



intelWATT

intelWATT Workshop on

**European leadership in action:
enabling technologies to boost
freshwater preservation**

22-23 February 2024 | Birmingham, UK

BOOK OF ABSTRACTS



"This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 958454"



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ORGANIZED BY



European leadership in action: enabling technologies to boost freshwater preservation.

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This international workshop on the latest developments in industrial wastewater treatment is organized in the frame of the intelWATT project and will be hosted by the University of Birmingham, UK. IntelWATT (www.intelwatt.eu - European Union's Horizon 2020 research and innovation programme under grant agreement No 958454) is a European project that aims to develop innovative, cost efficient, smart separation technologies applied in energy and water intensive industries. During this meeting, key academic and industrial actors from relevant fields of research and application (material engineering, process development, Artificial Intelligence, policy making, biogeography) engage with the most urgent challenges faced by the EU to maintain and ensure water security. These well-connected scientists propose the convergence of new approaches and techniques to fight water scarcity and pollution due to climate change as demonstrated in intelWATT. Furthermore, this event is a unique opportunity to boost cooperation between stakeholders, to disseminate new knowledge and to foster new partnerships (e.g. but not limited to: CE-SPIRE-07-2020 "Preserving fresh water: recycling industrial waters industry" and SC5-04-2019 "Building a water-smart economy and society"). These are essential steps to accelerate the rollout of the European Green Deal and overcome the current implementation gap.

The topics will be addressed during the workshop include:

- Advanced membranes for water technologies
- Digital characterization of membranes and membrane formation processes.
- Artificial water channels
- Graphene Oxide Membranes
- New industrial wastewater treatment processes
- Substance recovery
- Zero pollution initiatives
- Environmental Engineering
- New analytical methods for the determination of substances of interest
- Development of novel membranes and materials for demanding conditions
- Treatment and valorization of emerging contaminants
- Smart monitoring of wastewater treatment processes (sensors and IoT)
- Holistic water management, circular economy and energy recovery
- Challenges (fouling, corrosion , durability...)



AGENDA

Thursday 22nd February 2024

8:45 – 9:15 > Registration

9:15– 9:30 > Welcome

Prof. Philip Davies (University of Birmingham)

9:35 – 9:55 > Introduction and presentation of the workshop

Dr. Andreas Sapalidis (National Center for Scientific Research “Demokritos”)

10:00 – 10:30 > European Policies in the water sector

EU officer

10:30 – 11:00 > Coffee break

11:00 – 11:45 > Advanced membranes for water technologies

Prof. Mathias Ulbricht (University of Duisburg-Essen)

11:45 – 12:30 > Nutrients recovery and water reuse from distillery wastewater

Maria Celeste Gritti (Cranfield University)

12:30 – 13:45 > Lunch and Networking

14:00 – 14:45 > Assessing biofouling potential through seawater reverse osmosis pre-treatment

Prof. Maria Kennedy (IHE Delft Institute for Water Education)

14:45 – 15:30 > Aquaspice Symbiosis Enabling Platform

Dr. Athanasios Angelis-Dimakis (University of Huddersfield)

15:30 – 16:15 > Wetting phenomenon on homogeneous and patterned substrates: from fundamentals to applications

Dr. Fei Wang (Karlsruhe Institute of Technology)

16:30 – 17:30 > Poster Session

19:00 > Workshop Dinner

Friday 23rd February 2024

9:00 – 09:45 > Recent advances in ion exchange membranes and reverse electrodialysis for sustainable energy applications

Dr. Enrica Fontananova (CNR- Institute on Membrane Technology)

09:45 – 10:30 > Graphene Oxide Membranes: an enabling technology to fight water scarcity

Prof. Andrea Lamberti (Polytechnic University of Turin)

10:30 – 11:00 > Coffee break

11:00 – 11:30 > AI for water treatment and management: technologies, applications, and challenges

Ciro Navarro Aceto (Avvale S.A. Spain)

11:30 – 12:00 > Showcasing innovation in full-scale water treatment

Tuur van den Eijnde (Nijhuis Water Technology B.V.)

