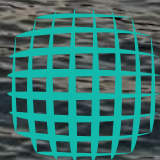


Mistra TerraClean Annual Report 2022



MISTRA
TERRACLEAN

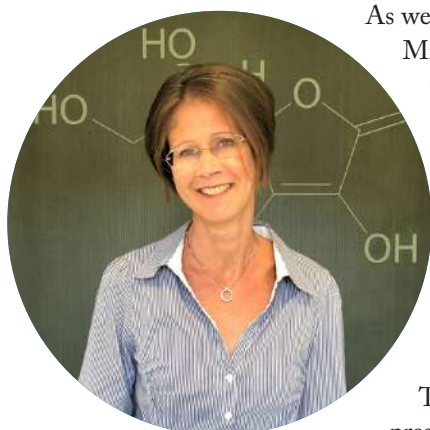
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LIST OF ABBREVIATIONS

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

A MISTRA TERRACLEAN PERSPECTIVE ON 2022



As we close 2022, we also close the first full year of phase II in Mistra TerraClean – a productive one for our research project thanks in large part to the valuable collaborations we have formed with academic, research institute, and industry partners. The established partnerships enable us to access cutting-edge research and resources, as well as provide us with valuable insights into real-world applications of our research. These partnerships have also allowed us to test and validate our findings in practical settings and have opened up opportunities for optimization and integration of components into more sophisticated systems. These partnerships have led to several joint publications and presentations and have allowed us to expand the scope of our project to include new and exciting research ideas.

The overarching goal of this programme, smart materials for clean air and water, felt ever as timely and important during the past year. The contaminants that we address are of increasing concern and significant material and sensor technologies will be needed to adequately deal with remediation, not the least PFAS substances, volatile organic compounds, and heavy metals. In light of the recent pandemic, we see an increasing interest in air quality issues and indoor air purification, as well as the need for further developments in anti-fouling materials. The research conducted within Mistra TerraClean addresses these issues and many more.

The many highlights of 2022 include:

- The continuous development of materials with fine-tuned chemical and morphological structures for efficient removal of impurities from water and air, risk mitigation plans for user cases to accelerate the safety of materials,
- An ambitious take on sensors to accelerate the smartness of materials. Designing a sensor that can accurately and reliably measure the desired parameter in complex systems is challenging and this is where the interdisciplinary collaborations and competence within Mistra TerraClean is a true asset,

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 interdisciplinary competence hub.

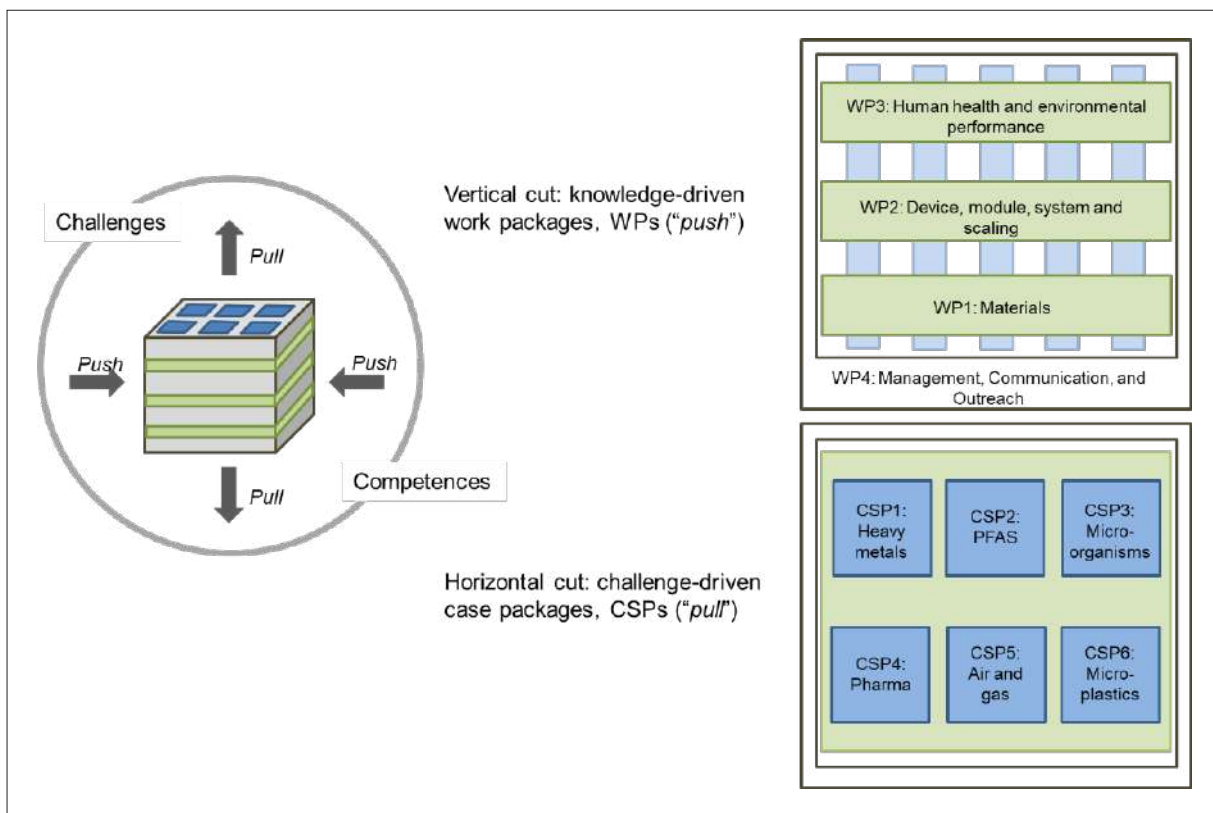


FIGURE 1.
The push-pull driven structure of Mistra TerraClean II.

