Book of Abstracts

Nanofiltration 2022: Principles, Applications and New Materials

26-30 June, 2022
Achalm (Reutlingen), Germany

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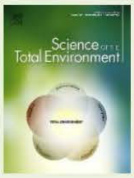

Science of the Total Environment

Separation and Purification Technology

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Nanofiltration 2022 Achalm, Reutlingen, Germany, 26–30 June 2022 — Introduction & Welcome

We made it! The Covid pandemic resulted in two postponements – from 2020 to 2021 and then 2022 – however these were needed for the book to be published (in August 2021, eventually) and the IAMT team to grow into the task of organising a conference. Two great team building weeks took place in lieu of the previous conferences.

We are welcoming about 125 participants to the Achalm in Reutlingen, Germany. This town – Reutlingen – in the Schwäbische Alb is my home. The place where I was born, educated in schools, gained good navigation skills with bike touring, developed leadership skills in church youth work and the character that has become my 'can do' and 'don't take no for an answer' signature. This is where I decided to become an engineer and discovered membranes, while living, working and training in a company called Berghof in the Arbachtal. At the young age of eight years I met Heiner Strathmann and before the end of high school Rudolf Graf showed me the fabrication of tubular UF membranes. Both are honoured guests at Nanofiltration 2022. After 20 years of international travel and working in truly amazing places around the world, I appreciate this region with its natural beauty. It is a wonderful dream come true to welcome my community of international membrane colleagues to my home. I hope that participants will enjoy the small selection of this special culture that we could incorporate in the programme.

The response to Nanofiltration 2022 has been amazing and despite many global regions still facing Covid restrictions that do not permit travel and participants not yet being comfortable with travel, we are full, in fact over-full, and are looking forward to stimulating discussions, fun activities and networking.

The book of abstracts of Nanofiltration 2022 is a snap shot of conference participant contributions. At this conference we do not have full proceedings, but there is the (signed!) ***Nanofiltration: Principles, Applications and New Materials*** book that participants receive and there will be a special issue launched after the conference entitled **Nanofiltration in the Global Water Cycle** in the open access *Nature Partner Journal Clean Water*, for which a considerable number of publication wavers will be available to conference participants.

Why so much interest in nanofiltration and why a separate conference?

Reverse osmosis with its thin film composite membranes is a well-established and unrivalled technology for seawater desalination. Ultrafiltration, with a more diverse choice of membrane materials and properties is the perfect choice for physical water disinfection. In between, nanofiltration offers a myriad of opportunities of separations at the nanoscale. These separations require a fundamental understanding not only of flow and interfacial phenomena in the pores – from two nanometres to subnanometer scale – but also of solute characteristics and interactions from molecular or ion properties through to dehydration and ion pairing. Such understanding is required to inform novel material developments as well as successful applications. Not only will such molecular phenomena reach the limits of our understanding, but also question the validity of assumptions that underpin common models.

The NF2022 conference aims to bring these topics together such that understanding can be enhanced and new ideas be stimulated. An opening and fourteen sessions with over sixty invited lectures and orals as well as over sixty posters make for an exciting programme.

Session 1: The Case for Nanofiltration: From Climate Change to Micropollutants

Session 2: Nanofiltration: Opportunities and Limitations for Water & Environment

Session 3: Nanofiltration Applications I: Water Treatment

Session 4: Nanofiltration Principles: Characterization/Fouling/Scaling

Session 5: Nanofiltration Principles: Transport Mechanisms

Session 6: Nanofiltration Principles: Nanofluidics

Session 7: Nanofiltration Applications II: Industrial & Resource Recovery

Session 8: Publish or Perish: Hot Topics in Publishing

Session 9: Nanofiltration New Materials I

Session 10: Nanofiltration Applications III Desalination & Reuse

Session 11: Nanoscale Imaging

Session 12: Nanofiltration New Materials II

Session 13: Renewable Energy & International Development

Session 14: The Potential of Nanofiltration for International Development

A big thank you to participants and friends for coming and taking part. Sponsors are supporting us in many different ways, which allowed us to waive a substantial number of registration fees for colleagues, have a live band and many other cool events: DOC Labor (Germany), Anton Paar (Austria), IFTS (France), Convergence (Netherlands), Dupont (Germany), BCC Research (USA), Undine Award (Germany), Wiley-VCH (Germany), European Membrane Society (EMS) for travel awards, *npj Clean Water* for many waivers for the forthcoming special issue, and *Nature Nanotechnology/Water* as well as Elsevier Journals *Science of the Total Environment, Separation & Purification Technology* and *Journal of Membrane Science* for oral and poster prizes, as well as Beckabeck (Germany) for a huge and most delicious cake.

Thanks also go to: Simon Scheuerle from KIT Events for handling our complicated registrations, the Achalm Hotel for hosting us, meeting many demands and delaying two times at zero costs (losing both income and staff). The DFG for supporting the conference and a number of international collaborations with grants – we hope that one day we will be able to access the funds that were granted despite impossible internal bureaucracy. Dr Fabio Pulizzi for chairing a session on publications. The IAMT team for being part of the organization and as a reward being able to all take part in the conference. A special mention goes to Dr Youssef-Amine Boussouga who has carried the lion's share of the organisational effort taking many tasks off my desk and patiently facing new challenges such as budgeting. The ultimate gift of this support was the fact that I could travel in the week prior to our meeting to participate in Miriam Balaban's EDS conference in Las Palmas and enjoy a heart-warming celebration of our inspiring 'Desalination Icon', who is blessing us with her participation at NF2022.

If I may express a wish then that is for our community brings all the talent together to solve one of our greatest societal challenges: providing safe water for all.

Happy nanofiltering!

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ABSTRACTS

I. Nanofiltration: Opportunities and Limitations for Water and Environment

The EU Globaqua project on multiple stressors in rivers under water scarcity and global change. Results of a reconnaissance study in selected European rivers and the need for advanced water treatment solutions

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Most ecosystems are exposed simultaneously to several stressors, in the so-called multiple-stress situation. Some stressors such as water scarcity can limit biodiversity and economic activities in entire regions. In addition of being a stressor on its own, water scarcity can drive the effects of other stressors acting upon river ecosystems. It leads to intermittency in water flow, and therefore has implications for hydrologic connectivity, negative side-effects on biodiversity, water quality, and river ecosystem functioning. Water scarcity can amplify the effects of water pollution by reducing the natural diluting capacity of rivers Interactions between stressors may be exacerbated by climate change. For instance, warmer temperatures and reduced river flows will likely increase the physiological burden of pollution on the aquatic biota, and biological feedback between stressors (e.g. climate change and nutrient pollution) may produce unexpected outcomes. Degradation of drainage basins, destruction of natural habitats, over-exploitation of fish populations and other natural resources, or the establishment of invasive species, are factors whose impacts combine and may give rise to synergistic effects, especially during periods of water shortage. The effects of these stressors are very relevant for the chemical and ecological status of water bodies as well as for the sustainability of ecosystem services they provide

Water scarcity is a key stressor with direct and indirect effects. The relevance of water scarcity as a stressor is most important in semi-arid regions such as the Mediterranean basin, characterized by highly variable river flows and the periodic occurrence of low flows and even no-flows. Climate change previsions forecast an increase in the frequency and magnitude of extreme events. Although extremes are part of the normal hydrologic behaviour in Mediterranean-type rivers, many already show a consistent trend towards decreased discharge.

This presentation will show different examples on the risk of emerging contaminants, nanomaterials and microplastics in Mediterranean river catchments affected by water scarcity. For example, the relevance of environmental factors (light, temperature, water flow) and chemical stressors (nutrients, pharmaceuticals, endocrine disruptors, pesticides,

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perfluorinated compounds and heavy metals) in the structure and functioning of epilithic biofilms in several Mediterranean watersheds, Ebro, Guadalquivir, Jucar, Llobregat and Evrotas, and others like Adige and Sava will be shown. Stressors co-occur and interact in specific manners, and the respective relevance of one or another in the response of the biota may be altered also by the flow regime.

As major conclusions of this reconnaissance study shows that under extreme events pollutants effects on the biota are more relevant that under regular river flow conditions. Flash -flood events will mobilize pollutants from sediments with an increase of bioavailable chemicals in the surface river. Under water scarcity there are combined effects of stressors, chemicals and water flow, affecting biota. Lastly, wastewater treatment plants (WWTPs) discharges affect river macroinvertebrate river biodiversity and pollutants discharged are bioaccumulated in fishes.

To overcome pollution problems in rivers under climate change effects, new solutions are required to improve river water quality and quantity like the use of advanced water treatment options. The thing is that conventional WWTPs were not designed to remove some organic compounds such as emerging pollutants. A wide array of micropollutants are usually found in WWTP effluents, so there is a need to develop and evaluate alternative treatments which could be efficient for their elimination. In short, several advanced treatments such membrane bioreactors (MBR), nanofiltration/ultrafiltration, reverse osmosis, eco-friendly- technologies likes algal-based solutions and advanced oxidation processes like photocatalysis that could improve the removal of many emerging pollutants and thereby diminish their presence in surface waters. An overview of the different water treatment technologies with practical examples will be reported. Lastly by improving the water treatment the river water will be less toxic on the biota downstream. By doing this we are providing an additional source for different reuse options, like agriculture or groundwater recharge being one of the mitigation strategies against climate change and water scarcity.

Plastic litter as raw material (source) for wastewater treatment and a fresh report from the Danube challenge https://www.cleandanube.org/?lang=en

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Plastic use continues to increase worldwide. Most of these plastics are only single used plastics. From1950 until 2015 8.3 Billion tonnes of Plastic were produced. After the use of these polymer products they end up mainly in land fill (79%). Only 9% are going to be recycled and the remaining 12%are combusted. Extrapolating the production rates of synthetic polymers, a worldwide mass of 34 billion tonnes will be produced until 2050. According to this development marine litter is ever increasing and consists of up to 80% of plastic. Accumulation of plastics due to its land based and maritime disposal is therefore recognized as one of today's major marine and within waters quality problems.

Without a dramatic increase of the worldwide recycling ratio of plastic products the negative effects on aquatic life and ultimately on human health at the end of the food chain can' t be reversed.

In nature anthropogenic debris have the potential to attract some of the pollutants from the chemical cocktail in river or marine waters. In addition to the ingredients of the debris itself the adsorbed pollutants can transfer from debris to fish, bivalves, shellfish etc. upon ingestion.

This contribution uses the adsorptive effect of small plastic litter, the so called microplastic, in order to remove chemicals from polluted waste water. The micoplastic filters are generated in a simple way using Makroplastic litter by disolving the material and direct precipitation in a second solvent. Applying this low cost process microplastic particles with very high surface areas can be produced (Fig. 1).

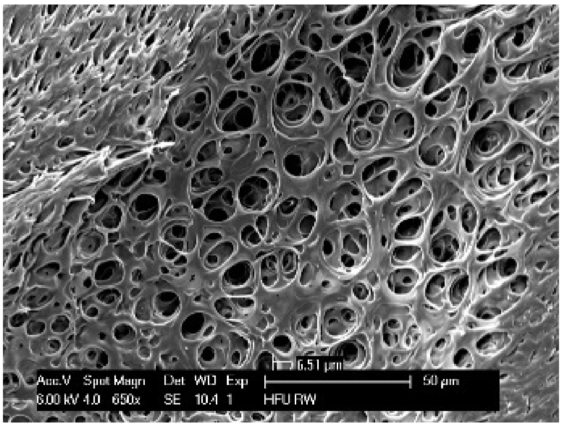

Fig. 1. SEM Image of a PA12 Micorplasticparticle

The low energy input in this process is considered as central economic criteria when it comes to recycling. As long as it is cheaper to produce petrol based plastic, instead of recycling plastic, there will be no increase of the recycling rate without legal regultions. Economic incentives are needed.

Keywords: Membranes; X-ray; Synchrotron; Imaging; Advanced characterization

Membrane technology in German water treatment: overview and historic development

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Membrane technology is used in German water treatment for two main purposes: removal of particles, turbid matter and microorganisms by microfiltration (MF) or ultrafiltration (UF) and removal of dissolved solids (e.g. salts, natural organic matter, micropollutants) by nanofiltration (NF) or low pressure reverse osmosis (LPRO).

Since 1998 more than 300 MF/UF-plants with a total capacity of 30,000 m^3/h were installed in water works of the public drinking water supply. Raw water resources are surface waters (river, lake, dam) and spring waters or well waters that are influenced by surface waters.

Most membranes do not remove substances selectively: MF/UF membranes remove particles larger than their pore size, NF/LPRO membranes remove substances larger than their molecular weight cut-off.

If coagulants are dosed into the feed of UF plants, it is possible to remove dissolved organic matter, such as humic substances as they are caught in the flocs formed with the coagulant and then being removed by sieving. The same principle also works for the removal of arsenic ions and other heavy metals. A couple of UF plants are operated especially with this objective.

The main application of NF/LPRO in Germany is softening of ground waters exhibiting a rather high hardness. A survey in 2021 showed that there are around 80 to 90 NF/RO-plants in operation or under construction in public drinking water supply in Germany with a total capacity of about 10,000 m^3/h [1]. However, there is a lot of discussion about using these processes for the removal of micropollutants, as there are some major drawbacks: the required usage of antiscalants and high concentrations of salts and micropollutants in the concentrate make its discharge into the environment complicated as authorities are uncertain how to deal with these issues. Within the research project "KonTriSol" different approaches to challenge these issues are being tested, e.g. the post-treatment of concentrates or strategies to minimize antiscalant-usage (closed circuit reverse osmosis).

Keywords: Membrane filtration; Drinking water treatment; Historic development

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Gravity-driven membrane filtration as nanofiltration pre-treatment: Effect of space reduction for biofilm growth and second-life membranes on flux performance and biopolymers removal

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Biopolymers (proteins and polysaccharides) play a major role in nanofiltration fouling. As biopolymers are poorly removed by conventional ultrafiltration (20-40% removal) but could be biodegraded by biofilm-membrane composites, a pre-treatment by gravity-driven membrane (GDM) filtration could be a strategic approach to improve nanofiltration performances. However, successful implementation requires to address two main challenges: (1) increase the GDM process compactness and (2) reduce GDM membrane capital expenditures (CAPEX). In the present study, we showed that the lower the space available for biofilm growth, the lower the flux of GDM filtration. For compact membrane geometry, i.e., inside-out hollow fiber membranes, we observed that maintain stable fluxes was only possible with biofilm basal layer destabilization via a mechanical biofilm growth control (daily gravity-driven backwash). The biofilm growth control strategy led to limited production loss (3%) and didn't impact the CAPEX and operation costs, given that the

backwash was gravity-driven. We therefore demonstrated that GDM filtration with compact membrane geometry was feasible. In addition, we showed that it was possible to considerably reduce membrane CAPEX using second-life membranes, i.e., recycled membranes from the drinking water industry, without decreasing the process performances. These membranes only had a flux 13 lower than new membranes. With calculations, we quantified that the use of second-life membranes would drop membrane CAPEX by 79.2% and 29.9 in comparison to GDM filtration with new membranes and to conventional ultrafiltration, respectively. Finally, we systematically studied the long and short-term effect of removal of different amount of biofilm on the biopolymer elimination by GDM filtration with second-life membranes. Irrespective the amount of biofilm removed by the backwash, the biopolymers were eliminated by 65%, showing that implementing GDM filtration with second-life membranes and daily gravity-driven backwash is a promising approach for nanofiltration pre-treatment.

Keywords: Nanofiltration pretreatment; Gravity-driven membrane filtration; Limited space for biofilm growth; Membrane capital expenditures

Recent advances of emerging pollutant mitigation in decentralized wastewater treatment processes: Potential of nanofiltration

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Emerging pollutants (such as micropollutants, microplastics) present in wastewater are of rising concern because their release can affect the natural environment and drinking water resources. In this decade, with increasing numbers of small-scale decentralized wastewater systems globally, the efforts on investigating emerging pollutant mitigation in the decentralized wastewater treatment processes has dramatically increased. This presentation aims to provide a comprehensive review on the mitigation efficiencies and mechanisms of micropollutants and microplastics in single-stage and hybrid decentralized wastewater treatment processes. As illustrated in previously documented studies, hybrid wastewater treatment facilities could display better performance compared to stand-alone facilities. This is because the multiple treatment steps could offer various microenvironments, allowing incorporating several mitigation mechanisms (such as sorption, degradation, filtration, etc.) to remove complicated emerging pollutants. The factors (such as system operation conditions, environmental conditions, wastewater matrix) influencing the removals of emerging pollutants from wastewater have been evaluated in terms of various treatment processes. In particular, nanofiltration based small-scale treatment facilities for water reclamation will be further discussed. Nevertheless, there is still very limited research work relating to synergised or conflicted effects of operation conditions on various emerging pollutants naturally present in the wastewater. Meanwhile, effective, reliable, and rapid analysis of the emerging pollutants in the complicated wastewater matrix is still a major challenge.

Keywords: Decentralized wastewater treatment; Microplastics; Micropollutants; Mitigation mechanisms

Micropollutants removal and partitioning in hybrid nanofiltration process

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More than 150 million of chemicals have been discharged in the environment in the last two decades, which exposes both humans and biota to a real and complex cocktail of pollutants globally distributed [1]. Anthropogenic organic chemicals, like pesticides, pharmaceuticals and per-fluorinated compounds (PFAS) as well as natural excreted pollutants, like steroid hormones, are ubiquitously found in water [2, 3].

While NF is proofed to be an effective process for the removal of pharmaceuticals (>90%) and pesticides (> 70%) due to interplay of size exclusion and/or charge repulsion [4, 5], there are still drawbacks for steroid hormones and PFAS.

NF is shown to be effective for concentration of long-chain PFAS in the retentate (range 90–99%) while retention of short-chain PFAS (carbon<6) is lower in a range of 30 to 70% due to reduced size exclusion [6]. Treating and disposal of PFAS contaminated concentrate remains still a challenge due to the high persistence to degradation of these contaminants

and combining NF with advanced technologies is suggested as promising solution [2, 7]. Steroid hormones removal by NF is not effective to meet the latest European drinking water guideline (EU, 2020/2184) of 1 ng/L of 17β estradiol for drinking water and 0.4 ng /L for surface water due to the breakthrough curve phenomenon [8, 9], which requires specific design of NF membranes with stronger binding property able to increase the energy barrier for transport.

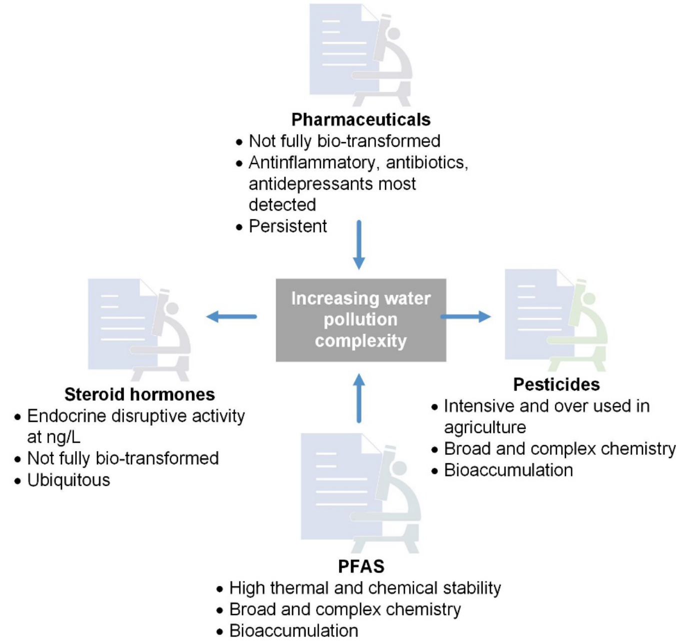

Fig. 1. Water pollution complexity and challenges for membrane technology.

Keywords: Steroid hormones; Per-fluorinated chemicals; Micro-nano plastics; Breakthrough curve; Hybrid process

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Nanofiltration of surface water with high organic content for reserve water supply

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High concentration of natural organic matter (NOM) is one of the main issues with surface water in Norway. Climate change leads to a rapid increase of NOM content in water supply sources, thus challenging drinking water treatment plants that use conventional coagulation and activated carbon adsorption. The new Norwegian drinking water regulation (2017) raises additional preparedness requirements to the treatment plants. Municipalities got the responsibility to provide solutions for reserve water supply, however many of them do not have an effective solution for reserve water supply. The objective of this study was to evaluate nanofiltration (NF) as a possible solution for reserve water supply using surface water with high NOM content. This goal was achieved by studying hydraulic and NOM retention performance of different NF membranes under various conditions of the pilot plant operation.

We carried out the pilot study during Feb-Mar 2019 at the Halden drinking water treatment plant using water from Femsjøen lake. During the pilot tests, the average water colour was at 37.2 mg-Pt/L, TOC 8 mg-C/L and turbidity 1.8 NTU. Four different NF spiral-wound elements were tested for 12 d each: SBNF (Trisep), NP010 (Nadir), Filmtec NF270 and NF90 (Dupont). Thus, we tested hydrophobic polyethersulfone, hydrophilic cellulose acetate and polyamide thin-film composite membranes with different molecular weight cutoff (200–2000 Da) and selectivity towards divalent ions (5-96%). The pilot unit was operated at constant pressure varying in three periods: 3, 4 and 5 bar. Flows were continuously recorded by digital flowmeters and used to calculate respective flux and permeability. In addition to TOC and TDS, the concentration of biologically degradable organic carbon (BDOC) was measured in permeate.

The results of the study show high removal of NOM by all the studied NF membrane elements. However, hydrophilic polyamide NF90, NF270 and cellulose acetate SBNF membranes demonstrated the highest TOC reduction rates: 97.5%, 95.5% and 93.9% respectively. The hydrophobic polyethersulfone membrane NP010 achieved only 83% reduction of TOC and experienced rapid fouling during the start of the operational period. With the best TOC reduction rate, NF90 was producing permeate at 15–30% lower flux than NF270. Three membranes NF90, NF270 and SBNF achieved low residual concentration of BDOC in permeate: <0.15 mg-BDOC/L for NF90 and NF270, while 0.18 mg-BDOC/L for SBNF. The concentration of BDOC after NP010 was significantly higher — 0.3 mg-BDOC/L. High BDOC removal rates indicate a low supply of organic carbon to the heterotrophic microorganisms and a low potential of biological growth in case of permeates after NF90 and NF270.

This study demonstrated that nanofiltration applying spiral-wound elements with hydrophilic polyamide thin film composite and cellulose acetate membranes is an effective solution for reserve water supply when surface water with high colour and TOC is used. It can achieve high TOC retention and sufficient removal of biologically degradable organic carbon from permeate at moderate membrane fouling rates.

Keywords: Nanofiltration; Drinking water; NOM; Reserve water supply

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Implementation challenges facing effective membrane-based groundwater remediation strategies in Bihar, India

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Contamination of groundwater from geogenic pollutants, such as arsenic and fluoride, is a major public health challenge impacting millions of people globally. Although a number of remediation technologies exist, including NF and/or RO-based systems, effective remediation can remain very challenging, particularly in rural or developing settings [1]. Using a case study in Bihar, India, we will provide an overview of remediation options and discuss some of the

implementation challenges regarding NF/RO-based systems in particular, including variable effectiveness, operational limitations, maintenance, monitoring, waste disposal, socio-economic barriers and/or access constraints. This presentation will highlight field results obtained from various types of NF/RO-based remediation systems currently in operation in Bihar, which indicate highly variable performance with regard to the removal of arsenic (retention ranging from ~ 40 to > 95 %) and other contaminants and high dependency on source water composition (particularly iron and phosphorus). Further, observed trends regarding cation and anion selectivity raises interesting questions for future research regarding if mechanistic trends related to dehydration observed in previous laboratory [2] and modelling-based studies [3] might also be applicable in field settings which are inherently far less controlled (*e.g.* complex water matrices, variable operating parameters, unknown membrane characteristics). The gap between technology availability and successful implementation in practice highlights the need for improved and locally-relevant technology selection and management strategies.

Keywords: Arsenic; Groundwater; Remediation; Implementation; Ion selectivity; Dehydration

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II. Nanofiltration Principles: Nanofluidics and Transport Mechanisms

Nanofluidic transport across nanoporous atomically thin graphene and its development as a next-generation membrane

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Nanoporous atomically thin graphene, wherein nanopores in the two-dimensional graphene lattice provide pathways for rapid and selective fluidic transport, constitutes the thinnest possible membrane and has potential for improving the efficiency, selectivity, productivity, versatility, and chemical resistance for a variety of membrane separations. Through controlled nucleation of defects via ion bombardment and oxidative etching, sub-nanometer pores are created in a single layer of graphene placed on a porous support. We discuss strategies for the design of membranes that are tolerant of defects in the graphene layer, and show that appropriate choice of the porous support is critical for exploiting the selectivity of nanoporous graphene. We further demonstrate that the impermeability of graphene can be exploited to selectively seal defects and tighten the pore size distribution to greatly improve its selectivity. Through these developments, we are able to realize centimeter-scale graphene membranes that show high selectivity between ions, molecules, and proteins for nanofiltration and dialysis, and ultrahigh permeance in organic solvent nanofiltration. These studies illustrate the interplay between material structure and transport in nanoporous graphene and demonstrate its potential for the realization of next-generation membranes for addressing emerging needs in water purification, resource recovery and recycling, and energy-efficient separations that demand the ability to operate under harsh conditions.

1.5 nm diameter carbon nanotube porins as model nanofluidic channels

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Controlling molecular transport on a molecular scale is important for the next generation membrane separations. Living systems move ions and small molecules across biological membranes using protein pores that rely on nanoscale confinement effects to achieve efficient and exquisitely-selective transport. Carbon nanotube porins (CNTPs)—pore channels formed by ultra-short carbon nanotubes assembled in a lipid membrane—can exploit similar physical principles to transport water, protons, and small ions with efficiency that rivals and sometimes exceeds that of biological channels. I will discuss the role of molecular confinement and slip flow in 1.5 nm diameter CNTPs pores and show how it can enhance water transport efficiency and influence the mechanisms of ion selectivity in these pores. In particular, I will highlight the mechanisms of ion selectivity and the importance of electroosmotic coupling in these nanofluidics channels. Overall, carbon nanotube porins represent simple and versatile biomimetic membrane pores that are ideal for studying nanoscale transport phenomena and building the next generation of separation technologies.

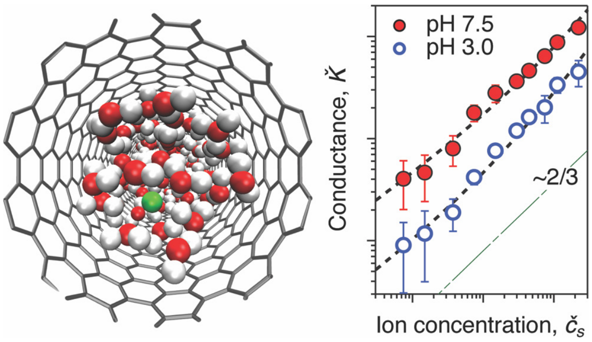

Fig. 1. (Left) A snapshot of the molecular dynamics simulations of water and ions in a 1.5 nm CNTP. (Right) Ionic conductance of 1.5 nm CNTPs.

Keywords: Nanofluidics; Carbon nanotube porins; Electroosmotic coupling

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Voltage induced reverse osmosis (VIRO)

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Worldwide access to fresh water is one of the key challenges of our modern society. The oceans represent 97% of the water on earth, making them the world's largest source of water. However, desalination of salted water is an energetically costly process usually carried out by reverse osmosis (RO). On the other hand, unsalted water sources such as rivers face the problem of the presence of micropollutants, present even after conventional treatments. In order to avoid the use of high pressure inherent to RO, we developed Voltage induced reverse osmosis (VIRO), a new technique for water filtration & desalination based on nanofluidic transport through composite membranes. This process exploits electro-osmosis and selectivity of nanostructured membranes. An electro-osmotic water flow is maintained in the first layer by applying an electric field on both sides of the membrane, while the selectivity of the second layer allows the filtration of micropollutants/salts. The performances of this process are discussed and compared to conventional techniques.

Keywords: Nanofluidics; Electroosmosis; 2D materials; Composite membrane

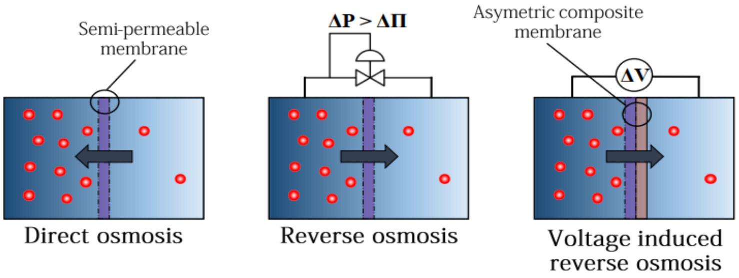

Fig. 1. Schematic representation (from left to right) of direct osmosis, reverse osmosis and voltage induced reverse osmosis

Electrodynamics of water at the nanoscale

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I will present the latest understanding of the structure and molecular dynamics of water from the viewpoint of condensed matter physics and based on the state-of-the-art experimental spectroscopic data available [1]. I will discuss the role of the quantum effects for the electrodynamics of water from direct current to terahertz that determine its spatial-time heterogeneity. Using this notion, I will demonstrate an approach that sheds light on the anomalous properties of water at the nanoscale, suggesting some new ideas for further interdisciplinary research. Finally, I will give some practical extensions of the fundamental physical models towards their applications in energy systems and nanofiltration.

