Module 2

Water softening methods: - Lime-soda, Zeolite and ion exchange processes and their applications.
Specifications of water for domestic use (ICMR and WHO);
Unit processes involved in water treatment for municipal supply - Sand Filtration- Sedimentation with coagulation- chlorination;
Domestic water purification – Candle filtration- activated carbon filtration; Disinfection methods- Ultrafiltration, UV treatment, Ozonolysis, Reverse Osmosis; Electro dialysis

External water softening methods

Lime soda process

- Soluble Ca and Mg salts in water are converted into insoluble compounds by addition of calculated amounts of lime ($Ca(OH)_2$) and soda (Na_2CO_3). $CaCO_3$ and $Mg(OH)_2$ are thus precipitated and then filtered off

For the removal of temporary hardness the reactions are:

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + 2H_2O$$
$$Mg(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + MgCO_3 + 2H_2O$$
$$MgCO_3 + Ca(OH)_2 \longrightarrow Mg(OH)_2 \downarrow + CaCO_3 \downarrow$$

for the removal of permanent hardness. The reactions are:

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 \downarrow + Na_2SO_4$$
$$MgSO_4 + Na_2CO_3 \longrightarrow MgCO_3 + Na_2SO_4$$
$$MgCO_3 + Ca(OH)_2 \longrightarrow Mg(OH)_2 \downarrow + CaCO_3 \downarrow$$
$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 \downarrow + 2NaCl$$

The reactions are slow and the fine precipitates can cause problems by depositing in pipes.

To avoid these

i)Thorough mixing is ensured

ii) Proper reaction time is maintained

iii) Accelerators like activated charcoal bring down the fine particles of precipitates

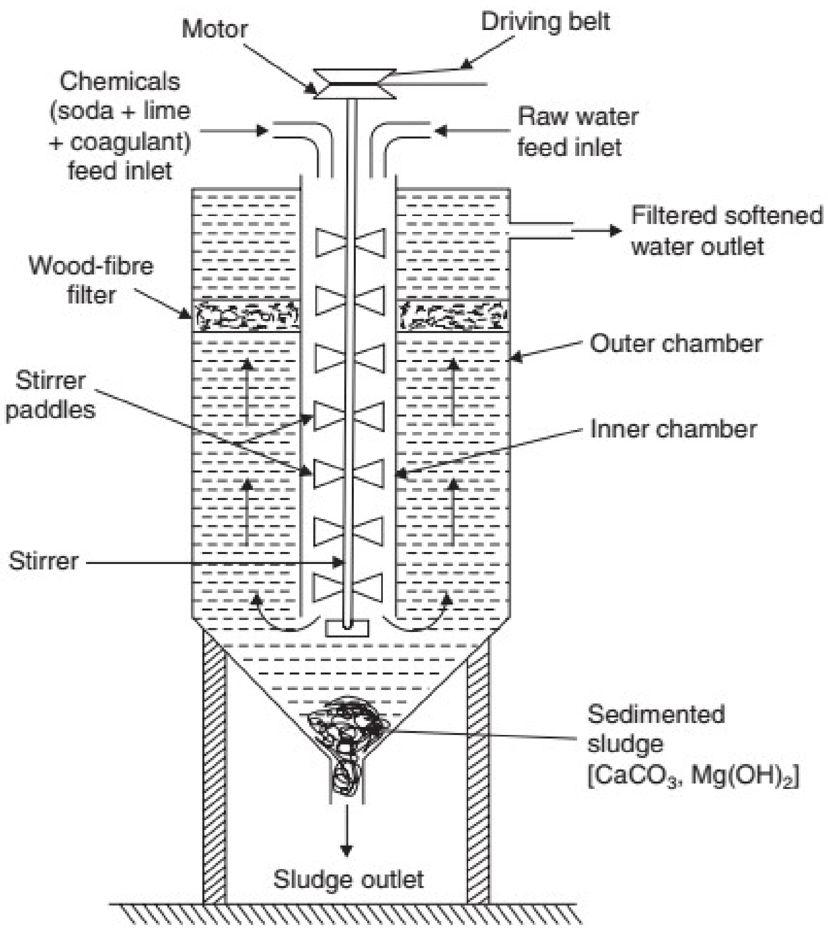
iv) Coagulants or flocculants like alum are added to trap the fine particles

$$\underset{\text{Coagulant}}{NaAlO_2} + 2H_2O \longrightarrow NaOH + Al(OH)_3$$

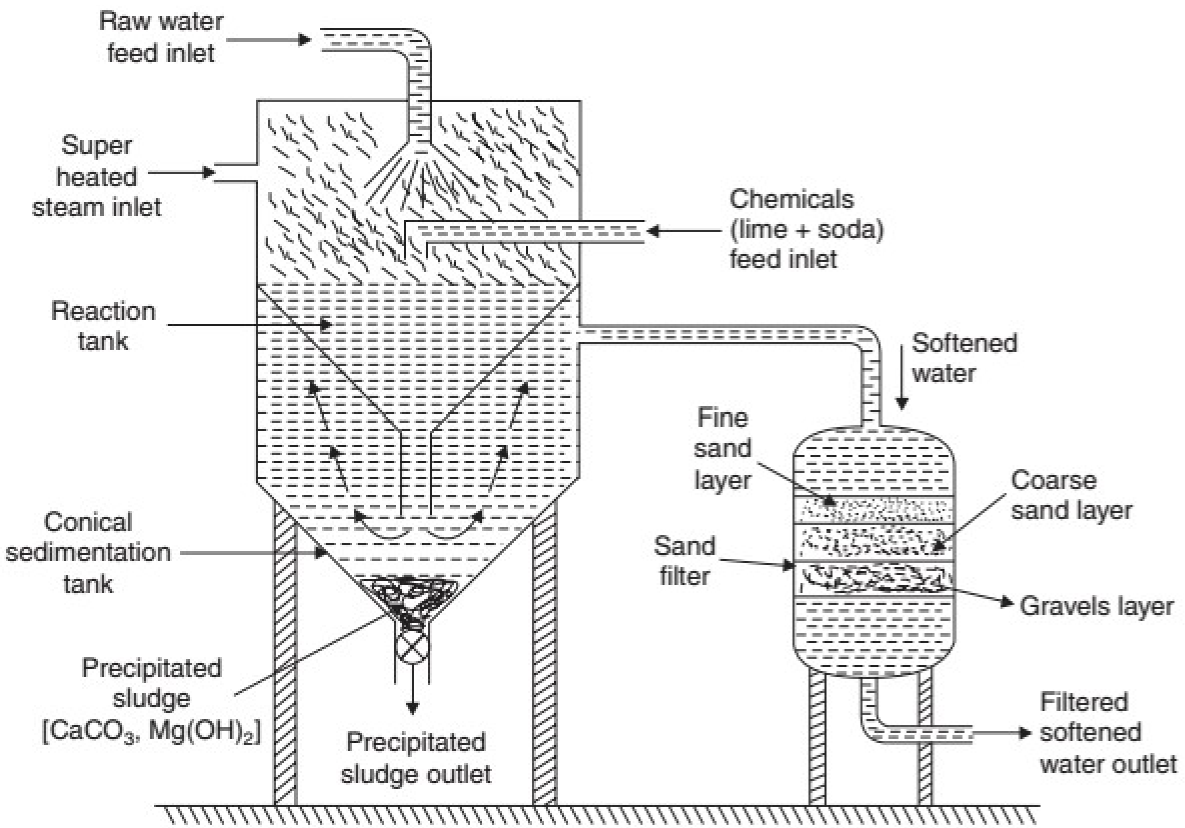
$$Al_2(SO_4)_3 + 3\,Ca(HCO_3)_2 \longrightarrow 2Al(OH)_3 + CaSO_4 + CO_2$$

Cold Lime soda process

- Calculated quantity of lime+soda+ coagulant are added to water
- Vigorous stirring is maintained
- Softened water rises up and heavier sludge and flocs settles down
- Softened water is then filtered off
- Residual hardness is brought down to 50 to 60 ppm



Hot Lime soda process



- 80 to 150 °C is maintained
- Reaction is faster, softening capacity increases, no coagulants are needed and dissolved gases are removed
- Residual hardness comes down to 15 to 30 ppm

