

Module- V

NANO MATERIALS

Introduction, properties (size dependent). Synthesis-bottom up approach (solgel,precipitation, gas condensation, chemical vapor condensation). Nano scale materials-nano crystals & clusters, nano crystalline, fullerenes, carbon nano tubes, nano wires, nano rods, dendrimers&nano composites.

Nanomaterials

- Nano materials are the physical substances with at least one characteristic dimension between 1-150 nm .
- A nanometer (nm) is one billionth of meter or 10^{-9} m.
- 1 nm is approximately the length equivalent to ten hydrogen or five silicon atoms aligned in a line.
- Any material of nano size with its properties distinctively different from its bulkform is considered as nonomaterial.
- Nanomaterials are the building blocks of practical nanotechnology and can be physically and chemically manipulated for specific applications.
- Nanotechnology is the study of all the phenomena and processes involved in the synthesis, properties and applications of nanomaterials and nanostructures.

Properties (size dependent):

Nanomaterialsin terms of particle size are in between bulk materials and atomic or molecular structures they show different physical,chemical,optical, electronicand magnetic properties compared to bulk materials. Few size dependent properties are

Surface area;When a bulk material is subdivided into individual nanomaterials, the total volume remains the same, but the collective surface area is greatly increased. Due to the increase in surface area the properties like catalytic activity,gas adsorption and chemical reactivity can be studied. For example **bulk gold** is catalytically inactive, but **gold nonoparticles** are catalytically very active for selective redox reactions.

Electrical properties:The electronic bands in bulk materials are continuous due to overlapping of orbitals of billions of atoms. But, in the nano size materials, very few atoms or molecules are present so the electronic bands become separate (discrete) and the separation between electronic state varies with the size of nanomaterial. Hence, some metals which are good conductors in bulk become semiconductors and nonconductors as their size is decreased to nano level.

Optical properties: The discrete electronic states of nanomaterials allow absorption and emission of light of specific wavelength. Hence nanomaterials exhibit unique colours which are different from bulk

materials. The nano particle of different size can scatter radiation of different wavelength. Colours of few colloidal solutions are due to this scattering effect.

When light hits the surface of metal particle, electrons present on the surface starts oscillating back and forth in a synchronized way in a small space, and the effect is called as **surface Plasmon Resonance (SPR)**. Resonating electrons have cross sectional area very much higher than the nanoparticles. Depending on the frequency of oscillation, resonating electrons can capture radiation of different wavelength.

Thermal properties: Certain nano materials have extraordinary thermal properties compared to their macroscopic counterparts. For example, silicon nanowires have a much smaller thermal conductivities compared to bulk silicon.

Synthesis of nanomaterials

1. Sol –gel process:

This is an important bottom-up approach for the synthesis of nanomaterials.

Following steps involved in the synthesis: a) Preparation of sol, b) Conversion of sol to gel, c) Aging of a gel, d) Removal of solvent and e) Heat treatment.

Inorganic salt is dissolved in water or suitable solvent to make a homogeneous solution.

The homogeneous solution is hydrolyzed using water in the presence of acid or base and converted into sol. Gel is obtained by condensing the dispersed colloidal particles in the sol. Gel is an interconnected rigid and porous inorganic network enclosing a continuous phase. This transition is called sol-gel transition.

The poly condensation reaction continues until the gel transforms into a solid mass of nano scale clusters accompanied by contraction of the gel network and expulsion of solvent from gel pores. The aging process can exceed 7 days and is critical to the prevention of cracks in the gel that have been cast.

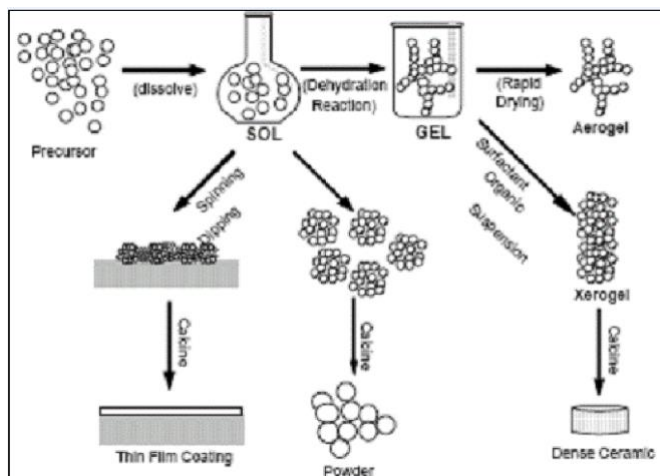
The encapsulated liquid is removed from the gel by evaporative drying.

The sample thus obtained is heat treated to obtain nanoparticles.

Ex: **CdSe semiconductor nanocrystals** are obtained by Sol –Gel method. A solution of dimethyl cadmium, a surfactant and tributylphosphine selenide is heated to 300 °C with continuous stirring. CdSe nanoparticles nucleate rapidly and then grow in size to become nanocrystals. The product is capped with surfactant, filtered and washed with acetone to remove the impurities.

TiO₂ nanorods are prepared by sol-gel method: A solution of Titanium isopropoxide is obtained by dissolving it in ethanol. A mixture containing acetyl acetone, ethanol and water is added to the above solution of titanium isopropoxide to obtain sol. Then Anodic Aluminium oxide membrane(AAO)(structure directing template) is dipped in this sol. A required volume of HCl is added to control hydrolysis

and condensation reaction in gel. The gel is dried by evaporation. AAO is removed by washing with NaOH solution. Nano rods are obtained by calcinating the sample at 400 °C for 24 hours.



Advantages;

Nanomaterials of high purity with good homogeneity can be obtained

Samples can be prepared at lower temperatures

Shape and size of the materials can be controlled.

Precipitation Method

In this method an inorganic metal salt (such as chloride, nitrate, acetate or oxychloride) is dissolved in water.

Metal cations in water exist in the form of metal hydrate species such as $\text{Al}(\text{H}_2\text{O})^{3+}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

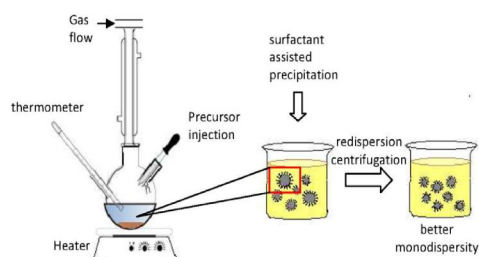
The species are hydrolyzed by adding a base solution, such as NaOH or NH_4OH .

On increasing the concentration of OH^- ions, the hydrolyzed species condense with each other to form metal hydroxides precipitates

The precipitate is washed, filtered and dried.

The dried powder is calcinated subsequently to obtain the final crystalline metal oxide.

Ex: Gold Nanoparticles are obtained by Precipitation method. Aqueous solution of gold is reduced with phosphorus (a mixed solution of carbon disulphide and water). A ruby coloured aqueous solution of dispersed gold nanoparticles is obtained. To prevent precipitation of gold metal, nanoparticles of gold are passed on to CS_2 solvent as soon as they are formed.



Advantages:

- The process is economical
- Wide range of single and multi components of oxide nanopowders can be synthesized.

Disadvantages:

- Inability to control the size of the particles
- Chances of aggregation of nano particles.

Inert-Gas condensation method

In this technique, a metal is vaporized using electron beam evaporation device in an inert atmosphere of helium or neon or krypton at the pressure of 1-50 mbar

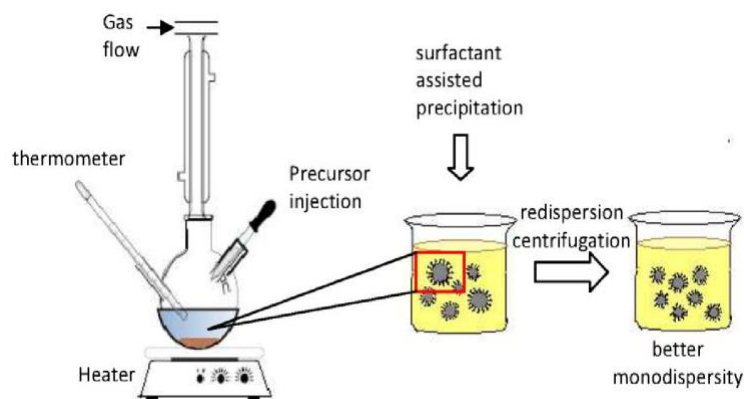
Metals atoms present in the vapour collide with the inert gas molecules and lose their energy. Due to collisions metal atoms are cooled down rapidly, become supersaturated and then nucleate homogeneously producing nanoparticles which collect at the bottom.

