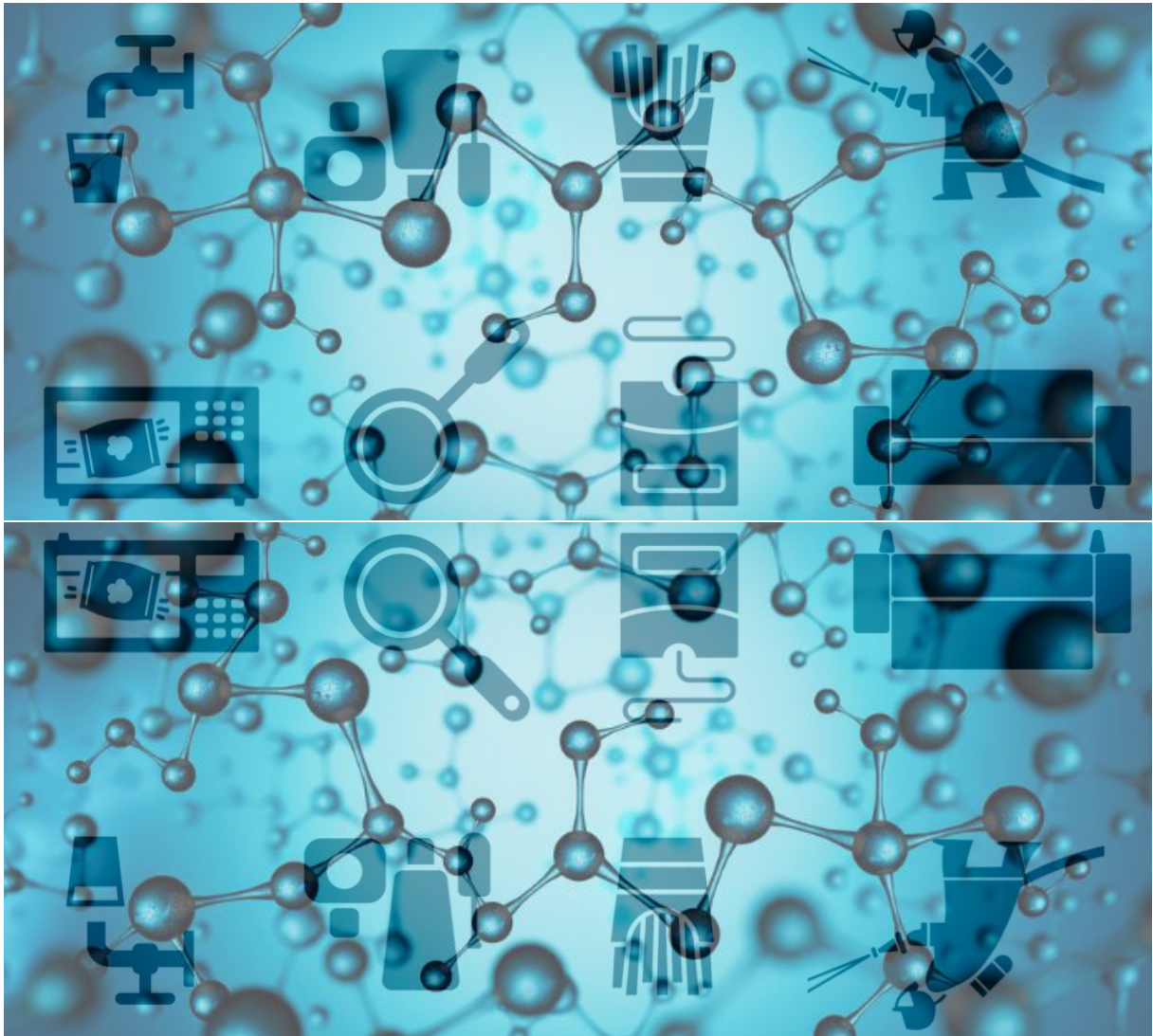

*Electrochemical degradation of PFAS contaminated
water with boron-doped diamond anodes*



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Electrochemical degradation of PFAS contaminated water with boron-doped diamond anodes

Additional Thesis Project

For the degree of MSc Applied Earth Sciences – Environmental Engineering

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Abstract

Since its production concentrations of the manmade chemical compounds PFAS found in the environment has increased significantly. The properties created by incorporating these chemicals, make them attractive for industrial usage and for many consumer products. These chemicals bioaccumulate and are very persistent. With known adverse health effects, its treatment to prevent release in the environment has become more and more important. To remediate PFAS in aquatic environments, such as groundwater and surface water helps protect our drinking water sources and reduces exposure to these harmful compounds. With this in mind the treatment technology, electrochemical oxidation of PFAS is applied here in various water matrices to study the destruction of these compounds.

Through galvanostatic EC experiments, water types in 10L continuously stirred reactor tanks, where pumped through an electrochemical cell consisting of boron-doped diamond electrodes at a constant current of either 30 or 40 A for a duration of either 3 or 6 hours. Samples were processed and then analysed for 29 PFAS through HPLC-MS/MS. Remediation of these compounds proved to be less efficient than in other studies.

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Nomenclature

Technical terms

| | |
|------------------|---|
| AFFF | Aqueous film-forming foam (also aqueous fire-fighting foam) |
| BDD | Boron-doped diamond |
| DOC | Dissolved organic carbon |
| DWTP | Drinking water treatment plant |
| HPLC | High-performance liquid chromatography |
| IS | Internal standard |
| MQL | Method quantification limit |
| MS/MS | Tandem mass spectrometry |
| PFAS | Per- and polyfluoroalkyl substances |
| \sum_{29} PFAS | Sum of 29 PFAS researched here |
| SPE | Solid phase extraction |
| TOC | Total organic carbon |

