Story behind the paper: 'Photocatalytic degradation of steroid hormone micropollutants by TiO_2-coated polyethersulfone membranes in a continuous flow-through process', scheduled for publication in Nature Nanotechnology on 31 March 2022

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Catalyst for water – removing steroid hormone micropollutants in flow through photocatalytic membrane!

Being able to remove micropollutants from water is one of the greatest global challenges, as micropollutants are often endocrine disrupters that affect basic human function such as behavior development and fertility. In a time of rapid decline in sperm counts, the exposure to pollutants must be limited, both for humans and the environment where such pollutants accumulate and are known to, for example, turn male fish female. Steroid hormones have been our pollutant of choice since about 2000 when the topic 'toilet to tap' sparked a huge media outcry as a result of proposals to potentially reuse wastewater for drinking. Notably, wastewater is always reused for drinking, it just depends how long the cycle is before we drink the water again. Hormones are everywhere where human beings are as we excrete them naturally, as well as using them in agriculture and medical therapies.

Working a lot on nanofiltration, our work focused initially on removing micropollutants such as steroid hormones. This was partially successful, but it soon turned out that these micropollutants partition into polymeric membrane materials and gradually make their way through to the clean filtrated water. Also, even if removal is successful, a concentrate stream is produced that requires further treatment. Nanofiltration, by nature, needs quite a lot of energy as it operates with pressures in the order of 10 bar. Thus, a classic engineering solution just creates new problems!

The idea of photocatalytic membranes to destroy these micropollutants was born in the early 2000s, when my (now) husband, Bryce Richards, was cursing about the quality of his TiO_2 coatings for solar cells. I had a quick look at his SEM images and said – wow, great membranes – given the amount of holes in his (hoped-for-dense) thin films. We submitted a grant – our first one - to the Australian Research Council at the time, but were not funded and had no other means to carry out the work. So, we forgot all about this, even though we always knew it was a great idea – and got busy with other things.

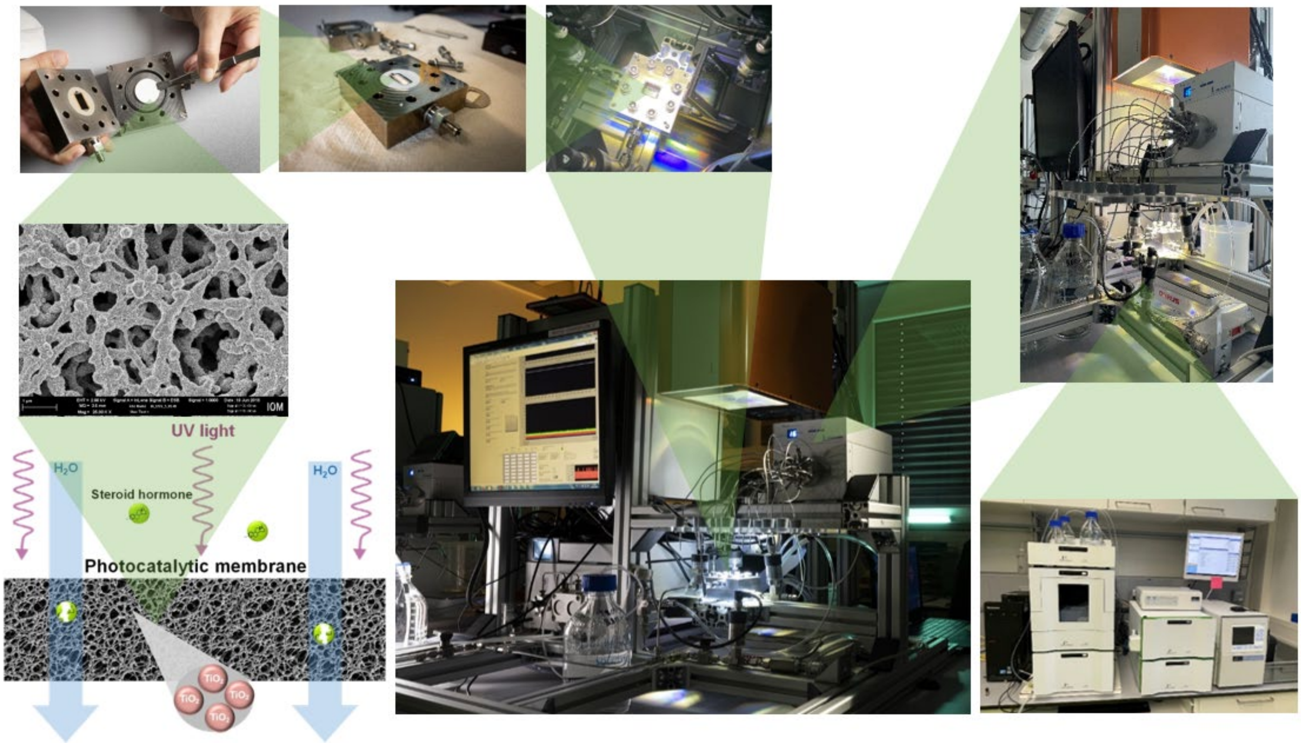
In 2014, I was invited to join a DFG consortium to work on a similar topic. I was invited primarily to add a female investigator to a group of 15 men. With a lot of engagement, I contributed great ideas and concepts, the consortium was funded, except for the project of the only woman! I declined the offer to be part of the consortium without funding and I decided to find ways and means to do the work anyhow. Instead, I found a number of great collaborators to develop the right analytical and membrane reactor tools. Clearly, it was the right time and the earlier set-backs have only served to fuel determination. The technical challenges to be overcome we could probably not have solved earlier.

