Green Ultrafiltration Membranes

Y. Medina-Gonzalez, J.C. Remigy*
Laboratoire de Génie Chimique,
Toulouse, France

remigy@chimie.ups-tlse.fr

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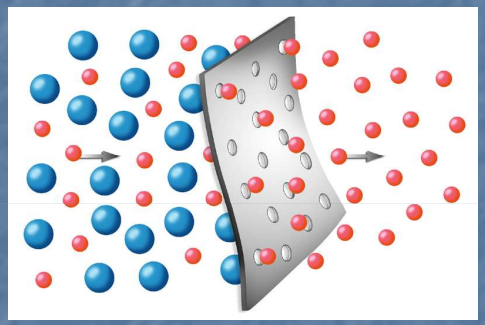
Membrane Processes

Membrane: barrier, selective.

- Appreciable energy savings

- Environmentally benign

- Greater flexibility in designing systems.



- Clean technology with operational ease

- Produces high quality products

- Replaces the conventional processes

Uses: Waste water treatment, separation of biological active components, refining of oils, gas separation ….
Membrane fabrication: Solvents, pollutants wastes.

Legal Context

Human health impact
Ecosystems impact
Greenhouse gas production
Global warming

Green production processes

Most recent European Environmental Law:

REACH (November 17th 2005)

The industries must prove the non-toxicity of their materials.

Green Solvents

Substitution of dangerous materials by green materials.

Green Solvents[§]

- Non toxic
- Non volatile
- From renewable resources

[§] **P. T. Anastas**, ACS Symposium Series 819, American Chemical Society, Washington DC. 2002, pp. 1-9.

Green solvents

Solvent	LD50	Vap. Pressure	Risks
Cyclohexane	Oral rat 12.7 g/kg Oral mouse 0.8 g/kg	96.8 mmHg at 20°C	Mutagen
DMSO	Oral rat 14.5 g/kg	0.42 mmHg at 20°C	Mutagen/Tumorigen
Acetone	Oral rat 5.8 g/kg	181 mmHg at 20°C	Highly flammable
Chloroform	Oral rat 1.2 g/kg Oral mouse 0.08 g/kg	158.3 mmHg at 20°C	Mutagen, teratogen
NMP	Oral rat 3. 9 g/kg Skin rabbit 8 g/kg	0.5 mmHg at 25°C	None
Ethyl lactate	Oral rat 5 g/kg Oral mouse 2.5g/kg	5 mmHg at 30°C	None
Methyl lactate	Oral rat 2 g/kg	2.6 mmHg at 20°C	None

Phase inversion Process

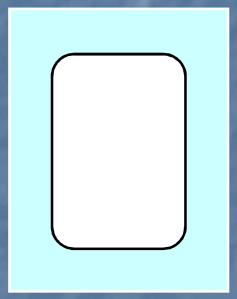
LiCl, PVP
NMP, DMF, DMSO, acetone, cyclohexane, chloroform…
Cellulose acetate: water treatment membranes, from renewable materials.

Polymer + solvent + porogen

(Solvent must solubilize polymer and porogen)

