Novel Membranes for Water Technologies
"Formation of Aligned Carbon Nanotubes (CNTs) with Tailored Physical and Chemical Properties"

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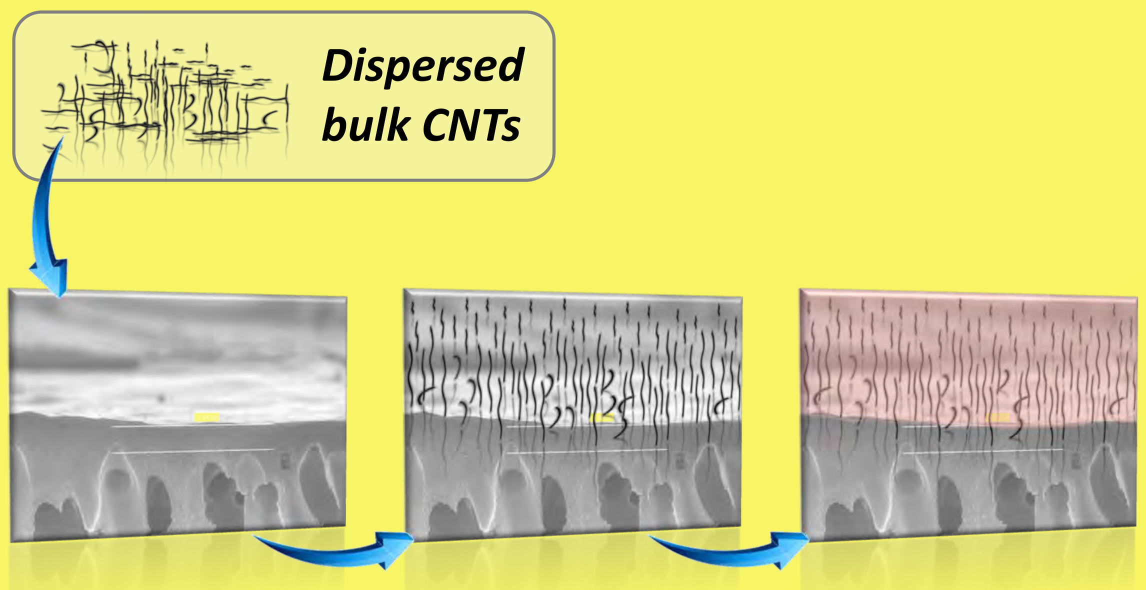
SEVENTH FRAMEWORK PROGRAMME

INTRODUCTION

The low quantities of fresh water worldwide for industrial, agricultural and municipal usage need to be well preserved by efficient, sustainable and cost-effective technologies. Membrane Bioreactors (MBR) consist a novel technology in water treatment and in combination with subsequent Nano-filtration (NF) or Reverse Osmosis (RO) membranes are well established preferably in industrial waste water treatment. Nevertheless, the subsequent combination of these 2 steps requires additional technologies resulting in additional costs and maintenance efforts while a major concern is the fouling of the membrane, the reversible and irreversible blocking of pores by colloidal/organic foulants. Thus, a new class of functional low fouling membranes for MBR technology with permeability and flux maintained or even increased and providing high rejection rate of low-molecular weight organic compounds or inorganic salts can be provided by the inclusion of CNTs into porous polymeric membranes, potent to overcome the immanent limitation of counterbalance between flux and selectivity, a challenging issue and the main focus of the EC funded project **BioNexGen**.

OBJECTIVE

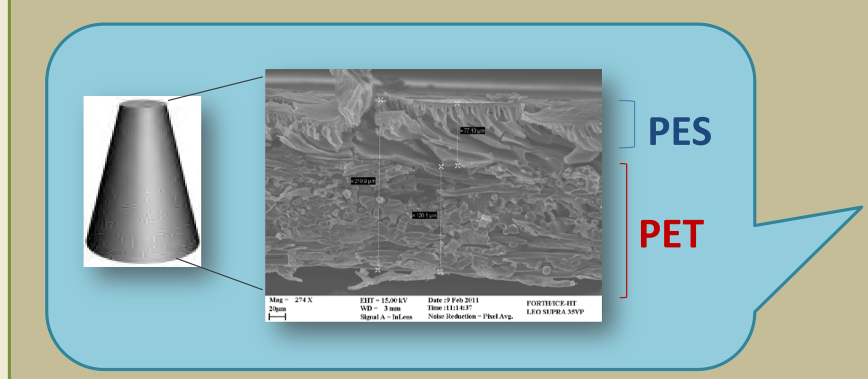
Development of a new class of functional membranes based on the embedment of CNTs in the thin selective layer of Ultra-filtration (UF) membranes using filtration methods, leading to **LOW FOULING MEMBRANES** for **MBR** with **HIGH WATER FLUX** & **HIGH REJECTION** of **low molecular weight** organic matter, potentially applicable to industrial wastewater treatment and reuse.



