Overview on nanotechnology and membranes For water applications

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CEO European Membrane House (a.i.s.b.l.)
Deputy-Director SIMEV (a UNESCO chair of the UNESCO water family partnership)

- EMH is a non-profit association (a.i.s.b.l.) aimed at enhancing industrial implementation of membrane-based technologies (Registr. 2008 / Start 2009)

- Background:

2008: Partners' will for sustainable structure

EMH European Membrane House

- European Network of Excellence on nanoscale-based membrane technologies (NMP – FP6 October 2004 / March 2009)

- IEM (Institut Européen des membranes) : a mixed unit of the CNRS and of the University of Montpellier (France)

- See : www.euromemhouse.com See : www.iemm.univ-montp2.fr

- UNESCO Chair SIMEV : a member of the UNESCO family partnership on water
  See : www.chaireunescosimev.euromemhouse.com

Chaire UNESCO SIMEV

Plan of the presentation

1. **You've said membrane technologies ?**

   A few reminders….

2. **Nanotechnology and membrane materials**

   The need for a correct understanding …

3. **What benefits for water treatment ?**

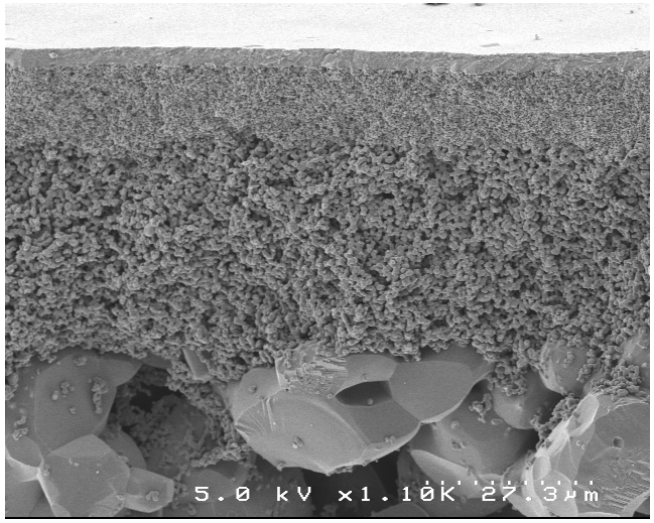
   Applications and future trends : a few examples

4. **Nanoscale based technologies and safety…**

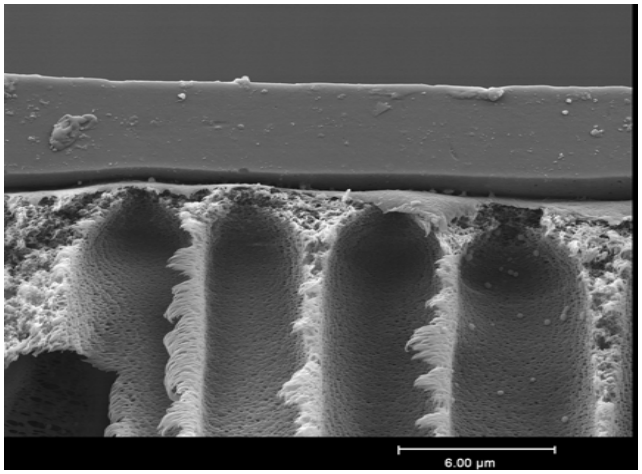
   A few remarks and proposals

1. You've said membrane technologies ?

- ***Artificial membrane materials : 2 examples***



Alumina / Support (10 µm) + 2 intermediate layers (0.8 & 0.2 µm) + separation layer (5 nm)



