

(WWM) Unit - II

Adsorption:-

Definition :- Adsorption is a natural process by which molecules of a dissolved substance collect on and adhere to the surface of an adsorbent solid.

- The Adsorbent is the solid material on which the adsorbate accumulates.
- The Adsorbate is the dissolved substance that is being removed from liquid phase to the solid surface of the adsorbent.
- Adsorption may occur at the outer surface of the adsorbent and in the Macropores, Mesopores and micropores in the inner cracks of the adsorbent.

Macropores $> 25 \text{ nm}$

Mesopores $> 1 \text{ nm}$ and $< 25 \text{ nm}$

Micro pores $< 1 \text{ nm}$

($1 \text{ nm} = 10^{-6} \text{ cm}$)

- Forces affecting adsorption:-

The principal forces leading to sticking the adsorbate to the surface of the adsorbent solid are:

(i) Vander Waals forces

(ii) Hydrogen bonding

(iii) Dipole - dipole Interactions.

- The following are main materials that are used as adsorbents.
 - Activated carbon
 - silica
 - Synthetic polymers

Activated carbon is mostly used adsorbent in water treatment.

- Activated carbon is a specially treated carbon, which possesses the property of absorbing and attracting impurities, such as gases, liquids and finely divided solids.

- It is available in granular as well as powder forms. It is highly porous, and absorptive and thus very useful for removing phenol type impurities.
- Activated carbon is mostly used in powdered form, and may be added to the water either before or after the coagulation, but before filtration.
- The most common method adopted is to add a portion in the mixing tank, and to add the remaining portion in water just before it enters the filter.
- This method of using activated carbon at two stages is called split method. Activated carbon may be applied at a constant rate or at varying rate.
- It may be applied either in a dry form or as a suspension or as a slurry. Its use as a suspension in water and then fed into the water to be treated as slurry, is generally preferred.
- Its use in powdered form may create problems, such as blown off due to winds. Nevertheless, in both the cases, the feeding equipments are similar to those used for adding coagulants.
- The usual dose of activated carbon varies from 5 to 20 mg/lit and optimum dose may be determined first in the laboratory and then in the field.

Activated carbon as granular form:-

- Activated carbon may also be used in the granular form as a filter media, instead of using sand in the rapid gravity filters or preferably in pressure filters.
- With passage of time, it loses its absorptive powers and requires to be rejuvenated.

- This regeneration is carried out by forcing the live steam upward through the perforated pipes placed in the gravel bed of filters.
- This process of rejuvenation may have to be carried out at interval of 1 month to 1 year, depending upon the quality of water being treated.

Advantages:-

The use of activated carbon may thus serve the following advantages:

- (i) When used in powdered form before coagulation, it aids in coagulation.
- (ii) It reduces the chlorine demand of treated water
- (iii) It removes the organic matter present in water
- (iv) It removes the tastes, odours and colours caused by the presence of Iron, ~~Iron~~ Manganese, phenols, hydrogen sulphide etc.
- (v) Its overdose is not harmful.

Reverse Osmosis:-

Osmosis:- It is the natural tendency of pure water with a low concentration of dissolved solids (TDS) to travel through a semi-permeable membrane into a solution of higher TDS in order to balance the solute levels on the both sides of the membrane.

- Reverse Osmosis is a membrane based demineralization technique used to separate dissolved solids such as ions from solutions. (Most applications involve water-based solutions).

- Reverse osmosis offers an ideal method of water purification, by rejecting most dissolved solids as well as suspended solids.

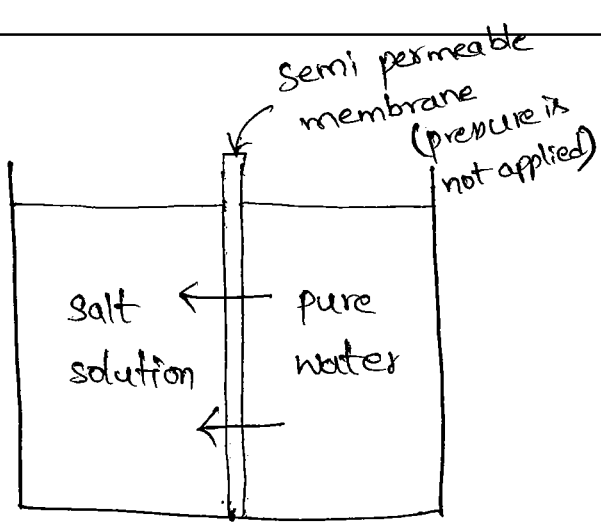
Definition Reverse Osmosis:-

Reverse osmosis is a process in which pressure greater than the natural osmotic pressure is applied on the high concentration side of the membrane, forcing the water to travel through the membrane from the higher TDS to lower TDS chamber, thus "reversing" the natural tendency of water flow.

