LEC-4

Water Treatment

Water Treatment

- 1. Physical treatment
 - a) Storage
 - b) Physical coagulation
 - c) Filtration
 - 2. Chemical treatment
 - a) Chemical coagulation
 - b) Water softening (Removing the Hardness)
 - c) Using Ion- Exchange units

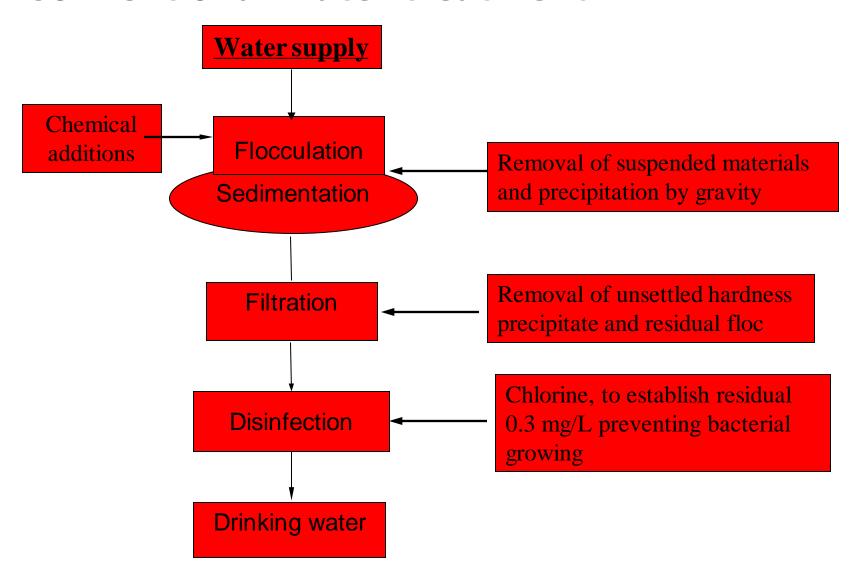
3. Biological Treatment

- a) Physical sterilization methods (Disinfection by):
 - Heating
 - Using Uv Radiation
- b) Chemical sterilization methods (Disinfection by):
 - Chlorination
 - Ozonation

Purification of Drinking Water

Flow diagram

Conventional water treatment



Purification of Drinking Water

Steps in a typical water treatment plan

- Coagulation (settling and precipitation)
- Hardness removal
- Disinfection

Coagulation

- Coagulation (or settling and precipitation)
- The finest particles, such as colloidal minerals, bacteria, and pollen do not settle in the raw water.
- Removal of this colloidal particles is necessary:
 - to give the finished water a clear appearance
- because they contain viruses and bacteria that are resistant to later disinfection.

Coagulation

- The capture of the fine particles is done by adding to the water either iron(III) sulfate, Fe₂(SO₄)₃, or aluminum sulfate, Al₂(SO₄)₃.
- In the case of aluminum sulfate, Al(OH)₃ is formed (in the pH range 6-8):

$$Al^{3+}(aq) + 3 HCO_3^-(aq) \rightarrow Al(OH)_3(s) + 3 CO_2(aq)$$

■ At this pH values, Al(OH)₃ is close to its minimum solubility and at equilibrium very little aluminum is left dissolved in the water.

Coagulation

- Aluminum hydroxide forms a very gelatinous precipitate, which settles very slowly and which incorporate the colloidal particles.
- With iron(III) sulfate the chemistry is analogous
- Fe³⁺ forms gelatinous iron hydroxide Fe(OH)₃.
- These reactions consume hydroxide
 - pH decreases (neutralize alkaline water)

- Hardness is characterized by the concentration of Ca²⁺ and Mg²⁺.
- Major problem caused by hard water: formation of mineral deposits.
- Calcium can be removed by addition of phosphate (see later).
- A more common way is by precipitation and filtering of insoluble CaCO₃

• When the calcium is present primarily as "bicarbonate hardness" (intermediate pH), it can be removed by direct addition of Ca(OH)₂ alone:

$$Ca^{2+} + 2HCO_3^- + Ca(OH)_2 \rightarrow 2 CaCO_3(s) + 2 H_2O$$

• When bicarbonate ion is not present at substantial levels, a source of CO₃⁻ must be provided at a high pH to prevent conversion of most of the carbonate to bicarbonate.

