



Bansilal Ramnath Agarwal Charitable Trust's

VISHWAKARMA INSTITUTE OF INFORMATION TECHNOLOGY

Department of Engineering & Applied Sciences

F. Y. B. Tech

Course Material (A brief reference version for students)

Course: Engineering Chemistry (2020 pattern)

Academic year 20-21

Unit 1: Water Technology

Disclaimer: *These notes are for internal circulation and are not meant for commercial use. These notes are meant to provide guidelines and outline of the unit. They are not necessarily complete answers to examination questions. Students must refer reference/text books, write lecture notes for producing expected answer in examination. Charts/diagrams must be drawn whenever necessary.*

Unit 1

Water Technology

Objective: To understand water technology for water analysis and water softening/purification methods

Content:(6 lectures): Introduction, Impurities in water, Specifications for drinking water (IS 10500: 2012), Hardness of water- Types, expression and units, Estimation of hardness by EDTA method, Disadvantages of hard water, Softening of water - Zeolite process, Demineralization by ion exchangers, Desalination methods - Reverse osmosis & Electro dialysis, Municipal water treatment

1.1 Impurities in water

The common impurities present in natural water are as follows:

A) Suspended impurities:

e. g. Clay, mud, organic matter, industrial waste.

They cause turbidity and give smell or odour to water

They can be removed by filtration.

B) Dissolved impurities:

They are subdivided into two types-

1. Dissolved gases like CO_2 , Cl_2 , H_2S , SO_x , NO_x
2. Dissolved salts like bicarbonates, sulphates, chlorides, nitrates of Ca, Mg, Fe, Al, Na, K etc.

They are removed by special softening procedures.

C) Colloidal impurities:

Colloidal particles of clay, mud, organic matter etc. which make the water turbid. They cannot be removed by filtration but are usually removed by coagulation followed by filtration. Coagulating agents commonly used are **potash alum, sodium aluminate**.

D) Biological impurities:

These impurities include microscopic algae, fungi, bacteria etc. They can be removed by sterilization process. Common sterilizing agents used are liquid chloride, ozone and UV light.

1.10 Specification of drinking water (IS 10500:2012 standards)

The water quality parameters are roughly divided into 3 categories.

1. Physical
2. Chemical
3. Biological

BIS (Bureau of Indian Standard) for drinking water give details of the permissible and desirable limits of various parameters in **drinking water**. As per **IS 10500:2012 standard** some specifications for **potable water** are as follows:

Sr. No.	Parameters	Requirement (acceptable limit)	Permissible limit in absence of alternate source
1.	Colour (Units) ,Hazen units	5	15
2.	Turbidity(Units), NTU	1	5
	Odour	Agreeable	Agreeable
	Taste	Agreeable	Agreeable
3.	Total dissolved solids(mg/lit)	500	2000
4.	pH	6.5-8.5	No relaxation
5.	Total hardness as CaCO ₃ equivalents (mg/lit)	200	600
6.	Iron (mg/lit)	0.3	No relaxation
7.	Manganese (mg/lit)	0.1	0.3
8.	Nitrate	45	No relaxation
9.	Chloride (mg/lit)	250	1000
	Residual free chlorine(mg/lit)	0.2	1
10.	Fluoride (mg/lit)	1.0	1.5
11.	Sulphate (mg/lit)	200	400
12.	Pathogenic Micro Organisms (Coliform)	-	Shall not be detected per 100 ml

1.2 Hardness of water

1.2.1Types of hardness

The water which does not form lather readily with soap, is known as hard water. The total hardness is due to the presence of dissolved bicarbonates, sulphates, chlorides and nitrates of calcium & magnesium.

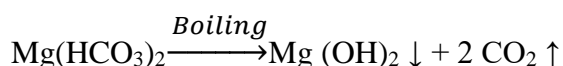
Hardness of water is classified into two types based on nature of impurities present, as

I) Temporary hardness II) Permanent hardness

I) Temporary Hardness of Water

Temporary hardness is the hardness that can be easily removed after boiling and filtration.

Dissolved impurities present in water like bicarbonates of Ca, Mg, Fe, Al and Mn can be removed from water by filtration after mere boiling. On boiling soluble bicarbonates get decomposed and form insoluble carbonates or hydroxides and CO₂ which escapes from water at boiling temperature.



Temporary hardness is also known as carbonate hardness or alkaline hardness.

II) Permanent Hardness of Water

Permanent hardness is the hardness that can not be removed by boiling and filtration

Dissolved impurities present in water like chlorides, sulphates, and nitrates of Ca, Mg, Fe, Al & Mn contribute to permanent hardness.

These dissolved salts can not be removed easily and therefore contribute **to permanent or non carbonate or non alkaline hardness.**

Total hardness = Temporary hardness + Permanent hardness

1.2.2 Units of Hardness

Hardness of water is the net amount of hardness causing impurities present in a water in a finite volume.

The concentration of dissolved impurities is usually expressed in terms of calcium carbonate equivalent. The choice of CaCO₃ equivalent is accepted universally as its molecular weight is 100 (and equivalent weight is 50) and is the most insoluble salt in water.

The CaCO₃ equivalent for any dissolved salt from water can be calculated, if its concentration in water is known as follows

$$\text{CaCO}_3 \text{ equivalent of any salt} = \frac{\text{Weight salt present per liter}}{\text{Equivalent weight of salt}} \times \frac{\text{Equivalent weight of CaCO}_3}{\text{Equivalent weight of salt}}$$

If the dissolved salt has bivalent cations, then the above formula can be modified as,

$$\text{CaCO}_3 \text{ equivalent of any bivalent salt} = \frac{\text{Weight salt present per liter}}{\text{Molecular weight of salt}} \times \frac{\text{Molecular weight of CaCO}_3}{100}$$

Units used of expressing CaCO₃ equivalent hardness are:

1) Milligrams per litre (mg/lit)

1 mg/lit hardness is 1 mg of CaCO₃ equivalent hardness present in 1 litre of water.

