



**UNIVERSITY OF ROME “LA SAPIENZA”
NANOTECHNOLOGIES ENGINEERING**

**MEMBRANE APPLICATIONS IN
NANOTECHNOLOGY:
PROCESS DESIGN EXAMPLES**

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Nanoparticles separation

CASE STUDY:

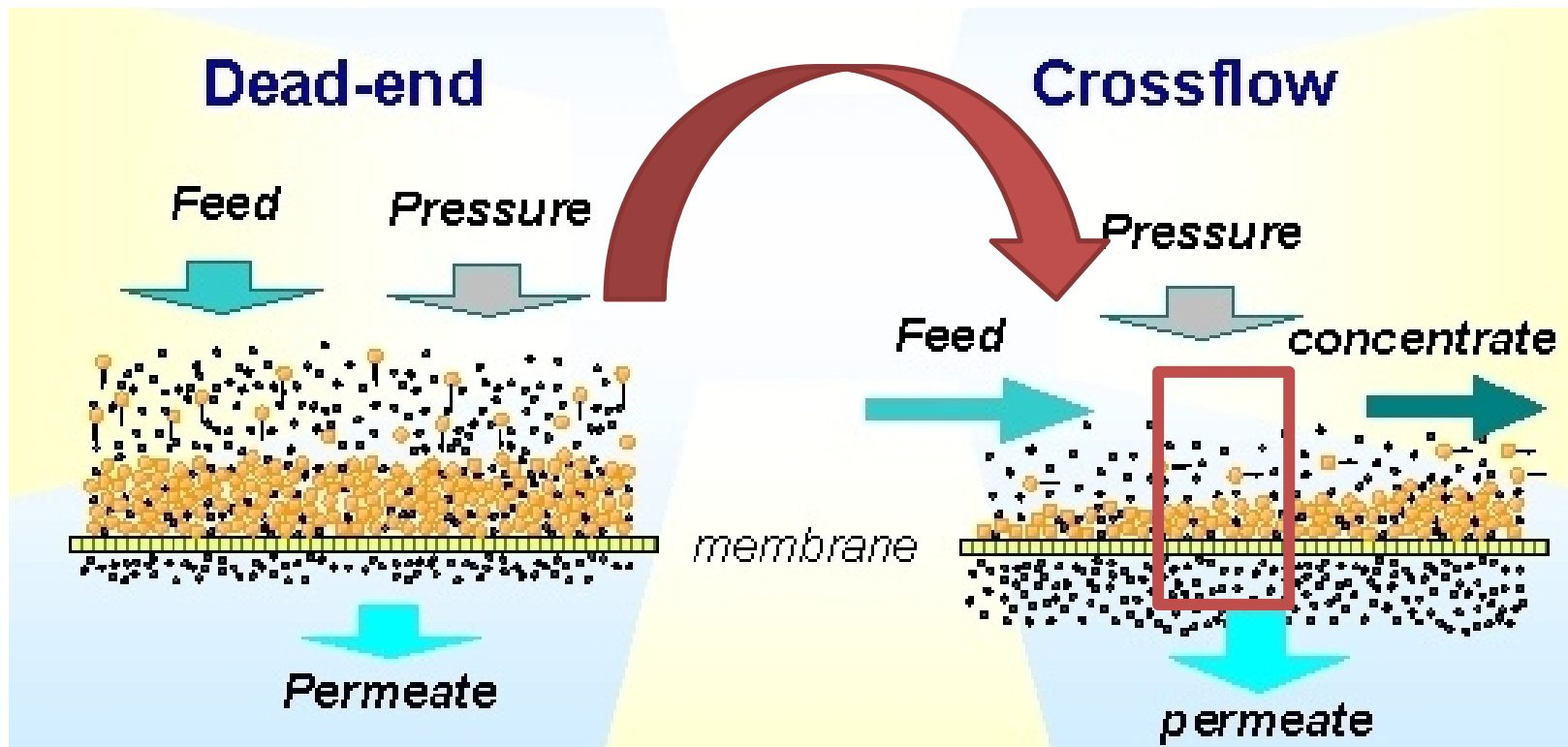
Separation of spherical, monodispersed silica particles of 47nm, 110nm and 310nm in size.

The used membrane is a ceramic one, with a mean pore size of 20nm.

The membrane module is tubular, with inner diameter of 7mm and 250mm in length.

Nanoparticles separation

It is possible to adopt locally dead end filtration relationships to crossflow filtration...



Nanoparticles separation

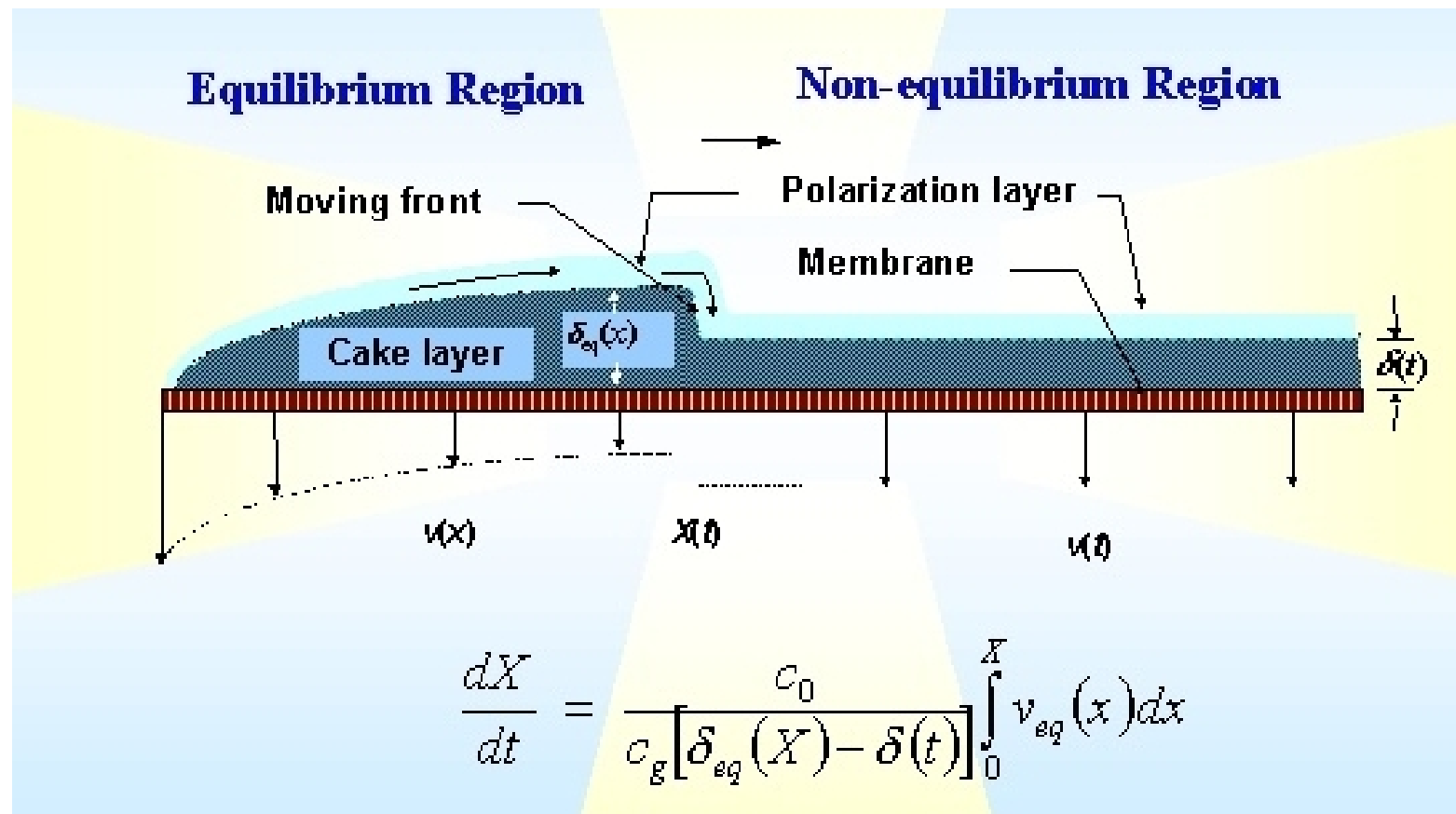
The filtration number N_f expresses the required energy to suspend a particle again to the bulk stream, depending on the particle radius a_p and the pressure drop across the polarization layer ΔP_p :

$$N_F = \left(\frac{4\pi a_p^3}{3kT} \right) \Delta P_p$$

- For $N_F < N_{FC}$: pure concentration polarization
- For $N_F > N_{FC}$: cake formation