PVDF support with polymeric top layer material

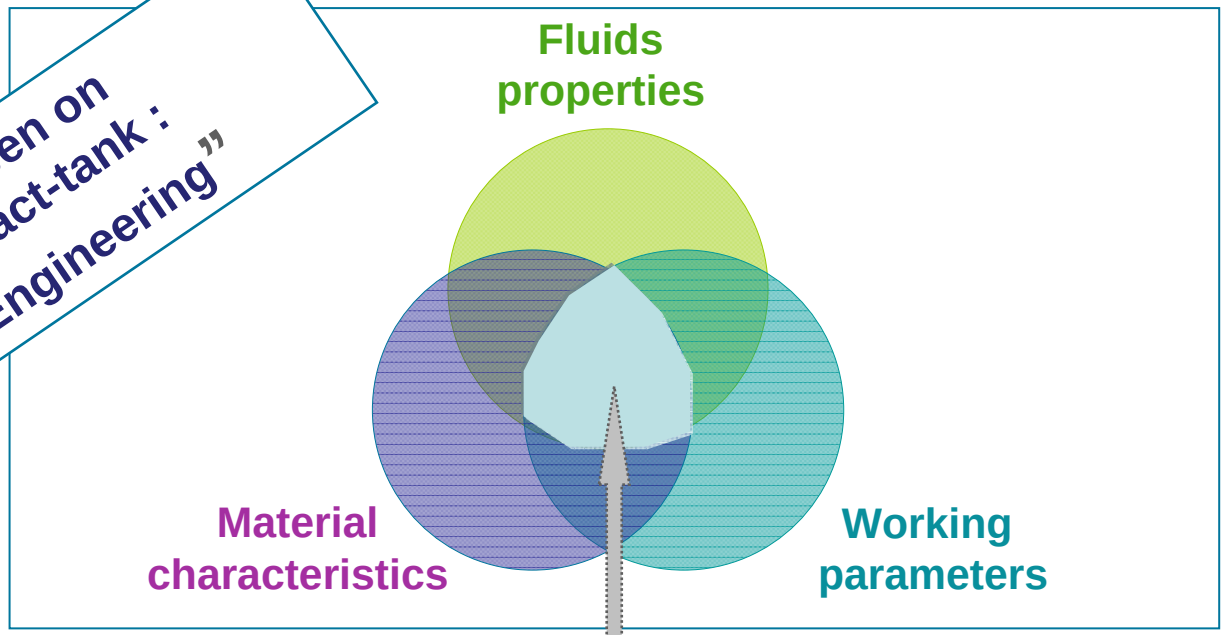
Architecture

Function

Gas or liquid separations

- ***A think-tank to develop around the "holy triptych"***

… so as to open on an improved act-tank : "Membrane Engineering"



➔Trying to integrate the data at all the scales in order to get an optimized "membrane function"

➔ The need to make the most of modeling to reach this objective through simulation

- ***A few remarks***

✓ A lot of specific properties and advantages : compactness, modularity, microstructures, improved functionalities, easy control and also in most case isothermal operations, with nearly no requirement for chemical additives…

✓A lot of possible functions to develop with thin layers : mass transfer, chemical reaction, fluid distribution or even energy transfer , information…

✓ "…membrane : the ultimate achievement for sustainable development and preservation of life…"

E. Sackmann in Handbook of biological physics
"Biological membranes . Architecture and function" - Elsevier 1995

- ***How to work correctly ?***

✓

✓ -level controlled properties : a really bright future …when needed !

…or even to manage together !

✓Improved operating modes, new original hybrid processes and set up of more holistic approaches better integrating experiments and modelling with a view to save time and money !

- ***When the material is responsible for the limiting step …***

=> The need to improve material characteristics in order to improve the overall performance

- "preparing a new material and asking after : what we can do with it?"

