Environmental Management

Experiment 14

Membrane methods in wastewater treatment

Theoretical material

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1. Classification of membrane methods.

There are many ways of division of membrane methods but the most often used is based on the membrane structure thus on the basis of driving force of this process.(Table 1) Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are classified as pressure driven processes are commonly used in liquid mixtures separation. (Table 2)

The separation of components in membrane techniques is based on selectivity of the membrane. The solution/mixture called as Feed is passed over the surface of specific semipermeable membrane at a pressure which called transmembrane pressure TMP. The permeating liquid is collected as the product usually it is purified water and concentrated feed is obtained which is called Retentate. (Figure 1)

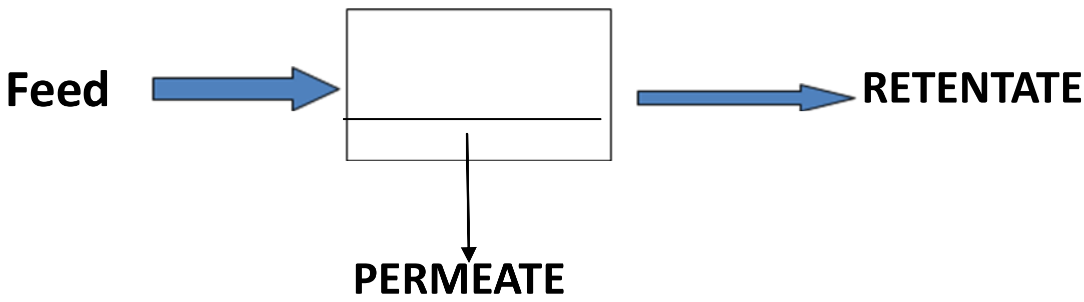


Figure 1. Flow diagram for membrane techniques.

Table 1

Driving forces in membrane methods

Pressure difference ΔP	Concentration difference ΔC	Temperature difference ΔT	Electric potential difference ΔE
Microfiltration (MF)	Pervaporation (PV)	Thermo-osmosis (TO)	Electrodialysis (ED)
Ultrafiltration (UF)	Gas separation (GS)	Membrane distillation (MD)	Electro-osmosis (EO)
Nanofiltration (NF)	Dialysis (D)		Membrane electrolysis (ME)
Reverse osmosis (RO)	Diffusion Dialysis (DD)		

The applied transmembrane pressure (TMP) depends on the kind of technique from 0.05-0.5 MPa in the microfiltration to 1-10 MPa in the reverse osmosis. (see Table 2). Membrane methods are environmentally friendly however yield of these methods is relatively low which was illustrated on Figure 1 in the form of a thin arrow for permeate flow. Table 2 shows what kind of materials can be removed from water with using pressure driven membrane methods. Bacteria and large viruses can be removed with using microfiltration, colloids, proteins with using ultrafiltration, organics compounds and divalent ions with using nanofiltration and completely desalination of water is possible with using reverse osmosis.

Table 2

Pressure driven membrane processes.

Technique	Pore size in membrane [μm]	TMP [MPa]	Types of materials removed
MF	1 – 0.01	0.05 – 0.5	Bacteria, yeasts clay, large viruses, suspended solids
UF	0.01 – 0.001	0.1 - 0.7	Proteins, viruses, fats, sillica, colloids
NF	10^{-3} – 10^{-4} (~1 nm)	0.3 – 2.4	Pesticides, sugars, herbicides, multivalent ions
RO	< 10^{-4}	1.5 – 7.0	Monovalent ions

2. Membrane classification.

The membrane is usually defined as selective barrier which separates two phases with different concentration of components. There are different methods of classifying of membranes based on their origin, morphology, structure, electric charge.

a) Origin (Figure 2)

Biological membrane made up of bilayers of phospholipids and synthetic: organic (made up of polymers) and inorganic (made up of ceramic, carbon, glass or stainless steel).