This method is commonly used to obtain metal nano materials with sizes in the range 2-100 nm.

For the formation of nanoparticles, the hot vapours of metal have to be cooled down quickly. Higher the cooling rate, higher will be the supersaturation resulting in the formation of large number of smaller particles.

Rate of cooling can be controlled by varying pressure of inert gas.

For example, evaporation of gold metal and condensation in the presence of helium gas produces gold nanoparticles which can be grown on various oxide substrates like titania and alumina.

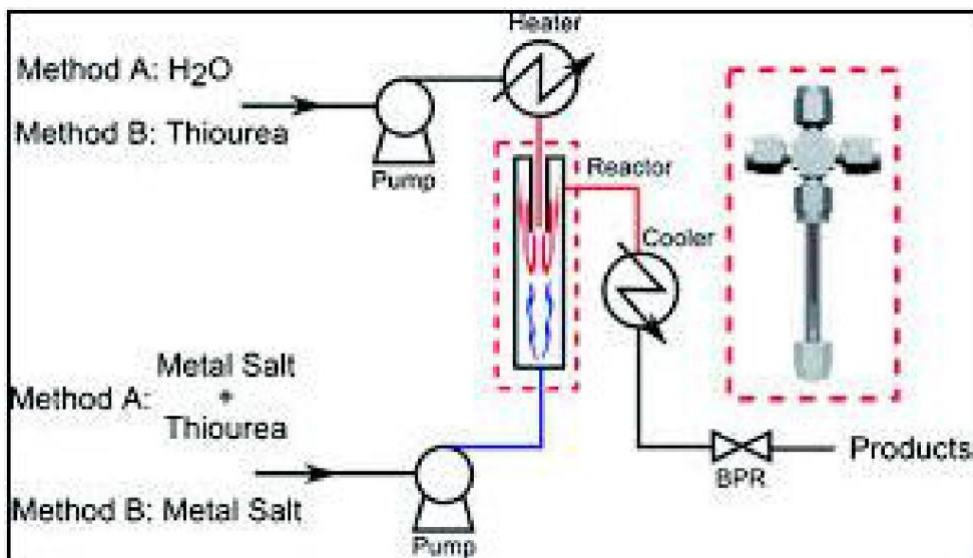


Chemical vapour deposition Method

This process involves the conversion of metal organic precursors (halides, carbonyls, organometallics and hydrides) into vapours in a reduced pressure atmosphere and subsequently dissociated by thermal energy to generate nuclei.

GaAs semiconductor nanoparticles are synthesized by chemical vapour deposition method from organometallic precursors. Trimethyl gallium and AsH_3 are used as precursors and hydrogen is used as a carrier gas as well as reducing agent. Reaction occurs at the temperature of 700°C at atmospheric pressure. Ga As nanoparticles are collected on a porous film downstream at a temperature of 350°C . The product obtained is sized single crystal Ga As with diameters ranging from 10 to 20 nm. The byproduct gas is easily removed out of reactor by carrier gas.

Silver nanowires are synthesized by chemical vapour deposition method: Silver seeds are first generated by heating silver nitrate at 160°C in ethylene glycol, which serves both as reducing agent and solvent. The surfactant used is polyvinyl pyrrolidone (PVP). If a separate solution of silver nitrate and PVP in ethylene glycol is then added dropwise to this seed solution highly elongated silver structures result.



Advantages:

- Simple technique and does not require ultrahigh vacuum
- Possible to deposit nanomaterials with almost any shape and any size
- Byproducts and leftovers are easily removed.

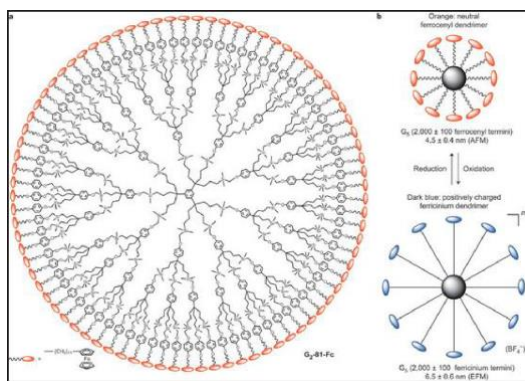
Disadvantages

Precursors used are volatile, and usually hazardous and extremely toxic. The byproducts are also toxic.

Nano Scale materials

Nanoparticle, nanocluster and nanocrystal, these three terms are often used interchangeably.

Nano particles are zero dimensional particles with their size varying between one to hundred nanometers. They are said to be zero dimensional because the movement of charge carriers are not free to move in any direction. Small nanoparticles with diameters of a few nanometers are comparable to molecules. Most of the properties of nanoparticles vary with size. In case of bulk materials properties vary with structure and composition but not on the size of material.



A nanocluster refers to a nanoparticle, usually in the size 0.1 to 1.5 nm. A nanocluster has a well-defined crystal structure in which the atomic positions can be exactly determined. Nanoclusters also exhibit properties that vary with size and shape. For example a nanocluster of gold containing 55 atoms is extremely more stable than a nanocluster with 56 atoms.

When the number of atoms in a nanocluster is increased, they assume the crystal structure same as that of bulk material. Such nanoclusters are called as nanocrystals. A nanocrystal is a crystal of nano size with its structure same as that of bulk material but properties vary with size of material.

GaAs semiconductor nanoparticles are synthesized by chemical vapour deposition method from organometallic precursors. Trimethyl gallium and AsH_3 are used as precursors and hydrogen is used as a carrier gas as well as reducing agent. Reaction occurs at the temperature of 700°C at atmospheric pressure. GaAs nanoparticles are collected on a porous film downstream at a temperature of 350°C . The product obtained is sized single crystal GaAs with diameters ranging from 10 to 20 nm. The byproduct gas is easily removed out of reactor by carrier gas.

Applications : Nanocrystals of metal oxides have the following applications

Light emitting Diodes (LED) Nano crystals display intense and narrow photoluminescence. Due to this property they are used in LED.

Biological labeling: nanocrystals exhibit size dependent fluorescence property, they become water dispersible, due to this property they are used for biolabelling and as scanning agents for MRI scan.

Full colour display: CdSe semiconductor nanocrystals also exhibit electroluminescence property. The colour (wavelength) of emitted radiation depends on the applied voltage. A single nanocrystal can emit

radiation of all the colours at different applied potential. Due to this property they are used in full colour display applications

Catalysis: Gold nanocrystals finely dispersed on high surface area oxide supports like silica or alumina are catalytically active, even at low temperature for the reaction like oxidation of CO and many hydrogenation and dehydrogenation reactions.

Nano rods: Nano rod can be considered as an elongated nanocrystal. A nanorod is a one dimensional nanostructure with the aspect ratio less than 10. Aspect ratio is defined as the ratio of length of a particle to its width. Length and width of nanorods usually vary from 10 to 100 nm. Nano rod is one dimensional, because the movement of charge carriers is allowed in only one direction and confined in two other directions.

Applications of nanorods

Nanorods are useful to study the effect of shape and size on magnetic, electronic, optical and chemical properties of the materials at nanoscale.

Gold nanorods exhibit very high fluorescence intensity. And also functional biomolecules like DNA, proteins can be attached to the selective locations of nanorods. Therefore nanorods find biomedical applications like biosensing and bioimaging.

Nano rods of alloys like Pt-Ru, Pt-Ni are used as catalysts in direct methanol oxygen fuel cell electro-oxidation of methanol.

Nanorods of metal oxides like TiO_2 , V_2O_5 and MnO_2 are used in catalysis.

