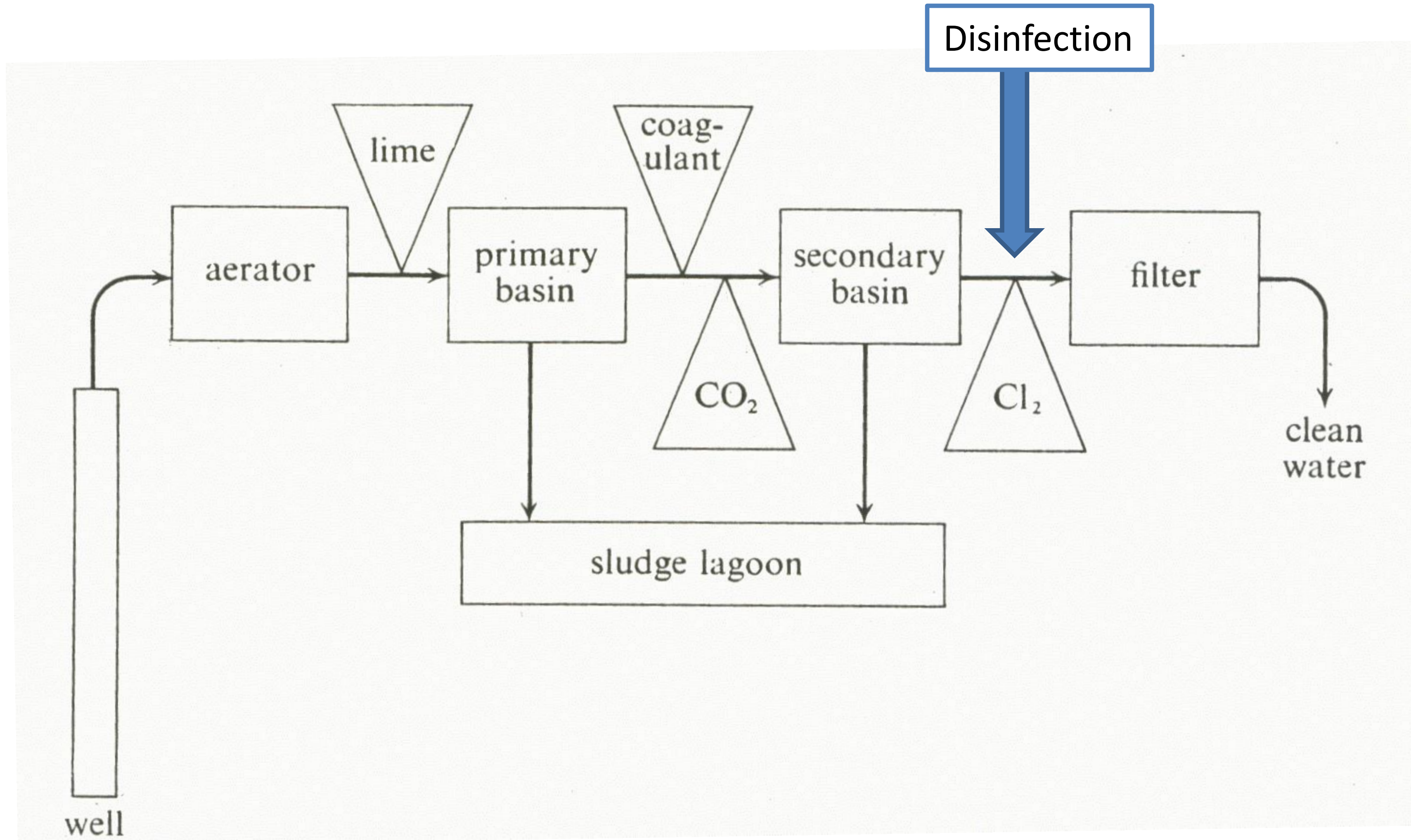
Methods of pollution control and waste management

Lecture 2

Water treatment processes (Part 2)

The main steps in water treatment



DISINFECTION OF WATER

Chlorine addition (as $Cl_{2(aq)}$)

$$Cl_2 + H_2O \rightleftarrows H^+ + Cl^- + HOCl \quad K_h = 4.5 * 10^{-4}$$

$$\underline{\color{red}{\mathbf{HOCl}}} \rightleftarrows H^+ + ClO^- \quad K_a = 2.7 * 10^{-8}$$

HOCl oxidizes enzymes in bacteria cells

Hypochlorous acid may react with compounds dissolved in water and cause subsequent reactions

A. L. Kowal, M Świderska-Bróż, Oczyszczanie wody, PWN 2009

DISINFECTION OF WATER

Chloroamines - combined available chlorine

$NH_4^+ + HOCl \rightarrow NH_2Cl + H_2O + H^+$ (monochloroamine)

$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$ (dichloroamine)

$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O$ (trichloroamine)

- NH_2Cl, $NHCl_2$, NCl_3 weaker disinfectant than chlorine (active in water distribution system)
- Chlorination with 8:1 weight ratio Cl: NH_3 denitrification

$2NH_2Cl + HOCl \rightarrow N_2 + 3H^+ + 3Cl^- + H_2O$

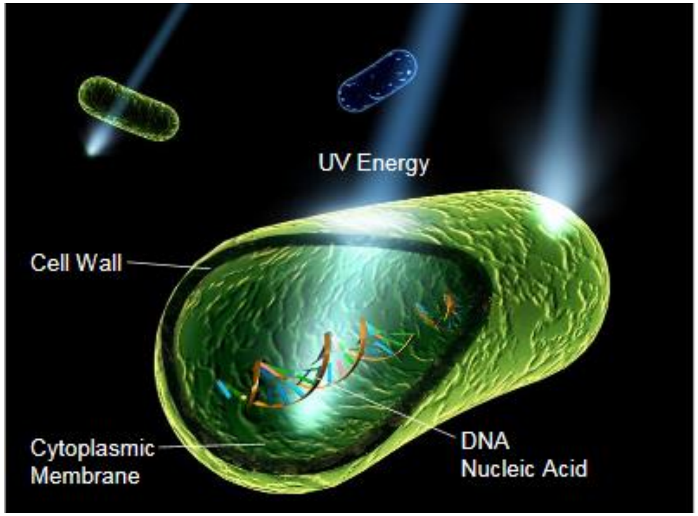
Disinfection by chlorine - disadvantages

DBPs (disinfection by-products) mainly trihalomethanes (THMs). Chlorine produces a number of by-products in the presence of organic matter in water. Among them $CHCl_3$ is the most important. Chronic chloroform exposure can damage the liver (where chloroform is metabolized to phosgene) and the kidneys.

