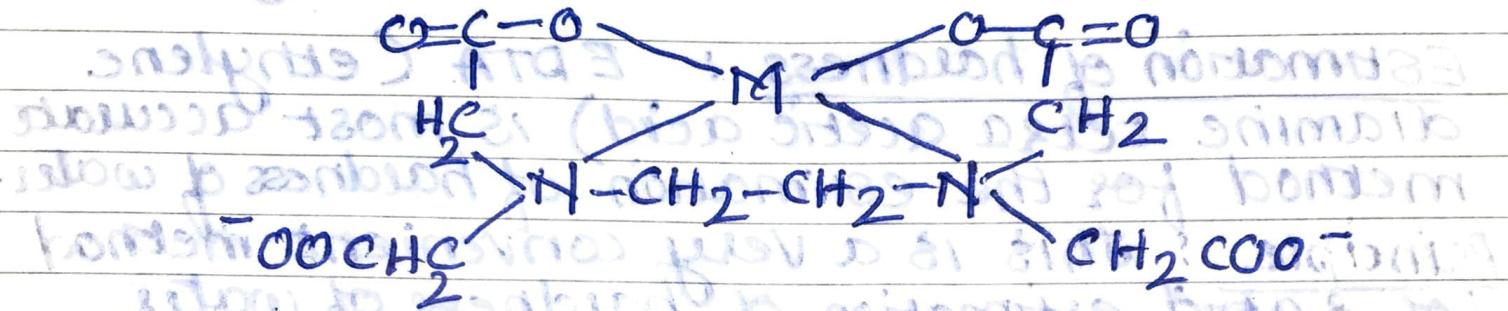
10



+ stable

= 101

$$101 = 88.58 + 1.5$$



### Metal complex of EDTA

calculation std prepared 1gm/lit of  $\text{CaCO}_3$

50ml of std hardwater -  $V_1$  ml of EDTA

50ml of unknown hardwater -  $V_2$  ml of EDTA

50ml of boiled hard water -  $V_3$  ml of EDTA

①  $V_1$  ml of EDTA  $\equiv$  50ml of std hard water  
 $\equiv$  50mg of  $\text{CaCO}_3$  equi hardness  
 $(1\text{ mg/ml } \text{CaCO}_3)$ .

$\therefore 1\text{ ml of EDTA} \equiv \frac{50}{V_1} \text{ mg of } \text{CaCO}_3 \text{ equi hardness}$

a. 50ml unknown hardwater  $\equiv V_2$  ml of EDTA  
 but we know that

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

$\therefore V_2 \text{ ml of EDTA} \equiv \frac{50 \times V_2}{V_1} \text{ mg of } \text{CaCO}_3 \text{ equi hardness.}$

(11)

$$50\text{ml unknown hard water} \equiv \frac{50 \times V_2}{V_1} \text{ mg CaCO}_3$$

equivalent hardness.

$$\therefore 1000\text{ml unknown hard water} \equiv \frac{50 \times V_2}{V_1} \times \frac{1000}{50}$$

$$= \frac{1000 V_2}{V_1} \text{ mg of CaCO}_3$$

$$\therefore \text{Total hardness} = 1000 \times \frac{V_2}{V_1} \text{ mg/lit (ppm)}$$

$$(3) 50\text{ml boiled hard water} \equiv V_3 \text{ ml of EDTA}$$

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

$$V_3 \text{ ml of EDTA} \equiv \frac{50}{V_1} \times V_3 \text{ mg of CaCO}_3 \text{ equi hardness}$$

$$50\text{ml of boiled hard water} \equiv \frac{50}{V_1} \times V_3 \text{ mg CaCO}_3 \text{ equi hardness.}$$

$$\therefore 1000\text{ml of boiled hard water} \equiv \frac{50}{V_1} \times V_3 \times \frac{1000}{50}$$

$$= 1000 \frac{V_3}{V_1} \text{ mg of CaCO}_3$$

$$\text{Permanent hardness} = \frac{1000 V_3}{V_1} \text{ mg/lit or ppm}$$

$$\text{Temporary hardness} = \text{Total} - \text{permanent}$$

(12)

$$= \frac{1000 V_2}{V_1} - \frac{1000 V_3}{V_1}$$

$$= 1000 \left( \frac{V_2 - V_3}{V_1} \right) \text{ mg/liter or ppm.}$$

### Problem

- i) calculate the hardness in ppm in a given sample of water from the following data.
- ① 50ml of std hard water containing 1mg  $\text{CaCO}_3$  per ml consumed 20ml EDTA using EBT as indicator.
- ii) 50ml water sample consumed 30ml EDTA using same indicator.
- iii) 50ml water sample after boiling and filtering consumed 20ml EDTA using the same indicator.

50ml of std hard water = 20ml EDTA

50mg of  $\text{CaCO}_3$  equi hardness = 20ml EDTA

$\frac{50}{20}$  mg of  $\text{CaCO}_3$  equi hardness = 1ml EDTA

1ml EDTA = 2.5mg of  $\text{CaCO}_3$  equivalent hardness.

50ml of water sample = 30ml of EDTA

But 1ml EDTA = 2.5mg of  $\text{CaCO}_3$

∴ 30ml EDTA =  $30 \times 2.5$  mg  $\text{CaCO}_3$

= 75mg  $\text{CaCO}_3$

(13)

50ml of water sample  $\equiv$  2.5 mg of  $\text{CaCO}_3$   
 $\therefore$  1000 ml of water sample  $\equiv$  1500 mg/lit

50ml of boiled water sample  $\equiv$  20 ml of EDTA  
 $\therefore$  1000 ml of boiled water sample  $\equiv$   $20 \times 2.5 \text{ mg CaCO}_3$   
 $\equiv$  1000 ppm.

$$\begin{aligned} \text{Temp} &= \text{total} - \text{permanent} \\ \text{TL} &= 1500 - 1000 = 500 \text{ ppm.} \end{aligned}$$

