Mistra TerraClean
Annual Report 2023

MISTRA TERRACLEAN

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LETTER FROM THE BOARD CHAIR

In 2023, the Mistra TerraClean research programme was halfway into its second phase of financing. All work packages within the programme are now up to full speed, and it is a pleasure to follow the great work that is carried out.

During the year we have seen good progress with both important standardisation work, academic publications, and international conference attendance. I would also like to highlight that the results have led to a patent application.

The research work conducted regarding recovery of rare earth metals has continued and has been intensified. This is very positive, as this area is likely to in increase in importance in different parts of the society in the future.

The programme was granted access to the MAX IV facility in Lund in southern Sweden, which was important for the continuation of the programme. All of us in the Programme Board are looking forward to learning more about the results and findings from the use of MAX IV, when the huge amount of data has been analysed.

The extensive transdisciplinary collaborations between academia, institutes, and industry through the partners within the consortium constitute a great success factor for the programme. It provides an important basis for learning and scaling up real life solutions and allows important insights into the challenges of implementing new results and concepts.

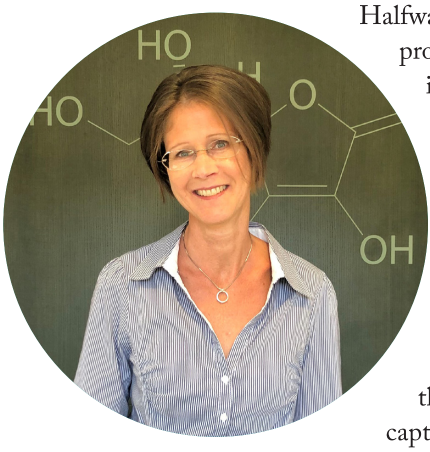
I am proud to be part of this excellent research programme with its accomplished researchers at universities and other partners, including a highly competent board. I am impressed by their extensive skills and competences. I would like to thank all participants of Mistra TerraClean for their great contributions and send a special thank you to our excellent Programme Director, Professor Ulrica Edlund, for keeping it all together during a great year filled with challenges and opportunities.

Katja Pettersson Sjöström
Chair of Mistra TerraClean Board
March 2024

LIST OF ABBREVIATIONS

ACC	Activated carbon cloth
AFM	Atomic force microscopy
AOP	Advanced oxidation process
API	Active pharmaceutical ingredient
BET	Brunauer–Emmett–Teller gas adsorption
CDI	Capacitive deionization
CFU	Colony Forming Unit
COD	Chemical oxygen demand
CSP	Case Study Package
DOM	Dissolved organic matters
FPT	Fibre and Polymer Technology
FTIR	Fourier-transform infrared spectroscopy
6:2 FTS	6:2 Fluorotelomer Sulfonate
GAC	Granular activated carbon
GC/MS	Gas chromatography/mass spectrometry
IKEM	Innovations- och Kemiindustrierna i Sverige
ICP-OES	Inductively coupled plasma-Optical emission spectroscopy
LC/MS	Liquid chromatography/mass spectrometry
LCA	Life cycle assessment
LCBRM	Life cycle based risk mapping
LCC	Life cycle cost analysis
LCIA	Life cycle impact assessment
MAC	Magnetic activated carbon
MNF	Material and nanophysics
MOF	Metal-organic framework
NMR	Nuclear magnetic resonance
PFAS	Per- and polyfluoroalkyl substances
PCR	Polymerase Chain Reaction
PEX	Cross-linked polyethylene
PFHxS	Perfluorohexanesulfonic acid
PFOA	Perfluorooctanesulfonic acid
PFOS	Perfluorooctane sulfonate
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
PoC	Proof-of-Concept
PoP	Persistent organic pollutant
RT-PCR	Reverse Transcriptase Polymerase Chain Reaction
REE	Rare Earth Elements
RMP	Risk Mitigation Plan
SEM	Scanning electron microscopy
SME	Small-medium enterprise
SGU	Statens Geologiska Undersökning
TEM	Transmission electron microscopy
TRL	Technology readiness level
UF	Ultrafiltration
VFE	Viral Filtration Efficiency
VOC	Volatile organic compounds
WP	Work Package
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

A MISTRA TERRACLEAN PERSPECTIVE ON 2023



Halfway into phase II, we are really up to speed with material production, analysis, sensor integration, and evaluation—both in terms of performance and environmental/safety considerations. Our understanding of the engineered materials' capacity to capture specific contaminants and the potential for incorporating sensing functions continues to grow. Hand-in-hand with life-cycle-based risk and opportunity mapping, the materials are evaluated and refined for improved sustainability.

Mistra TerraClean was conceived to directly respond to the pressing global and domestic needs to more effectively capture pollutants released into the air, water, and industrial effluents. Since then, the width of the problems with emissions containing for instance heavy metal ions, NOx gases, CO_2 and pharmaceutical intermediates are becoming even more apparent and new challenges have been added to the programme portfolio of target substances. Polluting substances like PFAS agents are more and more often on the societal agenda putting the spotlight on the need for efficient capture-and-destroy technologies. New achievements in this area are among the many highlights from the past year.

A few other snapshots of the many activities and advancements from 2023 include:

- Lifecycle-based risk and opportunity mapping was developed and implemented as an analytical approach. It considers all life cycle stages of new materials and technologies to identify advantages in comparison to state-of-the-art benchmark technologies as well as risks that might hinder further development and/or upscale in the future.
- The two-year case study on removal of active pharmaceutical ingredients from water was concluded with a pilot scale device, demonstrating efficient removal of tested compounds, including the notoriously difficult substance metformin.
- Novel and high-performing engineered activated carbons are prepared for gas adsorption.

- Metal organic framework (MOF) materials are developed for several target cases.
- The first rounds of bioreactor tests show promising performance of our engineered anti-fouling materials.
- Synchrotron experiments at the national laboratory facility MAX IV shed light on the mechanism of material structure formation.

A key to our progress is the transdisciplinary collaboration and the competence network with academic, institute, and industry partners. It is the shared expertise, the availability to relevant testbeds and sites, and optimal utilization of resources that enable us to perform at our best and expand the project's scope with new and exciting research ideas and findings.

Special thanks to our board for their invaluable support and guidance, and to Mistra for their confidence in advancing research and innovation in smart materials. We look forward to continuing to work together in the coming year and making further contributions to the field.

Ulrica Edlund
Director of Mistra TerraClean
March 2024

INTRODUCTION

Phase II of Mistra TerraClean runs from 2021 to 2025, with an ambition to level up the materials and technologies developed in phase I to industrial applications. The working structure (Figure 1) addresses current and future needs for clean water and clean air. With the know-how and attention developed in phase I, Mistra TerraClean has attracted attention from many new partners.

Six areas, CSPs, have been selected where Mistra TerraClean expertise could meet the needs. They include several activities on different TRL levels, where materials and devices are evaluated and developed in collaboration with stakeholders for specific contaminants.

The case topics are well motivated and responds to the needs of today while being pro-active for those of tomorrow. Mistra TerraClean phase I has surveyed the area, built a firm foundation and implemented an int+erdisciplinary competence hub.

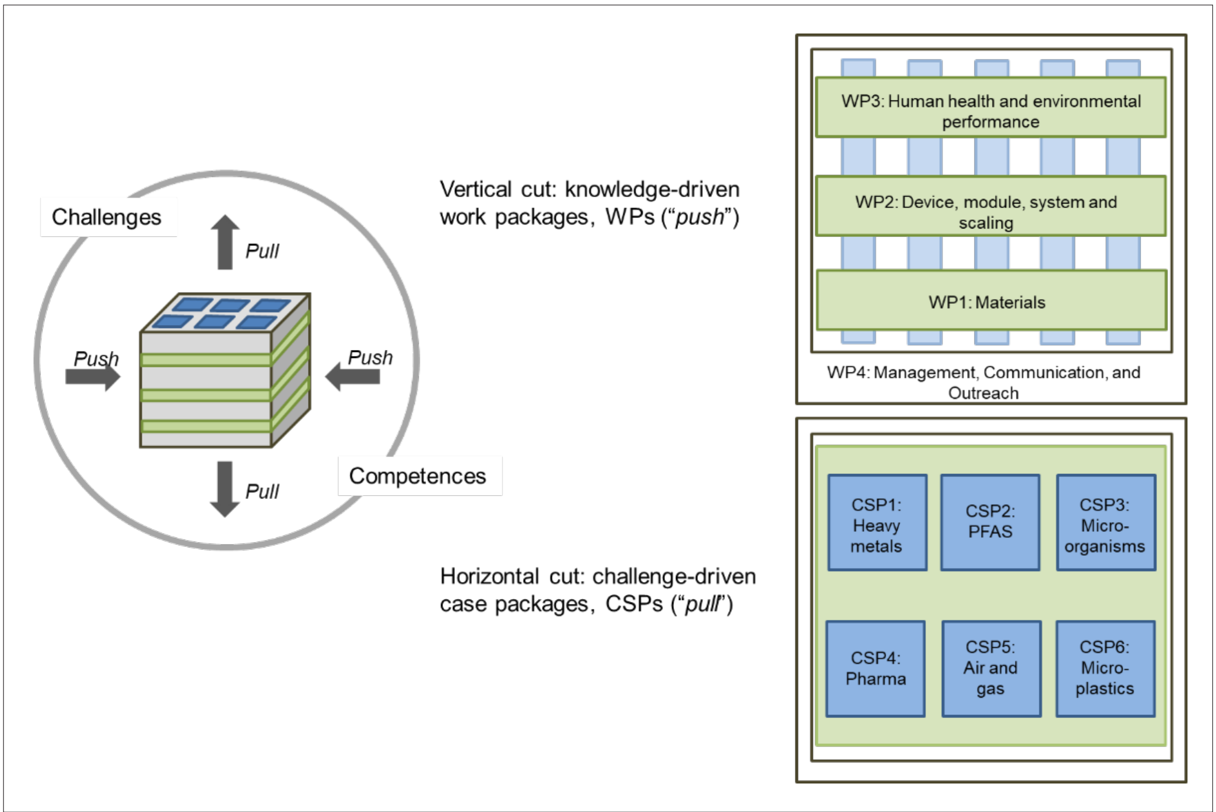


FIGURE 1.
The push-pull driven structure of Mistra TerraClean II.

COST-EFFECTIVE SOLUTIONS IMPORTANT FOR SUSTAINABILITY

What does it mean to engage in a programme like Mistra TerraClean? And what can different stakeholders gain from it? We asked three persons with different backgroud and affiliations.

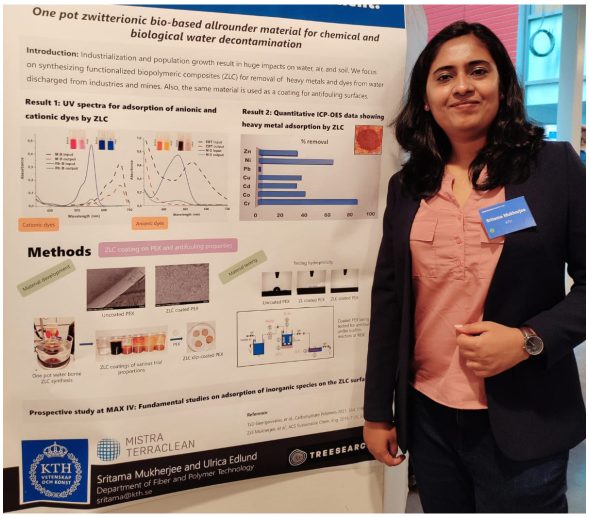
Sritama Mukherjee is a post-doctoral scientist at KTH, where she has been involved in Mistra Terra-Clean since 2022.

– I have been working on sustainable materials and composites for various applications, ranging from water treatment, sensors, bio-barriers to fire retardants, says Sritama. My interest lies in environmental impact assessment.

– My research is largely on industrially viable materials that are highly interdisciplinary in nature, she continues. In Mistra TerraClean II, I am currently involved in material synthesis and application for water treatment as well as antifouling surfaces.

Erik Ronne is research manager at Boliden with an extensive experience from large industry. Prior to Boliden, he worked at Akzo Nobel for 20 years with global responsibility for innovation strategies, stage-gate processes and open innovation.

– A key sustainability challenge for Boliden as well as the entire mining industry is the extractive waste, and my vision as research manager for sustainability is to make Boliden respected for the most sustainable and cost-efficient management of extractive waste in the mining industry, says Erik.