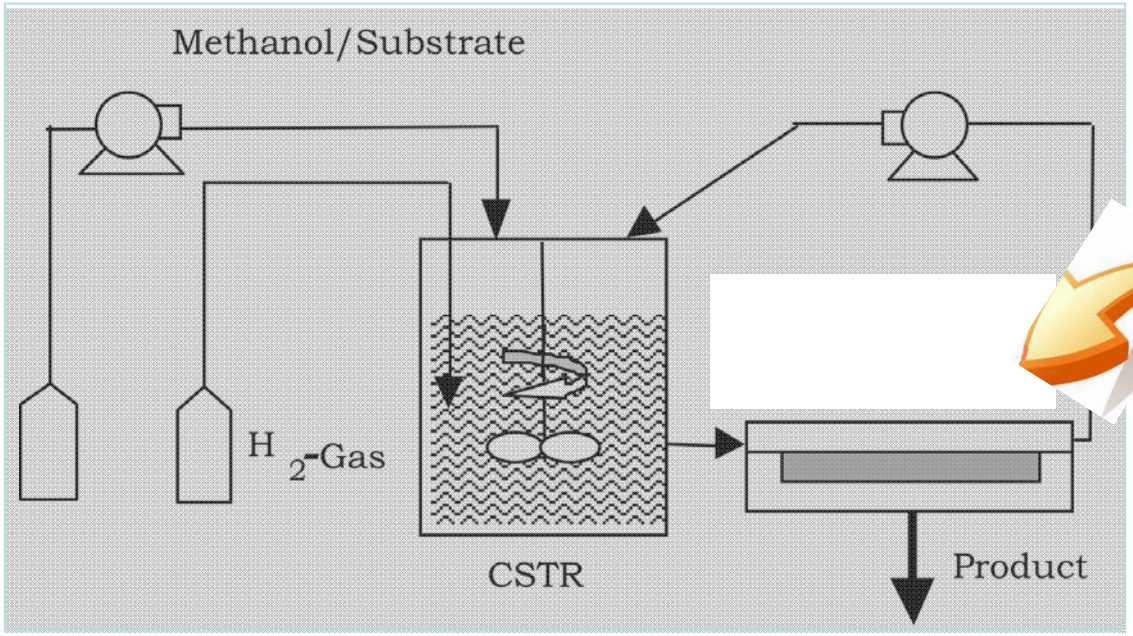
- With this prospect, much to expect from the implementation of nanotechnology to improve the materials, or to create new nanostructures adapted to the objectives which are focused : pore size, surface properties, new engineering concepts…

=> Two relevant examples

- ***NF for homogeneous catalysis***

  => Towards new membrane reaction technologies

- Preserving easy removal of catalyst after reaction and continuous operation mode
- Preventing high preparative effort and sometimes mass / heat transfer limitations
- Leading to higher chemo- and enantio-selectivity.



⇒ New solvent resistant NF membranes / MWCO 200-700 Daltons / nanopores (IUPAC)

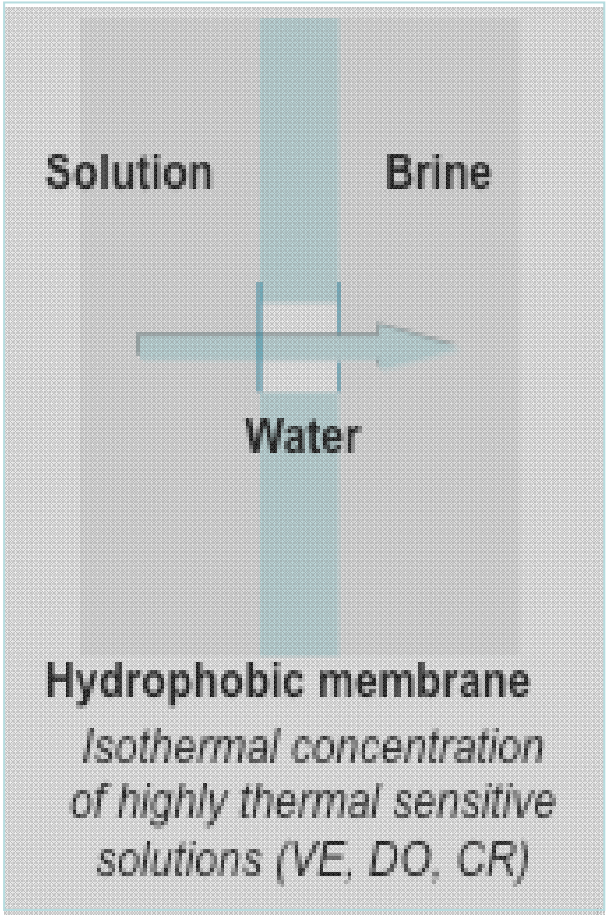
⇒ Chiral catalysis / Enantioselective hydrogenation