Nano wires: A nanowire is a one dimensional nanostructure of the order of a nanometer (10^{-9}). Width of nanowire is in the range of 1-100 nm but length can be more than nanoscale. Nanowire is considered as one dimensional nanomaterial, because the movement of charge carriers is allowed in only one direction (along the length) and confined in two other directions. Nanowires exhibit aspect ratio (length to width ratio) of more than a 1000. Many different types of nanowires exist, including metallic (ex: Ni, Pt, Au) semiconducting (Ex: Si,) and insulating (Ex: SiO_2 , TiO_2).

Applications of Nano wires

Nanowires are believed to be the building blocks of next generation nanoelectronics and molecular devices. They are likely to play a crucial role as interconnects and active components in nanoscale devices.

Silicon nanowires on stainless steel substrate are used as anode, which have power density 10 times greater than conventional Li-ion batteries.

AgCl nanowires are used in photocatalysis to decompose organic molecules in polluted water.

A solar cell using graphene coated with zinc oxide nanowires will allow the production of low cost flexible solar cells at high efficiency.

Nanocomposites:

A composite is a combination of two or more different materials that are mixed to get best properties of both. Nanocomposite material is obtained by inserting nano materials into the matrix layer. Such a material will have the properties of both nano phase as well as matrix. Matrices are polymers, glass and ceramics. In nano composite materials, particles are distributed in such a way that they do not touch each other.

The oldest known nanocomposite is “gold ruby glass”. In this composite, gold nano particles of almost spherical shape are distributed over glass matrix. Gold nanoparticles are soluble in glass matrix; therefore they need to be coated with tin oxide which acts as a colloid stabilizer.

Types of nanocomposites;

Zero dimensional composites; in which isolated nanoparticles are distributed in a matrix.

One dimensional composites; in which nano tubes, and nanorods are distributed in a matrix

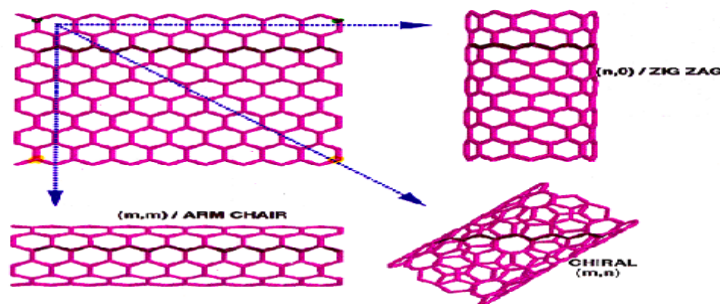
Two dimensional composites; in which thin nano films are placed between two matrix layers

Due to their large aspect ratio (i.e., size to volume ratios), submicrometer size, and unique properties, nanosensors, nanoprobe and other nanosystems are revolutionizing the fields of chemical and biological analysis.

They find applications in the important fields of catalysis, separation, sorption, and fuel cells.

Composite materials of nanorods with polymers as a matrix can have a combination of properties like good electrical conductivity and high tensile strength and are used in automotive industry.

Carbon Nanotubes (CNTs) are [allotropes of carbon](#) with a [cylindrical nanostructure](#). Nanotubes are members of the [fullerene](#) structural family. **Carbon nanotubes** are among the most exciting of nanomaterials. These rod-shaped carbon molecules are roughly one nanometer across. Although they're hollow, their densely packed structure makes them incredibly strong and they can be grown into fibers of virtually any length. Graphite is made up of layers of carbon atoms arranged in a hexagonal lattice. The nano tubes are typically longer than a micrometer, with diameter ranging from 1-20 nm. Each shell is made sp^2 trivalent carbon atoms. The tube is typically closed at each end.



Fullerene is a pure carbon molecule composed of a least 60 atoms of carbon, arranged as 12 pentagons and 20 hexagons. The diameter of the molecule is 1 nm. The molecule is composed of carbon in the form of a hollow sphere, ellipsoid, tube, and many other shapes. Spherical fullerenes are also called **buckyballs**, and they resemble the balls used in football (soccer). Cylindrical ones are called carbon nanotubes or buckytubes. Fullerenes are similar in structure to graphite, which is composed of stacked graphene sheets of linked hexagonal rings; but they may also contain pentagonal (or sometimes heptagonal) rings. The first fullerene molecule was named as buckminsterfullerene (C_{60}), as a homage to Buckminster Fuller.

Synthesis of fullerenes: Fullerene is synthesized by vaporization of graphite at very high temperature of 4000°C and condensing the vapour in inert atmosphere of helium gas. A mixture of various fullerenes is obtained by condensing the evaporated carbon. The main product is the fullerene C_{60} . It is extracted and crystallized using benzene as solvent.

Applications;

It is used in electrographic imaging, solar cells, nonlinear optical thin films, magneto optical recording etc.,

It is used in making carbon films, tunnel diodes, photolithography and double layer capacitor and storage devices

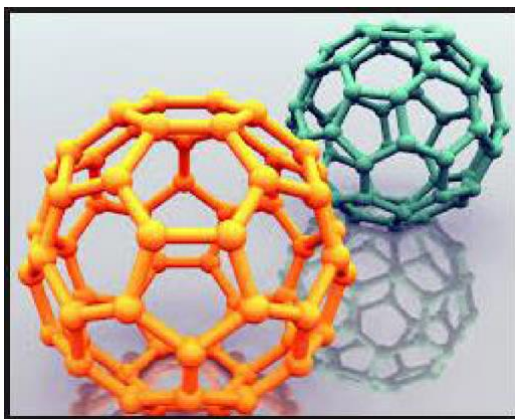
It is widely used for the conversion of diamond.

In the separation of chromatography materials, absorbent for gases etc.

It is used in gas sensors, temperature sensor, particle sensors and in detection of organic vapours.

Used as lubricants, adhesives, charge transfer complexes, cosmetics, catalysts.

It is used in secondary batteries, non aqueous batteries and fuel cell electrodes.



Dendrimers are repetitively branched molecules. The name comes from the Greek word (**dendron**), which translates to "tree". They have a central core of multifunctional molecule to which branched molecules are added repeatedly, step by step. Centre of a dendrimer is less dense compare to the exterior portion.

Dendrimers represent a class of novel polymers having unique molecular architectures characterized by their well-defined structure, with a high degree of molecular uniformity, low polydispersity and properties that make them attractive materials for the development of nano medicines. Dendrimers have well defined shape, size and molecular weight. Dendrimer can be grown up to 10-15 generations. Low generation dendrimers have a disc-like structure, while higher generations have a globular or spherical shape.

Applications:

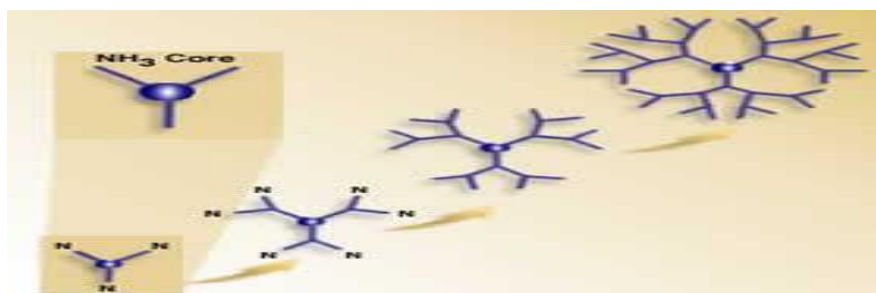
Used as contrast agents in MRI imaging. MRI imaging is used to produce anatomical images of organs and blood vessels.

Used in targeted drug deliveries: dendrimers can carry drugs and release it at specific infected part of the body in a controlled manner.

Dendrimers themselves are biologically active and used as antiviral and antibacterial agents.

Dendrimers can act as carriers called vectors in gene therapy. Vectors transfer through the cell membrane into nucleus.

Due to high surface area and high solubility of dendrimers they are used as nano scale catalysts in industrial processes.



5.14.4 Nano Composites: - Nano Composites are a class of material in which one or more phases with nanoscale dimensions (Zero- dimensional, One - dimensional, Two - dimensional) are embedded in a metal, ceramic or polymer matrix. Nano Composite material is obtained by inserting nano material into the matrix layer.

