

Mistra TerraClean PFAS case: executive summary

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This summary is a compilation of the main findings of the case study. The complete description of the methods, results of experiments, interpretation of the results and life-cycle comparison of the CDI-technology with a reference water treatment scenario is given in the internal reports:

Mistra TerraClean PFAS case: lab-scale trials internal report

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Mistra TerraClean PFAS case: pilot-scale testing of CDI-technology

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Mistra TerraClean PFAS case: Life cycle assessment and life cycle costing

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Introduction

Contamination of surface and ground waters with per- and polyfluoroalkyl substances (PFAS) is a global problem that pose an immediate threat to human health. PFAS are man-made chemicals that have found wide ranging industrial and consumer applications in oil, grease, soil and water repellents and as surfactants that have been applied in aerospace materials, garments, automotive vehicles, buildings and construction, chemicals and pharmaceuticals, electronics and semiconductors, energy production devices, oil and gas exploration equipment, first responder safety equipment and many health care applications in the modern economy. Given the high mobility and persistence of many PFAS, there are numerous cases where large aquifers used for drinking water production have been contaminated. One of the first examples of drinking water pollution with PFAS is the ground water aquifer in Tullinge (Stockholm), where high PFAS concentrations were identified in 2011 and a local water treatment plant needed to be shut down. Further identified cases of large-scale drinking water pollution include Ronneby and Uppsala. In these cases military activity at air bases and firefighting training were identified as the cause for PFAS pollution. There are even small-scale pollution cases where local firefighting efforts led to groundwater pollution. Moreover, high levels of PFAS are found in landfill leachate and some industrial effluents. The most established and used technologies for treatment of PFAS-contaminated waters are treatment with granular activated carbon (GAC), ion exchanger or application of membrane processes. GAC is the most widely used treatment option since it is a low-cost material, and can be reactivated, although at a substantial energy and financial cost. Frequent GAC replacement or reactivation is required to maintain effective PFAS removal, especially when influent PFAS concentrations are high or when short-chain PFAS removal is required.

A new process for the mitigation of PFAS contaminated water is the application of low-voltage electrochemical treatment by capacitive deionisation (CDI). Electrosorption has been successfully used to remove charged ions (desalination), polycyclic aromatic dyes, drug metabolites and herbicides, amongst others. The technology has been developed at KTH and is being commercialized by Stockholm Water Technology (SWT). The principle used for the removal of charged ions from water (example of saline water) is schematically represented in Figure 1.

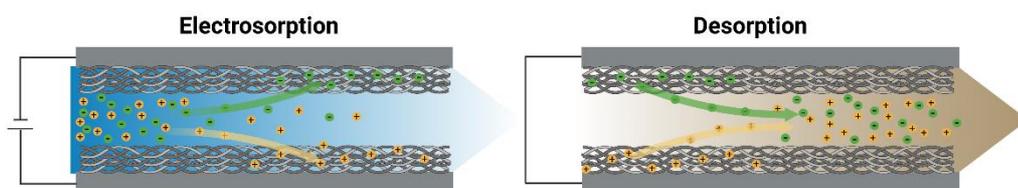


Fig. 1. Basic concept of electrosorption and desorption processes in a capacitive deionization device

Aims and objectives

The overall objective of this study was to electrically enhance the adsorption of PFAS onto activated carbon and electrically discharge them as an in-situ process to regenerate the activated carbon. The aim of this study was thus to pilot test the CDI-technology and study the mechanism of PFAS removal using synthetic solutions of PFAS for validating and benchmarking a continuous-flow capacitive electrochemical cell. Pilot-scale trials with an upscaled model of the CDI-unit and with water composition similar to that of real PFAS-polluted groundwater were performed and long-term performance of the device in real-life situation was evaluated. Life cycle assessment (LCA) and life cycle costing (LCC) were applied to evaluate environmental performance and costs associated with the device over its life cycle.

Materials and methods

The lab scale trials were performed by KTH using a CDI module and synthetic solutions of perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA). The pilot scale tests were performed by SWT and IVL at Hammarby Sjöstadsverk using a pilot system developed and built by SWT (Fig 2). The pilot was operated with water that had a composition similar to that of groundwater in Uppsala (PFAS concentration 120-160 ng/l including both short- and long-chain PFAS).



