ObservatoryNANO

BRIEFING No.16
ENVIRONMENT

SEVENTH FRAMEWORK PROGRAMME

NANOENHANCED MEMBRANES FOR IMPROVED WATER TREATMENT

Clean water is an essential requirement for all life and therefore the societal benefit from effective water treatment methods is significant. Global changes such as an increasing world population and the impacts of climate change will lead to drinking water scarcity, increased wastewater production, and increased contamination of surface water and groundwater. There are many different methods to treat contaminated water; one being filtration. However, membranes are not always cost-effective due to technical challenges such as limited flux and membrane fouling (deposition of biofilms on the membrane negatively affecting the membrane performance). The functionalisation of membranes with nanoparticles is one way to address these challenges and hence, improve membrane performance.

Nano-enhanced membranes in water treatment

Different types of membranes are used for drinking water production and for the treatment and recycling of industrial wastewater. However, the effectiveness of many membranes can be improved; for example by enhancing the flux or by reducing membrane fouling. Membrane characteristics that can be improved by the use of nanoparticles are: antifouling and antimicrobial properties; increased selectivity; increased flux (through increased hydrophobicity); or pore-size control by nanogels (shrinking/growing by change of pH or temperature). The application of nanoparticles in membranes can thus decrease the energy demand, the use of chemicals for membrane cleaning, and cost.

Box 1: Nano-enhanced membranes versus nano-structured membranes

There is a clear distinction between nano-enhanced membranes (NEM) where membranes are functionalised with discrete nanoparticles or nanotubes and nano-structured membranes (NSM) where the term “nano” refers only to the internal structure (pores) of the membrane. A separate briefing was published on nano-structured membranes (Briefing No.13). The technology readiness level and the risk associated with NEM and NSM differ significantly. Large membrane production companies are usually not active in the field of NEM.

Background

Membrane filtration for the treatment of water is a well established technology (see Briefing No.13). Despite the success and widespread application of NSM some challenges remain. These include;

- membrane fouling
- limited flux
- limited selectivity
- fixed pore size

To address these challenges, membranes can be functionalised with nanoparticles to improve membrane performance. This method is rather new, so it is not surprising that several different terms are being used to describe this technology; nano-activated, nano-enhanced, nanoparticle-enhanced, nanoparticle-based, and nano-functionalised membranes. To avoid any ambiguity, the terminology should be standardised. In this BRIEFING we will use the term “nano-enhanced membrane (NEM)” since “enhancement” best describes the function of the nanoparticles in the membrane.

A large body of literature on NEM exists; however, most of this work is still in the laboratory stage and relatively far from actual implementation. The most prominent nanoparticles being investigated are titanium dioxide (TiO_2), silver and carbon nanotubes (CNT). There are several possible methods for the functionalisation of membranes. In the case of thin film composites, nanoparticles can be integrated in the polyamide top layer of the membrane or applied on the surface of the membrane material (see ***Figure 1***). In the case of ceramic membranes or metallic microsieves nanoparticles are deposited on the surface and then combined at high temperature (***Figure 2***). Surface deposition of nanoparticles can be carried out by vapour deposition, electrophoretic coating or dip coating.