Depending on the dimension of nanomaterials distributed in the matrix, nanocomposites are as follows.

- 1) **Zero- dimensional Composites:** - Isolated nanoparticles are distributed in a matrix.
- 2) **One - dimensional Composites:** - The nanotubes and nanorods are distributed in a matrix.
- 3) **Two - dimensional Composites:** - The thin nanofilms are placed between two matrix layers.



Properties of Nano Composites

- 1) Nano Composite is "gold ruby glass," which was produced by Assyrians in the seventh century.
- 2) Composite materials of various nanomaterials with polymer as a matrix possess excellent mechanical and thermal properties.
- 3) Composites with well-aligned metal nanorods over polymer matrix can exhibit good electrical conductivity and high tensile strength.

Applications of Nano Composites

- 1) The excellent mechanical and thermal properties of composite materials are used to wide extent in the automotive industry.
- 2) The coated nanocomposite particles are widely used in the biology and medicine.

QUESTIONS

- 1) What are nano materials? Explain the synthesis of nano material by solgel & precipitation methods. 5m
- 2) What are nano materials? Explain properties of nano materials 5m
- 3) Explain synthesis of nano materials by chemical vapour condensation method. 5m
- 4) Write a note on i) Nano scale materials ii) Fullerenes iii) carbon Nano tubes iv) Nano wires v) Nano wires vi) Nano rods vii) dendrimers viii) nano composites 5m each
- 5) Synthesis & uses of Fullerenes?

WATER TECHNOLOGY

5.1 INTRODUCTION

Water is nature's most abundant and useful compound of many essential things, for the existence of human beings, animals & plants. Water is rated to be of greatest importance. It covers three fourth of earth's surface.

Water is not only essential for animals and plants but also occupies a unique position in industries. Probably its most importance use as an engineering material is in steam generation. Water is also used as a coolant in power & chemical plants. In addition to it water is widely used in other fields such as production of steel, rayon, papers, atomic energy, textiles, chemicals, ice & for air conditioning, drinking bathing, sanitary, washing, irrigation, fire fighting etc.

The main sources of water are

(A) Surface water (i) Rain water

(ii) River water

(iii) Sea water

(B) Underground water - spring & well water

IMPURITIES IN WATER-

All natural water supplies irrespective of the source contain impurities which may be broadly classified into four categories:

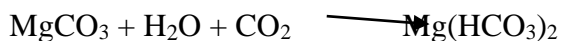
- 1) Dissolved impurities
- 2) Suspended impurities
- 3) Dissolved gases
- 4) Organic matter

Dissolved Impurities - Dissolved impurities mainly consist of bicarbonates, chlorides & sulphates of calcium, magnesium and sodium. In addition, small amounts of nitrates, nitrites, silicates, ammonium & ferrous salts are also present. These salts are derived from rock & soils with which the water is in contact. Thus water which is in contact with limestone contains calcium carbonate since the CO₂ dissolved in water

interacts with limestone



Similarly, water which is in contact with magnesite contains magnesium bicarbonate.



In general, ground waters contain more dissolved salts than surface waters.

5.2.2 Suspended matter - the suspended matter may be of inorganic or organic nature.

The inorganic materials include particles such as sand, clay, silica, hydroxides of iron & aluminium etc derived from the erosion of soil. Some of these particles have large size & therefore settle down readily. Others are fine particles & colloidal in nature. Such particles do not settle down easily.

The organic suspensions are decaying vegetable matter & due to microorganisms. These are also present in colloidal form. The presence of suspended matter, particularly the colloidal particles impart turbidity to water.

Dissolved gases: most waters contain dissolved gases such as oxygen, carbon dioxide, sulphur dioxide, ammonia & oxides of nitrogen, all of which are derived from atmosphere.

Organic matter: organic compounds derived from the decay of vegetable & animal matter including bacteria may be present in water. Water also gets contaminated with sewage & human excretal matter etc. Consequently the pathogenic bacteria such as typhoid bacillus & commensal bacteria of intestinal origin such as coliform group (streptococcus faecalis & clostridium welchii) are introduced into water.

BIOLER FEED WATER

A boiler is a closed vessel which operates under different pressures. Water heated in boiler under pressure is transformed to steam. The water used in these types of boilers is called as boiler feed water. (Boiler feed water is water used to supply a boiler to generate steam or hot water.) A boiler is a device for generating steam, which consists of two principal

parts: the furnace, which provides heat, usually by burning a fuel, and the boiler proper, a device in which the heat changes water into steam. The steam or hot fluid is then recirculated out of the boiler for use in various processes in heating applications.

Boiler feed water contains impurities.

These impurities result in many problems.

Boiler Problems

Impurities present in water can cause the following types of problems in boilers.

- i (i) Scale and sludge formation
- ii (ii) Priming and foaming
- iii (iii) Boiler corrosion

Scale and sludge formation

In boilers water is heated under high pressures to high temperatures. As boiling point of water is much lesser than that of many impurities, the impurities in water get progressively concentrated inside the boiler. These impurities get precipitated out on saturation. If the resultant precipitated is thick deposit is called as scale or if the precipitate is loosely held known as sludge.

Scales are due to the presence of MgCl_2 , $\text{Mg}(\text{HCO}_3)_2$, $\text{Ca}(\text{HCO}_3)_2$, CaSO_4 and silica in water and sludge is due to CaCl_2 , MgCl_2 , MgSO_4 , MgCO_3 etc.

Causes of scale formation

Loss of fuel

- i (i) Reduction in boiler efficiency
- ii (ii) Boiler explosion
- iii (iii) Decrease in the strength of boiler
- iv (iv) Cleaning process is expensive.

How to remove scales?

- i (i) Using wooden scraper or wire brush loose scales can be removed.
- ii (ii) Blow down operation for loose scales (removal of hard water from the bottom of the boiler and refilling soft water).
- iii (iii) By thermal shocks, it makes scales brittle.
- iv (iv) Treatment with HCl (5-10%) for carbonates and EDTA for Ca or Mg salt

Causes of sludge formation

- i (i) Loss of fuel
- ii (ii) Reduces boiler efficiency
- iii (iii) Leads to blockage of cooler and distribution pipes.
- iv (iv) Cleaning process is expensive]

How to avoid sludge?

- i (i) Using soft water
- ii (ii) By removing salty water from boiler time to time.

Priming and

Priming: It is the process of very rapid boiling of water in the boiler which makes some water droplets to be carried away along with steam in the form of spray into the steam outlet.

Priming is due to the presence of suspended and dissolved impurities in water and very high water level in the boiler and also due to defective boiler design.

Problems caused by priming

- i (i) Wet stem reduces the heating efficiency of the steam and causes corrosion.
- ii (ii) Impurities in water droplets may deposit on turbine blades to bring down its efficiency.

Priming prevention

- i (i) Maintaining low water levels.
- ii (ii) Good boiler design for proper evaporation of water.
- iii (iii) Avoiding rapid discharge of steam.

Foaming

It is the formation of small but persistent bubbles on the surface of boiler water. These bubbles are carried along with steam leading to excessive priming.

Prevention of foaming

- i (i) Using anti foaming agents like castor oil, polyamides etc.
- ii (ii) The removal of silica using ferrous sulphate.
- iii (iii) Removal of oils and grease from sodium aluminate
- iv (iv) Removal of clay and suspended matter using coagulating agents.

Boiler corrosion

Corrosion in boilers is due to presence of dissolved oxygen, dissolved CO₂ and MgCl₂.

(i) Due to dissolved oxygen

The dissolved oxygen reacts with iron at about 350-450 °C in the boiler and produces ferrous hydroxide.



Ferrous hydroxide oxidizes to ferric hydroxide by dissolved oxygen and deposits. This process repeats till all the dissolved oxygen is exhausted. The corroded parts are referred to as pits.

(ii) Due to dissolved CO₂



Further HCO₃⁻ may combine with Fe²⁺ giving Fe(HCO₃)₂ which decomposes giving Fe(OH)₂ and CO₂ thus continuing the process.