Non-solvent of the polymer, miscible with the solvent on dope solution

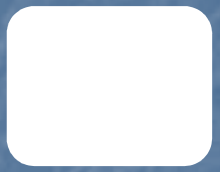
Dope solution



Casting on a glass plate

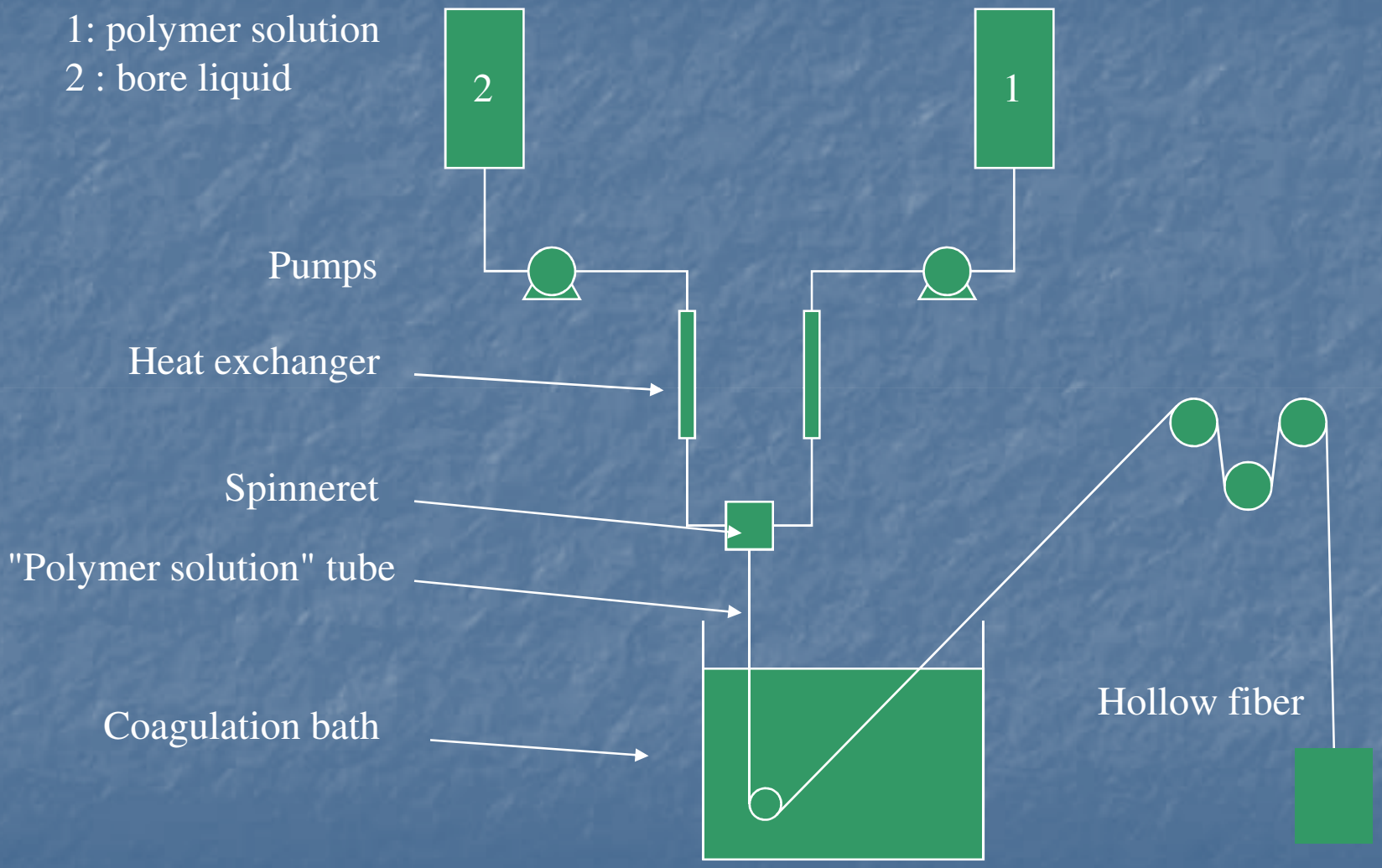
Immersion on a coagulation bath

Waste



Flat sheet membrane

Phase inversion Process: Hollow Fiber Fabrication



Phase Inversion and Green Materials

	Material	Water Soluble	Solvent Soluble	Solubilizes cellulose acetate	Natural	Suitable for green membranes?
SOLVENTS	**Methyl Lactate**	✓	-	✓	✓	**YES**
SOLVENTS	**Ethyl lactate**	✓	-	✓	✓	**YES**
SOLVENTS	NMP	✓	-	✓	×	NO
SOLVENTS	DMSO	✓	-	✓	×	NO
POROGENS	PVP	✓	✓	-	×	NO
POROGENS	**LiCl**	✓	✓	-	✓	**YES**
POROGENS	**$CaCl_2$**	✓	✓	-	✓	**YES**