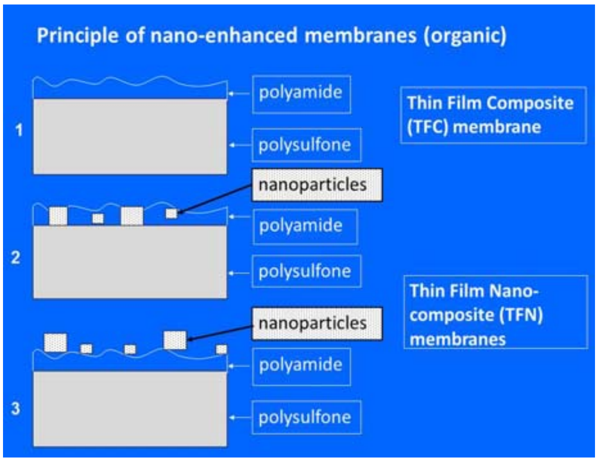

Figure 1: *Functionalisation of membranes with nanoparticles (adapted from [1])*

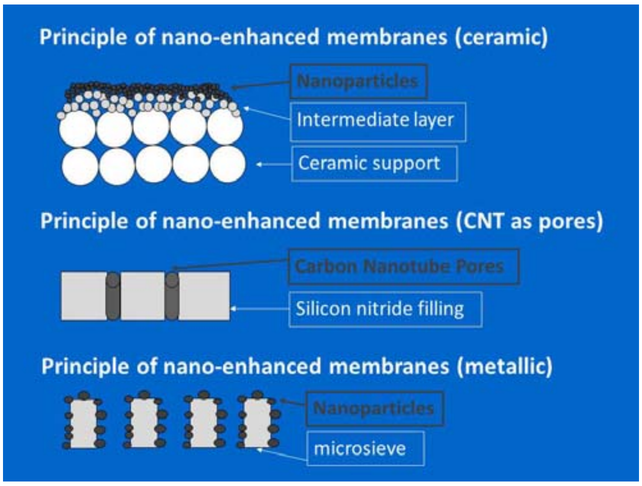

Figure 2: *Comparison of different NEM: ceramic membrane functionalised with NP (adapted from [1]), CNT as pores in a membrane and metallic microsieves functionalised with nanoparticles.*

An overview of manufacturing methods and performance of NEM in wastewater treatment is given in a review by Kim and Van der Bruggen[1].

Yet a totally different approach is the complete integration of CNT in a membrane as fine pores (***Figure 2***); in this case aligned CNT are grown vertically. The gaps are then filled with silicon nitride (or another material) and finally these pores are exposed by partial removal of the support material[2]. Another idea is the control of the pore size in the membrane by coating the pores with a nanogel that can be shrunk/grown by a change in pH or temperature to allow for easier cleaning. Recently, scientists were able to coat a mesh from stainless steel with CNTs (***Figure 3***)[3]; this filter can be used to separate oil and water. In initial experiments,

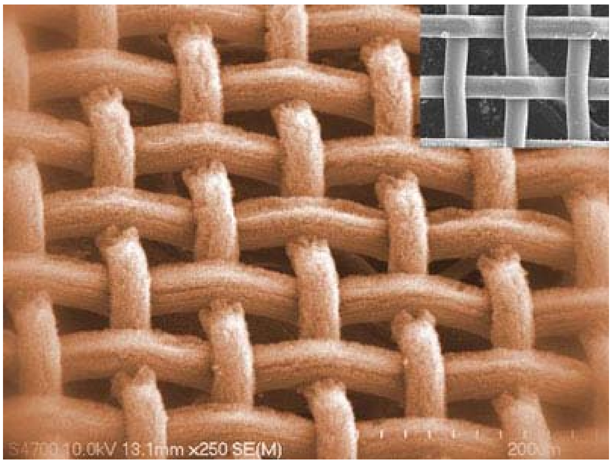

Figure 3: *A scanning electron microscopy image of the CNT -coated filter. For comparison, the inset is bare stainless steel mesh (Source: www.nanowerk.com)[3].*

80% of the water was rejected due to the hydrophobic properties of the CNTs.

The functionalisation of polymeric membranes is investigated in the EU-project nametech (www.nametech.eu).). In this project, Norit X-Flow (Netherlands) has tested the application of silver nanoparticles on ultrafiltration (UF) and microfiltration (MF) membranes as an antimicrobial agent. However, there are several challenges regarding the use of silver in full scale applications. Firstly, it is yet unknown if bacteria can develop a resistance to silver; publications exist indicating this can occur already after several weeks. Therefore, it can be debated if the application of silver in a product with a typical lifetime of 10 years is useful. Secondly, silver is antimicrobial due to slow dissolution into water as Ag^{+} ions, which means silver is consumed during its lifetime. Calculations of the silver lost by dissolution shows that a large amount of silver needs to be added to the membrane to have a lasting effect (up to 45wt% silver). Norit X-Flow concluded that silver may, however, find a potential application in membranes for point of use devices, where lifetimes are much shorter.

