Membrane filtration processes

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Contents

1   Introduction

The goal of membrane filtration processes is to separate molecules or particles from a solution by a membrane, while limiting its fouling in order to obtain a stable permeate flux during at least 20 hours. Two types of filtration processes are possible, tangential filtration and dead end filtration.

1.1   Principles and main parameters of filtration

1.1.1   Principle of tangential filtration

The fluid circulates along the membrane from a tank under the action of a pump. Only a part of the fluid, the permeate crosses membrane pores under a pressure difference (transmembrane pressure ptm) while the remaining fluid (retentate) is recycled in the tank or discarded. The membrane pores will retain macromolecules or particles of larger size, while microsolutes (molecules or particles smaller than pores diameters) will remain in permeate.

1.1.2   Principle of dead end filtration

In this case, the fluid must cross a membrane perpendicular to the flow and retentate concentration increases rapidly. Dead end filtration is mostly used with diluted fluids and membrane fouling occurs faster than in tangential filtration.

1.1.3   Main parameters of filtration

The filtrate flow rate Q_F is the flow crossing the membrane, expressed in m^3/s or in lit/hour (l/h). The permeate flux J is equal to Q_F/S, permeate flow per unit area of membrane, generally expressed in l/hm^2. The mean transmembrane pressure (ptm) is given by

$$\text{Ptm} = (p_a + p_r)/2 - p_P \tag{1}$$

where p_a is feed pressure, p_r retentate pressure at membrane exit and p_F the filtrate pressure. The sieving coefficient S of membrane is given by

$$S = C_F/C_r \tag{2}$$

where C_F is the permeate concentration and C_r that of retentate. The rejection rate is R= 1-S; it is complete if S=0 or R=1. For a membrane with uniform pores, there is no rejection (R=0) for solutes with diameter smaller than pores diameter and R will be equal to 1 for solutes with larger diameters than pores. In fact, since pores are not uniform, it frequently happens that solutes will only pass through larger pores and their rejection will be partial, with R<1.

Membranes are characterized by their hydraulic permeability Lp= J /ptm where J is the pure water flux. Permeability units are m/(Pa s) or l/(hm² bar). This permeability depends upon diameter and pores density as well as membrane thickness. Membrane resistance R_m (m^{-1}) is given by $R_m = (\mu \, Lp)^{-1}$ and, unlike hydraulic permeability, depends upon fluid viscosity.

1.2   Classification of membranes processes

A. Filtration processes using transmembrane pressure (ptm)

1.2.1   Microfiltration (MF).

These membranes are characterized by their mean pores diameter (d_p) ranging from 0.05 mm to 5 mm. The ptm varies from 0.1 to 3 bar as membrane resistance is relatively small. The membrane stops particles, but not molecules, so there is no osmotic pressure. It is possible to use MF in dead end filtration for low concentration fluids.

Applications: wine and fruits juice clarification, cell separation, membrane bioreactors. There are many applications in food industry and agronomy, biotechnology and mechanical industry.

Manufacturers: France: Orelis, Exekia,Tami.; Germany: Sartorius, Aaflow. USA: Pall, Millipore

1.2.2   Ultrafiltration (UF)

These membranes have smaller pores than microfiltration membranes: 2 nm $<d_p<$50 nm where 1nm = 10^{-9}m. They are characterized by their cut-off which is the smallest molar mass of molecules rejected by the membrane which ranges between 2000 and 10^6 Dalton (Da). The mean transmembrane pressure higher than in microfiltration varies between 1 and 8 bar, as pores are smaller, and osmotic pressure which decreases effective ptm, is higher.

With proper cut-off, UF membranes can reject macromolecules, proteins, and colloids in addition to particles.

Applications: proteins concentration for cheese fabrication, electrophoretic paints recovery in automotive industry.

Osmotic pressure is moderate, as molar concentration is not high, Permeate fluxes are high.

Manufacturers: Germany: Schumacher, Akzo. France: TAMI, Exekia. Holland: Xflow; England: PCI. USA: Amicon, Romicon, Koch, Pall, Millipore, Osmonics, Filmtech. Japan: Asahi, Kuraray.

1.2.3   Nanofiltration (NF)

Mean pores diameters of these membranes range from 0.5 nm to 2 nm, and their ptm between 5 and 25 bar because of higher osmotic pressure and membrane resistance. Membranes can reject mean molecules of molar mass <2000 Da. It is an intermediate process between reverse osmosis (RO) and ultrafiltration.

Applications: waste water treatment, extraction of small molecules, fractionation.

It is a more recent process as suitable membranes have appeared recently. Permeate fluxes are higher than in RO, but rejection rates are smaller.

1.2.4   Reverse osmosis (RO) d_p <0.5 nm   ptm: 10–100 bar

These membranes are dense, without pores and reject molecules of molecular mass <300 Da, for example, salt, sugar, etc…

Applications: sea water desalination, pure water preparation, treatment of effluents and lactoserum.

Osmotic pressure:. Osmotic pressure $\Delta\pi$ is given by

$$\Delta\pi = CRT \qquad \text{where C= molar concentration, R=8.31 (SI units), T= absolute temperature}$$

$\Delta\pi$ increases with molar concentration, which is the case for small molecules. For example, salt water with 30 g/L of salt has a concentration of 500 mole/m³ and $\Delta\pi$=12.5 bar. If pure water at pressure p_1 is separated from salt water at pressure p_2 by a semi permeable membrane, and if $p_1 = p_2$, pure water tends to dilute salt water to adjust these concentrations. There will be no transfer if $p_2 = p_1 + \Delta\pi$. Reverse osmosis corresponds to the case where $p_2 > p_1 + \Delta\pi$ and there will be a salt water transfer towards pure water. In microfiltration, osmotic pressure is negligible, as C is of the order of 1 mole/m³. In ultrafiltration, C will be of the order of 10 mole/m³ and $\Delta\pi$ varies from 0.1 to 1 bar. In nanofiltration, C is around 100 mole/m³ and $\Delta\pi$ varies from 3 to 10 bar. In reverse osmosis, $\Delta\pi$ varies from 10 to 40 bar. High transmembrane pressures are necessary to obtain important permeate flux in NF and RO. More generally, permeate fluxes decrease with decreasing pore size when changing from microfiltration to reverse osmosis. Solutes cross the membrane by solution-diffusion. Manufacturers of nanofiltration and reverse osmosis are often the same as those of ultrafiltration.

B. Processes based on diffusion or migration.

1.2.5   Dialysis

Solute transfer through the membrane is carried out by diffusion and is proportional to concentration difference between both sides of the membrane. Thin ultrafiltration membranes are used to limit the resistance to diffusion. Mass flux is given by $J_s = k(C_s - C_D)$ where k is the mass transfer coefficient, C_s is the solution concentration and C_D is the concentration of dialysate, which circulates at counter-current in order to maximize transfers.

Main application: Hemodialysis (artificial kidney), delivered 3 times a week to about 2 millions of patients worldwide, with a production of $10^8 m^2$ of membranes per year. The membrane eliminates water corresponding to the urine not produced by the patient. This process will be described in details in section 5.3.1.

Manufacturers: USA: Baxter, Extracorporeal. France: Hospal. Sueden: Gambro. Italy: Sorin. Germany: Fresenius. Japan: Toray, Nipro, Kuraray.

1.2.6   Electrodialysis

Electrodialysis membranes are electrically charged and alternatively anionic (+) repelling anions (-) and cationic (-) repelling cations (+) with an electrical field perpendicular to membranes and supplied by two electrodes. Modules are of plane filter type with rectangular parallel membranes. Ion migration takes place in even compartments and pure water is collected in odd compartments Membranes are made of hydrophobic ion exchange resins with fixed charges (PO_3^{2-}, COO^-, NR_3^+, PR_3^+) separated by a grid.

Alternative: bipolar membranes (with positive and negative sides) permitting to separate positive and negative ions and acid and base.

Applications: desalination of brackish waters, demineralization and denitrification of drinking water and food products (cheese, lactoserum), metal salts recovery from rinsing water. Waste water treatment, amino acid separation, production of lactic acid by bipolar membrane, extraction of organic ions produced by fermentation.

Manufacturers: Eurodia (Tokuyama), Corning EIVS.

1.2.7   Pervaporation

In this process, permeate is vaporized under vacuum and recovered by condensation on a cold plate.

Applications: fractionation of volatile fluids (water-alcohol), desalcoholisation of wines and beer, dehydration of organic solutions. Concentration of ethanol by hydrophilic membrane (PVA). Extractions of organic compounds in permeate with silicon organophilic membranes.

Advantage: this process requires less energy than distillation and is more selective for volatile compounds.

Manufacturer: France: Carbone Lorraine, GFT.

2   Fluid Mechanics

2.1   Poiseuille Flow

2.1.1   Plane Channel

Assumption: laminar steady flow, in a long duct, L >> h (thickness)
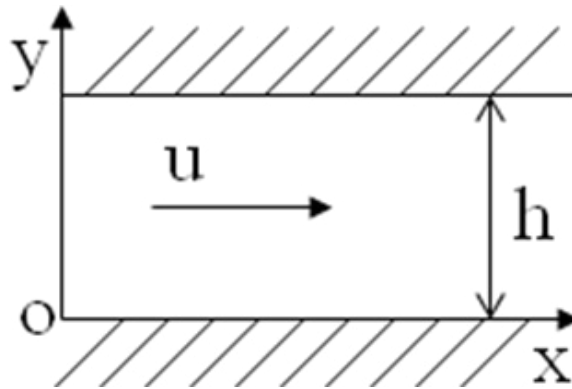
Fig.1. Plane channel of height h

If the Reynolds number Re $=\rho uh/\mu$ is < 2200, the velocity profile u is parabolic and given by

$$u = \frac{1}{2\mu} \ \frac{dp}{dx} \ (y^2 - yh) \tag{3a}$$

And the flow rate is Q = $\int_0^h b\,u\,dy$ = -bdp/dx (h^3/12μ)   (3b)

where h is the channel height and b the width.

Consequence: dp/dx is constant and negative

Poiseuille's law for pressure loss along a length L is

Δp =-Ldp/dx = 12 μQL/ (bh$^{3)}$ (4)

The shear rate at membrane is, γ_w = du/dy = 6Q/ (bh^2) = 6V/h   (5)

where V = mean velocity across the section

2.1.2   Cylindrical channel (hollow fibers and tubular membranes) with laminar flow

The velocity profile is also parabolic and given by (6) where d = 2R is the diameter, and μ is the dynamic viscosity
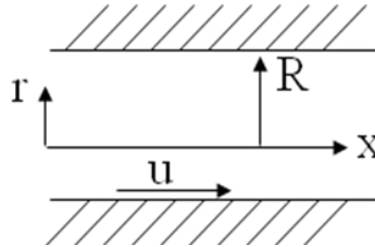
Fig. 2. Cylindrical channel of radius R.

$$u = \frac{1}{2\mu} \frac{dp}{dx} \left(r^2 - \frac{d^2}{4} \right) \tag{6}$$

The flow rate is

$$Q = 2\pi \int_0^R ru\ dy = -\ (dp/dx)\ \pi\ d^4/\ (128\mu) \tag{7}$$

The pressure drop is

$$\Delta p = 128\mu QL/\ (\pi d^4), \tag{8}$$

And the shear rate is given by $\gamma_w = 32Q\ /\ (\pi d^3) = 8v/d$ (9)

2.2   Turbulent flow (Re >2600)

A transition regime between laminar and turbulent flows occurs when 2200<Re<2600. When the Reynolds $\rho ud/\mu$ number exceeds 2600, the flow becomes turbulent and the pressure drop Δp is proportional to a friction coefficient f depending upon Re and wall roughness and is given by the Moody diagram

For a plane channel of height h $\Delta p = 1/2\ f\ (L/h)\ v^2$ (10)

For a cylindrical channel $\Delta p = 1/2\ f\ (L/d)\ v^2$ (11)

where v is the mean velocity across the section. The velocity profile is no longer parabolic, but flat in the channel center, its variation occurs in boundary layers near the walls, which increases the shear rate near the wall for the same flow rate as in laminar.

2.3   Laws of tangential filtration

With pure water, the flux J is proportional to the transmembrane pressure p_{tm} (law of porous media) and given by

$$J = p_{tm}/ (\mu R_m) = L_p p_{tm} \tag{12}$$
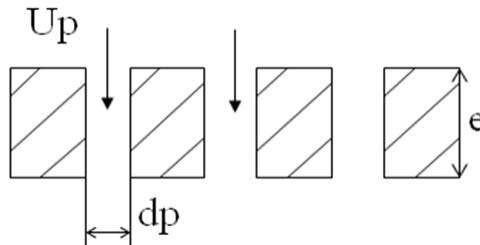
Fig. 3. Schematic of pores in a membrane.

R_m (m^{-1}) is the membrane resistance, which depends upon membrane thickness, and pore number per cm^2 N and their diameter d_p and L_p is hydraulic permeability.

For an ideal membrane with identical cylindrical pores, Poiseuille law (8) gives

$$R_m = 128e/ (\pi d_p N) = 32e/ (\varepsilon d_p^2) \tag{13}$$

where ε is the porosity equal to the ratio of pores volume /to total volume and

$$\varepsilon = N \,\pi d_p^2/4 \tag{14}$$

2.3.2   Solution containing macromolecules or particles suspensions

A layer of rejected molecules or particles deposits on the membrane and creates an additional resistance R_c which increases with time.

Rejected molecules create an osmotic pressure $\Delta\pi$ which must be deducted from p_{tm}.

$$J = (p_{tm} - \Delta\pi)/\,[\mu(R+R_c)] \tag{15}$$

Remarks: 1. R_c increases also with p_{tm} and the flux J is no longer linear with p_{tm}

2. If the temperature T increases, μ decays and J rises.

2.3.3   Concentration polarization

Definition: this phenomenon is due to the formation of macromolecules layer which occurs in UF, NF, and RO and limits permeate flux at high p_{tm}. It can form in less than 1 min on the membrane. This layer may disappear if p_{tm} is reduced
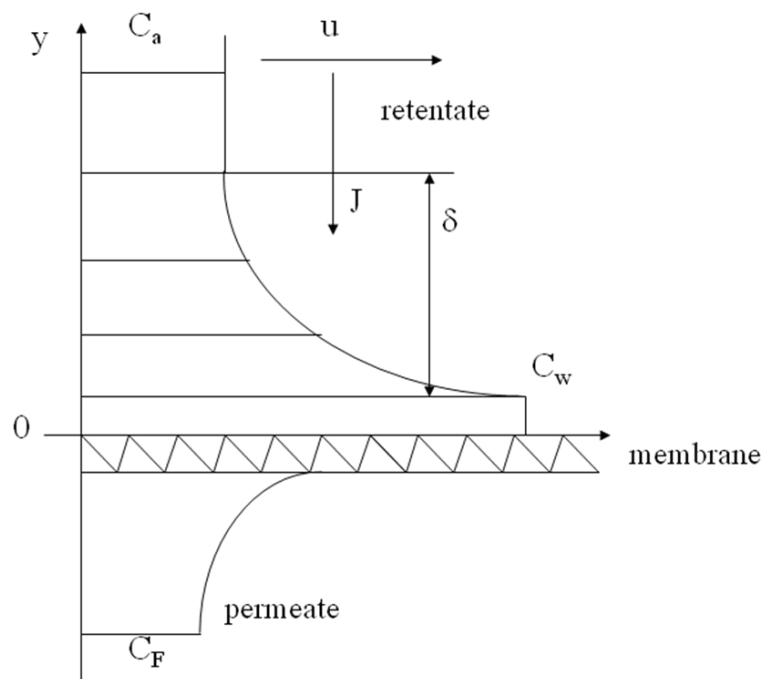
Fig.4: Concentration profiles on each side of membrane in presence of concentration polarization with a boundary layer thickness δ.

Consequences: This layer disappears if the ptm is cancelled. If the solute is completely rejected by the membrane, the condition of flux equality on each side of the membrane gives

$$JC = -D \ (dC/dx) \quad \text{where D is the solute diffusion coefficient} \tag{16}$$

By integrating (16) from x=0 where C=C_w (membrane concentration) to x= δ where C=C_a, concentration at the surface of polarization layer, one obtains for the flux a plateau J_{max} independent of ptm such that

$$J_{max} = (D/\delta) \ln (C_w/C_a) \quad \text{in case of total rejection} \tag{17}$$

where D/δ is the mass transfer coefficient. The macromolecule concentration C_w at membrane depends of the type of molecule. For instance, for albumin, C_w =300 g/L.

