CMR INSTITUTE OF TECHNOLOGY

Solution for Internal Assessment Test 2 – September 2021

Sub: Engineering Chemistry	Sub Code: 18CHE22		Branch: CSE & ISE
Date: 03-09-2021	Duration: 90 min's	Max Marks: 50	Sem / Sec: II / A to G

1 (a) Define BOD. 25 cm³ of sewage water was refluxed with 10 cm³ of 0.25 N $K_2Cr_2O_7$ in conc. H_2SO_4 medium. The un-reacted $K_2Cr_2O_7$ needed 16.1 cm³ of 0.05N FAS. 10 cm³ of 0.25 N $K_2Cr_2O_7$ when titrated under same condition using distilled water required 28.2 cm³ of 0.05N FAS. Calculate the COD. [06 Marks] CO4 L4

Solution: BOD: It is defined as the amount of oxygen required by microorganisms to oxidize the organic wastes present in one litre of waste water over a five-day period at 20 ºC.

COD of the sample   = $\dfrac{N_{FAS} \times (b\text{-}a) \times 8000}{V}$ mg dm^{-3} …………(1)

Where, N_{FAS} = Normality of FAS = 0.05 N

b = Volume of FAS required for blank titration = 28.2 cm³

a = Volume of FAS required for blank titration =16.1 cm³

V = Volume of waste water sample = 25 cm³

Substituting the values in eqution 1

COD of the sample   = $\dfrac{0.05 \times (28.2\text{-}16.1) \times 8000}{25}$ mg dm^{-3} …….(1)

= 193.6 mg dm^{-3}

1 (b) Write a short note on Fullerene. Mention their properties and applications. [04 marks] CO5 L2

Solution: Fullerenes are clusters made of carbon and are zero dimensional solids. They are allotropes of carbon with the formula C_{60} and have 60 C atoms arranged spherically. They are also called Bucky balls and have truncated icosahedrons structure with 20 hexagonal and 12 pentagonal rings forming the symmetry. Fullerenes have particle size of 2 nm, density of 1.65 g/cm³ and sublimes at 800 K. The carbon atoms are sp² hybridised**,** each carbon being bonded to three others in this material. Accordingly, there are two C-C bond lengths in fullerenes, the hexagonal bonds are shorter than pentagonal bonds. They behave as soft electrophile and readily accept electrons during reactions. C_{60} structure can be easily hydrogenated, methylated and fluorinated. They form exohedral complexes in which an atom or group is attached to the outside of the cage, as well as endohedral complexes in which an atom is trapped inside the cage structure. Bucky balls having more number of C atoms such as, 70, 76, 78, 84 etc arranged spherically have been isolated. ***More properties:*** Superconductivity is discovered in alkali doped fullerites at moderately high temperatures. Superconducting critical temperature (Tc) of doped fullerites increases with curvature of fullerenes cages, ie. as cluster size is reduced from C_{60} to C_{36}, C_{28} and C_{20}, their Tc increases. The index of

refraction for fullerenes is 2.2 at 600 nm and they have a resistivity of 1014 Ω/m. They function as catalysts in organic reactions.
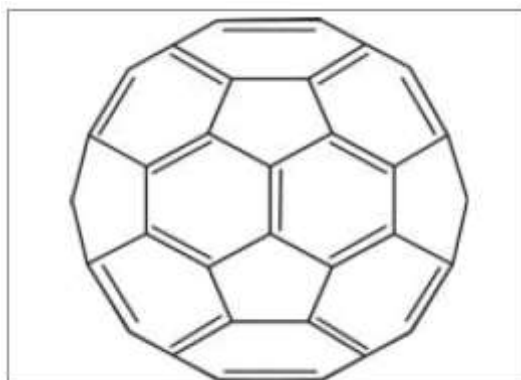

2 (a) What are nanomaterials? Discuss any two size dependent properties of nanomaterials. [05 marks] CO5 L2

Solution: Nanomaterials: are nano-sized materials having atleast one physical dimension in the size range of 1-100 nm.

(i) Surface Area: Nanomaterials have high surface to volume ratio and so exhibit good catalytic activity. For example, nano-structured metal clusters (Pd clusters) show improved catalytic properties for hydrogenation. Such clusters are integral part of cortex catalysts (heterogeneous type), where the active catalytic material is supported on solid oxide surface. These catalysts have improved life time and better catalytic activity. Nanomaterials can be used to construct efficient electrodes for fuel cells and in enantioselective catalysis where chiral modifiers are immobilised on the surface of metal particles.

Optical properties: Optical properties are connected with the electronic structure. A change in crystal size brings about changes in electronic structure and bandgap (electrons are more restricted in movement in nano-sized particles) leading to changes in absorption or luminescence behavior of the material. Example: Bulk gold appears yellow in colour, whereas nanosized Au appears red. In ZnO, the luminescence spectra shows blue-shift as particle size reduces. ie. The wavelength of the emitted light shifts towards lower wavelengths.
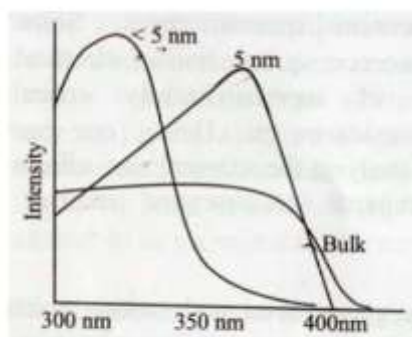
Luminiscence spectra of ZnO with change in particle size. Wavelength of PL shifts towards lower wavelengths (blue shift) with size.
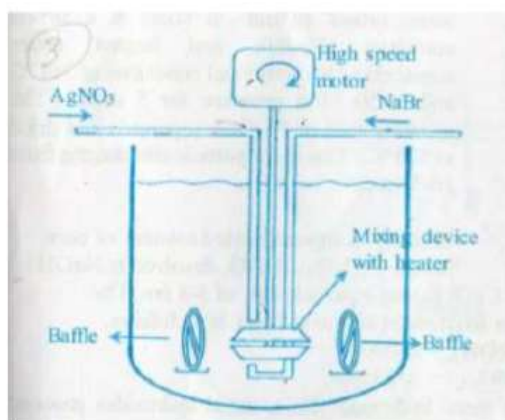
2 (b) Explain the synthesis of nanomaterial by precipitation method. [05 marks] CO5 L3