2. 50ml of std hard water ( $1.2 \text{ gm CaCO}_3/\text{lit}$ ) requires 32 ml of EDTA solution. 100ml of water sample consumes 14 ml of the EDTA solution. 100ml of boiled and filtered water takes 8.5 ml of EDTA solution. Find temporary and non carbonate hardness of the water sample.

$$\begin{aligned} \text{std. } 1.2 \text{ gm CaCO}_3/\text{lit} &= 12000 \text{ mg/liter} \\ &\equiv 1.2 \text{ mg/ml} \end{aligned}$$

$$\therefore 50 \text{ ml} \times 1.2 = 60 \text{ mg CaCO}_3.$$

$$\begin{aligned} \textcircled{1} \quad 50 \text{ ml of std hard water} &\equiv 32 \text{ ml of EDTA} \\ 60 \text{ mg of CaCO}_3 \text{ equi hardness} &\equiv 32 \text{ ml of EDTA} \\ \frac{60}{32} \text{ " " " " } &\equiv 1 \text{ ml of EDTA} \end{aligned}$$

$$1 \text{ ml EDTA} \equiv 1.875 \text{ mg CaCO}_3$$

$$\begin{aligned} \textcircled{2} \quad 100 \text{ ml water sample} &\equiv 14 \text{ ml of EDTA} \\ \text{But, } 1 \text{ ml of EDTA} &\equiv 1.875 \text{ mg CaCO}_3 \\ \therefore 14 \text{ ml of EDTA} &\equiv 1.875 \times 14 \text{ mg CaCO}_3 \end{aligned}$$

(14)

100ml water sample  $\equiv$  26.25 mg  $\text{CaCO}_3$  equiv.

~~1000ml water sample  $\equiv$  315mg  $\text{CaCO}_3$  hardness.~~

1000ml water sample  $\equiv$  262.5 ppm.

3. 100 ml of boiled water  $\equiv$  8.5 ml of EDTA  
 $\equiv 8.5 \times 1.875 \text{ mg } \text{CaCO}_3$   
 $\equiv 15.938 \text{ mg } \text{CaCO}_3$  equiv.

$\therefore$  1000ml of boiled water  $\equiv$  159.38 ppm hardness.

3) 50ml of a hard water sample required  
 6ml of N/20 EDTA solution for titration  
 20ml of the sample water after boiling and  
 filtering etc. required 4 ml of N/50 EDTA  
 solution for titration. calculate the hardness  
 in ppm.

[1000ml of 1N EDTA  $\equiv$  100 gm of  $\text{CaCO}_3$ .]  
 [1000ml of 1N EDTA  $\equiv$  50 gm of  $\text{CaCO}_3$ .]

(Since there no information regarding the standard is given, the above information is used.)

1000ml of 1N EDTA  $\equiv$  50 gm of  $\text{CaCO}_3$

1ml of 1N EDTA  $\equiv$   $50/1000$  gm of  $\text{CaCO}_3$   
 $= \frac{50}{1000} \times 1000 \text{ mg } \text{CaCO}_3$

$\equiv 50 \text{ mg } \text{CaCO}_3$

(15)

50ml hard water sample = 6ml of 1/20 N EDTA

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

6ml of  $\frac{1}{20}$  N EDTA =  $\frac{6}{20} \times 50$  mg  $\text{CaCO}_3$

= 15mg  $\text{CaCO}_3$  equi hardness

50ml hard water sample = 15mg  $\text{CaCO}_3$  equi hardness

∴ 1000 ml hard water sample =  $\frac{15}{50} \times 1000 = 300$  ppm.

20ml boiled sample = 14mg  $\text{CaCO}_3$  eq

∴ 1000ml boiled sample =  $\frac{14}{20} \times 1000 = 200$  ppm.

20ml of water sample after boiling = 4ml 1/50 N EDTA

But, 1ml of 1N EDTA = 50mg  $\text{CaCO}_3$  equi hardness

4ml of  $\frac{1}{50}$  N EDTA =  $\frac{4}{50} \times 50 = 4$  mg of  $\text{CaCO}_3$

20ml of boiled sample = 4mg of  $\text{CaCO}_3$  equivalent hardness.

∴ 1000ml of boiled sample =  $\frac{4}{20} \times 1000 = 200$  ppm.

(4) A standard hard water sample contains 0.25mg of  $\text{CaCO}_3$ /ml. 100ml of this water consumed 24.4ml 0.02N EDTA. 25ml sample of a boiler feed water consumed 10.8ml of the same EDTA. Another aliquot of the boiler

(16)

feed water consumed is boiled and filtered.  
 50ml of the filtrate consumed 3.1 ml of 0.01N EDTA. Obtain the hardness of boiled feed water and express as ppm 'Cl' and 'Fe'.

1ml of std water  $\rightarrow$  0.25 mg of  $\text{CaCO}_3$  equivalent hardness.

$\therefore 100\text{ml} \rightarrow 0.25 \times 100 \text{ mg of } \text{CaCO}_3$

100ml of std water sample  $\equiv$  24.4 ml of 0.02N EDTA

$0.25 \times 100 \text{ mg of } \text{CaCO}_3 \text{ equi} \equiv 24.4 \text{ ml of } 0.02 \text{ N EDTA}$

$$\frac{0.25 \times 100}{24.4 \times 0.02} = 51.23 \text{ mg} \equiv 1 \text{ ml of } 1 \text{ N EDTA}$$

25ml of sample water  $\equiv$  10.8 ml of 0.02N EDTA

$$\begin{aligned} \text{But } 1 \text{ ml of } 1 \text{ N EDTA} &\equiv 51.23 \text{ mg } \text{CaCO}_3 \text{ equi} \\ \therefore 10.8 \text{ ml of } 0.02 \text{ N EDTA} &\equiv 51.23 \times 10.8 \times 0.02 \\ &= 11.07 \text{ mg } \text{CaCO}_3 \end{aligned}$$

25ml of sample water  $\equiv$  11.07 mg of  $\text{CaCO}_3$  equi

$$\therefore 1000 \text{ ml of sample water} = \frac{11.07 \times 1000}{25} = 442.8 \text{ ppm}$$

$$\begin{aligned} 50 \text{ ml of boiled and fil water} &\equiv 3.1 \text{ ml of } 0.01 \text{ N EDTA} \\ &\equiv 3.1 \times 0.01 \times 51.23 \text{ mg } \text{CaCO}_3 \end{aligned}$$