In case of partial rejection, permeate concentration is C_F =SC_w ≠0, (18)

where S is the sieving coefficient, ratio of concentrations on each side of the membrane. In this case Eq. 16 becomes

$$JC = -D \ (dC/dx) + S \ C_w \tag{19}$$

By substituting C-C_F to C in (16), one obtains Eq. 20 by integration over y

$$J_{max} = k \ln \frac{C_w - C_F}{C_a - C_F} \tag{20}$$

J_{max} decreases if C_a increases, but is limited to $C_a = C_w$, which can be calculated by measuring J at various concentrations, and plotting it versus C in semi log coordinates and extrapolating at J=0 where C= C_w.

Demonstration of Eqs. 17 and 20

Assumption. In the boundary layer of thickness δ, C =C(y) and the solute flux towards membrane is equal to the flux leaving the membrane by diffusion. Eq. 16 is integrated over the thickness of the boundary layer from y=0 to y=δ, and from C=C_w to C= C_w -C_a

$$[Jy]_0 \ \delta = -D \ \ln C]^{Ca}_{Cw} \quad \text{or} \quad J = (D/\delta) \ln(C_w/C_a) \tag{21}$$

In case partial rejection, (19) becomes

$$JC = -DdC/dy + JC_F \tag{22}$$

Taking C'=C-C$_F$ and since dC$_F$/dy=0, dC=dC' and (22) gives

$$JC'=-DdC'/dy \hspace{6cm} (23)$$

 Hence, by integration we obtain

$$J=k\ln(C_a'/C_w') \hspace{6cm} (24)$$

Example of concentration polarization in milk ultrafiltration

Skim milk was ultrafiltered with a VSEP dynamic filtration module equipped with a vibrating membrane of 50 kDa cut-off at a TMP of 400 kPa. The permeate flux decays linearly in Fig. 5 with the logarithm of the volume reduction ratio (VRR= V_0/V) according to (.21), where V_0 is the initial volume and V the current one. The maximum VRR was determined by extrapolation at J=0 to be 8.66. The maximum VRR for a tubular module with the same membrane was only 5.6 and its permeate flux was lower.
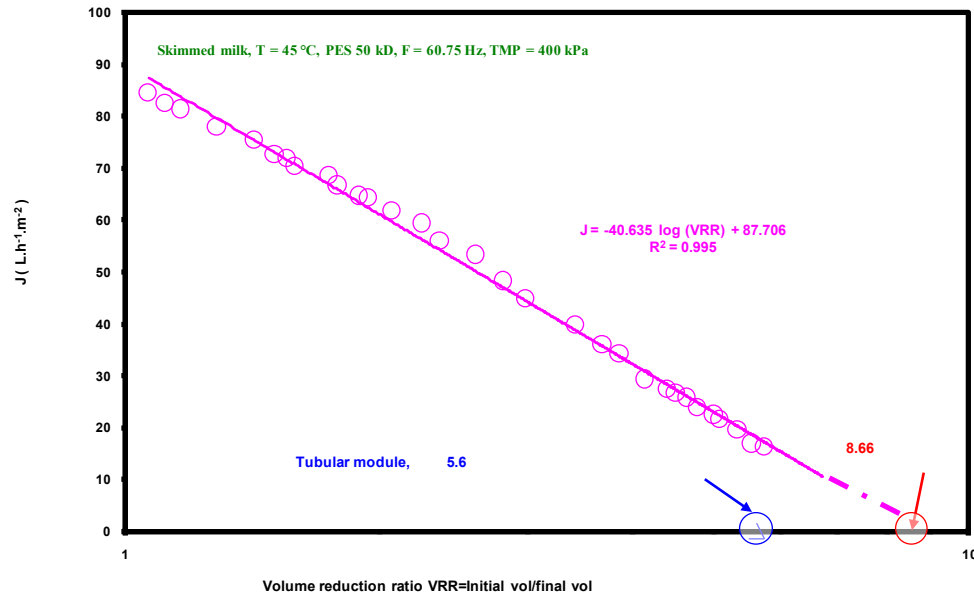
Fig. 5. Variation of permeate flux of a VSEP vibrating module with VRR during concentration of milk proteins by UF at 50kDa. Comparison with a tubular module.

Apparent rejection rate R'

The only concentrations easily accessible are those at the module inlet (C_e) or those of permeate (C_F) and retentate outlet. It is then practical to define apparent rejection rates R' and sieving coefficients S' based on concentrations C_e and C_F

$$R' = (C_e - C_F) / C_e \qquad\qquad (25a)$$

and $$S' = C_F / C_e = 1 - R' \qquad\qquad (25b)$$

2.3.4   Calculation of mass transfer coefficient k

This coefficient permit to calculate permeate fluxes in various situations, using the Sherwood number $Sh = k d_h / D$, where d_h is the hydraulic diameter $= 4\Sigma/P$, Σ is the cross section area, P the perimeter. Another parameter, the Graetz number is $G = v d_h^2 / (LD)$ where L is the membrane length and D the diffusion coefficient d. For a circular tube of diameter d, the section will be $\Sigma = \pi d^2/4$, the perimeter $P = \pi d$, and $d_h = d$, as expected.

For a plane filter, $\Sigma = bh$, $P = 2(b + h)$, where b=width, h=thickness <<b, $d_h = 2bh / (b + h) \approx 2h$

In the case of laminar regime, with a Reynolds number <2200, corresponding to hollow fibers or plane filters, Blatt et al [1] have shown that, in concentration polarization regime, a relation between Sherwood and Graetz numbers exists

a) In the case of tubular membranes and hollow fibers, this relation is, if G> 100

Sh =1.62 G$^{1/3}$,   (26)

which yields   (27)

$$k = \frac{DSh}{d} = 1.62 \frac{D}{d}\left(\frac{Vd^2}{LD}\right)^{1/3} = 0.81\left(\frac{\gamma_w D^2}{L}\right)^{1/3}$$

with γ_w=32Q/ (πd^{3}N) = 8v/d, if N is the number of fibers in parallel and by using (21) and (27), the permeate flux will be given by

J= 0.81(γ_wD^2/L)$^{1/3}$ln (C$_w$/C$_a$)   (28)

The permeate flux Q$_P$, with S= πdLN, where N is the fibers, number will be

Q$_F$=JS=2.56(SD/d)$^{2/3}$Q$^{1/3}$ln (C$_w$/C$_a$)   (29)

The filtration flow is independent from diameter and only depends upon the total length of fibers or tubular membranes NL. To increase permeate flux, it is necessary to augment the shear rate.

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b) In the case of a plane filter of width b and n compartments of thickness h, the relation becomes if G>330:

$$Sh = 2.2\, G^{1/3} \text{ with } G = 4vh^2/(DL) \tag{30}$$

$$\text{and } k = D\, Sh/(2h) = 1.1(D/h)(4vh^2/LD)^{1/3} = 0.96(\gamma_w D^2/L)^{1/3} \tag{31}$$

with $\gamma_w = 6Q/(bh^2 n) = 6v/h$,   hence

$$J = 0.96\,(\gamma_w D^2/L)^{1/3}\ln(C_w/C_a) \tag{32}$$

The permeate flow rate for a plane filter with n compartments, and S=2nbL becomes

$$Q_F = 2.2(SD/h)^{2/3}\, Q^{1/3}\ln(C_w/C_a) \tag{33}$$

Remarks: For both geometries, J rises if γ_w increases and L decreases. The permeate flux is proportional to $Q^{1/3}$ and $S^{2/3}$, and decreases along the membrane as the flow rate Q. In order to use these equations, one must know the diffusion coefficient D which is generally available for usual molecules.

In the case of turbulent regime, which occurs in tubular membranes, the empirical correlation of Chilton-Colburn gives

$$Sh = 0.04 Re^{3/4}\, Sc^{1/3} \tag{34}$$

And the mass transfer coefficient k_t becomes

$$k_t = 0.04\, D^{2/3}\, v^{3/4}/(d^{1/4} \nu^{0.42}) \tag{35}$$

Another correlation that of Harriot and Hamilton, writes

$$Sh_t = 0.0096 Re^{0,91}\, Sc^{0.35} \tag{36}$$

with Re $= vd/\nu$ Sc= Schmidt Nb $= \nu/D$, and gives

$$k_t = \frac{0.0096 D^{2/3} V^{0,91}}{d^{0,09} \nu^{0,57}} \tag{37}$$

Remarks: The 2nd correlation (36) gives more importance to the velocity than the 1st (34) as its exponent is higher. J increases faster with velocity than in laminar regime; it is independent from L and depends little from d. Eqs. 35 and 36 are only approximate and it is preferable to find empirical relations from experimental tests, of the type J =K v^n where n varies generally from 0.5 to 1.

For tubular membranes, one finds, with (31) and (35)

$$k_t/k = 0.00593\ Re^{0,57}(L/d)^{0.33} = 2.8 \tag{38}$$

for Re =2000 and L/d=200, which means that the laminar-turbulent transition augments the flux. It is then worthwhile to introduce turbulence promoters (obstacles inside the membranes) which increase turbulence inside plane filters and tubular membranes.

SI and traditional units relevant to membrane filtration are listed in Table 1

Parameter	SI Unit	Traditionnal unit	Parameter	SI Unit	Traditionnal unit
Length	Meter, m	1 μ=10^{-6}m	Dynamic viscosity μ	Pa s	1 cp=10^{-3}Pas Water at 20° = 1cp
Force	Newton, N	1 kg= 9.8 Newton	Kinematic viscosity ν	m^2/s	1 cs=10^{-4} m^2/s Water at 20° : 1 cs
Pressure	Pascal Pa	1bar=10^5 Pa	Flow rate	m^3/s	1 m^3/h = 0.27 10^{-3} m^3/s
Power	Watt, W	1 CV=736W	Flux, velocity	m/s	1 l/ (hm^2)= 0.27 10^{-6} m/s

Table 1. Usual units relative to membrane processes parameters.

3   Various types of membranes and modules

3.1   Organic membranes (cellulosic and polymeric)

These membranes are available as plane films and are used in microfiltration and ultrafiltration. Hollow fibers with internal diameter of 0.5 to 2 mm, are used in microfiltration, ultrafiltration, nanofiltration and reverse osmosis.

Examples: cellulose acetate, polysulfone, polyacrylonitrile, polyamide, polypropylene, cellulose acetate, teflon, polyethersulfone (PES).

Membranes characteristics: they are thin, with thickness from 10 µm (symmetrical membranes) to 200 µm (asymmetric or composites), available in the entire range of pores size from microfiltration to reverse osmosis. Asymmetric membranes contain a macroporous sublayer supporting the thin membrane.

Advantages: Their cost is moderate, from 30 €/m² for spiral modules for reverse osmosis to 800 €/m² for small plane cartridges for microfiltration. They are available in all configurations, tubular, hollow fibers, plane, and offer a large choice of cut-off and pores diameters.

Drawbacks: They do not allow steam sterilization, except for PVDF membrane. Their maximum pressure is low, 7–8 bars and their mean lifetime is 1 to 2 years.

Examples of ultrafiltration membranes

Pictures of Nadir® membranes PES 10, 50, 150 kDa and Ultran® PES 300 and 500 kDa are presented in Fig. 6.

Ultran®   Nadir®
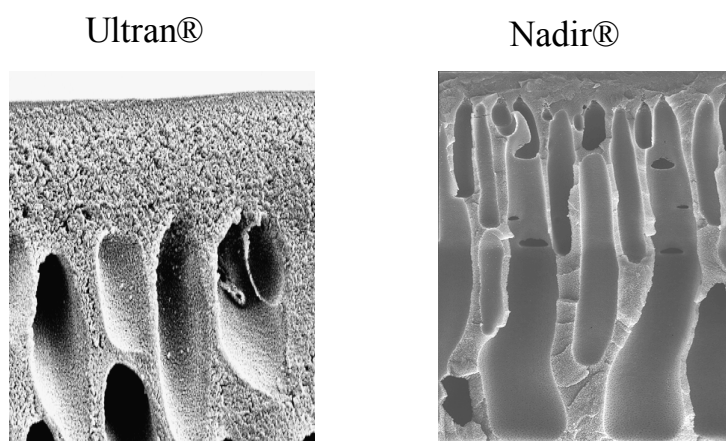
Fig 6. Examples of pores of ultrafiltration membranes

3.2   Mineral membranes

Most of them are made in ceramic, but they also exist in zirconium oxide, carbon, or porous glass. Their thickness ranges from 2 to 3 mm, and they are mainly available in tubular and multichannel types.

Advantages: They are strong and can sustain extreme pH, chemical products, high temperatures and pressures and their lifetime exceeds 3 years. They also have high permeabilities. Membrane cleaning can be made in situ by retrofiltration. They can be steam sterilized.

Drawbacks: Their price is generally high and their dead volume is important except for small TAMI flat cartridges. Some membranes are available in nanofiltration.

Main manufacturers: TAMI Co (Nyons, France) commercializes tubular and multichannel ceramic membranes from 10 to 43 mm of outer diameter. Some have single circular channels, but most membranes are multichannel of various cross sections to maximize membrane area and increase permeate flux for a given module diameter. Membralox Society (in Tarbes France, but purchased by US Filter) manufactures ceramic modules with hexagonal section containing 19 circular channels.

3.3   Various types of modules

3.3.1   Plane modules

Manufacturers: France; Orelis. USA: Millipore.UK: Dorr Olliver. Germany: Sartorius. DDS, DK.

Principle: they contain parallel compartments each composed of two parallel membranes supported by plates with grooves separated by gaskets.

Advantages: they are easy to take apart to facilitate cleaning and membranes exchange and have small dead volumes. The thickness of liquid veins is adjusted by gaskets. Plastic plates can be reused.

Drawbacks: they are difficult to clean without been taken apart, and not available with mineral membranes.

3.3.2   Plane cartridges

Manufacturers: USA: Millipore. France: Orelis, TAMI.

Principle: they are small plane filters consisting in several compartments assembled by glue, several cartridges are inserted inside a box. The presence of holes in plates permits fluid circulation.

Advantages: their dead volume is very small, they are compact, with adjustable area, and operate with small feed flows.

Drawbacks: they are costly, difficult to clean, because of glued membranes. They are mostly used in laboratories and in pharmaceutical industry. TAMI cartridges are the only ones with ceramic membranes.

3.3.3   Spiral wound modules with organic membranes

Manufacturers: US: Millipore, Koch, Osmonics.

Principle: these modules are frequently used in industry, as they offer large membrane areas, and consist of a membrane, a grid and a plastic foil rolled around a tube which evacuates the permeate. These components are placed inside a rigid cylinder to sustain large pressures. They are much used in ultrafiltration, nanofiltration and reverse osmosis for treatment of effluents and desalination of salt water.

Advantages: their cost is small (30$/m^2 for desalination of salt water) and their surface/volume ratio is high.

Drawbacks: they are subject to fouling, their performances are difficult to control, and their cleaning is difficult.

3.3.4   Tubular modules

They are available with organic or mineral membranes (multi-channels), with inner diameters from 2.5 mm to 30 mm.

Manufacturers: USA: Koch, PCI (organic), Millipore . France: TAMI (ceramic), Orelis, SCT. Germany: Schumacher, Aaflow, Wesfalia Separator.

Advantages: They are well suited to highly charged or very viscous liquids and are easy to clean.