Solution: The method employs mixing of reagents to get an insoluble material as a precipitate. For preparation of nanosized particles by this method, the reagents to be mixed are introduced at critical supersaturation limit. *For example, when $AgNO_3$ is mixed with NaCl, a precipitate of AgCl is formed. White $BaSO_4$ precipitate is formed when $BaCl_2$ is mixed with H_2SO_4.*

The process involves (i) nucleation and (ii) growth of nuclei to form a particle. During nucleation few molecules come together and aggregate to form several nuclei. In the growth phase, smaller precipitates dissolve and get deposited on the bigger ones. This is Ostwald's ripening. Bulk precipitates of the size of μm to mm are generally formed when saturation concentration is reached and in absence of a controlled reaction. For nano-sized particles, the reagents are mixed at critical supersaturation limit, beyond which nucleation begins.

Preparation of nano-sized AgBr from $AgNO_3$ and NaBr solutions: A double jet precipitation apparatus is used to prepare nanoparticles of AgBr by solution precipitation using equimolar $AgNO_3$ and NaBr solutions. The apparatus allows to regulate particle concentration, temperature, rate of reagent addition and mode of mixing for the reaction.

The reagents are introduced through fine tubes into the apparatus in regulated pulses and a mixing device is used that is attached to a high speed motor shaft and rotates at controlled speed of 2000 rpm . The rate of reagent addition through fine tubes is controlled using a remote pump. One of the reagents (0.01 M $AgNO_3$) is introduced above the inlet zone of the mixing device, while NaBr (0.01 M) is added below. The solution concentration is kept high (> 0.5 M) and the temperature of the system maintained at 70 $^{\circ}$C. Baffles are present around the mixing device that inhibits the vertical rotation of the contents in the vessel. At high rates of reagent addition, supersaturation is obtained at the introduction point leading to highnucleation rate for the particle formation. Supersaturation is relieved by stirring at regulated speed and the resulting emulsion will have particles of 7-60 nm AgBr. The use of capping agents and re-dispersion will stabilize the prepared nanoparticles.

Fig: Precipiation method

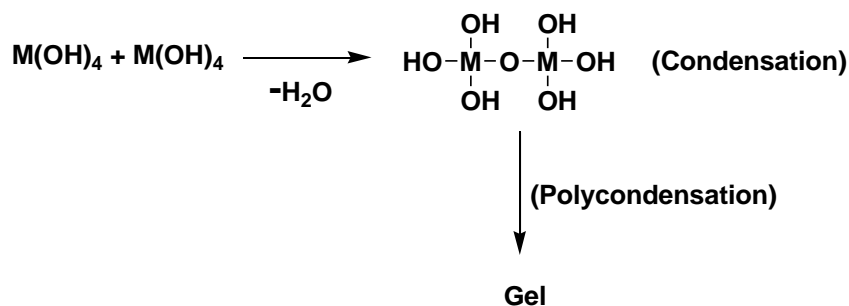**3 (a) Explain the synthesis of nano-material by sol-gel technique. Mention its advantages. [5] CO5 L3**

Solution: _Sol-Gel-Method._ The sol-gel process has been mainly used in the synthesis of monodispersed nanoparticles of metal oxide and temp sensitive organic- inorganic hybrid material. The following steps are involved in the synthesis of nanomaterials by sol-gel process.
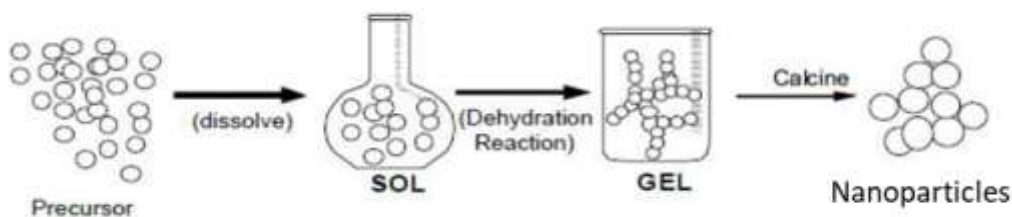
a) **Preparation of sol**: In this method, metal alkoxide is used a precursor (starting material) to synthesize nanoparticles of a metal oxide. First the sol is prepared by dissolving the precursor is suitable solvent. Then the sol is hydrolyzed.

$$M(OR)_4 + 4H_2O \longrightarrow M(OH)_4 + 4ROH \quad \textbf{(Hydrolysis)}$$

b) **Conversion of sol to gel**: The polycondensation reaction results in the formation of an oxide gel.

$$M(OH)_4 + M(OH)_4 \xrightarrow[\textbf{-H}_2\textbf{O}]{} \begin{matrix} \textbf{OH} \quad \textbf{OH} \\ \textbf{HO-M-O-M-OH} \\ \textbf{OH} \quad \textbf{OH} \end{matrix} \quad \textbf{(Condensation)}$$

(Polycondensation)

Gel

c) **Aging of the gel**: The gel on ageing for a known period of time condenses to nanoclusters of metal hydroxides.

d) **Removal of a solvent**: The encapsulated water and other volatile liquids are removal by drying from the gel network.

e) **Heat treatment**: The sample obtained is calcined (heat treatment) at high temperature to obtain nanoparticles. Nanoparticles formed by sol-gel process commonly have a size ranging from 1 to 100 nm.