12:00 – 12:30 > Biomimetic membranes incorporating artificial water channels for high-performance water reverse osmosis desalination

Prof. Mihail Barboiu (Institut Européen des Membranes)

12:30 – 13:30 > Lunch break

13:30 – 14:00 > Future perspective of Thermal Desalination

Dr. Alba Ruiz Aguirre (Plataforma Solar de Almería, CIEMAT)

14:00 – 14:30 > Molecular dynamics simulations of membranes assisted crystallization

Dr Elena Tocci (CNR- Institute on Membrane Technology)

14:30 > Closing



USEFUL INFORMATION

Location:

Edgbaston Park Hotel and Conference Centre

53 Edgbaston Park Rd, Birmingham B15 2RS, UK



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Oral presentations
22nd February 2024

ABSTRACTS

Advanced membranes for water technologies

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Membrane technologies have been established in a wide range of industrial applications; the most successful processes are nowadays realized in very large scale. Synthetic organic polymers are the dominating materials, and intense research and development is focused on innovations leading to advanced membranes with higher separation performance adapted to specific requirements of important applications [1]. In this presentation we will discuss how the efficiency of membrane-based separations can be improved by developing membranes with wanted selectivity at high intrinsic permeability along with high stability and resistance to fouling. Innovations in membrane materials are highly visible in the research community, but the focus of the talk will be on those that are also compatible with industrially scalable membrane fabrication processes. Another relevant research direction is devoted to easy-to implement post-modifications of membranes that can also be applied to membrane modules (e.g. [2]). Finally, emerging methodologies that will enable a “second life” of the rapidly growing number of end-of-life membrane modules and the resulting opportunities will be outlined [3]. All such generic innovations in membrane materials and the related life cycles will contribute to more sustainable membrane-based processes for important applications in water purification, water reuse and resource recovery from water.

References

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Nutrients recovery and water reuse from distillery wastewater

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Industrial effluents, often known for their complex composition, are increasingly targeted for resource recovery, particularly water and nutrients, owing to stringent discharge regulations and growing demands for these materials. Ultimate, is an international and interdisciplinary project funded by the European Commission, striving to promote water smart industrial symbioses, focused on mining resources (water, nutrients, heat) from industrial wastewaters, within the framework of circular economy. Among Ultimate's nine research case studies, case study 7 is centred around whiskey distillery wastewater and aims to investigate the integration of an existing treatment system with supplementary units to harvest N and P products and generate water for reuse (e.g. cleaning, cooling applications). This study focuses on a Scottish distillery, where the current on site plant treats the process wastewater with an anaerobic membrane bioreactor (AnMBR), harvesting energy and delivering a virtually solids-free, warm (38°C) permeate, yet rich in nutrients (700-800 mg TAN/L, 250 mg PO₄-P/L). This work explored the application of a precipitation unit followed by ammonia stripping and scrubbing on the AnMBR permeate, yielding fertilisers as struvite and ammonium sulfate, respectively. These processes have been assessed with in situ, pilot scale units (0.5 m³/h) operated in different periods between September 2022 – November 2023. It was aimed to demonstrate the treatments feasibility, evaluate their performances, products quality and identify challenges for resolution. Furthermore, reverse osmosis membrane filtration (RO) was tested for the production of water apt for reuse, at pilot scale, ex situ. The objective was to validate the treatment feasibility, define bottlenecks and advantages. Moreover, the sequence of the three treatment steps was investigated, to provide guidance in selecting combinations tailored to various requirements. During the pilot trials, it was proved that struvite precipitation with a fluidised bed reactor was able to reduce PO₄-P levels by 81±3%, when supplied with MgCl₂ and adjusting pH at pH 8.8 with NaOH. It was possible to successfully control precipitation and scaling, protecting the downstream stripping packed tower. Moreover, the treatment delivered high quality struvite pellets, whose morphology and size (up to 5 mm) were tuneable along pH changes. The stripping unit was operated at 30-35°C, exploiting the residual heat in the water, and 69±16% removal efficiency was achieved with pH 9.8, adjusted by NaOH dosing.

The ammonium sulfate solution formed in the scrubber was of high quality (up to 20 g N/L), yet it was affected by dilution by stripped water vapour. The RO tests investigated how the permeate quality changed depending on the position of the membranes unit along the treatment train. Directly treating the AnMBR effluent required a second pass RO unit (50-85% recovery rate), to achieve permeate composition suitable for cooling applications. On the other hand, during the first pass this option enabled nutrients concentration into a small volume, improving the recovery rate for ammonia when this was fed to the nutrients recovery steps. The best permeate quality, with single pass tests, was achieved by feeding the RO membrane with the nutrients-depleted water (post nutrients recovery steps). However this also led to the greatest increase in membrane resistance due to reversible fouling and high osmotic pressure, as a result of the high salinity caused by dosing pre - treatments' reagents. Overall, this study provided evidence that it is possible to produce water for reuse and recover nutrients in good quality products from distillery wastewater. The choice of the units sequence depends on trade-off of different aspects, including installations costs, water quality targets, fouling and resources available on site.



