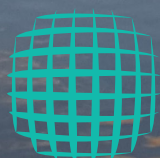


# Mistra TerraClean Annual Report 2023



MISTRA  
TERRACLEAN

# TABLE OF CONTENTS

Letter from the Board Chair.....	3
List of abbreviations.....	4
A Mistra TerraClean perspective on 2023.....	5
Introduction.....	7
Cost-effective solutions important for sustainability .....	8
Work Package 1: Materials.....	11
Work Package 2: Smart Filter design and validation.....	14
Work Package 3: Environmental and human health assessment.....	16
Work Package 4: Management, communication, and outreach.....	18
Case Study Package 1: Heavy metals.....	20
Case Study Package 2: PFAS and industrial water.....	23
Case Package 3: Microorganisms and fouling.....	26
Case Study Package 4: Pharma .....	29
Case Study Package 5: Air and gas.....	32
Case Study Package 6: Microplastics.....	34
Scientific output and outreach activities.....	36
Programme Participants.....	40
Programme Management .....	41

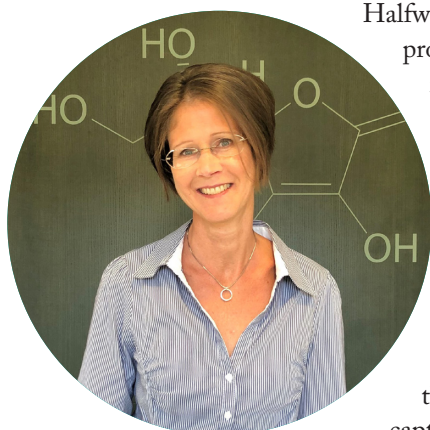


# LIST OF ABBREVIATIONS

<b>ACC</b>	Activated carbon cloth	<b>NMR</b>	Nuclear magnetic resonance
<b>AFM</b>	Atomic force microscopy	<b>PFAS</b>	Per- and polyfluoroalkyl substances
<b>AOP</b>	Advanced oxidation process	<b>PCR</b>	Polymerase Chain Reaction
<b>API</b>	Active pharmaceutical ingredient	<b>PEX</b>	Cross-linked polyethylene
<b>BET</b>	Brunauer–Emmett–Teller gas adsorption	<b>PFHxS</b>	Perfluorohexanesulfonic acid
<b>CDI</b>	Capacitive deionization	<b>PFOA</b>	Perfluorooctanesulfonic acid
<b>CFU</b>	Colony Forming Unit	<b>PFOS</b>	Perfluorooctane sulfonate
<b>COD</b>	Chemical oxygen demand	<b>PTFE</b>	Polytetrafluoroethylene
<b>CSP</b>	Case Study Package	<b>PVDF</b>	Polyvinylidene fluoride
<b>DOM</b>	Dissolved organic matters	<b>PoC</b>	Proof-of-Concept
<b>FPT</b>	Fibre and Polymer Technology	<b>PoP</b>	Persistent organic pollutant
<b>FTIR</b>	Fourier-transform infrared spectroscopy	<b>RT-PCR</b>	Reverse Transcriptase Polymerase Chain Reaction
<b>6:2 FTS</b>	6:2 Fluorotelomer Sulfonate	<b>REE</b>	Rare Earth Elements
<b>GAC</b>	Granular activated carbon	<b>RMP</b>	Risk Mitigation Plan
<b>GC/MS</b>	Gas chromatography/mass spectrometry	<b>SEM</b>	Scanning electron microscopy
<b>IKEM</b>	Innovations- och Kemiindustrierna i Sverige	<b>SME</b>	Small-medium enterprise
<b>ICP-OES</b>	Inductively coupled plasma-Optical emission spectroscopy	<b>SGU</b>	Statens Geologiska Undersökning
<b>LC/MS</b>	Liquid chromatography/mass spectrometry	<b>TEM</b>	Transmission electron microscopy
<b>LCA</b>	Life cycle assessment	<b>TRL</b>	Technology readiness level
<b>LCBRM</b>	Life cycle based risk mapping	<b>UF</b>	Ultrafiltration
<b>LCC</b>	Life cycle cost analysis	<b>VFE</b>	Viral Filtration Efficiency
<b>LCIA</b>	Life cycle impact assessment	<b>VOC</b>	Volatile organic compounds
<b>MAC</b>	Magnetic activated carbon	<b>WP</b>	Work Package
<b>MNF</b>	Material and nanophysics	<b>XPS</b>	X-ray photoelectron spectroscopy
<b>MOF</b>	Metal-organic framework	<b>XRD</b>	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, NO<sub>x</sub> gases, CO<sub>2</sub> 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.