Advantages

1. Nanomaterials of high purity with good homogeneity can be obtained.
2. Samples can be prepared at lower temperature.
3. Easy to control synthesis parameters to control physical characteristics like shape and size of resulting materials.
4. Simple and inexpensive equipment.
5. Size can be controlled.

3(b) Explain the reverse osmosis process of desalination. Specify the role of semipermeable membrane? [5] CO4 L3

Solution: <u>**Desalination of sea water by reverse osmosis**</u>: The process of partial or complete demineralization of highly saline water (such as the sea water) is referred to desalination. It is done by reverse osmosis.

Reverse Osmosis: Theory: Osmosis is the flow of solvent or water through a semi permeable membrane from region of lower concentration to higher concentration. This natural process can be reversed by applying a higher pressure on the sea water side than the osmotic pressure. Thus the process, which reverses the natural spontaneous osmosis, is called reverse osmosis. Sea water exerts an osmotic pressure of about 240 psi. Reverse osmosis can be effected by the use of pressure in the range of 410-510 psi.
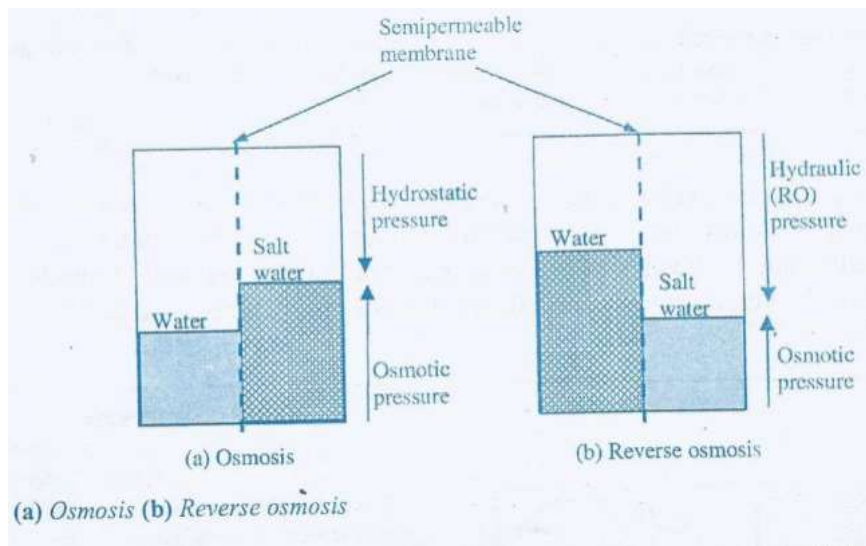
Fig: Reverse osmosis method of desalination

Process: A series of tubes lined on the inside with extremely thin semi-permeable membrane. These tubes are arranged in parallel array in fresh water. Sea water is pumped continuously at high pressure through these tubes. Water flows from sea water into fresh water. Concentrated salt water and fresh water are withdrawn through their respective outlets.
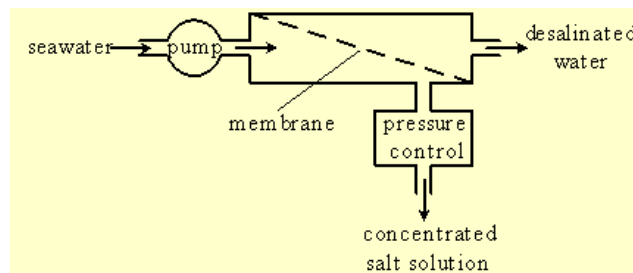
Figure: Desalination by reverse osmosis.

Advantages:
1. The energy requirements are low.
2. Process is simple and continuous.
3. It involves no phase changes

4. Provides odorless, crystal clear water.
5. Easy to maintain

Disadvantages: 1. This method is not used on large scale production of fresh water
2. It is only successful in recovery of fresh water from brackish water
Role of semipermeable menbranne: A semipermeable membrane removes larger solute particulates from drinking water. The membrane is designed to allow only certain molecules to pass through depending upon the molecule size, chemistry or solubility.

4 (a) What is desalination? Explain ion exchange process for softening of water. How is the exhausted resin regenerated in this process? [06 marks] CO4 L3

Solution: <u>Desalination</u>: The process of partial or complete demineralization of highly saline water (such as the sea water) is referred to desalination. It is done by reverse osmosis.