Aquaspice Symbiosis Enabling Platform

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AquaSPICE promotes the circular use of water in Process Industry and fosters awareness in resource-efficiency. It provides compact solutions such as water treatment and reuse technologies and recycling practices, while developing an innovative cyber-physical system to monitor, evaluate and optimize water use in real time.

The AquaSPICE innovations are categorized in three different pillars: (a) Circular innovations focus on water re-use options at different levels and closed loops practices for water, energy and substances; (b) Process innovations consist of the installation, operation, and assessment of advanced water treatment technologies and practices with energy and substances recovery; and (c) Digital innovations involve a real-time monitoring and distributed data management system, which connects the physical and digital worlds through smart sensor networks, IIoT and cloud/edge technologies, and a Water-specific Cyber-Physical-System (WaterCPS). The AquaSPICE innovations are tested and implemented in five different industrial case studies and seven different use cases.



Wetting phenomenon on homogeneous and patterned substrates: from fundamentals to applications

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Wetting effect occurs when a droplet contacts a solid substrate [1]. A fundamental understanding on the wetting phenomenon is of importance for comprehending daily life observations, such as dew on plant leaves, and for practical applications, such as water harvesting/preservation, inkjet printing, drug delivery, microfluidics, and lab-on-a-chip systems, to name a few.

When the solid surface is ideally smooth as a mathematical postulation, the wetting phenomenon is well described by the textbook theory of Thomas Young [2]. However, we should note that no real substrate in our daily lives is mathematically homogeneous and smooth. Examples are membranes, roughness, chemical heterogeneity. By considering these facts, we divide the present discussion into two parts: (P1) Microscopically inhomogeneous surface; (P2) Macroscopically inhomogeneous surface. In the case of P1, we will present a generalized Young's law with the consideration that the liquid partially penetrates into the solid phase at the microscale [3]. In this case, we derive the apparent contact angle as a function of the internal energy and the van der Waals force. In particular, fundamentals of contact angle hysteresis will be discussed, intrinsically differing from the Cassie-Baxter-Wenzel theory. In the scenario of P2, we will present wetting effect on macroscopically patterned surface [4-6], categorized as mechanically patterned and chemically patterned surfaces. We demonstrate that there are multiple energy minimum states for a fixed droplet volume via simulation, theory, and experiments. Application of our model to inkjet printing, liquid wells, drug discovery process, and cell culturing will be briefly elucidated, as an ending of the present talk.

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Oral presentations
23rd February 2024

ABSTRACTS

Recent advances in ion exchange membranes and reverse electro dialysis for sustainable energy applications

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Rivers, lakes, seas and oceans offer a vast renewable energy resource. Particularly, salinity gradient power (SGP) or “blue energy”, i.e. the energy available from the controlled mixing of two solutions with different salinity, has the second largest marine-based global sustainable energy potential, next to ocean waves [1]. Additional potential sources of SGP are wastewater brines produced by numerous energy and water intensive industries, such as mining and desalination industries. One of the most promising technologies developed to harvest SGP is the reverse electro dialysis (RED). This process uses alternate anion- and cation-exchange membranes (AEM and CEM) to control the ions transfer from high to low-concentration solutions to convert Gibbs free energy of mixing in electrical energy (Fig. 1).

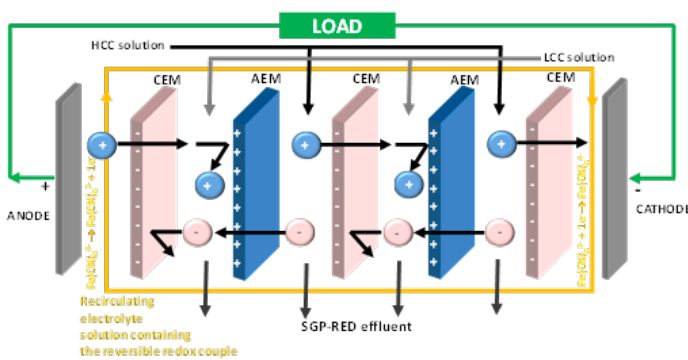


Figure 1 : Scheme of the operational principle of the reverse electro dialysis

SGP capture by RED can contribute in fulfilling the increasing world's energy demand without emitting greenhouse gases. However, RED technology is still limited by economic and technical barriers consisting of the high membrane costs and the strong performance drop when shifting from model monovalent solutions used in “standard” testing, to real multicomponent solutions. Fundamental electrochemical studies combined with RED experiments were carried-out in order to deeply understand the role of the saline solution concentration and composition on membrane transport properties and performance in applications of specific interest [2]. The outcomes of these studies are crucial for membranes selection and setting of the RED operative conditions, as well as, to contribute to the development of the next generation of AEM/CEM pairs specifically designed for RED [3].

