MODULE 3

WATER TECHNOLOGY AND NANOTECHNOLOGY

Syllabus:

Water Technology: Introduction, water parameters, hardness of water, determination of temporary, permanent and total hardness by EDTA method, numerical problems, Softening of water by ion exchange method, desalination of water by electrodialysis, determination of COD, numerical problems. Forward osmosis: Introduction, Process and applications.

Nanotechnology: Introduction, size dependent properties of nanomaterial (surface area and catalytic), Synthesis of nanomaterial by sol-gel method and co-precipitation method.

Nanomaterials: Introduction, properties and engineering applications of carbon nanotubes, graphene and nanomaterials for water treatment (Metal oxide).

Self-learning: Sewage treatment (Primary, secondary and tertiary)

Hard Water: Hard water is the one which contains salts of calcium and magnesium that is the water which contains sulfate nitrates chloride and bicarbonates of calcium and magnesium, and the hard water doesn't form leather easily with the soap this is because of the precipitation of the soap with the calcium and magnesium.

Types of the Hardness

1) **Temporary hardness:** temporary hardness is caused by the presence of bicarbonates of calcium and magnesium. This can be removed by boiling the water for about the 30 minutes. Upon boiling the bicarbonates of calcium and magnesium gets converted into insoluble carbonates and hydroxide forms which can be later on filtered and removed .
2) **Permanent hardness:** permanent hardness is caused by chloride and sulphate of calcium and magnesium. This cannot be destroyed by boiling.

Total Hardness is the sum of temporary and permanent hardness.

The hardness of the water is expressed in terms of ppm of $CaCO_3$.

Estimation of Hardness:

Principle: Metal ions responsible for hardness of water i.e., Ca^{+2} Mg^{+2} can be estimated by using standard solution of disodium salt of EDTA.

Disodium salt of EDTA is a hexa dentate ligand which forms metal EDTA complex. Which takes place readily at pH=10 to maintain this, NH_3-NH_4Cl.

Eriochrome Black-T indicator is used. When EBT is added to hard water at pH10, it forms wine red complex with few metal ions.

M^{+2} + EBT $\longrightarrow$ M-EBT (Wine Red Color)

When a water sample is titrated against standard EDTA solution, remaining metal ions react with EDTA forming M-EDTA complex.

M^{+2} + EDTA $\longrightarrow$ M-EDTA

M-EDTA complex is more stable than M-EBT complex, therefore at the end point EDTA replaces EBT from M-EBT complex and free EBT is released to the solution.

M-EBT + EDTA $\longrightarrow$ M-EDTA + EBT (Blue color)

Procedure:

Estimation of Total Hardness:

1. Pipette out 25 ml of hardwater into conical flask.
2. Add 5ml of NH_3-NH_4Cl buffer.
3. Add 2 to 3 drops of EBT indicator.
4. Titrate against standard EDTA solution, till the color changes from wine red to clear blue.

Calculation:

$$\text{Total Hardness} = \frac{(100 \times 10^{-3} \times V_1 \times z) \times 10^6}{V_s} = \underline{\qquad\quad} \text{ PPM}$$

Ion Exchange Method

The process of removal of calcium, magnesium, iron, salts and other metallic ions from water is called softening of water.

In iron exchange method, softening of water is done by exchanging the ions causing hardness of water with the desired ions from an ion exchange resin. Ion exchange resins are high molecular weight cross-linked polymer with a porous structure. The functional group which are attached to the chain are responsible for ion exchange properties. The resins containing acidic groups which are capable of exchanging H^+ ions for cations present in water are known as cation exchange resins. The resins containing the basic groups which are capable of exchanging OH^- ions for anions present in water as anion exchange resins.

Process: in this process cation and anion exchange resins are packed in separate columns. Hard water is first passed through cation exchange resin where cations like Ca^{+2}, Mg^{+2} are removed from hard water by exchanging with H^+ ions as follows.