50ml of boiled water  $\equiv 1.58813 \text{ mg } \text{CaCO}_3$

$$\therefore 1000 \text{ ml of boiled water} \equiv 31.76 \text{ ppm.}$$

$$\text{Temp} = \text{Total} - \text{Perm} = 442.8 - 31.76 = 410.86 \text{ ppm}$$

(17)

$$\text{Total} - 442.8 \text{ ppm} = 30.98^\circ \text{Cl} = 44.262^\circ \text{Fe}$$

$$\text{Temp} - 410.86 \text{ ppm} = 28.76^\circ \text{Cl} = 41.086^\circ \text{Fe}$$

$$\text{Ptemp} - 31.76 \text{ ppm} = 2.223^\circ \text{Cl} = 3.176^\circ \text{Fe}$$

(5). calculate the hardness of water sample whose 20ml required 30ml of EDTA soln?  
10ml of  $\text{CaCl}_2$  solution (strength 300mg  $\text{CaCO}_3$ /200ml) required 20ml EDTA solution

$$200\text{ml of } \text{CaCl}_2 \equiv 300 \text{ mg } \text{CaCO}_3 \text{ equivalence}$$

$$\therefore 10\text{ml of } \text{CaCl}_2 \equiv \frac{10 \times 300}{200} = 15 \text{ mg } \text{CaCO}_3$$

$$10\text{ml of } \text{CaCl}_2 \text{ solution} \equiv 20\text{ml of EDTA solution}$$

$$15 \text{ mg of } \text{CaCO}_3 \equiv 20\text{ml of EDTA solution}$$

$$\therefore \frac{15}{20} \text{ mg of } \text{CaCO}_3 \equiv 1\text{ml of EDTA solution}$$

$$0.75 \text{ mg of } \text{CaCO}_3$$

$$20\text{ml of hard water sample} \equiv 30\text{ml of EDTA}$$

$$\equiv 30 \times 0.75 \text{ mg } \text{CaCO}_3$$

$$20\text{ml of hard water sample} \equiv 22.5 \text{ mg } \text{CaCO}_3$$

$$1000\text{ml of hard water sample} \equiv \frac{22.5 \times 1000}{20}$$

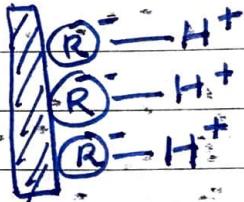
$$\text{below board, return to position 3} - 1125 \text{ ppm.}$$

Ion exchange method is one of the method used for softening of water. It is also called as demineralisation process. (deionised water)

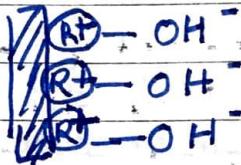
For many years distillation was the only method available for complete removal of soluble salts from water. However with the advent of development of commercial cation exchange resins ( $R-SO_3H$ ,  $R-COOH$ ) and anion exchange resins ( $R-CH_2-NH_3^+$ ,  $OH^-$ ,  $C_2H_4N^+H_3$ ) it has been possible to produce de-ionised water of highest purity by two step ion exchange process.

Principle : Ability of ion exchange resin to exchange their functional group like  $H^+$  with cations like  $Ca^{+2}$ ,  $Mg^{+2}$ ,  $Na^+$  using cation exchange resin and  $OH^-$  with all anions ( $Cl^-$ ,  $SO_4^{-2}$ ,  $CO_3^{2-}$ ) with  $OH^-$  anions using anion exchange resin.

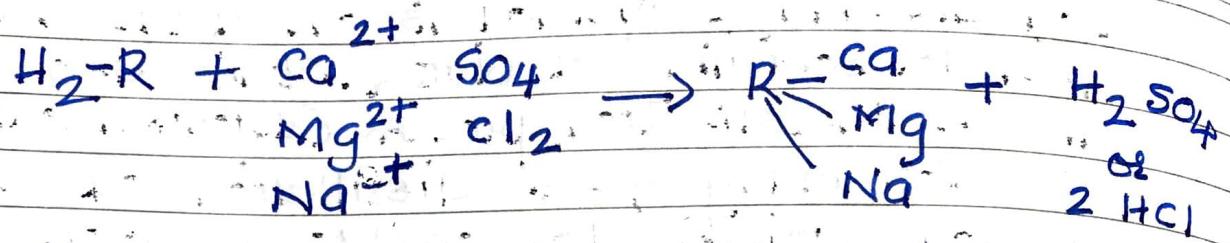
cation exchange Resin - is a polymeric anion to which active cations are attached.



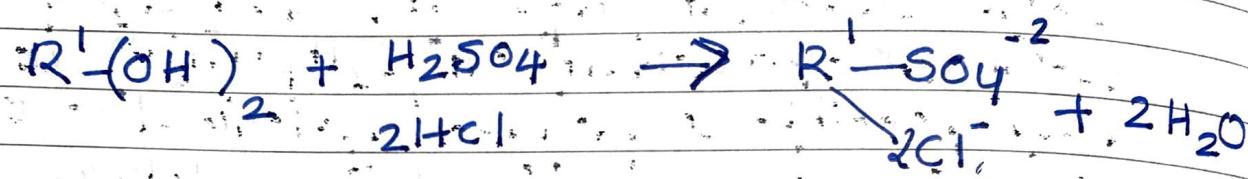
Anion exchange Resin is a polymeric cation to which active anions are attached.