2) Parts per million (ppm):

1 ppm hardness is 1 part of CaCO₃ equivalent hardness present in million litres of water i.e. 10⁶ parts of water

Relation between mg/lit and ppm:

$$1 \text{ mg/lit} = 1 \text{ ppm}$$

Other units of CaCO₃ equivalent are degree clark (°Cl) and degree French (°Fr).

$$1 \text{ ppm} = 1 \text{ mg/lit} = 0.07^\circ\text{Cl} = 0.1^\circ\text{Fr}$$

1.2.3 Solved Numerical on: Hardness Calculation

Example 1: Calculate the hardness of water sample having following analysis: Mg(HCO₃)₂ = 7.3 ppm, Ca(HCO₃)₂ = 16.2 ppm, MgCl₂ = 9.5 ppm, CaSO₄ = 13.6 ppm, Fe₂O₃ = 8.5 ppm, Mg(NO₃)₂ = 14.8 ppm. Also calculate carbonate and non carbonate hardness.

Solution: Calculation of CaCO₃ equivalent for dissolved impurities.

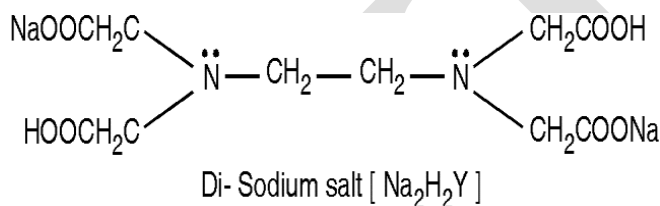
Impurity	Amount given in ppm	Molecular weight	CaCO ₃ equivalent
Mg(HCO ₃) ₂	7.3	146	$7.3 \times \frac{100}{146} = 5$
Ca(HCO ₃) ₂	16.2	162	$16.2 \times \frac{100}{162} = 10$
MgCl ₂	9.5	95	$9.5 \times \frac{100}{95} = 10$
CaSO ₄	13.6	136	$13.6 \times \frac{100}{136} = 10$
Fe ₂ O ₃	8.5	-	Not hardness causing impurity
Mg(NO ₃) ₂	14.8	148	$14.8 \times \frac{100}{148} = 10$
NaCl	11.7	-	Not hardness causing impurity

$$\begin{aligned}
 \text{Total hardness present} &= [\text{Mg}(\text{HCO}_3)_2 + \text{Ca}(\text{HCO}_3)_2 + \text{MgCl}_2 + \text{CaSO}_4 + \text{Mg}(\text{NO}_3)_2] \\
 &= [5 + 10 + 10 + 10 + 10] \\
 &= 45 \text{ ppm} \\
 \text{Carbonate hardness} &= [\text{Mg}(\text{HCO}_3)_2 + \text{Ca}(\text{HCO}_3)_2] \\
 &= [5 + 10] \\
 &= 15 \text{ ppm} \\
 \text{Non carbonate hardness} &= [\text{MgCl}_2 + \text{CaSO}_4 + \text{Mg}(\text{NO}_3)_2] \\
 &= [10 + 10 + 10] \\
 &= 30 \text{ ppm}
 \end{aligned}$$

1.2.4 Estimation of hardness by EDTA method

The total hardness of a water sample is found accurately by titration of the water sample with disodium salt of ethylene diamine tetra-acetic acid (disodium EDTA).

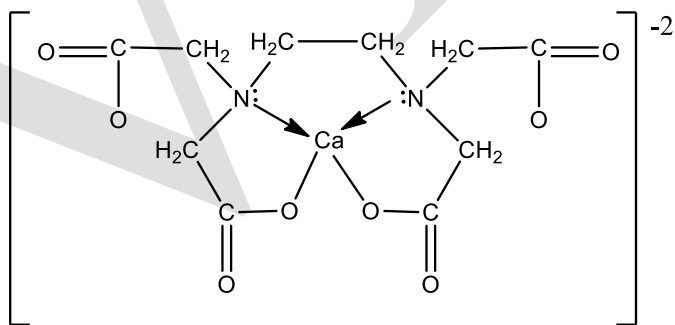
Structure of EDTA:



EDTA is ethylene diamine tetra-acetic acid which is water insoluble, but disodium salt of EDTA is water soluble.

Na_2EDTA forms 1:1 complex with divalent cation like Ca^{+2} or Mg^{+2}

Structure of M-EDTA complex:



Theory:

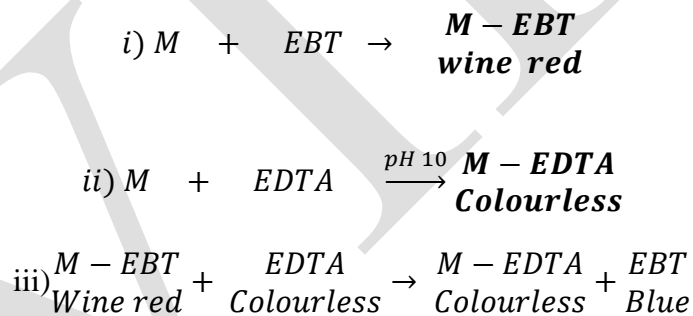
i) Disodium EDTA reacts quickly with the hardness causing metal ions in water, even in very low concentration of salts. i.e. it is highly sensitive towards heavy metal ions in water.

- ii) A suitable pH is required for the reaction between the metal ions present in water and disodium EDTA, otherwise the reaction is reversible and cannot go to completion in forward direction.
- iii) During the reaction, H^+ ions are formed and decreases the pH of reaction mixture.
- iv) Hence, ammoniacal buffer solution (ammonium hydroxide + ammonium chloride) of **pH about 10** is necessary during titration, so that it will not allow the decrease of pH.
- v) The reaction between disodium EDTA and heavy metal ion, results in the formation of cyclic co-ordination complex (chelate) and hence the titration is known as complexometric titration
- vi) Generally, organic dyes such as Eriochrome Black –T (EBT) act as indicator for the EDTA titrations

Principle:

- i) The hardness causing ions like Ca^{++} and Mg^{++} present in water form unstable complexes with the indicator EBT (M-EBT), having **wine red** colour.
- ii) EDTA then reacts with all hardness causing metal ions present in water to form stable complexes (EDTA- metal complex).
- iii) EDTA then reacts with metal ions from M-EBT complex to form stable EDTA-metal complex with the regeneration of **blue** colour of EBT.

Reaction:



Procedure:

Titration part I: Standardization of EDTA solution:

- i) Prepare standard solution of $ZnSO_4$.
- ii) Fill a burette with disodium EDTA solution and pipette out 5 ml standard $ZnSO_4$ solution in a conical flask.
- iii) Add about 3 ml buffer solution of pH about 10 and 2-3 drops of EBT indicator in it.

- iv) Titrate the wine-red coloured mixture against the EDTA solution till it changes to sky blue.
- v) Let the titration reading be V_1 ml.

