Environmental Quality Management

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Membrane Separation Processes in Environmental Protection – laboratory

Choose yourself and new technologies

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1. ***The influence of membrane cut-off on the transport and separation properties of ultrafiltration membranes***
2. ***Separation of organic dyes using ceramic membranes***
3. ***Desalination of water by electrodialysis***
4. ***Water softening by Donnan dialysis***

Wednesday 13^{15}–16^{55} room 20, b. D-2	**Section**	
	A	**B**
22.04.2020	Introduction	
29.04.2020	3	1
06.05.2020	1	3
13.05.2020	4	2
20.05.2020	2	4

EXERCISES

I. The influence of membrane cut-off on the transport and separation properties of ultrafiltration membranes.

II. Separation of organic dyes using ceramic membranes.

III. Desalination of water by electrodialysis.

IV. Water softening by Donnan dialysis

I. The influence of membrane cut-off on the transport and separation properties of ultrafiltration membranes

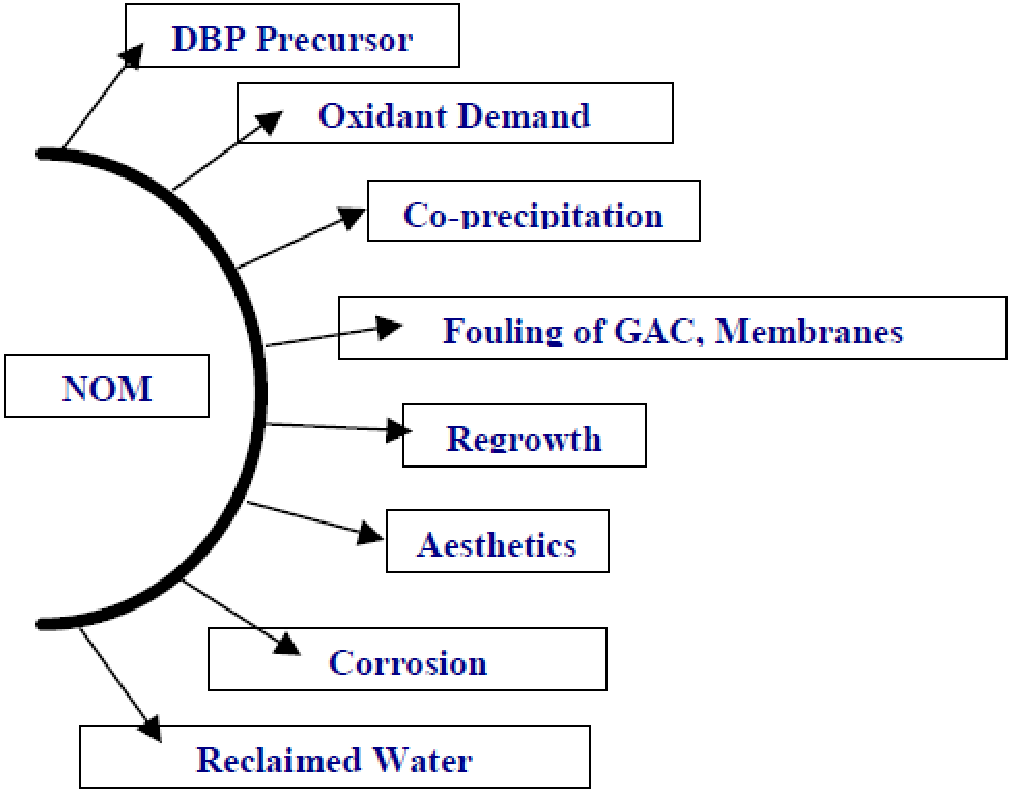
OBJECTIVES:

1. To determine the influence of membrane properties and feed solution composition on permeate flux.

2. To determine the influence of transmembrane pressure and feed solution properties on permeate flux (for membranes of various cut-offs).

3. To determine the influence of transmembrane pressure and membrane cut-off on separation efficiency of natural organic matter.

Natural organic matter (NOM)