In the framework of the IntelWATT project a RED process was successfully implemented in an integrated membrane system for the valorisation of brine streams from mining activities in order to recover energy and water, exploiting renewable energy resources (i.e. salinity gradient and solar power) [4]. Technical targets of this case study are the recovery of 3 MJ of electric energy /m³ of treated brine and 1 m³/hour of deionized. The integrated pilot unit comprises the following sections: a) an ultrafiltration (UF) unit for the brine pre-treatment; b) a RED unit for converting the chemical potential difference between two streams with different salinity (brine and well water) into electrical energy; c) a solar assisted membrane distillation (MD) unit that operates on the mixed solutions outgoing from RED in order to recover distillate water. Moreover, the concentrated from MD unit operating at high recovery factor could be potentially re-used as high salinity solution for RED in a closed loop. The integrated system has buffer tanks between the three sections to comply with the different operative flow rates of each process. Tailor made sensors and automated decision-making mechanisms will optimize the process conditions in real time. A challenge of this case study is the possibility to recover valuable minerals from the waste brine by membrane assisted crystallization.

Research activities in progress on the development of green and high performing ion exchange membranes for energy application will be also presented.



Acknowledgements

This work has received funding from the European Union's Horizon 2020 research and innovation program within the project "intelligent Water Treatment Technologies for water preservation combined with simultaneous energy production and material recovery in energy intensive industries - intelWATT" (Grant agreement n. 958454).

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Graphene Oxide Membranes: an enabling technology to fight water scarcity

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As global initiatives intensify to meet the United Nations' 2030 Agenda for Sustainable Development, the simultaneous pursuit of Goals 6 and 7 becomes paramount. Goal 7 emphasizes the necessity for access to affordable, reliable, and clean energy, while Goal 6 underscores the urgency in ensuring clean water and sanitation for all. This groundbreaking study introduces graphene oxide (GO) membranes, an unprecedented technology with dual applications—revolutionizing sustainable energy generation (SDG 7) and transforming water treatment methodologies (SDG 6).

At the heart of this research lies the innovation of reverse electrodialysis (RED), a technology harnessing the Nernst potential between water streams of differing salt concentrations to generate electricity. The efficacy of RED is intricately tied to the performance of ion-exchange membranes (IEM). Here, 2D materials, particularly GO membranes, emerge as game-changers, exhibiting enhanced transport properties, superior ionic conductivity, mechanical strength, and antifouling characteristics in comparison to traditional polymeric IEM.

A key breakthrough in this work is the scalable production of GO membranes, achieved through the doctor blade technique, addressing scalability challenges encountered in non-scalable methods documented in the literature. Notably, these membranes demonstrate exceptional stability under harsh conditions, including exposure to highly concentrated H₂SO₄, NaOH, NaBr, and NaI, as well as compatibility with organic solvents. Further optimizations focus on increasing permselectivity and reducing ionic membrane resistance, positioning the GO membranes as leaders in monovalent cation selectivity compared to state-of-the-art polymeric membranes.

Electrical impedance spectroscopy unveils the intricacies of membrane dynamics, revealing a direct relationship between thickness and lateral size of GO flakes with permselectivity and ionic resistance. In a groundbreaking move, UV irradiation is introduced as a chemical-free reduction mechanism, resulting in reduced GO (rGO) membranes. These rGO membranes exhibit a 10% increase in permselectivity, attributed to a reduction in nanochannels and membrane swelling degree. The introduction of binders, particularly Polyvinylpyrrolidone (PP), further enhances mechanical stability, permselectivity, and ionic resistance.

Expanding the scope to address water-related challenges aligns seamlessly with the ambitions of SDG 6. The scalable roll-to-roll process for membrane production and the detachment of self-standing large area membranes pave the way for practical applications. These membranes showcase promise in contaminants removal below their solubility limit in water and raw material recovery from wastewater brines, thus contributing significantly to the broader goals of ensuring clean water and sanitation for all (SDG 6) and advancing sustainable, clean energy access (SDG 7). This study not only presents a technological advancement but also embodies a holistic approach towards achieving multiple Sustainable Development Goals through the convergence of innovative materials and applications.



AI for water treatment and management: technologies, applications, and challenges

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As the demand for efficient and sustainable water solutions for treatment and management purposes intensifies, the integration of AI technologies emerges as a crucial catalyst. The current pace of AI innovations is rapid and keeping up with it can be challenging, even for AI professionals. This presentation aims to simplify the understanding of AI to an audience with no previous AI background.