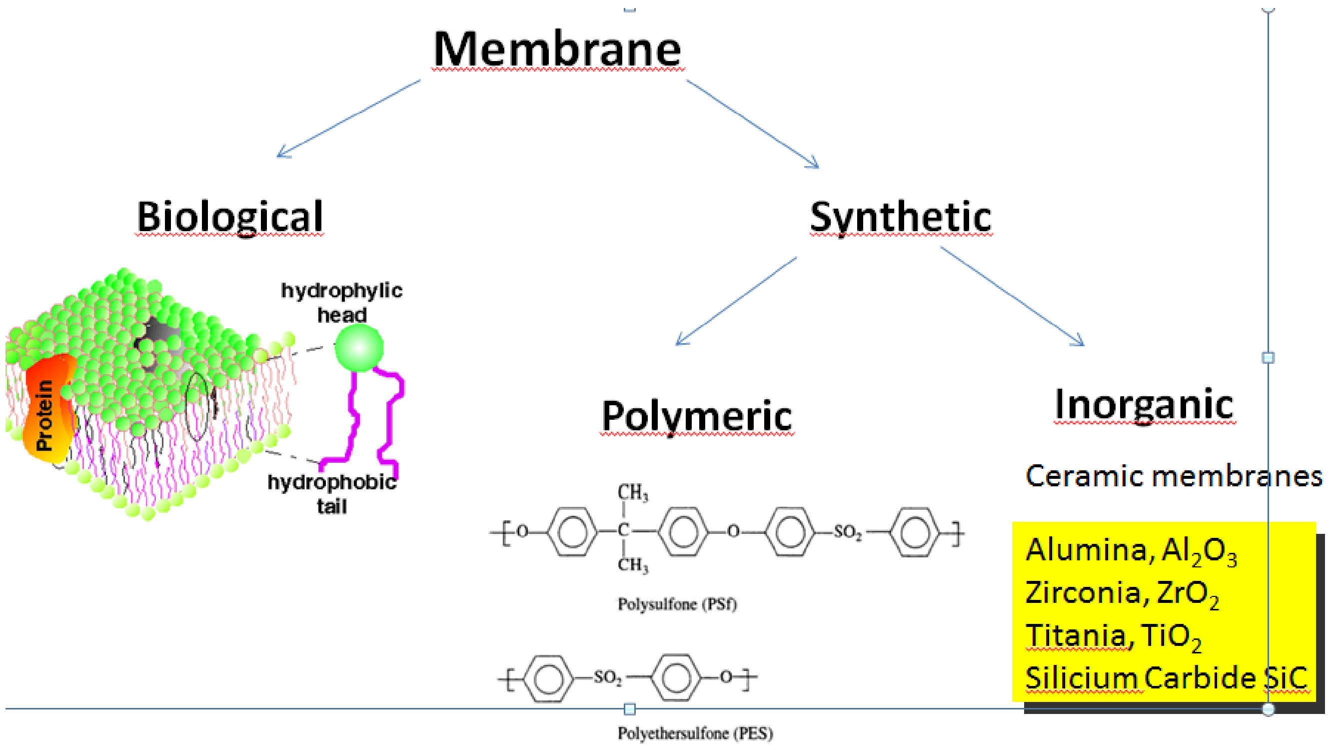


Figure 2. Types of membrane on the basis of their sources.

Polymers which are the most commonly used for obtaining of membranes are following: cellulose acetate, polysulfone, polyethersulfone, polyethylene, polyamides. Polymeric membranes are relatively cheap and easy for preparation, however are not well resistant for temperature and their physical properties worsening in relatively short time (aging of polymers phenomena). The inorganic membranes are resistant for high temperature, stable but usually characterized by brittleness, additionally capital cost for the systems with inorganic membrane is higher in comparison with system with polymeric membrane.

b) Morphology (Figure 3)

Homogeneous membrane The separation of components is related to their transport rates within phase of membrane**.** The components differ in relative diffusion rates and solubility in membrane. Homogeneous membranes are used in reverse osmosis and nanofiltration.

Porous membrane retains particles larger than pore size. This type of membrane is used in microfiltration, ultrafiltration and dialysis.

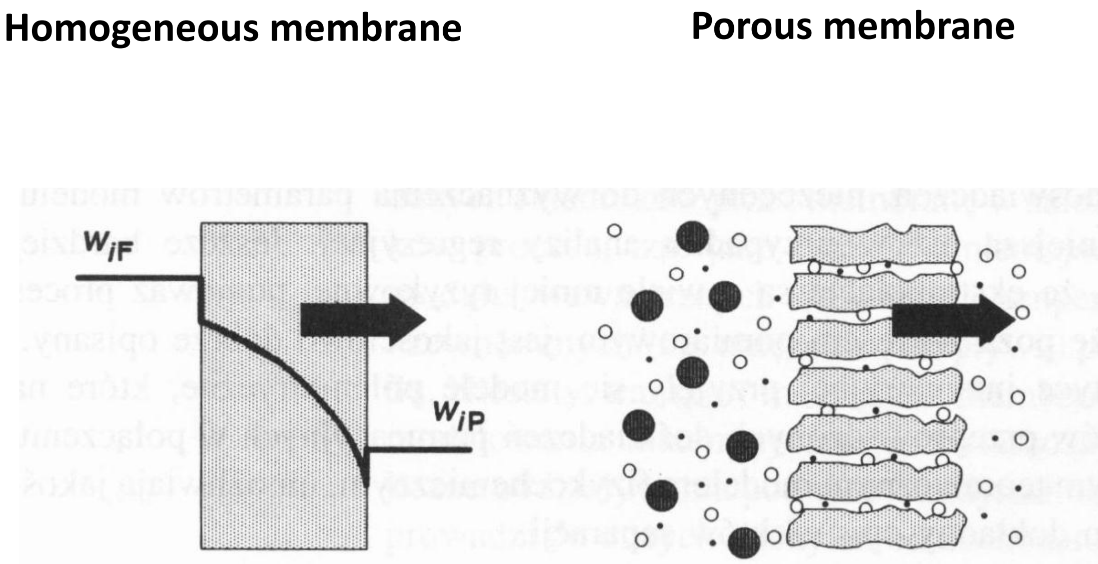


Figure 3. The models of membranes.

c) Structure

Symmetric membrane are rarely used. Typically asymmetric membranes are used on industrial scale. This type of membrane consists of two of 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. (Figure 4)

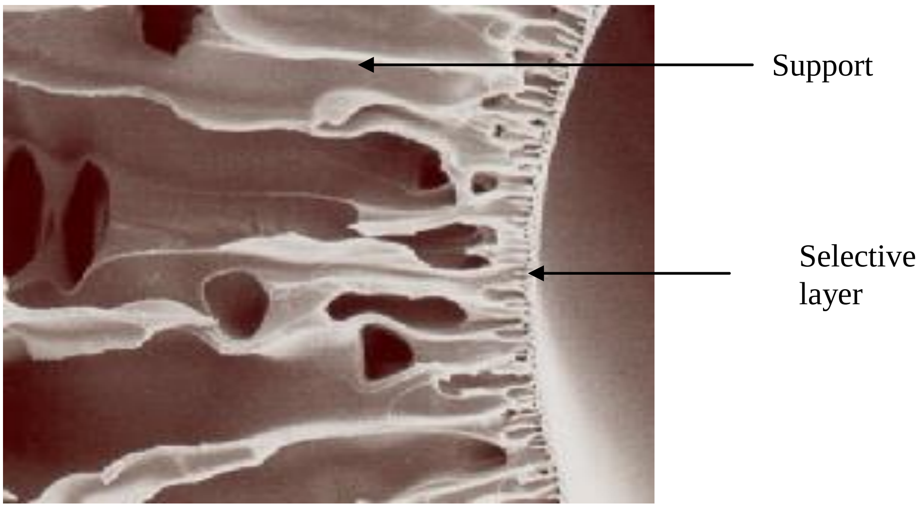


Figure 4. Cross-sectional microscopic picture (SEM) of asymmetric membrane.