- ***Surface nanostructuration of UF / MF materials***

=> Towards new routes for crystallization

their saturation limit => a metastable state (supersaturation) => crystals may nucleate and grow.

-The membrane material : not simply a support for solvent evaporation => decreases also the work required to create critical nuclei / changes locally the probability of heterogeneous nucleation with respect to other locations in the system => importance of the surface nanostructure (contact angle)



3 . What benefits for water treatment ?

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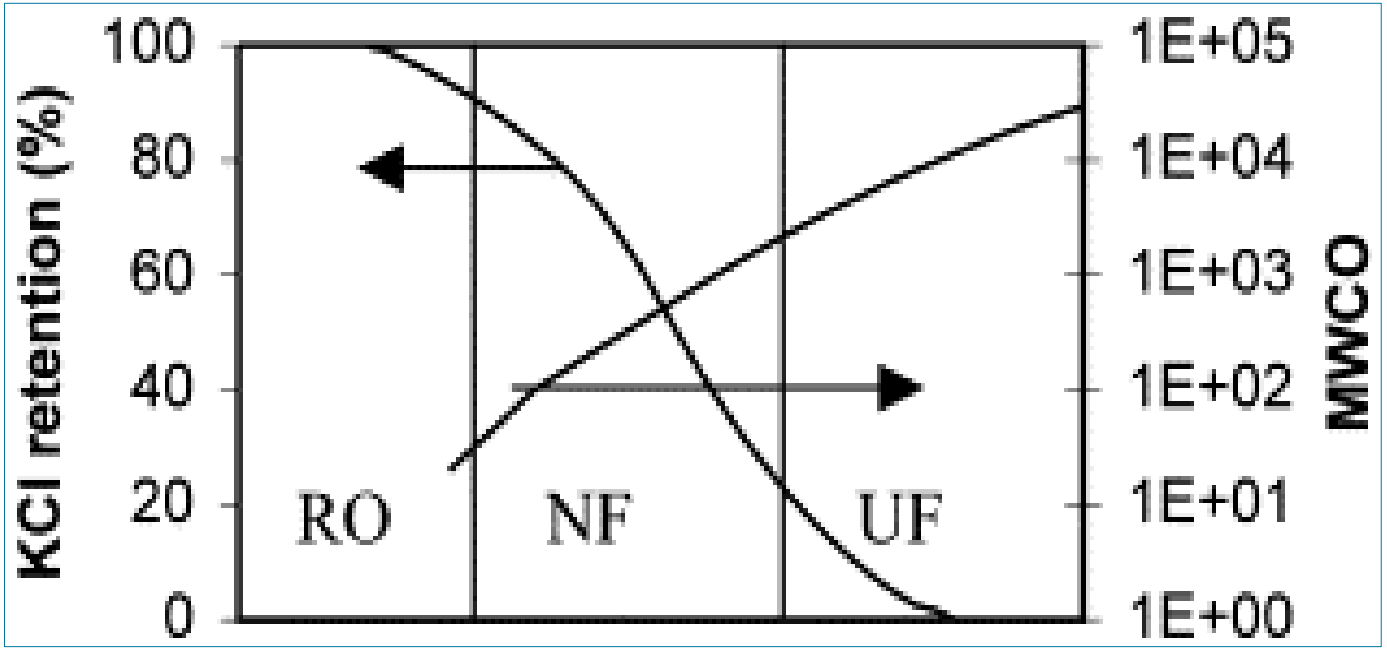
⇨ **A technology which allows the removal from water of :**

differences in diffusion rates (RO).