Advantages of Lime soda process

- Economical
- Process increases pH and hence reduces corrosion
- Removes much of the minerals
- Pathogenic bacteria are also removed considerably

Disadvantages of Lime soda process

- Careful operation and skilled supervision required
- Sludge disposal is a problem
- Hardness is not completely eradicated by this method

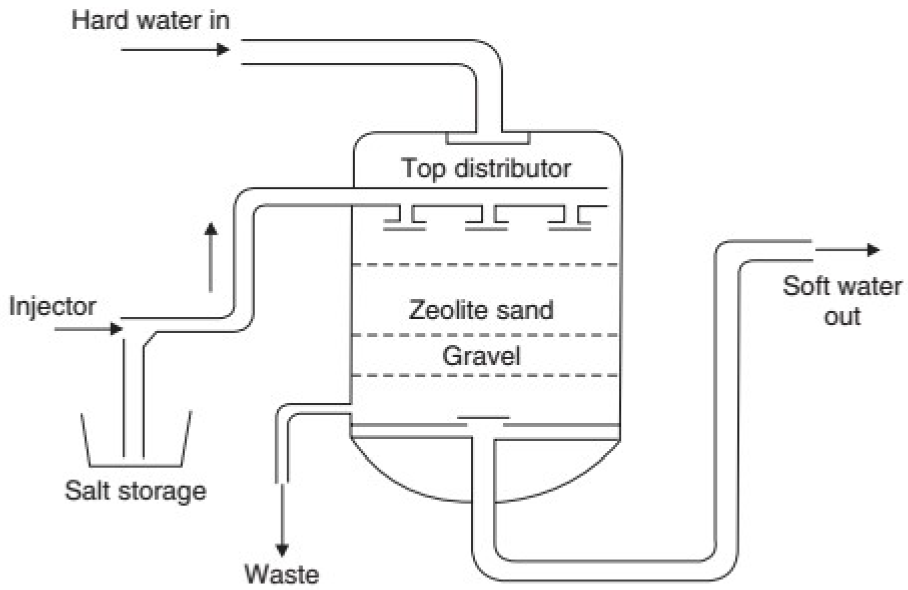
Zeolite or permutit process

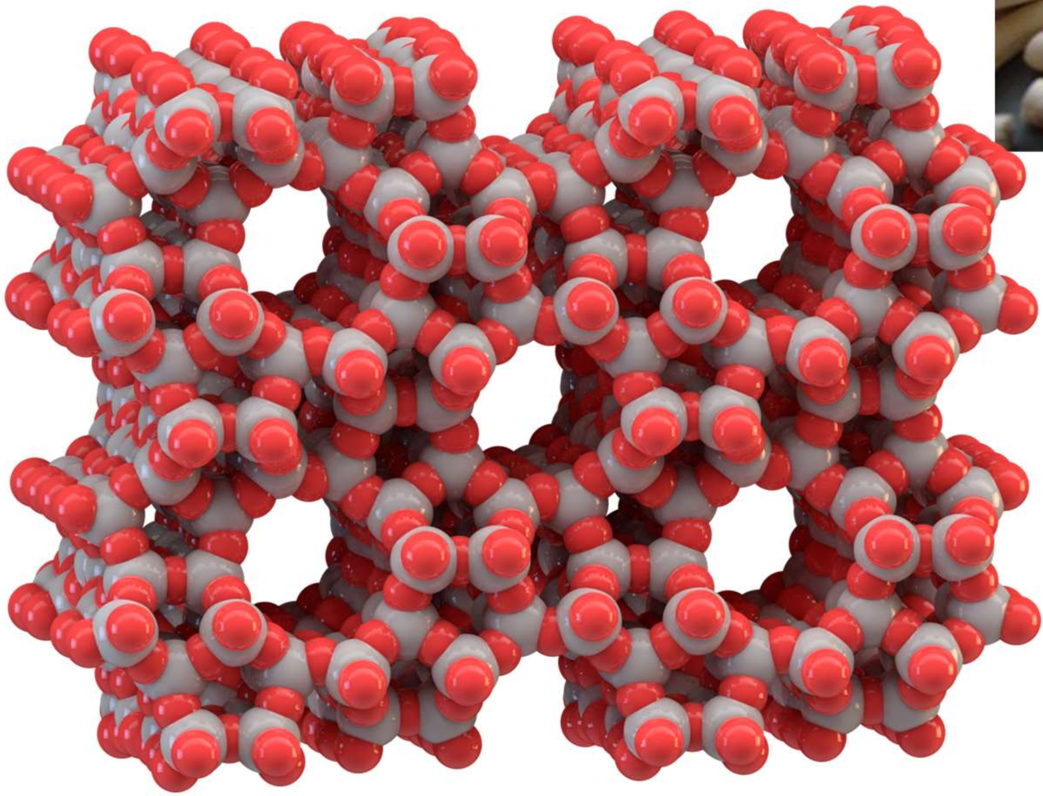
- Zeolite is a Hydrated Sodium Alumino Silicate (HSAS), capable of exchanging reversibly its sodium ions for hardness producing ions in water.
- Natural zeolites are non-porous but synthetic zeolites are porous and possess gel structure

- Hard water is percolated through a bed of zeolite. The hardness causing ions are retained by the zeolite bed

$$Na_2Ze + Ca(HCO_3)_2 = 2Na\ HCO_3 + CaZe$$
$$Na_2Ze + Mg(HCO_3)_2 = 2NaHCO_3 + MgZe$$
$$Na_2Ze + CaSO_4 = Na_2SO_4 + CaZe$$
$$Na_2Ze + CaCl_2 = 2NaCl + CaZe$$

- After a while, Ze is completely converted to Ca and Mg Ze and needs to be regenerated
- 10% brine solution will regenerate the zeolite for further softening of hard water



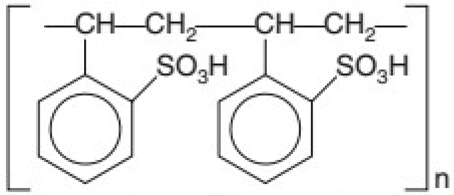
- **Limitations-** turbid water can cause clogging of the pores
- Coloured metal ions like Fe^{2+} or Mn^{2+} must be removed first, as they bind very firmly and cannot be removed easily from the zeolite
- Mineral acids can destroy the Ze bed and so must be neutralised before use

- **Advantages-** hardness comes down to around 10ppm
- The equipment is compact, less skill needed for maintenance, no sludge formation

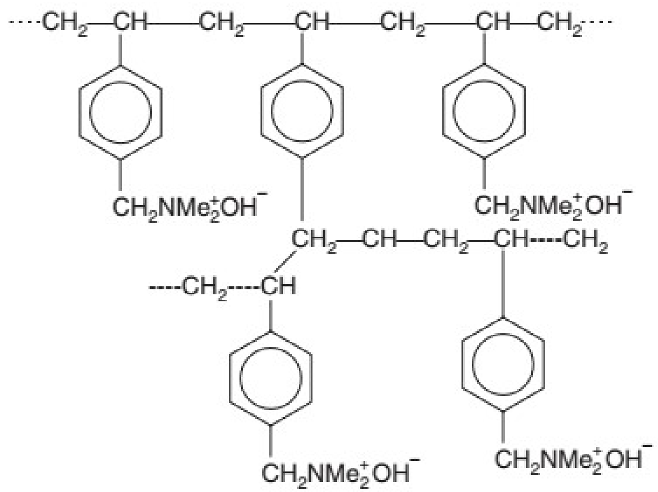
- **Disadvantages-** the process introduces excess of sodium than the lime soda process
- The method only replaces Ca^{2+} and $Mg^{2+,}$ but leaves behind all the anions like HCO_3^- and CO_3^{2-}
- The HCO_3^- decomposes to give CO_2 which causes corrosion and CO_3^{2-} decomposes to NaOH which can cause caustic embrittlement