WORK PACKAGE 1

MATERIALS

**WP1 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, and PFAS from water, in addition to the reduction of microorganisms and fouling in water and gas tubes, and the removal microplastics, and for gas purification in relation to, for example, the removal of VOC and CO₂. 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	UU; RISE
1.2 Carbon-based smart materials	SU; RISE; BrightDay Graphene
1.3 Lignocellulosic materials	KTH; SU; RISE; MoRe
1.4 Chemically modified materials	KTH; SU; UU; RISE; Alfa Laval
1.5 Characterization platform	RISE; KTH; SU; UU

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

Progress and achievements during 2022

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 use for pollutant removal. Additionally, we are exploring high temperature regeneration of heat-resistive mineral materials will be evaluated in CSP2 and CSP4.

Zirconium and hafnium-based inorganic oxides (related to carbonates and hydroxides) have been synthesized and optimized for high temperature CO₂ sorptions. Primary studies are completed, and manuscripts are being prepared for publication.

The work of developing a detailed model of the surface-adsorbate interaction on carbonates/hydroxides has begun. It will continue as follow up studies, after the publications of manuscripts mentioned above.

Different coating techniques are explored for a potential scale-up, such as roll, dip- and spray-coating, and aerosol-based techniques. Moreover, we investigate the preparation of green composite aerogels and foams of cellulose and protein nanofibrils like amyloid nanofibrils. These protein fibrils can be easily prepared from whey, the byproduct of dairy industries. The aerogels are prepared via freeze-linking and the foams are prepared via oven drying. This eliminates the need for freeze-drying or other highly energy-consuming methods.

The SU team has successfully developed hybrids of cellulose and metal organic frameworks and used it in membrane and filter processing. Membranes were prepared by a vacuum filtration method that produced Cello-MOF paper, which showed multiple functionality towards adsorption of metal ions and dyes, electrochemical sensing of Pb^{2+} as well as CO_2 capture. These materials also showed recyclability and possibility for multiple use.

Filters were prepared from these materials via 3D printing which resulted in 3D filters which showed adsorption of metal ions and CO_2 .

Both these methods are scalable and selective towards multiple charged pollutants in water medium.

Work is performed on relating adsorption and conductivity in the domain of electro-adsorption, which is of importance in the understanding of capacitive deionization technologies.

Task 1.5 Characterization platform

The focus here is on documenting the characterization and validation of the sorbent materials developed for the project. This involves the documentation of the variety of surface characterization techniques such as XPS, SEM, TEM, XRD, IR, ICP-OES and solid-state NMR spectroscopy.

The knowledge transfer approach about current and future capacities for cutting-edge techniques for characterization is getting analyzed.

The approach for collecting and sharing protocols for advanced analyses proceeds continuously throughout the programme lifetime.



FIGURE 3. Dimitrios Georgouvelas became the programme's first PhD student to graduate. The picture is taken at his dissertation.

WORK PACKAGE 2

SMART FILTER DESIGN AND VALIDATION

WP2 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; SU
2.3 Scaling and Techno-economy	RISE; IVL; SU; Alfa Laval

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

In exploration of suitable working and meeting modes, bimonthly meetings were held during the spring, where the meetings were themed on CSPs. Orientation on each CSP, progress, needs for evaluation of materials, devices, sensors were discussed, as well the prospects for commercialization and scaling of the technology.

A common view was that the work in most CSPs were not mature enough for an evaluation of commercialization plans. For this reason, the meeting mode was changed to workshops in the fall.

Two workshops were held, presenting the benchmark systems and new materials for clean water, and clean air, respectively. The workshops included a lecture on materials and devices (filters and sensors), describing the compatibility issues, and a demonstration of materials developed in WP1 for the purpose. The goal for the workshops was to present the benchmark systems currently in use and describe their bottlenecks. The benchmark systems should act as template for new setup and evaluation. Another goal was to present a proposed decision process for upscaling.

The workshops were appreciated and acted as push and pull to assist faster implementation of materials in the different cases.

Progress and achievements during 2022

Task 2.1 Connected filter devices and integration

This task is to build on the sensor-absorbent concept developed in task 2.2 and has not produced results under 2022. The development of the optical sensing methods, UV fluorescence, to detect presence of biofilms is reported in CSP3.

Task 2.2 Sensors and sensor materials

In this task, the original focus has been more specified to develop PFAS sensors based on metal-organic frameworks (MOF). Further, the target to develop sensors for perfluorinated pollutants has been changed to include devices for detection of PFAS-substances by low-cost dose-exposure indicators. This change and specification in ambition is motivated by the abundance of reports on selective accumulator materials that can work as responsive materials or together with sensors at concentrations that are in the range of regulatory concentrations. On the other hand, we have not found reports on sensors with a reversible and dynamic response in the concentration ranges of relevance for health effects and regulatory concentration limits. Dose indicators operating by exposing an accumulator or accumulator-responsive material for a specific time or water volume exposure can potentially solve problems for field studies, provided the product is low cost.

A new method to functionalize porous adsorbents such as carbons was developed. This method employs works by impregnating the porous material with polymerizable compound to afford stable immobilized functions at the surface by polymerization. The method starts from bio-based phenols to produce benzoxazines and phenols polymerized with the benzoxazines and produces immobilized functions, stable to extreme pH, chemicals and high temperature, to a low cost of materials and processes. Here, we have employed the chelating and redox functionalities of the polymerized materials onto porous carbons to afford sensor-adsorbent materials.