Calculations:

Standardization of EDTA:

Let the molarity of ZnSO_4 solution prepared be M_2 molar. Calculate the molarity of disodium EDTA using volume of ZnSO_4 solution pipetted for titration and volume of disodium EDTA (burette reading) by formula,

$$M_1 V_1 = M_2 V_2$$

$$\text{EDTA} = \text{ZnSO}_4$$

M_1 = Exact molarity of EDTA = ?

Titration part II: Total hardness of water sample:

- i) Take 5 ml of the water sample in a conical flask.
- ii) Add about 3 ml of the buffer solution of pH 10 and 2-3 drops of EBT indicator solution in it.
- iii) Titrate this wine-red mixture against the EDTA solution till the colour changes to **blue**. Let the titration reading be 'y' ml.

Calculation: Determination of Total hardness of water sample:

In general,

$$\text{Total hardness of water sample} = \frac{y}{V} \times Z \times 100 \times 1000 \text{ ppm CaCO}_3 \text{ equivalent}$$

V = volume of water sample titrated

y = volume of disodium EDTA (burette reading)

Z = molarity of disodium EDTA solution.

Titration part III: Permanent hardness of water sample:

- i) Take 5 ml of the water sample (**boiled and filtered**) in a conical flask.
- ii) Add about 3 ml of the buffer solution of pH 10 and 2-3 drops of EBT indicator solution in it.
- iii) Titrate this wine-red mixture against the EDTA solution till the colour changes to **blue**. Let the titration reading be 'z' ml

Calculation:

a) Determination of Permanent hardness of water sample:

$$\text{Permanent hardness of water sample} = \frac{x}{V} \times Z \times 100 \times 1000 \text{ ppm CaCO}_3 \text{ equivalent}$$

V = volume of water sample titrated

x = volume of disodium EDTA (burette reading)

Z = molarity of disodium EDTA solution.

b) Determination of Temporary hardness of water sample:

Temporary hardness = Total hardness – permanent hardness

Thus, using EDTA method total, permanent and temporary hardness can be easily calculated for any sample water.

Disadvantages of hard water (Significance of Hardness Determination):

Though hard water is as palatable as soft waters, a knowledge of the magnitude and type of hardness is important in determining the suitability of a water for domestic and industrial purposes. Use of hard water for cleaning purposes is unsatisfactory as they increase the consumption of soaps. This drawback has been partly overcome by the use of synthetic detergents but for personal hygiene, soap is preferred and hard water remains objectionable. Hard water offers difficulties in dyeing of textiles, is uneconomical and even hazardous in steam generation and imparts many of the undesirable characteristics to the finished products in paper industry, beverages, dairies, and allied industries. Soft water is required for an innumerable number of other industries also.

In devising an efficient and economical softening process, determination of total hardness and the relative amounts of Carbonate Hardness & Non Carbonate Hardness is important.

1.2.5 Solved Numerical on: EDTA Method

1) 50 ml of standard hard water containing 1.2 gm of CaCO₃ per litre required 16 ml of EDTA solution for end point. Whereas 50 ml of water sample required 20 ml of same EDTA solution and 50 ml boiled water sample required 12 ml of EDTA solution for end point. Calculate total, temporary and permanent hardness of water in ppm.

Solution:

i) As 1 litre of standard hard water contains 1200 mg CaCO₃.

∴ 1 ml standard hard water contains 1.2 mg CaCO_3

∴ 50 ml standard hard water contains 60 mg CaCO_3

As 16 ml EDTA \equiv 50 ml standard hard water \equiv 60 mg CaCO_3 hardness

∴ 1 ml EDTA \equiv $60/16 = 3.75$ mg CaCO_3 hardness

As 50 ml water sample consumes 20 ml EDTA

∴ 1000 ml water sample will consume $\frac{1000}{50} \times 20 = 400$ ml EDTA.

As 1 ml EDTA \equiv 3.75 mg CaCO_3

∴ 400 ml EDTA \equiv $400 \times 3.75 = 1500$ mg CaCO_3

Hence **total hardness** of water sample = **1500 ppm CaCO_3 equivalent.**

Permanent hardness

Boiled and filtered water contains only permanent hardness

As 50 ml boiled water sample requires 12 ml EDTA

∴ 1000 ml boiled water sample requires $1000 \times 12/50 = 240$ ml EDTA

240 ml EDTA \equiv $240 \times 3.75 = 900$ ppm CaCO_3 equivalent permanent hardness

Temporary hardness = Total hardness – Permanent hardness

$$= 1500 - 900 = \mathbf{600 \text{ ppm } \text{CaCO}_3 \text{ equivalent.}}$$

2) 50 ml of water sample requires 19 ml of 0.05 M EDTA during titration. Whereas 50 ml of boiled water sample requires 13.5 ml of same EDTA in the titration. Calculate total, temporary and permanent hardness of the water sample.

Solution:

Given, molarity of EDTA is $Z = 0.05$, $y = 19$ ml, $V = 50$ ml

Total hardness = $y \times Z \times 100 \times 1000 / V$

$$= 19 \times 0.05 \times 100 \times 1000 / V$$

= 1900 ppm CaCO_3 equivalent.

After boiling, temporary hardness gets removed and the boiled water contains only permanent hardness.

Boiled water titration $x = 13.5$ ml $V = 50$ ml and $Z = 0.05$ M

Hence, Permanent hardness = $x \times Z \times 100 \times 1000 / V$

$$= 13.5 \times 0.05 \times 100 \times 1000 / 50$$

= 1350 ppm CaCO_3 equivalent

$$\begin{aligned}\text{Temporary hardness} &= \text{total hardness} - \text{permanent hardness} \\ &= 1900 - 1350 = \mathbf{550 \text{ ppm CaCO}_3 \text{ equivalent}}\end{aligned}$$

1. 5 Softening of water - Zeolite process

1.5.1 Introduction of zeolite

The name zeolite came from Greek word, 'Zein' – boiling, lithos – stone, meaning 'boiling stone'. The zeolite was first used in 1756 by Cronsted (Swedish geologist). The chemical structure of sodium zeolite may be represented as,



Thus, **zeolite is hydrated sodium alumino silicate, capable of exchanging reversibly their sodium ions for multivalent cations present in water. Therefore, zeolites find application in softening of water.** Zeolites are also known as 'permutit'

Two types of zeolites are commonly used in water softening

- a) Natural zeolites (nonporous, green sand)
- b) Synthetic zeolites (porous, gel structure)

Natural zeolites are derived from green sand by washing, heating and treating with caustic soda (NaOH). They are nonporous and are more durable.