4   Modelisation of membrane circuits

4.1   Conservation of volume and mass flow rates

At a bifurcation

Volume flow rate: $Q_3 = Q_1 + Q_2$ (39)

Mass flow rate: $Q_3 C_3 = Q_2 C_2 + Q_1 C_1$ (40)

where C is solute concentration
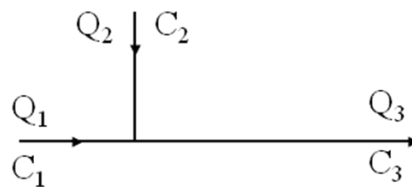
Fig. 7. Conservation of volume and mass flow rates at a bifurcation

In a filtration module
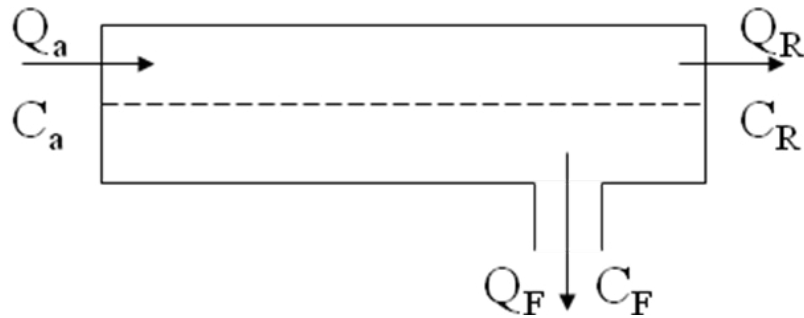
Fig.8. Conservation of volume and mass flow rates in a flat module

Volume flow rate $\qquad Q_R = Q_a - Q_F$, $C_{F\,=}\,S\,{}^{\prime}C_a$ $\hfill$ (41)

Mass flow rate $\quad Q_a C_a = Q_R C_R + Q_F C_F = Q_R C_R + Q_F S\,{}^{\prime}C_a$ $\hfill$ (42)

Hence

$$C_R = \frac{Ca(Q_a - S'Q_F)}{Q_a - Q_F}$$ (43)

If S'=1, there is no rejection $C_R = C_a$ $\hfill$ (44)

4.2 Single batch filtration circuit

Fluid conservation: $dV/dt = -Q_P$, $\hfill$ (45)

Solute conservation: $d(VC)/dt = -QC$ $\hfill$ (46)
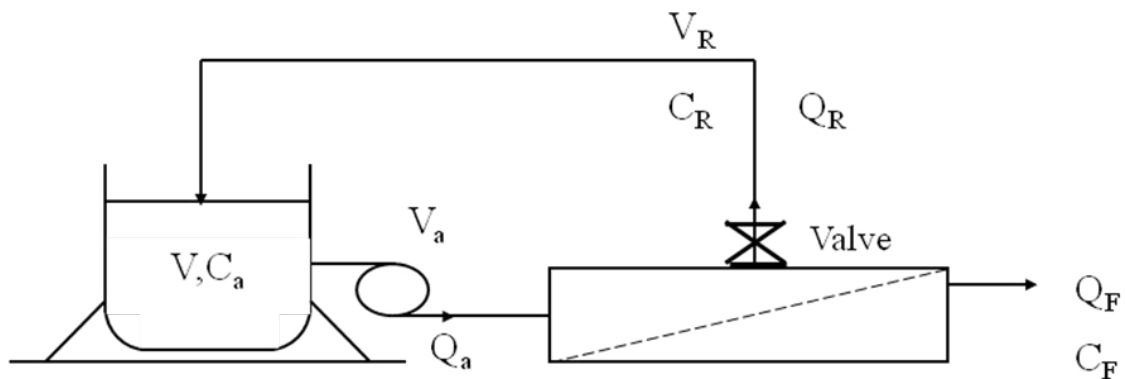
Fig. 9. Schematic of filtration bench in single batch

Assumption: The retentate volume in circuit is much smaller than the tank volume. The retentate is recirculated by a pump into the feed tank, while permeate is collected. This type of bench is used for pilots and small units.

Nomenclature

V_R = Retentate dead volume, V= fluid volume in tank

V_a = feed dead volume

C_a, C_P, C_R = feed, filtrate, retentate concentrations increase with time

Advantages: This bench permits to concentrate solutions to high ratios, due to recirculation.

Drawback: the recirculation into the tank requires a pump with high flow rate which must be volumetric to keep flow rate independent from ptm.

4.2.1   Modelisation of single batch with partial rejection

Fluid: $dV/dt = -Q_F$ (47)

Solute: $d(Vc_a)/dt = -Q_F C_F = -S'C_a Q_F$ (48) with $C_F = S'C_a$

Subtracting Eq.47xC_a from Eq.48 gives

$$V dC_a/dt = (S'-1)C_a dV/dt \qquad (49)$$

Hence if S' = const

$$C_a V^{1-S'} = Const = C_{a0} V_0^{1-S'} \qquad (50)$$

even if Q_F is time dependent

If S' =1, no rejection, $C_a = C_{a0}$, and there is no concentration

If S' <1, C_a increases when the tank gets emptied

If Q_F = Const (stabilized fouling) $V = V_0 - Q_F t$ (51)

$$\frac{C_a}{C_{a0}} = \frac{1}{(1 - Q_F t/V_0)^{1-S'}} \qquad (52)$$

As VRR= V_0/V, we obtain

$$C_a/C_0 = (VRR)^{R'} \qquad \text{where R'=1- } C_F/C_a \text{ is apparent rejection rate} \qquad (53)$$

And, if R '=1, we have

$$\mathbb{C}_a/C_0 = VRR \qquad\qquad (54)$$

While with R'<1 partial rejection, C_a/C_0 will be less than VRR

The recovery factor in retentate r_R is given by

$$r_R = C_a V/(C_0 V_0) = (VRR)^{R'-1} < 1 \text{ for partial rejection} \qquad (55)$$

$$= 1 \text{ for total rejection}$$

4.3   Diafiltration in single batch

The goal of diafiltration is to eliminate microsolutes without concentrating the rejected solute in retentate. The tank receives a water flow rate $Q_d = Q_F$. Thus, fluid volume in circuit remains constant and rejected solute concentration does not change.
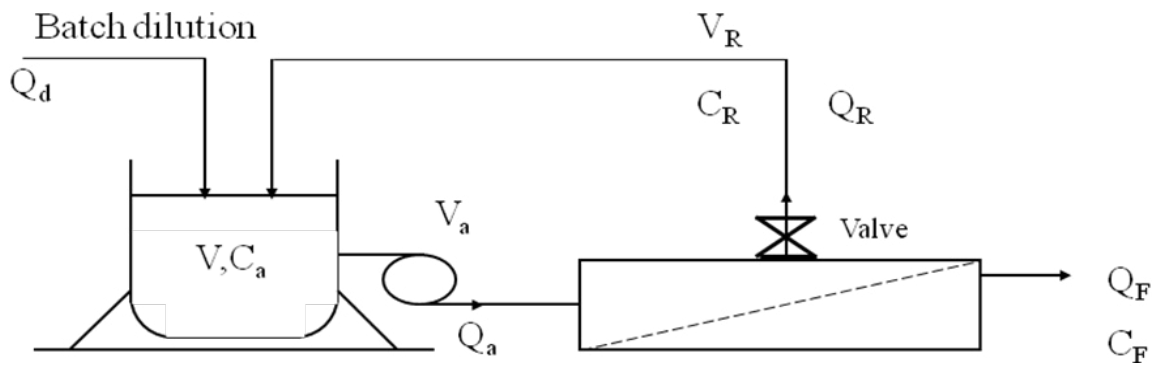
Fig.10. Diafiltration circuit with water feeding in the tank to diluate retentate.

Modelisation of diafiltration

$$dV/dt = Q_d - Q_F = 0 \qquad \text{hence } V = V_0 \tag{56}$$

Mass conservation on tank gives

$$V_0 dC_a/dt = -Q_F C_F = -Q_F (1-R') C_a \tag{57}$$

If Q_F=const, and V_F is permeate volume, integration of (57) over time gives

$$C_a = C_0 \exp[-Q_F(1-R')t/V_0] = C_0 \exp[-V_F/V_0] \tag{58}$$

With partial rejection (R'<1), C_a decays exponentially while, if R'=1, $C_a = C_{a0}$ and the retentate does not concentrate.

Example: if R'=1, $V_F = V_0$, $C_a/C_0 = 0.36$, 64% of microsolute has been eliminated. To eliminate 99% requires a filtration volume $V_F = 4.6 \, V_0$, according to (58).

Optimisation of a diafiltration

If the rejected solute is concentrated before diafiltration, this reduces the initial volume V_0, but also the flux given by $J=k\ln(C_w/C)$. It can be shown that diafiltration will be shorter if the fluid is concentrated until the optimal concentration $C_{opt} = C_w/2.73$.

4.4   Batch with recirculation loop
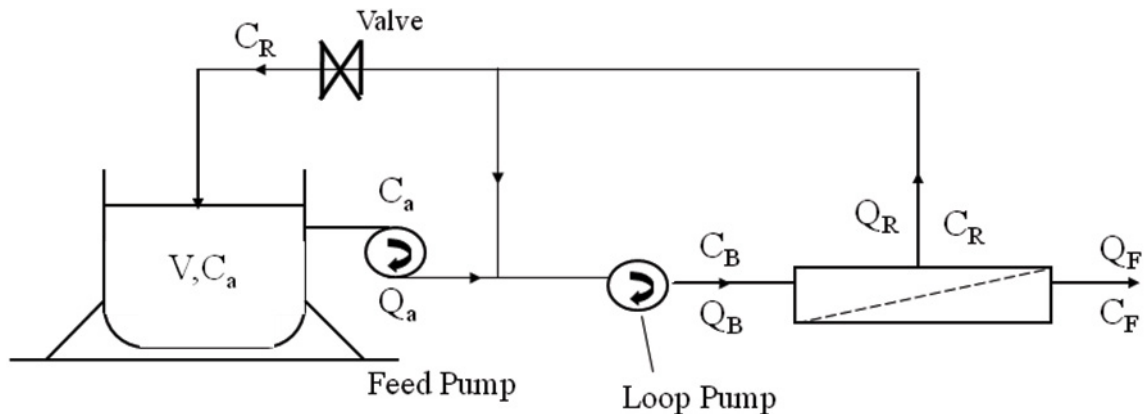
Fig. 11. Bench with filtration module in recirculation loop

Advantage: by recirculating the retentate through the filter in the loop with a 2nd pump, fluid velocity v is increased along the membrane. The loop pump does not need to be volumetric as it only needs to overcome the pressure loss along the membrane. The feed pump, which supplies the loop pressure, will have a smaller flow rate than the loop pump, which saves energy. Loop concentration will be higher than the tank one and the rejection rate will be decreased.

Drawback: two pumps are necessary and concentration is higher in filter than in tank.

Modelisation of circuit with recirculation loop

Volume conservation: $dV/dt = -Q_F$, $Q_R = Q_B - Q_F$, $Q_c = Q_a - Q_F$ (59)

Solute conservation writes

On system: $d(V C_a)/dt = -Q_F C_F = -Q_F C_B (1-R')$ avec $C_F = C_B (1-R')$ (60)

On filter: $C_B Q_B = C_F Q_F + C_R (Q_B - Q_F)$ (61)

On loop $Q_a C_a = Q_F C_F + C_R (Q_a - Q_F)$ (62)

If $Q_B >> Q_F$, $C_B \approx C_R$ fluid in filter on retentate side is weakly concentrated. With total rejection

$C_F = 0$ and (61) gives

$$C_R/C_a = Q_a/(Q_a - Q_F)$$ (63)

This ratio may be high if Q_a is close to Q_F.

4.5   Continuous operation with loops in series and parallel modules
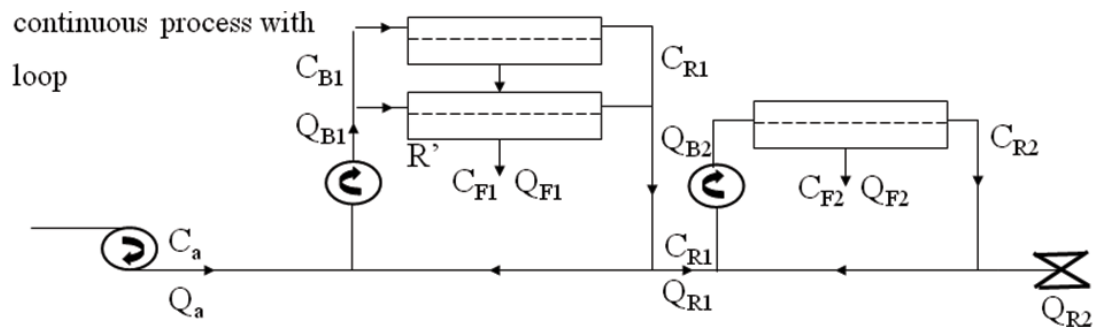
Fig. 12. Continuous process with recirculation loops

The system, presented in Fig.12, is fed continuously by a pump. Recirculation takes place in a series of loops. The VRR will not vary with time, but with the number of loops. Several steps are necessary to reach a high VRR, which requires a large membrane area and the system will be more complex.

Advantage: A feed tank is not necessary, and this circuit will consume less energy than a batch system with a tank. This process is used in plants with a large production.

Drawback: Membrane area is higher than in previous systems.

4.5.1   Modelisation of continuous operation

Case of total rejection

1st stage:

Flow rate conservation writes

$$Q_a = Q_{R1} + Q_{F1} \tag{64}$$

And solute conservation is

$$Q_a C_a = Q_{R1} C_{R1} \tag{65}$$

The concentration factor is given by

$$C_{R1}/C_a = Q_a/(Q_a - Q_{F1}) \tag{66}$$

2nd stage:

The concentration factor between 2 stages is:

$$C_{R2}/C_{R1} = Q_{R1}/(Q_{R1} - Q_{F2}) \tag{67}$$

So, the global concentration factor is

$$C_{R2}/C_a = Q_a/(Q_a - Q_{F1} - Q_{F2}) \tag{68}$$

In the case of several stages in series, the global concentration factor becomes

$$C_{Rf}/C_a = Q_a/(Q_a - \Sigma Q_F) \tag{69}$$

Case of partial rejection

Permeate concentration is

$$C_F = C_{R1} (1-R') \tag{70a}$$

And mass balance on 1st stage becomes

$$Q_a C_a = Q_{R1} C_{R1} + Q_{F1} (1-R') C_{R1} \tag{70b}$$

By solving Eq. 70 for C_{R1}/C_a with (66), one finds

$$C_{R1}/C_a = Q_a / (Q_a - R'Q_{F1}) \qquad (71)$$

The concentration factor is smaller than with total rejection.

4.6   Experimental tests on pilots

Precautions

It is necessary to use a pilot with a complete instrumentation and pressure transducers before and after the filter. Pumps must be volumetric.

It is preferable to use the same filter type (tubular membrane, hollow fibers or plane module) as in the final system, in order to get a permeate flux representative of the industrial module.

Tests procedure

One can start with tests at constant concentration with full recycling of permeate and retentate on the tank. The pressure rise progressively during starting conditions and the flux J(t) and the pressure drops at constant ptm are measured for various fluid velocities. Then fluxes are measured at various ptm in stabilized conditions. Different membranes must be tested for screening. Concentration tests are carried out without permeate recycling at optimal ptm. The maximum VRR is given by

$$VRR_{max} = V_0/V_{dead} \qquad (72)$$

where V_0 is the initial fluid volume and V_{dead} the dead volume of pipes.

4.7   Membranes cleaning

A periodic cleaning is generally necessary to eliminate fouling layers and pores plugging in order to retain membranes performances. Membranes used in the food industry must be cleaned every day. This cleaning must be followed by rinsing with soft water demineralized by ion exchanger resins to eliminate traces of cleaning products. More generally, cleaning agents must eliminate organic compounds, micro-organisms and dissolve mineral salts.

4.7.1   Deposits composition

They include mineral salts (calcium carbonate, sulfates), hydroxides, biological films and organic matters (proteins, pectins) which constitute the main cause of fouling in, biological and food applications. Proteins must be eliminated with alkaline detergents as they are compatible with mineral membranes and a majority of polymeric membranes.

Modes of chemical cleaning vary according to deposits composition

Chemical Agents	**deposits**
❖ nitric acid, 5g/L,70°	carbonated deposits, hydroxides
❖ basic (soda NaOH, 4 g/L, N/10, 65°)	organic deposits
❖ oxidant solutions, chloride	biological deposits
❖ detergents (enzymes 1%+rinsing)	organic deposits of proteins

Hydrodynamic cleanings

❖ counter-current cleaning. The permeate valve is shut and the flow direction in module is reversed.

❖ retrofiltration. The permeate circuit is briefly pressurized to reverse filtration direction through the pores, into the retentate.

❖ sair retrofiltrations (Memcor process). The permeate circulates inside hollow fibers and is pressurized by compressed air, while retentate circulates between hollow fibers.
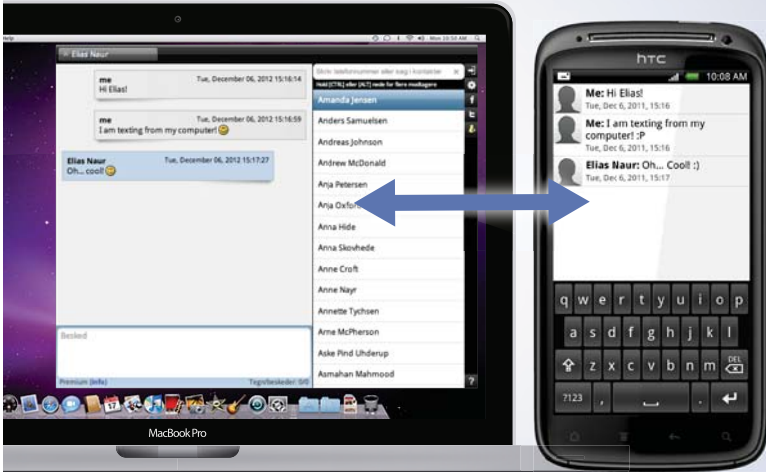
Cleaning efficiency can be evaluated by measuring the hydraulic permeability of membranes with pure water after each cleaning. This permits to calculate the membrane resistance R_m defined by (12). Fouling resistance R_c defined by (13) can then be calculated from permeate flux of filtered solution. This resistance can be divided into an irreversible part R_{ir} which remains after cleaning, and a reversible one R_r removed by cleaning. But the absence of chemical contamination by cleaning products and by living micro-organisms must be verified.