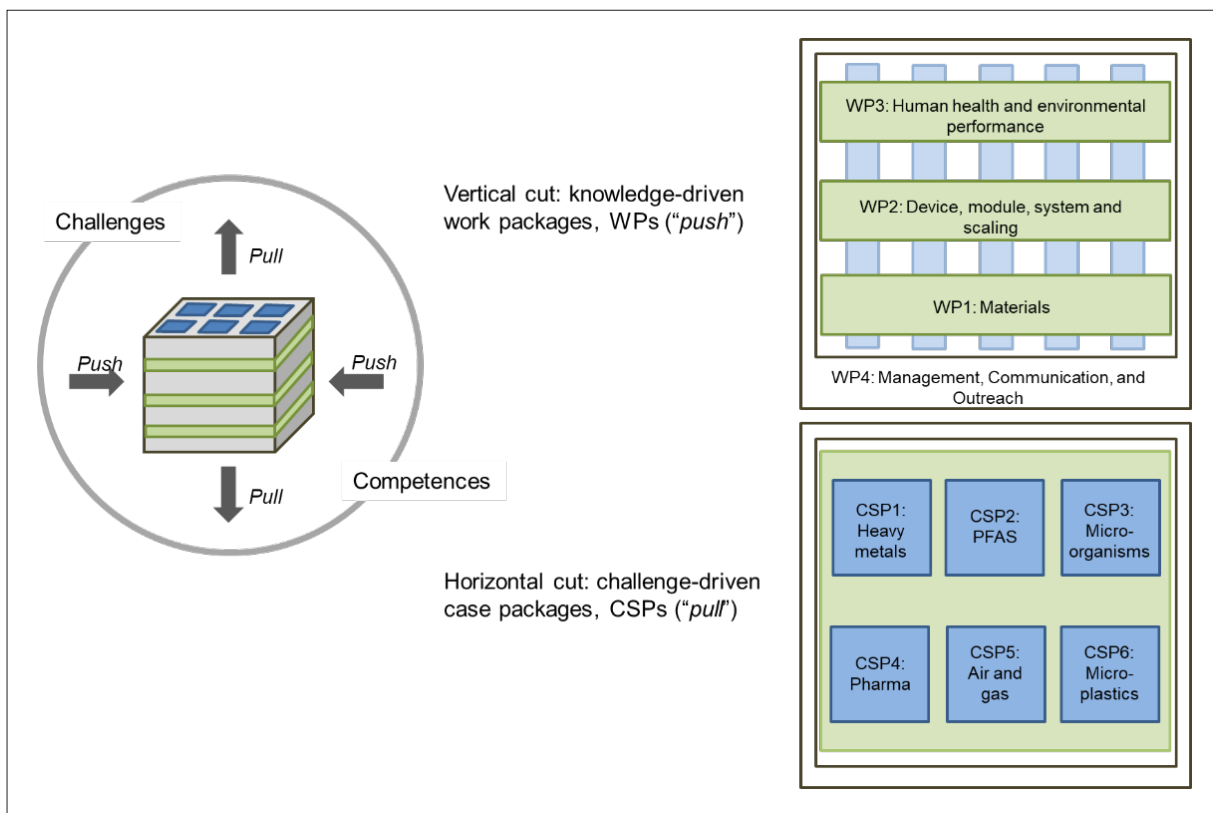


# INTRODUCTION

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 inter-disciplinary 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 background and affiliations.*

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

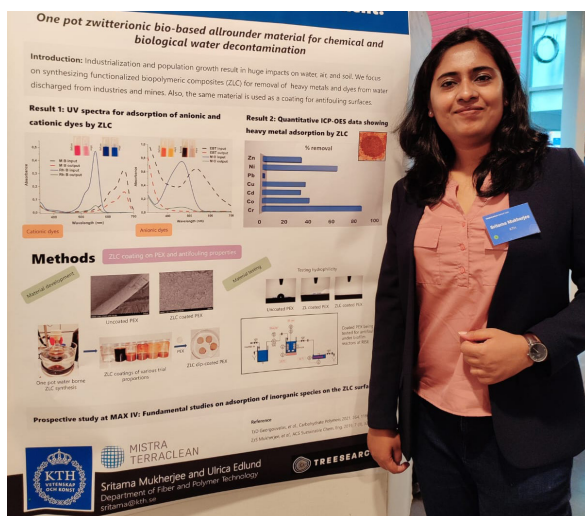
– I have been working on sustainable materials and composites for various applications, ranging from water treatment, sensors, bio-barriers to fire retardants, says Sritama. My interest lies in environmental impact assessment.

– 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.



# 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<sub>2</sub>. 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.