The SU team developed cellulose-metal organic framework hybrid paper which acts as adsorbents and

sensing material simultaneously. A scalable water-mediated processing of nanocellulose - Zeolitic Imidazolate framework hybrid paper was developed. The produced papers, i.e. CelloZIFPaper, were applied as adsorbents for the removal of the heavy metals from water, with adsorption capacities of 66.2–354.0 mg/g. CelloZIFPaper can also be used as a ‘self-standing’ working electrode for the selective sensing of toxic heavy metals, i. e. lead ions (Pb^{2+}), using electrochemical-based methods with a detection limit of 8 μM (Figure 4). The electrochemical measurements may advance ‘Lab-on-CelloZIFPaper’ technologies for label-free detection of Pb^{2+} .

Another track of this task develops low-cost tools for robotized analysis of adsorbents and sensor materials. The objective here is to aid the development of electrochemical sensor-adsorbents for water pollutants using robotized dispensing of test solution and electrode preparation and enable software supported tools for materials development. This methodology development is needed to generate the large number of analytical data needed to establish sensor and adsorption parameters for all materials under development and for all relevant water matrices. The concept is tested on a new class of sensor adsorbents developed in this task and in phase one of this programme, and that is immobilization of chelating and redox functions on porous electrode materials using coupling polymerization of bio-derived benzoxazines. The function of a sample of this materials class is shown below (Figure 5).

A pre-study report on possible approaches for PFAS sensor development was delivered, presented, and up-loaded in connection with the consortium meeting in October 2022.

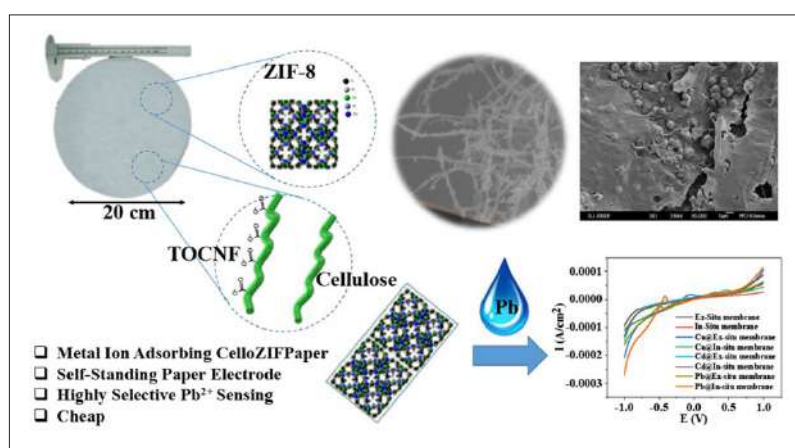


FIGURE 4. CelloZIFPaper combines adsorbent- and sensor functions to form a “smart Mistra TerraClean filter material” for water contaminated by heavy metal ions.

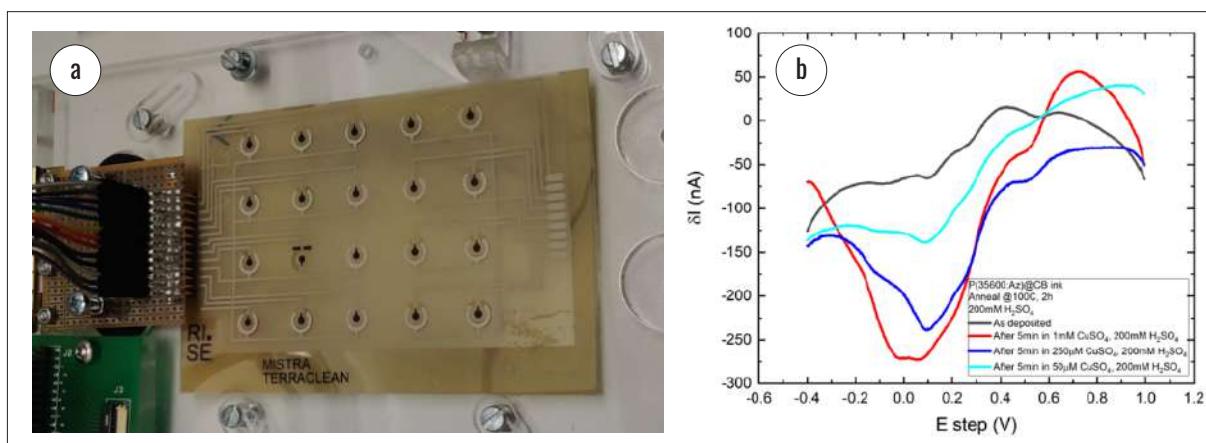


FIGURE 5. a) A printed array of electrochemical cells, an enabler for robotized characterization of sensor absorbents. b) A sensor-absorbent electrode material, functionalized porous carbon, analyzed for the ability to capture and respond to metal ions.

Task 2.3 Scaling and techno-economy

To organize and keep track of development and evaluation of materials being developed, two actions were taken in this task. First, a list of materials ready for techno-economical evaluation was established, and second a procedure on how the evaluation of materials should be processed within WP2 was proposed, where the latter was one of the deliverables during 2022. The aim of the evaluation decision process is to provide early feedback to material developers and to keep track of material cases under development in the process.

A proposed formalized decision process for selecting upscaling cases was presented and up-loaded in connection with a workshop in October.

A list of material candidates, regarding scalability, techno-economical, and performance evaluation of materials developed in WP1, and devices can be found in a continuously updated document. It is considered the rolling report of this delivery.



FIGURE 7. Mistra TerraClean Board visiting RISE facilities in Stockholm.