Fouling mechanisms

Membrane fouling reduces permeate flux with time, fast at first, as the reduction is due to the formation of a concentration polarization layer. Later, the reduction becomes slow and irreversible. Surface fouling is due to rejected particles forming a cake, deep fouling occurs by adsorption of particles or solutes which shrinks pores diameters.

Variation of permeate flux with time is measured at constant concentration, various circulation speeds of the fluid and different pressure rises. Internal fouling of pores can be evaluated by electronic microscopy. Biologic fouling caused by microorganisms is a major challenge in many processes. Its control requires an analysis of the biofilm deposited on the membrane, that can be made with confocal laser microscopy and image analysis. Biofilms can form during treatment of effluents containing inorganics salts with limited solubility, colloids and macromolecular organic compounds by nanofiltration and reverse osmosis. These biofilms accelerate permeate flux decline.

Enzymatic cleaning

This cleaning permits to improve the efficiency of fouling removal when chemical treatments are not adapted. It consumes less energy than chemical treatments, but enzymatic detergents are more expensive and their action is slower. Enzymatic cleaning is frequently associated with alkaline and acid treatments. Most used enzymes are modified proteases (alcalase, durazyme, esperase, savinase) with pH from 7 to 11. This cleaning efficiently decreases the hydraulic resistance, but its disinfection may be insufficient as tension-active agents fixed on membrane may consume a good part of des disinfectants and chemical agents. Liquid enzymatic detergents actually seem to be the best, as their activity is conserved during storage.
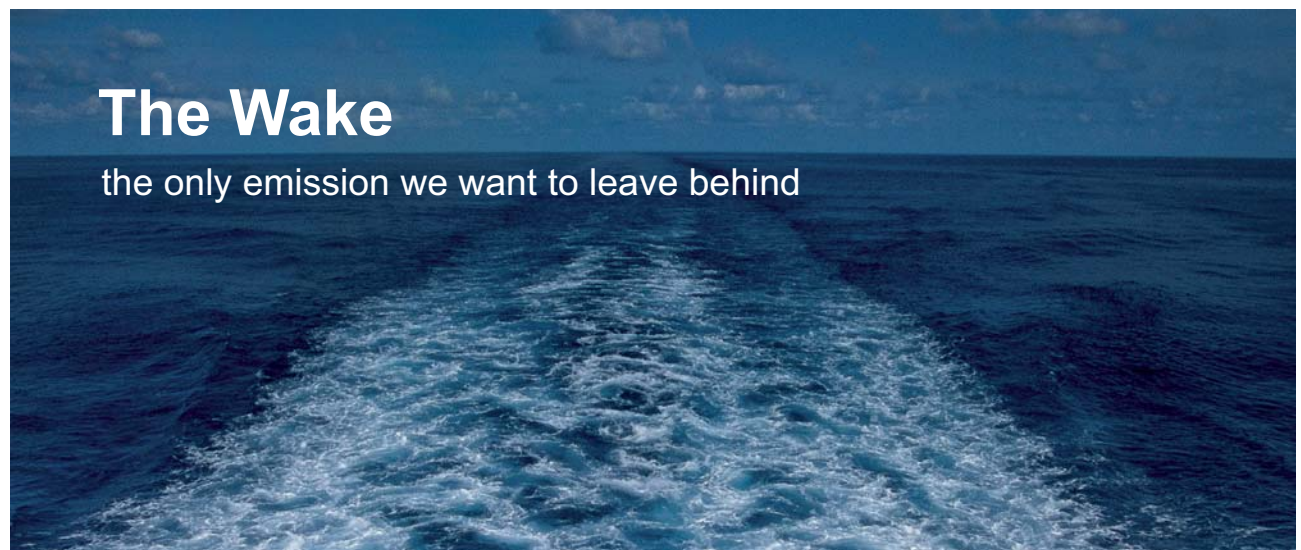
5   Applications of membrane processes

5.1   Cross flow filtration against the concurrence

Microfiltration is frequently used for clarification of fluids in the food industry and as pretreatment before ultrafiltration or nanofiltration. Competitive processes are centrifugation, adsorption on kieselguhr, dead end filtration and decantation.

Ultrafiltration is well suited for concentration and fractionation of various components. Its competitors are distillation and evaporation.

Nanofiltration and reverse osmosis are used for waste water treatment by elimination of small molecules such as ions and lactose in dairy industry and for desalination of salt water by reverse osmosis. Their main competitor is chromatography.

Advantages of membranes relatively to traditional processes

Membrane processes are continuous, and are easily automatized. They can operate during long periods without regeneration (24 hr in food industry). They offer better quality products, especially concerning water obtained from effluents. They permit the recovery of various constituents in permeate and retentate.

5.2   Applications to dairy industry

World dairy industry is one of major membrane consumers for lactoserum treatment and proteins valorization. Three membranes generations have been or are still utilized.

- Cellulose acetate is no longer present because of its limitations in PH from 3 to 8 and in temperature with a maximum of 50°C.
- Polysulfone manufactured by Amicon, Romicon and Techsep can support PH from 1 to 12, and a 75°C temperature, but does not resist well to chlorine disinfectantss.
- Mineral membranes manufactured by TAMI and Pall (Membralox) can be steam-sterilized.

A. Microfiltration

5.2.1   Milk debacterisation by membrane (cold pasteurization)

The goal is to retain bacterias by the membrane while transmitting all proteins. A problem is that casein micelles are retained even with 0.8 μm pores and form a cake which rejects proteins. An alternative is the Bactocatch process of Alfa Laval using mineral membranes of 1.4 to 0.8 μm pores and a high fluid velocity of 8 m /s. To avoid a high inlet ptm, the permeate is recycled by a pump in the same direction as the retentate, that permits to keep a uniform ptm of 0.4 bar. This process is efficient, but energy cost is high.

5.2.2   Casein extraction for cheese products

Casein micelles are retained in retentate, while soluble proteins cross the membrane into permeate. The process starts with a 1st microfiltration in order to concentrate the retentate three times with microfiltration membranes of 0.1 to 0.2 μm pores, followed by diafiltration until a VRR of 5. The purified micelles suspension is then dried and called native phospho-caseinate.

5.2.3   Selective proteins separation

Casein is separated from soluble proteins αLa and βLg in order to make cheeses from UHT milk. It is concentrated until VRR =3. It is also possible to prepare milk with a reduced soluble proteins /casein ratio, after retaining micellar caseins by microfiltration. This ratio is reduced by a diafiltration diluting soluble proteins in permeate.

B. Ultrafiltration:

5.2.4   Milk proteins standardisation

In order to compensate seasonal variations of milk proteins concentration which can perturb cheese fabrication in plants, a part of production is concentrated to a VRR of 2 to 4 and is mixed to the initial milk according to the needs to obtain the selected proteins concentration (from 35 to 45 g/L). This standardization permits to increase cheese proteins content and consequently to reduce the coagulant enzyme quantity, while insuring a stronger gel. Brewing and casting will be easier.

5.2.5   Cheese Fabrication

The draining of traditional process is replaced by an ultrafiltration of proteins with a 10–15 kDa cut-off membrane. This process, called MMV from the initials of its inventors (Maubois et al) has been implemented and patented at INRA (National Institute of Agronomic Research) of Rennes. The ultrafiltration eliminates the major part of water, mineral salts and lactose, but retains all soluble proteins representing 20% of total proteins and caseins. The product is more homogeneous and reduces losses of nitric matters at 4% against 23%by draining. Rennet and ferments are introduced into the retentate together with the necessary cream quantity. Temperature is set at 60°C because of the high viscosity. The draining produces a proteins loss of 25% in lactoserum which is a polluting product. With ultrafiltration, 100kg of milk contains 19 kg of proteins and 81 kg of lactoserum, against respectively 15 and 85 kg by draining. Rennet is added after ultrafiltration, permitting to save a part of it. The MMV process is utilized to make feta and soft cheese, camembert, brie, etc… The choice is between making cheese at low temperature <10°, to protect it from bacterial developments, but create prohibitive pressure losses because of the high viscosity at high concentrations, or to work at 50°C to diminish pressure losses with a risk of bacteria proliferation.

The best solution is to work at low temperature until a concentration ratio of about 3, and to reach the desired final concentration by heating the retentate at 50°C. This process is applied to the fabrication of Swiss cheese and feta, pressed cheese, such as saint Paulin and gruyere cheese. It permits to save 15% of milk. For fresh cheeses which contain 82 % of water, the concentration ratio is limited to 2 and since the viscosity is moderate, one can operate at low temperature. For camembert and goat cheeses the temperature is limited to 4°C until the dry matter, essentially nitric proteins reach 10%, then the temperature is raised to 50°C until a concentration of 20% in nitric matters. Losses of nitric matters are only 5% with ultrafiltration against 17 to 23% with the traditional process.

Drawbacks

The augmentation of ions concentration (Ca, Mg, and Potassium) mixed with caseins in the same proportion as proteins may modify the cheese taste, which becomes more acid. To avoid this acidity, one can add salt at the end of ultrafiltration or diafiltrate the cheese for the saint Paulin and start a lactic maturation for fresh cheeses. It is also possible to ultrafilter a milk acidified by lactic ferments which will fix Ca et Mg ions on soluble micelles, and will permit their elimination in permeate..

Fabrication of fresh cheeses

This process begins by concentrating milk by ultrafiltration before its acidification and coagulation by rennet. To avoid an excessive acidity, the milk is heated during 20 s at 80°C, which reduces the acid taste.

Fabrication of soft cheeses

For camembert, milk is concentrated 5 times until a dry matter content of about 35%. Milk is slightly acidified until a pH of 6.4 and the retentate is diluted par diafiltration to adjust ionic balance. 90% of feta is prepared by the MMV process. Milk is also concentrated 5 times before being directly coagulated during cheese packing and this process is very much developed, especially in Denmark.

The MMV process cannot be applied to hard cheeses (gruyere), as it does not permit to obtain a high enough concentration for their fabrication.

5.2.6   Thermal treatment of milk at the farm

Normally, once milk has been collected from animals, it is kept at 4°C at the farm. Then, before distribution, it is heated at every four days at 72°C in order to destroy germs. It is not necessary to transport water and lactoserum, as only 20% of collected milk is consumed as milk or cheese. To avoid energy losses by heating, cooling, or transportation, milk can be ultrafiltered at the farm in order to add proteins and fat mass to retentate which represents only 20% of milk produced by the cows, while lactose and mineral salts that constitute the permeate are consumed in the farm by animals. This system is commercialized by Alpha Laval.

5.2.7   Fractionation of lactoserum by draining

The lactoserum is a by-product of cheese fabrication, and a pollutant because of its high content in organic compounds exposed to aerobic fermentation. Its composition for cheese obtained by draining is the following: lactose: 47 g/l, proteins: 8 g/l, mineral salts: 7 g/l, fat mass: 1.5 g/l.

Production of one kg of cheese generates from 5 to 10 kg of lactoserum. Its evaporation gives a dry product containing 12 to 14% of proteins, which is not enough to be commercialized.

To reduce COD (chemical oxygen demand, responsible of pollution) and to augment proteins content, 80% of proteins are recovered by ultrafiltration at 10 kDa, and permeate containing lactose is then treated by reverse osmosis. The retentate contains concentrated lactose, while the permeate, with a small quantity of organic pollutants can then be recycled in the plant. This process has been generalized since 1965. Proteins can be concentrated 20 times and the final product containing 80% of proteins, as well as lactose, are valorized in children food. Concentrated lactose is also used in food industry.

C. Nanofiltration and reverse osmosis

5.2.8   Water treatment in processes from dairy industry.

This process is close to that of preceding section, but the ultrafiltration step is not necessary and is replaced by a nanofiltration, since milk is diluted in these effluents. Recovered proteins and lactose are valorized outside the food sector. To discharge effluents in rivers, a COD of less than 125 mgO_2/l is necessary. For recycling them in a plant, the COD must be reduced to less than 50 mgO_2/l and a final step of reverse osmosis is necessary. These processes are presently being developed.

5.2.9   Yogurts fabrication

This fabrication starts with a nanofiltration replacing reverse osmosis or vacuum evaporation, as energy consumption during concentration is higher to that of nanofiltration. Yogurts prepared by nanofiltration are fat-free with a small acidity and their organoleptic qualities are better than those of yogurts made by reverse osmosis or vacuum evaporation.

5.3   Other applications to food industry

5.3.1   Wines production

Musts concentration

Concentration of grapes musts by reverse osmosis improves their quality by eliminating part of contained water by reaching a dry matter concentration of 45° Brix with very good sugar content, higher than 99.5%. Dupont de Nemours Co manufactures a filtration module operating at a pressure of 120 bar to exceed 45° Brix (1° Brix = 1 g of sucrose in 100 g of solution). Wines prepared from these musts are richer in phenol compounds and more suitable for aging. Ultrafiltration may also be used for treating musts in place of centrifugation and for reducing SO_2 content. Microfiltration, with pores from 0.2 to 0.6 μm, clarifies musts by eliminating residues from fermentation, yeasts and lactic bacterias and permits their sterilization. Microfiltration may also replace a pasteurization of musts with few germs or stop a microbial development.

Wine clarification

After fermentation and the first removal of yeast wastes, microfiltration can replace filtration steps on membranes and kieselguhr. Pollution by kieselguhr can be avoided, which saves time. Dead end filtration on a 0.2 μm pores cartridge is also used to sterilize the wine before bottling. Microfiltration increases the treatment efficiency of tartaric stabilization by cooling, due to colloids retention and avoids precipitation of potassium hydrogen tartrate. This treatment may also be made by electro- dialysis, which is used for treating rinsing water from tanks. It eliminates color matters and 70% of COD in permeate and recovers tartric acid and anthocyanes in retentate to valorize them.

Reverse osmosis permits to remove alcohol from wines after concentration, and replacing the permeate by the same water volume, which reduces the ethanol percentage. A preliminary step of ultrafiltration augments permeates fluxes of reverse osmosis.
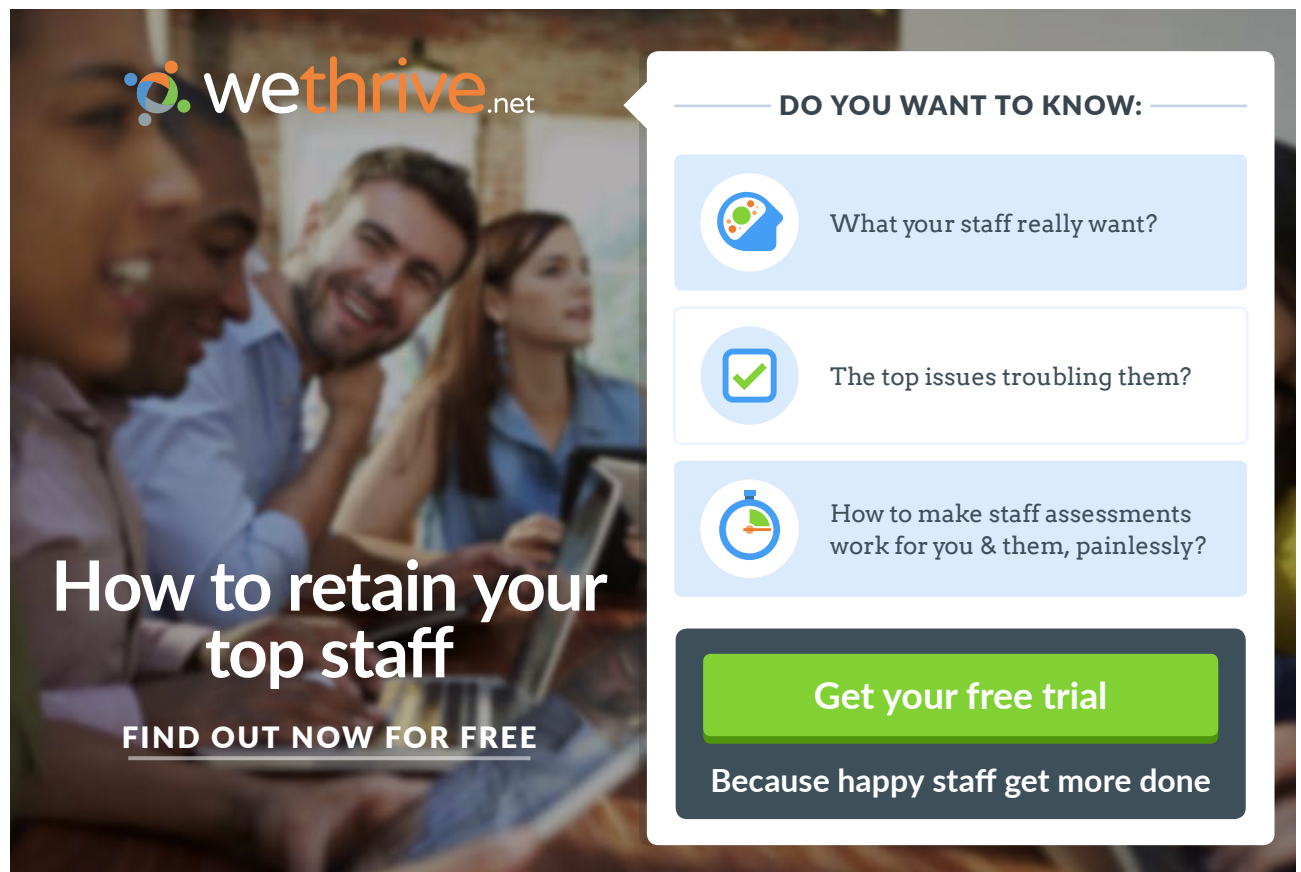
Membrane filtration is mainly used for white and young wines. Trucks carrying filtration modules visit small producers who can filtrate their wines without having to purchase equipment.