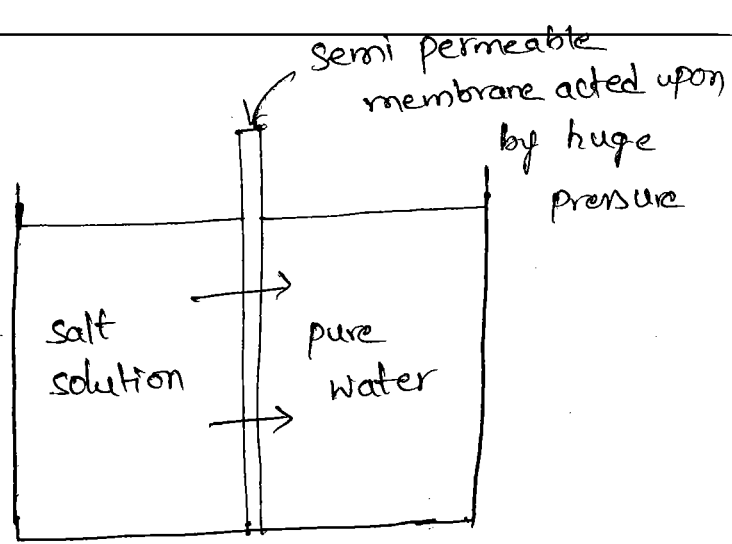
- Reverse osmosis works on the same principle as osmosis, but in the reverse direction that is way it is called "Reverse osmosis".
- Reverse osmosis membranes also hold back suspended impurities, such as silt, colloidal particles and micro organisms by virtue of their ultra-fine pore size.

Principle:- Reverse osmosis is a basically "membrane separation process" to draw fresh water through a membranes from high TDS solutions (TDS = Total Dissolved Solids) such as sea water, brackish water, Industrial effluent and other sources.

- In natural osmosis, when salt solution is separated from pure water by semi-permeable membrane, the pure water flows across the membrane until the pressure on the pure water side become equal to the osmotic pressure of the salt solution.
- But in "reverse osmosis" process, the natural osmotic pressure is opposed by exerting an external pressure on the side containing the salt solution.



(a) Osmosis



(b) Reverse Osmosis

- The osmotic pressure is proportional to the TDS of the water and a pressure of at least twice osmotic pressure is required to achieve an economically feasible flow.
 - The semi-permeable membrane used in this process is thin but dense and strong enough to withstand the high external pressure.
 - There are 3 major types of membranes:
 - (1) cellulose
 - (2) Fully aromatic polyamide
 - (3) Thin Film Composite.
- The pore size for RO membrane is around 0.0001μ .
- Reverse osmosis does not work below 600 kg/cm^2 and usually operated at about 1000 kg/cm^2 pressure.
 - It should be ideally be tolerant of wide ranges of pH and temperature and should be resistant to attack by chemicals like free chlorine and by bacteria.
 - Ideally, it should also be resistant to scaling and fouling by contaminants in the feed water.

Reverse osmosis Applications :-

1. Sea water Desalination
2. pharmaceutical water purifications
3. Municipal water purification & Rural well water purification
4. Brackish well water Desalination
5. Laboratory water purification.
6. Industrial water purification
7. Bottled Drinking water production.

- In order to accurately measure the performance of an Reverse Osmosis system. we need following parameters.

- (1) Feed pressure
- (2) Feed conductivity
- (3) Feed flow
- (4) permeate - pressure, conductivity & flow

- Higher salt rejection, the better the system is performing. A low salt rejection can mean that membranes require cleaning or replacement.

$$\% \text{ Salt Rejection} = \frac{(\text{conductivity of Feed water}) - (\text{pure water conductivity})}{\text{conductivity of Feed water}} \times 100$$

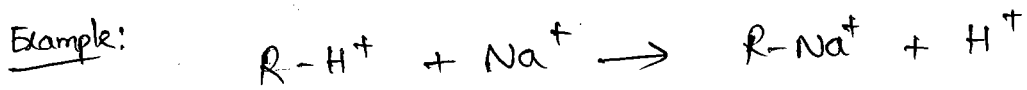
- The higher the recovery % means less water to drain as concentrate and saving more permeate water.

$$\% \text{ Recovery} = \frac{\text{permeate flow rate}}{\text{Feed flow rate}} \times 100.$$

Ion Exchange:-

principle:- Reversible exchange of ions between the ions present in the solution and those present in the ion exchange resin.

- Ion exchange is an adsorption phenomenon where the mechanism of adsorption is electrostatic. Electrostatic forces hold ions to charged functional groups on the surface of the ion exchange resin.
- The adsorbed ions replace ions that are on the resin surface on 1:1 charge basis.