$Ca^{+2} + 2R^- \text{-} H^+ \longrightarrow R_2^{-2}\text{-}Ca^{+2} + 2H^+$

$Mg^{+2} + 2R^- H^+ \longrightarrow R_2^{-2}\text{-}Mg^{+2} + 2H^+$

Hard water is then passed through anion exchange resins where ions like SO_4^{-2}, Cl^- are exchanged with OH^- ions as follows:

$R^+\text{-}OH^- + Cl^- \longrightarrow R^+\text{-}Cl^- + OH^-$

These H^+ and OH^- ions released combine to form water molecules.

Regenerations: When resins are exhausted and lose their capacity to exchange ions, they are regenerated. The process of regeneration is the reverse of the reaction taking place for ionic change. The cation exchange resin is regenerated by passing a solution of dilute HCL or H_2SO_4

$$R_2^{-2}\text{-}Ca^{+2} + 2H^+ \longrightarrow Ca^{+2} + 2R^-\text{-}H^+$$

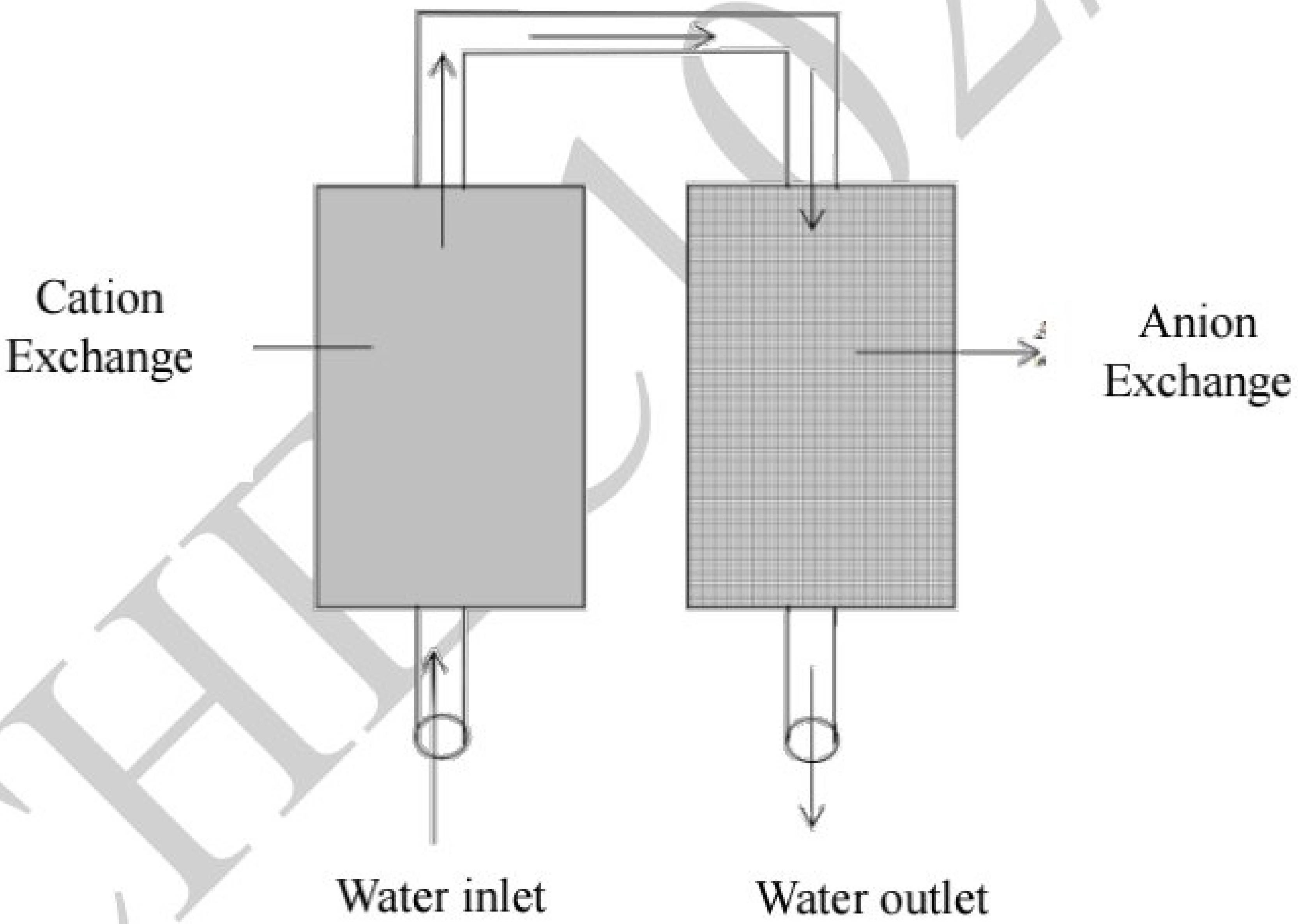
Similarly, anion exchange resin is washed with ammonium or sodium hydroxide solutions.

