

FutureCarbon



Helmholtz-Zentrum
Geesthacht
Zentrum für Material- und Küstenforschung



European Union
European Regional
Development Fund



HELLENIC REPUBLIC
Ministry of Economy
and Finance

Special Secretariat for
ERDF & CF Programmes
Managing Authority of "Competitiveness" Programme

GSRI
GENERAL SECRETARIAT FOR
RESEARCH AND INNOVATION

ΕΡΑνεΚ 2014-2020
OPERATIONAL PROGRAMME
COMPETITIVENESS
ENTREPRENEURSHIP
INNOVATION

ΕΣΠΑ
2014-2020
ανάπτυξη - εργασία - αλληλεγγύη
Partnership Agreement
2014 - 2020

Co-financed by Greece and the European Union

ECOTECH – NCSR Demokritos

NAMED 2nd Meeting

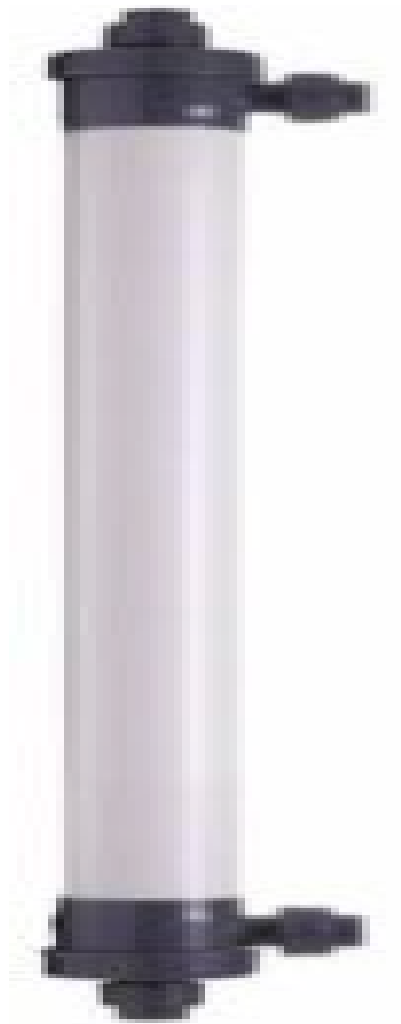
ECOTECH
ΣΥΣΤΗΜΑΤΑ ΠΡΟΣΤΑΣΙΑΣ ΠΕΡΙΒΑΛΛΟΝΤΟΣ

- For the development of the pilot unit we have two engineering designs, namely:
- (I) a design based on the preliminary design presented in the submitted proposal, which requires the development of four membranes (NF high Mg^{2+} rejection, NF high Na^+ rejection, FO and MD modules, all of them up scaled to 0.5 m³/day.
- (ii) a design based on the preliminary design presented in the submitted proposal, which requires the development of only three membranes (NF high Mg^{2+} rejection, NF high Na^+ rejection and FO, up scaled to 0.5 m³/day (there is no need for MD development).

- develop to TRL 6 of “next-generation” membranes.
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- **Forward Osmosis (FO) membranes** based on recent advances of nanotechnology, namely:
 - (a1) PIM/SWCNT (German side?) and
 - (a2) development of high flux single wall carbon nanotube (SWCNT) FO hollow fibre membranes by partner(Greek side).
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- Development to TRL 6 of “next-generation” **nanofiltration hollow fibre** , NF_{Mg} high Mg^{2+} rejection (Greek side).

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- **Development to TRL 6 of “next-generation” high flux membrane distillation (MD) membranes:**
- **(d1) PIM? (German side?)**
- **(d2) dual layer hollow fibre hollow fibre membranes hollow fiber membranes by partners(Greek side).**

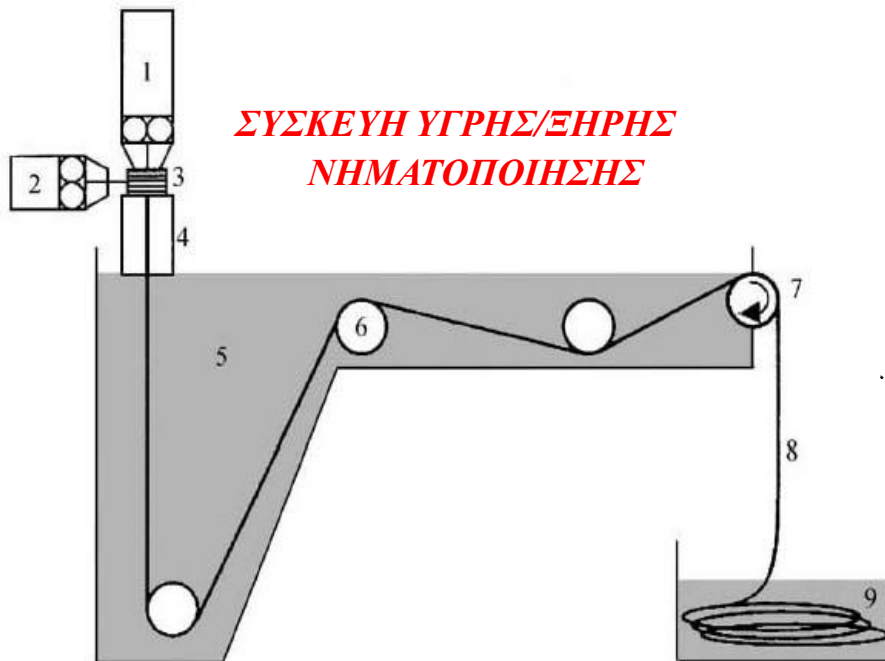
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- Upscale the best membranes to 0.5 m³/day.
- We need modules of the order of 0.5 m³/day.
- Design, development, operation and optimization of innovative combinations of the best NF₁/NF₂/FO/MD.



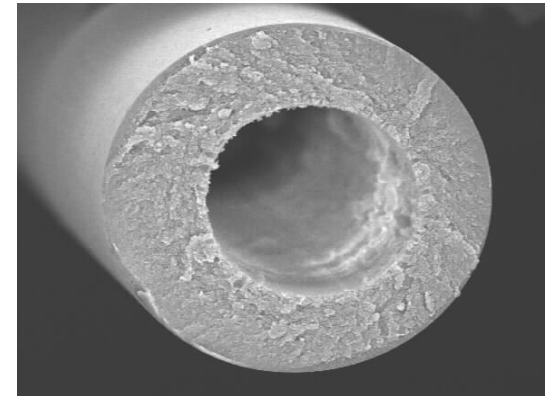
- ECOTECH has upgraded the design, we have two designs, one $NF_1/NF_2/FO/MD$ and a second $NF_1/NF_2/FO$, reducing the number of the membranes that need to be developed down to three.
- Feasibility study for the selected pilot unit
-