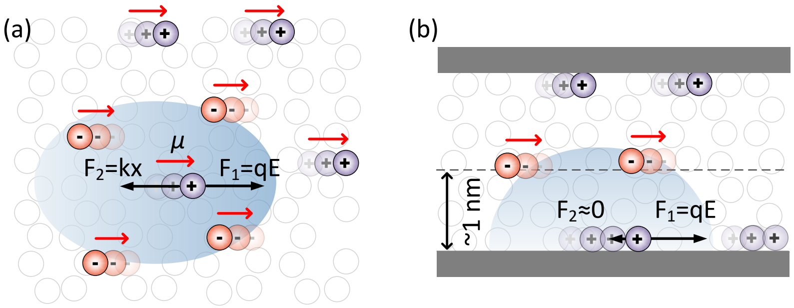

Fig. 1. Instantaneous structure of bulk water ($\varepsilon = 80$, low σ_{dc}), and b interfacial water ($\varepsilon << 80$, high σ_{dc}). Colored circles are short-lived spontaneously formed ionic species of H_3O^+ (excess proton) and OH^- (proton hole). White open circles are neutral water molecules. The blue "cloud" is the ionic atmosphere. F_1 and F_2 are the driving and restoring (friction) forces, respectively. The red arrows are the effective dipole moments μ due to the relative displacement of ions caused by external field.

Keywords: Water; Electrodynamics; Strong confinement; Protonic transport; Dielectric properties; Nanofluidics

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Electrical conductance of charged nanopores

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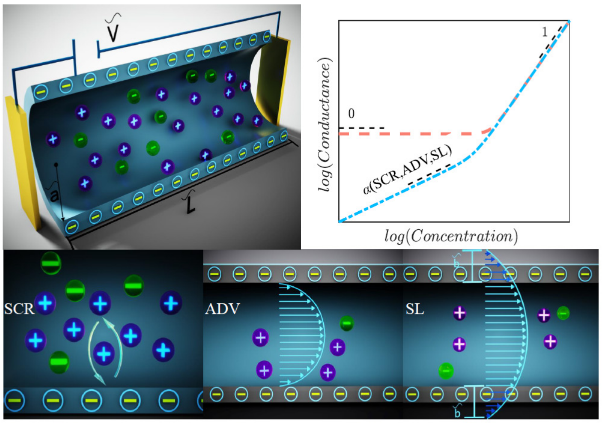
The nanofluidic's community paradigm that the low-concentrations conductance is concentration-independent is under scrutiny. Recent works have shown that the conductance depends on the concentration and that the slope, α, ranges between zero and one-half [1–3]. However, experiments have also measured slopes of two-thirds and unity [4,5]. In this talk, I will present novel results from our new comprehensive analytical model [6,7]. Our new model accounts for surface charge regulation (SCR), advection (ADV), slip-lengths SL), and the interplay of these mechanisms. We show that surface charge regulation predicts slopes of α between zero and one-half. Upon inclusion of convection combined with a slip length, the slope doubles from α to 2α. Importantly, our model, free of fitting parameters, shows remarkable correspondence to numerical simulations and predicts that the previously mentioned slopes of 0, 1/3, 1/2/, 2/3, and 1 are particular solutions of the more general solution that predicts that the slope ranges between zero and one. Consequently, our results imply that all three phenomena are essential in all nanofluidic systems' design stages.



Keywords: Nanofluidics; Ion-transport; Electrical conductance

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Next-generation desalination and water purification membranes: Where are we now?

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Water scarcity is one of the greatest global crises of our time. Increasing water supply beyond what is available from the hydrological cycle can be achieved by seawater desalination and wastewater reuse. Highly effective, low-cost, robust membrane-based technologies for desalination and wastewater reuse are needed, with minimal impact on the environment. However, progress in current state-of-the-art water purification membranes has been limited. This presentation

will critically discuss and evaluate recent research efforts in the past 15 years to (i) lower energy consumption for water desalination by improving membrane water permeability, (ii) reduce the cost of water desalination via increased water-salt selectivity, and (iii) enhance membrane ion-ion selectivity for applications at the water-energy nexus. The presentation will focus on the emerging area of ion-ion selectivity, where high precision ion separation is desired. We will highlight how insights from nanofluidics and ion-selective biological channels establish the basis for a new class of membranes with ion-ion selectivity. A few examples will be provided to elucidate the mechanisms of ion transport and selectivity in membranes with sub-nanometer pores. The presentation will conclude with a discussion on research directions and critical challenges for developing ion-selective membranes.

Ion association as a key element in NF modeling

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Despite wide use of NF and RO membranes, understanding ion transport in NF still presents a challenge, as current model are unable to reconcile all observations. Mean-field models such as Donnan, Poisson-Boltzmann or Manning have long been the standard, yet they fail to reproduce some observed trends, e.g., permeation of divalent-ion salts and multi-ion mixtures without questionable ad hoc adjustments.

This failure has been related here to the use of mean-field approaches, which were originally devised for high-T* (high-dielectric) media, in which potential variations are small compared to kT, and salts nearly completely dissociate. Unfortunately, this condition is strongly violated in NF, which are low-T*, i.e., the local potential variations largely exceed the thermal potential (Fig. 1). As a sounder treatment, we introduce a solution-diffusion model that adds ion association in a manner of classical Bjerrum theory. Association acts as a charge-regulating and ion-immobilizing mechanism that modifies the effect of fixed charges on ion permeation and the interpretation of "observed" membrane charge. In the new treatment, ion uptake and mobility become inter-related thus ion content no more simply correlates linearly with ion permeability. Our analysis also highlights the fact that simple continuum electrostatics is unable to supply an accurate quantitative description of association and solvation, for which the new model defines relevant ion-specific parameters, potentially deducible from molecular simulations.

The model can explain our recent NF data for NaCl+$CaCl_2$ mixtures and other published data, e.g., reported very high ion uptake in RO membranes, seemingly inconsistent with their high ion rejection. It thus presents a step towards more physically consistent predictive modeling of ion-selective membrane separations in water-, environment- and energy-related applications.

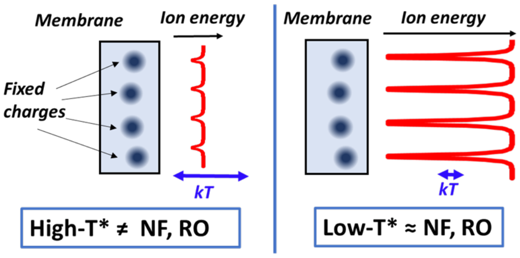

Fig. 1. A sketch illustrating high-T* and low-T* regimes of charged membranes: variations of electrostatic energy vs. kT.

Keywords: Nanofiltration; Charge exclusion; Ion association; Ion permeability; Membrane charge

Multifaceted role of modelling in membrane science and technology

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Exponential development of computer power and high-level computational tools makes modelling ever more accessible even to not-expert users. As a result, lots of unreliable modelling is produced and published, in particular, because there is no easy way for peers to verify the correctness of “fully-numerical” procedures. In membrane science and technology (similarly to many other engineering fields) there is an additional fundamental problem of poorly-defined membrane structure and properties. This situation made some membrane researchers effectively “write-off” modelling as a serious research tool.

In this lecture, we will argue that the situation is actually not that bad since in our field there are several kinds of useful modelling. However, they not necessarily go along the classical lines of the so-called mechanistic modelling of experimental data. This is because a major part of membrane phenomena occurs at nanoscale where satisfactory mechanistic description of equilibria and transport are still lacking.

This will be illustrated by the deficiencies of nano-pore model of nanofiltration where the laws of macroscopic hydro- and electro-dynamics are applied at sub-nano-scale. Due to sufficient number of adjustable parameters, this model sometimes can reproduce limited sets of experimental data. However, it often sorely fails when used outside the range employed for parameter fitting. As an alternative, we will present an advanced engineering model of NF based on solution-diffusion-electro-migration equations and briefly discuss equipment and experimental protocols required for determining its parameters.

Another useful kind of modelling is often practiced by physicists. It considers strongly simplified systems that reflect only principal qualitative features of reality. The use of this is twofold: better understanding the physics and formulating reference cases for verification of numerical analyses of more complex systems. This approach will be exemplified by the limiting case of ideal ion perm-selectivity of ion-exchange membranes widely used in electro-membrane processes.

Keywords: Nanofiltration; Modelling; Electrolyte solution; Multi-ion

Insights into the application of transition-state theory to transport in nanofiltration membranes

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Nanofiltration (NF) have been widely implemented in water purification and desalination processes. Separation between species at the molecular level is achievable in NF membranes due to complex and poorly understood set of transport mechanisms that have attracted the attention of researchers within and beyond the membrane community for many years. Minimizing existing knowledge gaps in transport through NF membranes can improve the sustainability of current water-treatment processes and expand the use of these membranes to other applications that require high selectivity between different species. Since its establishment in 1949, Eyring’s transition-state theory (TST) for transmembrane permeation has been applied in numerous studies to mechanistically explore molecular transport in dense membranes and more recently in NF membranes. In this work, we critically assess TST applied to transmembrane permeation in NF membranes focusing on mechanistic insights into transport under confinement that can be gained from this framework and the key limitations associated with the method. We first demonstrate and discuss the limited ability of the commonly used solution-diffusion model to mechanistically explain transport and selectivity trends observed in NF membranes. Next, we introduce the underlying principles and equations of TST and establish the connection to transmembrane permeation with a focus on molecular-level enthalpic and entropic barriers that govern water and solute transport under

confinement. We then critically assess the application of TST to explore transport in NF membranes, analyzing trends in measured enthalpic and entropic barriers and synthesizing new data to highlight important phenomena associated with the temperature-dependent measurement of the activation parameters. We also discuss major limitations of the experimental application of TST and propose specific solutions to minimize the uncertainties surrounding the current approach. We conclude with identifying future research needs to enhance the implementation and maximize the benefit of TST application to permeation through NF membranes.

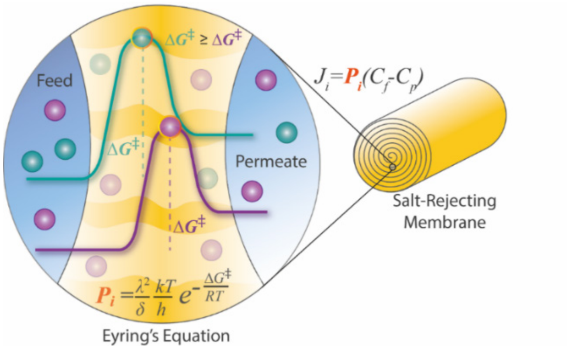

Fig. 1. Application of the Eyring equation to explore transport and selectivity in nanofiltration membranes. Using this equation, the permeability coefficient from the solution-diffusion model can be explored in terms of enthalpic and entropic barriers that govern the transport of species. Solute-solute selectivity is a result of the difference between the free-energy barriers of different solutes.

Keywords: Activation energy; Arrhenius equation; Eyring equation; Enthalpic barrier; Entropic barrier; Ion dehydration.

Progress in understanding concentration-polarization in nanofiltration

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Concentration polarization (CP) adversely affects membrane-based separation processes. We studied features of CP that were primarily overlooked, revealing interesting theoretical aspects with industrial implications.

First, we address the peak in the observed rejection of neutral solute and its subsequent decline with increased permeate flux. Although this phenomenon was previously reported (however scarcely), a theoretical analysis was not performed thus far, nor the practical implications were discussed. We investigated the equation describing the observed rejection as a function of flux based on the solution-diffusion-film model. This simple analysis revealed a surprising relationship between the maximal observed rejection peak rejection and the flux to mass-transfer coefficient ratio. Although fundamental, we could not find this connection in the published literature. We evaluated the practical implications of this CP-induced rejection peak both theoretically and experimentally for the case of organic micropollutants removal by nanofiltration membranes. The results indicated that a decline in micropollutants rejection could occur even when operating at typical operating conditions, especially when CP is enhanced by particulate fouling.

Second, we addressed the CP of charged solutes for the case of a feed solution containing trace-ions and one dominant salt, a good approximation in many nanofiltration applications. Although a theory for-trace ion transport including CP was previously presented by others, most of the later work on NF/RO modeling did not include CP. However, it may have a profound effect on process performances. This may be attributed to the lack (until-now) of a closed-form analytical solution accounting for the mostly ignored electromigration CP component. Here we revisited the solution-diffusion-electromigration-film model, deriving a fully analytical solution for the CP of trace-ions in a dominant salt solution. We used this theory to quantify the effect of electromigration on the CP of scale-forming trace-ions in RO and arsenic rejection in NF. We found significant deviations from the classic film model for some of the cases when accounting for electromigration.

This work shed new light on the effect of CP on both solute rejection and mineral scaling. We introduce new simple and accessible theoretical relations with practical significance that can contribute to the modeling and design of membrane processes.

Keywords: Solution–diffusion; Film model; Rejection peak; Electromigration; Micropollutants

Can pressure induce dehydration of ions in polyamide membranes?

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Membrane-based separation technologies such as nanofiltration (NF) and reverse osmosis (RO) are at the forefront of water purification and desalination processes. Rising demands for resource recovery have emphasized the need for improved solute-solute selectivity in these processes; however, achieving such precise selectivity with current membranes is a highly challenging task, which requires fundamental understanding of the transport mechanisms in play. Selectivity is a result of differences in the species permeability, which is a function of the intrinsic properties of the species (e.g., size and hydration energy) and the membrane (e.g., pore size and charge). In this study, we examined the permeability of different ions through commercial polyamide membranes (SW30, NF90, and NF270) under different pressures and varying operating conditions. To minimize the effect of concentration polarization, we first found the optimal crossflow rate where concentration polarization is negligible. Then, we measured water and salt permeabilities at different pressures for the different membranes. Our results expose increased salt permeabilities with higher pressures for all the membranes (Fig. 1), a somewhat surprising result considering the common notion that the salt permeability is independent of pressure. We suspect that the resultant trends of increased salt permeability with pressure is due to the dehydration phenomenon, as pressure may assist ions to detach their water shell and permeate more easily through the membrane. Higher permeation rates of smaller bare ions with larger hydration shell (e.g., lithium) compared to larger bare ions with smaller hydration shell (e.g., cesium) at higher pressures further support our hypothesis that ion dehydration is affected by pressure. We further support our theory that ion dehydration is affected by pressure by applying the transition-state theory for transmembrane permeation to measure the enthalpic and entropic barriers of ion permeation at different pressures. Overall, our insights on the permeation of small ions through polyamide membranes point out the potentially important role of ion dehydration in salt transport through NF and RO membranes.

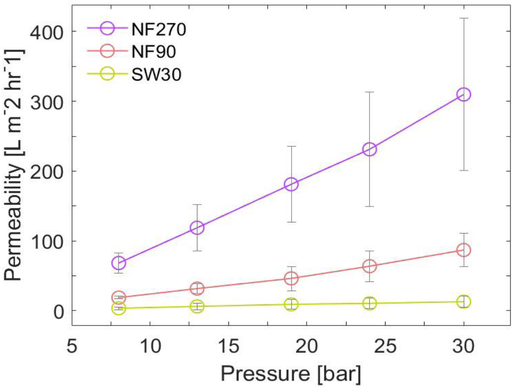

Fig. 1. Sodium permeability as a function of pressure, measured in SW30 (yellow), NF90 (red), and NF270 (purple) membranes in a temperature of 20°C and crossflow velocity of 6.4 m s^{-1}.

Keywords: Nanofiltration; Permeability; Selectivity; Transition-state theory

Selectivity of ionic species in polyamide membranes and the relation to the dehydration phenomenon

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Elucidating new transport mechanisms in polyamide membranes is a crucial step to design selective membranes for more sustainable water purification processes. In this study, we explored the selectivity trends of different ions, from small ions to notorious anionic pollutants and examined their transport mechanisms in loose and tight polyamide nanofiltration membranes. Applying transition-state theory, we broke down the intrinsic permeabilities of these species into enthalpic and entropic components. We analysed trends in these parameters to elucidate molecular phenomena that induce solute-solute selectivity at different pH values and pressures. Our results suggest that ion hydration is a key mechanism affecting ion transport in dense polymeric membranes. We speculate that the thermal activation of ions in the form of ion dehydration is less likely in pores that are either too small or contain a charged mouth, resulting in entropically-driven selectivity with steric exclusion of hydrated ions. Alternatively, ion dehydration in larger uncharged sub-nm pores is more feasible, inducing enthalpic selectivity that is driven by differences in the ion hydration properties. The dehydration phenomenon is further emphasised by the opposite rejection trends observed for monovalent cations compared to monovalent anions with respect to the ion bare size, as well as by the opposite cation rejection trends observed in the loose and tight nanofiltration membranes. Furthermore, we compared the selectivity of monovalent ions in a diffusion-only system to that in a pressure-driven system. The resultant opposite trend between the two systems indicates that ion transport due to dehydration is more likely when additional energy is supplied, i.e., activation due to pressure, temperature, etc. (Fig. 1). Overall, insights from this study can promote the design of membranes with improved solute-solute selectivity for various applications.

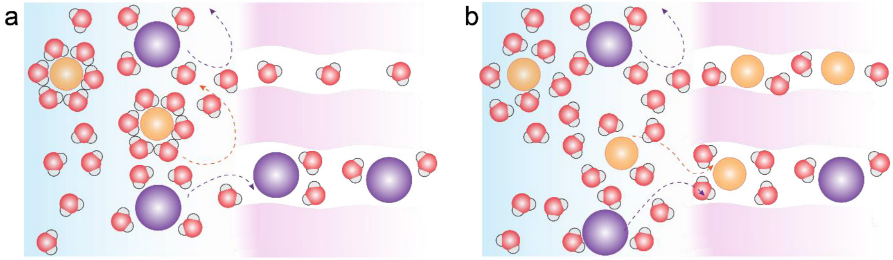

Fig. 1. Conceptual drawing of dehydration-assisted selective ion transport in polyamide membranes. (a) No energy is supplied, the larger ion (purple) can more easily detach its surrounding water molecules and enter the membrane compared to the smaller more strongly hydrated (orange) ion. (b) Applied energy enables the smaller ion to undergo dehydration and occupy more pores.

Keywords: Nanofiltration; Selectivity; Dehydration; Transition-state theory

Energy barriers for steroid hormone adsorption and transport in nanofiltration

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A breakthrough phenomenon is commonly observed during the nanofiltration (NF) of micropollutants (MPs) [1]. Experimental evaluation of the energy barriers associated with MPs transport in NF may contribute to a better understanding of the mechanisms responsible for breakthrough and helps improve MPs removal [2,3].

In this study [4], the energy barriers for adsorption, surface diffusion, and permeation encountering four steroid hormone MPs in tight and loose NF membranes are quantified at environmentally relevant concentrations using the Arrhenius concept (Fig. 1a).

Results show that the energy barriers for steroid hormone transport in tight NF membrane are entropically driven and underestimated due to the dominance of size exclusion at the pore (void) entry (Fig. 1b). In contrast, the loose NF membrane structure enables steroid hormone partitioning with a permeation energy barrier ranging from 96 to 116 kJ/mol. Evaluating the energy barriers for steroid hormone adsorption and surface diffusion reveals that surface diffusion transport contributes significantly to the measured energy barrier for permeation (Fig. 1c). Findings demonstrated that the breakthrough phenomenon observed during the NF of MPs is facilitated by the low energy barrier for adsorption. Experimental evidence of such principles is relevant for enhancing MPs removal in NF. One potential approach can be directed towards fabricating an NF membrane with binding sites that can give rise to a higher energy barrier for adsorption compared to the current commercial NF membranes, and hence limit the observed breakthrough.

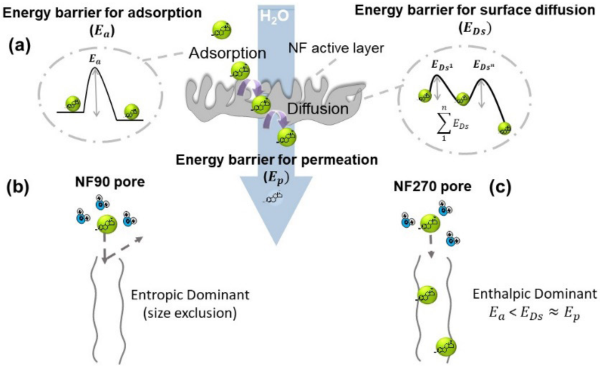

Fig. 1. (a) NF membrane active layer and the energy barriers for steroid hormone adsorption, surface diffusion, and permeation. (b) Energy barriers for steroid hormone are dominated by size exclusion (entropy) at the pore entry of NF90. (b) Energy barriers for steroid hormone adsorption (E_a) into NF270 is low, and surface diffusion transport controls the permeation energy barrier ($E_p = E_{DS}$).

Keywords: Micropollutant; Activation energy; Nanopore; Polyamide membrane; Arrhenius equation

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New compact expressions for concentration polarization of trace-ions in pressure-driven membrane processes

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Accounting for concentration-polarization (CP) is critical for modeling solute transport in membrane separation processes. In a mixed-electrolyte solution, ion CP is not only affected by diffusion and advection but also by electromigration. Yet, the classic film model, lacking an electromigration term, is still frequently used for modeling ion CP, probably due to the lack of a simple mathematical description. Moreover, ion CP tends to be altogether neglected in elaborated simulations to reduce the computational load. Herein, we present a compact CP expression, accounting for electromigration, that emerges as a seamless extension to the classic film theory. This equation can be used in the case of multicomponent mixtures with one dominant salt, which is relevant for nanofiltration applications such as removing trace ionic contaminants. To demonstrate the applicability and significance, we used the theory to quantify the effect of electromigration on ion CP in different dominant salt solutions. Finally, by analyzing an environmental membrane process case, we demonstrate how the new compact expression for CP deviates from the conventional one and quantify the implications on membrane scaling potential and the transport of trace ionic contaminants.

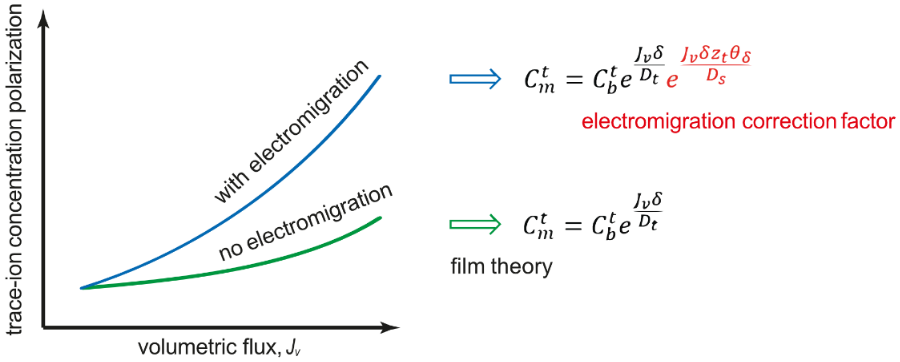

Fig. 1. A qualitative description of the electromigration correcting factor and its influence on concentration polarization predictions by film theory.

Keywords: Concentration polarization; Electromigration; Multi-component transport

New testing protocols and evaluation models for robust evaluation and comparison of nanofiltration and reverse osmosis membranes

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Efforts devoted to the improvement of nanofiltration and reverse osmosis membranes are often impaired by impossible comparison among these new materials obtained by different research groups and by means of dissimilar testing conditions. Fair comparison should be performed using intrinsic membrane properties. However, these are frequently ambiguously or not reported, in part due to difficulties in modeling the experimental results. To overcome these issues and accelerate membrane development, standardised testing and modeling protocols for NF/RO membranes are needed. The goal of this research is to support this commitment by demonstrating how certain testing conditions should be pursued while others abandoned, additionally proposing procedures that allow full membrane characterization and the extraction of the necessary data to conduct robust and simple modeling aimed at calculation of membrane intrinsic properties. To this purpose, commercial and non-commercial membranes were rigorously tested and the results applied in a new simplified model developed to describe the mass transfer through NF/RO. An in-depth investigation of the operating parameters affecting the characterization protocol was performed, defining the guidelines for a fast and correct evaluation of the intrinsic membrane parameters, namely, the water and salt permeability coefficients. Evaluation of the concentration polarization affecting the water and salt flux showed its dependency upon the testing conditions. Finally, the model was validated with experimental data releasing a new non-dimensional equation that can be used to check the replicability and the robustness of the new membranes developed. The simplified model reported in this study may represent a valuable tool to be integrated within the already known Open Membrane Database, while being available also for membrane manufacturers.

Keywords: Nanofiltration; Reverse osmosis; Testing; Permeance; Permeability coefficients; Concentration polarization

Hydrodynamic and electrostatic forces governing the membrane-organic solute interactions in asymmetric flow field flow fractionation

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The interaction of organic matter (OM) in aqueous solution with membranes during a filtration process largely influences the fate of the OM. The estimation of hydrodynamic and electrostatic forces involved in the separation of OM over different molecular weight cut-off (MWCO) membranes is essential for understanding the filtration process. Understanding the force-fractionation relation would also aid the selection of a suitable membrane for the characterization of OM properties and OM-membrane interactions.

This work targets to evaluate the role of UF membranes of MWCO (1–30 kDa) used in an asymmetric flow field flow fractionation (FFFF) system, on the hydrodynamic and electrostatic forces for a model organic solute polystyrene sulfonate sodium salt (PSS) (10–65 kDa), on their fractionation. The role of pH, ionic strength, permeate flow (Q_p) and concentrate flow (Q_C) were also evaluated.

A better fractionation (represented by low retention ratio of ≤0.2) was achieved under the conditions of low tangential drag force (2–5 aN) and moderate transverse drag force (800–1200 aN) when using low membrane MWCO (1 kDa), high Q_p (1.5–2.0 mL/min), low Q_C (0.2–0.3 mL/min) and low ionic strength (10 mM NaCl). The transverse drag force (F_{Dp}) is observed to be the most significant force determining the transport of solutes in fractionation. The electrostatic force is significant only when the solute is very close to the membrane. Ionic strength and pH does not have any effect on the retention ratio of PSS of a given size. However, ionic strength considerably affects the relative peak recovery of small-sized PSS, 10 kDa. The fractionation was correlated with the ratio of transverse drag force over tangential drag force (F_{Dp}/F_{Dt}) (Fig. 1). The fractionation increases with F_{Dp}/F_{Dt}. Smaller the PSS and higher MWCO membrane, higher the FDp/FDt required. In brief, a better fractionation (low F_{Dp}/F_{Dt}, retention ratio approaching 0.2) was achieved for bigger particles (> 10 kDa) in a high electrostatic repulsive environment (i.e. a low ionic strength medium ≤ 0.01 M) with low MWCO (≤1 kDa) membranes. The better fractionation with the low MWCO (1 kDa) membrane point out that nanofiltration membranes could offer better fractionation conditions in FFFF.

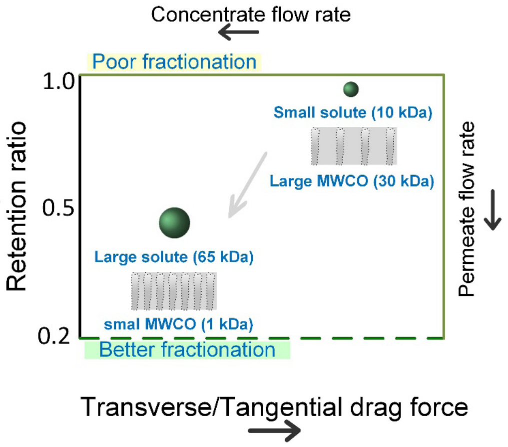

Fig. 1. Schematic representation of the relation of retention ratio of organic solute with transverse/tangential drag force balance (F_{Dp}/F_{Dt}). The retention ratio changes as a function of PSS molecular weight (10–65 kDa), membrane MWCO (1–30 kDa), permeate flow rates (Q_p) 1.0-2.0 mL/min and concentrate flow rates (Q_c) 0.2–0.6 mL/min

Keywords: Cross-flow ultrafiltration; Drag force; Lift force; Polystyrene sulfonate; Field-flow fractionation

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Adsorption of steroid hormone micropollutants in the nanoconfinement of vertically aligned single-walled carbon nanotube membranes

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Vertically aligned carbon nanotube (VaCNT) membranes are state-of-the-art membranes that allow water to conduct rapidly through their hydrophobic, smooth, and low tortuosity pores [1, 2]. The advantage in water flow may affect the surface interactions with contaminants. VaCNT membranes present an opportunity to understand the interactions inside nanopores thanks to the good membrane pore homogeneity.

In this study, hormone adsorption was quantified and explained via the interplay of forces that act on the hormone molecule. These forces are the i) hydrodynamic drag force that acts along the flow direction, ii) opposing hormone-wall friction force that restrict the hormone movement, iii) adhesive force that is directed toward the pore wall, and iv) repulsive force caused by the repulsion between the electrons of the wall and those of the hormone (Figure 1).

Filtration experiments were performed in dead-end mode with 100 ng/L hormone (17β-estradiol (E2), estrone, testosterone and progesterone) feed solutions. The effective area of VaCNT membranes was 2 cm^2. Given the high sensitivity of liquid scintillation counting for hormone analysis, the adsorbed mass of hormone is determined in small quantity, of sub-nanograms per square centimeter of membrane area.