Source of carbonate ion: sodium carbonate, Na₂CO₃.

■ The precipitation of magnesium as the hydroxide requires a higher pH than the precipitation of calcium as $Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3(s)$

 The high pH required may be provided by the basic carbonate ion from soda ash (Na₂CO₃)

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2(s)$$

- There are two main problems:
 - Supersaturation effect: Some CaCO₃ and Mg(OH)₂ usually remain in solution. They need to be removed.
 - Use of highly basic sodium carbonate, which gives the product water an excessively high pH, up to pH 11.
- Solution: water is recarbonated by bubbling
 CO₂ into it.
 - The carbon dioxide converts the slightly soluble calcium carbonate and magnesium hydroxide to their soluble bicarbonate forms

Disinfection

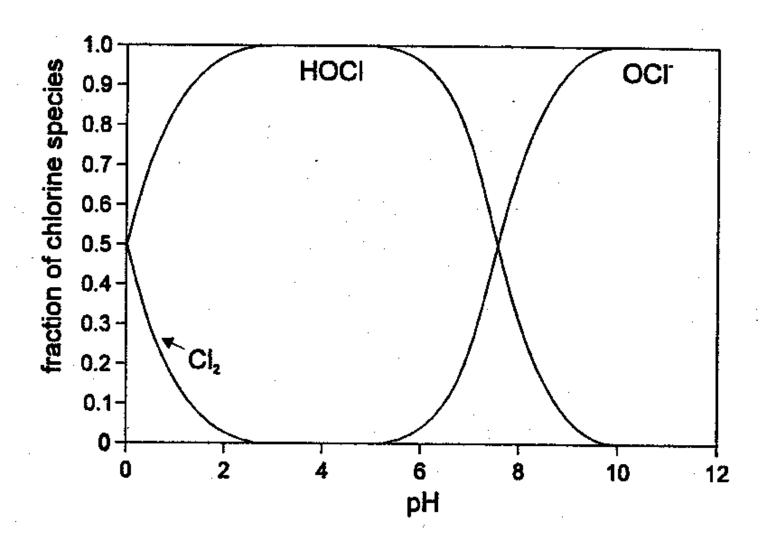
- Disinfection is the most essential part of water treatment
- Disinfectant used in water treatment:
 - chlorine
 - chlorine dioxide
 - ozone
 - ultraviolet radiation

Chlorine dissolves in water:

- Aqueous chlorine rapidly hydrolyzes to form hypochlorous acid: Cl₂(g) ↔ Cl₂(aq)
- Hypochlorous acid is a weak acid that dissociates according to the reaction: $Ka = 3 \times 10^8 \text{ mol/ L}$

$$Cl_2(aq) + H_2O \leftrightarrow H^+ + Cl^- + HOCl(aq)$$

$$HOCl(aq) \leftrightarrow H^+ + OCl^-$$



- Sometimes (e.g. swimming pools) hypochlorite salts, Ca(OCl)₂, are substituted for chlorine gas as a disinfectant.
- The hypochlorite salts are safer to handle than gaseous chlorine.
- Sodium hypochlorite, NaOCI, can also be used as a substitute for chlorine.
- The hypochlorite ions is then converted to hypochlorous acid:

$$OCl^{-} + H_{2}O \leftrightarrow HOCl + OH^{-}$$

- The two chemical species formed by chlorine in water, HOCl and OCl⁻, are known as free available chlorine.
- Free available chlorine is very effective in killing bacteria (in particular HOCl).
- HOCl(aq) about 10× more effective than ClO⁻(aq) –result of the more lipophilic HOCl crossing bacterial membranes more easily
- water with pH > 7.5 requires more chlorine or longer disinfection time – than water with pH < 7.5
- In the presence of ammonia chloroamines are formed.
- Alkaline pH will prevent the formation of these chloroamines.
- The chloroamines are called combined available chlorine.
- Breakpoint (Cl:N (wt/wt) = 8:1)