hollow fiber

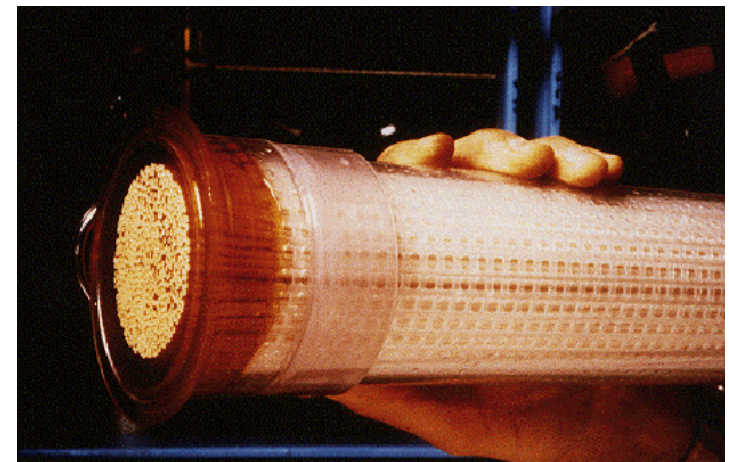
MEMBRANE DISTILLATION carbon membranes



1. Πολυμερές – Διαλύτης
2. Μη Διαλύτης
3. Spinneret
4. Air Gap
5. Λουτρό Θρόμβωσης
- 6-7. Τύμπανα Μεταφοράς - Συλλογής
8. Πολυμερική Κοίλη Ίνα

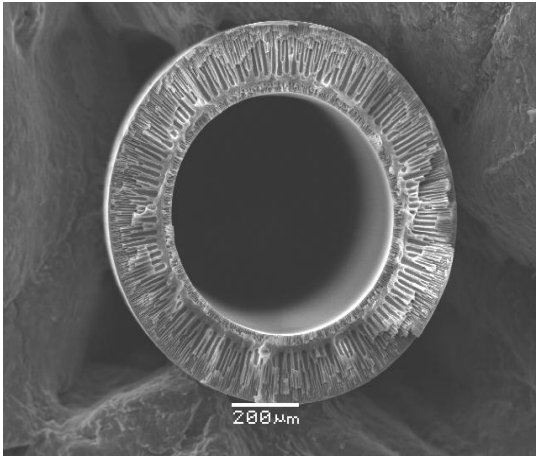


Φωτογραφία SEM

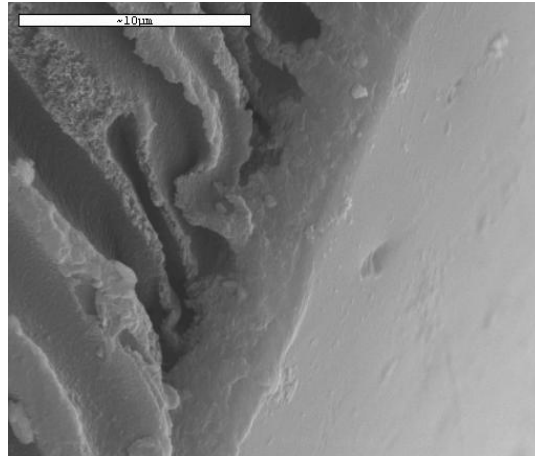


**Module Κοίλων Ίνων για
Διαχωρισμό Αερίων**

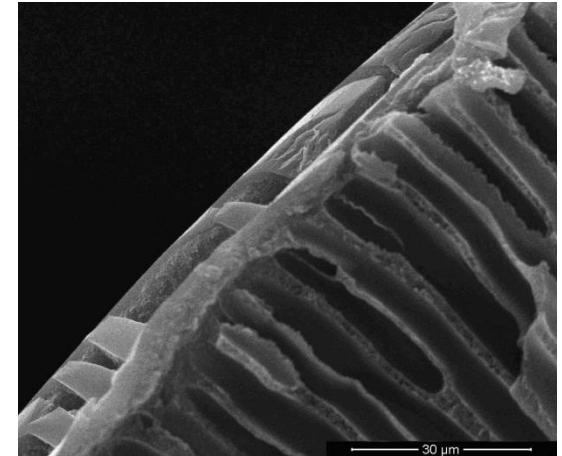
SEM PICTURES OF PRODUCED HOLLOW FIBER MEMBRANES



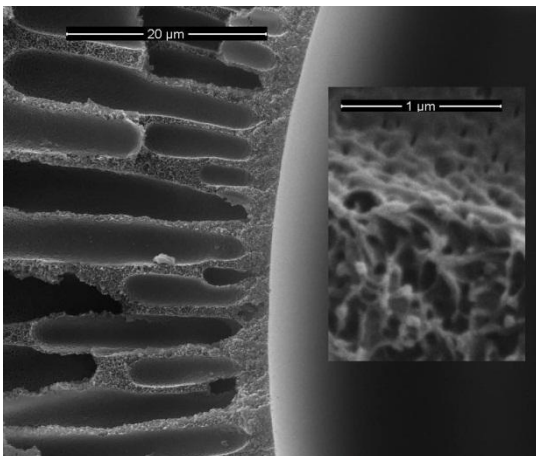
CROSS SECTION



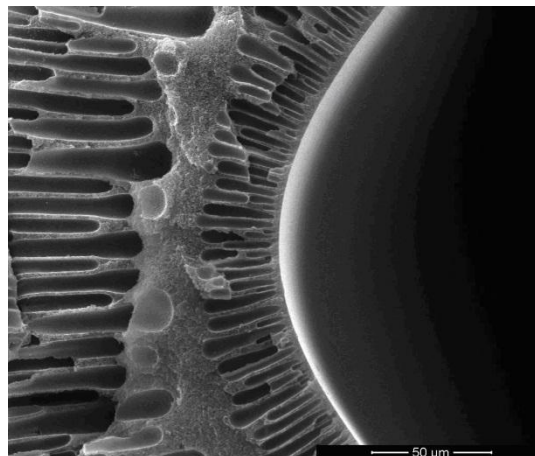
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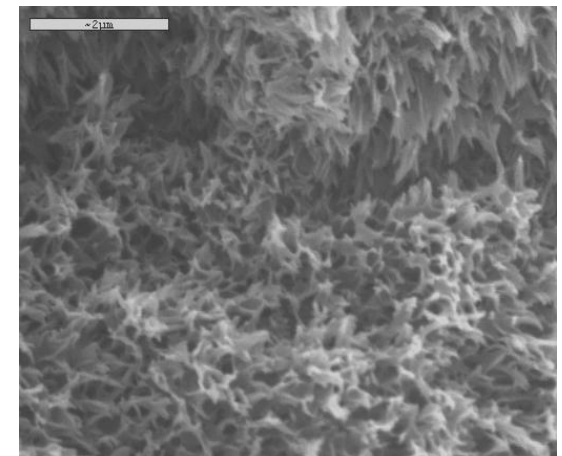
CROSS SECTION



