Water

Applied chemistry I

2020-21

✓Hardness

- **Soft water- Water which forms lather with a soap easily on shaking is called soft water**
- **Hard water-Water which does not forms lather with a soap easily on shaking is called hard water.**
- **Hardness is the soap consuming capacity of water and caused mainly due to dissolved salts of calcium and magnesium.**
- **Responsible for hardness-Heavy metal cations. Examples- Ca+,Mg+,Fe+,Al+++,Zn+etc.**

$$\underset{\text{(Present in Hard water)}}{Ca^{2+}} + \underset{\text{Sodium stearate (Soap)}}{2C_{17}H_{35}COONa} \longrightarrow \underset{\text{Calcium stearate}}{(C_{17}H_{35}COO)_2Ca} + 2Na^{+}$$

$$\underset{\text{(Present in Hard water)}}{Mg^{2+}} + 2C_{17}H_{35}COONa \longrightarrow \underset{\text{Magnesium stearate}}{(C_{17}H_{35}COO)_2Mg}$$

Hardness

- . **Hardness of water is of following two types.**

  1. Temporary or carbonate hardness:-

Hardness due to presence of carbonates & bicarbonates of heavy metals (mainly Ca and Mg) and carbonates of iron is called temporary hardness. It is removed by boiling of water. Due to heating soluble bicarbonates are converted into insoluble carbonates or hydroxides.

Ca(HCO)3 -------→ CaCO3 + H2O +CO2

Soluble Boiling Insoluble

Mg(HCO3)2- -----→ Mg(OH)2 + 2CO2

2 . Permanent or noncarbonate hardness:-

It is caused by soluble salts of heavy metals other than bicarbonates. (Generally dissolved Cl^- , SO_4^{--} &NO_3^- of heavy metals. Permanent hardness is not removed by boiling but needs chemical treatments)

Hardness

CALCULATION OF EQUIVALENTS OF CALCIUM CARBONATE

Example 1. Sample contains 180 mg/L of $Mg\ SO_4$

- Molar mass of $MgSO_4 = 24 + 32 + (16 \times 4) = 120$
- Chemical equivalent of $MgSO_4 = 120/2 = 60$
- Chemical equivalent of $CaCO_3 = 50$

$$\text{Equivalents of } CaCO_3 = \frac{\begin{pmatrix}\text{Mass of hardness}\\ \text{producing substance}\end{pmatrix} X \begin{pmatrix}\text{Chemical equivalent}\\ \text{of } CaCO_3\end{pmatrix}}{\begin{pmatrix}\text{Chemical equivalent of}\\ \text{hardness producing substance}\end{pmatrix}}$$

$$\text{Equivalents of } CaCO_3 = \frac{180\ X\ 50}{60} = 150\ mg/L \text{ or } ppm$$

Hardness of the sample = 150 mg/L or ppm

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✓Units of hardness

1) ppm $CaCO_3$ equivalent or mg/litre

This is the most common unit . It is defined as the number of parts by weight of calcium carbonate per million (10^6) parts by weight of water.

1 ppm = 1 part of CaCO3 in 10^6 parts of water

2) Degree Clarke (^{0}Cl)

It is defined as the of grains og CaCO3 equivalent present per gallon of water or it is number of parts of CaCO3 equivalent hardness in 70,000 parts of water.

3) Degree French (^{o}Fr)

It is defined as the parts of CaCO3 Equivalent present in 10^5 parts of water.

Relationship between the degrees:-

- **1 mg/litre =1 ppm = 0.07^{o}CL= 0.01^{o}Fr**

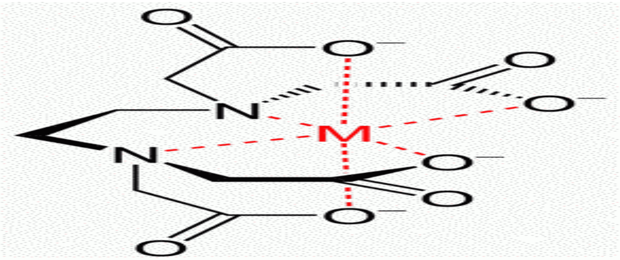
✓Undesirable Effects of Hard Water in Industries

Industries:

- **Paper industry**: Strength of paper becomes poor
- **Sugar industry**: Improper crystallization of sugar during crystallization.
- **Dyeing industry**: Dye and hardness causing ions like Fe^{++},Mn^{+2} may react to form undesirable products of different colour.
- **Textile industry:** If hard water is used for the washing and soap as cleaning agent, then there is wastage of soap due to reaction of soap and hardness causing ions in the water to form sticky ppt.
- **Pharmaceutical industry**: Hardness causing ions in water may react with them to produce undesirable products. Such products may either be having no action or adverse action.
- **Concrete making** : If the water contains chlorides, sulphates etc., then they may affect the hydration of compounds in cement and final strength of concrete mass will be affected
- **Steam generation**: Boiler corrosion, scale and sludge formation, caustic embrittlement etc

Estimation of hardness of water by EDTA method

- **The EDTA method of estimating hardness of water is an accurate , convenient and rapid method and hence more commonly used.**
- **EDTA is ethylene diamine tetra-acetic acid and its more convenient form is disodium EDTA.**
- **Disodium EDTA reacts quickly with the hardness causing metal ions in water. A suitable pH (about 10) is required for the reaction. During the reaction H+ ions are formed and decrease the pH of reaction mixture. Hence the buffer solution of pH about 10 is necessary during titration, so that it will not allow decreasing of pH.**
- **The reaction between disodium EDTA and heavy metal ion results in the formation of cyclic co-ordinate complex (chelate).**



(M is the hardness causing ion like Ca++, Mg++, Fe++etc.)

- **Organic dyes such as Eriochrome black-T (EBT) , calcon etc. act as indicators for the EDTA titrations**
- **EBT shows colour change at pH about 10, whereas colour shows colour change at about 12.5.**

Estimation of hardness of water by EDTA method

Principle: The principle of this method is based on the following facts.

- The hardness causing ions Ca++ and Mg++ present in water to form unstable complexs (M-EBT) with the indicator EBT having wine red colour.
- EDTA then reacts with all metal ions present in water to form stable complexes.(EDTA-metal complex).
- EDTA then extracts metal ions from M-EBT complex to form stable EDTA-metal complex with the regeneration of blue colour dye.

1) M^{++} + EBT → M-EBT + $2H^{+}$

(Blue) (Wine Red)

2) M-EBT + EDTA $\xrightarrow{\text{pH 10}}$ M-EDTA + EBT

red olourles colourless Blue

✓External Treatment (Softening Methods)

- **Lime soda process**
- **Zeolite process or permutit process**
- **Ion-exchange or deionization or demineralisation process**
- **Membrane filtration**

Ion Exchange Process

The ion-exchange resins are classified as follows :

1) Cation Exchange Resins (RH_2) : These resins are capable of exchanging rapidly cations like Ca^{2+} and Mg^{2+} by hydrogen ions. For example; sulphonated coals, tannin, formaldehyde resins, Amberlite IR-120, etc

$$H_2R + Ca^{2+} \longrightarrow RCa + 2H^+$$
$$H_2R + Mg^{2+} \longrightarrow RMg + 2H^+$$

2) Anion Exchange Resins ($R'(OH)_2$): These resins are capable of exchanging rapidly anions (Cl, SO_4^{2-}) by OH ions. For example amino-formaldehyde resins copoJymer of styrene and divinyl benzene, Amberlite 400, Zeolite - FF, etc.

