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German-Israeli Cooperation in Water Technology Research

Proceedings of the Status Seminar 2024
Koblenz, Germany
June 18 – 19, 2024

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The German-Israeli Cooperation in Water Technology Research

The bilateral cooperation in water technology was established already in 1974. Since then, more than 164 projects with Israeli and German partners have led to trusted relations between Israeli and German researchers.

The objectives of the German-Israeli Water Technology Cooperation Program are:

- To improve the water situation in Israel, its direct neighborhood and/or Germany
- To facilitate access to new markets for Israeli and German enterprises in the water and environmental sector
- To support and strengthen bilateral and multilateral cooperation in the water sector as well as facilitate cooperation between science and industry

Israel and Germany have a unique and vast pool of knowledge to share. Their innovative water technology solutions are recognized around the world. Israel has implemented advanced water reuse systems, resulting in a water reuse rate of around 85%. Israel is a leader in seawater desalination technology, which contributes significantly to the national drinking water supply. Modern drip irrigation was invented in Israel as well.

Germany also relies on innovative technologies for water treatment and purification to make efficient use of the resource while protecting the ecosystem. Germany is a global market leader in the export of water technology and is renowned for its expertise in the development of water filters, wastewater treatment plants, pumps and other water technology solutions.

The key topics of the 2024 status seminar are:

- Water technology to reduce the CO_2-footprint of the water sector or to adapt to major impacts of climate change
- Economical optimization in the water sector
- New approaches for asset management of water infrastructure
- Wastewater: recycling, reduction and reuse
- Organic micro-pollutants, pathogens and microplastic in drinking water resources and freshwater systems

Even greater efforts will be needed in the future to respond to the growing pressure on global water resources. According to the UN World Water Development Report 2024, roughly half of the world’s population currently experiences severe water scarcity for at least part of the year.

Efficient water technology and its appropriate use are key to achieve the United Nations´ Sustainable Development Goal 6 (Ensure availability and sustainable management of water and sanitation for all). The German-Israeli water technology research cooperation aims to contribute to the SDGs by ensuring the necessary innovation.

Projects Started in 2021

LowGHGWatt: Toward Ozone Disinfection in Reverse Osmosis Desalination: Enhancing Membrane Stability and Developing Novel Electrolyzer

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ABSTRACT

Reverse osmosis (RO) desalination is a promising solution to global water scarcity, yet it significantly contributes to greenhouse gas emissions due to the process's high energy demand. One approach to reduce RO energy demand is by mitigating biofouling, which can be achieved through ozone oxidation. However, conventional RO polyamide (PA) membranes are unstable when exposed to ozone. Enhancing membrane ozone stability can be achieved by surface coating with an ozone protective layer, such as metal oxide. In addition, ozone disinfection can be accomplished in situ via electrochemical water decomposition. Nevertheless, to realize this technology, the optimization of the catalytic layers is needed.

The overall goal of this ongoing study is to reduce the energy demand of RO desalination by mitigating biofouling through ozone disinfection. Specifically, we are (a) investigating the deposition of a protective ultrathin alumina layer by atomic layer deposition on membranes to enhance ozone stability. (b) Developing new polymer electrolyte membranes (PEM) by exploring novel based catalytic layers.

Our results indicate the formation of homogeneous alumina coating on PA membranes. It also shows that this coating can enhance the membrane's ozone stability, albeit with some impact on the membrane's selectivity. We also found that coating the anode of an ozone PEM electrolyzer with antimony-doped tin chloride as a catalytic layer can improve the electrolyzer ozone production compared to commercially available PEM.

Future research will include investigating the combination of the coated membrane with ozone treatment on membrane stability and biofouling formation during desalination, exploring the long-term stability and ozone production in seawater of the new PEM, and measuring the ozone-based DBPs in saline solutions.

KEYWORDS

Desalination; reverse osmosis; ozone; atomic layer deposition; polyamide membranes.

INTRODUCTION

Increased water scarcity is an acute problem worldwide. One attractive solution to produce freshwater from marginal water is desalination. The most common and energy-efficient desalination technology is reverse osmosis (RO). However, RO desalination is still an energy-intensive technology that contributes a major fraction of the total greenhouse gas (GHG) emissions of the water technology sector. Currently, the specific energy consumption of RO desalination exceeds its theoretical value due to different factors, such as fouling. Specifically, biofouling, the consequence of biofilm formation on the membrane's surface, is responsible for approx. 15% of the specific energy demand in RO desalination plants. Thus, hindering biofilm formation can help attain the theoretical energy demand of RO. One approach to mitigate biofouling is ozone disinfection of the feed water before desalination. Unfortunately, the polyamide (PA) RO membranes are sensitive to oxidation. In contrast, metal oxides (MOs) are resistant to oxidation by dissolved ozone. Therefore, the deposition of nanoporous MOs on top of PA membranes, at a uniform coverage and minimal thickness that can also be permeable to water, is a promising approach to impart chemical resistance to PA membranes. The deposition of such a MO layer can be achieved through atomic layer deposition (ALD).

Ozone is commonly generated by the corona discharge method, which requires an oxygen gas stream and a system to facilitate the transfer of ozone gas into water. An alternative approach is electrolysis using polymer electrolyte membranes (PEM). PEM enables on-site ozone production and enhances its dissolution efficiency. However, for PEM technology to become more widespread it must become more cost-effective, robust, simpler in design, and easier to maintain. A key area of research in this direction is the optimization of catalysts.

EXPERIMENTAL

Commercial RO PA membranes (ESPA1, Hydranautics) were utilized in this study. The PA membranes were coated with alumina, as described in our previous studies (Chaudhury et al., 2020; Wormser et al., 2021). Briefly, before the ALD coating, the membranes were modified by grafting poly(hydroxyethyl methacrylate) to enhance the process efficiency and then soaked in glycerol to prevent pore collapse. The dried membranes were placed in an Arradiance Gemstar XTTM benchtop reactor and coated with alumina for 5, 25, and 50 cycles. Following coating, the membranes were soaked for at least three days before being tested. Ozone was produced using the 4.CH+ Ozone-Micro-Cell (Innovatec, Germany) and measured by UV_{258} absorption and the Indigo method. The transmission electron microscope (TEM) images were acquired by TEM microscope (Tecnai T12) after separating the PA layer for the polysulfone, embedding the PA in epoxy, and cutting a thin layer by an ultramicrotome as described before (Freger, 2003). The membrane performance (flux and salt selectivity) was studied using a dead-end filtration cell, as described in Bernstein et al. (2010).

RESULTS AND DISCUSSION

Coating PA membrane with alumina to increase ozone stability

The research explores the possibility of coating the PA membrane with alumina ALD as a protective layer to enhance the membrane stability to ozone oxidation. First, the membrane was modified with a thin layer of HEMA to enhance the coating by introducing a high concentration of hydroxyl group to its surface as anchor points for the ALD process. Then, alumina coating was performed by ALD at 5, 25, and 50 cycles. The alumina coating was initially confirmed by SEM (results not shown) and TEM analysis. SEM images revealed noticeable changes in the

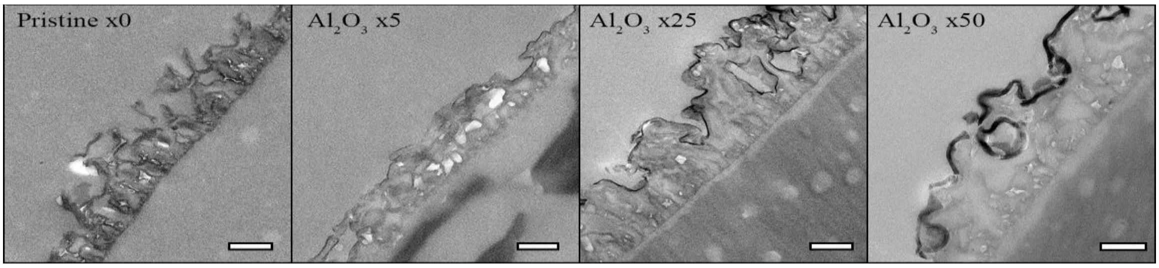

Figure 1: TEM images of pristine and alumina-coated PA RO membranes after 5, 25, and 50 cycles. Scale bar 200 nm.

PA surface morphology, while SEM-EDX analysis demonstrated the presence of Al, which increased from about 3% at 5 cycles to 5.3% after 25 cycles to 8.7 % after 50 cycles. TEM images (Figure 1) demonstrated a uniform alucone layer, approximately 5, 7, and 25 nm thick, after 5, 25, and 50 cycles, respectively.

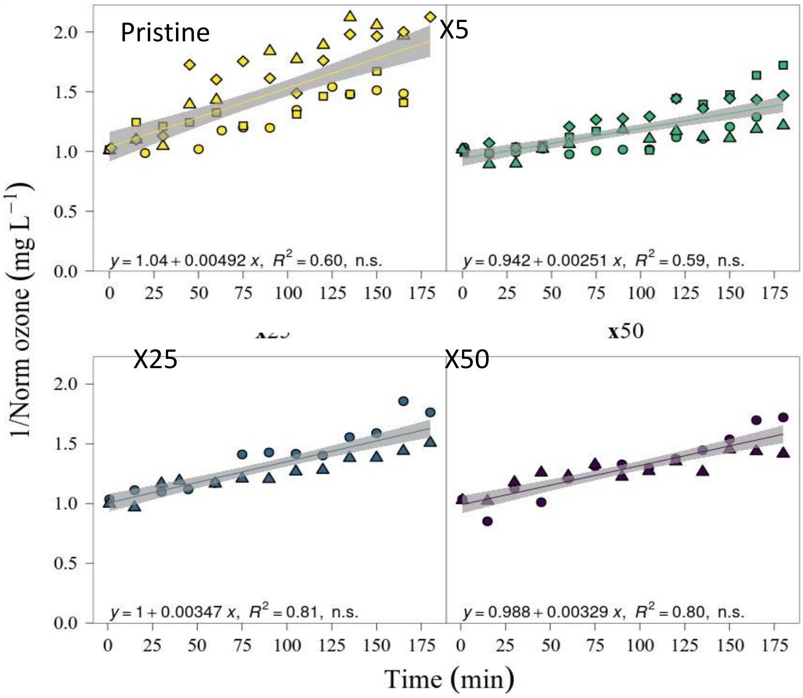

Figure 2: ozone decay rate when exposed to pristine membranes and 5, 25, and cycle alumina coted membrane (n=4).

The impact of the coating was estimated by measuring the change in the ozone concentration with time. The degradation of dissolved ozone can occur spontaneously or via oxidation of solid surfaces. Initial results (not shown) indicated that, as expected, dissolved ozone degradation significantly accelerates in the presence of pristine PA membranes. Comparing the ozone degradation rates between pristine PA membranes and alumina-coated PA membranes (Figure 2) revealed that the slowest rate was obtained for PA membranes coated with 5 ALD cycles. Measurements of normalized salt rejection (before and after exposure to ozone) demonstrated that the reduction in salt rejection (1 g/L NaCl) of the 5 cycles-coated membranes occurred at a higher ozone exposure dose (about 9 ppm·h) compared to the pristine PA membrane (about 6 ppm·h) and that its normalized permeability was more stable. These findings suggest that the coating enhances ozone stability. The impact of ozone on biofilm formation and membrane performance of pristine and 5-cycled PA membranes is currently being studied.

Development of the new catalytic layer for PEM

To improve ozone production by PEM, we investigated a new catalytic layer on the PEM and one. Antimony-doped tin chloride catalytic layer on titanium anode was studied as the new catalytic layer. Titanium was chosen since it is the preferred anode material for ozone generation due to its chemical resistance. Preliminary results indicated that the catalytic coating is unstable; therefore, a pre-treatment process of the anode was explored: (a) chemical cleaning to remove organic and inorganic layers that can destabilize the coating. The cleaning was done with acetone in an ultrasonic bath, 30 minutes degreasing in 15% caustic soda at 80 °C, and rinse in ultrapure water. (b) Etching in order increases the surface area of the carrier material, improves the adhesion of the growing layer, and enhances ozone production. The etching was done by boiling the electrode in hydrochloric acid (65%), rinsing it with ethanol, and drying it under vacuum. Then, the coating process with antimony-doped tin chloride was performed. During the annealing process, in addition to tin dioxide, two crystalline titanium dioxide phases, anatase and rutile, were formed. This resulted in cracks and a very uneven coating negative and impacted reproducibility. Therefore, we explored the coating of the anode with a sublayer of gold to protect the substrate and improve the coating layer. The current is therefore identified as an important parameter for adjusting the particle size, and the samples coated at 20 mA for 40 seconds showed the densest coverage. X-ray fluorescence and Laser Induced Breakdown Spectroscopy microscopy revealed that the layer thickness was 10 to 15 µm. The new coating was studied for ozone production (measured by the DPD method and compared to reference anodes. It was found that the catalyst with 15 µm thickness sublayers improves ozone production compared to the reference PEM Long-term stability has to be tested in further experiments.

CONCLUSION

PA membranes were successfully coated with a uniform layer of alucon using ALD. The membrane coated with 5 ALD cycles showed enhanced ozone stability, evidenced by a lower ozone degradation rate and more stable performance at high ozone doses compared to pristine PA membranes and those coated with 25 and 50 ALD cycles.

In addition, a titanium catalytic layer for ozone production via electro-catalytic reaction was prepared. A multi-step cleaning process was developed to ensure a substrate that ensures a high surface area and low flaws. The formation of the catalytic layer requires a gold sublayer with a dense coating that was archived electrochemical deposition. The current was identified as the important parameter for adjusting the particle size. Measurement of produced dissolved ozone compared to reference anodes demonstrates improvements in ozone production.

ACKNOWLEDGEMENTS

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Red-CO2-PNA: Reducing CO_2 Emissions from Municipal Wastewater Treatment – Comparing Different Partial Nitritation/Anammox Applications

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ABSTRACT

Nitrogen removal remains one of the most energy intensive parts of wastewater treatment and is therefore a potential target for reducing CO_2 emissions. Two different process strategies to overcome this limitation were investigated in the joint research project, both employing technologies based on partial nitritation/anammox (PN/A) for nitrogen removal from municipal wastewater (MWW). The first strategy (Israeli side) was based on an ion exchange and bioregeneration process for the selective removal and treatment of ammonium from mainstream MWW. The second strategy (German side) tested and optimized membrane aerated biofilm reactors (MABR) for energy efficient nitrogen removal.

At the conclusion of 3 years of research, promising results have been achieved. In Israel, an ion exchange – bioregeneration via PN/A system has been successfully developed for deammonification of mainstream wastewater. In Germany, the MABR technology showed promising results as it is very efficient in providing oxygen and at the same time keeping N_2O emissions low. The implementation of these new technologies has the potential to significantly reduce energy consumption and CO_2 emissions during nitrogen removal of mainstream MWW.

KEYWORDS

Partial nitritation; anammox; deammonification ion exchange; biofilm reactors; nitrous oxide

INTRODUCTION

Conventional wastewater treatment plants (WWTPs) are energy intensive and about 25% of their total energy consumption is spent on nitrogen removal. Instead of the traditional nitrification/denitrification processes used today, partial nitritation and anammox (PN/A) can offer significant energy savings and lower the CO_2-footprint of WWTPs when applied to mainstream municipal wastewater (MWW). While PN/A is a proven technology for side-stream treatment, i.e. applications dealing with concentrated wastewater streams, the technology has not yet been effectively applied to the much larger market of the mainstream due to the high COD/N ratio of MWW, lower temperatures, and low and fluctuating ammonium concentrations.

In order to overcome the limitations of implementing PN/A in MWW treatment, two different process strategies were investigated. The first strategy (Israeli side) is based on an ion exchange (IX) and bioregeneration process. MWW is first passed through an IX column where ammonium is separated from MWW and absorbed by zeolite. After breakthrough, the IX column is regenerated with brine yielding a regenerant solution with high ammonium concentrations and no COD that is suitable for stable and controlled treatment in a PN/A reactor. The treated regenerant is continually reused in subsequent cycles of IX absorption and regeneration. The German strategy uses a direct approach were an innovative biofilm reactor concept (the membrane aerated biofilm reactor, MABR) is investigated as technology with low energy requirements and low greenhouse gas emissions for nitrogen removal.

MATERIALS AND METHODS

Strategy 1: Ion exchange and bioregeneration via partial nitritation/anammox

Ammonia oxidizing bacteria (AOB) and anammox bacteria were first cultivated separately under hypersaline conditions (4% salinity). Both biomasses were harvested and seeded together in a 20L hypersaline PN/A reactor which was used to treat regenerant water from a bench scale ion exchange column filled with 1L of zeolite (chabazite). The ion exchange – bioregeneration system was operated for three different periods with the initial period consisting of 48 absorption and bioregeneration cycles, followed by two periods of 30 cycles each. Synthetic wastewater (50 mg/L NH_4^+-N; 200 L/cycle) was used in the first and third periods and real wastewater with similar NH_4^+ concentration used during the second period. The ion exchange column was regenerated after each absorption cycle with a 4% brine solution (24 L/cycle) starting with sea water. Sodium loss during absorption was compensated by adding NaCl to the regenerant and NaOH dosing in the PN/A reactor to compensate for nitritation.

Strategy 2: Operation and optimization of MABRs for PN/A

Two lab-scale MABRs were operated, each composed a gas compartment and a liquid compartment (volume of 1.8 L), separated by a flat sheet silicon membrane (thickness 300 µm) with a membrane surface area of 0.048 m². Synthetic feed was used with approximately 75 mg-NH4-N L^{-1}. Acetate was used as carbon source and added according to the desired C/N ratio (0, 0.5, 1.7, 3). The membrane lumen was aerated intermittently in one of the two reactors (iMABR) and continuously in the other reactor (cMABR). Intermittent aeration followed an hourly repeating pattern with an aeration phase (mostly 5 min) followed by a nitrogen flush (1 min) and an unaerated phase (54 min).