Phase inversion and Green Materials

Green solvents must **solubilize** the **polymer** and the **porogen**

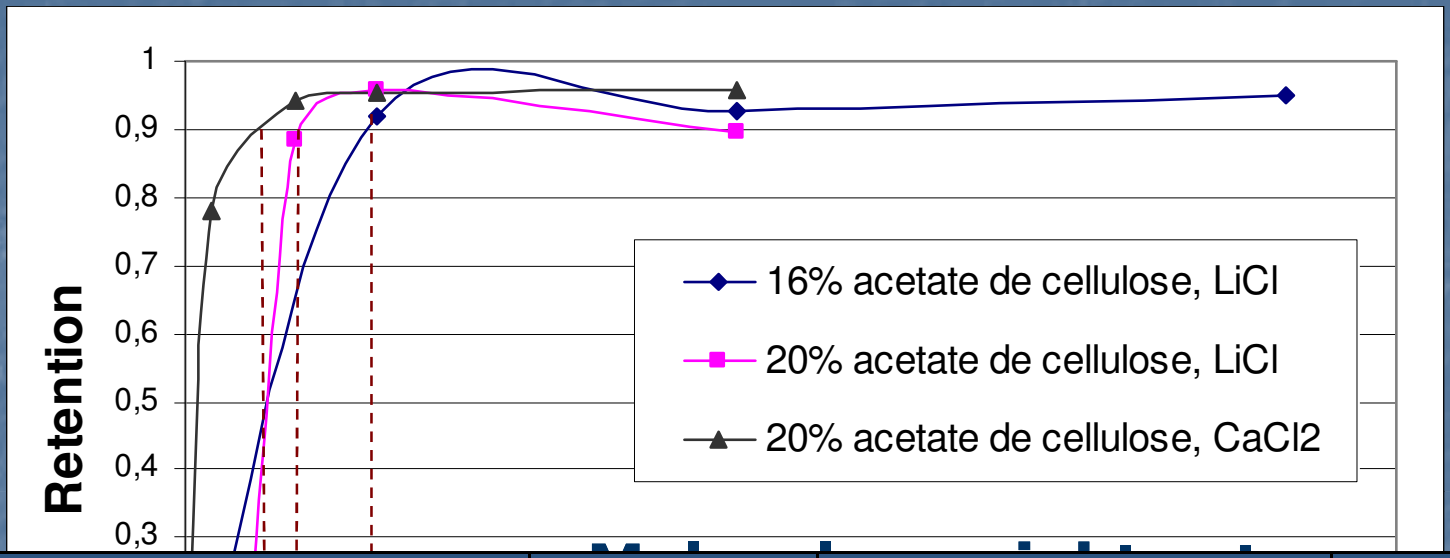
Green solvents must be **miscible** with the coagulation bath (currently **water**)

Methyl lactate
Ethyl lactate
$CaCl_2$ and LiCl
Cellulose acetate

Biodegradable and natural

From renewable raw materials

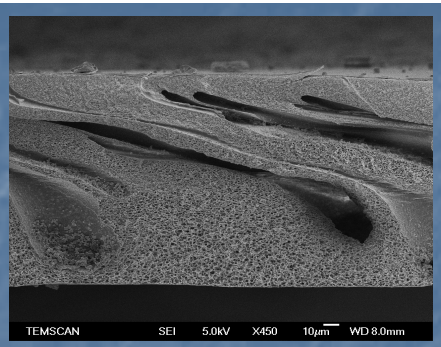
Results



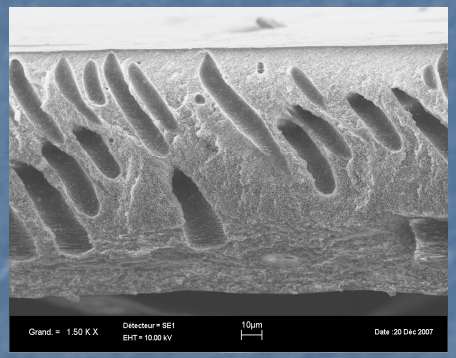
Membrane	MWCO (PEG, kDa)	Pure water permeability at 20°C ($Lh^{-1}m^{-2}bar^{-1}$)	Pressure at break (bar)
16% cellulose acetate, LiCl	35	177	4.5
20% cellulose acetate, LiCl	20	23	3
20% cellulose acetate, $CaCl_2$	15	13	>>5