First, an overview of the differences between AI, Machine Learning and Deep Learning and the main technologies applied to water solutions. Each of these technologies will be briefly explained, in simple terms, as well as the main applications. The presentation concludes by addressing the challenges hindering widespread adoption, paving the way for the understanding of opportunities and obstacles presented by the integration of AI in water treatment and management.

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Showcasing innovation in full-scale water treatment. Showing the value of wastewater as a resource

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Wastewater treatment has always been seen as a necessity for companies to comply with local or global regulations. Most industrial parties in history have therefore always focused on low-cost, efficient removal strategies for specific pollutants that legislation prescribes. With the growing ambition in circular processes, higher sustainability, and new insights this is changing. Innovation has shown that new technologies can treat wastewater in a competitive way, while harvesting many valuable components from wastewater. Nijhuis Saur Industries provides solid and adaptive solutions for sustainable and resilient water use, energy - and resource recovery. With our unique Customer for Life approach, we protect water resources, contribute to the water-, energy- and food transition, and help to restore and close the water loop.

We believe that wastewater is not the correct term. It is, in fact, a new source of value. There are various examples of large industrial scale water treatment technologies, applied to increase the sustainability of the production plants. In this presentation various examples are showcased of innovations applied. Cases include recovery of cellulose and nutrients and removal of micropollutants from municipal wastewater, recovery of fat from poultry wastewater, metal-recovery from the electroplating industry and the large-scale reuse of water to preserve natural reserves of groundwater.



Biomimetic membranes incorporating artificial water channels for high-performance water reverse osmosis desalination

¹* Mihail Barboiu

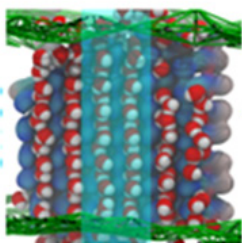
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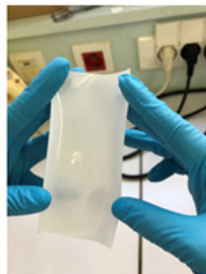
Inspired by biological models, artificial water channels can be used to overcome the permeability/ selectivity trade-off of traditional desalination membranes. We demonstrate that rational incorporation of I-quartet artificial water channels in composite polyamide membranes synthesized via interfacial polymerization, provide defect free biomimetic membranes with intrinsic water-to-salt permeability on the operational SWRO-BWRO/TWRO desalination pressure and high/medium/low salinity conditions. The best biomimetic composite membranes, which can be easily scaled for industrial standards (> m²), provide remarkable 99.5% rejection of NaCl and 91.2% boron rejection with water flux of 75 L m⁻² h⁻¹ at 65 bar applied pressure with a 35000 ppm NaCl feed solution at pH 8, representative of seawater desalination. This flux is more than 75% higher than that observed with current state-of-the-art membranes with equivalent solute rejection, translating into an equivalent reduction of the membrane effective area for the same water output and a ~12% reduction of the required energy for desalination.

« Towards the ultimate reverse osmosis desalination membranes »

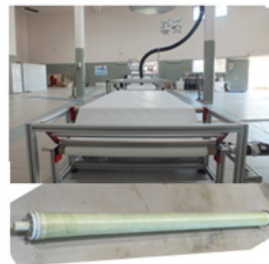
Fundamental science Artificial Water Channels



Lab scale Membranes



Industrial Modules



Acknowledgments

"This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement INTELWATT No 958454".

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Future perspective of Thermal Desalination

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Desalination represents a process to obtain freshwater coping with the lack of availability of it. There were about 15,906 operational desalination plants worldwide on 2020, which represented a total desalination capacity of 95.37 million m³ of desalinated water/day. The desalination plants with high production capacities are mostly installed in the MENA region, especially Middle East representing 47.5 % of the global capacity. This region combines water scarcity with a high availability of solar energy, making it a good candidate for thermal desalination. However, although in 80s, the technology installed was multi-stage flash distillation (MSF), little by little, they have been replaced by reverse osmosis (RO). Currently, the most installed technology is RO (69%), followed by MSF (18%) and multi-effect distillation (MED) (7%). However, desalination is not yet sustainable because it consumes a lot of energy, mainly from fossil fuels which can be hard to supply to remote areas and the prices of which are highly volatile. According to International Renewable Energy Agency (IRENA) technology statistics, only 1% of total desalinated water is renewable energy based. Renewable energy sources are consistently becoming more reliable and common as the costs associated with renewable technology decrease every year, thus resulting in a widespread use of renewable energy in many parts of the world, in part because there is a substantial capacity in rural and remote areas and the rest of the world, and islands too, where grid electricity or fossil fuels may not be the best option to generate energy at economical cost. The average specific electric energy consumption of RO is around 2.5-4 kWh/m³, while in thermal desalination considering MSF and MED, the specific thermal energy consumption is close to 45 kWh/m³. If thermal desalination wants to be competitive with RO, thermal energy consumption must be minimized. Different strategies have been addressed to reach this goal. Some of them are the increase of the number of effect in a MED plant, or coupled this one to a heat pump or a thermo-vapour compressor or even combine the production of freshwater and electricity by combining this technology with a concentrating solar power (CSP).