RESULTS AND DISCUSSION

Strategy 1: Ion exchange and bioregeneration via partial nitritation/anammox

Ammonium was successfully removed from simulative and real wastewater during the 108 absorption cycles of the ion exchange-bioregeneration process with no reduction in zeolite capacity during the experimental period. At complete column breakthrough (influent [NH_4^+-N] = effluent [NH_4^+-N]), 46.6% of the NH_4^+-N and 52.5% calcium were removed from the wastewater, demonstrating the similar affinity ammonium and calcium have for the ion exchange zeolite media (chabazite). As a result, the sodium concentration in the effluent wastewater rose by 100 mg/L while the calcium concentration in the regenerant increased from cycle to cycle (see below). Magnesium and potassium concentrations remained largely unchanged. Ion exchange column regeneration with 4% brine resulted in an ammonium rich brine regenerant (207.5 mg/L) without COD, ideal for treatment in the PN/A reactor. More than 90% of ammonium was successfully removed in the PN/A reactor (Fig. 1). The nitrate concentration increased in the recycled regenerant due to anammox activity. Average N_2O emissions as percent of ammonium removed was 1.05% ± 0.40% and could be reduced by 50% by the addition of a low acetate dose (0.35 g acetate/g NH_4^+-N removed). Microbial community analysis of the PN/A reactor revealed an obligately halophilic anammox bacteria from the genus *Candidatus Scalindua* and AOB from the halotolerant genus of *Nitrosomonas*. Stable operation of the PN/A reactor was mostly observed with no apparent growth of nitrite oxidizing bacteria (NOB) demonstrating the advantages of the ion exchange-bioregeneneration strategy. However, due to zeolite's affinity for calcium and the practice of minimal regenerant blowdown (field capacity only; approximately 1%), calcium increased in the recycling regenerant to very high concentrations (3000 mg/L as Ca^{2+}) and eventually impaired the activity of anammox bacteria in the PN/A reactor. With the appearance of high NO_2^--N concentrations, the PN/A reactor had to be taken off-line for recovery and reseeded with AOB and anammox bacteria. Following a period of continuous operation on sea water, the PN/A reactor was again ready to treat regenerant brine.

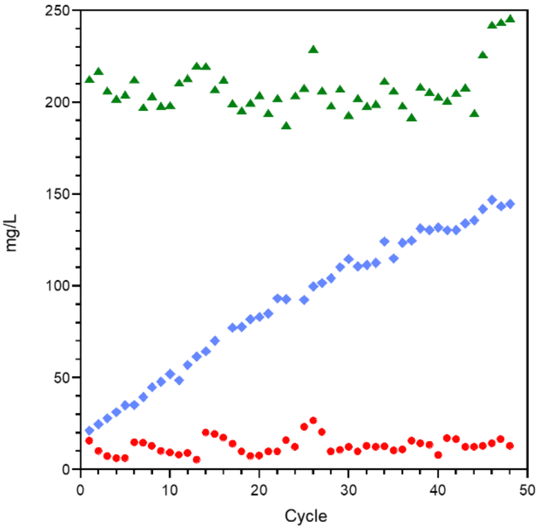

Fig. 1. Regenerant NH_4^+-N concentration before (green triangles) and after (red circles) PN/A reactor. Increase in NO_3^--N (blue diamonds) was due to anammox activity.

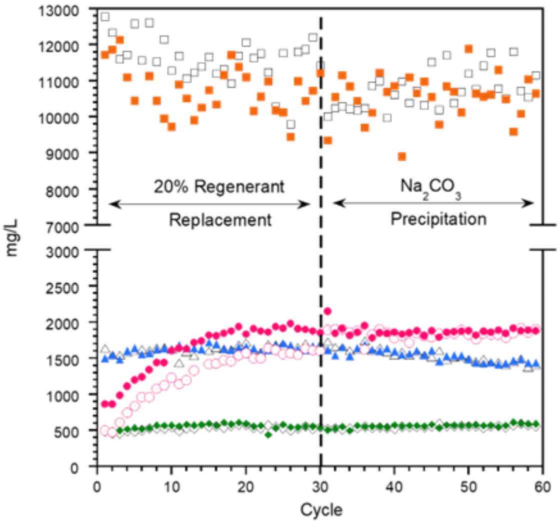

Fig. 2. Cation composition of regenerate before and after ion exchange regeneration. Sodium (squares), calcium (circles), magnesium (triangles) and potassium (diamonds).

Two methods were tested to stabilize the increase of calcium concentration in the recirculating regenerant. The first was regenerant replacement, i.e. 20% of the recycling regenerant solution was replaced after treatment in the PN/A reactor with fresh sea water (Fig. 2). In this method there was no need to add NaCl to replace sodium lost during ion exchange. The method ran for 30 cycles when actual wastewater was used. Using regenerant replacement, it took 15 cycles for the calcium concentration to increase from 490 mg/L (sea water) and then stabilize at 1879±39 mg/L as Ca2+. The system was run for a further 15 cycles with no problem. This approach would be effective in coastal areas with access to sea water. In the second method, calcium removal was carried out by precipitation using sodium carbonate (Fig. 2). After IX column regeneration, a dose of approx. 1 g Na2CO3 was given per liter regenerant. This resulted in the precipitation of 280±50 mg/L Ca2+ and a stable regenerant Ca2+ concentration of 1858±50 mg/L. The method was run for a further 30 cycles using synthetic wastewater. Both methods were shown to be effective in keeping calcium concentrations from accumulating in the regenerant and allowed for stable PN/A reactor performance and continued process operation

Strategy 2: Membrane aerated biofilm reactors

Two main aspects were considered for the MABRs, the aeration strategy and the impact of the C/N ratio. Limiting the air supply is key for successful implementation of PN/A processes and therefore continuous and intermittent aeration was tested. The results indicated that intermittent aeration was favourable in producing nitrite and establishing anammox activity. However, the turnover of the iMABR was also lower compared to the continuously aerated system (cMABR). The iMABR reached a percentage removal for ammonium of around 70 % at maximum, and of about 30 % for total nitrogen. The cMABR reached higher values for ammonium, but the total nitrogen removal was a bit lower. The highest surface removal rates were 4.1 g-N m^{-2} d^{-1}

(iMABR) and 4.5 g-N m^{-2} d^{-1} (cMABR) at a C/N ratio of 0. The best performance was observed with the C/N ratio of 3 when it comes to TN removal.

In terms of N_2O emissions, the MABRs showed significant differences between the aeration strategies and C/N ratios. Without the addition of biodegradable organic carbon, the iMABR showed N_2O emissions from both the gas and liquid phases. These N_2O concentrations resulted in a total emission of approx. 2 % of the ammonium removed.

Intermittent aeration, however, led to generally lower N_2O emissions of 0.05 – 0.79 % of the converted ammonium nitrogen, compared to the values of the cMABR with the exception of the C/N ratio of 0 as mentioned before (Fig. 3). Also, higher C/N ratios resulted in lower N_2O emissions, again with one exception for the cMABR for a C/N ratio of 1. The limiting conditions with respect to the organic carbon can be one possible explanation that led to the higher N_2O values in this operation phase.

In addition to the continuous monitoring of N_2O concentrations, batch tests were also carried out directly in the reactor to look into more short-term effects of changes in the C/N ratio or the carbon availability.

Fig. 4 shows an example of such a test for the operation period with a C/N ratio of 0. Immediately after the addition of a carbon source (here acetate, first red line), the N_2O concentration fell rapidly and was maintained at a very low level for approx. 12 hours. After the acetate was completely consumed (second red line), the N_2O concentration began to rise again and reached significantly higher values than before the addition of acetate. These experiments demonstrate the complexity and dynamics of nitrous oxide production and reduction.

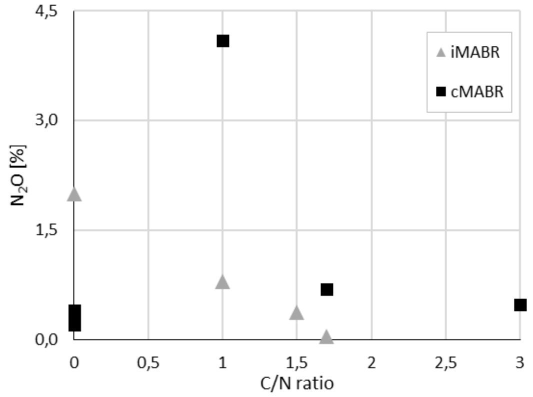

Fig. 3: N_2O emissions as percentage of the converted ammonium nitrogen for the intermittently aerated MABR (iMABR) and the continuously aerated reactor (cMABR). Emission estimates included off-gas analysis and the N_2O measured in the water phase.

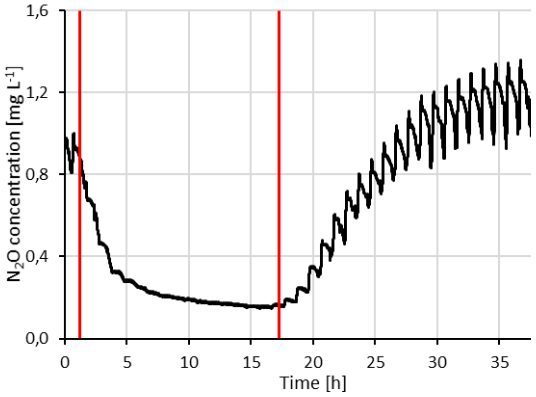

Fig. 4: N_2O concentration in the liquid phase of the iMABR during an approx. 2-day batch operation. The first red line shows the addition of the DOC (acetate), the second red line marks the time at which the DOC was completely consumed.

CONCLUSIONS

This collaborative project could demonstrate that two different technologies were successfully implemented for sustainable mainstream PN/A. Both showed high potential, with the ion exchange-bioregeneration process delivering good and stable effluent quality with low N2O emissions. The MABR as a technology with very low energy demand showed promising results with low N_2O emissions, while effluent quality still needs further improvements esp. with fluctuating C/N ratios.

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CatMemReac: CO_2 Reduction in the Oxidation of Micropollutants – Energy-Intensive vs. Novel Solar-Based Processes

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ABSTRACT

A photocatalytic reactor is a simple, effective, lost-cost-point of use, and efficient technology to remediate organic micropollutants (OMPs) from water sources. The focus of the present work is to showcase the potential of photocatalytic reactor technology in remediating pollutants from water sources while reducing CO_2 emission by making it more sustainable, efficient, and cost effective with the use of different catalyst and substrate source. In this work, a solar photocatalytic reactor fitted with organic light emitting diodes (OLEDs) was designed and tested with three different photocatalyst- bismuth tungstate, graphitic carbon nitride, and titanium dioxide. The photocatalysts were also coated on two different substrates and assessed for their performance. The findings highlighted that depending on cationic and anionic nature of the pollutants, different catalysts could be used to optimize the performance of the reactor. The results of actinometry and residence time distribution experiments suggested the reactor design to be very efficient in photocatalytic performance. Currently, a large-scale modular reactor is designed, manufactured, and placed in the TAU facility, Israel, as a pilot system.

KEYWORDS

Wastewater treatment; micropollutants; advanced oxidation process; photocatalysis; catalytic membrane; CO_2-reduction.

INTRODUCTION

With increase in population, climate change, and uneven water distribution, there is increased competition over existing water resources and the spread of issues related to water quality, water scarcity, and variability in hydrological events. Organic micropollutants (OMPs) are compounds having bio-accumulative, persistent, and toxic traits (Fonseca et al., 2021). These compounds have been detected in different water sources, generally in ng/L-µg/L range, worldwide (Aus der Beek et al., 2016; Fonseca et al., 2020). Significant terrestrial and aquatic health risk exist from the presence of OMPs. Considering these challenges in the water industry, the focus of our German-Israeli cooperation is to develop 'innovative renewable energy-based technology' to degrade OMPs and produce high quality water, also being energy efficient and having reduced carbon footprint.

The focus of our work is to develop a sustainable photocatalytic reactor capable of eliminating OMPs from water while taking into account the environmental impact, reducing the cost of manufacturing of the reactor, and optimizing its operation. We have developed a solar based reactor utilizing visible light using OLEDs which provide a more efficient sustainable water treatment solution. This innovative flow through reactor design was also characterized and optimized by testing different catalyst and substrate sources. A pilot-scale reactor is also developed in Israel and performance results are awaiting.

METHODS

An advanced flow-through solar based reactor was designed by fitting OLEDs, and realized via 3D printing (depicted in Figure 1(a)). Three different catalysts were selected for the photocatalytic investigations under visible light- titanium dioxide (KronoClean 7000), bismuth tungstate, and graphitic carbon nitride. These catalysts were also coated on two different substrates- 3D printed PLA material using a geopolymer based coating (potassium silicate and a calcium aluminate-based hardener, 5.7 wt.% catalyst), and nickel foam. The coated supports are shown in Figure 1(b). Further, the actinometry and residence time distribution experiments were also carried out in the solar reactor to characterize it.

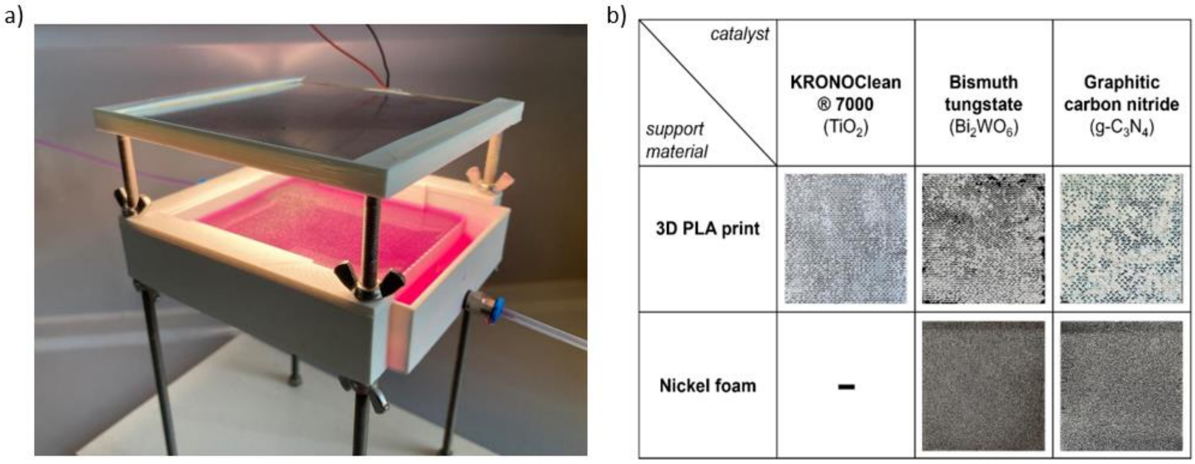

Figure 1 a: 3D printed solar reactor, **b:** Investigated combinations of catalysts and substrates.

RESULTS

Batch tests were carried out in the OLED based solar reactor to test the different catalysts (also coated on two different substrates) for photocatalytic activity using cationic methylene blue (MB) and anionic rose bengal (RB) as the test pollutants. The degradation of MB and RB using different catalyst is depicted in Figure 2.

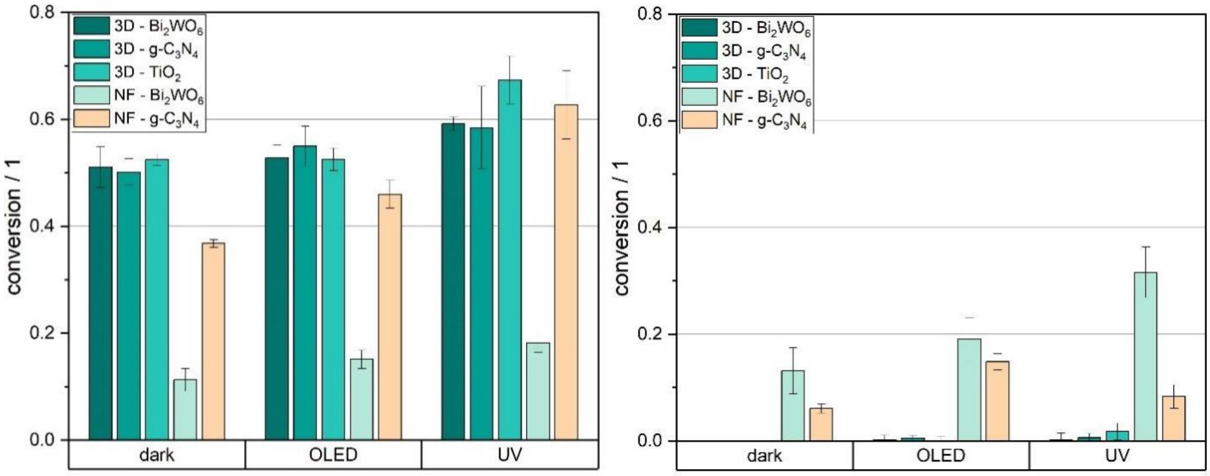

Figure 2: Degradation of MB (left) and RB (right) under different catalysts and irradiation.

Taking into account the adsorptive behavior of the substrate materials, high adsorption of MB on the immobilized geopolymer catalyst was observed, while RB was not significantly adsorbed. On the other hand, the two nickel foams coated with catalyst showed interactions with both dyes. Under OLED irradiation, the catalyst geopolymer coating showed differences compared to the dark sample, while a clear difference was observed under UV irradiation. Photocatalytic activity was observed with the bismuth tungstate coated on nickel foam under OLED and UV irradiation. The graphitic carbon nitride (CN) showed similar adsorption of MB as the geopolymer coatings and a photocatalytic effect when exposed to visible and UV light. Under UV conditions, the graphitic carbon nitride showed a lower conversion for RB.

The actinometric experiments in the solar reactor quantified the available photon flux in the reactor volume to a comparably high rate of 5.76 µmol/s. The external photonic efficiency was determined to be 93.3 %, which indicates a very efficient use of light. The residence time experiments with the reactor showed that the flow conditions in the OLED reactor are good, especially at the beginning of the mixing time. No long-lasting dead zones in the OLED reactor were observed, which indicates a positive design of the reactor systems.

CONCLUSION

The present work shows the development of a novel OLED based solar reactor which showcased its potential in achieving good photocatalytic activity. The highest photocatalytic activity was shown by graphitic carbon nitride on geopolymer coating for cationic MB, whereas for anionic RB, bismuth tungstate coated on nickel foam worked the best. Overall, the lab-scale solar reactor was found very efficient in utilizing light, and no long-lasting dead zones indicated an efficient design of the reactor. The outcomes drawn from this study will be helpful in conducting degradation studies on OMPs and maximizing their removal. These inferences could also be used for the upscaling process and further catalyst development, hence benefitting the water industry while being sustainable and cost-effective.