- important terms:
- >chlorine dose = concentration originally used
- ➤ chlorine residual = concentration in the finished water
- ➤ chlorine demand = concentration consumed by oxidizable substances present in the water
- Free available chlorine = sum of concentrations of HOCl(aq) and ClO-(aq)
- chloroamines the concentration of

Problems with the use of chlorine as a disinfectant:

- Simultaneous production of some toxic chlorinated organic compounds (e.g. chlorinated phenol).
- Production of trihalomethanes (THMs), CHX₃. Of particular concern is the formation of chloroform, CHCl₃ (carcinogen, suspected to affect reproductive system)
- chlorination byproducts, notably trihalomethanes.
- Example: chloroform CHCl₃ which is often present at 10ppb or more. Source is natural substances (humic acids)
- >C(=0)CH₃ + 3HOCl -> -CO2⁻ + CHCl₃ + 2H₂O

Disinfection/Chlorine Dioxide

- Chlorine dioxide, ClO₂, is an effective water disinfectant
- In the absence of impurity Cl₂, it does not produce THMs in water treatment.
- Chlorine dioxide oxidize organic molecules by extracting electrons from them.
- Chlorine dioxide is a gas that is violently reactive with organic matter and explosive when exposed to light.

Disinfection/Chlorine Dioxide

Chlorine dioxide is generated on-site, for example by the reaction of chlorine gas with solid sodium hypochlorite:

unstable, must be made in situ

$$2 \text{ NaClO}_2(s) + \text{Cl}_2(g) \leftrightarrow 2 \text{ ClO}_2(g) + 2 \text{ NaCl}(s)$$

- an oxidizing agent. not a chlorinating agent no taste and $10 \text{ NaClO}_2 + 5\text{H}_2\text{SO}_4 \rightarrow 8\text{ClO}_2 + 5\text{Na}_2\text{SO}_4 + 2\text{HCl} + 4\text{H}_2\text{O}$
- no residual effect rapidly decomposes must add Cl₂ afterward
- Some concern has been raised over possible health effects of its main degradation byproducts, ClO₂⁻ and ClO₃⁻ (chlorate) ions.