<u>Softening of water by ion exchange process:</u>
Theory: (i) Water softening is the process of reducing the dissolved salts of Ca, Mg and Fe in water, thus reducing its hardness. **(ii)** In the ion exchange method, softening of water is done by exchanging the ions causing hardness of water with desired ions from an ion exchange resin. **(iii)** Ion exchange resin is a cross-linked organic polymer having some ionisable group. It is of two types: (a) **Cation exchange resin or cation exchanger:** These resins have acidic group group such as $-SO_3H$, -COOH group. They contain replaceable hydrogen (H^+) ion. (b) **Anion exchange resin or anion exchanger:** These resins have basic group such as OH^- and are capable of exchanging their OH- group with the anion present in water.
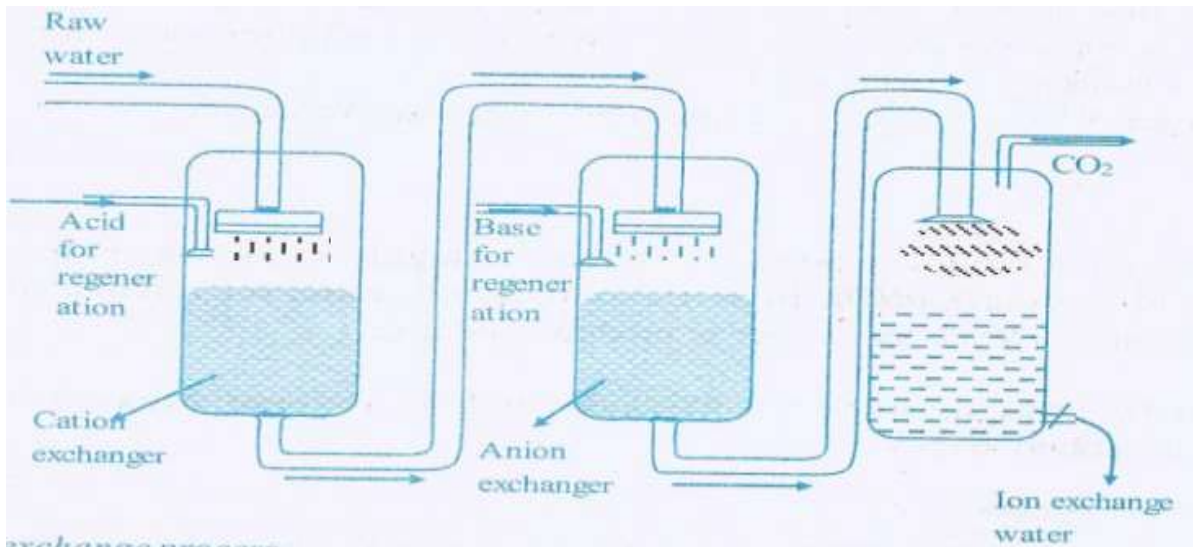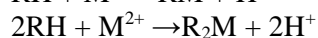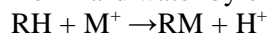

Fig. Ion Exchange process
**Process:** The ion exchange process is shown in the figure below:
(1) Hard water is first passed through cation exchange resin where cations like Ca^{2+}, Mg^{2+} are removed from hard water by exchanging H^+ ions as follows:
$RH + M^+ \rightarrow RM + H^+$
$2RH + M^{2+} \rightarrow R_2M + 2H^+$
Where R is part of resin, M^+ is monovalent ion like Na^+ and M^{2+} is divalent ion like Ca^{2+}, Mg^{2+}.

(2) The cation free water is passed through the anion exchanger tank, which absorbs all the anions present in water.

$ROH + X^- \rightarrow RX + OH^-$

$2ROH + X^{2-} \rightarrow R_2X + 2OH^-$
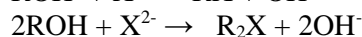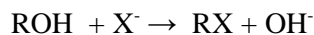
Where X^- and X^{2-} represent the anion such as Cl^-, NO_3^-, SO_4^{2-}

Thus the cation and anion impurities in water are replaced by an equal number of H^+ and OH^- ions respectively. The water obtained after this process is ions free and called as ion exchanged water or deionized (demineralized) water.

(3) **Regeneration of Resin**: After some time when the resins need to be regenerated again. The cation exchange resin is regenerated by flushing it with hydrochloric acid (HCl)

$RM + H^+ \rightarrow RH + M^+$

$R_2M + 2H^+ \rightarrow 2RH + M^{2+}$
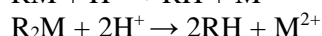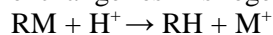
The anion exchange resin is regenerated by reacting it with sodium hydroxide (NaOH).

$RX + OH^- \rightarrow ROH + X^-$

$R_2X + 2OH^- \rightarrow 2ROH + X^{2-}$
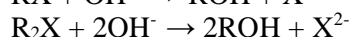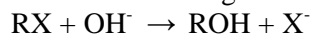
4 (b) What voltage will be generated by a single electrode that consists of an iron electrode immersed in 1.73 M FeSO₄ solution at 35 °C. Given standard reduction potential of Fe = -0.45 V. [04 marks] CO1 L4

Solution: Given: T= 35 °C = 273+35 = 308 K

$E^o{}_{Fe^{2+}/Fe}$ = **-0.45 V**
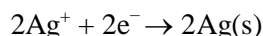
$[Fe^{2+}]$ = **173M**

Cell representation: $Cu(s)/CuSO_4(0.1M)//AgSO_4(0.05M)/Ag(s)$

Cell Reaction: At anode: $Cu(s) \rightarrow Cu^{2+} + 2e^-$

At Cathode: $\{Ag^+ + e^- \rightarrow Ag(s)\} \times 2$

$2Ag^+ + 2e^- \rightarrow 2Ag(s)$

....