- ions (mainly multivalent) by electric charge effect



⇨ **During the last decade main breakthroughs and ambitious projects with NF for improving drinking water quality**

– *Hardness* : for softening process, in competition with traditional ion exchange systems or lime softening (regeneration, sludge and wastes)

Typical NF rejections : 70 to 90%

– *Natural organic material (NOM)* : today various membranes with MWCO below 500

Major part of humic and fulvic acids

– *Micro pollutants* : pesticides and organohalide compounds having very negative effects (carcinogenic…). In competition with activated carbon adsorption, a very expensive method with large fractions of NOM (competition, regeneration…)

Very good TR

⇨

– *Abatement of fluoride :* elimination of excess F^- (Senegalese water from the endemic region of Fatick as an example…)

– *Separation of arsenic , lead, aluminium and uranium :*

As (V) and As (III) < 10 mg/l in France. In a lot of countries > 50 mg/l ! (Bengladesh, India, China… and even USA.)

More adapted than ion exchange, adsorption or biological treatment for large water production in rural countries

– *Treatment of wastewaters containing dispersed oils and suspended particles :*

"Produced waters" (PWs) : the largest waste stream from oil and gas exploration! Also in food and metal production….

– *New integrated operations :*

NF for MBR (micropollutants and POPs), NF+ED (amino-acid separation/recovery)…

- ***Photocatalytic water treatment technology***

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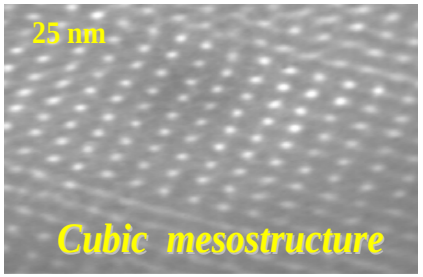
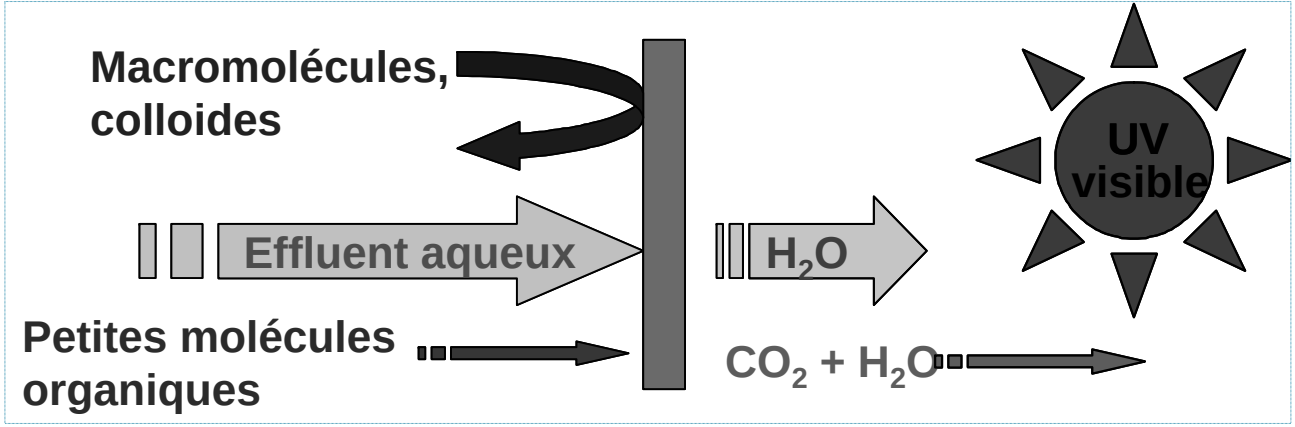
A very promising tool : => Membranes