10kDa<UF<500kDa

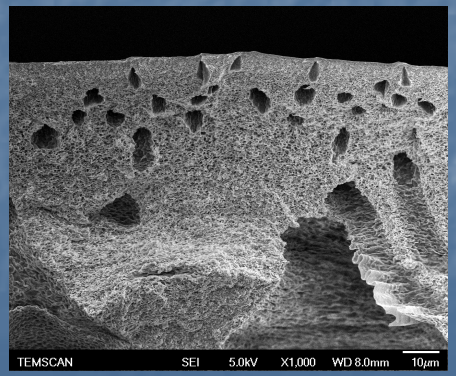
Results



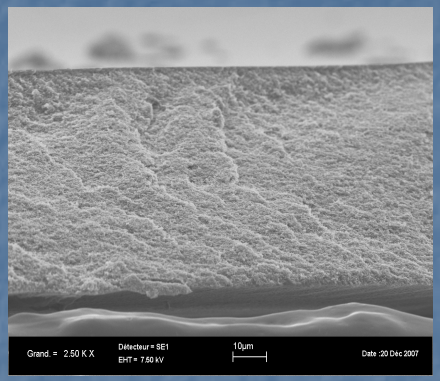
16% Cellulose acetate
6% LiCl
Solvent: methyl lactate



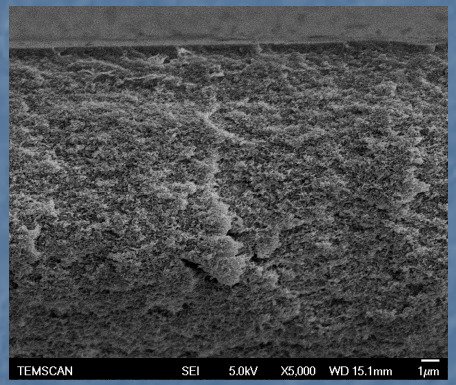
20% Cellulose acetate
6% LiCl
Solvent: methyl lactate



