Nanotechnologies and membrane engineering at the core of water and related questions in the Mediterranean and Middle-East countries

Rios G.M.

in

El Moujabber M. (ed.), Mandi L. (ed.), Trisorio-Liuzzi G. (ed.), Martín I. (ed.), Rabi A. (ed.), Rodríguez R. (ed.).
Technological perspectives for rational use of water resources in the Mediterranean region

Bari : CIHEAM
Options Méditerranéennes : Série A. Séminaires Méditerranéens; n. 88

2009
pages 141-147

Nanotechnologies and membrane engineering at the core of water and related questions in the Mediterranean and Middle-East countries

Gilbert M. Rios

Coordinator of the NanoMemPro[1] (NoE/EC /FP6)
Executive Director of the European Membrane House[2] (EMH)
Member of the UNESCO chair SIMEV[3]

Abstract. After a short recall on the importance of water questions for Mediterranean countries, membranes are presented as breakthrough technologies for the field of desalination. Then basic recalls are done concerning membrane materials and processes. A few examples of new very promising materials and processes operating at the nanoscale, not only for desalination but also with other water treatment applications, are presented. As a conclusion, a few ideas are proposed about the best ways to approach all these questions in the future. Undoubtedly, with cell membranes as an ultimate model, all these breakthrough bio-mimetic approaches offer a privileged direction to reach sustainable development.

Keywords. Membranes – Nanomaterials and processes – Desalination – Water treatment – Mediterranean countries.

Les nanotechnologies et les technologies à membrane au centre des questions relatives à l'eau dans les pays méditerranéens et du Moyen-Orient

Résumé. *Après avoir précisé la centralité des questions relatives à l'eau dans les pays méditerranéens, on va parcourir les technologies à membrane qui représentent une avancée significative dans le domaine du dessalement, en illustrant dans les grandes lignes les matériaux et les processus. Des exemples sont présentés concernant de nouveaux matériaux et processus très prometteurs, utilisés à l'échelle du nanomètre, non seulement pour le dessalement mais aussi dans le cas d'autres applications pour le traitement de l'eau. En conclusion, des propositions sont avancées pour aborder ces questions à l'avenir d'une manière appropriée. Sans aucun doute, avec les membranes cellulaires comme modèle ultime, ces approches biomimétiques innovantes s'avèrent être une voie importante à suivre pour atteindre un développement durable.*

Mots-clés. *Membranes – Nanomatériaux et processus– Dessalement – Traitement de l'eau – Pays méditerranéens*

I – Introduction

«Before conceiving His Creation, God was in a cloud in the sky. Then He created His Throne above water» (Hadith) - For the Koran, water is the essential element of Creation and there is really a sort of "charm" for water in the Holy Book with more than 60 mentions! The religions of the Book - Judaism, Christianity and Islam - took all birth in arid zones, where water remains invaluable -"a gift of God". It was the same with the old Egyptian (with the Nile divinity) or Mesopotamian (Gilgamesh story) civilizations. Thus it is easy to understand why water represents such a huge cultural heritage for all the religions and civilizations born in this part of the world!

Water production for human consumption, irrigation... has become today a crucial question for a lot of countries all over the world, and not only for the MENA countries. Even to a less extent, its importance is great for the south of Europe. The need for replacing this question in a "global situation", by taking into account energy considerations, new waste generation and citizen health, is a new trend. In this way, it is at the core of a huge debate on sustainable development,

preservation of natural resources and well-being of population in a quickly changing world (increase of population, new ways of life, climate changes…)
What solutions? Probably the need for:

- new technologies having the capacity to address the challenges with which we are faced,
- technical skills and expertises necessary for the implementation of these technologies,
- companies working to develop these new solutions,

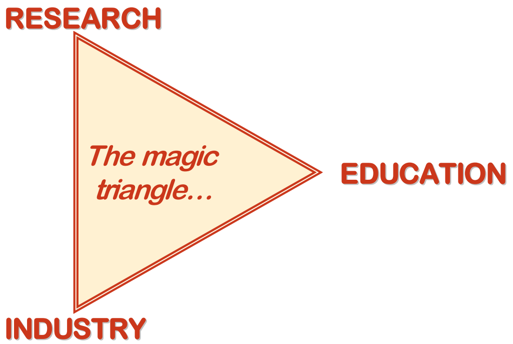

Figure 1. The magic triangle as well as rules to provide the necessary framework for these very ambitious integrated actions and their acceptance by population (information/communication).