CROSS SECTION



CROSS SECTION



INNERT

MD up scaled module to 0.5 M³/day MD

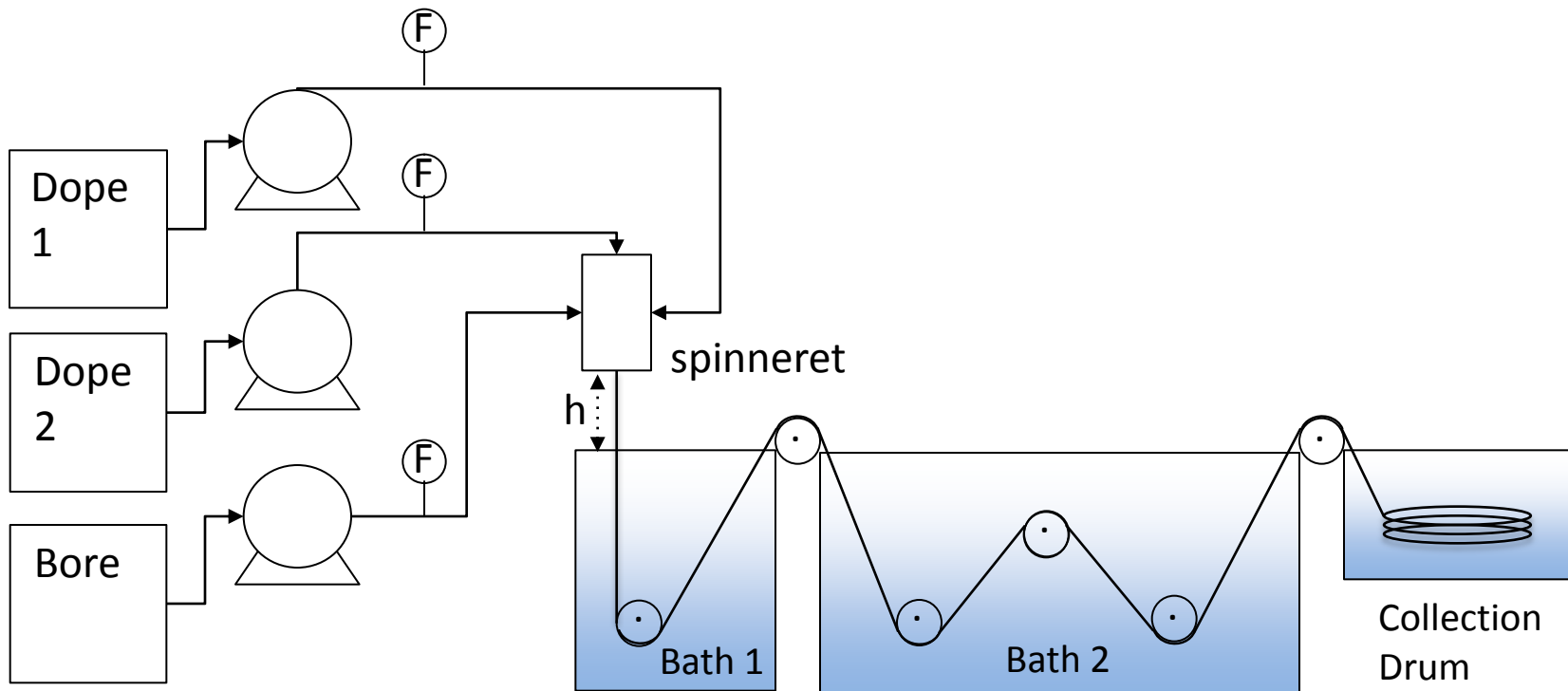
1. MD (Membrane distillation) Carbon hollow fiber fragile, not readily scalable

- **2. A better alternative is the readily scalable double layer PVDF/PEI (hydrophobic/hydrophilic) hollow fiber membrane**

Membrane Fabrication – Hollow Fiber and Flat

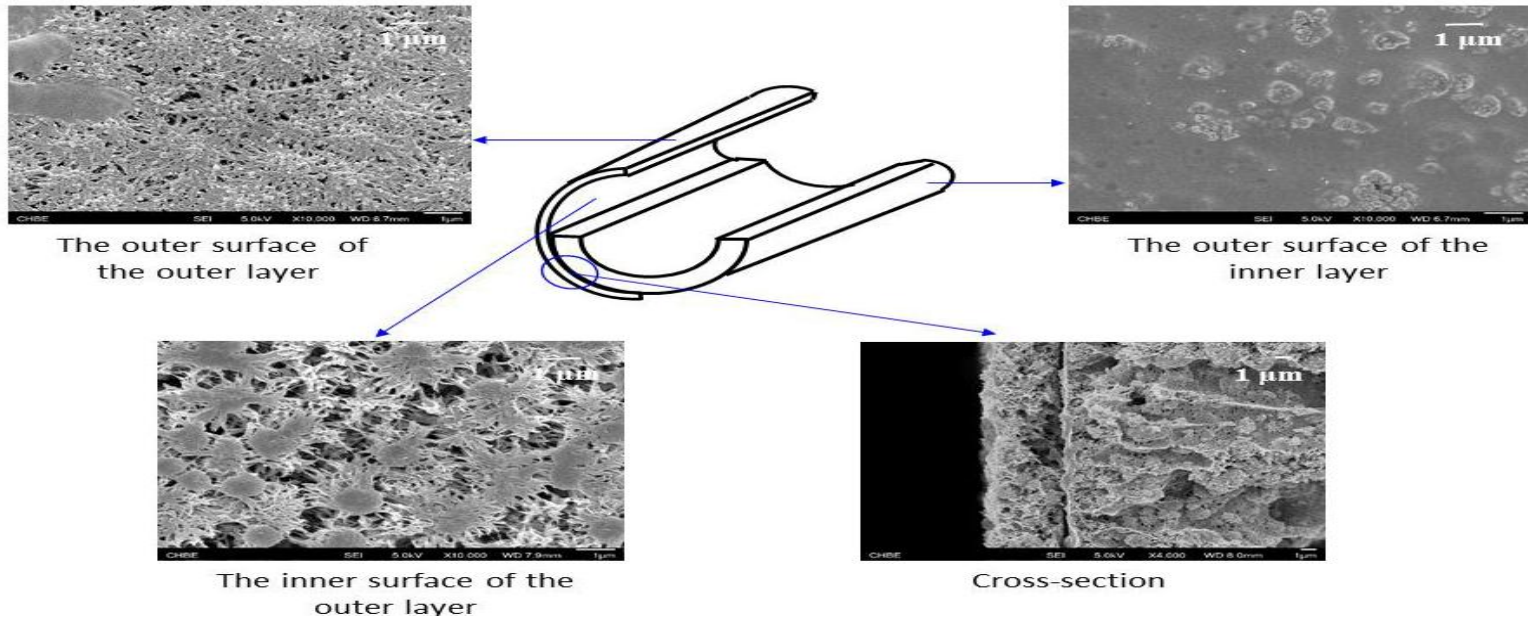
Goal: To fabricate flat and hollow fiber membranes for a MD, FO and NF application.