$$R^+\text{-}Cl^- + OH^- \longrightarrow R^+\text{-}OH^- + Cl^-$$

The columns are finally washed with deionized water and the washings are discarded.

Significance:

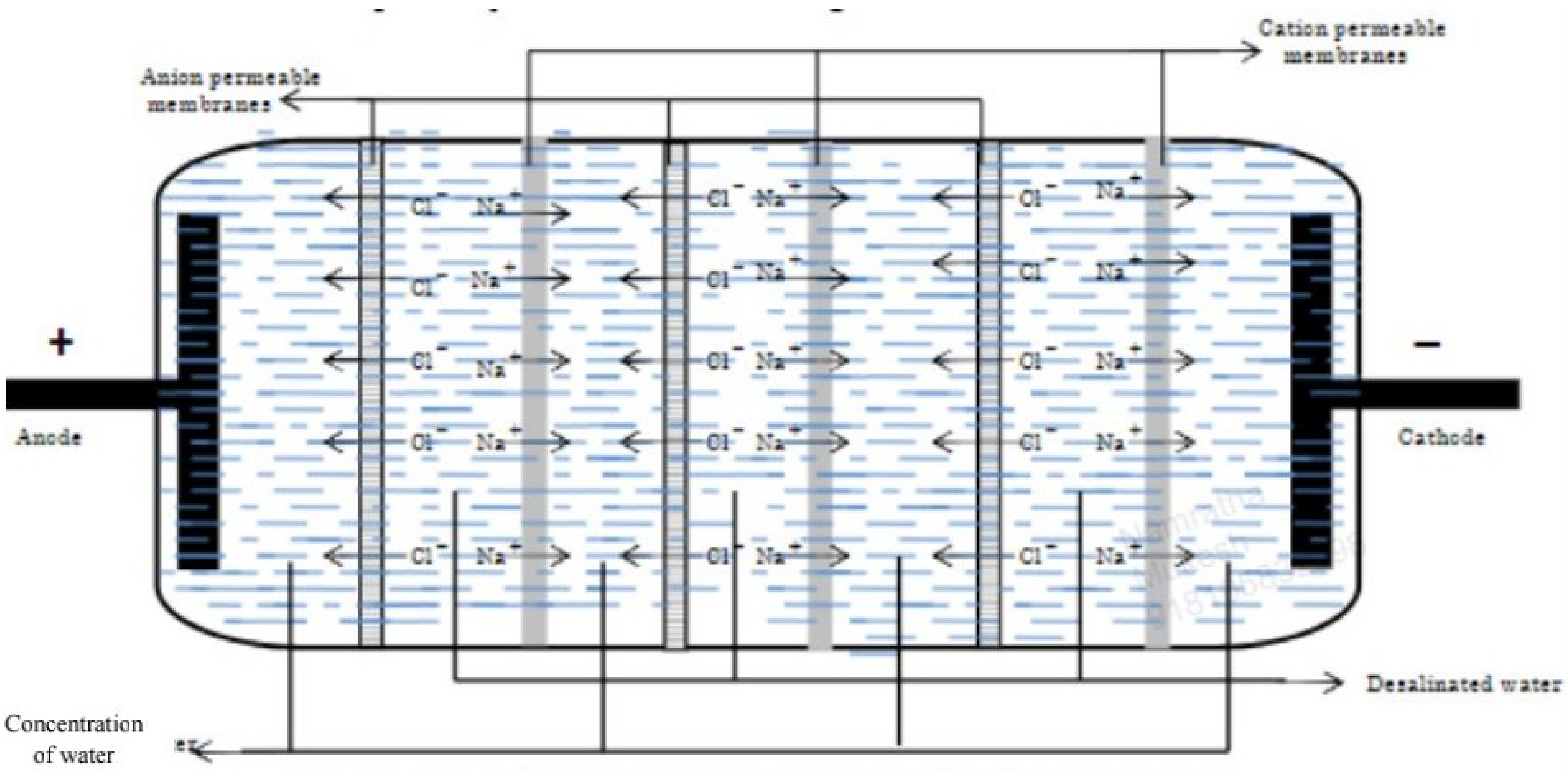
- Both acidic and alkaline water can be softened
- The ion exchange apparatus once set up is easy to operate and control.
- Residual hardness is very low and thus water is suitable for high pressure boilers also.