II – Desalination and new breakthrough membrane technologies

Desalination is probably as old as human civilization. Socrates already taught students how to distil seawater to obtain fresh water…Today, two groups of technologies must be distinguished: thermal or distillation processes which involve some form of boiling or evaporation with steam generators, heat boilers (Multiple Effect –MED- and Multiple Stage Flash –MSF- distillation) and membrane / RO processes (ordinarily isothermal operations with a significant energy saving … but which produce brines).

The current situation may be quickly summarized as follows (Proceedings of the EuroMed conference, 2006): all the annual fresh water supply for the planet comes from evaporation from the seas; only about 1% of the world potable water is derived from desalination plants; only a lower % is used for industrial needs and practically zero for irrigation; the total capacity of desalination was in 2000 of about 26 million m^3 per day (60% from seawater and 40% from brackish water) and it represents a quickly growing billion-dollar business!

Among the major impetus for strategic opportunities in these fields: a fast growing population (particularly in mega cities along the sea costs), breakthroughs in the reduced energy requirement and investment costs of desalination (from 3 to 5 $/ m^3 10 years ago to 0.4 to 0.8$ today before distribution, particularly due to the development of Membrane/RO processes) and in parallel a cost increase of traditional water supply. The very large-scale seawater desalination installations ordered by Israel, Saudi Arabia, Jordan, Florida, Spain… may treat today up to 200,000 m^3/day. Next important challenges will be to change traditional fossil energy supply into renewable energy sources such as solar, photovoltaic, fuel cell technologies or even to set-up nuclear power plant to feed huge desalination plants.

Up to recent years, there has also been a strong and emotional opposition to desalination as too costly, too large in scale, too technical for universal solutions… and some misunderstanding with the traditional water supplier's culture. But today innovative forces and entrepreneurial creativity result from our increased awareness of a world-wide water problem!

Concerning the life cycle assessment (LCA), it appears that desalination based on RO provokes significantly lower environmental load than thermal desalination; but thermal desalination technologies have a great environmental impact reduction when integrated with other production processes as shown in table 1. Thus analysis needs to be done on a case-by-case basis. Concerning marine environment and water quality, there is a potential negative impact of brine discharge (RO) on the ocean floor and benthic environment; but according to the more recent studies conducted in Cyprus or in the USA (Electric Power Research Institute, California Coastal Commission…), it should be managed correctly with appropriate environmental regulations (reject at a depth of 10–15 m, limitations on the chemicals used in the maintenance processes…).

Table 1. LCA details.

	MSF	MED	RO
kg. CO_2 / m^3	23.41	18.05	1.78
g. dust / m^3	2.04	1.02	2.07
g. NO_x / m^3	28.3	21.41	3.87
g. NMVOC[1] / m^3	7.90	5.85	1.10
g. SO_x / m^3	27.91	26.48	10.68

1 non-methane volatile organic compounds

m^3 of desalted water

	MSF	MED
Kg. CO_2 / m^3	1.96	1.11
g. dust / m^3	2.04	1.02
g. NO_x / m^3	4.29	2.42
g. NMVOC / m^3	1.22	0.59
g. SO_x / m^3	14.80	16.11

For processes driven by residual thermal energy

Looking at the market place, it appears that membrane technologies have the main advantages over thermal solutions to be very versatile (applicable to both large- and small-scale needs), and also to be competitive not only in the desalination of seawater but also for water recycling from effluents. All that represents an enormous challenge and opens very bright perspectives for membrane technologies!

You said "artificial membranes"?