Dry-wet hollow fiber spinning set-up



Membrane Fabrication – For MD application

Goal: PVDF/PEI (hydrophobic/hydrophilic) dual hollow fiber membrane with alumina nanoparticles.

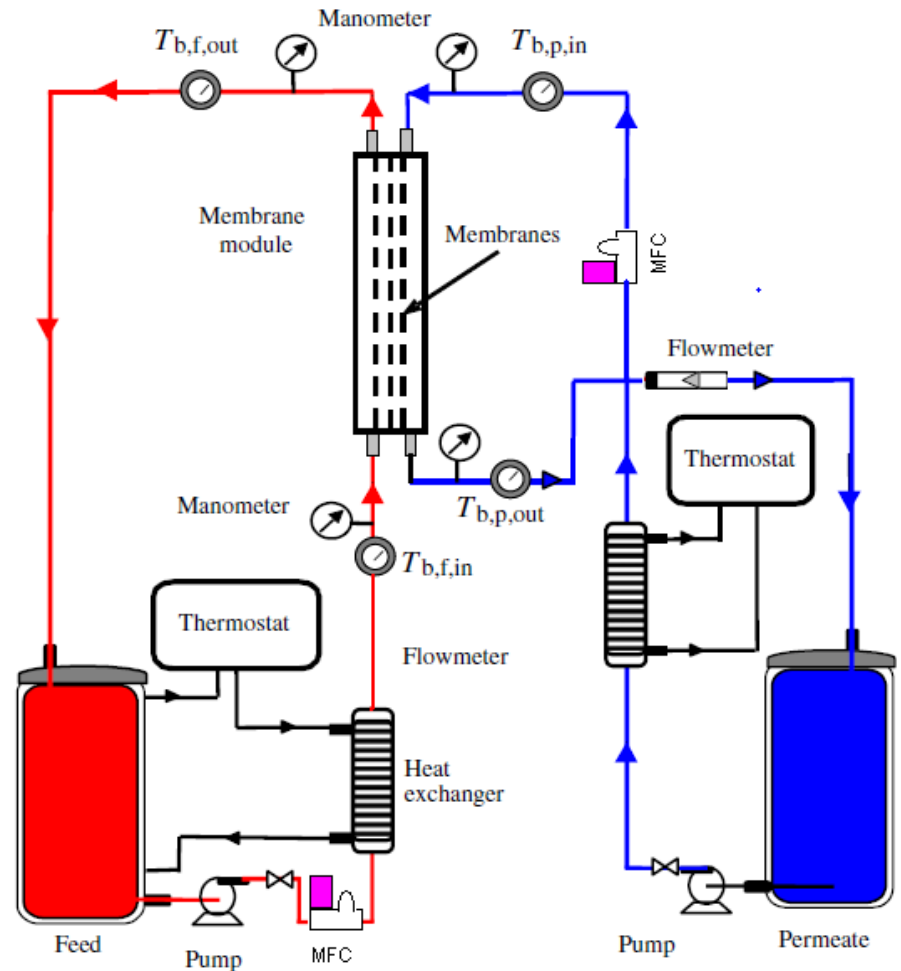
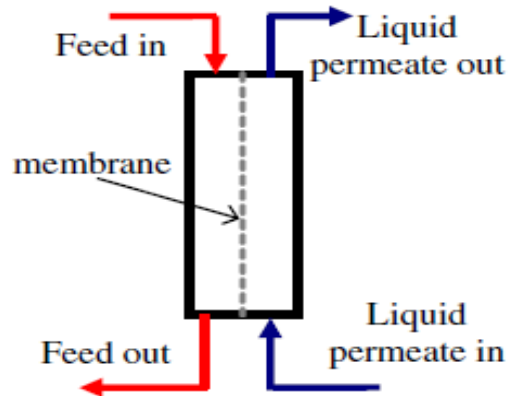


Membrane Fabrication – For FO and NF application

Goal: PES polyelectrolyte layering hollow fiber membrane with GA cross-linking, this creates a positive charge on the inner surface of the membrane that increases the rejection of salts.