Involved Societies: USA: Romicon. Germany: Sartorius All, France: Orelis, SIVA. Australia: Memcor.

5.3.2   Beer Microfiltration

Beer is traditionally filtered on kieselguhr or on press type filters. Cross flow microfiltration permits to avoid using kieselguhr and its pollution and to combine, in a single operation, beer clarification and sterilization by replacing pasteurization with an automated microfiltration. The two most interesting applications of microfiltration are presently the filtration of vintage beer and the recovery of left over beer in tanks that represents between 1.5 and 3% of produced volume, by concentrating it to 23% of dry weight. Microfiltration is carried out with tubular ceramic membranes of 0.4 to 0.8 μm pores and channel diameters of 4 to 6 mm, as yeast suspensions are quite viscous. Recovered beer is added to the main production. Membrane filtration of vintage beer is not competitive by itself, but it can be, if combined with tank bottom recovery.

It is, however, possible that the quality of microfiltered beer be worse in case of strong fouling due to loss of some molecular or colloïdal solutes such as polypeptids and polyphenols contributing to organoleptic characteristics of beer. Permeate fluxes vary from 10 to 50 $lh^{-1}m^{-2}$, but with membrane pores larger than 0.8 μm, beer would be cloudy. Fouling is principally due to internal pores blocking and only retrofiltration with transmembrane pressure reversal (backshock) during 0.1s at intervals of 1 to 5 s is efficient.

5.3.3   Clarification of fruits juice (Apple, ananas)

Microfiltration can replace decantation to stabilize juices and avoid fermentation. It is especially interesting for apple juice, which requires a good clarity and may be also used for cider clarification, but the technology is more complex. To augment flux, apple juices are treated with pectinase and filtered at 50°C. Pores sizes from 1 to 0.2 μm give good results, but it is also possible to use ultrafiltration with a cut-off larger than 50 kDa. To reduce transportation costs, apple juices may be concentrated to 25° Brix by reverse osmosis at 50°C.

Cider contains yeasts and fermentation residues, ethanol and CO_2 and must be treated by microfiltration. Permeate fluxes reach 70–110 $lh^{-1}m^{-2}$ on mineral membranes of 0.2 μm pores.

5.3.4   Other applications

Sugar refining

Ultrafiltration is used to decolorize sugar cane or beets syrups by eliminating polysaccharides and colloids. Syrup fabrication is rather complex and starts with cane crushing or cutting beets in small pieces. The next steps are liming by limestone milk, a first carbonation by CO_2, and a decantation with elimination of muds. A 2nd carbonation is carried out producing a cloudy juice, which is clarified by ultrafiltration at 15° Brix. After evaporation, the syrup reaches 70° Brix. One can also filtrate membrane juices obtained by hydrolysis of starch.

Concentration and clarification of gelatin.

Gelatin is a colloidal protein substance obtained by acqueous extraction at high temperature from animal skins and bones. Its clarification is made by microfiltration in case of high COD and liquid gelatin can be concentrated until 20% of proteins by ultrafiltration.

Recovery of vegetal proteins (ultrafiltration of soya juice).

Ultrafiltration at high temperature of soya juice (tonyu) permits to concentrate dry matter while eliminating trypsic inhibitors and unwanted soluble sugars. Ultrafiltered tonyu is mellower, more viscous and gelatinizes at high concentration. Curdled of soya (tofu) may be concentrated by ultrafiltration on mineral membranes.

Pectins concentration by ultrafiltration and reverse osmosis

Pectins are used as additives in fabrication of jellies, jams, desserts and children food. They stabilize and thicken also dressings for salads and ice creams. They permit to elaborate some medicaments and cosmetics due to their colloidal properties. Pectins also reduce cholesterol. They are extracted mainly from apple and lemon waste by alcoholic precipitation and evaporation.

The membrane process begins by an extraction from a tank containing water and acid, pectins are then pressed before ultrafiltration. The retentate supplies liquid pectins at a concentration of 60g /l while permeate is recycled on the tank. This permeate can also be recycled into a reverse osmosis module to recover valorizable products, while permeate of pure water is returned to the extraction tank.

The advantages of membrane processes are a better purification of sugar and mineral salts, by elimination in permeate of microsolutes, a partial bleaching of the product by elimination of colored compounds in permeate and a diminution of consumed power relatively to evaporation. High temperature treatments are also avoided.

5.4 Medical and biotechnological applications

5.4.1 Treatment of renal insufficiency by artificial kidney (Hemodialyzers)

Hemodialysis (blood dialysis) is used in case of chronic insufficiency (glomerules sickness) or renal arteries injuries when 90% of nephrons do not function. It consists in circulating patient's blood at a flow rate between 200 and 300 ml/min in a hemodialyzer containing an ultrafiltration membrane which eliminates urea and uremic toxins of blood by diffusion into the dialysate, an ionic fluid circulating on the other side of the membrane. A schematic of dialysis equipment is presented in Fig.13. Blood is collected by a needle in an arm artery by a roller pump and circulates in the dialyzer before being reinjected in a vein. The circuit also includes an arterial pressure transducer, an heparin injector to avoid formation of blood clots and a photoelectric detector of bubbles in blood.
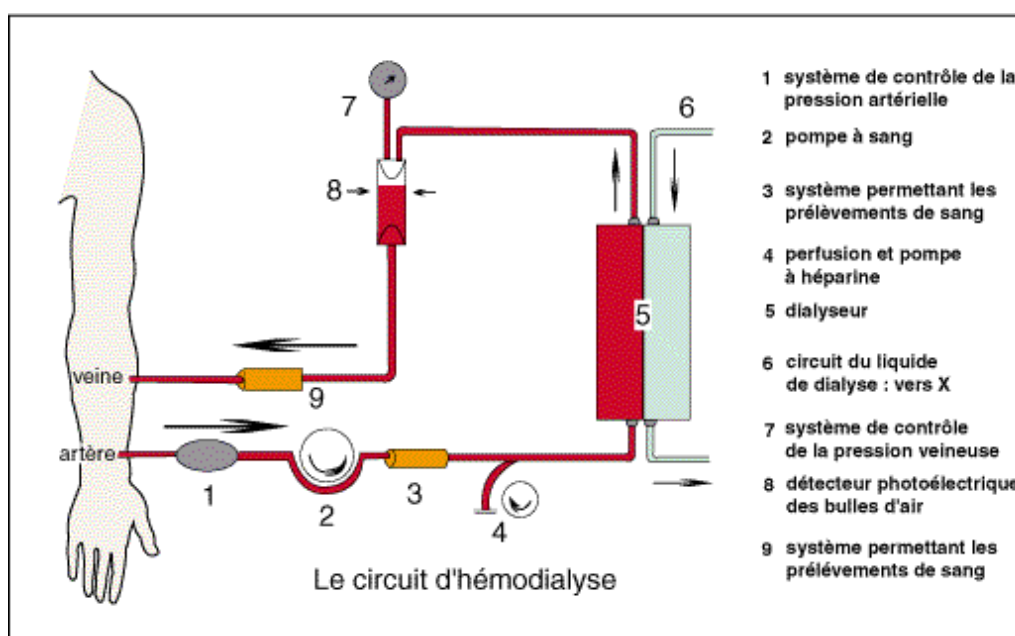
Fig 13. Schematic of a hemodialysis circuit and hemodialyzer

The dialysate eliminates toxins and excess water, but retains plasma ions as they have the same concentration as in dialysate, preventing their diffusion. It circulates in opposite direction to blood at a flow rate of 500 ml/min in order to maximize transfers and is not normally recycled. This treatment requires 3 dialysis sessions of 4h per week, together with dietetic restrictions to limit water and potassium intake. They are in France more than 30000 dialyzed patients and about 2 millions in the world. Hemodialyzers, which were initially plane filters are now mostly made of hollow fibers. These fibers are either cellulosic, cuprophan, or polymeric, (polysulfone, poly acrylonitrile, PMMA) more hemocompatible and with higher permeability than cuprophan.
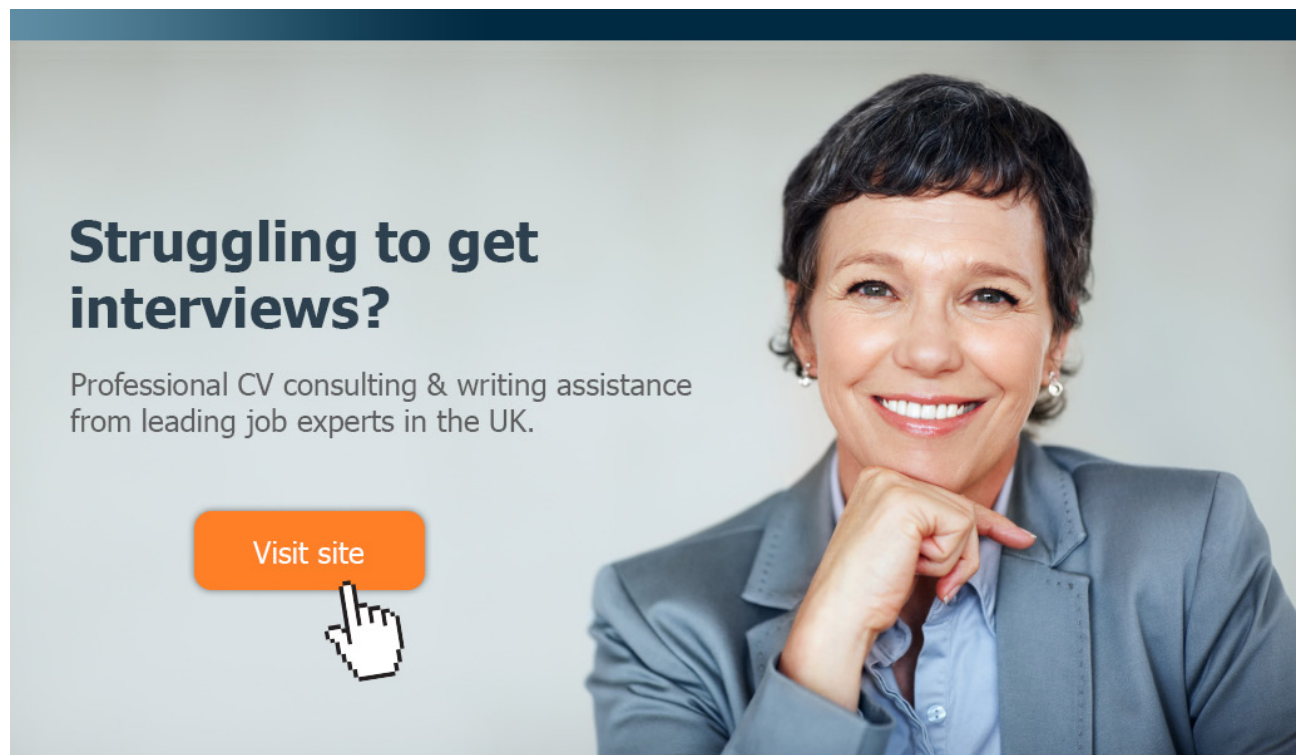
Toxins removal is measured by the clearance K in ml/min which is the ratio mass flow rate crossing the membrane, $Q_{Bi}C_{Bi} - Q_{B0}C_{B0}$, divided by the toxin concentration at the hemodialyzer inlet C_{Bi}, giving

$$K = (Q_{Bi}C_{Bi} - Q_{B0}C_{B0})/ C_{Bi} \tag{73}$$

where Q_{Bi} et $Q_{BO} = Q_{Bi} - Q_F$ are respectively inlet and outlet blood flow rates and C_{Bi}, C_{BO} the corresponding toxin concentrations. If ultrafiltration is small or zero, the clearance K is calculated as function of blood and dialysate flow rates, membrane area S and filtration resistance R_T of the hemodialyzer by

$$K = (e^{\alpha} - 1)/(e^{\alpha} - Q_B/Q_D) \tag{74}$$

where $\alpha = (S/ R_T)(Q_B^{-1} - Q_D^{-1})$ (75)

This clearance does not depend upon toxin concentration in blood and patient condition. However, for a dialysate solute present in the hemodialyzer such as sodium ion Na^+, the clearance is replaced by the dialysance D, defined by

$$D = (Q_{Bi}C_{Bi} - Q_{B0}C_{B0}) / (C_{Bi} - C_{Di}), \tag{76}$$

where C_{Di} is solute concentration at inlet of dialysate compartment of hemodialyzer.

Hemofiltration

This treatment consists in purifying blood only by convection using ultrafiltration without dialysate. The filtration rate Q_F must be of the order of 120 ml/min, which requires a blood flow rate through the needle of at least 300 ml/min. Mass balance on the hemodialyzer will be

$$Q_{Bi}C_{Bi} - Q_{B0}C_{B0} = Q_F C_F \tag{77}$$

And clearance becomes

$$K = C_F C_{Bi} / C_{Bi} = T_r Q_F \tag{78}$$

where $T_r = C_F / C_{Bi}$ is the transmittance. This transmittance is equal to 1 for small solutes and decays towards zero when the solute molar mass becomes close to membrane cut-off.

The advantage of this process is its simplicity and the fact that clearance of various toxins decreases more slowly with molar mass than in dialysis where transfer is diffusive. This transfer is more physiologic and gives a better hemodynamic stability. It necessitates, however, polymeric membranes with high permeability and an accurate control of ultrafiltration. Sterile dialysate must be injected into the blood returning to patient to replace a part of permeate, which can reach 28 l, exceeding the water volume that will be withdrawn and varies from 1 to 4 l. This sterile dialysate is expensive.

Hemodiafiltration

Hemodiafiltration is used more frequently than hemofiltration. It combines hemodialysis and a strong ultrafiltration, with 12 to 15 l of ultrafiltered volume. This process gives the best clearance as it combines an efficient diffusion of urea and a good convection for middle molecules, toxins of high molar mass. Its clearance is more difficult to calculate as blood and dialysate flow rates vary along the membrane. An empirical equation, also valid in conventional hemodialysis with a small UF is [3]

$$K_{HDF} = K_D + 0.46 Q_F \tag{79}$$

15% of renal patients in France are treated by hemodiafiltration.

### 5.4.2   Preparation of human albumin in transfusion centers

This process necessitates three steps after collecting human plasma in a bag. Ethanol is added to precipitate immunoglobulins. Then, alcohol is eliminated by diafiltration of supernatant albumin. The last step is a concentration of retentate proteins by ultrafiltration at 10kDa until albumin concentration reaches 210 g/L, which is required for an injection. The process temperature is less than 10° C to avoid denaturing proteins.