Ion exchange deionisation/demineralisation

- Ion exchange resins are synthetic insoluble, cross linked long chain organic polymers with a microporous structure
- The polymer chain contain functional groups for ion –exchange
- **Cation exchange resins** have **Acidic** functional groups (-COOH or $–SO_3H$) exchange H^+ with the **cations**
- **Anion exchange resins** have **Basic** functional groups (amines/imines based) exchange **anions** with OH^-
- **Usually styrene based polymers are utilised**

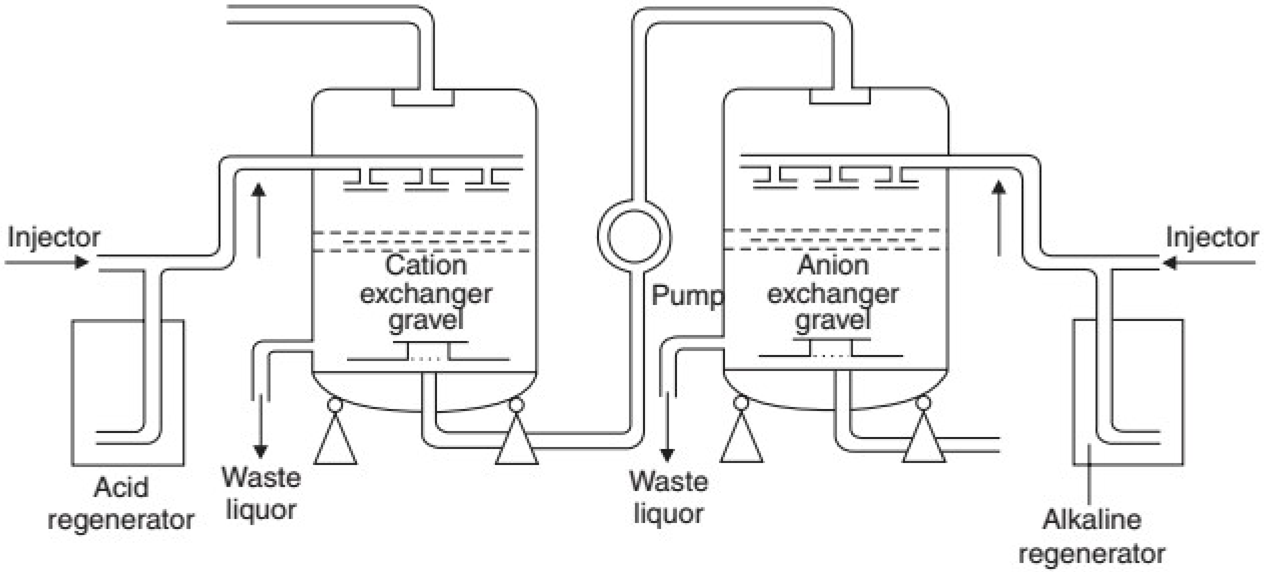


cation exchange resin



Anion exchange resin

Water purification by Ion exchange



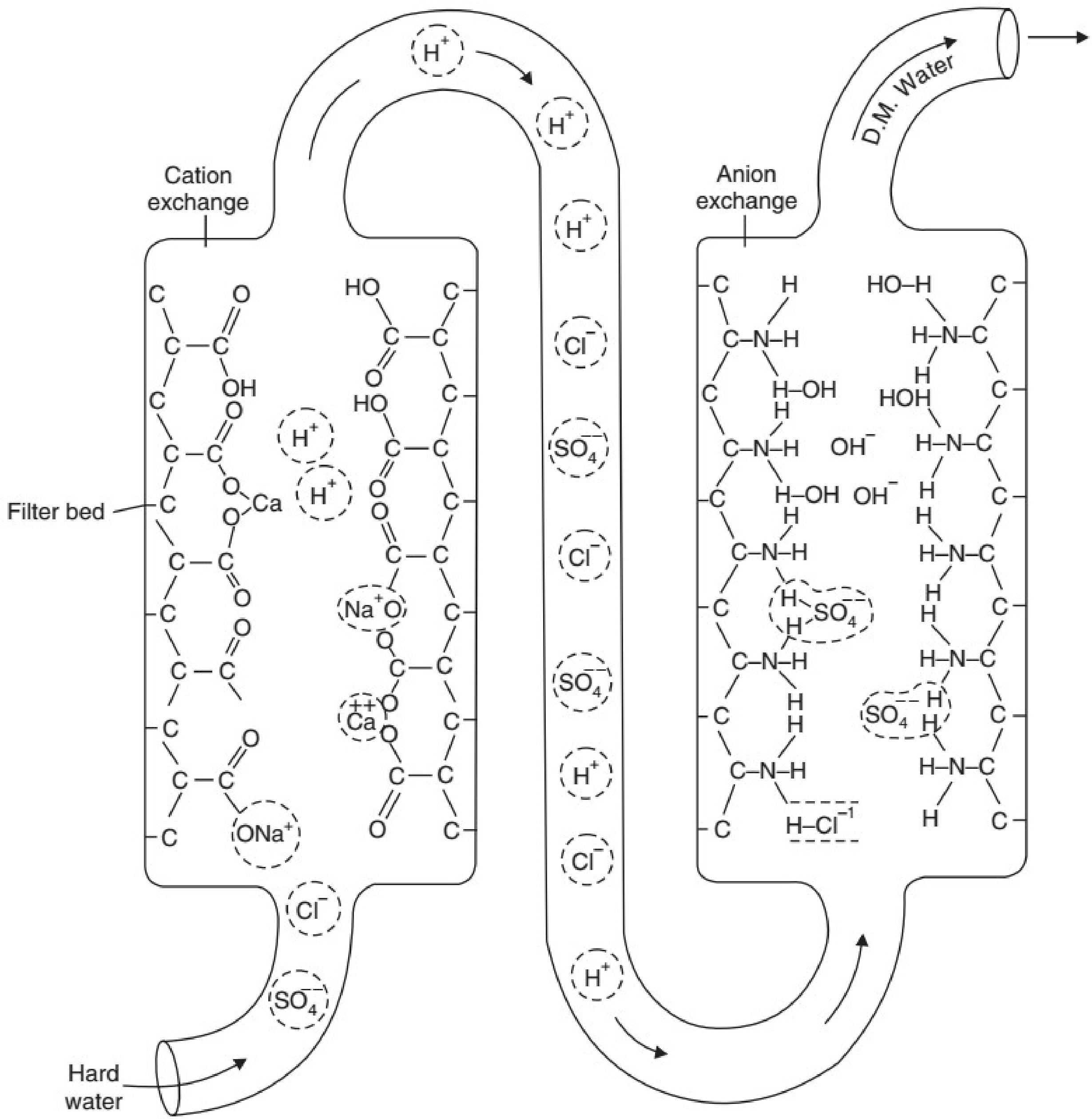
Hard water is passed first through the cation exchange column, removing all Ca2+ and Mg2+

$$2RH^{+} + Ca^{2+}/Mg^{2+} \longrightarrow R_2Ca^{2+}/R_2Mg^{2+} + 2H^{+}$$

Then it is passed through the anion exchange column, removing all anions like SO_4^{2-}, Cl^-

$$ROH^{-} + Cl^{-} \longrightarrow R^{+}Cl^{-} + OH^{-}$$

Water is thus de-ionised (DI water)



Cation exchange reaction:

$$2R^-H^+ + Ca^{+2} \rightleftharpoons CaR_2 + 2H^+$$

Anion exchange reaction:

$$RNH_2 + H_2O \rightleftharpoons R\overset{+}{N}H_3OH^-$$

$$R\overset{+}{N}H_3OH^- + Cl^- \rightleftharpoons R\overset{+}{N}H_3Cl^- + OH^-$$

Regeneration of ion exchange resin

- After a while, the resin loses all its H^+ and OH^- content and is exhausted and needs to be regenerated
- A cation exchange resin is regenerated by passing dil HCl or dil. H_2SO_4

$$R_2Ca^{2+} + 2H^+ \longrightarrow 2RH^+ + Ca^{2+}$$

- An anion exchange resin is regenerated by passing dil NaOH

$$R_2SO_4{}^{2-} + 2OH^- \longrightarrow 2ROH^- + SO_4{}^{2+}$$

- After regeneration, the resins are washed with DI water and the washings discarded