Per- and polyfluoroalkyl substances

| Acronym | Name | Carbon-atoms, n |
|--------------|---|-----------------|
| 4:2 FTSA | 4:2 Fluorotelomer sulfonic acid | 4 |
| 6:2 FTSA | 6:2 Fluorotelomer sulfonic acid | 6 |
| 8:2 FTSA | 8:2 Fluorotelomer sulfonic acid | 8 |
| 9Cl-PF3ONS | 9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid | |
| 11Cl-PF3OUdS | 11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid | |
| Et-FOSAA | N-ethylperfluorooctane sulfonamide acetic acid | 8 |
| FOSA | Perfluorooctane sulfonamide | 8 |
| HFPO-DA | Tetra-2-(heptafluoropropoxy)propanoic acid (GenX) | |
| Me-FOSAA | N-methyl perfluorooctane sulfonamide acetic acid | 8 |
| NaDONA | Sodium dodecafluoro-3H-4,8-dioxanonanoic acid | |
| PFBA | Perfluorobutanoic acid | 4 |
| PFBS | Perfluorobutane sulfonic acid | 4 |
| PFECHS | Perfluoroethylcyclohexane Sulfonate | |
| PFDA | Perfluorodecanoic acid | 10 |
| PFDoDA | Perfluorododecanoic sulfonic acid | 12 |
| PFDS | Perfluorodecanoic sulfonic acid | 10 |
| PFHpA | Perfluoroheptanoic acid | 7 |
| PFHpS | Perfluoroheptane sulfonic acid | 7 |
| PFHxA | Perfluorohexanoic acid | 5 |
| PFHxS | Perfluorohexane sulfonic acid | 6 |
| PFNA | Perfluorononanoic acid | 9 |
| PFNS | Perfluorononane sulfonic acid | 9 |
| PFOA | Perfluorooctanoic acid | 8 |
| PFOS | Perfluorooctane sulfonic acid | 8 |
| PFPeA | Perfluoropentanoic acid | 5 |
| PFPeS | Perfluoropentane sulfonic acid | 5 |
| PFTeDA | Perfluorotetradecanoic acid | 14 |
| PFTriDA | Perfluorotridecanoic acid | 13 |
| PFUnDA | Perfluoroundecanoic acid | 11 |

1 Introduction

Per- and polyfluoroalkyl substances (PFAS) are man-made fluorinated organic compounds from the 1950s and have been in use ever since for a wide range of consumer products and industrial purposes because of their unique physicochemical properties. When added in consumer products properties such as oil and water repellence and high durability are made (Franke et al., 2019). Consumer products, include shampoo, paint, food-packaging and many more (Ahmed et al., 2020). In industry examples of usage are aqueous film forming foams (AFFF)(Pelch et al., 2019).

The result of the widespread use and production of PFAS is contamination of the environment through industrial emissions, usage of consumer products containing PFAS, leachate from landfills, firefighting foam and WWTPs (Pistocchi & Loos, 2009). In the environment conditions needed to naturally break down the C-F bonds and mineralize the PFAS compounds do not occur (Uwayezu et al., 2021). Their unique properties make them extremely persistent in the environment. The majority of the compounds are non-degradable or transform into other terminal stable PFAS (Cousins et al., 2020). Therefor these chemicals are also described as “forever chemicals”.

The spread and persistency of PFAS is of major concern as they bioaccumulate and are toxic to human health, causing severe health problems, including cancer, immune system dysfunction, liver damage, development and reproductive harm and hormone disruption (Pelch et al., 2019; Li et al., 2020). Most regulatory actions concern perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), as these are the most well researched compounds from the PFAS. They have been included in the international Stockholm Convention and their usage is restricted under the EU’s Persistent Organic Pollutants (POPs) regulation. However over 4700 PFAS have been identified till now by the Organisation for Economic Co-operation and Development (OECD) and evidence is increasing that all those compounds pose similar threats to human health and the environment (Pelch et al., 2019).

Moreover, increased concentrations of PFAS in soil and industrial waste contaminate more and more ground and surface water and therefor limit these sources to be used for the production of drinking water (Uwayezu et al., 2021). According to Boone et al., (2019) Conventional remediation technologies, such as air stripping, thermal treatment, soil vapor extraction and hydroxyl-based chemical oxidation are not effective in removing PFOS and PFOA. Most used treatment technologies are extraction through carbon adsorption, reverse osmosis (RO), and nanofiltration, which are relatively expensive and affected by other contaminants present in the groundwater. Other technologies such as chemical oxidation, chemical reduction, electrochemical and sonochemical methods are under development and are promising (Kucharzyk et al., 2017).

The aim of this work is to research PFAS degradation through electrochemical oxidation in different water matrices with an existing electrochemical cell.

1.1 Per- and polyfluoroalkyl substances

PFAS are a subset of fluorinated substances, namely the highly fluorinated aliphatic substances. They can be divided into polymers and non-polymers. The polymers are highly weighted molecules and not viewed as problematic, however the non-polymeric PFAS are mobile in the environment and known to affect human health (Franke, 2020). Here the focus lies on non-polymeric PFAS and further usage of 'PFAS' in this work refers to the non-polymeric PFAS.

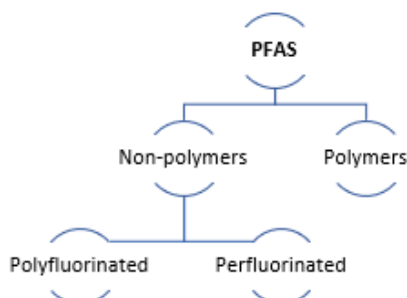


Figure 1: The condensed family tree for PFAS

PFAS contain perfluoroalkyl substances and polyfluoroalkyl substances, where the first one is characterized by the substitution of every H atom by F atoms with exception of the functional group, and were the latter as seen in the figure below shows that not all H atoms are replaced by an F atom, also excluding the functional group. The substitution of H atoms with F atoms gives PFAS the perfluoroalkyl moiety C_nF_{2n+1} . The C – F bonds convey these compounds their strength and stability.