Disinfection/Chlorine Dioxide



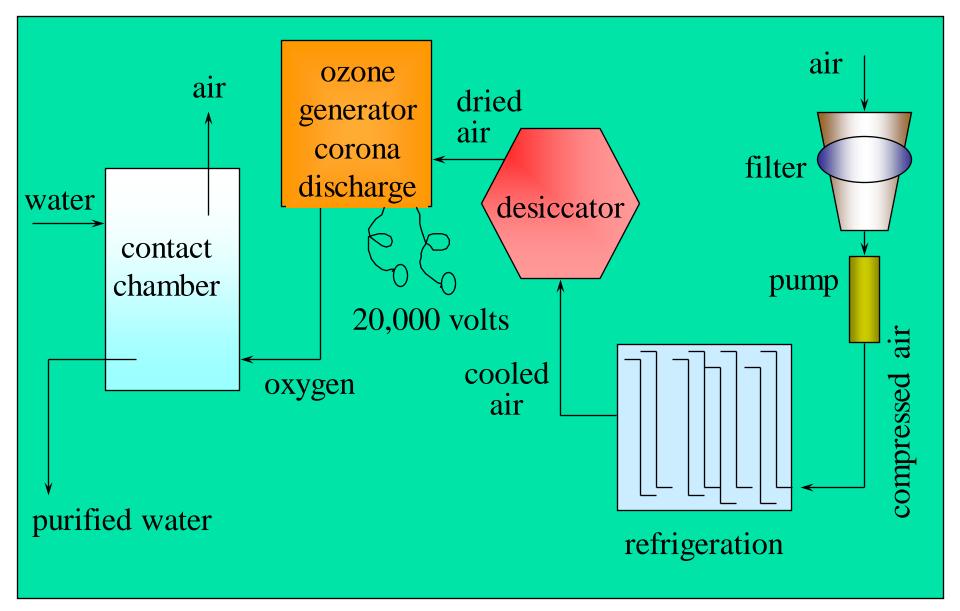
Disinfection/Ozone

- Ozone (stronger oxidizer than O₂) is sometimes used as a disinfectant instead of chlorine, particularly in Europe.
- unstable, must be made in situ by electric discharge on dry O₂ (air)
- Process: air is filtered, cooled, dried, and pressurized, then subjected to an electrical discharge of approximately 20,000 volts.
- 3O₂ —> 2O₃ formed as a dilute mixture in air
- The ozone produced is then pumped into a contact chamber where water contacts the ozone for 10-15 minutes.

Disinfection/Ozone

- ozonation equipment is expensive, only economic on a large scale
- an oxidizing agent, not a chlorinating agent
 no taste and odour problems, but cannot be used like ClO₂ as a temporary replacement for chlorine
- no residual in the water, decomposition is pH dependent (also faster at higher water temperature)

A typical ozone water-treatment system



Disinfection/Ozone

- Interest in ozonation arises from the possible production of toxic organochlorine compounds by water chlorination.
- ozone is more destructive to viruses than is chlorine.
- Unfortunately, the solubility of ozone in water is relatively low, which limits its disinfective power.

Disinfection/Ultraviolet light

- Ultraviolet radiation having wavelenghts below 300 nm is very damaging to life, including microorganisms by photochemical cross-linking of DNA, which absorbs strongly at this wavelength
- Mercury lamps (germicidal lamps) are available, having their output radiation principally at 254 nm (UV-C at 254 nm – major output of a low pressure)

Advantage of UV method:

Short contact time: 1-10 s. Ozone and chlorine both require contact of 10-50 minutes, therefore construction of a large reaction tank. UV disinfection can be run on a simple "flow-through" system (no holding tank)

Disinfection/Ultraviolet light

Advantage of UV method:

- Low installation costs. Ozone generators are complex and expensive to install; chlorine equipment is less so.
- Not influenced by pH or temperature. Chlorination and ozonation work best at lower pH, chlorine because more of it is in the HOCl rather than the OCl- form, ozone because it decomposes more rapidly at high pH.
- applicable to large and small scale installations, even domestic use
- No toxic residues.
- water must be clear and free of absorbing solutes

Disinfection/Ultraviolet light

Cost comparison between the various disinfectants:

Disinfectant	Plant capacity ^a	Cost ^b
Cl_2	0.05	26.0
	0.5	3.0
	1.0	1.7
ClO_2	0.05	52.5
	0.5	11.1
	1.0	8.6
O_3	0.05	72.5
	0.5	9.6
	1.0	6.6
UV	0.05	21.9
	0.5	7.2
	1.0	5.3

small installations: UV is cheapest, then chlorine

• large installations: chlorine is cheapest by a wide margin

The Treatment of Wastewater and Sewage

Pollutants in Sewage

- Typical municipal sewage contains oxygen-demanding materials, sediments, grease, oil, scum, pathogenic bacteria, viruses, salts, algal nutrients, pesticides, refractory organic compounds and heavy metals.
- Major disposal problem with sewage: the sludge produced as a product of the sewage treatment process.

Pollutants in Sewage

Constituent	Potential sources	Effects in water
Oxygen-demanding substances	Mostly organic materials, particularly human feces	Consume dissolved oxygen
Refractory organics	Industrial wastes, household products	Toxic to aquatic life
Viruses	Human wastes	Cause disease (possibly cancer); major deterrent to sewage recycle through water systems
Detergents	Household detergents	Esthetics, prevent grease and oil removal, toxic to aquatic life
Phosphates	Detergents	Algal nutrients
Grease and oil	Cooking, food processing, industrial wastes	Esthetics, harmful to some aquatic life
Salts	Human wastes, water softeners, industrial wastes	Increase water salinity
Heavy metals	Industrial wastes, chemical laboratories	Toxicity
Chelating agents	Some detergents, industrial wastes	Heavy metal ion solubilization and transport
Solids	All sources	Esthetics, harmful to aquatic life

Sewage Treatment

- Three main categories:
- primary treatment: primary settling, mechanical treatment
- secondary treatment: biological treatment, include the related problem of disposal of sewage sludge
- tertiary treatment: include advanced treatment.