ACKNOWLEDGEMENT

We thank the Israeli MOST (project numbers 3-17762 and 3-17763) and the German BMBF (funding code 02WIL1605) for funding the project CatMemReac in the context of the German-Israeli-Cooperation on Water Technology Research. We also thank our dear colleagues for contributing to the project: Vered Blass and Rajhans Negi from Tel Aviv University (ISR), Sabine Langkau, Jana Thomann, and Felix Tettenborn from Fraunhofer ISI (GER).

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EconWatSim: The EconWatSim Modelling Framework for Integrated Water Management – Cost Recovery Under Economies of Scale

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ABSTRACT

In this study economic simulation models are integrated to investigate the implications of different water pricing schemes on the Israeli economy. Model results suggest that the current pricing scheme can be optimized from an efficiency perspective, but different pricing schemes have discernable effects on households' welfare. The study demonstrates the potential of the model-linking approach to provide complementary results in terms of sectoral detail and economy-wide perspectives, which go beyond the capability of the single models. This allows for a more holistic assessment of the implications of changes in the water sector and can help to design coherent policies for the water and other sectors in the context of the water-energy-food nexus. Thereby this modelling framework can contribute to more efficient, sustainable, and integrated management of scarce water resources.

KEYWORDS

Water policy, Boiteux-Ramsey pricing, marginal cost pricing, integrated water management, water-energy-food nexus, cost recovery

WATER MANAGEMENT IN ISRAEL

In response to a prolonged drought over the past decade, Israel has implemented various technological innovations to enhance water supply, including desalination and wastewater reclamation. Additionally, quantitative instruments, such as user charges and fees, have been implemented to regulate water demand in the country. International organizations promote such measures mostly based on two arguments: 1) pricing constitutes essential incentives for efficient water use, and 2) fees are necessary for cost recovery, funding the water system's operation and maintenance, and facilitating investment in infrastructure (OECD, 2010). Accordingly, in 2010, Israel adjusted the water law. Since then the water tariffs are supposed to cover the pumping and supply costs, including the investments required for the efficient development of the water sector. However, a typical water sector tends to exhibit economies of scale, mainly as a result of the substantial share of capital investments in total costs. Also, physics and hydrology contribute to create economies of scale in the conveyance of the water. With a simple proportional pricing, cost-covering requires to set the price at the average cost level, while economic efficiency calls for setting prices equal to the marginal cost of supply. Scale economies imply that the two differ. This was confirmed for Israel by Reznik *et al.*, (2016), who estimated substantial deadweight losses due to the above pricing conflict in Israel.

Acknowledging the fact that under these conditions a pricing rule that implements the first best is infeasible, Ramsey (1927) and Boiteux (1971) suggested a pricing rule that minimizes the deadweight losses, according to which the relative markup of the water price above the marginal cost should be proportional to the inverse own-price demand elasticity of water. Thus, water consumers with less elastic demand pay more. Dierker (1991) formulated the conditions, under which the Boiteux-Ramsey pricing rule indeed achieves the second best and is thus optimal under the cost coverage requirement. Much in the spirit of the above Boiteux-Ramsey pricing rule, since the 2010 reform, the water economy in Israel is characterized by intersectoral cross subsidization, where the lower demand elastic urban sector subsidizes the agricultural sector with a larger demand elasticity as described in Luckmann, et al (2014).

In this study we investigate the implications of different pricing options to increase the economic efficiency in the water sector under economies of scale, while allowing for cost recovery inside or beyond the water sector using an economic simulation modelling framework integrating a high-resolution nation-wide model of the water sector with a computable general equilibrium (CGE) model.

METHODS

This study is based on the integration of two economic simulation models with a focus on the water sector. Both models have been updated and calibrated to the case of Israel and the year 2019 as a common base-year. The first model is the water sector optimization model MYWAS (Multi Year Water Allocation System Model), which depicts topography and water supply infrastructure in detail (Reznik *et al.*, 2016). For this study MYWAS has been enhanced to integrate income changes in the municipal demand function.

The second model is the CGE model STAGE_W (Luckmann *et al.*, 2014). This model includes the linkages of the water sector with the rest of the economy, by depicting all relevant economic agents, such as households, firms and the government, which are connected through economic transactions on commodity- and factor-markets. It has been expanded specifically to capture the relevant peculiarities of the Israeli water sector, including the use of different water qualities and sources (natural fresh water, desalination, reclaimed wastewater, brackish water) as well as price-differentiation between users.

The models are run in an iterative setup. MYWAS is used to optimize the water sector under the different pricing rules. The resulting average water prices, differentiated by water quality and user group as well as water supply quantities are then transferred to STAGE_W. The same is done for the water quantities consumed by agriculture, industries and municipalities. STAGE_W in turn, is then used to investigate the multiplier effects these changes in water policy have throughout the economy. The change in water supply, among others, affects the demand for energy and hence its price. Further, changes in water pricing have implications for households' disposable income, which again affects the demand for water. Therefore, the changes in water supply costs, energy and household income are fed back to MYWAS, which is recalibrated and re-run. This procedure is continued until the changes of the exchanged model parameters remain below a predefined threshold, which defines convergence. In this study the threshold has been set to 0.1% and convergence is reached after five to six iterations.

The model-framework is applied to investigate three scenarios: 1) Boiteux-Ramsey (B-R) pricing, in which water provision costs are covered through a regionally differentiated one-tier tariff that minimizes deadweight losses as described above, 2) Marginal cost (MC) pricing and cost recovery through a fixed annual water connection fee levied on all water users independent of consumption volume. 3) MC pricing and cost recovery through a multiplicative (and hence distribution-neutral) adjustment of the direct taxes on households. Therefore, in this scenario the deficit resulting from MC pricing under economies of scale is covered outside the water sector. The implications of these three scenarios within and beyond the water sector are discussed in the following.

PRELIMINARY RESULTS

As can be seen from Table 1, all three scenarios lead to a considerable drop in water prices in the agricultural sector. Yet, urban prices only fall in case of MC pricing, given the low demand elasticity of urban water users, resulting in a considerable markup in case of B-R pricing. These price changes result in an increase in water consumption of the agricultural sector in all scenarios, as well as a higher urban water use in case of MC pricing. Compared to analysing these pricing rules with MYWAS alone (results not reported), we see an increase in efficient prices in both sectors, which is a consequence of increasing energy prices and therefore a decrease in quantities of freshwater consumed.

Table 1: Comparison of water pricing rules

		Actual Pricing 2019	**B-R Pricing**	**Marg. Cost + Fee**	**Marg. Cost + Tax**
Water Consumption (MCM)	Urban	898	899	961	961
	Agriculture	1,174	1,448	1,447	1,447
	Neighbors	140	140	140	140
	Environment	0	0	0	0
	Total	2,213	2,487	2,548	2,549
Efficient Prices (NIS/CM)	Urban	9.06	9.59	5.01	5.01
	Agriculture	1.92	1.16	1.17	1.17

Note: In 2019 the average conversion rate was: 1 NIS = 0.2808 USD

The distributional effects of the different water pricing rules are visible in Figure 1. Panel a) shows that with B-R pricing the disposable income for Jewish households slightly declines, while it increases for all except the richest Arab-and-other households. This is mainly driven by differences in wages, which fall for Jewish labour categories by 0.3% on average and rise for Arab labour categories by 1.6%, driven by differences in occupations.

In both MC pricing scenarios income is increasing for all household groups. Yet, comparing the two cost-recovery options, reveals that cost recovery outside the water sector, i.e. through an income tax increase results in higher benefits for poorer households. This is due to the progressive income tax system in Israel, placing a heavier burden on richer households. In this scenario the income tax rate would be increased by 4% for all households.

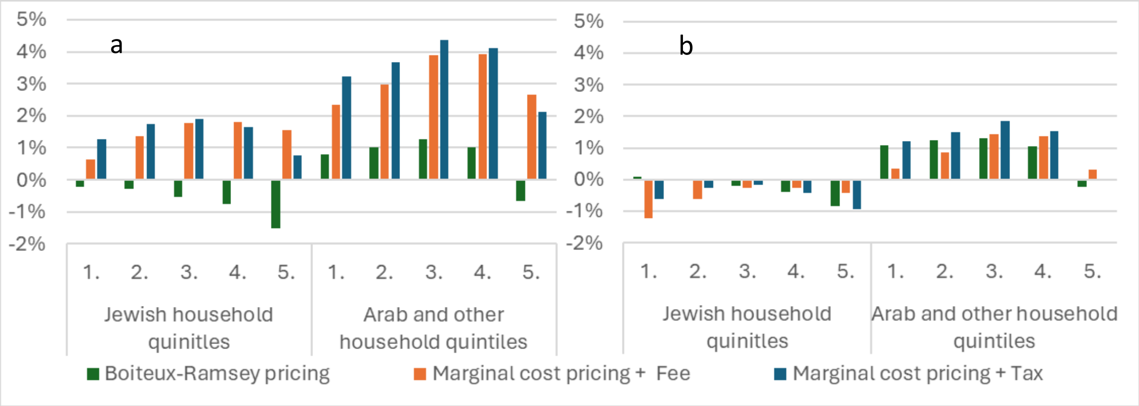

Figure 1: Distributional implications compared to the actual pricing in 2019; Panel a) Changes in households' disposable income; Panel b) Changes in equivalent variation compared to base household income. *Note: The equivalent variation is the change in household income required in the base situation to achieve the same level of consumption as in the respective scenario.*

Finally, Panel b) in Figure 1 shows the overall welfare effects on households, which are a composition of income and consumption effects. As can be seen the overall welfare effects turn negative for Jewish households. This is due to the overall increase of the price level with MC pricing, leading to an inflation rate of 2.3%, which is slightly above the income gains for Jewish households but below the income gains for Arab and other households. Still the gross domestic product slightly increases by between 137 million NIS and 145 million NIS annually with B-R and MC pricing, respectively.

CONCLUSIONS

This study shows for the case of Israel, that there are different pricing schemes which allow for cost recovery and at the same time enhance economic efficiency in the water sector as compared to the currently applied water pricing system. Yet, the modelling framework presented here also allows to study the economy-wide and distributional effects beyond the water sector. As shown, due to indirect effects on factor markets and income and price changes of consumer goods, the final effects on households' welfare vary considerably between the pricing policies applied.

While the results presented in this analysis are preliminary, as the EconWatSim model framework is still work in progress, the study demonstrates the potential of the approach of model-integration in allowing to address water policies in a new way, providing complementary perspectives in terms of a detailed and spatial representation of the water sector on the one hand and an economy-wide perspective on the other hand, allowing for an in-depth welfare analysis at the household level, which could not be provided by the single model components alone as MYWAS ignores fixed costs, while STAGE_W overlooks spatial heterogeneity, and the resulting policy ramifications.

The EconWatSim model framework thus allows for a more holistic assessment of the implications of changes in the water sector, including more complex pricing schemes, with different further options of cost recovery. That way, the framework can help to design coherent policies for the water and other sectors (such as agricultural subsidies, tariffs) and thereby enhance the integrated management of water resources, considering direct and indirect implications for other sectors in the wider context of the water-energy-food nexus.

ACKNOWLEDGEMENT

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Projects Started in 2022

ELARIA: Elimination of Antibiotic Resistances, Pathogens, and Faecal Indicators, and Risk Assessment in Advanced Wastewater Treatment

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ABSTRACT

Minimising the release of these biological contaminants by wastewater treatment plants (WWTPs) is becoming increasingly important to improve the quality of surface water sources and safe water reuse. The objectives of the ELARIA project are to generate reliable data on advanced wastewater treatment for the removal of multi-resistant pathogens, antibiotic resistance genes (ARGs), enteric viruses, protozoan parasites and indicator microorganisms in order to assess the microbial risk associated with the applications of the effluent produced. The first phase of the project focused on harmonising detection methods, investigating wastewater treatment plants that already have advanced wastewater treatment, and enumerating ARGs using PCR-based detection of long gene fragments instead of the usual short fragments. The harmonised detection methods were used to investigate WWTPs already using advanced treatment methods, including one WWTP with chlorination and UV treatment in Israel and three WWTPs with ozonation in Germany. All three treatment methods resulted in significant reductions in microbiological parameters at the applied doses, with the highest log removal rates for chlorination, followed by UV disinfection and ozonation. However, bacteria, antimicrobial resistant bacteria and ARGs of high hygienic relevance are still detectable after the treatment processes. ARGs quantified by short amplicon PCR were not efficiently reduced by the advanced treatment compared to the microbial indicators. Bench-scale studies comparing qPCR targeting short and long ARG fragments, showed higher reduction rates for the long amplicons. These data demonstrate that long amplicon (LA)-PCR provides important information for improved risk assessment, as only complete genes actually mediate antibiotic resistance.

KEYWORDS

Indicators; pathogenic viruses; antibiotic resistance genes; antibiotic resistant bacteria; wastewater, advanced wastewater treatment

INTRODUCTION

Water scarcity (< 1000 m^3/capita/year) has increased extremely rapidly, with the proportion of the world's population living in chronic water scarcity increasing from 9 % (280 million people) in 1960 to 35 % (2300 million people) in 2005 (Kummu et al., 2010). Water reuse can be used to alleviate water scarcity by groundwater recharge, restricted and unrestricted irrigation, or non-potable domestic use. This is achieved through conventional or advanced treatment trains, which can be optimised based on local wastewater characteristics to achieve water quality consistent with the intended use and regulatory framework (Gerardi and Zimmerman, 2005). The water quality of treated domestic wastewater is a key factor in the safety of surface waters and irrigated food crops. Treated wastewater may contain waterborne pathogenic microorganisms that can be transmitted via surface waters or irrigated food crops. These emerging pathogens are playing an increasing role in water quality management and safety.

METHODS

Sampling and sampling sites

In Israel, raw and treated effluent samples were collected from the Hod-Hasharon Kfar Saba WWTP. The treatment process consists of primary physical sedimentation, biological activated sludge, followed by sand filtration and either chlorine disinfection (dosing of 1-2 mg/L free chlorine) or UV irradiation (40 mW/cm^2). At this WWTP, eleven sampling campaigns were carried out, taking samples after secondary biological activated sludge treatment, gravity sand filtration, disinfection with either UV irradiation or chlorine disinfection.

In Germany, three WWTPs using ozonation as an advanced treatment step were investigated. The ozonation systems were operated under different conditions (variable ozone dosage: ΔSAC254 ≈ 30%, 40% or constant ozone dosage 3mg/L). The plants were sampled monthly. Samples were taken from the effluent of the secondary clarifier, the effluent of the ozonation and the effluent of the sand filter.

Determination of microbiological parameters

Within the ELARIA project, a wide range of hygienically relevant and representative microorganisms are analysed using a variety of cultivation and enumeration methods like faecal coliforms and *E. coli* (Colilert, IDEXX), enterococci (Enterolert, IDEXX), sulphite-reducing clostridia (TSC agar, ISO 14189), somatic and F-specific coliphages (ISO 10705-1 and 2), extended-spectrum beta-lactamase (ESBL) producing *E. coli* (Chrom ID agar), and antibiotic resistance genes (ARGs) *sul1*, *ermB*, bla_{TEM}, *tet*A, *tet*C, *vanA* (quantitative real time PCR).

Bench scale ozone treatment experiments

Bench-scale experiments were conducted using WWTP effluent inoculated with antibiotic-resistant model organisms at a known concentration. The ozonation experiments were performed as batch experiments in 250 mL glass vessels filled with drinking water. The ozone stock solution was prepared by sparging ozone gas through a cooled reactor column filled with ultrapure water. The ozone concentration (20–30 mg/L, in duplicates) was measured by a photometric test kit (NANOCOLOR Ozone, Macherey-Nagel) before adding the solution to the batch vessels. After an incubation time of 5 min, the reaction was stopped by adding sodium thiosulfate (1.5 %)

Long-amplicon PCR (LA-PCR)

Standard qPCR detection of viruses, bacteria and ARGs using quantitative real-time PCR detects small fragments of up to 300 base pairs. Depending on the organism, these small fragments represent only a small portion of the genome or, in the case of ARG, only a portion of the gene itself. When validating treatment procedures by PCR, short amplicons tend to underestimate damage at the nucleic acid level and therefore contrast strongly with the results of culture-based assays. Therefore, long amplicon PCRs were performed to detect ARGs.

RESULTS AND DISCUSSION

Investigation of the WWTPs using advanced treatment methods showed high prevalence of bacterial indicators, viral indicators, antibiotic-resistant bacteria and selected ARGs in the raw wastewater. At the Israeli WWTP, the reduction of the investigated microbial indicators faecal coliforms, *E. coli* and sulphite-reducing clostridia and somatic coliphages by chlorine disinfection (1-2 mg/L) was greater than that recorded by UV irradiation (40 mW/cm^2). The highest concentration of ARGs was found for *sul1* followed by *intl1* and *tet*A. A negligible reduction of ARGs was observed for UV irradiation using short amplicon PCR, whereas chlorine disinfection resulted in at least two log reduction of all genes analysed. The protozoan parasites *Cryptosporidium* and *Giardia* were detected in secondary effluent at higher concentrations during the summer months, but were below the detection limit in the tertiary effluent. In Germany, the three ozone treatment plants, which are designed to reduce micropollutants by at least 80 % (DWA, 2015), showed a reduction of 1-2 log levels in the cultured parameters. Similar to the UV treatment in Israel, the ozone treatment in these three WWTPs did not result in a reduction of ARGs detected by amplification of short fragments. The results of the analysis of samples from advanced treatment plants in Germany and Israel are summarised in Table 1. In both Germany and Israel, the concentration of F-specific coliphages in the influent was too low to calculate a log reduction for the treatment processes. Therefore, the suitability of these coliphages for such studies is limited.

Table 1: Log reduction of the various microbiological parameters by secondary wastewater treatment + sand filtration (SE), UV irradiation (UV), chlorine disinfection (Cl) and ozonation + sand filtration (O3)

	SE	**UV**	**Cl**	**O3**
E. coli	2.89	1.83	3.53	1.69
Faecal coliforms	2.55	3.12	3.71	1.47
ESBL *E. coli*	1.82	1.77	3.30	1.47
Sulphite reducing *Clostridia*	1.18	1.65	3.25	Not analysed
Somatic coliphages	2.16	2.80	3.52	1.70
16S rRNA gene	3.28	-0.21	0.23	0.34
sul1	3.17	-0.19	1.56	0.23

Overall, the results show that all treatment methods lead to a decrease in microbiological parameters, but bacteria, antibiotic-resistant bacteria and ARGs with high hygienic relevance can still be detected after treatment.