$Cu(s) + 2Ag^+ \rightarrow Cu^{2+} + 2Ag(s)$
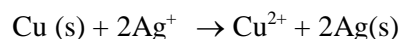
According to Nernst equation:

$E = E^o + \dfrac{2.303\ RT}{nF}\ log\ [Fe^{2+}]$

$E = (-0.45) + \dfrac{2.303 \times 8.314 \times 308}{2 \times 96500}\ log\ [1.73]$

$E = (-0.45) + (0.03056) \times (0.2380) = -0.45 + 0.00727$

$E = -0.4427\ V$

5 (a) Discuss the mechanism of scale and sludge formation in boiler. Mention their ill effects. [4] CO4 L2

Solution: **Scale and Sludge formation:** water is heated under high temperature and high pressure inside the boiler. It gets evaporated to get steam and thus the impurities present in water get

progressively concentrated, when impurities reach a saturation point it precipitates out.

- If precipitate formed is hard, dense and adherent coating on the boiler surface, it is called as scale.
- On the other hand if the ppt formed with in the boiler are soft, loose, greasy silky ppt, it is known as sludge.

Scales:
These are hard deposits which stick to inner wall/surface of the boiler and are difficult to remove. The composition of boiler scales varies over a wide range. However they may be broadly classified into 3 types.

1. **Scales containing salts of Ca and Mg** such as $CaCO_3$, $CaSO_4$ etc. These scales are characterized by their names such as carbonate scale, sulphate scales etc.
   - Salt of Mg form scale due to the formation of $Mg(OH)_2$, which has low solubility.

     $Mg(HCO_3)_2 \longrightarrow Mg(OH)_2 + 2CO_2$
   - Calcium bicarbonate decomposed on heating produces calcium carbonate which has low solubility in water and hence forms scales
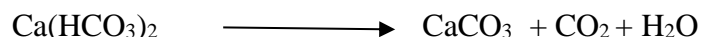
     $Ca(HCO_3)_2 \longrightarrow CaCO_3 + CO_2 + H_2O$
   - Solubility of $CaSO_4$ decreases with increase in temperature. In boiler the temperature at the walls will be higher than in the interior. The $CaSO_4$ gets saturated in the water which is in contact with surface and it gets precipitated out in the form of scales.
2. **Scales containing ferrous and ferric compounds** such as oxides, carbonates and phosphates.
3. **Silicate Scales:** Silica react with Ca and Mg present in water to form silicates of calcium and magnesium. These silicates form hard and glassy scale on the inner surface of boiler.

Sludge:
The loose accumulation of suspended solids on colder and less turbulent section of the boiler and in distribution pipes is known as sludge. It is formed by substances that have greater solubility in hot water then in cold water. Eg. $MgCl_2$, $MgCO_3$, $CaCl_2$ etc. It decreases boiler efficiency, wastage of fuel takes place and if not removed periodically it gets converted into scales.

Harmful effects of boiler scales and sludge:
1. **Wastage of fuel:** scales is a bad conductor of heat. It is like coating of insulating layer on metal surface. This leads to reduced rate of heat transfer and thus loss or wastage of fuel.
2. **Lowering of boiler efficiency:** Excessive scaling results clogging of boiler tubes or boiler parts may get chocked by deposition of scales. This may reduce the water circulation and thus efficiency of boiler.
3. **Boiler explosion:** Scales forms a coating on inner surface of boiler. On heating metal gets heated faster than scales as metal is a very good conductor of heat. This results in expansion of metal but scales do not expand much. Due to this, scales crack and water from inside the

boiler comes in contact with hot metal and immediately forms steam. This steam exerts a pressure on the boiler wall which may crack under pressure and burst.

4. **Loss of strength of boiler:** Because of overheating boiler material gets softer and weaker and thus make boiler unsafe to use.
5. **Expanse of cleaning:** Cleaning process of scale is very much expensive.

Removal of scales and sludge:

1. With the help of scapper or piece of wood, loosely adhering scale can be removed.
2. Brittle scale can be removed by thermal shock i.e. heating the boiler and suddenly cooling it with cold water.
3. By dissolving them by adding chemicals. For eg HCl is used for removal of $CaCO_3$ scale and EDTA is used for removal of $CaSO_4$ scales.

Prevention of scales and sludge:

The quality of natural water is usually improved through various treatments. The plant in which natural water undergoes treatment are known as water treatment plant and this water is known as treated water. When it is supplied to boiler it is known as feed water. Prevention of scales can be done by following ways.

1. **External Treatment** – By feeding soft in boiler. In this methd salts responsible for scale formation are removed by precipitation before sending this water to boiler.
2. **Internal Treatment** – Process of adding chemicals directly to water in boiler to remove scales forming impurities, which were not removed during external treatment. In this process ion is converted either into its more soluble salt or into its complex.
3. **Blow Down** – It is defined as periodical removal of boiler water and its replacement by feed water.

5 (b) Define Free energy. Derive the Nernst equation for single electrode potential. [6] CO1 L3

Solution: _**Free Energy**_: The thermodynamic free energy is the amount of work that a thermodynamic system can perform. The free energy is the internal energy of a system minus the amount of energy that cannot be used to perform work.

Nernst Equation

The potential of an electrode depends on concentration and temperature. In 1889, W. H. Nernst derived a quantitative relationship between electrode potential and concentration of electrolyte species.

Consider an electrode assembly undergoing a spontaneous reaction.

$$M^{n+} + ne^- \rightleftharpoons M$$
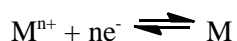
The equilibrium constant (Kc) is related to change in free energy by Vant Hoff equation as follows

$\Delta G = \Delta G^\circ + RT \ln Kc$ ----------------------------------(1)

For above reaction $Kc = \dfrac{[M]}{[M^{n+}]}$ -------------------------------------(2)

According to thermodynamics, decrease in free energy ($-\Delta G$) represents maximum amount of work that can be obtained from a chemical reaction.