Softening of water by ion exchange method

Desalination Of Water By Electrodialysis:

1. The process of removal of dissolved salts present in water is called desalination.
2. In electrodialysis method Salts present in water are removed by applying direct current method.
3. The unit consists of alternately placed cation and anion exchange membranes.
4. Two electrodes, a cathode and an anode are placed at two ends.
5. Salt water is taken in compartment and direct current is passed.
6. Under the influence of electric current, the anions move towards anode and cation move towards cathode.
7. This each compartment gets concentrated with anions and cations. Meanwhile other compartments get diluted.
8. Highly concentrated and desalinated water can be removed separately.

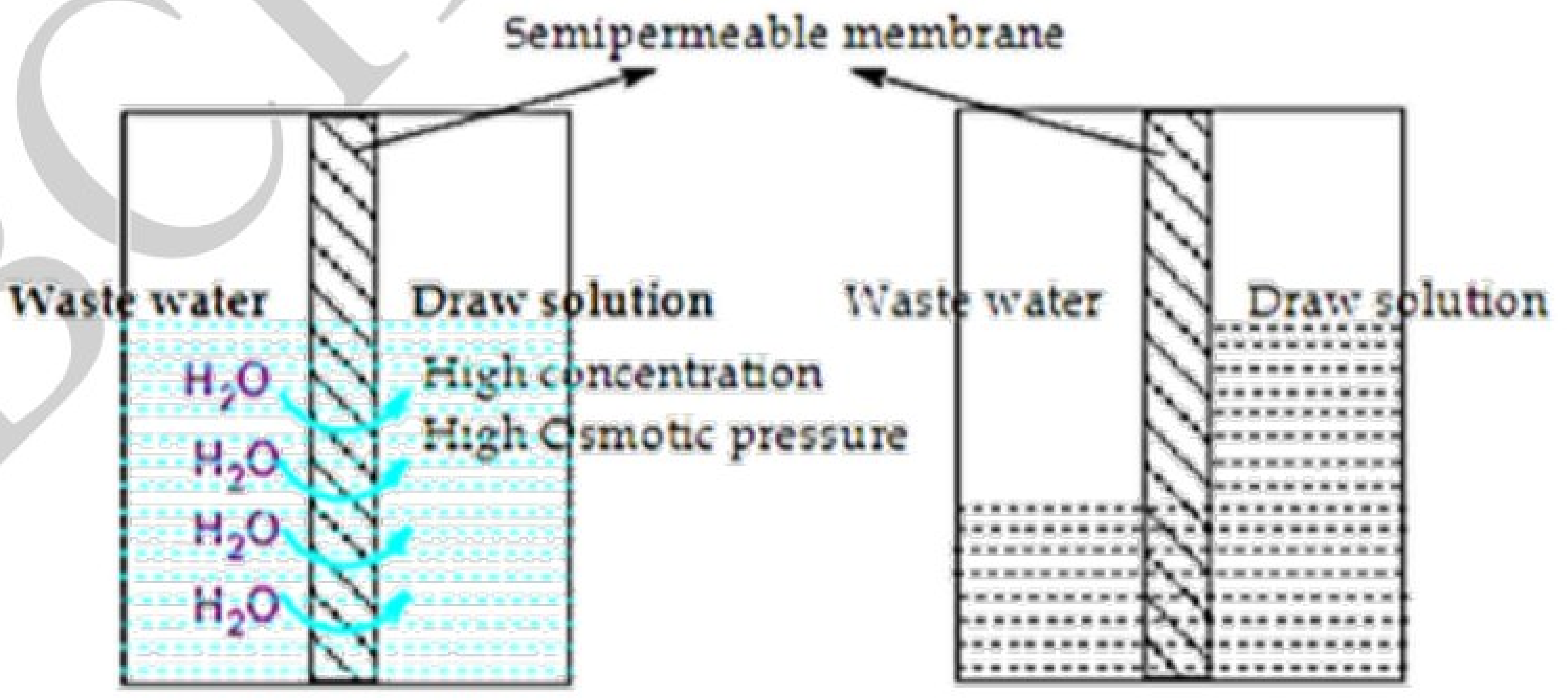


Desalination of water by electrodialysis using ion selective membrane

Forward Osmosis:

Forward osmosis. It's based on the principle of direct osmosis. In this method, Pure water is separated from wastewater without applying hydraulic pressure, just by direct osmosis. In forward osmosis technique, the wastewater sample from which clear water must be removed, is taken in one side of the membrane. On the other side, Solution of higher concentration with higher osmotic pressure is taken. This solution is called draw solution.

The concentration and osmotic pressure of draw solution is higher than the concentration and osmotic pressure of feed solution. Due to this difference, pure water molecules move from waste to feed solution to draw solution. Pure water from diluted draw solution is recovered by conventional process like reverse osmosis. Concentrated, solution is again used for drawing pure water from wastewater. Pure water can be recovered by thermal process as well. For example, when concentrated ammonium carbonate is used as a draw solution, pure water can be recovered by Thermal decomposition of ammonium carbonate.