Membrane distillation is another thermal desalination technology designed for small scale. Also, in this field, progress has been made in the configuration to reduce thermal energy consumption. These are internal heat recovery by changing plate and frame configuration to spiral wound configuration, combination of multichannel with great length and finally, the extraction of air in the permeate channel. The application of everything has reached to decrease the thermal energy consumption up to 43 kWh/m³. Besides being a good candidate in remote areas where the population is low and lack of infrastructure makes the installation of other desalination technology difficult, membrane distillation has its application niche in which reverse osmosis is not suitable. Some examples are the regeneration of industrial wastewaters, valorisation of urban wastewater and reverse osmosis brine and production of water for the generation of hydrogen by electrolysis. However, the most demanded is its possible coupling to desalination plants with reverse osmosis for the concentration of brines, reducing its discharge.



Molecular dynamics simulations of membranes assisted crystallization

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Membrane-assisted crystallization (MCr) is a hybrid membrane separation crystallization process in which a solution (at the retentate side) first becomes saturated, then supersaturated, and finally, the crystals are obtained [1,2]. MCr can promote crystals nucleation and growth in a well-controlled pathway, thus modulating the final properties of the crystals produced in terms of structure (polymorphism) and morphology (habit, shape, size, and size distribution).

It is generally difficult to monitor the growth mechanisms of crystal formation. The limitations of experimental techniques are due to the small number of molecules involved. However, molecular modelling helps to investigate the mechanism of nucleation and crystal growth [3,4].

In this work, molecular simulations have been performed to give insights into the experimental results.

Here, with an integrated experimental-computational approach, we demonstrate that hydrophobic membranes of polyvinylidene fluoride (PVDF) assist the crystal growth for monovalent salts, speeding up crystal nucleation in comparison to the bulk solution.

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Poster presentations
ABSTRACTS

Non-isothermal Donnan dialysis: a novel method beyond conventional water treatment methods for energy reduction in desalination

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Water treatment is a key step before the desalination to remove membrane fouling agents such as divalent cationic species (e.g. Ca^{2+} , Mg^{2+}). However, the energy intensity of water treatment methods such as nanofiltration is an increasing environmental, economic, and societal concern in many regions. To address this issue, a method so-called Donnan dialysis (DD), employs a concentration gradient between a feed and concentrate solution which are separated by an ion exchange membrane. Although DD is an economical, simple technological, and energy-saving process, it is not applied widely in industry because of its slow kinetics [1]. In this work, we proposed that applying low-grade waste heat can accelerate the kinetics of DD. As a first step in this UKRI-funded Marie Skłodowska-Curie postdoctoral proposal, we developed the theory of modified Donnan potential that can predict the required membrane potential under stationary and non-equilibrium conditions. Subsequently, the maximum possible amount of depleted target ions from the feed solution will be predicted. Furthermore, by developing the phenomenological ionic fluxes which consist of thermodynamical forces including temperature gradient and concentration gradient, we predicted the impact of temperature gradient on the kinetics of DD. As the next step, we are setting up a stack of nanochannels in which a temperature and concentration gradient will be applied across the nanochannels. This experimental investigation aims to understand how these thermodynamical forces could impact the kinetics of Donnan dialysis and how they could be employed to smartly add/remove ionic species from the feed solution. Finally, we aim to develop a bench-scale membrane-based setup to study the transport of ionic species through available commercial membranes. The foundation of our understanding in this step lies in the theories and nanofluidic experiments that we have performed in previous steps.