Fig. 2. CDI-modules used in the tests: left – lab scale device; right – pilot-scale plant with two CORE® CDI modules.

Chemical analysis of 11 PFAS substances was carried out by IVL labs with some of the analysis done at a third party laboratory (Synlab). IVL has developed a method for analysing possible PFAS degradation products and the analysis was performed for some samples from the lab-scale trials.

In parallel with pilot study execution, life cycle assessment (LCA) and life cycle costing (LCC) were conducted, to support further optimization of the capacitive deionization (CDI) device. In a dialogue with KTH Royal Institute of Technology and Stockholm Water Technology (SWT), a life cycle inventory for the manufacture and operation of the CDI in a capacity and size suitable for pilot studies was derived. In a prospective scenario this system model was scaled up, based on learnings from the pilot. As a reference scenario for established technology, based on literature data for a full-size application, the conventional water treatment using granulated activated carbon (GAC) was modelled. Characterization of potential toxicity and ecotoxicity impacts across the life cycle of the device was made possible by the inclusion of a system model in the novel method ProScale and calculation of new per- and polyfluoroalkyl substances (PFAS) characterization factors. Life cycle impact assessment (LCIA) was focussed on climate change and (eco)toxicity indicators. A broader set of indicators were investigated with a screening approach based on normalized results (person equivalents) for the recommended environmental footprint categories. An LCC was conducted based on inventory of energy demand and relevant costs associated with the CDI device and reference GAC scenario over their respective life cycles.

Results and conclusions

In the laboratory experiments, an electric potential was applied after pre-conditioning the electrodes. Upon application of a potential higher than that required for water splitting, free radicals can be created leading to degradation of organic compounds adsorbed on the

electrodes. During regeneration of the electrodes, the system is either short-circuited and/or a reverse potential is applied to facilitate desorption of charged ions in the solution. During laboratory tests, the electrodes were cleaned by alcohol in order to collect all the molecules and reaction products for analysis.

The lab-scale experiments provided a better understanding of underlying principles for PFAS removal by the CDI technology which can enable further optimisation of the technology in a large scale. Removal rate/efficiency of PFOA is considerably increased in the presence of PFOS. The presence of both compounds in solution increased the removal level of PFOA to 86 % (mix of PFOS and PFOA).

Several voltages were applied to study the degradation process and no substantial increase in removal rates were observed for voltages above 3.0 V and thus it was recommended to limit the voltage to 3.0 V for the pilot studies. Regeneration of the electrodes were achieved by short-circuiting the electrodes. In Fig. 3, results of a set of experiments are presented. The conditioning phase represents the physisorption, while the degradation phase is shown under applied voltage. The PFAS adsorbed on the electrodes increases significantly with time upon continuous applied voltage. During the regeneration phase the sorbed amount decreases but some PFAS remain attached on the electrodes even after regeneration (determined by organic solvent cleaning). Mass balance calculations showed that not all of removed PFAS was eluted during the regeneration and chemical cleaning phase. Missing PFAS is represented by the bars at cleaning phase in Fig. 3. This deficit in the PFAS balance is believed to be the result of PFAS degradation during the treatment. More careful evaluation shows that roughly 50 % of the sorbed PFAS was degraded at pH6 and about 20 % was degraded at pH 8.