Life is based on biological membranes which basically are thin layers separating two media in order to protect one medium from the other, while allowing selective exchanges between them. All the cells of living organisms are surrounded by membranes; our skin is also a fantastic high-tech membrane… Artificial membranes are simplistic industrially-manufactured copies of these biological models. The exchanges are regulated by the external forces - as an example a transmembrane pressure as for reverse osmosis (RO) or an electrical potential for electrodialysis (ED) as shown on figure 2-, the properties of the fluids -which ordinarily circulate in a tangential way as regards the wall to limit fouling and to increase the whole process/system efficiency- and the characteristics of the thin film material – which may be polymeric, inorganic or hybrid, dense or porous, neutral or electrically charged…-. The main performance criteria are the flux (which represents the quantity of fluid crossing the layer) and the selectivity (associated to the balance between the retained and non-retained species) (Basic principles of membrane technology, 1991).

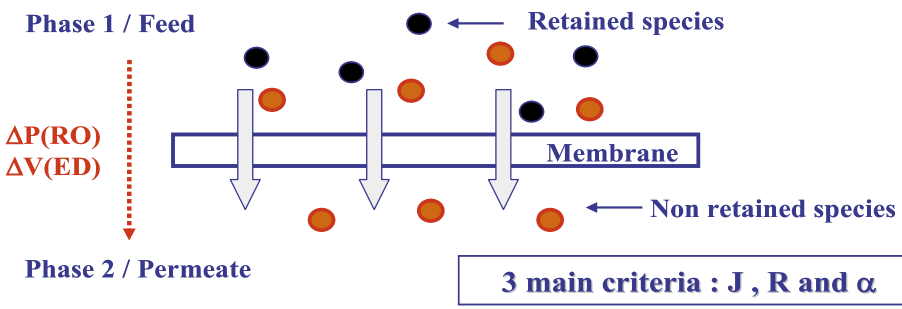

Figure 2. Schema presenting membrane technologies.

The key factor to improve the performance of a membrane operation is to keep the right balance between the limitations induced by the supporting material on the one side, and the fluid phases flowing along it on the other side. With the development of nanotechnology, new materials and concepts have emerged which seem promised to a really bright future.

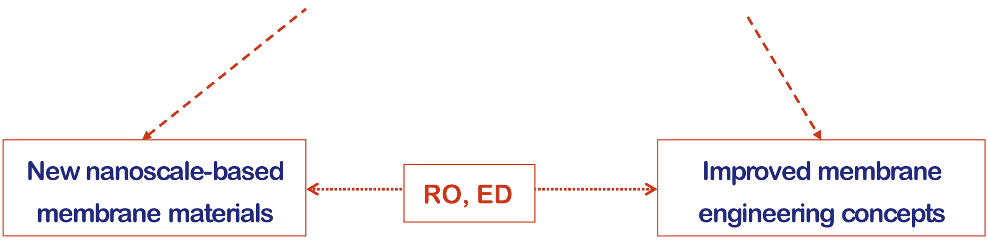

Figure 3. The ways to improve RO and ED.

Due to their intrinsic and well-known characteristics - modularity, easy control, low operating costs, isothermal working, no chemical addition…- membrane operations participate already to pre-treatment, purification and even finishing steps in water and effluents treatment processes like:

- Microfiltration for the separation of small particles and bacteria…
- Ultrafiltration for rejection of colloids, recovery of colorants in textile industries, concentration of oil-water emulsions
- Reverse osmosis for water desalting
- Electrodialysis for recovery of heavy metals from effluents, acid regeneration…

Beyond these "classical" techniques, a lot of other more recent technologies are developing such as membrane contactors and reactors.

III – A few examples of new promising membrane materials

The mixed-matrix membranes (MMMs) are merely hybrid membranes consisting of nanoparticles imbedded into polymeric matrix as represented on figure 4. The presence of nanoparticles allows getting much higher selectivity without compromising the flux. Different concepts are under investigation, which involve zeolites, carbon molecular sieves, other porous particles…or non-porous fillers. The selectivity is linked to the polymer-free volume, the particle size and surface, the presence of covalent bonding…

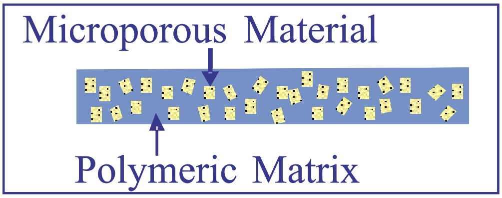

Figure 4. Scheme of an MMM.