- The THMs are carcinogenic compounds and their total concentration in drinking water should not be more than 0.1 mg/l.
- Another dangerous DBPs is the halogenated acetic acids HAAs as it may cause cancer.
- THMs and HAAs can be minimized by removing the organic matter before disinfection (for instance by using AC).
- When chlorine is added it reacts first with the reducing compounds and the chlorine will be reduced to the none effective chloride ion Cl^-

Disinfection – UV applications

How does UV disinfect?

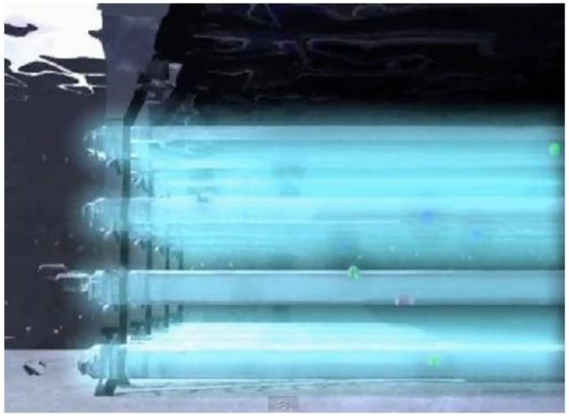


- UV light at the 254 nm wavelength penetrates the cell wall of the microorganism
- The UV energy permanently alters the DNA structure of the microorganism in a process called thymine dimerization

- The microorganism is “inactivated” and rendered unable to reproduce or infect

- Effective for protozoa, bacteria and viruses

UV disinfection – advantages and disadvantages



- No hazardous chemicals storage
- No known byproducts
- Not affected by temperature and pH
- Requires short time (seconds vs. minutes)

  smaller contact chamber
- No danger overdosing
- Higher Equipment cost
- No disinfectant residual (non-active in water distribution system)
- Not as effective for certain viruses

Ozone as disinfectant

- O_3 that is typically produced on-site by electrical discharge into high pressure O_2 vessels is another disinfectant

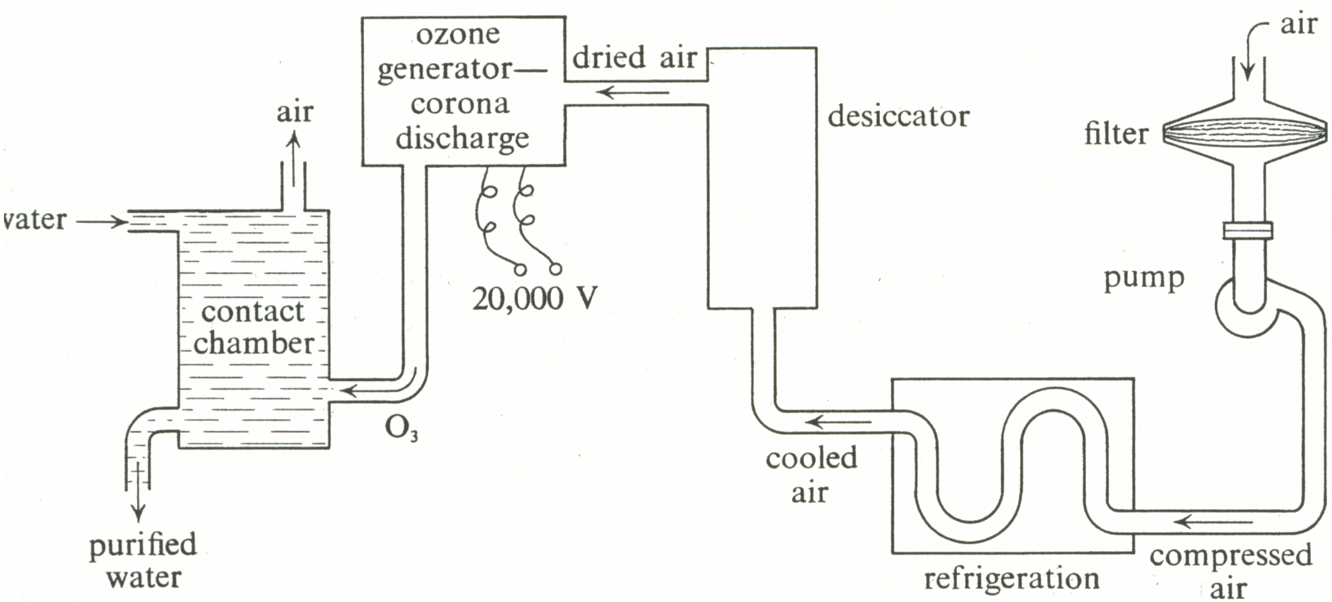


FIGURE 8.4 A schematic diagram of a typical ozone water-treatment system. *

*S. E. Manahan „Environmental Chemistry" Brooks/Cole Publishing Company , 1984

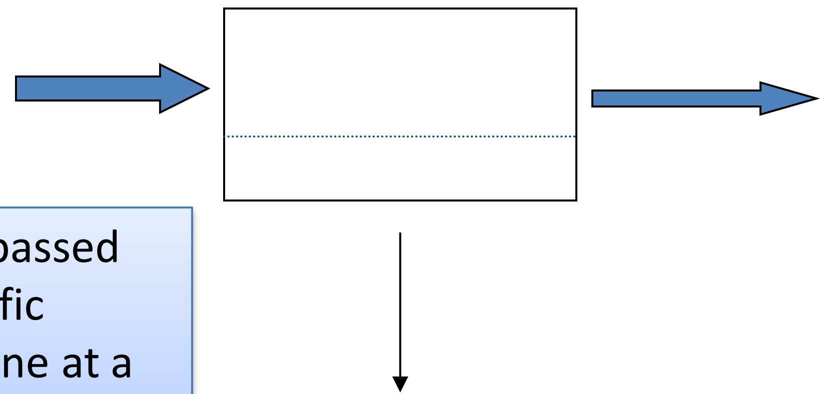
DISINFECTION OF WATER

O_3 as a disinfectant

- More destructive for viruses than chlorine, does not produce halocarbons,but
- costly, solubility of ozone in water is relatively low,
- decomposes spontaneously in water,
- some chlorine must be added.