Primary Treatment

- Primary treatment of waste water consists of the removal of insoluble matter such as grit, grease, and scum from water.
 - First step: screening to remove or reduce the size of trash and large solids that get into the sewage system. The solids are collected on screens and scraped off for subsequent disposal.
 - Second step: Grit removal.

Primary Treatment

- In the second step the sewage enters a large lagoon and moves through slowly enough that any solid particles settle out.
- Some materials float at the surface of the sewage (Those materials are called grease).
 They are removed by a skimming device.
- The effluent form the primary settler is almost clear, but has a high BOD (several hundred milligrams per liter).

Secondary Treatment

- Objective of the secondary treatment: to reduce the BOD to acceptable level (below 100 mg/L).
- The basic principle consists of the action of microorganisms provided with added oxygen degrading organic material in solution or in suspension.
- Two main systems:
 - Trickling filter
 - Activated sludge

Trickling Filter

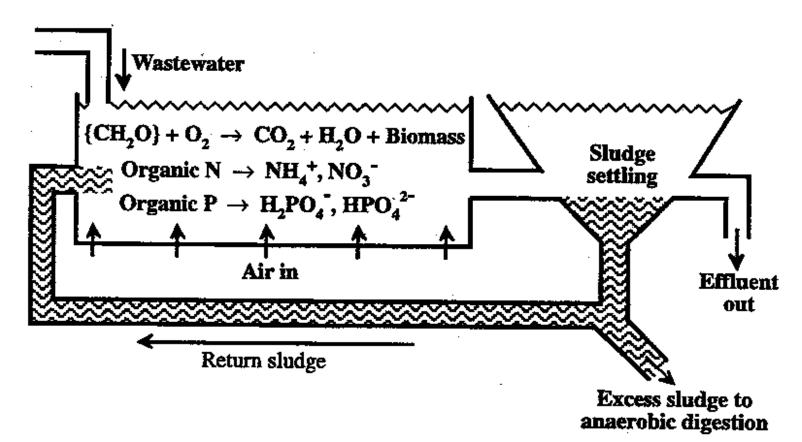
- The simplest biological waste treatment.
- The trickling filter is a large round bed of sand and gravel.
- A rotating boom sprinkle sprays the wastewater over rocks or other solid support material covered with microorganisms.
- Main threat: presence of toxic substances, which would kill the microorganisms.
- Disadvantage: require large space
- Advantage: low energy consumption

Activated Sludge Reactor

- Very effective wastewater treatment.
- Require less land and, being enclosed, can be maintained at the optimum temperatures for biological activity.
- The reactor is a large tank in which the wastewater is agitated and aerated to provide the oxygen required by the microorganisms.
- A portion of the sludge of microorganisms is removed from the exit stream of the reactor and recycled into the influent stream.

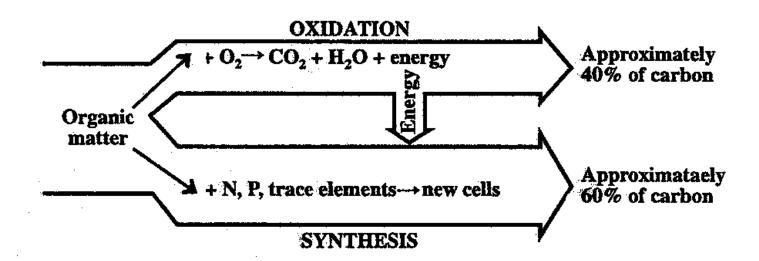
Activated Sludge Reactor

Schematic of activated sludge reactor:



Activate Sludge Reactor

- BOD may be removed by:
 - oxidation of organic matter to provide energy for the metabolic process.
 - Synthesis, incorporation of the organic matter into cell mass.