NOM

DBP Precursor

Oxidant Demand

Co-precipitation

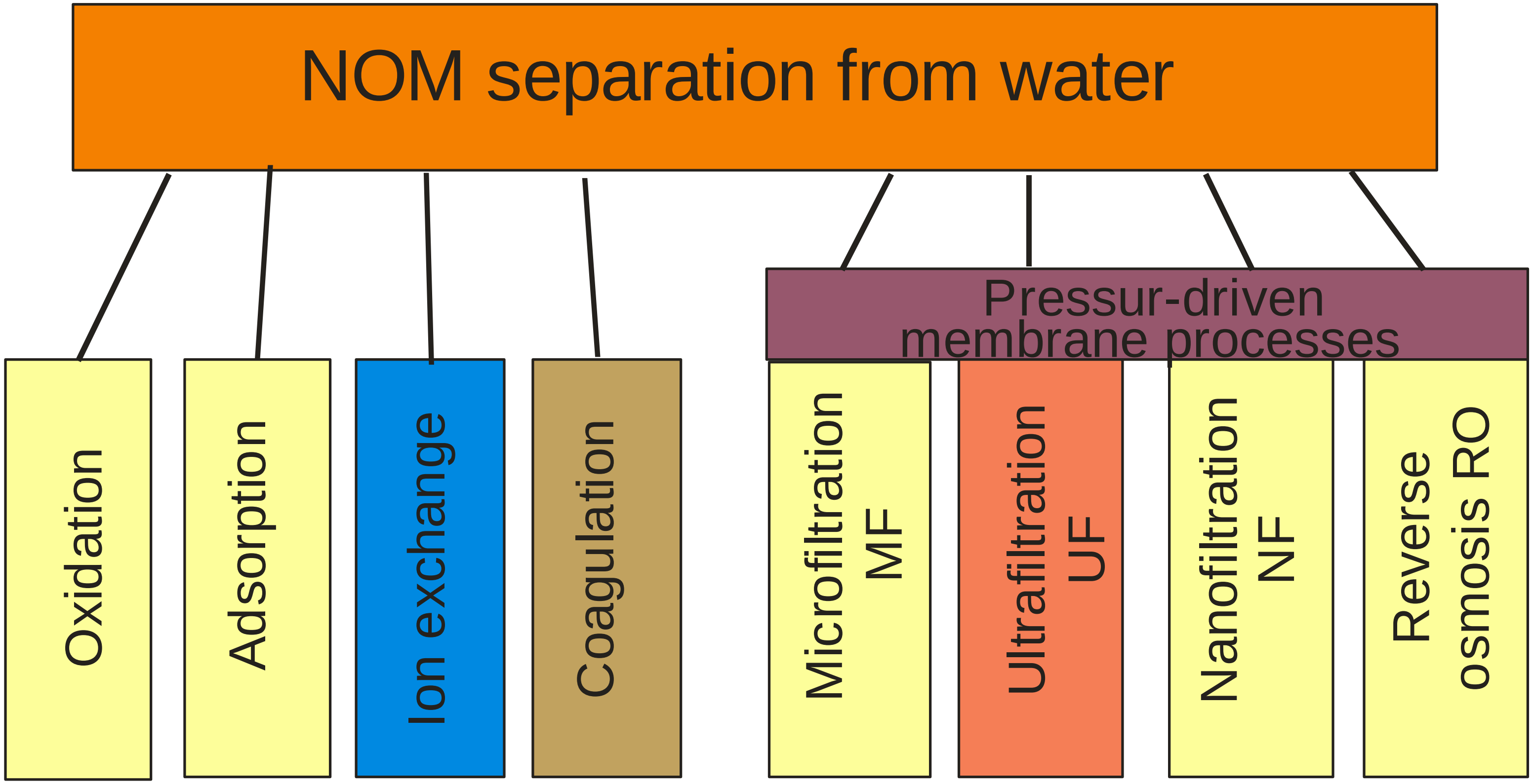
Fouling of GAC, Membranes

Regrowth

Aesthetics

Corrosion

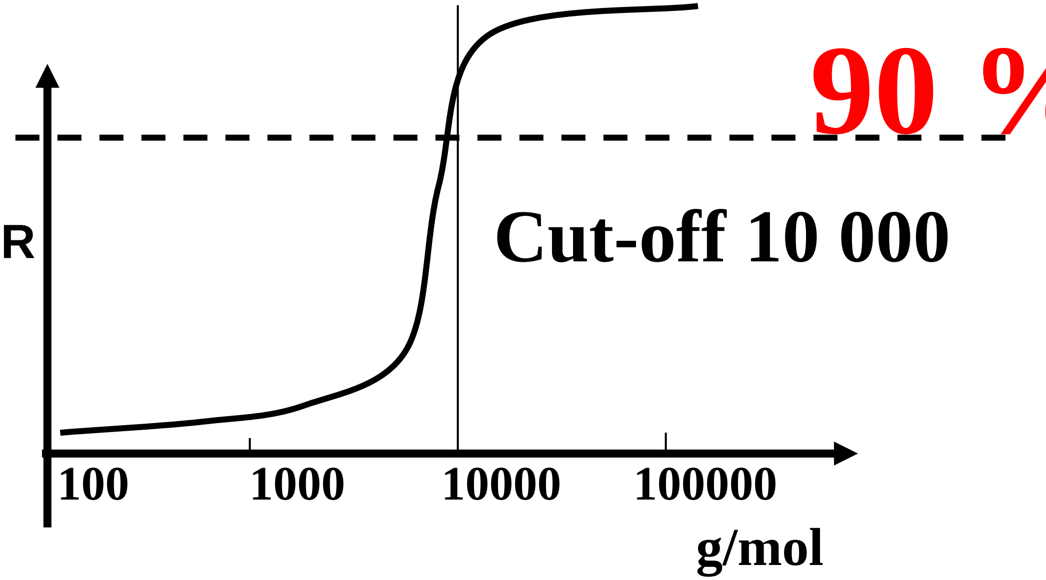
Reclaimed Water

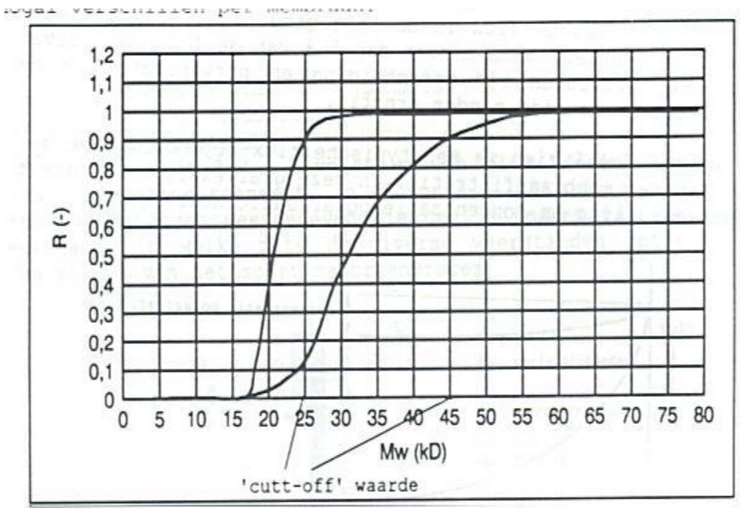


NOM separation from water

- Oxidation
- Adsorption
- Ion exchange
- Coagulation
- Pressur-driven membrane processes
  - Microfiltration MF
  - Ultrafiltration UF
  - Nanofiltration NF
  - Reverse osmosis RO

Membrane cut-off (molecular weight cut-off)





Molecular Weight Cut Off (MWCO) is a number expressed in Daltons indicating that 90% of the species with a molecular weight larger than the MWCO will be rejected.

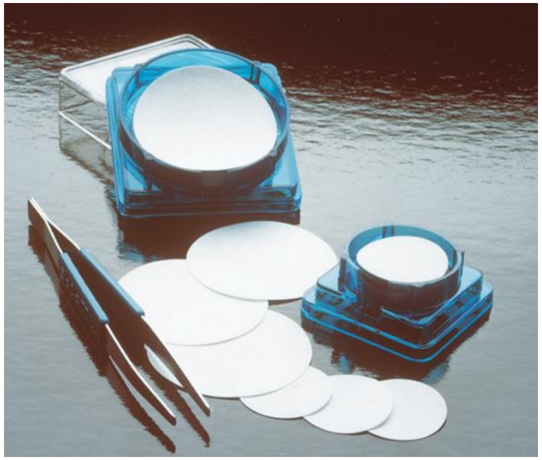
The influence of membrane cut-off on the transport and separation properties of ultrafiltration membranes

Materials and methods

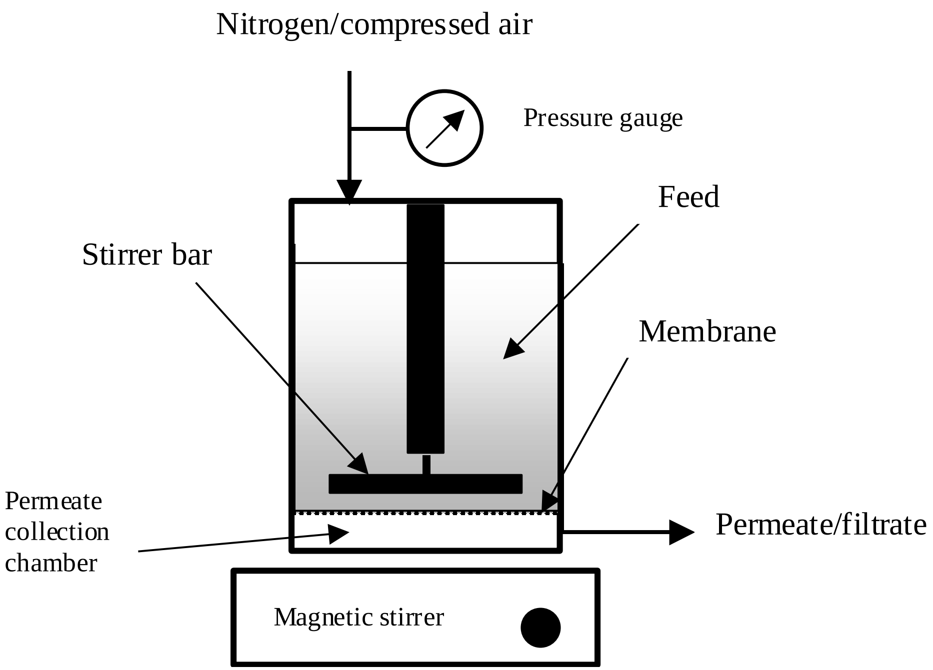
Flat ultrafiltration membranes of cut-off:
5, 10, 30 and 150 kDa

Transmembrane pressure: 0.05 – 0.2 MPa

Model solution containing natural
organic matter particles



Experimental set-up



The main part of the system is an Amicon 8400 ultrafiltration cell with a total volume of 350 cm^3 and a diameter of 76 mm. The effective surface of the membrane amounts to 4.52×10^{-3} m^2.

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TRANSPORT PROPERTIES = PERMEATE FLUX

Determine the influence of transmembrane pressure on permeate flux:
a) for distilled water
b) for water containing natural organic matter

Permeate flux (J): the volume of treated water obtained per time unit per unit of membrane surface area (m^3/m^2day)

$$\boxed{J = \frac{V}{A \cdot t}}$$

V – volume of permeate (cm^3, m^3)
A – membrane surface (cm^2, m^2)
T – time (s, day)

SEPARATION PROPERTIES = RETENTION COEFFICIENT

Determine the influence of transmembrane pressure and membrane cut-off on the retention of:

a) color, g Pt/m^3
b) absorbance UV at 254 nm, cm^{-1}

$$R = \frac{C_f - C_p}{C_f} \times 100\%$$

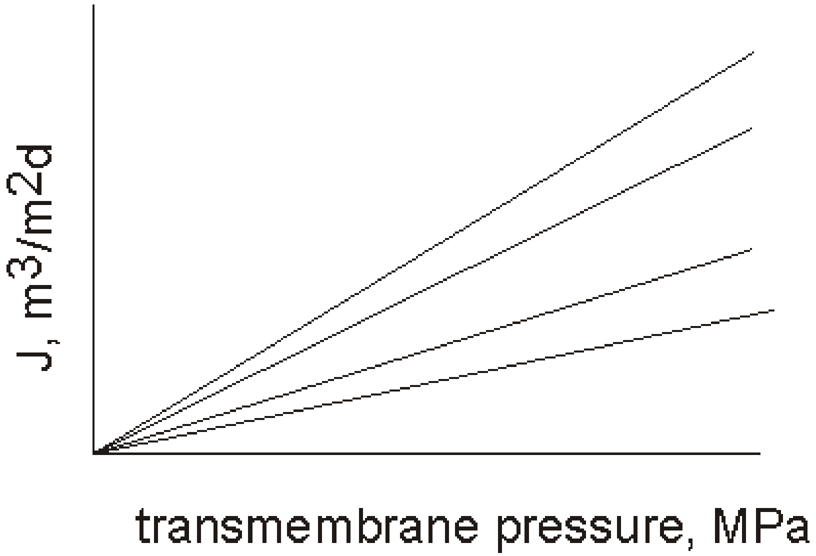
R – retention coefficient, %
C_f – feed stream color intensity or abs 254 nm
C_p - permeate color intensity or abs 254 nm