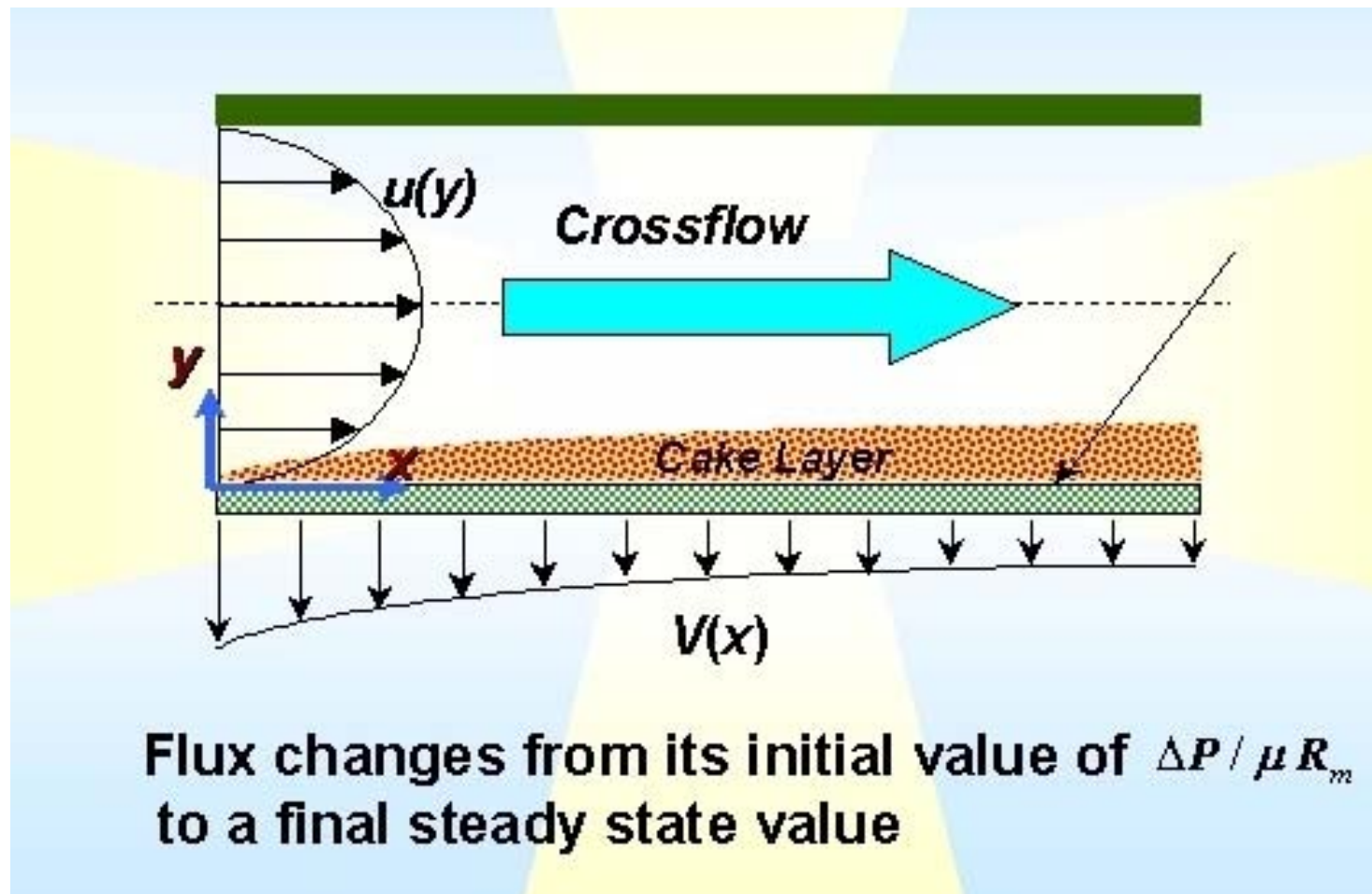
Nanoparticles separation

Development of the polarization layer:



Nanoparticles separation

Hydrodynamics affecting polarization:



Nanoparticles separation

Assumptions:

- Time for the CP layer to reach steady state is very fast
- Initial flux decline is independent of tangential flow

The Final Expression:

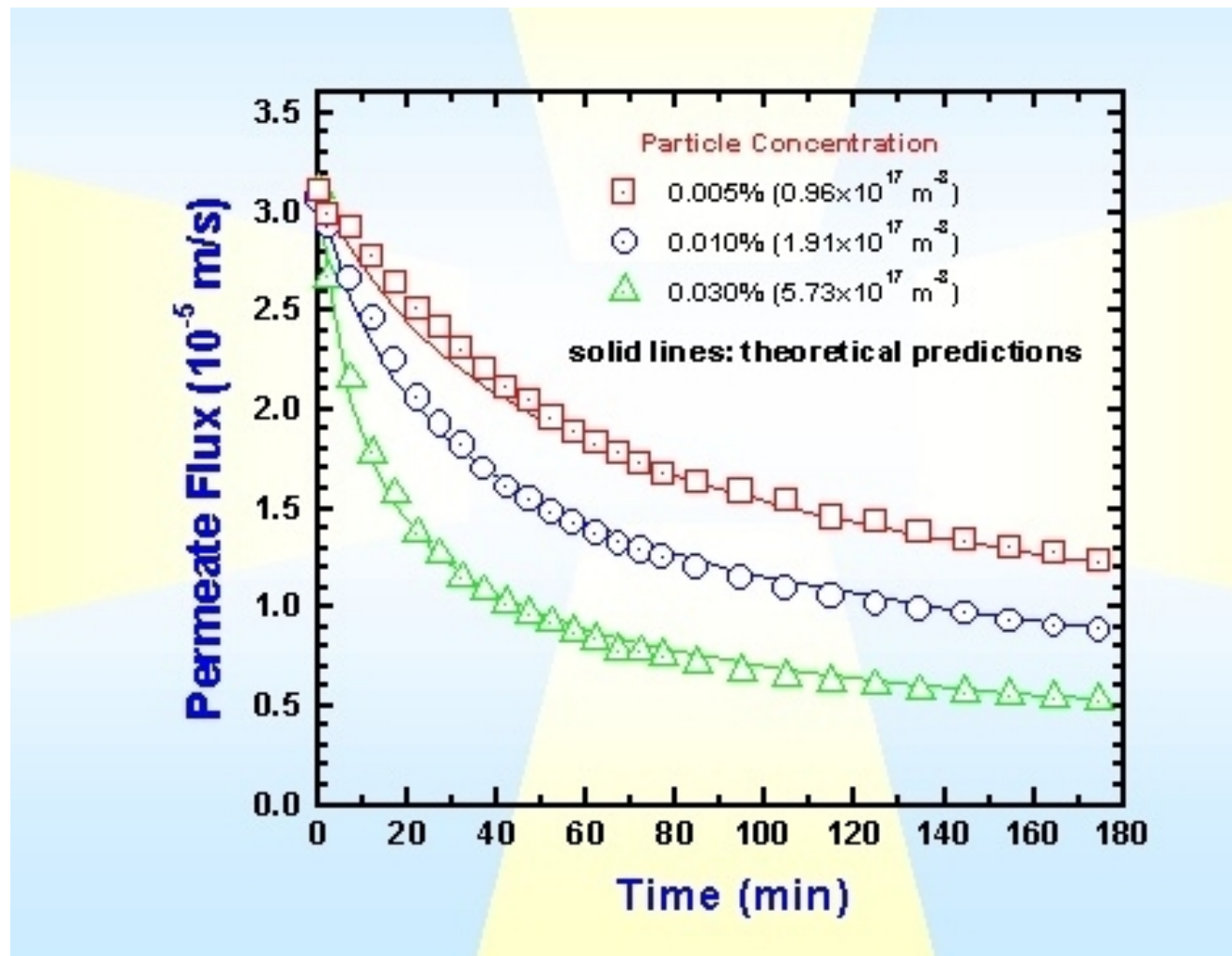
$$\frac{v_w}{v_0} = \left(1 + \frac{3kTA_s(\theta_{\max})C_0\Delta P}{2\pi a_p^3 DR_m^2} t \right)^{-\frac{1}{2}}$$