$$R(OH)_2 + 2Cl^- \longrightarrow RCl_2 + 2OH$$

- **1. Cation-exchange resins**

  (a) Strongly and (b) Weakly acidic types

- **2. Anion-exchange resins**

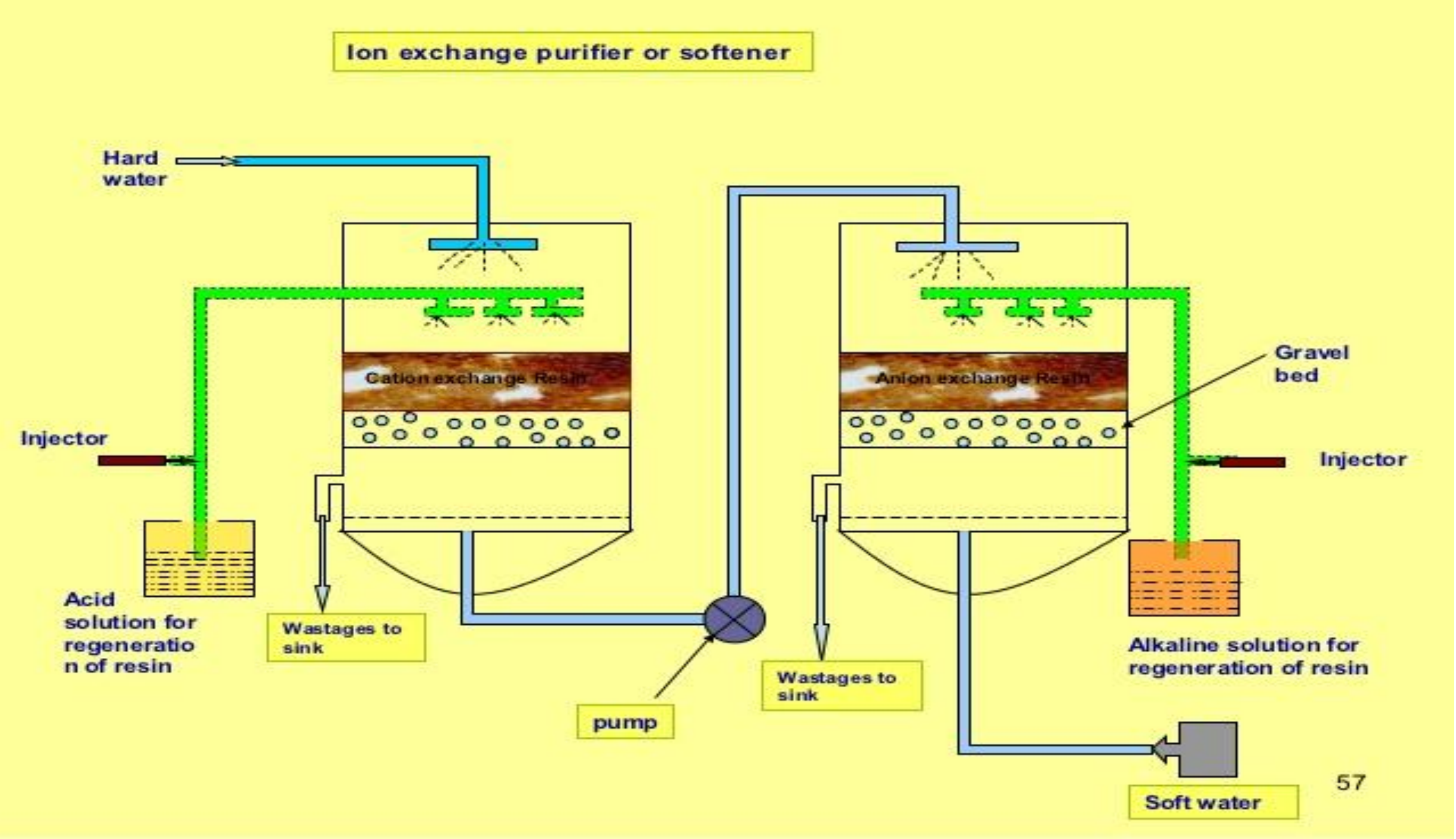
  (a) Strongly and (b) Weakly basic types.

- **Strong acidic and basic resins are further modified as highly porous type. These resins are available in different sizes and forms, e.g. granular or bead-like.**

1) Cation-exchangers: SO_3H, COOH or -OH

2) Anion-exchangers

NR_3^+,-CH_3, =P^+, etc NH_2,-$(C_2H_4)_x$ $(NH)_y$-


Ion exchange purifier or softener
Hard water
Injector
Cation exchange Resin
Anion exchange Resin
Gravel bed
Injector
Acid solution for regeneratio n of resin
Wastages to sink
pump
Wastages to sink
Alkaline solution for regeneration of resin
Soft water
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❖ Regeneration of ion exchanger resins:

The exhausted cation exchanger is regenerated by passing dilute HC1 or H_2SO_4 solution. The anion exchanger resin is regenerated by dil. NaOH.