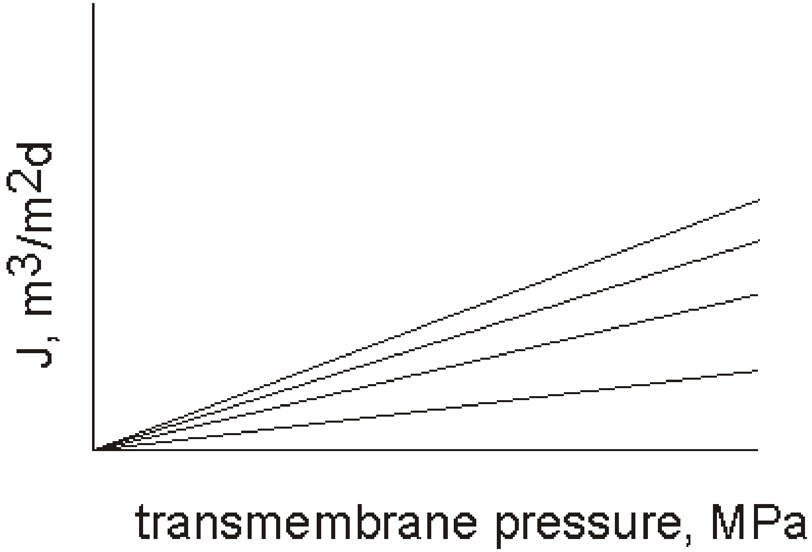
The obtained results should be listed in a table and/or plotted in figures

Example of a table for J = f(ΔP) and R =f(ΔP)

ΔP, MPa	Q_p cm^3/min	J_p m^3/m^{2}day	J_{NOM} m^3/m^{2}day	Absorb 254 nm, cm^{-1}	Color, g Pt/m^3	R_{abs}, %	R_{colour}, %
0.05							
0.1							
0.15							
0.2							

Exemplary relationships of J = f(ΔP)


Distilled water


Water containing NOM

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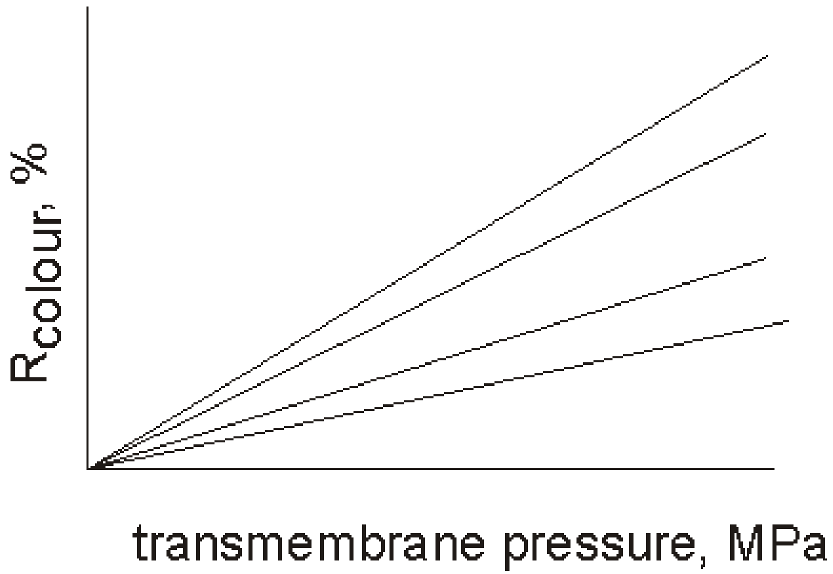
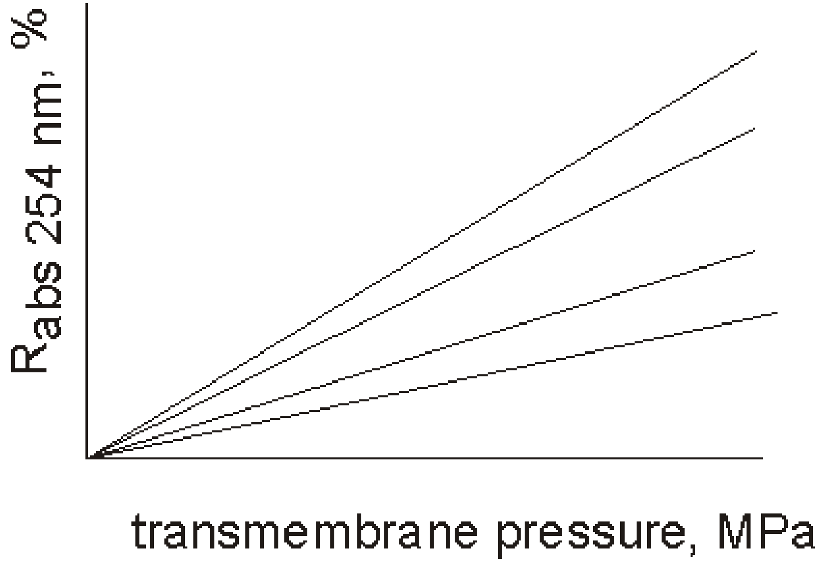
Exemplary relationships of R = f(ΔP)





II. Separation of organic dyes by ultrafiltration (UF) with the use of ceramic membranes

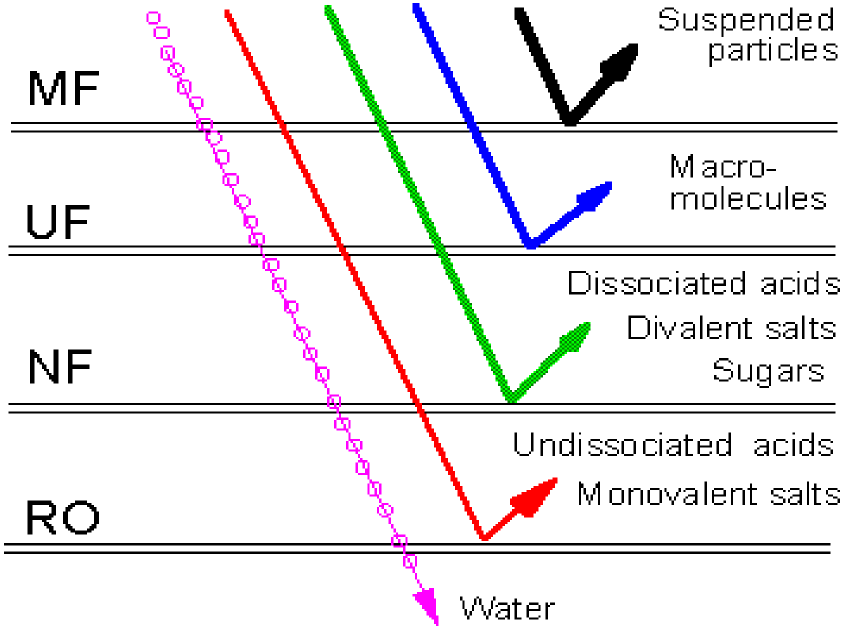
OBJECTIVES:

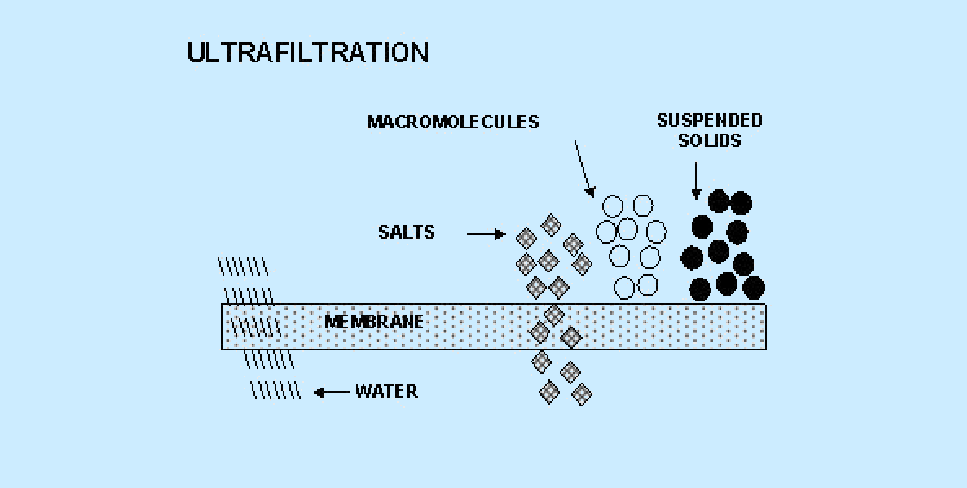
1. To determine the influence of transmembrane pressure and feed solution composition on permeate flux.