Membrane methods in water treatment

Feed



RETENTATE

The solution/mixture is passed over the surface of specific semipermeable membrane at a pressure which called transmembrane pressure TMP

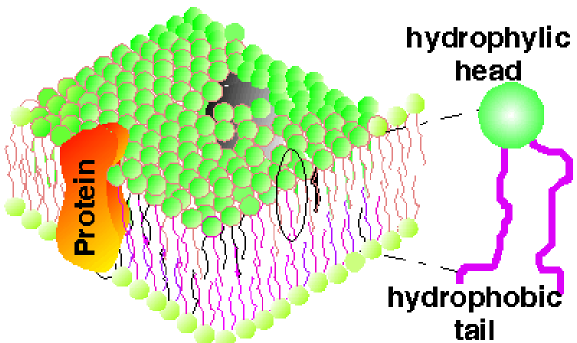
The concentrated feed

PERMEATE

The permeating liquid is collected as the product usually it is purified water

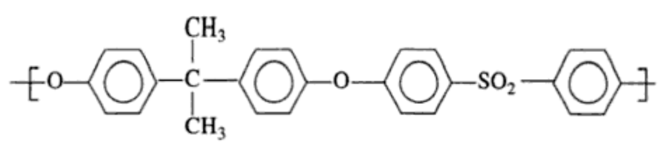
Membrane

Biological

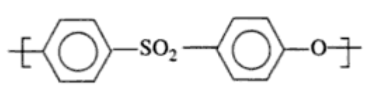


Synthetic

Polymeric



Polysulfone (PSf)



Polyethersulfone (PES)

Inorganic

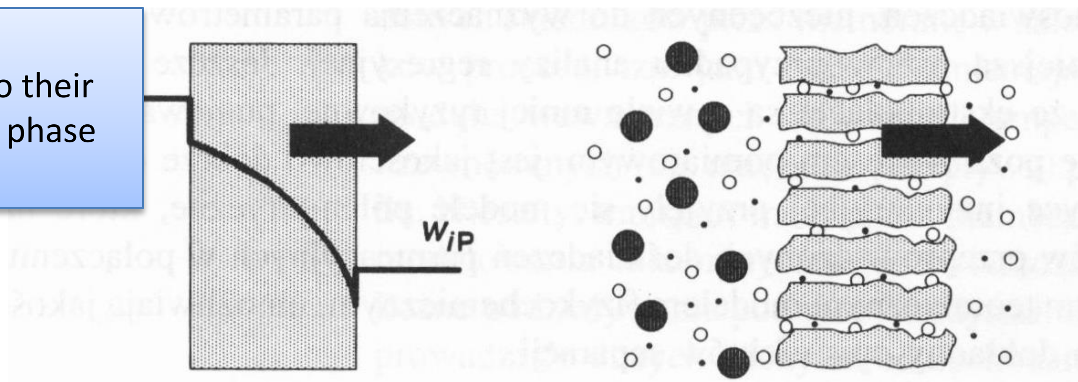
Ceramic membranes

Alumina, Al_2O_3
Zirconia, ZrO_2
Titania, TiO_2
Silicium Carbide SiC

Membrane methods in water treatment

Homogeneous membrane **Porous membrane**

The separation of components related to their transport rates within phase of membrane.



Membrane retains particles larger than pore size.

Reverse osmosis
Nanofiltration

Microfiltration
Ultrafiltration
Dialysis

‚cut-off' is defined as the molecular weight which is 90% rejected by the membrane

Driving Forces in Membrane Methods

ΔP	Δc	ΔT	ΔE
Microfiltration	Pervaporation	Thermo-osmosis	Electrodialysis
Ultrafiltration	Gas separation	Membrane distillation	Electro-osmosis
Nanofiltration	Vapour permeation		Membrane electrolysis
Reverse osmosis	Dialysis		
Piezodialysis	Diffusion dialysis		

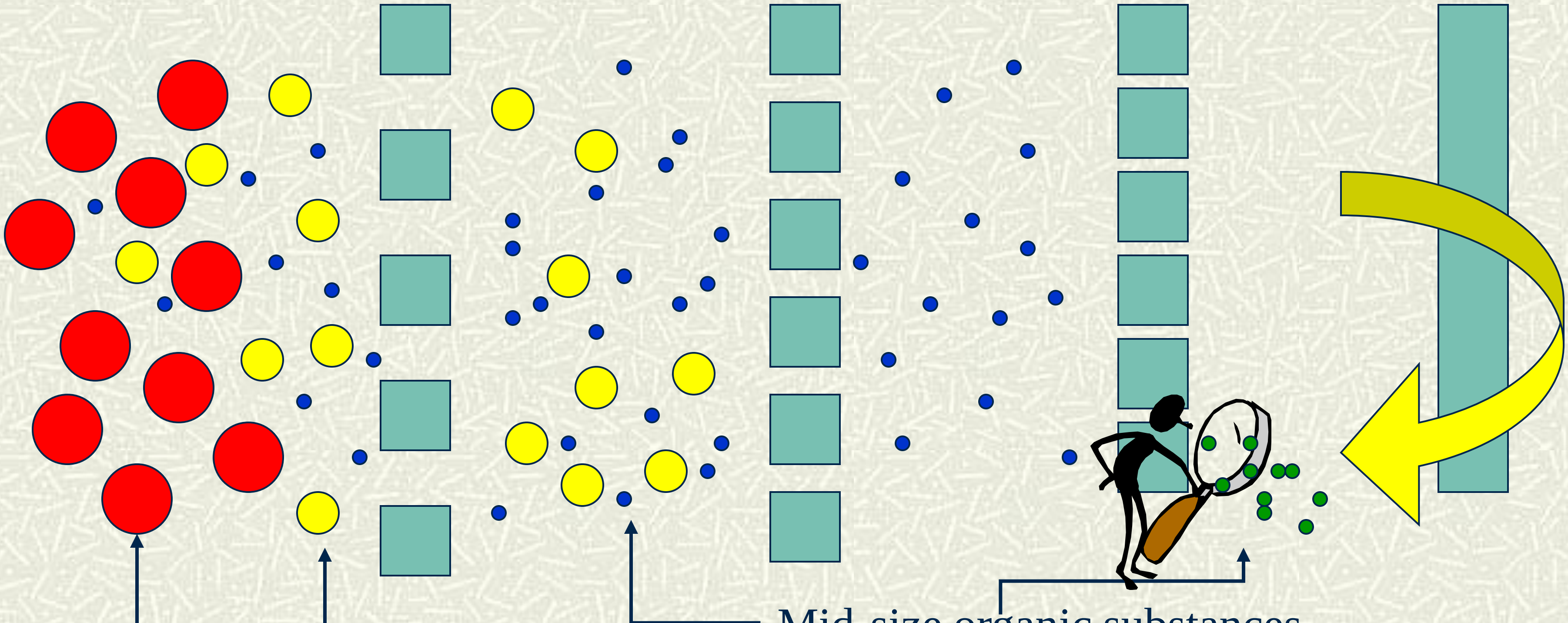
Filter type	Symbol	Pore Size, μm	Operating Pressure, psi	Types of Materials Removed
Microfilter	MF	1.0-0.01	<30	Clay, bacteria, large viruses, suspended solids
Ultrafilter	UF	0.01-0.001	20-100	Viruses, proteins, starches, colloids, silica, organics, dye, fat
Nanofilter	NF	0.001-0.0001	50-300	Sugar, pesticides, herbicides, divalent anions
Reverse Osmosis	RO	< 0.0001	225-1,000	Monovalent salts