d) Charge

The synthetic membranes can be neutral or charged. An ion-exchange membranes have electric charge which is positive or negative. The function of ion-exchange membranes is determined from the species of the charge of the ion-exchange groups fixed in the membranes and their distribution:

1. Cation exchange membranes, in which cation exchange groups (negatively charged) exist and cations selectively permeate through the membranes.
2. Anion exchange membranes, in which anion exchange groups (positively charged) exist and anions selectively permeate through the membranes.
3. Amphoteric ion exchange membranes, in which both cation and anion exchange groups exist at random throughout the membranes.
4. Bipolar ion-exchange membranes which have a cation exchange membrane layer and anion exchange membrane layer (bilayer membranes).
5. Mosaic ion exchange membranes, in which domains having cation exchange groups exist over cross-sections of the membranes and domains of anion exchange groups also exist. An insulator may exist around the respective domains.

Typical cation-exchange group are following SO_3H, COOH, AsO_3H and typical anion-exchange group are NR_3^+, NR_2H^+, NH_3^+. However, sulfonic acid and carboxylic acid groups are mainly used as cation exchange groups, and quaternary ammonium groups such as benzyl trimethylammonium groups and *N*-methyl pyridinium groups are mainly used as anion exchange groups in practical ion-exchange membranes.

Degree of the ions retain by ion-exchange membranes:

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

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

3. Membrane formation methods.

- For ceramic membranes a post-synthetic coking treatment method can be used in which first impregnating is performed for example with 1,3,5-triisopropylobenzene, next calcining in temperature above melting point usually > 500^0C and after this rapid cooling causes crystallites appear with microscopic pores (with size > 1 μm in diameter).

- ·For polymeric membranes mechanical stretch method can be used. Polymer foil is mechanical stretched in perpendicular directions and pores with size > 0.02 μm in diameter are obtained.
- Radiation with alpha particles (0.03μm > pores with size < 12 μm)
- Phase inversion (Loeb – Sourirajan method) - the most often used. Phase inversion refers to a process during which a homogeneous, polymer solution is converted into two phases, i.e. a solid polymer rich phase forming the rigid membrane structure and a polymer lean phase representing the liquid filled pores. Phase inversion can be induced by changing the thermodynamic properties of the system, e.g. by changing temperature or composition. Phase separation mechanisms can generally be subdivided in three main categories depending on the parameters that induce demixing. By changing the temperature at the interface of the polymer solution (temperature induced phase separation or TIPS), by reaction which causes phase separation (reaction induced phase separation) (RIPS) and by diffusion induced phase separation (DIPS) with using addition of non-solvent to homogenous solution of polymer.
- Solution coated composite membranes preparation method based on coating of microporous membrane (support) thin layer of dense non-porous membrane made from other polymer (composite membranes) by immersion of the porous membrane in solution of polymer and next evaporation of solvent.

Depending on the chosen method of membrane formation shape, size and distribution of pores can differ very significantly. (Figure 5)

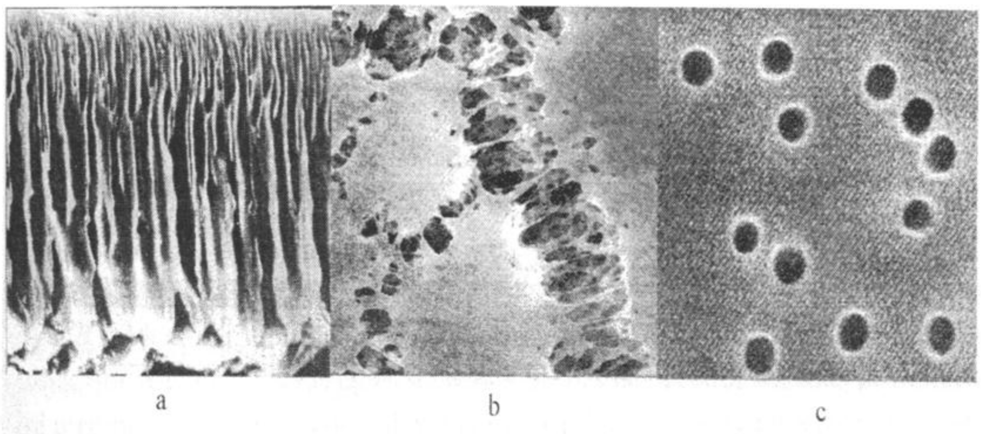


Figure 5. Cross-sectional picture of membranes formed with using methods a) phase inversion, b) mechanical stretch, c) radiation with alpha particles.

4. Selected parameters characterizing membrane process

- a) flux of permeate (yield)

J_V [m^3 s^{-1}m^2], J_N [mol s^{-1}m^2]

Flux of permeate is volume determined in cubic meters of solution or number of moles of major component which can permeate across the membrane per seconds per square meter of membrane surface

b) effectivity of separation

Retention factor:

$R = (C_F – C_p) / C_F$

Where: C_F –concentration of feed, C_p – concentration of permeate

c) Molecular weight cut off *(*MWCO) the lowest molecular weight of solute (usually given in Daltons) which is in 90% retained by the membrane or the molecular weight of the molecule that is 90% retained by the membrane determined with using polyglycols as standards.

5. Membrane modules.

Membrane module this is device in which the membrane is installed. Membrane modules must meet such requirements as their production costs, their packing density, energy consumption, and especially the control of concentration polarization and membrane fouling. A large number of different module types are described in the literature. But, on a large industrial scale mainly six basic types are used today. (Table 3)

a) The cartridge membrane module (Figure 6)

The feed solution enters the filter from the housing side and the product is collected in a center tube which is sealed against the housing by an O-ring.