Studies were also carried out on the relevance of amplicon length in PCR-based detection. For the bench scale ozone treatment experiments using treated wastewater spiked with model organisms (E. coli DSM4690 [tetA] and E. faecium DSM 13590 [vanA]), the ARGs of the model organisms were detected by PCR with short and long amplicons in addition to the culture method. The results show, that the concentrations of genes were overestimated using short amplicon PCR (see Figure 1).

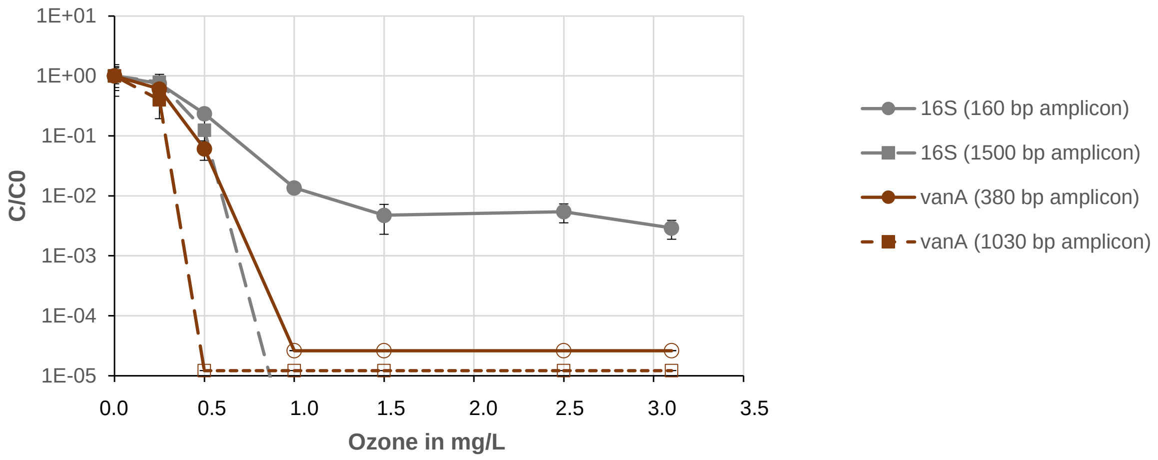

Figure 1: Comparative analysis of antibiotic resistance genes by short and long amplicon PCR for ozonation of wastewater treatment plant effluent spiked with resistant *E. coli* und *E. faecium* model bacteria. The unfilled marking points give values below the limit of detection.

While short 16S rRNA gene fragments were above the limit of quantification even at higher ozone concentrations, the gene could no longer be detected in LA-PCR at ozone concentrations above 0.5 mg/L. A similar picture emerges for the *vanA* gene, which becomes undetectable even earlier due to the detection of a long fragment.

These data illustrate the advantages of LA-PCR in reactive wastewater treatment. Overall, LA-PCR provides important information for improved risk assessment, as only complete genes actually mediate antibiotic resistance.

CONCLUSIONS AND OUTLOOK

This study showed that microbial indicators such as faecal coliforms, sulphite-reducing clostridia and somatic coliphages are prevalent at high concentrations in raw wastewater and secondary effluent. ARGs are also highly prevalent in both matrices. For the Israeli WWTP studied, chlorine disinfection was found to be more effective than UV irradiation in reducing the microbiological parameters analysed. Although the transmittance was adequate, the UV dose was relatively low at 40 mW/cm^2. In Germany, the ozone treatments of three WWTPs, designed to reduce micropollutants by at least 80 %, showed a reduction of 1-2 log levels in the parameters enumerated by culture methods. Overall, the results demonstrate that all treatment methods lead to a reduction in organisms, but bacteria, antibiotic-resistant bacteria and ARGs with high hygienic relevance can still be detected after treatment.

ARGs quantified by short amplicon PCR were not efficiently reduced by the advanced treatment compared to the microbial indicators. However, the bench-scale studies analysed comparatively by qPCR targeting short and long ARG fragments showed higher reduction rates for the long amplicons. These data illustrate that LA-PCR provides important information for improved risk assessment, as only complete genes actually mediate antibiotic resistance.

In the further course of the project, dose-response experiments with UV and UV-LED irradiation, ozone, chlorine and electrochemical treatment will be carried out to determine and compare the optimal conditions. The bench scale results will allow the optimisation of a multi-barrier pilot plant to produce high quality effluent with minimal health risk. The data generated will be used for quantitative microbial risk assessment, to compare the economics of treatment processes and to recommend key monitoring parameters.

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re:PM: Removal and Degradation Platforms Tailored for Persistent Mobile Organic Compounds in Drinking Water Sources

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ABSTRACT

Persistent and mobile chemicals (PMs) compromise the quality of our water resources and are difficult to remove by the established methods of drinking water treatment. Among these compounds are pesticide metabolites, pharmaceuticals, industrial chemicals and transformation products thereof, many of which have not been searched for, yet. Short-chain and ultrashort-chain per- and polyfluorinated alkyl substances (PFAS) are a very prominent group of PMs. Only recently the tolerable weekly intake for PFAS was reduced drastically. The project re:PM is dedicated to (I) characterizing the occurrence of PMs in groundwater and surface water used for drinking water production in urban, rural and industrial areas. (II) to develop innovative and efficient removal processes for PMs for drinking water production on the basis of metal oxides and modified metal oxides as sorbents and catalysts for PMs.

At Technion, work in the first year focused on the development of new composites for the adsorptive removal and catalytic destruction of short-chain PFAS and other PMs by combining positively charged polymers with clay minerals for a potentially stronger adsorption affinity to anionic short-chain PFAS. The HUJI group explored the conditions of PFAS adsorption on the three metal oxides zirconium oxide, manganese oxide and magnesium oxide more closely.

At UFZ, the activities were directed to improving the analytical method for PMs from groundwater based on supercritical fluid chromatography-mass spectrometry (SFC-MS) and to validate the final methods. The method was eventually applied to groundwater and tap water from Germany.

KEYWORDS

Persistent and mobile chemicals, per- and polyfluorinated alkyl substances, drinking water, groundwater, innovative treatment technologies, emerging analytical methods

INTRODUCTION

The occurrence of persistent and mobile organic chemicals (PMs) in the water cycle poses a real threat to the quality of our drinking water sources. PMs are challenging to analyze, to monitor and to remove from water, due to their high polarity and recalcitrance. The state-of-the-art remediation technologies are at times ineffective. For many PMs in source waters no removal technology is available (Reemtsma *et al.* 2016). The pool of PMs is supposedly very large but only partially explored (Neuwald *et al.* 2021). It comprises pesticide metabolites, pharmaceuticals and industrial chemicals registered under REACH, and transformation products thereof. A very prominent group of PMs are short-chain per- and polyfluorinated alkyl substances (PFAS). The most recent health-risk assessment drastically decreased the tolerable weekly intake of PFAS in Europe (EFSA 2020). Consequently, PFAS levels in drinking waters are exceeded on a broad scale. Additionally, technologies to remove PFAS from raw waters are inadequate for broad application. This example of PFAS drastically outlines that a protection gap exists for drinking water. This gap is, however, much larger: it comprises a largely unknown number of other PMs, with potential consequences for human health.

METHODS

For improving the knowledge regarding PMs in water resources we developed innovative analytical methods based on SFC-MS established at UFZ and dedicated to the screening for a large set of PMs. With these we will characterize the PM profile of source waters (mainly groundwater) for drinking water production in Israel and Germany.

For developing techniques specifically tailored to mitigate the impact of PMs on water resources we advanced adsorption and degradation processes of PMs using novel catalytic oxide materials. Adsorption-oxidation platforms based on our developed iron-oxide decorated clays modified by polymers that can trap PMs, and one-step adsorption-degradation in-situ by simple metal oxide platforms will be designed.

RESULTS AND DISCUSSION

1. Synthesis of Iron-decorated clay-polymer composites

This task is dedicated to synthesis and characterization of Fe-decorated clay with adsorption-enhancing polymers. Two positively charged polymers and several clay minerals were tested for removing PFOA, PFOS and PFBA. The best performance was observed by a PDADMAC -montmorillonite (MMT) composite. Thus, the MMT-PDADMAC composite was chosen, and the amount and type of PDADMAC was optimized by PFBA test which reached a high adsorption capacity of 83% removal. The adsorption isotherms for these PFAS were constructed (Fig. 1A and Fig. 1B). At low PFAS concentrations, the adsorption follows the Langmuir model. At high concentrations, adsorption increases, forming an S-shaped isotherm that suggests multi-layer adsorption due to increased surface hydrophobicity. The adsorption of PFBA varies with environmental conditions like salinity, pH, and humic acid presence. Notably, higher salinity significantly reduced adsorption affinity, attributed to surface charge screening and competition from other ions. Lastly, we investigated the adsorption of PFBA to iron-oxide MMT-PDADMAC to test the possibility of an adsorption - Fenton oxidation platform for PFAS. However, iron-oxides inhibited the adsorption significantly because Fe-MMT hinders the expansion of the clay layers which significantly reduces the SSA. To rectify this, iron-oxides were deposited on the composite after PDADMAC and enabled PFBA adsorption at levels similar to those measured before the deposition of iron oxides.

2. Removal of selected PMs by MnO_2, MgO, and ZrO_2

PFOA and PFOS were selected as initial model PFAS to test their removal by three metal oxides – MnO_2, MgO, and ZrO_2. The removal efficiency and adsorption rate correlated to the zeta potential of the oxides MnO_2 (-37) < MgO (+11) < ZrO_2 (+29). This suggests an electrostatic interaction mechanism between the negatively charged head groups of the PFAS and the positively charged surfaces. In addition, PFOS had a higher affinity and outcompeted PFOA in all cases, probably due to the electronegativity of the sulfonic group. Adsorption isotherms were constructed for PFOS and PFOA to these oxides. Like the clay-polymer composite, an S shape isotherm is observed for the adsorption of the PFOS to the positively charged surfaces. This is in line with the behavior of micelles that form a bilayer upon surface adsorption. In correlation with these findings, contact angle measurements show the increase in hydrophobicity of the PFOA-covered zirconium oxide surface in comparison with the MnO_2, where minimal adsorption is observed. The removal of 11 PFASs from groundwater increased as the chain length increases, as expected (Fig. 1C). The removal of short chain PFAS was negligible but was enhanced in the presence or upon pre-adsorption of the oxides with the long chain PFAS (Fig. 1D).

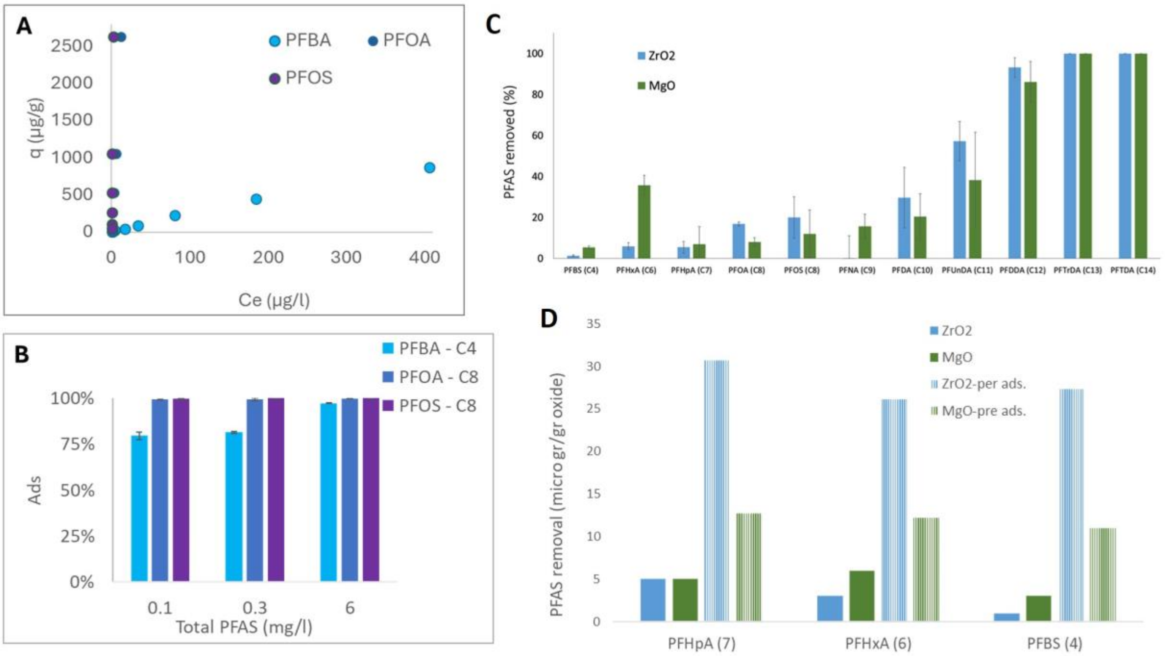

Figure 1: Removal of PFAS by the PDADMAC-MMT composite (A and B) and the oxides (C and D).

3. Adaptation of analytical method

In the section of refining our analytical method for PMs to effectively analyze and quantify them in water at trace level. 19 PFAS including ultrashort, short-chain and novel PFAS spiked at different levels in tap water and groundwater from Germany were applied for sample enrichment (for higher recoveries) and SFC-MS method (for better peak separation and higher sensitivity) development test. The optimized analytical workflow consists of freeze-drying, azeotrope evaporation, high-speed centrifuge, and SFC-MS measurement (Fig. 2A) with a method detection limit (MDL) of below 1 ng/L for most PFAS and is valid for analyzing PFAS in drinking water and its source water with a lower limit value from 2026 onwards (sum of a set of PFAS below 100 ng/L).

4. Selection of suspect/target PM List and screening of water samples

Apart from PFAS, a target list containing 151 PMs is selected with the help of Norman Suspect List Exchange, with particular attention on those PMs with a JChem Log D value (pH = 7.4) below 1, including pesticides, pharmaceuticals, cosmetics, and industrial materials, along with their parent compounds and/or transformation products. The analytical method validation for these PMs in tap water and groundwater was consistently conducted using the same established protocols. 94% of the PMs on the list were found detectable with their MDL mainly ranging from 0.1 to 100 ng/L in both waters, indicating that our analytical method is effectively valid for quantifying most PMs at trace levels. Interestingly, our analysis revealed no significant correlation between the recoveries of the PMs and their log D. By target screening of both PMs and PFAS in our tested water samples, tap water and a groundwater which is known for its minimal contamination levels, we found that the tap water contained 7 PFCAs, 5 PFSAs, and 4 novel PFAS. TFA (C2) was the most abundant, with a concentration exceeding 600 ng/L, followed by PFPrA (C3) at 6.5 ng/L. In the groundwater only 3 PFCAs and 2 novel PFAS were identified, with TFA similarly dominating at a concentration of 48 ng/L (Fig. 2B). For the remaining PMs, 73 were detected in tap water and 62 in groundwater, with their major concentrations ranged from below 0.1 ng/L to a few hundred ng/L (Fig. 2B and Fig. 2C).

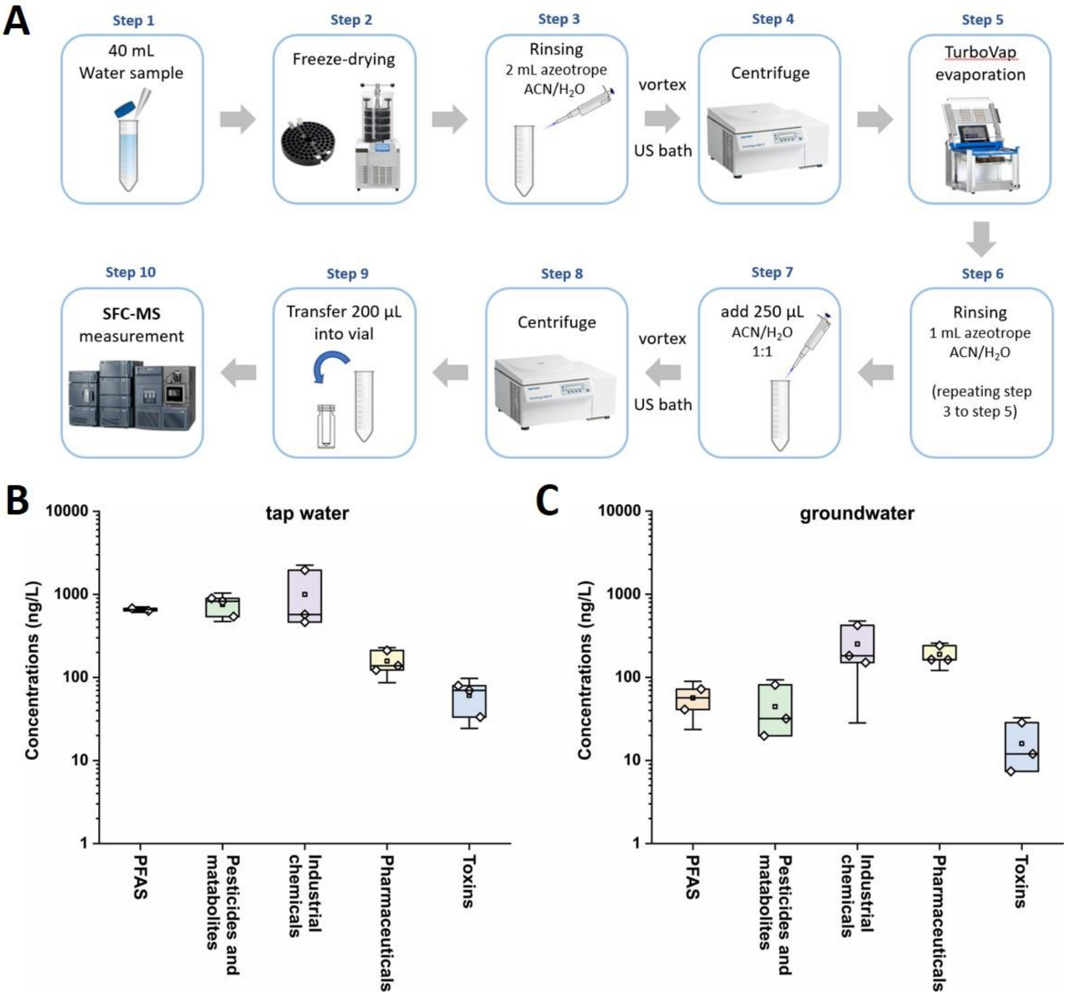

Figure 2: The optimized analytical workflow for PMs in water (A) and the quantified results of the detected PMs in tap water (B) and groundwater (C).