2. To determine the influence of transmembrane pressure and dye properties on UF separation efficiency.

3. To determine the influence of the concentration factor on the quality of permeate and membrane permeability.

Pressure membrane processes





Pressure range

MF: < 0.2 MPa
UF: 0.1-1.0 MPa
NF: 0.5 - 2.0 MPa
RO: 1.0 - 6.0 MPa

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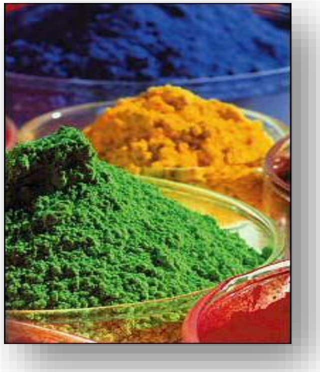
Dyes and textile wastewaters

Dye - a colored substance that has an affinity to the substrate to which it is being applied. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber.

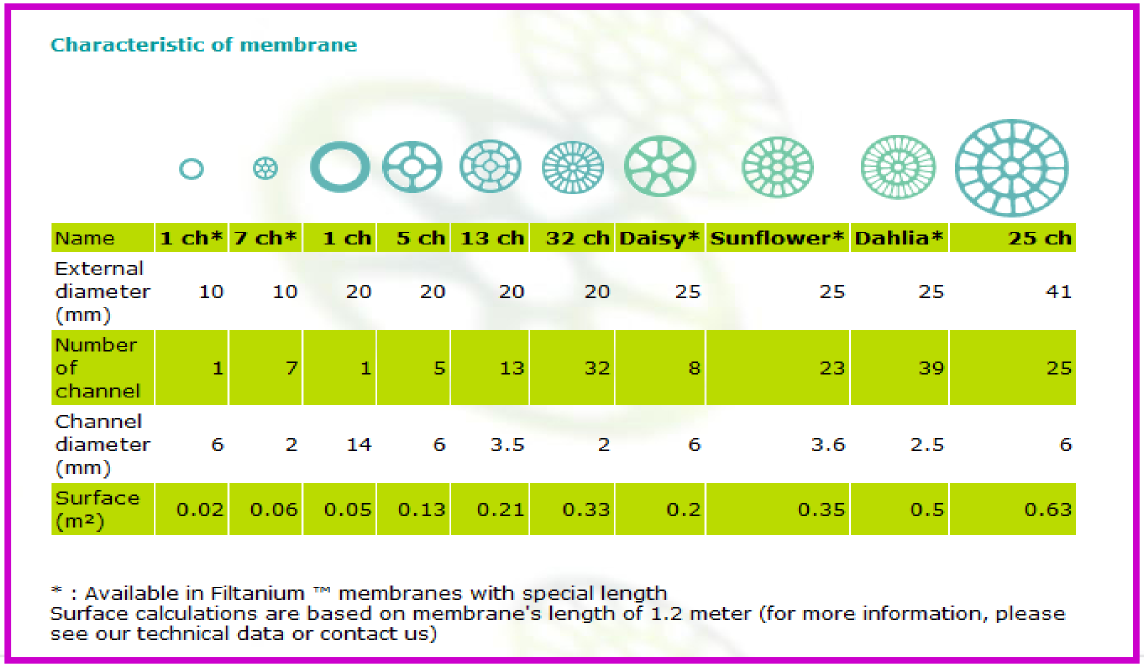
Dyes and pigments appear to be colored because they absorb some wavelengths of light preferentially. In contrast with a dye, a pigment generally is insoluble, and has no affinity for the substrate.



Dyes in water environment:
- aesthetic problem,
- deterioration of water taste,
- limitation of water usage in households and industry,
- toxic impact to water animals and plants,
- possibility of accumulation in animal bodies,
- dangerous to human health (carcinogenic),
- worsening of light transmittance in water,
- reducing of water self-treatment.

Ceramic membranes

Advantages:
- extremely high chemical and physical stability,
- outstanding separation characteristics,
- long life,
- ability of steam sterilization and back flushing,
- high abrasion resistance,
- high fluxes,
- bacteria resistance,
- possibility of regeneration,
- dry storage after cleaning,
- good mechanical stability.



Characteristic of membrane

Name	1 ch*	7 ch*	1 ch	5 ch	13 ch	32 ch	Daisy*	Sunflower*	Dahlia*	25 ch
External diameter (mm)	10	10	20	20	20	20	25	25	25	41
Number of channel	1	7	1	5	13	32	8	23	39	25
Channel diameter (mm)	6	2	14	6	3.5	2	6	3.6	2.5	6
Surface (m^2)	0.02	0.06	0.05	0.13	0.21	0.33	0.2	0.35	0.5	0.63

* : Available in Filtanium ™ membranes with special length
Surface calculations are based on membrane's length of 1.2 meter (for more information, please see our technical data or contact us)

Separation of organic dyes by ultrafiltration (UF) with the use of ceramic membranes

Materials and methods

- ceramic ultrafiltration membrane (cut-off 1-50 kDa)
- transmembrane pressure: 0.03 – 0.12 MPa
- model solutions containing organic dyes of various molecular weights (MW) (dye concentration 10-100 g/m^3)

CROSS-SECTIONS OF MULTI-CHANNEL CERAMIC MEMBRANES

METHYL ORANGE
MW 327 Da

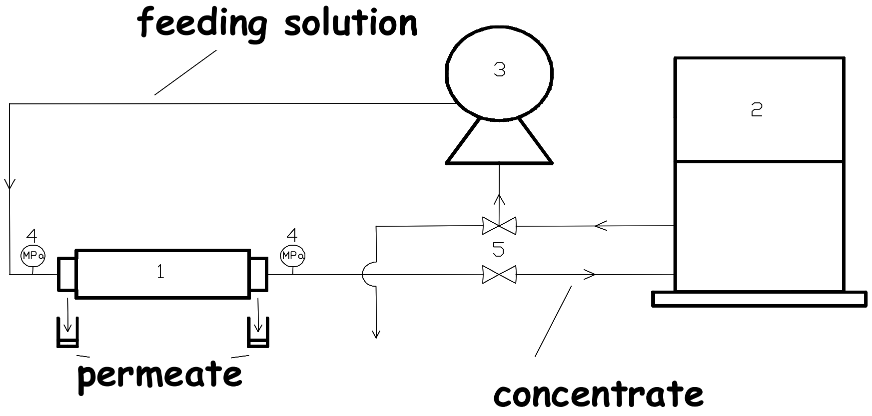
INDIGO CARMINE
MW 466 Da

TITAN YELLOW
MW 695 Da

DIRECT BLACK
MW 1060

Separation of organic dyes by ultrafiltration (UF) with the use of ceramic membranes

UF installation ProFluxM12 (Millipore)



1 – ceramic membrane module, 2 – feed tank,
3 – pressure pump, 4 – pressure sensor, 5 – valve

1-channel module

3-channel module

Feed tank volume – 2 dm^3
Membrane surface area – 42 cm^2
(1-channel module, length - 25 cm)

Separation of organic dyes by ultrafiltration (UF) with the use of ceramic membranes

Run of the exercise

1. Determine the influence of transmembrane pressure on permeate volume flux:
- for distilled water,
- for aqueous solutions of various dyes.

Permeate volume flux (J): the volume of treated water obtained per unit time per unit of membrane surface area (m^3/m^2day)

$$\boxed{J = \frac{V}{A \cdot t}}$$

V – volume of permeate (cm^3, m^3)
A – membrane surface (cm^2, m^2)
T – time (s, day)

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Separation of organic dyes by ultrafiltration (UF) with the use of ceramic membranes

2. Determine the influence of transmembrane pressure on the dye retention coefficient R for various dyes.

$$\boxed{R = 1 - \frac{C_p}{C_f} \times 100\%}$$

R – dye retention coefficient, %
C_f – dye concentration in feed stream, g/m^3
C_p - dye concentration in permeate, g/m^3

Separation of organic dyes by ultrafiltration (UF) with the use of ceramic membranes

3. Determine the influence of concentration factor on the quality of permeate and membrane permeability:

- **monitoring of volume flux J, dye retention R, volume of permeate and concentrate at 15 min intervals,**
- **constant pressure (0.1 MPa),**
- **operation at concentration mode (continuous discharging of permeate).**

$$CF = \frac{V_o}{V_c}$$

CF – concentration factor
V_o – initial volume of dye solution (i.e. 2 dm^3)
V_c – volume of concentrate after time t, dm^3
$V_c = V_o - V_p$
V_p - permeate volume after time t, dm^3