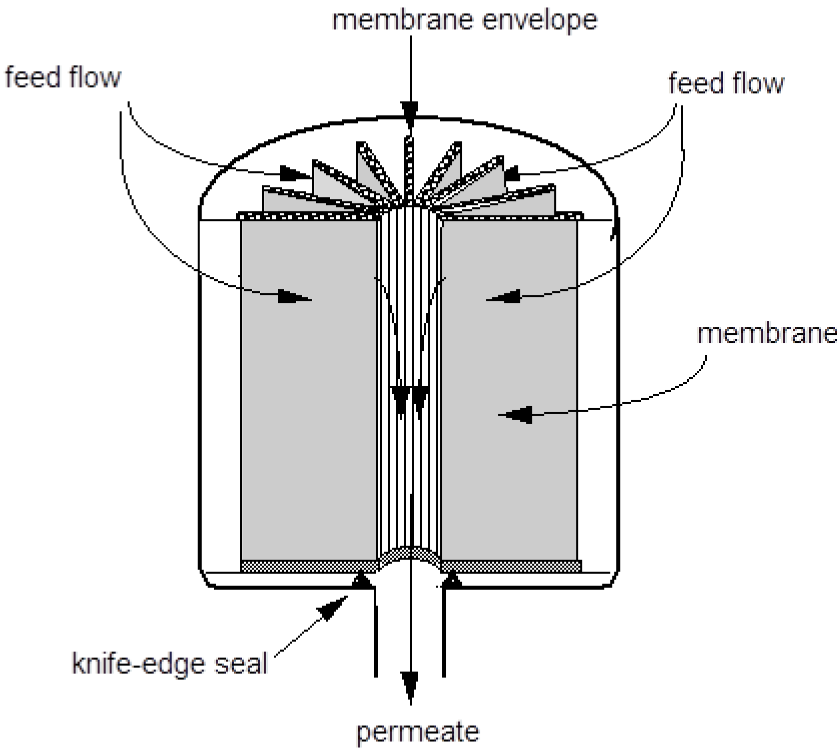


Figure 6. Scheme of cartridge filter unit

b) The plate-and-frame membrane module (Figure 7)

The design of this type of module is similar to the conventional filter press. The membranes, porous membrane support plates, and spacers forming the feed flow channel are clamped together and stacked between two endplates and placed in a housing.

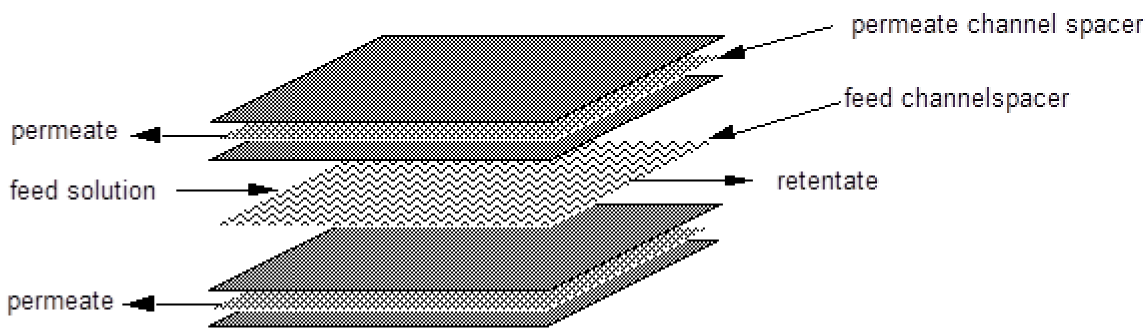


Figure 7. Scheme of a plate-and-frame membrane module

The feed solution is pressurized in the housing and forced across the surface of the membrane. The permeate is leaving the module through the permeate channel to a permeate collection manifold which in circular devices is central tube.

c) The spiral-wound module. (Figure 8)

The feed flow channel spacer, the membrane, and the porous membrane support form an envelope which is rolled around a perforated central collection tube and inserted into an outer tubular pressure shell. The feed solution passes in axial direction through the feed channel across the membrane surface. The filtrate is moves along the permeate channel and is collected in a perforated tube in the center of the roll.

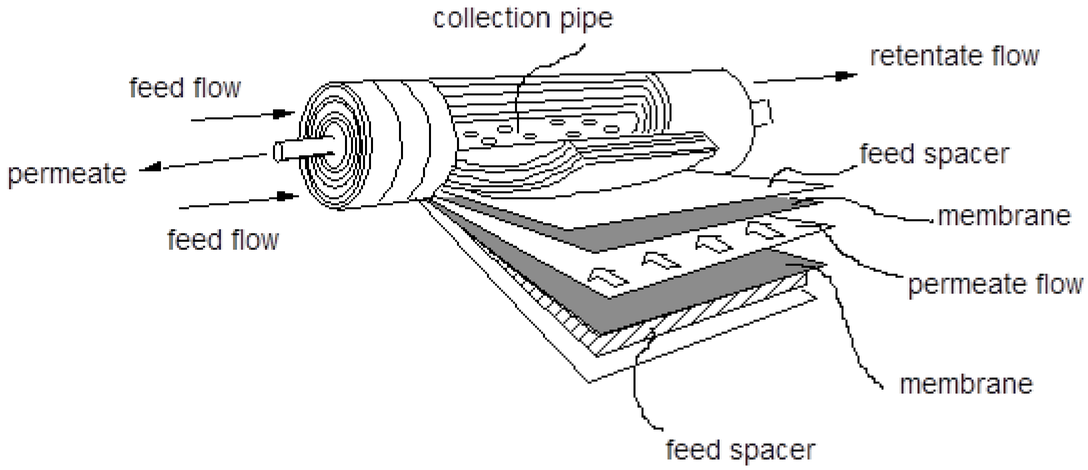


Figure 8. Scheme of a spiral-wound membrane module

The spiral-wound module provides a relatively large membrane area per unit volume. The major application of the spiral-wound module is in reverse osmosis sea and brackish water desalination. But it is also extensively used in ultrafiltration and gas separation.

d) The tubular membrane module. (Figure 9)

The tubular membrane module consists of membrane tubes placed into plastic pipes. The pressurized feed solution flows down the tube bore and the permeate is collected on the outer side of the porous support pipe.