Consortium meeting

Following several years of meetings and travel restrictions, we were thrilled to once again arrange a full-scale annual consortium meeting. Meeting was held in Norrköping on October 3-4, joining partners from near and far together – academia, institutes, authorities, organizations, and industry (Figure 8). The site for the consortium meeting was chosen with care. Norrköping is the home for RISE Printed Electronics Arena, Sweden’s main site for printed electronics research, where several of the consortium’s researchers work. The scientific field is multi-disciplinary, at the intersection of electronics design, chemistry, and physics, and ranges from fundamental research in polymers (materials science) to applied research with confidential applications in a multitude of market segments, like humidity sensors, batteries for power supply, printed solar cells on paper or plastic and wireless “labels” for network connection. A site visit to RISE was an obvious part of the meeting agenda.

The first day included discussions and group workshops on the smartness of filter materials, in the exiting venue of Visualization center. What is really a smart material, what benefits can smartness bring, and what are the weak points with the concept? How do we make new smart innovative solutions competitive with existing technology? Scaling and market readiness level? Smart materials solutions may seem expensive. But it could in the end be costlier to not embrace innovations.

The second day was a day rich in insights and inspiration. We enjoyed a tour around the facilities of Freudenberg Home and Cleaning Solutions in Norrköping to learn more about the products and process from a chemical and manufacturing perspective. Here, more than 6 million m² of the well-known Wettex cloth is produced annually. The Wettex cloth, invented in 1949, is an ingenious example of a bio-based all-cellulose wet-stable and high absorptive material and of high relevance for Mistra TerraClean.



FIGURE 8. Snapshots from the annual consortium meeting in Norrköping.

CASE STUDY PACKAGE 1: HEAVY METALS

CSP1 Leader: Johan Strandberg, IVL Swedish Environmental Research Institute

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

Key questions and scope

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.

Description of cases within the package

Lovisagruvan

Since 2004, Lovisagruvan (Figure 9) has been running an underground mine in Bergslagen, just north of Lindsberg, 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 (Håkanboda) is also owned by the Lovisagruvan company. This mine and its leachate, which is not governed actively, might contain rare earth elements, REE.

Svärträsk

The Geological Survey of Sweden is the governmental authority responsible for acting as the operator in cases where contaminated areas lack an owner. Svärträsk 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.



FIGURE 9. Basin for infiltrating groundwater in Lovisagruvan.

Boliden mines

Boliden operates several mines in Sweden and abroad. Many of them are based on sulphide-rich ores containing, for example, copper, zinc, gold, silver and lead. The residues are reactive in an aerobic environment, creating an acidic leachate that contains dissolved metals. Hence, Boliden's water treatment requirements 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 2022

The CSP aims to find feasible options for use in the cases presented by the industry to the group of researchers (Figure 10). 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.

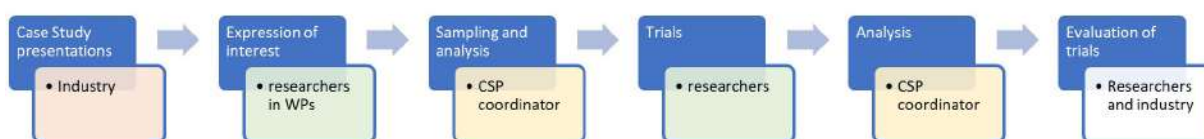


FIGURE 10. Process description for the stepwise engagement of mine operators and scientists in CSP1.

Case Study presentations

Industry representatives from Lovisagruvan and Svärträsk presented their cases to a group of researchers from the WPs and companies in June 2022. From the presentations and the following discussions, it was evident that the needs of Svärträsk were going to be difficult to meet using the materials and processes in the project. Lovisagruvan's case attracted interest from four research groups and three companies within the program.

Trials

Separation of metals and REE were tested on the following materials from the program with the following methods:

- Electroflotation
- Magnetic activated carbon
- Coagulation, Chromafora
- Metal-organic frameworks
- Polymeric filters based on lignocellulose
- Standard FeSO_4 precipitation (benchmark)

Sampling and analysis of real water

Water from Lovisagruvan was collected at different points, as per below, to allow researchers to try sorbents and processes on a lab scale on actual water:

1. Untreated water from Lovisagruvan at 235 m depth, expected to contain high concentrations of Pb and Zn.
2. Treated water (NaOH and FeSO_4) from Lovisagruvan.
3. Treated water (NaOH , FeSO_4 and peat filter) from Lovisagruvan
4. Untreated water from Håkanboda open pit mine (Figure 11), expected to contain As, Cu, Pb, Co and possibly rare earth elements (REE)
5. Untreated leachate from slagpiles in Håkanboda



FIGURE 11. Water sampling from Håkanboda open pit mine.



FIGURE 12. The Alfa Laval test unit used for microfiltration.

Since only some PFAS substances are removed by microfiltration, it is not useful to utilize the sorption phenomenon for practical application since most polluted waters contain a mix of PFAS substances.

An unexpected observation was made, namely that the concentration of 6:2 FTS was very high in all the samples even though the substance was not added to the tap water. These results were confirmed by both IVL and RISE analytical lab. Several hypotheses explaining the phenomenon were proposed, including presence as impurity in other PFAS standards, leaching from the pilot unit and leaching from membrane.

The experiments were conducted by IVL in cooperation with RISE and Alfa Laval. Even though no additional experiments with the membrane are planned within the CSP2, Alfa Laval will use the results for further product development outside the project.

Application of CDI

Performance of the CDI process when treating PFAS polluted water from SAAB was studied in two sets of experiments (Figure 13). In the first set, industrial scale electrodes were used.

A voltage of 2V and 4V respectively was applied during the electrosorption/destruction phase. After the sorption phase, the polarity was reversed for a short period followed by a longer period of short-circuiting the electrodes. The run was ended by circulating isopropanol solution to wash out the PFAS sorbed but not electrochemically released.

It was expected that during the first phase when the electrosorption or destruction of PFAS occurs, the concentration of PFAS in water should decrease. During the regeneration phase, the PFAS which was electrosorbed but not destroyed would be released,

leading to increase of the PFAS concentration. A third run (0 V) was also performed for reference.