Direct Contact Membrane Distillation - DCMD

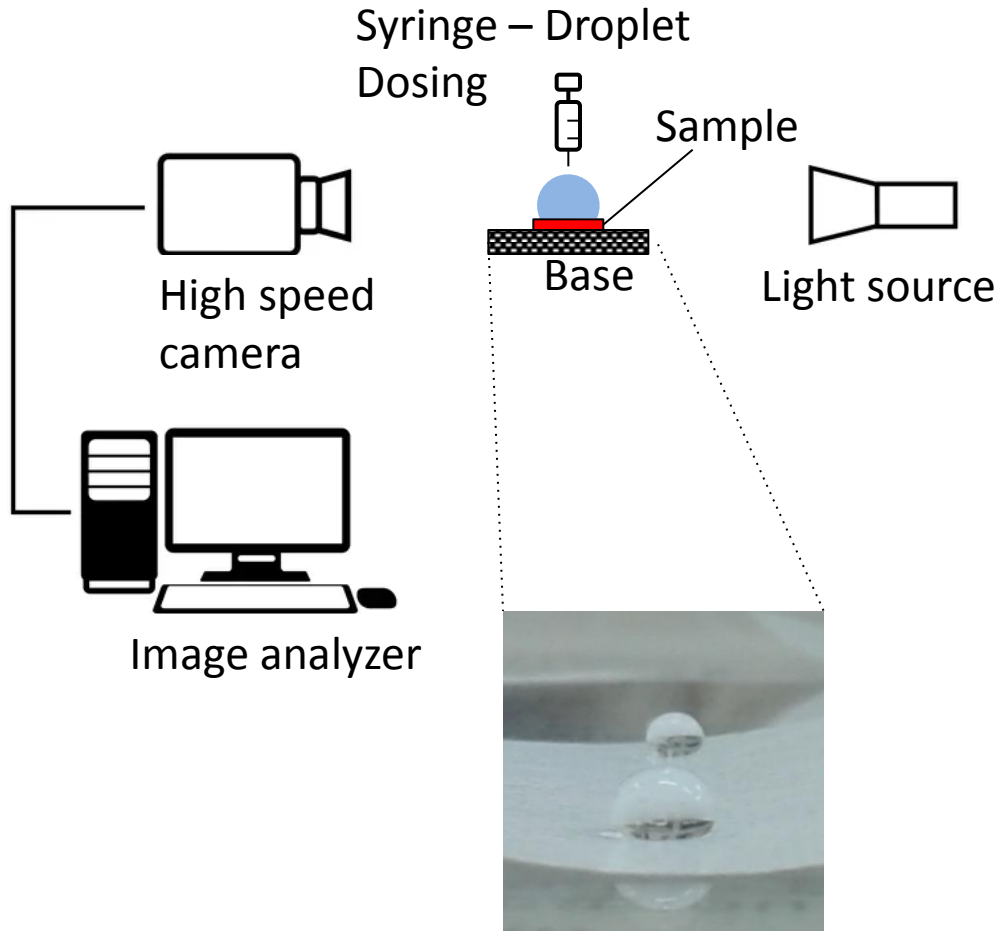


Commercial Membranes tested in the MD system

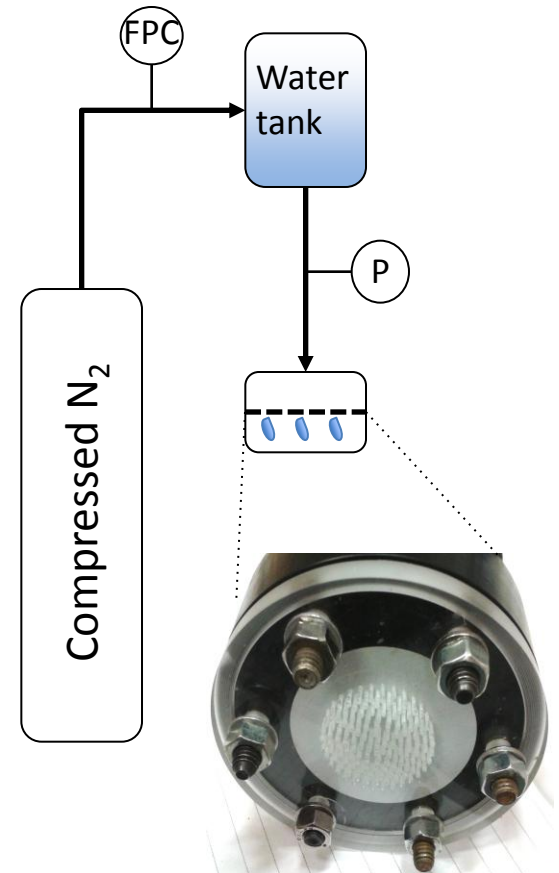
	M1B	M2B	M3L	M4L	M5L
Company	Filtres-Fiorini	Merck	Millipore	Filtres-Fiorini	Whatman
Type	Flat	Flat	Flat	Flat	Flat
Material	PTFE	PVDF	GTTP	NYLON	NYLON
Diameter [mm]	47	47	47	47	47
Pore size [μm]	0,22	0,22	0,2	0,22	0,2
Hydrophobicity	Hydrophobic	Hydrophobic	Hydrophilic	Hydrophilic	Hydrophilic

Characterization of Membranes

Water Contact Angle – WCA



Liquid Entry Pressure – LEP



Results from MD testing

Hydrophobic membranes proved too hydrophobic, no vapour was observed to pass through pores.

Hydrophilic membranes are not suitable for MD, the system resembles a FO operation.

Next plan 1: Membrane modification of surface to decrease hydrophobicity.

Next plan 2: Membrane modification of surface to increase hydrophobicity.

Membrane Modification - Method

Goal: To reduce hydrophobicity of hydrophobic membrane surface.

Step 1:

PTFE flat membranes were immersed for 24 hrs in various PVA solutions: 1 wt%, 0,5 wt% and 0,1 wt%.

Step 2:

Momentarily dipped in ethanol (bad solvent for PVA).

Step 3:

Immersed in GA (glutaraldehyde) solution for cross-linking of PVA for 24 hrs.

Step 4:

Washed with distilled water and dried.

Step 5:

Immersed in distilled water at high temperature ($\sim 65^{\circ}\text{C}$) for 24 hrs.

Step 6:

Stored dry at room temperature.

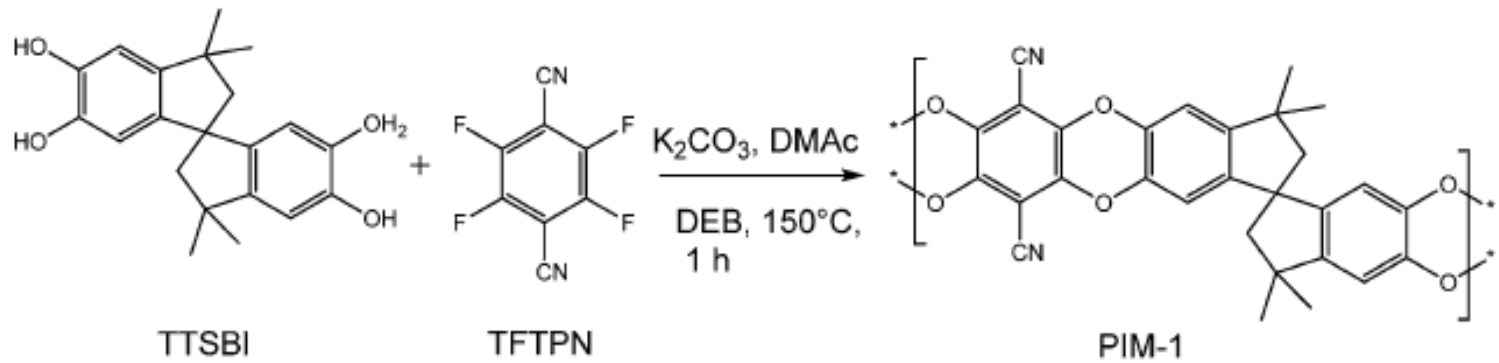
Results from PVA modification

The membrane modified with PVA 0,1% had a decreased contact angle and LEP but remained hydrophobic.

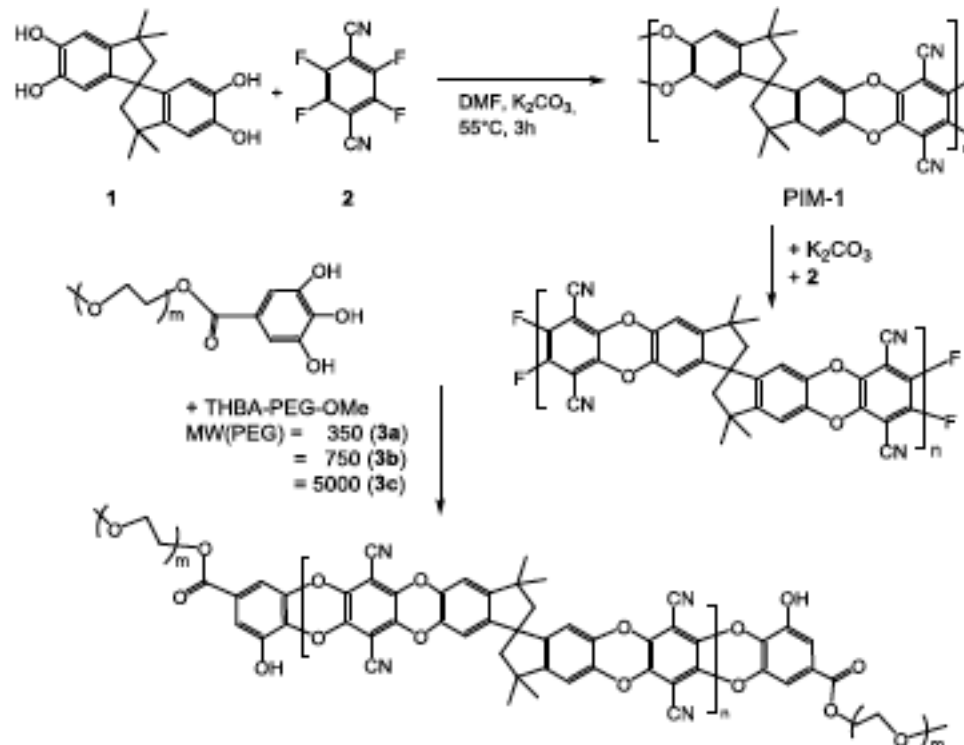
While, the membranes modified with PVA 1% and PVA 0,5% became hydrophilic.