The photocatalytic membrane reactor => Engineering



Ordered mesoporous TiO_2 membrane for coupled separation and photodegradation

New materials produced by sol-gel

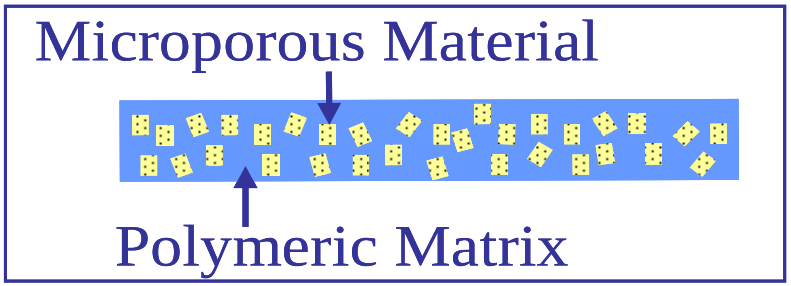


Water treatment / VOCs separation-degradation treatment

Low UF membrane material
Colloîd rejection / Low MW molecules (such as VOCs) non retained
Photodegradation on the right side of the membrane

⇨ What are MMs ?

- Hybrid membranes consisting of nanoparticles imbedded into polymeric matrix. Different new concepts under investigation.



- Much higher selectivity than polymeric membranes
- Zeolites, carbon molecular sieves or other porous particles
- With non-porous fillers, selectivity is linked to polymer free volume, particle size and surface, covalent bonding…

⇨ **A new RO membrane to reduce the cost of sea-water desalination and waste-water reclamation (Eric Hoek - University of California)**

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=> a 25% reduction of the overall cost of desalination including energy demand and environmental issues

Water production & recycling : a key topic for California
The fifth largest economy in the world !

⇨ **Also the use of block-copolymers…**

– A new kind of nano-membrane at the University at Buffalo (Javid Rzavev) : for an age-old public health problem => how to separate bacteria from drinking water ?

– Pores that are about 55 nm in diameter : large enough for water to slip through easily, but too small for bacteria.

– The largest pore-size obtained to date with block copolymers, and special properties of evenly spaced holes

Nanoletters, 31 January 2011, 11 (3) pp.998-1001

=> cost and time savings
=> safety insurance

(Such as against emerging health risk s : see those recently mentioned with amoebae and the bacteria they carry, through inhalation of aerosol droplets *Legionella or Mycobacterium*
Environmental Science& Technology 45(3) pp. 860 – 869

⇨ **New original materials and promising operations…..**

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+ well-performing flat-sheet FO modules + development of draw solutions : high osmotic pressure , low energy for …. : => previous slide "materials and process aspects "!

– "Nanoporous polyethersulfone (PES) membrane with enhanced flux applied for forward osmosis process"

J.Memb. Sci. 375 (2011) 63-68 South Korea

⇨ **But also new important engineering concept s….**

–

Membrane technology August 2007, p.8

– In its bulk liquid form, water is a disordered medium that flows very readily. When most substances are compressed into a solid, their density increases. But water is different. When it becomes ice, it becomes less dense.

=> when water is compressed (as an example in a nanometer sized channel), liquid properties are maintained and not akin to a solid.
=> In a nanometer-sized channel, fluid organized into layers !

⇨

http://www.nanoh2o.com/newsDetail.php5?newsID=68

Veolia and NanoH2O to Partner (Water Desalination Report) - November 10, 2009

Veolia Water Solutions & Technologies has entered a five-year partnership with California's NanoH2O to jointly explore opportunities for a new, higher flux SWRO membrane product. Under the agreement, which is best characterized as a technology partnership, NanoH2O will supply its 8-inch diameter nanocomposite seawater elements to Veolia Water Solutions for use in SWRO projects.