Results show that with a fast flow velocity inside the VaCNT membrane ($4.7 \cdot 10^{-4}$ m/s, faster than UF and similar to NF), E2 adsorption was insignificant because the strong drag force ($3.3 \cdot 10^{-3}$ pN) pushed the hormone molecules along the wall. When the drag force was reduced to $2.2 \cdot 10^{-3}$ pN, the effect of the opposing hormone−wall friction force is significant. When the drag force was further reduced to $4.3 \cdot 10^{-4}$ pN, the hormone movement is restricted and the E2 adsorbed mass increased from 0 to 0.4 ng/cm^2. At a constant drag force magnitude that permitted adsorption ($1.6 \cdot 10^{-3}$ pN), the adsorbed mass of four hormones is correlated to the hormone−wall adhesive force. This adhesive force drives the hormone towards the pore wall until it balances the repulsive force; and influences the friction force that resists the hormone movement with the flow.

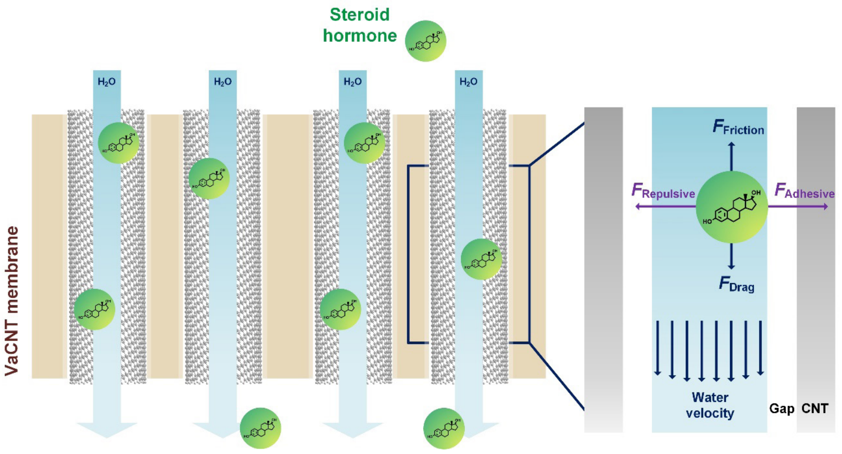

Fig. 1. Schematic of the VaCNT membrane and representation of the forces acting on a hormone (E2) molecule confined in the membrane pore. Adapted from Nguyen et al. [3].

From the above results, a framework where micropollutant adsorption in nanopores (including those of VaCNT and UF/NF) can be explained by the interplay of those four forces. The understanding of these forces can be exploited to improve selectivity.

Keywords: Nanofluidics; Ultrafiltration; Nanofiltration; Flow enhancement; Water treatment

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Energy harvesting: a universal model for reverse-electrodialysis

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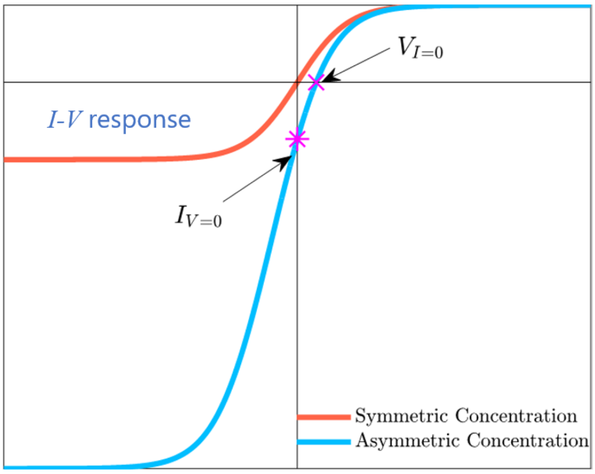
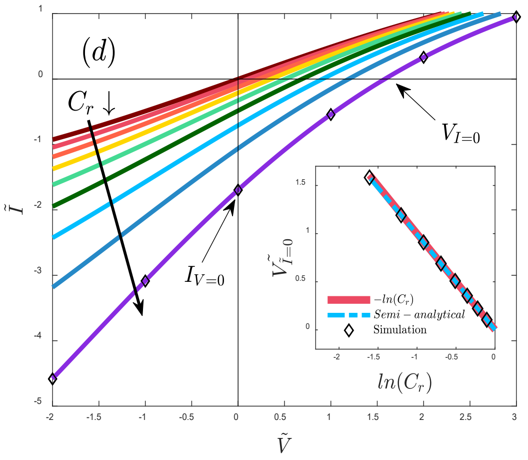
Reverse electrodialysis (RED) is a process that leverages a difference in salt concentrations to harvest energy. This asymmetry of salt concentrations includes naturally occurring freshwater rivers flowing into seawater. Thus, RED presents a potential to introduce a sustainable source of electricity that could revolutionize the global energy market. While the process of harvesting this essentially 'free' electric current using an ion-selective membrane in RED is well established, the microscopic details are still not completely understood. As such, this has led to the conventional reliance on trial and error for tuning and improving RED systems. To overcome these challenges, we introduce a universal model for RED systems, that accounts for the key parameters of these systems. We have derived several nonlinear relations that provide a robust understanding of the underlying physical principles of RED systems. Thus far, we have validated our model against existing analytical models and numeric simulations and are currently attempting to extend our analysis to provide new and novel relations that can be used to characterize blue energy harvesting.





Keywords: Nanofluidics; Ion-transport; Reverse electrodialysis

Bipolar nanochannels: A systematic approach to asymmetric problems

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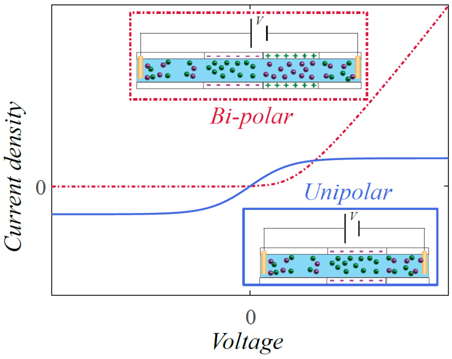
Nanofluidic systems are characterized by their current−voltage (I-V) response, where it is known that there are two distinct limits: unipolar and bipolar responses. In this work, we investigate the differences and similarities between these two responses. To this end, we show that the response is determined by a control parameter, S, that accounts for the geometry and surface charge properties of the system. We focus on both the time-dependent response and the steady-state response. First, we show that instead of manifesting the classical signature of concentration polarization in unipolar systems, such as ionic depletion and enrichment, bipolar and semi- bipolar systems exhibit a more complicated behavior such as the formation of two depletion layers. We further show that by tuning the control parameter S, we vary the current-voltage response between the two extreme limits. The finding of our work can be used to further elucidate the complicated behavior of ion transport in nanofluidic diodes and to rationalize experimental results. The insights of this work can be used to enhance and improve the design of all nanofluidic diodes.



Keywords: Nanofluidics; Ion-transport; Bipolar channels.

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Electrical circuit modelling of nanofluidic systems

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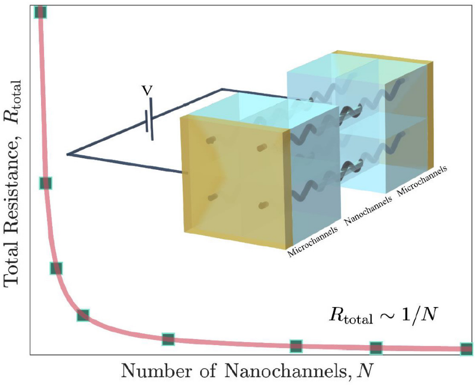
Nanofluidic systems exhibit transport characteristics that have made technological marvels such as desalination, energy harvesting, and highly sensitive biomolecule sensing possible by virtue of their ability to influence small currents due to the selective transport of ions. Traditionally many of these applications have relied on the use of nanoporous membranes. The immense complexities of membrane geometry often impede a comprehensive understanding of the underlying physics. To that end, we consider the much simpler nanochannel array to elucidate the effects of interchannel interactions on the Ohmic response of the array. We demonstrate that a nanochannel array is equivalent to an array of mutually independent but identical unit-cells whereby the array can be represented by an equivalent electrical circuit of unit-cell resistances connected in a parallel configuration. We validate the theoretical model underlying these electrical abstractions using numerical simulations and experiments. This simple framework enables the accurate interpretation of experimental data and the direct characterization of geometric parameters and surface charge properties of realistic systems.



Keywords: Nanofluidics; Ion-transport; Electrical circuits; Equivalent circuit

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III. Nanofiltration Principles: Characterization, Nanoscale Imaging, Fouling and Scaling

Zeta potential analysis of nanofiltration membranes: A review

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With the availability of a commercial instrument for the streaming potential measurement in the 1990s and the publication of a comprehensive paper by Childress and Elimelech (J. Membr. Sci. 119, 1996, 253), the zeta potential has started to become an indispensable parameter for the characterization of nanofiltration (NF) membranes. In the past 25 years, the diversity of information provided by the zeta potential has been exploited to better understand the performance of NF membranes.

The zeta potential shows responsible for the electrostatic interaction between the membrane surface and solutes in the feed with different consequences. Surface charge determines the rejection of solutes by the NF membrane. The zeta potential contributes to the fouling propensity of NF membranes. The sensitivity of the zeta potential to the outermost membrane surface and the separation of surface and interfacial phenomena from the bulk properties of the feed make the streaming potential method suitable for the characterization of the dynamics of solute-on-membrane surface adsorption processes.

This contribution highlights some pioneering attempts to apply the zeta potential to study the effect of solution chemistry, to model salt rejection, to determine the initial rate of membrane fouling, to qualify membrane surface modification, to evaluate the efficiency of cleaning cycles, to demonstrate the attack of harsh cleaning chemicals, and to illustrate adsorption processes of different solutes on the membrane surface. Representative papers and the results reported therein have been selected to review the scope of the zeta potential analysis for the characterization of NF membranes and their behaviour in the NF process.

Keywords: Surface characterization; Zeta potential; Streaming potential; Surface charge

Advanced nanoscale imaging of membranes: Opportunities and (related) examples

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Advanced characterization plays a significant role in many scientific fields, including chemistry, physics, materials science, and chemical engineering. Synchrotron methods provide unique opportunities to quantitatively probe and image structural, chemical and dynamical properties of matter down to the nanoscale. Over the last few decades, they have provided significant insight into the atomic and molecular scale processes underlying electrochemical energy storage and energy conversion. Considering the advent of novel and improvement of existing synchrotron methods, opportunities exist to utilize them towards advanced nanoscale characterization of membranes (e.g. for nanofiltration) and other clean water technologies. In the first part of this talk, some of these opportunities will be discussed. The second part focusses on two examples where synchrotron methods were utilized to advance the understanding of functional materials. These include imaging Si and the chemical forms of Ca on fouled reverse osmosis membranes, which allows for insight into the formation mechanism. Specifically, we identified specific Ca minerals in the fouling layer, however these covered only a small fraction of the membrane surface compared to organic-bound Ca and SiO_2, which formed a layer coating the entire membrane. We thus concluded that the latter caused the majority of fouling-related performance decline. Moreover, it will be shown how diffraction imaging of electrodes for energy storage allows us to reveal and quantify their degradation mechanisms. Specifically, we investigated extreme fast-charged Li-ion batteries with the goal to quantify capacity mechanisms. We found that the origin lies in parasitic Li plating on the anode caused by locally high overpotentials and in the evolution of the solid electrolyte interphase; cathode degradation is negligible.

Keywords: Membranes; X-ray; Synchrotron; Imaging; Advanced characterization

Nanoporous silicon – polypyrrole hybrids as electrically switchable membrane materials

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Membranes with electrically switchable wettability provide new means for nanofiltrations with stimuli-sensitive hydraulic permeabilites. Here we present experiments on nanoporous silicon (np-Si) functionalized by electropolymerization with pyrrole (PPy). Depending on the oxidation state polypyrrole is known to be either hydrophilic or hydrophobic, see Fig. 1.

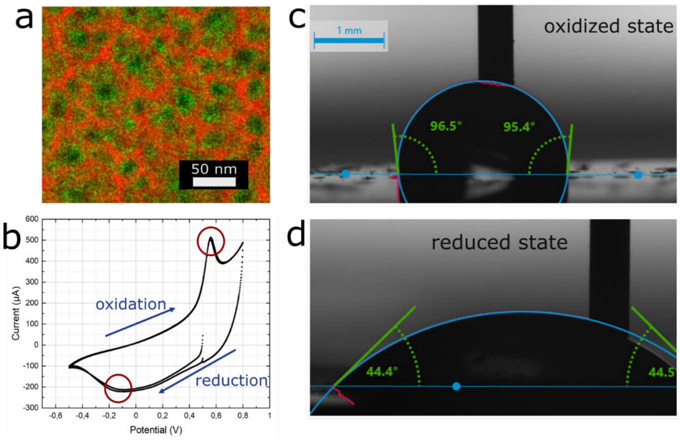

Fig. 1. (a) Dark-field scanning transmission electron micrograph (top view) of a np-Si membrane (red) filled by electropolymerisation with pyrrole (green). (b) Cyclic voltammetry indicate oxidation/reduction transitions at characteristic voltages. Using these values PPy was succesfully electrochemically switched from the oxidized to the reduced state. (c,d) Distinct wetting states of an aqueous electrolyte on the oxidized and reduced PPy state, respectively.

In this work, the different oxidation states of np-Si-PPy composites are studied through cyclic voltammetry measurements, where wetting-transition voltages are identified. We explore the switchable wettability originated at these oxidation state transitions both for bulk polymer layers and np-Si-PPy membrane geometry and its impact on the hydraulic permeability of aqueous solutions.

Keywords: Conductive polymer; Nanoporous silicon; Switchable wettability

Porosimetry of nano-pores in thin polymer films by depth resolved positron annihilation lifetime spectroscopy

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The quantitative characterization of pore sizes and distributions in thin polymer layers (< 50 nm) is a challenging task, especially for free volume structures enclosed inside the material without any connection to the surface. Positron annihilation lifetime spectroscopy (PALS) offers the possibility for non-destructive investigations of nanoscopic pores in the range of ~ 0.2 – 3 nm. With a pulsed, monochromatic positron beam of variable energy one determines the time between positron implantation and annihilation in a certain depth (5 nm – 5 µm) beneath the surface. In insulating materials such as polymers, positrons and electrons may form a bound state – Positronium (Ps). From the Positronium lifetime, one can calculate an effective pore radius by a semi-empirical, quantum-mechanical model (Tao-Eldrup-model). For this purpose, the pulsed low-energy positron system (PLEPS) [1] was developed. It is operated at the reactor-based, high intense positron source NEPOMUC and offers the possibility for non-destructive investigations of nanoscopic free volume elements inside porous materials.

At present, it is possible to obtain with PLEPS positron and Positronium lifetime spectra of membrane samples including 4 × 106 counts in less than 10 min for a single implantation energy. Changing the beam energy allows positron implantation in various depths. A full depth-profile of 10 - 15 energies requires about 2–4 h.

The system also allows in situ manipulation of the sample temperature between 80 K and 600 K during lifetime measurements. This enables to investigate free volume elements as a function of the temperature, and thus, to determine material phase transitions, e.g. the glass transition temperature.

In this talk we describe the method and the present setup of PLEPS, its performance, and show a selection of exemplary applications (e.g. [2,3]) to polymer problems.

Keywords: Positron annihilation; Porosimetry; Free volume; Thin films; Nano pores

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Photostability determination of polymeric photocatalyst-loaded membranes using accelerated ageing

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Photocatalytic membrane (PM) can degrade under light exposure and this is a setback against the application of PM in water treatment [1]. Prior to this work, it was unclear which characterization techniques are suitable for the stability evaluation of the membrane support and photocatalyst [2]. Based on this, a systematic approach is needed to assess PM photostability under laboratory conditions [2].

Three support membranes (hydrophilic polyethersulphone – PES-h/phil; hydrophilic polyvinylidene fluoride – PVDF-h/phil; hydrophobic PVDF – PVDF-h/phob) were loaded with two types of photocatalysts (titanium dioxide – TiO_2 [3]; palladium-porphyrin – PdTFPP [4]) and subsequently in an irradiation chamber (Fig. 1). Light intensity (365 nm–981 W m^{-2} and 405 nm–1242 W m^{-2}) and exposure time (up to 250 h) were controlled to simulate up to six months of PM usage. PM characterization was performed by several methods to detect changes in the aged membranes, including visual observation, scanning electron microscopy (SEM), and UV-Vis spectroscopy. The photocatalytic performance of aged PM was evaluated with methylene blue (MB) degradation in a photocatalytic membrane reactor [4].

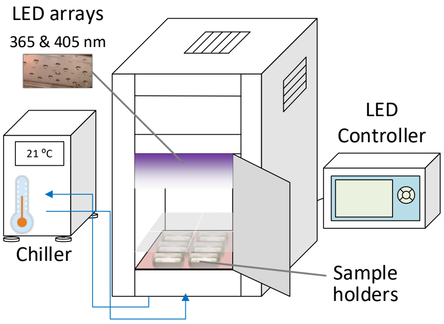

Fig. 1. Schematic of the irradiation chamber used in the PM ageing.

The PdTFPP-PVDF-h/phob membrane had a significant reduction of the characteristic PdTFPP absorption bands with irradiation time, a process called photobleaching. With TiO_2-PES-h/phil, SEM surface images of aged membranes showed damages on morphology with pore network collapse. The photocatalytic experiments with MB revealed that, unlike TiO_2-PES-h/phil and PdTFPP-PVDF-h/phob membranes, TiO_2-PVDF-h/phil retained the MB degradation efficiency after accelerated ageing.

In summary, inorganic photocatalyst (TiO_2) has superior stability when compared with porphyrin, which suffered photobleaching, as observed visually and on UV-Vis spectra. PVDF had higher photostability than PES, promoting stable photocatalytic MB removal. Overall, the support membrane and the photocatalyst must be considered when determining the techniques for PM photostability evaluation since a unified protocol is not appropriate. This systematic approach applies to all polymeric membranes, as well as the promising nanofiltration PMs.

Keywords: Photostability; Accelerated ageing; Titanium dioxide (TiO_2), Porphyrin; Polyvinylidene fluoride (PVDF); Polyethersulphone (PES)

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Characterization of estradiol micropollutant breakthrough curve in nanofiltration

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Water contamination by steroid hormone micropollutants (MPs) poses a risk for human health as it is related with alteration of the reproductive system and cancer [1]. Nanofiltration (NF) cannot remove efficiently organic MPs as they adsorb and permeate subsequently through the membrane, a phenomenon that is known as breakthrough curve [2-5]. The understanding of its variation with the mass transfer (external and intra-porous) and hydrodynamic is not clear.

In order to address this knowledge gap, a systematic investigation of estradiol (E2) breakthrough curve variation of tight and loose NF membranes has been performed in three filtration systems with different configurations (dead end and cross flow) and concentration polarization condition [6]. Tight NF membrane, like NF90, shows a flat breakthrough curve shape independent on operative conditions because E2 transport is controlled by the intra-porous mass transfer of diffusion (see Fig. 1) [7].

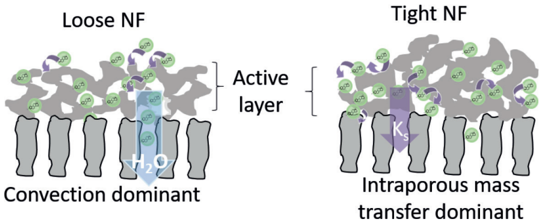

Fig. 1. Transport mechanisms controlling breakthrough curve in NF90 and NF270.

In case of loose NF270, the breakthrough curve variation is observed when hydrodynamics and pressure are changed as the convective transport is dominant. The variation of breakthrough curve shape is consistent with the concentration on the membrane surface which controls E2 membrane adsorption.

These findings are useful for the breakthrough curve characterization of new NF membrane materials in laboratory scale devices with different hydrodynamics and operated at different conditions (hence external mass transfer), which is relevant to evaluate the micropollutant removal achievable.

Keywords: Concentration polarization; Intra-porous mass transfer; Diffusion; Convection

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Interactions of alginate/toluidine blue complexes with PES membrane and examination of fouling development mechanisms

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This study explored fouling of polyethersulfonate (PES) membranes induced by the typical model foulant sodium alginate. The nominal pore size of the PES membranes was 50 nm. Interactions between PES surfaces and alginate were quantified based on the data of ATR-FTIR and UV-Vis transmission spectroscopy. The cationic probe toluidine blue (TB) that forms complexes with alginate was present in the examined system, typically at a 10^{-5} M concentration. The data indicated that the alginate molecules forming a fouling layer on PES surface strongly interacted with the cationic probe, and these interactions were qualitatively different from those in solution. Transmission spectra generated for PES membranes using a Cary 5000 instrument showed that interactions between TB cations and the alginate molecules present in the fouling layer lead to the formation of a complex system of TB_n oligomers while TB/alginate interactions in solution resulted in TB_2 dimers only. This indicated that the alginate molecules retained on the surface formed an increasingly organized network of distributed immobile charges. A strong correlation between the retention of the TB probe and development of the transmembrane pressure at varying ionic strengths was observed (Figure 1). The results demonstrate that the use of molecular probes combined with measurements of the transmission spectra of membrane/foulant systems allows tracking transformations in the surface films and thus elucidating microscopic-level transitions involved in the development of membrane fouling.

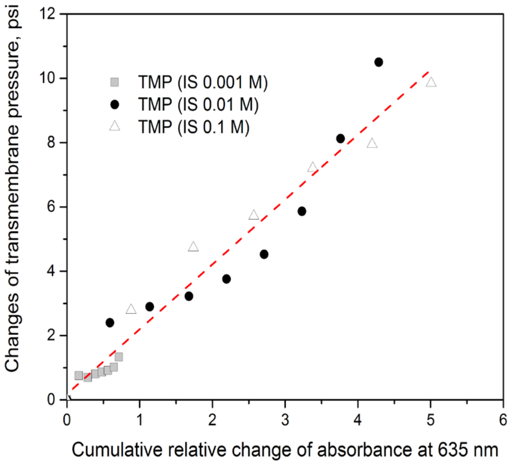

Fig. 1. Correlation between cumulative differential absorbance of TB probe vs. transmembrane pressure measured at varying ionic strengths (alginate concentration 2.8 mg/L as DOC; pH 7.0).

Keywords: Alginate; Cationic probe; Fouling; Membrane; PES, spectroscopy

Investigating fouling behavior of nanofiltration capillary membranes in water treatment and its impact on separation performance

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Nanofiltration (NF) membranes have recently regained attention due to emerging of more restrictions regarding pollutants levels in surface water as well as quality of drinking water. Ultrafiltration (UF) membranes have been frequently employed for treatment of surface water; however, low molecular weight fractions of NOMs, e.g., building blocks and

certain biopolymers are challenging the permeate quality and causing severe internal fouling. Instead, NF capillary membranes can produce permeates of better quality; nevertheless, their fouling behavior and its impact on retention ability for ions existing in surface water are still questionable. Here, fouling propensity of novel polyethersulfone-based NF capillary membranes (400 Da, supplied by NX Filtration B.V. Netherlands), during mini-plant multiple-cycles filtration experiments was investigated using different potting soil extracts (PS1, PS2) imitating moderately loaded surface water. PS1 and PS2 contained comparable humic substances portions, but with different fractions of biopolymers and hydrophobic organic carbon. Complex feed solutions comprising potting soil extracts (5 mg/L TOC) and MgSO4 (600 mg/L) were additionally employed. In contrast to UF membranes, PS caused limited fouling of NF membranes (cf. Fig.1), whilst severer permeability decline was noticed in case of complex feed solutions; more fouling was observed in case of PS with higher biopolymer contents. Nevertheless, fouling of NF capillary membranes, by both PS and complex feed mixture, was interestingly mechanically washable indicating that permeability decline is most likely due to surface fouling (cake filtration mechanism) rather than internal fouling, what is often observed in UF membranes using PS. Moreover, TOC and salt retention were found to increase for later filtration cycles that may be correlated to a possible contribution of the formed cake layer. Further experiments are performed for better understanding the fouling mechanisms and their impact on salt retention.

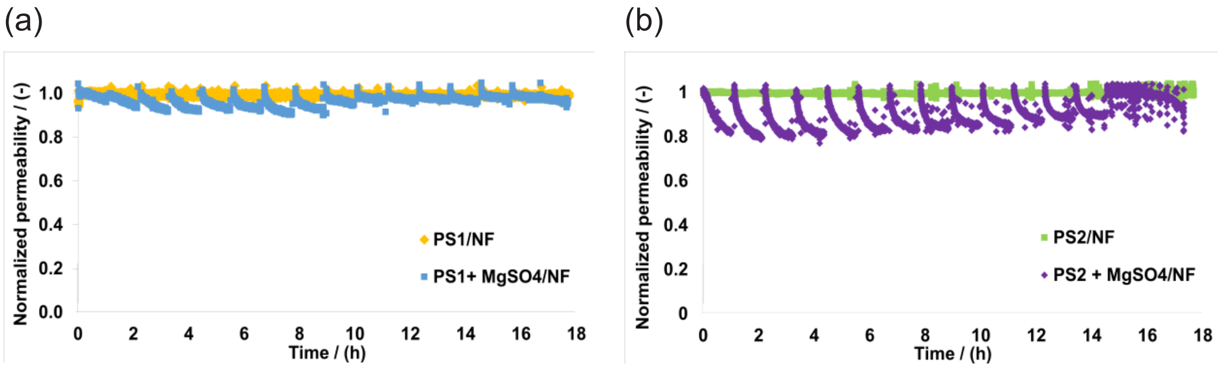

Fig. 1. Performance of NF capillary membrane during mini-plant filtration experiments of PS and complex feed mixture at constant pressure of 2.5 bar and crossflow velocity of 0.2 m/s; (a) PS1: DOC = 3700 ppm-C, biopolymer content = 35 ppm-C, hydrophobic organic carbon = 35 ppm-C; (b) PS2: DOC = 5200 ppm-C, biopolymer content = 410 ppm-C.

Keywords: Nanofiltration; Hybrid; Seawater desalination; Osmotic limitation; Scaling prevention; High recovery

Mitigating NF fouling with micronanobubbles

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Proteins purified by nanofiltration NF membranes are crucial in biotechnological and pharmaceutical applications. Membrane fouling occurs inevitably during the purification and results in reducing transmembrane flux or raising operational expenses. Periodical cleaning is imperative to prevent or eliminate fouling, enhance protein yield, and maintain membrane selectivity. Membranes are largely cleaned chemically despite the method's inherent drawbacks, such as additional cost, environmental sustainability, and potential damage of membrane surface. Membrane surface modification, flow manipulation (turbulence promotion, back-flushing, and pulsing), ultrasonic treatment, feed pretreatment, and gas sparging can avoid or minimize the drawbacks. The air sparging is promising due to its relative efficiency and reduced impact on the environment due to the absence of cleaning chemicals.

On this account, we studied the existing fouling prevention mechanisms and proposed an optimal bubble flow regime for preventing and controlling organic fouling in flat sheet NF membranes. Our findings revealed that the various mechanisms by which air bubble flows control or prevent organic fouling vary depending on the size of the bubbles. Small-sized air bubbles <0.05 mm improved BSA retention but also led to flux decline. In contrast, larger bubbles of about 2mm minimized fouling despite not improving BSA retention. Interestingly, a flow of 0.5–1.0 mm air bubbles enabled continuous 3 h run, suggesting the possibility of combining these fouling-combat mechanisms. It was worth noting that the effects of bubbles on flat sheet NF membranes differed from that of submerged hollow fibers.

In summary, given the strong influence of filtration mode and bubble size on the fouling and retention in NF membrane-based systems, knowledge of bubbles sizes and their related effects is vital in evaluating the effectiveness of different fouling prevention scenarios. The exact mechanisms for preventing organic fouling are rather complicated, it involved multiple processes, including the adsorption of impurities by small bubbles and fouling layer distortion by large bubbles.

Keywords: Two-phase flow; Gas–water mix; Leonardo paradox; Bubble diameter; Oscillating flow; Vortex chamber

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Micropollutants partitioning in combined magnetic ion exchange (MIEX) membrane processes

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Endocrine disruptors, like natural and synthetic steroid hormones, are micropollutants of emerging concern in drinking water produced from treated waste water as these contaminants are not efficiently removed [1].

This poses a challenge for application of hybrid membrane processes, like nanofiltration (NF) and ultrafiltration (UF) combined with MIEX in water reuse as the partitioning of micropollutants with the resin, membrane material and natural organics (like humic acid) may occur [2-4]. In order to elucidate these interactions, estradiol uptake by MIEX, membrane and humic acid (HA) is determined at different pH and in presence of fouling caused by HA and calcium.

The results show that partitioning with MIEX in batch is dependent on pH and it is higher at alkaline pH (pH>10) due to deprotonation of E2 phenolic groups [5]. In case of fouling condition, E2-HA partitioning is reduced due to calcium interference that compete with E2 molecules. In hybrid MIEX-NF process, E2-MIEX interaction is dominant at all pH conditions resulting in E2 uptake up to 40% (Fig. 1) [6, 7].

These results demonstrate that the accumulation of steroid hormones is significant in hybrid membrane processes that treat waters containing natural organics (like in water reuse) and it poses a risk of accidental release into the environment.