$$RCa\ (or\ RMg) + 2HC1 \longrightarrow 2RH + CaCl_2\ (or\ MgCl_2)$$

$$2RCO_3 + NaOH \longrightarrow Na_2CO_3 + ROH$$

- **Advantages of ion exchange process**

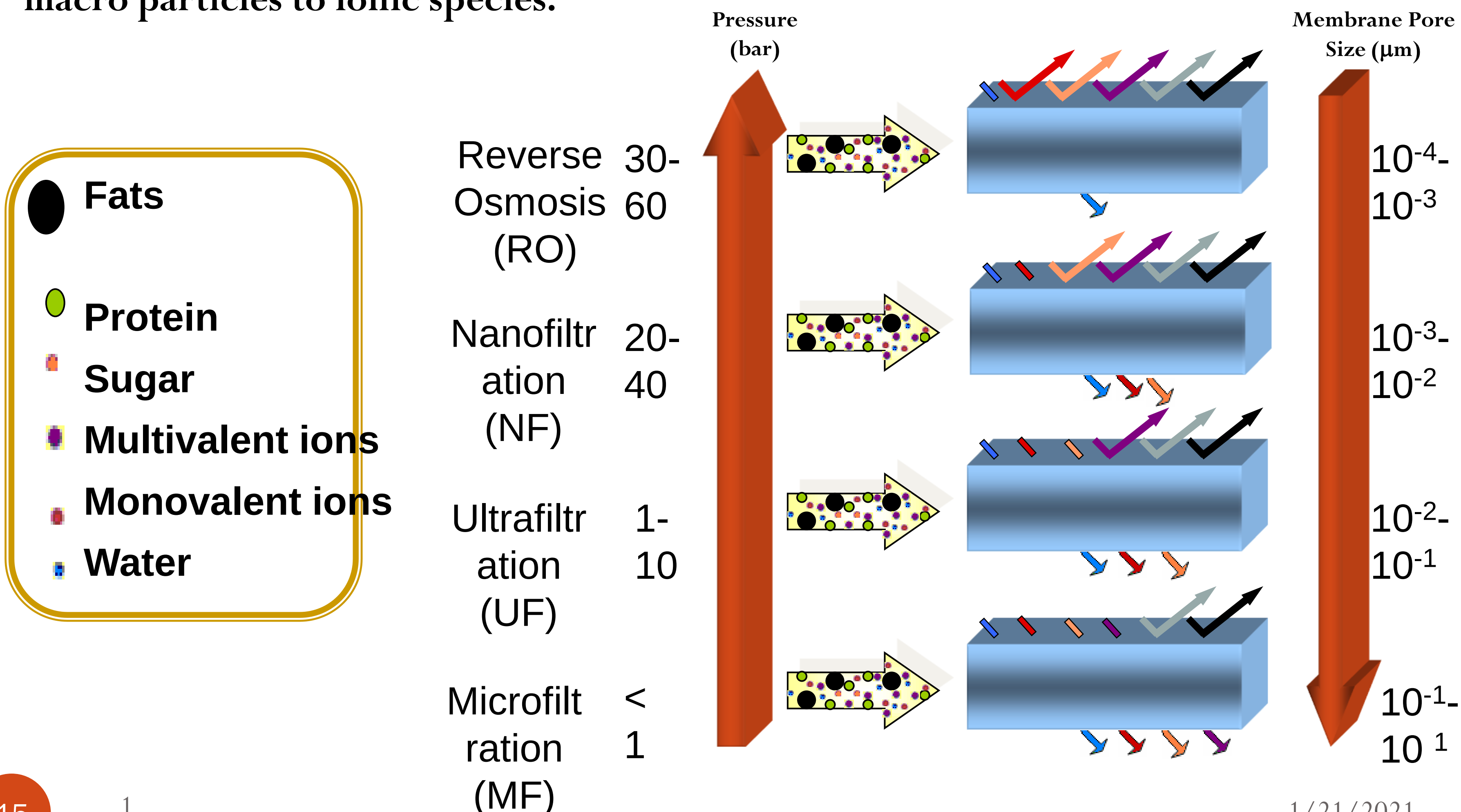
1. The process can be used to soften highly acidic or alkaline water.
2. It produces water of low hardness (2 ppm), therefore, it is good for high pressure boilers.

