BRIEFING No.13
ENVIRONMENT

NANOSTRUCTURED MEMBRANES FOR WATER TREATMENT

Potable water is a precious resource as without it human life is not possible. The increasing world population is a critical issue since it leads to higher water demand, increased wastewater production, and increased stress on surface water. This challenge requires innovative solutions for the production of potable water, wastewater treatment, and water recycling.

Membranes with nanosized pores have been in use by the water industry for decades and are an established method for the treatment of contaminated water and drinking water production. This BRIEFING outlines the most important application areas of nanostructured membranes (NSM), their economic and social impact, and challenges that remain to be addressed. It further points out open issues regarding the definition of nanostructured materials, which have direct implications for policy making, and highlights the difference between nanostructured membranes and membranes incorporating nanoparticles.

Filtration for clean water

Nanostructured membranes (NSM) can be used to reject suspended particles, bacteria, macromolecules, viruses, colloids, organic compounds, and multivalent ions. They are therefore mainly utilised for drinking water production (for water softening or disinfection), and the treatment of landfill leachate and industrial wastewater (decolouring). Other application areas include the dairy industry.

Filtration with NSM can be considered as a well established technology. Nanofiltration – the latest filtration method – was introduced in the 1980s. Competing technologies include:

- Activated carbon, ozonation/chlorination, UV-light (for the removal of micropollutants in drinking water production);
- Ion exchange, lime softening (for the reduction of hardness); and
- (Membrane) distillation, pervaporation, electrodialysis, adsorption, crystallisation etc. (for the recycling of industrial wastewater).

The advantages of NSM compared with other treatment methods depend upon the substances present in the feed water and the water that is subject to cleaning. One advantage is that different pollutants can be removed in the same filtration step. Depending on the membrane this removal can be selective towards certain substances, or compounds can be only partially removed; for example calcium carbonate in the case of water softening. It is therefore crucial that the membrane is exactly tailored to the needs of the treatment plant in order to achieve the maximum removal of the target compound(s). Additional advantages are[1]: no resistant/deadened organisms are left; the use of chemicals is minimal; and the cleaning capacity is not detracted by turbidity, or economic factors such as costs or energy use. In addition, in wastewater treatment, filtration methods are ideal for plants with space restrictions since the filtration elements are relatively small thanks to their modular structure and no large basins are needed.

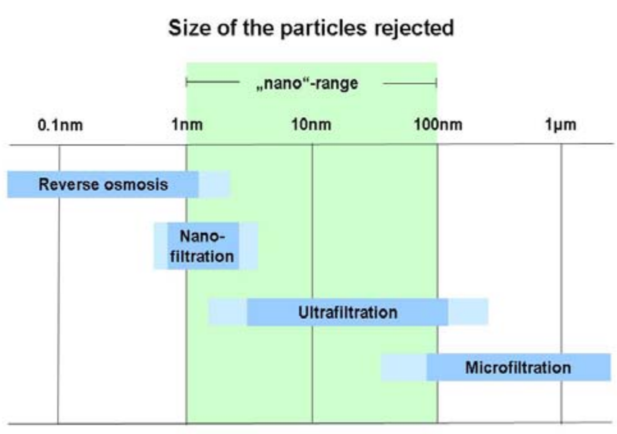

Figure 1: *Filtration spectra of the different membranes. In the range of 1-100nm mainly nanofiltration and ultrafiltration membranes are applied.*

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".

Background

Nanostructured membranes (NSM) can be made from ceramic materials or, most commonly, from polymers. Ceramic membranes have the advantage of being more resistant to mechanical forces, chemicals and temperature (they can be sterilised), but are significantly more expensive to manufacture. The membranes generally have a life time of 5-15 years depending on the application area. Mechanical, thermal and chemical properties are crucial to ensuring the stability of the membrane under pressure and to allow for cleaning and regeneration [2]. Working parameters (such as hydrodynamics) have to be adapted to the membrane accordingly. In NF and UF a pressure of about 1-10 bar is generally applied [3].