1 psi = 0,0680 atm

http://web.evs.anl.gov/pwmis/techdesc/membrane/index.cfm

Pressure driven processes

$\Delta P=$	MF	UF	NF	RO
	10-300 kPa	50-500 kPa	0.5-1.5 MPa	0.5-1.5 MPa



Bacteria, parasites, particles

Mid-size organic substances,
multiple charged ions

single charged ions

Membrane methods in water treatment

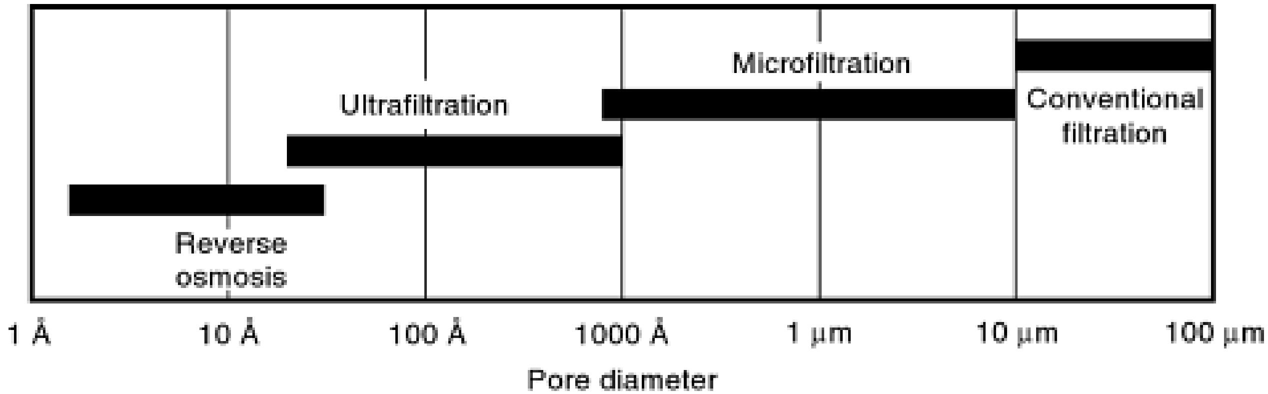


Figure 1.2 Reverse osmosis, ultrafiltration, microfiltration, and conventional filtration are related processes differing principally in the average pore diameter of the membrane filter. Reverse osmosis membranes are so dense that discrete pores do not exist; transport occurs via statistically distributed free volume areas. The relative size of different solutes removed by each class of membrane is illustrated in this schematic

R. W Baker „Membrane technology and applications" Wiley, 2004

Transport equations

The Hagen-Poiseuille and the Kozeny-Carman equations can be applied to demonstrate the flow of water through membranes. The use of these equations depends on the shapes and sizes of the pores.

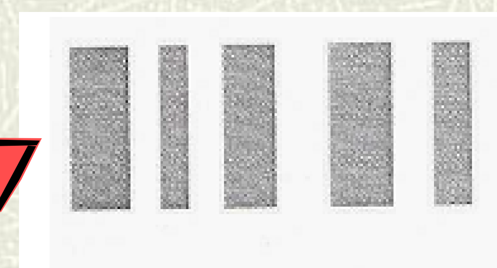
1. Hagen-Poiseuille

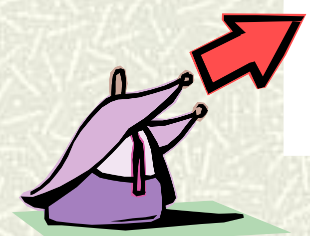
J – the solvent flux
ΔP – pressure difference
Δx – thickness of membrane
τ– tortuosity
η – viscosity
r – the pore radius
ε – surface porosity

$$J = \frac{\varepsilon \cdot r^2}{8\eta\tau}\frac{\Delta P}{\Delta x}$$

Flux is proportional to TMP and inversly proportional to the thickness

cylindrical pores



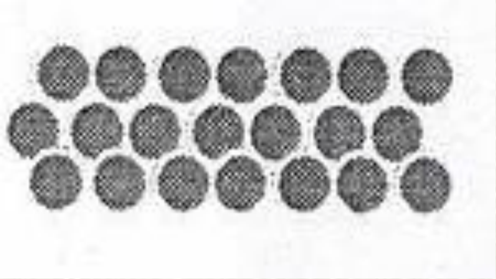


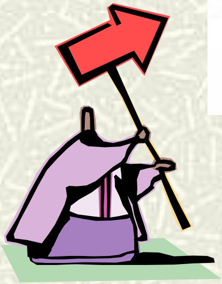
Transport equations

2. Kozeny-Carman

$$J = \frac{\varepsilon^3}{K\eta S^2}\frac{\Delta P}{\Delta x}$$

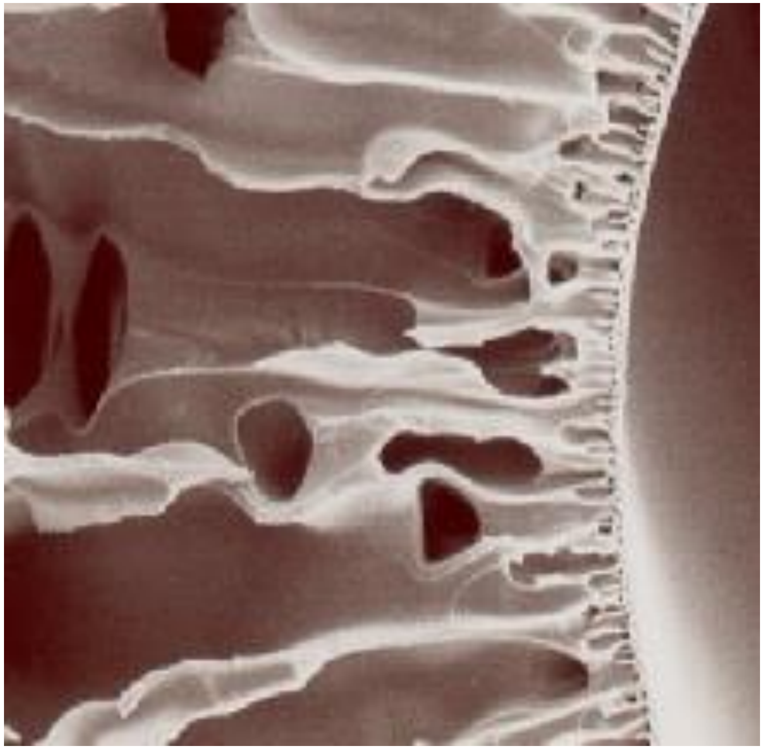
closely packed spheres





S – surface area per unit volume
K – Kozeny-Carman constant
(depends on the pore geometry)