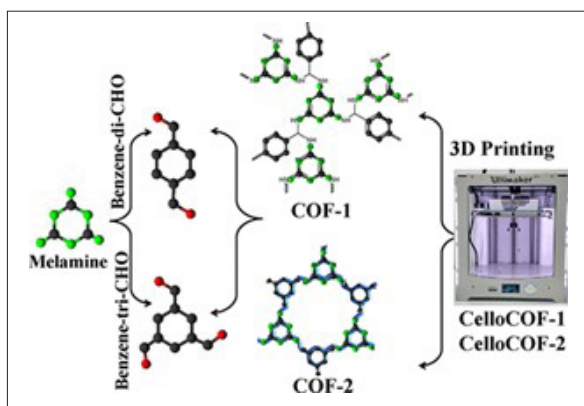
We synthesized a novel sodium hafnium oxide (Na<sub>2</sub>HfO<sub>3</sub>) by solid-state synthesis and found that its CO<sub>2</sub> sorption properties are high at high temperatures. The work has been published.

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  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ . 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  $\text{CO}_2$  chemisorption on aminated carbons. Various porous carbons were evaluated on  $\text{CO}_2$  adsorption with polyethyleneimine (PEI) modification. Films rich in carbon and aminated carbons have been prepared using cellulose nanofibrils as a structuring agent.

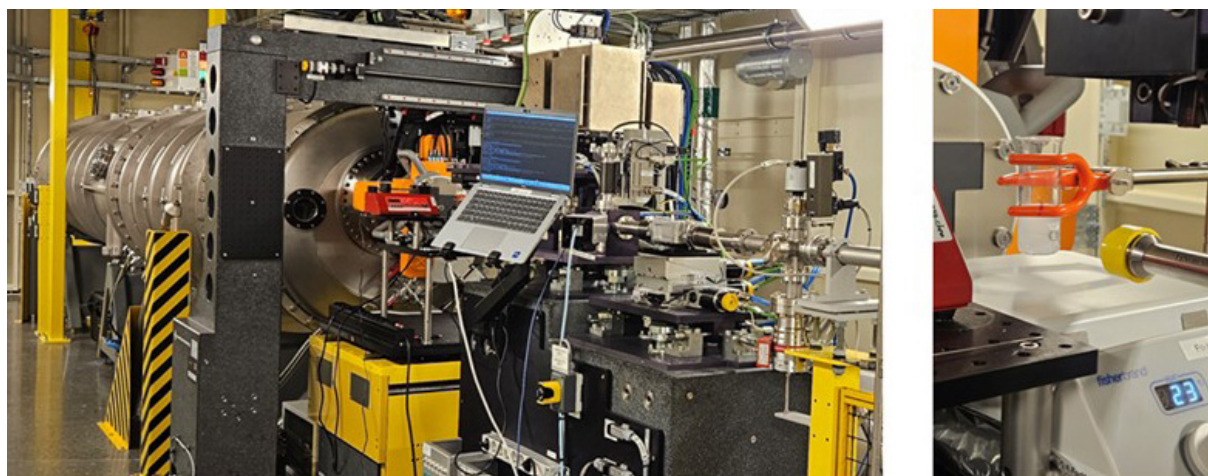
## Task 1.3 Lignocellulosic materials

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  $\text{CO}_2$  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.



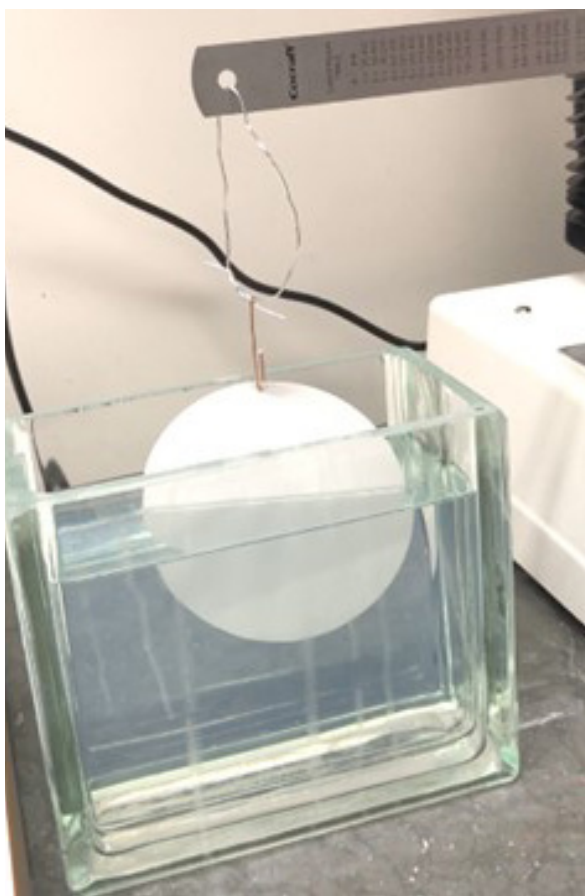
**FIGURE 3.** Photographs showing the experimental step at ForMAX beamline. A custom-built reactor was used to ensure adequate mixing and for preventing beam damage during the reaction time.