The results showed very little difference between the three runs (Figure 14). The removal efficiency towards PFAS was 96-99 %, with no release of PFAS during the regeneration phase. Since the same performance was observed in the reference run, it indicates that the main mechanism of PFAS removal was physical sorption of PFAS. Moreover, it shows that isopropanol is not effective for chemical regeneration of electrodes.

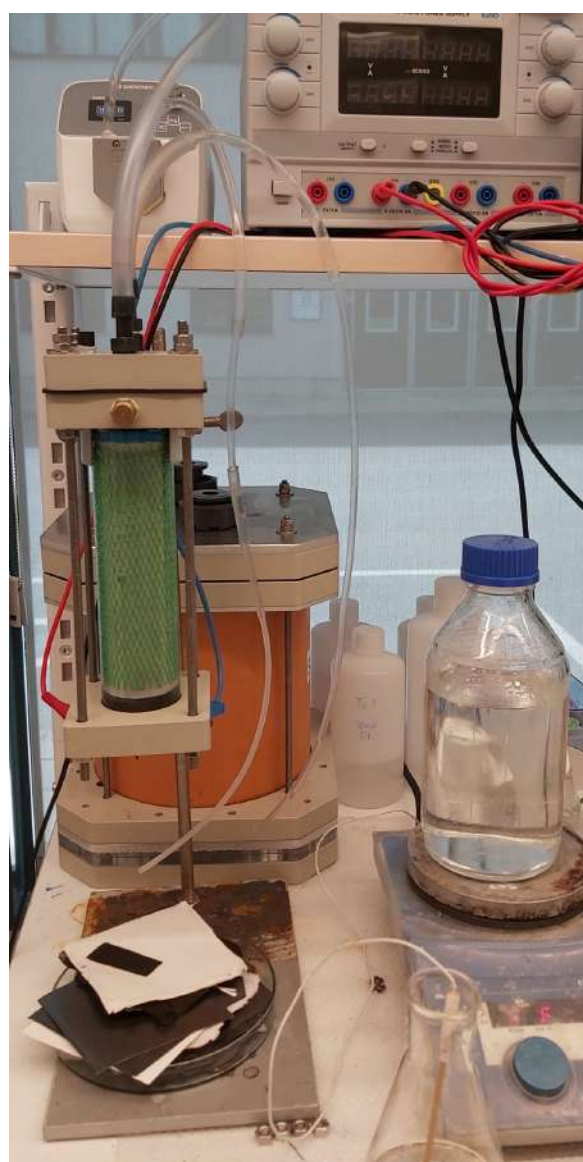


FIGURE 13. The CDI cell, cylindrical disposition, connected to a power supply. Two electrodes (450 cm² each) separated by cellulosic paper are inside the device.

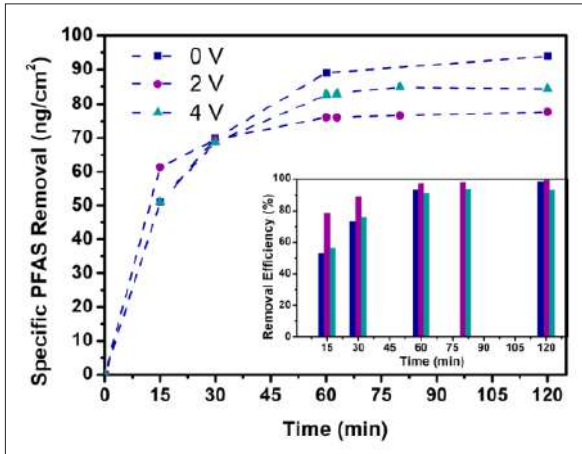


FIGURE 14. Removal of PFAS in the first run of experiments with CDI.

In the second test, the strategy was to fully saturate the electrodes with PFAS before the actual voltage application, to observe the effect of the electrochemical processes.

The electrode was saturated in two consequent runs of physical sorption (A-1 and A-2 in Figure 15). Deionized water was circulated through the cell to break down or regenerate the sorbed PFAS. The test was then repeated to show if the sorption capacity of the electrode was regenerated. Further, another trial of electro-regeneration was performed using a saline solution followed by a final sorption trial.

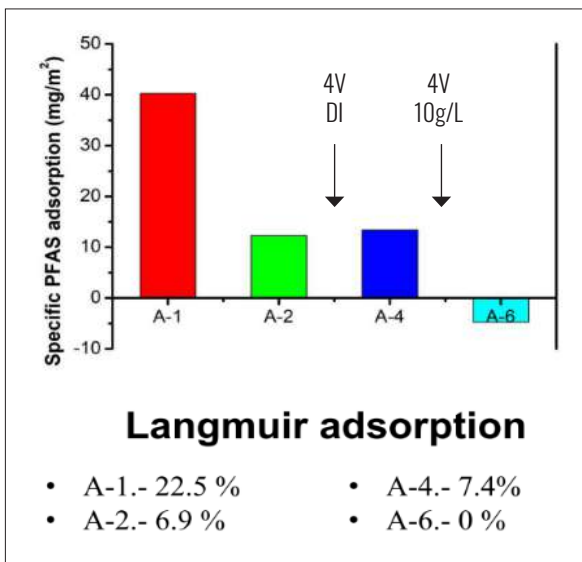


FIGURE 15. Removal of PFAS in the second run of experiments with CDI.

The conclusion was that the electro-regeneration with deionized water was effective. Conversely, regeneration with salt solution does not seem to be effective since no net removal of PFAS in A-6 is observed.

It is noted that the efficiency of PFAS removal was negligible, probably due to an overload of PFAS on the electrodes. The uncertainty of the analysis does therefore not allow any definitive conclusion.