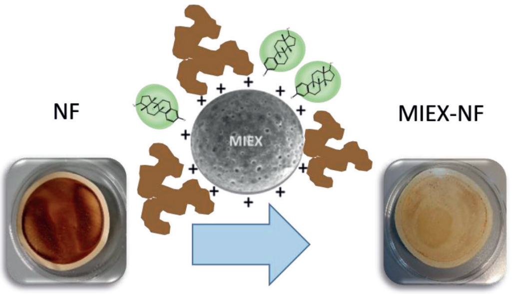

Fig. 1. Fouling reduction of NF90 in presence of MIEX in the feed solution and E2 partitioning

Keywords: Water reuse; Fouling; Humic acid; Hybrid membrane processes

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Spontaneous osmotic backwash for fouling control in batteryless photovoltaic powered nanofiltration/reverse osmosis systems

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Drinking water scarcity is a severe issue in arid rural regions where electricity is not always accessible. Solar energy is an underutilised energy resource in many such regions. The idea of integrating photovoltaic panels and nanofiltration/reverse osmosis (NF/RO) membranes was proposed to address this issue [1]. Mineral scalants and organic matter in feedwater may deposit on the membrane surface, causing scaling and fouling problems and increasing the maintenance effort and costs. Solar energy fluctuations induce a spontaneous direct osmotic backwash (OB) when the operating pressure is less than the osmotic pressure of feedwater, potentially alleviating the scaling/fouling.

In this study, the feasibility (cleaning efficiency) of spontaneous OB on scaling and organic fouling was investigated via a bench-scale crossflow NF/RO system powered by a solar array simulator (SAS) with different feedwater chemistries and two membrane types (BW30 and NF270). The SAS simulates the solar irradiance fluctuations and induces the OB process, which is quantified by a bi-directional flow sensor. Calcium carbonate and calcium sulfate were used as model scalants and humic acid with calcium as model organic foulant.

Results demonstrate that the spontaneous OB restores 30–98% flux and removes partial scalants/organic foulants (Fig. 1), depending on the feedwater chemistry (scalants content, salinity, pH, and water hardness), membrane types, and fluctuating conditions. The insights obtained from this work include; i) early recognition of scaling/ fouling and implementing OB at the initial stage are important; ii) osmotic backwash is most effective at neutral pH, low hardness and salinity in such systems; iii) on sunny days, it is worth considering turning off the pump to induce the OB process as a routine maintenance measure [2].

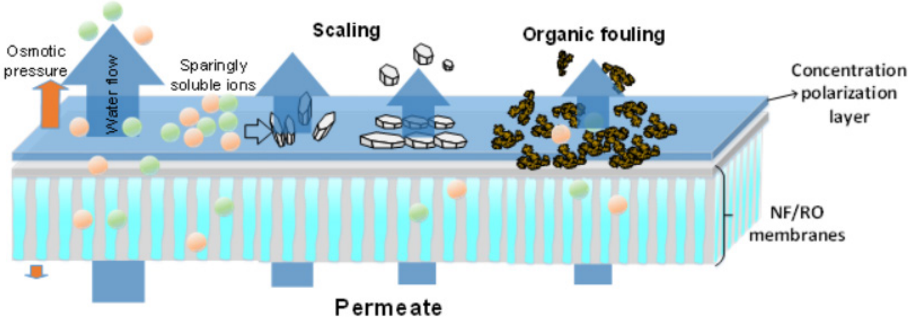

Fig. 1. Schematic of spontaneous osmotic backwash for scaling and organic fouling control, adapted from [3].

Keywords: Decentralised; Water treatment; Solar desalination; Physical membrane cleaning; Self-cleaning; Inorganic scaling; Organic fouling

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Enhancing polyvinylidene fluoride nanofibers membrane wetting properties by alkaline surface treatment

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Surface treatment of polyvinylidene fluoride (PVDF) nanofibers membrane with alkaline solutions has been shown to enhance PVDF wetting properties and decrease membrane hydrophobicity. PVDF nanofibers were treated with different sodium hydroxide (NaOH) concentrations under elevated temperatures in presence of isopropanol. The PVDF nanofibers were laminated with a nonwoven polystyrene layer and tested in a cross-flow filtration setup simulation unit. The surface treatment resulted in a decrease of the water contact angle to 67° from a pristine starting angle of 160.4° when treated with 0.5 M aqueous NaOH, 2 h, 80°C. Furthermore, the membrane sample treated with 1 M NaOH, 2 h, 80°C showed an increase in the water flux of about 400% (Fig. 1).

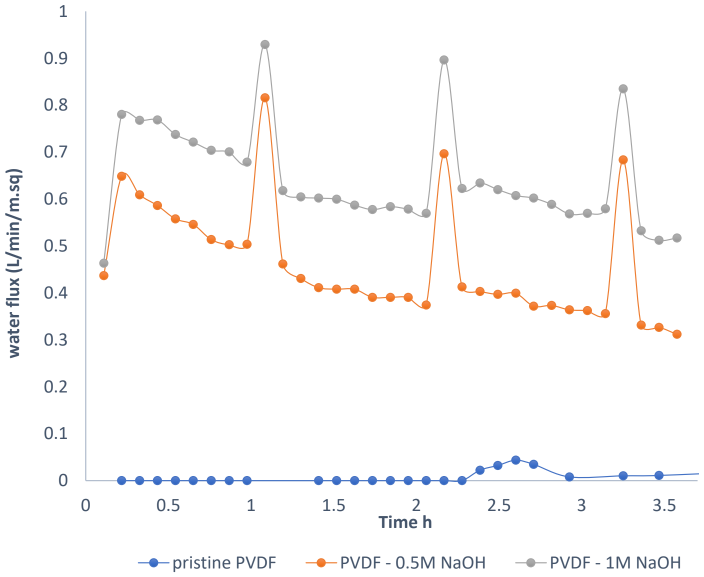

Fig. 1. Membrane water flux change over time

Keywords: Nanofibers; Plyvinylidene fluoride; Membrane; Wetting properties

IV. Nanofiltration Applications: Desalination and Water Treatment

Low-pressure nanofiltration coupled with ultrafiltration: an efficient solution for drinking water treatment

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In recent years, society has become more concerned about the environment and thus triggers the search for more ecological solutions in the field of drinking water treatment. In this context, low-pressure nanofiltration (NF) stands out for its advantages: (1) less chemical consumption and sludge production; (2) less sensitive to water quality; (3) negligible salt removal and (4) low-pressure operation (<5 bar), resulting in low operational costs.

The project's aim is to evaluate the performance of low pressure NF combined with ultrafiltration (UF) for the treatment of groundwater and colored surface water. Furthermore, the project aims to obtain water losses below 10%, contrary to similar studies which accomplished the same task but with water losses in excess of 30%.

UF unit operates dead-end mode with 200 kDa membrane, while NF operates cross-flow mode with 1kDa membrane. Both UF and NF membranes are chlorine resistant.

UF-NF system produced a colorless permeate (<5 mg/l Pt/Co) with a DOC below 1.5 ppm-C; indifferently of the water source used: spiked groundwater or groundwater. NF membrane is highly efficient in removing large molecules such as humic substances (~1000 g/mol) and building blocs (~300-500 g/mol), accomplishing a removal of 79% and 49% respectively. In contrast, low molecular weight neutrals and acids (<350 g/mol) are partly removed (below 10%).

UF cleaning procedures resulted in water loses around 5%, while NF were 5% due to concentrate flow. In summary, UF-NF combined presents water loses below 10%.

NF permeability performance -shown in Fig. 1- remained stable with a loss of 12% of its original value. A cleaning in place -after 13 months of operation- accomplished a permeability recovery above 95%.

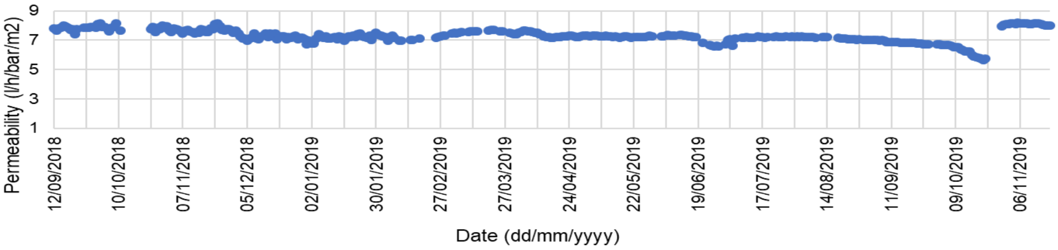

Fig. 1. NF permeability performance.

Motivated by the encouraging results, a new campaign on river water will begin in 2020 (Bretagne, France) where UF-NF will operate with direct feed from the river.

Keywords: Nanofiltration; Ultrafiltration; Groundwater; Drinking water

Hybrid RO-NF for reduced applied pressure requirement in high recovery water treatment and desalination

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Nanofiltration (NF) membrane technology for water treatment and desalination provides the benefit of lower applied pressure requirement relative to reverse osmosis (RO) processes, while providing unique separation capabilities for deployment for municipal and industrial wastewater reclamation and reuse, agricultural drainage water salinity reduction, and for upgrading impaired groundwater. In order to reduce membrane fouling propensity and tune membrane performance, NF membrane surface nano-structuring with tethered polyacrylic acid (PAA) chains was introduced demonstrating low fouling propensity and the ability to overcome the typical permeability/selectivity tradeoff. In addition, the integration of NF with RO water treatment/desalination was evaluated with the goal of reducing the required applied pressure. Fundamental process modeling of the hybrid NF-RO configuration revealed that a minimum (optimal) a pressure reduction exists with respect to the NF stage solute rejection. Also, analysis of the hybrid system configurations (including with stream recycling and interstage pumping), along with experimental studies with a small spiral-wound RO-NF system (~13 m^3/d capacity), demonstrated the potential for significant feed pressure reduction relative to conventional RO.

Keywords: Nanofiltration; Reverse osmosis; Applied pressure; Hybrid RO-NF; Water treatment; Desalination

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NF in hybrids desalting seawater

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The pressure for increasing recovery in desalination processes is driven by environmental concerns related to brine disposal, reduced pretreatment costs, and increased productivity from existing plants with sunk costs. This is so for most feeds. However, in seawater desalination, many sites allow brine discharge to the sea which is often sustainable if properly done. However, there are seawater sites where brine discharge is still a challenging environmental issue. In the case of seawater there is also the potential for salt and minerals production which could defray the costs of increased recovery.

Nanofiltration can play a role, both in increasing recovery in seawater desalination (by removing scaling ions) and in producing minerals from SWRO concentrate (by carrying out a divalent-monovalent split of the salts, allowing each stream to be purified into mineral products). This talk will survey the potential of NF to carry out those roles as well as the experience to date. In its ability to selectively remove divalent ions, NF can serve as pretreatment both in thermal desal (pioneered by the SWCC allowing reduced thermal energy consumption), and pressure-driven SWRO. The various schemes for using NF for mineral production from SWRO concentrate in tandem with other processes will be presented.

Osmotic limitations also place a ceiling on recovery in conventional SWRO processes. The lower salt rejection of NF can allow its use in cascade processes such as EERO that allow higher recoveries while minimizing energy consumption. Such schemes will be touched upon, highlighting the particular properties of NF that are required.

Keywords: Nanofiltration; Hybrid; Seawater desalination; Osmotic limitation; Scaling prevention; High recovery

Chitosan-functionalized biochar for simultaneous sorption of ciprofloxacin and heavy metals in hybrid nanofiltration-adsorption process

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For years, nanofiltration has been successfully tested for removal of heavy metals and organic pollutants from water. However, most of the studies focused on individual removal efficiency of only one group of contaminants: inorganic or organic, even though they co-exist in the environment. Their simultaneous elimination may be difficult due to potential synergistic or antagonistic interactions. The example is ciprofloxacin (CIP), a metal-complexing fluoroquinolone antibiotic. The complexation usually leads to alteration of the physicochemical properties of organic and/or inorganic pollutant. To overcome it, the authors propose to combine nanofiltration with adsorption, which would additionally treat the concentrate from potential complexes. The study aiming to produce chitosan-biochar adsorbent (CH-BB) was conducted and the tests of its efficiency in the simultaneous removal of CIP, and three metal(loid)s (As, Cd and Pb) was evaluated. Modification of raw pig manure biochar resulted in an increase in its adsorption capacity; the highest increment was observed for As (almost 6-fold) and the lowest was observed for CIP (1.1-fold). The adsorption capacity of CH-BB followed the order: Pb > Cd > >As > CIP. The adsorbent was able to successfully remove all targeted contaminants, individually and in the mixture, however it was confirmed that the presence of metal(loid)s led to mobility alteration of CIP. The future perspective is to test the removal efficiency of nanofiltration-adsorption hybrid system to remove CIP and targeted potentially harmful elements.

Keywords: Nanofiltration; Conference; Membrane; Adsorption; Biochar; Chitosan

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Partial desalination of saline groundwater by nanofiltration within the use of Abstraction-Desalination-Recharge methodology

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Saltwater intrusion is a growing problem in areas with close proximity to saline water, showing a shrinking groundwater level due to excessive use of fresh groundwater resources. According to the high concentrations of sodium, chloride and nitrate, saline groundwater might not be suitable for domestic, irrigation or industrial use. Managed aquifer recharge is one option to support the natural groundwater recharge in order to remediate saline aquifers. In semi(-arid) areas, where water in adequate quality and quantity is often not available for artificial recharge, the partial desalination of costal saline groundwater presents a cost effective technology within the Abstraction-Desalination-Recharge (ADR) methodology. Which desalination technique is suitable within this remediation concept depends thereby on the composition and temperature of saline groundwater and the local threshold concentration for infiltration.

In our study, nanofiltration membranes showing a high retention rate for sodium, chloride and nitrate seems to be sufficient for partial desalination of saline groundwater. The desalination performance of the FILMTEC™NF90 were examined within lab-scale tests and simulations using WAVE Design Software for a slightly saline groundwater (1.0 g/L TDS; 14°C), a moderately saline groundwater (2.2 TDS; 29°C) and a very highly saline groundwater (18 g/L, 22°C). The results show that slightly saline groundwater and moderately saline groundwater can be desalinated sufficiently by nanofiltration with 0.01-0.16 kWh/m^3 regarding sodium and chloride threshold concentrations. However, high nitrate concentrations due to agriculture (>0.4 g/L) would be more sufficiently desalinated by membrane capacitive deionization, brackish water membranes or reverse osmosis. Considering the desalination cases were nanofiltration is the most energy efficient technology, the required energy for desalination of saline groundwater within a 4 year remediation period can take 900 to 35 000 €/km of coastline. Since nanofiltration membranes are more efficient in retention of divalent ions, nanofiltration membranes show a high potential implemented in membrane capacitive deionisation for a selective retention of monovalent ions. This study was supported by the European Social Fund (ESF).

Keywords: Nanofiltration; Managed aquifer recharge; Abstraction-Desalination-Recharge (ADR); Saline groundwater

Comparative study on the performance of nanofiltration and reverse osmosis for the elimination of sulphate from well water

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The excessive presence of sulphate in the water of the borehole utilized as a source of potable water supply for the village of Garpéné, located at the Centre Region of Burkina Faso, was revealed through laboratory experimentation. The use of membrane technologies for the elimination of sulphate contaminants has been considered by previous studies. This present study thus proposes to evaluate the removal efficiencies of nanofiltration and reverse osmosis for the elimination of sulphate ions from water sourced from this borehole. A combined nanofiltration (NF270 membrane) and reverse osmosis (TW30 membrane) pilot was used for the filtration of the real borehole water and prepared synthetic solutions. Several experimental conditions made it possible to evaluate the effect of the pressure, the nature of the solution to be filtered, and the ions accompanying the sulphate. The results obtained demonstrated that retention rates of sulphate ions ranging from 95% to 99% and 97% to 99% were obtained respectively with the nanofiltration and reverse osmosis membranes. The results also demonstrated that the operating conditions have a significant effect on the retention of sulphate by the reverse osmosis and nanofiltration membranes. In particular, a linear correlation has been demonstrated between the conversion rate and the transmembrane pressure for the two types of membrane. With regard to the effect of the counter-ion, it has been observed that during nanofiltration, the retention of sulphate ions in the water to be treated is lower in the presence of calcium ions than in the presence of sodium ions whereas in reverse osmosis, little influence of the counter-ions was observed. In view of the results obtained, it appears that the nanofiltration technology alone is suitable for the removal of sulphate with a low energy consumption. Coupling with solar energy could be ensigaged in the Sahelian climatic context.

Keywords: Borehole; Drinking water treatment; Garpéné; Nanofiltration; Reverse osmosis; Sulphate removal

Nanofitration vs. reverse osmosis for brackish water desalination process considering wide range of salinity: pilot scale investigation

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Nanofiltration (NF) may provide the opportunity to reduce feed pressures and operating costs associated with reverse osmosis (RO) for brackish water desalination while providing similar permeate quality. Since NF membranes are supplied in the same configurations as RO membranes, utilities could replace RO with NF spiral-wound elements without the need for significant additional capital investment. In this study, the tradeoffs in choosing NF membranes over

RO were investigated. Pilot-scale testing was performed at brackish water RO (BWRO) desalination facility (VEOLIA-ONEE) located in the south of Morocco. Three feed TDS concentrations of 4, 6 and 10 $g.L^{-1}$ were employed where NaCl was spiked to the real brackish water for TDS adjustment. Two NF membranes (NF90, NE90) with two RO membranes (REBLF, BW30) were targeted for this study. The water permeability of each membrane was evaluated at different feed TDS concentrations.The NF membranes have permeability coefficients up to three times higher than the traditional BWRO membrane BW30.Rejection experiments were conducted at a permeate flux rate of 26 $L.m^{-2}.h^{-1}$ under three different recovery (10%, 45% and 70%) for each feed concentration value. The system was operated by controlling the feed pressure as a variable to obtain the selected values for permeate flux and recovery. The BW30 membrane exhibited the highest TDS rejection and showed more or less steady value (99%) with increasing feed salinity followed by REBLF (92% - 98%) which showed similar behavior as the NF membranes, with rejection decreasing when feed concentration increases. The salt rejections of NF90 were excellent even at high concentrations (between 91% and 98%). This membrane presents hybrid behavior; high rejection that does not change much with salinity (<3%) and the highest water permeability related to its rough surface as evidenced by AFM study. NE90 membrane was more sensitive to salinity changes with rejection decreasing from 96% to 80% with increasing feed concentration and recovery. This membrane could be preferred for long term performance, at low salinity conditions, because of its higher negative charge, hydrophilicity and smooth surface. The required pressures for brackish water desalination with NF membranes were 50% lower than the BW30 membrane to produce the same average flux. Such low pressures reduce power consumption and might be helpful in optimizing the process.

Keywords: Nanofiltration; Reverse osmosis; Desalination; Brackish water; Salinity

Separation of calcium and magnesium from seawater using diananofiltration

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The brine residue from the seawater desalination is returned to the sea which must be done by diluting as far as possible from any marine ecosystem in order not to damage it. Reverse osmosis (RO) retains over 99% of dissolved salts in seawater and produces water that lacks the alkalinity and hardness needed to be consumed, as well as being corrosive. Therefore, it must be remineralized by adding substances such as calcium, magnesium and bicarbonates and adjusting the calcium-carbon balance. As an alternative to RO, nanofiltration (NF) uses membranes that have a higher permeability and the operation consumes less energy when working at lower pressure, in addition, the water produced already has a significant mineral content.

The remineralization of desalinated water was studied by incorporating ions (Mg^{2+} and Ca^{2+}) obtained by diananofiltration of brine from a seawater desalination plant using nanofiltration in two stages. At a pilot scale, the use of the NF270 membrane was determined as an operation condition for the diananofiltration and operating for 15 min with brine at a pressure of 20 bar, a concentrate with enough calcium and magnesium contents is obtained to remineralize desalinated water and obtain a final hardness of 150 ppm. With this system, it is possible to retain 53% of Magnesium, 38% of calcium, while 95% of chloride is eliminated. The remineralized product water using the concentrate obtained by the brine diananofiltration contains 150 ppm of Cl^-, 150 ppm of hardness and pH 7.5. When carrying out the microbiological analysis of the product concentrate, no total coliforms, aerobic bacteria, gram-negative bacteria, gram-positive bacteria, or *Echerichia Coli* are observed, therefore, a post-treatment is not required as ultrafiltration to eliminate possible contamination before remineralizing the desalinated water. The remineralization cost of the m^3 of desalinated water is approximately US $ 0.06.

Keywords: Diananofiltration; Remineralization; Desalination; Seawater

Hardness removal from groundwater by nanofiltration: Experimental and modeling

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Water hardness causes potentially costly nuisance problems in homes and in industry, such as disabling washing, formation of tartar carbonate and magnesium hydroxide in the pipe network of hot water. In this work, the ability of two commercial nanofiltration membranes (NF90, NF270) to remove hardness from the Maâmora groundwater (North of Morocco) was studied. Experiments were carried out in the pressure range of 5–40 bar and for different total hardness (TH) of the feed water. The effects of the trans-membrane pressure on the permeate flux and retention rate were investigated for each membrane. The results show that the nanofiltration membranes are capable of retaining the total hardness present in groundwater.

Experiment results were correlated and analysed using Spiegler–Kedem model. Model parameters (the reflection coefficients and the solute permeability) have been determined for the two membranes using an adequate mathematical optimization procedure (Levenberg-Marquardt´s algorithm: LMA). Model predictions of Ca^{2+} and Mg^{2+} rejection were used to calculate rejection for Total Hardness. The modeling results were in good agreement with the experimental data for both NF90 and NF270 membrane.

The correlation coefficient was greater than 0.9 in all cases. Also, statistical analysis of residual errors based on the root mean square error (RMSE), the normalized root mean square error (NRMSE) and the Nash-sutcliffe efficiency (NSE) coefficient demonstrates the good performance of the model and the optimization procedure. Results of this study are of great importance for local managers since waters of Maâmora groundwater are locally used in many areas and are part of several water management plans.

Keywords: Nanofiltration; Total hardeness; Spiegler–Kedem model; Maâmora groundwater

Insights into the removal of selenium and arsenic by nanofiltration in the presence of organic matter

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Selenium (Se) and arsenic (As) are toxic contaminants in groundwater. Their immobilisation in water is associated with the presence of organic matter (OM), which increases with temperature increase exacerbated of global warming [1]. Selenium and arsenic contamination can be found in groundwater at different salinities [2]. Organic matter and salinity require a roust process. Nanofiltration (NF), which is known to be effective to retain multivalent ions, may be well suited technology for the treatment of different water types contaminated with Se and As.

Nanofiltration experiments were carried with a cross-flow filtration set-up at constant flow rates mode. The experiments were conducted with the emphasis on the role of speciation (Se^{IV}, Se^{VI}, As^{III}, As^{V}), membrane charge screening on the retention mechanisms and in the presence of organic matter (OM), such as humic acid (HA). Asymmetric flow field-flow fractionation coupled on-line with inductively coupled plasma – mass spectrometry (FFF-ICP-MS) was used to quantify OM complexation.

Selenium and arsenic retention with NF showed a strong dependence on pH, which was due to speciation [4-6]. The membrane charge screening, at higher salinity (up to 20 g/L NaCl), had no significant impact on Se and As retention with NF [4-6]. The presence of OM (at 10 mgC/L) enhanced the retention of Se and As^{V} by 10-20%, while 40% of increase was observed for As^{III} when increasing HA concentration to 100 mgC/L. The presence of HA enhanced the membrane negative charge and hence the Donnan exclusion mechanism with the negative Se and As^{V} species (Figure 1B) [4,5]. For the neutral As^{III} species, FFF-ICP-MS measurements showed that As^{III}-HA complexation was the responsible mechanism (Figure 1A) [6]. While NF failed to treat As, this technology was effective in removing Se from real water (Gahard groundwater, Ille et Vilaine, France) achieving both EU (20 μg/L) and WHO (30 μg/L) drinking water guidelines.

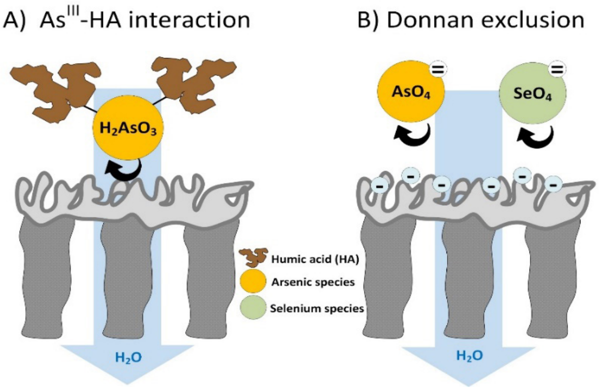

Fig. 1. Proposed mechanisms for As^{III} retention in presence of humic acid and Se and As^{V}.

Keywords: Water treatment; Arsenate; Arsenite; Selenite; Selenate; Membrane filtration.

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Nitrate removal from brackish water by electrodialysis

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The deterioration of the quality of global natural water resources is often shown by its pH variation as well as by an increasing salinity and nitrate concentration leading to serious public concerns, especially in drinking water production. The objective of this study is to evaluate the impact of pH (3 – 11) on nitrate (100 mg/L) removal from brackish water (0 – 10 g/L NaCl; 1 mM $NaHCO_3$) by electrodialysis (ED).

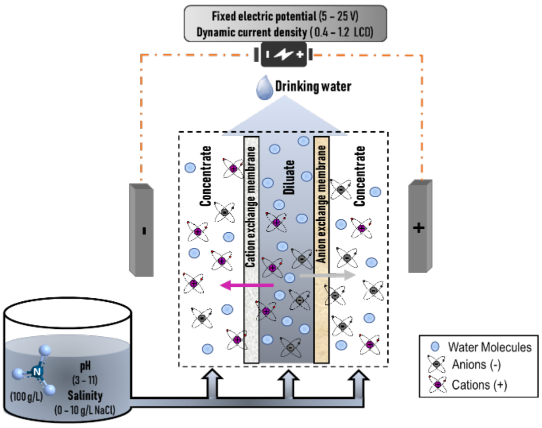

Fig. 1. Schematic illustrating the water treatment by electrodialysis.

Specific energy consumption (SEC) and current efficiency (CE) of the ED process on fixed voltage (5 – 25 V) and dynamic current density (DCD), as function of the limiting current density (0.4 – 1.2 of LCD), were assessed. The results show that the pH and salinity variation did not significantly affect (<5%) the nitrate removal by ED [1]. A similar result was found in the literature for nanofiltration (NF) process, where nitrate retention was pH independent but the retention was reduced with water salinity [4, 5]. The increase in electric potential at fixed or dynamic ED operation caused an increase in nitrate removal and SEC, while the CE was higher at dynamic operation comparing to fixed voltage operation. In all ED experiments at fixed electric potential and DCD, TDS and nitrate concentration reached the drinking water guideline, except at the low extremes of 5 V and 0.4 of LCD. In conclusion, this experimental study has shown that the application of ED is useful for drinking water treatment of brackish water containing nitrate.

Keywords: Batch electrodialysis; Physico-chemical water treatment; Desalination; Nitrogen compound; Dynamic current density

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Lake water utilisation via HDPE intake systems

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The principle of using seawater / lake water is to extract clean deep water from a certain depth, which is raised to a higher storage tanks / basins, before it will be treated, e.g. by nanofiltration and / or UV treatment for the use as potable water.

The company Hydrokarst Swiss is specialized in the installation, welding of high quality HDPE pipes and connecting the system to a special inlet screen which has the advantage of easy cleaning from Quagga Mussels and other marine growth and is designed to allow the use of cleaning tools such as the ones produced from the swiss company Reinhart Hydrocleaning, expert in the internal pipe cleaning. AGRU is expert for the special parts, such as 6 m high sweep bends, which are characterized by very low flow resistance and easiness for cleaning from Quagga Mussels and marine growth on the inside. The pre-assembled pipelines are provided with concrete ballast and pulled over large distances to the installation-site on the water surface. In order to avoid kinks, the commercial divers and specialists of Hydrokarst Swiss lower the pipelines in an S-shaped curve down to depth of 80 m and more. There, the temperature is almost constant between 4° and 8°C all year round.

Fig. 1. floating HDPE Pipeline before sinking to the ground

Keywords: Lake water intake; Subsea pipeline; Deep water pipe; Off-shore; Quagga Mussels.

V. Nanofiltration Applications: Waste Water Treatment and Water Reuse

Solvent tolerant nanofiltration and reverse osmosis membranes for the purification of industrial aqueous streams

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Nanofiltration (NF) and reverse osmosis (RO) membranes are widely used for the purification of aqueous streams. However, the presence of solvents in feed water streams generally affects the performance of these membranes, due to swelling and deterioration, leading to lower permeabilities and unpredictable rejection behavior. To overcome these limitations, the development of cost and energy efficient methods for stable NF and RO membranes are needed, able to separate and substantially concentrate organic compounds from industrial processes and waste streams.

New types of NF/RO membranes are being developed (Solsep, U Twente and KU Leuven) and are expected to have a competitive performance in a wide range of solvent/water mixtures whereby both water and solvent might pass the membrane, while organic compounds and salts are rejected.

VITO is currently testing well-known commercial NF and RO polymeric membranes using a laboratory bench-top cross-flow membrane unit with different model mixtures. These mixtures contain organic compounds like toluene and monoethylene glycol and salts. The experimental trials are conducted with flat sheet membranes, at room temperature and at transmembrane pressures between 10 and 40 bar. Membrane rejection, permeability and stability are thoroughly studied and analyzed. The most performing commercial membranes are also being tested with real relevant industrial streams, using spiral wound modules.