## 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<sub>2</sub>. 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<sub>2</sub> and SF<sub>6</sub>. The regulation of the pore structures of two very different adsorbents has been explored to tune the selection of CO<sub>2</sub> sorption. The mechanism of weakly-temperature-dependent CO<sub>2</sub> 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.





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.

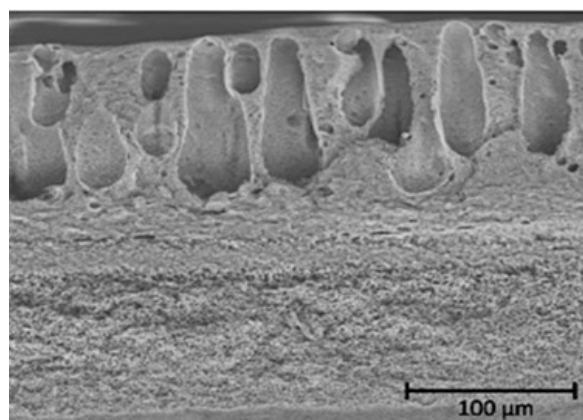
A more detailed workshop was held in March on techno-economical assessment describing the professional approaches and tools. A follow-up was made in October during the session "Techno-economic Assessment – System Boundaries to Visualizing Hotspots".

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 Mimby. 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<sub>2</sub> 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, COMMUNICA- TION, AND OUTREACH

**WP 4 Leader: KTH, Communication leader: IKEM**

**Progress and achievements during 2023**

## 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.

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.

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.



Together with Svenskt Vatten, we arranged an open seminar on the EU's Proposal for a revised Wastewater Treatment Directive in April. Various aspects of the said directive - pharmaceuticals, 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.



## 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.

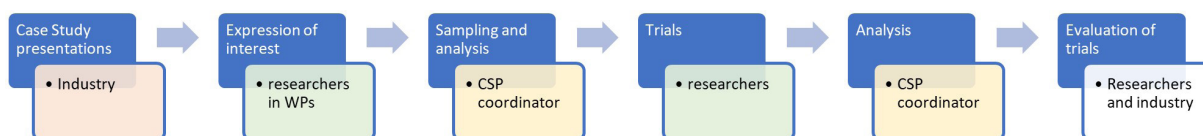


FIGURE 8. Process description for the stepwise engagement of mine operators and scientists in CSP1.

## Analysis

Water samples from different points in Lovisagravan 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 shows 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.