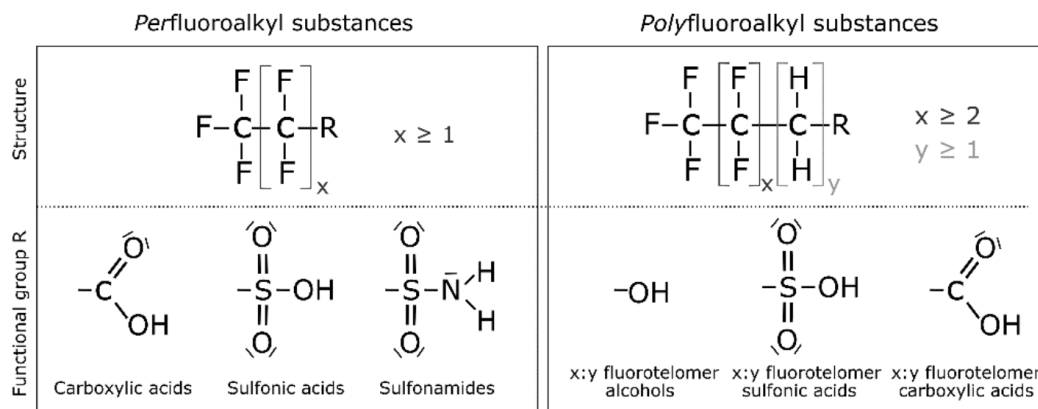


Figure 2: Common PFAS chemical structures (Franke, 2020).

Moreover, polyfluoroalkyl substances can transform under certain conditions (abiotically or biotically) to perfluoroalkyl substances. The Long chained PFAS has been the focus in the global regulatory community, specifically perfluoroalkyl carboxylic acids ($C_nF_{2n+1}SO_3H, n \geq 6$) and perfluoroalkyl carboxylic acid ($C_nF_{2n+1}COOH, n \geq 7$) as they show to be more bio accumulative compared to their short-chain counterparts (Buck et al., 2011). Due to the regulations, resulting in the phasing out and banning, of long chained PFAS, such as PFOA and PFOS, a swift has been made to the production of short chained PFAS. The percentage of these short-chained compounds will increase in the environment and waterbodies in addition to their formation by the degradation of the long-chained counterparts. However for these compounds the potential health risks are also feared as they are less absorbable, more persistent and mobile in soil and groundwater (Li et al., 2020).

1.2 Electrochemical treatment

PFAS treatment technology consist of destructive and non-destructive treatment processes. Destructive treatments make use of redox reactions to degrade the PFAS into smaller compounds (organic and inorganic). The best situation would be defluorination, where fluoride is formed and mineralization, where the carbon is transformed into CO_2 . This minimizes costs that would result from residual waste processing. For this work electrooxidation is looked into. Electrooxidation is one of the most widely studied water treatment process and have been researched mainly regarding wastewater, contaminated groundwater, and fundamental electrolyte matrices. Recently drinking water is also studied in this context. There are several advantages in using this technology, e.g. on-site generation of water treatment chemicals, decentralized operation, scalable and modular processes for optional increase in capacity (Ryan et al., 2021).

Electrochemical treatments employ electrolyte cells, which basically comprise of an electron source, an anode and a cathode (the latter two can be in multiples). The reductions reactions happen on the cathode, whereas the oxidation reactions occur on the anode. Determined by the desired reactions, specific electrode materials are chosen.

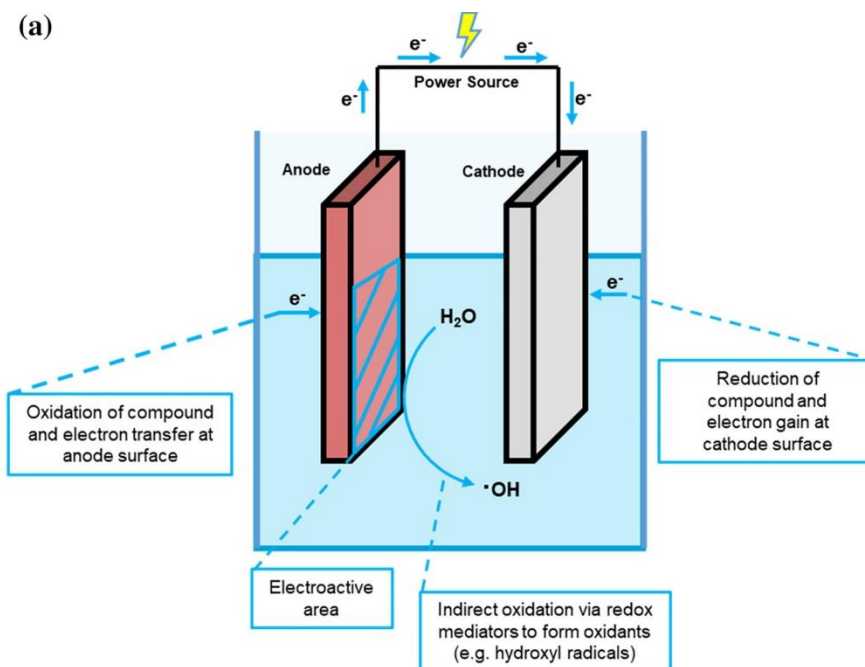


Figure 3: Basic schematics of an electrolytic cell in electrochemical water treatment reactors (Ryan et al., 2021)

For the experiments in this work boron-doped diamond on niobium (Ni) electrodes were used. These electrodes are favourable due to their mechanical, chemical and thermal stability and high electron transfer ability (Wanninayake, 2021). This technique allows for full mineralization of PFAS. These electrodes can oxidize PFAS directly on the anode surface through electron transfer or with indirect oxidation through hydroxyl radicals ($\bullet\text{OH}$) or in situ produced oxidants (Schaefer et al., 2017). When the radicals react with the PFAS, a stepwise degradation process occur with corresponding sequence of chain reactions (Wanninayake, 2021), resulting in shorter chained PFAS.

The current density is the amount of current per surface area of the electrode. This is an important parameter as it directly influences the amount of oxidative species produced (Veciana et al., 2022). For remediation of PFAS high voltage and current are needed.

1.3 Water matrices

For researching PFAS remediation various electrolytes have been used, such as sodium sulphate (Na_2SO_4), sodium chloride (NaCl), sodium perchlorate (NaClO_4) and sodium nitrate (NaNO_3). However sodium sulphate and sodium nitrate are preferred due to the formation of toxic products by chloride, such as chlorate (ClO_3^-) and perchlorate (ClO_4^-) (Veciana et al., 2022).