Activated Sludge Reactor

- The water content in the sludge may be removed by some drying process and the resulting dewatered sludge may be incinerated or used as landfill.
- To a certain extent, sewage sludge may be digested in the absence of oxygen by methane-producing anaerobic bacteria to produce methane and carbon dioxide
- A well-designed plant may produce enough methane to provide for all of its power needs.

Tertiary Treatment

- In some cases a portion of the drinking water is actually water that has been discharged from a municipal sewage treatment.
- Tertiary waste treatment (also called advanced waste treatment): term used to describe a variety of processes performed on the effluent from the secondary waste treatment.

Tertiary Treatment

- The contaminants removed by tertiary treatment fall into three general categories:
 - suspended solids: responsible for residual biological oxygen demand in secondary sewage effluent waters.
 - dissolved organic compounds: they are potentially the most toxic
 - dissolved inorganic materials: the major problem: nitrates and phosphates (nutrient for algae). Also, potentially hazardous toxic metals may be found among the dissolved inorganics.

Removal of Solids

- Some of the colloidal particles are removed using aluminum salt which forms Al(OH)₃.
- Similar to the process described during the purification of the drinking water.

Removal of Dissolved Organics

- The standard method for removal of dissolved organic material is by adsorption on activated carbon.
- Activated carbon is characterized by a very large surface area.
- The carbon is regenerated by heating it to 950°C in a steam-air atmosphere.
- Adsorbent synthetic polymers can also be used instead of activated carbon. They are regenerated by using solvent such as isopropanol and acetone.

Removal of Dissolved Inorganics

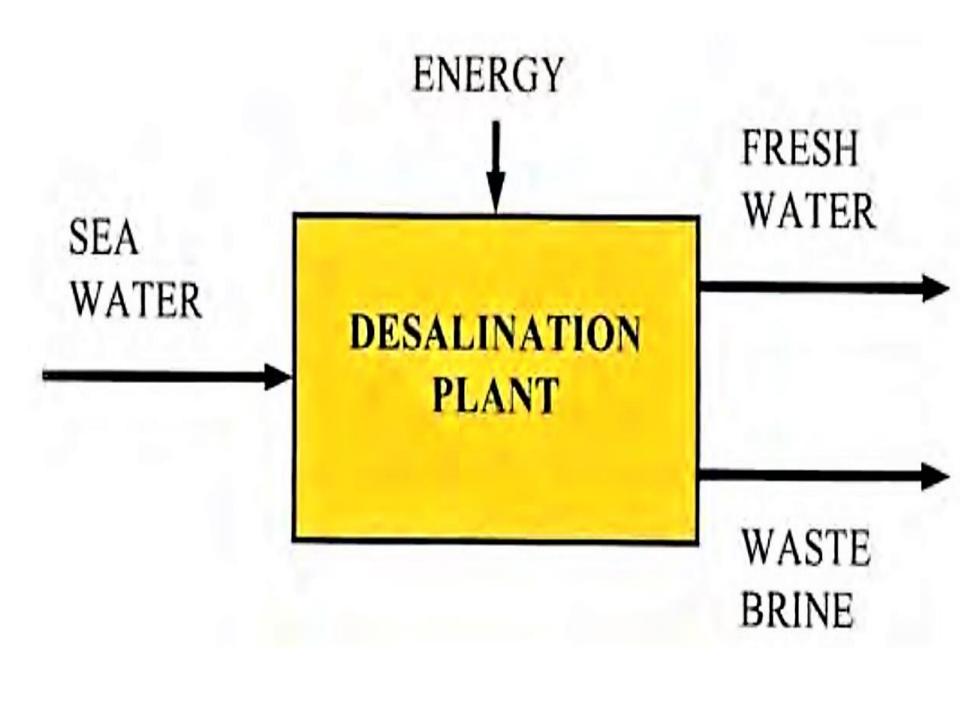
- The effluent of secondary waste treatment generally contains 300-400 mg/L more dissolved inorganic material than does the municipal water supply.
- The most cost-effective methods of removing inorganic material from water is currently membrane processes.
- Methods considered: reverse osmosis, electrodialysis, and ion exchange.