5.4.3   Plasma collection from donors

Treatment of auto-immune diseases consists in replacing pathologic plasma by a healthy one. Donor's blood is withdrawn by a needle connected to a peristaltic pump and circulates in a filter to separate plasma, collected in a bag, from permeate, while platelets and red cells in retentate are returned to the donor. These filters were made initially of hollow fibers type with pores diameters from 0.2 to 0.5 μm, but, in 1985, Hemascience Co (Ca, USA) introduced a dynamic filtration module with a cylindrical polycarbonate membrane of 58 cm^2 area and 1.34 cm radius, rotating inside a concentric cylinder at 3600 rpm/min. This single use filter, represented in Fig. 14, permitted to collect 600 to 700 ml of plasma in 30 min, more rapidly than a hollow fibers filter of 300 cm^2, because of its high shear rate due to Taylor vortices generated by rotation (Fig. 15).
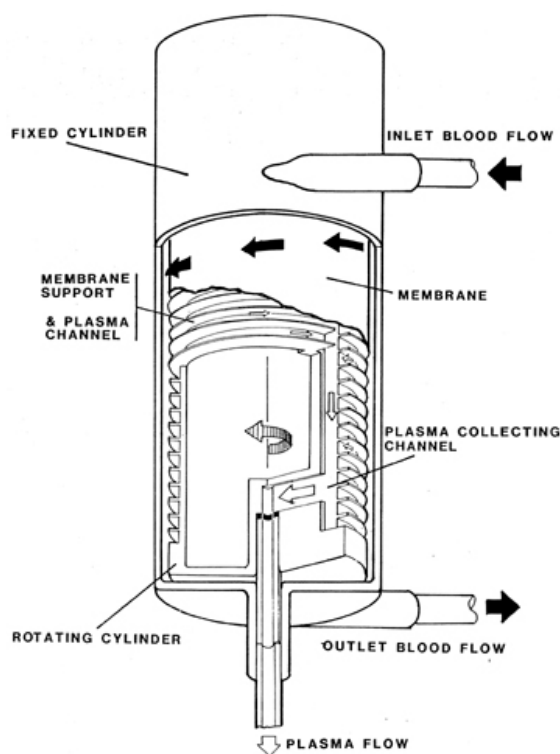
Fig. 14. Schematic of Plasmacell filter for plasma donation.
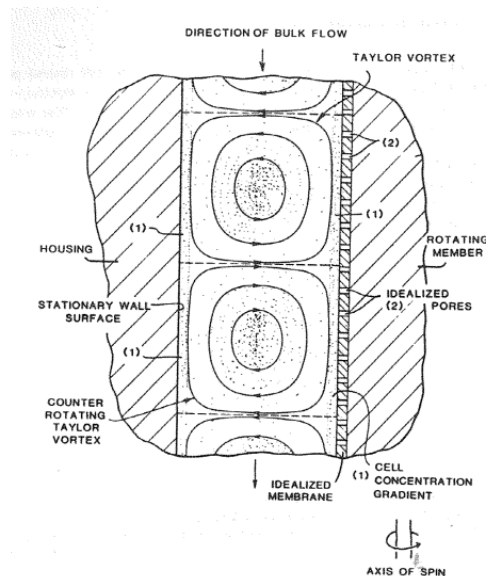
Fig.15. Taylor vortices in the gap between rotating filter and housing.

The small internal volume of this rotating filter limits the residence time of blood inside, reducing hemolysis risks for red cells and damages to platelets. This Plasmacell filter, commercialized later by Baxter Co and now by the German Company Fresenius Kabi with a nylon membrane, is very successful for plasma donation as it is automatized.

5.4.4   Other applications

Preparation of bioethanol by membrane

European production of bioethanol from fermentation of sweet compounds has been mutiplied by two from 2005 to 2006 with 1.6 millions of liters produced and this trend will continue if the project of mixing 10% of bioethanol to gasoline will take place. The necessary water must be treated by nanofiltration and reverse osmosis, while the biomass will be clarified by microfiltration and ultrafiltration before its fermentation. Ultrafiltration is used for concentrating the product before its treatment in an anaerobic digester. Effluents resulting from this fabrication may be treated by membrane bioreactors.

A new type de bioethanol is produced from vegetal biomass issued from straw, trees and herbs in order not to use beets and other products consumed by man. In this case, biomass is purified by a microfiltration ad an ultrafiltration so as to limit risks of contamination of the fermentor. Nanofiltration and reverse osmosis permit to pour concentrate the product before anaerobic digestion.

Production of pure apyrogenic water for dialysis centers and pharmaceutical industry

This process combines microfiltration + reverse osmosis with a final microfiltration, before utilization.

Cell culture on membrane permitting oxygen supply

An example is the macro-encapsulation of Langerhans islets inside hollow fibers for a bioartificial pancreas or of hepatocytes for hepatic support.

5.4.5   Biological treatment of effluents by membrane bioreactors (MBR)

The principle of this treatment is to intensify bacterias proliferation in effluents by air injection and to use them to degrade pollutants. The MBR consists in a tank receiving water and containing biomass, or activated sludge, which is recirculated on the tank after crossing membrane modules of ultrafiltration or microfiltration. The retentate returns to the tank and excess sludge is discarded while permeate is recovered as rinsing water. MBR replace decantation ponds of the conventional process for separating biomass from effluent by gravity. Anaerobic processes are used to eliminate carbonic pollutants from concentrated dairy effluents. This process includes a 1st step of hydrolysis in which proteins and fats are hydrolyzed into amino-acids, fatty acids and small molecules. The 2nd step is a methanization converting metabolites in methane and CO_2.

Advantages:

Biomass concentration in the MBR is about 20g/L instead of 3g/l in a reservoir, which increases effluent purification and reduces sludge production. Effluent is less polluted. Concentrations can reach 300 g/l for yeast and more than 120 g/l for bacterias. The replacement of decantation ponds by MBR saves a lot of space. This process is used in new buildings in Japan and spreads rapidly in industry.

Drawbacks

The cost of filtration plant (investment and electricity) is higher and technology is more complex. In France, Biarritz is one of the few large cities using MBR for water and waste cleaning.

Systems types and manufacturers

Degremont MBRs are equipped with mineral membranes and Orelis MBR with organic membranes. Initially the filter was in a loop outside the MBR. But Japanese companies, and Veolia Environment, have proposed to immerse U-shaped hollow fibers inside the MBR to avoid recirculation and reduce energy consumption. Permeate fluxes were smaller because of dead-end filtration, but compressed air could be used to clean membranes.

5.4.6   Treatment of specific effluents

Paper industry

This industry produces 100 m³ of effluents per ton of paper pulp. Ultrafiltration is used to recover and concentrate before recycling lignite and colour compounds. Mineral membranes permit to work at 120°C. The effluent is purified by nanofiltration. These processes are frequently used in Scandinavia.

Textile industry

Filtration permits to recover gluing agents of threads, non biodegradable polyvinyl alcohol, colour agents and indigo.

Oil removal from cutting fluids

During parts machining, the tool is lubricated by spraying oil to cool the part and evacuate the chips, then the part is rinsed by spraying water. This water contains less than 1% of emulsified oil forming droplets of 0.1 to 1μm diameter. Resulting pollutant emulsions can be separated by chemical methods or by microfiltration or ultrafiltration at 70°C. The membrane retains oil drops. Water from ultrafiltration permeate is recycled and oil from retentate, representing 5 to 10% of initial effluent volume, can be reused as cutting oil or be concentrated to more than 50% and incinerated

Waste water treatment from nuclear plants

The radioactivity of water from cooling circuits is due to iron hydroxide in saline medium. This water is concentrated by ultrafiltration or microfiltration to obtain recyclable water and a small volume of radioactive sludge, which will be vitrified.

Electrophoretic paints recovery

The part to be painted, for instance an automobile door, is immersed into a paint tank with pigments electrically charged. These pigments are projected on the door by an electric field created in the tank which produces a uniform paint layer. This process creates three problems:

- the presence of external ions issued from the part may perturb ionic balance by keeping the paint as colloïdal suspension and make the paint inadequate.
- a large quantity of deionized water is necessary to rinse the metal part and get rid of excess paint.
- the paint must be separated from rinsing water to recover pigments and to avoid pollution.

To this effect, an ultrafilter must be inserted in the recirculation circuit of paint on the tank. Paint particles and pigments are rejected by the membrane while external ions are removed in permeate. Paint contained in rinsing water is returned to the tank and permeate is recycled as rinsing water which reduces water consumption. Membranes are in cellulose acetate or in polyacrylonitril. Paint consumption is greatly reduced and this process is much used in the car industry.

5.5   Process optimization by a technico-economic method

The goal of this method is to minimize by an optimal choice of fluid velocity v, the total cost per par m^3 of permeate (investment, operating and energy costs, and maintenance).

Method

Permeate flux data are obtained from experimental tests on pilots as

$$J=C_1 v^m, \qquad (80) \qquad \text{and the pressure drop by} \qquad \Delta p=C_2 v^n \qquad (81)$$

Economic data

The investment cost I of circuit +membranes is given by the ratio of price to utilization duration and maintenance M, will be assumed to be a fraction of I, for example: M=0.2 I.

Costs proportional to pumps power (consumed energy) are separated. For example, the power of loop pump P_B with flow rate Q_B will be augmented by 20% to take into account power of feed pump and cooling circuit, to give.

$$P_B = Q_B \Delta p_B \text{ with } Q_B = \Sigma v, \text{ where } \Sigma = \text{ section area between parallel membranes} \qquad (82)$$

The cost per m^3 of permeate C_p, if η is the pumps efficiency, C_j the cost of electric joule, S the membrane area, is given by

$$C_p = P_B P_j/(\eta Q_F) = C_3 v^{n+m-1} \text{ with } C_3 = C_2 \Sigma/(C_1 S \eta) \qquad (83)$$

(83) shows that C_p increases when v rises.

Costs proportional to membrane area S, are amortization A and maintenance M. This cost per m^3 of permeate I_A is equal to

$$I_A = (A+M)/Q_F = C_4 v^{-m} \qquad (84)$$

If v increases, I_A decreases. There is an optimal speed v minimizing $I = I_A + I_p$ that can be found from a graph or by calculating the value of v giving dI/dv=0.

This calculation is described in Fig. 15 which displays variations of amortization and operating costs as function of fluid speed along membranes.
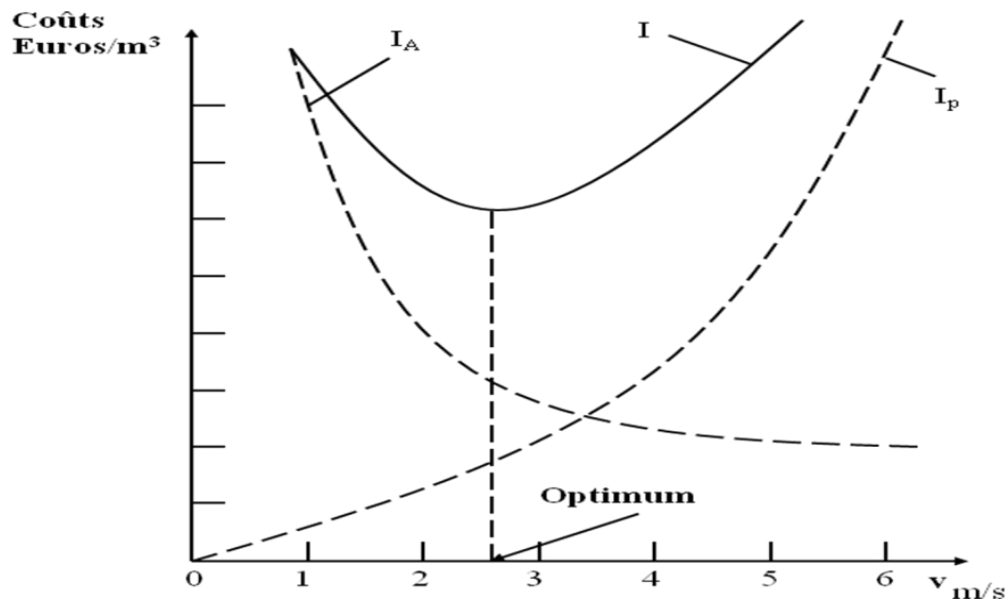
Fig. 16. Determination of optimal fluid velocity (2.6 m/s) to minimize process cost per m³ of permeate

6 High shear rate dynamic filtration

Dynamic filtration is a relatively recent process which necessitates special filtration modules, able to generate shear rates at membrane much higher than in crossflow filtration. A review of these systems can be found has been made by the author [4].

6.1 Principle of dynamic filtration

The axial fluid velocity is replaced by the rotation of a disk relatively to the membrane (rotating disk modules) or by the rotation of the membrane around an axis or by fluid inertia in modules with vibrating membranes such as the VSEP of New logic, CA USA.

Advantages:

In classical cross flow filtration, the high axial fluid velocity produces a large pressure loss along the module and a high inlet ptm, while the high shear rates independent from the flow rate of dynamic filtration eliminates the fouling layer on membrane, and reduces concentration polarization in ultrafiltration and nanofiltration. The main advantages are

- A smaller feed flow rate, producing a smaller ptm, which is ideal for extracting macromolecules.
- Permeate flux larger than in crossflow filtration for microfiltration, ultrafiltration, nanofiltration and reverse osmosis.
- An excellent transmission of solutes in microfiltration and a higher rejection of micro-solutes by the membrane in ultrafiltration, nanofiltration and reverse osmosis, since diffusive transfer is reduced by the diminution of concentration polarization.
- The possibility to operate at very high concentrations, even in reverse osmosis.

These modules offer the choice to increase permeate fluxes by 3 to 5 times with slightly higher energy consumption or to produce fluxes equivalents to those of crossflow filtration by reducing the rotation speed of disks or membranes. In this case, the reduction of consumed energy per m^3 of permeate can reach 60%.

Drawbacks:

Dynamic filtration modules are more complex and expensive per m^2 of membrane. The cost of their maintenance is also generally higher than for crossflow filtration modules.

6.2   Industrial systems of dynamic filtration

6.2.1   Modules with rotating cylindrical membrane

These systems consist in a cylindrical membrane rotating inside a concentric cylindrical housing like the Plasmacell of Fig 14 and take advantage of Taylor vortices which develop in the gap like in Fig. 15 and increase the shear rate by comparison with a Couette flow between two parallel plates with one moving relatively to the other. These vortices are created above a specific rotation speed such that the Taylor Nb Ta given by

$$Ta = (\omega\, R^{1/2}e^{3/2})/\nu \tag{85}$$

exceeds 42, where ω is the membrane angular velocity in radian/s, R is the membrane radius, e the radial gap between membrane and outer cylinder and ν the kinematic viscosity.

GI Taylor [5] has also proposed the following equation for the shear rate γ at membrane

$$\gamma = 0.23\, Ta^{1/2}\, \omega R/e = 0.23\, \omega^{3/2}R^{5/4}e^{-1/4}\, \nu^{-1/2} \tag{86}$$

which is valid for 60<Ta< 3000, and covers laminar and turbulent regimes.

Holeschowsky and Cooney [6] have used a Membrex module with a rotating cylindrical membrane to ultrafilter bovine albumin at a ptm of 800 kPa and have proposed for Sherwood number Sh

$$Sh = k_m\, e/D = 0.93 Ta^{0.5}Sc^{1/3} \tag{87}$$

where k_m is the mass transfer coefficient and D is the diffusivity.

The first industrial modules of this type were the Biodruckfilter of Sulzer AG, (Winterthur, Switzerland) and the Benchmark Rotary Biofiltration of Membrex (Garfield, NJ, USA) with membranes area of the order of 2 m². It is in fact possible to mount a 2nd membrane fixed inside the concentric housing which would supply the same permeate flux as the other membrane. But these modules have a large volume/ membrane area ratio which is a drawback. The main application of this concept is still the Plasmacell used for plasma donation described in section 5.4.3. It can be noted that the permeate rotates with the membrane, which produces a counter-pressure decreasing the ptm.