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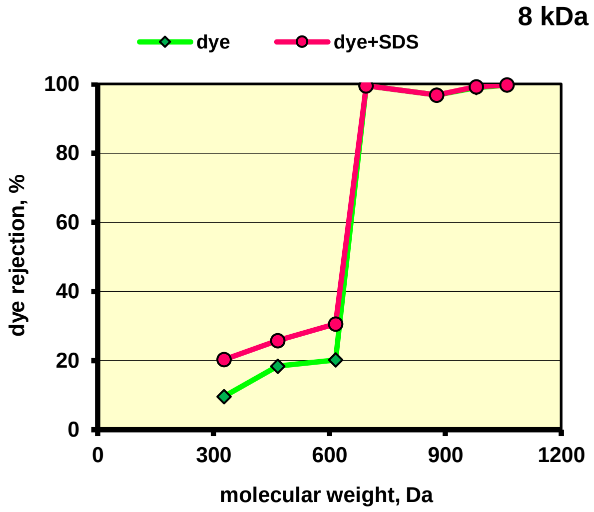
Separation of organic dyes by ultrafiltration (UF) with the use of ceramic membranes

The results obtained should be listed in a table and/or plotted in figures

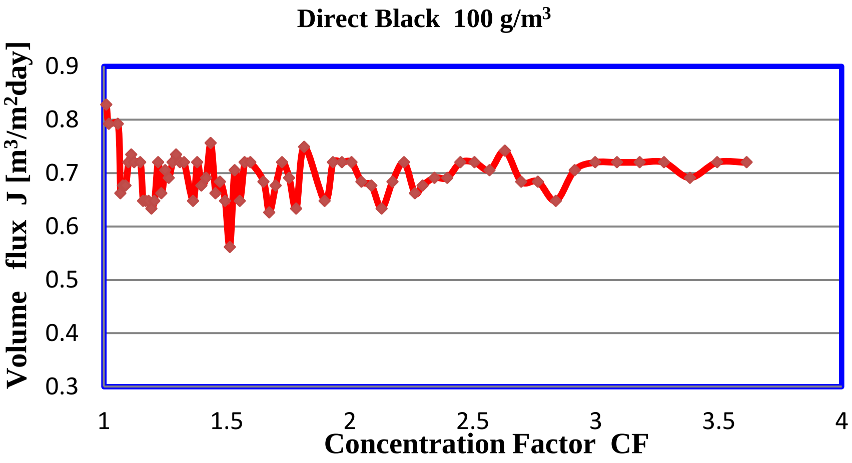
Example of table for J = f(ΔP) and R =f(ΔP)

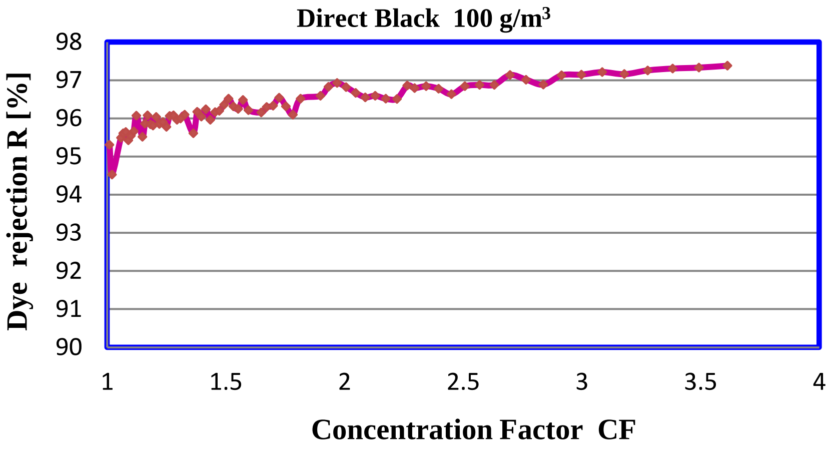
ΔP, MPa	Q_p cm^3/min	J_p m^3/m^{2}day	J_{av} m^3/m^{2}day	absorb	C_p g/m^3	R, %	R_{av} %
0.03							
0.06							
0.09							

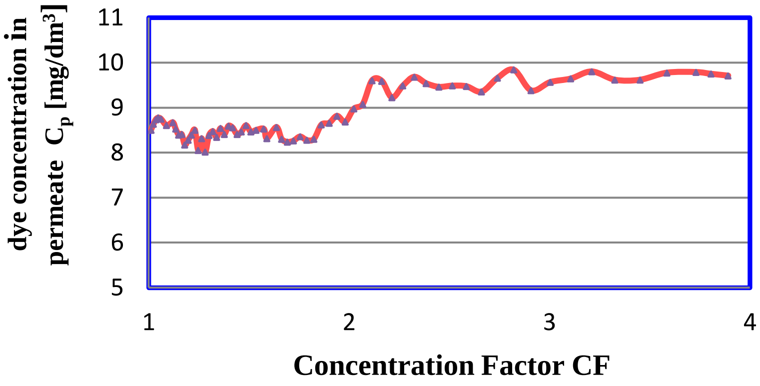
Exemplary rejection curve



EXEMPLARY RELATIONSHIPS
$J=f(CF)$, $R=f(CF)$, and $C_p=f(CF)$


Direct Black 100 g/m^3


Direct Black 100 g/m^3



EXAMPLE 1

Estimate the quantity and quality of concentrate from an ultrafiltration installation in the dyeing section of textile factory. In the installation 4000 m^3/day of water (= amount of permeate) is reused for rinsing baths. It is assumed that both recovery and dye rejection rates are equal to 90% and the dye concentration of the feed stream is 400 g/m^3.

1. Determine the flow rate of the concentrate Q_c and the total amount of exhausted dye bath that must be processed Q_f

Recovery rate r

$$r = \frac{Q_p}{Q_f} \times 100\%$$

Feed flow rate Q_f

$$Q_f = Q_p + Q_c$$

Q_p - permeate flow rate

$$Q_c = \frac{Q_p(1-r)}{r}$$

$$Q_c = \frac{4000\,(1-0.9)}{0.9} = 444\,m^3/day$$

$$Q_f = 4000 + 444 = 4444\,m^3/day$$

or

4000 m^3/day – 90% of feed flow rate
x – 100 % of feed flow rate

X = 4444 m^3/day

EXAMPLE 1 (continuation)

2. Determine the concentration of the permeate stream C_p

Dye rejection

C_f – dye concentration in the feed stream

$$R = \frac{C_f - C_p}{C_f} \times 100\%$$

$$C_p = C_f(1 - R) = 400(1 - 0.9) = 40\ g/m^3$$

3. Determine the concentration of the concentrated stream C_c

Mass balance equation

$$Q_f C_f = Q_p C_p + Q_c C_c$$

$$C_c = \frac{Q_f C_f - Q_p C_p}{Q_c}$$

$$C_c = \frac{4444x400 - 4000x40}{444}\left[\frac{\frac{m^3}{day} x \frac{g}{m^3}}{\frac{m^3}{day}}\right]$$

$$C_c = 3643\ g/m^3$$

EXAMPLE 2

The dyeing section of a textile factory generates 10 m^3/day of exhausted dye baths (Q_f). How many UF modules should be applied to treat this wastewater?

Assumptions: recovery rate r = 84%, module permeability at 0.4 MPa J = 4 m^3/m^2day, Membrane surface area/module S_m = 1.2 m^2, operation cycle t = 6h/day.