NSM have proven their efficiency in removing particles, bacteria/viruses, (natural) organic matter, hardness, metals (such as arsenic, uranium, lead, chromate), sulphate, and a number of organic and inorganic substances (such as pesticides and some pharmaceuticals) sometimes even in one single treatment step. Uncharged compounds and monovalent ions like nitrates are rejected to a lower extent while the rejection of multivalent ions is higher (up to 99%). For groundwater, seawater and brackish water treatment usually reverse osmosis (RO) is needed while for softening tight nanofiltration (NF) is generally sufficient [4]. The different filtration methods overlap in their application range (***Figure 1***) and in practice each company has their own criteria to distinguish between for example a loose RO-membrane and a tight NF-membrane. A general way of differentiation is based on the ability of the membrane to reject dissolved species: RO- and NF-membranes may be called dense membranes that are able to reject dissolved species such as ions while ultrafiltration (UF)- and microfiltration (MF)-membranes can usually only reject suspended particles [2]. It becomes evident that the choice of the membrane type requires a trade off between the pore size and the contaminant rejection. Generally, for smaller pores rejection will be increased but also the pressure needed and thus the energy demand is greater. The electric charge of the membrane material is another very important parameter with regards to ion rejection.

Several studies have shown the effectiveness of NSM for cleaning industrial wastewater (such as fish meal wastewater, solutes from etching processes, wastewater from textile industry)[5]. The filtration process is able to reduce the contaminant level significantly and makes the reuse of the water possible. In 2003 an extensive pilot study was conducted with 30 types of coloured wastewater over a period of 6 weeks [5]. Depending on the composition of the dyes, decolouring efficiency of 70-100% was obtained with running costs around €0.25-1.4 per m^3.

NSM may be combined with other treatment steps using either different membranes (such as NF followed by RO) or conventional methods such as active carbon. A combination of methods might be effectual to reduce the costs, energy use or fouling, and also to ensure the complete removal of undesired compounds.

Box 2: Definitions of nanostructured membranes

The International Union of Pure and Applied Chemistry (IUPAC) defines the following (nanostructured) membranes [6]:

Reverse osmosis (RO): Liquid-phase pressure-driven separation process in which applied trans-membrane pressure causes selective movement of solvent against its osmotic pressure difference.

Nanofiltration (NF): Pressure-driven membrane-based separation process in which particles and dissolved macromolecules smaller than 2 nm are rejected.

Ultrafiltration (UF): A separation process whereby a solution containing a solute of molecular size significantly greater than that of the solvent molecule is removed from the solvent by the application of a hydraulic pressure forcing only the solvent to flow through a suitable membrane, usually having a pore size in the range 1-100 nm.

Microfiltration (MF): Pressure-driven membrane-based separation process; particles and dissolved macromolecules larger than 100 nm are rejected.

Impacts

Societal impact on European Citizen

The positive impact of membranes in society is evident since the improvement of water quality and the treatment of wastewater concern issues that will become even more critical in the future. NSM can be used for water desalination and therefore offers the possibility of providing drinking water in arid regions with access to sea water. Filtration with NSM also allows for the recycling of wastewater and can remove even trace contaminants. The land area required for filtration plants is significantly lower than for conventional wastewater treatment plants, and additionally the use of chemicals in filtration is usually restricted to the membrane cleaning agents and is thus low. New jobs for trained professionals may also be created as the membrane maintenance requires specialised expertise.

Economic/Industry Impact

The water treatment industry is faced with increasingly stringent regulations and challenges through emerging contaminants in the wastewaters and in sources (ground and surface water) for potable water production. This trend is evident in the very positive growth estimates for the NSM markets. According to publicly available data on various studies published by BCC Research the estimated Compound Annual Growth Rate (CAGR) for the related markets and components is in the range of 7.3% for RO system components[7], 13.8% for RO desalination applications[8], and 5.7% for UF applications[9]. The global market for RO components is currently greater than $2.6 billion[7]. The segment of the membrane module is estimated to be smaller than 25%. The RO system component market is expected to reach $3.7 billion by 2014[7].

In 2007 BCC Research estimated that the market for NF-membranes was $89.1 million in 2006, reaching $310 million by 2012 with a CAGR of 26.1%[10]. From this water treatment applications would generate $238.2 million in 2012 with a CAGR of 27.4%. Experts from the Technologiezentrum Wasser (TWZ) Karlsruhe also expect a rising demand for NF-membranes in drinking water production [3]. If we expect the CAGR to remain constant, the size of the markets would reach around $390 million by 2014, which in turn would represent a third of the US UF markets, 10% of the global RO system component markets, and about 7% of the global RO-based desalination applications markets. In Europe, UF-plants are widespread and have usually been in use for a number of years. NF and RO-plants are also installed in numerous locations. The TWZ[3] reports five RO-plants and six NF-plants in Germany, some of them operating since 1998, mainly for reduction of hardness. In Norway NF-plants are widespread (more than 100 plants since 1989) for the removal of natural organic matter in drinking water [4].