- **Advantages-** Highly acidic or alkaline water can be softened
- Softening upto 2ppm

- **Disadvantages-** expensive
- Turbidity can cause troubles

Mixed bed de-ioniser

- A single cylinder with an intimate mixture of cation and anion exchangers
- Hard water comes in contact very effectively, a number of times – equivalent to passing through a series of cation and anion exchangers
- Results in hardness less than 1ppm

Lime Soda process-Numericals

Calculation of lime and soda required for the softening of hard water by the lime soda process

Hardness producing substance	Chemical reaction with lime and soda	Need (Lime (L) or Soda (S))
Permanent Hardness		
$CaCl_2$	$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2NaCl$	**S**
$MgSO_4$	$MgSO_4 + \mathbf{Ca(OH)_2} \longrightarrow Mg(OH)_2\downarrow + CaSO_4$ $CaSO_4 + \mathbf{Na_2CO_3} \longrightarrow CaCO_3\downarrow + Na_2SO_4$	L + S
	$MgCl_2 + Na_2CO_3 \longrightarrow MgCO_3\downarrow + 2NaCl$	S
Temp. Hardness		
$Ca(HCO_3)_2$	$Ca(HCO_3)_2 + \mathbf{Ca(OH)_2} \longrightarrow 2CaCO_3\downarrow + 2H_2O$	L
$Mg(HCO_3)_2$	$Mg(HCO_3)_2 + \mathbf{2Ca(OH)_2} \longrightarrow 2CaCO_3\downarrow + Mg(OH)_2\downarrow + 2H_2O$	2L
Acids		
HCl	$2HCl + Na_2CO_3 \longrightarrow 2NaCl + H_2O + CO_2\uparrow$	S
H_2SO_4	$H_2SO_4 + Na_2CO_3 \longrightarrow Na_2SO_4 + H_2O + CO_2\uparrow$	S

Rules

1. When the impurities are given as $CaCO_3$ and $MgCO_3$ present in water it should be considered as due to bicarbonates of calcium and magnesium respectively
2. If Ca^{2+} and Mg^{2+} is given, 1 equivalent of lime and 1 equivalent of soda is required for Mg^{2+} whereas 1 equivalent of soda is required for Ca^{2+}. The ions Ca^{2+} and Mg^{2+} are treated as permanent hardness due to Ca and Mg.
3. Substances like NaCl, KCl, Na_2SO_4, SiO_2, Fe_2O_3 etc do not contribute to hardness and therefore, they do not consume any soda or lime and hence if these present need not be taken in to consideration during calculation.
4. Soda (Na_2CO_3) neutralizes only permanent hardness
5. If the lime and soda used are impure and if the percentage purity is given, then the actual requirements of the chemicals should be calculated accordingly. Thus, if lime is 90% pure, then the value obtained must be multiplied by 100/90 to get actual lime requirement.

Molecular weight of lime = 74

Molecular weight of soda = 106

Molecular weight of $CaCO_3$ = 100

Therefore, 100 parts by mass of $CaCO_3$ are equivalent to

(i) 74 parts by mass of $Ca(OH)_2$

(ii) 106 parts by mass of Na_2CO_3

Therefore, Lime requirement for softenening

$$= \frac{74}{100}\left[\text{T.H of } Ca^{2+} + (2 \times \text{T.H of } Mg^{2+}) + \text{P.H of } (Mg^{2+} + Fe^{2+} + Al^{3+}) + CO_2 + H^+ + HCO_3^- - NaAlO_2\right]$$

T.H = temporary hardness

P.H = Permanent Hardness

Soda requirement for softenening

$$= \frac{106}{100}\left[\text{P.H of } (Ca^{2+} + Mg^{2+} + Fe^{2+} + Al^{3+}) + H^+ - HCO_3^-\right]$$

Problem 1

Calculate the amount of lime required for softening 5,000 litres of hard water containing 72 ppm of $MgSO_4$ (mol wt = 120) Ans = 222g

Solution

Step 1 List out the given data

Given data : Amount of $MgSO_4$ is 72 ppm; water qty = 500 litres; mol. wt. MgSO4 = 120

Step 2 calculate the $CaCO_3$ equivalent

Hardness producing substance	Quantity (ppm)	Multiplication factor	$CaCO_3$ equivalent hardness (ppm or mg/L)
$MgSO_4$	72	100/120	72 X (100/120) = 60

Step 3 calculation of lime requirement

Lime required = 74/100 (hardness due to $MgSO_4$) x vol. of water

= 74/100 (60 mg/L) x 5000 L

= 222,000 mg

= 222 g

Problem 2

Calculate the amount of lime and soda required for softening 5,000 litres of hard water containing: $MgCO_3$ = 144 ppm, $CaCO_3$ = 25 ppm, $MgCl_2$ = 95ppm, $CaCl_2$ = 111ppm, Fe_2O_3 = 25ppm and Na_2SO_4 = 15ppm

Solution

Step 1 List out the given data

Given data : $MgCO_3$ = 144 ppm, $CaCO_3$ = 25 ppm, $MgCl_2$ = 95ppm, $CaCl_2$ = 111ppm,

Fe_2O_3 = 25ppm and Na_2SO_4 = 15ppm

Step 2 calculate the $CaCO_3$ equivalent hardness

Hardness producing substance			
$MgCO_3$ $CaCO_3$ $MgCl_2$ $CaCl_2$ Fe_2O_3 Na_2SO_4			

$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 + 2H_2O$; $Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_3 + Mg(OH)_2 + 2H_2O$

$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2 + CaCl_2$; $CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$

Step 3 Calculation of lime requirement

Lime required = 74/100 (hardness due to (2 x $MgCO_3$)+ $CaCO_3$ + $MgCl_2$) x vol. of water

= 74/100 (2 x 171.4) + 25.0 +100.0 mg/L x 5,000 L

= 74/100 (467.8) mg x 5,000

= 17, 309,00 mg

Answer = 1.731 kg

Step 4 calculation of soda requirement

soda required = 106/100 (hardness due to $MgCl_2$ + $CaCl_2$) x vol. of water

= 106/100 (100 +100.0) mg/L x 50,00 L

= 106/100 (200) mg x 5,000

= 10, 6,00,00 mg

Answer = 1.06 kg

Calculate the amount of lime and soda required for the softening of 50000 litres of water containing the following hardness causing salts:

$Ca(HCO_3)_2$ = 30.5 mg/L;

$Mg(HCO_3)_2$ = 45.3 mg/L;

$CaCl_2$ = 22.0 mg/L;

$MgCl_2$ = 62.4 mg/L,

$MgSO_4$ = 21.1 mg/L;

[Molecular weight of $Ca(HCO_3)_2$ = 162; $Mg(HCO_3)_2$ = 146; $CaCl_2$ = 111; $MgCl_2$ = 95; $MgSO_4$ = 120].

Specifications for potable water

1. The water should be clear, colorless and odorless
2. It should be free form dissolved gases such as CO_2, H_2S etc
3. Water should be free from pathogenic microorganisms
4. The hardness should not be high (not more than 125ppm)
5. The turbidity in drinking water should not exceed 25 ppm
6. The pH of the drinking water must be 7.0 – 8.5
7. The total dissolved salts (TDS) should be less than 500ppm
8. It should be devoid of arsenic and heavy metals such as Cr, Hg etc

Specifications of water for domestic use

Parameter	Table	World Health Organization
Arsenic	As	10µg/l
Barium	Ba	700µg/l
Benzene		10µg/l
Boron	B	2.4 mg/l
Cadmium	Cd	3 µg/l
Calcium	Ca	
chlorides		250 mg/l
Chromium	Cr	50µg/l
Copper	Cu	2.0 mg/l
Cyanide		50 µg/l
Fluoride		1.5 mg/l
Lead	Pb	10 µg/l
Mercury	Hg	6 µg/l
Nitrate		50 mg/l
Pesticides — Total		0.50 µg/l
Pesticides (individual)		0.10 µg/ l
Selenium	Se	40 µg/l
Tetrachloroethene and Trichloroethene		40µg/l

Treatment of water for municipal supply

Municipal water treatment involves the following steps:

1. **Screening-** removal suspended impurities by passing raw water through scrrens with large number of holes. Floating matters gets removed