Natural organic matter, dissolved carbon species and hydrocarbons co-contaminants connected to AFFF releases compete with PFAS for hydroxyl radicals and therefore inhibit PFAS reactions (Schaefer et al., 2017).

An indirect pathway for the formation of PFAS is through precursors. These compounds are existing contaminants or end up in the environment with the release of PFAS. The problem of these compounds is their ability to transform to PFAS consequently resulting in higher concentrations. The water samples used in the experiments were retrieved from an area highly contaminated with AFFF, and precursors are associated with AFFF releases (D'Agostino & Mabury, 2017).

High level of ions in the water will increase the electrical conductivity, resulting in lower electrical power demands, which will make the usage of this treatment technology more economically attractive. Low conductivity in for example drinking water treatment can be a challenge as adding salts should be within certain ranges corresponding to drinking water norms. The ions in water matrices influences which oxidants are produced and these in turn significantly impact the chemical reactions pathways (Ryan et al., 2021).

2 Methodology

2.1 Water matrices

The water matrices used here, were from an industrial site of the company Cytiva. The grounds are highly contaminated due to incidents with PFAS containing firefighting foam. From different wells around the compounds ground water at two different depths were collected. Treated process water and stormwater were also evaluated from this site, however concentrations were very low from the latter two, which made the result less trustworthy and therefore not included in this report.

Below an overview can be seen for the general chemistry of the water types used.

Table 1: The general chemistry of the untreated water types.

| ELEMENT | SAMPLE | Shallow groundwater | Deep groundwater 1 | Deep groundwater 2 |
|-------------------------------|-------------------------------------|---------------------|--------------------|--------------------|
| Ca, calcium | mg/L | 54.4 | 125 | 144 |
| Fe, iron | mg/L | 2.49 | 2.86 | 3.84 |
| K, potassium | mg/L | 7.53 | 52.4 | 20.3 |
| Mg, magnesium | mg/L | 8.84 | 23.7 | 32.8 |
| Mn, Mangan | µg/L | 125 | 721 | 382 |
| Na, sodium | mg/L | 442 | 185 | 109 |
| nitrite, NO ₂ | mg/L | 0.011 | 0.013 | <0.010 |
| Nitrite, NO ₂ -N | mg/L | 0.003 | 0.004 | <0.002 |
| chloride | mg/L | 308 | 337 | 253 |
| COD-Cr | mg/L | 338 | 18.8 | 13.2 |
| fluoride | mg/L | 0.799 | 0.707 | 0.752 |
| ammonium NH ₄ | mg/L | 3.63 | <0.050 | <0.050 |
| ammonia- + NH ₄ -N | mg/L | 2.82 | <0.040 | <0.040 |
| nitrate, NO ₃ | mg/L | <2.00 | 6.32 | 16.8 |
| Nitrate, NO ₃ -N | mg/L | <0.500 | 1.43 | 3.8 |
| total phosphor, P | mg/L | 1.69 | 1.34 | 0.346 |
| Total nitrogen | mg/L | 7.2 | 1.7 | 3.5 |
| Chlorate | µg/L | <10 | <10 | <10 |
| turbidity | FNU | 13.1 | 32.8 | 84.6 |
| alkalinity | mg HCO ₃ ⁻ /L | 596 | 453 | 430 |
| TOC | mg/L | 112 | 8.86 | 6.09 |

The degradation efficiency of the electrochemical cells was tested by using demineralized water in which a mixture of PFOA and PFOS was added. Below the added amounts can be seen. The sodium sulphate was added to increase the conductivity of the water used.

Table 2: Synthetic solution components

| Components | Amount | Concentration |
|-----------------|--------|---------------|
| Demi water | 10 L | - |
| Sodium sulphate | 10 g | 1 g/L |
| PFOA | 0.1 mL | 0.1 mg/L |
| PFOS | 0.1 mL | 0.1 mg/L |

2.2 General study design

Table 3 shows an overview for the various water matrices and experimental conditions. For the first two experiments shallow and deep groundwater, the current density was 15 mA/cm². After gathering the results, a current density of 20 (at maximum current intensity) was used for the experiments with system 1. For system 2 the current density was 40 mA/cm² (also at maximum current intensity). All experiments were performed in duplicates.

Table 3: Overview experiments conditions and water types

| Water type | Electrochemical Cell* | Duration (hr) | Current density [mA/cm ²] | Flow rate L/min |
|---------------------|-----------------------|---------------|---------------------------------------|-----------------|
| Groundwater shallow | System 1 | 3 | 15 | 8 |
| Deep Groundwater 1 | System 1 | 3 | 15 | 8 |
| Deep Groundwater 1 | System 1 | 6 | 20 | 8 |
| Deep Groundwater 2 | System 2 | 3 | 40 | 8 |
| PFOS/PFOA mix 1 | System 1 | 3 | 20 | 8 |
| PFOS/PFOA mix 2 | System 2 | 3 | 40 | 8 |

*System 1: cell with 20 dm² anode surface

System 2: cell with 10 dm² anode surface

2.3 Experimental set-up

See Figure 4 for the experiment set-up. The studied water type was poured into the 10 L reactor and continuously stirred with a motorized mixer at 10000 rpm. To create a constant flow of 8L per minute in the system a pump was connected. Lastly the water type was pumped through the electrochemical cells from NOVA Diamant AB (Uppsala, Sweden). Here one cell with 10 dm² anode surface and another cell with 20 dm² anode surface were used. The power source was a lab grade switching mode power supply with a maximum output of 16 Volt and 40 Ampere.