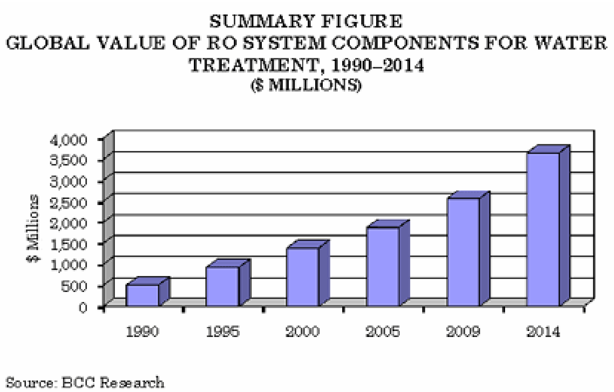

Figure 2a: *BCC Research expects the RO system component markets to grow to $3.7billion by 2014[7].*

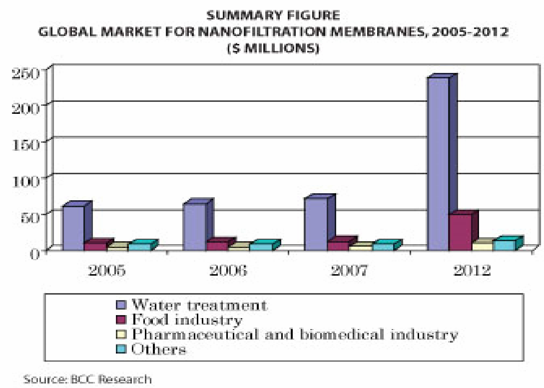

Figure 2b: *By 2012 BCC Research estimate that the NF-membranes markets would grow to $310 million[10].*

Technology Readiness Level (TRL)

The TRL indicates technology development status; NSM are a well established technology and are thus classified as mature market technology.

Challenges

Although filtration with NSM is a mature market, there are a number of technical challenges that require further research and development. Some of the challenges mentioned can be addressed by nano-enhanced membranes (subject of a BRIEFING on nano-enhanced membranes, to be published in May 2011). Relevant issues are[11];

- reduction of membrane fouling and scaling
- increased flux/reduced pressure (and thus reduced energy demand)
- accurate modelling and simulation of membrane performance
- even pore size distribution in the membrane (all pores having similar size)
- increased membrane resistance and lifetime
- increased membrane selectivity
- solutions for the treatment of the concentrate

Membrane fouling is the major technical challenge; this is the accumulation of the rejected material on the membrane. Fouling leads to clogging of the pores and thus reduced flux. It is thus inevitable to have to flush or clean membranes regularly. A further problem for NF-membranes is the modelling of the membrane performance which is usually not accurate enough to predict performance in large-scale plants. Lab-scale experiments and pilot tests are recommended since the performance of the membrane depends on the different contaminants or other substances present in the specific water source used.

It is evident that the membrane selectivity towards certain substances is crucial. Unfortunately, the rejection rate in NF and UF is limited depending on the pore size and charge of the membrane. However, in most cases, such as for water recycling and the removal of trace contaminants, a total rejection of the substances is desirable. Another challenge in industrial wastewater treatment is the resistance of the membrane towards specific compounds (for example organic solvents). Recent research is also focused on the development of solvent resistant nanostructured membranes and great advances are being achieved here.

Economic reasons may also prohibit the widespread installation of NSM-plants. It must be emphasised that UF is a standard treatment in drinking water production (for removal of bacteria or viruses) while NF is much less common. Generally, the water industry is conservative and reluctant to try new methods as long as the current methods comply with regulations. In many cases, conventional methods are cheaper and the installation of NSM-plants would require a totally different infrastructure and maintenance expertise. Therefore the market for NSM at the moment is mainly in new plants and in areas where specific substances need to be removed or recovered.