ACKNOWELDGEMENTS

The authors gratefully acknowledge the financial support of the project re:PM in the framework of the German- Israely Water Technology Cooperation by BMBF and MOST (BMBF FKz 02WIL1658; MOST Project Number 1001541168).

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MICROLAKE: Dynamics of Micropollutants and High Affinity Particulate Matter in Lake Kinneret and its Watershed

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ABSTRACT

Lake Kinneret is a key source of drinking and irrigation water for Israel and the kingdom of Jordan. The Lake's major source (Jordan River) is tainted with various micropollutants, including DDT and Endosulfan, banned decades ago. Yet, these are barely detected in the receiving lake water but were found in Jordan River mouth sediments and the Lake's fish. In this study the link between the water's particulate matter, microplastics and pollutants is investigated to understand the transport processes in the lake and the food web. First results provided insights on seasonal pollutant levels and the presence of microplastics. Investigations between the link of particulate organic matter, microplastics and pollutants could not yet be determined and will be investigated in the future.

KEYWORDS

Particulate matter, sediments, affinity, micropollutants sorption, Lake Kinneret, Jordan River.

INTRODUCTION

Freshwater sources used for drinking and agricultural irrigation may include chronic low concentrations of micropollutants (pesticides, petrochemicals, healthcare products, etc.). While focussing on the water medium, in some cases, these harmful components that have been recorded in the freshwater origins (rivers and streams) are all but missing at the sink (i.e. the Lake). These harmful compounds that in many cases cause severe health issues, may bioaccumulate in aquatic organism's tissues or adsorb to particles that sink to the lake bed. One such example is the case of Lake Kinneret. The Kinneret is mainly fed by the Jordan River that receives inputs from a large watershed in northern Israel. Lake Kinneret is the biggest freshwater body in the middle east, supplying water to both Israel and the kingdom of Jordan. Additionally, the Lake's finfish population is harvested and sold for human consumption. A survey conducted in 2004 on Lake fish revealed high levels of pesticides (micropollutants), including DDT and Endosulfan in their tissues (Kinneret Lake Laboratory 2004). These pesticides have been banned for many decades, and are almost undetectable in the Lake water. However, they were found in relatively high levels in the Jordan river mouth sediments (David et al. 2007). In the present study we examine the adsorption of micropollutants, to particulate matter in the Lake and its spatial deposition in the sediment layer. In this project, we assess the presence of micropollutant contaminated sediments with material collected from the Lake. One of the requested results is the formation of a distribution map, implying on the location of polluted sediment hot spots, and the assessment of dominant adsorbing features in the sediment material such as lipids, microplastics and polysaccharides. Since the distribution of these components most likely varies in different seasons, samplings are carried out at different time points per year to capture seasonal patterns. An additional goal of this project, focuses on the translocation potential of different sediment particles. This task is achieved by an indirect measurement of the particles settling velocities, focussing specifically on the fluffy layer that has the greatest translocation potential. Further, to fully understand the potential of pollutants "sponge like" particles translocation and settling in hot spots, we conduct affinity tests of the pollutants found in the Lake, and the various fluffy sediment particles sampled.

MATERIAL AND METHODS

Sampling locations

This study tracks the location of polluted sediments or particulate matter including microplastics, and tries to assess their potential translocation and ability to adsorb pollutants. Several sampling cruises were conducted from August 2022 till March 2024 following the transects depicted in Figure 1A. All sampling cruises are repeating the same stations.

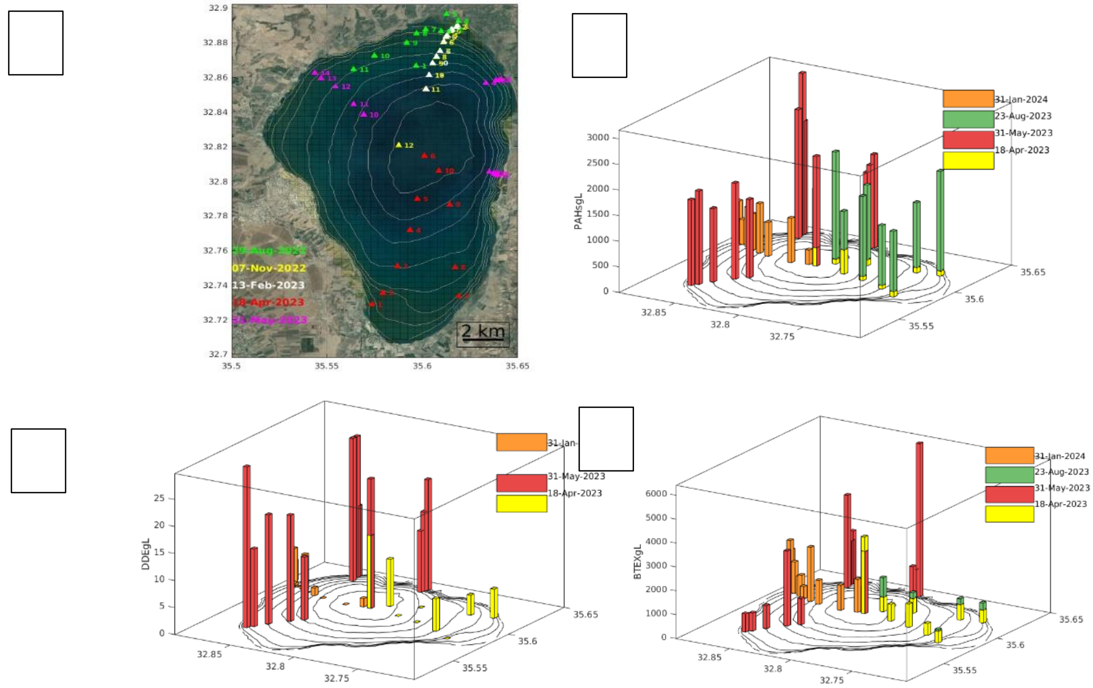

Figure 1: Sampling locations (A) and ∑PAHs (B) , ∑BTEX (C) and DDE (D), recorded at the transects conducted between August 2022 to March 2024.

Sampling methodology

This project focuses on particles that have the highest translocation potential in the lake. Thus, we chose to sample the sediment's top fluffy layer (<1 cm in depth). This layer has a high water content and is readily suspended. Hence, it must be sampled with great care. In order to sample the fluffy layer with a plastic-free instrument, a special brass corer was constructed. In each one of the stations depicted in Figure 1, a core sample was taken and the top 1 cm was collected using a piston with a special iron knife, and temperature and depth were recorded.

Chemical analysis

All sediments were kept in an ice box till the samples reached the laboratory (<4 hours) and then immediately separated from the top water. This procedure may prevent the formation of white aggregates that are formed in freshwater bodies after freeze-drying, due to the presence of dissolved inorganic carbon. Thereafter fluffy layer samples were freeze-dried and stored at −20°C until further processing. Efficient multi-extractions of up to six samples at a time, were conducted by placing 0.2 grams of each freeze-dried sample in a multi-extractor (BUCHI), followed by concentration in a multi-evaporator (E-916 by BUCHI). The extracts were worked up by specially designed glass columns containing silica beads, concentrated again by the multi-evaporator, and finally analyzed by the laboratory GC/MS against commercial standards.

FTIR analysis

Fluffy layer samples were analyzed by diffuse reflectance infrared Fourier transform (DRIFT) measurements (Bornemann et al., 2010) using a Bruker Tensor 27 spectrometer coupled to an infrared plate reader unit (Bruker HTS-XT, Bruker Optik, Ettlingen, Germany). Measurements were performed using mercury-cadmium-tellurid (MCT) detector cooled by liquid nitrogen in the range of 4000 to 620 cm^{-1} with 32 co-added scans and a resolution of 4 cm^{-1}. Prior to measurement the flully layer sampled was grounded in an agate mortar and placed in five wells of a 96-well plate. Each well was measured four times during the automated process.

MP analysis

To analyse for microplastics 500 mg of fluffy layer (six stations + procedural blank) were treated using Fenton's reagent according to literature (Leistenschneider et al., 2024) using syringes instead of an automated system. Afterwards, the sample was remobilized in a saturated NaBr (ρ=1.54 g/cm³) solution and given into a separation funnel for density separation following the approach of Leistenschneider et al., 2024. Analysis for MP was performed using focal plane array (FPA) based Fourier transform Infrared (FTIR) microscopy. Therefore, the samples were concentrated onto Anodisc filters (Anodisc, Ø 25 mm; 0.2 µm pore size, Whatman, UK), dried for 48h hours in a desiccator rack and placed on a BaF_2 window for measurement. The measurement was performed according to literature (Leistenschneider et al., 2024) and the measured data analysed using siMPle (Primpke et al., 2020) and the database of Roscher et al., 2022.

RESULTS AND DISCUSSION

While the concentrations of DDE (Figure 1D) as a representative of the pesticides are below 25 ppb, concentrations of nine dominant PAHs (Figure 1B) were up to 3000 ppb. The sum of the six BTEX (Figure 1C) reached up to 6400 ppb.

Figure 2 depicts the results of the first series of complementary analysis for organic matter composition using IR measurements, microplastics and micro pollutant concentrations.

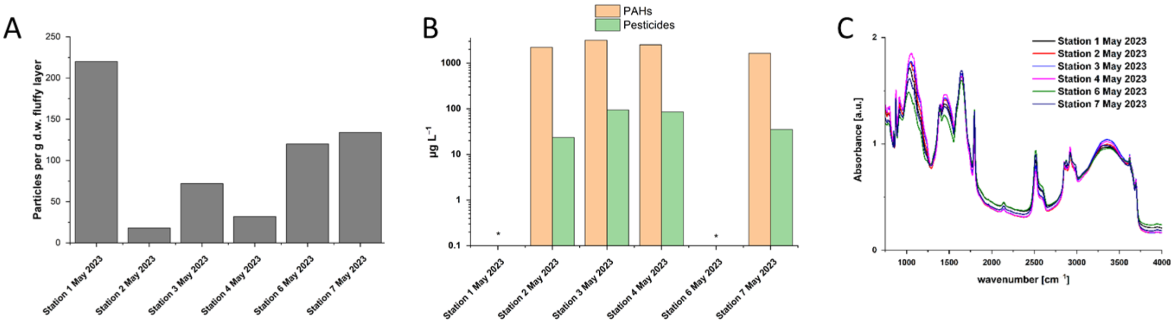

Figure 2: Overview on the blank corrected concentration of microplastics (A,), micro pollutants (B) and infra-red analysis results (C) for organic matter determination of the fully layer for sediments samples with the brass sediment corer on May 31 2023.

The first analysis of the Fluffy layer showed the presence of microplastics (Figure 2A) in the fully layer together with micropollutants (Figure 2B).Though relative to the bulk number of particles in the sediment, microplastics number is low, a high affinity of hydrophobic pollutants was shown to these particles (van der Hal et al. 2020). Due to the low number of samples analysed for microplastics a current trend or correlation between the concentrations could not be determined yet. Here, it was found that the performed analytical procedure needs to be optimized for a more rapid handling of the high number of samples and the comparably low amount of sample. This process is currently still ongoing.

CONCLUSIONS

The first joined analysis results of this study indicate that microplastics and micropollutants are present in the same samples. Still, due to the limited amount of data currently available any investigations regarding links between the particle identities, micro pollutants found and the organic matter of the fluffy layer are still ongoing to determine hotspot areas.

ACKNOWLEDGEMENT

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DEFEAT-PFAS: Detection, Quantification, and Treatment of Per- and Polyfluoroalkyl Substances (PFAS) in Groundwater

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ABSTRACT

The research project focuses on tackling the detection, measurement, and elimination of per- and polyfluoroalkyl substances (PFAS) from polluted groundwater, with a particular emphasis on addressing short (C4-C7) and ultrashort (C1-C3) chain PFAS. Given the widespread use of PFAS in various products, they are commonly found in groundwater near industrial and military sites in Germany and Israel. Moreover, recent regulations limiting the use of long chain PFAS have led industries to shift towards shorter chain alternatives. Hence, our efforts are geared towards refining detection, quantification, and removal methods for short and ultrashort chain PFAS. In terms of detection, ww are developing passive sampling devices capable of collecting and tracking the temporal distribution of PFAS species in groundwater. This will enable us to analyze contaminations in German and Israeli groundwater using cutting-edge analytical techniques. Additionally, contaminated groundwater will undergo a two-stage treatment process aimed at concentrating the relatively low PFAS concentrations using innovative membrane technologies such as closed-circuit reverse osmosis and mixed matrix composite nanofiltration membrane adsorbers. Subsequently, the streams containing higher PFAS concentrations will be treated through coagulation, with the remaining PFAS being adsorbed onto carbonaceous nanomaterials. The outcome of this research will include the creation of advanced tools for detecting, measuring, and eliminating PFAS from polluted groundwater, while also enhancing our understanding of the scope of these contaminations.

KEYWORDS

Closed-circuit reverse osmosis, mixed matrix composite nanofiltration membranes, adsorption, carbonaceous nanomaterials, emerging pollutants, passive sampling

INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are a diverse group of organofluorine surfactants found in many consumer products, including non-stick cookware, fast-food packaging, and water-repellent clothing. These compounds, which can be anionic, cationic, or zwitterionic, have been linked to various health issues such as immune and thyroid dysfunction, liver damage, disruptions in lipid and insulin levels, kidney problems, reproductive and developmental harm, and potential carcinogenic effects.

Due to these adverse effects, regulations have curtailed the use of long chain (≥C8) PFAS, pushing industries to adopt shorter chain (C_4-C_7) and ultrashort chain (C_1-C_3) alternatives (Neuwald et al. 2022). However, the high polarity, water solubility, and persistence of ultrashort-chain PFAS lead to their accumulation in the environment, particularly in water bodies, posing risks to aquatic life and increasing human exposure via drinking water.

In regions like Europe, the US, Germany, and Israel, PFAS contamination in groundwater has been detected. This study focuses on developing methods for the detection, quantification, concentration, and removal of PFAS from contaminated groundwater, as illustrated in Figure 1 of our proposed treatment approach.

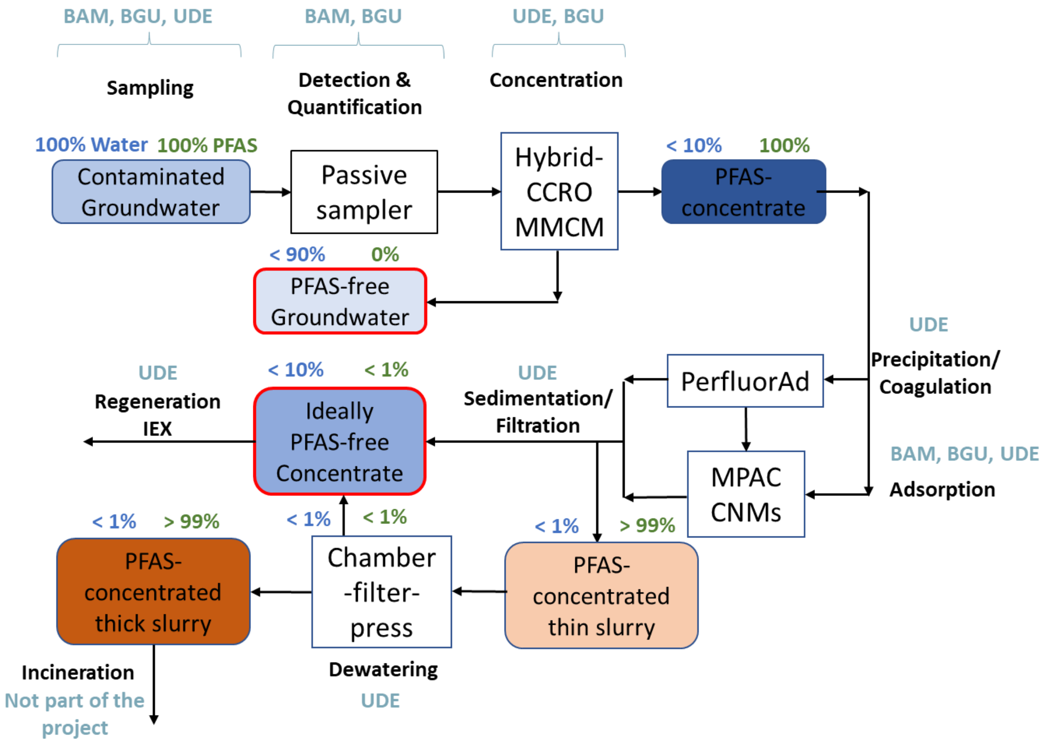

Figure 1: Schematic presentation of the treatment train in the project. The blue numbers show the water volume flow, and the green numbers show the PFAS pathway. Acronyms include hybrid closed-circuit reverse osmosis (CCRO), mixed matrix composite nanofiltration membranes (MMCM), carbonaceous nanomaterials (CNMs), and magnetically separable powdered activated carbon (PAC).

RESEARCH AIMS

Our project seeks to enhance our understanding of how to detect, measure, and remove PFAS from groundwater, with a focus on both short (C_4-C_7) and ultrashort (C_1-C_3) chain PFAS. These efforts include using innovative materials not only for coagulating and adsorbing PFAS in drinking water treatment processes but also for creating selective solid-phase extraction methods for analytical purposes and designing effective passive samplers. Our strategy involves evaluating various technologies to concentrate PFAS-contaminated groundwater and remove PFAS through coagulation and adsorption techniques. We have outlined the following specific objectives:

Aim 1: Develop and characterize new sampling and analytical methods to detect and analyze ultrashort- and short-chain PFAS in groundwater, enhancing accuracy and efficiency.