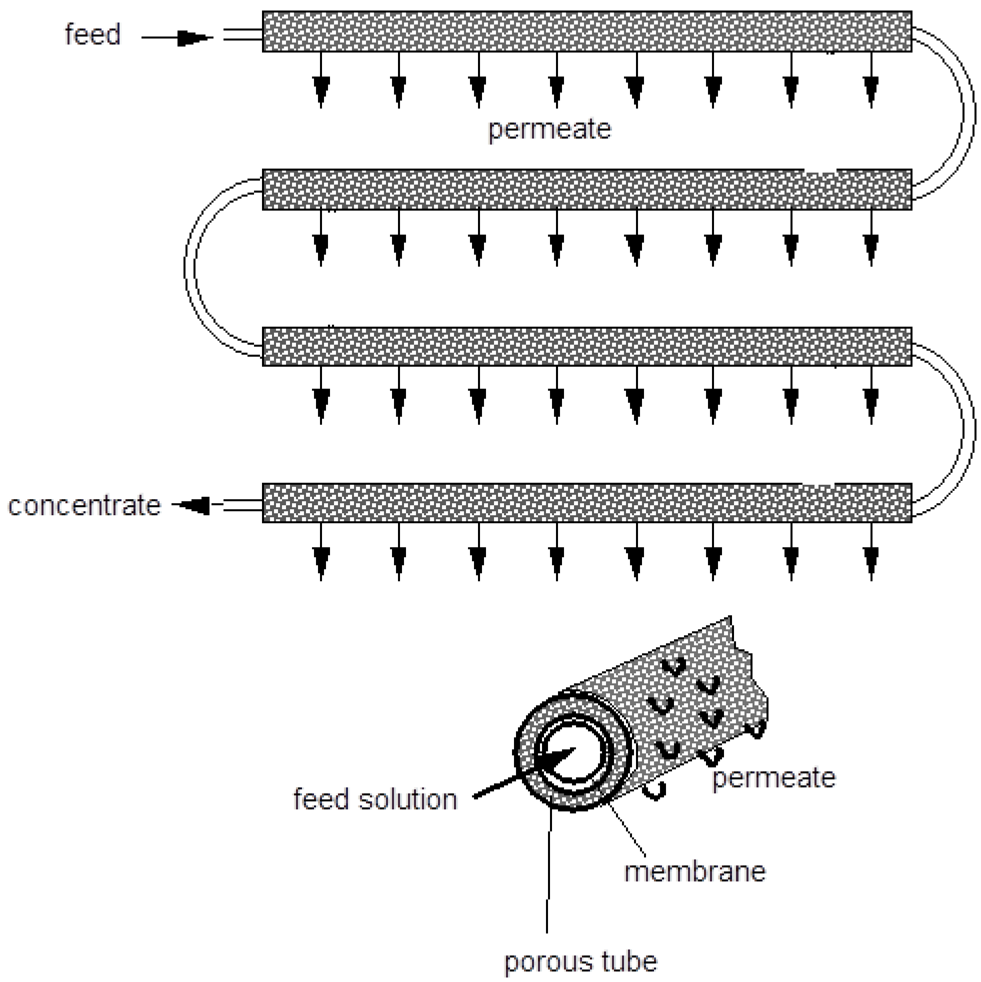


Figure 9. Scheme of the tubular membrane module.

The main advantage of the tubular module is that concentration polarization effects and membrane fouling can be easily controlled. The disadvantage of the tubular module design is the low surface area, that can be installed in a given unit volume, and the very high costs. Therefore, tubular membrane modules are generally only applied in applications where feed solutions with high solid content, and high viscosity have to be treated and other module concepts fail due to membrane fouling.

e) The capillary membrane module. (Figure 10)

This module consists of a large number of membrane capillaries with an inner diameter of 0.2 to 3 mm arranged in parallel as a bundle in a shell tube. The feed solution is passed down the center of the membrane capillary and the filtrate, which permeates the capillary wall, is collected in the shell tube.

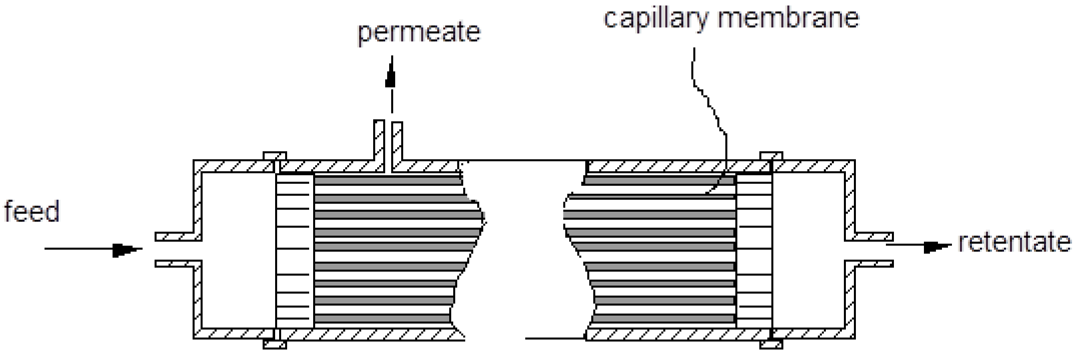


Figure 10. . Scheme of a capillary membrane module.