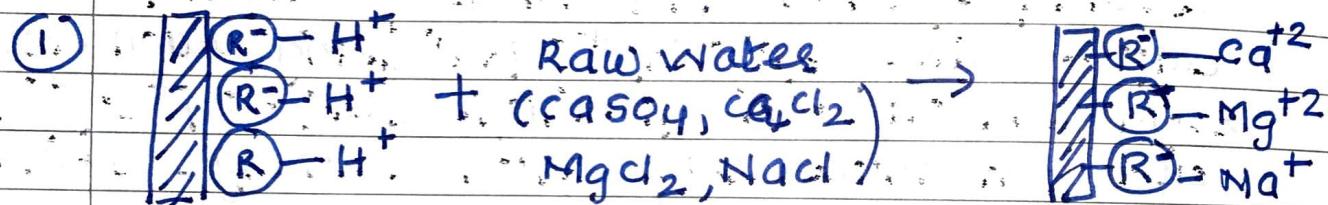
The process of softening water involves passing raw water through cation exchanger



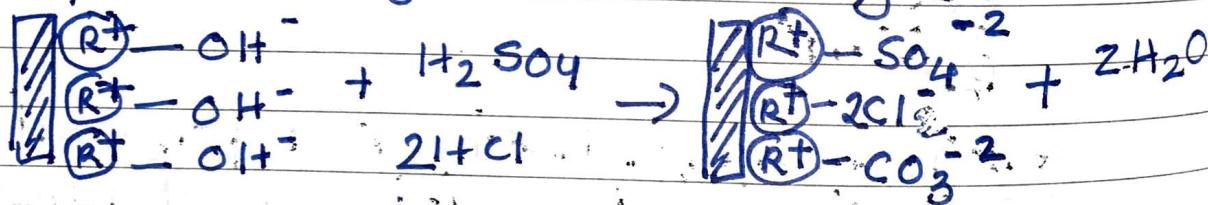
The effluent from this step is then passed through an anion exchanger.



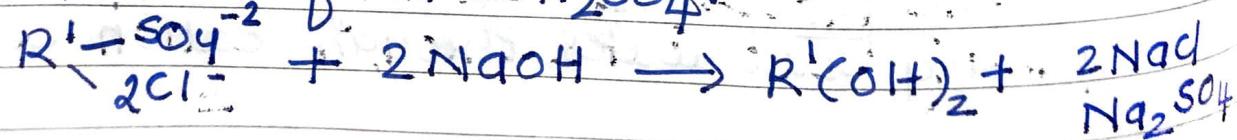
Thus all the ions present in water are removed and deionised water is produced.

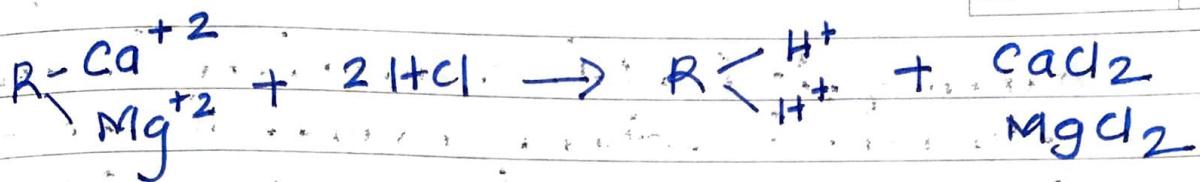


(2) The acid (effluent) from above is allowed to pass through anion exchanger.

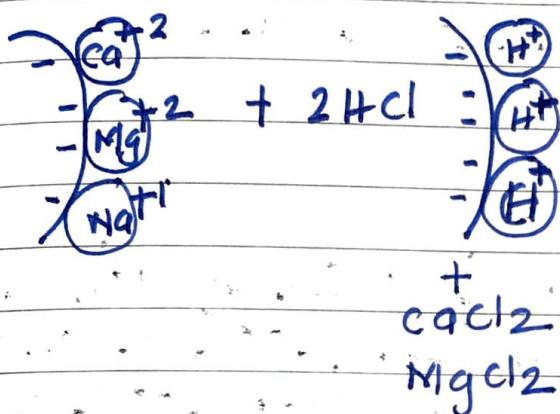


Regeneration: The anion exchanger may be regenerated by treating it with dilute NaOH soln. The cation exchanger is regenerated by passing a solution of HCl or H2SO4.

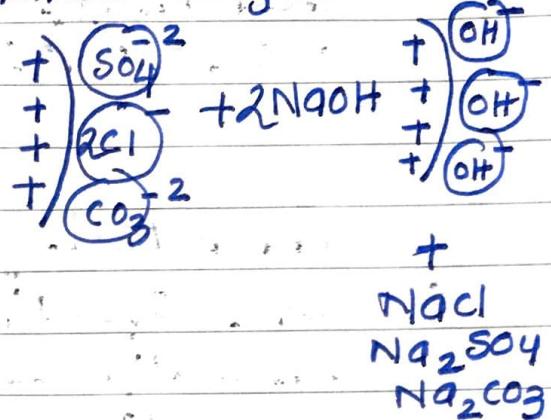




### cation Regeneration.



### Anion Regeneration



### Equipment

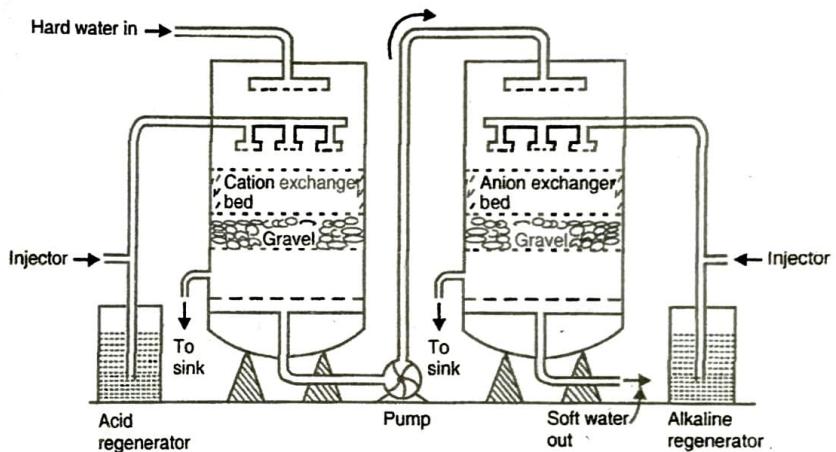


Fig. 8. Demineralization of water.

The equipment consist of two cylinders which contain the cation exchange resin and the anion exchange resin. The outlet from cation exchanger is connected to anion exchanger. Separate outlets are provided for draining purposes. Tanks provided at the bottom contains the regeneration chemicals.