Also TiO_2 cannot be successfully applied in or on organic membranes because the membrane is – just like the target compounds - degraded by the photoreactivity of TiO_2. Research on TiO_2-functionalised membranes thus mainly focuses on ceramic membranes and metallic microsieves. At the Fraunhofer Institute (Germany) microsieves are coated with TiO_2 or TiO_2/Ag composites to achieve anti-fouling properties. The coatings are applied by vacuum coating and sintering and were found to be physically and chemically resistant; however, the photocatalytic activity needs to be improved. Additional illumination with UV-light is tested to directly degrade organic contaminants in the source water. The advantages of microsieves are the stability of the metallic support and the uniform pore and pore size distribution.

Membranes with CNT-pores could be used instead of reverse osmosis (RO) membranes for the production of ultrapure water with the advantage of an increased flux. By increasing the flux, the energy demand and costs can be decreased significantly. However, this technology is still at the basic research stage and it is estimated that the technology will at the earliest be ready for scale up in 5-10 years if all technical challenges can be overcome.

Type of Nanoparticle	Intended membrane improvement	Compatible membrane types
TiO_2	Increased flux, antifouling	Ceramic, metallic
Ag	Antimicrobial	all
CNT	Increased flux	
Al_2O_3, silica, zirconia	Increased flux	all

Table 1: *Nanoparticles used in membranes*

Impacts

Societal/Impact on European Citizen

The beneficial impact of a technology that may potentially improve water quality is beyond question. However, great care has to be given to the potential risk posed by the release of nanoparticles – especially from materials in contact with (drinking) water such as nano-enhanced membranes (see section on **Challenges**). Depending on the type of membrane, the benefit of nano-enhanced membranes for society differs. Nano-enhanced membranes with CNT used as pores for the production of drinking water from seawater may potentially become cost-effective and environmentally friendly by reducing the energy demand through an increased flux. Nano-enhanced anti-fouling membranes could lead to cost savings in industry due to a decreased energy demand and reduced need of chemicals for cleaning; a reduction of cleaning agents and energy demand will also have a positive impact on the environment. The NGO European Environmental Bureau (EEB) considers nanotechnology based water treatments as a promising solution, but is concerned about EHS impacts in particular of CNT and remarks that: "Clean water is only partly a technological issue; societal and political dimensions, such as local production and control, are much more important to address".[4]

Economic

NEM have implications for several stages of the water treatment value chain. The economic arguments for NEM are focused on more efficient and less energy intensive processes. Additionally NEM may enable combination of mechanical and chemical processes that are currently performed individually. In terms of economic impact the effect on the energy consumption is considered to be greater than the benefit of combined processing.

Assuming that ~1% of total energy consumption (2900TWh in 2008)[5] is spent on water and wastewater treatment and that approximately 5%[6] of these electricity costs are due the filtration and that electricity costs are at 0.08€ for one kWh[7], we can calculate that approximately €116M is annually spent on electricity related to water and wastewater filtration within EU27. In comparison the energy consumption of the whole water and wastewater process, which is around 4% of total national energy consumption, is a total of €9.3bn; the majority of this is due to pumping the water through the distribution system[6]. The estimated Compound Annual Growth Rate (CAGR) for the related electricity demand in the U.S. is around 0.8% by 2015 and thus represents a relatively stable market[6].

The above numbers are valid for conventional water processes. Potable water supply from seawater through desalination consumes at least six times more energy than supply from surface or ground water [6, 8]. Thus there are major economic impacts expected from making seawater desalination less energy intensive, especially in the areas with limited access to fresh water.

Technology readiness levels

There are no NEM available on the market yet. Due to technical challenges, the technology is still in its infancy. The technology readiness level is considered to be between basic research (for CNT-pores in membranes), applied research (TiO_2 in membranes) and pilot projects (silver enhanced membranes). The time to market for NEM is estimated at around 5-15 years.

Challenges

At this stage, there are still major technological problems to be overcome before NEM can enter the market. For membranes with CNT-pores, major issues are:

- There are too many CNT/pores per m^2;
- Production of CNTs with a small, uniformly distributed diameter;
- High temperature needed for the growth of the CNT makes the use of polymers as carrier impossible; and
- Production of a sufficiently thin polymeric membrane as the support structure.

The scale up from laboratory to industry will take another estimated 5 years from the time when the first prototype is available. Once prototypes are available, CNT-membranes must undergo a sound risk assessment process to assure that no CNTs are released to the water. Otherwise society will be reluctant to use this new technology. Additionally the method must be cost-effective compared to other methods. Trained professionals will also be needed to handle the membranes which might be challenging in many developing countries with water scarcity.