Next step: To coat membranes with PVA solutions of 2% and 0,05% and test the modified membranes' performance in the MD system.

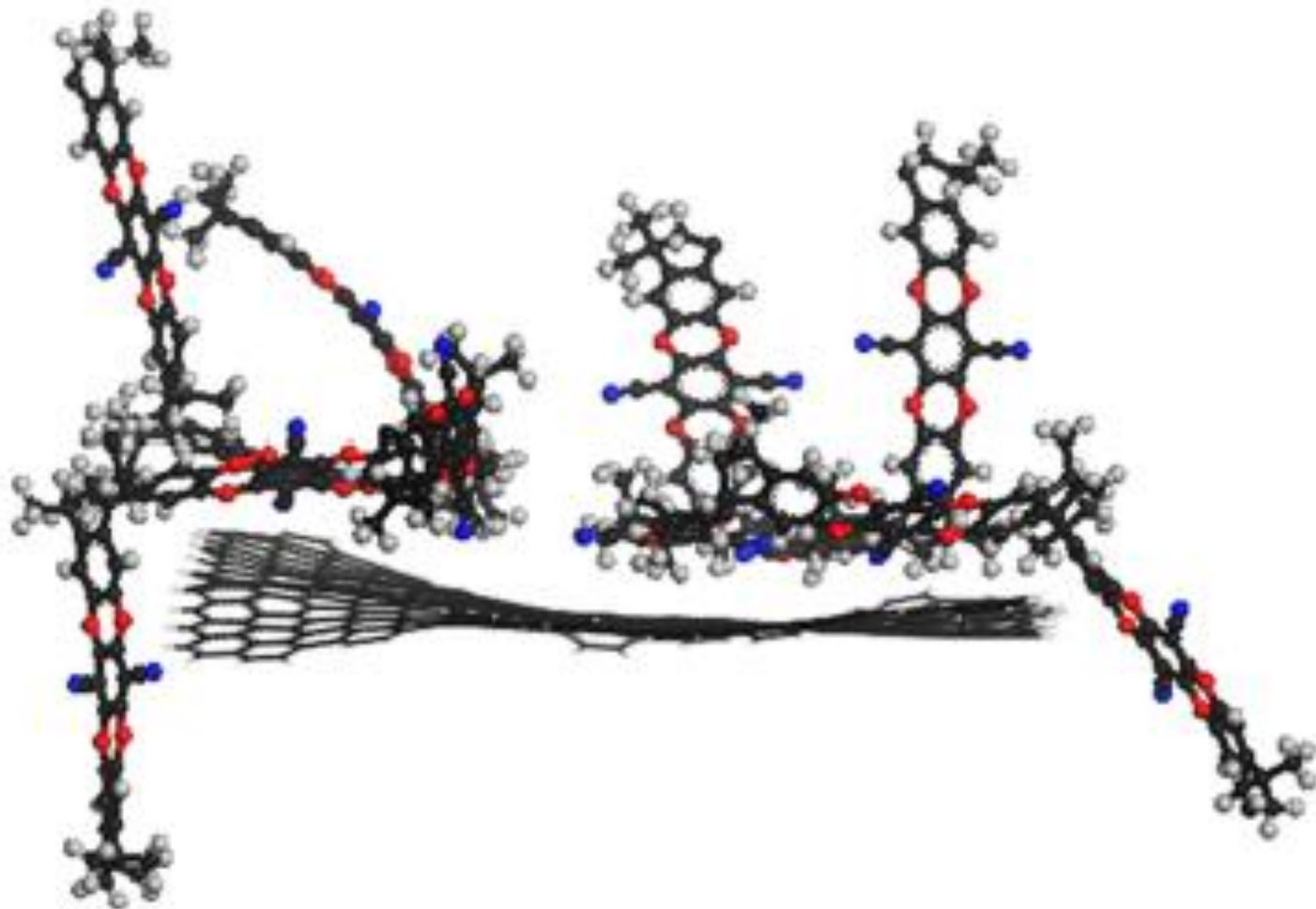
PIM-1



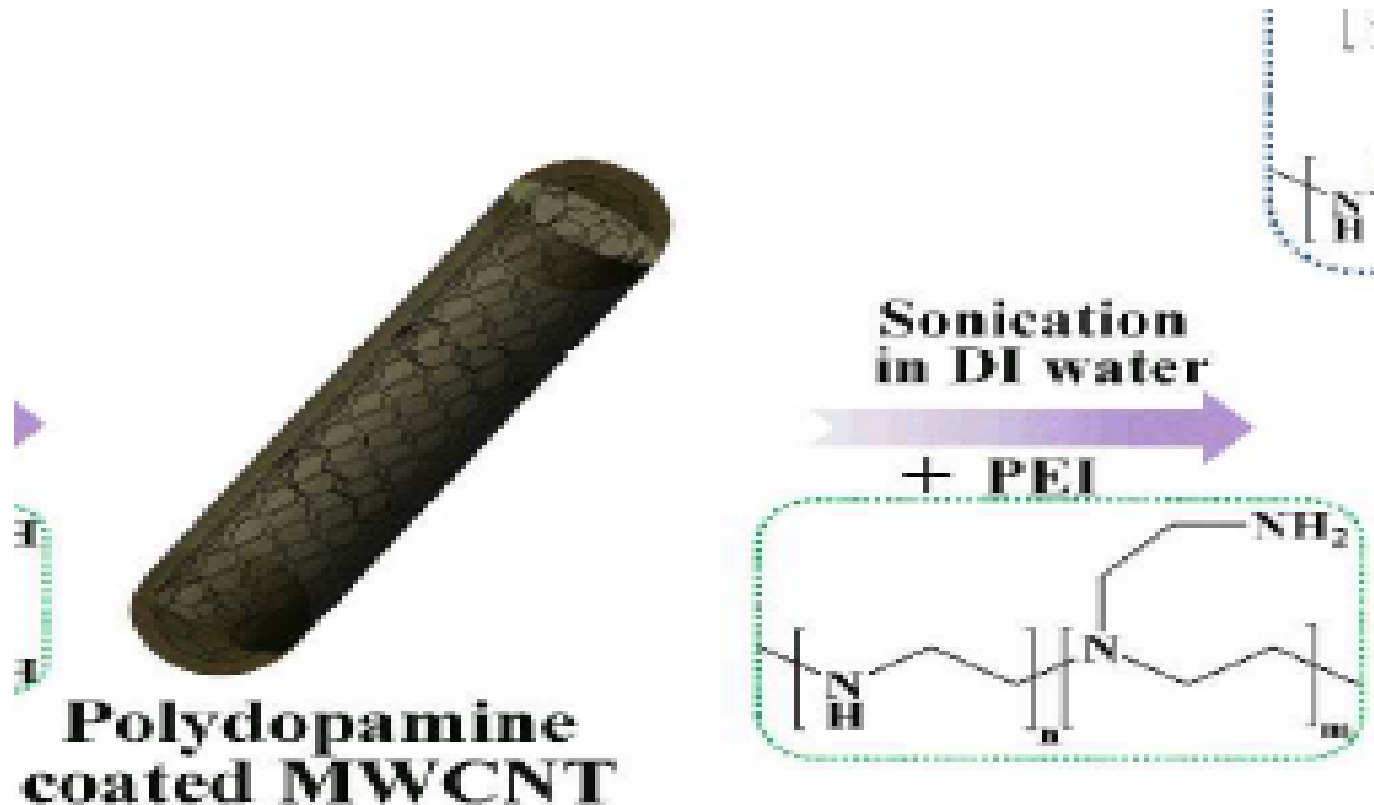
PERVAPORATION OR NANOFILTRATION OR FO?