Limitation: Water containing turbid or suspended matter block the pores of the resin hence decrease its efficiency.

Advantage:- ① acidic or alkaline water can be softened. ② Residual hardness is less than  $2 \text{ ppm}$ . ③ Water free of all minerals can be obtained.

Disadvantage : ① Resin is costly ② Highly turbid water do not give best results.

### Numericals :

① After treating  $10^4$  lit water by ion exchanger, the cation resin required  $200\text{L}$  of  $0.1\text{N HCl}$  and anion exchanger required  $200\text{L}$  of  $0.1\text{N NaOH}$  solution. Find the hardness of water.

Note : In an ion exchanger, all hardness causing cations are separated by cation exchanger, while the anion exchanger removes anions of the constituent present in water. Consequently the amount of acid for regeneration of cation resin refers hardness part.

1gm equivalent of  $\text{HCl} \equiv 1\text{ gm equivalent of } \text{CaCO}_3$

$1000\text{ ml of } 1\text{N HCl} \equiv 50\text{ gm of } \text{CaCO}_3$

$1\text{ ml of } 1\text{N HCl} \equiv 50\text{ mg of } \text{CaCO}_3 \text{ equivalent hardness.}$

$$200 \times 1000\text{ ml of } 0.1\text{N HCl} \equiv \frac{50 \times 200 \times 1000 \times 0.1}{1 \times 1}$$

mg of  $\text{CaCO}_3$  equi hardness

$\equiv 10^6 \text{ mg of } \text{CaCO}_3 \text{ equi hardness}$

$10^4$  litres of water contains  $10^6 \text{ mg of } \text{CaCO}_3 \text{ equi hardness}$

$$\therefore 1 \text{ litre of water contains} = \frac{10^6 \times 1}{10^4} = 100 \text{ mg/lit } \text{ or } 100 \text{ ppm}$$

2. In an ion exchange process the sample of hard water having hardness 375 ppm was demineralised. For regeneration of column's 75 lit of 0.1N HCl and 75 lit of 0.1N NaOH was required for cation and anion exchangers respectively. calculate the total quantity of water softened by these softeners.

1000 ml of 1N HCl  $\equiv$  50 gm of  $\text{CaCO}_3$  equivalent hardness

1 ml of 1N HCl  $\equiv$  50 mg of  $\text{CaCO}_3$  equivalent hardness  
 $75 \times 10^3$  ml of 0.1N HCl  $\equiv$   $50 \times 75 \times 10^3 \times 0.1$  mg of  $\text{CaCO}_3$   
 $1 \times 1$

$375 \times 10^3$  mg of  $\text{CaCO}_3$  equivalent hardness

1 lit of sample water contains 375 mg of  $\text{CaCO}_3$  equivalent hardness

$\therefore x$  lit of sample water contains  $375 \times 10^3$  mg of  $\text{CaCO}_3$  equivalent hardness

$$\therefore x = \frac{375 \times 10^3 \times 1}{375} = 1000 \text{ lit}$$

3. In demineralization process 20,000 lit of hard water having hardness 375 ppm was softened. How much 1tcl of 0.2N would be required for regeneration

1 lit of hard water sample contains 375 mg of  $\text{CaCO}_3$  equivalent hardness

20,000 lit hard water sample contains  $375 \times 10^5$  mg of  $\text{CaCO}_3$  equivalent hardness.

1 ml of 1N HCl  $\equiv$  50 mg of  $\text{CaCO}_3$  equivalent hardness  
 $x$  ml of 0.2N HCl  $\equiv$   $75 \times 10^5$  mg of  $\text{CaCO}_3$  equivalent hardness.

$$x = \frac{75 \times 10^5 \times 1 \times 1}{0.2 \times 50} = 750,000 \text{ ml} = 750 \text{ lit}$$

### Extra Questions

1. In regeneration of 75% exhausted ion exchanger, 200 litres of 1N NaOH was required. If the hardness is 75 ppm, calculate how many litres of water was softened by that softener.  
(Ans - 33.33. 33 litres - Ans)
2.  $10^5$  litres of hard water was passed through an ion exchanger. Calculate how much the hardness of water sample in ppm, if 215 lit of N/50 HCl and same amount of NaOH was required for regeneration  
(Ans - 2.15 ppm)
3. In demineralization process 30,000 lit of hard water having 150 ppm hardness was softened. How much NaOH of 0.2N would be required for regeneration of anion exchanger.  
(Ans - 150 lit)

## Biological and chemical oxygen demands:

The presence of free oxygen is necessary for the livelihood of organisms, present in sewage water. The aerobic action continues, till the free oxygen is present. As the oxygen exhausts the anaerobic action of putrefaction starts, when complex organic compound split up, setting free gases like  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ ,  $\text{CH}_4$  etc and foul smell starts coming. The length of aerobic action can be increased, if the percentage of free oxygen in the sewage is increased in the beginning.

### Biological oxygen demand (Definition) - (Qmp)

BOD of a sewage is defined as the amount of free oxygen required for the biological oxidation of organic matter under aerobic conditions at  $20^\circ\text{C}$  and for a period of 5 days.

The unit of BOD is mg/L or ppm.

Significance - BOD is the most important in sewage treatment, as it indicates the amount of decomposable organic matter in the sewage. Larger the concentration of decomposable organic matter, greater the BOD and consequently more the nuisance potential.

BOD has a special significance in pollution control, as it enables us to determine the degree of pollution at any time in the sewage.

(More the BOD Value less is the dissolved oxygen in water)

Dissolved oxygen - The measurement of DO gives a ready assessment of purity of water. The determination of dissolved oxygen is the basis for BOD test, which is commonly used to evaluate the pollution strength of waste waters.

The dissolved oxygen content determination is also essential for maintaining aerobic conditions in the receiving waters and also in the aerobic treatment of sewage and industrial waste water.