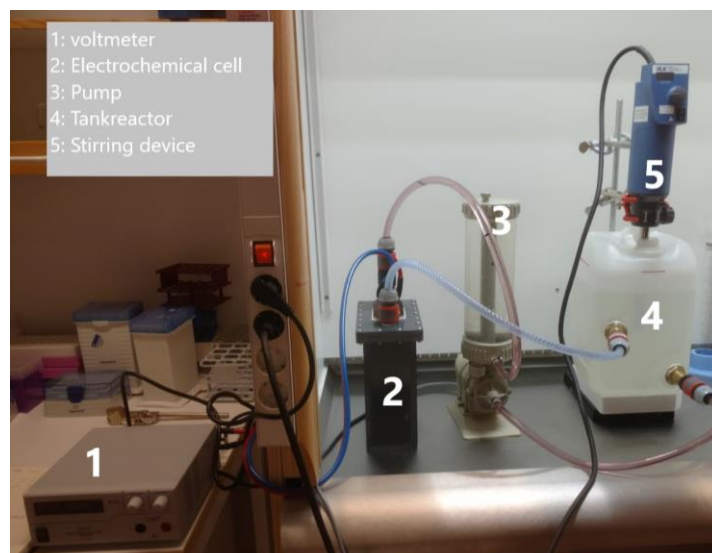


Figure 4: Set up of the experiments

The system was rinsed 3 times with demineralized water after each experiment and the order of experiments went from the least PFAS contaminated water type to the most contaminated one, to avoid cross contamination between them. The demineralized water was used for rinsing as it was found to consist of approximately 200 ng/L PFAS, which was relatively low compared to the concentrations in the tested water types.

For scaled systems it was recommended that the system is operated under constant current (galvanostatic). By maintaining a constant current, the potential (V) will be analogous to it based on the cell resistance, which is mainly influenced by the matrix conductivity. The electroactive area of the electrodes in the electrochemical cell and the current used, gives the current density in mA/cm^2 .

Sampling was done on 0, 15, 35, 60, 90, 130, 180 minutes respectively for the 3hour duration and on 0, 40, 90, 150, 210, 280, 360 minutes respectively for the 6hour duration. For every sample the pH and temperature were measured as an extra check on the experimental conditions.

The next step was to filter the samples. Equipment was rinsed three times with methanol before usage. 0.45 μm microfiber filters were used. To pull the liquid through the filter a vacuum pump was attached and switched on for short periods. To reduce cross contamination samples went in the order from least contaminated to highest. See below the filtration method.



Figure 5: Filtration of the samples

After filtration the samples were processed following to the method, solid-phase extraction (SPE) according to the ISO 25101:2009 method (ISO, 2009). The samples were poured into the reservoir (right picture), where then it would pass the cartridge (Oasis® WAX cartridges, 6cc, 150 mg, 60 µm; Waters, Ireland). Due to the ionic characteristics of the cartridges the PFAS compounds are gathered within. Then to subtract the analyte from the cartridges an elution solution of 1% of NH_4OH in methanol was used for the cartridges (Left picture). PP tubes were set beneath the cartridges to catch the washed out PFAS.

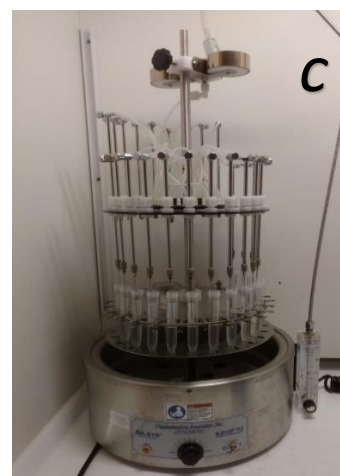
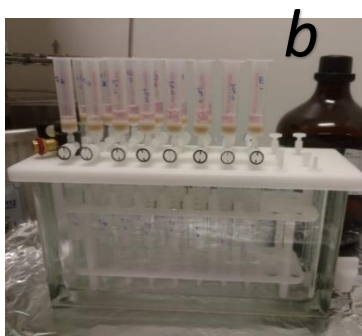


Figure 6: a: filling the reservoirs with the sample, b: removing the analytes from the cartridges, c: nitrogen evaporator.

Then the analytes are put into the nitrogen evaporator to increase its concentration to 1mL and transferred into 2 mL vials. These vials were shaken before entering the HPLC-MS/MS for analysis.

3 Results and discussion

3.1 PFAS degradation in PFOS/PFOA spiked water

3.1.1 System 1

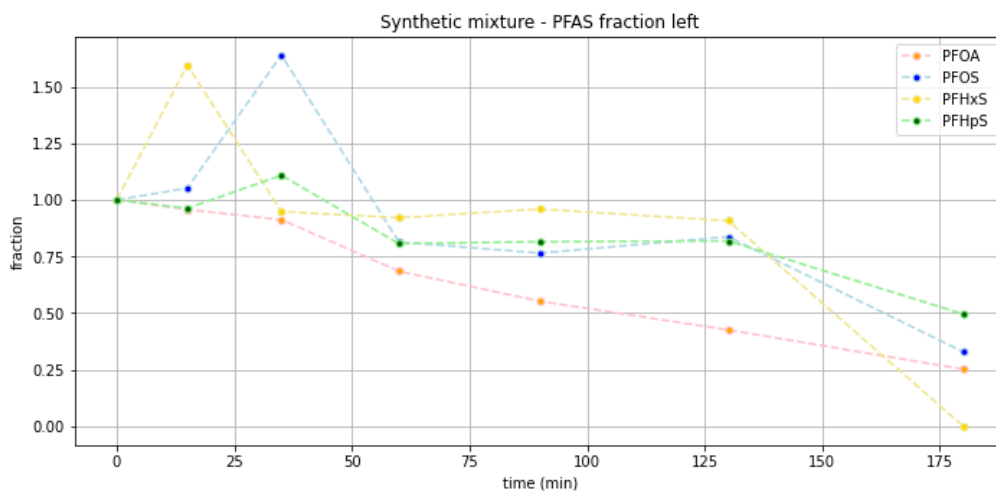
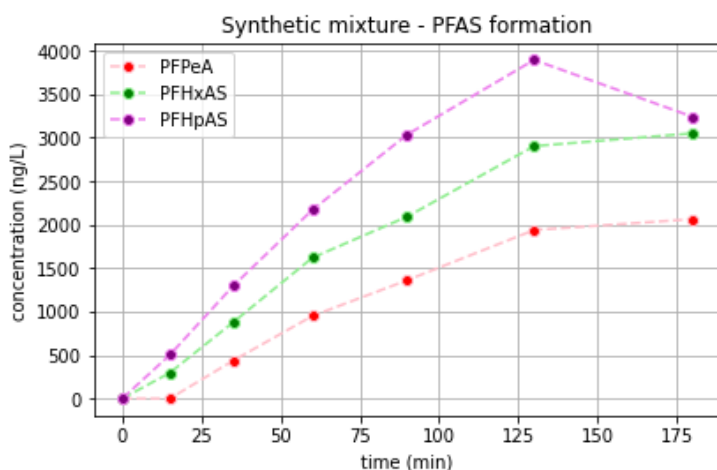


Figure 7: Remediation of PFOA/PFOS spiked demineralized water at sampling points.