***Filtering CNT suspensions** through nano-porous membrane*

***Coating of anti-microbial polymeric film** over the vertically embedded CNTs on the membrane surface*

MATERIALS



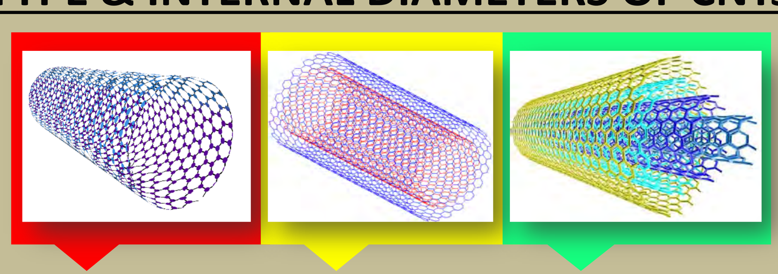
PES/PET NANO-POROUS UF COMMERCIAL MEMBRANES OF CONICAL-SHAPE STRUCTURE
(SEM CROSS SECTION IMAGE)

Properties of CNTs:

- High aspect ratio
- Chemically inert hydrophobic graphitic walls
- Internal diameters of nano-scale range

"Excellent combination for high flow rate[1,2] and high rejection of low molecular weight organic molecules"

TYPE & INTERNAL DIAMETERS OF CNTs

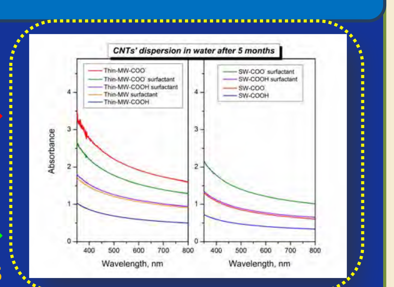


Single walled	Double Walled	Thin-Multi walled
0.8-1.4 nm	2.0-3.0 nm	1.0-6.5 nm

EXPERIMENTAL

Dispersion of *Thin-MWCNTs* functionalized with *-COOH* groups in H_2O

From left to right: Thin-MWCOO⁻, Thin-MWCOO⁻ (+surfactant), Thin-MWCOOH (+surf.), Thin-MWCOOH, Thin-MW (+surf.).



Dispersion of *SWCNTs* functionalized with *-COOH* groups in H_2O

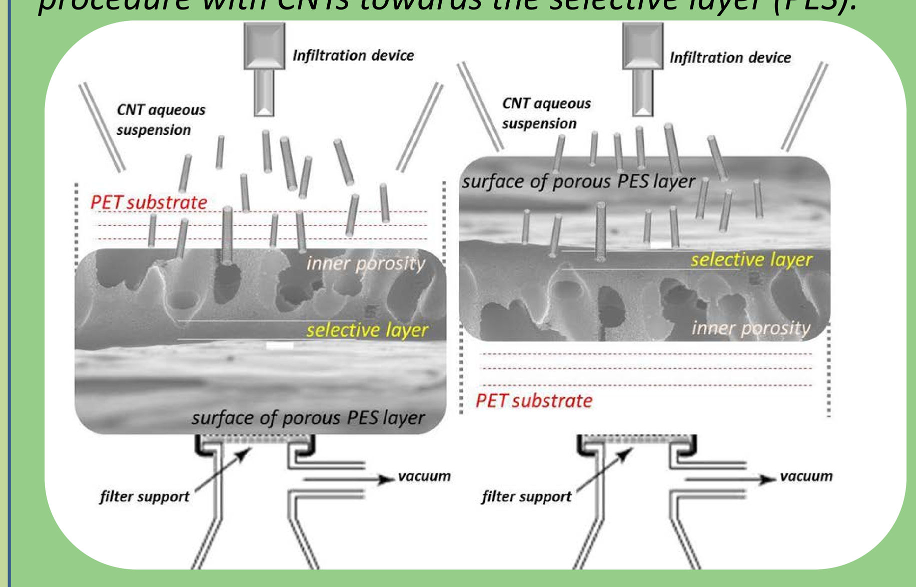
From left to right: SWCOOH (+surf.), SWCOO⁻ (+surf.), SWCOO⁻, SWCOOH.