Synthetic zeolites are derived from green sand by washing, heating and treating with caustic soda (NaOH). They are nonporous and are more durable.

Synthetic zeolites are prepared by heating together China clay, feldspar and soda ash followed by cooling and granulating the resultant mass. They can be prepared by heating solutions of sodium silicate, aluminium sulphate and sodium aluminate. Such zeolites are porous and possess gel structure and has higher exchange capacity than natural zeolites.

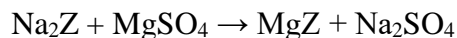
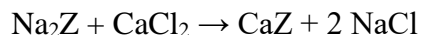
1.5.2 Zeolite process of water softening

Theory:

Principle: zeolite is hydrated sodium alumino silicate, capable of exchanging reversibly their sodium ions for multivalent cations present in water. Therefore, zeolites find application in softening of water.

Zeolites hold sodium ions loosely and can easily exchange their sodium ions with other cations like Ca^{+2} , Mg^{+2} etc. Thus if water containing dissolved calcium magnesium salts is passed over a bed of sodium zeolite, Ca and Mg are exchanged sodium as follows,

(Abbreviation given to sodium zeolite as Na_2Z or Na_2P)



From the above exchange reaction, sodium zeolite is converted into calcium magnesium zeolite, whereas water becomes free from Ca and Mg salts but becomes richer in sodium salt.

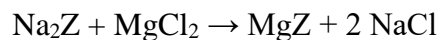
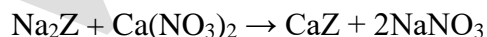
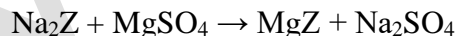
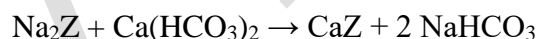
When zeolite is exhausted i.e. when it loses its sodium exchanging capacity, it can be regenerated by washing the bed with a concentrated solution of sodium chloride (brine) as follows.



The regenerated zeolite (Na_2Z) can be used again for softening of water.

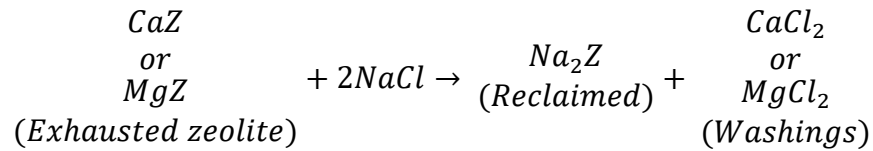
Process

For softening of water by zeolite process, hard water is percolated at specified rate through a zeolite bed as shown in the fig. 1.7.1. The hardness causing impurities are retained by zeolite crystal as CaZ or MgZ. whereas outgoing water contains sodium salts.

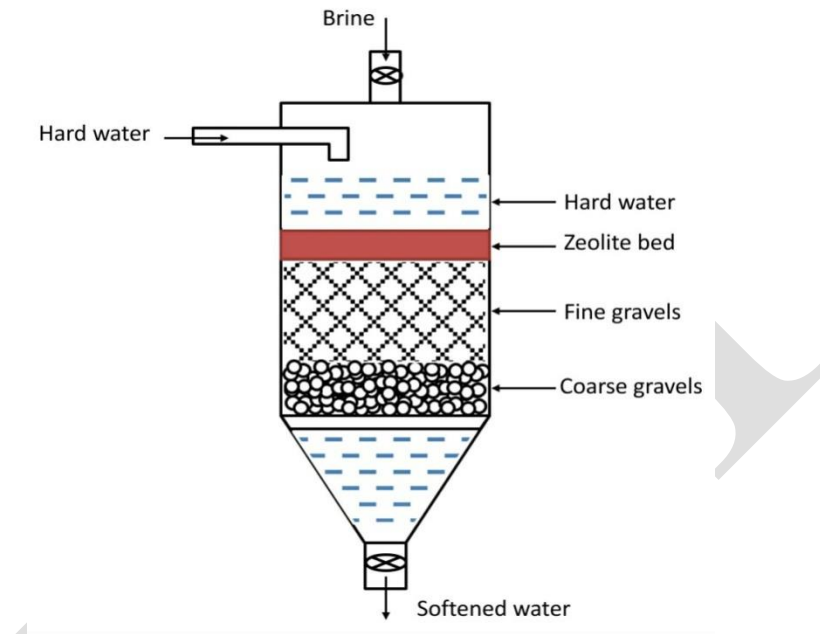


Regeneration

After sometime, when zeolite is completely converted into calcium and magnesium zeolite, it is unable to soften water further i.e. it gets exhausted. At this stage, the supply of hard water is stopped and exhausted zeolite is reclaimed by treating the zeolite bed with concentrated **brine** solution (**10 % NaCl solution**)



The washings containing CaCl_2 and MgCl_2 are drained and regenerated zeolite bed is used again for softening purpose.



Advantages

1. Hardness is completely removed.
2. Equipment used is compact and occupies less space.
3. No impurities are precipitated, so there is no danger of sludge formation.
4. The process automatically adjusts itself for variation in hardness of incoming water.
5. It is quite clean process and requires less time for softening.
6. Soft water obtained has hardness between 5 – 10 ppm.

Limitations

1. Water having turbidity and suspended matter should not be directly fed to the zeolite softener because the pores of zeolite bed will be clogged and the rate of flow will unduly decreased.

Thus, turbidity and suspended matter from the water should be removed before subjecting it to the zeolite treatment.

2. Water containing excess acidity or alkalinity may destroy zeolite crystals. Therefore, it is preferable to have pH 7 of the water passing through zeolite softener.

3. Water containing Fe^{+2} and Mn^{+2} cannot be used as their respective zeolite cannot be regenerated easily with brine.

1.5.3 Solved Numerical on Zeolite process

1) An exhausted zeolite was regenerated by 200 litre of NaCl having strength 160 gm/litre. How many litres of a hard water having hardness 300 ppm as CaCO_3 can be softed by this softener?