The outcome of this research study will contribute towards a circular economy, by enabling the recovery and re-use of water, solvents and organic compounds and by less waste handling or discharge to the environment.

Keywords: Organic solvent nanofiltration; Polymeric membranes; Water recovery; Solvent recovery; Process intensification

Enhancing chloride rejection in NF for water reuse in evaporative cooling towers

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Evaporative cooling towers are essential in commercial and industrial settings to dissipate excess heat to the atmosphere through evaporation. While evaporation of cooling water takes place, vast amounts of water are discharged from the water reservoir and replaced with fresh clean makeup water. The addition of fresh clean water prevents critical ions in the cooling water from concentrating, which otherwise could cause scaling and corrosion issues.

For reducing water consumption from cooling towers, a dNF40 hollow fiber membrane with a 400 Da MWCO (NX filtration BV, The Netherlands) was chosen for side stream filtration of cooling water, because of its high fouling resistance and possibility for backwashing. Our mass balance model shows that a 70% reduction of the water discharged from cooling towers can be achieved with this specific membrane, which consequently reduces the makeup water consumption by 22%. However, actual water savings depend on rejection of the specific ions and their concentrations in the makeup water. As chloride has a poor membrane rejection, this ion could in some cases limit the achievable water savings.

During batch filtration of cooling water, it was observed that NF rejection of chloride decreases as batch water recovery increase (Fig. 1 left panel), resulting in a low to negative overall rejection of chloride of the batch. In literature, rejection of chloride has been reported to depend on the properties of the ion itself, but also the interaction with other ions, especially sulphate. With this in mind, a novel filtration control concept was developed which utilized the difference in NF rejection of specific ions. By splitting the NF permeate in different fractions, ionic interactions in these fractions were altered. Subjecting the last fraction of the permeate to an additional filtration, hereby increased the overall chloride rejection from around 3.3% and up to 11.2%.

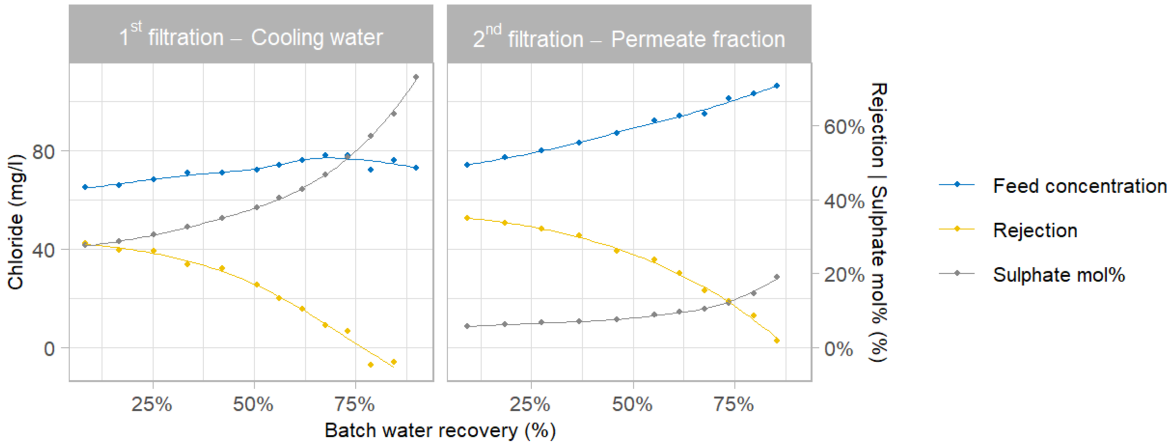

Fig. 1. Membrane rejection and feed concentration of chloride as a function of water recovery during filtration of, cooling water (left) and the last fraction of permeate (right). Sulphate mol% is the mole ratio between chloride and sulphate in the feed water.

Keywords: Nanofiltration; Batch filtration; Chloride rejection; Ionic interactions; Cooling tower; Water reuse

Advances in nanofiltration for landfill leachate treatment

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Landfill leachate is defined by the European Environment Agency as: “Liquid that has seeped through solid waste in a landfill and has extracted soluble dissolved or suspended materials in the process” (EEA, 2004). The treatment of landfill leachate, which is contaminated potentially by e.g. high levels of ammonia, various salts and poorly biodegradable organics, is a challenging technical task. Treatment schemes typically involve different stages including mechanical, physico-chemical, biological and chemical processes. Membrane processes such as membrane bioreactors (MBR) with ultrafiltration for biomass separation as well as reverse osmosis as stand-alone treatment have been applied in landfill leachate treatment for decades.

Nanofiltration (NF) is an established separation technology which employs membranes with a molecular weight cut-off around 200-400 Dalton and surface charge properties which allow for retention of multivalent ions. Next to membrane materials such as organic thin film composites, also inorganic NF membranes are in industrial use and many new materials such as layer-by-layer modified membranes with NF properties are under development.

NF has been tested and applied for landfill leachate treatment as well, but is mostly used in process combinations as not all contaminants contained in the raw leachate can be retained to a sufficient degree by NF alone. Advanced landfill leachate treatment schemes include e.g. MBR plus NF as a polishing stage to achieve stringent direct environmental discharge standards. Process configurations employed include also options for retentate treatment and recycling to the biological stage.

The status and recent advances in research on and technical application of NF in landfill leachate treatment will be presented mainly based on Meier et al. (2020).

Keywords: Nanofiltration; Landfill leachate; Membrane bioreactors; Concentrate treatment.

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Description of polar mobile organic compounds (PMOC) removal by tight nanofiltration (NF90) using decision tree methodology

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Polar mobile organic compounds (PMOC, referred also as Persistent Mobile Organic Compounds) are highly polar chemicals and tend to accumulate due to their low degradation properties and slow adsorption kinetics in short water. Due to their properties, PMOC might be partially eliminated by advanced technologies such as activated carbon adsorption, membrane processes and advanced oxidation processes. Several researches were conducted using deep learning tools such as neural network, principal component analysis, quantitative structure activity relationship (QSAR). Yangali-Quintanilla et al. (2009) developed a model for emerging contaminants removal on NF membranes. Their model underlines the importance of geometric properties of MPs, the membranes' molecular weight cut-off, salt rejection and MPs hydrophobicity (logD) values in rejection mechanisms. The present study investigates the rejection of 22 PMOC selected from the Water JPI project PROMOTE on NF membranes at three different TMP. In order to better describe rejection mechanisms the decision tree methodology was employed to link PMOC properties to rejection values. Compared to neural network modelling, decision tree methodology is easier, faster and provides more information on modelling process. Globally, PMOC are highly rejected by membranes whatever the considered experimental conditions. Less rejected compounds are positively charged aromatic amine compounds and TMP has a strong impact on compounds passage. Decision tree methodology was employed to investigate rejection mechanisms. Results underline that PMOC rejection on NF membranes depends on the hydrophilicity and MW (Fig. 1).

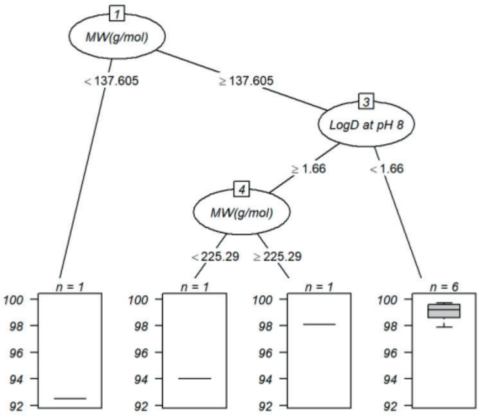

Fig. 1. Rejection mechanisms modelling of PMOC on NF90 at 8 bars by decision tree methodology.

Keywords: Nanofiltration; Polar mobile organic compounds (PMOC); Decision tree

Reference

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Nanofiltration membrane bioreactor + reverse osmosis for wastewater reclamation

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This study examines the feasibility of a novel nanofiltration membrane bioreactor (NFMBR) followed by reverse osmosis (RO) process for water reclamation at both lab-scale and pilot-scale. The lab-scale NFMBR (hollow fibre NF)+RO system was applied to treat municipal wastewater and the results showed that (1) the NF-MBR (at a constant flux of 10 L/m^{2}h) achieved superior MBR permeate quality due to enhanced biodegradation and high rejection capacity of the NF membrane, leading to lower RO fouling rates (~3.3 times; RO was operated at 90% recovery) compared to that fed with an ultrafiltration (UF) MBR permeate. (2) The cake layer fouling that caused the cake-enhanced osmotic pressure effect contributed predominantly to NF membrane fouling. With extending sludge retention time (SRT) of NFMBR, more severe NF membrane fouling was observed, attributing to the greater formation of calcium phosphate scale and Ca-polysaccharides complex. (3) Extending SRT could improve the microbial bio-flocculation capability, but did not influence the microbial activity, viability, and community structure in the NFMBR. (4) Extending SRT did not impact NFMBR permeate quality, but led to a higher RO membrane fouling rate, implying organic compositions in NFMBR permeate may influence RO performance. (5) The calculated energy consumption of the NFMBR+RO system at 90% recovery was comparable to that of the UFMBR+RO at 75% recovery, which proves the economic feasibility of NFMBR+RO for high recovery water reclamation. Furthermore, the pilot-scale NFMBR (4″ hollow fiber NF module)+RO system was continuously operated for ~290 days, which achieved excellent treatment efficiency at 90% recovery due to superior NFMBR permeate quality (total organic carbon less than 2 mg/L). The pilot NFMBR+RO system successfully demonstrated its long-term stability, feasibility, and scalability for water reclamation.

Keywords: Nanofiltration; Membrane bioreactor; Reverse osmosis; Wastewater

Nanofiltration in integrated membrane processes for the biorefinery of agri-food wastes

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The food industry generates a large amount of waste rich in functional compounds that can be used for the development of high-added value products that have applications in the agricultural, nutraceutical and pharmaceutical sectors. The use of by-products and wastes from food processing offers the possibility of generating additional profit and making the industry self-sustainable from a circular economy perspective. The use of appropriate membrane processes enables the recovery and concentration of bioactive compounds from wastewaters (e.g. olive mill wastewaters, OMWWs), vegetable food residues and leaves.

The selection of suitable membrane processes with high selectivity and stability for long-term applications are prerequisites for the use of membrane systems in various industrial fields. The nanofiltration process has been studied in detail as part of an integrated process for recovery, fractionation, and concentration of bioactive compounds, using a pretreatment step to mitigate fouling of nanofiltration membranes. The presentation will focus on the recovery and valorization of functional molecules from real matrices such as OMWWs and tomato leaves extracts. OMWWs are considered a rich source of biophenols with health benefits, while tomato leaves extracts can be a renewable source of oligogalacturonides, used as biopesticides for natural protection of tomato plants. The nanofiltration process (polymeric membranes with MWCO in the range of 150-300 Da and ceramic membrane with a pore size of 2 nm) was investigated

using a laboratory-scale prototype for the biorefinery of OMWWs. High rejection of biophenols (98±1%) was achieved while producing purified water with a recovery factor of 80%. Based on the best performing membrane, a production scale plant for the integrated membrane process was developed and installed at the site of an olive mill. In case of tomato leaves their aqueous extract were treated with membrane processes (30-50 kDa ultrafiltration and 1 kDa nanofiltration membranes) to fractionate their biomolecules (carbohydrates, biophenols and proteins) and allow the better study of their biological activity. The fractionated extract was then used to protect tomato plants against *Pseudomonas syringae*, which can affect crop yield and tomato fruit quality. Promising suppression of bacterial growth was achieved when the carbohydrate-enriched fraction was applied to tomato leaves prior to bacterial infection.

Keywords: Nanofiltration; Integrated membrane process; Bioactive compounds; Biorefinery; Olive mill wastewaters; Tomato leaves.

Towards the valorization of acidic effluents from hydrometallurgical copper plants by acid-resistant polymeric nanofiltration membranes

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The exhaustion of mineral reserves has made necessary to adopt circular economy policies to recover raw materials from secondary sources (i.e. wastes). Due to the depletion of high-purity ores, hydrometallurgical copper plants tend to treat low-quality minerals that contain impurities (e.g. Fe, As and Zn). The presence of such undesired compounds forces to adopt the application of solvent extraction–electrowinning process to obtain copper cathodes (99.999%). However, after the solvent extraction process, the aqueous stream depleted of copper, containing H_2SO_4 (up to 60 g/L) and metals (Fe, Zn) must be appropriately handled. Traditionally, this stream is treated by adding CaO(s) to neutralize acidity and remove metals as hydroxides. Nonetheless, this stream can be used to recover Zn due to its high concentration (around 15 g/L), but it would be necessary to concentrate it up to 50 g/L to make feasible its recovery in a solvent extraction unit prior to electrowinning. This step can be achieved by nanofiltration (NF) membranes due to the high rejection of multivalent species, but also acid can be recovered in the permeate to be reused internally due to the low rejection of monovalent species.

This work evaluates the performance of the acid-resistant Duracid (Suez) NF membranes to valorize acidic effluents from a hydrometallurgical copper plant. The solution was characterized by 55 g/L H_2SO_4, 15 g/L Zn, 1.2 g/L Cl, 0.9 g/L Na and 0.5 g/L Ca, while other elements such as Fe, Pb and Cu were at µg/L levels. Experiments were carried out under a spiral-wound configuration (2.4 m^2) where pressure was varied up to 20 bar. The transport of species was characterized by using the Solution-Electro-Diffusion-Film model (SEDFm), considering chemical equilibria between species. In addition, PHREEQC was used to determine the scaling potential.

Results showed high Zn rejections (>98%) at pressures higher than 12 bar. Additionally, H^+ rejections remained below 15%, revealing the possibility to recover acid in the permeate (mixture of H_2SO_4 and HCl). Simulations using the SEDFm revealed the possibility of concentrating Zn up to 50 g/L after recovering 75% of permeate. However, scaling can occur due to the precipitation of anglesite ($PbSO_4$(s)), anhydrite ($CaSO_4$(s)) and gypsum ($CaSO_4$:$2H_2O$(s)).

Keywords: Nanofiltration; Acidic effluents; Hydrometallurgical copper plants; Duracid; Solution-Electro-Diffusion-Film model

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Multi-objective operation for improving municipal wastewater regeneration with nanofiltration

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The removal of microcontaminants, such as pharmaceuticals or pesticides, which is one of the main concerns in municipal wastewater regeneration jointly with harmful microorganisms, can be performed through the combination of appropriate nanofiltration (NF) systems with advanced oxidation post-treatments, as it has been already demonstrated at pilot-scale. In this research work, the optimization of the NF process operation is analyzed to contribute to the industrialization of this application for the separation and pre-concentration of microcontaminants from municipal wastewater treatment plant effluents. A NF pilot plant, fully instrumentalized (see Figure 1), has been deeply analyzed from the control point of view. The optimal operational points (defined as those that minimize the specific electrical consumption and maximize the high quality permeate production) have been experimentally evaluated at different feed-water salinities (in the range of 1500-5000 μS/cm). Operational constraints (maximum pressure drop, maximum operating pressure and maximum permeate conductivity) have also been taken into account. The main process variables (pressures and flow rates) have been modelled with first order plus dead time transfer introducing typical step changes in the velocity of the NF pump (B1) and in the apertures of recirculation (VR) and concentrate (VC) valves. With the results obtained, a control strategy has been proposed to maintain the process in the optimal operational point despite changes in the feed-water salinity. The analysis carried out suggests that the use of appropriate control structures in NF plants can guarantee safety operation and reduce maintenance costs.

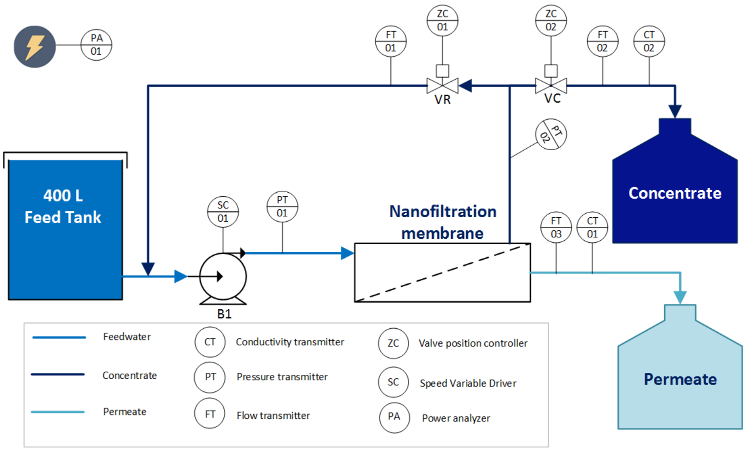

Fig. 1. Schematic diagram of the automatized NF pilot plant

Keywords: Nanofiltration; Wastewater treatment; Process control; Optimization

Interference of organic matter with steroid hormone adsorption in single walled carbon nanotube – ultrafiltration composite membranes

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The occurrence of micropollutants (MPs) in waters results in substantial health burdens [1]. Nanofiltration membranes (NF) can partially remove MPs at significant energy costs while ultrafiltration membranes (UF) cannot remove such small molecules. A way to improve MP removal of UF is to couple filtration and adsorption through a particle-UF composite membrane [2]. Single-walled carbon nanotubes (SWCNTs) are incorporated in the permeate side of an UF for dynamic adsorption of steroid hormones [3]. The UF can retain turbidity, bacteria, and organic matter (OM) from interacting with SWCNTs. This study investigates the interference of various OM types with the adsorption, and the retention of the most interfering OM by the UF (Fig. 1).

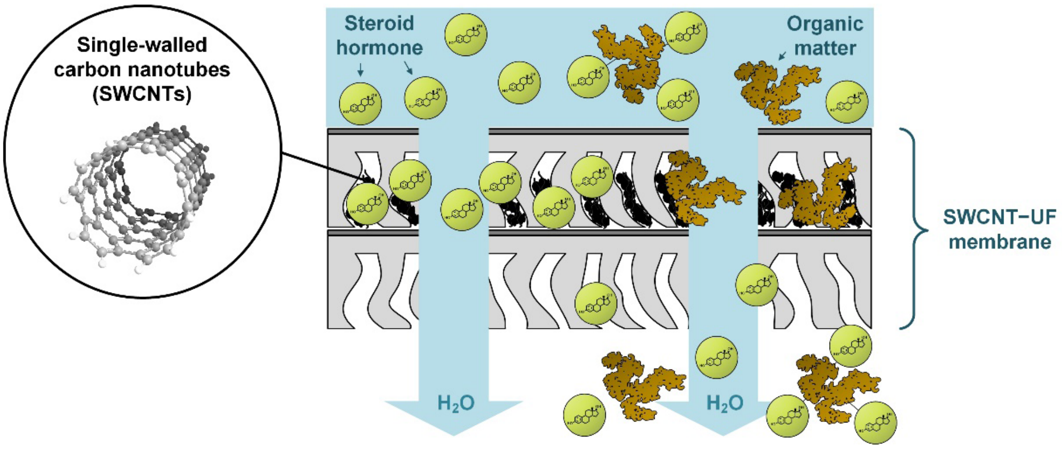

Fig. 1. Schematic of the interference of organic matter that prevents steroid hormone adsorption by the SWCNT-UF composite membrane. Adapted from Nguyen et al. [4].

SWCNT–UF membranes with commercial SWCNTs deposited in the support structure of UF (MWCO range 3–100 kDa, supplied by Millipore, USA) were used. Filtration experiments were conducted with a micro-crossflow filtration system (membrane area 2 cm^2) [5]. Feed solutions contain tritium-labelled steroid hormone (100 ng/L) and OM (10 mgC/L). The OM types include humic acid (HA), Australian natural OM, tannic acid (TA), tea extract, tannin, glucose, alginate, fermentation products and worm farm extract. OM composition was determined with various analytical techniques (UV-Vis spectroscopy, liquid chromatography – organic carbon detection, etc.). The concentrations of hormones were determined with a liquid scintillation counter.

In the presence of certain OM types, E2 removal reduced from 35% to 5–20% because OM interfered with E2 adsorption by SWCNTs. Tannic acid (TA), a polyphenol, caused the most prominent reduction. Nevertheless, with the top UF membrane of compatible pore size, OM can be shielded and its interference is mitigated. For example, a significant amount of TA (80%) was removed by UF 5 kDa, allowing the SWCNT–UF membrane with such MWCO to remove 48% of E2 [4]. In conclusion, with permeate-side incorporation of nanoparticles, good steroid hormone removal can be maintained although the use of nanoparticles may raise toxicity concerns.

Keywords: Carbon-based nanoparticles; Cross-flow filtration; Liquid chromatography – organic carbon detection; Dynamic adsorption; Support layer deposition.

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Removal of glyphosate (GLY) by polymer-based spherical activated carbon (PBSAC)

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Glyphosate (GLY) is the most used herbicide worldwide and exists in the environment at high concentrations from 0.2 to 400 µg/L [1]. Conventional water and wastewater treatment technologies have not shown adequate removal of GLY [2]. PBSAC is an efficient carbon-based adsorbent toward micropollutants [3]. In this regard, this study employs polymer-based activated carbon (PBSAC) to remove GLY and its main metabolite aminomethylphosphonic acid (AMPA) in waters, then integrates PBSAC with ultrafiltration (UF) membrane for removal in a low-pressure filtration process (Figure 1).

PBSAC (Blücher Co., Germany) was evaluated for GLY and AMPA (initial concentrations of 1 µg/L) removal in static adsorption experiment. A composite of UF membrane (10 kDa PLHGC, Millipore Corp., USA) with PBSAC placed in the permeate side was prepared in a stirred cell system [4]. Filtration of feed with GLY and AMPA at concentrations of 1 µg/L was performed through the UF-PBSAC in dead-end mode. Liquid chromatography with tandem mass spectrometry (LC-MS/MS) was used to determine GLY and AMPA concentration with a detection limit of 20 ng/L.

95 % of GLY and 57 % of AMPA were removed from a 1 µg/L (each) mixture of GLY and AMPA by PBSAC 0.5 g/L. Different PBSAC parameters and water quality were determined for adsorption characterization. Higher GLY and AMPA adsorption capacities were observed with PBSAC at higher activation levels, and lower oxygen contents, and at lower pH conditions.

Meanwhile, a thin layer of UF-PBSAC can remove 75 % GLY and 45 % AMPA in preliminary experiments. The saturation was not reached due to the tremendous adsorption capacity of PBSAC. However, the permeate concentration did not reach EU guidelines for pesticides (0.1 µg/L for each pesticide) in the current configuration. In comparison with nanofiltration membrane, UF-PBSAC cannot reach the reported GLY and AMPA removal of typical NF membrane of 85% [5].

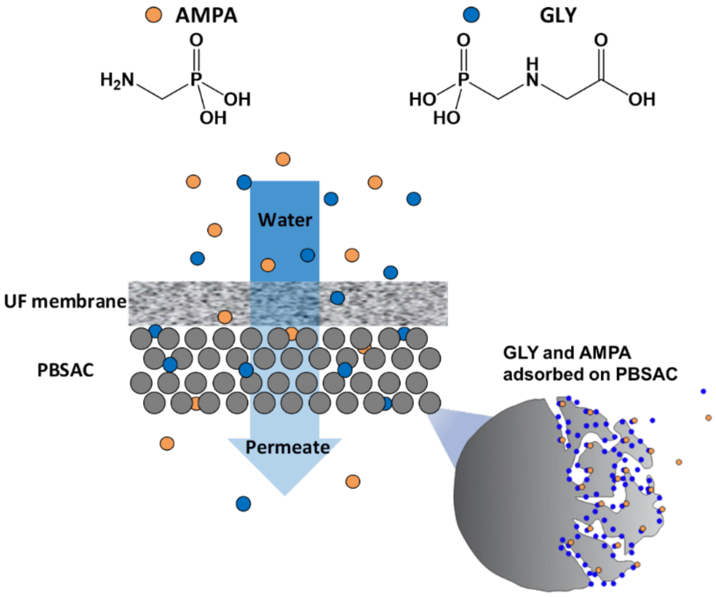

Fig. 1. GLY and AMPA removal by PBSAC and UF-PBSAC

Keywords: Glyphosate (GLY), aminomethylphosphonic acid (AMPA), ultrafiltration membrane, filtration, PBSAC, activated carbon.

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VI. Nanofiltration Applications: Industrial and Resource Recovery

NF membranes in the chemical processing industry

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The chapter chemical Industry includes inorganic and organic chemical Industry but also the pharmaceutical and biotechnology industry. (pp. 543-597)

NF is an established separation technique in the chemical, pharmaceutical, and biotechnology – and they are the least published! In the early 80 I started to sell NF type membranes and elements to the chemical Industry in Switzerland. Looking back, it was somehow funny to understand that they used the membranes for classical "nanofiltration" processes, a few years bevor "nanofiltration membrane" was introduce as a new product. The membrane type which used was a tight UF (G"-Type" from Desalination System. Inc. short "DESAL"). The "G"-type membranes were very tight with a molecular weight range as low as 500 D. Belong others, tight UF and (later) NF membranes were used in the desalination and concentration of water-soluble dyes, purification (desalting) and concentration of optical brightening agents (OBA); In general, the goal was to concentrate and purify small molecules (>150 D) from salty solutions in one step. (Page 564-566). NF rejects the organic molecules and monovalent salts are passing the membrane and get washed out by diafiltration. "G5-type" had very low A-value and therefore required a high operating pressure as high as 30–40 bar to create acceptable fluxes. Later, newer NF membranes based on piperazine amide were introduced having much higher A-Values (water fluxes) and therefore lower feed pressures and better economics.

The new type of NF membrane in spiral wound configuration invoked many other applications. I would like to name brine treatment in the chloralkali industry, where Cl_2 gas and NaOH is produced from NaCl brines. This worldwide dominant process works at 80°C and 300–350 g/L NaCl (at the beginning) and about 200 g/L NaCl at the end of the electrolyzing process). Although the salt used for this process is clean but still contains minor contamination of impurities such as sulfate and divalent cations. To avoid precipitation by Ca- or $BaSO_4$ at the electrolyze cells it is important to purge a part of the salt brine for desulfurization and return it in the bath in order to maintain the SO4 level at or below approx. 5000 ppm. The idea using NF membrane to selectively reject Na_2SO_4 solutions from brine streams was first done in 1992, and between 1993-1995 the performance of several different NF membranes was tested in Kverner Chemetics laboratory in Canada. After patenting, a first full scale SRS plant was built. (SRS: sulfate removal system). Na_2SO_4 was rejected by NF in a brine solution having > 200 g/L NaCl salt at 70°C. This process is very membrane dependent. There are NF membranes in the market which reaches up to 98% rejection for sulfate ions even at 75°C and >99% at lower temperature. (book page 549 – 553). A new aspect: Seawater RO brines are treated increasingly using NF. The NF permeate after reconcentration at 120 bar is a potential source for NaCl brine for chemical industry. (pp. 546-548).

Dominant NF applications are also found in pharmaceutical and biotechnical Industry. Examples are antibiotics recovery from fermentation processes, enzyme recovery, amino acid concentration and purification, protein or polysaccharides purification and concentration, also purification and concentration of contrast media products (X-ray). NF is nowadays one of the key processes in antibiotics production. Proven antibiotic applications include the production of cephalosporin-C, clavulanic acid, erythromycin, 6-APA, 7-ADCA and others. NF can achieve high activity concentration at regular temperatures without stressing the product due to thermal shocks. NF spiral wound systems are working with optimal performance after ceramic microfiltration (MF) or ultrafiltration (UF) which are used to filter the fermentation broth. (pp. 571–575).

Acid-stable (or acid tolerant) polymer NF spiral wound elements are increasingly available to purify and reuse acids and for the recovery of metals which are dissolved in acids. Some of the chemical and biotechnology processes are operated at low pH and NF is used to concentrate and purify the products at low pH whereas the monovalent acids are passing the membrane and reused while the products are rejected and separated.

Solvent stable NF membrane in spiral wound configuration are in use to purify solvents and recycle expensive catalysts. A NF system is described which is fed by a solvent/oil/wax mix and where the solvent is recycled and reused for a dewaxing process. (page 581-584). The successful introduction of solvent stable polymeric and ceramic membranes with a MWCO of 150 (polymer) and 200-400 (ceramic) will probably invoke more applications in the chemical and pharmaceutical Industry.

Ceramic nanofiltration membranes in process- and wastewater treatment

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Ceramic (TiO_2/ZrO_2) nanofiltration membranes have been successfully developed to industrial scale. These membranes, which are stable in the pH range from 0-14 and show a high temperature stability, have proven their performance in many industrial water treatment applications. Typical applications focus on the separation of organic molecules, the retention of multivalent ions, the decolorization of waters, the retention of micropollutants or a combination thereof.

Over the past 20 years two types of ceramic nanofiltration membranes with typical cut-off values of 450 Da and 200 Da in aqueous mixtures have been developed. Furthermore, the membrane geometry and specific membrane area were developed further. Whereas the development started on small single channel tubes the ceramic nanofiltration membranes are now available on an industrial scale with specific membrane areas of up to 1.2 m^2 per membrane as 151 channel tubes from project partner Rauschert. Newest developments focus on rotating disc membranes. Nanofiltration membrane layers on rotating disc filters are a worldwide novelty. Membrane systems with rotating disc filters are considered to be operated more efficiently in terms of energy, since the energy required to rotate the disc filters is lower than the pump energy required to operate the crossflow filtration systems.