(iii) Due to MgCl₂

Mineral acid are produced by the hydrolysis of salts like MgCl₂ and FeCl₂ in boiler feed water.

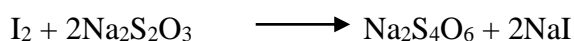
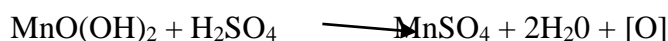
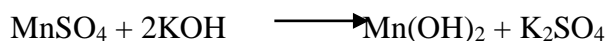


Determination of Dissolved Oxygen by Winklers or Iodometric method:

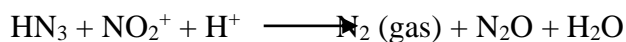
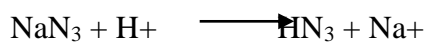
The analysis of dissolved oxygen (DO) in water is a key test to assess raw water quality & to keep a check

on stream solution. The DO forms the basis for Biochemical Oxygen Demand (BOD) which constitutes an important parameter to evaluate pollution potential of wastes. DO test is used to control the amount of oxygen in boiler feed water by physical, chemical & mechanical methods. The measurements of the amount of oxygen actually dissolved in a water sample are of great importance as the oxygen content is important for many biological & chemical processes.

Principle: The principle involved in the determination of dissolved oxygen is that the divalent manganese solution along with a strong alkali is added to water sample. The DO present in water sample oxidizes divalent manganese to tetravalent manganese. The basic manganic oxide formed acts as oxygen carrier to enable the dissolved oxygen in molecular form to take part in the reaction. Upon acidification, tetravalent manganese reverts to divalent state with the liberation of nascent oxygen, which oxidizes KI to I₂. The liberated iodine is titrated against standard sodium thiosulphate solution using starch as indicator.



KI is added as alkaline KI which consists of a solution of sodium azide, KI & NaOH in water. Sodium azide destroys the nitrites in water & thereby reduces the error due to nitrites.



Procedure: Pipette out 300 cm³ of water sample into a clean glass stoppered bottle. Add 3 cm³ of manganous sulphate solution dipping the pipette below the surface of water. Add 3 cm³ of alkaline potassium iodide solution. Stopper the bottle & shake well and allow the precipitate to settle down. Now add 1 cm³ of concentrated sulphuric acid slowly & mix well until the precipitate dissolves completely. Pipette out 102 cm³ of this solution into a clean conical flask & slowly titrate against 0.02N sodium thiosulphate solution using 2 cm³ of starch indicator near the end point. Record the volume of sodium thiosulphate solution used.

Calculation:

$$\text{Normality} \times \text{volume of oxygen solution} = \text{Normality} \times \text{volume of Na}_2\text{S}_2\text{O}_3$$

$$\text{Therefore, normality of oxygen solution} = \text{Normality} \times \text{volume of Na}_2\text{S}_2\text{O}_3$$

$$\text{Volume of oxygen solution}$$

$$= N \times V = a$$

$$\text{Weight of dissolved oxygen/dm}^3 = \text{Normality} \times \text{Equivalent weight of oxygen}$$

$$= a \times 8.0 \times 1000 \text{ mg/l}$$

BIOLOGICAL OXYGEN DEMAND :

Definition: BOD is usually defined as the amount of oxygen required by bacteria while stabilizing decomposable organic matter under aerobic condition. The BOD Test is widely used to determine the pollutional strength of domestic & industrial waste in terms of oxygen that they will require if discharged in natural water sources in which aerobic condition exists.

Natural water contains dissolved oxygen (8.7ppm or 8.7 mg dm⁻³) and the dissolved oxygen (DO) is capable of oxidizing many of these pollutants particularly the organic wastes such as dead plant matter & animal wastes. In this way the dissolved oxygen is consumed. However in running water such as streams and rivers there is a continuous replenishment of oxygen maintaining the DO level & hence the degradation is aerobic. The degradation products are CO₂ and water which are harmless. On the other hand, in stagnant waters such as in lake and well waters, there is gradual decrease in the DO level ultimately causing anaerobic (absence of air) degradation of organic wastes releasing obnoxious gases such as H₂S, CH₄ & NH₃.

BOD is defined as “ the quantity of oxygen required by microorganisms to oxidize the organic wastes present in one litre of waste water over a five day period at 20 °C.

Characteristics of BOD parameter:

The unit of BOD is mg dm⁻³ or ppm.

It is empirical and semiquantitative.

It represents only biodegradable organic load in sewage.

Strictly aerobic conditions are needed.

Determination is slow & time consuming method ▪ Polluting power of sewage or its nuisance value. ▪ The load of organic matter on the sewage treatment plant. The amount of clean diluting water required for disposal of sewage. BOD indicates the amount of decomposable organic matter in the sewage. It is an expression of how much oxygen is needed for microbes to oxidize the organic matter in the sewage. It gives information's about the following: It is important to know the BOD of sewage before disposing into rivers or lakes because dissolved oxygen content in the water will be decreased by the sewage if its BOD is high resulting in the death of fishes and other aquatic animals. **Determination of BOD :** The parameter is commonly measured by the quantity of oxygen utilized by aerobic bacteria during 5 days period. (CHONS)

$$+ O_2 \rightarrow CO_2 + H_2O + NO_3^- + SO_4^{2-}$$
 The BOD test is based on determination of oxygen. BOD may be measured directly in a few sample but in general a dilution procedure is required.

Direct method: with samples whose 5 day BOD does not exceed 7mg/l it is not necessary to dilute them providing that they are aerated to bring D.O level nearly to saturation at the start of the test. Procedure is to adjust a sample to about 20 C & aerate with diffused air to increase or decrease the DO gas content of the sample to near saturation. Two or more BOD bottles are then filled with the sample. Atleast one is analyzed for BOD immediately & the other are incubated for 5 days at 20 C. After the 5th day the amt of DO remaining in the incubated sample is determined & the 5th day BOD is calculated by subtraction of the 5th day result from that obtained on the 1st day.

Dilution method: here measuring of BOD is based upon the fundamental concept. The rate of biochemical degradation of organic matter is directly proportional to the amt of unoxidised material existing at that time. According to this concept the rate at oxygen is used in dilution of waste is in direct ratio to the percentage of waste in the dilution provided that all factors are equal. The environmental & nutritional factors that has to be controlled to obtain reproducible result include.

1. Freedom from toxic material. 2. Favourable pH & osmotic pressure. 3. Presence of available essential nutrients. 4. Std temperature. 5. Presence of significant population of mixed organisms of soil origin.

A synthetic dilution water prepared from distilled water is best for BOD testing because most of the variables like contamination from chlorine residue for variation of DO & presence of microorganisms, algae or nutrients etc can be kept under control. The dilution water should be seeded with waster water or other materials to ensure a uniform population of organisms in various dilution& to provide an opportunity for an organic matter present in the dilution water to be exposed to the same type of organic matter as those involved in the stabilization of waste. The dilution water should be aerated to saturate it with oxygen before use.

The BOD can be calculated as

$$\text{BOD} = D_1 - D_2 \times B \text{ mg. dm}^{-3} \text{ A}$$

Where D1 is DO in mg. dm⁻³ in solution at the start.

D2 is the DO in mg. dm⁻³ in solution after 5 days.

A is the volume of sample in ml before dilution.

B is the volume of sample in ml after dilution.

CHEMICAL OXYGEN DEMAND:

BOD refers to biologically oxidisable impurities and does not account for non-oxidizable& slowly oxidizable impurities. COD is a faster method of determining the amount of oxygen required to oxidize both the biologically oxidizable and biologically non-oxidizable but chemically oxidizable organic & inorganic wastes.

Definition: the amount of oxygen consumed in the chemical oxidation of organic & inorganic wastes present in 1 litre of waste water.

Characteristics of COD parameter:

1. It is a satisfactory, quantitative method for measuring total organic load and inorganic load.
2. it is preferable to BOD as the results are reliable.
3. rapidly measurable parameter & needs about 3 hours for completion.
4. in general $COD > BOD$ since both biodegradable and non biodegradable organic load are completely oxidized.
5. when use along with BOD test, it gives biologically resistant organic matter.