Sritama Mukherjee, KTH

Erik Ronne, Boliden

Malin Alpsten, Bright Day Graphene

Malin Alpsten is the CEO and co-founder at Bright Day Graphene, a startup company that produces biobased graphene. And Malin is optimistic about the future.

– We are here to make a change regarding new materials and new technologies. The world needs a big change fast – away from the use of fossil materials and towards sustainable and toxic-free solutions. We want to contribute to this transition by offering a biobased graphene with excellent properties, that can revolutionize the technology industry.

Why are you engaged in the Mistra TerraClean II?

– MTC II addresses challenging water research problems, says Sritama Mukherjee. The programme compels us to devise smart solutions to problems, including opportunities to collaborate and work together with the large industry-academia consortium members.

From Malin Alpsten's perspective, one reason for engaging in the programme is to test the biobased graphene material in new applications.

– There is a lot of research going on, where graphene and related 2D materials will have an impact in the near future, says Malin Alpsten. Air filtering is for example one area where graphene can add value, in comparison to conventional methods.

Participating in research programmes is important for Boliden, and the company is involved in more than 30 national and international research projects.

– We are interested in the use of smart advanced materials and technologies, says Erik Ronne. However, as a mining company we are handling very large volumes of waste and water, so at the end of the day it is always the cost efficiency that is the key.

What are the benefits working in a consortium with academia and industry?

– The possibility to work with experts and to interact with potential customers at the same time is a major benefit, especially for a startup company like Bright Day Graphene, says Malin Alpsten. Unfortunately, we have been forced to take a more passive role in the project during the past year due to a lower production capacity.

– To my knowledge, mixed consortia like the MTC II are the best format for research problems regarding environmental issues, says Sritama Mukherjee. The consortium not only gives different perspectives to look at problems on lab scale and large scale, but also allows a check on the feasibility of the solution implementation and technology development. Moreover, it is useful in sharing research infrastructure, expertise, and ideas.

– The focus on pilots and tests under real conditions is a key to success, says Erik Ronne. Many public funded R&D projects are done at the laboratory with no ideas about the final implementation, and it is often the implementation rather than the technology development as such which is the big challenge.

What, and how, do you plan to contribute to the programme?

– To put it bluntly, we are adding a realistic view to the research results from a large company's perspective, says Erik Ronne. Businesses need to balance costs against effectiveness, and the techno-economic analyses, as well as the life cycle-based risk and opportunity mappings within the programme are methods that we support to the largest extent. MTC II is a very good platform for discussions around these questions.

Sritama Mukherjee sees many opportunities in the programme where her competence is useful.

– With my expertise and a collaborative effort, I hope I might contribute to solutions for the separate case studies. As a scientist, I can see that the research will lead to publications, and possibly new IP. The ultimately target is to develop technologies that can be scaled up and tested in real-time.

– We planned to contribute by producing the graphene material to CSP3 regarding airborne biofouling, but due to circumstances we could not anticipate, the production has been delayed, says Malin Alpsten. We are however planning to be more active in the programme, moving forward.

What will be the best outcome that you can think of when the programme ends? What have you achieved?

– The best outcome would be a material, or a technology that can be useful in real-time, Sritama Mukherjee says. I do believe that the work relationship that has been developed between different partners will be helpful in the future.

– I agree with Sritama, and hope that the programme will lead to commercially available technologies, says Erik Ronne. Innovative and smart materials may very well be a tool the reach the goal, but the goal as such is only cost efficiency.

WORK PACKAGE 1
MATERIALS

WP 1 Leader: Niklas Hedin, Stockholm University

Key questions and scope

In this WP, materials are developed and functionalized, and they are further studied in the CSPs and their targeted applications. The four tasks of the WP have a focus on developing materials with specific functions for the removal of heavy metals, pharmaceuticals and related molecules. Moreover, removal of PFAS from water, in addition to the reduction of microorganisms and fouling in water and gas tubes, and the removal of microplastics from water are of interest, as well as gas purification by removal of VOCs and CO_2. The tasks involve efforts to make the materials adaptive, responsive, or interactive, preparing them for integration in devices in WP2 and in the CSPs.

Tasks	Partners
1.1 Carbonates, hydroxides, and related compounds	Uppsala University; RISE
1.2 Carbon-based smart materials	Stockholm University; RISE; BrightDay Graphene
1.3 Lignocellulosic materials	KTH; Stockholm University; RISE; MoRe
1.4 Chemically modified materials	KTH; Stockholm University; Uppsala University; RISE; Alfa Laval
1.5 Characterization platform	RISE; KTH; Stockholm University; Uppsala University

TABLE 1. Overview of WP1, tasks and involved partners.

Progress and achievements during 2023

Task 1.1 Carbonates, hydroxides, and related compounds

This task explores the compositions and applications of carbonates and hydroxide materials, and how existing materials such as Upsalite can be improved and optimized for pollutant removal. High-temperature regeneration of heat-resistive mineral materials is explored together with CSP2 and CSP4.

We synthesized a novel sodium hafnium oxide (Na_2HfO_3) by solid-state synthesis and found that its CO_2 sorption properties are high at high temperatures. The work has been published.

The work on developing a detailed model to understand the surface-adsorbate interaction on carbonates/hydroxides has begun and will continue in 2024.

Task 1.2 Carbon-based smart materials

Here, we focus on developing magnetic activated carbons from biomass, 3D-arrangement of graphene, and the modification of activated carbon cloth to create smart, multifunctional electrochemical electrodes. These materials are explored for e.g. the removal of short-chained PFAS molecules, air and gas purification, and the removal of metal ions and pharmaceutical intermediates/residues.

We studied the uptake of VOCs in activated carbon with included iron phosphates. Activated carbons modified with iron-rich nanoparticles were studied for the removal of Cd^{2+} and Pb^{2+}. Furthermore, studies on the uptake of PFAS on activated carbons that are magnetic have been performed.

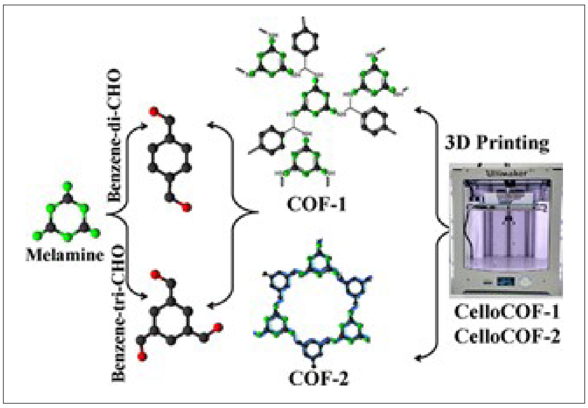


FIGURE 2. Schematic representation for synthesizing COF-1 and COF-2 for 3D printing into scaffolds. The figure originates from the article, ACS Applied Materials Interfaces 2023, 15, 51, 59795-59805.

To get a detailed understanding of the carbon-adsorbate interaction and kinetics, we have a simple model for the uptake of PFAS on carbons, and similarly for the CO_2 chemisorption on aminated carbons. Various porous carbons were evaluated on CO_2 adsorption with polyethyleneimine (PEI) modification. Films rich in carbon and aminated carbons have been prepared using cellulose nanofibrils as a structuring agent.

Task 1.3 Lignocellulosic materials

This task focuses on the synthesis and preparation of hybrids and composites using cellulose, hemicellulose, and lignin, three components that make up a large portion of the biomass on earth. These materials are relevant for the carrier of inorganic components, support for membranes/filters, and functional materials for selective capture/rejection of water and air pollutants.

We have conducted performance screening on structured lignocellulosic materials with respect to adsorption capacity, selectivity, and kinetics. Moreover, we studied the 3D printing of cellulose and zeolitic imidazolate frameworks and the adsorption of CO_2 and heavy metal ions, and cellulose and covalent organic frameworks for the same applications (Figure 2).

We also studied the kinetics of nucleation and growth of ZIF-8 on a suspension of cellulose nanocrystals by combined SAXS/WAXS at ForMax beam line at MAX IV, Lund (Figure 3).

Finally, we are compiling a database for adsorption of molecules and ions of lignocellulosic materials.

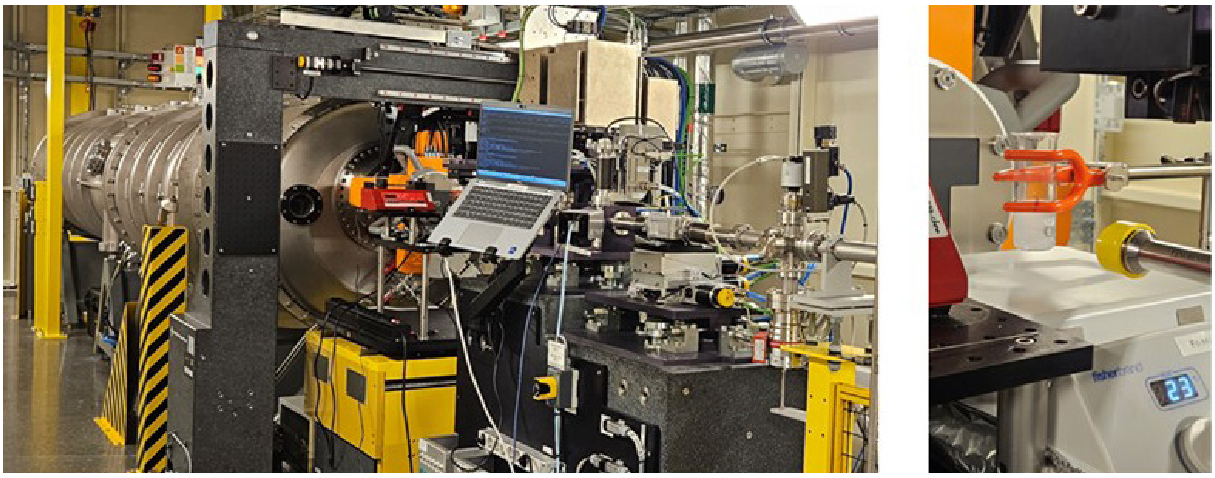


FIGURE 3. Photographs showing the experimental step at ForMAX beamline. A custom-built reactor was used to ensure adequate mixing and for preventing beam damage during the reaction time.

Task 1.4 Chemically modified materials

Here, we study materials that sometimes need to be chemically modified to gain the intended functionality. For this, we are using so-called molecular layer-by-layer assembly to provide intended functionalities for the surface. We are exploring surface chemistry modifications to achieve low-fouling membranes, and amine modification to enhance the materials' affinities for CO_2. Different coating techniques are explored for a potential scale-up, such as roll, dip- and spray-coating, and aerosol-based techniques, (Figure 4).

Moreover, we investigate the preparation of green composite aerogels, foams of cellulose, and protein nanofibrils like amyloid nanofibrils. These protein fibrils can be easily prepared from whey, by-product of dairy industries. The aerogels are prepared via freeze-linking and the foams are prepared via oven drying, therefore, there is no need to use freeze-drying or other high energy-use methods.

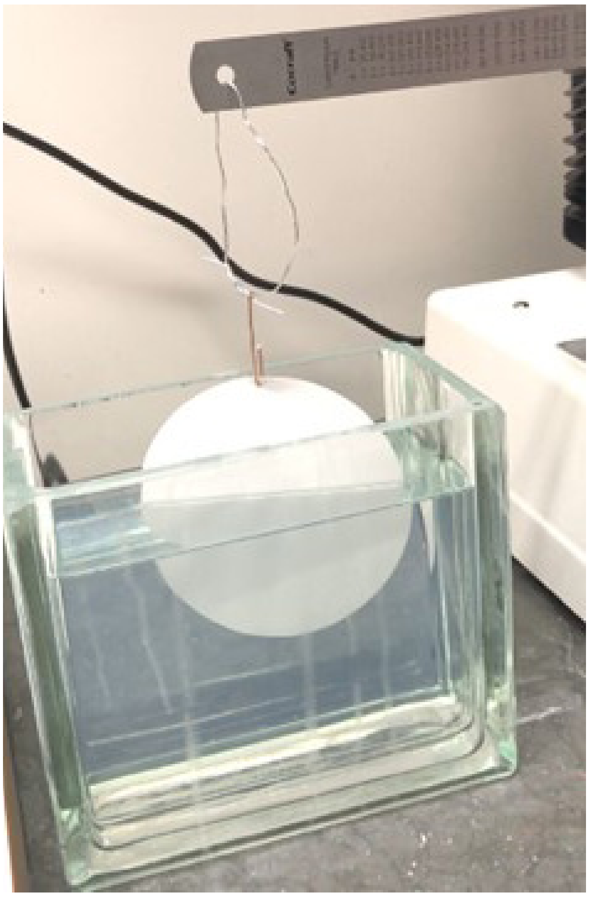


FIGURE 4. Using dip-coating technique to produce low-fouling membranes.