Properties of CNTs

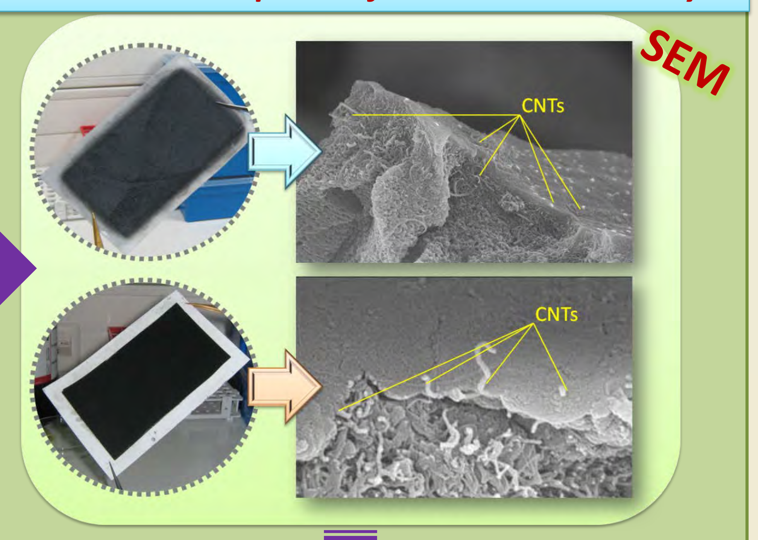
	SWCNT *Cheaptubes	SW-COOH	SW-COO⁻	Thin – MWCNT *Nanothinx	T– MWCNT-COOH	T– MWCNT-COO⁻
Carbon Purity (%)	>90	>90	>90	94	94	94
External Diameter (nm)	1-2	1-2	1-2	6 – 15	6 – 15	6 – 15
Internal Diameter (nm)	0.8 – 1.6	0.8 – 1.6	0.8 – 1.6	1.0 – 6.5	1.0 – 6.5	1.0 – 6.5
Length	5-30μm	≤ 1μm	≤ 1μm	≥ 10μm	≤ 1μm	≤ 1μm

RESULTS

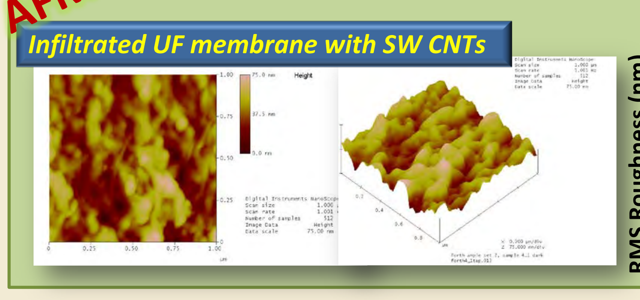
***Left:** Membrane infiltration procedure with CNTs from the support layer (PET side) and **Right:** Membrane infiltration procedure with CNTs towards the selective layer (PES).*