Water Desalination

Removal of Dissolved Inorganics

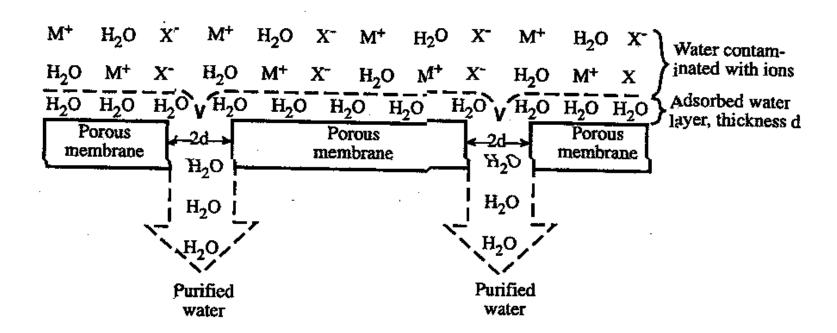
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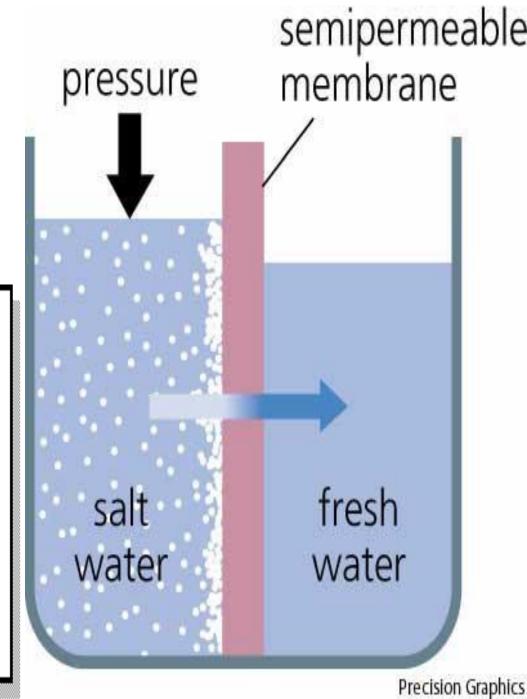
 These methods used for: Desalination process which helps to remove salts from sea water to make it drinkable

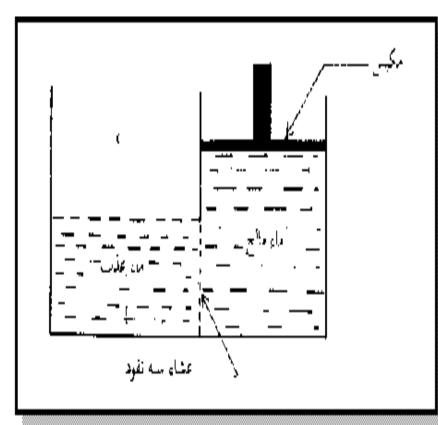


Reverse Osmosis

 Basic principle: force water through a semipermeable membrane that allows the passage of water but not other material.