2. **Aeration-** passing compressed air removes odour and iron as $Fe(OH)_3$

3. **Sedimentation and coagulation –** settling in a large tank to remove suspended impurities

- Coagulants such as $NaAlO_2$ or $\mathbf{Al_2(SO_4)_3}$ added to trap fine clay & colloidal particles.
- Generally used coagulants are Alum (K_2SO_4, $Al_2(SO_4)_3 . 24H_2O$)and green vitriol ($FeSO_4.7H_2O$)

4. **Filtration-** Filtration through a bed of granular material such as sand would remove bacteria and other microbes and colloidal impurities

5. **Sterilization and disinfection**

6. **Storage and distribution**

Sterilization and disinfection

- **Bleaching powder ($CaOCl_2$)**
- **Chlorination by passing Cl_2**
- **Use of Chloramines**
- **Ozonisation (O_3)**
- **UV Treatment**

Bleaching powder ($CaOCl_2$)

- 1Kg per 1,000 kiloliters of water
- Hypochlorous acid is produced which is a germicide
- Ca is introduced which raises the hardness of water

$$Ca(OCl)Cl + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

Chlorination by passing Cl_2

- Either gas or concentrated solution is used to chlorinate water. 0.3 – 0.5ppm is sufficient
- **Break point chlorination** involves the addition of enough chlorine to oxidise a) Organic matter, b) reducing substances and c) free ammonia
- Trichloromethanes and haloacetic acid by-products are carcinogenic

- Excess chlorine gives bad taste and causes eye irritation
- Over-chlorination after breakpoint can be removed by adding sulphur dioxide or sodium sulphite
- 2:1 mixture of Cl_2 and NH_3 gives chloramine $ClNH_2$, which is a better disinfectant than just chlorine

Use of Chloramines

- When Chlorine and ammonia are added in 2:1 ratio of volume, chloramines are formed

$$Cl_2 + NH_3 \rightarrow ClNH_2 + HCl$$

- Chloramine is most effective than chlorine in disinfection. HOCl is generated here as well

$$ClNH_2 + H_2O \rightarrow HOCl + NH_3$$

- In addition to formation of HOCl which is bactericidal, nascent oxygen is also formed by its decomposition , which adds to bactericidal activity

- Chloramines do not impart any odour nor affects the taste of water and so is becoming popular as a disinfecting agent

Sterilization by ozone

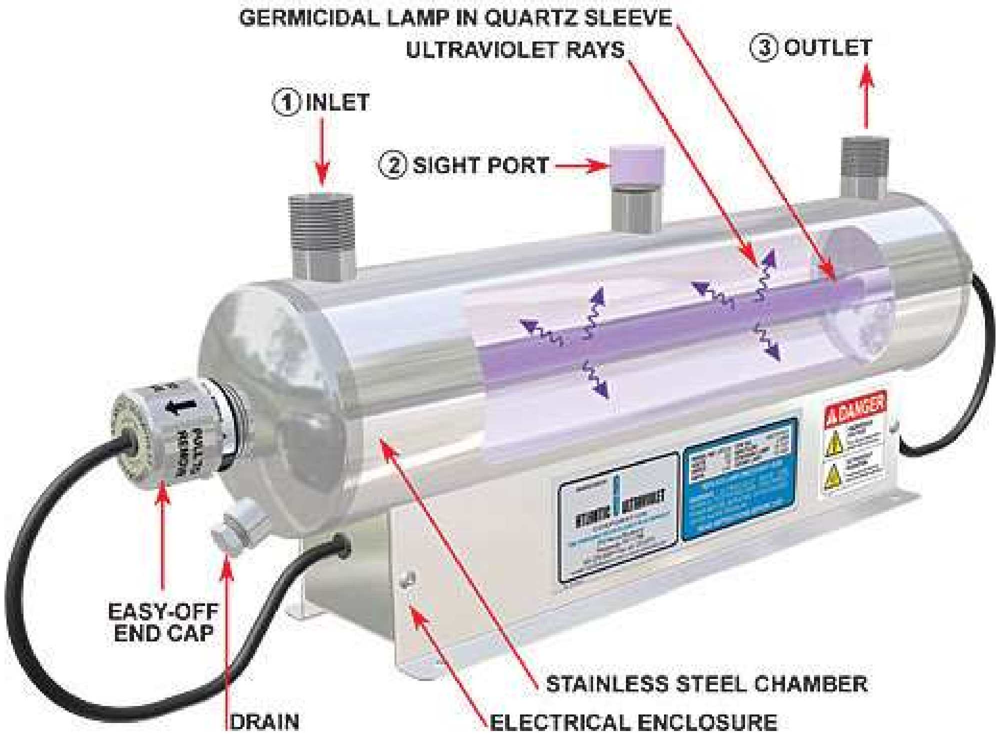
- Ozone is produced by passing silent electric discharge through cold and dry oxygen

$$\boxed{O_3 \longrightarrow O_2 + \mathbf{[O]}}$$

- O_3 thus produced is unstable and so liberates nascent oxygen, which is strongly bacteriocidal
- Ozone and water are mixed in a tank for 10-15 minutes with a usual dosage of 2-3ppm
- Though its very effective in killing microbes and removing odour and taste with no harmful side products, the process is very expensive

Treatment with UV

- UV light is very effective in inactivating microbes, as long as the water has low level of colour
- Like ozonisation, UV treatment leaves behind no residual disinfectant and so the water may gain bacteria while storage and transport.



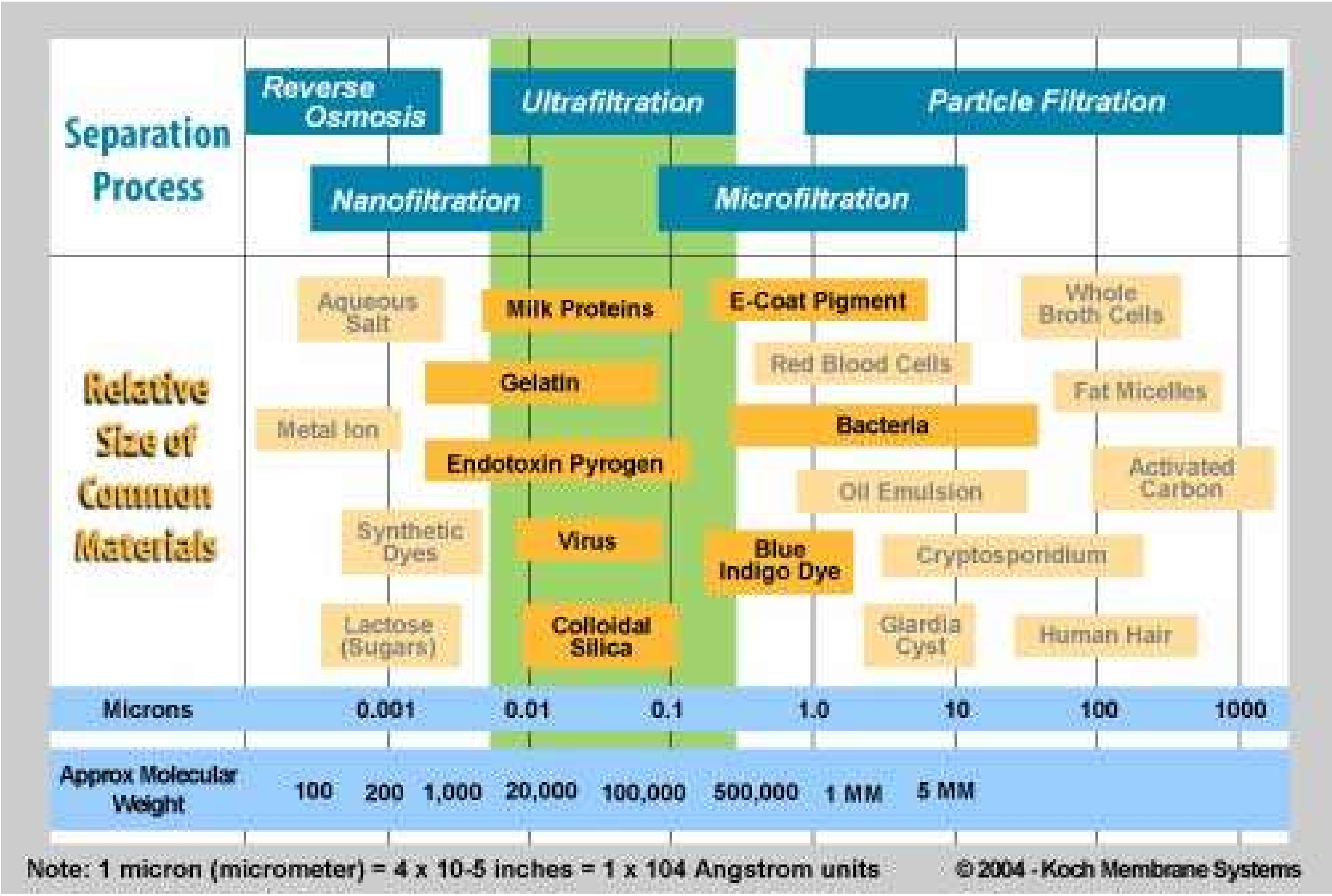
Ultrafiltration and nanofiltration for disinfection