Firstly, the analytical tool that we developed for steroid hormone analysis to the required sub-ng/L concentrations was liquid scintillation counting for radiolabeled steroid hormones. For photocatalytic degradation, this method is not suitable as the tritium is detected in both intact and degraded molecules. A separation step was required and it was hard work to make for this to succeed.

Secondly, photocatalytic membranes require light in a flow through cell to make use of the enhanced mass transfer in a micro- or nano-reactor (the pores of a microfiltration membrane are a few hundred nanometers in size, while for nanofiltration this is in the order of 1 nm or less). Small scale, small volumes, meaningful hydrodynamics and needing to get light into the system required a lot of collaborative efforts, in particular with Bryce Richards whose optics and solar energy harvesting knowledge once again came in handy.

Thirdly, choosing good membranes was critical and we are lucky to be able to produce or modify our own membranes and work with a number of great collaborators. In this case the membranes are produced at the Leibniz Institute of Surface Engineering (IOM) in Leipzig by Agnes Schulze and Kristina Fischer. Highly photocatalytic active TiO_2 nanoparticles are synthesized via hydrothermal synthesis and immobilized on microfiltration membranes. The material is simple and abundant.

In essence, we have been able to attain a steroid hormone removal such that the new drinking guidelines of 1 ng/L can nearly be achieved - the analytical detection limited of 4 ng/L was reached. Naturally, we are very proud of what we have achieved and this work is a huge milestone as well as a solid foundation for future developments.



Photocatalytic membrane filtration system with solar simulator, micro-crossflow cell operated in dead end mode membranes coated with TiO_2 nanoparticles at IOM, sampling through switching valve and analysis via

There is a myriad of possibilities to now create other materials that achieve the degradation to lower concentrations, even faster, at lower energy requirements at different wavelengths and using natural light, and perhaps most importantly, degrade other pollutants such as per- and polyfluoroalkyl substances (PFASs) or pesticides like glyphosate. Interference of real water contaminants, effectiveness in mixtures, potential generation of by-products especially when treating real waters, are topics that will keep researchers busy in the coming decade. The challenge to upscale photocatalysis considering the long term (5-10 year) stability of polymeric membranes and good engineering to guide the light into membrane modules require creative engineering minds. No doubt, ‘water catalysts’ are coming!

Read our paper in Nature Nanotechnology: https://www.nature.com/articles/s41565-022-01074-8 news & views

NANOFILTRATION

Membranes that filter and destroy pollutants

Decoration of nanofiltration membranes with catalysts lead to efficient removal and degradation of micropollutants.