(Below determination is just for understanding)

Determination - Winkler's Method or Iodometric method

(By adding Reagents molecular O<sub>2</sub> is converted to I<sub>2</sub>)

Bottle - 1 - 50ml sewage sample diluted with aerated distilled water and made up to 900ml

25ml of the above sample from bottle one is pipetted in conical flask + Reagents are added and titrated versus Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.

and dissolved oxygen content is calculated.

This is DO<sub>Initial</sub>

Bottle - 2 - 50ml sewage sample diluted with aerated distilled water and made upto 900ml. This bottle is kept in an incubator at 20°C for 5 days

After 5 days - 25ml of the above sample is taken + Reagents are added and titrated versus Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and dissolved oxygen content is calculate. This is DO<sub>Final</sub>.

In order to find the BOD of the sample we have to multiply by dilution factor.

BOD = Dissolved oxygen<sub>initial</sub> - Dissolved oxygen<sub>final</sub>

$$\text{BOD} = (\text{DO}_{\text{initial}} - \text{DO}_{\text{final}}) \times \text{dilution factor}$$

$$\text{BOD} = \frac{(\text{DO}_{\text{initial}} - \text{DO}_{\text{final}}) \times \text{volume of sewage water after dilution.}}{\text{volume of sewage water before dilution}}$$

example

$$\text{BOD} = (\text{DO}_I - \text{DO}_F) \times \frac{900 \text{ ml (Total dilution)}}{50 \text{ ml (sewage sample taken)}}$$

### Problems

- (1) 100ml of waste water containing 920 ppm dissolved oxygen was diluted with 100ml of distilled water and kept in a bottle at 20°C for 5 days. The oxygen content of the resulting water was then found to be 250 ppm. calculate the BOD of the sample.

$$\text{BOD} = (\text{DO}_{\text{initial}} - \text{DO}_{\text{final}}) \times \text{dilution factor}$$

$$= (920 - 250) \times \frac{200}{100} = 1,320 \text{ ppm.}$$

2. 25 ml of sample contains 350 ppm of dissolved oxygen was diluted to 100 ml with distilled water and kept for 5 days at 20°C. The oxygen content was found to be 200 ppm. calculate BOD of the sample

$$\text{BOD} = (\text{DO}_I - \text{DO}_F) \times \text{dilution factor} = (350 - 200) \times \frac{100}{25} = 600 \text{ ppm}$$

Definition - The amount of oxygen required by (biologically inert and biologically oxidizable) organic matter in a sample of water for its oxidation by a strong oxidising agent is known as chemical oxygen demand. (The unit of COD is mg/L or ppm)

Significance - COD is important water quality parameter because, similar to BOD it provides an index to assess the effect discharge wastewater will have on the receiving environment.

Higher COD value indicates greater amount of oxidizable organic matter in sample, which will reduce dissolved oxygen levels. A reduction in DO (dissolved oxygen) can lead to anaerobic condition, which is harmful to aquatic life form.

It is a quickly measured parameter for stream, sewage, and industrial waste sample to determine their pollutional strength. It takes only 3 hrs as compared to 5 day for BOD.

since it oxidises all type of organic matter, so the COD values will greater than BOD.

Principle involved in the determination of COD is that when the waste water sample is refluxed with a known excess of potassium dichromate in 50%  $H_2SO_4$  solution in presence of  $Ag_2O$  and  $HgSO_4$ , all organic matter of the sample is oxidised to water,  $CO_2$  and  $NH_3$ . The excess dichromate (remaining unreacted in the solution) is treated with a standard solution of FAS (Ferrous ammonium sulphate) Estimation - Emp.

A blank determination is also carried out which

contains the same amount of  $K_2Cr_2O_7$  added to distilled water (same as the sample) and titrated vs FAS  $\rightarrow$  3 ml formula

$$COD = \frac{(\text{Blank - Estimation}) \times N_{FAS} \times 8 \times 1000}{\text{volume of sample}}$$

$$= \frac{(B-E) \times N_{FAS} \times 8 \times 1000}{\text{volume of sample}} \quad \begin{matrix} \text{mg/lit or} \\ \text{ppm.} \end{matrix}$$

1. 25ml of a (sample) sewage water was refluxed with  $K_2Cr_2O_7$  solution in presence of dil  $H_2SO_4$ . The uncorrected dichromate required 5.5ml of 0.1N FAS solution. 10ml of the same  $K_2Cr_2O_7$  solution and 25ml of distilled water under the same conditions as the sample required 26ml of 0.1N FAS. calculate COD of the sample.

(Normality of FAS should only be considered)

### Method 1

1000ml of 1N FAS  $\equiv$  8gm of oxygen

1ml of 1N FAS  $\equiv$  8mg of oxygen.

$(26-5.5)$ ml of 0.1N FAS  $\equiv$   $(26-5.5) \times 0.1 \times 8$  mg  
of oxygen.

25ml of sample contains  $= (26-5.5) \times 0.1 \times 8$  mg  
of oxygen.

1000ml of sample contains  $= \frac{(26-5.5) \times 0.1 \times 8 \times 1000}{25}$

$= 656 \text{ mg/lit or ppm.}$

Method 2  $COD = \frac{(B-E) \times N_{FAS} \times 8 \times 1000}{\text{volume of sample}}$

$= \frac{(26-5.5) \times 0.1 \times 8 \times 1000}{25} = 656 \text{ ppm}$

2. Calculate the COD of the effluent sample when  $25 \text{ cm}^3$  of an effluent requires  $8.3 \text{ cm}^3$  of  $0.001\text{M}$   $\text{K}_2\text{Cr}_2\text{O}_7$  for oxidation (mol wt - 294)

$$\text{Eq. wt of } \text{K}_2\text{Cr}_2\text{O}_7 = \frac{\text{Mol wt}}{6}$$

$$\text{Normality} = \frac{\text{Mol wt}}{6}$$

$$6N = \text{Mol wt}$$

Given.  $0.001\text{M}$   $\text{K}_2\text{Cr}_2\text{O}_7$  which  $6 \times 0.001 \text{ N}$

$\text{K}_2\text{Cr}_2\text{O}_7$

$1000\text{ml of } 1\text{N } \text{K}_2\text{Cr}_2\text{O}_7 = 8 \text{ gm of oxygen}$