* Hong, S., Faibish, R.S., and Elimelech, M. (1997) *J. Colloid Interface Sci.*, 196: 267-277.

As: correction parameter to Stokes law evaluated at the maximum packaging of the cake layer, that is the minimum cake porosity; D: particle diffusion coefficient; Rm: membrane resistance.

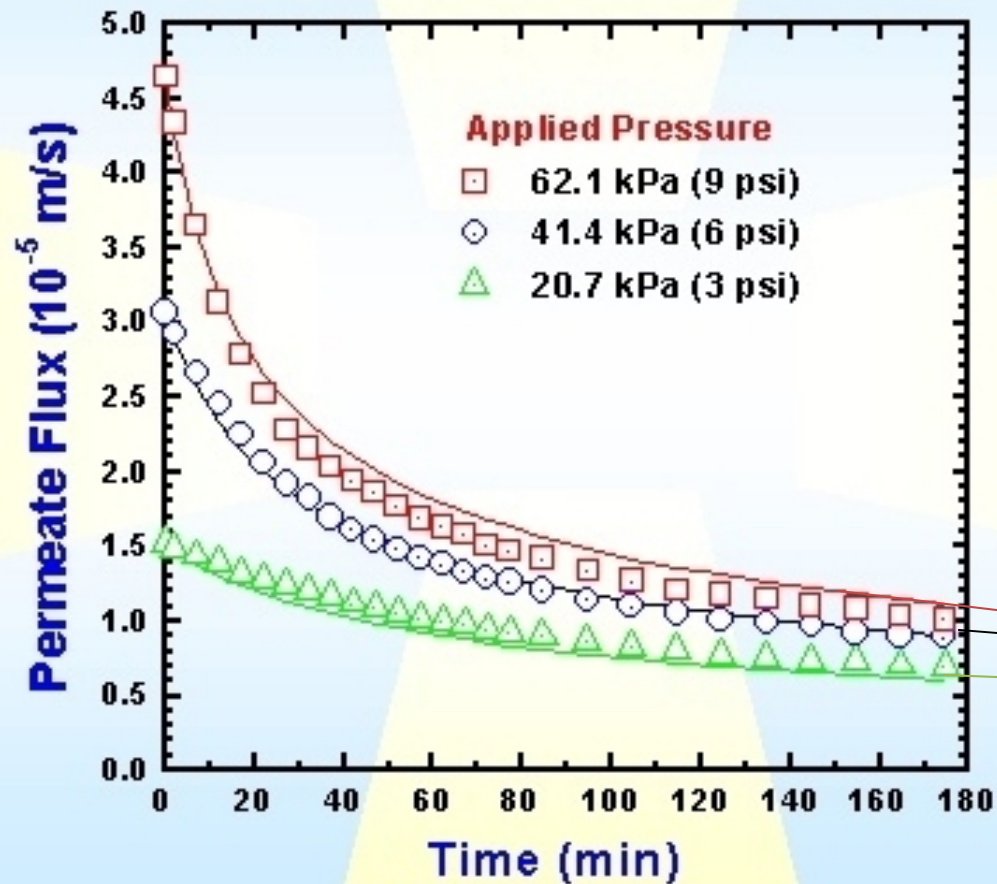
Nanoparticles separation

Permeate flux as a function of particle concentration



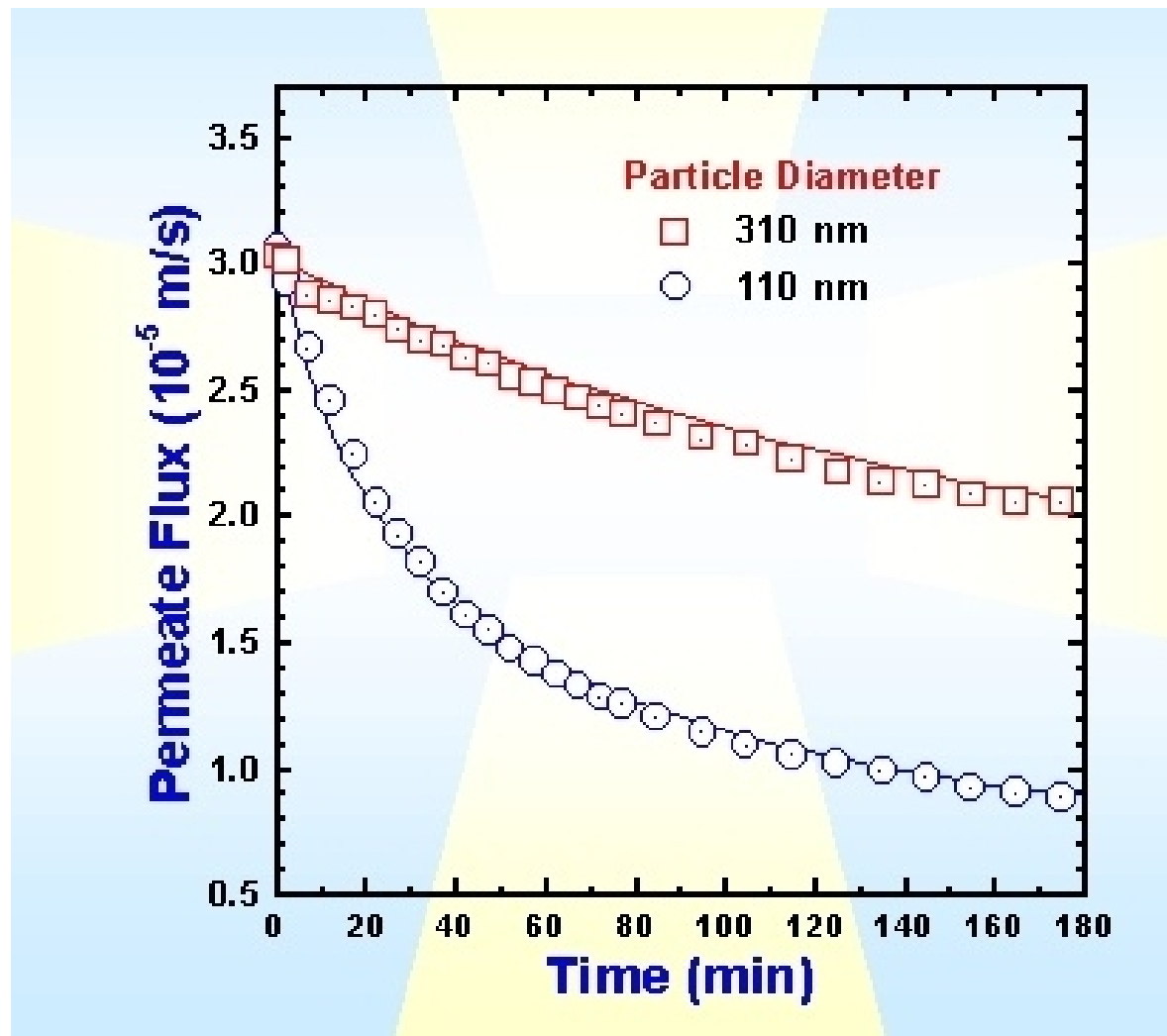
Nanoparticles separation

Permeate flux as a function of applied pressure