Application of MAC

Initial testing of the MAC was performed. Different MAC doses were tested (Figure 16) and compared to the same doses of polycyclic aromatic compounds, PAC. It was found that at different concentrations of MAC, (200–500 mg/L), the removal of PFAS exceeds 80 %. The comparison with commercial PAC showed however that application of as low as 100 mg/L of PAC gives the same performance as the application of 500 mg/L of MAC.

It is therefore crucial that the MAC can be reused and regenerated effectively for the technology to be competitive with PAC.

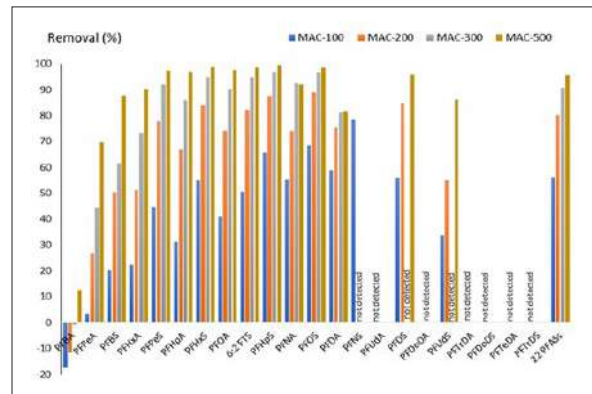


FIGURE 16. Removal of PFAS with different MAC doses.

This included “old” PEX from Uponor, and new PEX from two commercial sources.

PEX from different sources and ages perform equivalently in allowing biofilm accumulation in the RISE bioreactor set-up (Figure 18).

In a parallel track, attempts to utilize fluorescence detection in quantification of biofilm on the PEX surfaces have been made by RISE. Initial work focussed on potential background interference from intrinsic fluorescence of the PEX polymer.

Varied responses have been noted, but the pipe material tested so far seems to have a background fluorescence that may allow for biofilm detection. There are indications that the level of this potentially interfering background fluorescence may be dependent on the pipe production method. Current focus is on extending measurements to other materials, testing the approach for different cases, using known amounts of biofilms on neutral surfaces. An important area for development is also the design of the “in-pipe” device that might allow biomonitoring in real time *in situ*.

Air-borne biofouling

A pivotal achievement has been the establishment by RISE of a bioreactor-based test system for testing material/chemistry solutions in air-borne biofouling. Camfil collaborated with RISE to generate a standardized system for assessing viral contamination of

air filtration material. Thirteen basic filter materials have so-far been tested.

The Viral Filtration Efficiency (VFE) method allows quantitation of viral particles recovered from filter material (Figure 19). The work has initially centered on the use of bacteriophage phi-X 174. Various “lifting” techniques have been tested and a bacterial (phage killing of bacteria) growth assay established as quantitative measure. Further experiments are ongoing to test if direct quantitation of live/dead phage can be achieved using quantitative RT-PCR.

Different buffers and methods have been tested, and a protocol for recovery of viable bacteriophages from filters has been developed. The next step has been to establish a live/dead test with a quantitative PCR method. The method has now been standardized according to ISO 18184 and is currently being extended beyond phage X-174 towards the use of other more pathogenic viruses, adenovirus and murine norovirus (Figure 20). The work is a result of collaboration with the Department of Infectious Diseases at Sahlgrenska Academy in Gothenburg and RISE Bioeconomy and Health.

In addition to assay establishment, work has begun on chemical modification of filter surfaces with ZnO. This has begun by establishing a risk assessment for its use at RISE. The coated filter materials are currently being created and will be tested using the phage-based assay initially. There are also plans to test both nano-carbon- and chitosan-based coatings.



FIGURE 19. Setup of the VFE assay.

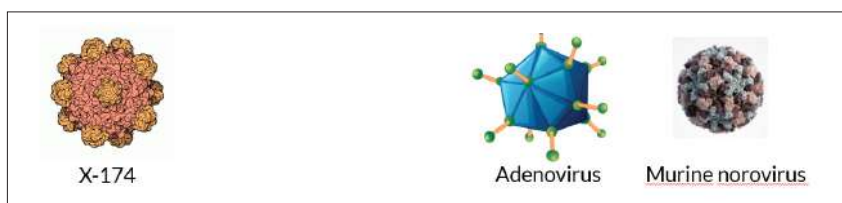


FIGURE 20. The viruses tested in this work.

CASE STUDY PACKAGE 4: PHARMA

CSP4 Leader: Ian Cotgreave, RISE

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

Key questions and scope

The case study centres on the use of 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 laboratory scale and attempts to transfer to 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 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 2022

The AstraZeneca case

AstraZeneca has been very active in the collaboration, providing both API standards for analytical approaches, and providing spiked API samples for use by SWT/KTH and Axolot. The company has also hosted visits for KTH, SWT, IVL and RISE during the year, which is vital to cement ties and lay the

ground for collaboration, particularly with respect to the need for establishing pilot studies on-site.

Development of analytical techniques

The analytical approaches have been developed by RISE and involve appropriate LC-MS/MS methods. Initial work successfully established quantitative analytical techniques for the 21 APIs identified by AstraZeneca as important.

The work was initially focused on three pure compounds for lab scale work, namely metoprolol, metformin (a substance difficult to remove with conventional approaches) and esomeprazole (a suspected chemically unstable substance) (Figure 21).