- Examples of Ion exchanger materials are: proteins, soils, coal metal oxides and Alumino silicates (zeolites)

process:-

- The process here, however, uses a strong base anion exchange resin (zeolite) in the chloride form.
- As the water passes through the bed of the resin contained in a pressure vessel, Fluorides and other anions like Arsenic, nitrates etc. present in the water are exchanged with the chloride ions of the resin, thus releasing chlorides into water and adsorbing fluorides, nitrates, Arsenic ions into the resin.
- When the resin gets saturated with anions like Fluoride, nitrate, Arsenic etc. as indicated by their increased concentration in the out flowing water, the same can be cleaned and regenerated with 5-10% sodium chloride solution (brine) and the bed is returned to service.

- To ensure that a flow is maintained during regeneration, ideally 100% standby units should be provided.
- During regeneration, the exchange process get reversed, as the anions absorbed on the resin get replaced by chloride ions and discharged to waste water with chloride ions.
- The capacity of a plant based on this technology may range from 500 l/h to 5000 l/h.
- Although the method ensures high efficiency of fluoride removal, yet it requires regular replacement of resin, ~~material~~ and large amount of salt (NaCl) for regeneration of resin saturated with fluorides.
- The method is hence found to be very costly, ~~is~~ ~~poor~~ after sales service in villages.

Applications :-

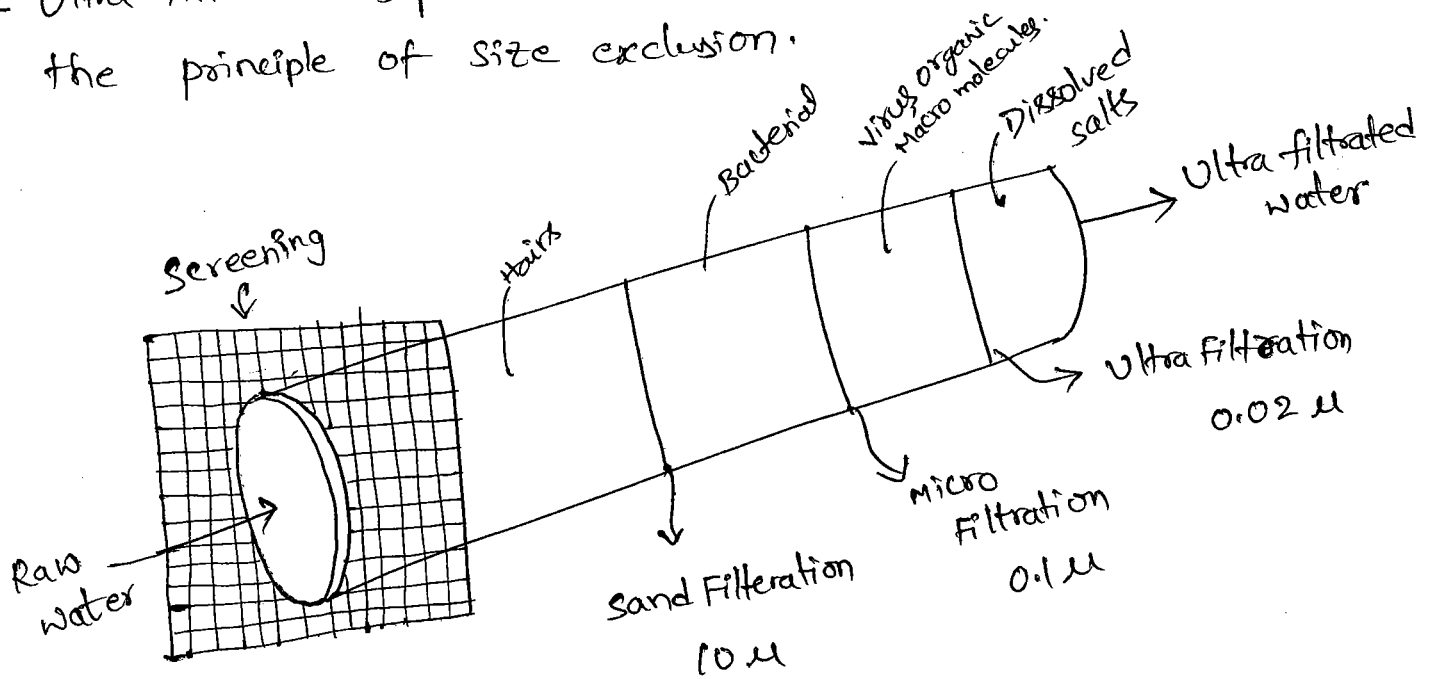
- Ca, Mg (hardness removal) exchange with Na or H
- Fe, Mn removal from ground water
- Recovery of valuable waste products Ag, Au, U.
- Removal of NO_3 , NH_4 , PO_4 (nutrient removal)
- Demineralization [exchange all cations for H all anions for OH].