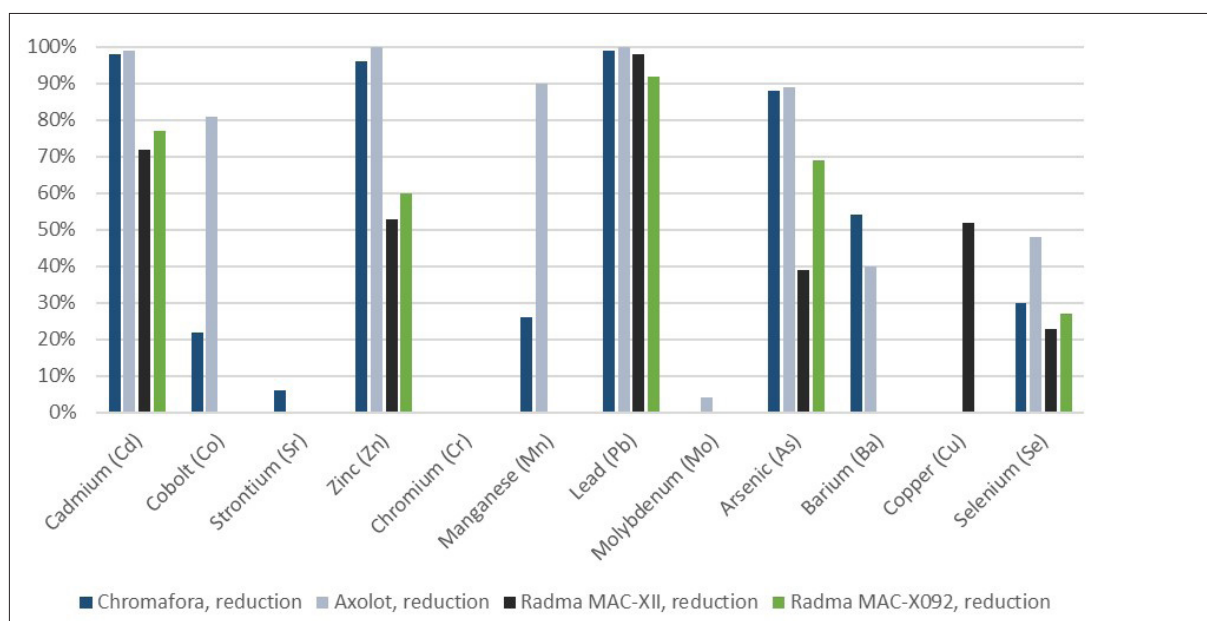
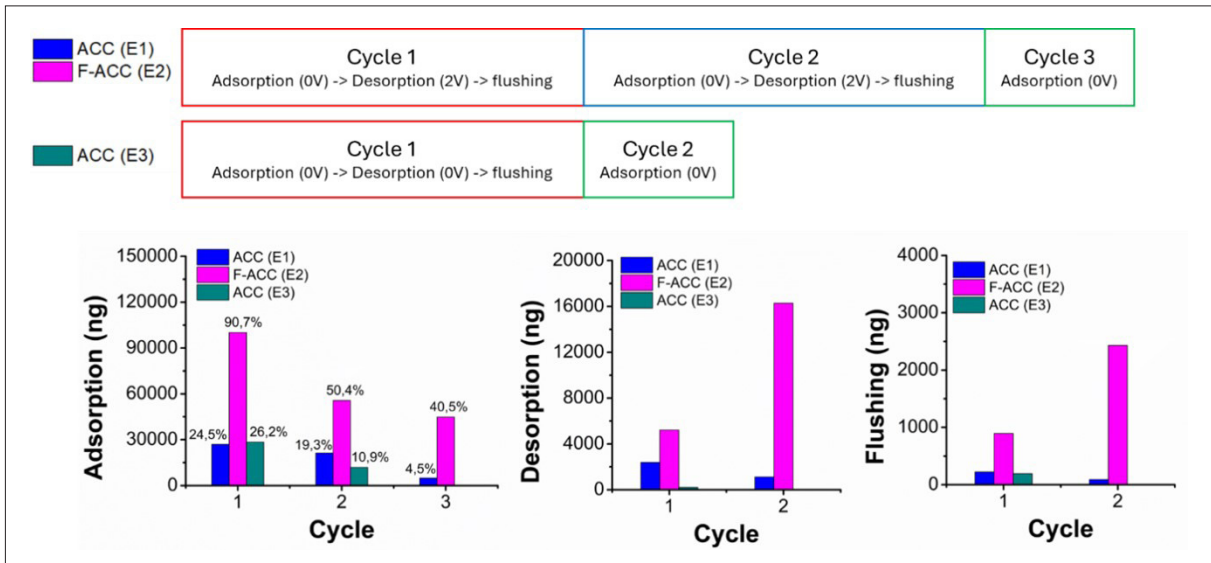


FIGURE 9. Reduction rates for various metals with different treatment methods.