The presentation will give an introduction into relevant membrane properties and realized applications using ceramic NF membranes.

Fig. 1. From left to right: Tubular ceramic nanofiltration membranes of different geometry, IKTS mobile pilot filtration system, retention of painkiller Naproxen by ceramic nanofiltration membrane

Keywords: Ceramic nanofiltration; Micropollutants; Water treatment

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Nanofiltration as a part of nitrogen recovery concept

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Wastewater nutrient recovery has two-way benefits by removing impurities from usable water as well as by concentrating nutrients to be utilized as chemical products. In this study, nanofiltration (NF) was studied as a part of nitrogen recovery concept for both municipal and industrial wastewaters. Good pre-treatment, such as flocculation aided belt filtration and subsequent microfiltration (MF) for fibers removal, and/or precipitation, settling and MF for scalants removal was essential for fouling prevention in NF. Pre-treatment also affected the purity of recovered nutrients. The fibers removal by flocculants, which was carried out at neutral pH, had minor influence on the concentration of nitrogen for subsequent NF. Removal of scalants at low pH had no effect on ammonium concentration whereas at high pH 10, ammonium concentration decreased more than 20%. Scalants removal had minor effect on nitrate concentration. Recovery of ammonium nitrogen, which was the main component in the studied wastewaters, was pH dependent. Ammonium starts at pH over nine to be in gaseous ammonia form, and on the other hand, gas releases easily from liquors and permeates the membranes. Ammonium rejection using loose NF, such as NF270 having cut-off rate of ~400 Da, was only 20-50% at near neutral or high pH. By using tighter membrane, such as NF90 having cut off rate of ~200 Da, and decreasing pH of the wastewaters, ammonium rejection could be increased even to over 90%. However, nitrate rejection using NF membranes was poor at tested pH range. Based on the results, there are possibilities for NF to be part of nitrogen recovery, when the main nitrogen component of the wastewater is ammonium.

Keywords: Nanofiltration; Nitrogen; Ammonium; Nitrate; Recovery; Fouling.

Nanofiltration of saline oil-water emulsions: Combined effect of salt concentration polarization and fouling by oil on flux performance

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The exploration and production of oil and gas generates a large volume of oily wastewater known as produced water. Produced water composition varies significantly depending on the type of hydrocarbon product generated, the geographic location of the field, and the amount of time the water remains in contact with the geological formation. However, the main constituent is suspended oil (100–5000 mg/L) often accompanied by elevated levels of salt. The high salinity in produced water is primarily attributed to the dissolved sodium and chloride ions where the concentration of total dissolved solids can reach ~ 300 g/L. If not properly treated, the discharge of produced water can pose significant environmental risks.

The present study focused on the separation of saline oil-in-water emulsions by nanofiltration membranes. We show that the interaction of emulsified oil and rejected dissolved species (NaCl and surfactant) in the vicinity of the membrane surface affects permeate flux and selectivity of separation. Concentration dependences of both the salt permeability coefficient and the reflection coefficient are determined and used to evaluate relative contributions of osmotic pressure and oil fouling to the overall flux decline. The decrease in the reflection coefficient with solute concentration minimizes the effect of concentration polarization and makes oil layer formation on the membrane surface the dominant fouling mechanism. The overall performance of a nanofiltration membrane treating saline oil-water emulsion is determined by emulsion stability and is relatively insensitive to feed salinity. More generally, understanding the behavior of oil within the mass transfer boundary layer with high salt concentration should help devise better strategies for minimizing membrane fouling.

Keywords: Nanofiltration; Reflection coefficient; Oil-water emulsion; Concentration polarization; Salt permeability coefficient; Fouling.

Commercial nanofiltration membranes applied in an integrated route for the reclamation of gold mining effluent

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Pressure oxidation (POX) is a hydrometallurgical process that is widely used to release gold occluded in the mineral matrix. This process is responsible for a high consumption of water, generating a large volume of effluent (63 m^3/h), which is composed of several metals and sulfuric acid in high concentrations. In this way, the successful implementation of the ultrafiltration (UF) - nanofiltration (NF) - reverse osmosis (RO) membrane route can produce water for reuse and concentrate solutes for later recovery in order to decrease the water footprint of the mining sector. Despite the potential

of this route, the interaction between the effluents and the membrane, mainly NF, represents key factors that impact the operation and should be better understood. In this study, commercial NF membranes (NF90, NF270, MPF34, DK, and Duracid) were evaluated in terms of performance, such as permeate flux, metal rejection, acid recovery, and scale potential. The DK showed the greatest potential for application in the treatment of POX effluents. In the NF process, an average concentration factor of 2 was observed for the concentration of retentate metals at 50% RR permeate. The results showed the importance of NF membrane selection to increase the sustainability of the treatment route performance due to the effluent characteristics.

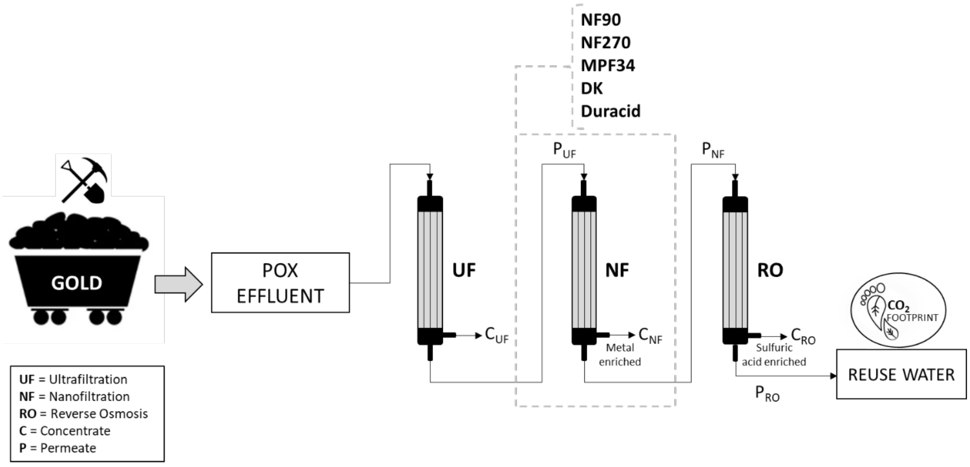

Fig. 1. Schematic diagram of the UF-NF-RO treatment route

Keywords: Nanofiltration membranes; Gold mining effluent; Wastewater treatment; Reuse water.

Application of hollow fiber nanofiltration membrane to reduce water footprint of evaporative cooling towers

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Evaporative cooling towers are critical for cooling in large industrial and commercial buildings. It is a major water consuming process as it involves dissipating waste heat through evaporation of tap water quality water. This requires constant supply of fresh make-up water while generating a brine (blowdown) that is periodically drained to prevent scaling/corrosion issues. We developed a novel concept using hollow fiber nanofiltration (HFNF) to reduce the water footprint of cooling towers. The HFNF is integrated as a side-stream filtration unit to remove critical salts from the cooling water, consequently lowering the blowdown waste and saving make-up water without exceeding cooling water quality limits. The membrane used is a polyelectrolyte multilayer (PEM) membrane (dNF40) from NX Filtration, which was selected for its high tolerance to fouling (back-washable) and chlorine (a common biocide applied in cooling towers). The concept was tested in pilot/demo scale for treatment of cooling water in two industrial facilities in Denmark. Results show that dNF40 can maintain levels of critical ions (i.e., calcium, sulphate) in cooling water well below the water quality limits, while the low membrane rejections of dissolved silica and chloride define the maximum water savings attainable in the cooling tower at the allowable limits. Experimental and modelling data demonstrated make-up water savings of 17-25% and blowdown discharge reduction of 50-75% are attainable, depending on the cooling tower load and make-up water quality. The side-stream HFNF also removed suspended solids, nutrients, organics and planktonic bacteria (including Legionella) from the cooling water, thereby reducing fouling and biological risk during cooling tower operation. We have deployed two side-stream HFNF units operated with an auto-adaptive control algorithm in two industrial cooling towers, which confirmed actual water savings and operational robustness of the concept (Fig. 1).

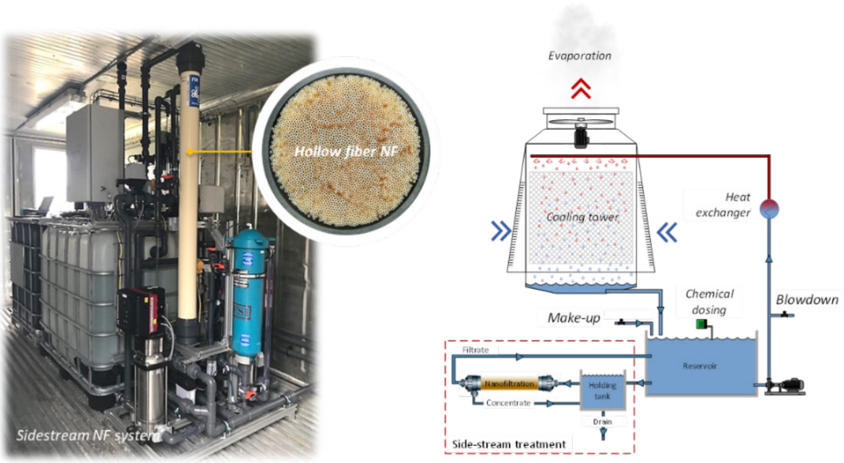

Fig. 1. The side-stream treatment unit with PEM hollow fiber NF (left) and schematic diagram of the unit installed in a cooling tower (right).

Keywords: Nanofiltration; PEM membrane; Cooling tower; Water reuse; Control algorithm

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Advanced organic solvent nanofiltration in food and pharma industry – from scratch to production scale

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A new optimised synthesis route was established for a product in the food and pharma sector at DSM. However, a new impurity in the intermediate production disturbed the further processing and needed to be removed. Several separation methods in the laboratory were investigated (e.g. thermal separation, crystallisation, adsorption etc.). However, only the separation via nanofiltration produced results which are implementable later in production scale.

This OSN (organic solvent nanofiltration) purification method is advanced, since a four-component-mixture must be processed: two solutes – the impurity and the precursor, and two organic solvents. Not only, the membrane and the operation conditions must be suitable to retain the impurity and at the same time provide a reasonable flux for the precursor. Also, the ratio of the two organic solvents must be kept in a narrow range where a sufficient solubility of the precursor is assured, despite the different permeation properties of the solvents. In addition, long-term effects regarding scaling have to be considered.

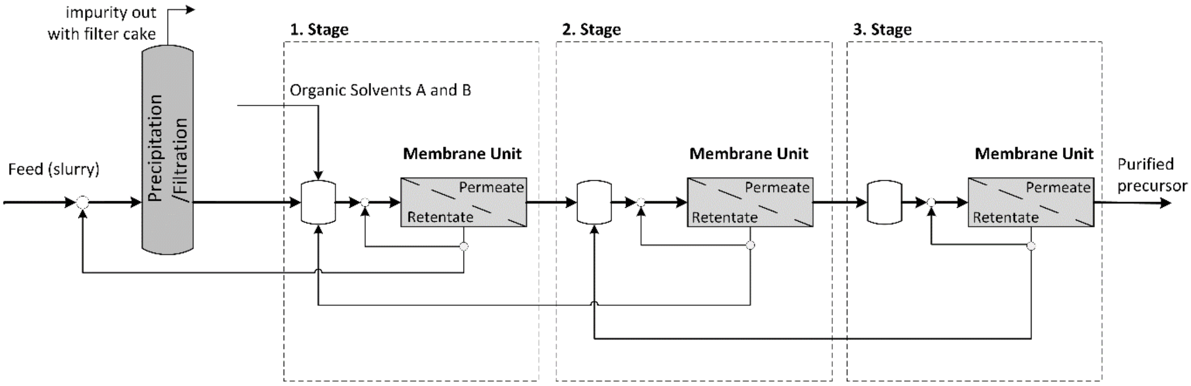

Fig. 1. Three-staged process design of the OSN system

During lab and piloting trials a three-staged process was developed which combines a precipitation/filtration unit with a subsequent OSN unit and advanced recycle systems as shown in Fig. 1. This process is currently under construction in one of the production plants of DSM.

Keywords: Organic solvent nanofiltration; Scale up; Process design; Industry

Generation of sulfuric acid and sodium hydroxide from the sodium sulphate salt by electro-electrodialysis (EED)

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The electro-electrodialysis process (EED) is used to generate H_2SO_4 and NaOH from sulphate sodium salt Na_2SO_4. The key phenomenon limiting the current efficiency of this process is the proton leakage through the anion selective membrane was not observed.

The electro-electrodialysis was carried out with a three-compartment cell with two platinum-coated titanium electrodes separated by three compartments. The couple membrane used in this work is AFN and CMX. The experiments were carried out for four current densities 8.33 $mA.cm^{-2}$,11.11 $mA.cm^{-2}$, 13.88 $mA.cm^{-2}$ and 27.77 $mA.cm^{-2}$.

For each current density, a voltage variation of cell and concentrations of H_2SO_4 and NaOH in the two compartments with the current density was used. The concentration of H_2SO_4 and NaOH increases with current density and with time, but higher for NaOH. The current efficiency increases with the current applied to the cell.

The request for the electro-electrodialysis operation power was calculated in terms of the electrical energy consumed to produce H_2SO_4 and NaOH for 6 h of electro-electrodialysis and it was found floating with the current applied and concentration sodium sulphate used and the concentration of H_2SO_4 and NaOH products, but is comparable for both initial concentrations of sodium sulfate.

Keywords: Electro-electrodialysis; Sodium sulphate; Sulfuric acid; Sodium hydroxide.

This work was supported by TIA Co. (France). The authors express their thanks for this support.

VII. Nanofiltration New Materials

Artificial water channels — toward biomimetic membranes for desalination

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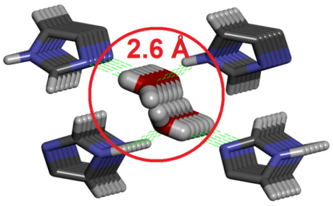

This lecture discusses the incipient development of the first artificial water channels systems. We include only systems that integrate synthetic elements in their water selective translocation unit. Therefore, we exclude peptide channels because their sequences derive from the proteins in natural channels. We review many of the natural systems involved in water and related proton transport processes. We describe how these systems can fit within our primary goal of maintaining natural function within bio-assisted artificial systems. In the last part, we present several inspiring breakthroughs from the last decade in the field of biomimetic artificial water channels. All these examples demonstrate how the novel interactive water-channels can parallel biomolecular systems. At the same time these simpler artificial water channels offer a means of understanding water structures useful to understanding many biological scenarios. Moreover, they can be used for the preparation of highly selective membranes for desalination.

Keywords: Artificial water channels; BWRO; SWRO; PA membrane

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Polyelectrolytes and polymeric ionomers for tailoring selectivity and permeability of nanofiltration membranes

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Numerous successful applications provide evidence that nanofiltration (NF) can be an efficient and sustainable technology to solve relevant separation problems in a wide range of scales. The scope could be further expanded with NF membranes that have tailored selectivity at competitive permeance and sufficient stability for specific separation problems with aqueous or organic mixtures, and that can be fabricated by easily scalable processes [1]. The focus of this presentation will be on polymers containing fixed charged groups, but having different macromolecular structure and architecture, and their potential as building blocks for barrier layers in NF membranes. One can qualitatively distinguish with respect to the content of ionic groups between "polyelectrolytes" (relatively high) and "polymeric ionomers" (relatively low). However, it is more appropriate to consider the interactions between the ionic groups and the consequences for polymer structure in solution and bulk states [2]. This is most relevant with view on potential utilization as barrier layer of a NF membrane and suited processing conditions to obtain such layers. This will be discussed also using examples for thin-film composite NF membranes, including synthesis and evaluation of a library of anion-exchange poly(arylene ethersulfone) multi-block copolymers as NF-selective materials [3], cross-linked polyelectrolyte layers on ultrafiltration membranes [4], or ongoing attempts to utilize tailored polyelectrolyte nanogel particles in combination with polyelectrolytes or polymeric ionomers of opposite charge as building blocks for layers with unconventional ion selectivity.

Keywords: Nanofiltration membrane; Polyelectrolyte; Ionomer; Cross-linking; Ion selectivity.

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Functionalized thin-film nanofiltration membranes

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The implementation of thin-film composite membranes has revolutionized the seawater desalination decades ago. The integration of thin coatings on membranes is currently the most effective and versatile way to promote high permeance and selectivity also for nanofiltration. Our group has been proposing new functionalizations, new materials and methods for nanofiltration membranes. We have been conducting interfacial polymerization with monomers such as porphyrin, dendrimers, and more recently macrocycles such as cyclodextrin. Other methods under investigation are the deposition of covalent organic framework (COF), covalent organic networks (CON), by in situ reaction on a porous asymmetric support. Furthermore, nanochannels can be strictly engineered in the interlayers of 2D materials, such as graphene oxide, inducing the formation of paths with dual-dimensions to balance selectivity and permeance or crosslinking to enhance the stability. The membranes have been tested for nanofiltration in water and in organic solvent medium.

Keywords: Nanofiltration; Thin-film; Interfacial polymerization; COF/CON; 2D layers

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Epoxides as a novel platform chemistry for water purification membranes

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Epoxide chemistry has been applied for many decades in a variety of industries owing to their excellent chemical, physical, and thermal resistance and the simple tunability of their chemical composition. However, in membrane technology, the use of epoxides for the synthesis of thin top-layers for thin-film composite (TFC) membranes has only recently been demonstrated by our group [1,2]. The same principles of polyamide interfacial polymerization (IP) were successfully transferred to the synthesis of epoxide thin films. Further densification of the interfacially polymerized thin film by inducing additional cross-links allowed to improve membrane performance from the loose to the tight nanofiltration range. By careful consideration of the epoxide functionality and initiator type, the salt rejection and water permeance could be tuned to achieve permeances between 1.5 and 3 L/m^{2}hbar with monovalent salt rejection between 60 and 90%. The epoxy-based top-layers are also highly cross-linked and intrinsically robust as demonstrated by their full stability in sodium hypochlorite (NaOCl, 500 ppm), and in caustic (NaOH, pH 12) and acidic (HNO_3, pH 1) environments. Stability tests for 5 days in organic solvents such as toluene, ethanol and isopropanol showed no degradation in the desalination performance nor in the physicochemical properties of the robust membranes. As a consequence, these membranes can be cleaned with these chemicals or even used under these harsh conditions, contrary to state-of-the-art polyamide-based membranes which would degrade. Epoxy-based membranes may therefore lay the foundation for a new generation of stable (solvent-resistant) nanofiltration TFC membranes with a wide range of performance that is tunable for specific applications.

Keywords: Nanofiltration; Epoxide chemistry; Water softening; Interfacial polymerization; Chemical resistance.

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Aromatic porous polymer network membranes for organic solvent nanofiltration under extreme conditions

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Aromatic porous polymer networks (PPNs) are promising candidate materials for organic solvent nanofiltration (OSN) membranes, in which molecular-sieving selectivity, high permeability, and chemical/structural stability can be integrated. In this work, aromatic PPN membranes p-PPN, m-PPN and tri-PPN are fabricated by in situ aldol triple condensation cross-linking. These membranes demonstrate high stability, permeability and sharp selectivity in OSN, thanks to the aromatic nature of the backbone, high surface area (up to 1235 m2/g), and narrowly distributed pore sizes. They possess a high organic solvent permeability so that a good permeance is achieved despite a thickness over 100 μm. Molecular weight cut-off and molecular weight retention onset of these membranes are ~600 g/mol and 350 g/mol, respectively, making it possible to efficiently separate molecules from a complex mixture composed of compounds with only marginally different molecular weights. As a result of the highly stable nature of the aromatic backbones, these PPN membranes show retained structural integrity and OSN performance in the presence of either strong acid or strong base for over 50 h. The extraordinary stability, integrated with the excellent permeability and selectivity, render these PPN membranes promising candidate for challenging OSN applications under extreme conditions.

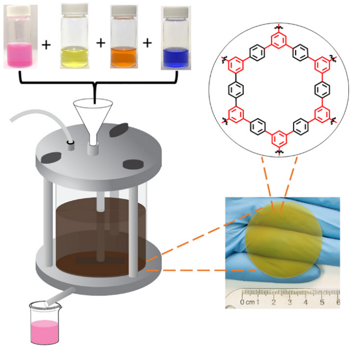

Fig. 1. Highly robust aromatic porous polymer networks: the backbone structure and organic solvent nanofiltration in harsh conditions.

Keywords: Nanofiltration; Porous; Polymer network; Stability; Organic.

Direct treatment of various water sources using hollow fiber nanofiltration membranes

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Introduction

Warm and dry summers are becoming a reality in the north western part of Europe. The shift in climate is already resulting in alarmingly low levels of groundwater. This water is intended to be used for irrigation and industrial use. At the same time, groundwater is also one of the most important sources for producing potable water in many European countries. This results in water scarcity, also in traditionally wet regions of Europe. Next-generation hollow fiber NF membranes based on polyelectrolyte multilayers are suitable for direct treatment of alternative water sources, such as surface water and (biologically treated) wastewater. In the last years, these membranes have come of age and are now commercially used in various water treatment processes. The main benefits of these new chemistries for NF membranes on hollow fibers include micropollutant and organics removal, fouling resistance, chlorine tolerance, minimal pretreatment, reduced chemical usage, and cleanability at a wide pH range. These benefits lead to significantly lower operating costs and considerable CO_2 footprint reduction.

Summary

In this presentation we will provide an overview on how polyelectrolyte multilayer bases membranes are used in a multitude of (commercial) applications. The inherent nature of the layer-by-layer production method of the membranes allows for precise tuning of membrane properties. As such, dense NF membranes (MWCO < 400 Da) can be made that reject organic micropollutants, such as medicines or PFAS from fresh water sources. Chemically stable NF membranes can be obtained that are used to recover high concentrations of caustic soda from waste streams and to reduce both water and chemical consumption. We will also show that more open NF membranes (MWCO 400-800 Da) are perfectly suited in hybrid processes with advanced oxidation for cost effective wastewater treatment for reuse purposes and decentralized processes. To summarize, in this presentation we will show the versatility, stability, and maturity of these selective commercially available polyelectrolyte multilayer based hollow fiber membranes.

Keywords: Nanofiltration membrane hollow fiber; Water reuse; Micropollutants; Wastewater treatment.

Molecular-level design of highly selective nanofiltration membranes

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Industrial separation and purification processes consume 10–15% of the world's energy production. The replacement of distillation by membrane separation without phase change could reduce this energy demand drastically. But for energy-efficient separation, there is still a strong need for highly permeable and selective membranes with a sharp cut-off in a targeted size range. This presentation will give a brief overview of recent approaches of a molecular level design of nanofiltration membranes for aqueous and non-aqueous applications. Examples of such a design are the use of polymers with intrinsic microporosity (PIMs), the self-assembly of block copolymers, or the integration of selective cavitands into the membrane-forming polymer structure. This presentation will focus on the latter approach. One of the best-known organic cavitands is cyclodextrin, which contains defined hydrophobic cavities able to embrace guest molecules selectively. Cyclodextrins are attractive for size-selective molecular separations, and cyclodextrin-based cross-linked polymers have been in preparation for some time. However, manufacturing mechanically and chemically stable pure cyclodextrin films has remained challenging. We performed cyclodextrin interfacial polymerization on a commercial ultrafiltration PAN membrane (GMT, Rheinfelden). We started with pure and continued then with aminated cyclodextrin. Sub-10 nm thin but mechanically and chemically highly stable NF membranes could be manufactured. The high reactivity of the amino-CD allows a very short reaction time. This enables, in principle, the manufacturing of ultrathin coatings using state-of-the-art membrane manufacturing machines. Particularly noteworthy is the ability of this new membrane-type to discriminate between molecules with nearly identical molecular weights but different shapes. Comparing this membrane with the best commercial and state-of-the-art membranes reveals its outstanding properties.

Practical problems of industrial upscaling will be discussed briefly.

Keywords: Interfacial polymerization; Thin-film composite; Cyclodextrin; Shape-selectivity.

Polyelectrolyte self-assembly for the next generation of sustainable nanofiltration membranes: From ultra-thin coatings to complete membranes

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The intensification of the use and reuse of fresh water resources comes at a cost. Reports on rising levels of emerging contaminants in our water are numerous. New and better membranes are urgently needed to come to better and more sustainable water treatment processes. Over the past decade polyelectrolyte multilayers have established themselves as one of the most promising new materials in membrane Science and Technology [1]. Novel nanofiltration membranes are prepared by the self-assembly of oppositely charged polyelectrolytes at the interfaces of a porous ultrafiltration support membrane. In this so-called Layer-by-Layer (LbL) assembly, the support membrane is alternatively exposed to polycations and polyanions, to build polyelectrolyte multilayer's (PEMs) of controllable thickness. After coating the separation properties of the membrane are completely determined by the applied PEM layer.

In this contribution, we will discuss how a novel asymmetric approach to PEM membrane preparation can lead to membranes with unique separation properties. We present a membrane with an active separation layer of just 4-6 nm in thickness. The membrane retains small organics at high fluxes, while allowing ions to easily pass through the membrane. The unique membrane properties also allow for new processes to more efficiently treat both surface and waste water [2].

And we can even push this one step further. By a carefully controlled 1-step precipitation process, we can prepare polyelectrolyte complex based membranes, where the polyelectrolyte complex functions as the porous support membrane and as the separation layer. This aqueous phase separation (APS) approach, has strong similarities to the traditional non-solvent induced phase separation process, but without producing water streams contaminated with aprotic organic solvents. Indeed, also in APS it is possible to create very promising nanofiltration membranes [3], with excellent stability in organic solvents and at extreme pH values [3].

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Composite hollow fiber nanofiltration membranes via chemistry in a spinneret

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The fabrication of composite membrane structures typically requires several procedurally complex membrane modification steps. In recent years, we have demonstrated that the scalable technology basis of "Chemistry in a Spinneret" serves as a one-step fabrication process for composite hollow membranes, providing an intelligent alternative for the multi-step membrane modification processes. The formation of a porous hollow fiber membrane acts as an underlying process superimposed with chemical reactions and/or ionic interactions of additives occurring at the interface of the polymer solution and lumen fluid.

In this paper, we present three different material systems that have been successfully converted into composite hollow fiber nanofiltration membranes using the "Chemistry in a Spinneret" technology.

The formation of composite hollow fiber membranes with crosslinked separation layers is enabled by applying the crosslinking reactions of polyethylenimine with trimesoyl chloride and glutaraldehyde during hollow fiber spinning. Both created layers exhibit similar nanofiltration properties and were investigated for solvent, pH, and backwash stability.

The combination of ionic crosslinking of oppositely charged polyelectrolytes and covalent crosslinking of the polyelectrolytes with glutaraldehyde during hollow fiber spinning results in nanofiltration membranes. The fibers show high salt retentions and a low molecular weight cut-off of 280 Da.

In the last material system, sulfonated polyethersulfone (SPES) serves as a polyanionic additive in the polymer solution that ionically complexes with polycations in the lumen fluid during fiber spinning. The spun fibers have a positively charged lumen surface, which enables subsequent coating with the polyanion polystyrene sulfonate (PSS) in a coating bath. The resulting composite hollow fiber membranes have open to dense nanofiltration characteristics depending on the used polyelectrolytes.

The various material systems investigated establish the "Chemistry in a Spinneret" as a universal technology base for the fabrication of nanofiltration hollow fiber membranes. The results provide a broad basis for further membrane material and morphology developments.

Keywords: Nanofiltration; Composite hollow fiber membranes; Crosslinking; Phase inversion; Polyelectrolyte; Chemistry in a spinneret.

Preparation and characterization of flat and tubular nanofiltration membranes of polypyrrole. Application in Congo Red dye and Na_2SO_4 removal

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The present study consists in the development of composite membranes by deposition of polypyrrole polymer layer on flat pozzolan and tubular carbone-ZrO_2 microfiltration supports. In order to evaluate their performances, the prepared membranes were applied to eliminate congo red dye and inorganic salt.

The polypyrrole membranes were successfully developed using the interfacial polymerization process. A thin layer of polypyrrole was synthesized on the support surface by the chemical polymerization method. The polypyrrole was prepared using the pyrrole solution (0.05 M) with ultrapure water, followed by the addition of $FeCl_3$ (0.1M) as oxidizing agent. This preparation was kept unagitated for 24 h to achieve decantation of polypyrrole.

The chemical synthesis of the polypyrrole polymer was confirmed by infrared spectroscopy and X-ray diffraction analyses, whereas scanning electron microscopy and contact angle techniques revealed the coherence, homogeneity and hydrophobicity of 108° and 138° for the flat and tubular polypyrrole membrane respectively.

To study the filtration efficiency, the flat polypyrrole membrane was tested for congo red dye removal, and the tubular polypyrrole membrane was applied for congo dye and Na_2SO_4 removal. The experimental results at optimized conditions determined that the polypyrrole flat and tubular membranes have a permeability of 10.3 and 6.0 $L.h^{-1}.m^{-2}.bar^{-1}$ respectively. The polypyrrole flat membrane removes 98% of congo red. The polypyrrole tubular membrane removes Congo red (99.7 ± 2%) and Na_2SO_4 (92.6 ± 3%) at high pH.

Keywords: Polypyrrole; Composite membrane; Nanofiltration; Salt; Dye; Wastewater.