~~Applications :-~~

~~Applications :-~~

Ultra filtration:-

- Ultrafiltration (UF) is a variety of membrane filtration in which forces like pressure or concentration gradients lead to a separation through a semi-permeable membrane.
- Ultra filtration separates solids from liquid streams based on the principle of size exclusion.



- Ultra filtration process similar to Reverse osmosis, using hydrostatic pressure force to water through a semi-permeable membrane.
- The pore size of ultra filtration membrane is usually 10^3 - 10^6 Daltons.
- Ultrafiltration is a pressure driven barrier to suspended solids, bacteria, viruses, endotoxins and other pathogens to produce water with very high purity and low silt density.
- Suspended solids and solutes of high molecular weight are retained while water and low molecular weight solutes pass through the membrane.
- Ultra filtration is not fundamentally different from Reverse osmosis, Microfiltration, nano filtration, except in terms of the size of the molecules it retains.

pore size of membrane

Reverse osmosis	←	0.0001 - 0.001 μm
Ultra Filtration	-	0.001 - 0.1 μm
Micro Filtration	-	0.1 - 10 μm
Sand Filtration	-	10 - 100 μm .

- Ultra Filtration membranes are used where essentially all colloidal particles (including most pathogenic organisms) must be removed but most of the dissolved solids may pass through the membrane without causing problems in the finished water.
- Ultrafiltration will remove most turbidity from water.

Working:

- Ultrafiltration uses hollow fibers of membrane material and the feed water flows either inside the shell, or in the lumen of the fibers.
- Suspended solids & high molecular weight solutes are retained, while water and low molecular weight solutes pass through the membrane.

Benefits:-

- No need for chemicals (coagulants, flocculants, disinfectants, pH adjustment)
- size exclusion filtration as opposed to media depth filtration.
- Good and constant quality of the treated water in terms of particle and microbial removal
- process and plant compactness
- Simple Automation
- Environmentally friendly.

Maintenance :-

- Ultrafiltration system contains extremely fine membrane filters which need to be properly cleaned.
- The cleaning process used depends on whether a UF system is being used to remove organic or inorganic contaminants ^{or} even both.
- To remove organic contaminants the general cleaning protocol for the cleaning of tubular membranes is to use a low foam, medium alkaline detergent at 0.6-1%. For a maximum of 40-60 min.
- To remove inorganic contaminants the best treatment is with citric acid at a maximum concentration of 3%.
The acid should circulate for 1-3 hrs.
- Hydrochloric acid can also be used to clean membranes, ~~and~~ as can oxalic, sulfuric and nitric acid.

Freezing:

- This method is based upon the principle that when salt water freezes, ice formed in the beginning is almost free from salt.
- This ice, when melted, can give us good water. The quality of water obtained is satisfactory, but the cost of production is high and prohibitive.

- When water freezes, the ice is theoretically free from the saline concentration of the water.
- Basically, a freezing process involves cooling the incoming sea water, freezing it to obtain fresh water ice, separating the ice and brine liquid, melting the ice to give fresh water and using the purified water and concentrated brine to chill the incoming sea water.
- There are four basic components in all freezing desalination processes:
 - Freezer
 - Washer
 - Melter
 - Heat Removal Systems.

i) Freezer:- A freezer consists of a vessel in which ice crystals and vapour are formed simultaneously.

- In this heat removes from the brine in order to produce ice crystals which can be easily transferred, removed, separated, washed and then melted.

- The design and operation of the freezer are to producing high proportion of discrete ice crystals rather than clumps of ice so that the amount of brine entrapped between the crystals formed is minimised.

- The size of ice crystals are formed is very important because fine crystals are difficult to wash. (size of ice crystals is 0.5 mm size i.e. minimum)

(ii) Washer

- Ice crystals formed in the freezer are pumped as slurry to the washer where ice crystals are separated from the brine.

- The counter current wash column is usually utilized as the washer, in which a small part of the product fresh water, flowing in a direction counter to that of ice motion, is used to wash the ice to remove the brine adhering to the crystal surfaces.