Figure 7 shows the decrease of PFOA, PFOS, PFHxS and PFHpS. These four compounds were present at the first sampling point. Initially an increase in PFOS, PFHpS and PFHxS concentration occurred. Either they were formed during treatment or contamination occurred during processing of the samples. Only PFOA was reducing in concentration for every sampling point. Percentage of these compounds left after treatment can be seen in Table 4. Only the data of the duplicate were used here, as the first experiment appeared to have high contamination in some of the samples.

Table 4: system 1, PFAS fraction left after 3 hours of treatment.

| Type | PFAS left after treatment [%] | Amount treated [ng/L] |
|------------------|-------------------------------|-----------------------|
| PFOA | 25.22 | 51778.00 |
| PFOS | 32.86 | 17025.18 |
| PFHxS | 0.00 | 59.05 |
| PFHpS | 49.58 | 599.72 |
| \sum_{29} PFAS | 37.47 | 69461.94 |



Shorter chained PFAS; PFPeA(n=4), PFHxA(n=5) and PFHpA(n=6) were formed during treatment as they were not present in the initial sampling point.

Figure 8: System 1, PFOS/PFOA mixture, compound formation of PFPeA, PFHxA and PFHpA.

3.1.2 System 2

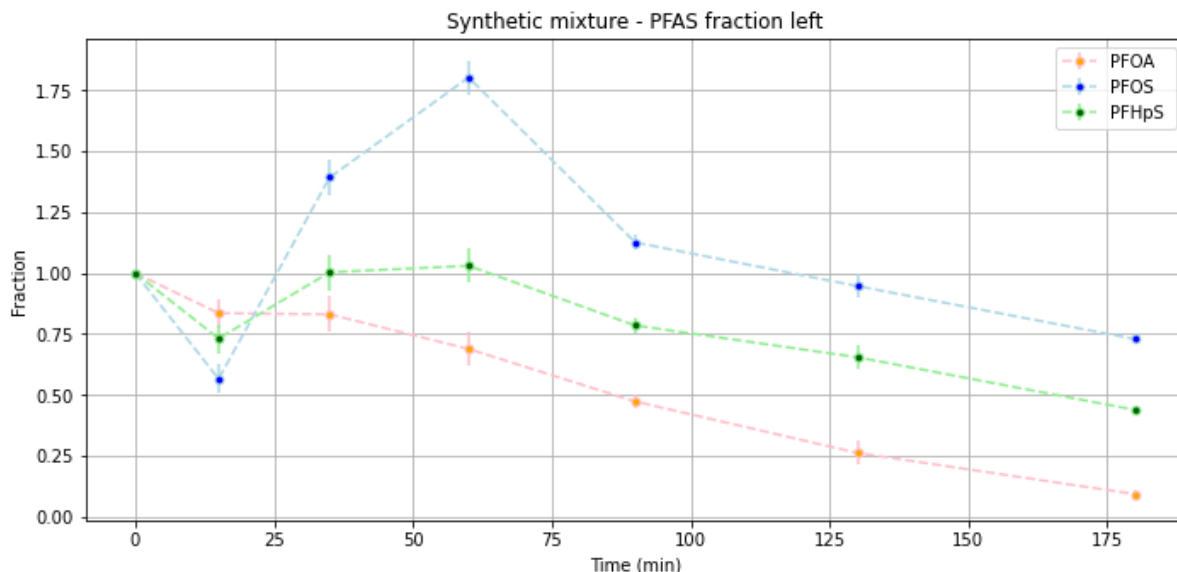
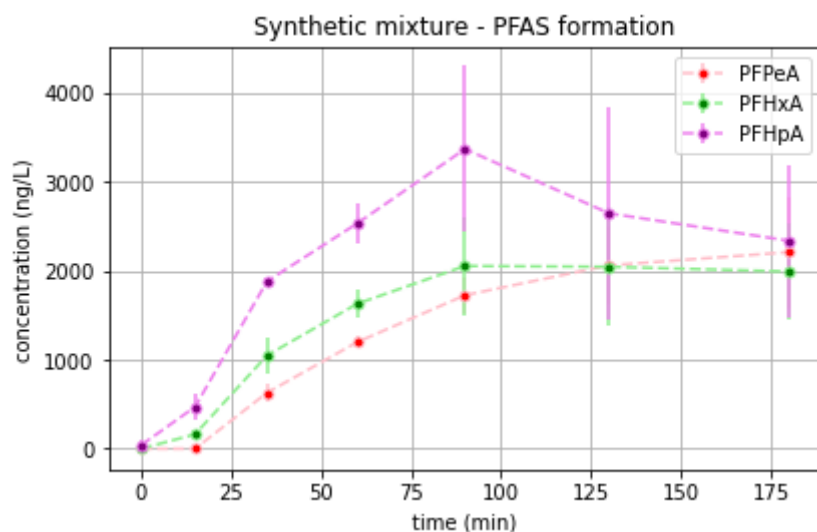


Figure 9: PFOA/PFOA mixture system 2, PFAS fraction left over time.

For system 2 an initial decrease followed by an increase of concentration can be seen for PFOS and PFHpS. The increase corresponds to the compounds behaviour found with system 1. PFHxS is not found here, which was probably due to the concentration being under the detection limit. PFOS (n=8) degradation is significantly lower compared to the other system. However, more PFOA (n=7) has been treated comparatively. This was not expected as longer chained PFAS ordinarily have an higher oxidation rate (Veciana et al., 2022).