Forward Osmosis

Applications:

1) Mainly used in industries for the concentration recovery of fruit juices, sugar concentration etc
2) Can be used for desalination of sea water to obtain potable water.
3) Used to extract pure water from sewage water.

Chemical Oxygen Demand (COD)

COD is defined as the amount of oxygen required to oxidize all oxidizable impurities presenting 1 liter of wastewater using a strong oxidizing agent such as acidified $K_2Cr_2O_7$.

Determination of COD

Principle: a known volume of wastewater sample is refluxed with $K_2Cr_2O_7$ solution in sulphuric acid medium. $K_2Cr_2O_7$ oxidizes oxidizers impurities. The amount of unreacted $K_2Cr_2O_7$ is determined by titration with the standard solution of ferrous ammonium sulphate. The amount of $K_2Cr_2O_7$ consumed corresponds to the COD of the wastewater sample to find out this a blank titration without waste water is carried out.

Ag_2SO_4 is used as catalyst for the oxidation of straight chain aliphatic compounds. And mercuric sulphate is added to hinders the interference of chloride ions.

$$Hg^{+2} + 4Cl^{-} \longrightarrow [HgCl_4]^{-2}$$

Procedure:

Back titration: 25 cm^3 of wastewater sample and 25 cm^3 of $K_2Cr_2O_7$ into 250 cm^3 of conical flask and one test tube full of 1:1 sulphuric acid containing the silver sulphate and mercuric sulphate is added. Reflux the mixture for half an hour and cool add two to three drops of ferroin indicator is added and titrate against standard for ferrous ammonium sulphate solution till the colour changes from bluish green to reddish brown.