Lidietta Giorno

Chronic exposure to trace micropollutants found in water, food and the environment poses a serious threat to public health and the economy. Indeed, some recalcitrant pesticides and hormones mimic neuronal receptors and can impair biological functions, causing cognitive and neuronal diseases. Removing and degrading these pollutants from the environment is challenging. Membrane technologies such as nanofiltration and reverse osmosis have been shown to be very efficient in removing small molecules from water[1–3]. Nanofiltration membranes can efficiently separate small molecules (>100 g mol^{-1}) and divalent ions thanks to size and charge-exclusion mechanisms. Reverse osmosis membranes can only pass water molecules through, while retaining even monovalent ions, thanks to their dense structure — with no discernible pores — and the solution/diffusion mechanism of molecules through the free volume of the polymer matrix in the membrane; therefore, these processes can efficiently remove micropollutants and purify water. The retentate (that is, the solution that remains upstream of the membrane) is, however, a concentrated solution of harmful micropollutants and, if not properly treated, can pose an even greater risk, with the overall result that the problem is simply transferred from one level to another.

To address this problem, micropollutants must not only be separated from water, but also eliminated by either degrading them to the point of mineralization or at least degrading them to harmless substances. The combination of catalysis with nanoengineered membranes makes it possible to simultaneously control mass transport and reaction rate at the nanoscale[4]. Nanostructured porous membrane matrices decorated with catalysts enable the creation of catalytic membrane reactors with a high surface-to-volume ratio, where each nanoscale pore acts like a continuous microreactor, making the overall membrane an extremely efficient high-throughput system[5]. Considerable research efforts have been devoted to the development of different types of catalyst (inorganic, organic, biological) loaded into polymeric and inorganic membranes, and also, combined with UV radiation, advanced oxidation processes for degradation of various micropollutants from water[4].

Andrea Schäfer and her colleagues have been working intensively on the degradation of micropollutants[6,7], and as they describe in *Nature Nanotechnology*, have recently demonstrated the high efficiency of a photocatalytic membrane reactor composed of TiO_2 nanoparticles deposited on the surface of porous polyethersulfone membranes (PES) for the degradation of steroid hormones (SHs) under UV light[8]. Although previous studies used either the catalyst or the membrane,