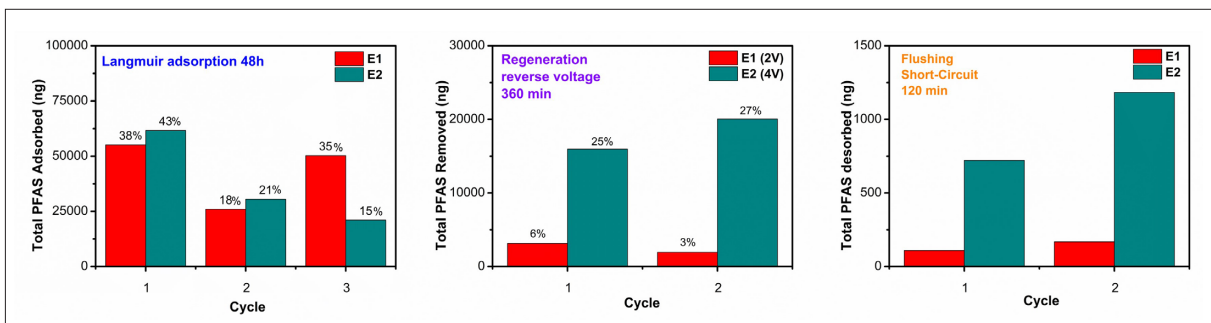




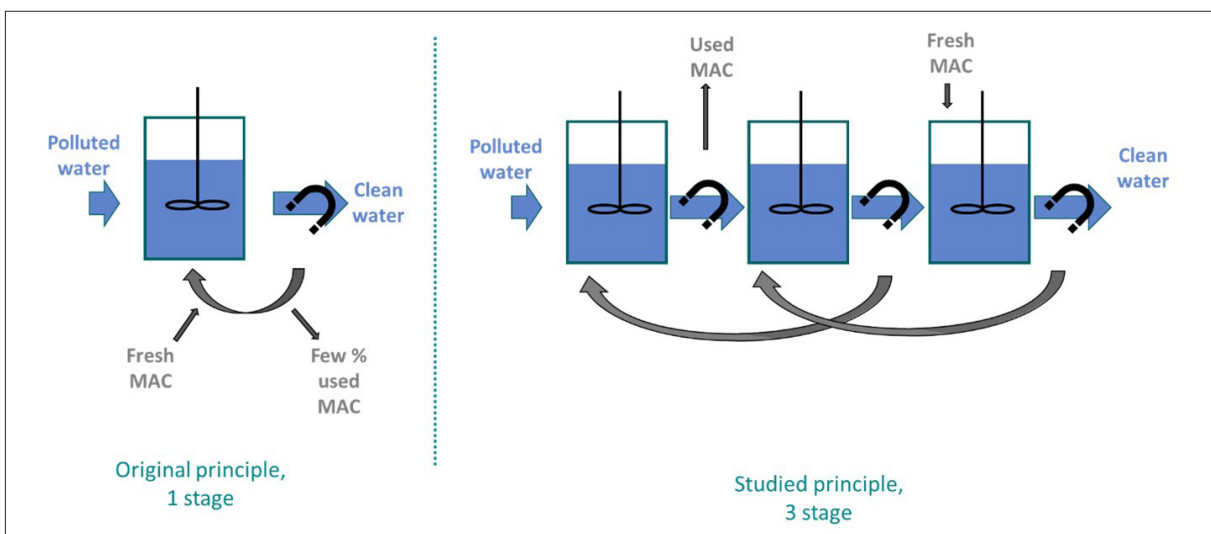




**FIGURE 10.** Experimental procedure (above) and results (below) for the first run of experiments. Numbers above the bars in the adsorption diagram show the PFAS removal efficiency.



**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.





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.

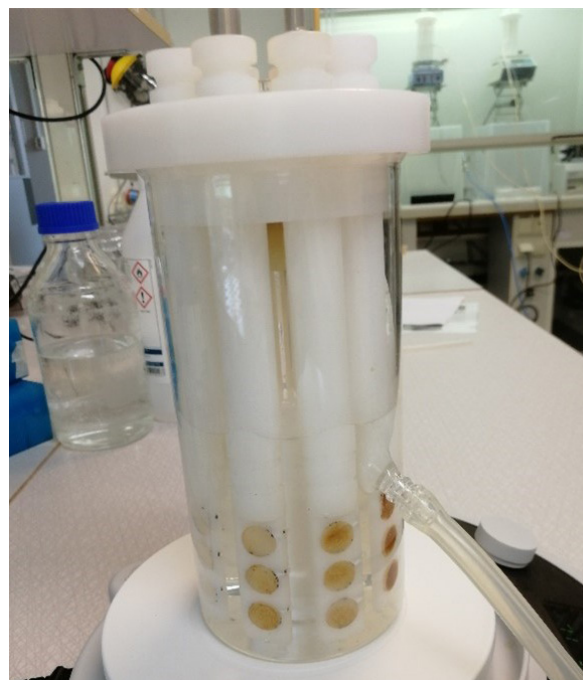
The bioreactor has also been adapted to use bacterial biofilms, created using both *Staphylococcus aureus* and *Escherichia coli* as probe organisms, both of which are associated with risks for infection. Here, initial work has focused on the use of photocatalytic illumination of ZnO-impregnated cellulose 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

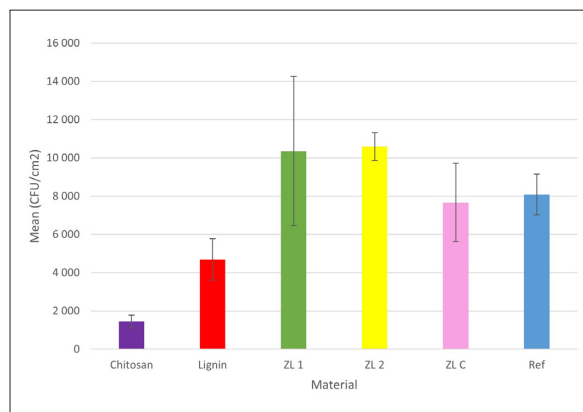
There are two areas of endeavor within this sub-case study, one involving the testing of chemically modifying the PEX material normally used in water pipe manufacturing (Uponor), and one involving modification of ultrafiltration membranes (Alfa Laval) with cellulose nanocrystals.