Let the normality of the sample solution be z N

Let the volume of FAS solution consumed in titration be y cm^3

Blank titration: pipette out 25 cm^3 of $K_2Cr_2O_7$ solution into clean conical flask. Add one test tube full of 1:1 sulphuric acid followed by 2 to 3 drops of ferroin indicator and titrate against the standard FAS solution till the colour of solution turns from bluish green to redish brown.

Calculations:

$1\ cm^3$ of 1 N FAS solution = 1milli equivalent of oxygen = 8 mg of oxygen

$(x\text{-}y)\ cm^3$ of z N FAS solution = $8 \times (x\text{-}y) \times z$ mg of oxygen

i.e., $25.0\ cm^3$ of waste water sample = $8 \times (x\text{-}y) \times z$ mg of oxygen

$$1000\ cm^3 \text{ of the waste water sample} = \frac{8 \times (x-y) \times z \times 1000}{25} \text{ mg of oxygen}$$

$$\text{COD of waste water sample} = \frac{8 \times (x-y) \times z \times 1000}{25} \text{ mg of } O_2/dm^3$$

Nanotechnology

Any material with nano size with different properties from their bulk material is called nano material.

Size Dependent Properties

- **Surface area:** if a bulk material is subdivided into individual nano material, the total volume remains same but the collective surface area increases.
- **Catalytic properties**: nano materials have significant proportion of atoms at the surface, properties like catalytic activity, adsorption and chemical activity which are surface phenomenon, which depend on surface area.
- There for nanomaterials show some specific surface related properties which are not observed in bulk materials. Example, bulk gold is catalytically inactive, but gold nano particles are catalytically active.
- **Electrical properties**: the electronic bands in buk material is continuous where as in nanomaterials is discrete due to this even though bulk material is conducting its nano materials may become semiconductor or insulators

SOL-Gel Process

Preparation of SOL:

A sol is prepared by dispersing precursors in suitable solvent. Either a metal salt of metal alkoxide is used as precursor.

Conversion of SOL to gel: Sol further undergoes hydrolysis and condensation reaction forming a gel.

$M(OC_2H_5)_4 + x\ H_2O \longrightarrow M(OC_2H)_{4\text{-}X}(OH)_X + x\ C_2H_5OH$

Condensation:

$M(OC_2H_5)_{4-x}(OH)_x$ + $M(OC_2H_5)_4$-$x(OH)_x$ → $(OC_2H_5)_{4-x}(OH)_{x-1}M$-O-$M(OH)_{x-1}(OC_2H_5)_{4-X}$ + H_2O

Ageing of a gel: gel on ageing of known period, finally condenses to nanoscale clusters of metal hydroxides.

Removal of solvent: the solvent is removed by evaporation.

Heat treatment: the sample thus obtained is calcinated to obtain nano particle.

Co-Precipitation Method

In this method solid nanoparticles are obtained by careful precipitation from their solution.
The process involves 2 steps:

1. **Nucleation:**
   - A solution of metal salt (nitrate or acetate) is obtained by dissolving in water.
   - Precipitating agents like NaOH, NH4OH are added which changes the pH and causes condensation of precursors.
   - Thus, the concentration of the solution increases and reaches a super saturation level and at this stage nucleus formation is initiated.
2. **Growth of particle:**
   - A nucleus further grows into nano particle, which gets precipitated.
   - The product obtained is filtered, washed with water, air dried and finally calcinated at high temperature to remove counter anions like nitrate, acetate which are readily decomposed.
   - Precipitation synthesis can be used to prepare nano particles of metal oxide, metal sulphides and metals.
   - For the production of metallic nanoparticles, reducing agents are added to the solution.
   - Metal sulphides are produced by adding H_2S.