- **Disadvantages**

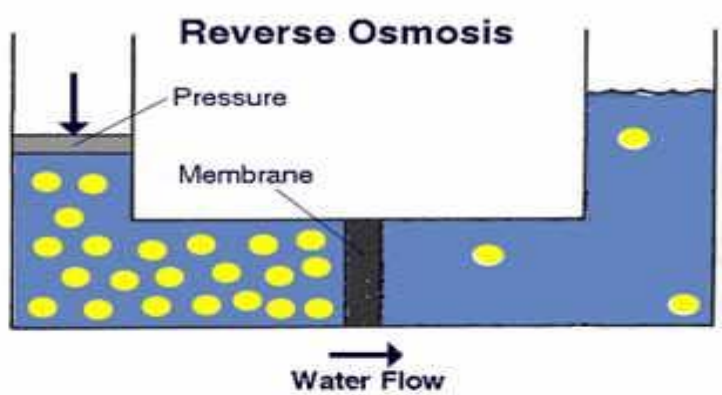
1. The equipment is costly.
2. If water contains turbidity, then the output reduces

❖Memberane methods for softening of water

Pressure driven membrane processes are specially useful where a wide range of possible contaminants have to be removed over the entire removal spectrum i.e. macro particles to ionic species.



Reverse osmosis



Osmosis
Reverse osmosis
Hydrostatic Pressure> Osmotic pressure
Pressure: 15-40 kg/cm2
SPM (Semipermeable membrane): cellulose acetate, PMMA, polyamide

- **Application of an external pressure to the salt solution side equal to the osmotic pressure will also cause equilibrium.**
- **Additional pressure will raise the chemical potential of the water in the salt solution and cause a solvent flow to the pure water side, because it now has a lower chemical potential.**

Reverse osmosis

Advantages:

- **Removes ionic and non ionic, colloidal and high molecular weight organic matters**
- **Removes colloidal silica**
- **Life time is 2 years**
- **Low capital cost, simplicity, high reliability, the RO is gaining ground at present for converting sea water into drinking water for obtaining water for high pressure boilers.**

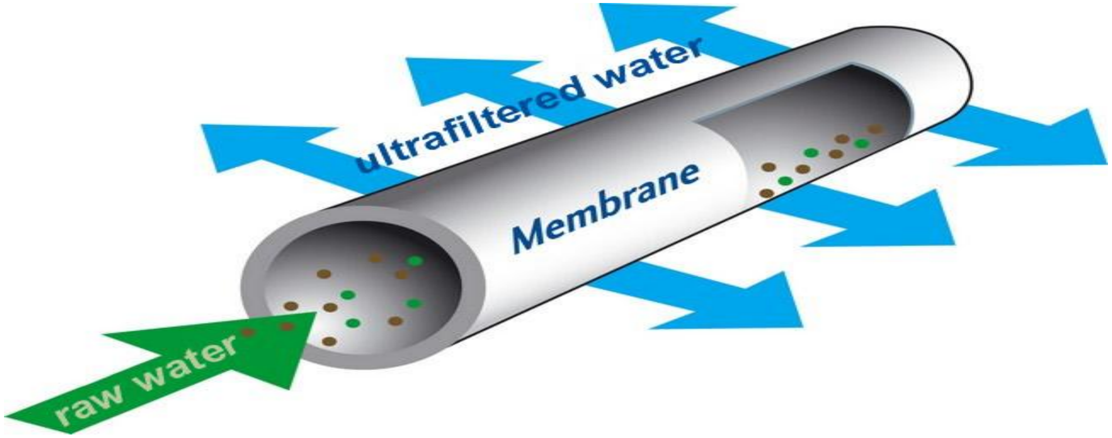
Features of the RO membranes :

- **The membranes are formed of thin film of polymeric material several thousand Angstroms thick cast on polymeric porous material.**
- **Commercial membranes have high water permeability and a high degree of semi-permeability.**
- **The membrane must be stable over a wide range of pH and temperature, and have good mechanical integrity.**
- **The life of commercial membranes varies between 2-3 years.**
- **This depends on the feed water quality, pretreatment conditions, and stability of operation.**