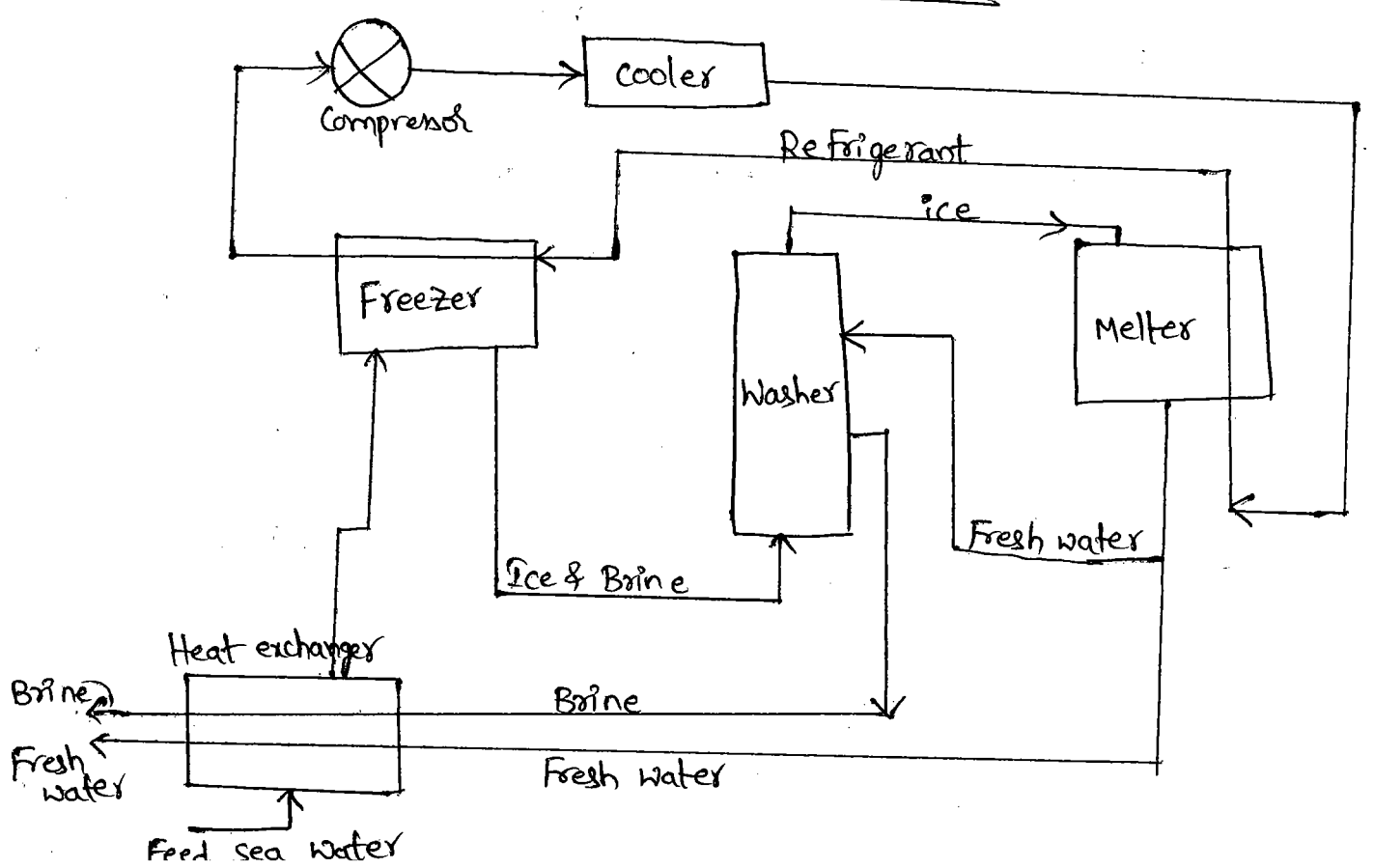
(iii) Melter:-

- In the melter the ice from the washer is usually melted by transferring the heat of crystallization removed from the brine in the freezer to the melter
- This is usually done by discharging the refrigerant into the melter where the ice picks up heat and melts.

(iv) Heat exchangers:-

- Heat exchangers are used between the product and feed water streams in order to reduce the temperature of the feed water and conserve energy.