Solution:

Module permeability in one cycle : $q = J \times t = 4 \times 6/24 = 1\ m^3/m^2$

It means that 1 m^3 of membrane allows to produce 1 m^3 of permeate in one cycle

Permeate flow rate: $Q_p = r \times Q_f = 0.84 \times 10 = 8.4\ m^3/day = 8.4\ m^3$ in one cycle

Desired membrane area:

$$S = Q_p/q = 8.4/1 = 8.4\ m^2$$

Number of UF modules:

$$n = S/S_m = 8.4/1.2 = 7 \text{ modules}$$

III. Desalination of water by electrodialysis (ED)

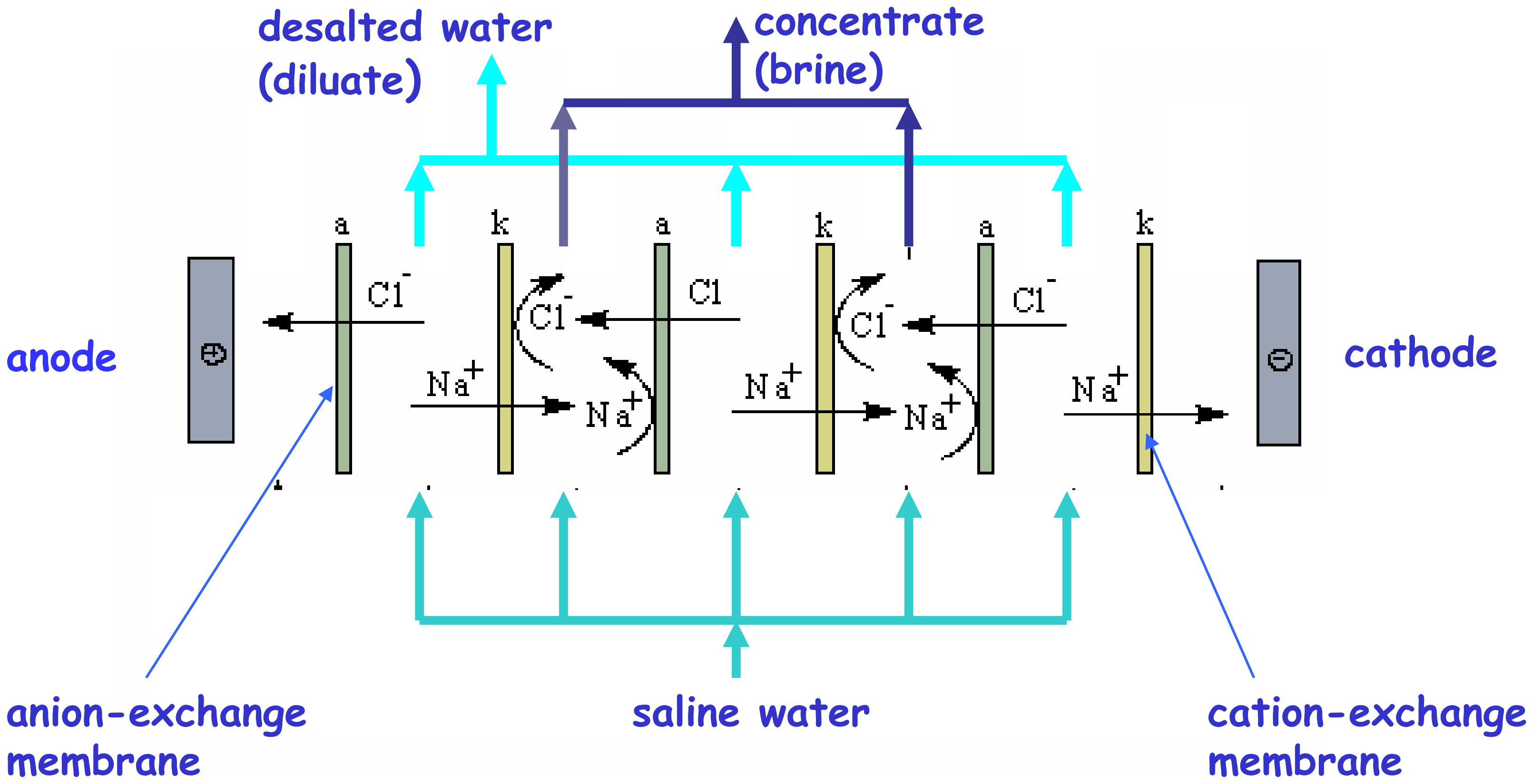
Objectives:

1. To evaluate the suitability of electrodialysis in the desalination of brackish water.
2. To determine the ED process efficiency, desalination degree and diluate quality.
3. To calculate the energy demand in the ED process.

The principle of electrodialysis (ED)

- transport of ions through alternately set pairs of ion-exchange membranes – anion-exchange and cation-exchange membranes
- ion transport is caused by the difference in electric potential on both membrane sides, i.e. electric current is needed
- effect of the process – 2 streams: desalted and concentrated
- desalted stream- diluate is the feed water from which the cations and anions have been removed
- concentrated stream – the stream in which the cations and anions removed from the diluate stream have been concentrated

The principle of electrodialysis (ED)



ED application - examples

- water desalination (salinity up to 5 g $NaCl/dm^3$) for drinking water production (salinity < 0.5 g/dm^3),
- salt production from seawater
- treatment of industrial effluents and reuse of diluate as process water,
- water treatment for boiler water,
- desalination and deacidification of solutions of organic compounds, separation of aminoacids:
- removal of inorganic salts from raw whey (desalted whey can be used in food production),
- deacidification of fruit juices,
- production of milk with a low content of Na^+ ions (by replacing Na^+ ions for Ca^{2+}, K^+ or Mg^{2+}).

Desalination of water by electrodialysis (ED)

Materials and methods

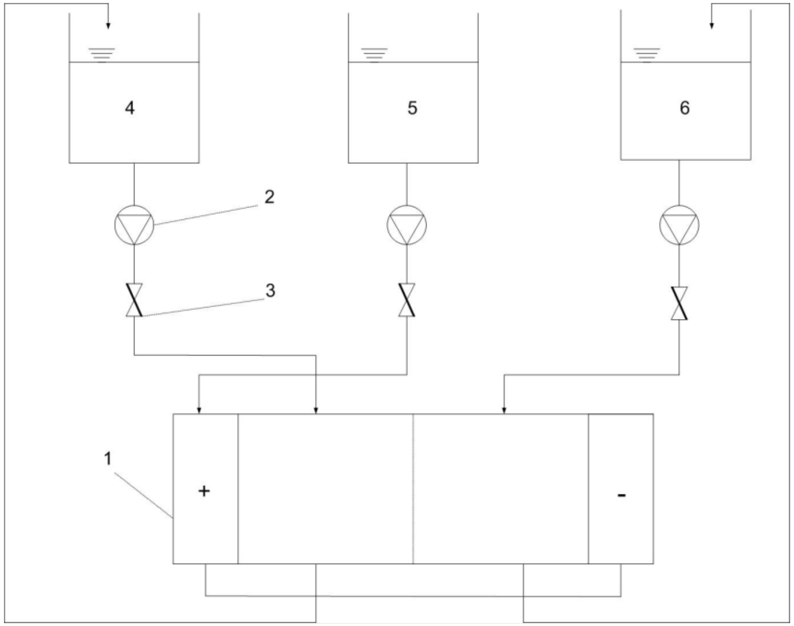
- set of anion-exchange and cation-exchange membranes
- membrane installation with ED stack (n pairs of cells)
- model solution of brackish water (5% $CaCl_2$)

ED stack

Operational parameters:
- current intensity in the range from 0.5 to 1 A
- operation time – max 2 h
- voltage range - 10-60 V

Desalination of water by electrodialysis (ED)

ED installation GOEMASEP 136



1- ED stack, 2 – pump, 3 – rotameter, 4 – diluate tank,
5 – electrode solution tank, 6 - concentrate tank

Back view

Front view

Maximal number of cell pairs n = 20
Effective area of one membrane – 36 cm^2
Pump flow rate – max 150 dm^3/h

Volume of tanks – 10 dm^3

Desalination of water by electrodialysis (ED)

Run of the exercise

1. Fill the diluate tank with 2 dm^3 of $CaCl_2$ solution.
2. Set up the current intensity to the desired value.
3. Determine the raw water quality (Ca^{2+} and Cl^- concentration, conductivity, pH and alkalinity).
4. Monitor the quality of diluate and concentrate at 20 min intervals by determining the following parameters:
   Ca^{2+} and Cl^- concentration,
   conductivity, pH and alkalinity.
5. Monitor the applied voltage at 15 min intervals.