6.2.2   Systems with disks rotating on a single shaft

These systems are composed of separate compartments, each containing a metal disk rotating between two fixed circular membranes. A membranes change requires taking apart the module. One of first systems was the Pall DMF (USA) with 5 m^2 of organic membranes, but it is no longer sold. Bokela Co (Germany) commercializes the Dyno filter, along the same principle, with 1 to 12 m^2 of organic or inorganic membranes of 0.14 to 0.85 m of diameter, represented in Fig.17. Maximum pressure is 6 bar, and permits ultrafiltration.
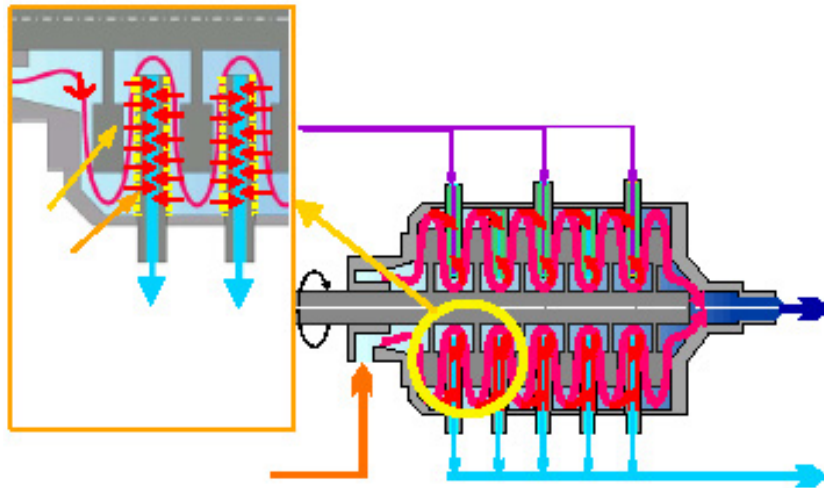

Fig. 17. Dyno module of dynamic filtration with metal disks rotating between circular membranes.

Another system produced by Metso Paper Co at Raisio (Finland) may include from 2 to 140 m² of organic membranes with diameters up to 1 m (Fig. 18). Disks are replaced by rotors with a peripheral velocity reaching 14 m/s with a 132 kW motor. Modules of 84 m² and 75 kW or 15 m² and 30 kW with membrane diameters of 0.55m are also available. These modules are frequently used in paper mill industry and for pigments recovery.
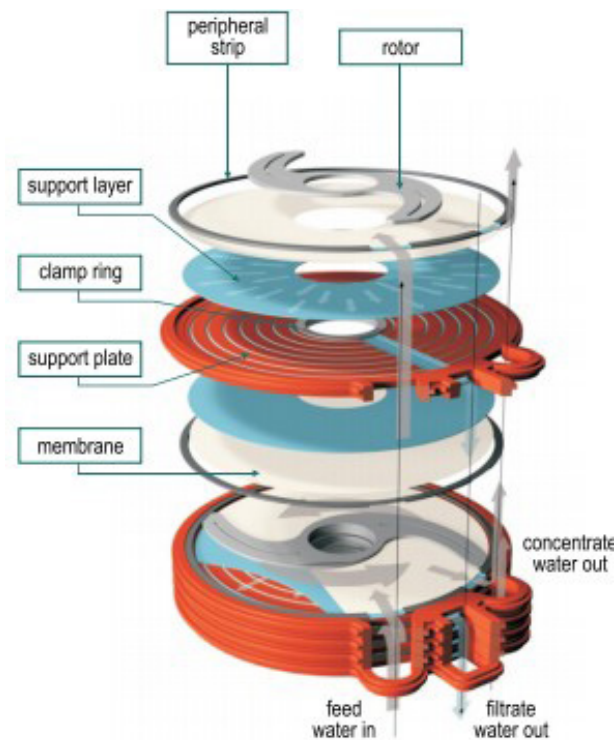
Fig 18: Optifilter CR module with rotating disks

Bouzerar et al [7] have proposed, from Navier Stokes theory, equations for local membrane shear rate as function of radius r. In laminar regime, this shear rate is given by

$$\gamma_l = 0.77 \, (k_e \, \omega)^{1.5} \, r \, \nu^{-0.5} \tag{88}$$

where k_e is the coefficient of fluid stirring by the disk equal to 0.42 for a flat disk and which can reach more than 0.82 for a disk equipped with radial vanes. In turbulent regime, they found, by using Blasius friction coefficient, the local shear rate $\gamma_t(r)$

$$\gamma_t = 0.0296 \, (k_e \omega)^{1.8} \, r^{1.6} \, \nu^{-0.8} \tag{89}$$

The averaged shear rate on a disk of radius R becomes, by integrating (89) on the disk area

$$\gamma_{tm} = 0.0164 \, (k_e \omega)^{1.8} \, R^{1.6} \, \nu^{-0.8} = 0.55 \, \gamma_{max} \tag{90}$$

where γ_{max} is the maximum shear rate at r=R, at membrane periphery.

The Spintek, produced in United States, use circular membranes rotating between fixed plates (Fig. 19) whose area may reach 2.3 m^2 and is available with organic or ceramic membranes. These modules, with separate compartments, have limited membrane area unlike modules described in section 6.2.2.
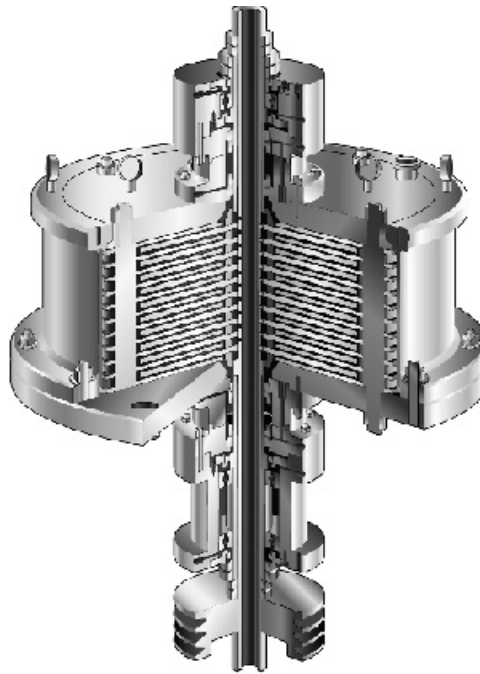
Fig. 19. Spintek module with organic or ceramic membranes of 2.3m^2 total area

Their membrane shear rate is, however, higher than for fixed membranes and is given by,

in laminar regime $\gamma_{dl} = 1.81\ (k_e\omega)^{1.5}\ r\ v^{-0.5}$,   (91)

and in turbulent regime $\gamma_{dt} = 0.057\ (k_e\omega)^{1.8}\ r^{1.6}\ v^{-0.8}$ (92)

Since permeate rotates with the membrane, it produces a counter pressure which reduces ptm like for cylindrical membrane modules.

6.2.3   Systems with membrane disks rotating around parallel axes

These systems consist in a housing in which ceramic membranes rotate around one or several shafts. Replacing membranes is then easier than in preceding modules and they can receive large membrane areas. The MSD (multishaft disks) from Westfalia Separator (Aalen, Germany), is available with ceramic membrane disks of 31 cm diameter mounted on 8 shafts for 20 to 80 m^2 of membranes area as shown in Fig. 20. The partial membranes overlap augments their shear rate and the permeate flux. Another system, the RotoStream, from Canzler (Germany) is available with ceramic membrane disks membranes with areas up to 154 m^2 and Hitachi (Japan) commercializes filtration modules with up to 100 m^2 of membranes area. These two modules have parallel shafts located in one plane and not on a cylinder as the MSD, which reduces membranes overlap.

Ding et al [7] have investigated the membrane speed in the overlap zone on a small MSD pilot with two shafts and have found that speed difference between two membranes constant and equal to d ω
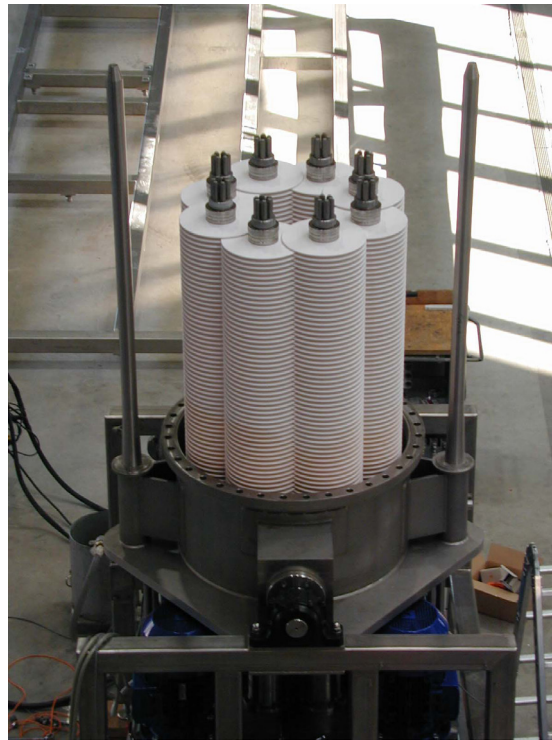

Fig 20. MSD Module with 80 m² membrane area

where d is the inter-shaft distance. This speed was 7.4 m/s at 1037 rpm and 13.7 m/s at 1930 rpm, which is 50% higher than the peripheral membrane speed.

The SSDF module of KMPT (Germany) can receive up to 15m² of ceramic membranes on two shafts but is also available with 25 m² of composite membranes for microfiltration, ultrafiltration and nanofiltration, The Novoflow (Oberndorf, Germany), sells two single shaft modules with ceramic membranes of UF and MF, the CRD with 15.2 cm diameter membranes of 5 m² area and the SSDF with membranes 31.2 cm diameter membranes of 15 m² area. The module SSDF can also receive composite membranes of 55 cm diameter for MF, and NF with an area of 25 m².

6.3   Systems with vibrating membranes

The most popular system is the VSEP (Vibratory shear-enhanced processing) introduced by New Logic Research (Ca, US) in 1992 [9] which consists in a stack of circular organic membranes separated by gaskets and permeate collectors vibrating azimuthally around a vertical axis at a frequency of about 60.3 Hz and an amplitude of 2.5 to 3 cm. The membrane shear rate is created by the fluid inertia, out of phase relatively to membranes. Fig. 21a represents a laboratory pilot equipped with a single membrane and Fig. 21b shows details of membrane and its gaskets and support in the housing. Oscillations frequency is close to the resonant frequency, which minimizes the power necessary to create these oscillations, which is only 9 kW for a total membrane area of 150 m². Laboratory pilots have 30 cm diameter membranes, while those of industrial modules are 60 cm in diameter. Fig. 22 displays fluid circulation inside a VSEP with several compartments and Fig. 23 shows industrial modules with 150 m² of membrane area.
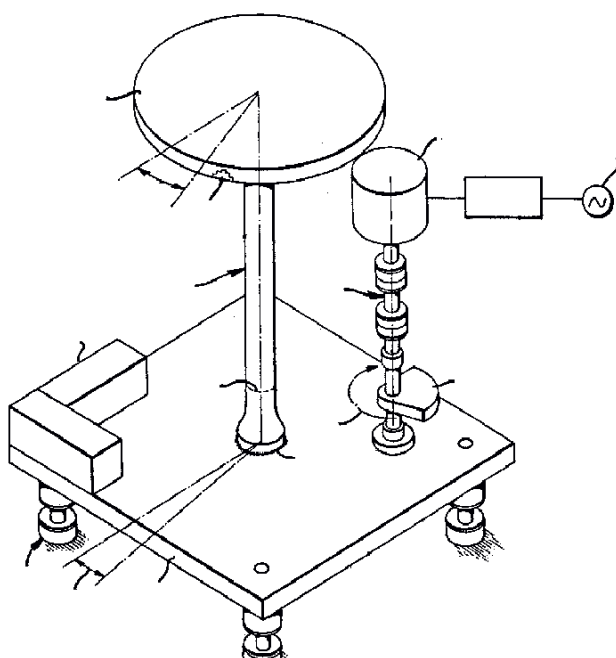

Fig. 21a. Laboratory pilot VSEP L 101
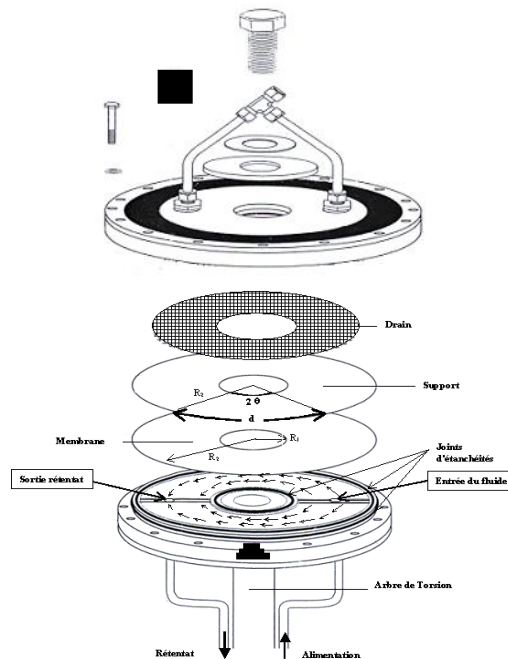
Fig. 21b. Details of VSEP L101 pilots

These systems can sustain pressures of 40 bar, permitting nanofiltration and reverse osmosis in addition to microfiltration and ultrafiltration. The membrane shear rate is determined by oscillations frequency and varies sinusoidally with time according to the following equation [10]

$$\gamma (r, t) = (rd/R_2) \ d \ (\pi F)^{1.5} \ \nu^{-0.5} \ (\cos\omega_1 t - \sin\omega_1 t) \tag{93}$$
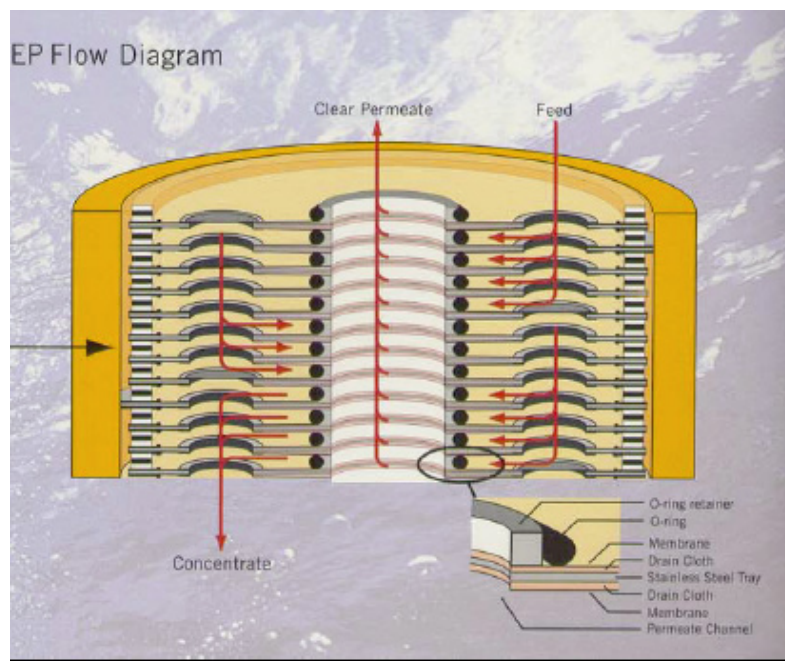
Fig 22. Schematic of fluid circulation inside a VSEP module

where d is the displacement amplitude of membrane at periphery, R_2 the membrane outer radius, F the oscillations frequency and $\omega_1 = 2\pi F$. The maximum shear rate with time at membrane periphery is given by

$$\gamma_{max1} = 2^{0.5}\, d\, (\pi F)^{1.5}\, \nu^{-0.5} \tag{94}$$

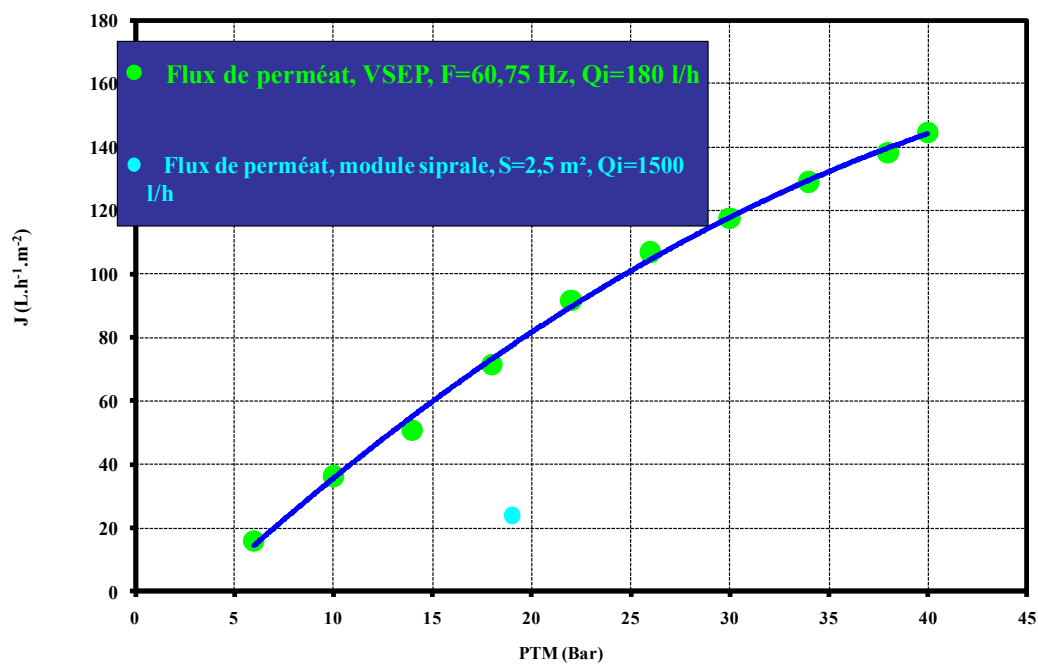**Fig 23**. Industrial VSEP modules with 150 m^2 of membranes

The mean shear rate on membrane is given by

$$\gamma_m = \ = \frac{2^{3/2}(R_2^3 - R_1^3)}{3\pi R_2(R_2^2 - R_1^2)} \ \gamma_{max1} = 0.330 \ \gamma_{max1} \qquad (95)$$

where R_1 is the radius of membrane central hole for the shaft.