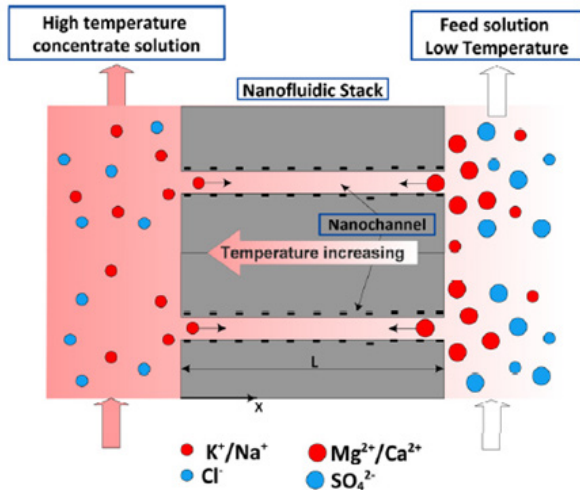


Figure 1. Schematic illustration of nanofluidic stack under temperature and concentration gradients

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The Study of Boron Rejection Relation to Salinity and pH by RO Membrane

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Boron removal by reverse osmosis (RO) membrane has been improved by increasing pH due to the effect of pH on the ratio of boron species. At high pH, boron transforms from the uncharged boric acid ($B(OH)_3$) to negatively charged borate ($B(OH)_4^-$) and sized-increased borate ion which is more favorably rejected by the SWRO membrane. The interplay between pH and ionic strength is believed to be the key to understand for the boron removal by RO membranes. However, the effect of ionic strength in the solution on boron removal was not taken into consideration in most cases. In fact, it has been reported that higher ionic strength is theoretically suggested to be the cause of lower pKa value and that means we can expect better boron removal at lower pH with higher ionic strength (salinity) [Wilf, 2007]. In this study, effect of salinity and pH on boron removal efficiency by Dow Filmtec SW30-2540 commercial polyamide reverse osmosis membrane was investigated. The boron rejection increased from around 62-94% at pH 4 to over 99% at pH 10. When the solution pH is higher than 9.2, boron transforms into anionic form of borate ion ($B(OH)_4^-$) with increased size and could be effectively rejected by the RO membrane primarily due to size sieving effect. Also, the result revealed that boron rejection at higher salinity was slightly higher than that at lower salinity and same pH. Boron rejections at pH 10 were found to be 97.38% and 99.65% at 500 mg/L and 30,000 mg/L NaCl, respectively. This phenomenon can be attributed to the decrease in the apparent pKa of boric acid as the ionic strength increases, which probably resulted in increased boron rejection at pH 10. However, in conditions where pH is higher than boric acid pKa the contribution of the salinity for rejection is negligible. This observation suggested that the high pH effect at any given feed salinity was the dominant factor for boron rejection by RO membrane.

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Chitosan/curcumin/activated carbon nanoadsorbents for the removal of hexavalent chromium from wastewaters

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Heavy metal contamination has sparked extensive scientific interest due to its long-term toxicological consequences on human health and the environment. A great deal of heavy metals have been dumped directly into the environment from anthropogenic sources, causing hazards to human health through polluted waterways (Vu et al., 2017). Chromium ions (Cr³⁺) play an important part in the maintenance of triglyceride, cholesterol, and glucose levels in the body. At specific circumstances, yet Cr³⁺ is quickly oxidized to Cr⁶⁺, which is hazardous to the ecosystem. It can also harm the respiratory system, skin, kidneys, liver, and lungs, causing nasal septum rupture, dermatitis, and lung cancer (Rahaman et al., 2024). The maximum allowable value for Cr in drinking water is 0.05 mg/L, according to WHO guidelines. As a result, it is critical to lower Cr⁶⁺ to a safe level before they are released into water bodies. Due to its accessibility, simplicity, cost, and efficacy, adsorption has been employed more frequently than conventional strategies (Priya et al., 2024).

Carbon-based nanomaterials have been investigated as superior adsorbents in aqueous solutions for the separation of organic and inorganic contaminants. The current study recommends the usage of adsorbents based on activated carbon (AC). Activated carbon has been proven to be an excellent adsorbent for the purification of a wide range of contaminants present in aqueous solutions. This can be attributed to its extraordinarily immense surface area, well-developed internal microporosity structure, and the existence of a diverse range of active sites on its surface (Owlad et al., 2010). However, because it is mainly nonpolar, it hinders the attraction of charged metal species to its surface and has low adsorption selectivity. For this reason, it is combined with other materials to improve its effectiveness. In the present study, chitosan and curcumin were used. Curcumin (Cur) is a natural polyphenolic substance derived from the plant *Curcuma longa* L. Previous research has shown that encapsulating curcumin in nanoparticles improves its capacity to absorb metal ions as a chelating agent (Rezagholizade-shirvan et al., 2023). Chitosan (Cs) is a biopolymer with outstanding adsorption capabilities, that could be due to the numerous kinds of bonds or forces created in its framework (hydrogen bonds, Van der Waals forces, and ionic forces) (Kekes et al., 2021).