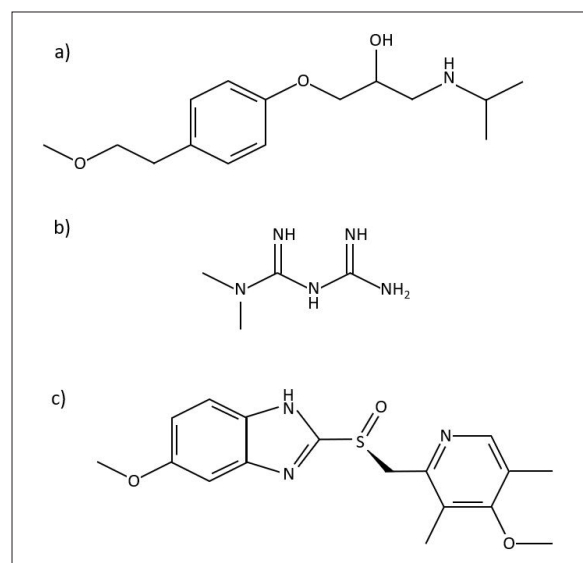


FIGURE 21. Molecular structure of a) metoprolol b) metformin and c) esomeprazole.

The methods have also been adapted to the analysis of APIs spiked into process water. Here process samples are filtered through a 0.22 μM PVDF membrane prior to further analysis by LC-MS.

A deeper investigation of the breakdown products emanating from esomeprazole was undertaken as initial experiments revealed instability under a variety of experimental conditions used in the lab-scale experiments. This also gained essential knowledge for interpretation of the experiment utilizing the CDI techniques on API spiked solutions. This work revealed a clear dependence on acidity for the breakdown process.

Application of the CDI technique to API remediation

Capacitive deionization (CDI) is an emerging technology that is showing considerable promises as a sustainable low energy process for purification of water from process and wastewater. It offers the possibility of both electrosorption/desorption as well as oxygen free-radical mediated degradation of bound molecules upon desorption (“catch and kill”). Its simplicity and cost-effective operation, together with potential energy recovery possibilities during its operation, makes it a promising technology to be implemented as part of treatment process of drinking water and industrial wastewater plants. The CDI technology has been described more fully in previous MTC reports.

Lab-scale phase

The lab-scale tests have been conducted at division of Functional Nanomaterials Group at KTH, whereas the analytical work was performed by researchers at RISE. The API spiked solutions used during the lab trials were provided by AstraZeneca. The solutions were immediately stored under freezing conditions until the experiments were performed. The lab-scale system comprised of a CDI flat cell of 5x5 cm, with a flow-through architecture (close to the SWT solution). The technicalities of the setup are out of scope for the report, but a schematic representation of the lab-scale rig is shown below (Figure 22).

Initial experiments revealed that metformin was not removed from water flow when only pure adsorption was applied, whereas metoprolol and esomeprazole were almost quantitatively removed after 120 minutes of circulation (Figure 23). Application of a between 2V and 5V potential did not greatly enhance the rate of removal of metoprolol and esomeprazole, but metformin was clearly more effectively adsorbed, indicating that metformin removal is mediated by electrosorption, whereas metoprolol and esomeprazole desorb rather poorly, reacting poorly to the reverse polarity. It may also be possible that degradation of the latter two APIs occurs on the electrodes, with release of by-products. This is the subject of further investigation, but esomeprazole is clearly subject to this (see above).

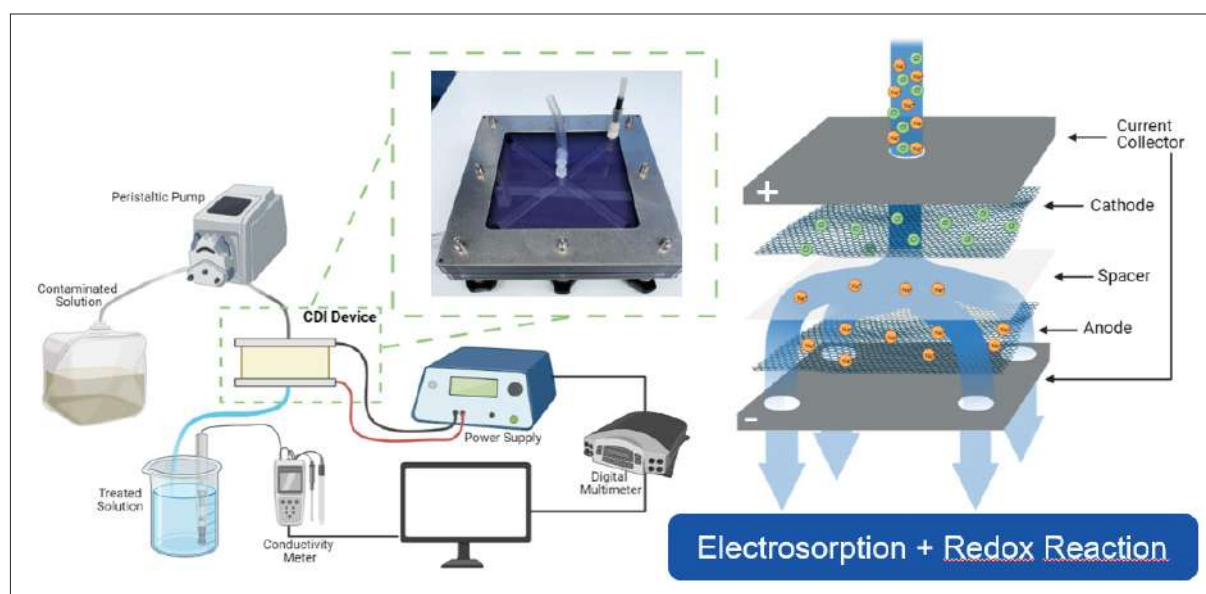


FIGURE 22. A schematic representation of the capacitive deionisation technique.

Latterly experiments are being performed focused on the use of the flat cell CDI architecture to investigate further aspects of the adsorption/desorption mode with respect to potential breakdown of the API. This is focused on a mass balance approach where either primary breakdown products are sought in the circu-

lating solution and the API and potential breakdown products are retained on the electrode. The effects of pH and applied voltage are also included.