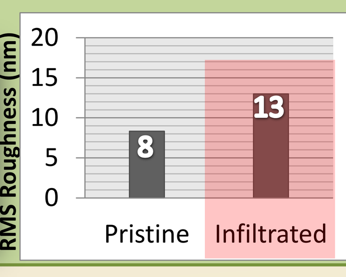


CNTs' intrusion into the pores of the PES selective layer

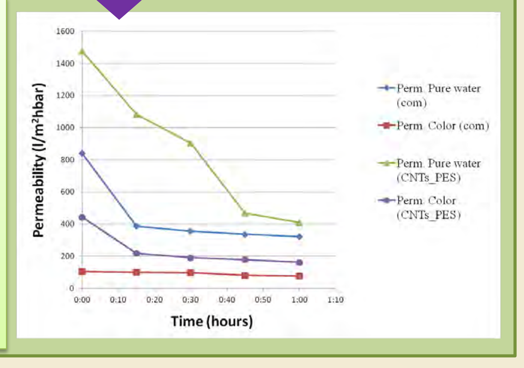


Infiltrated UF membrane with SW CNTs

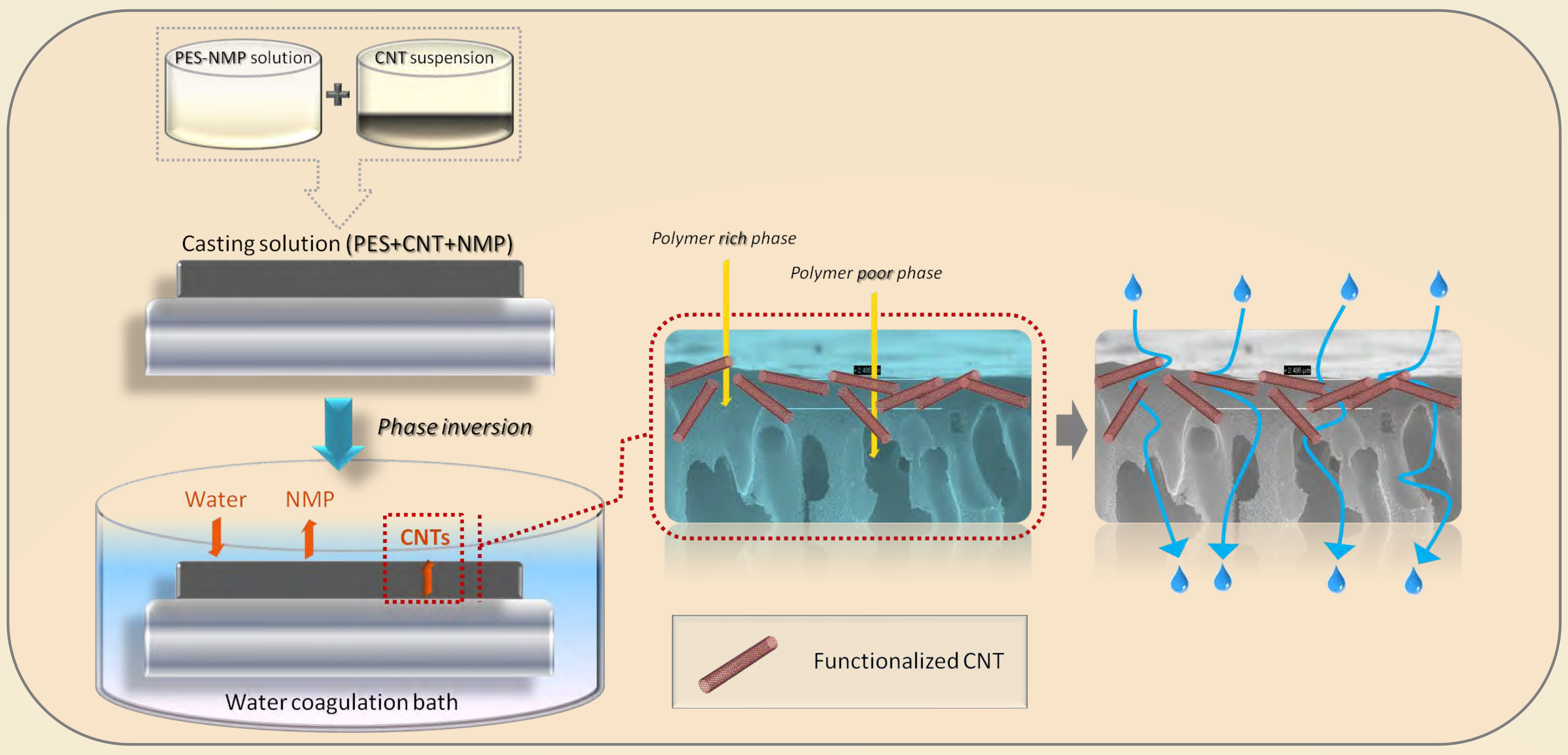




Modified membranes' characterization regarding the permeability of pure water and the permeability of a low molecular weight model organic colored foulant