Asymmetric membrane



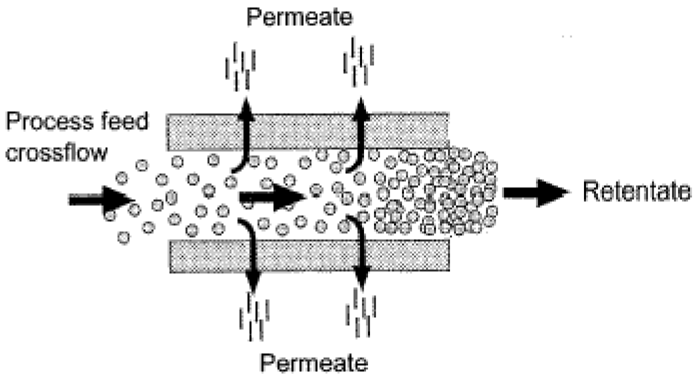
Cross-section of asymmetric membrane

The assymetric membrane consists of two layers, each with different structures and permeabilities has a relatively dense, extremely thin surface layer (i.e. the "skin", also called the permselective layer) supported on an open, much thicker porous substructure

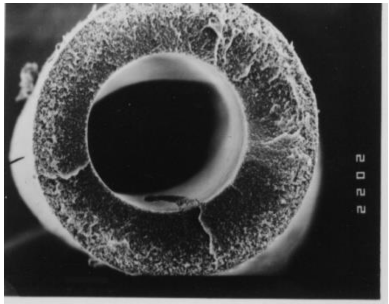
http://www.cnr.it/sitocnr/Iservizi/Edizioni/Catalogopubblicazioni/

Membrane methods in water treatment

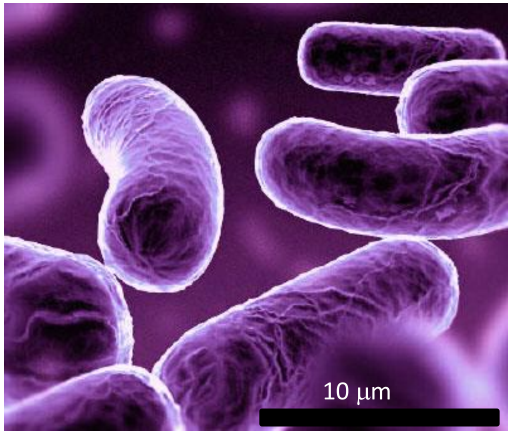
- Microfiltration (MF) and Ultrafiltration (UF) in removal of pathogens



•A membrane is a thin material that has pores (holes) of a specific size
•Membranes trap larger particles that won't fit through the pores of the membrane, letting water and other smaller substances through to the other side
•Membranes for MF have pores 1.0-0.01μm, for UF 0.01-0.001 μm
•The pressure TMP for MF < 3 bars, UF < 10 bars



Photomicrograph of a hollow fiber/capillary membrane



Bacillus bacterium Gram-positive

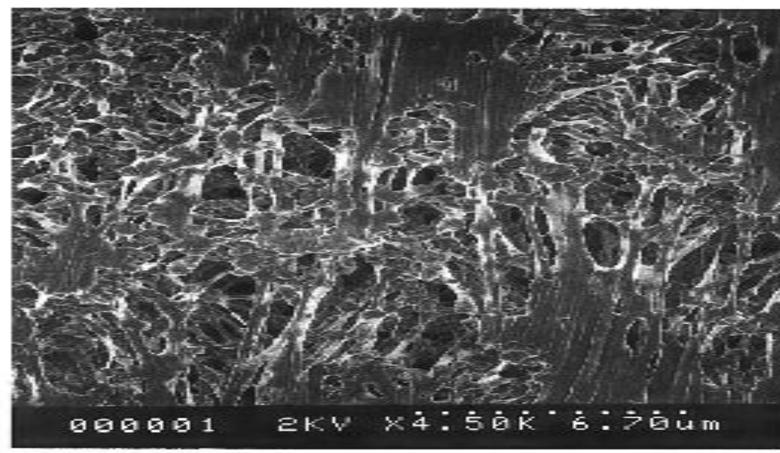
J. Dittrich, R.Gnirss, A. Peter-Frohlich,E. Sarfert, Wat. Sci. Tech. 1996, 34, 125.; http://www.turbosquid.com/FullPreview/Index.cfm/ID/274625

Microfiltration

- Types of materials which can be removed:

clay, bacteria, large viruses, suspended solids

Microfiltration water plant, USA



A microfilter membrane (image from SEM)

http://www.waterworksmw.com/rack%201%20&%202b.jpg http://www.imc.cas.cz/sympo/41micros/Image126.gif

Ultrafiltration

Types of materials which can be removed:
viruses, proteins, starches, colloids, silica
Does not filter ionic particles like lead, iron, chloride ions; nitrates, nitrites; other charged particles

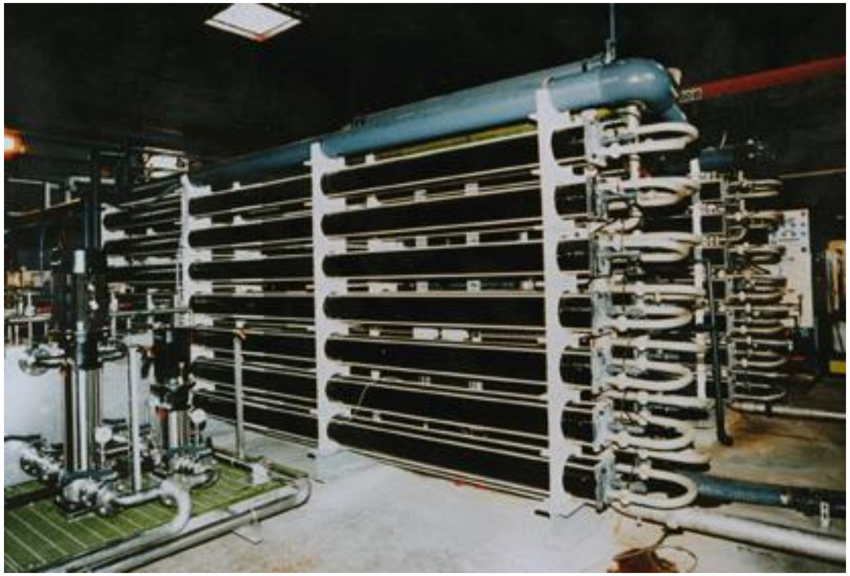
An ultrafiltration plant in Jachenhausen, Germany

http://www.inge.ag/bilder/presse/bildmaterial/referenzen/jachenhausen.jpg

Why Choose Membrane Filtration?