- Filtration is a process of removing particulate matter from water by forcing the water through a porous media
- The size of materials that can be removed during filtration depends upon the size of the pores of the filter
- An ultrafiltration filter has a pore size around 0.01 micron
- A nanofiltration filter has a pore size around 0.001 micron
- Reverse osmosis filters have a pore size around 0.0001 micron

Ultrafiltration would remove large particles, macromolecules, bacteria, protozoa and may remove some viruses.
Ultrafiltration cannot remove dissolved substances unless they are first adsorbed (with activated carbon) or coagulated (with alum or iron salts).

Nanofiltration removes most organic molecules, nearly all viruses, most of the natural organic matter and a range of salts. Nanofiltration removes divalent ions, which make water hard, so nanofiltration is often used to soften hard water.

polysulfone and cellulose acetate are the most commonly used membrane materials



Separation Process
Reverse Osmosis
Ultrafiltration
Particle Filtration
Nanofiltration
Microfiltration
Relative Size of Common Materials
Aqueous Salt
Milk Proteins
E-Coat Pigment
Whole Broth Cells
Red Blood Cells
Gelatin
Fat Micelles
Metal Ion
Bacteria
Endotoxin Pyrogen
Activated Carbon
Oil Emulsion
Synthetic Dyes
Virus
Blue Indigo Dye
Cryptosporidium
Lactose (Sugars)
Colloidal Silica
Giardia Cyst
Human Hair
Microns
0.001
0.01
0.1
1.0
10
100
1000
Approx Molecular Weight
100
200
1,000
20,000
100,000
500,000
1 MM
5 MM
Note: 1 micron (micrometer) = 4 x 10-5 inches = 1 x 104 Angstrom units
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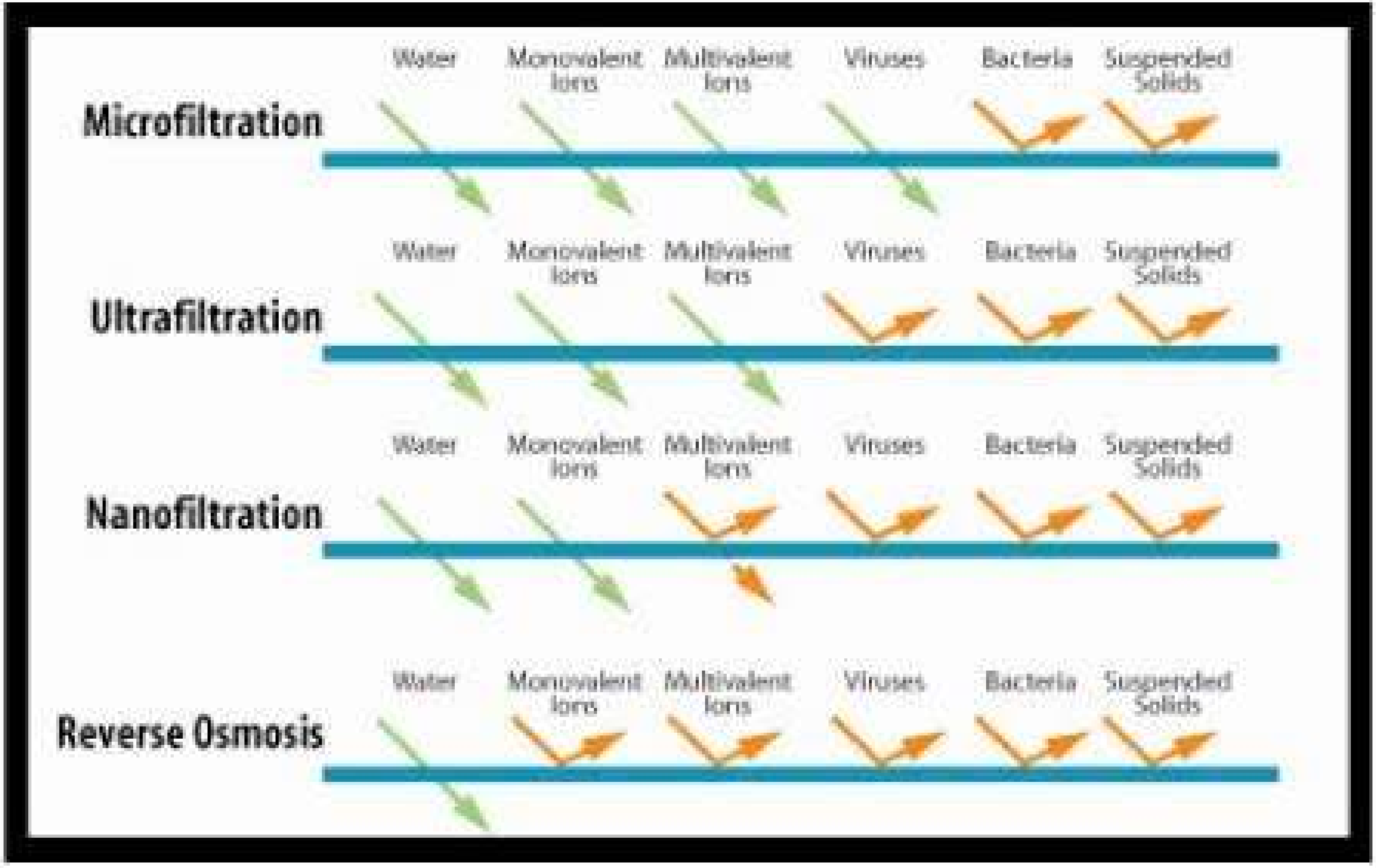
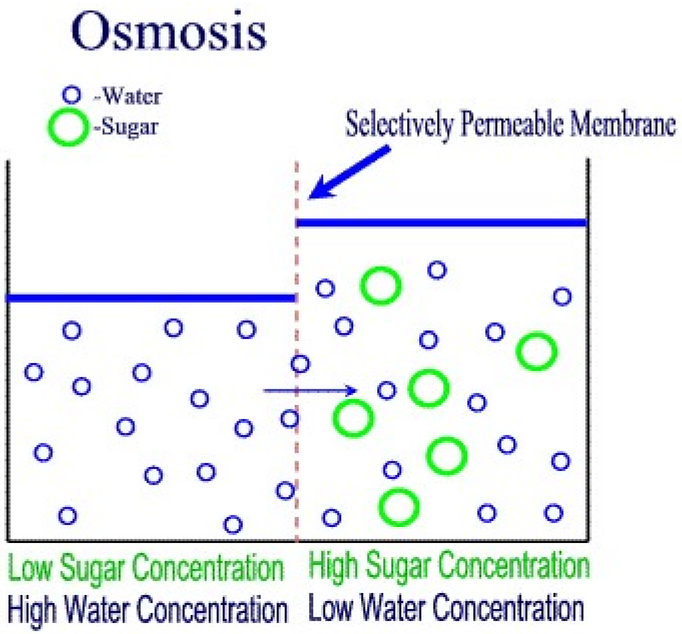
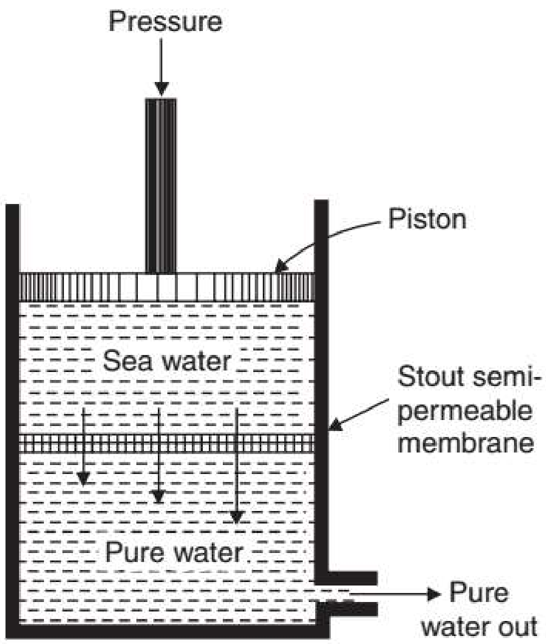