Carbon Nano Tubes (CNT)

Carbon nano tubes are cylindrical tubes with central hollow core, formed by rolling up of graphite sheets.

Types:

1. **Single walled carbon nano tubes (SWCNTs):** They are formed by rolling up of single layer of graphite. The diameter of SWCNT is 1.4 nm and length can go up to few micrometers.
2. **Multi- walled carbon (MWCNTs):** They consist of two or more concentric graphenes cylinders with van der waals forces between them. The diameter of MWCNTs varies from 30 to 50 nm and length can go up to few micrometers.

Properties of CNTs

1. They have high electrical and thermal conductivity.
2. They have low density and very high mechanical strength
3. They can emit electrons when subjected to high electric field
4. They have sp^2 carbon-carbon bonds which ae stronger than sp^3bonds found in diamond and provides CNTs with very good mechanical properties.
5. They are strongest and stiffest
6. SWCNTs efficiently absorb radiation in the near infra red range

Applications

1. As electrode material for lithium ion rechargeble batteries
2. Metallic interconnect between the components of integrated circuits.
3. Used in field emission X-ray tubes.
4. Used to obtain composite material with enhanced mechanical properties.
5. SWCNTs are used in cancer thermotherapy to selectively kill cancer cells without affecting the nearby healthy tissues.

Graphenes

- Graphene is a two-dimensional nano material made up of single atomic layer of carbon atoms present in hexagonal honeycomb like lattice.
- It is just one atom thick but extends in two directions.
- From a layered graphite material if a single layer is separated then it results in graphene.

Properties Of Graphenes

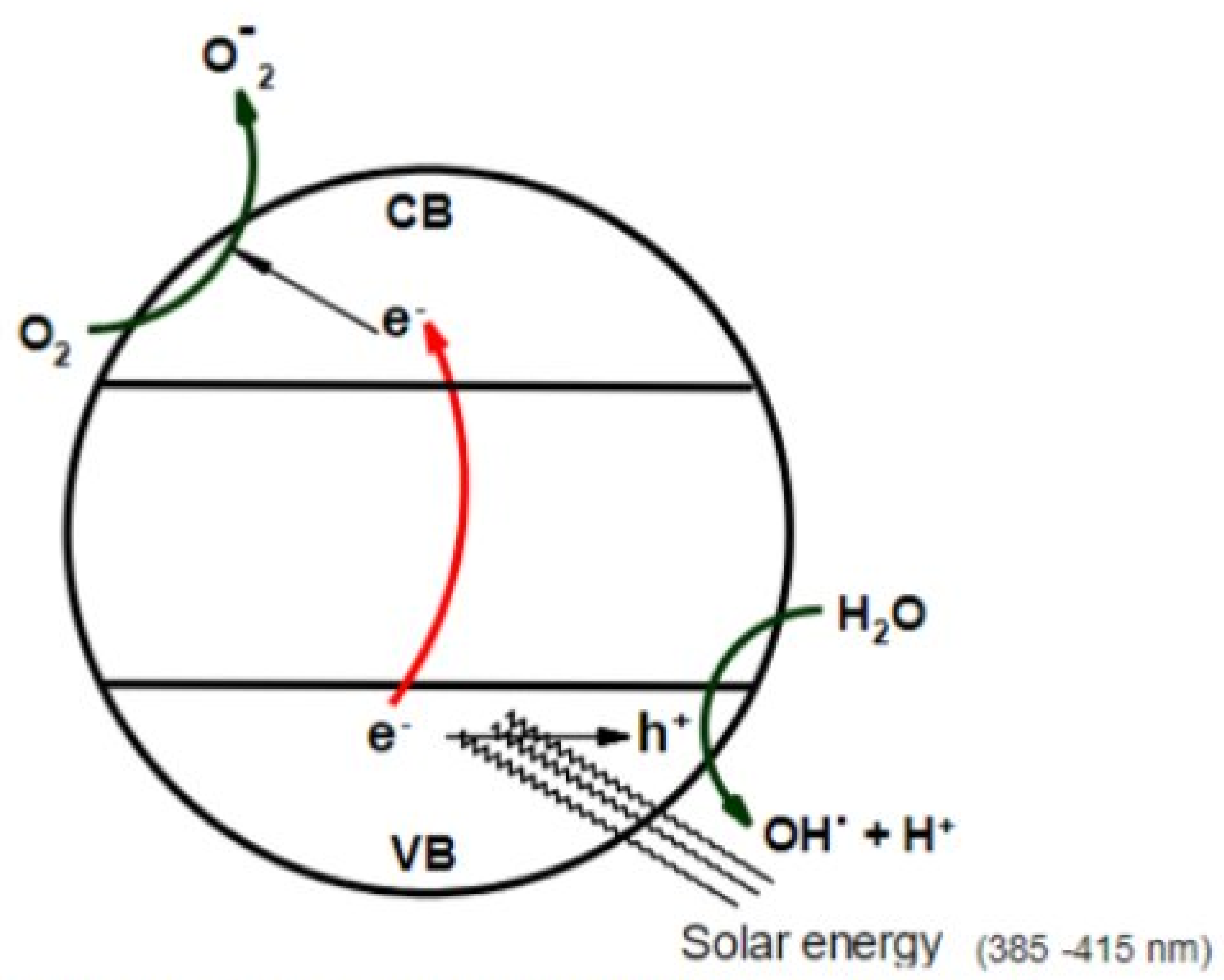
1. Graphene is transparent, flexible material with excellent mechanical, optical, thermal, electronic and chemical properties.
2. It has very high mechanical strength almost 100 times higher than steel
3. It is the best conductor of heat and electricity. Its thermal conductivity is higher than CNT, graphite and almost 10 times higher than Cu metal.
4. It has very wide optical band.it can absorb 2.3% radiation in visible and IR region which is 2-3 times higher than other semiconductors.