This work was supported by MESRSFC (Ministère de l'Enseignement Supérieur et de la Recherche Scientifique et de la Formation des Cadres – Morocco) and CNRST (Project number PPR/2015/72).

Preparation and characterization of low-cost NaA zeolite membrane on kaolinite support

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In the last two decades, zeolite membranes have attracted a lot of interest, not only for their well-defined channels structure and uniform pore size, but also for their high thermal and excellent chemical stability. Additionally, zeolite membranes are characterized by high performance in terms of selectivity and separation factor, which make them very demanded in industrial applications, such as dehydration of acids and alcohol, organic/organic and gas separation, as well as desalination. However, the estimated cost of zeolite membranes for industrial applications is estimated between 1000 and 3000 €/m^2, noting that 80% of this cost is related to the support and only 20% dedicate to zeolite layer itself. For this, there is a great interest in using local materials that are abundant and cheaper for the preparation of the support that provides the mechanical strength of the membrane.

In this work, a systematic approach is described for the preparation of NaA zeolite membrane on inexpensive ceramic kaolinite support through hydrothermal synthesis. Firstly, ceramic support was prepared from local kaolinite clay via uniaxial pressing method, followed by sintering. Secondly, the zeolite layer was grown on the substrate via in-situ crystallization and secondary growth methods. The prepared membrane was deeply characterized using several techniques in order to investigate the layer deposition as well as the membrane hydrophobicity.

To evaluate its performance, NaA zeolite membrane was tested for ethanol dehydration via pervaporation process. The prepared zeolite membrane exhibited high permeate flux (8.49 kg.m^{-2}.h^{-1}) and a separation factor over 10000.

Keywords: Zeolite; Ceramic membrane; Hydrothermal synthesis; Pervaporation.

This work was supported by MESRSFC (Ministère de l'Enseignement Supérieur et de la Recherche Scientifique et de la Formation des cadres – Morocco) and CNRST (Project number PPR/2015/72).

Two-dimensional materials with intrinsic microporosity

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Perforated graphene and similar single-layer materials are pursued as ultimately thin separation membranes for ensuring high throughput and selectivity. However, the size distribution in artificial pores is difficult to control because of their defective origin, and the permeability attainable with such 2D membranes is compromised by the reduced mechanical stability. This contribution presents recent advances in mass transfer studies with naturally open planar nanomaterials that feature high areal densities of uniform pores. The intrinsic 2D membranes span both inorganic (bilayer oxides) and organic structures (covalent organic frameworks (COFs)) and can be prepared on a centimeter scale. There is a custom-designed vacuum apparatus in place to enable model permeation measurements with free-standing membranes. Bilayer silicon dioxide (Fig.1a) is found to impede the transport of atmospheric and noble gases, while vaporous substances like water and alcohols readily cross the membrane upon physisorption. In turn, 2D boronate ester COF (Fig.1b) allows for the free molecular flow, but the membrane architecture also favors the passage of condensable species, including aromatic hydrocarbons. The surface processes appear to play a major role in the permeation through nanoscopic layers as the transmembrane flux is revealed to depend on the number of adsorbates. Given the pore dimensions in the inherent 2D membranes ranging from 0.5 to 2 nm, the materials promise great potential for nanofiltration applications.

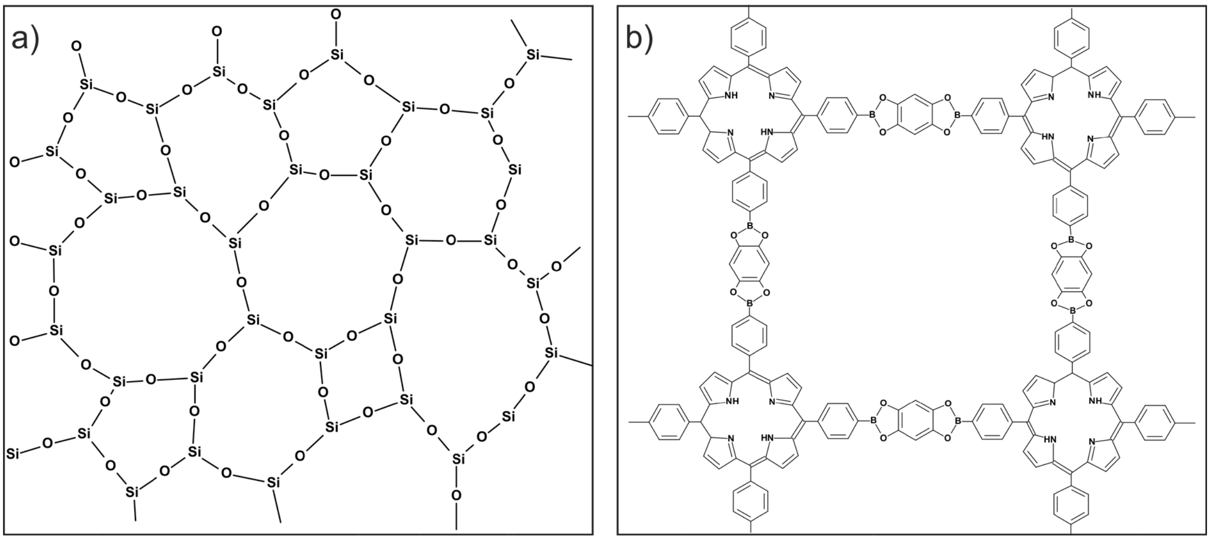

Fig. 1. Chemical structures of intrinsically porous 2D membranes: a) Bilayer silicon dioxide; b) Boronate ester COF.

Keywords: 2D Membranes; Bilayer oxides; Covalent organic frameworks

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Mixed matrix composite nanofiltration membranes for enhanced removal of PFOA from contaminated water

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Sustainable removal of organic micropollutants (MPs) such as per- and polyfluorinated alkyl substances from different water matrices is a long-standing goal. These MPs may harm human health even in the nanogram range (ng/L). Several technologies have been described in numerous studies to remove PFOA from water/wastewater. Nanofiltration (NF) and adsorption stand out as efficient and accessible options among these technologies. Polyamide NF membranes can efficiently remove PFOA (90-99 %), but their performance deteriorates during prolonged runs. Adsorption effectively removes most MPs but has disadvantages like early saturation of active sites, competition with other organic and inorganic solutes, and high footprint.

Layer by Layer (LBL) deposition of polyelectrolyte layers on porous support became a popular method for synthesizing composite NF membranes with tunable performances and high mechanical, chemical, and biological stability. However, PFOA rejection by NF is often insufficient. The present work aims to significantly enhance PFOA removal by NF by developing a regenerable mixed-matrix-composite LBL nanofiltration membrane (MMCNF) - hybridization of polyelectrolytes-based NF with adsorption in the support layer (Fig. 1b).

We fabricated the mixed-matrix porous support by casting polyethersulfone (thickness ~ 400 μm), together with commercially available cyclodextrin-based adsorbents (<20 μm) regenerable with methanol/ethanol. Then, a polyelectrolytes-based NF layer was deposited on this substrate, resulting in MMCNF. PFOA retention experiments were carried out in crossflow recirculation mode using membranes with different adsorbent loadings. At higher loading, PFOA removal performance and pure water flux of MMCM improved significantly (Fig. 1a). Preliminary perfluorooctanoic acid (PFOA) rejection results (Fig. 1) are promising and revealed that MMCNF could be potentially utilized for producing PFAS free drinking water.

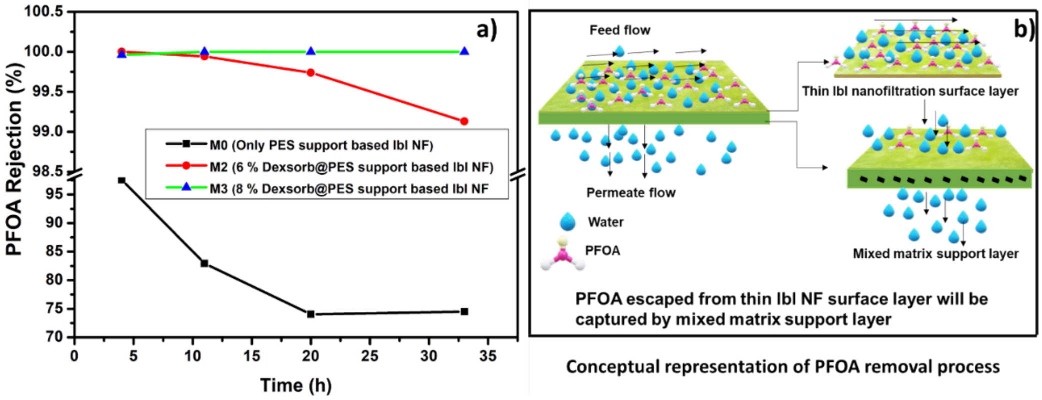

Fig. 1. a) Effect of adsorbent loading on PFOA removal performance of M0, M2, and M3 membranes b) Conceptual representation of PFOA removal process)

Keywords: Nanofiltration; Mixed matrix composite nanofiltration membrane; Adsorption.

Arsenic removal in water treatment via tailored anionic nanofiltration membrane

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Membrane processes are used for a wide range of purposes and are also a preferable technology for arsenic (As) removal treatment. The recommended limit of arsenic in drinking water from WHO guidelines (2001) is 10 µg/L. Prominent results were shown by a negatively charged "loose" porous nanofiltration (NF) membrane, where the rejection of As(V) was ~90% for feed concentrations from 10 to 316 mg/L. However, the rejection of As(III) decreased from 28 to 5% in the same concentration range [1]. To remove As(III) is more complicated and challenging due to its non-ionic state. Thus, the aim for this work is to obtain NF membranes that have a high rejection independent of As-speciation with adequate permeance.

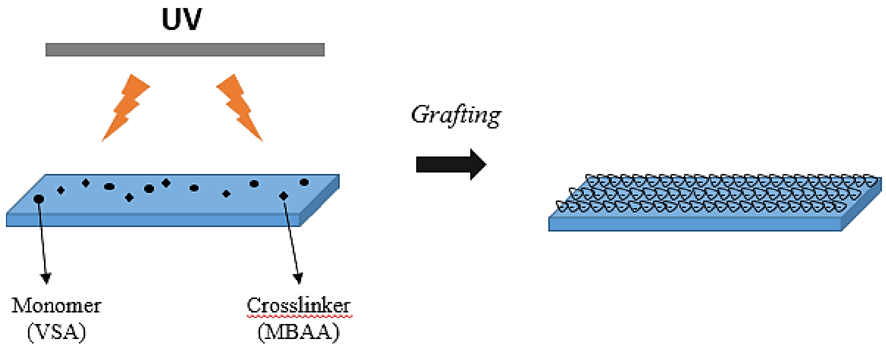

Fig. 1. Schematic of surface functionalization using UV-initiated cross-linking graft copolymerization.

The modification of ultrafiltration (UF) membrane towards NF application could be achieved by using polyelectrolytes as the active layer on the membrane through post-functionalization of the membrane surface, e.g. via photo-grafting. Surface functionalization with ionic hydrogels had been previously shown by using vinyl sulfonic acid (VSA) monomer with N,N′-methylenbisacrylamide (MBAA) as the cross-linker monomer on polyethersulfone (PES) UF membrane[2]. VSA as a functional monomer was chosen because it yields high charge density polyelectrolyte hydrogel that is ionic throughout the entire pH range. PES membrane was also chosen due to its reactivity upon excitation with the UV light, which can be used to initiate the graft copolymerization from the membrane surface.

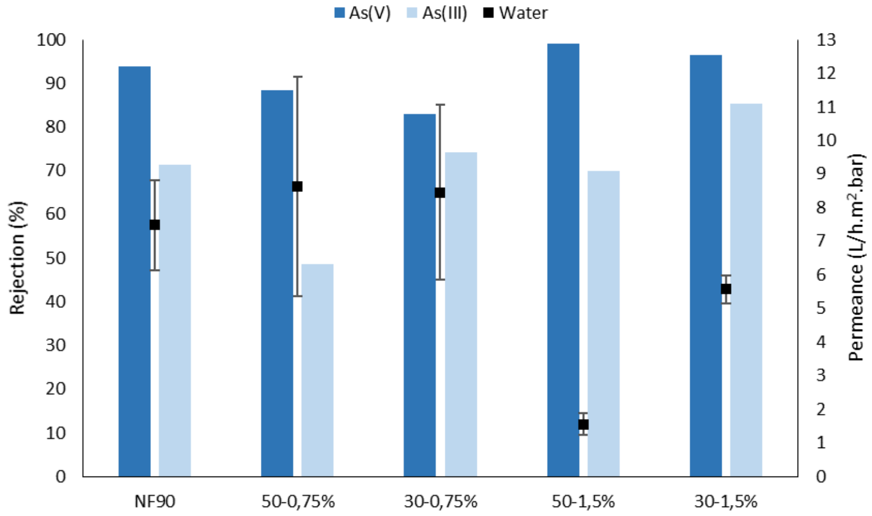

Fig. 2. Permeance and rejection of As species for tailored anionic NF membranes prepared with 25 wt% VSA on two different UF base membranes (nominal cut-off 50 and 30 kDa) and using two different crosslinker concentrations (0.75 and 1.5 mol% MBAA) at 18 minutes UV irradiation in comparison with commercial NF90 membrane.

The separation mechanism of NF membrane regarding the charge and size effects is more apparent in the tailored anionic NF membranes with 1.5%mole MBAA due to its higher rejection of anionic compound (As(V)) and non-ionic compound (As(III)) than with the lower concentration of crosslinker (Fig. 2). In comparison to NF90, the rejection of As(III) by the "30–1.5%" membrane is even higher with adequate water permeance. Salt rejection for sodium sulphate (Na_2SO_4) and sodium chloride (NaCl) has reached ~89% and ~64%, respectively, which is also a suitable performance for NF membrane application.

Essentially, the tailored anionic NF membranes "30–1.5%" is favorable for removing the different As species for production of safe drinking water. Furthermore, a reactive coating method in another modification approach using VSA monomer to fabricate a NF-selective layer on PES hollow-fibre membranes is currently investigated as well.

Keywords: Nanofiltration; Arsenic; Graft copolymerization; Water treatment.

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Development of reduced graphene oxide membrane on flat Moroccan ceramic pozzolan support. Application for soluble dyes removal

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A novel reduced graphene oxide composite membrane was successfully prepared on ceramic pozzolan support by chemical grafting and spin-coating method. The graphite was firstly oxidized and exfoliated to form graphene oxide (GO) that was grafted on modified ceramic surface using 3-Glycidoxypropyltrimethoxysilane (GLYMO). Then, the GO layer was thermally treated to obtain reduced graphene oxide (rGO) membrane. The concentration effect of GLYMO grafting agent was studied in the range of 0.01–0.1 M in ethanol. The composite membrane was characterized using XRD, FTIR, Contact angle, SEM, EDX, and AFM Techniques. The morphology analysis showed that rGO layer is homogenously adhered on pozzolan support with 2.0 µm ± 0.1 in thickness using 0.05 M of GLYMO. The experimental results indicated that water permeability decreases from 75 to 2 L/m^2.h.bar when GLYMO concentration is increased from 0.01 to 0.1 M. The prepared membranes were applied for filtration of bromothymol blue, methyl orange and murexide solutions under pressure of 4 bar during 2 h. The membranes showed a good efficiency in rejection of soluble dyes. For membrane prepared with 0.1 M of GLYMO (optimized membrane), experimental values of rejection achieved 94, 93 and 97% for bromothymol blue, methyl orange and murexide respectively (Fig. 1).

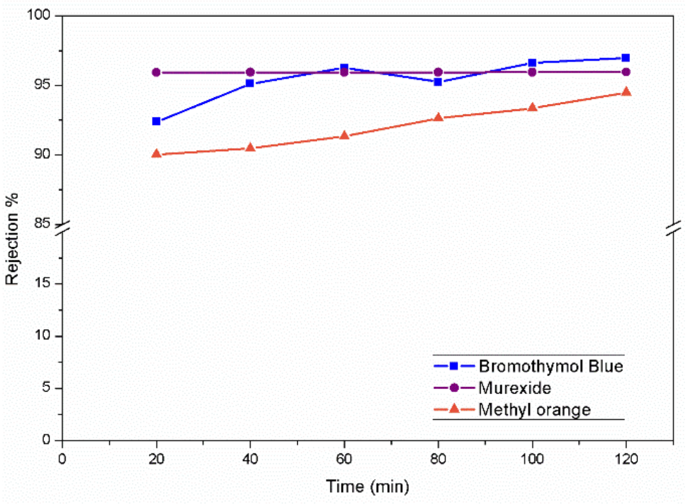

Fig. 1. Rejection of dye

Keywords: Nanofiltration; Grafting; Reduced graphene oxide; Composite membrane; Dye rejection.

Innovative Halar® LMP-ECTFE membranes for the recovery of natural compounds from *Sambucus Nigra* L. by organic solvent filtration

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The development of the nanofiltration (NF) membrane, together with new trends in the use of innovative materials, paves the way for the next generation of NF membranes, with high resistance to organic solvents and with the possibility to convert waste into resources. Halar® LMP ECTFE, developed from Solvay Specialty Polymers (SpA, Bollate, MI), an ideal polymer for its excellent chemical stability and mechanical properties and its lower melting point grade respect the standard Halar® ECTFE. As a result, these characteristics make it more processable, preserving chemical–physical stability, hydrophobicity and mechanical properties. In this work, LMP ECTFE flat-sheet membranes were prepared via TIPS (Thermally Induced Phase Separation), using d-ethyl adipate (DEA) as suitable non-toxic solvent. The produced membranes were characterized in terms of morphologies (SEM and AFM), porosity, pore size, contact angle and mechanical tests. The chemical stability was evaluated by swelling test using dense film, in contact for 192h in pure organic solvents (DMF, DMA, NMP, Acetone, Toluene, EtOH, MetOH, Tetrahydrofuran). Membranes performance was evaluated via organic solvent filtration using pure EtOH, MetOH and DMF, confirming that LMP ECTFE membranes are promising candidates to be use in separation filtration processes under harsh conditions. The results obtained show that with varying polymer concentrations from 15 wt.% to 25 wt.%, in dope solution, it is possible to tailor the produced membranes in the NF and UF range [1]. Finally, the LMP ECTFE membrane at 25 wt.% of polymer was used for concentrating the phytochemicals compounds obtained from flowers and leaves extracts in EtOH and MeOH, of *Sambucus Nigra L*. The obtained results suggest the use of retentate fractions that possesses higher tyrosinase inhibitory and ABTS radicals scavenging activity, with IC50 of 53.9 μg/mL and 46.4 μg/mL, respectively.

Keywords: Nanofiltration; Pharmaceutical compounds; Halar® LMP ECTFE membranes.

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Selectivity of artificial water channel-polyamide composite membranes towards inorganic contaminants

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The rising need for improved permselectivity in desalination and water treatment is addressed by the water selective artificial water channel-polyamide composite (AWC-PA) membrane. AWC-PA is expected to selectively transport water over all other ions providing excellent water-ion permselectivity. Investigating the transport of hydrated ions through these water selective AWCs incorporated into the active layer of a thin film composite membrane, contributes to a better understanding the selectivity of such membranes. Rejection and permselectivity for ions (Cl^-, NO_3, F^-, SO_4^{2-} Na^+, K^+ Ca^{2+}, Mg^{2+}) with varying hydration properties by AWC-PA were investigated and compared with a commercial BW30LE membrane.

With the exception of strongly hydrated cations, the AWC-PA membrane provided a comparable rejection (80-96%) and permselectivity (1.0-1.7 bar^{-1}). It was observed for anions (F^-, NO_3^-) with lower hydration number, a reduction in surface charge through variation of pH (12-2) decreased the rejection from 90 to 40% for NO_3^- and 90 to 40% for F^-. The influence of charge shielding was investigated by varying ionic strength (0.58-20 g/L) which reduced the rejection from 80 to 40% for both anions. The increase in osmotic pressure with salinity was from 0.4-8.4 bar. This suggested that charge repulsion between the bare ion and membrane surface compared with size exclusion as a possible rejection mechanism for ions in water selective AWC-PA membranes. The observation from this study further warrants future research using molecular dynamics simulations on the transport of strongly hydrated ions through water selective channel membranes. Due to the scalable nature of AWC-PA, another potential research area would be investigating their performance in scaled up operations.

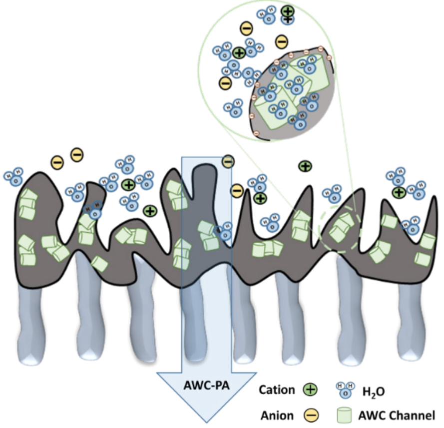

Fig. 1. Schematic illustrating water transport through AWC-PA

Keywords: Biomimetic membranes; Ion hydration; Ion transport; Nanofiltration; Desalination

Reference

J. Joseph, Y.A. Boussouga, M. Di Vincenzo, M. Barboiu, A.I. Schäfer, Selectivity of artificial water channel-polyamide composite membranes towards inorganic contaminants, submitted to Journal of membrane science (under revision)

The impact of morphology of polyethersulfone membrane on micropollutant adsorption

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Polyethersulfone (PES) has been commonly used in nanofiltration (NF)/reverse osmosis (RO) thin-film composite (TFC) membranes as a support layer [1]. In a TFC membrane, the active layer is typically composed of polyamide (PA) which can absorb more micropollutants (MPs) compared with other polymers [2]. Although the adsorption of organic solute in the active layer had been studied, the role of the PES support layer on MPs adsorption is often neglected [3] and the adsorption variation with morphology is not yet understood.

In this study, the PES membranes were fabricated by phase inversion with different coagulation bath temperature (CBT) (from 10 to 70°C). The morphology was characterized using scanning electron microscope (SEM). Estradiol (E2) was used in the dynamic filtration for micropollutant removal with both fabricated PES membranes and commercial PES membranes (Biomax® Ultrafiltration).

Findings demonstrated that CBT controlled pore size and permeability (CBT from 10 to 70°C; permeability from 13 to 1300 L/m^2·h·bar). Higher CBT increases the diffusivities of both water and solvent and creates larger macro void structure which allows water easily to pass through [4,5]. Membranes with smaller pore size and lower permeability exhibit higher E2 adsorption (0.61 ng/cm^2) compared with the loose membranes (0.27 ng/cm^2). Because of the morphology difference in fabricated PES membranes, the residence is independent on E2 adsorption. However, the residence time governs the E2 adsorption below the residence time of 4·10^{-3} s in the active layer of Biomax®. By elucidating the influence of morphology in the PES support layer on micropollutant adsorption, membrane manufacturers can fabricate a tight support layer to enhance adsorption or fabricate loose one to reduce the adsorption for long-term usage.

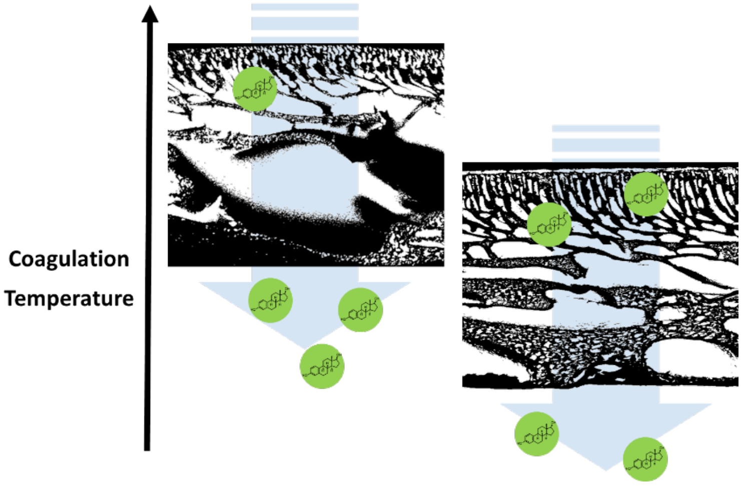

Fig. 1. Fabricated PES membranes coagulate at different temperature which show varied E2 adsorption.

Keywords: Nanofiltration; TFC membrane; PES; Micropollutant; Adsoption.

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VIII.Reactive Nanofiltration: Materials and Applications

Electrochemical membranes for monitoring and treatment of recycled water

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Combining electrochemistry and filtration in a flow-through electrochemcial cell provides additional significant advantages as electrochemistry can be used for both monitoring and treating of the effluent. We have developed a flow-through electrode made of a carbon nanotubes (CNTs) film deposited on a polytetrafluoroethylene (PTFE) membrane and employed for the determination of different materials, such as organic pollutants and heavy metals (Figure 1) [1-3]. Very low detection limits were achieved by this approach. For example, the detection of 6.4 ppb of Cu^{2+} was accomplished in 30 seconds. More recently, we have studied the detection and removal of the micropollutant 4nonylphenol (4-NP). The latter can be detected very efficiently due to its adsorption on the CNTs followed by its electrochemical oxidation. The level of detection (LOD) for the system was $1.92 \cdot 10^{-10}$ M (equals to 42.3 ppt) of 4-NP. Moreover, the electrochemical membrane could also be used for the removal of 4-NP. Yet, the oxidation of the 4-NP fouls the CNT membrane and therefore a second membrane was added and an entire flow-through cell was 3D printed.

The principles of applying an electrochemical membrane will be presented and the perspective of such systems will be discussed.

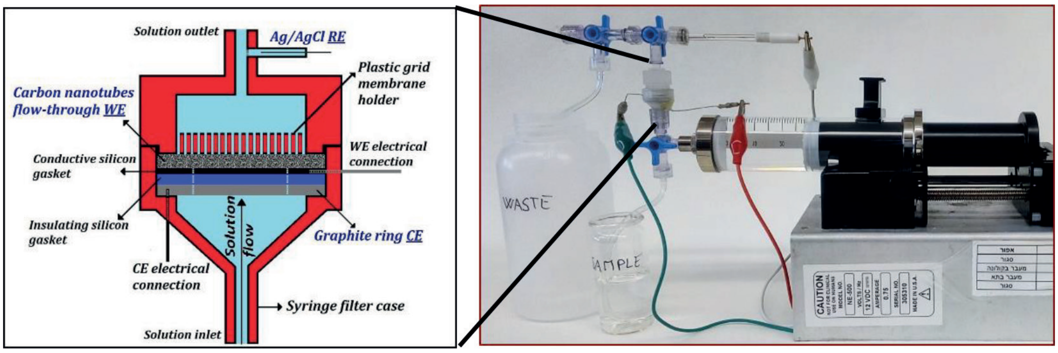

Fig. 1. Left: schematics of the electrochemical membrane; right: the entire system.

Keywords: Electrochemistry; Monitoring; Micropollutants; Carbon nanotubes

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Photocatalytic decoloration of methylene blue by Vis-responsive Ag-nanoparticles/TiO_2 composite thin films fabricated by molecular precursor method (MPM)

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The Ag-nanoparticles (Ag-NP)/TiO_2 composite thin films with various amounts of Ag (10 mol% ≤ n ≤ 80 mol%) were examined as a potential photocatalyst by decoloration reaction of methylene blue (MB) in an aqueous solution. These composite thin films of ca. 100 nm thickness were fabricated by the MPM at 600 ºC in air. The XPS measurements revealed that silver particles were obtained mainly in metallic form. Homogeneous distribution of Ag-NP in the composite thin films were clarified by the FE-SEM and TEM observations. The absorption spectra of Ag-NP/TiO_2 composite thin films were analyzed by using Kubelk-Munk equation for diffuse reflectance spectra (DRS), to study the plasmonic effect of Ag-nanoparticles (Ag NP) in dielectric TiO_2 matrix. The relationship between the unprecedentedly high amounts of metallic silver in TiO_2 and photocatalytic decoloration rate of methylene blue was examined. The decoloration rates monitored by the absorption intensity of the MB solution (fig.1) indicated that the composite thin films of Ag amount less than 40 mol% are not effective under Vis-irradiation, though they can work as a photocatalyst under UV-irradiation. Further, the UV-sensitivity of the composite thin films gradually decreased to almost half level of that of the TiO_2 thin film fabricated under the identical conditions, when the Ag amount increased from 10 to 40 mol%. Contrarily, the composite thin films of Ag content larger than 50 mol% showed the Vis-responsive activity, whose level was slightly lower than the decreased UV-sensitivity. Diffuse reflectance spectra suggested that the Vis-responsive activity of the composite thin films is due to the localized surface plasmon resonance (LSPR).