During the year, devised adsorbents and membranes with several simultaneous functions have been developed, for example antifouling properties combined with high and specific molecular adsorption.

We have gained new understanding of the interconnections of molecular adsorption with properties of the support for example the electrical conductivity. Furthermore, different MOFs have been studied for capturing greenhouse gases, including CO_2 and SF6. The regulation of the pore structures of two very different adsorbents has been explored to tune the selection of CO_2 sorption. The mechanism of weakly-temperature-dependent CO_2 sorption has been studied.

Task 1.5 Characterization platform

In Task 1.5 we focus on documenting the characterizing and validation of the sorbent materials developed for the project. This involves the documentation of a variety of surface characterization techniques such as XPS, SEM, TEM, XRD, IR, ICP-OES, and solid-state NMR spectroscopy.

The work has been focused on establishing secured knowledge transfer about current and future capacities for cutting-edge techniques for characterization, as well as collecting and sharing protocols for advanced analyses.

WORK PACKAGE 2: SMART FILTER DESIGN AND VALIDATION

WP 2 Leader: Mats Sandberg, RISE

Key questions and scope

WP2 connects materials at the molecular level with the device level by creating devices with connected materials. At the organizational level in the project, WP2 is to provide early feedback from techno-economical evaluation of materials developed in WP1 and connects to LCA work in WP3.

Tasks	Partners
2.1 Connected Filter Devices and Integration	RISE; KTH
2.2 Sensors and Sensor Materials	RISE; Stockholm University
2.3 Scaling and Techno-economy	RISE; IVL; Stockholm University; Alfa Laval

TABLE 2. Overview of WP2, tasks and involved partners.

Progress and achievements during 2023

Task 2.1 Connected Filter Devices and Integration

The work on optical sensors for the detection of materials from living organisms for air filters continued with a fluorescence analysis of pure cellulose substrates, to see if spontaneous substrate fluorescence could interfere with signals from materials originating from cells. The results showed that background interference would not be a problem. Tests with filters intentionally contaminated with the target microorganisms could not be carried out due to restrictions in shipping and handling the organisms. Future work will be carried out with sterilized samples.

The work on realizing a connected filter device is based on building a sensor with a material with identical properties as the filter material. To this end, the method to modify carbons, mentioned below under sensor materials, has been extended to the modification of granulated activated carbons to realize a smart filter where the absorbent and sensor are based on materials with identical absorption properties.

Task 2.2 Sensors and Sensor Materials

The work on sensor absorbents for heavy metal ions was concluded in 2023. The method of chemically modifying porous carbons to improve absorption properties and sensor functions was published as a patent application in January. This was also presented orally at the EMRS Spring Conference in June.

In an outreach to probe for specific interests in modified carbons and sensor absorbents, a project partner pointed out the need for aluminum ion sensors. Aluminum is an element of concern due to its importance in water purification processes and its negative health effects. Possibilities of determining aluminum with low-cost sensors could lead to better quality assurance and lower costs in water purification.

In response to this, the challenges of constructing sensor electrode materials for electrochemical detection of aluminum ions were approached with our method to modify and functionalize porous carbons. Electrochemically, the challenge is associated with the high reduction potential of aluminum ions. The use of modified carbon in aluminum sensors has the effect of producing a distinct redox peak in response to exposure to aluminum ions while a non-modified carbon mainly produces a capacitive response.

The printed low-cost arrays reported last year were used for the characterization of both heavy metal and aluminum sensor materials.

Task 2.3 Scaling and Techno-economy

Educational workshops on benchmark systems in 2022 were proved successful and were continued during 2023. Workshops were held on the use of software tools to estimate costs for processes. Such tools can be applied for filtration processes as well as for filter material manufacturing processes. These activities and discussions around techno-economic aspects aimed for a more holistic approach on developed materials and their incorporation in new or existing devices and systems.

Among 2023 publications, background information important for techno-economical assessment and scaling has been provided to a larger extent. It is also recognized that the formalized process within the consortia including requests for upscaling is not used by the researchers. Therefore, a common effort to pull out candidates was initiated by WP2 and WP3. This initiative was addressed during the consortium meeting and has resulted in a constructive evaluation and screening of viable concepts. Status in cases originating from CSP1 and CSP2 was disseminated in the late fall and the remaining CSPs will be in focus beginning of 2024.

A more detailed workshop was held in March on techno-economical assessment describing the professional approaches and tools. A follow-up was made in October during the session ”Techno-economic Assessment – System Boundaries to Visualizing Hotspots”.

The rolling report on developed material continues to grow. The need to handle air and water materials separately is considered for 2024. CSP5 has provided a good report template to describe essential properties and limitations of air filter materials. The new materials are clearly described in comparison to currently used materials.

Work on the manufacturing of antifouling membranes ready for scaling tests has been carried out by the team at Stockholm University (Figure 5). Here, commercial cellulose acetate solution and commercial substrates provided by Alfa Laval are the starting points for scaled manufacturing, where the approach is to increase the cellulose acetate solutions followed by phase inversion using water as the non-solvent. Developed formulations were used to produce membranes at the facility of Alfa Laval in Nakskov, Denmark, and showed acceptable quality (with respect to homogeneity, thickness, percentage load of CNCs, etc.). However, more systematic basic characterizations are needed before a decision on upscaling can be made.

Furthermore, Stockholm University has carried out studies on scalable production of filters with 3D-printing methods for microplastic removal, in collaboration with CSP6. The team developed a method to produce biobased water purification filters by 3D-printing, using the fused deposition modelling. The filters consisted of reinforced polylactic acid-based composites. Our target is set on the removal of microplastics from laundry effluents and to evaluate capacity for removal of metal ions of the selected materials, something that has been demonstrated for removal of copper ions. Small rectangular filters with dimensions of several centimeters in a lab scale were prepared. The filter size will be scaled up dimensions suited for direct testing at the facilities of Mimbly. The possibility of scaling up the composite material from commercial sources is under consideration and will require a technoeconomic analysis.

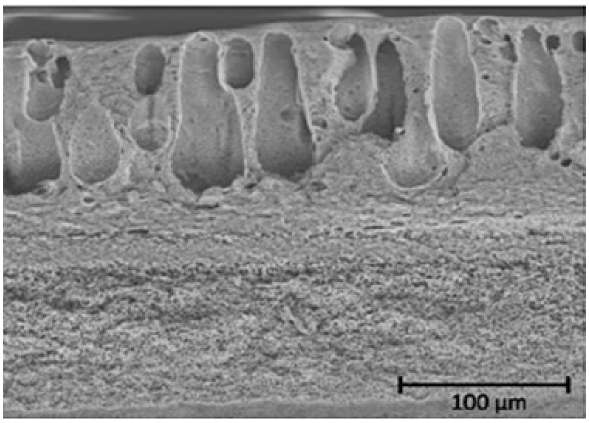


FIGURE 5. Cellulose acetate and cellulose nanocrystal-based phase inversion membranes developed at Stockholm University in collaboration with Alfa Laval.

WORK PACKAGE 3
ENVIRONMENTAL AND HUMAN HEALTH ASSESSMENT

WP 3 Leader: Maja Halling, IVL

Key questions and scope

The aim is to provide input regarding human health and environmental impacts to the various CSPs for developing smart, flexible, and effective materials. WP3 will utilize several tools for reaching valuable input to the CSPs: Life cycle-based risk and opportunity mapping (LCBROM), Life cycle assessment (LCA), Life cycle costing (LCC), and Safety assessment and ecotoxicological tests.

Tasks	Partners
3.1 Appraisal process development and risk mitigation plans	IVL; RISE; SLU
3.2 Tier 1: Toxicological appraisal of the material and identification of most important environmental and human health aspects of material production, application, post-consumer fate and management	IVL; RISE; SLU
3.3 Tier 2: Environmental (LCA) and economic (LCC + external costs) performance of material and devices in individual case studies. Applied toxicological testing of filter treatments in individual case studies with focus on ecotoxicity.	IVL; RISE; SLU

TABLE 3. Overview of WP3, tasks and involved partners.

Progress and achievements during 2023

Life Cycle Based Risk and Opportunity Mapping

In 2023, work on the LCBROM has been intensified. LCBROM intends to streamline the initial process of identifying hot spots along the entire life cycle for selected materials and devices, usually based on existing publications for comparable items. A first LCBROM on ferrous sulfate activated carbon used in CSP1 has been completed and the working method has been refined by, among other things, updating and improving the report template based on the lessons learned after the first LCBROM. We have also developed a questionnaire to facilitate the initial information gathering. The questionnaire is distributed to the technology owners before the start-up meeting and the information provided by the technology owners serves as a springboard and forms the basis for further work. In connection with improving the methodology, we chose to change the name from Life cycle-based risk mapping (LCBRM) to Life cycle-based risk and opportunity mapping (LCBROM) as we also want to signal that the screening focuses on identifying both opportunities and risks.

In total, five LCBROMs will be performed. During 2022, an LCBROM focusing on magnetic activated carbon (MAC) used in CSP2 and CSP4 was initiated.

During the year, LCBROM for the following technologies has been initiated:

- Modified organic framework (MOF), with the aim of purifying PFAS, used in CSP2.
- Hollow fiber renewal liquid membrane (HFRLM) with the aim of extracting REO from various sources (such as abandoned mines), used in CSP1.
- Modified PEX tubes used in CSP3.
- Carbonized cellulose used in CSP5.

A project leader within WP3 has been assigned for the assessments and contact with involved partners has been established.

A collaboration with WP4 has been initiated where information on the state of the art and available technology in the field is currently inventoried and can be shared and incorporated into LCBROM.

Workshop

In September, an internal workshop was held at SLU in Uppsala. All partners in the programme were welcome to join. The theme of the workshop was ”Introduction to ecotoxicological methods”, and representatives from SLU introduced the field of ecotoxicology and how the methods could be applied in the Mistra TerraClean programme. Attendees were also invited to a visit to the lab where ecotoxicological studies are performed (Figure 6).

Complementary LCA

Work on the complementary LCA continued during the year, with continued contacts with Stockholm Water Technology and AstraZeneca, with a focus on the effects of replacing existing fossil-based activated carbon with CDI treatment.

Chemical risk assessment

Chemical risk assessments have been performed on substances used in the modification of the surface of PEX tubes aiming to inhibit bacterial growth. The risk assessment showed that several of the substances used for modification had CMR (carcinogenic, mutagenic, and reprotoxic) properties. Fortunately, the most successful modification process, kraft lignin, does not contain any chemicals with hazardous properties.

A chemical risk assessment was also performed at amines used in the development of amine-modified materials (activated carbon or graphene oxide) developed by researchers at Stockholm University and mainly used in CSP5 for CO_2 removal.

Ecotoxicological experimental studies

No ecotoxicological studies have been performed yet. However, discussions with CSP4 have been initiated to find out how such studies can be applied and utilized to further advance the material development. Additionally, as the LCBROMs are moving forward, new opportunities for ecotoxicological experimental studies are being identified.

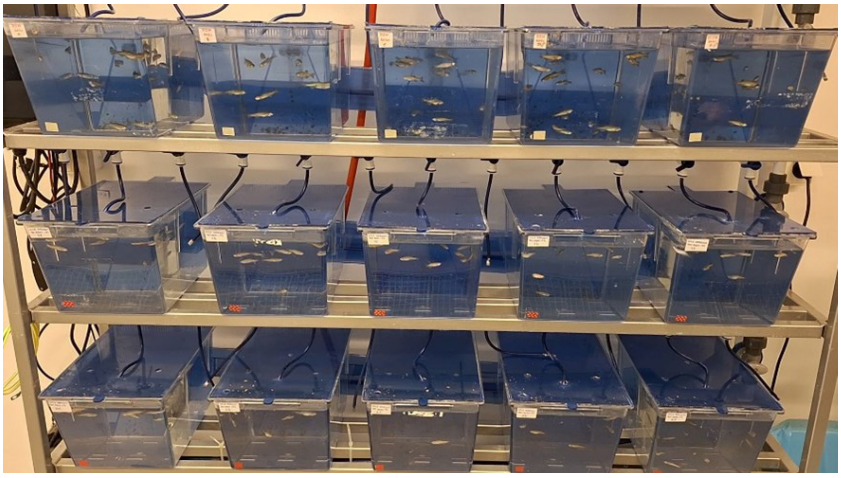


FIGURE 6. Fish tanks for ecotoxicological studies at SLU.