20% Cellulose acetate
3% LiCl
Solvent: ethyl lactate



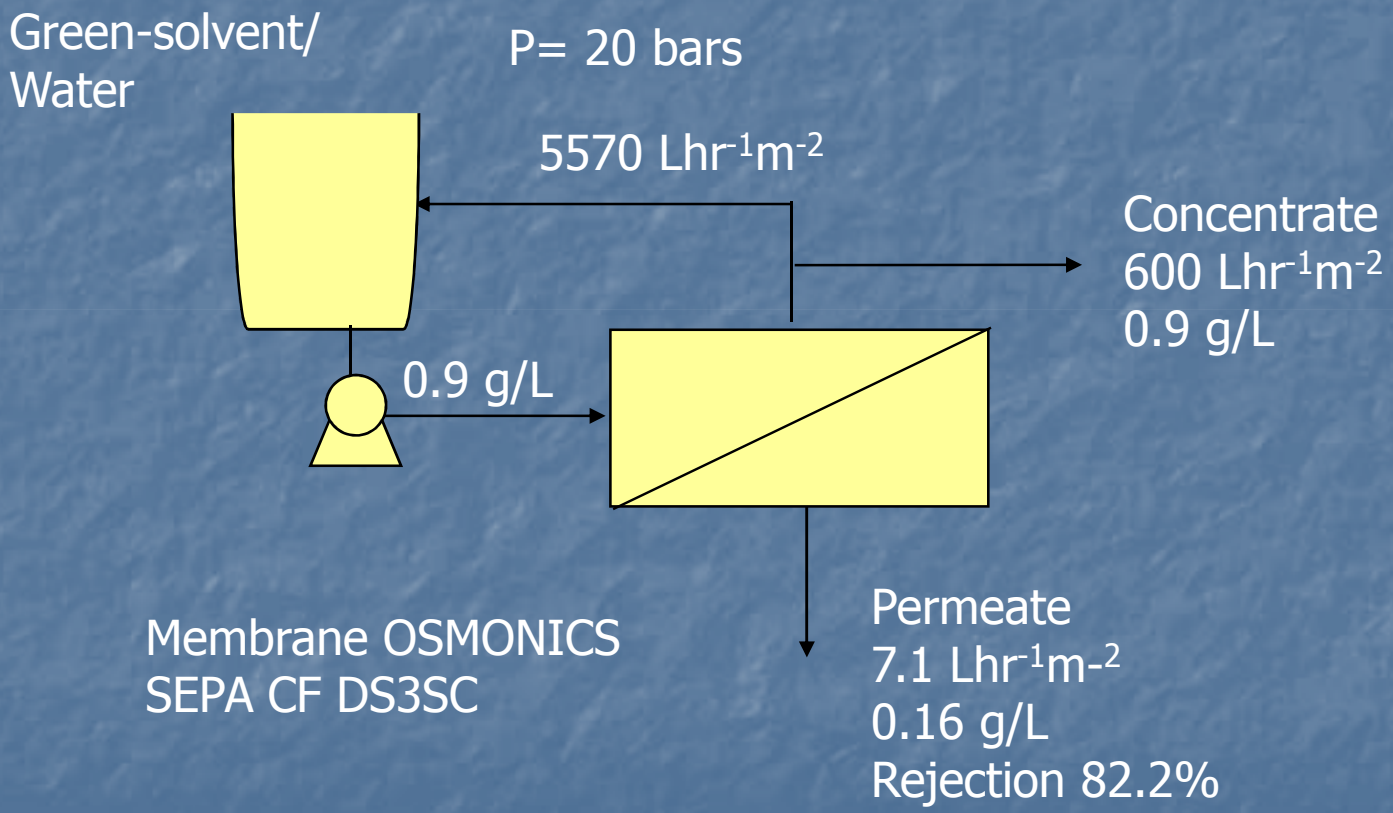
20% Cellulose acetate
6% $CaCl_2$
Solvent: Methyl lactate
Pores < 0.1 µm