Membrane Process Characteristics

Reverse osmosis

- **Osmosis** is the **spontaneous** net movement of solvent molecules through a semi-permeable membrane into a region of higher solute concentration, in the direction that tends to equalize the solute concentrations on the two sides.
- When pressure more than the osmotic pressure is applied from the concentrated solution, the flow of solvent reverses.
- In RO, pure water is separated from contaminants rather than removing the contaminants.
- Also known as super-filtration or hyper-filtration





Reverse osmosis - method

- Pressure applied is around 15 to 40 Kg /cm^2
- Both ionic and non-ionic impurities are left behind
- Membranes are made of cellulose acetate, poly methacrylate, polyamide polymers

Advantages

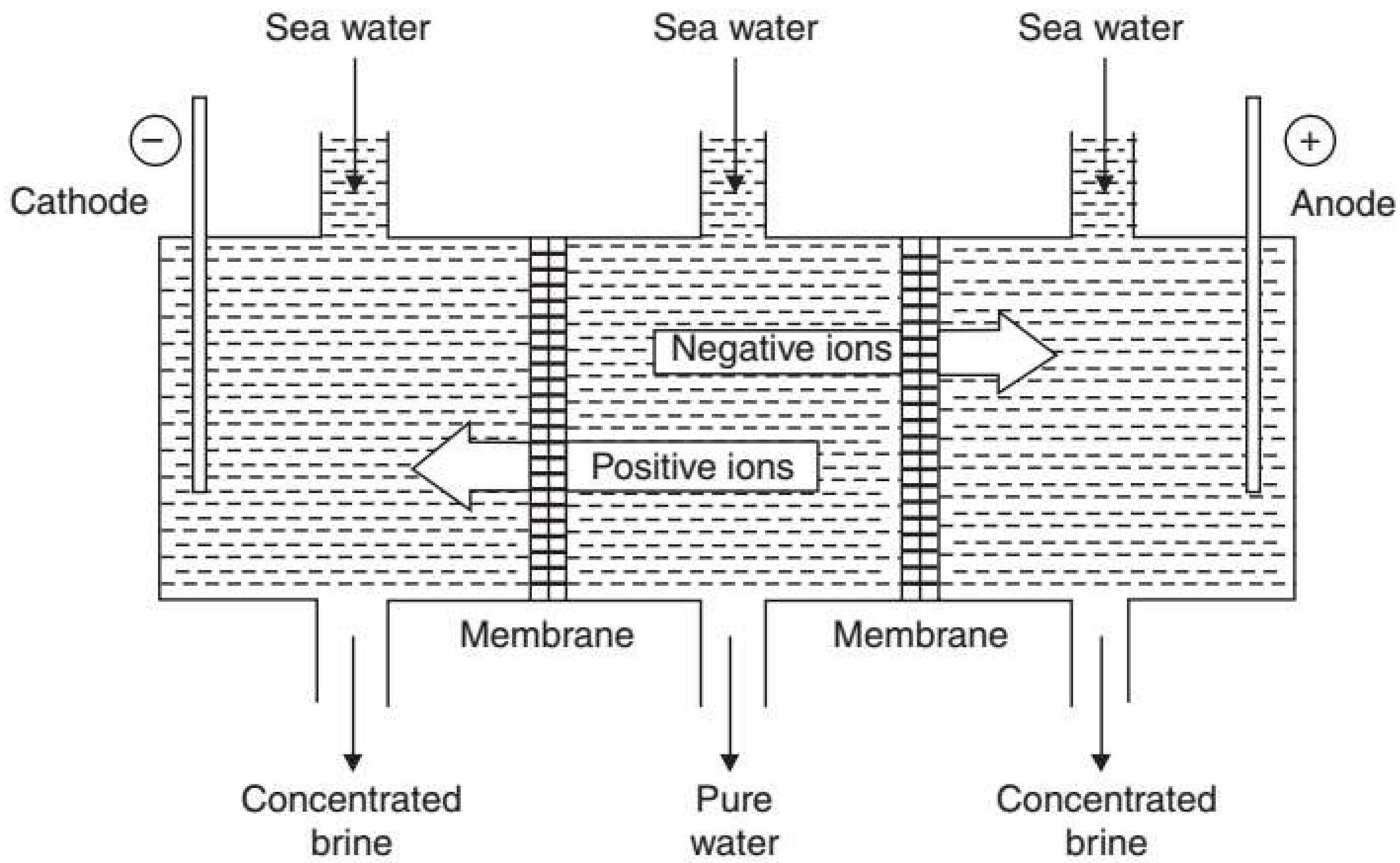
- All sorts of impurities are removed- ionic, non-ionic, high molecular organic matter, particles, dyes and bacteria
- Colloidal silica, which is not removed by other methods, is easily removed by RO
- Replacing the membrane is almost the only maintenance required
- Life of the membrane is high (~2 years) and can be replaced in minutes

Semipermeable membranes are fragile:

- Hard water can clog membrane
- Chlorine can destroy membrane
- Membrane must be rinsed regularly to prevent scaling
- Prefiltration usually required