WORK PACKAGE 4
MANAGEMENT, COMMUNICATION, AND OUTREACH

WP 4 Leader: KTH, Communication leader: IKEM

Key questions and scope

WP4 is responsible for administrative and financial management, assuring that deliverables, prototypes and demonstrations are on time within the given budget. Key questions are the following: Programme management plan, Programme organization, Communication within programme, Materials and results flow within the programme, IPR agreements between partners and securing base for further commercialization in Sweden of the programme results, Communication to stakeholders, Dissemination to public, society, and policy makers, and To facilitate an effective cooperation and communication between the different WPs.

Tasks	Partners
4.1 Administrative and financial management	KTH
4.2 Programme monitoring, quality control and risk management	KTH
4.3 Case-oriented outreach activities	IKEM
4.4 Connect to relevant policy instruments	IKEM
4.5 Ongoing communication and reporting	KTH; IKEM

TABLE 4. Overview of WP4, tasks and involved partners.

Progress and achievements during 2023

WP4 regularly arranges steering group meetings, board meetings, facilitates knowledge transfer and outreach, and maintains control of programme finances and resources on a regular reporting period basis. Monthly steering group meetings is an important instrument in keeping momentum, sharing the latest insights, and providing a forum for continuous co-creation.

An ambitious case-oriented analysis exercise was initiated and will continue into 2024, aiming at mapping where the best available technologies are today and how Mistra TerraClean research can supply and fit in the development of more effective cleaning, as well as what current obstacles exist toward better technology.

Continuing our ambition to raise the competence and expertise within and beyond our consortium, internal workshops, site visits to partners, and open seminars were arranged throughout 2023.

During the year we have continued following the policy work and implementation of the Industrial Emissions Directive, IED, i.e. by participating in a national reference group connected to the Swedish Environmental Protection Agency, looking at Best Available Technologies (BAT). With IKEM participating in IRISS, an international ecosystem for accelerating the transition to Safe-and-Sustainable-by-Design materials, products, and processes, the consortium has gained a deeper understanding of adequate policy issues.

Together with Svenskt Vatten, we arranged an open seminar on the EU's Proposal for a revised Waste-water Treatment Directive in April. Various aspects of the said directive - pharmaceutics, nitrogen, urban wastewater treatment, and sludge, among others - and their implications on stakeholders were discussed together with invited speakers.

The programme and its activities in the water purification arena were presented to the public with a specific target group of high school students at the event "ForskarFredag", the Swedish part of a Europe-wide public event called European Researchers' Night.

This year's consortium meeting was held in late October (Figure 7), joining partners from near and far together – academia, institutes, authorities, organizations, and industry. We started the meeting in Skellefteå, a rapidly expanding city, bustling with entrepreneurship and, therefore, an inspiring venue for clean-tech enthusiasts like us. The first day included updates from all case study packages, and discussions. How do we foster co-creation and make the best use of strategic funding? A "self-audit" exercise was launched to provide an inventory of material and device candidates developed within the programme and their maturity in terms of function, scaling, and environmental footprint.

An inspiring guest lecturer from the company Racoon Miljöfilter AB gave a user´s view on the challenges in air filtration, and delivered the story of how a global company has been formed in Robertsfors, thanks to a trade fair and a microwave oven in the garage.

The next day was truly inspiring and educational. Thanks to the hospitality and generosity of Boliden, a full day of site visits at Skelleftefältet, including Maurliden, a concentrator plant, active and decommissioned sites, demonstrated the challenges and opportunities of clean technologies in the mining industry with relevance to Mistra TerraClean.

FIGURE 7. Snapshots from the annual consortium meeting in Skellefteå and Boliden.

CASE STUDY PACKAGE 1: HEAVY METALS

CSP 1 Leader: Johan Strandberg, IVL

Involved partners: IVL; KTH; Stockholm Water Technology; Stockholm University; RISE; SGU; Lovisagruvan; Boliden; Nordic Water (Sulzer)

Key questions and scope

There is a growing industrial and societal interest in capturing and enriching rare earth elements to support the green transition. CSP1 addresses the treatment and separation of heavy metals from water streams in active and closed mining operations. The applied methods may also be applicable for treating other waters contaminated by heavy metals, e. g. leachate water or contaminated stormwater.

The scope of this case package is to find new methods with higher efficiency, less waste and lower cost than the methods available today.

CSP1 continues to address the separation and treatment of heavy metals from water streams in active and closed mining operations. Noteworthy progress in reducing key heavy metals like lead and zinc has pivoted the project towards an additional goal: the concentration of Rare Earth Elements (REEs) from various sources such as closed mines and heavy metal separation processes using technically simpler equipment.

Description of cases within the package

Lovisagruvan

Since 2004, Lovisagruvan has been running an underground mine in Bergslagen, just north of Lindesberg, with high concentrations of zinc, lead, and minor silver. The continued decrease of the release of zinc and lead to the surrounding environment is the aim target in this case for Mistra TerraClean. In addition, a nearby closed cobalt mine (Håkansboda) is also owned by the Lovisagruvan company. This mine and its leachate, which is not governed actively, might contain REE.

Svärtträsk

The Swedish Geological Survey is the governmental authority responsible for acting as the operator in cases where contaminated areas lack an owner. Svärtträsk is such a case, where a rock landfill of mining residues has been constructed in a former open pit mine. Acidic water runs from the landfill through ditches in the area, directed to a water treatment station. The performance of this treatment with respect to passive operation and low running costs are the challenges for the researchers in the program.

Boliden mines

Boliden operates a number of mines in Sweden and abroad. Many of them are based on sulphidic-rich ores containing, for example, copper, zinc, gold, silver and lead. The residues are reactive in an aerobic environment, creating a low-pH leachate that contains dissolved metals. Hence, Boliden's water treatment needs are both in the active and closed phases of a mine. The specific challenge to be addressed by the program has not been defined but is more general.

Progress and achievements during 2023

CSP1 aims to find feasible options for use in the cases presented by industry to the group of researchers. If this occurs, the applications and cases may be subjected to additional research within the program or as a result of collaboration between companies and industry, depending on where the IP of the chosen solution resides. The process is described in Figure 8.

Analysis

Water samples from different points in Lovisagruvan and Håkanboda mines were collected for lab-scale testing of sorbents and processes. The evaluation of these was finalized during 2023.

Evaluation of trials

A range of materials from the program were tested for the separation of metals and REEs. Figure 9 showcases the reduction rates for various metals using different treatment methods.

Figure 9 indicates significant reductions in the concentration of key heavy metals, with the applied methods showing potential for broader application in the treatment of contaminated water streams.

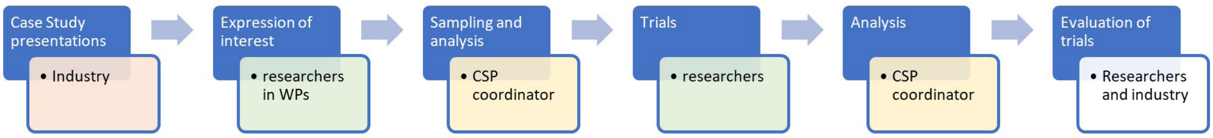


FIGURE 8. Process description for the stepwise engagement of mine operators and scientists in CSP1.

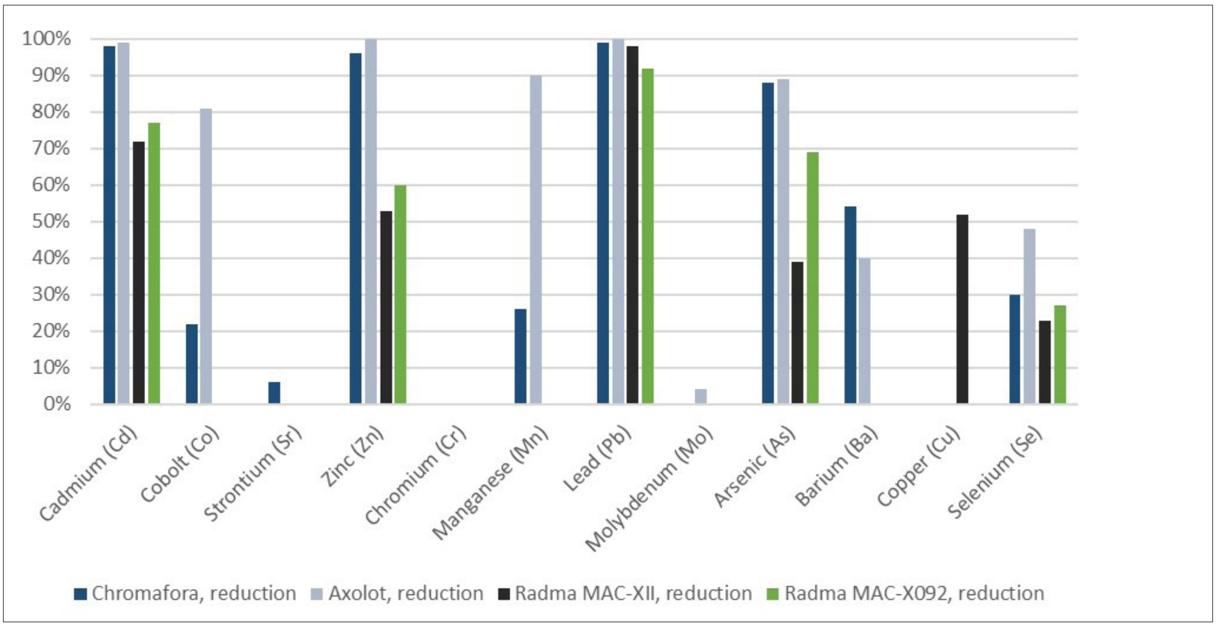


FIGURE 9. Reduction rates for various metals with different treatment methods.

New Direction within CSP1

A new initiative aims to develop a technology to concentrate REEs, creating a high-value concentrate (REO) that can be sold for the separation of individual REEs. The case study focuses on water from Håkansboda, a discontinued mine in Bergslagen. The potential value of REO will depend on the constituents, their concentrations, and the separation cost relative to water quality.

The tasks performed within this new field, during 2023 were:

Literature Review: An initial literature review established a benchmark of techniques utilized by other researchers and identified challenges to reduce operational costs. Based on this review, and prior knowledge, the Mistra TerraClean consortium formulated hypotheses regarding material development within the program. This work will be developed into an application for funding from the programme's strategic reserve.

Pilot Plant Construction: The pilot plant setup has been completed, providing flexibility in changing separation technologies, and understanding capacity requirements.

Market Analysis: To determine the market value of REO and the elements that dictate its value, a comprehensive market analysis is being conducted. This analysis will guide the pilot trials.

Pilot Trials: Pilot runs are being carried out using liquid membranes, with the dual aim of examining separation efficacy and building expertise, as well as preparing for potential modifications in membranes and pretreatments.

CASE STUDY PACKAGE 2: PFAS AND INDUSTRIAL WATER

CSP 2 Leader: Tove Mallin, RISE

Involved parners: RISE; KTH; SU; IVL; Alfa Laval; SAAB; Stockholm Water Technology; Radma Carbon

Key questions and scope

The aim of CSP2 is to test the practical application of materials and devices partly developed within the project for the removal of persistent organic pollutants from water of two test sites; PFAS polluted ground and surface water from SAAB's airport in Linköping and polluted slope water from SKF's industrial process. Due to the acquisition of the SKF branch by another company, the experiments at the SKF's site were canceled. The case study will further focus only on the SAAB site.

Progress and achievements during 2023

Application of CDI

Experiments on PFAS removal by CDI were designed based on the findings from the research conducted during 2022. In the previously performed experiments, the strategy was to study the influence of the process parameters (e.g. voltage, polarity, regeneration solution) by firstly saturating the electrodes with PFAS (physical sorption, no voltage application) followed by different strategies for regeneration with voltage application and, lastly, performing the final physical sorption stage to see if the regeneration was effective for renewing the sorption capacity.

The first set of experiments performed during 2023 investigated the process performance using the same methodology, although with a substantially decreased PFAS loading. Two types of electrodes were studied, a conventional activated carbon cloth (ACC) electrode in experiment 1 (E1), and a new fluorine-modified activated carbon cloth (F-ACC) in experiment 2 (E2). In both cases, the physical adsorption and electrically enhanced desorption were alternated in three cycles. Additionally, a reference experiment with ACC but only chemical regeneration (no voltage supply) was performed (E3).