$\therefore 1\text{ml of } 1\text{N } \text{K}_2\text{Cr}_2\text{O}_7 = 8 \text{ mg of oxygen}$

$8.3\text{ml of } 0.001 \times 6 \text{N } \text{K}_2\text{Cr}_2\text{O}_7 = 8.3 \times 0.001 \times 6 \times 8 \text{ mg of oxygen.}$

$25\text{ml of sample contains } 8.3 \times 0.001 \times 6 \times 8 \text{ mg of oxygen.}$

$\therefore 1000\text{ml of sample contains } \frac{8.3 \times 0.001 \times 6 \times 8 \times 1000}{25} = 15.94 \text{ ppm.}$

#### Assignment 4

- i. A  $25\text{ml}$  sample for COD analysis was reacted with  $15\text{ml}$  of  $0.25\text{N}$   $\text{K}_2\text{Cr}_2\text{O}_7$  solution and after the reaction, the unreacted  $\text{K}_2\text{Cr}_2\text{O}_7$  required  $18\text{ml}$  of  $0.1\text{N FAS}$  for reaction. Under identical condition  $15\text{ml}$  of same  $\text{K}_2\text{Cr}_2\text{O}_7$  solution mixed with  $25\text{ml}$  distilled water required  $30\text{ml}$  of  $0.1\text{N FAS}$ . What is the COD of the sample  
(Ans -  $384 \text{ ppm}$ )

Osmosis is the movement of any solvent through a selectively permeable membrane into an area of higher solute concentration, the result of which will be an equalizing of solute concentration on either side of the membrane.

(Phenomenon - seen at cellular level in animals, plants)

The definition of reverse osmosis best understood if we understood osmosis concept.

In osmosis it the passage of solvent, but not solute, between two solution of different concentration separated by semi permeable membrane.

Let us take a U tube with a semipermeable membrane at the centre of the tube, separating the two arms of the U-tube. In one arm we take a ~~base water~~ (solvent) with sugar (solute) mixed in it to make a solution.

In the other arm we pour colourless, tasteless water.

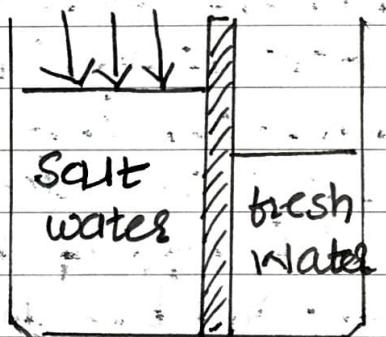
The liquid level in the sugar water arm will slowly increase, as the solvent (Water) move through the membrane to make both sides of the U-arm closer to equal in sugar to water ratio.

But why does this happen? because water wants to find the balance. And because one side of the arm is full of sugar, the pure water on the other side decides to move to match the concentration or until osmotic pressure is reached.

In reverse osmosis we literally are reversing the process. making our solvent move from high concentration to low concentration solution. But we know that's not something the solution really wants to do. so how do we make reverse osmosis happen? So we put the concentrated solution under pressure.

Reverse osmosis : If a solution is separated from the pure solvent by a semipermeable membrane and the pressure applied on the solution is more than the osmotic pressure, the solvent starts flowing from the solution towards the pure solvent. This phenomenon is known as reverse osmosis. (In case of solution of different concentration solvent moves from the solution of higher concentration to lower conc.) Thus in reverse osmosis method, pure solvent (water) is separated from its contaminates rather than removing contaminants from water. This membrane filtration is sometimes also called super-filtration or hyper-filtration.

Semipermeable membrane - eg. cellulose acetate  
Polymethacrylate, Polyamine  
pressure ( $15-40 \text{ kg cm}^{-2}$ )



### What Reverse osmosis treats

1. Reverse osmosis filtration improves the taste, odour, colour (appearance) of water by removing contaminants that cause taste and odour problems. (Chloride, sulphates)
2. It removes contaminants from water, including nitrates, pesticides, herbicides, arsenic,

mercury, lead, fluorides. (high level of fluoride in natural water causes fluorosis)

### Advantages

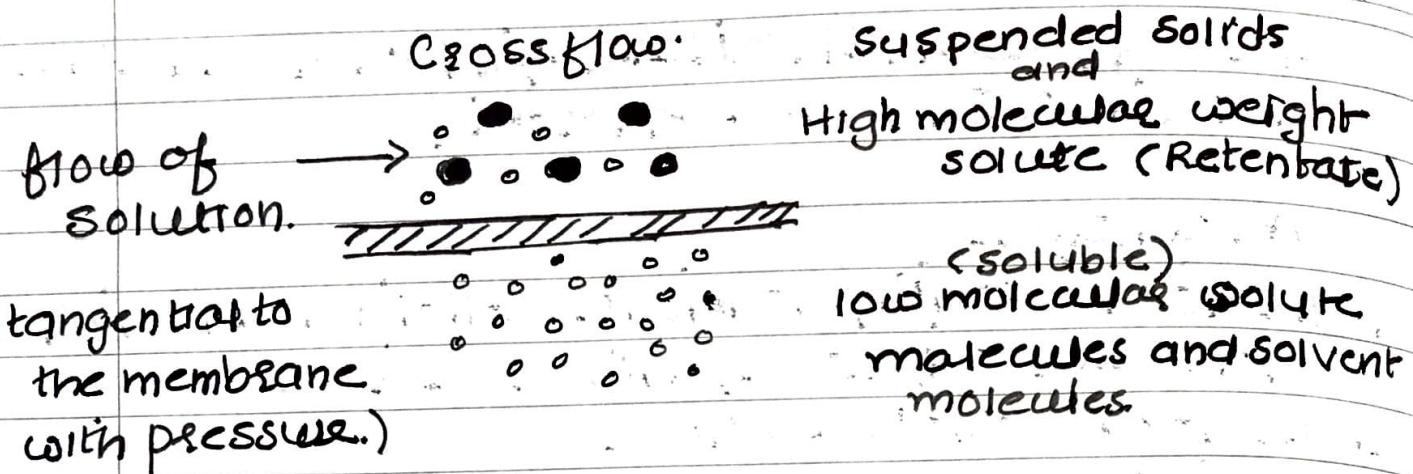
1. Removes ionic/non ionic colloidal and high molecular weight organic matter.
2. Removes colloidal silica.
3. Maintenance cost is low.
4. Life time of membrane is 2 years, easily replaced.
5. Due to low capital cost, simplicity, low operating cost and high reliability, the reverse osmosis is gaining ground at present for converting sea water into drinking water and for obtaining water for very high pressure boilers.