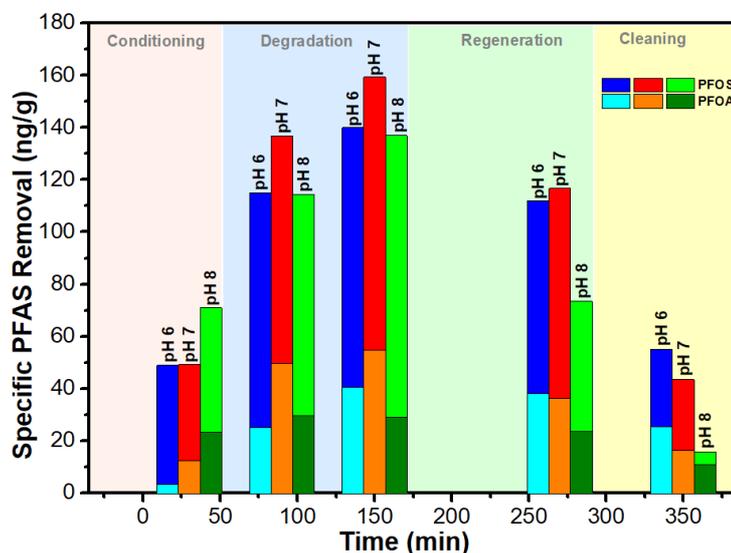


Fig. 3.- Specific removal of PFOA and PFOS in aqueous solution with buffer at different pH between pH 6 to pH 8

Since short-circuiting was identified as limited option to completely regenerate the electrodes, a reversed voltage pulsing was recommended as a more efficient means of regeneration, which was tested during the pilot-scale trials.

In order to confirm that the deficit in PFAS mass balance is due to a complete mineralisation and not a partial degradation of PFOA and PFOS, the samples of the treated water and produced concentrate were further analysed for traditional short-chain PFAS (PFAS 11) and for possible degradation products due to incomplete defluorination of PFAS. No degradation products were however found in the treated spiked water samples in considerable concentration which suggests that the mineralisation of the missing PFOA and PFOS is complete. This was further confirmed by organic fluorine analysis which showed that the remaining PFOS and PFOA in the samples were the only fluorocarbons present in the samples in considerable concentrations.

During the pilot-scale study conclusions of the lab-scale study were considered in order to improve performance (e.g. applied voltage of 3 V, reverse voltage pulsing etc.) but also similar experiments were run in parallel in order to investigate difference of performance in system of different scale and treating water of different composition. The electrosorption experiments with different voltages and different treatment time (number of cycles of sorption/regeneration) clearly showed that both short-chain and long-chain PFAS can be electrosorbed using an applied potential and can be released into a concentration tank, upon short-circuiting the electrodes or upon the application of a reverse potential to the electrodes.

Removal of PFAS by CDI in a larger scale showed to be more complicated than anticipated in the beginning of the project and required significant amount of testing of different operational conditions and flow patterns within the unit in batch tests. The performed work will however benefit in further application of CDI for both PFAS removal and other applications.

The performed work on system optimisation resulted in selection of operational conditions for long-term continuous operation experiments. The long-term test was run until a total of ca 25 000 litres of PFAS-contaminated water was processed during the pilot run. The total operation time for the pilot study in the long-term test mode was 7 weeks, which included time required for filling the tanks and the actual treatment time. If the filling time is excluded the effective operation time is 24 days. Optimized modules from lessons learnt during the first tests were installed before the continuous operation phase. The pilot was operated at a voltage of 2.0 V, treatment time of 60 min and a short reverse voltage pulsing during the regeneration phase. The system showed good performance from the beginning of the period until at least 6 000 L of contaminated water was treated reaching PFAS 11 removal of 90 % (Fig. 4). Even after treatment of 12 000 L of water the PFAS-removal of the system was sufficient to reduce the PFAS concentration under the legal limit (reduction from 120 ng/l to 81 ng/l).

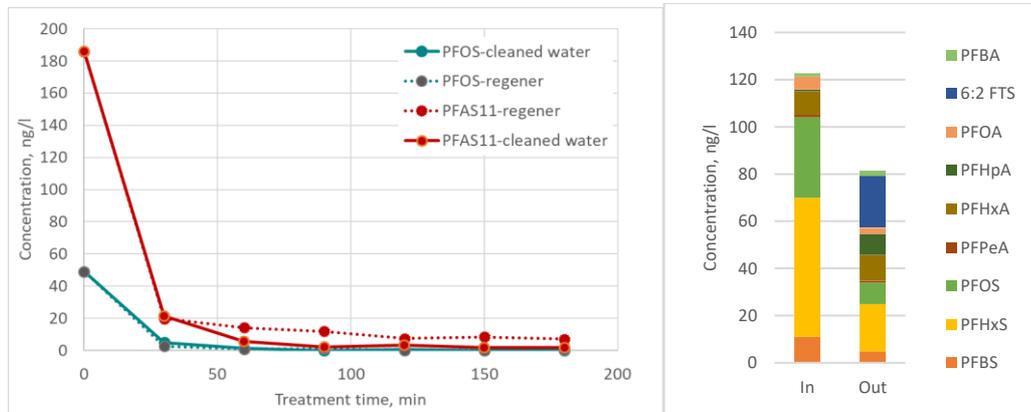


Fig. 4. - PFAS removal in continuous operation mode: lefts – with newly installed modules, right – after treating 12 000 L of water.