Aim 2: Advance and refine membrane processes designed for effective PFAS rejection and producing PFAS-free water, focusing on integrating hybrid closed-circuit reverse osmosis (CCRO) and mixed matrix composite nanofiltration membranes (MMCM).

Aim 3: Innovate and evaluate PFAS removal techniques using novel coagulation and adsorption processes incorporating carbonaceous nanomaterials (CNMs) and magnetically separable PAC, aiming for high efficiency and easy recovery.

RESULTS AND DISCUSSION:

For Aim 1, the project successfully developed gas chromatography-mass spectrometry (GC-MS)-based methods to directly analyze (ultra) short chain PFAS in water samples. Given the volatility of these compounds, headspace techniques are employed to capture and inject the gas phase above the water sample. The process involves heating the sample, and in the case of perfluorocarboxyl acids (PFCAs), simultaneous methylation occurs to ensure the PFAS are efficiently volatilized into the gas phase without loss. Figure 2 illustrates a GC chromatogram displaying the separation profiles for various PFCAs and fluorotelomer alcohols (FTOHs).

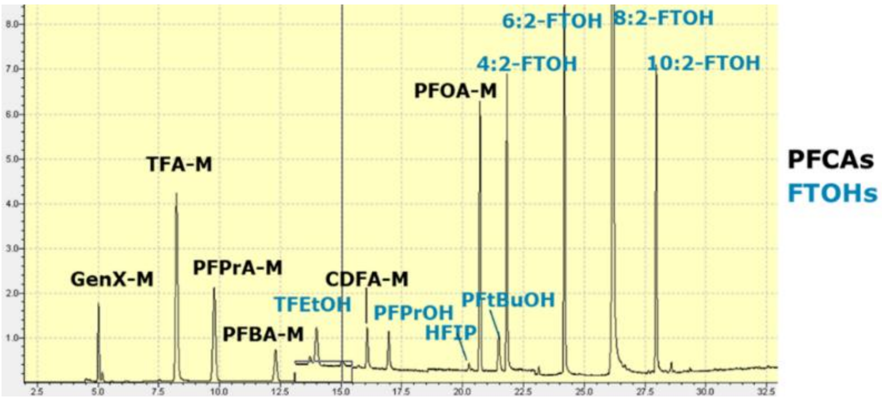

Figure 2. GC-MS chromatogram from a standard mixture of various (ultra-)short PFCAs and various FTOHs; -M = methylated form of PFAS

For Aim 2, MMCM comprising a thin multilayer polyelectrolyte film deposited on thick (~400 µm) polyethersulfone supports incorporating β-cyclodextrin microparticles were prepared. These membranes achieved near complete removal (>99.9%) of model PFAS (perfluorooctanoic acid) for significantly longer filtration times (Figure 3). The exhausted MMCM was regenerated using ethanol, showing consistent performances in three filtration cycles. Perfluorooctanoic acid (PFOA) was concentrated ~38-fold in the ethanol eluent (Chaudhary et al. 2023).

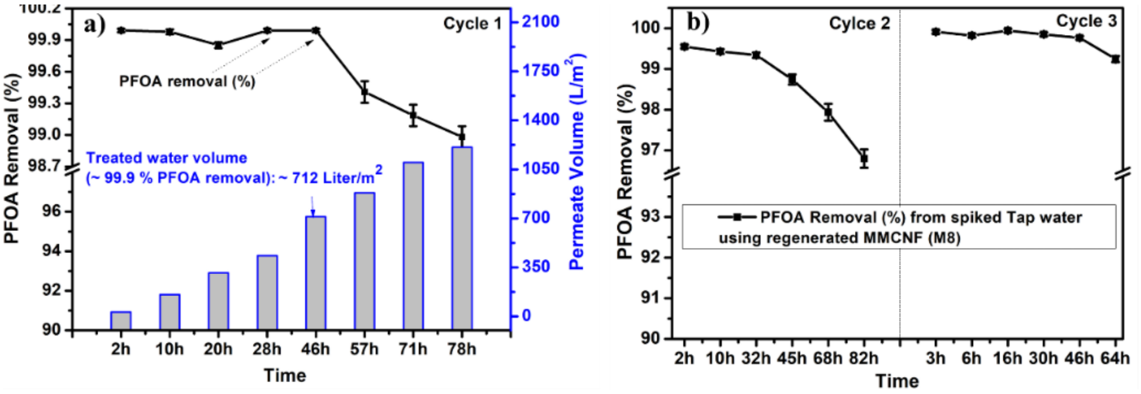

Figure 3. (a) Permeate volume and PFOA retention during spiked tap water experiment (cycle 1), (b) two additional consecutive cycles after regeneration. Feed PFOA concentrations during cycle 1, cycle 2, and cycle 3 were 540, 334, and 344 µg L^{-1}, respectively. During cycle 1, the treated volume was estimated based on the average flux of 15.4 Lm^{-2}h^{-1}.

Additionally, the feed water for the hybrid closed circuit reverse osmosis (CCRO) system underwent pre-treatment using ion exchange (IEX) to remove key scaling-forming ions, such as calcium (Ca^{2+}), to enhance the overall recovery efficiency of the RO process. The effectiveness of using a cation exchanger to soften the water was initially explored through simulations. These simulations involved calculating the saturation index for calcite, a primary scaling agent, based on varying recovery rates or concentration factors. The findings indicated that the relatively low concentration of Ca^{2+} in the raw water, combined with a pre-treatment strategy that treated only 50% of the inflow using a weakly acidic cation exchanger (WAC), enabled the water to be safely concentrated by a factor of up to 10.

For Aim 3, pristine and modified carbon nanotubes (CNTs, CNTs-F, and CNTs-NH_2) were evaluated for PFOA and perfluorobutanoic acid (PFBA) adsorption. CNTs modified with fluorine (-F) groups exhibited the highest adsorption capacity (5902 µg/g) for PFOA, while for PFBA, the highest adsorption capacity was attained with CNTs modified with amin (-NH_2) functional groups (1312 µg/g) resulting from hydrophobic and fluorophilic interaction for PFOA and elevated surface charge and electrostatic interactions for PFBA. Next, the CNTs were used to fabricate porous electrodes by pressure deposition on a porous polymeric support. The electrodes were characterized by cyclic voltammetry, which shows they are conducting and electroactive. Electro-adsorption of PFBA was evaluated at a range of external potentials, revealing that at 0.75V, PFBA exhibited the highest adsorption capacity on CNTs-F (4344 µg/g). Conversely, the highest adsorption capacity for PFBA on CNTs-NH2 occurred at 1 V (2888 µg/g). Both results indicate that electrostatic interactions govern PFBA adsorption.

CONCLUSIONS AND OUTLOOK

The DEFEAT-PFAS project develops selective passive samplers based on CNTs for (ultra)short PFAS and integrates the GC-MS with a headspace setup to quantify ultrashort chain PFCAs and FTOHs in water samples directly. Regarding adsorption enhancements, amine and fluorine-modified CNTs have improved the specific adsorption rates for short and long-chain PFAS, such as PFBA and PFOA. This improvement is attributed to the fluorophilicity of CNT-F adsorbers and the positive charge of CNT-NH2. Additionally, mixed matrix composite membranes have proven highly effective in removing various PFAS types from synthetic and real tap water. Moreover, simulations have shown that employing a weakly acidic cation exchanger for partial pre-treatment can effectively double the concentration factor in the CCRO process. Finally, magnetically separable powdered activated carbon and the coagulant PerfluorAd will be employed to treat the concentrate.

ACKNOWLEDGEMENT

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Projects Started in 2023

PEC-NF: Polyelectrolyte-Complex Nanofiltration: Optimal and Tunable Membrane Solution for Treatment and Reuse of Urban and Industrial Waste Water

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ABSTRACT

In the frame of the “PEC-NF” project, novel membranes for nanofiltration (NF) will be developed, that can be utilized for the tertiary treatment of wastewater (for purification and reuse). The thin-film composite membranes have a separation layer from a polyelectrolyte complex (PEC) on a suited porous ultrafiltration membrane as support. It consists of charged polymers (polyanions and polycations, amphiphilic ionomers or water-soluble polyelectrolytes) and can in the PEC be adjusted so that it is electrically neutral and provides efficient rejection of organic micropollutants (OMP). Furthermore, the PEC membranes can be designed to be more hydrophilic and chemically more robust compared to established polyamide NF membranes. A platform will be established that comprises the combination of materials (commercial ionomers, polyelectrolytes and PECs accessible therefrom) and fabrication methods (coating of suited support membranes) for PEC-NF membranes. The performance of the PEC NF membranes as novel, promising alternative for removal of OMPs from wastewaters will be investigated in detail, and the membranes will be adapted to specific separation problems. In cooperation with the partners from academia, the project partner from industry will transfer and upscale most promising PEC-NF formulations and coating methods to tubular membranes, a format, that has high potential for the treatment of complicated specialized industrial wastewater streams, in order to enable an industrial utilization. The application potential of the novel membranes that are developed in „PEC-NF“ will finally be evaluated in the treatment of real wastewater streams.

KEYWORDS

Nanofiltration, thin-film composite membranes, polyelectrolytes, ionomers, polyelectrolyte complex, selectivity, organic micropollutants

INTRODUCTION

Nanofiltration (NF) membrane technology offers a vast range of solutions for water treatment [1]. Most of today’s NF membranes are thin-film composites [1], produced by interfacial polymerization of a polyamide top layer [2] or, less commonly, by coating with a negatively charged sulfonated polysulfone top layer [3]. Recently, polyelectrolyte complexes (PEC) prepared, e.g., by layer-by-layer (LbL) technique, and combining two oppositely charged polyelectrolytes emerged as an attractive and scalable alternative [4]. However, this technique demands a tedious multi-step coating process and the films held by reversible ionic bonds may be prone to destabilization at high salt concentrations and extreme pH. In previous work, we reported a conceptually different approach to preparation of PEC NF membranes using a reasonably simple and scalable two-step coating of two polyelectrolytes of opposite charge [5,6]. In this process, the overall thickness is controlled by the first coated layer of an amphiphilic polyelectrolyte, the ionomer Nafion, while the second coating with a water-soluble amino-functional polycation, polyvinylamine (PVAm), and subsequent drying produce a PEC of a tunable charge. A single step coating with cross-linking of anionic polystyrene sulfonate particles and cationic polyethyleneimine was also established, but the overall separation performance of these PCE-NF membranes was not yet competitive [7].

The aim of this project is to adapt and necessarily modify novel PEC membranes for nanofiltration that can be utilized for the tertiary treatment of wastewater (for purification and reuse) and have a high rejection for organic micropollutants (OMP). A platform shall be established that comprises the combination of materials (commercial ionomers, polyelectrolytes and PECs accessible therefrom) and fabrication methods (coating of suited support membranes) for PEC-NF membranes. In cooperation with the project partner from industry, the transfer and upscale of the most promising PEC-NF formulations and coating methods to tubular membranes will be performed. In this paper, we report on results obtained in the first phase of the project that had started in fall 2023.

RESULTS AND DISCUSSION

In our previous project, commercially established membranes, either base membranes for the fabrication of the PA TFC membranes or ultrafiltration membranes, had been used for the coating with the PEC layer [5-7]. However, this has also caused complications due to non-ideal wetting by the coating solution or delamination of the barrier film because of insufficient adhesion / lamination strength as well as loss of permeance because of susceptibility of the support membrane to used solvents or cross-linking and drying conditions applied during the coating with the barrier film.

Therefore, we started in the “PEC-NF” project by adopting knowledge from literature and we fabricated - first in lab, then in pilot scale – porous polymer membranes that can be tailored as supports for PEC-NF membranes and that are compatible with all relevant coating conditions.

One support membrane is fabricated from polyacrylonitrile (PAN) and then aminated on the surface (“aPAN”) to yield cationic groups [8], that facilitate the lamination of anionic ionomers or polyelectrolytes. The other support membrane is fabricated from a blend of polyethersulfone (PES) and sulfonated PES, so that it has anionic groups on the surface [9] that are in this project expected to facilitate the lamination of cationic ionomers or polyelectrolytes. This sulfonated PES membrane (“sPES”) will later in the project also be fabricated as tubular membrane to be utilized as porous support in the scale-up of promising PEC-NF membranes.

Dip-coating using the solution of a polymer is a method to fabricate films on supports with thicknesses of less than 1 µm. Based on method development in a previous project, a thin-film composite membrane with the commercial anionic ionomer Nexar as barrier layer was fabricated using the aPAN membrane as support (see Figure 1). The thickness of the barrier layer was about 600 nm, and stability of the membrane indicated that the lamination to the porous support membrane was effective. The rejection of polyethylene glycol of 600 g/mol indicated that the membrane is in the NF range, the data for rejection of different salt are as expected for a membrane with a significant contribution of Donnan exclusion (here by negatively charged fixed ions in the barrier layer). Permeance is relatively low, in particular in relation to the rejection values. This will now be increased by reducing the barrier film thickness.

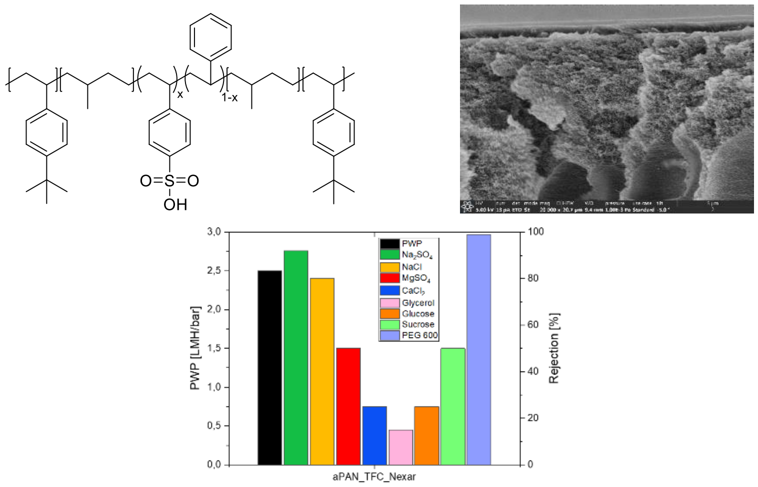

Figure 1: a) Chemical structure of Nexar, b) SEM image of the cross-section, c) pure water permeance (PWP) and solute rejection, both for a first Nexar aPAN composite membrane.

Recently, the differences in rejection mechanisms for salts and for OMPs were analyzed theoretically, which indicated that PECs with high content of ionic groups or intrinsic ion-pairs can potentially produce a significant selectivity [10], e.g., as desired for tertiary wastewater treatment. However, recent reports on LbL-based NF membranes indicate that OMP/salt selectivity strongly vary between specific positively and negatively charged groups of the polyelectrolyte/ionomer [11]. Therefore, we continue to exploit the Nafion-polyamine PEC system [5,6] to better understand the relation between the preparation and the performance, in particular, selectivity towards OMPs versus salts. To clarify the effect of PEC charge, the trend of rejection of ions and different OMPs, a series of Nafion-PVAm membranes was prepared with the degree of Nafion neutralization varied via PVAm concentration in the second dip-coating solution (0.5, 2 and 5 g/L), following established protocol [5,6] (see Figure 2).

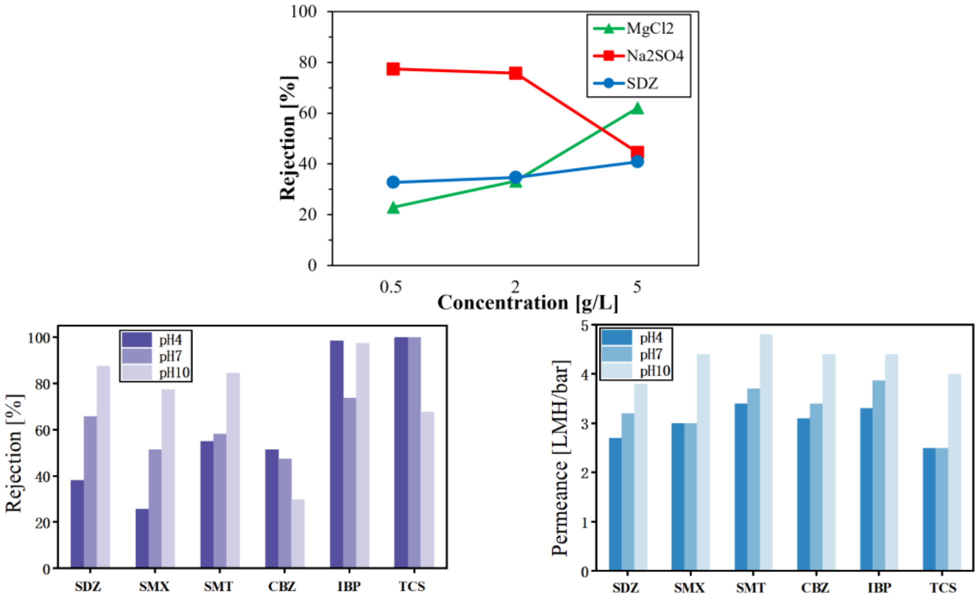

Figure 2: a) Rejection of sulfadiazine (SDZ) and salts by Nafion-PVAm PEC membranes of nominal thickness of 155 nm prepared using different PVAm concentrations in the second coating. b) Rejection of different OMP by Nafion-PVAm membranes at different pH; sulfadiazine, sulfomethoxazole (SMX) and sulfamethazine (SMT) are hydrophilic and negatively charged at higher

pH, carbamazepine (CBZ) is hydrophilic and neutral, ibuprofen (IBP) and triclosan (TCS) are hydrophobic. c) Water permeance measured for respective OMP solutions and pH.

Figure 2a compares variation of representative salts and SDZ, a model OMP that is negatively charged at pH 7 ($pK_a = 6.5$). The results are consistent with PEC charge changing form negative to positive with increasing PAVm concentration. Although the salt and OMP rejections are still comparable, this demonstrates that varying the PEC charge balance can tune salt/OMP selectivity. Figure 2b and c also shows the effect of varying pH, as another way of controlling the charge of both PEC and OMPs, which may also tune OMP rejection and, to a lesser degree, permeability that correlates with membrane swelling that in turn correlates with unbalanced polymer charge. The results also show that PEC membrane more strongly rejects hydrophobic neutral OMPs (IBP and TCS), compared with the other, more hydrophilic and charged OMPs. This trend is opposite of that displayed for NF270, a conventional polyamide NF membrane (not shown), indicating that the two types of NF may offer complementary choices for rejecting different groups of OMPs.