Desalination of water by electrodialysis (ED)

Calculations

The following parameters should be calculated:

1) The current efficiency η_p (separately for Ca^{2+} and Cl^- ions)

$$\boxed{\eta_p = \frac{Ł_{ac}}{Ł_{th}} \bullet 100\%}$$

$Ł_{ac}$ – ACTUAL total cations or anions removed from diluate cell to concentrate cell (expressed as equivalent concentration), eq

$Ł_{th}$ –THEORETICAL total cations or anions removed from diluate cell to concentrate cell (expressed as equivalent concentration), eq

Calculations (continuation)

$$Ł_{ac} = V_i C_i - V_f C_f$$

We express concentration as eq/m^3 no as usually in g/m^3

V_i – initial volume of diluate, m^3

V_f – final volume of diluate, m^3

C_i – initial total concentration of cations or anions in the diluate cell, eq/m^3

C_f – final total concentration of cations or anions in the diluate cell, eq/m^3

Assumption $V_i = V_f = V$ (2 dm^3)

Calculations (continuation)

Faraday's law gives the relationship between the electrical charge measured in Ampers and ions transported through the membrane (for one cell pair)

$$Ł_{th} = \frac{I \cdot t}{F}$$

$$Ł_{th} = \frac{n \cdot I \cdot t}{F}$$

n – number of diluate cells

I – current intensity, A

t – time of the process, s

F – Faraday constant, 96500 As/eq

Calculations (continuation)

2. Specific energy demand W_e

$$W_e = \frac{E_c}{V} = \frac{I \cdot \sum U \cdot \Delta t}{V}$$

Wh/m^3

$$W_e = \frac{E_c}{Ł_{ac}} = \frac{I \cdot \sum U \cdot \Delta t}{Ł_{ac}}$$

Wh/eq

E_c – total energy demand, Wh

$Ł_{ac}$ – total cations or anions removed (expressed as equivalent concentration), eq

V – volume of treated solution (volume of diluate with the assumption that $V_{initial} = V_{final} = V$), m^3

Calculations (continuation)

Energy demand

The energy demand can be calculated as:

$E = I\,(Ut)$

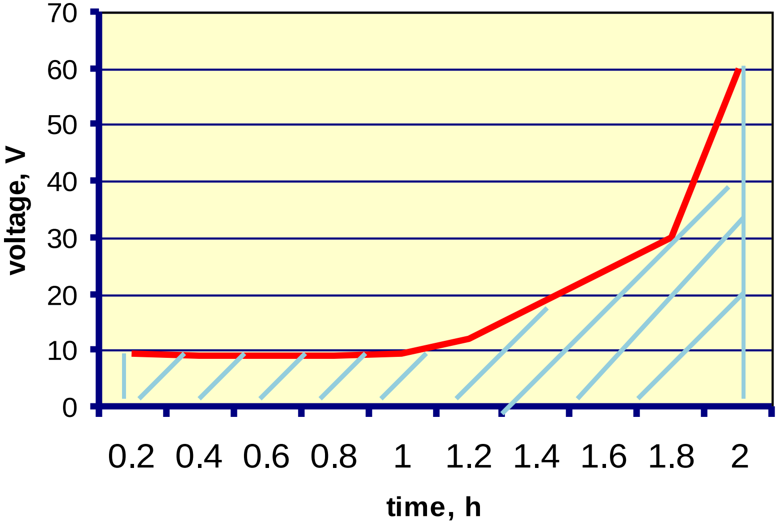
The surface area under the curve U = f(t) should be determined

I – current intensity, A

U – voltage (measured during process), V

t – time of the process, h

U = f(t)



Calculations (continuation)

3. Determine the degree of water desalination R by calculating the removal coefficients of determined parameters (Ca^{2+} and Cl^- concentration, conductivity)

$$R = 1 - \frac{C_f}{C_i} \text{ x } 100\ \%$$

C_f - concentration of the component in the diluate after ED process
C_i - concentration of the component in the raw brackish water

The results obtained should be listed in a table and plotted according to the following relationships:
U = f(t),
conductivity = f(t), Ca^{2+} = f(t), Cl^- = f(t) (in diluate and concentrate)

Example 3

The electrodialysis of 10 dm^3 of $CaCl_2$ solution was carried out. The concentration of salt in the solution amounted to 6 g/dm^3.

Problem: calculate the theoretical final concentration of $CaCl_2$ in the dialysate cells. Number of cell pairs: 10. The process was carried out for 1 hour at the current intensity 0.6 A.

Data: $V_i = 10\ dm^3$ $n=10$
$C_i = 6\ g\ CaCl_2/dm^3$ $I = 0.6\ A$
$t = 1h$

unknown: C_{fth}

Example 3 - solution

The theoretical amount of ions removed from the diluate cell to the concentrate cell (from Faraday's law):

$$\boxed{Ł_{th} = \frac{n \cdot I \cdot t}{96500} = \frac{10 \cdot 0.6 \cdot 3600}{96500} = 0.22\,eq}$$

calculation of the salt concentration in miliequivalents:

Miliequivalent of $CaCl_2$: {40 + (2 x 35.5)}/2 = 55 mg/meq

$CaCl_2$ concentration: 6000 mg/dm^3 : 55 mg/meq = 109 meq/dm^3

Example 3 - solution (continuation)

Calculation of C_{fth}

According to slide 38

$$Ł_{ac} = 0.22\ eq = 220\ meq = V(C_i - C_{fth}) = 10\ dm^3(109\ meq/dm^3 - C_{fth})$$

1 eq = 1000 meq

$$C_{fth} = 109\ meq/dm^3 - 22\ meq/dm^3 = 87\ meq/dm^3$$

Calculation of the salt concentration in mg/dm^3:

$$C_{fth} = 87\ meq/dm^3 \cdot 55\ mg/meq = 4785\ mg/dm^3 = 4.79\ g/dm^3$$

ANSWER: the theoretical salt concentration in the dialysate after the process will be equal to 4.79 g/dm^3

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Example 4

What is the time required to reach 70% desalination effect for the electrodialysis of 5 dm^3 of $CaCl_2$ solution with a concentration of 3 g/dm^3? Number of cell pairs: 10. The process is carried out at a current intensity of 1A, whereas the current efficiency is equal to 0.8.

Data: $V_i = 5\ dm^3$
$C_i = 3\ g\ CaCl_2/dm^3$
$n = 10$

$\eta_o = 70\% = 0.7$
$\eta_p = 80\% = 0.8$

Unknown: time of process duration t

EXAMPLE 4 - solution

calculation of salt concentration in miliequivalents:

Miliequivalent of $CaCl_2$: {40 + (2 x 35.5)} : 2 = 55 mg/meq

$CaCl_2$ concentration: 3000 mg/dm^3 : 55 mg/meq = 54.5 meq/dm^3

Actual amount of ions removed from dialysate assuming $V_i = V_f = V$

$$Ł_{ac} = V(C_i - C_f) = 5 dm^3 (54.5\, meq/dm^3 - 0.3 \cdot 54.5\, meq/dm^3) = 191\, meq$$

Where $C_f = 0.3 \cdot C_i$ (70% desalination)

Example 4 – solution (continuation)

current efficiency

$$\eta_p = \frac{\text{Ł}_{ac}}{\text{Ł}_{th}}$$

theoretical amount of ions removed

$$\text{Ł}_{th} = \frac{\text{Ł}_{ac}}{0.8} = \frac{191\ meq}{0.8} = 238\ meq$$

= 0.238 eq

On the other hand:

$$\text{Ł}_{th} = \frac{nIt}{96500}$$

$$t = \frac{\text{Ł}_{th} \cdot 96500}{nI} = \frac{0.238eq \cdot 96500}{10 \cdot 1} = 0.64h$$

= 2296.7 s

ANSWER: To reach 70% desalination effect the process should be carried out for 0.64 h

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EXAMPLE 5 - Engineering problem

A light brackish water of the specification below requires desalination to produce drinking water (according to English standards) with the use of 500 cell pairs, 1x0.75 m electrodialysis stack:

Na^+	830 mg/dm^3	Mg^{2+}	60 mg/dm^3
Ca^{2+}	100 mg/dm^3	HCO_3^-	120 mg/dm^3
SO_4^{2-}	50 mg/dm^3	Cl^-	1530 mg/dm^3

Assumed operational parameters:

- current efficiency η_p = 95%
- product recovery Θ = 85%
- average production rate Q = 500 m^3/day
- specific cell pair resistance $r = 10 + (10^4/C_{av})\ \Omega cm^2$, where C_{av} – average concentration in dilute (in meq/dm^3)

Question: what will be the specific energy demand?

EXAMPLE 5- solution of engineering problem

According to drinking water standards the sodium content should be halved. It is also known that hardness (i.e. Ca^{2+} and Mg^{2+}) is removed at twice the rate of sodium.

Recalculation of ion concentration (C_o) from mg/dm^3 to meq/dm^3 :

Na^+	36 meq/dm^3	Cl^-	43 meq/dm^3
Ca^{2+}	5 meq/dm^3	SO_4^{2-}	1 meq/dm^3
Mg^{2+}	5 meq/dm^3	HCO_3^-	2 meq/dm^3
Total	45 meq/dm^3	Total	46 meq/dm^3

After the process the composition of the desalted product (C), the amount of the ions removed (ΔC) and the average concentration of the diluate (C_{av}) should be:

	C	ΔC	C_{av}
Na^+	18 meq/dm^3	18 meq/dm^3	27 meq/dm^3
Ca^{2+}	1.25 meq/dm^3	3.75 meq/dm^3	3.13 meq/dm^3
Mg^{2+}	1.25 meq /dm^3	3.75 meq/dm^3	3.13 meq/dm^3

EXAMPLE 5- solution of engineering problem (continuation)

Taking into account the theoretical amount of ions removed from the diluate cell to the concentrate cell (Ł_{th}), the current intensity I can be caculated:

$$\text{Ł}_{th} = \frac{n \cdot I \cdot t}{F} = \frac{V(C_i - C_f)}{\eta_p}$$

C_p – initial ion concentration in diluate cell, meq/dm^3
C_k - final ion concentration in diluate cell, meq/dm^3
η_p – current efficiency

$$I = \frac{QF\Delta C}{n\eta_p} = \frac{500 \times 96500 \times 25.5}{24 \times 60 \times 60 \times 500 \times 0.95} = 30A$$

EXAMPLE 5- solution of engineering problem (continuation).