The results of this set of experiments clearly showed that the newly developed electrode material has considerably better sorption properties compared to ACC and allowed reaching around 90% PFAS removal in the first cycle of E2 (Figure 10). Moreover, the electrical potential during the regeneration phase improves the process performance, and it is clear that the regeneration of the electrodes is the limiting stage of the overall process.

Based on these findings, a new set of experiment was conducted using only F-ACC. The regeneration phase was adjusted so that only fresh NaCl solution was pumped through the cell and the polarity of the cell was reversed intermittently. The new regeneration

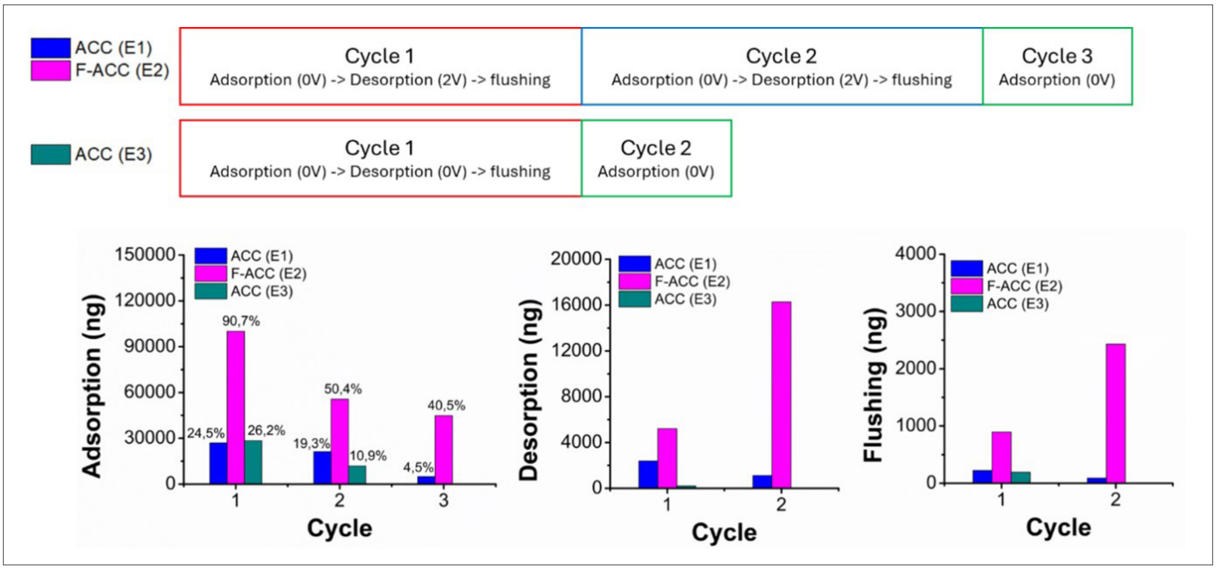


FIGURE 10. Experimental procedure (above) and results (below) for the first run of experiments. Numbers above the bars in the adsorption diagram show the PFAS removal efficiency.

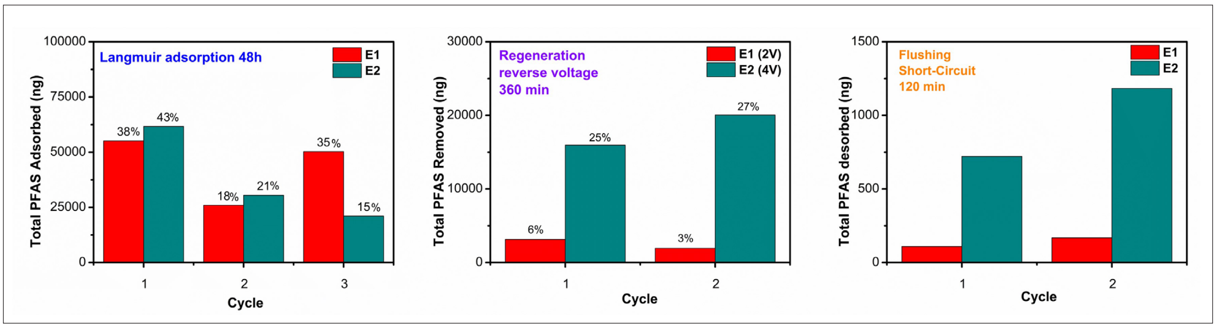


FIGURE 11. Experimental results for the second run of experiments. Numbers above the bars in the adsorption diagram show the PFAS removal or regeneration in percent of initial content in the treated water.

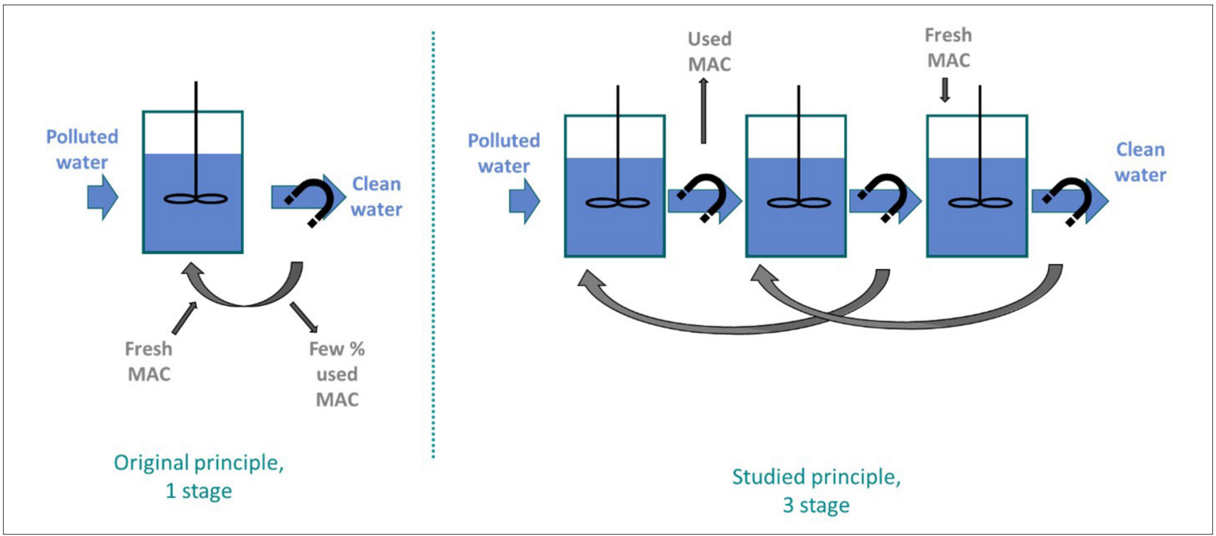


FIGURE 12. Studied principle of 3-stage counter-current MAC application in comparison to original principle.

strategy resulted in a more stable removal efficiency in the consecutive runs (Figure 11).

Further discussion of the results of the second run within the CSP2 is planned. The coming experiments will focus on verification of the technology as a whole aiming at good PFAS removal, high regeneration degree and high-volume reduction of polluted water.

Application of MAC

Application of MAC for PFAS removal was further tested by three experiments, investigating the influence of contact time, number of sorption stages, and the type of solvent used for regeneration. The contact time of 30 min was found to be sufficient for the practical application, even though some minor increase of sorption was observed at longer contact times.

The number of stages were investigated simulating the original principle of the Radma Carbon technology with one-stage adsorption in comparison with a modified concept with three stages and counter-current flow of MAC and water (Figure 12). It was shown that with three stages the required dose could be decreased by more than 60% and reach the same low dose as what is required for conventional powder activated carbon (PAC).

Since MAC is expected to have a higher price than conventional PAC, the regeneration of MAC with organic solvent for further reuse is still a vital part of the technology. Application of methanol and acetone was tested in three consequent sorption cycles. It was shown that recovery of PFAS in the regeneration solution was nearly complete, however decrease of removal efficiency was observed for the regenerated MAC motivating further experiments on the optimization of the process.

Application of MOF

Preliminary evaluation of MOF for PFAS removal was performed using synthetic solutions of PFAS-spiked deionized water and compared to parallel tests with conventional PAC. Four different MOFs were tested in four to five different doses. Only a minor PFAS removal was observed in some experiments. The testing of MOF will be further continued during 2024.

CASE STUDY PACKAGE 3: MICROORGANISMS AND FOULING

CSP 3 Leader: Ian Cotgreave, RISE

Involved partners: RISE; KTH; SU; Uponor; Camfil; Alfa Laval; Stockholm Water Technology

Key questions and scope

The case study focuses on the use of advanced chemical/material/sensing techniques in preventing biofouling from water- and air-borne sources. The work was divided into two sections at the onset of 2022 and will be reported according to this.

During 2023 the anti-biofouling case study has been driven in two separate work streams, one involving airborne biofouling and one involving waterborne biofouling.

Airborne biofouling

Key to both areas of material design and testing has been the establishment of bioreactor techniques, with specific bacterial and viral contaminants. In the case of airborne biofouling, we have established a bioreactor platform in which porous filters and solid surface

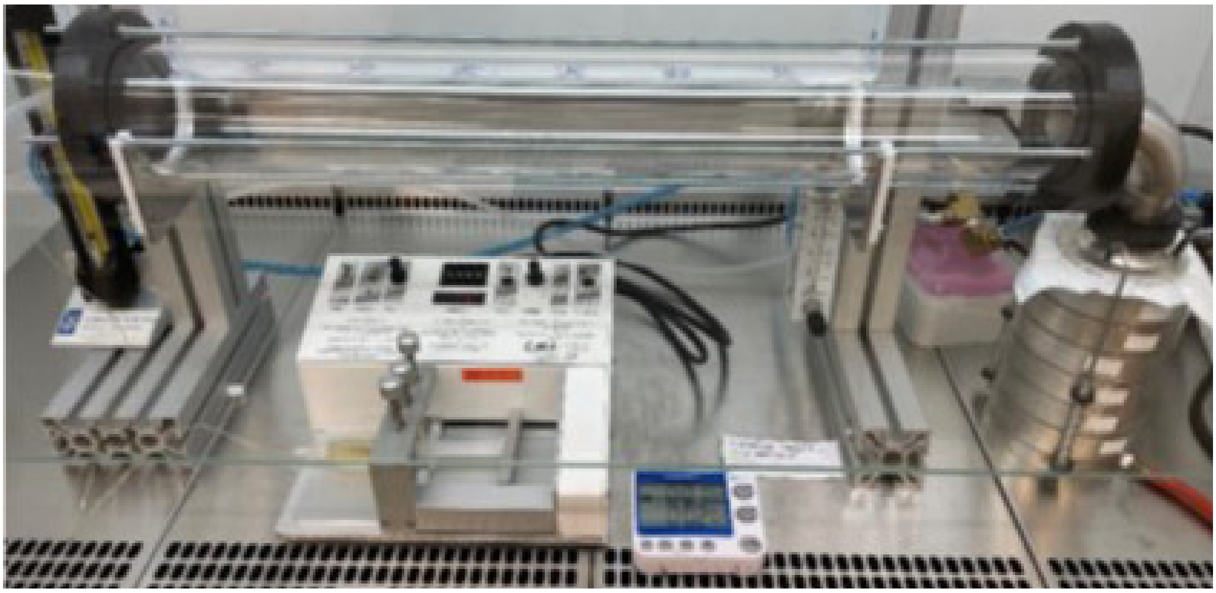


FIGURE 13. Set up of the VFE assay.

materials can be placed and seeded with bacteriophage and viruses. Camfil has collaborated with RISE to generate a standardized system for assessing viral contamination of air filtration material (Figure 13).

The initial work reported in 2022 has been extended to allow routinized use of the bioreactor not only using the initial bacteriophage surrogate species (phi-X 174), coupled to the live/dead PCR-based quantitation method, but also to the use of the more pathogenic viruses like adenovirus, and murine norovirus. The work is a collaboration between Department of Infectious Diseases at Sahlgrenska Academy in Gothenburg and RISE. The method has now been standardized according to ISO 18184.

The bioreactor has also been adapted to use bacterial biofilms, created using both *Staphylococcus aureus* and *Escherichia coli* as probe organisms, both of which are associated with risks for infection. Here, initial work has focused on the use of photocatalytic illumination of ZnO-impregnated cellulose filters, of the type used by Camfil for their air outlet filters, as well as ZnO-coated glass surfaces, have failed to reveal anti-fouling activities with the two bacterial strains utilized. This has led to a change in focus in the airborne anti-biofouling case study towards the use of graphene-impregnated materials. These materials potentially support direct biocidal activity, as well as the potential to optimize this using heating. This work is now continuing with extra funding from the programme's strategic reserve.