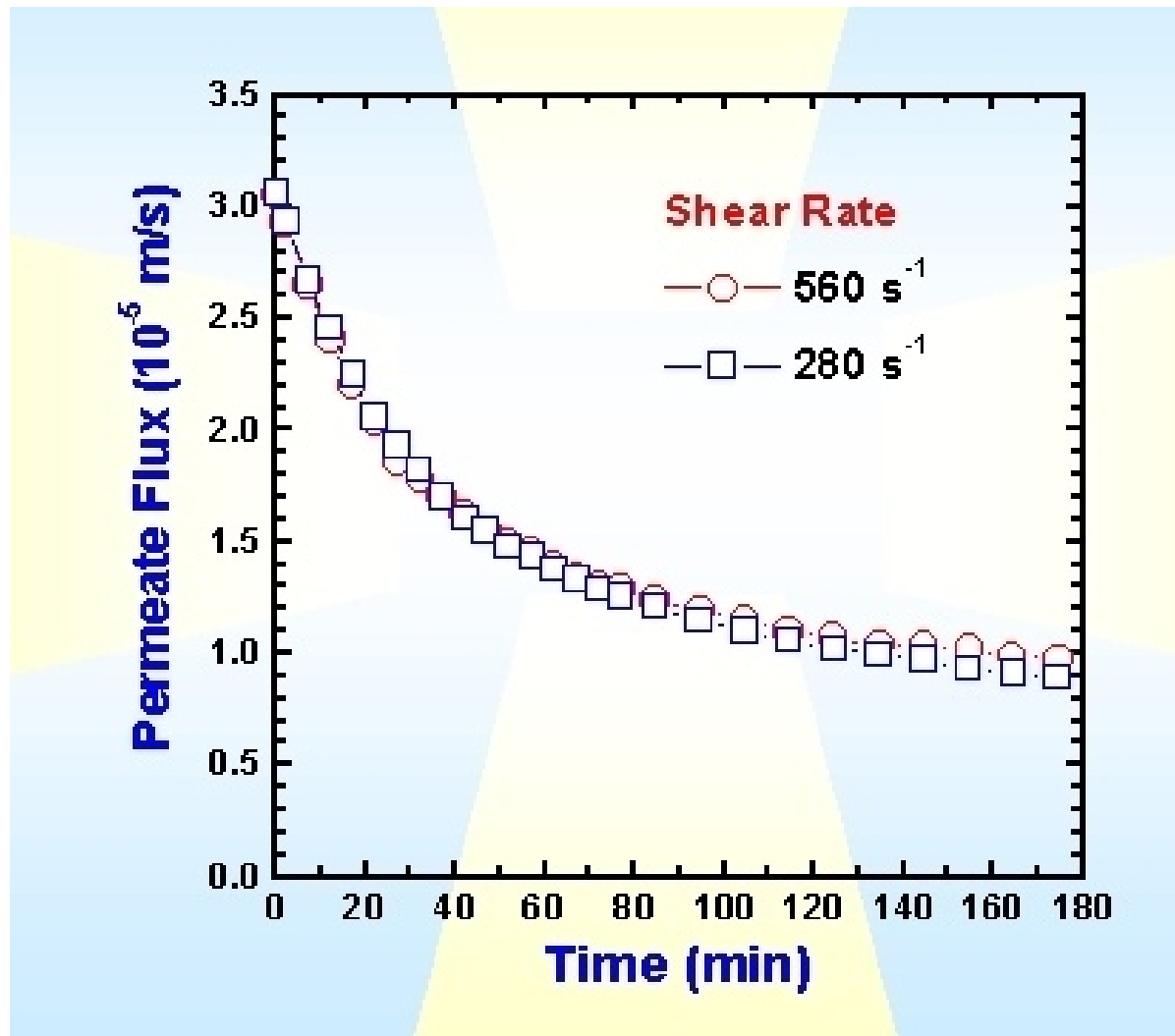
Nanoparticles separation

Permeate flux as a function of particle size

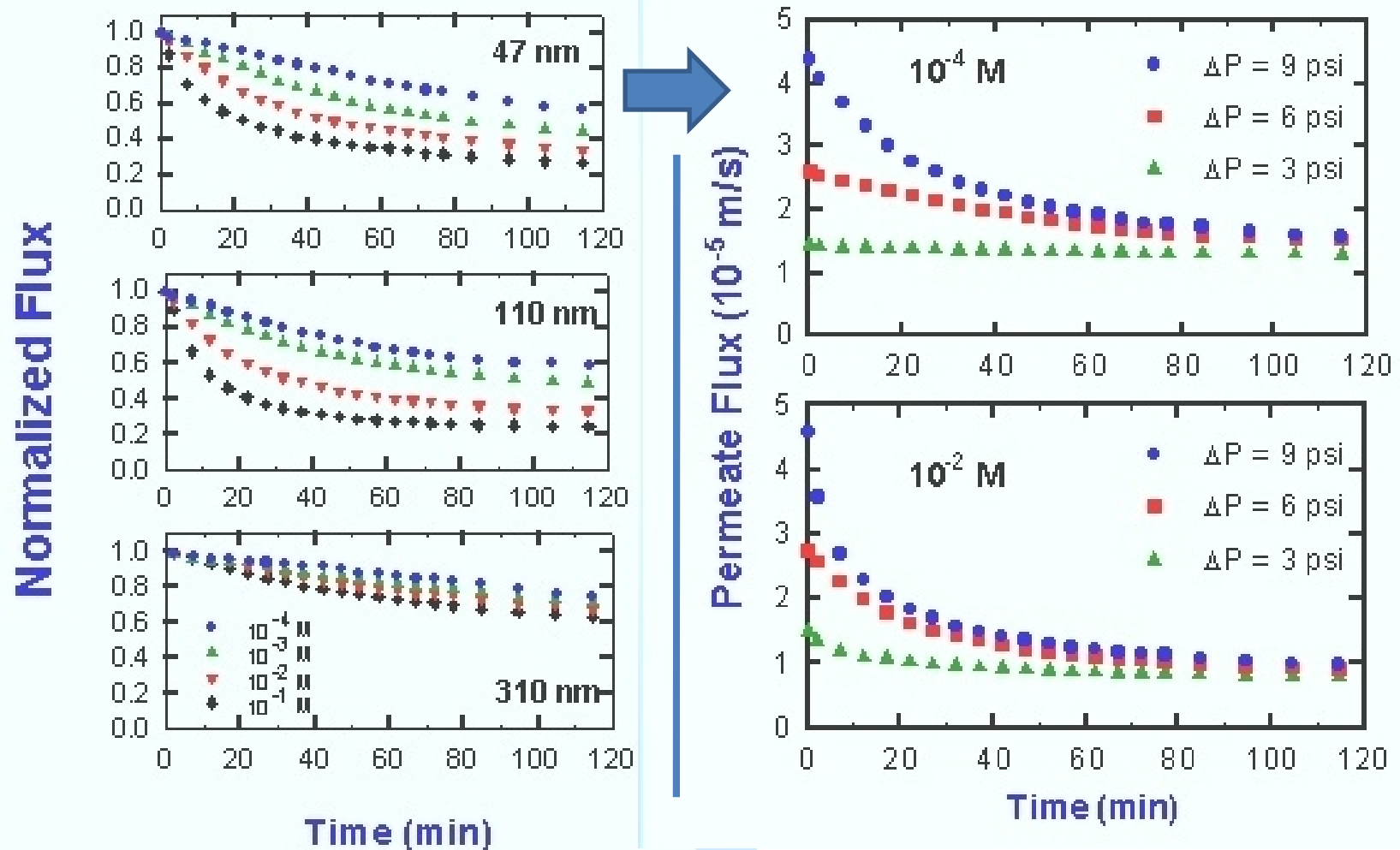


Nanoparticles separation

Permeate flux as a function of feed flow rate

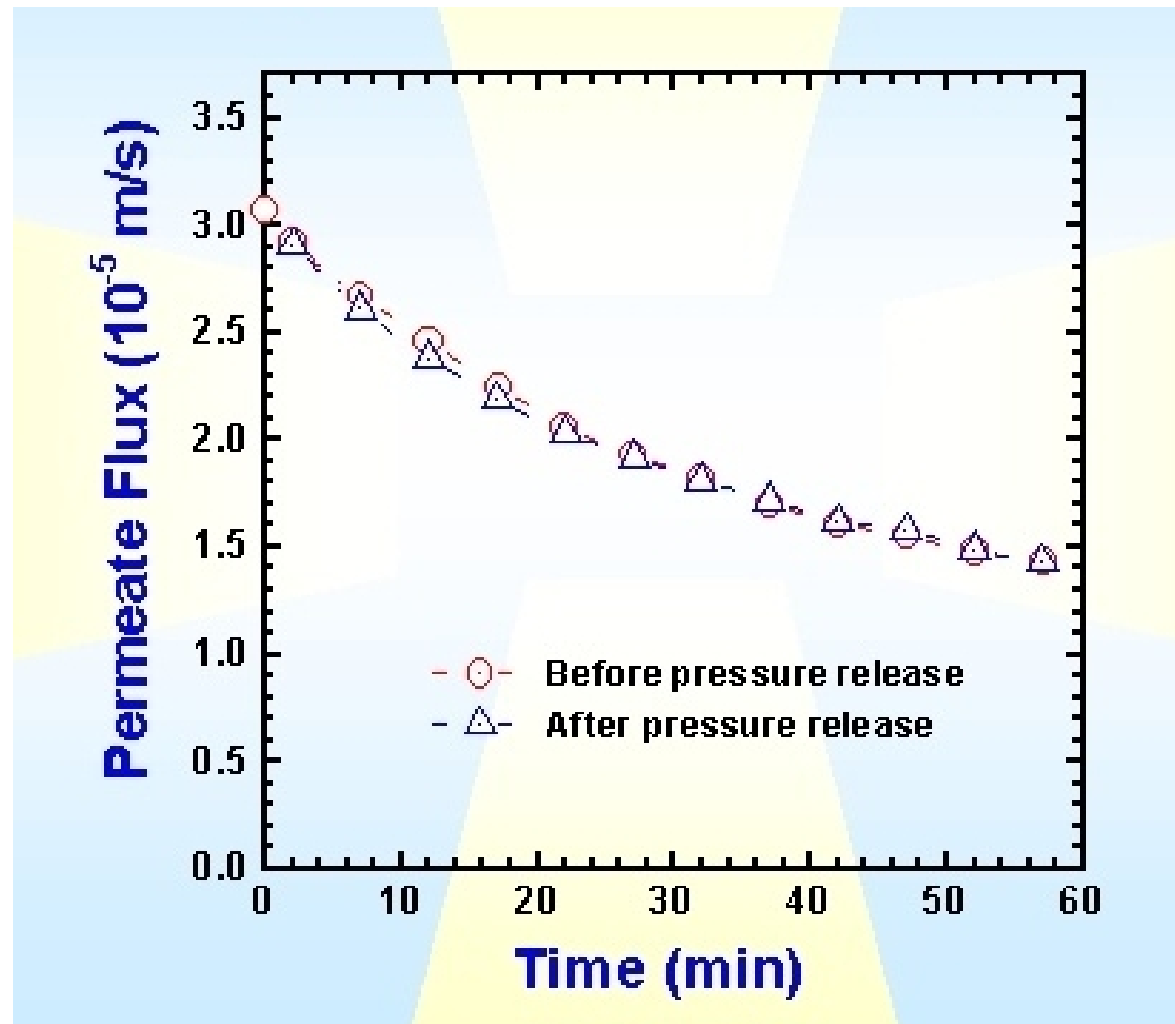


Nanoparticles separation



Nanoparticles separation

Irreversible fouling after 3 psi experiment:



Case study II

❖ **CASE STUDY: PRELIMINARY STUDY ON A PURIFICATION PROCESS OF OLIVE VEGETATION WASTEWATER (OVWW).** The olive mill produce daily 10m³ of OVWW. Coagulation + membrane process was chosen.