The capillary membrane module provides a high membrane area per module volume. The production costs are relatively low and concentration polarization and membrane fouling can be effectively controlled. The main disadvantage of the capillary membrane module is the required low operating pressure.

f) The hollow fiber membrane module. (Figure 11)

In hollow fiber membranes, the selective layer is on the outside of the fibers, which are installed as a bundle of several thousand fibers in a half loop with the free ends. The filtrate passes through the fiber walls and flows up the bore to the open end of the fibers.

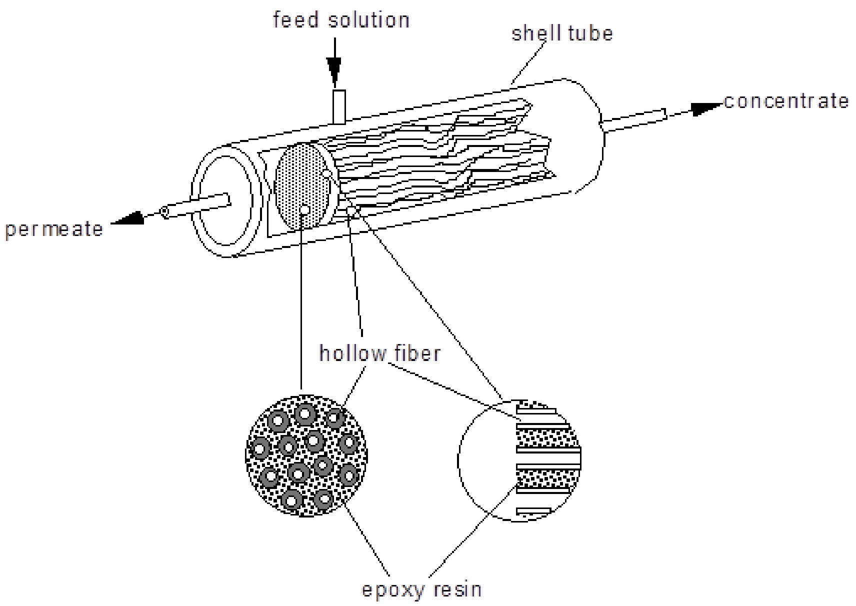


Figure 11. Scheme of a hollow fiber module.

The hollow fiber membrane module has the highest packing density of all module types. Unfortunately its production is rather cost effective and control of concentration polarization and membrane fouling is difficult. The modules do not tolerate any particles, macromolecules or other materials that may easily precipitated at the membrane surface.

Table 3

Commercially available membrane modules, there costs and major applications.

Membrane module	Membrane area per unit volume ($m^2 m^{-3}$)	Membrane costs	Control of concentration polarization	Application
Filter cartridge module	800 -1000	low	Very poor	Dead-end MF
Plate-and-frame module	400 - 800	medium	good	MF, UF, RO, D, ED
Spiral-wound module	800 - 1200	low	good	UF, RO, GS
Tubular module	20 - 100	very high	very good	MF, UF, RO
Capillary module	600 - 1200	low	very good	UF, MF, D, SLM
Hollow fiber module	2000 - 5000	very low	very poor	RO, GS

6. Types of continuous flows used in membrane modules. (Figure 12)

a) **co-current flow:** flow pattern through a membrane module in which the fluids on the upstream and the downstream sides of the membrane move parallel to the membrane surface and in the same directions

b) **completely-mixed (perfectly-mixed) flow** flow through a membrane module in which fluids on both the upstream and downstream sides of the membrane are individually well-mixed

c) **counter-current flow:** flow through a membrane module in which the fluids on the upstream and downstream sides of the membrane move parallel to the membrane surface but in opposite directions

d) **dead-end flow:** flow through a membrane module in which the only outlet for upstream fluid is through the membrane

e) **cross flow:** flow through a membrane module in which the fluid on the upstream side of the membrane moves parallel to the membrane surface and the fluid on the downstream side of the membrane moves away from the membrane in the direction normal to the membrane surface

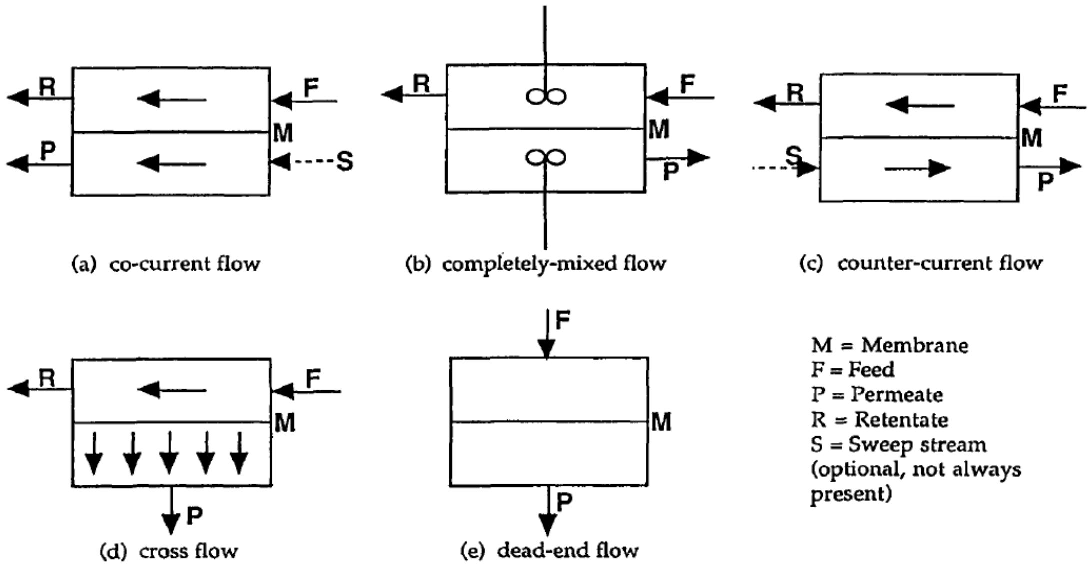


Figure 1: Types of ideal continuous flows used in membrane-based separations

Figure 12. Types of continuous flows in membrane modules.