Permeate fluxes in dynamic filtration are 3 to 5 times higher than in cross flow filtration, as shown in Fig. 24.

Fig.24. Comparison between permeate fluxes from a VSP pilot and a spiral module in NF of diluted milk with the same membrane at same tmp.

VSEP modules are relatively frequent in USA, Canada and in Eastern countries (Japan, Malaysia, and China). They are less used in Europe, perhaps because of the presence of German dynamic filtration modules. It is also possible to vibrate longitudinally vertical hollow fibers cartridges close at the bottom at a frequency of 30 Hz amplitude of 0.4 to 2.4 mm. (Fig. 25, Beier et al [11]). But these systems are not yet commercialized as their shear rates are smaller than those of VSEP.
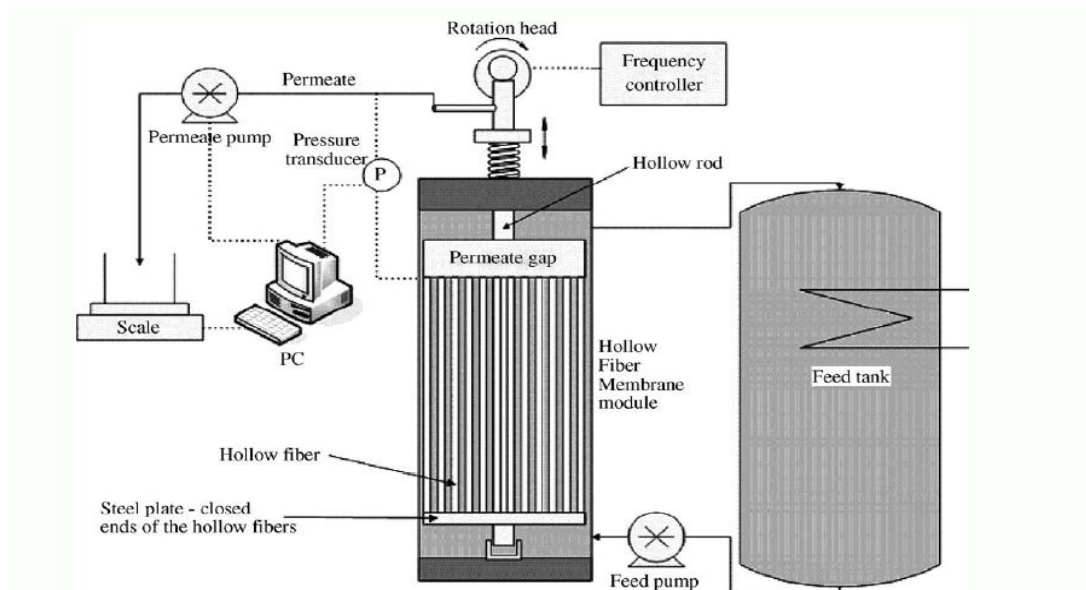
Fig. 25. Schematic of a vibrating vertical hollow fibers cartridge which oscillates longitudinally to increase its shear rate. (From Beier et al [11])

7   Summary

The various processes of membrane filtration (microfiltration, ultrafiltration, nanofiltration, reverse osmosis, electrodialysis and pervaporation) used in industry have been presented in the 1[est] chapter. A review of basic fluid mechanics has been given in the 2nd chapter in order to supply equations describing the flow inside filtration modules and their circuits. Methods for calculating permeate fluxes in laminar and turbulent regimes were also given. Chapter 3 describes various types of membranes and modules together with their advantages and drawbacks. Chapter 4 presents a modelisation of flows in filtration circuits including recirculation loops with modules in series and in parallel, which are frequent in industry. This modelisation permits to calculate variations of permeate and retentate concentrations with time.

Chapter 5 presents the main applications of these processes, especially those of food and dairy industries and a technico-economic method permitting, from filtration experimental and economic data, to calculate the power consumed and the process cost and to determine the optimal fluid velocity inside the membranes leading to a minimum cost per m³ of permeate. Chapter 6 describes the principle of dynamic filtration, a recent process, creating very high shear rates by using rotating disks, and rotating or vibrating membranes. These modules produce permeate fluxes much higher than in cross flow with smaller feed flow rates, since the shear rate is independent of feed flow rates. They also permit excellent solute transmissions in microfiltration and a higher rejection of microsolutes in ultrafiltration, nanofiltration and reverse osmosis, since the diffusive transfer is reduced by a diminution of concentration polarization.

Nomenclature

b: width

C: concentration

D: diffusivity or dialysance   d: diameter

e: thickness

h: height

J: permeate flux

K: clearance

k: mass transfer coefficient

k_e: fluid stirring coefficient

L: length L_p: hydraulic permeability

p: pressure   ptm: transmembrane pressure, P: power

Q: flow rate

R: radius or rejection rate, r: local radius

R_m: membrane resistance, R_c: fouling resistance, R_t: total resistance

S, S': sieving coefficient

T_r: transmittance

U: local fluide speed

V: volume,   v: mean velocity on section

c: abscissa   y: ordinate

Indices

a : feed, B :loop, F : filtrate, l : laminar R : retentate, t : turbulent, w : membrane (for shear rate)

Abbreviations: VRR: volume reduction ratio, G : Graetz nb, Sh : Sherwood nb,

Ta : Taylor nb

Greek Symbols

Δp: drop; γ: shear rate, ε: porosity, μ: dynamic viscosity, ν : kinematic viscosity,

π: osmotic pressure, ω: angular speed

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Application exercices

Exercice 1.

A suspension of $CaCO_3$ particles of initial concentration C_0 is concentrated with a tubular membrane of length L= 1 m and 1mm.thickness. The local mass transfer coefficient k (x) is given in these conditions by the equation

$$k(x) = 1{,}047 \ 10^{-5} \ x^{-1/3} \text{ in m/s}$$

1. Calculate the mean permeate flux if the suspension pressure is constant and equal to 2.3 bar (with a negligible pressure drop) and permeate pressure is equal to 1 bar.

Data: filtrate viscosity: $\mu=1.1 \ 10^{-4}$ Pa s, $CaCO_3$ density: $\rho=2600 \text{ kg/m}^3$

Membrane resistance $R_m = 1.56 \ 10^{12} \text{ m}^{-1}$. Porosity of formed cake: $\varepsilon= 0.4$ (see Eq. 14)

Initial suspension concentration $C_0= 20 \text{ kg/m}^3$

Exercice 2. Diafiltration process with variable volume

A solute of total mass M_p and concentration C_p (t) is concentrated by diafiltration with a membrane module operating in single batch (voir Fig 10), while eliminating another solute of concentration C_a (t) which is not rejected. Initial concentrations are C_{p0} et C_{a0} and final ones are C_{pf} et C_{af}. Permeate flux is given in l/hm² by

$$J_v = (B_1 + B_2\, C_p + B_3\, C_a)^{-1} \text{ when concentrations are expressed in g/l}$$

1. Calculate the duration t_1 of concentration phase (without adding water) to concentrate the solute C_p until its final concentration C_{pf}. Deduce the normalized duration T_1 for treating 1 kg of solute with 1 m² of membrane. Assume $B'_1 = B_1 + B_3\, C_{a0}$

2. Calculate the normalized duration T_2 of diafiltration phase at constant volume which brings C_a to its final value C_{af}, if concentration is finished when $C_p = C_{pf}$. Assume $B'_2 = B_1 + B_2\, C_{pf}$

3. The goal is to combine these 2 operations in a single phase by adding a water flow rate Q_D related to permeate flow rate Q_F by $Q_D = Q_F (1 - 1/\alpha)$ where α is constant. Determine, with mass conservation equations, a relation between C_a and C_p, initial concentrations and α. Find the value of α permitting to reach the final state. Calculate the normalized duration T_3 of this single phase process.

   Numerical application. Calculate T1, T_2 and T_3 for C_{p0} = 7.5 g/l, C_{a0} = 200 g/l, C_{pf} = 210 g/l, and C_{af} = 1 g/l , B_1 =5 10⁻³, B_2 = 0.9 10⁻⁴, B_3 = 1.7 10⁻⁴. Which is the best process?

Exercice 3. Process optimization by a technico-economic method.

A industrial filtration unit is composed of p chains of parallel modules including each chain including q tubular modules in series. The fluid cross section of each module is Σ =72 cm² and its membrane area de is S=5,73m². The permeate flux in l/hm² is J =15v^{0,8}, the pressure drop in Pascal of each module is Δp=7 10-7v², where v is is the fluid velocity in m/s,

1. Calculate the power P_B of loop pump in watt and the permeate flow rate in m3/s. and the specific energy P_B/Q_F consumed per m3 of permeate. This energy will be increased by 20% to account for the feed pump and the cooling system. Calculate the cost of electricity per m³ of permeate, if the Kwh price is 0.07 €.

2. Membranes cost is 4300€/m² and they are amortized over 3 years. The price of de filtration unit (without membranes) is 1400 €per m² of membrane, amortized over 8 years with 7000 h/year of utilization. Calculate the cost of amortization per m³ of permeate which should be increased by 20%to include maintenance. Calculate the total costs per m3 of permeate.

3. Find the fluid velocity in modules which minimizes this cost and calculate it. What will be the permeate flux?

4. Calculate the optimal velocity if the price of Kwh becomes 0.09 €?

Exercice 4.

The goal is to concentrate, by a factor of 8 in volume, milk proteins using a continuous process with 2 loops (see Figure.below). Inlet proteins concentration is C_a, their sieving coefficient S', based upon retentate concentration (to simplifiy its calculation) is S' = C_{Fi}/C_{Ri} = 0.1 for both loops (i =1,2). The feed flow rate is Q_a = 3 m³/h.

1) Calculate flow rates Q_{F1} et Q_{R1} so that the volume reduction ratio (VRR$_1$ = Q_a/Q_{R1}) of 1ˢᵗ loop to 2.5. Find Q_{F2} et Q_{R2} so that the total VRR =Q_a/Q_{R2} be equal to 8.

2) From mass balances of each loop, calculate proteins concentration ratio of each loop, C_{R1}/C_a, C_{R2}/C_{R1} and the total concentration ratio C_{R2}/C_a, and deduce the final recovery factor in retentate r = $C_{R2}Q_{R2}/C_aQ_a$.

3) It is assumed that permeate fluxes of each loop (i = 1, 2) are given by J_i = kLn(C_w/C_{Ri}) where k = 25 l/hm² and C_w = 10 C_a are the same for each loop. Calculate membrane areas A_1 and A_2 of each loop.

4) Because of internal pores fouling, the permeate flow rate decayed to 1.44 m³/h in the 1ˢᵗ loop and to 0.61 m³/h for the 2ⁿᵈ. Calculate the new retentate flow rates, the total VRR, the total concentration ratio C'$_{R2}$/C$_a$, and the new recovery factor r' in retentate.

5) Find the feed flow rate Q'$_a$ necessary to obtain the initial VRR of 8, with filtration flow rates of question 4. Calculate the total protein concentration factor in this case.

Fig12
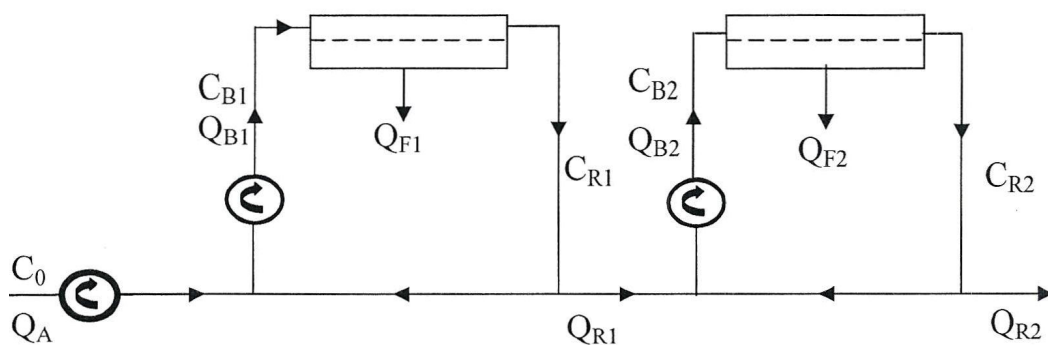
Exercice 5.

An industrial microfiltration system consists in a recirculation loop with 10 parallel chains of 3 modules in series. Each module contains tubular membranes of total area S=11.46 m². The inner cross section of tubes is Σ= 144 cm². The permeate flux and pressure drop for each module are given by

J_i= 15 V $^{0.8}$ in l/hm² et V in m/s Δp_i =0 .07 V² in bar

It is assumed that the flow rate Q_B crossing each module is the same as Q_{Fi} <<Q and V=3 m/s.

1) Calculate the total permeate flux J and the total filtration rate Q_F.
2) Calculate the loop flow rate Q_B and the total pressure drop in chain.
3) Calculate the power P_B consumed by the loop feed pump if its efficiency is 0.8.
4) If the membranes number is 2000, calculate the length L of each membrane, and the Reynolds Nb if μ=1cp and ρ= 1kg/lit.

Exercice 6. Cake filtration law

It happens that the membrane is covered by a particles cake which makes an additional filtration resistance $R_c = aV_F$, proportional to filtered volume V_F which deposit particles on the membrane. The permeate flux J(t) decays with time according to the relation

$$J(t) = \frac{ptm}{R_m + aV_F(t)}$$

where R_m denotes the membrane resistance. Deduce that the flux variation J(t) is given by

$$J(t) = \frac{J_0}{(1+\frac{2aJ_0 At}{R_m})^{1/2}}$$

where J_0 is the initial flux and A the membrane area. Roots of a 2nd degree equation

$ax^2 + bx + c = 0$ are $x = (-b \pm \sqrt{(b^2-4ac)})/2a$.

Exercice 7. Cascade filtration

A solution contains two solutes a and b at concentrations C_{a0} and C_{b0}. The goal is to eliminate solute a with higher molecular weight while recovering and concentrating solute b. The filtration system is given in the figure below. The solution is divided in 2 tanks 1 and 2 containing respectively initial volumes V_{10} et V_{20} The 1st filter retains solute a in tank 1 with a rejection rate R'_a given by $C_{Fa} = C_a(1-R'_a)$ and transmits completely solute b. Tank 2 is fed by permeate of filter 1. The 2nd filter, completely rejects both solutes, and is used to concentrate solute b. All flow rates, including Q_{F1} et Q_{F2}, are constants.

1) 1st circuit. Write volume and mass balance equations on this circuit (Tank 1+filter 1). Calculate variations of $V_1(t)$ and $C_a(t)$ with time. Find solute b concentration in permeate flow rate Q_{F1}. Integral of $dx/(A+Bx) = (1/B)\ln(A+Bx) + C$.

2) Concentration stops when tank 1 and circuit volume reaches a value V_m. Calculate the circuit VRR, the process duration and the final concentration ratio of solute a (C_{af1}/C_{a0}). Numerical application: $V_{10} = 900$ L, $V_m = 30$ L, $Q_{F1} = 120$ L/m, $R'_a = 0.95$.

3) 2nd circuit. Solute b is in tank 2 and filter 2 which operates simultaneously with the 1st circuit (same filtration duration). At t=0 this circuit is filled with a volume $V_{20} = 20$ L containing solutes at their initial concentrations C_{a0} and C_{b0}. Calculate the final volume in tank 2 V_{2f} if $Q_{F2} = 0.8$ Q_{F1} together with final concentration ratios C_{af2}/C_{a0} et C_{bf}/C_{b0} in this tank, for data of question 2.

4) Using volume and mass balance equations on circuit 2, find a differential equation for C_b which would permit to find the variation $C_b(t)$.