- Effective barrier to bacteria and viruses
- Can reduce/delete problem DBPs
- Cost-competitive to conventional treatment
- Better quality of obtained water than conventional treatment
- Highly-automated methods and easy to operate

Nanofiltration (NF)



Nanofiltration water cleaning serving Mery-sur-Oise, a suburb of Paris, France

Ion-exchange membrane with typical pore size 1nm

Cation-exchange group SO_3H, COOH, AsO_3H

Anion-exchange group NR_3^+, NR_2H^+, NH_3^+

Degree of the ion retain in the following order

$$NO_3^- < Cl^- < OH^- < SO_4^{2-} < CO_3^{2-}$$

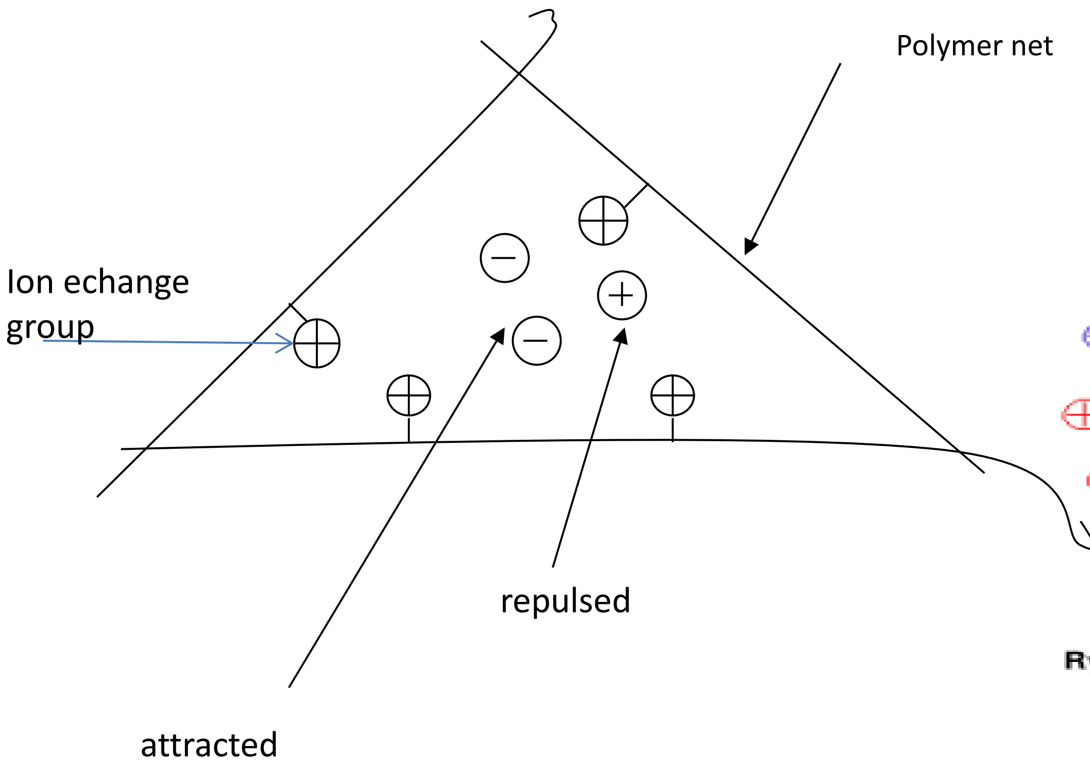
$$H^+ < Na^+ < K^+ < Ca^{2+} < Mg^{2+} < Cu^{2+}$$

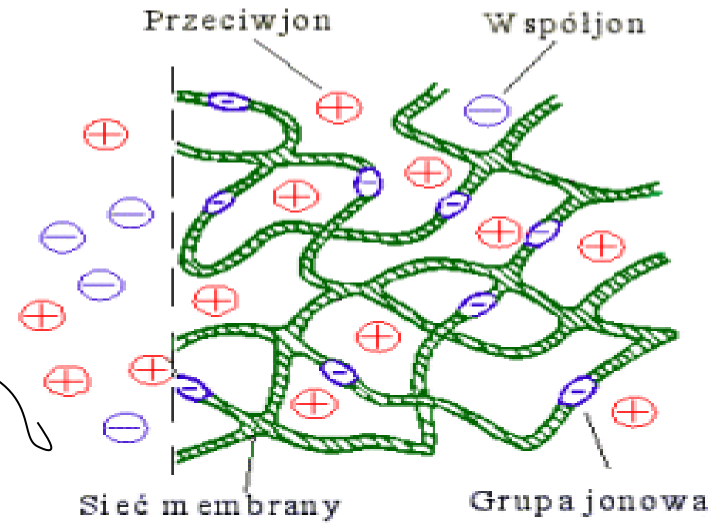
NF can be used in water softening proces and removing of toxic or unwanted bivalent ions (ions with 2 or more charges), such as lead, iron, nickel, mercury (II)

Cut-off $\cong$ 500 Da   TMP = 5 -30 bar

http://www.wateronline.com/crlive/files/Images/10899070-E891-11D3-8C1F-009027DE0829/newwater1.gif

Nanofiltration (NF)





Rys. 1. Membrana kationoselektywna w kontakcie z zewnętrznym roztworem elektrolitu

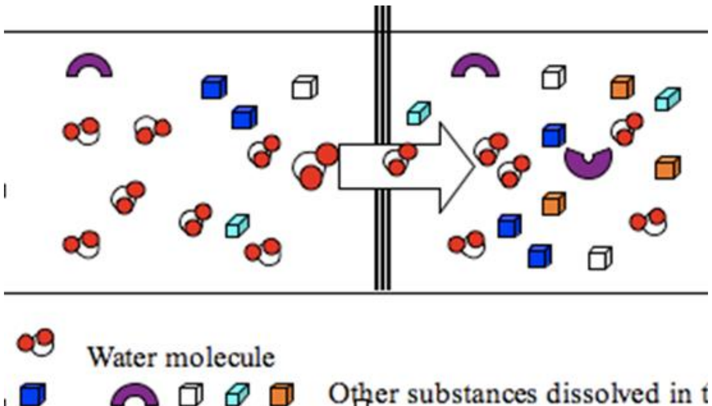
Membrane methods in water treatment

Nanofiltration and lime-soda method in water treatment

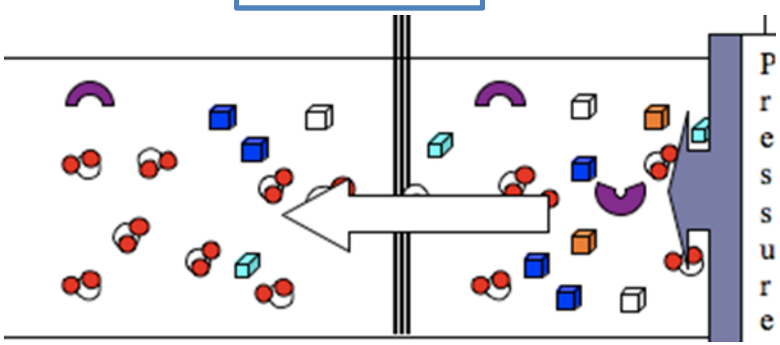
Parameter mg/dm^3	Raw water	Lime-soda method	NF	WHO requirements
Ca^{2+}	91	18	12	
Mg^{2+}	5	4	2	
Na^{+}	16	16	7	200
K^{+}	0	0	0	
Fe^{3+}	0.3	0.02	0.02	0.3
HCO_3^{-}	264	33	23	
CO_3^{2-}	0	4	0	
Cl^{-}	35	35	15	250
SO_4^{2-}	17	17	4	400
pH	7.2	9.3	7.4	