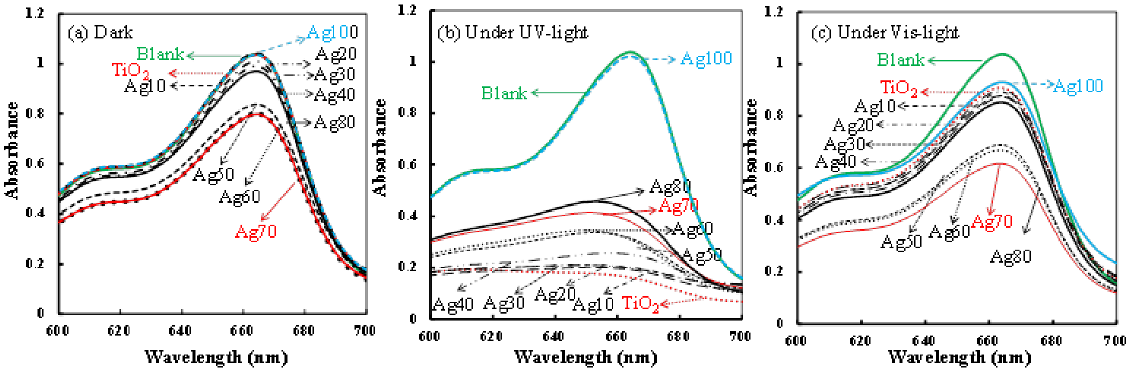

Fig. 1. Absorption spectra of decomposition of 0.001 mmol of MB aqueous solution in the presence of different Ag-NP/TiO_2 thin films after kept under (a) dark (b) UV and (c) Vis-light irradiation for 18 h.

Keywords: Thin films; Nanoparticles; Composites; Photocatalyst; Methylene blue.

Photocatalytic nanofiltration reactors

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Heterogeneous photocatalysis permits to meet stricter environmental limits by using green chemistry concepts. Drinking, industrial and waste water, which are often polluted by toxic organic species, can be treated by complete degradation of organic pollutants to small and non-noxious species, without using chemicals and avoiding sludge production and disposal. Photocatalytic Membrane Reactors (PMRs) are hybrid processes coupling heterogeneous photocatalysis and membrane separation. The membrane allows the confinement of photocatalyst and pollutants in the reaction environment while operating in continuous. In particular, Nanofiltration (NF) membranes enable the retention of larger recalcitrant molecules in the reactor while the small and non-noxious photodegradation products permeate through the membrane.

Some basic principles of heterogeneous photocatalysis are presented, then the most important factors affecting the performance of PMRs are summarized, as reactor configuration, photocatalyst type/amount, light source, feed and membrane characteristics. System configurations with suspended or immobilized photocatalyst are discussed evidencing their effects on system performance. Some laboratory applications of PMRs on pollutants as 4-nitrophenol, humic acids, patent blue dye (also at high concentration) in batch and continuous membrane photoreactors, using NF membranes are described evidencing how the use of these systems can give improved purification of various types of waters without producing sludge and saving chemicals. It is expected that these hybrid processes could be considered particularly when plant upgrading is planned and, especially, if sunlight energy can be used for irradiation.

Keywords: Heterogeneous photocatalysis; Membrane processes; Hybrid membrane processes; Photocatalytic membrane reactors; Nanofiltration; Wastewater treatments.

Fe-zeolite colloids as photocatalysts for PFAS removal: degrading 'forever chemicals'

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Perfluorinated aliphatic substances (PFAS) are compounds of high concern due to their extreme persistence in the environment which lead to the term 'forever chemicals'. They are nearly ubiquitous in the environment and show adverse effects on human health such as oxidative stress, immunosuppression (including decreased response to vaccines), impairing reproductive health, and increasing the risk of cancer. Decomposition of PFAS in water remains a huge challenge, as they are almost inert to conventional biological and technical water treatment processes. Nanofiltration has been shown to efficiently remove PFAS from water; however, disposal of the resulting PFAS-enriched concentrates remains an unsolved problem. Thus, combined approaches of membrane filtration for removal and novel catalytic processes for destruction of PFAS offer the potential for safe and efficient treatment strategies for PFAS-contaminated water.

In this work, we describe the application of colloidal (~ 1 μm) Fe(III)-loaded zeolites of the BEA framework as adsorbents and photocatalysts for degradation of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) under ambient conditions. In a system containing 1 g L^{-1} suspended Fe-zeolites, outstanding PFOA decomposition (> 99%, starting concentration 20 mg L^{-1}) was achieved within 24 h under slightly acidic conditions (pH ≤ 5.5) using irradiation with UV-A light (360 nm) [1]. Degradation of the even more persistent PFOS required irradiation with UV-C light (254 nm). 20 μM PFOS loaded on 0.5 g L^{-1} Fe-zeolites in aqueous suspension was degraded > 95% within 48 h under acidic conditions (pH ≤ 5.5) in the presence of oxygen [2]. Short-chain perfluorinated carboxylic acids (PFCAs) are the main intermediates, besides fluoride and CO_2 (and sulfate in case of PFOS). No significant PFOA/PFOS degradation occurs with Fe-free zeolites. Furthermore, we investigated the effects of pH, inorganic ions and gas atmospheres on PFOA degradation.

A photochemical degradation mechanism with zeolite-bound iron species as catalytic sites for ligand-to-metal charge transfer from the PFAS carboxylate or sulfonate head group is proposed. Oxygen is the only terminal oxidant. We also successfully applied the system to real groundwater samples where trace PFOS was present.

The presented study offers a novel catalyst material which can be applied in future functional membrane developments or in combined membrane filtration/concentrate treatment technologies.

Keywords: PFAS; Adsorption; Oxidation; Photocatalysis; Functional membranes.

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Photodegradation of textile pollutants in wastewater by nanocomposite membranes

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In this research, the PVDF (polyvinylidene fluoride) – PANI (polyaniline) –titanium nanotube (TNT) based nanocomposite membranes were synthesised through phase inversion method. The composition and structural properties of nanocomposite membranes were characterised by X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), atomic force microscopy (AFM) and scanning electron microscope (SEM). The significant properties of synthesised membranes such as distribution of pore size, thermal properties, mechanical properties, and photocatalytic behaviour of membranes were also studied. The hydrophilic properties of the composite membranes increased with filler content (PANI-TNT) and results in improved pure water flux (484.8 ± 2.9 $L/m^2\,h^{-1}$) compared to that (312.0 ± 1.91 L/m^2h^{-1}) of the pure PVDF membrane. The pure PVDF and nanocomposite membrane were further analysed in terms of their filtration properties such as adsorption of dyes (methyl orange, Allura red) and UV self-cleaning properties. The newly developed nanocomposite membranes showed excellent pollutant removal efficiency (~90%). The synthesised nanocomposite membranes also showed photocatalytic activities due to the presence of TNTs, and adsorption of methyl orange (MO) reduces significantly with the UV light irradiations. The UV self-cleaning property of the composite membrane was further confirmed due to their high flux recovery ratio of about 94%. The results show that embedded PANI-TNT within nanocomposite was photo-catalytically active and degrade the dye molecules from the surface of the nanocomposite membrane.

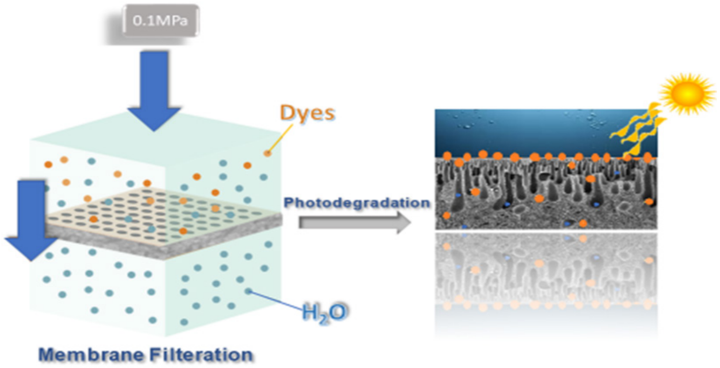

Fig. 1. Photodegradation of textile pollutants in wastewater by nanocomposite membranes

Keywords: Membrane; Nanofiltration; Phase inversion; Anti-fouling; Photodegradation

Carbon-based functionalized materials and catalyst composites

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Catalytically active and surface-functionalized colloidal carbon particles (CCP) are a versatile tool to accomplish targeted contaminant removal from aqueous media. CCP were both, bottom-up generated by a special hydrothermal carbonization process from sugar precursors and top-down ground from granular activated carbon [1]. Further tuning of pore structure but especially of surface chemistry allows the tailoring of the material for target contaminant affinity.

The adsorption of per- and polyfluorinated alkyl substances (PFAS) to CCP was found to relate strongly to their surface characteristics [2]. Cation and anion exchange capacities at pH 7, as well as point of zero net proton charge (PZC), were identified as suitable indicators for PFAS affinity. Unexpected high adsorption affinity (K_d up to $10^7…10^8$ L/kg) was found for PFAS of C6 to C8 chain length. The superposition of hydrophobic interactions and electrostatic attraction between PFAS anions and positively charged sites of CCP, esp. due to proton adsorption to π-electron-rich regions on the basal plane of carbon, was identified as beneficial.

As shown for PFAS, also other persistent halogenated micropollutants, such as pharmaceuticals (e.g. diclofenac), herbicides (e.g. atrazine, bromacil) and disinfectants (e.g. triclosan) are subject to improved adsorption by surface-tuned CCP. Detoxification of these adsorbed micropollutants was achieved by selective dehalogenation by reduction functions built into the CCP [3]. Most efficiently worked hydrodehalogenation using bimetallic Pd/Fe catalysts with only traces of Pd on Fe clusters which were precipitated within the CCP pores. Pd can also be used as protected membrane-embedded catalyst for the extension of the membrane function by a catalytic dehalogenation function as the Pd-based dehalogenation takes place extremely fast [4].

Carbon-based functionalized materials and catalyst composites offer a broad spectrum of targeted contaminant affinity and degradation abilities and could be applied in future functional membrane developments.

Keywords: Carbon-based particles; Reduction function; Hydrodehalogenation catalysis; PFAS-specialized adsorption.

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Separation of ions using capacitive deionization with nanofiltration membrane by N and S doped graphene quantum dot-decorated on highly ordered mesoporous carbon electrode

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Capacitive deionization (CDI) has emerged as a promising strategy for water desalination because of its low energy consumption, low cost, easy operation, and low environmental impact for desalination of the sea or brackish water. However, a single CDI system showed low removal efficiency with a high-concentration (TDS> 3000 mg L^{-1}) because of the ion saturation on the electrode surface. Thus, the new CDI system combines with nanofiltration (NF) membrane to enhance and then achieve high removal. The NF membrane is ion-selective. because of the surface properties of the membrane, electrostatic repulsion/attraction forces may occur between the components in the liquid and the membrane surface, which results in a certain degree of ion selectivity. Thus, the NF membrane can help the ion separation between the CDI electrodes. The mechanism of CDI uses the electro-absorbance process, in which ions are adsorbed on the electrode surface. Therefore, carbon materials with high surface area, high specific capacitance, and high desalination efficiency are essential to CDI technology for water resources recycling. Herein, the nanocomposites of nitrogen- and sulfur-doped graphene quantum dots (N,S-GQDs) decorated onto three-dimensional highly ordered mesoporous carbon (HOPC) have been developed for enhanced CDI process. The N,S-GQDs@HOPC nanocomposites show an electric double layer feature with specific capacitances of 301 F g^{-1} and 195 F g^{-1} at 10 and 300 mV s^{-1}, respectively. The electrochemical performance of N,S-GQDs@HOPC is attributed to the increased charge storage sites and good electrical conductivity, due to the high surface area and heteroatom doping. The results show the electrode improvement of the charge transfer and ion transport. The design of the CDI-NF system shows in Fig. 1. In the system, the permeate flow passes through NF membrane and the current collector. This design can achieve high ions removal of brackish water, and then this is environmentally friendly technology for water desalination.

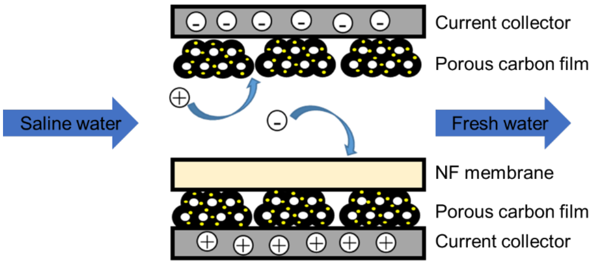

Fig. 1. The scheme of CDI-NF device

Keywords: Water; Electrodynamics; Strong confinement; Protonic transport; Dielectric properties; Nanofluidics.

Photodegradation of organic pollutants using photosensitized membranes

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Photocatalysis can solve environmental pollution, however, the use of semiconductor photocatalysts (*e.g.* TiO_2) is limited by the requirement of ultraviolet light irradiation [1]. Photosensitizers, such as porphyrins, are an alternative to TiO_2 because visible light (that comprises most of the solar spectrum) can activate these compounds [2]. The combination of microfiltration membranes with porphyrins has potential to degrade organic pollutants such as steroid hormones, allowing the achievement of the guideline limit of 1 ng L^{-1} for steroid hormones in water proposed by the European Union [3].

A hydrophobic PVDF microfiltration membrane (GVXAL, 0.2 µm, Millipore) was used as support for the porphyrin, loaded *via* adsorption [3]. Three porphyrin types were evaluated: palladium (Pd), zinc (Zn), and free-base (H_2) [5]. The photocatalytic activity was evaluated in a single-pass continuous-flow photocatalytic membrane reactor [4], using three light sources: green light (gLED, 528 nm) [3], white light (WLED, 400-800 nm) [4], simulated solar light (SolSim, 350-1150 nm) [5]. Photocatalysis was performed on methylene blue (MB) [3] and the steroid hormones (SH) 17β-estradiol (E2), estrone (E1), progesterone (P), and testosterone (T) [4-5].

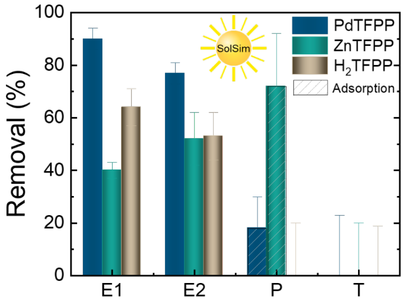

Fig. 1. Steroid hormones removal using different coordinated metal porphyrins.

Using gLED, 59% of MB was photodegraded with PdTFPP and the performance was stable over 90 h of experiment. PdTFPP achieved the best removal of E2 when irradiated with SolSim (89±4%), under the same flux of absorbed photons as gLED and WLED. The effect of the coordinated metal of porphyrin on reactive species production was observed under SolSim irradiation (Fig. 1), where PdTFPP had an overall better SH removal. Pd and ZnTFPP removed P by adsorption only; however, none of the evaluated porphyrins was able to adequately remove P and T via photodegradation.

In conclusion, membranes photosensitized with porphyrin were able to degrade the organic pollutants MB, E1, and E2. PdTFPP was successfully activated under the irradiation of gLED, WLED and SolSim. The coordinated metal of TFPP leads to different performances on SH degradation, between 40% (ZnTFPP) and 90% (PdTFPP) for E1. The methods presented are promising for photocatalytic nanofiltration systems where SHs are retained by the membrane and photodegraded by the porphyrin.

Keywords: Photodegradation; Steroid hormones; Porphyrin; Solar simulator.

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Poly(vinylidene fluoride) membrane with immobilized TiO_2 for degradation of low concentrated steroid hormones in a photocatalytic membrane reactor

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Steroid hormones (SHs) in water resources have raised concerns in human and aquatic health. Nanofiltration (NF) and photocatalytic membrane reactors (PMRs) can efficiently remove SHs [1, 2]. UV irradiation causes the chain scission of the polymer bonds and functional groups, leading to the decrease of the photocatalytic performance [3]. Thus, the SHs removal and degradation kinetics on the polymeric membrane that is less prone to destruction by the UV exposure (such as poly(vinylidene fluoride), PVDF) remains to be studied.

The photocatalytic degradation of SHs at environmentally relevant concentration (<200 ng/L) using a PVDF membrane with immobilized TiO_2 (PVDF-TiO_2) operated under UV light (365 nm) in a continuous flow-through PMR was examined. The rate-limiting step was identified at various operating, solution chemistry, and membrane preparation conditions. Scanning electron microscopy equipped with an energy-dispersive X-ray spectroscopy (SEM-EDX) was used to characterize the membrane surface morphology and elemental analyses.

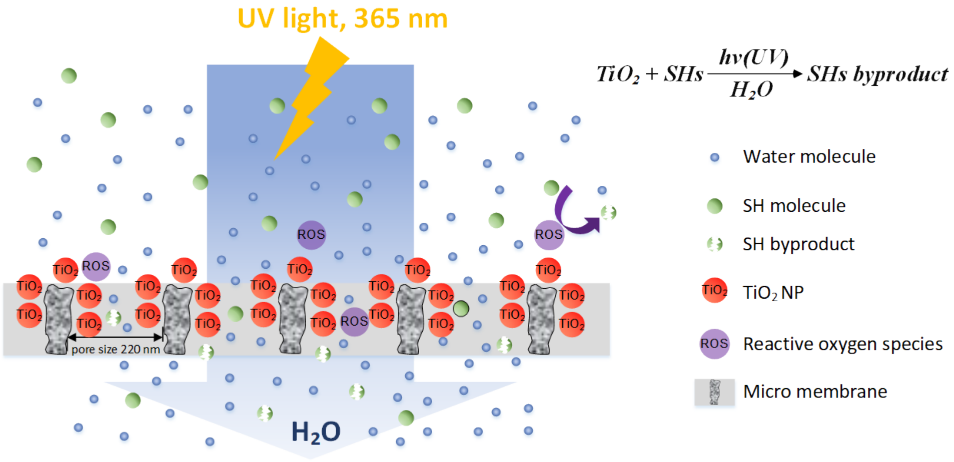

Fig. 1. Mechanism of the SH degradation on the PVDF-TiO_2 photocatalytic membrane in a flow-through PMR.

The apparent rate of disappearance (r''_{E2}) increased linearly as increasing the water flux from 60 to 900 L/m²h, which is indicative of a molar-flux-controlled degradation regime [5]. The E2 removal and was significantly enhanced by increasing the surface Ti content from 4 to 6.5%, while the threshold value of the surface Ti content was 5% [5]. The E2 removal and was independent of the spatial distribution of TiO_2 throughout the membrane, indicating the limitation of the light penetration depth. A E2 removal of 96% was achieved at 60 L/m²h, 25 mW/cm², 6.5% Ti [5]. The results demonstrated that a higher E2 removal at a significantly lower pressure (0.15 bar) can be achieved on the PVDF-TiO_2 membrane compared with NF at a pressure of 3–20 bar [4].

Keywords: Steroid hormones; Flow-through photocatalytic membrane; Immobilized TiO_2; Microfiltration; Water treatment

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IX. Renewable Energy Powered Nanofiltration

Renewable energy for membrane filtration

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This talk will explore the opportunities for powering membrane filtration systems via renewable energy sources. In terms of feedwater, the focus will be on brackish water, which is a relatively untapped resource in many continents and can be effectively desalinated using nanofiltration or low-pressure reverse osmosis membranes. In terms of electrically powering such systems via renewable energy, a brief overview of all possible technologies will be presented, however the main focus will lie in the area of photovoltaics (PV). PV has proven to be popular due to its: i) modularity – like with membranes, greater capacities are achieved by placing more PV modules in parallel and/or series; ii) robustness – PV modules are issued with performance guarantees lasting up to 40 years; which iii) gives great confidence in implementing these for operation in harsh conditions.

Uniquely, PV-powered membrane filtration systems are one of the only renewable energy powered systems that is able to operate well without the use of energy storage components. In such a directly-coupled system the "making hay while the suns shines" approach allows for all possible energy to be used for producing permeate, which can then be stored in a tank. While such systems are able to cope with fluctuating (clouds) and intermittent (day/night) solar irradiation, long term testing under such conditions is still needed to evaluate whether this directly-coupled operation is detrimental to either the membrane or the pump.

The addition of more system control could allow for more optimal use of available energy as well as, for example, backwash processes. To allow for more flexible energy consumption, now energy storage components are required, such as: i) lithium ion batteries; ii) supercapacitors; iii) pressure accumulators. The pros and cons of these technologies will be discussed, along with implications for the robustness of the entire system.

Keywords: Desalination; Solar energy; Photovoltaics; Energy fluctuations; Energy storage; Energy buffering.

Nanofiltration powered by renewable energy for the treatment of nitrated groundwater: case study of Sidi Taibi plant

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The groundwater in the region of Sidi Taibi (Province of Kenitra, Morocco) is intended for human consumption and agriculture. However, this water is largely contaminated with nitrate, which poses a serious threat to human health. This situation is at the origin of the construction in 2014 of the first nitrate removal plant in Morocco, using nanofiltration (NF) coupled to an electrochemical disinfection system, and powered with renewable energies (photovoltaic and wind). The unit was installed at Al Annouar high school in Sidi Taibi to supply 1200 students with potable water, with a production capacity of 500 L/h (3 L/d/student). The local groundwater is nitrated and slightly brackish. This Sidi Taibi plant was built by a European consortium of three companies located in the south of France: Belectric Co. (solar energy), Firmus Co. (membrane treatment) and Comodos Co. (wind energy). The Moroccan partners of these companies are: Ibn Tofail University (ITU), the Moroccan Membrane and Desalination Society (MMDS) and the Regional Education Authority (REA). The aim of this work is to describe the Sidi Taibi plant and to assess its performances (recovery rate, retention, energy consumption and sensitivity of the membrane to the fouling). In addition, this study provides an evaluation of the economics involved in using NF membrane combined to renewable energies to produce potable water from nitrated water. The results of this study will be presented and discussed.

Removal of inorganic contaminants (As, Se, U, NO_3, F) in decentralised nanofiltration

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Two-thirds of the global (urban and rural) world population (4 billion people) are under water stress as per the most recent statistics made by The World Bank [1]. Remote areas are the most challenging to address as low population densities and lack of infrastructure in terms of water supply, adequate sanitation and electricity grid. In addition, waterborne contaminants such as selenium (Se), arsenic (As), uranium (U), fluoride (F) and nitrate (NO_3), which cause several health issues at μg/L and mg/L levels, require a sustainable and effective treatment. Nanofiltration (NF), which is known to be effective to retain multivalent ions, is an alterative decentralised drinking water treatment. This technology is technically established for large scale desalination [2], as well as decentralised systems powered with renewable energy, in which the costs are comparable with water charges, such as in Africa [3].

Nanofiltration has demonstrated its effectiveness to remove Se [4], As in oxic conditions [5], uranium [6], fluoride [7] and nitrate [8]. Treatment of NF with Se, As and U are generally known to be affected by pH and ultimately by the speciation. This means that the charge exclusion is the most mechanism for treatment [4-6]. Although, NF showed its robustness to water quality variations, such salinity. On the other hand, F and NO_3 are removed by NF with the contribution of both charge and size exclusions [9].

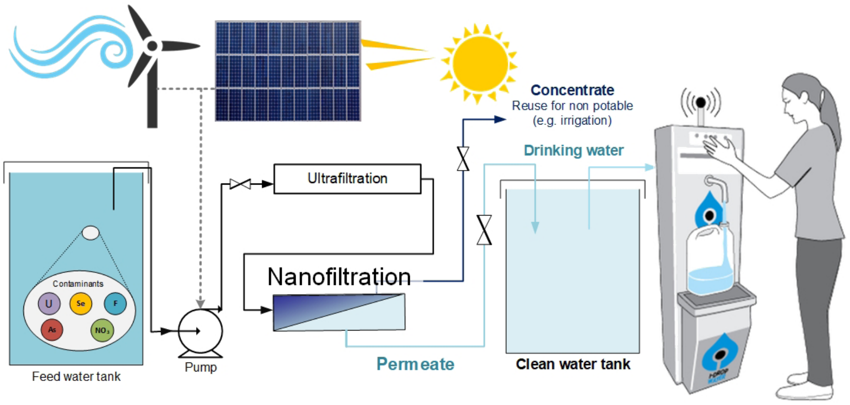

Fig. 1. Decentralised nanofiltration system powered by renewable energy.

In the context of decentralised system, NF is a promising technology for the treatment of the above contaminants. This has been demonstrated in previous field study using renewable energy powered decentralised nanofiltration powered (Figure 1) [10-12]. This strongly renders decentralised nanofiltration is a favourable solution for drinking water treatment in remote and rural areas. It can also be adopted in urban areas to reduce the stress on existing centralised water systems [13] and reuse water locally, hence avoiding transport.

Keywords: Water treatment; Membrane filtration; Trace contaminants; Speciation; Retention mechanism.

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Solar-powered nanofiltration/reverse osmosis system for fluoride removal from brackish water: System resilience

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Batteryless photovoltaic nanofiltration/reverse osmosis (PV-NF/RO) filtration systems are exposed to power fluctuations due to variability in solar irradiance caused by passing clouds. This disruption results in variations of the hydrodynamics, thus a decline in the permeate quantity and quality. Although, the resilience of the PV-NF/RO system to such variable operation can be defined by the performance loss and the recovery time (Fig. 1) [1].

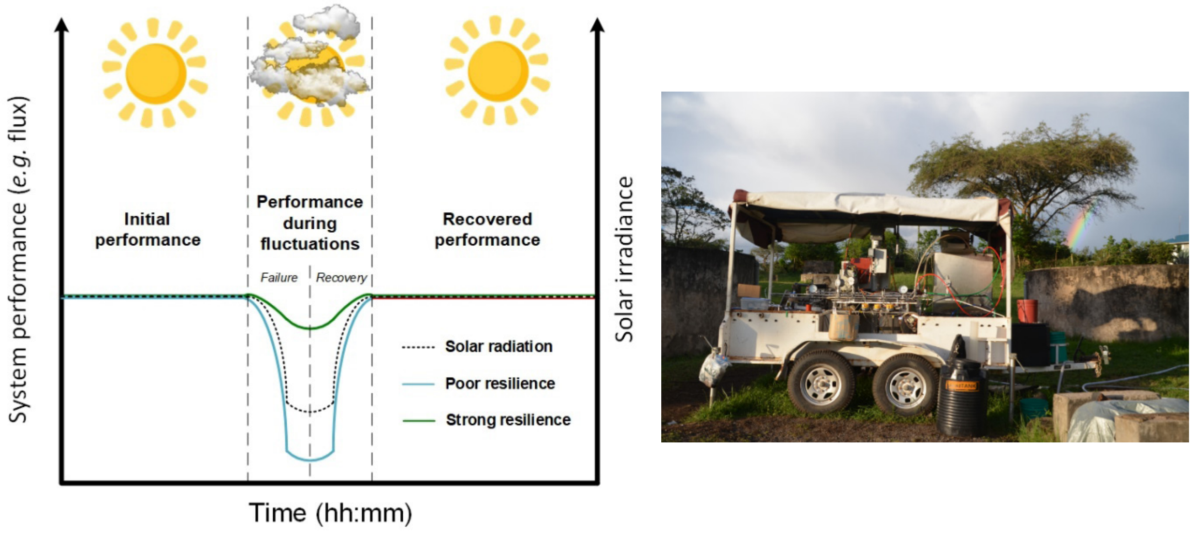

Fig. 1. Graphical representation defining the concept of system resilience for a PV-membrane system (photo in the right) in Tanzania

A PV-NF/RO system [2] that can be equipped with four different (4”) membranes – NF270, NF90, BW30 – was investigated. The system was used to treat northern Tanzanian waters having different salinity, with all being characterised by high fluoride (F) contamination (>1.5 mg/L) [3]. For meaningful comparison, all experiments have been conducted with identical data of a recorded solar day characterized by four cloudy events. The resilience indicators of the PV-NF/RO system were resilience factor (RF) and recovery time [4].

Results showed that the PV-NF/RO system equipped with tighter a NF membrane (NF90) and BW30 exhibited high resilience to variations in permeate quality [5]. This was in contrast to the loose NF membrane (NF270), which exhibited a higher resilience to specific energy consumption (SEC) variations, but with a large decrease in permeate quality, in terms of F, during fluctuations [5].

System resilience exhibited a recovery time range of 50–350 s depending on duration of the fluctuation period and regardless of water quality or membrane type [5]. This work demonstrates the robustness of the decentralised PV-NF/RO system designed for drinking water production in remote conditions.

Keywords: Drinking water; Membrane filtration; Decentralised system; Energy fluctuations; Performance recovery.

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Energy storage options for photovoltaic-powered membrane filtration systems for desalination of brackish water

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It has long been established that photovoltaic-powered membrane filtration (PV-membrane) systems can successfully operate without relying on energy storage components. However, due to the fluctuating and intermittent nature of solar energy, energy storage can possibly enhance the performance of such brackish water desalination systems. In this paper, three scenarios are examined: i) the reference system that is directly coupled to the PV modules with no energy storage capability; and then either using: ii) lithium-ion batteries, which can provide around one-day's-worth of energy storage; or iii) supercapacitors, which afford more like 5-6 min of energy buffering. The pros and cons of each of these PV-membrane system configurations are examined using three atypical solar days: i) a sunny day; ii) a partly cloudy day; and iii) a very cloudy day. The key figures-of-merit are: specific energy consumption (SEC), daily permeate production, permeate quality, number of shut-down events (or the shut-down duration), and the overall system efficiency. In addition, the likely robustness of such systems is estimated. The latter is important parameter given that: i) the capital costs of such systems are high and, therefore, to achieve the lowest cost of water, the system lifetime needs to maximised, ideally to 20-years; and ii) reduced operations and maintenance costs will also result in a lower cost of water. What also impacts on the cost of water from such a system is the throughput, or the daily permeate production, which – for the same ultrafiltration (UF) and nanofiltration (NF) membranes and pumps – can be higher when energy storage components are included, simply because the equipment can be operated during night-time as well. These outcomes are discussed in the context of small-scale PV-powered hybrid UF/NF membrane filtration systems for deployment in remote locations in Africa.

Keywords: Desalination; Solar energy; Photovoltaics; Energy fluctuations; Energy storage; Energy buffering.

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