Freezing process

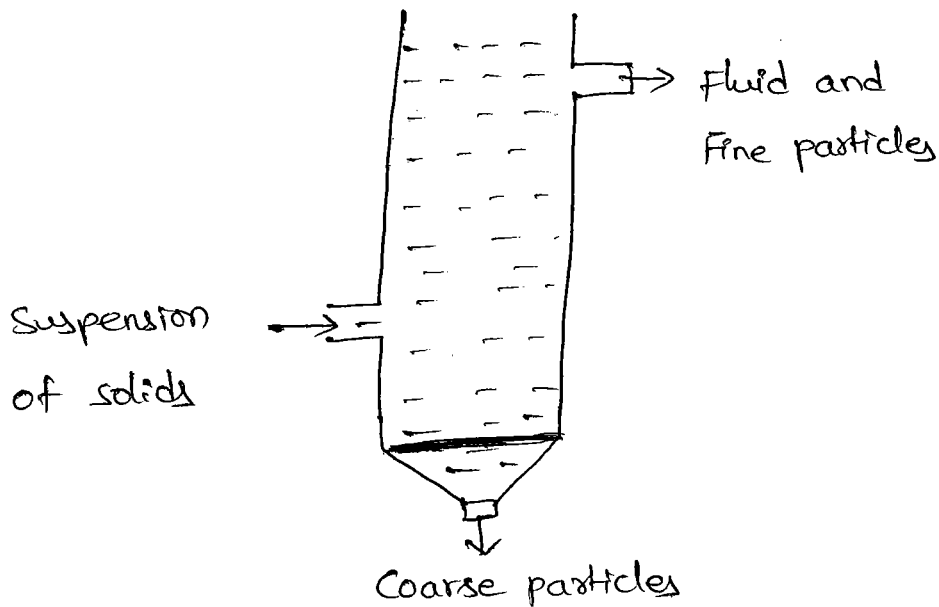


process:-

- In this process saline water does not come into contact with refrigerant directly. Ice is formed on a surface by mechanical refrigeration.
- A feed sea water is first pumped through a heat exchanger, to reduce its temperature, then entered into the freezing chamber, where it is cooled further to the temperature at which ice crystals are formed.
- The ice and brine slurry is pumped to a wash column, where the ice and brine are separated.
- The ice is transported to the melter, where ice is melted by heat released from condensation of compressed refrigerant.
- A small part of the product fresh water is passed to the wash column and is used to wash the ice crystals and major part is passed through the heat exchanger to cool the feed sea water and is then discharged for storage.
- The brine from the wash column is returned to the heat exchanger to cool the feed sea water and discarded.
- The freezing process will be ~~not~~ widely used in the field of industrial waste water treatment and food industry.
- The equipment used in the process is complex, expensive and difficult to operate and maintain.
- Therefore this process is seldom utilized practically in desalination.

Elutriation :-

- Elutriation is a process for separating particles based on their size, shape and density, using a stream of gas or liquid flowing in a direction usually opposite to the direction of sedimentation.
- This method is mainly used for particles smaller than 1 μ m.
- In Elutriation, movement of fluid against the direction of sedimentation of the particle.
- The apparatus consists of a vertical column. An inlet near the bottom and outlet at the base for coarse particles.
- An overflow near the top for fluid and fine particles.
- Velocity gradient across the tube results in the separation of particles of different sizes.



Simple Apparatus for Elutriation of Water

Elutriation of sludge :-

- It is the process of washing the sludge to remove the organic and fatty acids.

- During the sludge digestion, the volatile acids, alcohols and organic acids are developed, which if not removed, will interfere with coagulation process during dewatering.
- If elutriation of sludge is done before the dewatering or concentration it will much reduce the quantity of coagulants.
- Sludge elutriation is carried out in a single or multiple tasks by washing the sludge with water.
- During washing the solids are continuously kept in suspension by air or mechanical agitation.
- There are 3 methods of elutriation
 - (1) Single stage
 - (2) Multiple stage
 - (3) Counter Current Washing.
 the water requirement being dependent upon the method used.
- For a given alkalinity reduction, single stage elutriation requires 2.5 times as much water as the two stage and 5 times as much water as counter current washing.
- Therefore single stage washing is used for small plants.
- Counter current washing, although higher in initial cost, is adopted in large plants.
- Water requirement also depends on alkalinity of dilution water, alkalinity of elutriated sludge and desired alkalinity of sludge.
- Sludge and water are mixed in a chamber with mechanical mixing arrangement, keeping 20secs detention period.
- The sludge is then settled in ~~settling~~ settling tanks and excess water decanted.

- The maximum surface loading on settling tank may be $40 \text{ m}^3/\text{m}^2/\text{day}$ with a detention period of 4 hours.
 - Counter current elutriation is generally carried out in twin tanks similar to sedimentation tanks, in which sludge and water enter at opposite ends.
 - piping and channels are so provided that wash water entering the second stage tank comes first contact with sludge already washed in the first stage.
 - About 2-3 times quantity of wash water is required than sludge volume elutriated.
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Removal of Iron and Manganese :-

- Iron and Manganese are generally present in water supplies, either in suspension as hydrated oxides or in solution as bicarbonates.
- Water has iron dissolved in it as the result of carbon dioxide coming in contact with iron ore to form soluble ferrous bicarbonate.
- Iron in natural waters may be in ferric or ferrous condition, soluble, colloidal or insoluble.
- When Manganese is also associated with iron, removal becomes more difficult.
- When they are present in amounts greater than 0.3 ppm, either alone or as total, the following objectionable effects may be noted:
 - (i) Unpleasant taste & odour
 - (ii) Cause staining of plumbing fixtures, clothing and textiles.
 - (iii) Accumulation of precipitated iron in water mains.

(iv) Growth of Crenothrix in water mains.