❖ **OBJECTIVE: TECHNICAL OPTIMIZATION OF THE MEMBRANE PROCESS.** Target value was COD < 500 mg/l.

❖ **PROBLEMS: FOULING.** Need to be avoided.

OLIVE VEGETATION WASTEWATER CHARACTERISTICS:

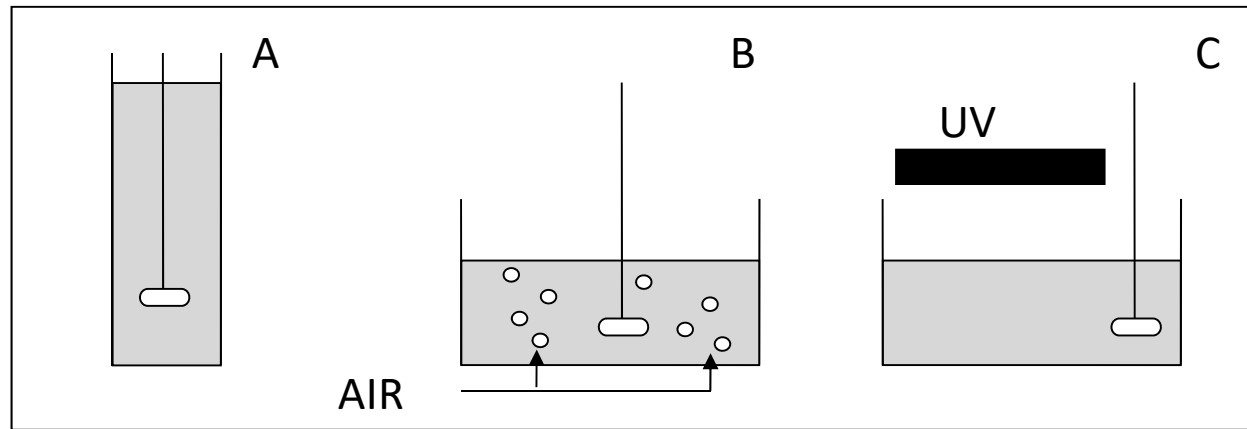
EC	COD	TPh	pH
6,37 mS/cm	55000 mg/l	350 mg/l	4,2

Preliminary experiments

With only 300 micron gridding of the waste water, on all membranes a zero-flux condition was observed within minutes, using low pressure values!