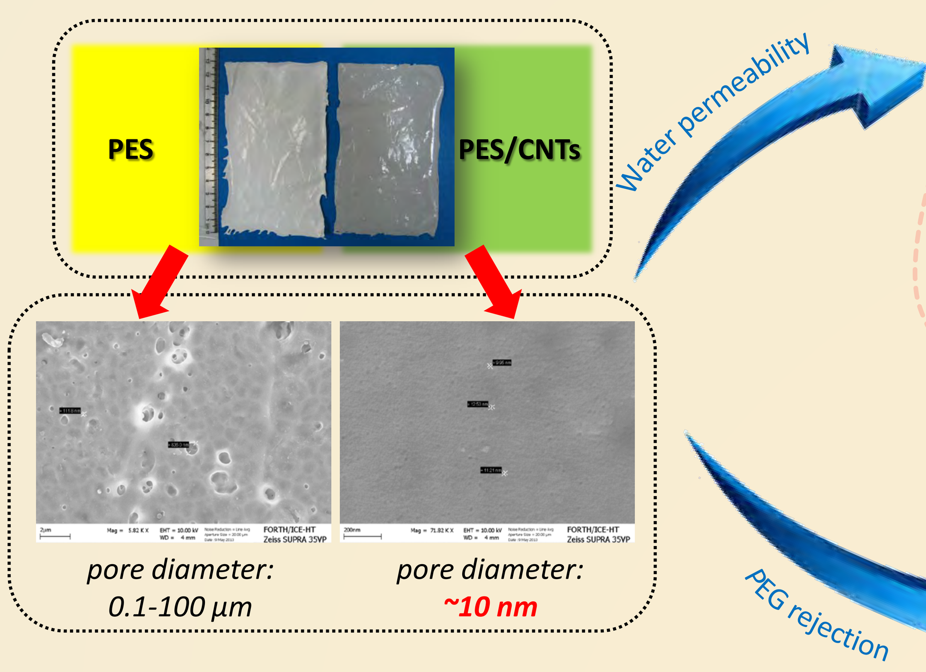


2nd APPROACH: MIXED MATRIX MEMBRANES



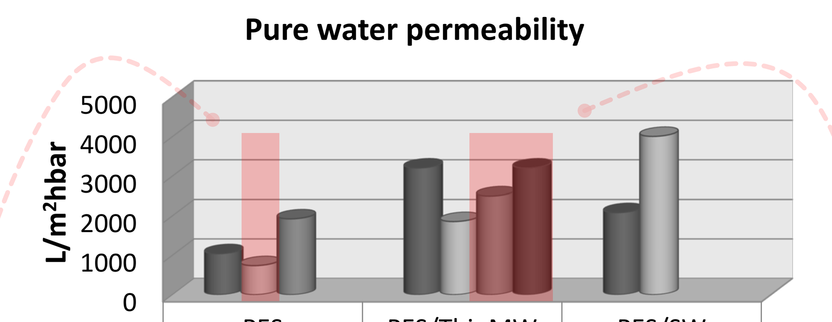
RESULTS

Membrane Morphology

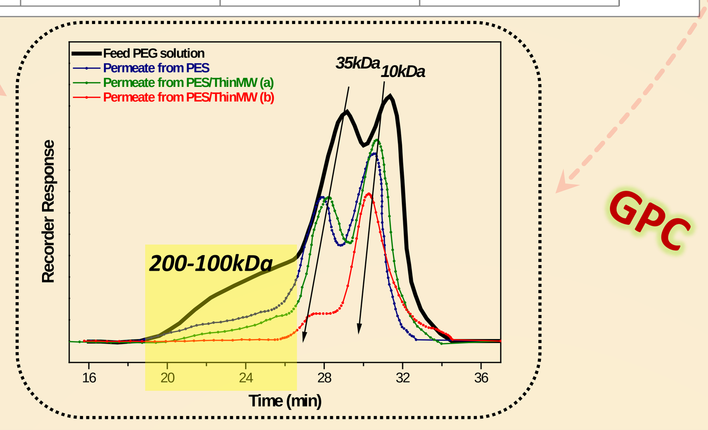


pore diameter: 0.1-100 μm

pore diameter: ~10 nm



	PES	PES/ThinMW	PES/SW
MN 1	1041	3205	2082
MN 2	737	1855	4006
MN 3	1923	2500	
MN 4		3205	



CONCLUSIONS

The embedment of CNTs into the anisotropic, porous polymeric membranes was achieved using a filtration unit while a specific infiltration device was used for two reasons: first to maintain CNTs well dispersed in the aqueous suspensions and second -and parallel to the use of vacuum- to shove, align and direct CNTs towards to the membrane pores .

A number of parameters were studied regarding the infiltration process and CNTs' suspension concentration resulting in development of certain infiltration protocols.

The conversion of an ultra-filtration membrane to a nano-filtration one by the embedment of CNTs in the thin selective layer is not an easy task. There are many challenges that must be addressed, although innovative filtration methods have been developed. SERS can be proved as a valuable tool for the quantitative assessment of foulants and/or CNTs in aqueous solutions even at a very low concentration range.

Other approaches regarding the incorporation of CNTs into porous PES membranes are being studied. Synthesis of composed, anisotropic, porous membranes with CNTs is investigated and fruitful results lead to comparative study.

Surface Enhanced Raman Scattering (SERS) proves to be a powerful method to use in the detection and quantification of CNTs in aqueous suspensions at notably low concentrations for any eventual release from CNT-modified membranes.

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