$-\Delta G = W_{max}$-- (3)

Work done in electrochemical reaction depends on

(i) Number of coulombs of electricity that flow and   (ii) Energy available per coulomb.

Number of coulombs = n × F (Where n = number of electrons involved in the cell reaction and F = Faraday constant)

Energy available per coulomb = E (V) or JC^{-1}

Thus,

$W_{max} = n \times F \times E$ -------------------------------------- (4)

n = moles of electrons, F = $Cmol^{-1}$, E = JC^{-1}

Equating equations (3) & (4)

$-\Delta G = n \times F \times E$ or

$\Delta G = -n \times F \times E$ ------------------------------ (5)

Under standard conditions, when concentrations of all species is unity, standard free energy change is given by equation

$\Delta G^\circ = -n \times F \times E^\circ$------------------------------(6)

Where ΔG° = Change in free energy under standard conditions, E° is a constant called **standard electrode potential**.

E° is the potential when a metal is dipped in 1M solution of its ions or when an inert electrode is in contact with a gas at a pressure of 1 atm at 298 K.

Therefore by substituting values of ΔG, ΔG° and Kc from equation (2), (5) and (6) into equation (1), we get

$$-nFE = -nFE^\circ + RT \ln \frac{[M]}{[M^{n+}]}$$

$$-nFE = -nF\, E^\circ + RT \ln [M] - RT \ln [M^{n+}]$$

Dividing whole equation by $-nF$

$$\frac{-nFE}{-nF} = \frac{-nF\, E^\circ}{-nF} + \frac{RT \ln[M]}{-nF} - \frac{RT \ln[M^{n+}]}{-nF}$$

$$E = E^\circ - \frac{RT \ln[M]}{nF} + \frac{RT \ln[M^{n+}]}{nF}$$

Under standard condition $[M] = 1$,

$$\therefore\ E = E^\circ + \frac{RT \ln[M^{n+}]}{nF} \quad \text{-----------------------------------} (7)$$

Converting natural log to base 10 in eqn (7) we get

$$E = E^\circ + \frac{2.303 RT \log[M^{n+}]}{nF} \quad \text{----------------------------------} (8)$$

Substituting the values for R (8.314 $JK^{-1}mol^{-1}$), F (96500 $Cmol^{-1}$) and T (298K) in eqn (8) we get

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

This is the mathematical representation of Nernst equation.

6 (a) Explain the activated sludge treatment of waste water with suitable diagram. What is the role of supply of excess oxygen in the biological digestion of organic matter? [6] CO4 L3

Solution: Secondary(Biological) treatment (Activated sludge process).
- The waste water after the primary treatment is allowed to flow into large tanks where biological treatment is carried out.
- *Activated sludge* containing microorganisms (from a previous operation) is sprayed over the water. The microorganisms present in the sludge form a thin layer and thrive on the organic wastes in the sewage.

- Air is passed vigorously from the centre of the tank in order to bring good contact between the organic wastes and bacteria in presence of air and sunlight. Under these conditions, aerobic oxidation of organic matter occurs.
- The sludge formed is removed by settling or filtration. A part of the sludge is reused and the rest is used as fertilizer.
- The residual water is chlorinated to remove bacteria and finally discharged into running water or used for watering plants. The activated sludge process operates at 90-95 % efficiency of BOD treatment.
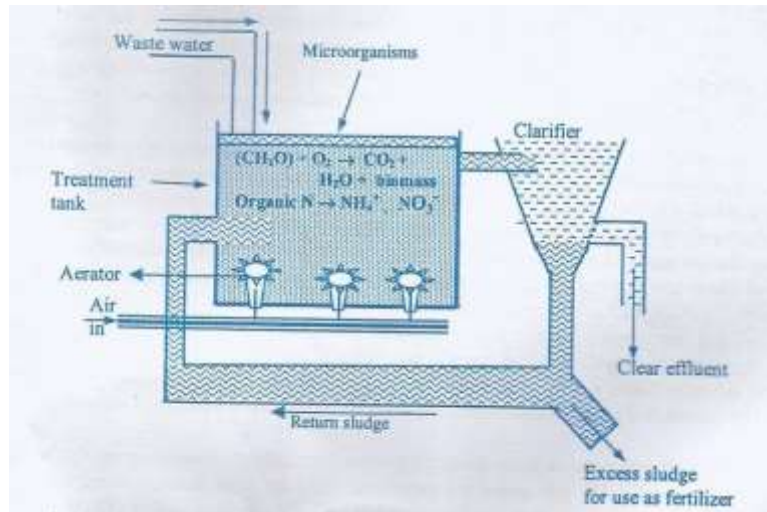
Fig. *Activated sludge process*

Excess of oxygen is needed by the bacteria to allow biodegradation to occur. The supplied oxygen is utilised by bacteria in the wastewater to break down the organic matter.

6(b) Discuss the causes, effects and disposal methods of biomedical- waste. [4] CO4 L2

Solution: Bio medical waste (BMW) may be defined as any solid, fluid or liquid waste material including its container and any other intermediate products which is generated during short term and long term care consisting of observational, diagnostic, therapeutic and rehabilitative services for a person suffering or suspected to be suffering from disease or injury or during research pertaining to production & testing of biologicals during immunization of human beings. From total quantity of waste generated by health care activities almost 80-90% is general waste comparable to domestic waste. This comes from the administrative and housekeeping functions of Hospital and laboratories. The balance 10-20% of waste is considered hazardous and / or infectious.