Electrodialysis

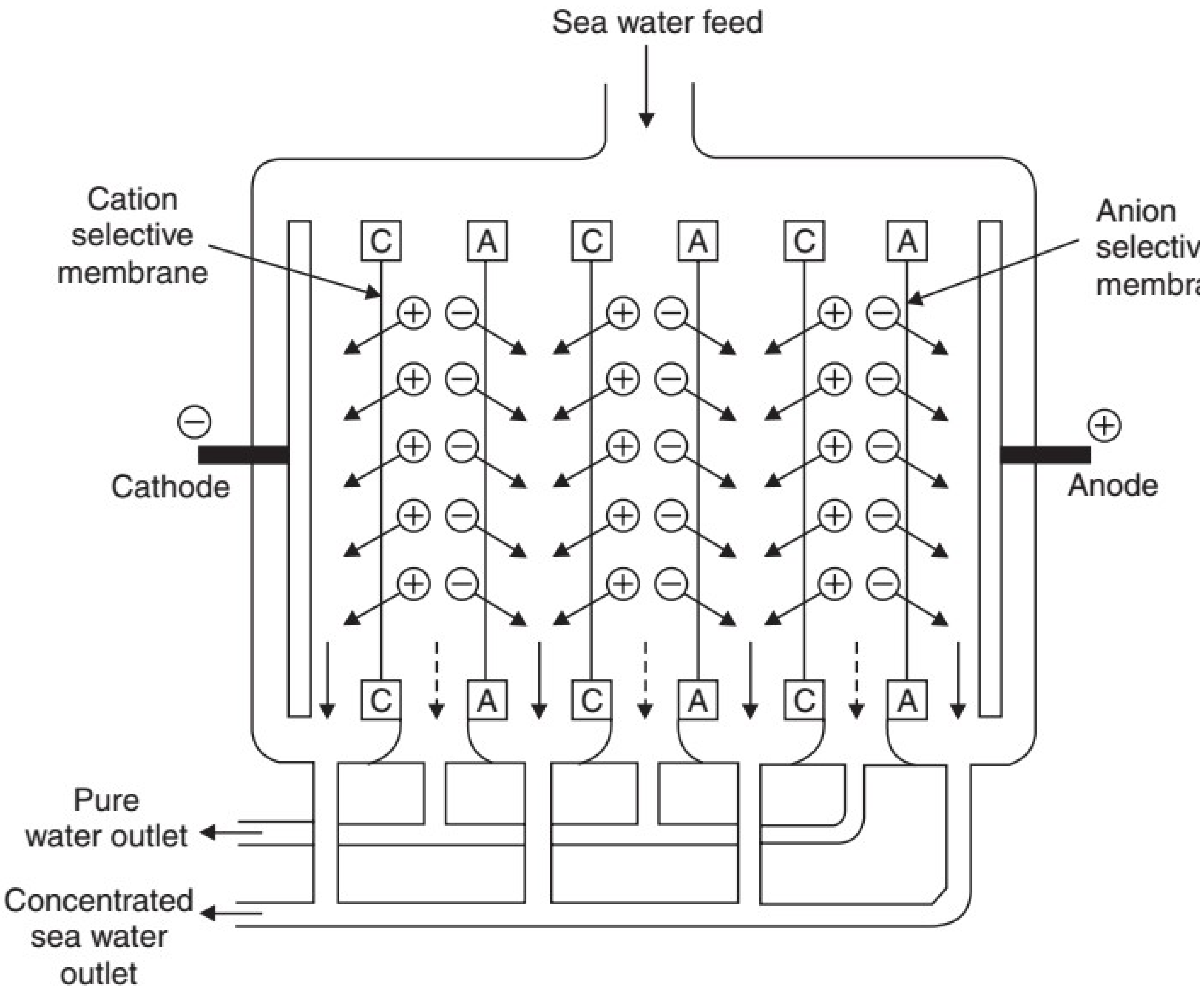
- Ions are transported through ion-permeable membranes from one solution to another under a potential gradient (DC)
- On passing DC, Na^+ ions move towards the cathode (negative electrode) and Cl^- moves towards anode ; the concentration of ions in the middle compartment decreases
- Pure water is thus removed from time to time



- Ion selective membranes are used, which have permeability to only one kind of ions of specific charge
- A cation selective membranes is permeable to only cations, due to charged functional groups (RSO_3^-, $RCOO^-$), which reject ions of same charge
- An electrodialysis cell consists of a large number of paired sets of rigid plastic membranes.
- Electric field applied perpendicular to the water flow direction

Ion permeable membranes

- They are sheets of ion-exchange resins, with other polymers for strength & flexibility
- Ions with a charge opposite to the fixed charge on the resin are freely exchanged. The free ions carry most o f the current
- Ions of opposite charge are repeled

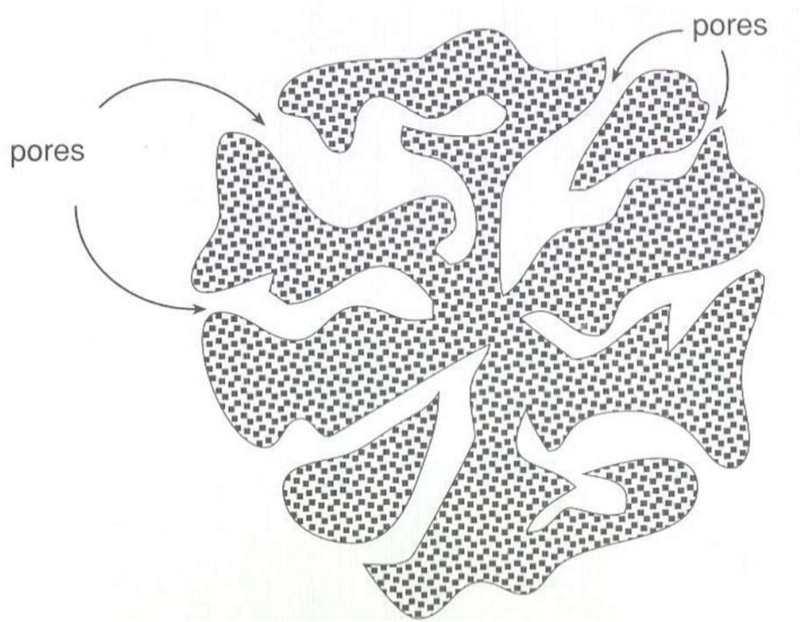

Sea water feed
Cation
selective
membrane
Anion
selectiv
membra
Cathode
Anode
C
A
Pure
water outlet
Concentrated
sea water
outlet

Activated charcoal filtration

- Activated carbon adsorption is an effective means for reducing organic chemicals, chlorine, lead, and unpleasant tastes and odors in water
- The solid material used in an activated carbon filter is typically petroleum coke, bituminous coal, lignite, wood products, coconut shell, or peanut shells, all of which are sources of carbon.
- The material is activated by subjecting it to high temperature (~1300 °F) and steam in the absence of oxygen.
- This process produces a carbon substance with many small pores and thus a very large surface area, which is then crushed to yield a granular or pulverized product
- The huge number of tiny pores in activated charcoal is very efficient in filtering off pollutants, by the phenomenon of adsorption

Effectiveness of Activated Carbon in the Removal of certain contaminants

- Bacteria, viruses.
- Cysts (*Cryptosporidium, Giardia lamblia*) that can cause respiratory problems
- Chlorine and chlorination by-products
- Color/odor
- Organic chemicals
- Petroleum/gasoline by-products
- Radon
- Volatile organic chemicals (VOCs)

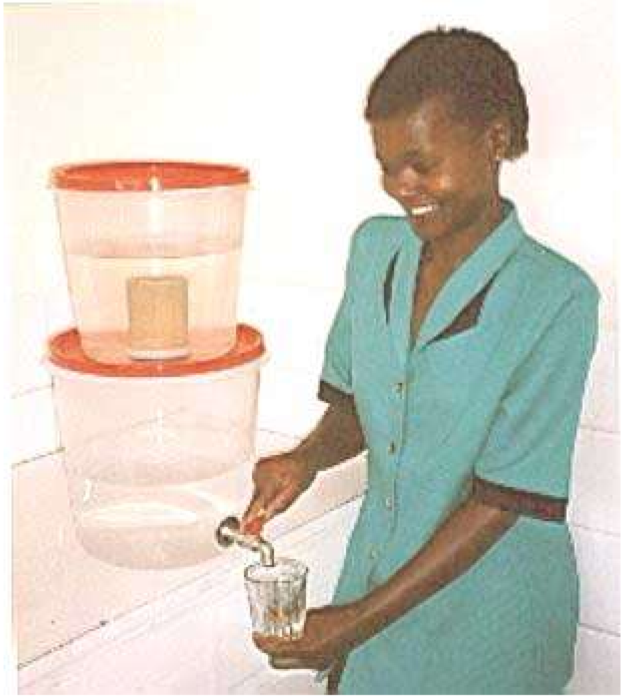


Cross-section of a carbon particle

What is a Candle Filter?

- The most common ceramic water filter.
- Looks like an upside-down candle, screwed into the base of the upper portion of a two container water filter.
- Water poured into the upper basin, where it filters through the candle and collects in the lower container.
- A ceramic filter physically traps microorganisms and other suspended contaminants in its pores.

Candle Filters



Kisii Filter bucket with
ceramic filter

Candle Filter Design

- Mix clay with water and sawdust or flour
- Compress into mold
- Heat in oven to vaporize sawdust and leave open pores
- Pore size ~ 1 – 5 micron diameter
- Can add more specialized filter material to remove fluoride, arsenic
- Doulton filters made of Diatomaceous Earth (DE) + activated carbon inside (for taste, odor)
- Often includes oligodynamic silver – kills bacteria, slows biofilm formation (bacteriostatic effect)

What is removed

- parasitic worms, cysts (Crypty, Giardia), spores, bacteria

What *isn't* removed

- Many viruses are small enough to fit through pores
  - but viruses are often charged, and adsorb to filter surfaces
- Any dissolved substances, unless they adsorb (not guaranteed) or additional filter materials are included (activated carbon)