

Project context and main objectives

The main objective of the NATIOMEM project was to develop a novel photocatalytically active membrane for drinking and waste water treatment. The membrane consists of a porous substrate with a photocatalytic coating on the surface. The coating is made of nitrogen-doped titanium dioxide (TiON), which can induce photocatalysis by irradiation in the visible range of the solar spectrum.

The coated membrane should be integrated into a point-of-use treatment system for rural application in areas where electricity is not available, and for decentralized treatment of waste water for non-potable recycling.

Prototypes of the novel photocatalytic treatment should be constructed, tested and demonstrated. The combined filtration and oxidation process should trap and inactivate microorganisms, as well as mineralize chemical micropollutants. It was envisaged to develop the point-of-use treatment system into a technically and economically viable treatment option for:

- Production of safe drinking water from contaminated ground water and surface water after simple pre-treatment, in rural areas with limited infrastructure (*e.g.* no electric power grid).
- Disinfection of microbial unsafe piped drinking water.
- Treatment of grey wastewater after pre-treatment, for non-potable reuse.

In South Africa, the targeted application was local production of safe drinking water for people living in rural communities, which is around 38% of the South African population. The available raw water sources are rain, ground and surface water. Due to the lack of electric power and infrastructure, the photocatalytic membrane unit should be inexpensive and easy to use, and only require minimum maintenance. The treatment solution would provide the water supplier Umgeni Water with a treatment system suitable for remote villages within their region. When fully optimised and commercialised, the low-tech treatment unit should bring safe drinking water to villages also in other disadvantaged regions.

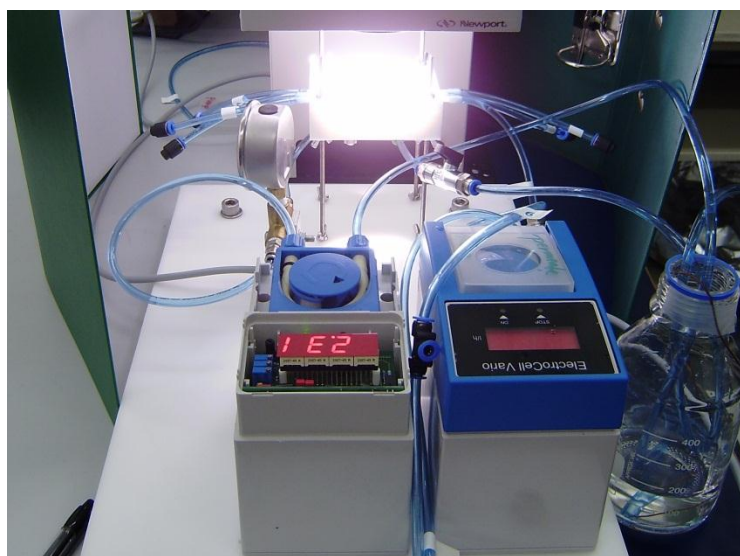
In Jordan, the government has issued an official strategy to reuse grey wastewater for non-potable purposes. The NATIOMEM consortium decided to develop a photocatalytic unit to treat domestic grey water. The design aims at a roof-top solution for urban areas. NATIOMEM's Jordanian end user partner Kawar Energy should promote the technology from their base in Amman. Decentralised reuse of treated grey water for toilet flushing and irrigation would reduce fresh water consumption and alleviate the drastic water scarcity in the region.

Work performed and main results

The NATIOMEM consortium applied several coating techniques such as sol-gel, sputter deposition, atmospheric pressure plasma jet and filtered vacuum arc deposition. Several of these techniques have produced TiON coatings with good photocatalytic activity (PCA) under solar irradiation.

The coatings were characterized with various techniques, such as X-ray photoelectron spectroscopy (XPS), X-ray Diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM), atomic force microscopy (AFM) and spectrophotometry. The findings regarding composition, structure and morphology were correlated to the coating parameters to optimize the coating processes. The analytical methods were also applied to identify contamination on the membrane substrates, and to verify the effect of methods for cleaning the membranes.