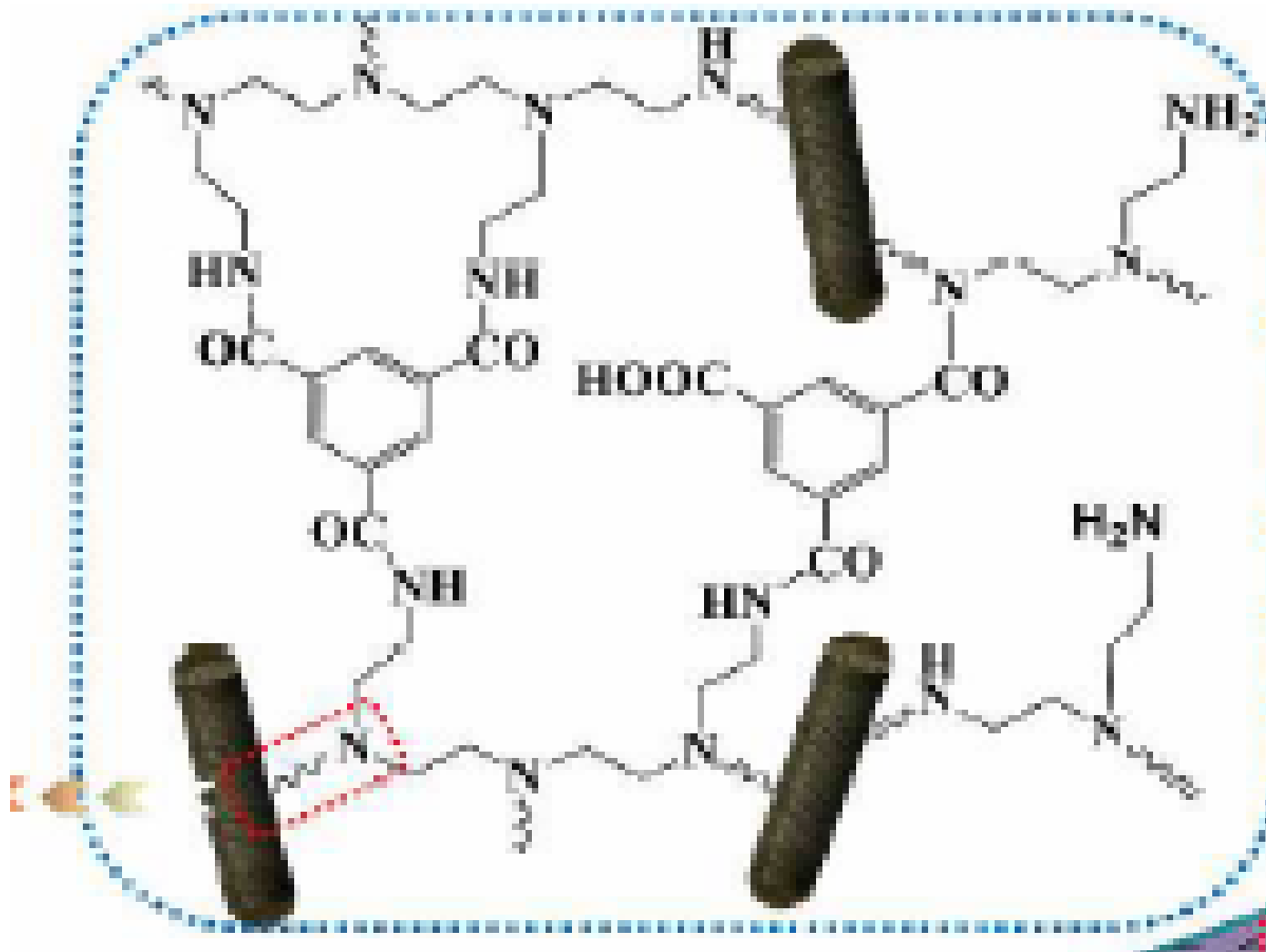
PIM1-GO up scalable PVDF hollow fiber FO membranes