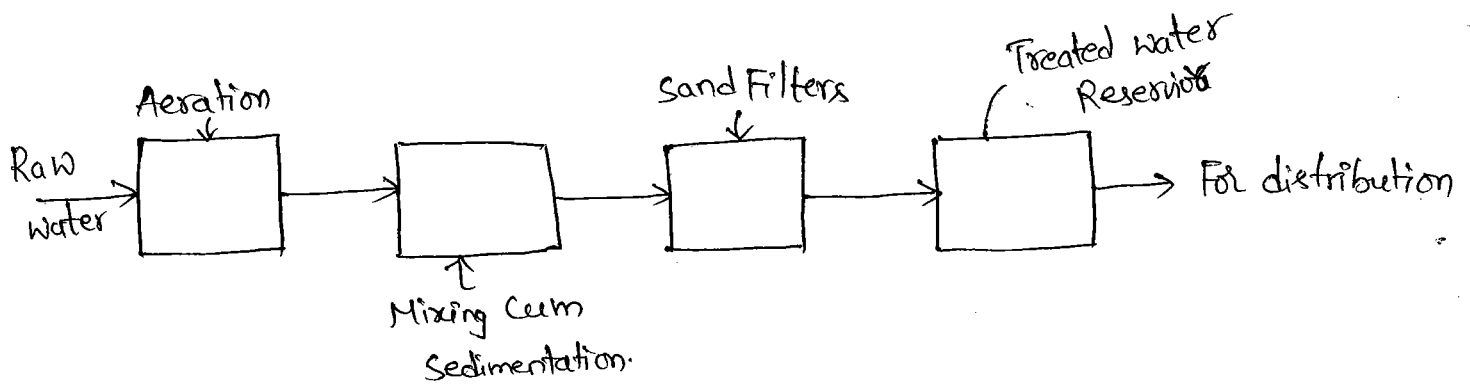
(v) Cause troubles in various manufacturing processes.

(vi) Sulphate iron cause acidity and corrosive action on Iron and Brass.

- The Reddish tinge in water is due to presence of iron while the Brownish tinge is due to presence of Manganese.

Method:- ①

When Iron and Manganese occur in water without organic matter, they can be removed by aeration, followed by coagulation, sedimentation and filtration.

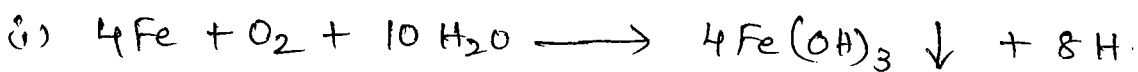


Flow diagram of Iron and Manganese removing plant

- By Aeration, dissolved Iron is oxidized to Ferric oxide which is insoluble in water. Similarly, dissolved Manganese Compounds are converted to insoluble Manganese Compounds.

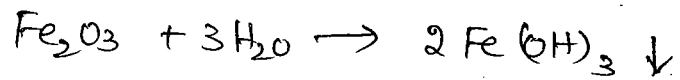
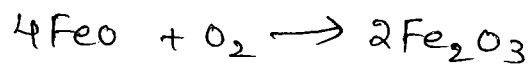
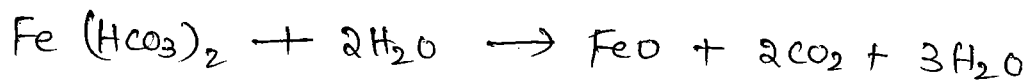
- The precipitated floc can be settled down in settling tanks or be further removed in Gravity or pressure Filters.

The following reaction takes place:



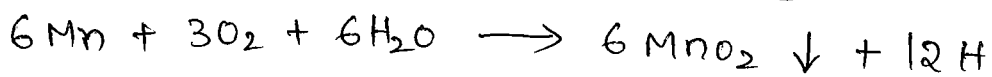
A reaction period of about 5 minutes or less, at a pH of 7 to 7.5 and 0.14 mg of oxygen is required to convert 1 mg of Ferric Iron to Ferric hydroxide.

(i) When Iron is present as Ferrous bicarbonate.



Here also, we find that 0.14 mg O_2 is required for 1 mg of Iron.

(iii) In case of Manganese, the following reaction takes place:



It shows that 1 mg Mn requires 0.29 mg of O_2 .

Manganese removal requires a pH adjustment upto 9.4 to 9.6

- This method of Iron and Manganese removal is most extensively used.
- In order to accelerate the oxidation particularly in waters with high CO_2 , addition of lime, soda ash or caustic soda is done.
- Combination of Iron and Manganese, or Iron alone, loosely bound to organic matter, make their removal difficult. The bond between them is broken by adding lime and thus raising pH value more than 9, so that Iron & Manganese can be precipitated.

Another method - (2)

- When water does not contain large amounts of Iron or Manganese these can be removed by means of a Manganese Zeolite.
- As Raw water passes through the bed of zeolite, the Iron and

Manganese are oxidised to insoluble hydrated oxides that are removed by mechanical filtering action of the zeolite bed.

- The bed must be washed and must be regenerated occasionally with potassium permanganate.

Another method:- (3)

- Oxidation of Iron compounds may also be obtained by chlorination followed by sedimentation and filtration.
- Iron and Manganese can be removed in oxidized condition, by softening water by excess lime process.
- As pH of 8.2 is needed for Iron removal while a pH of 9.6 is needed for removal of Manganese.