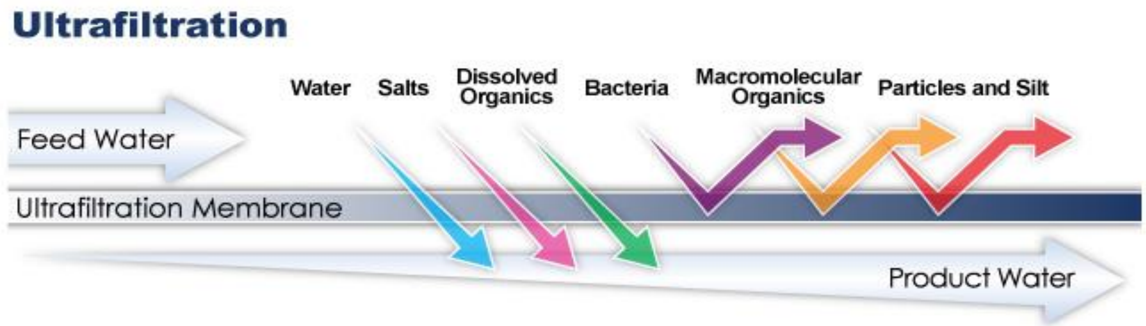
Application

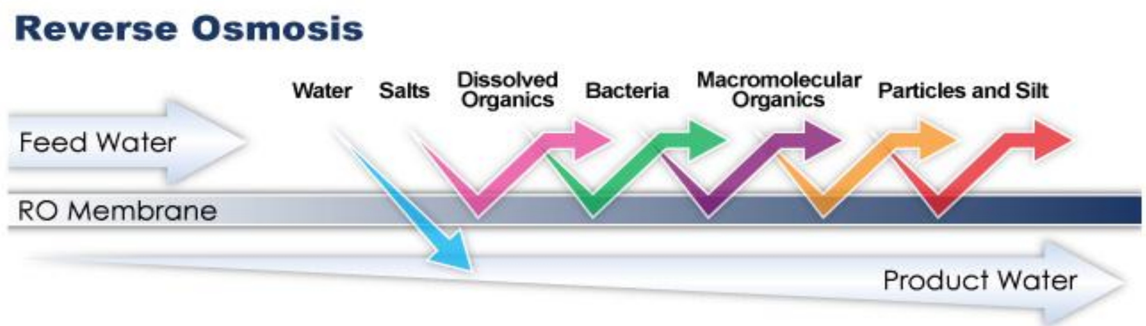
- **Desalination of sea water**

Ultrafiltration



Selective fractionation technique, a cross flow separation process
Pressure-145 psi
Pore size of memberane - 0.1 – 0,001 micron
Removes fats and protein
Permeate and concentrate
Efficiency in Flux- gallons of filtered water/foot2/day


Ultrafiltration
Water
Salts
Dissolved Organics
Bacteria
Macromolecular Organics
Particles and Silt
Feed Water
Ultrafiltration Membrane
Product Water