….

Nielsen told *WDR*, "We're always looking for the newest and greatest technology to maintain a leadership position in the market, and we think their technology has a lot to offer..."

…..

NanoH2O chief executive Jeff Green said the membranes are a true composite membrane – not a coating – where porous, inorganic and hydrophilic nanoparticles are encapsulated within a polyamide membrane film. "We have shown we can get a salt rejection greater than 99.7 percent while operating our nanocomposite membranes at a flux of at least 30 gfd [50 Lmh].

…..

Nielsen likes the fact that the elements are directly interchangeable with those in existing installations. "Best of all, they are competitively priced with conventional elements," he said. NanoH2O is currently completing construction of its own membrane manufacturing facility. …..

- ***Today a lot of enthusiasm with the topic….***

⇒ **Recent books …**

- Handbook of membrane separations – Ed. A.K Pabby, S.S.H Rizvi and A.M.Sastre - Taylor and Francis Group – 2009
- NanoMaterials for the Energy and the Environment – Ed. G.M.Rios, G.Centi and N.Kanellopoulos – Pan Stanford Publishing - 2011

⇒ **Workshops & Congresses…**

- Zurich – January 2011 – Nano Observatory
  => NMS and NEM concepts…
- Nano and Water 2011 – IWA – Asconia - May 15-18
- Membranes and nanotechnologies – Montpellier – June 6, 2011….

⇒ **EU projects…**

- Nano4water cluster ….
- Nanoforum.org…..

⇒ **A very recent article about nanoparticles and membranes….**

Environmental Pollution 158 (2010) 2335–2349

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Review

The use of nanoparticles in polymeric and ceramic membrane structures: Review of manufacturing procedures and performance improvement for water treatment

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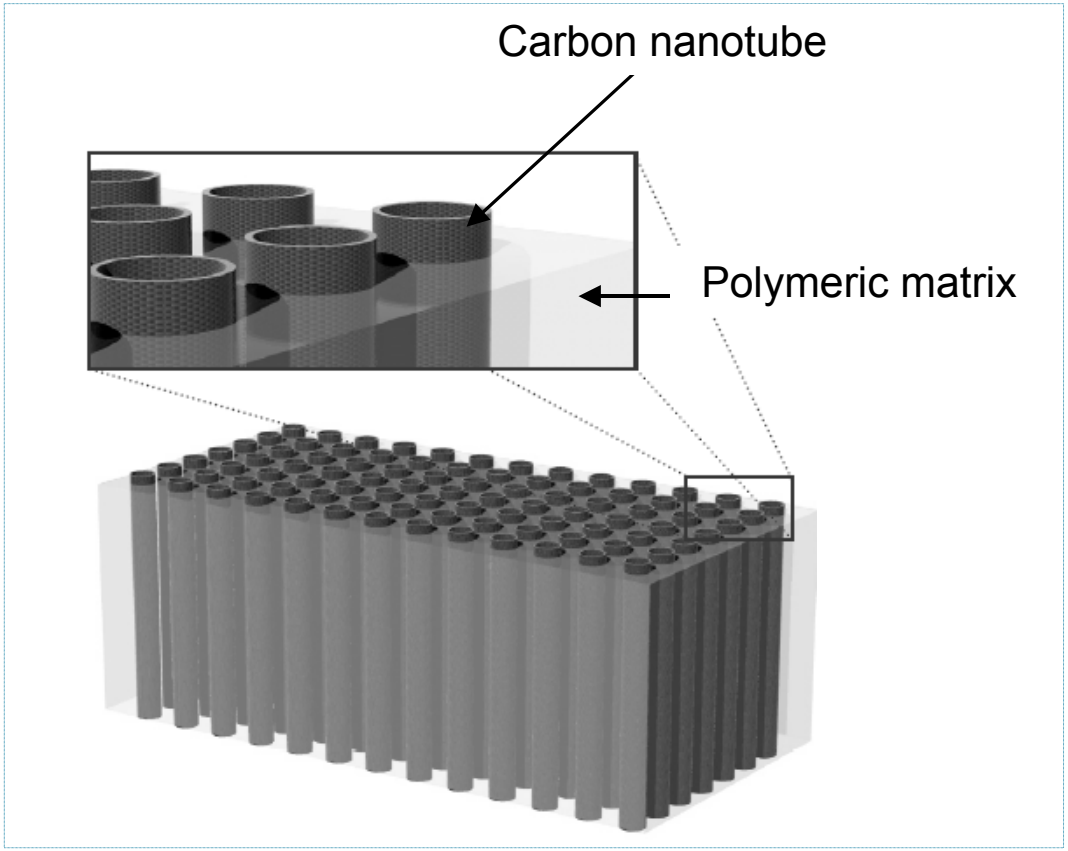
Nanoparticles show a great potential for application in polymeric and ceramic membrane structures, in view of fouling mitigation and catalytic breakdown processes.