Determination of COD

Principle: The principle of the method is the oxidation of organic matter using chemical oxidizing agents such as acidified potassium dichromate in the presence of a catalyst such as silver sulphate (which catalyses the oxidation of organic matter) & mercuric sulphate (which forms a complex with chloride ions present in water thus preventing its interference).

A typical reaction representing the oxidation of organic matter is given below:



The method consists in adding excess of a standard solution of potassium dichromate acidified with sulphuric acid to a known volume of effluent sample and back titrating the excess of potassium dichromate against a standard solution of ferrous ammonium sulphate. COD values are also expressed in $mg\ dm^{-3}$.

Procedure: To a measured volume of waste water sample taken in a flask, add 10 cm^3 of 0.25N $K_2Cr_2O_7$ solution followed by 30 cm^3 of 6N H_2SO_4 . Add 1g of Ag_2SO_4 followed by 1g of Hg_2SO_4 . Attach a reflux condenser & reflux the contents for 2 hrs. Cool and titrate the excess $K_2Cr_2O_7$ against ferrous ammonium sulphate solution using ferroin as indicator till the bluish green colour turns sharply to reddish brown. Let the volume of titrant required be 'a' cm^3 . Perform a blank titration taking the same amount of water in place of the waste water. Let the volume required be 'b' cm^3 .

Calculations:

Volume of $K_2Cr_2O_7$ required for the sample = $b - a\ cm^3$.

$$COD\ of\ the\ sample = N \times (b - a) \times 8\ g\ dm^{-3}\ V$$

$$= N \times (b - a) \times 8000\ mg\ dm^{-3}\ V$$

Where N = normality of ferrous ammonium sulphate

V = volume of waste water sample

b = volume of std FAS used in blank titration

a = volume of std FAS used in sample titration

SEWAGE TREATMENT

The domestic sewage contains heavy load of BOD, pathogenic bacteria, colour & annoying smell. If such raw waste water is discharged into natural water bodies they may cause detrimental effects such as

destruction to aquatic life, depletion of dissolved oxygen, disagreeable colour & odour and not to forget the waterborne diseases caused by the pathogenic bacteria. Therefore sewage has to undergo proper treatment before being discharged in natural water bodies.

The sewage treatment is carried out in 3 stages, namely:

1. Primary treatment
2. Secondary treatment
3. Tertiary treatment

Primary treatment (Physical & chemical): It involves

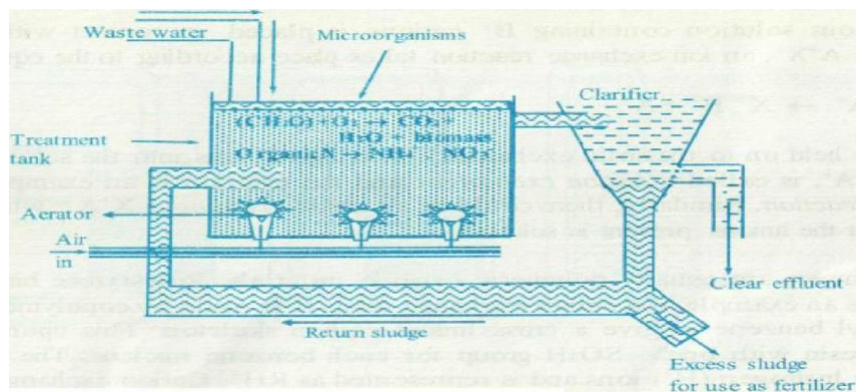
- (a) Screening - physical process of removing large suspended or floating matter in sewage using bar screens & mesh screens which retain the matter while allowing the sewage water to pass through them.
- (b) Silt & grit removal - is done by passing through grit chambers where velocity of sewage flow is reduced. Silt & grit being heavier they settle down in the bottom.
- (c) Oil & grease removal - by passing through skimming tanks. Here compressed air is blown through the sewage water converting it into soapy mixture & lifted to the surface. The floating mixture is skimmed off.
- (d) Sedimentation process removes finer suspended impurities. This process may be of 2 types: i) by plain sedimentation which is carried out in a continuous flow type sedimentation tank. ii) Sedimentation with coagulation (coagulants like alum, ferrous sulphate etc.)

Secondary treatment (biological): After Primary treatment waste water is made to pass into large tanks where biological treatment is carried out. This process involves aerobic biochemical oxidation or aeration. The organic matter is converted into CO_2 , the nitrogen into ammonia & finally into nitrites and nitrates. Bases present in the sewage water form salts like ammonium nitrite, ammonium nitrate, calcium nitrate, etc.

Secondary or biological treatment is carried out by trickling filter method or activated sludge process

Trickling filter method - it consists of a rectangular or circular vessel with a filter bed made of broken bricks or large anthracite coal. Sewage is sprayed over this bed by means of a rotating distributor. As the sewage trickles or percolates downwards through the filter bed, microorganisms grow on the surface of aggregates using organic materials of the sewage as food. Aerobic conditions are maintained & purified sewage is removed from the bottom. This method removes 90% of biologically oxidisable impurities.

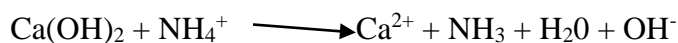
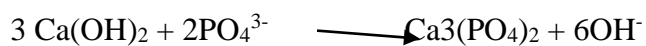
Activated sludge process - it involves extensive aeration of the sewage water & the process of aerobic oxidation by addition of activated sludge (i.e., part of sludge previously oxidized) into the sewage water. Activated sludge contains large number of aerobic bacteria & other micro organisms.



The sedimented sewage water is mixed with proper quantity of activated sludge and the mixture is sent to the aeration tank, in which the mixture is aerated and agitated for several hours. During this process, organic matters are oxidized. After the process is complete, the effluent is sent to a sedimentation tank, where sludge is deposited & water free from organic matter is drawn off. A part of the settled sludge is sent back for seeding fresh batch of sewage. The activated sludge process operates at 90-95% efficiency of BOD treatment. If the treated water contains a high concentration of phosphates, heavy metal ions, colloidal impurities & non-degradable organic compounds, the water is subjected to tertiary treatment.

3) Tertiary treatment: The aim of tertiary treatment is further purification of waste water as well as its recycling. The tertiary treatment consists of

(a) Removal of phosphate - The phosphates are removed by adding Ca(OH)_2 . A flocculant precipitate of calcium phosphate is formed at pH 10-11. At this pH, ammonium salts are converted into ammonia.



(b) Coagulation and Sedimentation: The suspended fine particles are removed by sedimentation in the presence of coagulants like alum, ferrous sulphate, etc. The flocculant precipitates of Al(OH)_3 or Fe(OH)_2 formed by the coagulants entrap the fine particles & help them to settle down. The highly charged ions of the coagulants also neutralize the charges on colloidal particles and make them to coagulate and settle down.

(c) Filtration: the water is passed through conventional sand filter beds to remove the last traces of suspended matter.

(d) Stripping of ammonia and other gases is done in a degasifier. The degasifier consists of a large tower fitted with a number of perforated plates. The hot water trickles through these plates. Large surface area and higher temperature promote stripping of dissolved gases like NH_3 , CO_2 , H_2S , etc.

(e) Disinfection: The pathogenic bacteria are destroyed by disinfection. Among many disinfectants, chlorine is cheap & effective



Un ionised HOCl attacks the cells of bacteria and kills them.

The final composition of tertiary treated waste water is.

$\text{BOD} < 1\text{ppm}$

$\text{NH}_4^+ < 1\text{ppm}$

$\text{PO}_4^{3-} < 1\text{ppm}$

The treated water has high clarity free from odour, low BOD & therefore, it is nearly equivalent to drinking water & can be recycled.

SLUDGE DISPOSAL: Sludge which is collected from sewage treatment processes are disposed off by the following methods.

(i) Burial at sea: sludge is dumped at places near sea.

(ii) Land spreading: the sludge is uniformly spread over soil, followed by ploughing. It acts as fertilizer.