Solution:

Given 1 lit. of NaCl solution contains $\rightarrow 160 \text{ gmNaCl}$

\therefore 200 lit. of NaCl solution contains $\rightarrow 200 \times 160 \text{ gm}$

$\rightarrow 32000 \text{ gmNaCl}$

$\rightarrow 32 \times 10^6 \text{ mg}$

Given, 1 litre water sample contains 300 mg CaCO_3 equivalent hardness

\therefore Quantity of NaCl required for regeneration of zeolite softner in terms of CaCO_3 equivalent

$$\frac{50}{58.5} \times 32 \times 10^6 \text{ mg} = 273.50427 \times 10^5$$

[Quantity of NaCl required for regeneration in terms of CaCO_3 equivalent = Total hardness]

\therefore 300 mg CaCO_3 equivalent hardness \rightarrow present in 1 lit of water

$\therefore 273.50427 \times 10^5 \text{ mg hardness} \rightarrow ?$

$$\frac{273.50427 \times 10^5}{300} \text{ litre of water}$$

$$= 91168.09 \text{ lit}$$

\therefore Quantity of water sample softened = 91168.09 lit.

2) A zeolite bed exhausted by softening 3000 liters of water require 10 liters of 15% NaCl solution for regeneration. Calculate the hardness of water sample

Solution:

15% NaCl solution is used for regeneration.

i.e. 15 gm NaCl dissolved in 100 ml water.

∴ 1 lit of 15% NaCl solution contains → 150 gm NaCl

∴ 10 lit of 15% NaCl solution contains → 1500 gm NaCl

$$\rightarrow 15 \times 10^5 \text{ mg NaCl}$$

∴ CaCO_3 equivalent of total NaCl required for regeneration

$$\frac{50}{58.5} \times 15 \times 10^5 \text{ mg} = 12.820512 \times 10^5 \text{ mg}$$

∴ CaCO_3 equivalent of NaCl required for regeneration = Total hardness present in 3000 lit. of sample water.

3000 lit. of sample water → $12.820512 \times 10^5 \text{ mg CaCO}_3$ equivalent hardness

$$1 \text{ lit. of sample water} \rightarrow \frac{12.820512 \times 10^5}{3000} \text{ mg}$$

∴ 1 lit. of sample water contain 427.35 mg CaCO_3 equivalent hardness.

∴ **Hardness of water sample = 427.35 ppm**

1.6 Demineralization by ion exchangers

1.6.1 Introduction to ion exchangers

This method is commonly used for obtaining pure water from an ordinary water.

There are two synthetic resins used (in separate vessels) i.e. a cation exchanger resin and an anion exchanger resin.

a) Cation exchanger resin/ Cation exchangers:

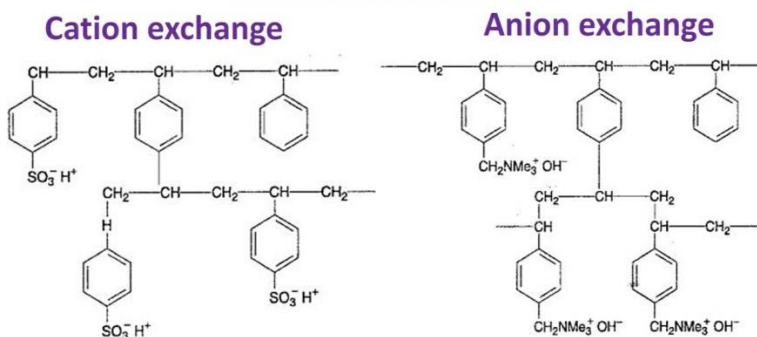
i) This is a polymer having carboxylated/ sulphonated aromatic rings attached to the chain

ii) The H^+ ions are loosely held on $-SO_3H$ or $-COOH$ groups and are easily exchanged with cations from water.

b) Anion exchanger resin/ Anion exchangers:

i) This is a polymer having aromatic rings linked to the polymer chain and the rings are with quaternary ammonium group:

ii) The $-OH$ ions are loosely held and are easily exchangeable with all the negative ions from water.



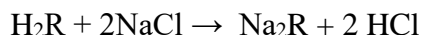
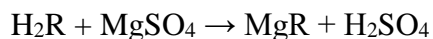
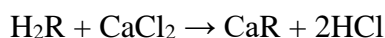
1.6.2 Ion exchange process

Principle:

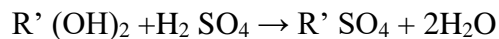
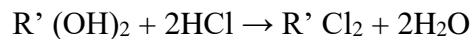
When water containing cations and anions, is passed through the resins, cation exchanger resin captures all cations (in exchange of H^+) and anion exchanger resin captures all anions (in exchange to OH^-), to give pure and all ions-free water.

Process:

i) The water to be treated, first enters in porous cation exchanger resin, where all cations are captured by the resin and H^+ are released in exchange.

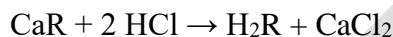
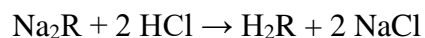


ii) Then the acidic output water from first resin, enters in the porous anions exchanger resin where all anions in water are captured and OH⁻ are released in exchange.

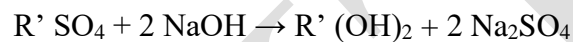
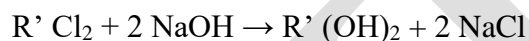


Regeneration:

i) The exhausted cation exchanger, is regenerated by washing with **dil. HCl** solution



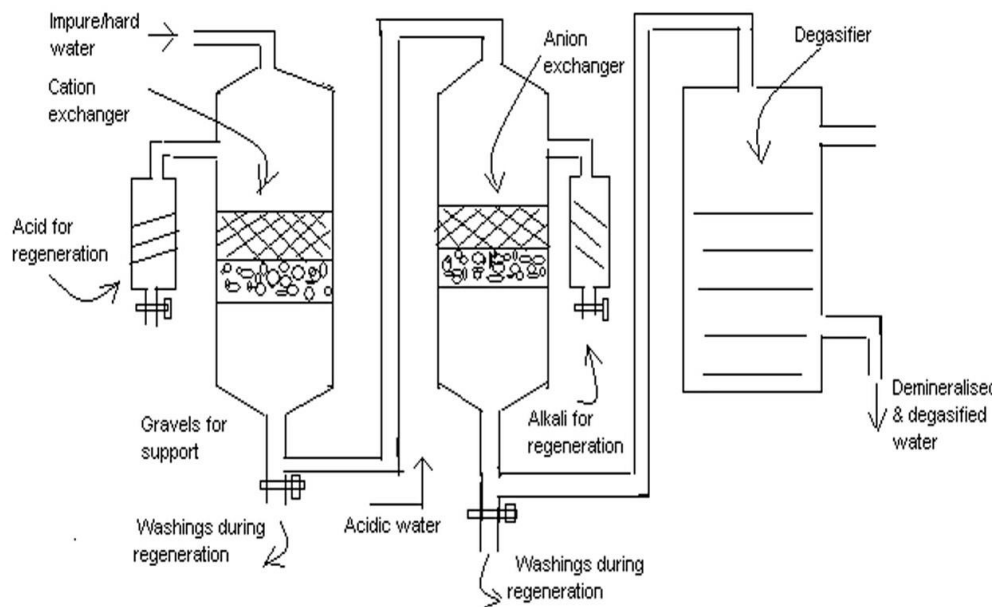
ii) The exhausted anion exchanger resin is regenerated by washing with **dil. NaOH** solution.