The TiON coatings were transferred to microfiltration membrane substrates, including ceramic and metal membranes. The photocatalytic activity of the coated membranes was quantified in the laboratory, using a custom-made flow cell equipped with a solar simulator. The main test parameter was photocatalytic degradation of the organic model pollutant carbamazepine (CBZ). The best results were achieved with a sol-gel coating on an aluminium oxide (Al_2O_3) membrane. Compared to undoped TiO_2 , the TiON-coated membranes had significantly higher photocatalytic activity when illuminated with the full solar spectrum, lower dependence on wavelength in the UV region, and some activity in the visible range of the spectrum. Also, a high inactivation of bacteriophages (model virus) could be achieved.



Laboratory testing of photocatalytic membranes at Tel Aviv University

The effect of physical and water quality parameters on the PCA of TiON coated membranes was investigated. Among the physical parameters were: wavelength dependence of PCA, transmittance of filtration cell cover, temperature, catalyst loading, filtration mode and water flux. The effect of the water quality was examined by addition of commonly found ions and natural organic matter. In this way, the boundaries for the applicability of the photocatalytic membranes were established. Also the efficacy of chemical cleaning agents was investigated for recovering the PCA after use. The coated membranes were furthermore characterised for pore size distribution, hydrophilicity, water permeability and retention of well-defined particles.

Based on the results from laboratory testing, three pilot plants with photocatalytic membranes were designed and constructed, each holding 16 coated membranes with a total effective area of 0.35 square metres. The pilot plants were set up in South Africa and Jordan, and used to quantify the performance of the coated membrane treating natural waters, to investigate fouling tendencies and to develop suitable cleaning strategies.



Installation of photocatalytic membranes into the pilot plant



Pilot plant with NATIOMEM membranes in Amman, Jordan

Performance on the pilot scale was less than in the lab. The normalised CBZ degradation rate was about an order of magnitude lower than in the laboratory. Also disinfection was less efficient, and produced conclusive results only when the water was passed over the coated membrane several times. Part of the explanation for the low efficiency of the pilot plants is the interference from constituents in pre-treated, natural feed water. Another major factor was the hydraulic conditions in the system. Lengthening retention time by reducing the flux in the pilot plants was not advantageous.

Even in low-fouling waters, dead-end operation at low-flux with simple pre-treatment caused heavy fouling. Cleaning in place (CIP) at low flux, with the same chemicals that were efficient in the lab, failed to restore the membrane permeability. Manual cleaning of the membranes was necessary in the pilot plants.

The poor hydraulic and photocatalytic performance in pilot-scale was analysed, and translated into updated recommendations for the design and the technical application of the coated membranes.

Expected final results and potential impact

A broad range of coating methods was applied in parallel to develop the photocatalytic TiON coatings for the membrane substrate. The coating laboratories at University Pierre & Marie Curie, University of L'Aquila and Tel Aviv University optimized the coatings for performance, and gained a deeper understanding of the fundamental properties of the materials.

In the course of the project, some novel coatings were developed. These include TiO₂/TiN bi-layer thin films created by RF reactive magnetron sputtering, and TiON formation by oxidation of titanium nitride (TiN).

The coatings developed within NATIOMEM also have potential for other applications, such as hydrogen production and 3rd generation low cost solar cells. The bilayer strategy developed during this project demonstrated effective separation between the photo-generated electron-hole pairs which enhanced photoactivity. This strategy can be applied to coat glass or quartz substrates, since very high photocurrents were obtained during water splitting measurements and further applications for hydrogen production could be developed.

To conclude, good progress was made within NATIOMEM on TiON doping and material science. The results on the coatings produced by the partners were published in seven peer-reviewed articles so far, and presented at numerous conferences and workshops.

In the laboratory tests, the photocatalytic membrane has shown promising performance for disinfecting drinking water. In the pilot plant tests, the low pressure, low flux, low fouling strategy proved to be ineffective. This makes the concept unsuitable for the envisaged low-tech application. The treatment unit would require more effective pre-filtration and the use of electric energy, which would also increase the cost.

After integrating the findings from the lab and pilot tests, the coated membrane has good potential for commercialisation. The involved coating and engineering partners have initiated a product development phase.