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





# CASE STUDY 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.

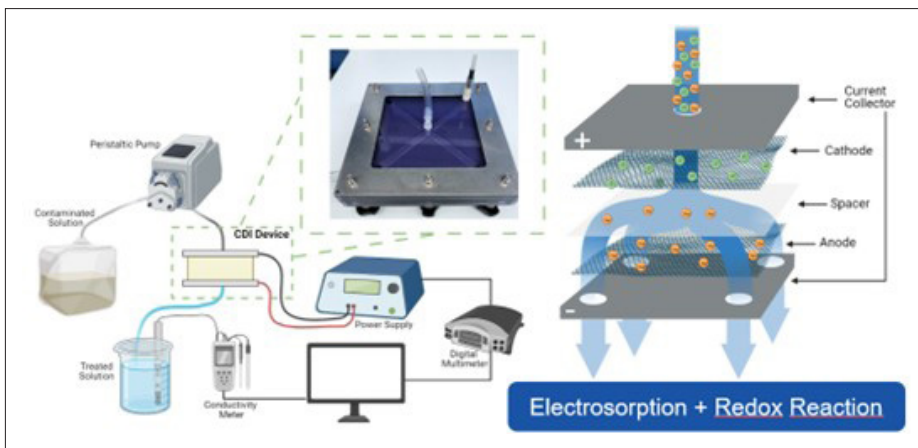
The capacitive deionisation technology (CDI) from Stockholm Water Technology (SWT) is primarily in focus, but some work has been performed with

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 pre-treatment 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/Pyrimetazol, 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; Insplosion*

### Key questions and scope

The principal purpose is to design and evaluate the sorbents used for the removal of SO<sub>x</sub> and NO<sub>x</sub> 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 SO<sub>x</sub> and NO<sub>x</sub> is challenging, as SO<sub>2</sub> influences the efficiency of the NO<sub>x</sub> removal. In, for example, an adsorbent media impregnated with a base, the presence of SO<sub>2</sub> would cause the premature desorption of NO<sub>2</sub> and NO. A system on which SO<sub>x</sub> and NO<sub>x</sub> are co-adsorbed is preferred.

### Progress and achievements during 2023

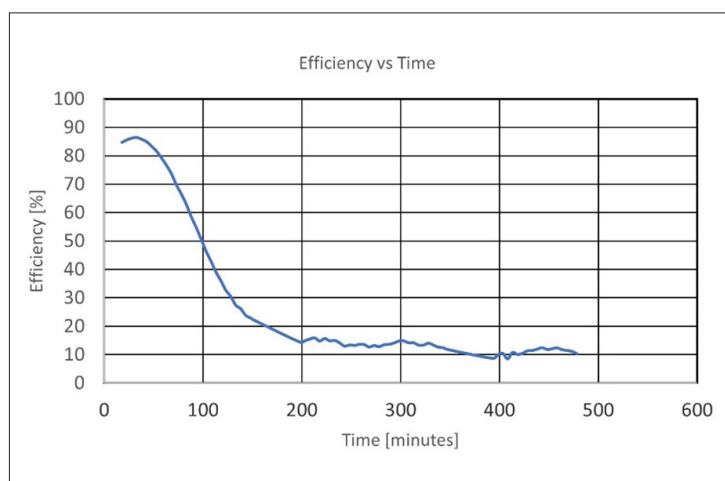
Considerable effort was made to find relevant sites for gas adsorption case studies. Recent studies have revealed that volatile organic compounds such as formaldehyde may impact the yield in IVF clinics and may cause considerable suffering for the involved customers. Isopropanol and acetone in the air 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. SO<sub>x</sub> and NO<sub>x</sub> 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.

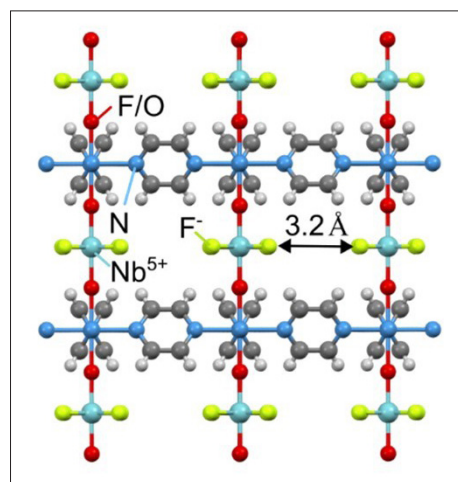
CSP5 has several activities targeting the addition of adsorbents in films and filter papers. Here, functional surface coatings based on silica nanoparticles, with amine groups added in a second step, were prepared on filter paper (see more details in section WP1). To create a large surface area for gas 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<sub>2</sub> and formaldehyde at Camfil, and NO<sub>2</sub> at IVL.

For SO<sub>2</sub> and formaldehyde gas adsorption, high removal efficiencies were noted initially for the silica + amine coated papers (100% and 85% for SO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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.