Reverse Osmosis
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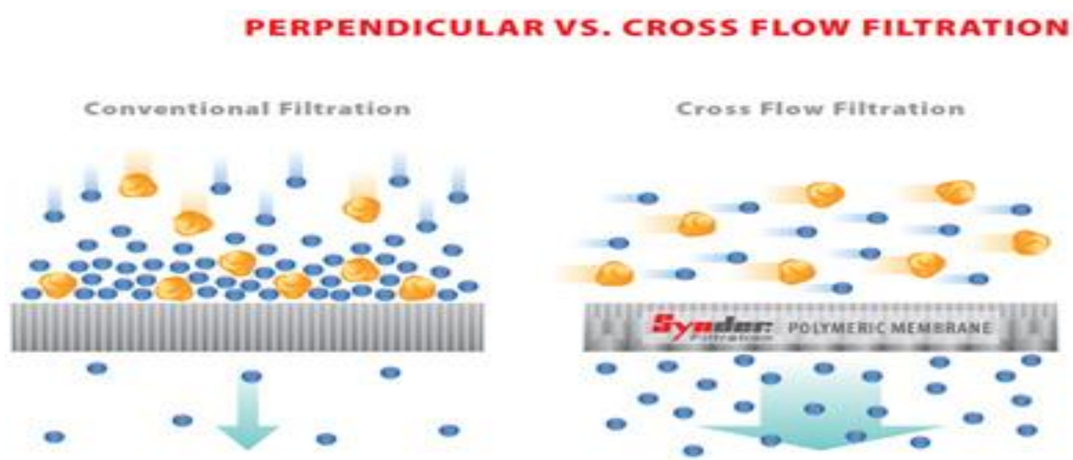
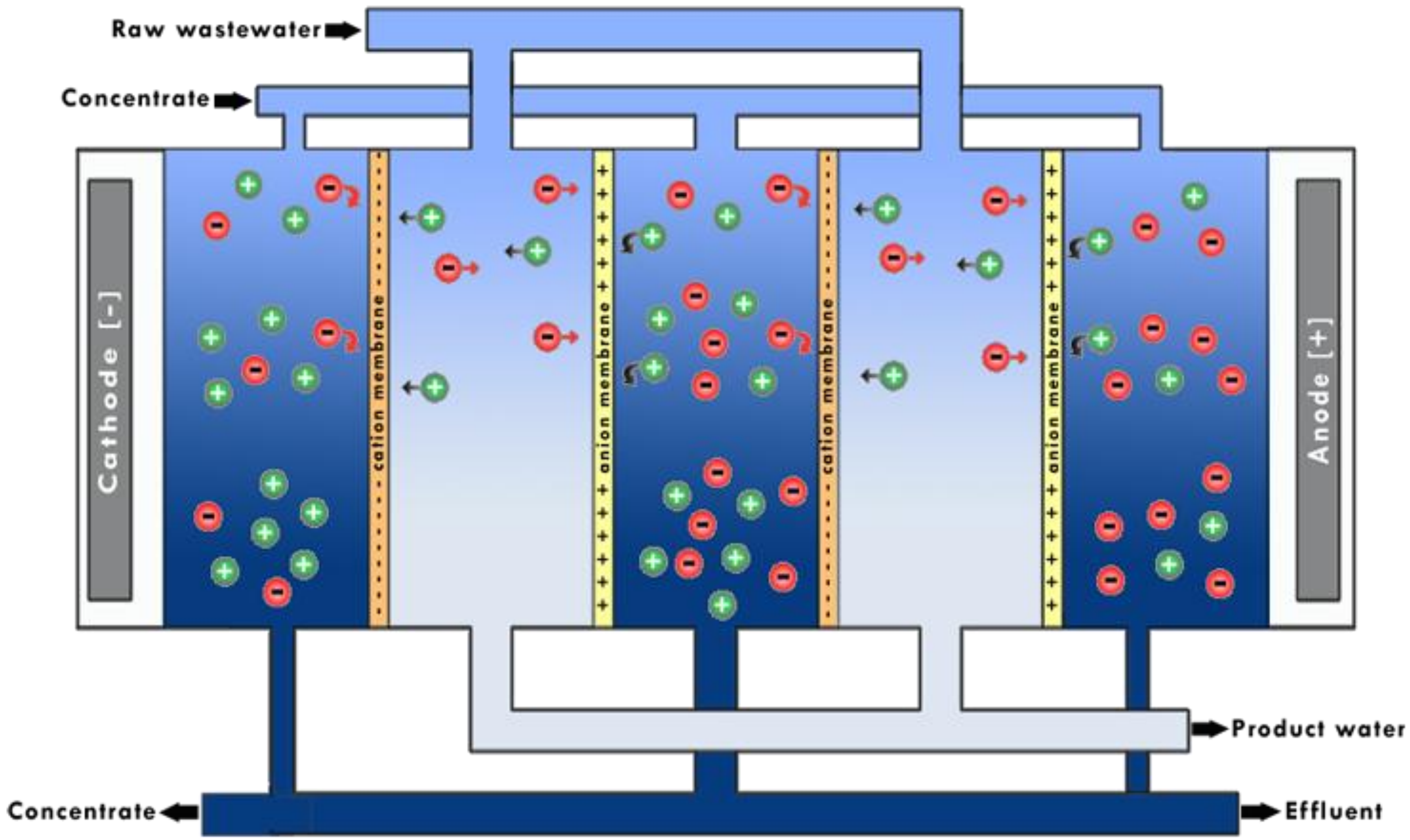

PERPENDICULAR VS. CROSS FLOW FILTRATION
Conventional Filtration
Cross Flow Filtration
POLYMERIC MEMBRANE

Applications of Ultra filtration

- Paint recovery in automobile industry
- Fractionation of milk and whey proteins
- Removal of colloids
- Clarification and concentration of fruit juices

Electrodialysis



Basics of electrodialysis:

Memberane are barriers made up of cross linked polymers allows only ions to pass but not water. There are two types of memberanes.