CONCLUSIONS

First results of the “PEC-NF” project show that the Nafion-PVAm PEC NF membranes can be further developed toward tunable and high rejection of organic micropollutants. The insights gained for this system will also be utilized for the development of PEC NF membranes using non-fluorinated ionomers as building block. The development of porous support membranes that are compatible with the coating of PEC layers will be the basis to obtain stable membranes with high separation performance. The feasibility to use a non-fluorinated ionomer for fabrication of PEC NF membranes has already been demonstrated.

ACKNOWLEDGEMENTS

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DASAM: Data-Driven Sewer Asset Management in Germany and Israel

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ABSTRACT

Sewer networks represent an enormous investment in physical assets for a city. In many cities worldwide, the underground infrastructure is nearing the end of its technical lifetime and will soon reach the age of renewal. This requires large investments, for which municipalities often lack the financial resources. This investment gap results in degrading water and drainage services, escalating flood risk, increasing environmental impacts, and raising expenditures for emergency repairs. Municipalities must develop cost-effective approaches for managing their assets due to tight financial constraints. Within this context, DASAM ambitions to develop new approaches for asset management of sewer infrastructure by harnessing the potential of 1) the growing availability of system-wide CCTV data and geographic information systems, 2) the uptake of automatic defect detection from inspection data with AI and 3) recent innovations in artificial intelligence algorithms. Solutions will be fully implemented and demonstrated in large German (Berlin) and Israeli (Netanya and Maayanot HaSharon) cities. Finally, the scientific assessment of the operational and strategic benefits provided by DASAM innovations is expected to increase the confidence of utilities for data-driven asset management and foster the large-scale market uptake of smart solutions in Germany, Israel, and beyond.

KEYWORDS

Sewer, asset management; machine learning; monitoring; condition assessment

INTRODUCTION

Sewer asset management

CCTV has been applied since the 1980's as industry standard for sewer system inspection and remains the main source of information for planning rehabilitation needs. It provides visual data (images or videos) of the internal surface of the inspected sewers. Pipe defects recorded during CCTV inspections are manually or automatically coded according to standard coding systems (e.g. EN 13508-2) and the overall sewer condition is assessed using an automatic classification methodology (e.g. DWA 149-3). Sewer deterioration models traditionally use sewer condition data to infer the current and future condition of sewers based on influencing factors in the form of exogenous variables (Tscheikner-Gratl *et al.*, 2019). Those exogenous variables include (but are not limited to) factors that influence deterioration processes, such as the pipe's diameter, material, shape, construction age, surrounding soil conditions, or sewerage type (e.g., stormwater, wastewater, or combined sewer). Modelling outcomes can support utilities in 1) developing short-term inspection and rehabilitation programs by estimating the current structural condition of all sewers in the network and 2) planning long-term investment needs by forecasting the future condition of the network. Thanks to the growing data availability (In

Germany and in Israel, local regulations commit sewer operators to inspect their network regularly), a new generation of projects has been exploring the potential of machine learning in asset management. OZEK (2005-2009, DBU), AUZUKA (2016-2020, BMBF) and KIKI (2021-2023, BMBF) developed software for automated damage detection to enrich current inspection methods. Companies like E.sic and startups like Pallon are currently proposing cloud-based algorithms for automatic defect assessment, and large German utilities are accelerating the uptake of artificial intelligence (AI) to rationalize the condition assessment procedure. Within this context, KWB has developed the software SEMAplus together with Berliner Wasserbetriebe to support sewer inspection planning and long-term rehabilitation planning.

Software for data-driven asset management

SEMAplus is a modelling software which predicts the structural condition of uninspected sewer sections and the future development of the network condition. It is composed of two main modules, the SEMAplus pipe simulator and the SEMAplus strategy simulator. The pipe simulator uses a tree-based machine learning (ML) model and available data on sewer condition, sewer characteristics and relevant environmental factors to determine the current structural condition of each sewer pipe. The result is a ranked list of all inspected and uninspected pipes, sorted by their immediate need for rehabilitation. The strategy simulator is based on a statistical aging model and provides long-term predictions of the condition of the sewer network, considering different investment scenarios. The sewer aging model integrates different rehabilitation methods to simulate the effect of repairs, pipe lining or renewal on the structural condition.

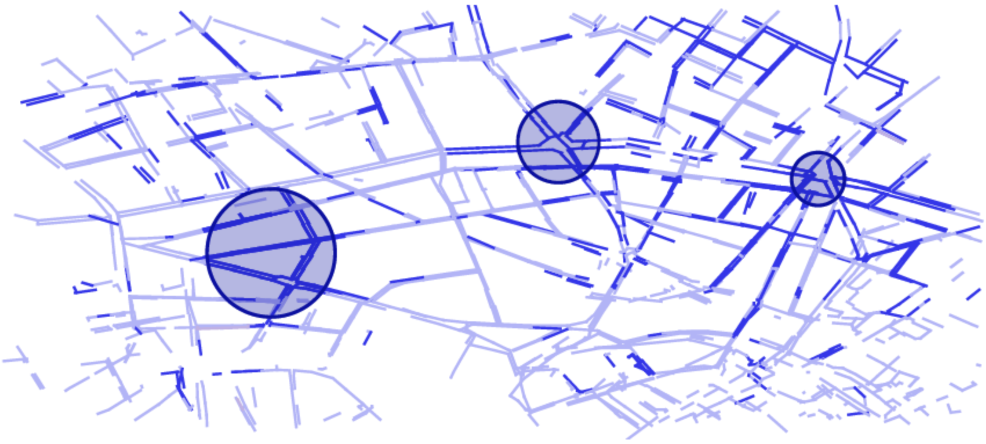

Figure 1: The pipe simulator enables sewer inspections to focus on pipes in urgent need of rehabilitation, and can be used as evidence to negotiate rehabilitation priorities at the city level, along with other critical infrastructures.

In a push to make smarter investments, the industry is accelerating the adoption of digital solutions to improve and optimize their strategic and operational planning capabilities (Stein *et al.*, 2022). Over the past two decades, researchers started to utilize new data from sparsely available visual inspections (CCTV) and built data-driven modelling solutions to improve future pipe assessment and rehabilitation strategies. Nevertheless, most of these models remain in the academic field and failed to support effectively utility investment planning. Main factors hampering their uptake were the lack of data availability, deficient data quality and the poor accuracy of statistical models. Recent progress in digital water are now paving the way for a much deeper digital transformation.

OBJECTIVE

DASAM develops new approaches for asset management of sewer infrastructure by harnessing the potential of the growing availability of system-wide CCTV data and geographic information systems, the uptake of automatic defect detection with AI and recent innovations in AI algorithms. Asset management is undergoing major transformations over the last 20 years toward an age of full knowledge of the system, where each single pipe has been inspected or monitored at least once in its lifetime. This knowledge opens up novel insights into the mechanisms of pipe aging and promising pathways to generate new insights on physics through mathematical modeling. Nevertheless, this massive increase of data availability hides large disparities between utilities and countries in terms of quantity (incompleteness) and quality (uncertainty) that need to be addressed by future data-driven solutions.

Within this context, the recently started DASAM project (2023-2026) will transfer novel advancements in artificial intelligence in the water asset management domain and integrate environmental assessment into the asset management decision making process. Solutions will be co-created by a multidisciplinary consortium composed of German and Israeli scientific partners, industry and end users from the water and digital sectors. SEMAplus will be fully implemented and demonstrated in large German (Berlin) and Israeli (Netanya and Kfar Yona) demonstration sites reflecting the diversity of both countries' urbanization, networks, topography, climate and digital transformation. Innovations will be incorporated into the software and methods will be published in open access for the benefit of the industry and the research community. The next section present DASAM’s activities structured around the specific objectives.

METHODOLOGY

SO1 Unlock the full value of available inspection data to simulate asset management strategies

Data from Germany and Israel will be used to **assess the transferability of deterioration models** in a variety of geographic contexts as well as the **added value** for the operational teams (e.g., time and OPEX saved to identify sewer in poor condition with inspection programs) and strategic departments of the utilities (e.g., optimization potential for annual investments). Furthermore, the presence of ubiquitous pipe defect data (i.e., CCTV inspections of each pipe) and data on multiple inspections allows to **integrate previous defects** into deterioration modeling. The main innovation resides in the integration of the observed single defects (e.g. cracks) and their evolution over time (from multiple inspections) at the core of deterioration modeling.

SO2 Going further – building on most recent advancements in machine learning

DASAM will enhance the architecture of existing deterioration models by utilizing novel machine learning techniques. Aim are (1) to cope with missing or inaccurate data, (2) improve the accuracy of machine learning approaches by considering the right-censoring nature of CCTV data and (3) enhance the generalizability and transferability of modeling approaches across networks and cities. **Graph Neural Networks (GNNs)** from the field of geometric deep learning will be utilized to impute missing information on pipe properties and inspections. This can tremendously improve datasets with imperfect or missing information on both, pipe properties and inspection data, and will enhance the transferability of the models for systems where only few inspection data exist. **Random survival forests (RSF)** will be used to improve condition modeling by integrating aging processes in the form of survival curves in the models, and hence, bridge the gap between statistical and machine learning models. **Educated machines** coupled with mathematical and physical models will be used to alleviate the need for massive amount of data and to increase the generalizability and transferability of the solutions found here. The integration of RSF into an educated machine framework is expected to account for both spatial and temporal network characteristics, which potentially results in better inference than the state-of-the-art of the structural health of the various sewage network elements (Kendler et al., 2022).

SO3 Include environmental impact assessment into the decision-making process

The objective is to introduce new decision criteria into strategic planning that takes the environmental impact of pipe rehabilitation actions into account. More precisely, DASAM will develop specific life-cycle based CO2e-factors for standard pipe rehabilitation measures. This includes 1) identifying decisive factors for CO2e footprints and group rehabilitation measures accordingly (e.g. open/closed construction, in-liners, depth of sewer, pipe material, …) and 2) integrating CO2e factors into SEMAplus engine and dashboards for calculating embodied carbon of asset management strategies. Finally, DASAM will evaluate the sensitivity of a range of rehabilitation strategies and develop recommendations for a low-impact asset management of water utilities.

SO4 Create a long-term living community of users of data-driven asset management solutions

This objective focuses on strengthening bilateral cooperation in the water sector between Germany and Israel. It includes the creation of a DASAM community with participants in Europe and the Middle East. DASAM will create a platform for exchanging user experiences with data-driven asset management. Utilities will be able to share experiences, tips and best practices on the use of the developed data-driven asset management tools. The community will also allow utilities to exchange on the use of data-driven tools to efficiently support their asset management practices and address common issues of interest (e.g. such as how to communicate technical results with decision makers and stakeholders? How to consider uncertainties in the decision-making process? How to balance operational costs and investments?). Finally, this platform will create a fertile environment for technical exchange between German and Israeli utilities and the scientific community, where innovators and researchers can provide support and assistance on mutual issues. The Israeli Governmental Authority for Water and Sewage will support the establishment of the community by empowering the dissemination of the findings among practitioners.

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The authors are responsible for the content of this publication.

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PFASense: A Bio-Electrochemical Detection Array for PerfluoroAlkyl Acids

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ABSTRACT

Industrial pollutants, including perfluoroalkyl and polyfluoroalkyl substances (PFASs), pose serious health and environmental risks. Time-consuming and expensive traditional detection techniques, including liquid chromatography-mass spectrometry, impede prompt field examination. PFASense attempts to address this problem by the development of cost-effective, dependable, and sustainable electrochemical techniques for continuous PFAS evaluation in contaminated aquatic environments. The proposed approach combines a pretreatment phase employing nanofiltration membranes to remove interfering impurities, chemometric array-based analysis, as well as bacteria- and yeast-based whole cell biosensors. The sensors are examined in complex aqueous matrices, such as contaminated ground water, and mathematical models are employed for perfluorooctane sulfonic acid (PFOS) quantification. To date, we have demonstrated preliminary limits of PFOS detection in buffer of 151 ± 53 nM and 53.1 ± 19.0 nM, employing fluorinated and hydrophobic modified electrodes, respectively. We plan to eventually integrate the complementary PFASense technologies into a portable fluidic device for continuous PFAS monitoring.

KEYWORDS

Perfluoroalkyl and polyfluoroalkyl substances (PFAS) monitoring; electrochemical sensors; whole cell biosensors; intelligent multi-electrode arrays; nanofiltration; orthogonal multi-modal sensing.

INTRODUCTION

Per and poly fluoroalkyl compounds (PFAS) are widely used in products like water-repellent clothes, firefighting foams, non-stick cookware, and fast-food packaging, posing a major health risk due to their durable C-F bond and amphiphilic activity (O'Hagan, 2008). Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) are the most studied forms, with shorter chain counterparts like perfluorobutane sulfonate (PFBS), perfluorobutanoic acid (PFBA), and hexafluoropropylene oxide dimer acid. PFAS have harmful and long-lasting effects on the environment,

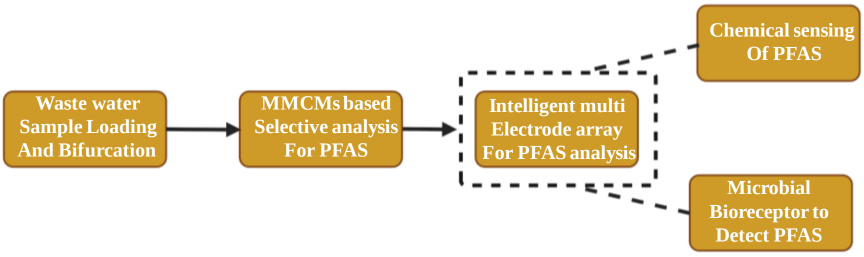

Figure 1. Scheme of the multi-sensors array for PFAAs analysis.

and can build up inside the human body, leading to increased cholesterol, diabetes, and kidney cancer. The U.S. Environmental Protection Agency recommends a 70 ppt concentration limit for PFOA and PFOS (PFAS Fact Sheets, 2024), but sensitivity and selectivity is needed for investigating them in various environmental matrices. Standard techniques exist for detecting PFAS, but they have deficiencies, require advanced instrumentation facilities, and are expensive and unsuccessful in determining PFAS at the earliest (Gremmel *et al.*, 2027).

The main PFASense objective is the development of a bio-electrochemical detection array for perfluoroalkyl acids. To achieve this ambitious aim, four research teams have joined forces: BGU (electrochemical array detection, Ben-Yoav), ZIWR (nano filtration and molecular imprinting, Ronen), HUJI (microbial bioreporters, Belkin) and BfG (yeast-based sensors, Buchinger). All components will be integrated in a microfluidic multi-array sensor device. The sensor-output will be used to train algorithms for an intelligent chemical analysis of perfluoroalkyl substances (PFAAs), focusing on interactions with different chain lengths, functionalities and biological activity. The envisaged device allows a portable cost-effective, dependable, and sustainable techniques for continuous PFAS evaluation in contaminated aquatic environments; pollution-impacted ground waters and industrial wastewaters will be tested.

METHODS

Mixed matrix composite ultrafiltration membrane fabrication

Mixed Matrix Composite Ultrafiltration Membranes (MMCM) consist of inorganic and organic fillers in a polymer matrix, merging high selectivity, desirable mechanical properties, and economic viability with high PFAS adsorption. While standalone sorption technologies often face challenges such as clogging and sorbent exhaustion by dissolved organics, integrating commercial sorbents (e.g., Dexsorb or carbon nanomaterials) into the porous support of an ultrafiltration (UF) membrane will allow capturing and concentrating PFAS from varying solutions while removing other contaminants (mainly organic matter) which could interfere with further analysis required. Following adsorption, the adsorbed PFAS will be released from the MMCM as concentrated solution using methanol/basic methanol and water or water. The concentrated solution will be further analysed by varying electrochemical/biological sensors.

For this task, we will (1) fabricate MMCM using solid fillers mixed into PES and cast as a thin, porous membrane. (2) PFAS (PFOS) adsorption will be evaluated for pristine MMCM and with varying loading percentages of fillers such as Dexsorb and functionalized CNTs (mainly CNTs with amine groups, according to preliminary data). The feed solution will include PFOS at concentrations typically found in contaminated industrial wastewater (100-1000 ppb) (3) we will assess the impact of organic matter and varying ions on the adsorption capacity of the MMCM, and (4) measure the ability and concentration factor of the MMCM to concentrate the PFAS in the feed solution.

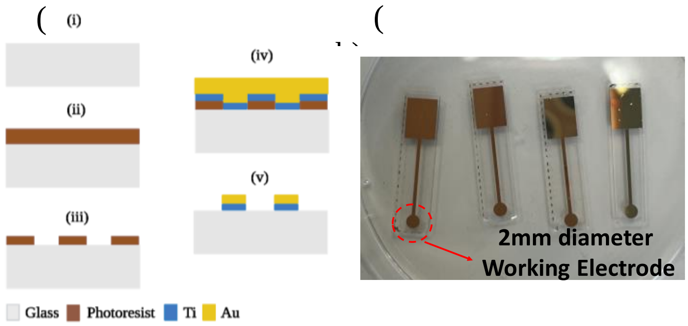

Figure 2: Fabrication of the macroelectrode system. (a) Fabrication process (b) Fabricated 2 mm gold electrode.

Electrochemical sensors

The team at BGU has developed an intelligent array of macrosystems modified with hydrophobic/fluorophilic materials for in-field detection of PFAS. The sensors were designed using computer-aided design software and conventional photolithography methods. The team (together with Prof. Mira Amiram’s group) modified elastin like peptides (ELPs) with hydrophobic and fluorine groups, anchored to gold surfaces, and activated with hydrogen peroxide and KOH. The platform was used for electrochemical selectivity testing of PFAS, and pretreatment membrane filtration will be integrated into a portable fluidic device for continuous monitoring.