7. Transport equation in membrane processes.

a) The Hagen-Poiseuille equation can be applied to demonstrate the flow of permeate through the membranes. The use of this equation depends on the shapes and sizes of the pores.

For cylindrical pores:

$$J = \frac{\varepsilon \cdot r^2}{8\eta\tau}\frac{\Delta P}{\Delta x} \qquad (1)$$

Where:

J – the solvent flux

ΔP – pressure difference (TMP)

Δx – thickness of membrane

τ - tortuosity

η - viscosity

r – the pore radius

ε -surface porosity

According to this equation flux is proportional to TMP and inversely proportional to the thickness.

This transport equation very well describes pressure driven techniques.

b) The solution-diffusion model - transport by a solution-diffusion mechanism

According to this model following equation describes transport across the membrane

$$J_n = k\, D(c_2 - c_1)/l \qquad (2)$$

Where:

J_n – flux [mol m^{-2} s^{-1}]

l -thickness of membrane

D - diffusion coefficient of permeated component

c_1 – concentration of permeated component in feed

c_2 – concentration of permeated component in permeate

k - partition coefficient (ratio of concentration of permeated component between membrane and feed)

i charakteryzuje daną membranę. Model dobrze opisuje procesy zachodzące podczas mikrofiltracji.

According to equation (2) flux is proportional to the difference in concentration between feed and permeate inversely proportional to the thickness of the membrane.

8. Technical difficulties in performing membrane process.

a) Membrane fouling – this is serious problem in membrane processes characterized by reduction of permeate flux results from: increased flow resistance due to pore blocking, concentration polarization and gel or "cake" layer formation as results mainly coagulation and adsorption processes. Fouling will not be observed when the flux is maintained below "critical flux", but beyond this critical value, the particles start to deposit on membrane surface as a "cake" layer. The "cake" layer is readily removable from the membrane by physical washing protocol, this being classified as reversible fouling. fouling caused by adsorption of dissolved matter into the membrane pore, and pore blocking is considered irreversible, and is generally removed by chemical cleaning. (Figure 13)

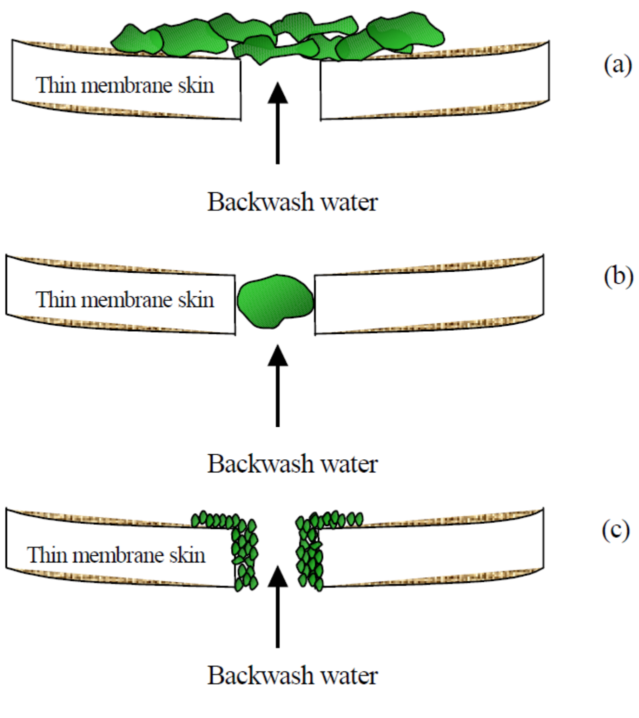


Figure 13. Mechanisms of membrane fouling; (a) gel/cake formation; (b) pore plugging; and (c) pore narrowing.

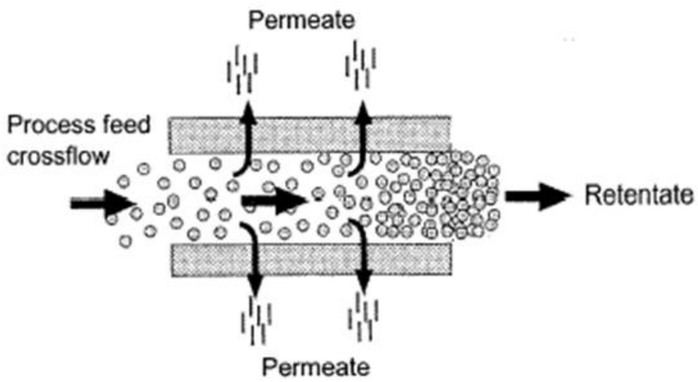
Fouling is especially visible microfiltration and ultrafiltration. It's worth to mention that membrane fouling cannot be completely excluded. Membrane cleaning is the major method of fouling reduction. The type of cleaning depends on the type of fouling and type of the membranes.

b) Concentration polarisation – formation of the layer of solution immediately adjacent to the membrane surface becomes depleted in the permeating solute on the feed side of the membrane and enriched in this component on the permeate side, which reduces the permeating components concentration difference across the membrane, thereby lowering the flux and the membrane selectivity. The application of cross-flow continuous flows in membrane modules allows reduce this phenomenon but it is not possible to exclude this phenomenon completely.

c) Deformation of pores under influence of pressure in pressure driven techniques.

9. The selected application of membrane processes in environmental protection.

a) Microfiltration (MF) and Ultrafiltration (UF) in removal of pathogens instead of water chlorination



- 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

b) Nanofiltration can be used in water softening process instead classical lime-soda method. Table 4 shows comparison of two methods in water softening.

c) Removing of toxic or unwanted divalent ions (ions with 2 or more charges), such as lead, iron, nickel, mercury (II) from water

Cut-off ≅ 500 Da   TMP = 5 -30 bar

Table 4

The effectiveness of Nanofiltration in softening of water - comparison with lime– soda method.