Praca zbiorowa pod red. Anny Narębskiej ”Membrany i membranowe techniki rozdziału” Uniwersytet Mikołaja Kopernika , Toruń, 1997

Osmosis and Reverse osmosis



Osmosis



Reverse Osmosis

TMP ≅ 10 – 200 bar

Osmosis is a natural process that moves water across a semipermeable membrane, from an *of low* solute concentration *to an area of greater concentration* until the concentrations are equal

To move water from a *more concentrated area to a less concentrated area* requires high pressure to push the water in the opposite direction that it flows naturally

Reverse osmosis

Very high pressures are required to desalination of seawater using RO.

Salty water cannot support life. People can’t drink it and plants can’t use it to grow.

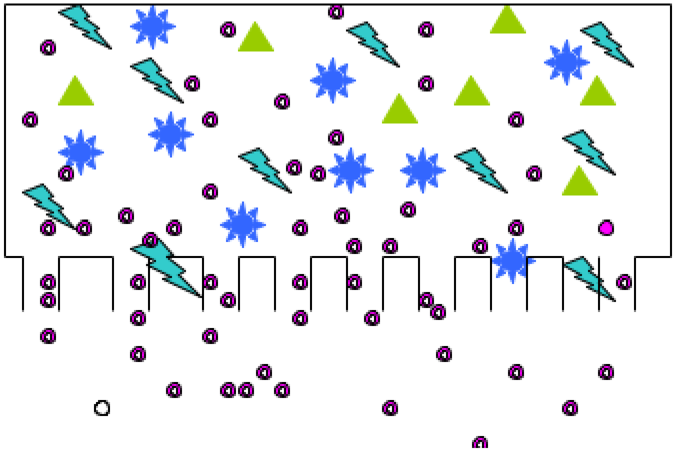
Reverse osmosis is the most expensive membrane filtration system.

Reverse osmosis (or desalination) water treatment plants, like this one, are often located close to the ocean

http://iclaro.com/users/18342/pictures/Desalination%20Plant.jpg

Reverse osmosis

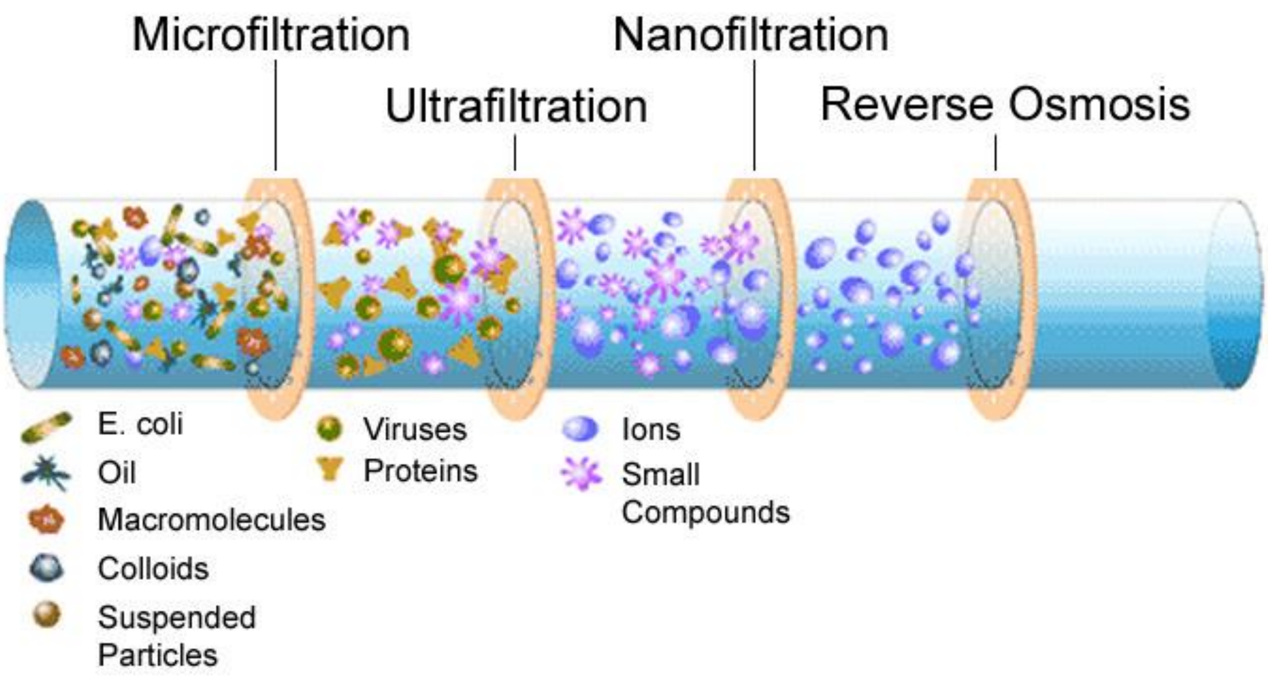
Fouling of RO membranes



Pores clogged with large objects
This makes the filtering membrane unusable

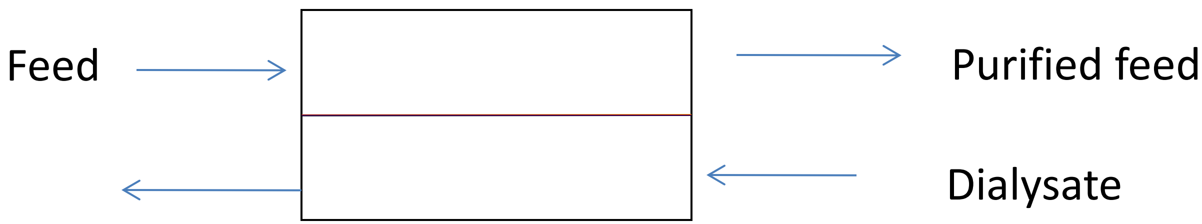
Series of membrane filtration

- Filters can be sequenced from large to small pore size to decrease fouling and they must still be cleaned regularly to remain usable