- Use of carbon nanotubes, silver, TiO2, block-polymers….

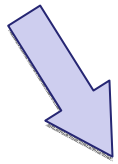


- For high flux, disinfection, photo-catalytic properties, antifouling behavior… and even responsive membranes mimicking nature….

- ***But also the need to pay close attention to securities issues !***

⇒ **NanoMemPro (2004-2009 / FP6 / NoE)**

Nanoscale-based membrane technologies



Nano structured membranes/NSM

Nano enhanced membranes/NEM

Meeting Zurich – January 2011
Article to be published on HazMat

ObservatoryNANO

BRIEFING No.13

ENVIRONMENT

SEVENTH FRAMEWORK PROGRAMME

NANOSTRUCTURED MEMBRANES FOR WATER TREATMENT

http://www.observatorynano.eu

Box 1: The term "nano" in nanofiltration

Figure 1 highlights clearly that the term "nano" in nanofiltration does not correspond to the definition of "nano" in nanotechnology. Instead it refers to the size of the particles (about 1 nm) that are rejected by the membrane. Since the term "nano" in membrane technology is already assigned to this specific type of membrane, we propose using the term "nanostructured membrane" (NSM) for any membrane with engineered nano-sized structures (e.g. pores) according to the current ISO definition of nanomaterials but explicitly excluding membranes with integrated nanoparticles (nano-enhanced membranes, NEM). The umbrella term for all membranes involving nanotechnology (NSM and NEM) - developed by the Network of Excellence NanoMemPro (EU FP6 project): is "nanoscale based membrane technologies".

Box 3: NSM versus NEM

There is a clear distinction between NSM where the term "nano" refers only to the pores (or the particles that are rejected) and NEM where membranes are functionalised with discrete nanoparticles. A separate briefing will be published on NEM because the technology readiness level and the risk associated to the membranes differ significantly. The membrane industry does not classify NSM as nanotechnology; large membrane production companies are usually not active in the field of NEM.

Conclusions

- An enthralling domain, with fascinating perspectives, which requires a broad view and a holistic approach … as well as some caution !

- One cannot expect everything from this kind of materials , but simply what can be reasonably expected. Having in mind the main limitations to process performance is a pre-requisite.

- The effects of new engineered materials should be determined not only from the point of view of process performance, but also from the point of view of potential (eco)toxicity effects.

- When nanoparticles can be released to the environment - TiO2 or carbon nanoparticles, nanotubes … - a careful control of this release from membranes is necessary …. but not always easy either regarding concentration measurement or interpreting concentration/toxicity relation… !

- Nanofiltration membrane materials (i.e. with nanopores according to IUPAC) and as a whole nanostructured membranes should not be confused with nano-enhanced membrane materials (surface or matrix modifications with nanoparticles). They are based on different concept, either considering their manufacture or applications.