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	

d) Reverse osmosis in desalination of water and ultrapure water preparation instead evaporation methods.

Figure 14 illustrates differences between osmosis and reverse osmosis.

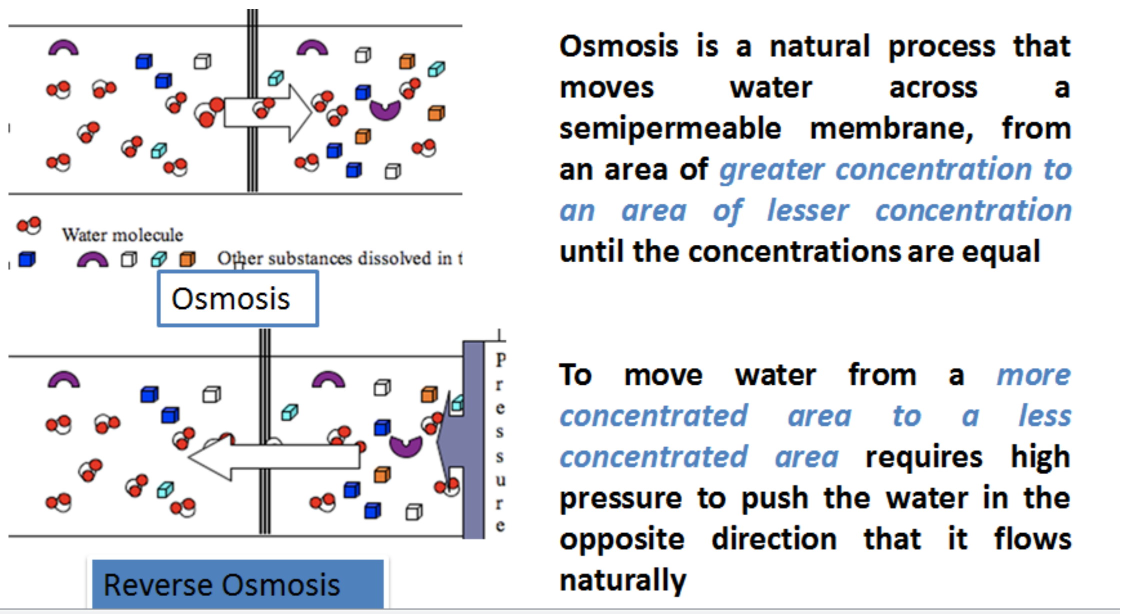


Figure 14. The mechanism of osmosis and reverse osmosis.

e) Series of membrane filtration in water treatment processes. (Figure 15)

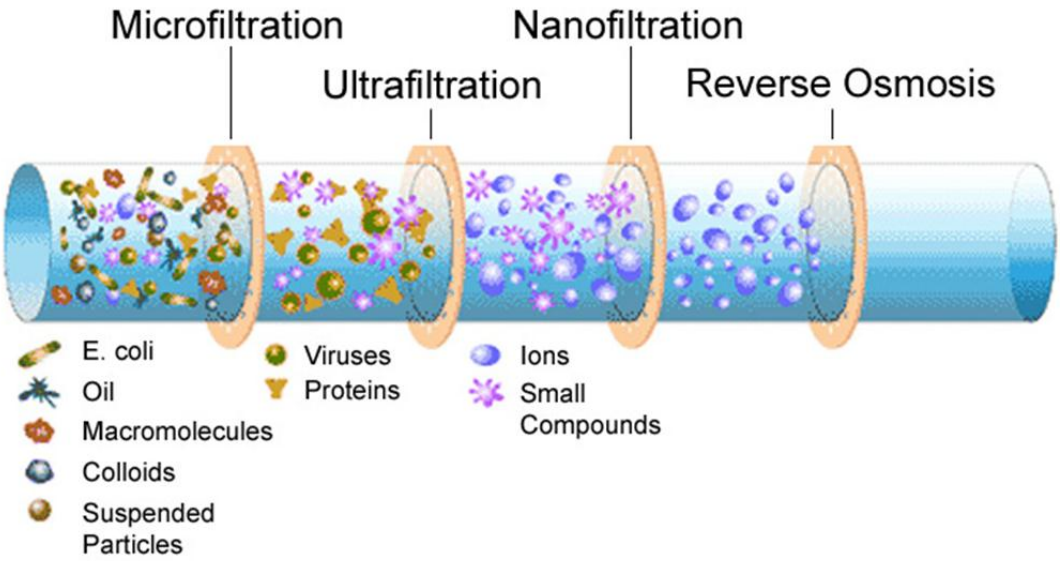


Figure. 15. Series of membrane methods in water treatment processes.

f) Microfiltration, Ultrafiltration, Dialysis in wastewater treatment. (Figure 16)

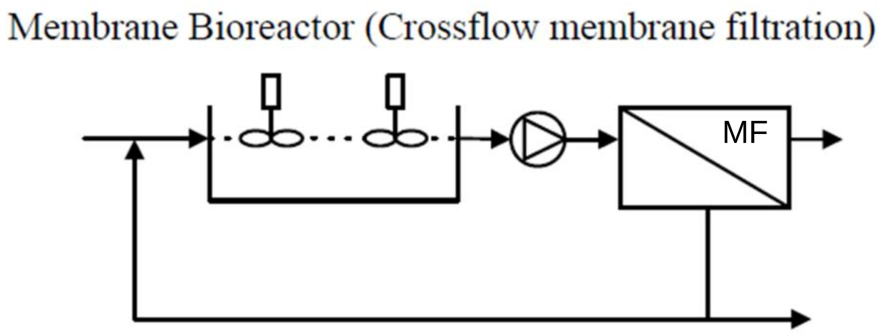


Figure 16. Membrane bioreactor with membrane module for Microfiltration in installation for wastewater treatment with active sludge.

Opracowano w oparciu o następujące pozycje literaturowe:

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