The results show that the applied DC potential can also partially degrade PFAS (both short-chain and long-chain) into shorter species, even at voltages as low as 2.0 V DC. As can be seen from Fig 4 there was substantial decrease in the PFOS, PFOA and PFHxS concentrations but the concentrations of PFHpA and 6:2 FTS increased instead.

The technology shows a good promise to be optimized for continuous and better removal of PFAS through modification and optimization of the system and control processes which were not evaluated in this pilot application but are discussed in the last section of this summary.

Based on the results of the pilot-scale testing the CDI technology was evaluated by LCA and LCC in order to identify potential hot-spots in environmental performance and assess the economic viability at the current stage of technology development and provide inputs for future developments. Important parameters considered for the assessment was the lifetime of the modules, treatment efficiency, volume of the produced concentrate and the need for its treatment. During the continuous operation in pilot-scale process the effective operation time was 24 d and to the end of the period there was a significant reduction of the treatment efficiency. Water recovery was 36-70 % in different phases of the trial. The results of the pilot-scale evaluation provided the basis for different scenarios evaluated in the LCC and LCA, using data from pilot scale operations and for a prospective optimized system based on KTH and SWT expertise and experience in the process.

The LCA was performed assuming that the life-time of the modules is 10 years with the refurbishment of modules every two years by changing the spacers. The removal efficiency was assumed to start at 90 % and gradually decrease to the end of the modules' lifetime, but still satisfying a maximum PFAS concentration of 85 ng/l. Water recovery was assumed to be 70% and the concentrate treatment was evaluated in different scenarios. Total electricity consumption was modelled in two scenarios: 1.8 kWh/m³ for pilot scale operations and 0.65 kWh/m³ in a scaled-up scenario.

LCA results indicate that, in pilot scale, energy use during operation is an important source of potential environmental impacts for the CDI for the indicators climate change, indirect human

toxicity in the non-cancer effects category and ecotoxicity, while the manufacturing life cycle stage has important contributions for indicators indirect human toxicity in the carcinogenicity effects category and direct toxicity effects. At pilot scale system auxiliary materials had a large contribution to the accumulated impact scores, but it was shown that in a larger scale system their importance would be drastically reduced in relation to core module components.

Quantification of potential impacts from PFAS emissions with the treated water, when the treatment goal is set to 85 ng/l (sum PFAS-11), indicate that potential impacts from the emitted water could still be, in relation to device manufacture and operation, an important contributor to overall potential impacts (indicator human toxicity, non-cancer effects). Thus, illustrating the relevance of the water treatment but also highlighting the great potential from in situ PFAS destruction.

A preliminary evaluation related to the scenario of the established GAC treatment showed that the CDI in a prospective large-scale scenario contributes less to climate change impacts, which is in line with avoiding a fossil-based material such as bituminous coal during operation. The pilot-scale device layout includes a comparably large amount of highly alloyed steel in the system, which is not required for the function of the device and can be replaced by other materials or solutions. A preliminary initial analysis showed that these parts contribute to indirect impacts on human health related to cancer, from material manufacture, and that those impacts can be reduced in the design on the device for large scale operations. Further investigation of scenarios with different energy sources and material choice are needed to guide the development.

Due to limited data availability for the GAC system, the level of completeness and detail are not equal for the two systems. Moreover, data for the GAC system were available mostly for an optimized large-scale application. Pressure driven systems are not considered.

The LCC analysis showed the CDI-system has a higher total cost than GAC-filter for a small-scale installation with a capacity of 1 m³/d. This is partly because of the production of concentrate that potentially must be treated and partly because the complexity of the system is rather high (which gives higher investment cost). However, the production cost of the CDI system is continuously reducing with manufacturing development and can lead to substantial cost reduction over time.