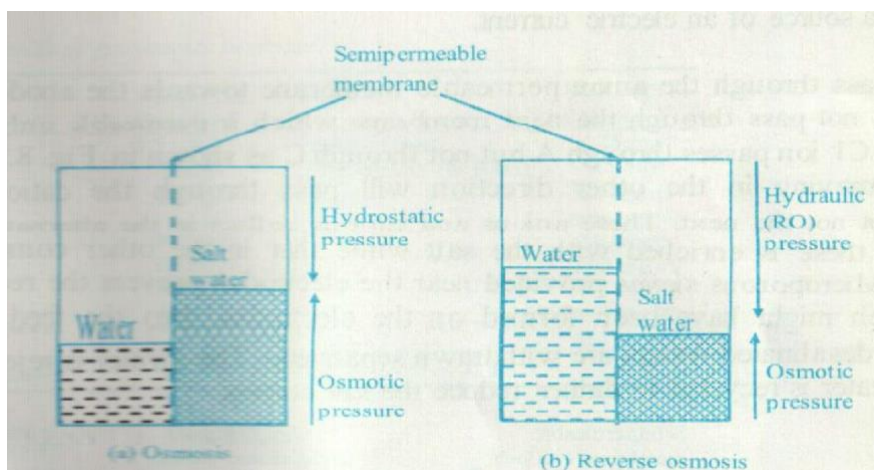
(iii) Septic tank treatment & sludge digestion: The sludge is kept in a closed tank in the absence of air for prolonged period (abt 30 days). The sludge undergoes anaerobic decomposition producing gases like methane, H_2S , phosphine, etc. The gas can be used as fuel for city supply or power generation.

POTABLE WATER

Water that is fit for human consumption and meets the stringent microbiological and chemical standards of quality to prevent waterborne diseases and health risks from toxic chemicals is called potable water.

Desalination: It is the process of partial or complete demineralization of highly saline water such as a sea water is referred to desalination. In partial demineralization, the amount of dissolved salts is reduced to such a level, that water is rendered potable. Several methods such as flash evaporation, reverse osmosis and electro dialysis are available for desalination.

Reverse osmosis is a separation process that uses pressure to force a solvent through a membrane that retains the solute on one side and allows the pure solvent to pass to the other side. More formally, it is the process of forcing a solvent from a region of high solute concentration through a membrane to a region of low solute concentration by applying a pressure in excess of the osmotic pressure. This is the reverse of the normal osmosis process, which is the natural movement of solvent from an area of low solute concentration, through a membrane, to an area of high solute concentration when no external pressure is applied. The membrane here is semipermeable, meaning it allows the passage of solvent but not of solute.



The membranes used for reverse osmosis have a dense barrier layer in the polymer matrix where most separation occurs. In most cases the membrane is designed to allow only water to pass through this dense layer while preventing the passage of solutes (such as salt ions). Sea water exerts an osmotic pressure of about 240 psi, brackish water has significantly lower value. Reverse osmosis can be effected by the use of pressures in the range of 410 - 540 psi. A reverse osmosis unit consists of a membrane, a vessel and high pressure pump. The membranes are generally made up of cellulose acetate or nylon and are usually fabricated in a cylindrical shape.

This process requires that a high pressure be exerted on the high concentration side of the membrane, usually 2–17 bar (30–250 psi) for fresh and brackish water, and 40–70 bar (600–1000 psi) for seawater, which has around 24 bar (350 psi) natural osmotic pressure which must be overcome.

This process is best known for its use in desalination (removing the salt from sea water to get fresh water), but has also purified naturally occurring freshwater for medical, industrial process and rinsing applications since the early 1970s. In RO, feed water is pumped at high pressure through permeable membranes, separating salts from the water (Figure 1). The feed water is pretreated to remove particles that would clog the membranes. The quality of the water produced depends on the pressure, the concentration of salts in the feed water, and the salt permeation constant of the membranes. Product water quality can be improved by adding a second pass of membranes, whereby product water from the first pass is fed to the second pass.

Flow Diagram of a reverse osmosis system

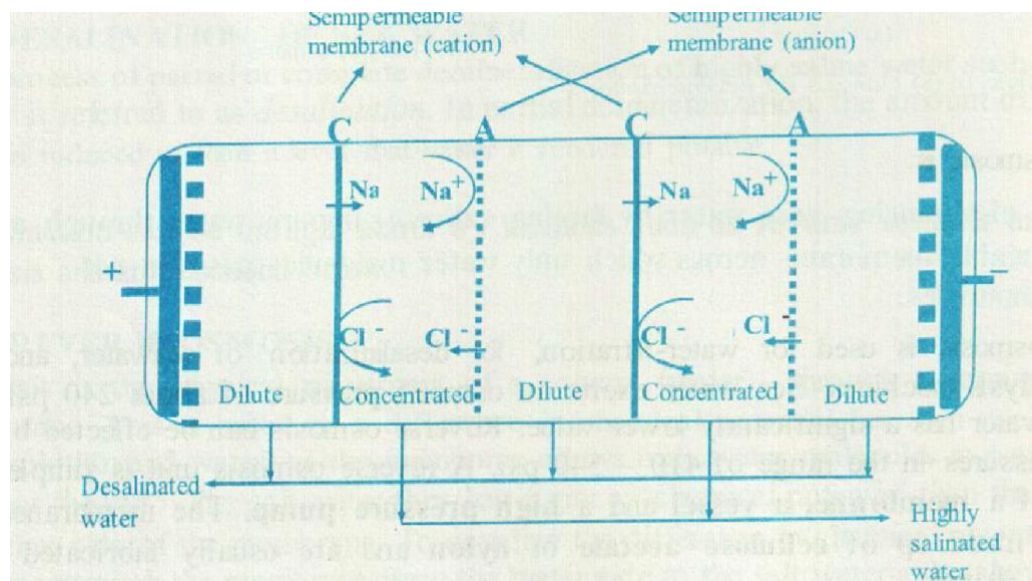
ELECTRODIALYSIS: Electrodialysis is an electro membrane process in which ions are transported through ion permeable membranes from one solution to another under the influence of a potential gradient. The electrical charges on the ions allow them to be driven through the membranes fabricated from ion exchange polymers. Applying a voltage between two end electrodes generates the potential field required for this. Since the membranes used in electrodialysis have the ability to selectively transport ions having positive or negative charge and reject ions of the opposite charge, useful concentration, removal, or separation of electrolytes can be achieved by electrodialysis.

Principle: Passage of an electric current through a solution of salt results in migration of cations towards the cathode & anions towards the anode. The use of semi permeable cation or anion exchange membrane in an electrolytic vessel permits the passage of only cations or anions respectively in the solution.

Construction: It consist of a chamber carrying a series of compartments fitted with closely spaced alternate cation (C) and anion (A) exchange semipermeable membranes between the electrodes. An electrodialyzer unit will have 200 to 1000 compartments. The feed is taken in the dialyzer and the electrodes are connected to a source of an electric current.

The anions pass through the anion permeable membrane towards the anode. However, these ions do not pass through the next membrane which is permeable only to cations. Similarly the cations moving in the

other direction will pass through the cation exchange membrane but not the next. These anions & cations collect in the alternate chambers; the



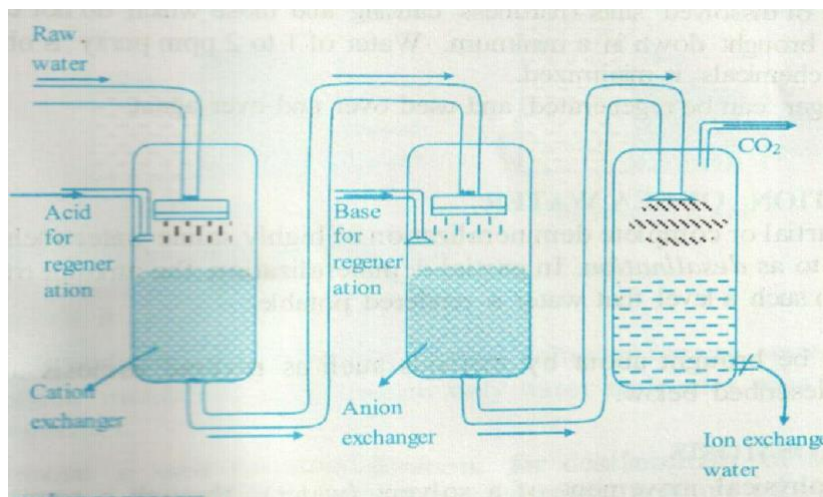
water in these is enriched with salt while that in the other compartments is desalinated. Micro porous sieves provided near the electrodes prevent the re-entry of any deposit, which might have been formed on the electrodes, into the feed water. The enriched and desalinated waters are withdrawn separately. The former is rejected and the desalinated water is recycled to further reduce the salt content.