Waterborne biofouling

There are two areas of endeavor within this sub-case study, one involving the testing of chemically modifying the PEX material normally used in water pipe manufacturing (Uponor), and one involving modification of ultrafiltration membranes (Alfa Laval) with cellulose nanocrystals.

Key progress has been made in establishing the routine use of the bioreactor for testing surface modification of PEX material, which includes a heat disinfection unit (Figure 14).

Initial work focused on a series of chemically modified PEX materials generated by KTH, using *Escherichia coli* as a model organism. It revealed that two of these chemical modifications, involving covalent coating with lignin or chitosan, facilitate the inhibition of biofilm generation in the closed bioreactor system (Figure 15).

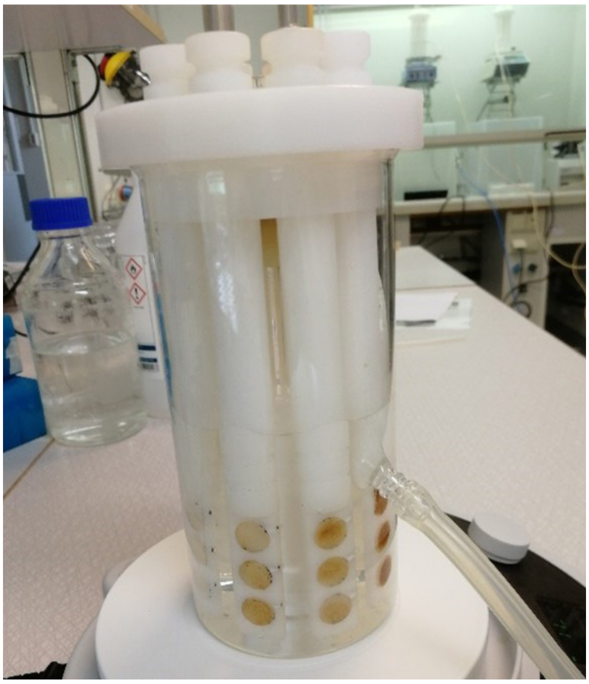


FIGURE 14. Multiple samples can be analysed simultaneously in the water biofouling bioreactor.

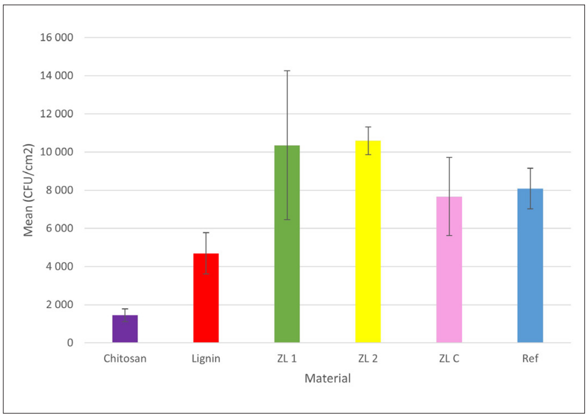


FIGURE 15. Inhibition of biofilm build up with E. Coli of several chemically modified PEX surfaces (n=3 on each, Ref=control unmodified surface).

This work is being continued using funding from the programme's strategic reserve, where the focus will be on understanding the properties of lignin which are involved in the anti-fouling effects, such as surface charge, position, and the number of phenolic groups, to optimise the activity of this material further.
In the second area of research, ultrafiltration membranes with potentially enhanced antifouling and antibacterial properties were prepared using phase inversion and incorporation of cellulose nanocrystals

(CNCs), which potentially improve the antifouling properties of membranes due to their hydrophilic nature. The work has developed formulations with increasing CNC concentration in commercial cellulose acetate solutions, provided by Alfa Laval, which have been successfully used as a coating for commercial PET substrates, followed by phase inversion, using water as non- solvent (Figure 16). The CNC content had a positive effect on water flow, as CNC/CA coated membranes had a better flow than the coating itself without CNC.

Due to their use in the dairy industry, where milk filtration is associated with biofouling by milk proteins. The anti-biofouling properties of this treatment were initially studied using a protein solution of bovine serum albumin (BSA), which demonstrated a >90% inhibition of adsorption of the protein to the membranes without increased resistance in flow across the membrane. Additionally, the membranes were stored aseptically in water for up to one month showed no biological film development. As these membranes are considered promising for potential scale-up, further investigations are planned to characterize the nature of the anti-biofouling function of CNCs and its longevity of activity on the membranes.

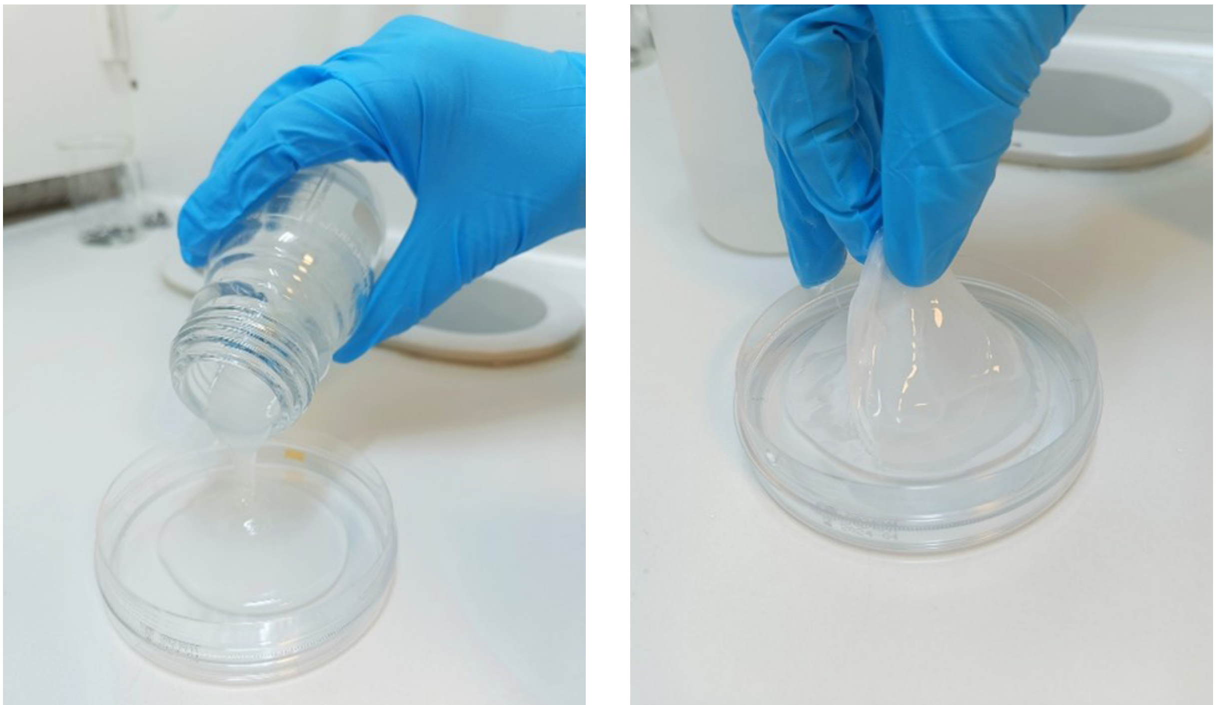


FIGURE 16. Photographs showing the processing of cellulose acetate and cellulose nanocrystals-based phase inversion membrane with antifouling properties (activities at Stockholm University in collaboration with Alfa Laval).

CASE STYDY PACKAGE 4: PHARMA

CSP 4 Leader: Ian Cotgreave, RISE

Involved partners: RISE; KTH; AstraZeneca; Stockholm Water Technology, Radma Carbon

Key questions and scope

The case study focuses on the use of a variety of techniques and materials in the removal of highly potent active pharmaceutical ingredients (APIs) from wastewater streams at the AstraZeneca wastewater treatment plant in Gärtuna. The case study is divided into work performed with spiked solutions at a laboratory scale and attempts to transfer to a small pilot scale on-site. The experimental work also rests on the development of appropriate chemical analysis techniques for the APIs in various water-based matrices.

The capacitive deionisation technology (CDI) from Stockholm Water Technology (SWT) is primarily in focus, but some work has been performed with the Axolot flocculation material, as well as the Radma Carbon material. These studies are at an early stage and will not be reported further here.

Progress and achievements during 2023

The case study on active pharmaceutical ingredient (API) removal from AstraZeneca waste process water has focused almost exclusively on performance testing CDI on site within the AstraZeneca plant at Gärtuna. The CDI approach (Figure 17) offers the ability to both "capture" agents using electrosorption, and "destroy" structures due to the electrochemical redox reactions elicited by reactive oxygen species within the equipment.

The work continues from the work of the previous year, which focused on proof-of-principle using lab scale apparatus, as shown (Figure 17) with the removal of three APIs from pure water using the lab scale flat-bed electrode system at KTH.

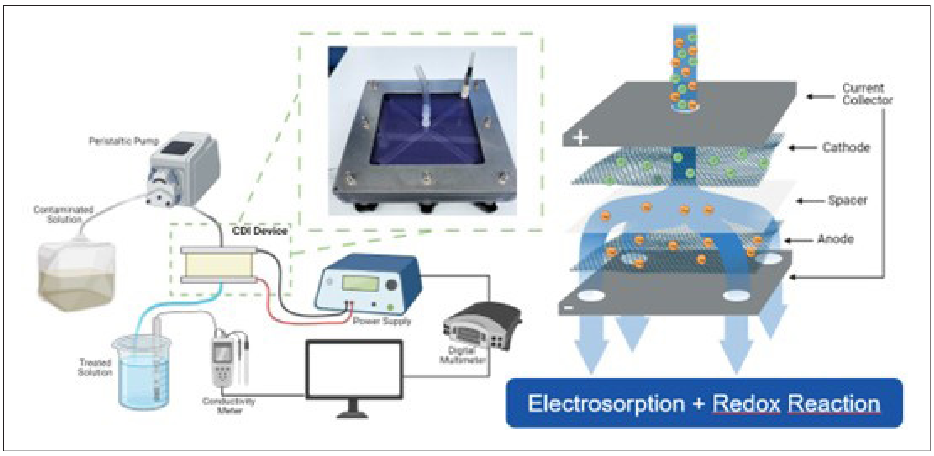


FIGURE 17.
Schematic of the CDI equipment, including a functional blow-up of the electrode structure.

Pilot scale experiments

Two rounds of pilot plant activities clearly demonstrate the scalability of the approach to industrial wastewater environments. In these experiments, RISE has functioned as coordinator for the case study and report compiler, as well as providing all technical support. SWT has provided the CDI test rig for the field trial at AstraZeneca and has supervised installment within the working environment, as well as providing technical support during each run of the rig. AstraZeneca has provided the working environment for the CDI test rig, as well as facilitating the sampling of water from various sections of the existing treatment line. The company has also supervised spiking experiments using process water, as well as sample collection and shipping for analysis. Furthermore, they have provided information on selected APIs where necessary. KTH has provided support to the interpretation of the results generated within the pilot experiments.

The experimentation focuses on testing the CDI approach against standard poly-aluminium chloride (PAC), at two specific stages in the AstraZeneca's cleaning process. This involves either the PAC pretreatment step, which is commonly used for certain applications, or a later stage use of PAC after bacterial treatment, in so-called final polishing.

The equipment was placed within the process environment near to the existing process plant equipment, and consisted of the CDI plant, coupled to three reservoirs (Figure 18).

The pilot studies focused on demonstrating the effectiveness of simultaneous removal of up to 21 selected active pharmaceutical ingredients (APIs), known to be common in the wastewater. These include Omeprazole/Pyrmetazol, Metformin and Metoprolol, as previously utilized in laboratory scale work, with the other structures remaining undisclosed at the request of AstraZeneca. The analytical approaches for the APIs have been developed by

FIGURE 18. The CDI test rig placed in Building B650 at the AstraZeneca Gärtuna site. From the left, the collection tank, CDI unit, reject tank (smaller tank behind the CDI unit) and the test water tank.

RISE and involve appropriate LC-MS/MS methods, coupled to water pretreatment by microfiltration. In the first experiment, the APIs were tested at the levels at which they constitutively occur, based on historical data from AstraZeneca. In the second pilot study, process water was spiked with up to 18 of these APIs in combination as the initial pilot study revealed that background levels of some of the APIs were under the detection limits for the individual APIs on the analytical platform.