→ PRETREATMENT IS NECESSARY!

Analyzed pretreatments



COAGULATION

Aluminium sulphate (AS)
Aluminium hydroxide (AH)

BIODIGESTION

Biodigestion (BIO)
(BIO + AS)

PHOTOCATALYSIS

Photocatalist nano-TiO₂
size 70nm (PC)

Pretreatment	Initial COD [mg/l]	Operation Time [h]	Recovery [%]	Δ COD [%]	Δ EC [%]
AS	55000	72	80.0	-52.7	+57.9
AH	55000	72	80.0	-56.5	+1.5
BIO	27000	168	90.0	-45.8	-
BIO+AS	27000	240	75.0	-67.0	-
PC	64000	24	95.0	-87.0	-

Coagulation

USED COAGULANT:

ALUMINIUM SULPHATE $\text{Al}_2(\text{SO}_4)_3$

VARIABLES:

COAGULANT DOSAGE [g/L] from 0 to 128 g/L

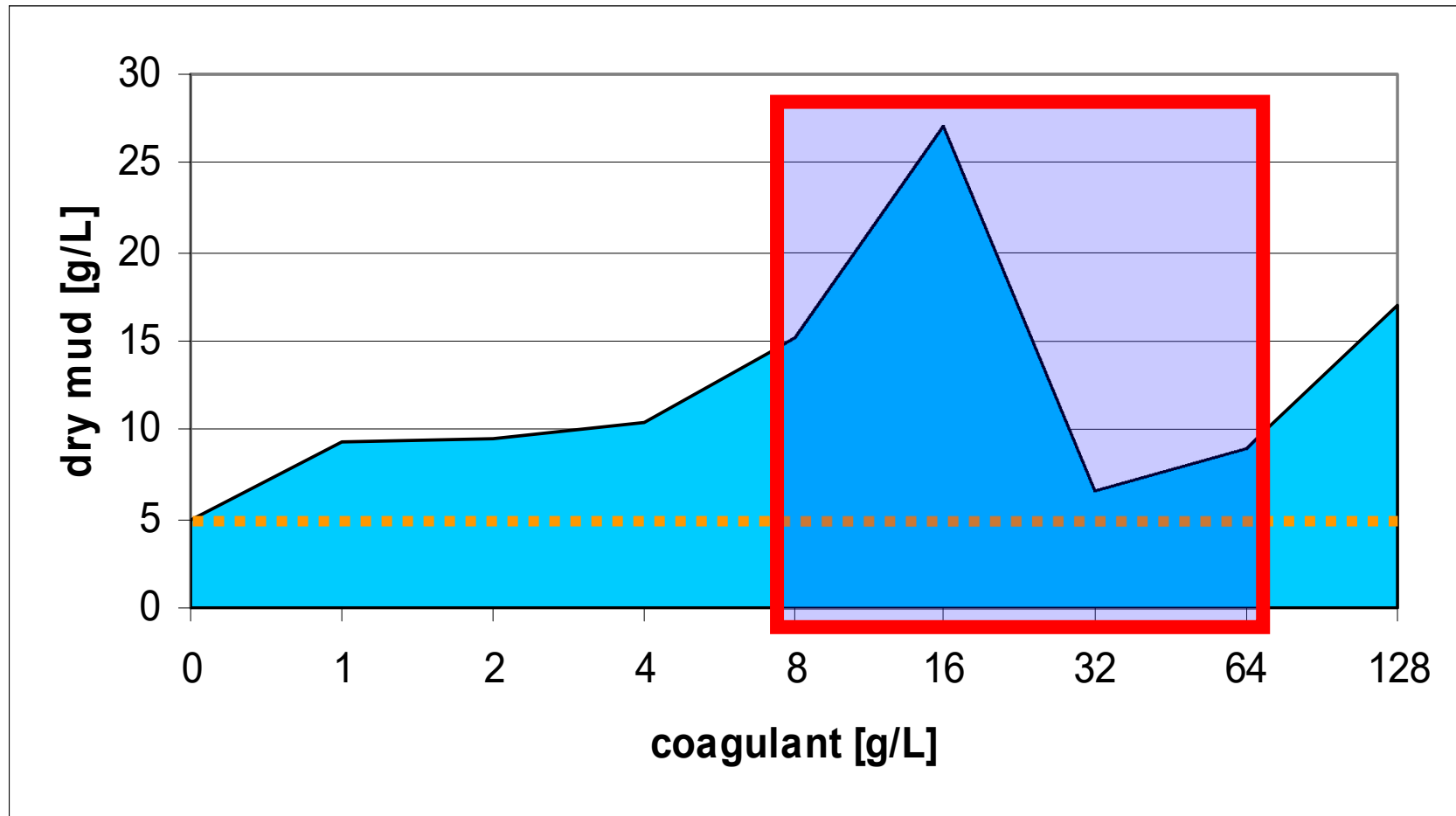
FAST MIXING TIME [min] 1.5 and 3.0 min

SLOW MIXING TIME [min] 20 min

SEDIMENTATION TIME [days] 1, 3, 7 and 14 days

ALLOWS HOMOGENEOUS DISPERSION OF THE
 ...
 ALLOWS FAST AND HOMOGENEOUS
 ALLOWS THE SEPARATION OF THE FORMED
 FLOCKS

Coagulation results



MF

Sample ID	Pre-treatment	R _{COD} [%]	J _{th} [l/hm ²]	TMP _{th} [bar]	d _p [nm]	v _p [%]
OVWW before pretreatment	AS	-	-	-	970.8	82.75
	AH	-	-	-	970.8	82.75
	BIO	-	-	-	879.4	84.14
	BIO+AS	-	-	-	1043.4	81.81
	PC	-	-	-	-	-

RELATIONSHIP BETWEEN THRESHOLD FLUX J_{th} AND PARTICLE SIZE DISTRIBUTION v_p

MF Y = 50%	AS	23.7	4.25	2.5	3980.9	69.03
	BIO+AS	22.0	4.16	3.0	>6000.0	70.56
	PC	18.9	5.23	1.5	150.7	66.66
MF Y = 90%	AS	-	-	-	-	-
	BIO+AS	18.7	2.74	3.0	>6000.0	73.54
	PC	22.8	5.12	2.0	224.1	67.65

UF

Sample ID	Pre-treatment	R _{COD} [%]	J _{th} [l/hm ²]	TMP _{th} [bar]	d _p [nm]	v _p [%]
UF Y = 0%	AS	21.8	5.52	4.0	54.2	58.98
	BIO+AS	43.1	6.36	5.0	145.8	51.29
	PC	59.2	14.92	7.0	123.3	45.87
UF Y = 50%	AS	17.8	5.99	4.0	66.5	61.75
	BIO+AS	29.9	3.02	4.0	396.2	67.45
	PC	63.1	7.65	4.0	340.1	51.08
UF Y = 90%	AS	-	-	-	-	-
	BIO+AS	32.9	2.43	5.0	514.2	74.10
	PC	61.1	4.54	4.0	350.9	66.87