An interesting example is provided by the new RO membrane presented by Eric Hoek (E.Hoek *et al.*, 2007) from the University of California to reduce the cost of sea-water desalination and waste-water reclamation. It is a uniquely cross-linked matrix of polymers and nanoscale engineered particles, which creates molecular tunnels through which water flows much more easily than nearly all the contaminants. The highly porous nanoparticles are soaking up water like a sponge, while repelling dissolved salts and other impurities such as organics and bacteria. As a result, driven-pressure is lower than in conventional systems. The overall cost of desalination is considerably reduced (25%), including energy demand and environmental issues. One must remember that water production and recycling is a key topic for California, the fifth largest economy in the world!

Molecular self-assembly is another way to obtain a new kind of membrane materials. Self-organization is an important building principle of biological membranes; with this concept as a guideline, efforts have been made during the last years to imitate nature, with molecules very different from the biological ones. Block copolymers represent one class of self-assembling materials attractive to fabricate well-ordered nanometer-scale structures (spheres, cylinders and lamellae…depending on the volume fractions : figure 5). With them it can be envisaged to manufacture membranes, with an extremely narrow pore size distribution, leading to superior selectivity without flux decrease.

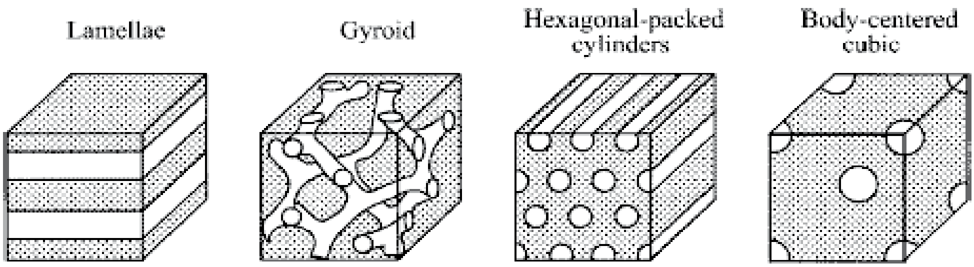

Figure 5. Ordered nanometer-scale structures obtained by self-assembly.

With such materials, a potential alternative has been recently proposed at Urbana and Cambridge in the United States which consists in coating commercial polyvinylidene fluoride membranes (PVDF) with self-assembling amphiphilic graft copolymers [poly (oxyethylene) methacrylate] to prepare new antifouling NF membranes. It is worth recalling that with traditional UF membranes employed in membrane bioreactors (MBRs), a high susceptibility to fouling by extracellular polymeric substances (EPS) is ordinarily observed.

IV – Nanofiltration (NF) a very quickly developing technology

NF is a quite new technology (Handbook of Membrane separations, 2008) which allows the removal from a liquid (see figure 6) of:

- nanoscale uncharged molecules by size exclusion and/or from differences in diffusion rates,

- ions (mainly multivalent) by electric charge effects.

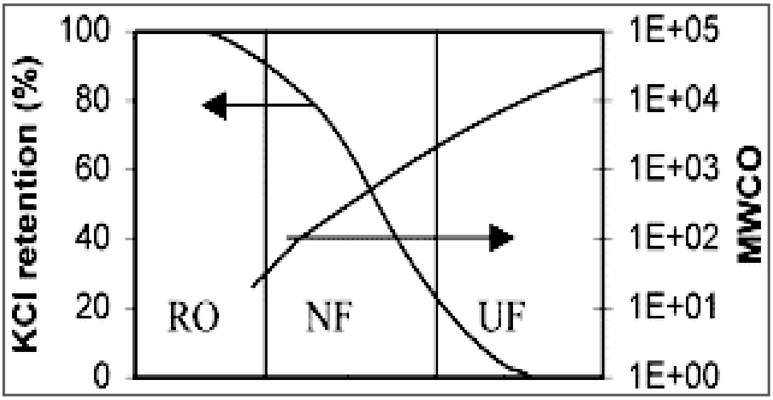

Figure 6. Classical NF performance.