Figure:

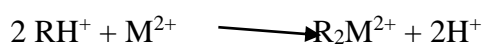
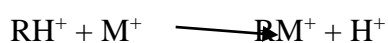
Softening of water by ion exchange process

In this method, softening of water is done by exchanging the ions causing hardness of water with desired ions from an ion exchange resin. Ion exchange resins are high molecular weight, cross linked polymers with porous structure. The functional groups which are attached to the chains are responsible for ion exchange properties. The resins containing acidic groups which are capable of exchanging H^+ ions for cations (Ca^{2+} or Mg^{2+}) present in water are known as cation exchange resins (RH^+). The resins containing basic groups which are capable of exchanging OH^- for anions (Cl^- , SO_4^{2-}) present in water are known as anion exchange resins (ROH^-).

Ion exchange process

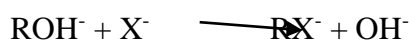


Process: Water is first passed through a cation exchange resin which removes the cations present in it.



Where M^+ is monovalent like Na^+ and M^{2+} is divalent like Ca^{2+} , Mg^{2+} .

The water is then treated by passing it through an anion exchanger to remove anions.

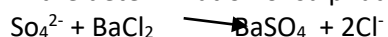


Where X^- and X^{2-} represent the anions Cl^- , NO_3^- , F^- and SO_4^{2-} .

Thus the cation and anion impurities in water are replaced by an equal number of H^+ and OH^- ions respectively.

Describe the determination of sulphates by gravimetric method: Suitable reagents are added to make precipitate, the precipitate is washed, dried and weighed.

In the determination of sulphates $BaCl_2$ is added to sulphates, $BaSO_4$ is formed



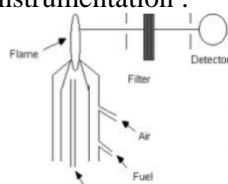
$BaSO_4$ ppt is filtered and is washed many times with hot water to remove chloride and other impurities and dried and finally weighed as $BaSO_4$

$$\text{Amount of sulphates present} = \frac{\text{Weight of } BaSO_4 \times}{233.33 \times 1000}$$

Explain the theory, instrumentation and applications of flame photometry

The principle involved in flame photometry is that when a solution containing a metallic compound is aspirated into a flame, a vapour containing metal atoms will be formed. Some of these metal atoms in gaseous state may be raised to an energy level which is sufficiently high to permit the emission of radiation, which is characteristic to the metal under investigation. This method is generally used for the analysis of sodium, potassium, calcium and lithium. The layout of a simple flame photometer is shown below

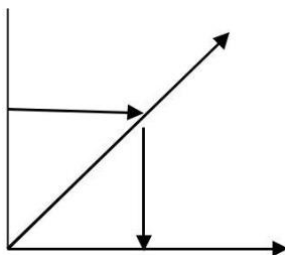
Instrumentation :



Liquid Sample from Aspirator

Procedure: Pipette out 2,4,6,8 and 10 ml of standard NaCl solution into four different 50 ml standard flasks. Make the solutions up to the mark and shake well for uniform concentration. Take the first standard solution and aspirate into the flame of the Flame photometer. The flame emission intensity is measured by flame photometer using sodium filter (598nm). The same

is repeated for all standard solutions with distilled water being sprayed to the flame in between the trials. Then aspirate the given sample of water into the flame and note down the value of emission response.



Result: Amount of Sodium/ Potassium present in the given sample of water =

Flame photometer uses/ Applications: Concentration of calcium in hard water, Concentration of Sodium, potassium in Urine, concentration of calcium and other elements in bio-glass and ceramic materials.

Explain the theory, instrumentation and applications of Potentiometry : Determination of equivalence point of acid base and redox titrations on the basis of potential measurements, when the titration is in progress.

$$E = E^{\circ} + \frac{0.0591}{n} \log[M^{n+}]$$

Instrumentation : Platinum electrode, calomel electrode, potentiometer,

Eg : determination of amount of FAS potentiometrically by using pot. Dichromate

In a beaker FAS is taken and 1 t.t of H_2SO_4 is added, the potential is measured after each addition of 0.5ml of potassium dichromate from the burette, the potential gradually increases and at equivalence point there is a sudden hike in potential, equivalence point is determined by plotting the graph of change in potential against volume potassium dichromate added, from the equivalence point and the normality of FAS, the amount of FAS present in the given solution is determined.

Explain theory instrumentation and applications of conductometry : basically acid base titrations where conductance is measured, and the change in conductance is due to the replacement of ions of different mobilities, reciprocal of resistance is conductance, specific conductance is the conductance of two platinum electrodes of $1cm^2$ area kept at 1 cm apart.

Instrumentation : conductivity cell, device to measure conductance conductivity meter

Eg 1. Acid mixture with strong base

1. Strong acid with strong base
2. Weak acid with strong base

Explain the theory, instrumentation and applications of Colorimetry :

$$A \propto \epsilon Ct$$

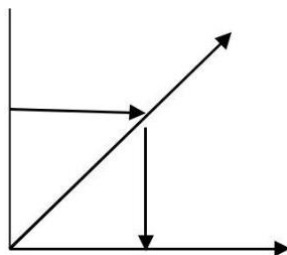
A absorption, ϵ molar absorptivity constant, c concentration, t path length, when t is kept constant $A \propto C$

Principle : colorimetry is applicable to coloured solutions, or forms colour when suitable reagents are added

In the estimation of copper in the given copper sulphate solution, when ammonia is added to copper sulphate cuprammonium sulphate complex is formed, which absorbs maximum amount of light at 620nm, so absorbance is measured at 620nm

Procedure: Pipette out 5,10,15,20,25ml of standard copper sulphate solution into four different 50 ml standard flasks. Add 5ml of ammonia solution, and make the solutions up to the mark and shake well for

uniform concentration. Set O.D zero for blank and the O.D for all the other solutions at 620nm, Plot a graph of Absorbance against volume of copper sulphate, and determine the amount of copper present in the given copper sulphate solution.



Explain the theory, instrumentation and applications of Atomic spectroscopy

Principle: When a solution having a mixture of metallic species is introduced into the flame, the solvent evaporates and vapour of metallic species is obtained. Some of metal atoms can be raised to an energy level sufficiently high to emit characteristics radiation of metal—a phenomenon that is used in flame photometry. Here a large amount of metal atoms remain in non-emitting ground state. These ground state atoms of a particular element are receptive of light radiation of their own specific resonance wavelength. In this way, when a light of this wavelength passes through a flame, a part of light will be absorbed and this absorption will be proportional to the intensity of atoms in the flame. So in atomic absorption spectroscopy the amount of light absorbed is determined because the absorption is proportional to the concentration of the element.

The apparatus consist of:

(1) Radiant Source (2) Atomizer (3) Mono chromator (4) Lenses and Slits and (5) Detectors.

The main components used in the instrument can be described as follows

Procedure: First of all, a meter is adjusted to read zero absorbance or 100% transmittance when a blank solution is sprayed into the flame and light of hollow cathode lamp passes on to photomultiplier tube. Now the solution to be investigated is introduced, a certain part of light is absorbed resulting in decrease of light intensity falling on photomultiplier. This gives a deflection in the meter needle which is noted immediately. As this is a comparative method hence standard solutions of elements are used to make a calibration curve from which the concentration of sample elements can be calculate