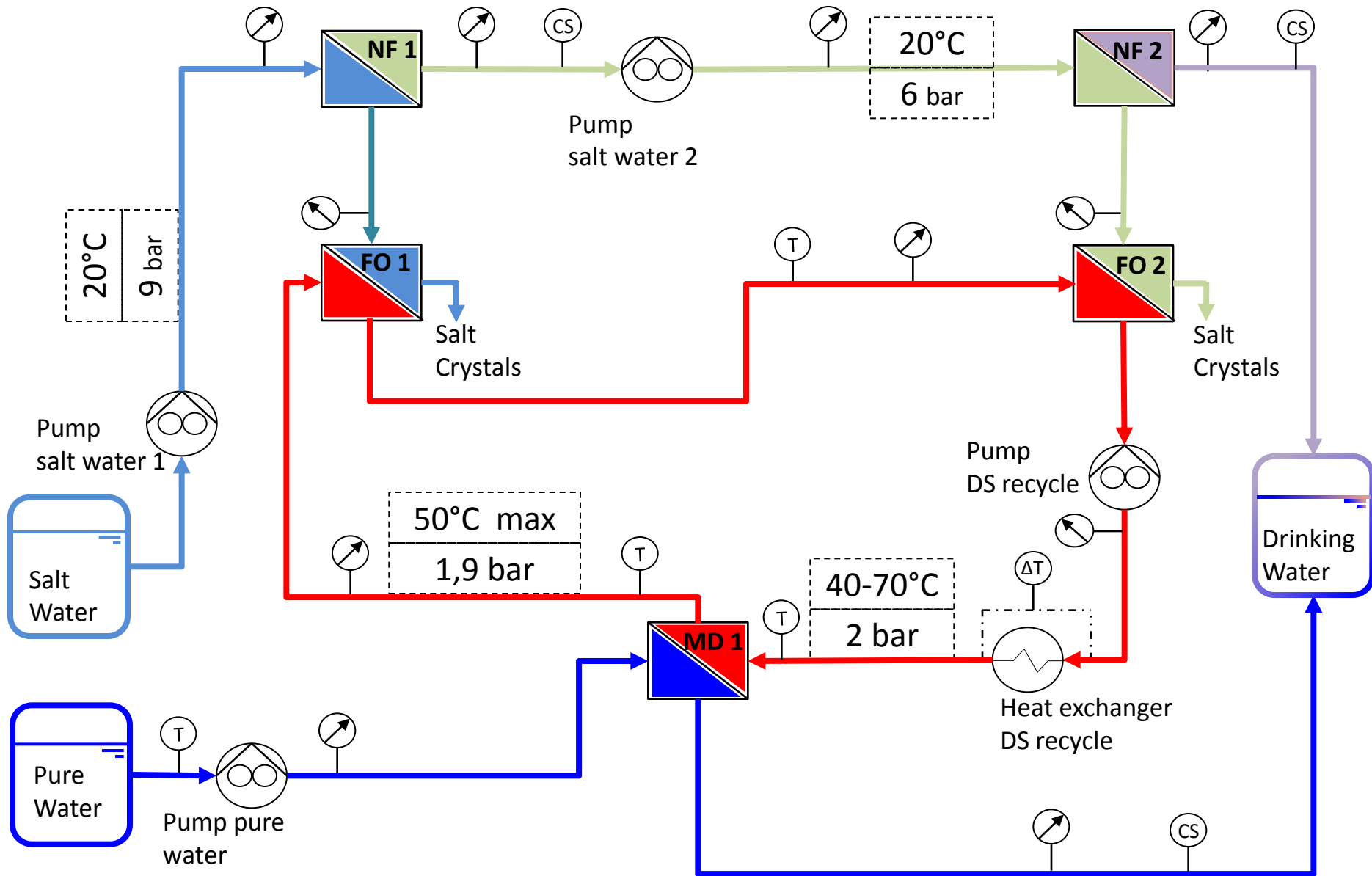
CNT-PEI-TMC hollow fiber FO membrane



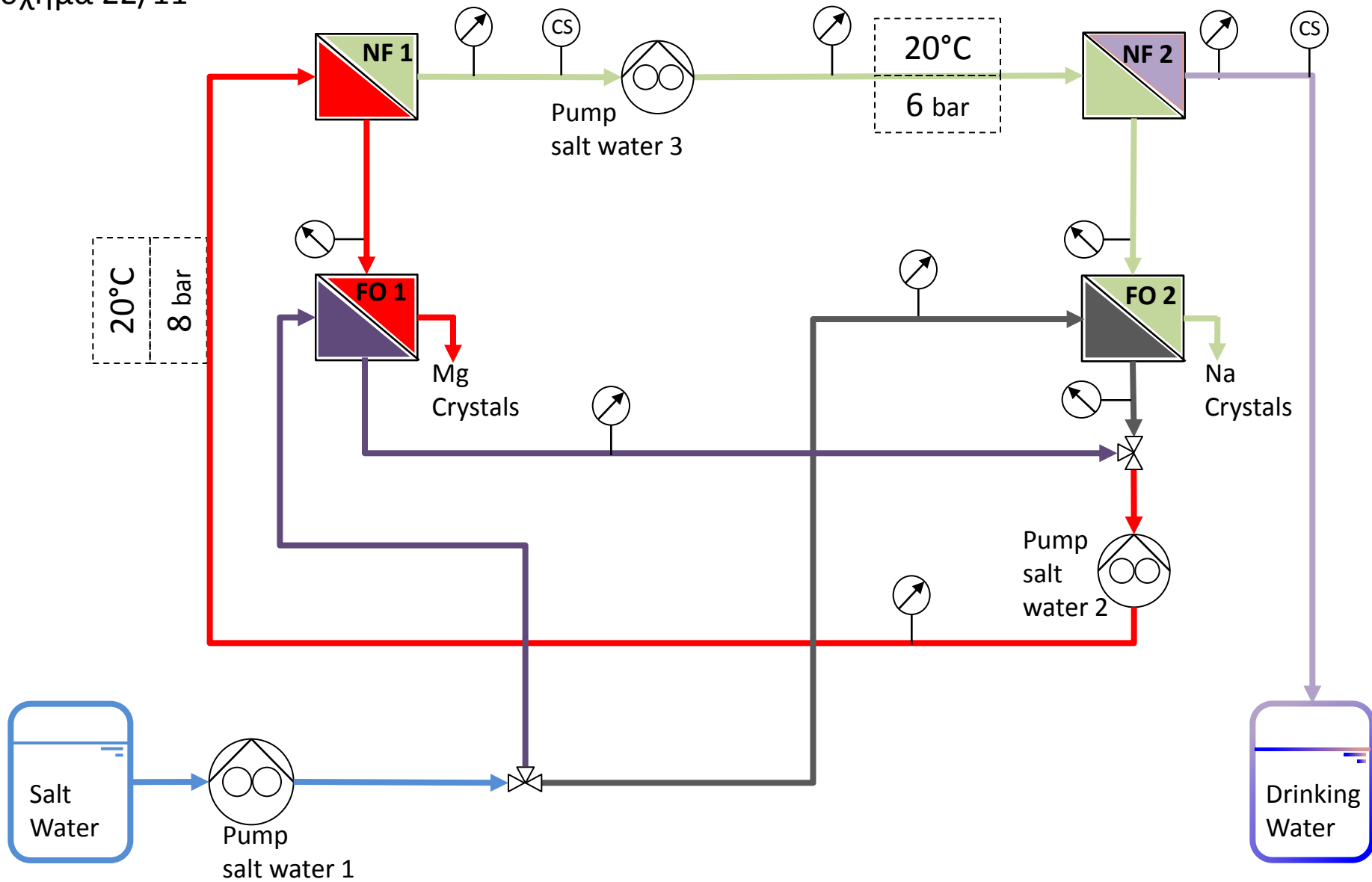
CNT-PEI-TMC hollow fiber FO membrane



Pilot Unit Schematic



σχήμα 22/11



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