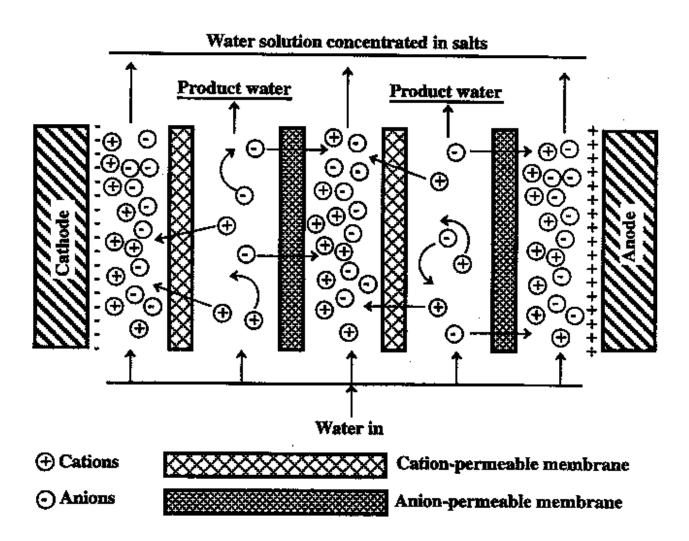




Electrodialysis

- Basic principle: apply a direct current across a body of water separated into vertical layers by membranes alternately permeable to cations and anions.
- Cations migrate toward the cathode and anions toward the anode.
- Layers of water enriched in salts alternate with those from which salts have been removed.

Electrodialysis



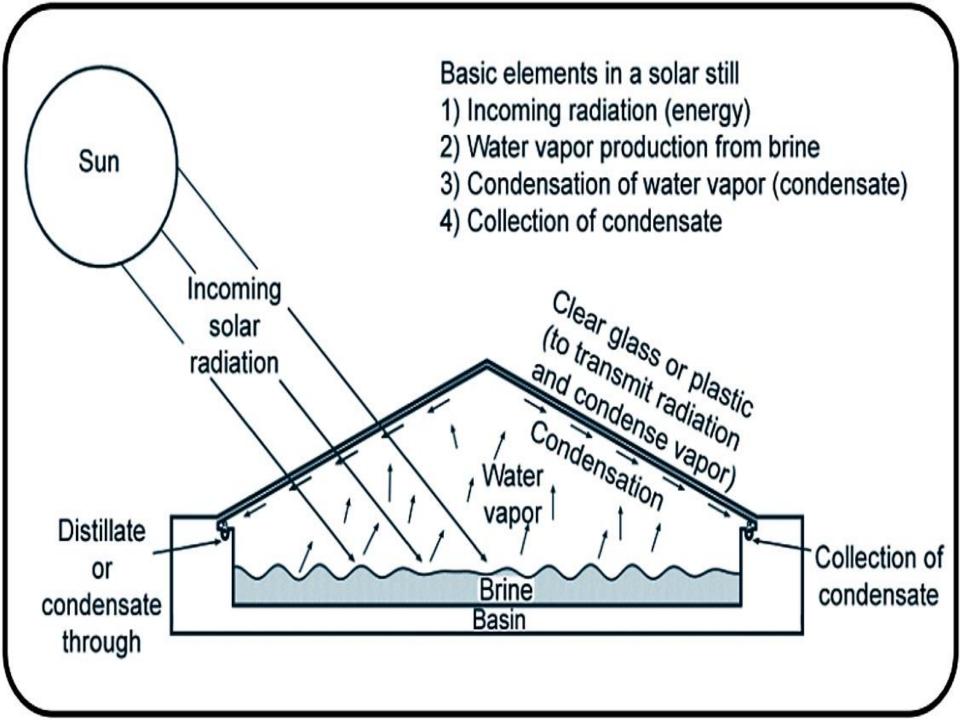
Ion Exchange

 Basic principle: passing the water successively over a solid cation exchanger and a solid anion exchanger, which replace cations and anions by hydrogen ion and hydroxide ion, respectively.

$$H^{+-}\{Cat(s)\} + M^{+} + X^{-} \rightarrow M^{+-}\{Cat(s)\} + H^{+} + X^{-}$$

$$OH^{-+}\{An(s)\} + H^{+} + X^{-} \rightarrow X^{-+}\{An(s)\} + H_{2}O$$

The cation exchanger is regenerated with strong acid and the anion exchanger with strong base.



Waste Water Treatment Methods

- aeration to remove volatile solutes
- precipitation of divalent cations
- coagulation and flocculation
- settling
- filtration
- disinfection

A typical municipal water treatment plant