Silver-enhanced membranes will not enter the mass market because the amount of silver washed out in ionic form is significant and thus enormous amounts of silver would need to be included in the membrane. Furthermore, there is not enough data on the time needed for the bacteria to become resistant against silver. However, some niche products for specialized applications might enter the market within a few years. As the use of silver as antimicrobial agent is widespread in products of daily life, there are no additional concerns to be expected from the public. Silver is most toxic in ionic form which is already covered in the current legislation.

Membranes with TiO_2 need to be resistant towards the radicals produced by the TiO_2 induced photocatalysis. This excludes all polymeric membranes. Ceramic and metallic membranes may be functionalized with TiO_2, but the strong binding of TiO_2 on the surface that is needed to avoid the release of TiO_2, leads to a decreased reactivity of TiO_2. However, research in this area is encouraging and pilot projects may be feasible within 5 years. Since TiO_2 is inexpensive, such membranes are expected to be cost-effective.

From a risk perspective care has to be taken when nanoparticles may be released and thus an exposure of humans and/or the environment cannot be excluded. This applies to production as well as during handling and use. Particularly all materials in contact with water that are functionalized with nanoparticles must be subject to leaching tests and strict regulation. It must be ensured that no particles are released and/or that the particles used are non-toxic.

EU Competitive Position

There are several companies active in research in this area including companies with knowledge on thin films and silver technology from the photo-industry are using this expertise to develop functional membranes. Also some small to medium scale membrane companies have activities with nano-enhanced membranes while larger membrane producing companies are usually not active in this area.

Several universities and institutes are working on NEM. The Fraunhofer Umsicht (Germany) has created a platform with own series of conferences (**nANO meets water:** 3rd conference 10th November 2011, www.nano-water.de) Under the umbrella of "nano for water" (www.nano4water.eu) the EU is also financing projects on NEM.

Summary

- Nano-enhanced membranes combine nanotechnology with membrane technology to improve membrane properties and thus increase their performance.
- There are several very diverse approaches to integrate nano-objects into a membrane: CNT as pores; nanogels in pores; and TiO_2/ silver/CNT coated on or integrated into different membrane materials.
- There are no products on the market yet. The TRL is, depending on the method, between "basic research" and "pilot projects".
- Due to some remaining technical challenges it is estimated that nano-enhanced membranes will enter the market at the earliest in 5 years.
- Since nanoparticles may potentially be released from nano-enhanced membranes, special attention has to be given to risk assessment. Governments must enforce regulations to ensure the safety of such membranes particularly those in contact with drinking water.

Further information

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References

[1] Kim, J. and Van der Bruggen, B. (2010). „The use of nanoparticles in polymeric and ceramic membrane structures: Review of manufactureing procedures and performance improvement for water treatment." Environmental Pollution 158: 2335-2349
[2] Holt, J. K., Park, H. G., Wang, Y. M., Stadermann, M., Artyukhin, A. B., Grigoropoulos, C. P., Noy, A., and Bakajin, O. (2006) Fast mass transport through sub-2-nanometer carbon nanotubes. Science 312, 1034-1037
[3] http://www.nanowerk.com/news/newsid=20987.php
[4] EEB, "Challenges and opportunities to green nanotechnologies," Nanotechnologies in the 21st century, issue 1, 2009, http://www.eeb.org/index.cfm/activities/industry-health/nanotechnology/
[5] Supply, transformation, consumption - electricity - annual data [nrg_105a] EUROSTAT
[6] Electric Power Research Institute, Inc. (EPRI), 2002. "Water & Sustainability (Volume 4): U.S. Electricity Consumption for Water Supply & Treatment - The Next Half Century." Palo Alto, CA: 2000. 1006787
[7] Electricity - industrial consumers - half-yearly prices - New methodology from 2007 onwards [nrg_pc_205] EUROSTAT
[8] von Gottberg, A., Pang, A., and Talavera, J. L., 2005. "Optimizing Water Recovery and Energy Consumption for Seawater RO Systems." General Electric, TP1021EN 0510

Related EU-Project: Ambio (Advanced Nanostructured Surfaces for the Control of Biofouling: www.ambio.bham.ac.uk)

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