Applications

- Graphene is used as reinforcement fiber material in polymer composites.
- Due to excellent electrical and thermal properties graphene is used to improve both energy capacity and charge rate in rechargeable batteries.
- In making superior supercapacitors and in lightweight, flexible photovoltaic cells.
- In biomedical applications such as targeted drug delivery (useful in cancer treatment), bio sensing and biomedical imaging.

Application of TiO_2 nanoparticle in disinfection of water

1. TiO_2 nanoparticle absorbs near visible UV radiation of wavelength 385 to 415 nm.
2. Electrons are ejected from valence band and jump to conduction band leaving behind hole.
3. Hole takes up an electron from water molecule and splits it to hydroxyl free radical.
4. Electron in conduction band reduces oxygen to superoxide radical anion.
5. These hydroxyl radicals can oxidize organic molecules in the cells of microorganisms to carbon dioxide and water and destroy their cell structure and kill them.



TiO$_2$ photo active material for water disinfection

Silver Nano Particles (SNPs)

The silver nanoparticles has unique optical, thermal, catalytic electromagnetic, adsorbent and anti-microbial activities.

AgNP's have antibacterial activity due to their large surface volume ratio. They penetrate the cell wall of bacteria and lead to cell death.

AgNPs exhibit antifungal and antiviral activity. They are effective in killing viruses and fungus in water. They also exhibit anti-inflammatory and anti-cancer activity. Due to their broad range anti-microbial activities, silver nano particles are used in water purification.

QUESTION BANK

1. Explain the determination of total hardness of water using EDTA method.
2. Explain the process of softening of water by ion exchange method.
3. Explain the determination of COD
4. Explanation of desalination of water by electro dialysis method.
5. Write a note of forward osmosis.
6. Write the properties and applications of CNT and Graphenes.
7. Explain the synthesis of nanomaterials by sol-gel and co-precipitation method.
8. Write the application of nanomaterials in water treatment.
9. Numerical problems on COD and hardness determination.