Results of the CDI pilot studies

Ambient levels of APIs

The initial pilot revealed between 75 and 100% removal of those APIs which were present at detectable ambient levels in water taken from the last stage for "polishing". For four APIs, the removal was superior to the conventional PAC treatment. Even at concentrations 1000-fold higher than those previously used in laboratory scale work, the CDI rig removed the APIs, but with proportionately lower efficiency under the standard conditions of the test.

Spiked levels of APIs

In this series of experiments, the water was spiked with the APIs to levels that bring them up to or above the levels used in laboratory-scale experiments. In the case of this complex mixture in of APIs, the CDI rig demonstrated the efficient reduction of all 18 measured APIs, ranging from the lowest, Metformin (72%), to the highest for the other APIs (>99%). In most cases the removal efficiencies, in terms of percent of the initial concentrations, were in parity with the traditional PAC method used in the AstraZeneca process. However, one structure was removed less efficiently and in the case of two others, including Metformin, the CDI method provided considerably better performance.

General conclusions from the CDI pilot experiments

The CDI treatment performs well in parity with conventional PAC treatment, with some superiority for Metformin and one other API. In general, the efficiency is higher in water of higher purity, which indicates that the eventual application would be as a polishing treatment close to the end of the process. It is not clear from the experiments if only electrosorption has been operative in the results, as the analyses were not targeted towards identification of potential break-down products. Further, the application of the process has not been optimised in terms of the time of running and regeneration of the electrodes during the process.

Thus, further work is required with selective APIs to demonstrate both "capture" and "destruction", using non-target analysis of potential breakdown products. Further studies are also required on extending the CDI treatment and the potential effect of intermittent electrode regeneration. This work will finally indicate whether the CDI technology provides an attractive alternative to conventional treatments, with diminished liabilities and hazards from the current PAC-based waste concentrates.

CASE STUDY PACKAGE 5: AIR AND GAS

CSP 5 Leader: Hjalmar Granberg, RISE

Involved partners: RISE; Stockholm University; Uppsala University; KTH; IVL; Camfil; Svensk Ventilation; Humlegården; Avanzare; Bright Day Graphene; Sally R; Insplorion

Key questions and scope

The principal purpose is to design and evaluate the sorbents used for the removal of SOx and NOx in applications with low concentrations for indoor air, as defined by the providers of ventilation solutions and users, typically in the ppb range up to 1 ppm.

For indoor air applications, the removal of SOx, and NOx is challenging, as SO_2 influences the efficiency of the NOx removal. In, for example, an adsorbent media impregnated with a base, the presence of SO_2 would cause the premature desorption of NO_2 and NO. A system on which SOx and NOx are co-adsorbed is preferred.

Progress and achievements during 2023

Considerable effort was made to find relevant sites for gas adsorption case studies. Recent studies have revealed that volatile organic compounds such as formaldehyde may impact the yield in IVF clinics and may cause considerable suffering for the involved customers. Isopropanol and aceton in the air at silicon processing sites need to be removed for the working environment of the personnel and low-cost solutions to solve this problem are sought. SOx and NOx can cause metal corrosion in server halls and hence reduce the life of their servers. Work is ongoing to find a good locality to test and show the results obtained within CSP5.

CSP5 has several activities targeting the addition of adsorbents in films and filter papers. Here, functional surface coatings based on silica nanoparticles, with amine groups added in a second step, were prepared on filter paper (see more details in section WP1). To create a large surface area for gas adsorption it can be advantageous to use silica nanoparticles, since they are commercially available, low cost and can be applied to paper-based filters. The prepared surface-coated filter papers were tested for gas adsorption of SO_2 and formaldehyde at Camfil, and NO_2 at IVL.

For SO_2 and formaldehyde gas adsorption, high removal efficiencies were noted initially for the silica + amine coated papers (100% and 85% for SO_2 and formaldehyde respectively, see Figure 19 for formaldehyde). The reason for the initial high adsorption followed by a decrease to a low level after ca 200 min, is most likely that the available amine surface groups get filled during the filtering of the gas. For NO_2 gas adsorption at IVL, we noted a similar trend with high initial efficiency.

Work is also progressing on the preparation of structured films comprising particulate activated carbons (AC) bound together with small ratios of cellulose nanofibers (<20%). The structured AC films were successfully stacked together and exposed to different gases. Initial trials indicate that CO_2 gas uptake in the AC films is comparable to the AC particles not bound together into films. This opens for engineering the geometry of the filtering media without compromising its efficiency. It also opens the possibility to design the sweet spot between pressure drop, filtering capacity and diffusion dynamics given by the require-

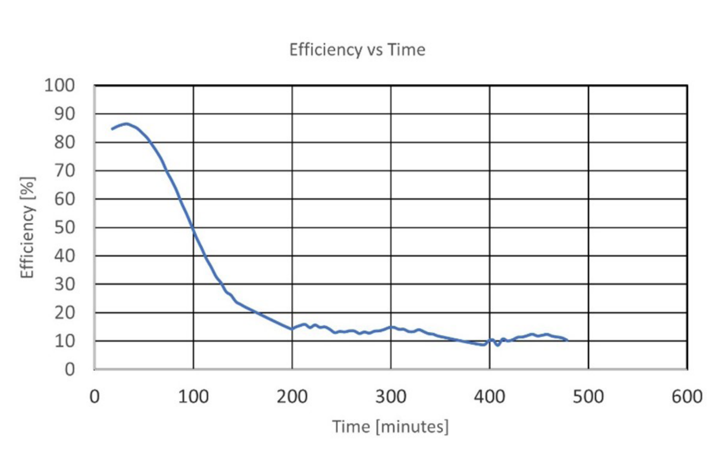


FIGURE 19. Removal efficiency data for formaldehyde gas adsorption trials on amine-coated silica-impregnated filter papers at Camfil.

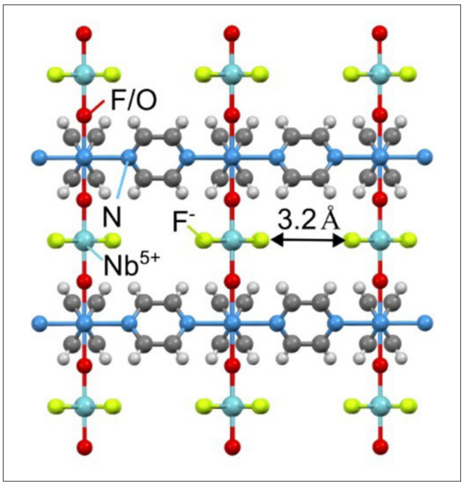


FIGURE 20. Structural representation of the ultra microporous material (HUM) named KAUST-7, with the F - - F distance highlighted.

ments for each specific case. A mathematical model is prepared to better understand the parameters that dictate the basic cost-performance parameters of such stacked film gas filters. The model is currently being compared to real data to determine its applicability and predictability.

Solid oxides and metal-organic frameworks were further explored and optimized for the adsorption of CO_2 and SF_6. Firstly, novel sodium hafnium oxide (Na_2HfO_3) was synthesized by us, structured by 3D printing, and tested its CO_2 sorption properties at high temperatures. We found that Na_2HfO_3 can adsorb CO_2 in high-temperature applications with good stability. Secondly, gallium and vanadium-based novel MOFs first synthesized by us showed enhanced interaction and good uptake of the greenhouse gas SF_6. Pore size optimization of these MOFs allowed us to tune the adsorption properties and target different gases.

Thirdly, hybrid ultra-microporous materials (HUMs) named KAUST-7 were investigated as a potential sorbent for direct air capture of CO_2 (Figure 20). We tuned the pore size of this material by inorganic pillar substitution. We found that tuning the pore size of this type of HUM by replacing the inorganic units can be used to effectively affect the diffusion rate of CO_2 gases as well as the strength of the CO_2 sorption. Furthermore, the extremely high CO_2 selectivity of this material may allow us to further develop them for CO_2 capture from other low-concentration sources, or for biogas upgrading (Figure 21).

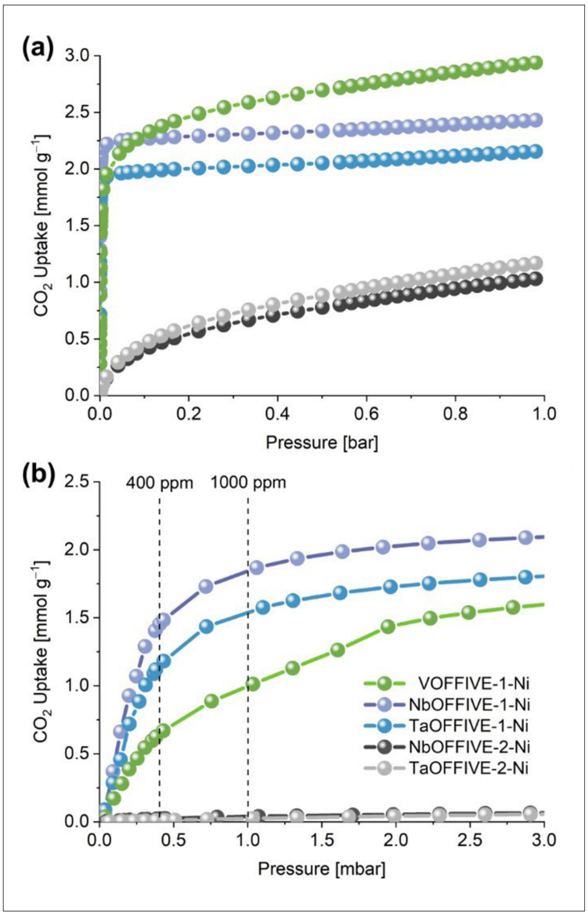


FIGURE 21. The CO_2 sorption isotherms of the isoreticular samples; VOFFIVE-1-Ni, NbOFFIVE-1-Ni, TaOFFIVE-1-Ni, NbOFFIVE-2-Ni, and TaOFFIVE-2-Ni (a) from 0 to 1 bar at 293 K (b) from 0 to 3 mbar at 293 K.

CASE STUDY PACKAGE 6: MICROPLASTICS

CSP 6 Leader: Sven Norgren, MoRe

Involved partners: Stockholm University; KTH; RISE; IVL; MoRe; Mimbly

Key questions and scope

One of the major indentified sources of microplastics in Sweden are particles generated in washing machine effluents. Early capture, and water-phase capture will lower the risk of particles becoming airborne and the risk of particle down-sizing.

CSP6 is addressing the treatment of microplastic-containing water from household washing machines and laundries with biobased filters.

Progress and achievements during 2023

In this CSP, Mimbly has engaged actively during 2023 and has provided the specifications for making units that can be used in the washing machines and they have also carried out washing trials with fleece, so the project has some washing machine effluents to study (Figure 22).

Literature studies conducted on microplastics have been summarized in a review "Strategies towards micro-/nanoplastics-free environment: Insights into tailored chemical approaches for their elimination" lead by postdoctoral researchers. This review gives an overview of the definitions, and different physical and chemical characteristics of the different size classes

FIGURE 22. New fleece was washed to make a washing machine effluent filled with microplastics. In the end of the project, we hope to have a non-fossil based filter that works excellent in the device that are putted into Mimbly's machines (to the right in the pictures above).

of plastics (macroplastics, microplastics, and nanoplastics). It discusses various detection and analysis techniques ranging from simple ways to sophisticated instrumentation, followed by existing and upcoming microplastic capture by methods such as membrane filtration, coagulation, adsorption, and so on. Lastly, it outlines the degradation processes, summarizing the gaps and scopes.

The team at Stockholm University developed and published on the synthesis of polylactic acid (PLA) – based composites reinforced with homogenously dispersed TEMPO-oxidized cellulose nanofibers (TCNF) or chitin nanofibers (ChNF). The 3D-printed monolithic, bio-composite filters were able to adsorb metal ions, and to reject microplastics from the water. The filters can be recycled and reused multiple times for the removal of microplastics from contaminated laundry water.

We have also developed similar 3D-printed filters using filaments based on waste textiles (Figure 23).