Bacterial based sensors

The construction of whole cell sensors involves three basic components: the two DNA fragments acting as a sensing element and as a reporting system, and the host cell that harbors the plasmid-borne fusion of these two molecular entities. As the host bacterial strain, we employ *Escherichia coli*, which is not only highly amenable to molecular manipulations but has been repeatedly demonstrated as an extremely efficient host for diverse sensing constructs for multiple applications. As a reporting system the intensively studied *lacZ* gene is used, encoding the β-galactosidase enzyme, a highly versatile molecular reporter of gene activation. With the appropriate substrate (for example p-aminophenyl-β-D-galactopyranoside, PAPG), LacZ activity, induced by the target compound(s), generates an electrochemically active product (p-aminophenol), the concentration of which can be monitored by an electrode. To identify PFA-responsive gene promoters that will act as the sensing elements in the new PFAS bioreporters, cells are exposed to model PFAS compounds and responsive genes are identified using either an RNAseq approach or the exposure of a suitable promoter-reporter fusion library.

Yeast based sensors

The already described interference of PFAS with thyroid-signaling in human and wild-life can be associated with various adverse health outcomes such as metabolic syndrome and diabetes mellitus. Recently, a mammalian cell-based bioassay was proposed for the effect-based detection of PFAS via thyroid-signaling, based on the competitive binding of PFAS and T4 to the transport protein transthyretin, and subsequent effects on thyroid receptor activation following a reporter gene assay as described above for bacterial bioreporters. Such an approach opens the door for effect-based biosensors detecting this relevant mode of action; however, due to demanding conditions for cell culturing and a short shelf-life, mammalian cells are only of limited use for lab-independent biosensors. Therefore, we design, construct and test *S. cerevisiae*-based bioreporters with enhanced sensitivity, e.g. by increasing cell wall permeability by the deletion of genes encoding for cell wall proteins. As for the bacterial biosensor the actual measurement of the signal will be adapted from a colorimetric to a electrochemical detection by making use of PAPG.

RESULTS AND DISCUSSION

Development and characterization of array of electrodes for quantification of PFAS

CAD software was used to design photomasks for macro sensors, which will be deposited using standard photolithography techniques. Titanium is deposited for binding, followed by an Au layer using E-GUN VST. SU-8 negative photoresist will coat the chip, except for the electrode, which was modified with Elastin-like peptides. The modified electrodes were then assessed for their electrochemical activity using a potential window spanning from -0.2 to 0.65 V, at a scan rate of 100mV/s and characterized using optical microscopy and Contact angle measurement. The modification process was done in collaboration with Prof. Amiram's team, with the goal of enhancing the performance of the electrodes.

PFAS analysis with the modified electrodes

This work uses electrodes modified with ELPs of different hydrophobicities to examine the effect of PFOS concentration on electrochemical signals. The interaction of PFOS and ELPs on the Au surface is what drives the sensing mechanism. Peak currents drop with increasing PFOS content, according to cyclic voltammogram data, with immobilized electrodes ELPs-tFF and ELPs-pPr exhibiting a considerable decrease. The linear regression analysis exhibits good co-relation for the charge transfer resistance vs concentration. The Limit of detection for the fluorinated and hydrophobic ELPs- modified electrode towards PFOS detection are 151 ± 53 nM and 53.1 ± 19.1 nM respectively.

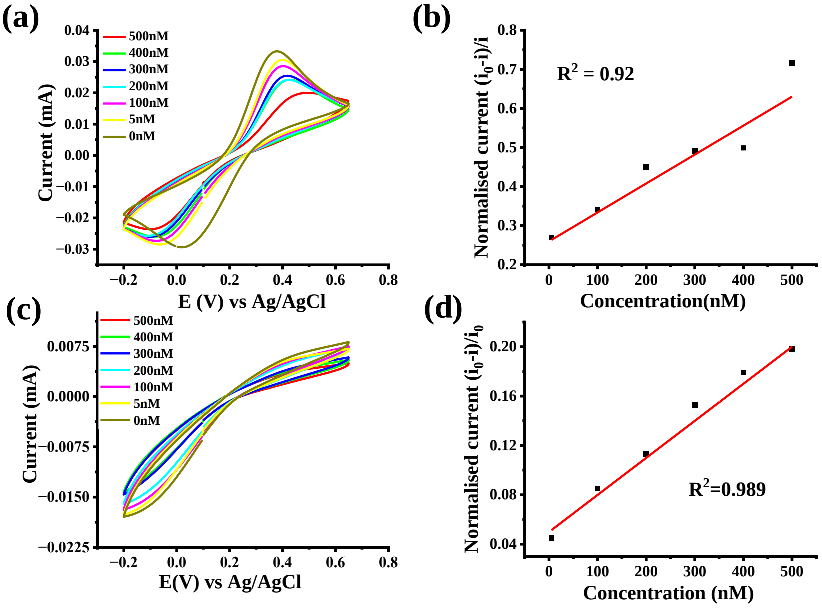

Figure 3: Cyclic Voltammetry was conducted on PFOS concentrations using ELPs integrated Au elec-trode, with CV graphs for fluorinated(a) and hydrophobic(c) electrodes, and linear regression curves for each electrode (b&d).

Bacterial based sensors

Current efforts focus on the identification of suitable PFAS-specific sensing elements. No reportable results are currently available.

Yeast based sensors

Currently we work on the adaption of electrochemical signal detection and the construction of enhanced sensor strains.

CONCLUSIONS TO DATE AND FUTURE PLANS

The study identifies PFOS using various ELP types and quantitatively analyzes PFOS. The electrochemical analysis of modified Au electrodes improves sensing capability, with hydrophobic ELPs showing an enhanced limit of detection of 53.1 ± 19.1 nM. Future research aims to incorporate yeast, bacterial, and electrochemical sensors to improve quantification and sensitivity.

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NEWR: Water Decontamination Through Sulfate-Radical Oxidation in a Nano-Enabled Catalytic Filtration Process for Non-Potable and Potable Water Reuse

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ABSTRACT

Potable and non-potable reuse of treated wastewater requires effective removal of chemical and microbial contamination. While these processes are generally resource-intensive and require advanced technology-using adequately treated wastewater is an economically and ecologically viable option in water-scarce regions. This project aims to develop a treatment concept alternative to conventional systems and subsequently upscale the design. A novel nano-enabled catalytic filtration process presents the core element applicable for non-potable and potable water reuse applications. Sulfate radicals are generated through the catalytic decomposition of peroxymonosulfate (PMS) via manganese oxide (MnO_2) based nanomaterials which oxidize the undesired contaminants in the water matrix. Integrating such nano-catalysts in reuse holds promise in the inactivation of pathogens, removal of various trace organic chemicals (TOrCs), and mitigating the spread of antibiotic microbial resistance (AMR) from municipal wastewater with high durability in long-term operation. By immobilizing the nanomaterial onto a granular media and packaging the resultant nanocomposite in a filtration unit, we allow efficient, sustainable, and practical use in reuse schemes at comparable costs to established processes. We hypothesize that through both material design and process engineering, optimal deployment of such nano-based technology can be utilized efficiently while avoiding the limitations of currently available technologies.

KEYWORDS

Water reuse; catalytic oxidation; water decontamination; trace organic chemicals; disinfection

SCIENTIFIC BACKGROUND

Treated wastewater effluents (WW) are a valuable source to augment future freshwater supplies (Friedler 2001). However, there is a need to develop new attenuation strategies for removing anti-microbial resistant pathogens and genes and chemicals from wastewater (Hiller et al. 2019). Oxidative processes applied in water reuse concepts include UV-based advanced oxidation processes (AOPs) and ozonation. AOPs involve the generation of reactive hydroxyl (•OH) radicals, which are often scavenged by non-targeted substances in WW, resulting in elevated radical- and energy demand. Application of sulfate-radical based oxidation can overcome limitations of traditional AOP technologies. Sulfate radicals may combine the advantages of both ozonation and AOPs with •OH radicals. Similar to ozone, sulfate radicals hold selectivity towards specific pollutants compared to the unselective OH radicals, and thus may be less prone to scavenging effects of the water matrix (Lee et al. 2020). Sulfate radicals can be generated *in-situ* through the activation of PMS or peroxydisulfate (PDS) by heat, photolysis, or catalytic reactions. Specifically, engineered nanomaterials—with unique properties that differ from their bulk counterparts, such as high reactivity, tunable surface properties, and tailored structure—may catalyze PMS activation, as we recently demonstrated (Yecheskel et al. 2024; Bein et al. 2023). In this project, we use a nano-enabled catalytic filtration process for efficient sulfate-radical oxidation using MnO_2 nanoparticles grown on activated carbon.

RESEARCH OBJECTIVES

The primary goal of this study is to develop an alternative treatment concept for non-potable and potable water reuse applications. Specific objectives include:

- Material design, characterization, and optimization of nano-based catalysts of MnO_2 grown onto an activated carbon (AC) platform.
- Evaluation and optimization of TOrCs elimination by the catalytic filtration process in a real WW matrix.
- Microbial and toxicological assessment of the final catalytic filtration process as integrated part of a water reuse concept
- Pilot-scale validation of water reuse during long-term operation in real-world conditions, Preliminary treatment (such as ultrafiltration) and post treatment (such as biofilter) will be integrated to optimize the entire advanced treatment scheme.
- Benchmarking of the optimized process against alternative oxidative processes

METHODOLOGY

The project's significant milestones began with Tel Aviv University synthesizing MnO_2 onto AC as a support material. The operational synthesis parameters are optimized for economic effectiveness (i.e., yield), catalytic performance, and scalability. Briefly, commercially available virgin granular ACs will be impregnated with MnO_2 using one-stage hydrothermal methods to form MnO_2@AC (Zucker et al. 2019; He et al. 2019). Precursors are dissolved in deionized water and heated in presence of AC to cause precipitation/coating. These nanocomposites are characterized (to assess properties such as crystallinity, morphology, and edge sites), and their activation of sulfate radicals is tested with PMS dosing.

Conversely, the Technical University of Munich focuses on engineering and optimizing the treatment process by designing a lab-scale, column-based filtration setup. The process is then optimized with regard to key operational parameters (i.e., empty bed contact time, PMS dosing and catalyst amount) before it is evaluated for a more extended operational period to study long-term stability and leaching. Parallel operation of multiple columns will allow to differentiate between adsorption and conversion, to identify the effect of different water matrices and to shed light on downstream biodegradability. This is followed by testing a feed water using secondary effluent from the Schweinfurt wastewater treatment plant, optimization of operational parameters; and reducing microbial counts in the effluent. It is then evaluated against existing treatment technologies available on-site.

The last component of the project is the design (scaling-up) and benchmarking of the catalytic filtration process in the Schweinfurt wastewater treatment plant. This system's process data and feasibility are compared against the existing pilot-scale ultrafiltration-ozone/biologically activated carbon (BAC) treatment system in the plant.

PRELIMINARY RESULTS

Synthesis and characteristics of MnO_2@AC

A literature survey was first conducted to map the work conducted on MnO_2 structures as catalysts. MnO_2 was shown to activate PMS for sulfate radical generation (Bein et al. 2023), and its phase was found to play a crucial role on its catalytic activity, influencing both the generation of sulfate radicals and the direct oxidation reactions with pollutants (Huang et al. 2019). Moreover, the growth of MnO_2 catalysts on substrates, such as AC and sand, has been reported (Fang et al. 2018).

The published synthesis protocol of MnO_2@sand was used as a starting point for the project. In parallel, two types of synthesis methods were tested to produce MnO_2: hydrothermal synthesis and wet synthesis in presence and absence of a platform. Preliminary results indicated challenges in achieving uniform MnO_2 coverage on AC substrates, possibly due to growth and deposition limitations (Figure 1). Consequently, various pretreatment techniques for AC grains were investigated to enhance MnO_2 deposition, such as sonication, H_2SO_4 soaking, UV/O exposure, etc. It should be noted that the formed MnO_2 layer had the desired α-MnO_2 phase (Figure 2).

As this project is in its initial phase, we are also developing methodological approaches which will be used for determination of the catalytic activity, stability, and yield. The MnO_2 coverage of the particles, for example, is examined qualitatively by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS), and quantitatively using inductively coupled plasma-mass spectroscopy (ICP-MS). The catalytic system tests will be conducted in a multi-channel system, as specified below.

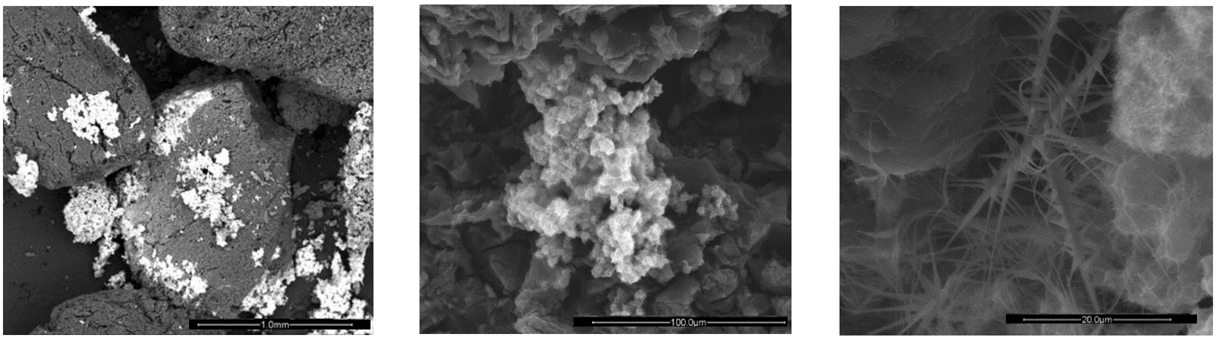

Figure 1: Scanning electron microscopy (SEM) micrographs of the synthesized MnO_2@AC. The bright areas represent the catalyst MnO_2 and the dark areas are the activated carbon (AC).

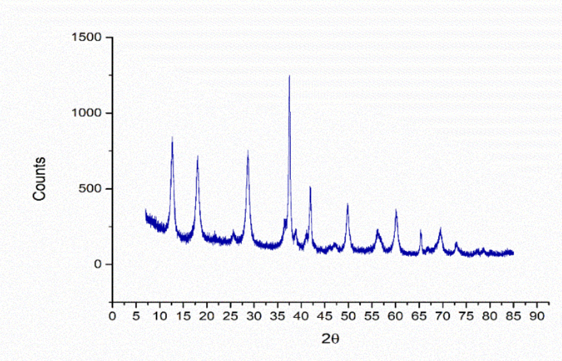

Figure 2: X-Ray Diffraction (XRD) pattern of the catalyst phase α-MnO_2

Design of lab-scale flow-through system

An experimental lab-scale flow-through system is designed with four stainless steel columns (bed volume of a few milliliters) as the focal point of the design to allow for parallel operation. Figure 3 below presents the preliminary layout of the setup. A multi-channel pump connects the columns to the feed tank with connections for in-line dosing of PMS. The setup allows for channel-dependent flow and dosing control. The columns (bottom-to-top operation) can be packed with different packing materials such as AC or sand with or without MnO_2 synthesized on its surface. These would then be filled in the columns and held in place using meshes and connectors. The feed solution consists of different water matrices spiked with known amounts of targeted TOrCs. The removal rate of the TOrCs is then determined and the effectiveness of the AC's adsorption and the sulfate radical oxidation are distinguished. The selection of target TOrCs will also provide insight into the reactive oxidant species. Other packaging material combinations (different substrates and synthesized catalysts) with various flowrates of PMS or feed can be tested accordingly.

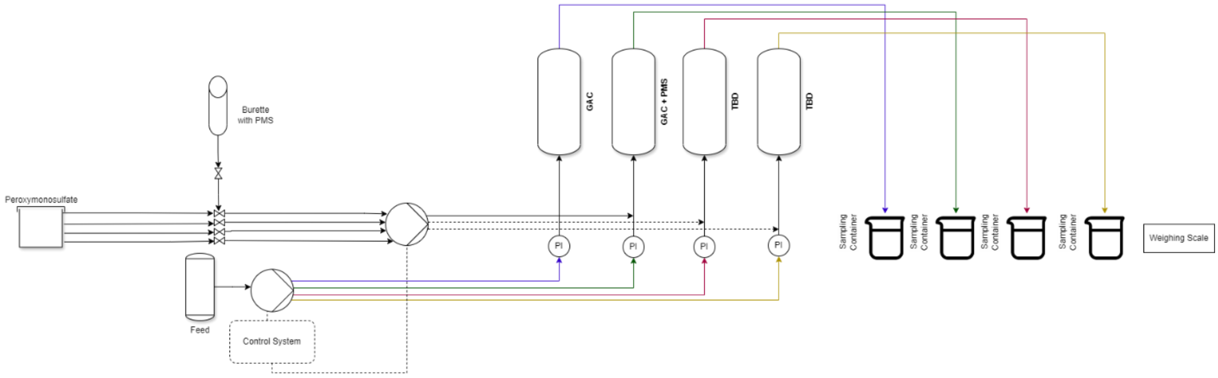

Figure 3: Lab-scale setup with multiple columns that can be operated in parallel. The columns are packed with catalytic material to allow for efficient elimination of TOrCs and microbial contaminants.

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Young Scientists Exchange Program (YSEP)

In order to encourage young scientists to participate in the Water Technology Research Program within the framework of the German-Israeli Cooperation, the BMBF and MOST have initiated a "Young Scientists Exchange Program" in 1999. More than 150 Young Scientists from both countries successfully completed their stay already.

Conditions

The program is open to Israeli and German diploma/M.Sc. students, post graduates, doctoral degree students, and post doctorates candidates who wish to spend a training period in Israel or Germany for up to 6 months, but not less than 1 month. Candidates are considered as "Young Scientist" if no more than 3 years have passed since receiving the PhD. Funding will be provided to cover all necessary expenses of the applicant's visit abroad (travel, accommodation, living expenses, extraordinary work expenses). In each case (Israeli scientist visiting Germany / German scientist visiting Israel) the grant will be transferred to the German cooperating institution. Therefore, the German institution has to direct the joint application to the Water Technology Project Agency of BMBF.

A work report has to be submitted latest two months after the end of the exchange period.

Allowance

Accommodation and living expenses (as lump sums):1.830 EURO for each month; 61 EURO for additional days as lump sums* Travel, extraordinary expenses: only on account

*) The lump sum includes the costs for additional insurances (health, accident, luggage, private liability) that shall be contracted by the candidates for the period of their stay abroad according to the agreement.

The full call text is available at: https://www.fona.de/en/measures/german_-israeli_cooperation_in_water_technology_research_copy.php

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