Ultrafiltration is a separation process using membrane with pore size in the range of 0.1 to 0.01 micron. It is a membrane filtration in which hydrostatic pressure forces a liquid against a semipermeable membrane. In this case only water and low molecular weight solutes are allowed to pass through the membrane and high molecular weight solutes and suspended solids are retained.

Those solvent molecules and other dissolved molecules which pass through the membrane are called permeate.

Those which do not pass through the membrane are called Retentate.

Ultrafiltration is achieved by pressuring the solution flow, which is tangential to surface of supported membrane (crossflow U.F)



Dead flow or perpendicular flow causes build up of solids onto the membrane surface, cross flow filtration increases the passage of permeate through the membrane.

### Application

- ① Industrial Process and wastewater treatment
  - Oil Removal in wastewater
  - dissolved natural organic matter in surface water.
- ② Dairy
  - whey Protein concentrate /
  - Milk Protein concentrate
  - Beline clarification
  - casein / whey fractionation
- ③ Biotech / Pharmaceutical
  - Enzyme / protein concentrate
  - Antibiotics production
  - Blood plasma processing
- ④ Food and Beverage
  - Fruit juice concentrate
  - Plant extract processing
  - Corn wet milling

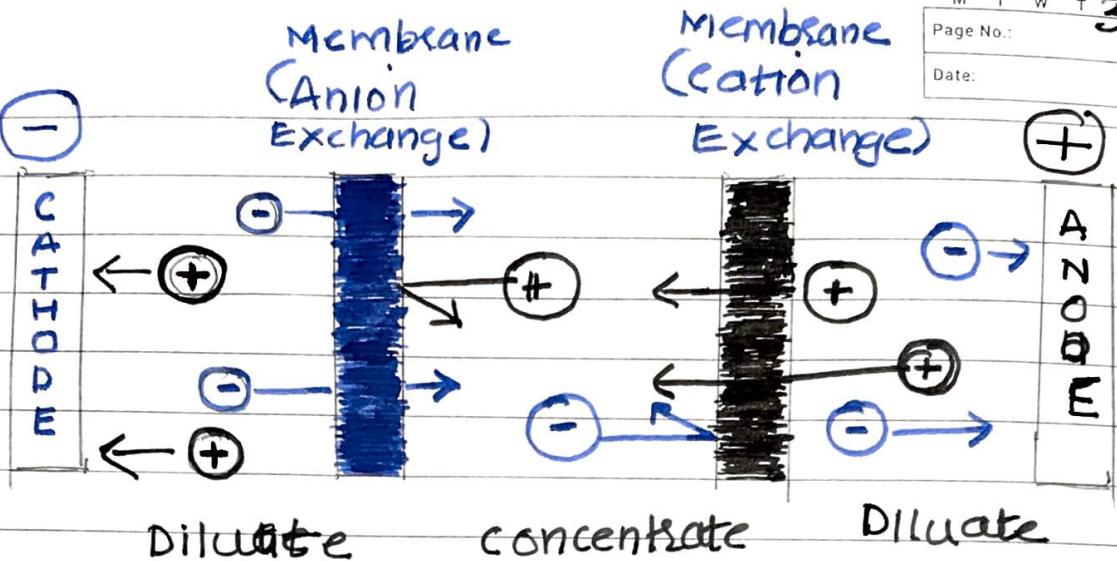
5. Automobile / Industrial  
 Electrocoat painting (Recovery of paints)  
 Industrial wastewater treatment.

ultrafiltration is done in different industries in order to recycle flow or add value to large products. Its main attraction is its ability to purify, separate, concentrate large molecules in continuous system.

### Electrodialysis:

Introduction Water, as one of the most vital substance for human life, is a limited resource. Increasing human activities generate an increasing demand for freshwaters. On the other hand, the scarce resources of natural water that fulfill drinking water quality standards are severely threatened by pollution, unsustainable use, climate change and many other forces. Treatment for the production of fresh water from any kind of water sources such as ground & surface water, as well as recycled process and wastewater, are becoming more and more important to cope with the rapidly increasing water demand.

Electrodialysis is applied for the removal of dissolved ionic substances from water. Amongst other desalination process, such as ion exchange, nanofiltration and reverse osmosis, the main advantage of electrodialysis are high water recovery, selective desalination, low chemical demand and low energy demand. (Removal of common salt from water is known as desalination).



Electrodialysis is a method in which the ions (of the salt present) are pulled out of the water by passing direct current using electrodes and thin rigid plastic membrane pairs.

When direct current is passed through saline water, the  $\text{Na}^+$  ion starts moving towards negative pole (cathode), while the  $\text{Cl}^-$  ion starts moving towards positive pole (anode) through the membrane. As result the concentration of brine decreases, i.e. get desaline water.

Electrodialysis cell consist of large number of paired sets of rigid plastic membranes. Saline water (also called brackish water as it has a salty taste) is passed under a pressure of about ( $5-6 \text{ kg m}^{-2}$ ) between membrane pairs and an electric field is applied perpendicular to the direction of water flow.

Just as magnets like charges repel each other, the fixed +ve charge inside the membrane repel positively charged ions ( $\text{Na}^+$ ) yet permit negatively charged ions to pass through. Similarly the fixed negative charge inside the other type

membrane repel -vely charged ions ( $\text{Cl}^-$ ) yet permit +vely charged Na<sup>+</sup> ions to pass through. Therefore, water in one compartment of the cell is deprived of salts, while the salt concentration in adjacent compartment is increased. Thus we get alternate streams of pure water and concentrated brine.