20% cellulose acetate
3% $CaCl_2$
9% water
Solvent ethyl lactate
Pores ≈ 0.1 µm

Green-solvent Recovery / Water Recycling

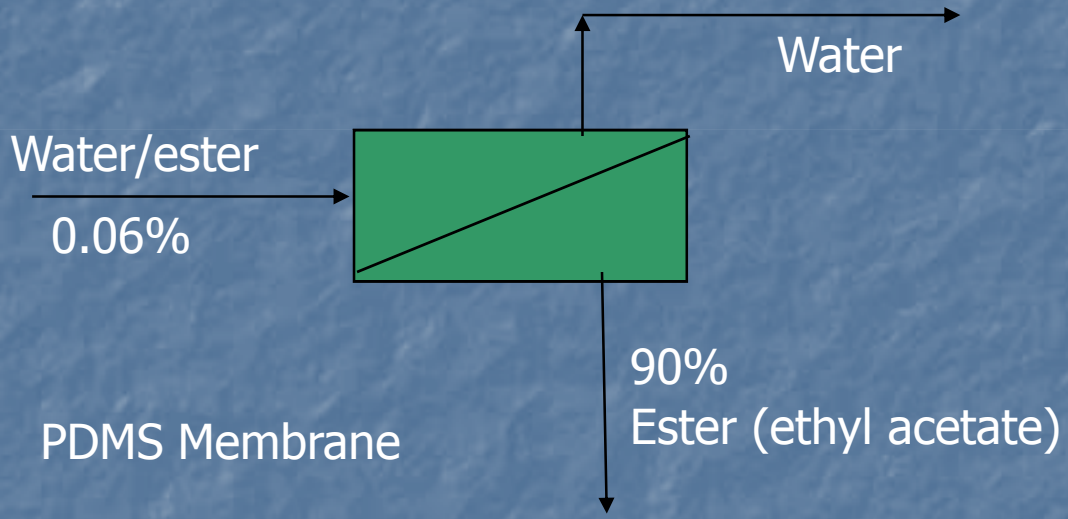
Reverse osmosis



Green-solvent Recovery / Water Recycling

Pervaporation

Bendjama, Z. PhD Thesis INPL 1993.
M.K.Djebar et al, J. Membr. Sci. 146 (1998) 125-133.



Conclusions

- Ultrafiltration cellulose acetate membranes were obtained only by using natural and biodegradable materials.

- $CaCl_2$ used as porogen produced membranes resistant to pressure higher than 5 bars.

- Reverse osmosis has been proved to be a good technique to recycle water from process. Pervaporation could be an ideal technique for green-solvent recuperation.

- Fabrication of green ultrafiltration membranes can be easily implemented on industry together with green-solvent recuperation in actual facilities.

Prospects

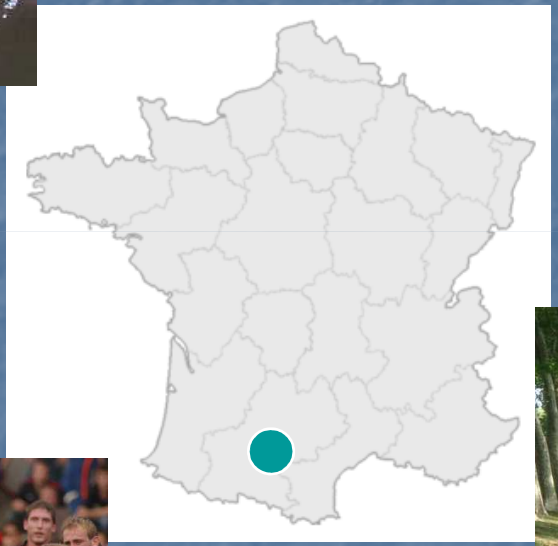
- Encouraging results.

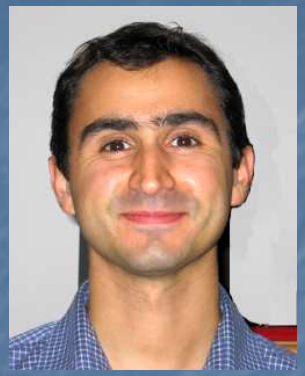
- We will try to improve the dope solution to obtain membranes with high permeability, and resistant to pressure. A low MWCO would be desirable.

- Fabrication of hollow fiber membranes.

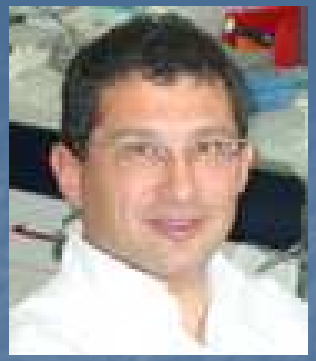
-Tests with other natural materials.

TOULOUSE





Dr. Lahitte

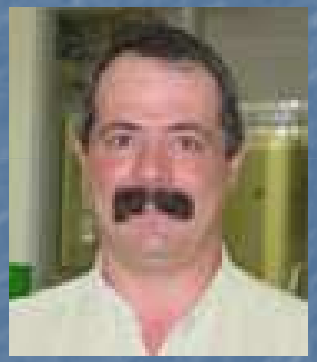


Dr. Aimar

Dr. Remigy

Membrane Elaboration Team

Ing. Desclaux



Ing. Rouch

Dr. Macanas

THANK YOU!!