For a large-scale system a proper LCC could not be done since it was hard to estimate the investment cost for the CDI-technology at that scale. Comparison of the major operating costs for a large-scale system for the CDI and GAC showed more research and development need to be done in order to match the costs of a GAC-based treatment system in case PFAS-rich concentrate stream is produced by CDI and needs to be treated. The operation costs for the combination of CDI and GAC are higher than for treatment only by GAC under the assumptions used for the evaluation, even for the scenario when very high PFAS removal is maintained by GAC.

It was, however, demonstrated in both lab- and pilot-scale trials that a part of PFAS was degraded during the treatment process. If further technology development leads to enhanced PFAS degradation during the treatment with only trace amounts of PFAS remaining in the concentrate, then it can be discharged without further treatments. This would positively influence the outcome of LCC, since treatment of the concentrate is currently a major cost component. Moreover, if the investment cost for CDI is considerably lower than for GAC-filters the total cost

might be lower for a CDI-based system. Lastly, the CDI system may be more cost-effective for treatment of more challenging water streams containing both PFAS and other pollutants, for which treatment by GAC is more costly comparing to treating groundwater.

In conclusion, LCA and LCC results proved already during pilot operations to be relevant guidance in the further development of the CDI for treatment of PFAS contaminated water. In future research and further development new knowledge gained can be incorporated into the systems models in a tiered approach to support the development of smart solutions for water and air purification.

Future work and potential for further development

Mechanism of PFAS removal

The performed research gave important insights in the mechanism of PFAS degradation. However, further experiments with different combinations of different PFAS in different concentrations are needed to fully understand the mechanism and be able to utilize the process most effectively in large scale. Experiments with sole short-chain PFAS compounds and in combination with long-chain PFAS needs to be performed. Moreover, comparative experiments done in lab scale and pilot scale with the same water and operation conditions would help to better link the findings of the experiments performed at different scale.

Optimisation of CDI in continuous operation

It is essential to perform more testing of the CDI in continuous operation in order to prolong the period of high-efficient PFAS removal. The measures which have not yet been fully investigated include serial operation, power pulsing optimization, flow optimization, etc. Furthermore, strategies for periodically cleaning the CDI electrodes to remove difficult to desorb PFAS molecules from the micropores of the activated carbon should be studied. Further investigation on how the system performs treating water with higher PFAS concentrations and with different chemical composition (e.g., higher content of dissolved organic carbon or hardness) also needs to be conducted to get a better grip of the PFAS removal efficiency and costing parameters in a larger scale. In addition, the projected water recovery ratio of 70 % needs to be confirmed by continued experiments. These measures may lead to more effective regeneration of the electrodes, a lower energy consumption and substantial prolonging the life-time of the modules ensuring that PFAS can be effectively removed by CDI devices with the application of a low voltage.

Life-cycle evaluation

Following the results obtained during the laboratory scale experiments and the pilot runs which was supplemented with LCC and LCA studies in order to obtain a global purview on what can be the next steps, it is obvious that important messages are obtained from this study. Notably amongst the obtained results, in the future, focus should be on scaling up the CDI systems to scales that can be more comparable to the current production level treatments. Furthermore, possibilities of integrating CDI with the GAC treatments to reduce the environmental impact and costs needs to be considered. Finally, long-term tests on the degradation of PFAS molecules and eco-toxicity tests of the by-products containing treated water should be carried out. Further LCA/LCC analysis with scaled up CDI systems would lead to a clearer cost-benefit analysis with the existing technologies.



Cost estimation for the CDI-technology for a large-scale system was not fully possible in this study and should be evaluated better in further studies. The cost of different components (e.g. electrode materials) is subject to change and it is expected that the total investment cost could be reduced in future. In addition, through economies of scale, large systems will have a much lower ratio of power consumption and cost of peripheral components with respect to the water volume treated, hence improving viability of the application.

A more thorough analysis and further optimization of the process could lead to potentially competitive treatment of PFAS using the CDI technology or tandem GAC-CDI technologies.