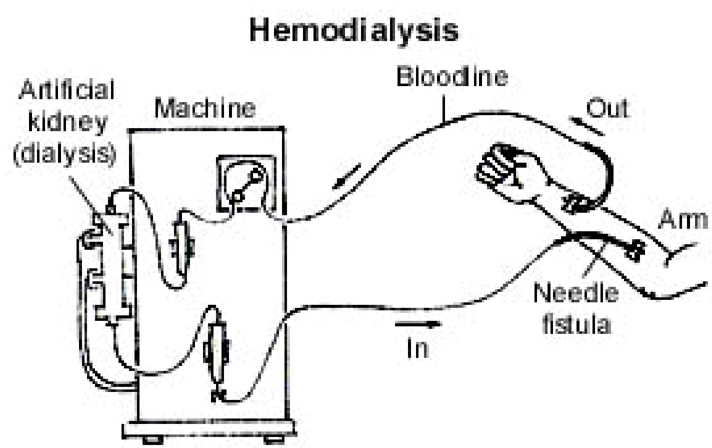
http://www.alting.fr/images/cross_flow_details.gif

Dialysis



Dialysis is a membrane process where solutes (MW~<100 Da) diffuse from one side of the membrane (feed side) to the other (dialysate or permeate side) according to their concentration gradient.

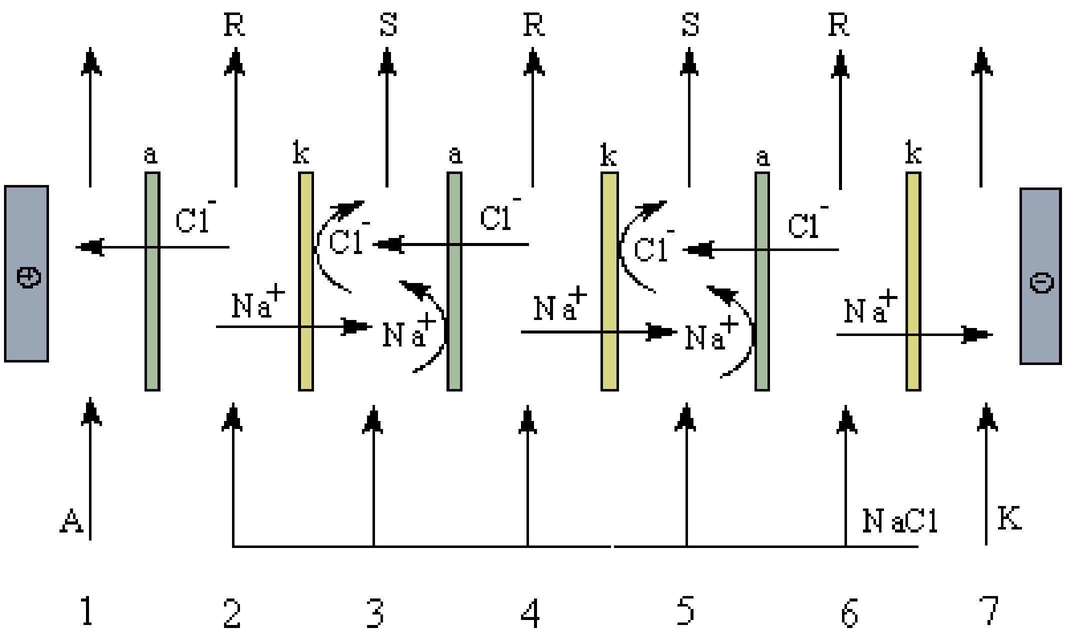
The most known application of membrane methods is hemodialysis



Removing waste products such as creatinina and urea from the blood when the kidneys are in renal failure.

Praca zbiorowa pod red. Anny Narębskiej ”Membrany i membranowe techniki rozdziału” Uniwersytet Mikołaja Kopernika , Toruń, 1997

Electrodialysis

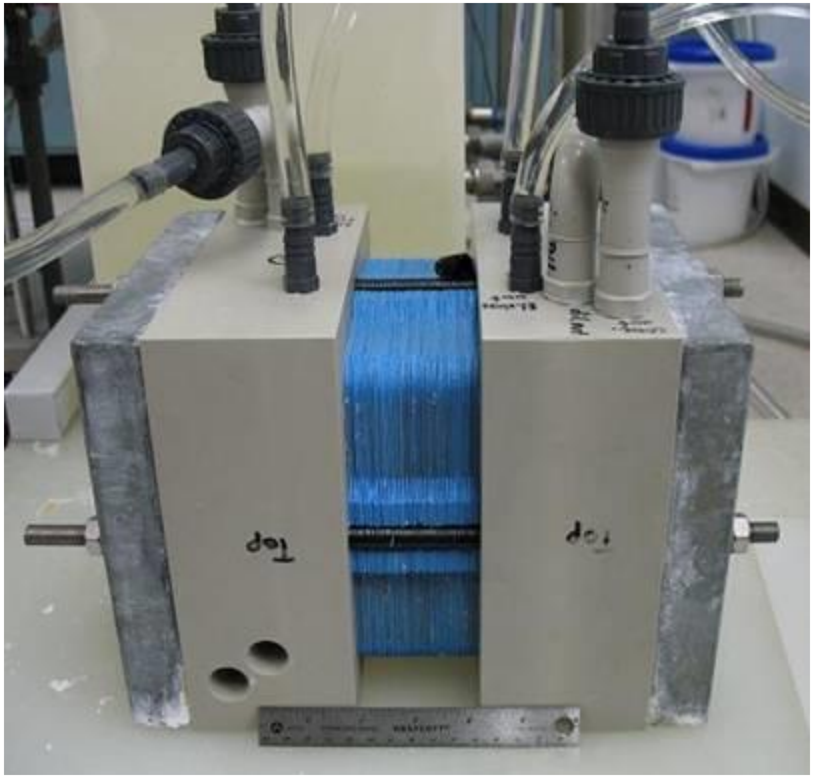


R diluate; S – concentrate; k-cation exchange membrane;
a – anion exchange membrane ; A – anode solution; B –catode solution

Electrodialysis is a membrane process in which ions are transported through ***ion permeable membranes*** from one solution to another under the influence of an electrical potential gradient. Hundreds of anionic and cationic membranes placed alternatively.
First applications in the 30's.

Praca zbiorowa pod red. Anny Narębskiej "Membrany i membranowe techniki rozdziału" Uniwersytet Mikołaja Kopernika , Toruń, 1997

Electrodialysis



Ion Permeable Membranes

- Non porous
- Sheets of ion-exchange resins and other polymers
- Thickness 100 - 500 μm

Anion - exchange positively charged groups
Cation – exchange negatively charged groups

Application: large scale brackish and seawater desalination and salt production