iii) Thus the water flowing out from second exchanger resin contains equivalent amounts of H⁺ and OH⁻ ions which combines to form H₂O and there is no ionic impurity in the final water. This method is also called as deionization or demineralization process.

Figure:

The flow sheet of the treatment, is shown in fig.



Advantages:

- i) This method gives water of zero hardness and no ionic impurities.
- ii) If the output water is passed through de-gassifier, then the gaseous impurities like O₂, CO₂ also get expelled, to get water of 'distilled water' standard.
- iii) Equipment occupies small space.
- iv) Process is easy to operate, with negligible running cost.

Limitations:

- i) Initial investment high.
- ii) Process can be operated only for small scale purification of water.

1.6.3 Comparison between Zeolite Process and Ion-exchange Process

Sr.No.	Zeolite Process	Ion-exchange process
1	Softener used in the process is zeolite crystals.	Softener used in ionexchange process is (synthetic resin) ion exchange resin.
2	Zeolite crystals can exchange sodium ions with multivalent cations present in water	Synthetic resins exchange either their cation or anion for impurities present in water.
3	On treatment with zeolite crystals, soft water obtained contains sodium salt.	On treatment with cation exchanger resin and anion exchanger resin, soft water obtained is free from mineral salts.
4	Zeolite process cannot be used for water containing iron, manganese salts and highly acidic or alkaline water.	Ion exchange process can be used for all types of water sample.
5	Exhausted zeolite can be regenerated by NaCl solution.	Exhausted resins can be regenerated, cation exchange resin using dilHCl and anion exchange resin using dil KOH.
6	Soft water has hardness 5-10 ppm.	Soft water has hardness 0 – 2 ppm

1.6.4 Solved numerical on ion Exchange process:

- 1) 10,000 litres of water was treated by ion exchange process for removing its hardness. The process then required 200 lit of 0.1 N HCl and 200 lit of 0.1N NaOH for regeneration. Calculate hardness of water

Solution:

when 0.1 N HCl is passed through cation exchanger, it replaces equivalent cations of CaCO_3 hardness

To calculate quantity of CaCO_3 equivalent hardness, HCl in terms of grams are to be calculated.

As 1 lit 1N HCl \rightarrow 36.5 gms

\therefore 200 lit 0.1 N HCl \rightarrow ? = 730 gms

As, 1 M HCl is equivalent to $\frac{1}{2}$ M CaCO_3

36.5 gms of HCl is equivalent to 50 gms of CaCO_3

\therefore 730 gms of HCl is equivalent to ? = 1000 gms

Thus, 1000 gms CaCO_3 equivalent hardness cations are replaced by HCl which was originally present in 10,000 lits of water

Therefore, CaCO_3 equivalent hardness present per liter of water = $1000/10,000 = 0.1\text{gm}$

Thus hardness of water = $0.1\text{gms/lit} = 100\text{ mg/lit} = 100\text{ ppm}$

1.7 Reverse osmosis

Principle:

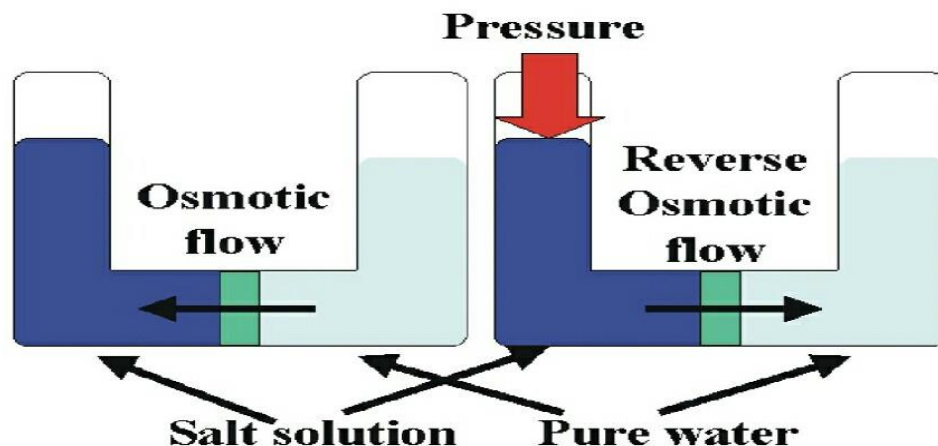
The reversal of solvent flow, from higher concentration solution to lower concentration solution through a semipermeable membrane, by applying an external pressure slightly higher than the osmotic pressure of higher-concentration solution, is known as reverse osmosis.

Normal osmosis process, is shown in fig. where the solvent flows from low concentration solution to higher concentration solution, through the **semipermeable membrane** (SPM), until difference in water levels creates a sufficient pressure to counteract the original water flow. The difference in levels represents osmotic pressure of the solution.

In the reverse osmosis, we apply external pressure on the higher concentration solution slightly higher than osmotic pressure.

The flow of solvent takes place in reverse direction i.e. from higher concentration solution to lower concentration solution, through the SPM.

Thus in RO, we separate water from its' contaminants rather than contaminants from water.



Method:

- i) Sea water or water polluted by ionic pollutants, is filled in reverse osmosis cell
- ii) A pressure of 200 psi is applied on it to force the solvent to pass through SPM. (SPM has such porosity that it allows only molecules to pass through and higher sized ions molecules are prohibited from passing).
- iii) Membrane consists of a polymeric material film made of proper porosity, from materials like acrylics, polyamides, aramids, etc.