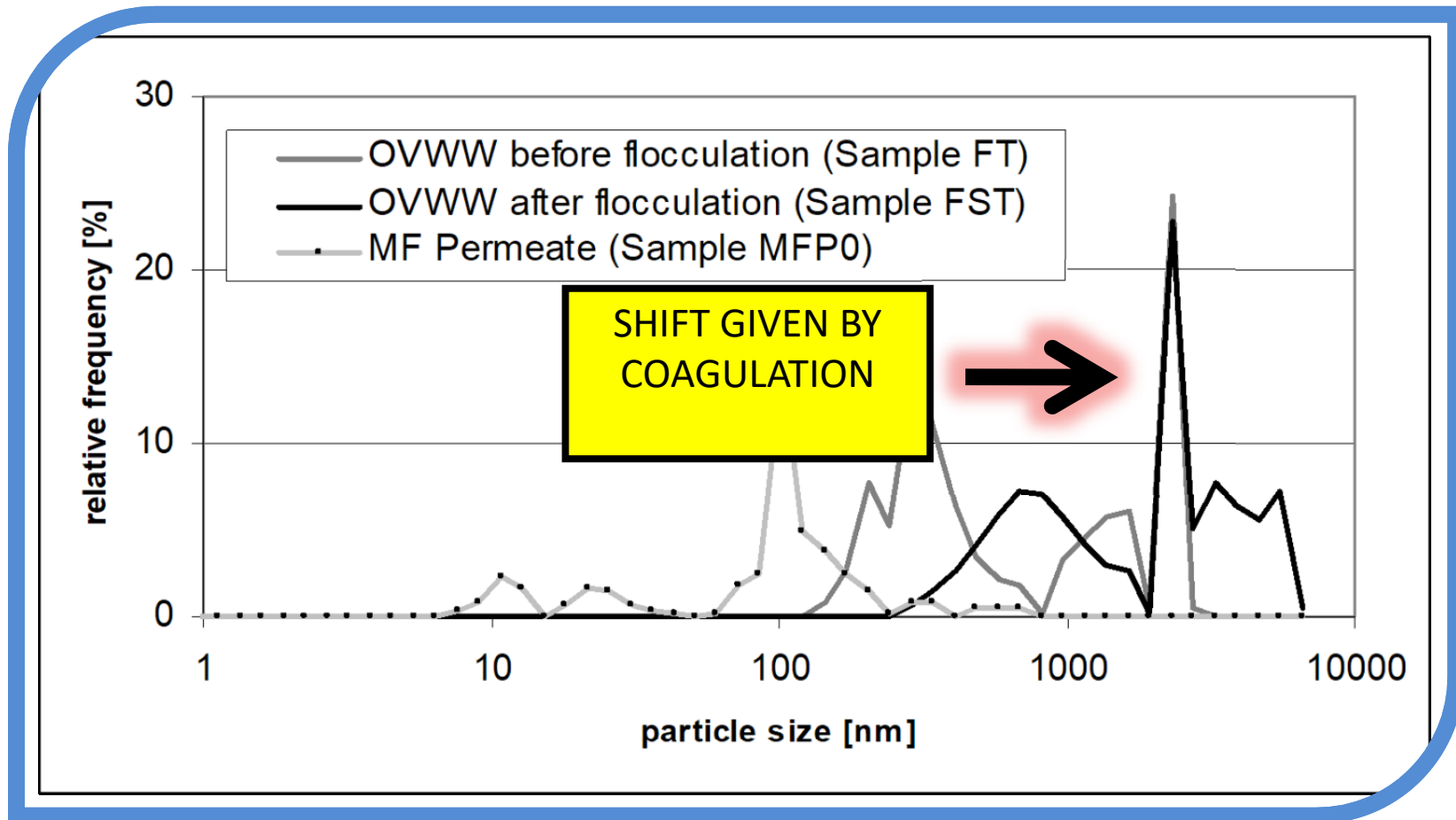
NF

Sample ID	Pre-treatment	R _{COD} [%]	J _{th} [l/hm ²]	P _{th} [bar]	d _p [nm]	v _p [%]
NF Y = 0%	AS	58.4	22.04	7.0	2.1	40.22
	BIO+AS	78.9	3.98	3.0	30.8	75.24
	PC	77.1	14.92	3.0	1.1	47.23
NF Y = 50%	AS	78.0	16.47	7.0	3.6	56.87
	BIO+AS	84.2	2.17	3.0	45.1	79.41
	PC	80.6	7.65	3.0	1.9	55.98
NF Y = 90%	AS	-	-	-	-	-
	BIO+AS	89.6	1.43	3.0	50.0	73.87
	PC	82.5	5.99	3.0	2.1	57.12

RO

Sample ID	Pre-treatment	R _{COD} [%]	J _{th} [l/hm ²]	P _{th} [bar]	d _p [nm]	v _p [%]
RO Y = 0%	AS	95.0	13.49	13.0	-	-
	BIO+AS	77.3	1.64	3.0	-	-
	PC	89.1	9.20		-	-
RO Y = 50%	AS	96.1	10.29	13.0	-	-
	BIO+AS	81.0	2.49	4.0	-	-
	PC	88.4	8.99	3.5	-	-
RO Y = 90%	AS	-	-	-	-	-
	BIO+AS	81.2	1.92	3.0	-	-
	PC	85.1	7.56	2.5	-	-

PSD shift by coagulation



Design results (1)

ECONOMICS WILL NOT BE TAKEN INTO ACCOUNT!

1. MF doesn't seem to be needed. Threshold flux values of UF are higher than those of MF. The PSD shift pulls particles towards the MF pore size!
2. Coagulation is taken into account due to better performances down to RO.
3. From a first rejection analysis, coagulation, UF, NF and RO are needed to reach the COD target. Since RO is needed, coagulation is the right pretreatment.

STEP	COD [g/l]
START	55,0
Coagulation	27,5
UF	22,0
NF	8,3
RO	0,4

Design results (2)

MEMBRANE AREA DETERMINATION

EQUATIONS:

$$OD1\% = 100 (1 - (J_b + a \text{ TMP}_b T_w) / J_b)$$

$$ODN\% = (N_w - 1) T_w m_w\%$$

$$ODT\% = OD1\% + ODN\%$$

T_w : operating time of one cycle

N_w : number of cycles before membran module substitution

Design results (3)

1. Jp of each step are determined by simulation code.
2. Membrane areas are evaluated based on minimum critical flux values, based on treating 2 mc of wastewater at 90% recovery each step in 8 hours.

STEP	Jp [lhbar/sqm]	Membrane area [sqm]
UF	2,32	775
NF	13,18	122
RO	8,73	166

Final considerations

The total square area needed to purify 1458 litres of waste water within 8 hours is 1063 sqm.

At 24 hour regime, the needed membrane area drops down to 354 sqm.