Biomedical waste any kind of waste that contains infectious material (or material that's potentially infectious). The sources includes waste generated by healthcare facilities like physician's offices, hospitals, dental practices, laboratories, medical research facilities, and veterinary clinics. The characteristic bio-medical waste is listed below:
Sharps. This waste includes anything that can pierce the skin, including needles, broken glass, staples, wires etc.
Infectious Waste. Anything infectious goes in this category (example tissues, excreta, and lab cultures

etc.).

Radioactive. This kind of waste include radiotherapy liquid.

Pathological. Human fluids, tissue, blood etc

Pharmaceuticals. This grouping includes all unused, expired, and/or contaminated vaccines and drugs. It also encompasses antibiotics, injectables, and pills.

Chemical. These are disinfectants and solvents used for laboratory purposes.

Genotoxic Waste. This is a highly hazardous form of medical waste that's either carcinogenic or mutagenic. Example: Drugs used in cancer treatment.

Disposal Methods:

1) Autoclaving: It is a low heat thermal process and it uses steam for disinfection of waste. Autoclaves are of two types depending on the method they use for removal of air pockets. They are gravity flow autoclave and vacuum autoclave. After it's been sterilized, the waste can be disposed of normally in solid waste landfills.

2) Chemical disinfection: These processes use chemicals that act as disinfectants (example: Sodium hypochlorite, peracetic acid, hydrogen peroxide etc.). Most chemical processes are water-intensive and require neutralizing agents.

3) Microwaving: is a process which disinfects the waste by moist heat and steam generated by microwave energy.

4) Incineration: Incineration of waste materials converts the waste into ash, flue gas and heat. The ash is mostly formed by the inorganic constituents of the waste and may take the form of solid lumps or particulates carried by the flue gas. The flue gases must be cleaned to remove gaseous and particulate pollutants before they are dispersed into the atmosphere

7 (a) Discuss the sources, harmful effects and prevention of oxides of nitrogen (NOx) [4] CO4 L2

Solution: <u>Oxides of Nitrogen</u>: Nitrogen oxides (NOx) are a group of gases made up of varying amounts of oxygen and nitrogen molecules. One of the most common nitrogen oxides is nitrogen dioxide (NO_2) which is a reddish, brown gas that has an unpleasant smell and is poisonous in high concentrations

Sources:

(a) Vehicular emissions or automobile emissions

(b) They are formed when fossil fuels are burned at high temperatures, but can also be formed naturally by lightning strikes.

(c) However significant amount of NO & NO_2 are emitted in to the atmosphere by natural activity.

$$N_2 + O_2 \rightarrow 2NO \text{ (at 1483 K)}$$
$$2NO + O_2 \rightarrow 2NO_2$$
$$NO + O_3 \rightarrow NO_2 + O_2$$
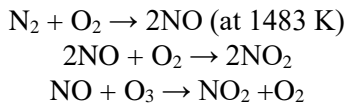
Effects:

(a) These can form secondary pollutants and can result in environmental problems such as acidification and nitrogen enrichment.

(b) It can increase the likelihood of respiratory problems, as it inflames the lining of the lungs, and can reduce immunity to lung infections. This can cause problems such as wheezing, coughing, colds, flu and bronchitis.

(c) NO_2 and other NOx interact with water, oxygen and other chemicals in the atmosphere to form acid rain.

(d) The nitrate particles that result from NOx make the air hazy and difficult to see though and accounts for global warming.

Control:

(a) Fuel switching is the simplest and potentially the most economical way to reduce NOx emissions.

(b) Use of catalytic converter which converts Pt-Rh catalyst which converts toxic gases to non-toxic Nitrogen.

(c) Installation of burners especially designed to limit NOx formation can reduce NOx emissions by up to 50%.

$$2NO \rightarrow N_2 + O_2.$$
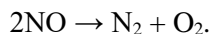
7 (b) An electrochemical cell consists of coper electrode dipped in 0.1 M cupric sulphate and silver electrode dipped in 0.05 M silver sulphate. Represent the cell, write the cell reaction and calculate the cell potential at 28 ^{o}C. Given standard reduction potential of Cu and Ag are 0.34 V and 0.80V. [6] CO1 L4

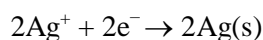**Solution: Given: T= 28 ^{o}C = 273+28 = 301 K**

$$E^o_{Cu^{2+}/Cu} = 0.34 \text{ V}; E^o_{Ag^+/Ag} = 0.80 \text{ V}$$

$$[Cu^{2+}] = 0.1M; [Ag^+] = 0.05M$$

Cell representation: $Cu(s)/CuSO_4(0.1M)//AgSO_4(0.05M)/Ag(s)$

Cell Reaction: At anode: $Cu (s) \rightarrow Cu^{2+} + 2e^-$

At Cathode: $\{Ag^+ + e^- \rightarrow Ag(s) \} \times 2$

$$2Ag^+ + 2e^- \rightarrow 2Ag(s)$$

……………………………..

$$Cu (s) + 2Ag^+ \rightarrow Cu^{2+} + 2Ag(s)$$
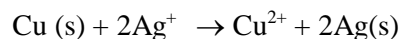
According to Nernst equation:

$E_{cell} = E^o_{cell} + \dfrac{2.303 \text{ RT}}{nF} \log \dfrac{[Ag+]^2}{[Cu^{2+}]}$

$E_{cell} = (E^o_{cathode} - E^o_{anode}) + \dfrac{2.303 \text{ RT}}{nF} \log \dfrac{[Ag+]^2}{[Cu^{2+}]}$

$E_{cell} = (0.80-0.34) + \dfrac{2.303 \times 8.314 \times 301}{2 \times 96500} \log \dfrac{[0.05]^2}{[0.1]}$

$E_{cell} = (0.46) + 0.02986 \log 0.025$

$E_{cell} = (0.46) + 0.02986 \times (-1.6020) = (0.46) - (0.0478)$

$E_{cell} = 0.4122$ V

8 (a) Explain the experimental determination of Fluoride in water using colorimetric method. [5] CO4 L3

Solution: Determination of fluoride by SPADNS Method: Fluoride ion severely affects the qualities of drinking water. If its concentration exceeds 1 mg/L, causes dental fluorosis. Its concentration can be estimated colorimetrically by using Zirconyl-SPADNS [sodium 2-(p-sulphophenylazo)-1,8-dihydroxy-3,6 naphthalene disulphonate] reagent.

Principle: Under Acidic conditions, fluoride ion reacts with Zr-SPADNS reagent and Color of

this reagent gets bleached. The extent of bleaching depends on the concentration of F⁻ ion.

Zr-SPADNS + F⁻ → $(ZrF_6)^{2-}$ + SPADNS
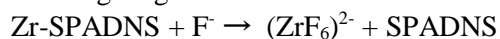
Procedure:

i.   Prepare a reference solution by adding 10 ml of SPADNS in HCl and dilute to 50 ml and use this solution to set the colorimeter to zero at 570 nm.

ii.   Prepare Zr-SPADNS reagent by dissolving $ZrCl_2. 8H_2O$ and SPADNS in HCl and dilute to 500 ml.

iii.   Prepare a stock solution of NaF by dissolving 0.022 g in 1000 ml.

iv.   Prepare a series of standard solutions by adding 2,4,6,8 ml of NaF Solution in 50 ml standard flasks.

v.   To each flask, 1 drop of sodium arsenite $(NaAsO_2)$ and 10ml of Zr-SPADANS reagent are added. Dilute up to the mark using distilled water. Mix well and measure transmittance at 570 nm.

vi.   Draw a calibration curve by plotting transmittance versus concentration of fluoride ion.

vii.   Take a known volume of water sample in which fluoride concentration has to be determined, add $NaAsO_2$ and 10ml of Zr-SPADANS and measure transmittance at 570 nm.

viii.   Calculate the F- ion concentration using calibration curve.
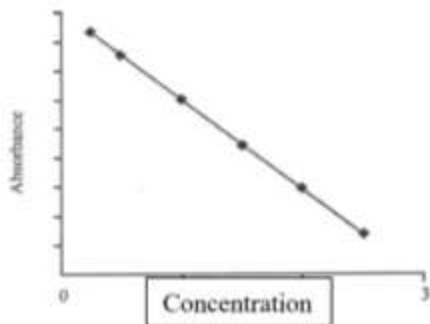
$$F \text{ mg/l} = \frac{(Absorbance\ of\ sample) \times (Concentration\ of\ Standard) \times 1000}{(Absorbance\ of\ Standard) \times (Concentration\ of\ Sample\ Taken)}$$

8 (b) Discuss the mechanism of ozone depletion. Mention its ill effects and control. [5] CO4 L2

Solution: Ozone in the stratosphere is a product of UV radiations acting on dioxygen (O_2) molecules. The UV radiations split apart molecular oxygen into free oxygen (O) atoms. These oxygen atoms combine with the molecular oxygen to form ozone.
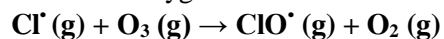
$$O_2 \text{ (g)} + O\text{(g)} \longrightarrow O_3 \text{ (g)}$$
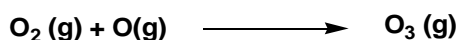
Destruction or depletion of Ozone Layer:

A Chlorofluorocarbon on decomposition gives Chlorine free radical

CF_2Cl_2 **(g)** → **Cl˙ + CF₂Cl˙ (g)**

(i) The chlorine radical then react with stratospheric ozone to form chlorine monoxide radicals and molecular oxygen.

Cl˙ (g) + O₃ (g) → ClO˙ (g) + O₂ (g)

(ii) Reaction of chlorine monoxide radical with atomic oxygen produces more chlorine radicals.

ClO˙ (g) + O˙ (g) → Cl˙ (g) + O₂ (g)
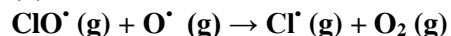
(iii) The chlorine radicals are continuously regenerated and cause the breakdown of ozone. Thus, CFCs are transporting agents for continuously generating chlorine radicals into the stratosphere and damaging the ozone layer. Coolants, Aerosols, and Refrigerators are main source for Chlorofluorocarbons

Effects of depletion of ozone layer:

• The depletion of ozone layer, increases UV radiation exposure. UV radiations lead to ageing of skin, cataract, sunburn, skin cancer.

• It is also responsible for killing of many phytoplanktons, damage to fish productivity etc.

Control of ozone depletion:

Ozone depletion can be controlled by using hydrochlorofluorocarbons (HCFCs) and hydrofluoroalkanes (HFAs) in place of CFCs. These contain hydrogen in their molecule and undergo oxidation readily.