Advantages:

- i) RO removes all ionic, colloidal, nonionic pollutants from water.
- ii) Simple to operate
- iii) Low cost process
- iv) Pure water for high pressure boiler can be obtained.
- v) If the SPM is specially prepared such that it allows limited quantity of salts to pass through it along with water, then RO technique is used to obtain drinking **mineral water**. Efficiency of the process depends upon the physical, chemical and mechanical (strength) characteristics of semipermeable membrane.

Proper porosity, resistance to attack by bacteria, salts, water and ability to bear the external pressure and pressure of water on the membrane, are important in selecting SPM.

1.8 Electrodialysis

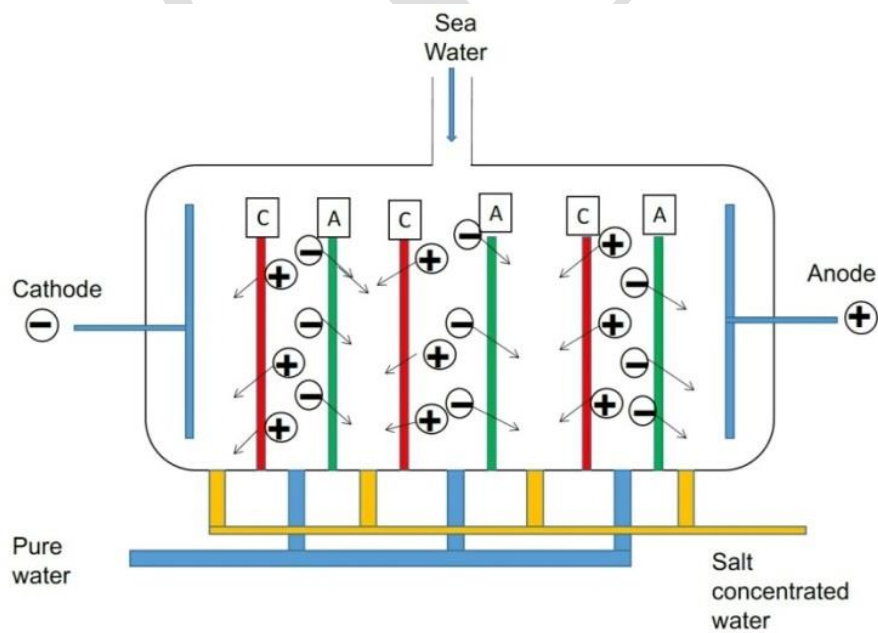
The process of removing ionic pollutants (salts, ionic dyes) from water by using membranes and electric field, is known as electrodialysis.

Principle:

Salt water is allowed to pass through ion selective membranes (cation and anion) under electric field to get salt free(pure) water.

Construction and Working:

An electrodialysis cell consists of a large number of paired sets of plastic membranes. The membranes are ion-selective. e.g. A cation selective membrane will allow only cations to pass through it, as this membrane consists of negatively charged fixed groups which repel anions and do not allow to go through (groups on membrane like SO_3^- , COO^- , etc)The anion selective membrane allows only anions to pass through and the plastic membrane has cations repelling groups like NR_3 .When an electric field is applied, perpendicular to the direction of flow of water, the anions move towards positively charged electrode through the anion selective membrane in the neighboring compartment but after that there is cation selective membrane and the movement stopped.



Similarly, cations move in the direction of negatively charged electrode and go in neighboring compartment. They cannot move further because next is anion selective membrane.

The result will be alternate compartments with very high concentration of electrolytes and neighboring compartments to them with negligible concentration of ionic substances. Thus we get alternate streams of pure water from the electrodialysis cell.

Applications:

- i) Removal of ionic pollutants (toxic salts, ionic dyes, etc.) from treated industrial waste.
- ii) Removal of salts from sea water, to get pure water.
- iii) Removal of limited quantity of salts from sea water to get drinking (mineral) water.

1.9 Municipal/ Domestic water treatment

Municipalities have to supply potable water, i.e. water which is safe to drink. Drinking water is safe to drink. Drinking or potable water, fit for human consumption, should satisfy the following essential requirements:

- It should be sparkling clear and odourless.
- It should be pleasant in test.
- It should be perfectly cool.
- Its turbidity should not exceed 10 ppm.
- It should be free from objectionable dissolved gases like hydrogen sulphide.
- It should be free from objectionable minerals such as lead, arsenic, chromium and manganese salts.
- Its alkalinity should not be high. Its pH should be about 8.0
- It should be reasonably soft.
- Its total dissolved solids should be less than 500 ppm.
- It should be free from disease-producing micro-organisms.

1.9.1 Purification of water for domestic use:

Natural water from rivers, canals, etc., does not confirm to all the required specifications of drinking water. For removing various types of impurities, the following treatment processes are employed:

Note: Municipal water treatment does not aim at removing the dissolved salts present.

Consequently, municipalities do not, generally, supply softened water

A) Removal of suspended impurities:

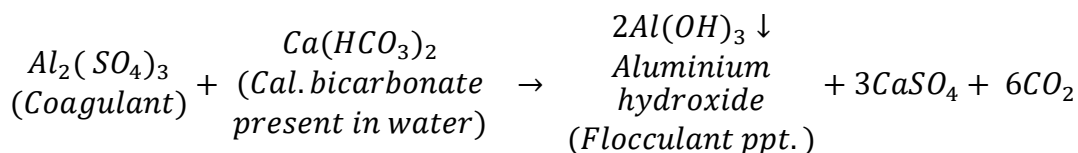
1) **Screening:** The raw water is passed through screens, having large number of holes, when floating matters are retained by them.

2) **Sedimentation:** It is a process of allowing water to stand undisturbed in big tanks, about 5 m deep, when most of the suspended particles settle down at the bottom, due to the force of gravity. The clear supernatant water is then drawn from tank with the with the help of pumps. The retention period in a sedimentation tank ranges from 2-6 hours.