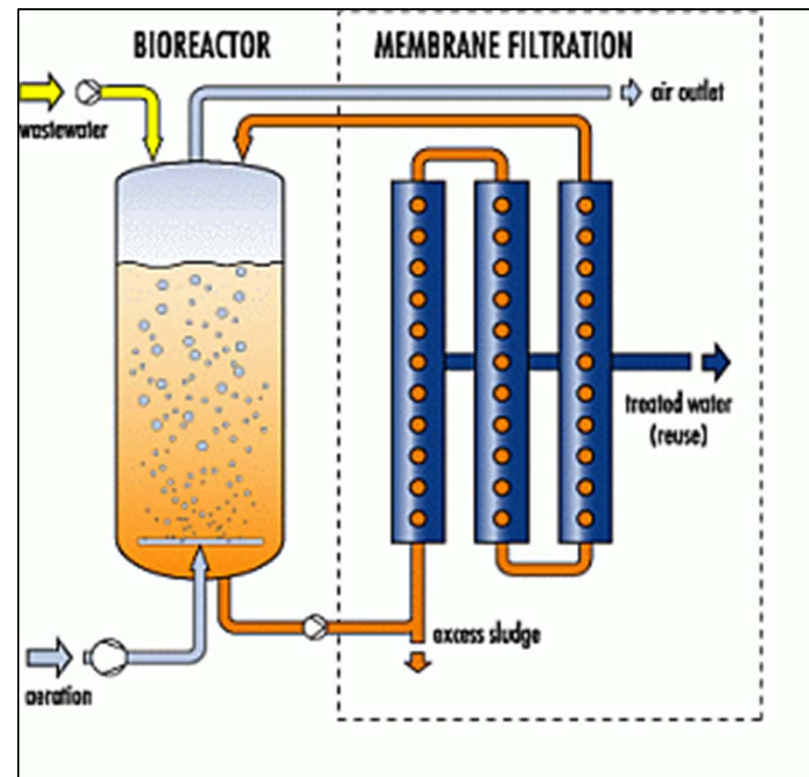
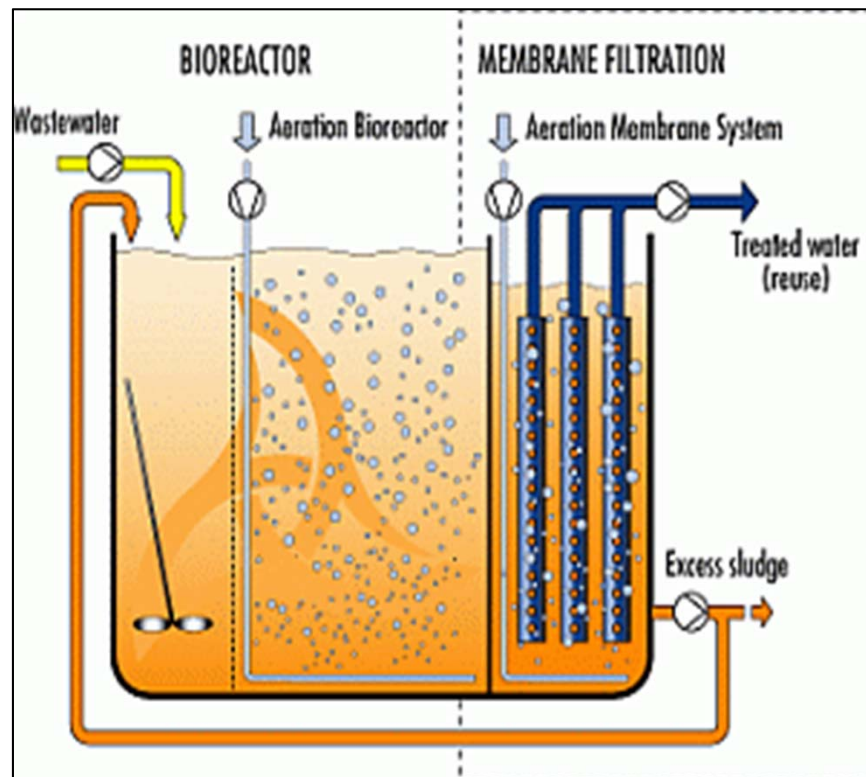
A standard module (SW) have 32 sqm of active area
→ 12 modules are needed (8 UF, 2NF, 2RO)

Life of modules has been estimated around 5 years.
→ membrane investment costs approx. 1,1 €/h

Without fouling control, 12000 € of membranes are lost within hours! (approx. 3500 €/h)

Case study III

MEMBRANE BIOREACTOR (MBR)



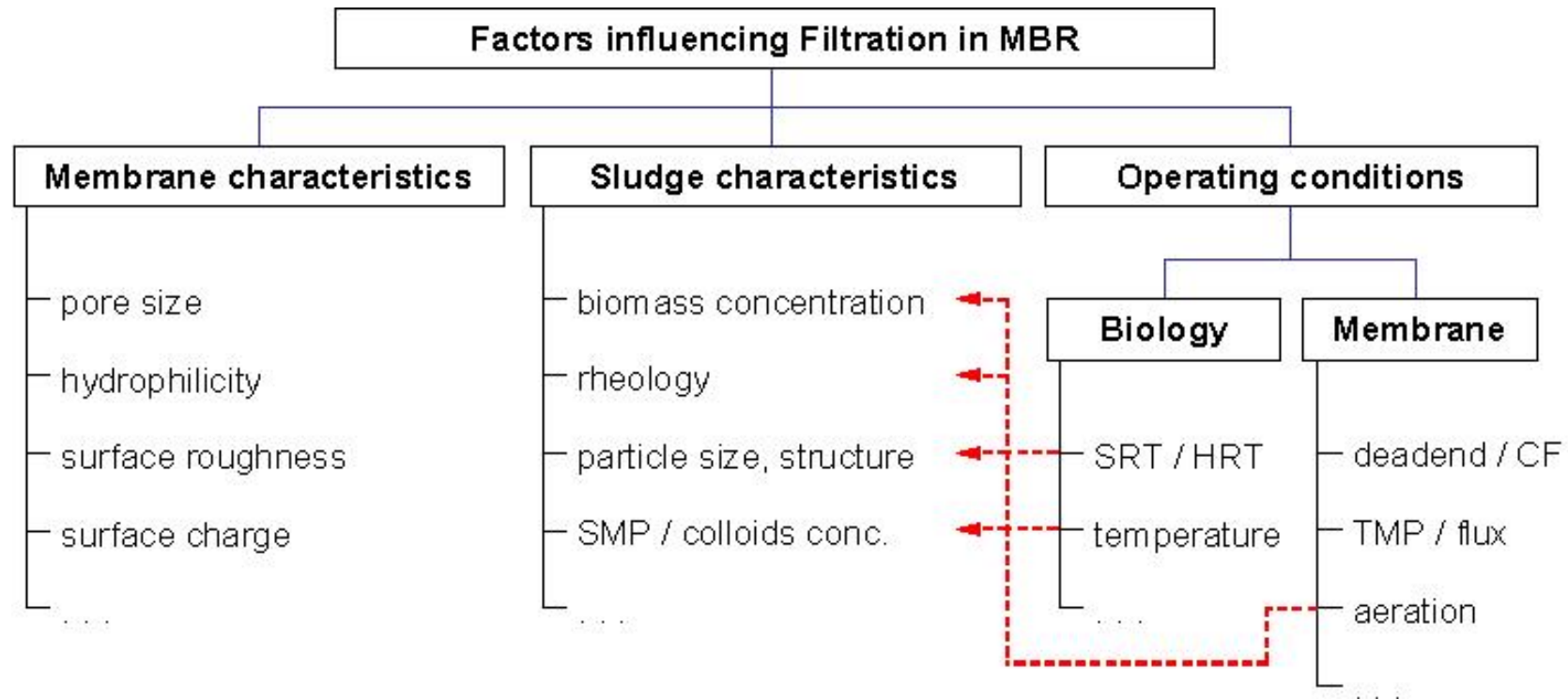
Case study III

MEMBRANE BIOREACTOR (MBR)

Submerged MBR	Side-Stream MBR
Aeration costs high (~90%) Very low liquid pumping costs (higher if suction pump is used ~28%) Lower flux (larger footprint) Less frequent cleaning required Lower operating costs Higher capital costs	Aeration costs low (~20%) High pumping costs (60-80%) Higher flux (smaller footprint) More frequent cleaning required Higher operating costs Lower capital costs

Case study III

MEMBRANE BIOREACTOR (MBR)



“ANTI-FOULING” STRATEGIES:

Intermittent permeation, Permeate backwash, Air backwash, Chemicals

Boundary flux

Case study III



Process parameter	Typical value	Comment
Sludge concentration	10 - 20 g MLSS[2]/l	Sometimes up to 30 g/l
Sludge load	0.05 - 0.25 g CZV/gMLSS.d	Comparable with conventional active sludge systems
Sludge age	30 - 90 days	Sludge load
Temperature	5 - 25 °C	Thermophilic applications also known
flux internal MBR	10 - 20 l/m ² .h	
flux external MBR	30 - 40 l/m ² .h	