The energy demand can be calculated from the following equation:

$$E = \frac{I \cdot n \cdot r' \cdot t \cdot F \cdot Q \cdot \Delta C}{\eta_p}$$

(where r' - cell resistance, Ω)

$$E = I^2 Rt = I^2 RV / Q$$

(in kWh)

where R – stack resistance, Ω

EXAMPLE 5- solution of engineering problem (continuation).

Specific energy demand (energy per unit volume of diluate)

$$E/V = I^2 R / \Theta Q$$ **where R – stack resistance**

$$R = \frac{rn}{A} = \frac{(10 + 10^4/33.2) \times 500}{1 \times 0.75 \times 10^4} = 20.7\Omega$$

$$E = \frac{30^2 \times 20.7 \times 24}{0.85 \times 500 \times 1000} = 1.05 kWh/m^3$$

Taking into account that energy demand for water pumping through the stack is equal to 0.2 kWh/m^3 the total specific energy demand in the process will be: 1.25 kWh/m^3

IV. Water softening by Donnan dialysis

Objectives:

1. To evaluate the suitability of Donnan dialysis for water softening

2. To determine the variability of water quality parameters in the course of Donnan dialysis

3. To assess type of water in view of total hardness

Water hardness

Water hardness is caused:

- mainly by the presence of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions, that are naturally present in water,
- by the presence of iron (Fe^{2+}), strontium (Sr^{2+}), and manganese (Mn^{2+}) ions (in a lesser extend).

Total hardness

Carbonate hardness

Non-carbonate hardness

Carbonates $CaCO_3$ and $MgCO_3$

Bicarbonates $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$

Hydroxides $Ca(OH)_2$ and $Mg(OH)_2$

Sulphates $MgSO_4$ and $CaSO_4$

Chlorides $CaCl_2$ and $MgCl_2$

Nitrates

Water hardness classifications

Water classification	Hardness			
	meq/dm^3	mg CaCO$_3$/dm^3	°dH (German degree)	mmol/dm^3
Very soft	< 2	< 100	< 5.6	< 1
Soft	2-4	100 - 200	5.6 – 11.2	1 -2
Moderately hard	4-7	200 -350	11.2 – 19.6	2 – 3.5
Hard	7-11	350 - 550	19.6 -30.8	3.5 – 5.5
Very hard	>11	> 550	>30.8	> 5.5

Adverse effects of hard water

- increasing of soap consumption for washing due to precipitation of calcium and magnesium compounds,
- skin irritation,
- deposition of Ca^{2+} and Mg^{2+} ions on textile fibers during washing,
- worsening of the nutrient quality of meat cooked in hard water,
- increasing of corrosion hazard in heat exchanger due to hydrolysis of magnesium salts and increase of hydrogen ion concentration,
- build-up of scales ($CaCO_3$, $Mg(OH)_2$, $CaSO_4$) in boilers, which impair the flow of heat into water, reducing the heating efficiency.

Recommended total hardness in drinking water: 60-500 mg $CaCO_3/dm^3$

Water softening

Water softening - removal of calcium, magnesium, and certain other metal cations in hard water

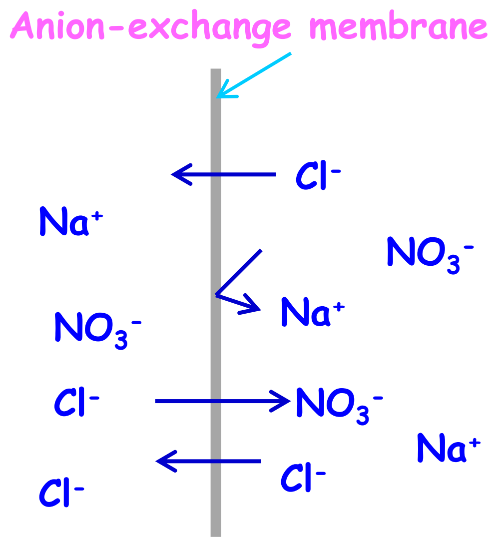
Water softening can be performed by:

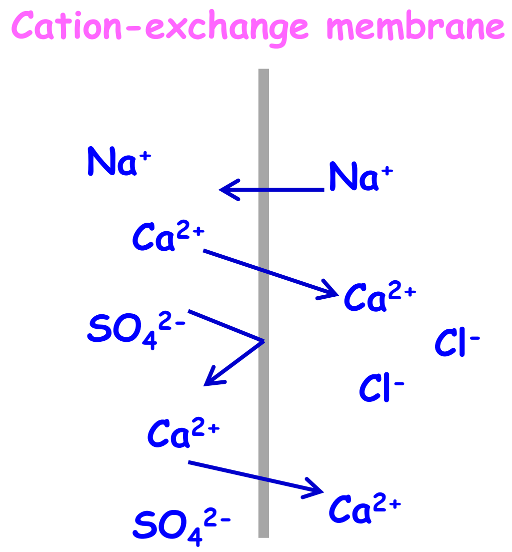
- distillation,
- thermal methods involving water heating to temperature of 100°C and, as a consequence of heating, decomposition of calcium and magnesium bicarbonates with separation of hardly soluble calcium carbonate, magnesium carbonate and magnesium hydrooxide,
- chemical methods involving precipitation of insoluble calcium and magnesium compounds. In these methods the following chemicals can be used: lime, soda, sodium hydrooxide, phosphates,
- chemical and physical methods involving ion-exchange process with the use of cationic exchangers and membrane techniques (nanofiltration, reverse osmosis, electrodialysis and Donnan dialysis).

The principle of Donnan dialysis

- exchange of ions having the same charge between two solutions separated by an ion-exchange membrane,
- driving force → difference in chemical potentials (concentrations) of solutions on both membrane sides,
- The ion-exchange membrane separates two solutions - feed and concentrate (receiving solution). Concentrate contains electrolyte in high concentration (0.1-1 mol/dm^3), whereas concentration of feed solution is significantly lower (0.001 to 0.1 mol/dm^3),
- diffusion of ions (anions or cations depending on ion-exchange membrane type) from receiving solution to feed solution,
- an equivalent ion flow in opposite direction from feed to concentrate.

Donnan dialysis





Feed solution
e.g. water + $NaNO_3$

Receiving solution
(concentrate)
e.g. NaCl solution

Feed solution
e.g. water + $CaSO_4$

Receiving solution
(concentrate)
e.g. NaCl solution

Application:
- removal of fluorides from drinking water,
- removal of nitrates in IEMB
- water pretreatment in RO (repleacing of harmful sulphate and bicarbonate ions by e.g. chloride ions)

Application:
- water softening

Softening of water by Donnan dialysis

Materials and methods

- set of cation-exchange membranes
- installation (see excercise 3) with membrane stack (20 pairs of cells; membrane area 0.14 m^2)
- feed solution (raw water) - model solution containing 5 mmol $CaCl_2/dm^3$ and 5 mmol $MgCl_2/dm^3$
- concentrate – NaCl solution (300 mmol/dm^3)

Feed to concentrate ratio 1:1

membrane stack

Water softening by Donnan dialysis

Run of the exercise

1. Fill the dialysate tank with raw water and concentrate tank – with NaCl solution. Start the pumps.
2. Determine the raw water quality (Ca^{2+}, Mg^{2+} , Cl^{-} concentration, total hardness, conductivity, pH).
4. Monitor the quality of dialysate and concentrate at 20 min intervals by determining the water quality parameters listed in item 2.

Water softening by Donnan dialysis

Analysis of results

1. Put in table all obtained results and make graphs of water quality parameters versus operation time.
2. Evaluate process efficiency (percentage decrease of Mg^{2+} and Ca^{2+} content and total hardness reduction).
2. Assess type of product water in view of total hardness.

= 0.238 eq

ANALITYCAL METHODS

- **Exercise 1:**
  - color
  - UV absorbance at 254 nm
- **Exercise 2:**
  - dye concentration (spectrophotometrically) – calibration curve
- **Exercise 3:**
  - pH
  - conductivity
  - alcalinity
  - calcium concentration
  - chlorides concentration
- **Exercise 4:**
  - pH
  - conductivity
  - total hardness
  - chlorides concentration

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