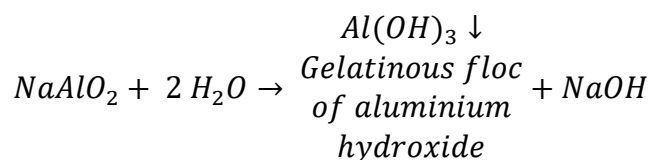
When water contains fine clay particles and colloidal matter, it becomes necessary to apply sedimentation with coagulation for removing such impurities. *Sedimentation with coagulation is the process of removing fine suspended and colloidal impurities by the addition of requisite amount of chemicals (called coagulants) to water before sedimentation. Coagulant, when added to water, forms an insoluble gelatinous, flocculent precipitate, which descent through the water, adsorbs and entangles very fine suspended impurities forming bigger flocs, which settle down easily.* Coagulants like alum or ferrous sulphate provide Al^{+3} or Fe^{+3} ions, which neutralize the negative charge on the colloidal clay particles. After losing their charge, the tiny clay particles come nearer to one another and combine to form bigger particles, which settle down, due to force of gravity. Thus, coagulant forces even colloidal particles to settle down. The coagulants (or flocculants) are, generally, added in solution form. For proper mixing of coagulants with water, mixers are employed. Properly mixed water is then *sedimented*.

Chemical coagulants: The following are the most commonly used coagulants:

(i) **Alum** [$\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$] is the most widely used in water treatment plants. Alum reacts in water in the presence of alkalinity of water. If natural alkalinity is not present, sufficient lime is also added.



(ii) **Sodium aluminate** (NaAlO_2) is obtained from bauxite refineries in the form of thick solution. This can very easily be used for treating water having no alkalinity (i.e, pH less than 7). pH range for best results is 5.5 – 8.0.



The aluminium hydroxide floc causes sedimentation. The sodium hydroxide thus produced, precipitates magnesium salts as Mg(OH)_2



3) **Filtration:** It is the process of removing colloidal matter and most of the bacterias, micro-organisms, etc., by passing water through a bed of fine sand and other proper-sized granular materials. Filtration is carried out by using sand filter.

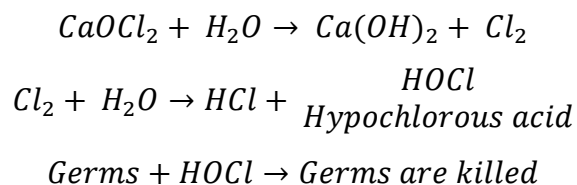
B) Removal of microorganisms:

Water after passing through sedimentation, coagulation and filtration operations still contains a small percentage of pathogenic bacteria (disease-producing). Consequently, water used, particularly for drinking or municipal purposes, must be freed from these disease-producing bacteria, micro-organisms, etc. The process of destroying/killing the disease producing bacteria, micro-organisms, etc., from the water and making it safe for use, is called disinfection. The chemicals or substances, which are added to water for killing the bacteria, etc., are known as disinfectants. The disinfection of water can be carried out by following methods:

(1) **By boiling** water for 10-15 minutes, all the disease-producing bacteria are killed and water becomes safe for use.

***Note:** This process can kill only the existing germs in water at the time of boiling, but does not provide any protection against future possible contamination. Moreover, this method is very costly and can be used only in individual cases, particularly during the break up of epidemics in the town or city, and it is impossible to employ it in municipal water-works.*

(2) **By adding bleaching powder:** In small water-works, about 1 kg of bleaching powder per 1,000 kilolitres of water is mixed and water allowed to stand undisturbed for several hours. The chemical action produces **hypochlorous acid (powerful germicide)**.

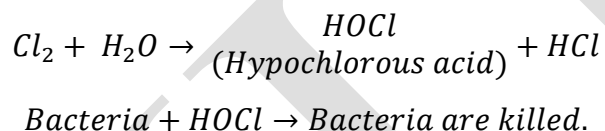


The disinfecting action of bleaching powder is due to the chlorine made available by it.

Drawbacks:

- Bleaching powder introduces calcium in water, thereby making it *more hard*
- Bleaching powder *deteriorates*, due to its continuous decomposition during storage. So, whenever it is to be added, it has to be analysed for its effective chlorine content.
- Only calculated quantity of bleaching powder should be used, since an excess of it gives a *bad taste and smell* to treated-water

(3) By Chlorination: Chlorine (either gas or in concentrated solution form) produces *hypochlorous acid*, which is powerful germicide.



Factors affecting efficiency of chlorine:

- Time of contact:** It has been experimentally shown that number of microorganisms destroyed by chlorine per unit time is proportional to the number of microorganisms remaining alive. Consequently, the death rate is maximum to start with and it goes on decreasing with time.
- Temperature of water :** The rate of reaction with enzymes increases with temperature . Consequently, death rate of micro-organisms by chlorine increases with rise in water temperature.
- pH value of water:** It has been found that at lower pH values (between 5-6.5), a small contact period is required to kill same percentage of organisms.

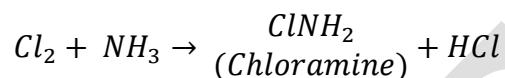
Advantages of chlorine:

- It is effective and economical.
- It requires very little space for storage.
- It is stable and does not deteriorate on keeping.
- It can be used at low as well as high temperatures.
- It introduces no salt impurities in the treated-water
- It is most ideal disinfectant.

Disadvantages:

- Excess of chlorine, if added, produces a characteristic unpleasant taste and odour. Moreover, its excess produces an irritation on mucus membrane. The quantity of free chlorine in treated-water should not exceed 0.1 to 0.2 ppm
- It is more effective below 6.5 pH and less effective at higher pH values.

(4) By using chloramine (ClNH₂): When chlorine and ammonia are mixed in the ratio 2:1 by volume, a compound *chloramine* is formed.



Chloramine is much more lasting than chlorine alone and consequently, it is a better bactericidal than chlorine alone.

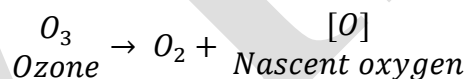


Note: Now a days, chloramine is used for disinfection of water, because its excess does not produce any irritating odour. Moreover, it imparts a good taste to treated-water.

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



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



The nascent oxygen is very powerful oxidising agent and kills all the bacteria as well as oxidises the organic matter present in water.

Disadvantage: This method is quite expensive and hence, not employed for disinfection of municipal water supply.

Advantage: Disinfection by ozone is costlier than chlorine, but it simultaneously removes colour, odour and taste without giving any residue. Its excess is not harmful, since it is unstable and decomposes into oxygen.

References

- 1) Engineering Chemistry by Jain and Jain
- 2) Engineering Chemistry by Wiley India First edition 2011
- 3) Engineering Chemistry by O. G. Palanna, Tata McGraw Hill Education Pvt. Ltd.
- 4) A Textbook of Engineering Chemistry by Dr.S.S.Dara and Dr.S.S. Umare, S.Chand publication

WILEY