1) Cation exchange membranes have fixed negative charges e.g $RSO3^-$, $RCOO^-$

2) Anion exchange membranes have fixed positive charges e.g : R_4N^+

- **There are two electrodes, Anode is kept near anion selective membrane and cathode is placed near cation selective membranes.**
- **Under influence of applied emf cations move towards cathode and anions towards anode through ion selective membrane.**
- **There is depletion of ions in central compartment while it increases in two side compartments.**
- **Desalinated water is collected from central compartment and brackish water from side compartments is replaced by fresh water.**

Electrodialysis:

Adv:

- **It is compact**
- **Economical**
- **If electricity available it is best suited technique**

Disadvantages:

Sometimes pretreatment of water is needed

Suspended particles with diameter that exceeds 10 micrometer need to be removed else they may plug the membrane.

BOD

Biochemical oxygen demand (**BOD**) is the amount of dissolved oxygen needed (i.e. demanded) by aerobic biological organisms to break down organic material present in a given water sample at 20 °C over a time period of 5 days. The BOD value is most commonly expressed in milligrams of oxygen consumed per litre of sample.

Significance:

BOD reduction is used as a gauge of the effectiveness and design of of wastewater treatment plants.

BOD of wastewater effluents is used to indicate the short term impact on the oxygen levels of the receiving water.

It is best test in assessing the organic pollution.

It is used assess the quantity of safe water which can be safely discharged in water bodies.

From BOD self purifying capacity of stream can be determined.

BOD

When dilution water is not seeded,

$$BOD_5 = \frac{DO_i - DO_f}{\left(\frac{V_s}{V_b}\right)}$$

where

BOD_5 = biochemical oxygen demand at t days (mg/L)
DO_i = initial dissolved oxygen in the sample bottle (mg /L)
DO_f = final dissolved oxygen in the sample bottle (mg/L)
V_b = sample bottle volume, usually 300 mL
V_s = sample volume (mL)
Note that the $\frac{V_b}{V_s}$ is the sample dilution.

COD

- Chemical **oxygen** demand (COD) is a measure of the capacity of **water** to consume oxygen during the **decomposition** of organic **matter** and the oxidation of inorganic chemicals such as Ammonia and nitrite by strong oxidizing agent.
- COD measurements are commonly made on samples of waste water or of natural waters contaminated by domestic or industrial wastes. Chemical oxygen demand is measured as a standardized laboratory assay in which a closed water **sample** is incubated with a strong chemical oxidant under specific conditions of **temperature** and for a particular period of **time**. A commonly used oxidant in COD assays is potassium dichromate ($K_2Cr_2O_7$) which is used in combination with boiling **sulfuric acid** (H_2SO_4). Because this chemical oxidant is not specific to oxygen-consuming chemicals that are organic or inorganic, both of these sources of oxygen demand are measured in a COD assay. COD measures oxygen requirement for both biologically oxidizable and biologically inert impurities, hence the value of COD is always higher than BOD for same sample of water.

- **Significance**
- The higher the chemical oxygen demand, the higher the amount of pollution in the test sample.
- It forms basis for calculation of efficiency of treatment plant
- As it is a fast process comparing to BOD it has become important in the management and design of treatment plants.
- It is important in proposing standards for discharging waste water in various water bodies.

- $COD = \frac{(V1-V2) \times N \times 8 \times 1000}{\text{Vol. of sample}}$

- where V1 is the volume of FAS used in the blank sample, *V2* is the volume of FAS in the original sample, and *N* is the normality of FAS. If milliliters are used consistently for volume measurements, the result of the COD calculation is given in mg/L.

BOD	COD
Biochemical oxygen demand (BOD) is the amount of dissolved oxygen needed (i.e. demanded) by aerobic biological organisms to break down organic material present in a given water sample at 20 °C over a time period of 5 days.The BOD value is most commonly expressed in milligrams of oxygen consumed per litre of sample.	Chemical oxygen demand (COD) is a measure of the capacity of water to consume oxygen during the decomposition of organic matter and the oxidation of inorganic chemicals such as Ammonia and nitrite by strong oxidizing agent
BOD measures oxygen requirement for only biologically oxidizable impurities,	COD measures oxygen requirement for both biologically oxidizable and biologically inert impurities,
Slow process takes 5 days	Fast process, It takes 2-3 hours
BOD values are generally leass than COD values	COD values are generally greater than BOD values