There are no concerns regarding the societal and environmental impacts of NSM; they are not expected to have any adverse effect on human health and ecosystems as they do not contain nanoparticles. Indeed, NSM could be used to filter out unwanted nanoparticles in wastewater treatment plants. In addition, all materials in contact with drinking water are subject to stringent regulations and approvals to ensure water quality standards. However, a remaining societal challenge is the installation of NSM-plants in developing countries. As the maintenance of the membrane requires specialised expertise, filtration plants are so far only installed in industrialised countries where trained professionals are available. Furthermore lack of economical power and political will, in addition to corruption and bureaucracy, can hinder the adoption of new technologies in developing countries. The installation of NSM in such countries is not only a societal challenge; they potentially represent a large market for the membrane industry.

EU Competitive Position

The majority of the existing NSM manufacturing capacity is in Japan and the US. Europe has only a few active companies in the field, but they have been able to secure specific niches where they have quite substantial market shares. For instance Norit B.V. from the Netherlands commands 50% market share of the beer filtration markets and 17% share of the global “ultrafiltration” markets. Europe also carries out high quality research in the field of nanofiltration.

Summary

- Nanostructured membranes (NSM) include membranes for ultrafiltration (UF) and nanofiltration (NF) (and in some cases also for microfiltration or reverse osmosis).
- NSM can be used for the removal of a wide range of pollutants from groundwater and surface water for the purpose of drinking water production [4]; however, currently the major application is in disinfection (UF) and water softening (NF).
- NSM are less widespread in municipal wastewater treatment but are used for industrial wastewater treatment (water recycling) such as in the textile sector.
- Full scale installations have proven the reliability of NSM in different areas. NSM are considered a mature market technology.
- The main challenge is membrane fouling.
- NSM do not contain any nanoparticles and must be clearly distinguished from membranes with integrated nanoparticles (nano-enhanced membranes).
- There are no adverse effects expected either for human health or the environment.

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.

Further information

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References

[1] W.E.T. GmbH, Einführung in die Ultrafiltration, 2005, available at: http://www.wet-gmbh.com/ger/docs/uf_allgemein_de.pdf
[2] Samhaber, Wolfang M., Erfahrungen und Anwendungspotential der Nanofiltration, 2004, available at: http://www.ivt.jku.at/Forschung/Publikationen/pdf/Membrantechnik%20in%20der%20Prozessindustrie.pdf
[3] Lipp, P., Erfahrungen mit Nanofiltration und Umkehrosmose, Membrantage Kassel 2004, DVGW-Technologiezentrum Wasser (TWZ), Karlsruhe, available at: http://www.dvgw.de/fileadmin/dvgw/wasser/aufbereitung/membranverfahren8.pdf
[4] Thorsen, T. and Fløgstad, H., Nanofiltration in drinking water treatment, 2006, EU FP6 project Techneau: D 5.3.4B, available at: http://www.techneau.org/fileadmin/files/Publications/Publications/Deliverables/D5.3.4b.pdf
[5] Mueller, Nicole C. and Nowack, Bernd, Report on the Technology Sector Environment, 2009, EU FP6 project ObservatoryNANO, available at: www.observatorynano.eu
[6] IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). XML on-line corrected version: http://goldbook.iupac.org (2006-) created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins. ISBN 0-9678550-9-8. doi:10.1351/goldbook
[7] Hanft, S., Summary of the report: Major Reverse Osmosis System Components for Water Treatment: The Global Market, Report Code: MST049C, September 2009, http://www.bccresearch.com/report/MST049C.htm
[8] Hanft, S., Summary of the report: Seawater and Brackish Water Desalination, Report Code: MST052B, September 2010, http://www.bccresearch.com/report/MST052B.html
[9] Hanft, S., Summary of the report: Ultrafiltration Membranes: Technologies and the U.S. Market, Report Code: MST044C, May 2010, http://www.bccresearch.com/report/MST044C.html
[10] Gagliardi M., Summary of the report: Nanofiltration, Report Code: NAN045A, September 2007, http://www.bccresearch.com/report/NAN045A.html
[11] Van der Bruggen, B., Mänttäri, M., Nyström, M., Drawbacks of applying nanofiltration and how to avoid them: A review, Separation and Purification Technology 63 (2008), 251–263