Together these studies form the basis of an academic publication which is being developed.

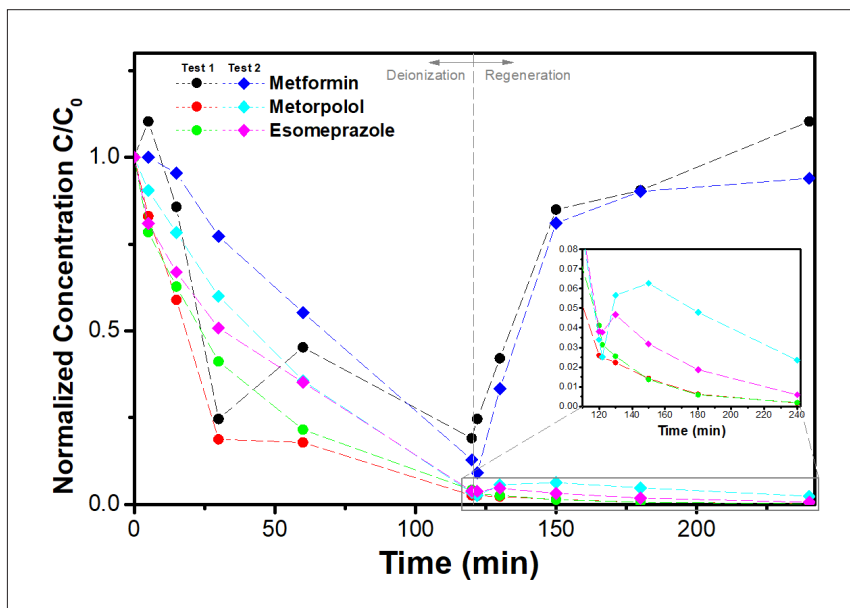


FIGURE 23. Normalized concentrations of esomeprazole, metformin and metoprolol in a spiked water mixture subjected to electrosorption at 2V.

AN INDUSTRIAL PARTNER PERSPECTIVE ON MISTRA TERRACLEAN II

Why are you engaged in the Mistra TerraClean II?

– The programme’s vision is to contribute towards clean soil, water and air by means of new technologies. This vision matches with Radma’s quest for efficient and affordable solutions for water remediation.

What are the benefits of joining a consortium for a company of your size and kind of business?

– Radma is a micro company and by participating in Mistra TerraClean II we get the opportunity to meet with experienced scientists and experts from academia and industry.

What do you expect from being a partner in Mistra TerraClean II?

– To evaluate and improve our magnetic carbon technology in real applications for water treatment in mining, pharmaceutical and ground water applications.

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

– To participate in “real life” projects and test the properties of our magnetic materials in laboratory and pilot scale and to assess the economic and environmental credentials for problem owners and society.



FIGURE 29. Radwa Ashour with a sample of Radma’s magnetic carbon.

MISTRA'S SUPPORT TO UKRAINIAN RESEARCHERS

In April 2022, Mistra's Board decided to allocate SEK 10 million to support researchers fleeing the war in Ukraine. The funding can be used to offer researchers employment for a limited period of time in Mistra's research programmes. One of the researchers is Serhii, currently working with Mistra TerraClean and hosted by Stockholm University.

The day the war began

When Mistra announced their support to Ukrainian researchers, Professor Serhii was sitting in a laboratory at Johannes Gutenberg University in Mainz, Germany, wondering where he and his wife could settle down and continue work and life together.

They decided to leave Kyiv and Ukraine before a full-scale war developed and headed westwards to the border in February, days before Russia's invasion. On February 24, they crossed the border to Poland.

Serhii used to work at the National Academy of Sciences of Ukraine and from time to time he also taught chemistry at various Kyiv universities. Both Serhii and his wife are chemists in materials science with extensive expertise in, among other things, nanocomposite materials.

– We looked for jobs as researchers in chemistry and sent our CVs near and far. It was important for us to be able to work, not just live on support, says Serhii. In the long term, they wanted to be able to continue working with their own research for a longer period of time.

Via a Ukrainian database for scientists they got in contact with Professor Niklas Hedin at Stockholm University, who found that Serhii's experience and competence could be an asset for the Mistra

TerraClean programme. Thanks to the Mistra special funding and additional support from the Swedish Foundation for Strategic Research and Stockholm University, they came to Stockholm in September 2022 for a two-year assignment.

– I have previously worked on developing products for the industry, such as new generations of sun protection cream where we used nanoparticles that provide stronger protection against UV radiation”, says Serhii.

– Serhii's research profile fits well into the Mistra TerraClean mission of eliminating pollutants in water, and Serhii and his wife are very appreciated among the other scientists here, says Niklas Hedin.

According to Serhii, his Ukrainian job network is still working, but funding has dropped drastically and is now 20–30 percent of what it used to be from the government. He believes that there are tangible risks that Ukraine's scientific and educational capacity will deteriorate sharply.

– The lack of sufficient funding and basic needs, like electricity and heating have a negative impact on scientific processes, says Serhii.

The future is still very uncertain for the Ukrainian couple, as their tenure at Stockholm University ends in September 2024

– Today I feel that I have no future, life is focused on one day at a time. I have a desire to continue a meaningful professional life, Serhii says, looking at the window.

(Due to the situation in Ukraine, Professor Serhii does not want to appear with surname or picture.)

“We looked for jobs as researchers in chemistry and sent our CVs near and far. It was important for us to be able to work, not just live on support.”

SCIENTIFIC OUTPUT AND OUTREACH ACTIVITIES

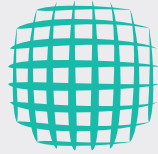
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