Table 5: system 1, PFAS fraction left after 3 hours of treatment.

| Type | PFAS left after treatment [%] | Amount treated [ng/L] |
|------------------|-------------------------------|-----------------------|
| PFOA | 9.35 | 53433.13 |
| PFOS | 72.94 | 11120.35 |
| PFHpS | 43.88 | 774.12 |
| \sum_{29} PFAS | 31.19 | 65327.60 |



PFPeA, PFHxA and PFHpA were also formed here during treatment.

Figure 10: System 2, PFOS/PFOA mixture, compound formation of PFPeA, PFHxAS and PFHpAS

3.1.3 Comparison of the two systems

The degradation development of the compounds was similar between the results of the two systems. As system 1 has a bigger anode surface it has treated higher concentrations of the compounds. As the formation of PFPeA, PFHxAS and PFHpAS depends on the degradation of the other compounds, also here more compounds were formed for system 1.

3.2 Shallow groundwater

3.2.1 System 1

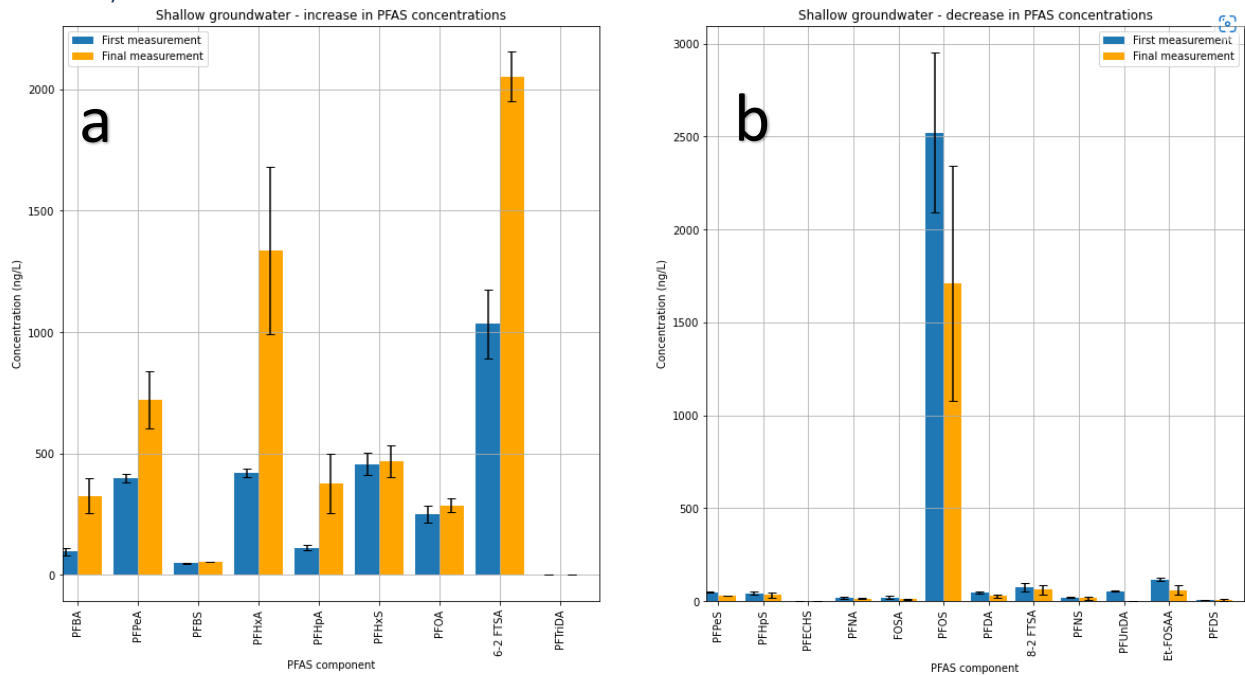


Figure 11: Shallow groundwater, a: compounds with increase in concentrations, b: compounds with decreasing concentrations

For shallow groundwater more compounds were formed see figure 8a, which is expected as the area is contaminated with AFFF and therefore precursors should be present. Also, with the presence of long chained PFAS, shorter chained PFAS are expected to be released when they oxidate. Next to the formation of PFPeA, PFHxA and PFHpA as seen with the synthetic water matrices now also PFBA, PFPeA, PFBS, PFHxS, PFOA, 6:2 FTSA and PFTriDA were formed. Only for PFOS a significant decrease in concentration can be seen. It could be that organic matter or microorganisms present limited the electron transfer efficiency (Schaefer et al., 2017).

Table 6: Shallow groundwater: Overview for the sum of the analysed PFAS components.

| | Initial concentration [ng/L] | Final concentration [ng/L] | Percentage removal [%] |
|-------------------------|------------------------------|----------------------------|------------------------|
| $\sum_{29} \text{PFAS}$ | 5791.22 | 7591.53 | -0.31 |

3.3 PFAS degradation in deep groundwater 1

3.3.1 System 1

3.3.1.1 Experiment duration: 3 hours

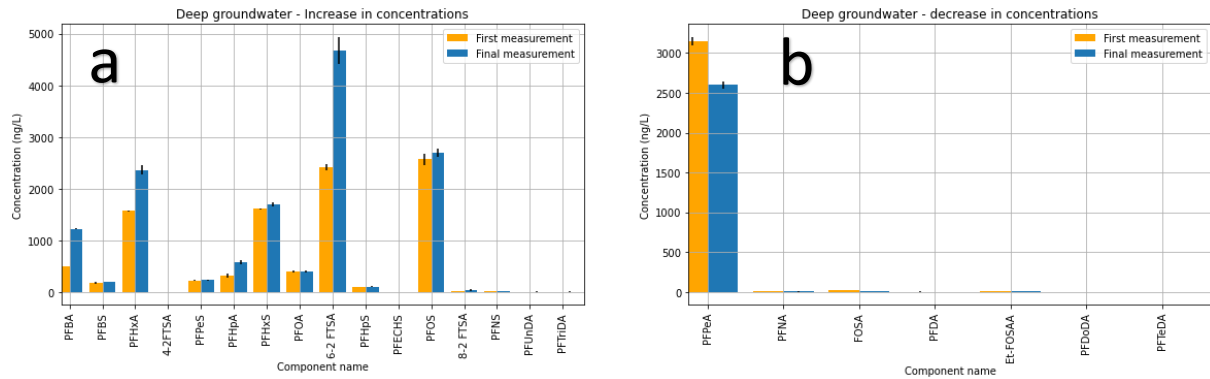


Figure 12: deep groundwater (3h), a: compounds with increase in concentrations, b: compounds with decreasing concentrations

The results from treating deep groundwater show an increase in various compounds, but only PFPeA had decreased in concentration. Also compounds such as, chloride, manganese, iron was decreasing in the range of 10~200 mg/L, which is much higher than the PFAS concentrations present and might have competed for the active sites on the anodes or for the free radicals produced.