The composites' morphology and structure were characterized by FT-IR, SEM, BET and XRD analysis. The effect of the pH value, contact time, adsorbent's dosage and initial chromium concentration was examined in order to evaluate the adsorption efficiency of the materials. According to the results, the modification of Cs/AC@ with Cur increased the removal of Cr ions, by using 0.5 g/L of the adsorbent. Experimental data of equilibrium were used to calculate adsorption isotherm at the temperature of 30°C and the obtained data were fitted to the Langmuir and Freundlich adsorption isotherm models. Two kinetic models were examined to fit the kinetics of chromium sorption pseudo first order and pseudo second order models. Overall, the results indicate that Cs/AC@Cur can be effectively employed for removal of chromium from aqueous solutions.

Acknowledgments:

We acknowledge support of this work by the project "Advanced Nanostructured Materials for Sustainable Growth: Green Energy Production/Storage, Energy Saving and Environmental Remediation" (TAEDR-0535821) which is implemented under the action "Flagship actions in interdisciplinary scientific fields with a special focus on the productive fabric" (ID 16618), Greece 2.0 – National Recovery and Resilience Fund and funded by European Union NextGenerationEU.



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Additively manufactured hydrophobic adsorbents for wastewater treatment

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Water is the most important natural resource as it is crucial for the survival of living organisms [1]. However, water scarcity has become a major threat. The usable quantities of freshwater on Earth are very limited, comprising only 4% of the total amount of water. Out of this 4%, only 1,1 % is suitable for consumption [2]. Despite that, the quality of water has been continuously deteriorated. Water pollution is strongly associated with industrial, agricultural and domestic activities, which release various compounds such as pesticides, fertilizers, endocrine disrupting chemicals, pharmaceutical products, personal care products and synthetic dyes. When concentrated in water in quantities greater than certain concentrations, these compounds lead to its degradation and make it unfit for use.[3] Conventional water treatment plants have the ability to treat various types of pollutants, but other types of pollutants such as emerging organic contaminants remain in the treated effluents and even in small quantities have an adverse impact on the environment and on human health [4]. In recent years, many advanced techniques have been developed to combat pollution. Adsorption is one of the most widespread advanced techniques for wastewater treatment due to its plethora of advantages including efficient removal of a wide variety of chemically diverse pollutants, low cost and environmental friendliness as it does not lead to the formation of toxic by-products.

The efficiency of the adsorption process depends strongly on the physical and chemical properties of the adsorbent materials, which can be organic, inorganic or polymeric [5],[6]. Polymeric adsorbents are one of the most important types of adsorbent material. These materials have several advantages, including mechanical stability, adjustable surface chemistry, controllable pore size, low weight and simple regeneration [7]. A new perspective for the creation of novel polymeric adsorbent materials is the utilization of additive manufacturing, or 3D printing, as it allows the creation of chemically diverse materials with complex geometric shapes owing large specific surface areas and channels that that can improve adsorption [8]. 3D printed polymers can have hydrophobic properties that optimize the adsorption capacity of non-polar and semi-polar substances [9]. Dong et al, created 3D printed super-hydrophobic materials able to rapidly adsorb isooctane, soybean oil, and dichloromethane [10]. Additionally, Yuan et al developed a super-hydrophobic 3D printed polysulfone membrane that was also able to separate oil from water [11]. Thus, the creation of hydrophobic materials holds significance importance for use in water treatment applications.

In this work, we present the synthesis and characterization of 3D-structured composite adsorbent materials by a vat photopolymerization method with a potential use as hydrophobic adsorbents in wastewater treatment. Powdered activated carbon was ultrasonically dispersed in a photocurable urethane acrylate-based resin which was solidified layer-by-layer by using light of a wavelength of 405nm. The 3D printed composite material was characterized by Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). Material's hydrophobicity was determined by contact angle goniometry measurements, while preliminary tests on the effect of pH on the removal of a frequently detected in wastewaters non-steroidal anti-inflammatory drug (NSAID), namely diclofenac, were performed. The results indicate that complex-shaped hydrophobic composite adsorbents, which can effectively remove NSAIDs from wastewaters, can be easily produced by 3D printing via photopolymerization.

Keywords: photopolymerization, activated carbon, 3D printing, composite adsorbent, pollutants of emerging concern, NSAIDs, diclofenac



Acknowledgement

We acknowledge support of this work by the project “Advanced Nanostructured Materials for Sustainable Growth: Green Energy Production/Storage, Energy Saving and Environmental Remediation” (TAEDR-0535821) which is implemented under the action “Flagship actions in interdisciplinary scientific fields with a special focus on the productive fabric” (ID 16618), Greece 2.0 – National Recovery and Resilience Fund and funded by European Union NextGenerationEU.

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