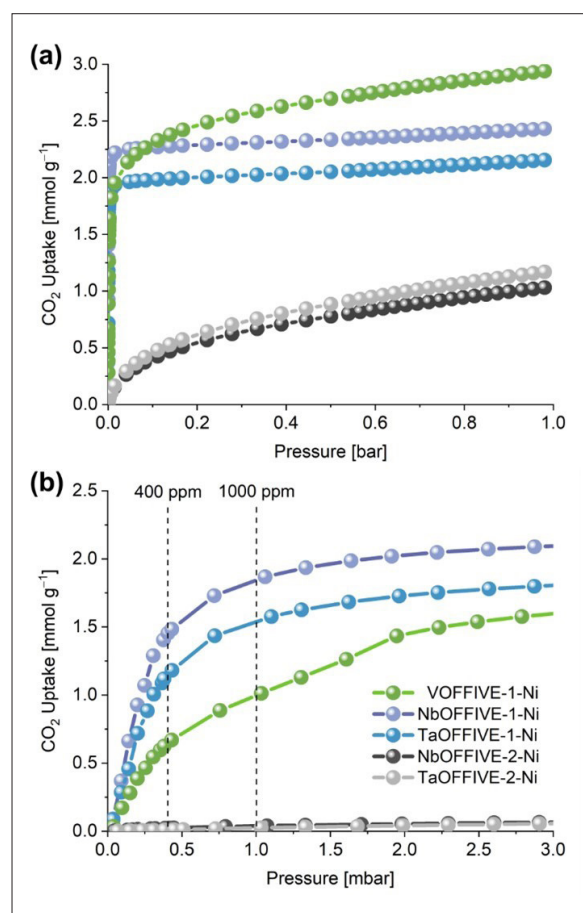


**FIGURE 20.** Structural representation of the ultra microporous material (HUM) named KAUST-7, with the F - F distance highlighted.

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  $\text{CO}_2$  and  $\text{SF}_6$ . Firstly, novel sodium hafnium oxide ( $\text{Na}_2\text{HfO}_3$ ) was synthesized by us, structured by 3D printing, and tested its  $\text{CO}_2$  sorption properties at high temperatures. We found that  $\text{Na}_2\text{HfO}_3$  can adsorb  $\text{CO}_2$  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  $\text{SF}_6$ . 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  $\text{CO}_2$  (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  $\text{CO}_2$  gases as well as the strength of the  $\text{CO}_2$  sorption. Furthermore, the extremely high  $\text{CO}_2$  selectivity of this material may allow us to further develop them for  $\text{CO}_2$  capture from other low-concentration sources, or for biogas upgrading (Figure 21).



**FIGURE 21.** The  $\text{CO}_2$  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.



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.

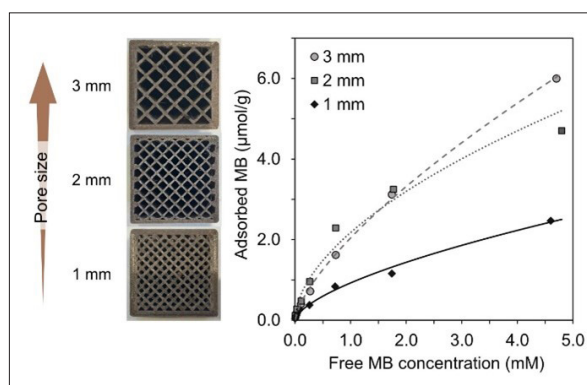
The team at Stockholm University developed and published on the synthesis of polylactic acid (PLA) – based composites reinforced with homogeneously dispersed TEMPO-oxidized cellulose nanofibers (TCNF) or chitin nanofibers (ChNF). The 3D-printed monolithic, bio-composite filters were able to adsorb metal 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).

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 Mimby 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 Mimby on utilizing the 3D printed filters in a pilot scale study at Mimby. Plans were made to provide the specifications for producing 3D printed units that can be used in the washing machines.



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





- Hao, W., Shi, Y., Ullah, L., Li, R., Hedin, N. (2023) Effects of the Ion-Exchange Sequence on the CO<sub>2</sub> Uptake and CO<sub>2</sub>-over-N<sub>2</sub> 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 imidazolate frameworks (CelloZIF-L) for adsorption of carbon dioxide (CO<sub>2</sub>) 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<sub>2</sub> 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<sub>2</sub>) 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<sub>2</sub> Capture and Utilisation Cycles. *Applied Catalysis B: Environment and Energy*, 338, 123053. <https://doi.org/10.1016/j.apcatb.2023.123053>

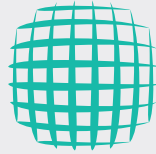












MISTRA  
TERRACLEAN

FUNDED BY



The Swedish Foundation for  
Strategic Environmental Research

## PARTNERS

**ALFA LAVAL ASTRAZENECA AVANZARE AXOLOT  
BOLIDEN BRIGHT DAY GRAPHENE CAMFIL AB  
HUMLEGÅRDEN IKEM INSPLOSION IVL LOVISAGRUVAN AB  
MIMBLY NORDIC WATER RADMA CARBON AB RISE  
ROYAL INSTITUTE OF TECHNOLOGY (KTH) SAAB  
SALLY R SGU SLU STOCKHOLM UNIVERSITY  
STOCKHOLM WATER TECHNOLOGY AB  
SVENSK VENTILATION UPONOR UPPSALA UNIVERSITY**