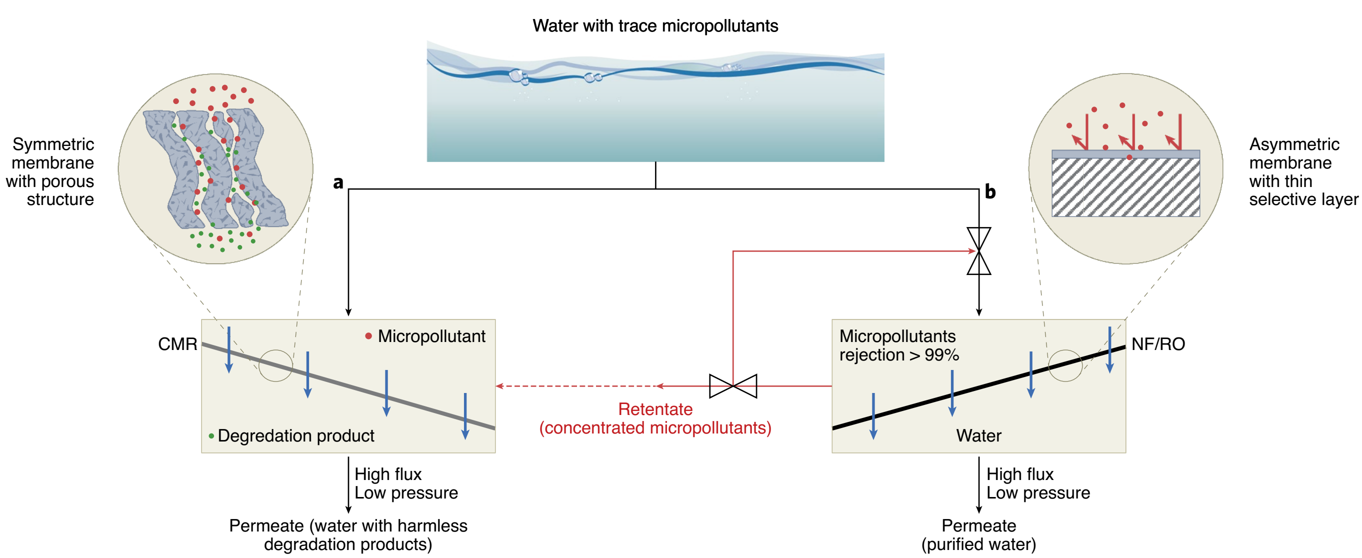


Fig. 1 | Illustration of the possible process routes for the treatment of water containing micropollutants. a, Water can be treated directly in the catalytic membrane reactor (CMR) if degradation of the micropollutants leads to their complete mineralization or to harmless intermediates. Schäfer and colleagues achieved 94% degradation of β-oestradiol in a photocatalytic membrane reactor. **b**, If the toxicity of the intermediates is uncertain, water for potable use can be purified by nanofiltration (NF) and/or reverse osmosis (RO) (rejection higher than 99% can be achieved), and the micropollutants concentrated in the retentate can be treated in the CMR to reduce their hazard.

the key combination of the 10-nm catalyst nanoparticles and their uniform distribution within the nanostructured porous membrane — with a pore size of 220 nm — together with tuned chemistry and fluid dynamics through the pores, resulted in an unprecedented 94% degradation of the hormone oestradiol at a residence time of 6.2 s (60 l m^{-2} h) and 44 mW cm^{-2} in continuous single-pass operation mode.

The study confirmed that the nanoscale structure of the photocatalytic membrane reactor improves the contact between reagents and catalyst even at a very low — but environmentally relevant — micropollutant concentration of 100 ng l^{-1}. Systematic characterization of the charge of various components as a function of pH allowed the team to clarify the conditions under which electrostatic repulsion leads to inefficient utilization of the reactive oxygen species generated by the photocatalytic reaction.

Schäfer and colleagues also found that the adsorption of the micropollutant on the membrane surface (decorated with TiO_2 catalyst) and the dissolved oxygen concentration controlled the photocatalytic removal. In fact, the rate of micropollutant removal increased with decreasing temperature, with a removal of micropollutants nine times higher at 11 °C than at 62 °C. This is because although diffusivity increases with temperature, surface adsorption of micropollutants and oxygen solubility decrease with increasing temperature.

It is interesting to note that a good removal rate was obtained in the temperature range of 10 to 25 °C, which implies that the photocatalytic membrane reactor can be operated with low energy consumption. The use of microfiltration PES membranes by Schäfer and colleagues was helpful in demonstrating that the technology can benefit from state-of-the-art commercial products. However, the adaptation of a membrane structure originally developed for a different application leaves room for improvement of the photodegradation reactor system by ad hoc-designed membranes with tailored thickness, channel tortuosity and hierarchical porous structure, allowing the adjustment of residence time, pressure, reagent concentration and product removal. It is expected that almost complete degradation of micropollutants can be achieved in the continuous single-pass flow-through reactor, where the reaction can be shifted to the left according to the Le Chatelier principle by removing the reaction product.

The work of Schäfer and colleagues has shown that it is possible to obtain high degradation of β-oestradiol at high flux through the membrane, thus preventing its accumulation in the retentate stream. The conversion of micropollutants into harmless substances is an important issue. Whether the technology is used for direct water treatment or whether the water is first purified (for example, by nanofiltration and/or reverse osmosis) and the micropollutant-enriched retentate solution then treated (Fig. 1) depends largely on the nature of the substances produced in the photodegradation process, an aspect that has not yet been fully clarified and requires a significantly greater research effort. ❐

Lidietta Giorno ✉
National Research Council of Italy, Institute on Membrane Technology (CNR-ITM), Rende, Italy.
✉*e-mail: l.giorno@itm.cnr.it*

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Competing interests

The author declares no competing interests.