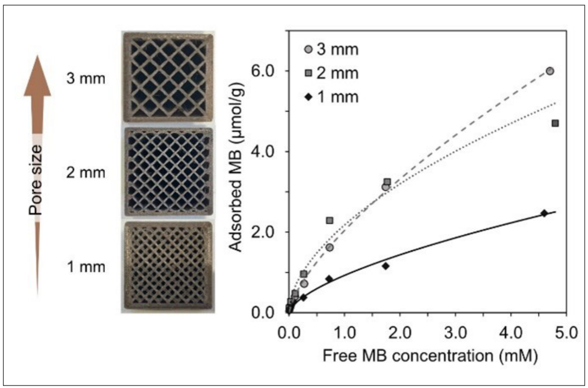


FIGURE 23. Textile-based 3D printed filters with tuneable porosity and adsorption isotherm for MB removal from water.

Here the TEMPO-functionalized nanofibers embedded in a polyester matrix functioned as adsorbent for dyes (Methylene blue used as model cationic dye). A manuscript reporting, synthesis, characterization, and dye removal has been submitted. This will be further studied for microplastic removal using water samples provided by Mimbly for microplastics removal evaluation.

Although our first target is in the removal of microplastics from laundry effluents, this system can be promising for the removal of other pollutant species, such as metal ions. However further work is required to expand the applications of the 3D filters to a broader area.

During the year some discussions were carried out with Mimbly on utilizing the 3D printed filters in a pilot scale study at Mimbly. Plans were made to provide the specifications for producing 3D printed units that can be used in the washing machines.

SCIENTIFIC OUTPUT AND OUTREACH ACTIVITIES

PUBLICATIONS

Al Soubaihi, R. M., Saoud, K. M., Dutta, J. (2023) Low-Temperature Co Oxidation by Silver Nanoparticles in Silica Aerogel Mesoreactors. Chemical Engineering Journal, 455, 140576. https://dx.doi.org/10.1016/j.cej.2022.140576

Chang, R., Åhlén, M., Cheung, O. (2023) Structural Tuning of Fluorinated Hybrid Ultramicroporous Materials (HUMs) for Low-Concentration CO_2 Capture. ChemRxiv, February 14. https://doi.org/10.26434/chemrxiv-2023-69g0g

Chang, R., Åhlén, M., Strømme, M., Cheung, O. (2023) Flue Gas CO_2 Capture with Hybrid Ultramicroporous Materials (HUMs). ChemRxiv, November 30. https://doi.org/10.26434/chemrxiv-2023-7gdss

Chang, R., Cheung, O., Menon, A., Grape, E. S., Broqvist, P., Inge, A. K. (2023) Deciphering the Existence of Hexagonal Sodium Zirconate CO_2 Sorbent. ChemRxiv, July 18. https://doi.org/10.26434/chemrxiv-2023-4c69m

Chang, R., Svensson Grape, E., Clairefond, T., Tikhomirov, E., Inge, A. K., Cheung, O. (2023) Synthesis and Characterization of Sodium Hafnium Oxide (Na2HfO3) and Its High Temperature CO_2 Sorption Properties. Journal of Material Chemistry A. 11, 7617-7628 https://doi.org/10.1039/D3TA00415E

Cheung, O., Åhlén, M., Chang, R., Strømme, M. (2023) Visible Light-Triggered Desorption of CO_2 in Green Coordination Polymers. ChemRxiv, November 30. https://doi.org/10.26434/chemrxiv-2023-n0lnl

Cheung, O., Åhlén, M., Ahlberg, E., Nehla, P., Salazar-Alvarez, G., Ershadrad, S., Sanyal, B., Öhrström, L. R. (2023) A Hexagon Based Mn (II) Rod Metal-Organic Framework–Structure, SF6 Gas Sorption, Magnetism and Electrochemistry. Chemical Communications 59, 2106-2109. https://doi.org/10.1039/D2CC06916D

Fijoł, N., Aguilar-Sánchez, A., Ruiz-Caldas, M., Redlinger-Pohn, J., Mautner, A., Mathew, A., P. (2023) 3D printed polylactic acid (PLA) filters reinforced with polysaccharide nanofibers for metal ions capture and microplastics separation from water, Chemical Engineering Journal, 457, 2023, 141153, https://doi.org/10.1016/j.cej.2022.141153https://doi.org/10.1016/j.cej.2022.141153

Georgouvelas, D., Nasser Abdelhamid, H., Edlund, U., Mathew A.P. (2023) In-situ modified nanocellulose/alginate hydrogel composite beads for purifying mining effluents. Nanoscale Advances, 5, 5892–5899. https://doi.org/10.1039/D3NA00531C

Hao, W., Shi, Y., Ullah, L., Li, R., Hedin, N. (2023) Effects of the Ion-Exchange Sequence on the CO_2 Uptake and CO_2–over–N2 Selectivity of Zeolite NaKA. Sustainable Chemistry for Climate Action, 3, 100030. https://doi.org/10.1016/j.scca.2023.100030

Metem, P., Toledo-Carrillo, E., Ye, F., Dutta, J. (2023) Enhanced Electrocatalytic Conversion of Nitrates to Ammonia: Fuel from Waste. ChemSusChem n/a (n/a), e202301570. https://doi.org/10.1002/cssc.202301570

Mohammad Al Soubaihi, R., Mohammad Saoud, K., Dutta, J. (2023) Low-Temperature CO Oxidation by Silver Nanoparticles in Silica Aerogel Mesoreactors. Chemical Engineering Journal, 455, 140576. https://doi.org/10.1016/j.cej.2022.140576

Nasser Abdelhamid, H., Sultan, Sahar, Mathew, A.P. (2023) 3D printing of cellulose/leaf-like zeolitic imidazsolate frameworks (CelloZIF-L) for adsorption of carbon dioxide (CO_2) and heavy metal ions. Dalton Transactions, 52, 2988. https://pubs.rsc.org/en/content/articlelanding/2023/dt/d2dt04168e

Nasser Abdelhamid, H., Sultan, Sahar, Mathew, A. P. (2023) Three-Dimensional Printing of Cellulose/Covalent Organic Frameworks (CelloCOFs) for CO_2 Adsorption and Water Treatment. ACS Applied materials and Interfaces, 15 (51), 59795–59805. https://doi.org/10.1021/acsami.3c13966

Nasser Abdelhamid, H., Sultan, Sahar, Mathew, A.P. (2023) Binder-free Three-dimensional (3D) printing of Cellulose-ZIF8 (CelloZIF-8) for water treatment and carbon dioxide (CO_2) adsorption. Chemical Engineering Journal, 468, 143567. https://www.sciencedirect.com/science/article/pii/S1385894723022982

Nordstrand, J., Toledo-Carrillo, E., Dutta, J. (2023) Tuning the Cation/Anion Adsorption Balance with a Multi-Electrode Capacitive-Deionization Process. Journal of the Electrochemical Society, 170 (2), 023502. https://doi.org/10.1149/1945-7111/acb84c

Nordstrand, J., Dutta, J. (2023) Potential-Driven Mechanisms for Raising the Intercalation Selectivity 100-Fold in Multi-Ion Removal from Water. Desalination 565, 116865. https://dx.doi.org/10.1016/j.desal.2023.116865

Saadattalab, V., Wu, J., Tai, C.-W., Bacsik, Z., Hedin, N. (2023) Adsorption of Volatile Organic Compounds on Activated Carbon with Included Iron Phosphate. Carbon Trends, 11, 100259. https://doi.org/10.1016/j.cartre.2023.100259

Svensson Grape, E., Chacón-García, A. J., Rojas, S., Pérez, Y., Jaworski, A., Nero, M., Åhlén, M., Martínez-Ahumada, E., Galetsa Feindt, A. E., Pepillo, M., et al. (2023) Removal of Pharmaceutical Pollutants from Effluent by a Plant-Based Metal–Organic Framework. Nature Water, 1 (5), 433-442. https://doi.org/10.1038/s44221-023-00070-z

Wang, X., Hao, W., Hedin, N. (2023) Colloidally Dispersible Activated Carbons and Yarn-like Colloidal Assemblies of Hydrochar. JCIS Open, 11, 100090. https://doi.org/10.1016/j.jciso.2023.100090

Yu, D., Basumatary, I. B., Kumar, S., Ye, F., Dutta, J. (2023) Chitosan Modified with Bio-Extract as an Antibacterial Coating with UV Filtering Feature. International Journal of Biological Macromolecules 230,123145. https://dx.doi.org/10.1016/j.ijbiomac.2023.123145

Zhang, X., Alvarado-Ávila, M. I., Liu, Y., Yu, D., Ye, F, Dutta, J. (2023) Self-Sacrificial Growth of Hierarchical P (Ni, Co, Fe) for Enhanced Asymmetric Supercapacitors and Oxygen Evolution Reactions. Electrochimica Acta 438,141582. https://dx.doi.org/10.1016/j.electacta.2022.141582

Zhou, X. Shen, B., Lyubartsev, A., Zhai, J., Hedin, N. (2023) Semiconducting Piezoelectric Heterostructures for Piezo- and Piezophotocatalysis. Nano Energy, 96, 107141. https://doi.org/10.1016/j.nanoen.2022.107141

Wu, X., Chang, R., Tan, M., Tao, L., Fan, Q., Hu, X., Tan, H. L., Åhlén, M., Cheung, O., Liu, W. (2023) An Investigation of the Ni/Carbonate Interfaces on Dual Function Materials in Integrated CO_2 Capture and Utilisation Cycles. Applied Catalysis B: Environment and Energy, 338, 123053. https://doi.org/10.1016/j.apcatb.2023.123053

Åhlén, M., Cheung, O., Xu, C. (2023) Low-Concentration CO_2 Capture Using Metal-Organic Frameworks–Current Status and Future Perspectives. Dalton Transactions, 52, 1841-1856. https://doi.org/10.1039/D2DT04088C

Åhlén, M., Zhou Y., Hedbom D., Cho H.S., Strømme M., Terasaki O., Cheung O. (2023) Efficient SF6 capture and separation in robust gallium- and vanadium-based metal-organic frameworks. Journal of Materials Chemistry A 11, 26435-26441 https://doi.org/10.1039/D3TA05297D

PATENT APPLICATION

Sandberg, M., Beni, V., Wijeratne, K., 2023-01-19, Porous Material. Patent Application WO2023285146A1 / WO2023285146A1, https://worldwide.espacenet.com/patent/search/family/082492517/publication/WO2023285146A1?q=EP2022067901

REPORTS

Nilsson, C. Toxicological health hazard evaluation of amines (CSP5). Internal report delivered to CSP5, October, 2023.

Nilsson, C. Toxicological information (CSP3). Internal report delivered to CSP3, October 2023.

Alvarado Ávila, M. (2023) PFAS Update report experiment 1 from KTH Functional and NanoMaterials Group, Mistra TerraClean internal report.

Alvarado Ávila, M. (2023) PFAS Update report experiment 2 from KTH Functional and NanoMaterials Group, Mistra TerraClean internal report.

Liliestråle, M. (2023) Magnetically Activated Carbon (MAC) Stage 2, Mistra TerraClean internal report.

Cotgreave, I. MTC CSP4/2023, Report to the Board concerning progress in 2023 Mistra TerraClean internal report.

CONFERENCES

Göksu Cinar Cifti, Jing Ai, Wei Zhao, Karin Hallstensson, Zoltan Bacsik, Niklas Hedin, Abhilash Sugunan (2023) "Smart Materials for Adaptable and Reversible Chemisorption of Indoor Carbon Dioxide". Poster presentation, Gordon Research Conference on Carbon Capture Utilization and Storage, May 2023.

Jing Ai, Zoltan Bacsik, Niklas Hedin (2023) "Environmental applications of bone char". Poster presentation. Biochar Summit on June 13-14 in Helsingborg, 2023.

Mats Sandberg, European Materials Research Society Spring 2023, May 29 – June 2, 2023. "Novel functionalized porous carbons as sensor-absorbents for water purification applications". Oral presentation.

Steffen Schellenberger, FLUOROS 2023, August 31 – September 1, 2023. "Novel post-treatment technologies for poly- and perfluoroalkyl substances (PFAS) and the application of a lifecycle-based risk mapping (LCBRM)", Poster spot presentation.

POPULAR SCIENCE AND OUTREACH

U. Edlund, Popular science lecture 'Smarta material för renare vatten' at 'Forskarfredag' (Part of European Researchers' Night), 2023.

MASTER THESES

H. Tefasse Belachew (2023) KTH. "Surface modification of crosslinked polyethylene to prevent biofouling". https://www.diva-portal.org/smash/record.jsf?pid=diva2:1777458

DOCTORAL THESES

J. Nordstrand (2023) KTH. "At the Mountains of Modeling: Multiscale Simulations of Desalination by Capacitive Deionization". https://kth.diva-portal.org/smash/get/diva2:1713552/FULLTEXT03.pdf

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