For the last decade, one can mention among the main breakthroughs and more ambitious projects involving NF for improving drinking water quality:

- the reduction of hardness with softening processes; in that case NF is in competition with traditional ion-exchange systems or lime softening (regeneration, sludge and wastes…) and typical rejections of 70 to 90% are obtained through the separation of natural organic material (NOM) : today there are on the market various membranes with MWCO below 500 daltons, sufficiently low to remove the major part of humic and fulvic acids
- the high elimination of micro pollutants such as pesticides and organohalide compounds which have very negative effects on health (carcinogenic…); in that case, NF is competing with activated carbon adsorption, a very expensive method in the presence of large fractions of NOM due to competition, regeneration…

New very promising projects of technological developments are today focused on the abatement of fluoride ions to prevent fluorose disease, or the separation of arsenic, lead, aluminium and uranium. The maximum fluoride concentration in drinking water has been fixed by the World Health Organization at about 1.5-2.0 mg/l; in some sub-Saharan African countries it may be higher than 20-25 mg/l ! As (V) and As (III) are limited to 10 mg/l in France: in a lot of countries in the world concentrations higher than 50 mg/l may be found (not only in Bangladesh, India, China… but also in the USA). For such applications and large water production in rural countries, NF appeared to be more adapted than ion exchange, adsorption or biological treatment.

Other works are devoted to membrane bioreactor coupling with nanofiltration for an improved removal of toxicity in the hospital effluent. In hospital discharges, and more generally in water resources, there are numerous toxic pollutants (estrogenic hormones and other bio-products) which are responsible for cancers, allergies, fertility losses, thyroid diseases … Until now there was no clear legislation anywhere in the world about this topic; but they are being developed very quickly. With the process here proposed, by adjusting the contact time between the pollutant and the purifying biomass (MBR) it is possible to eliminate a large part of contaminants with strong biological/chemical resistance and/or low concentration; the addition of a further NF step to an MBR may eradicate the residual pollution.

V – Conclusion

Nanotechnologies and membrane technologies represent definitely a central question for the future of all our societies in terms of health, environment, energy, industrial market! This is particularly true for the Mediterranean area due to the scarcity of the water resource! Let us hope that they will be able to bring positive contributions as large as the water service roads of the Roman Empire or the Arab kingdoms of Al Andalusia…

To be as efficient as possible, research and technological developments will ask for a strong and revitalized collaboration between Europe and MENA countries based on our huge cultural heritage, our geographical proximity, our historical contacts and other complementarity reasons. Holistic approaches based on a strong integration of disciplines and expertise on a case-by-case basis will have to emerge and all kind of synergies will be welcomed.
Among others and along with more classical bilateral actions, it seems that UNESCO through the actions of its chairs and centers, as well as the European Union through its various research and structuring programs, should play a main part in this whole process.

References

Jeong B.H., Hoek M.V., Yan E., Subramani Y., Huang A., Hurwitz X., Ghosh G. A.K. and Nano A.J., 2007. Interfacial polymerization of thin film nanocomposites: A new concept for reverse osmosis membranes. *Journal of Membrane Science,* 294 (1-2):1-7.

Mulder M., 1991. *Basic principles of membrane technologies* .Kluwer Academic Publishers (The Netherlands).

Pabby A.K., Rizvi S.S.H.and Sastre A.M. (Ed.,) 2008. *Handbook of Membrane separations* CRCPress (London).

Proceedings of the EuroMed Conference, 2006. Desalination strategies in South Mediterranean countries. Cooperation between Mediterranean Countries of Europe and the Southern Rim of the Mediterranean. Desalination, 204 21–25 May 2006, Montpellier, France.

[1] NanoMemPro : see www.nanomempro.com
[2] EMH: a Belgian international non-profit making association : see www.euromemhouse.com
[3] SIMEV – Head : Prof. L.Cot – « Membrane technologies applied to the environment »