Removal of Colour and odour:-

- The colour, odour in the water come due to presence of dissolved gases such as hydrogen sulphide, Organic matter, Micro organisms and Contamination due to Industrial wastes containing phenol, excessive chlorine etc.
- The following are the various treatments which are used in removing the colour and odour.
 - (a) Aeration
 - (b) Treatment with Activated carbon.
 - (c) Treatment with Copper Sulphate.
 - (d) Oxidation of organic matters.

(a) Aeration :- It is the process of bringing water in intimate contact with air, while doing so the water absorbs oxygen from the air.

- The CO_2 gas is also removed upto 70% and upto certain extent bacteria are also killed. Iron and Manganese and H_2S gas are also removed upto certain extent from the water.
- Following are the various methods of aeration which are commonly used.

(i) By air diffusion :-

- In this method perforated pipes are fixed in the bottom of the settling tanks.
- The compressed air is blown through the pipes which comes out in the form of bubbles and stir the whole water at greater speed.
- During the upward movement of air it is thoroughly mixed with water and does its aeration.
- The Aeration tanks are usually made 2.5 to 3 m deep and work on the principle of continuous flow, having minimum detention period of 15 minutes.
- The quantity of air consumed varies from 0.3 - 0.6 cum per 1000 lt of water.

(ii) By Trickling beds :-

- In this method the water is allowed to flow on the Trickling beds of coke, which are supported on the perforated bottom of the Trays.
- The water is allowed to trickle from the top to the bottom under gravitational force. During this downward movement, the water gets mixed up with air and the aeration takes place.

- The size of coke tray ranges between 50 - 75 cm.

- The efficiency of this method is more than "Cascades" but it is less effective than the method of "spray nozzles".

(iii) By using spray nozzles:-

- In this method the water is thrown up in the air into fine sprays to a height of 2-2.5 m under pressure of 0.7 - 1.15 kg/cm².

- When small particles of water come in contact of greater surface area of the air, they absorb it and the water is aerated.

- The dissolved gases like H₂S, CO₂ etc escape into the atmosphere and the oxidation of various substances and organic matter takes place.

(iv) By using Cascades:-

- In this method the water is allowed to fall over a series of concrete steps or over a weir etc. in thin film.

- During the fall, the water gets thoroughly mixed with air and gets aerated.

→ Excessive Aeration should not be done, otherwise excessive absorption of O₂ will increase the corrosive property of water and it may require de-aeration process.

(b) Treatment with Activated Carbon:-

- Activated carbon is the most widely used substance for removal of Tastes and odours from public water supply, because it has excellent properties of attracting impurities, such as gases, finely divided solid particles and other liquid impurities.

- Activated carbon is usually used in powdered form and may be added either before and/or after coagulation with sedimentation. But it is used always before filtration.
- Activated carbon can also be used in granular form as a filter media, instead of using sand in the rapid gravity filter. But if used as filter media of pressure filters, it will be much better.

Advantages:-

1. If used in powder form it will increase the coagulation power of the process.
2. The chlorine demand of the water is reduced after using activated carbon.
3. The activated carbon removes tastes, odour & colour which are due to presence of Iron, Manganese, phenols, H_2S , chlorine, CO_2 etc.
4. The excessive dose of activated carbon is not harmful.
5. The process is simple requiring less skill.

(c) Treatment with copper sulphate :-

- Copper sulphate ($CuSO_4 \cdot 7H_2O$) also helps in removing colours, tastes and odours from water.
- The advantages of copper sulphate is that it checks the growth of algae even before its production, and also kills some bacteria.
- It is usually applied at the rate of 0.5 - 0.65 mg/lit to the treated water, before it is allowed for distribution in the mains.
- The solution of copper sulphate is generally prepared and added just at the entry of the water in the distribution mains. It can also be added in the clear water storage reservoirs.

- It can also be added in the lakes or impounded Reservoirs for the prevention of algae growth, but if excessive dose is added it will kill the fish and other living creatures, so quantity of dose should be properly determined in laboratory and check it.

(d) By oxidation of organic matter:-

- chlorine, potassium permanganate, ozone etc are oxidising agents which are commonly used.
- The dose of potassium permanganate varies from 0.05 - 0.1 mg/lit. chlorine also helps in the removal of organic matter in addition to its disinfection work, if added beyond breakpoint chlorination (or) super chlorination followed by dechlorination.
- chlorine dioxide gas and ozone can be used for oxidation purpose, but due to their heavy cost, they are uneconomical, hence are not used anywhere.

Use of Municipal waste water in Industries:-

- Municipal waste water Reuse has been increasing particularly in countries where shortage of water resources is severe.
- A successful reuse application of waste water depends on many factors of which quality and quantity very useful.
- The presence of Heavy metals, pollutants and other Toxic organics can effect health without treatment.
- For direct and Indirect distribution systems, the municipal waste water used in Industries is 7-8%.