Table 7: Deep groundwater 1: Overview for the sum of the analysed PFAS components.

| | Initial concentration [ng/L] | Final concentration [ng/L] | Percentage removal [%] |
|------------------|------------------------------|----------------------------|------------------------|
| \sum_{29} PFAS | 13098.55 | 16852.94 | -28.66 |

3.3.2 System 1, experiment duration 6h

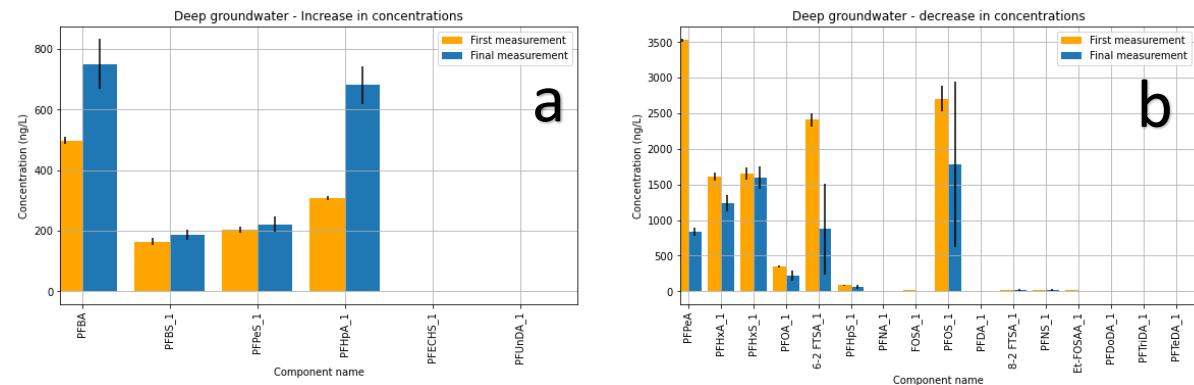


Figure 13: deep groundwater (6h), a: compounds that were formed, b: compounds with decreasing concentrations.

With longer treatment duration more compounds were being oxidized. The number of compounds increasing in concentration is much less compared to treating for 3 hours. It is possible that precursors need more time to form PFAS before they can actually be degraded.

Table 8: Deep groundwater 1: Overview for the sum of the analysed PFAS components.

| | Initial concentration [ng/L] | Final concentration [ng/L] | Percentage removal [%] |
|------------------|------------------------------|----------------------------|------------------------|
| \sum_{29} PFAS | 13616.71 | 8495.47 | 37.61 |

3.4 PFAS degradation in deep groundwater 2

3.4.1 System 2

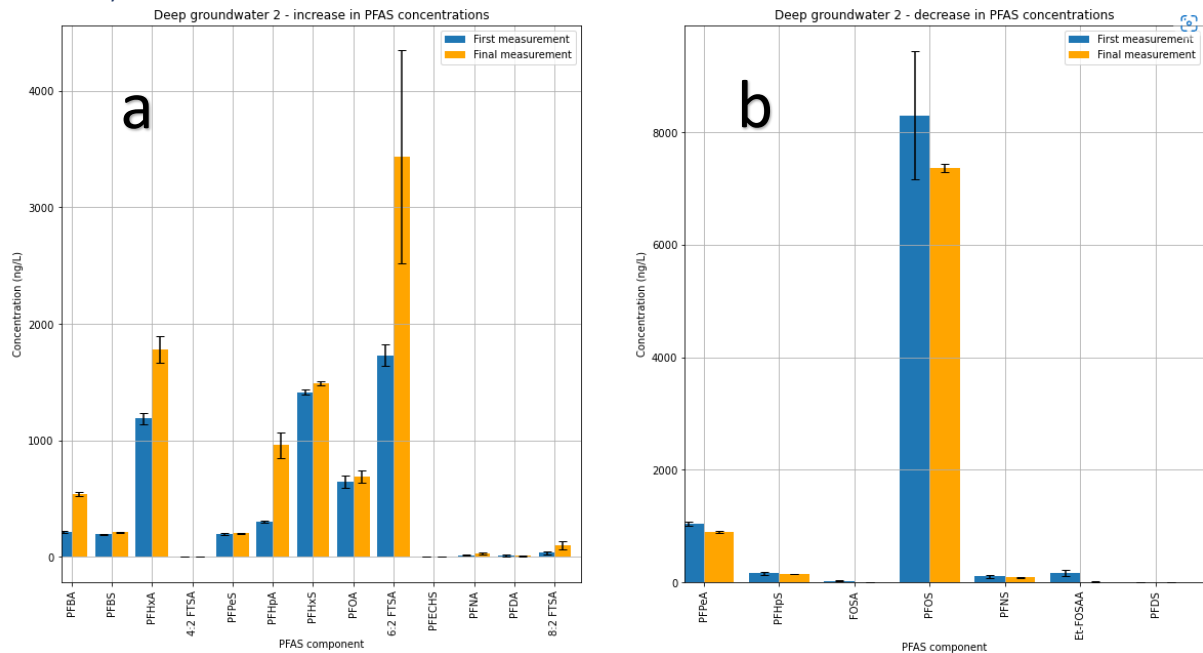


Figure 14: deep groundwater (3h), a: compounds with increase in concentrations, b: compounds with decreasing concentrations.

Here more PFAS were formed than were destroyed. Also, the amount of treated PFAS is low, however it is similar to system one. The formation of so many compounds is likely due to precursors.

Table 9: Deep groundwater 2: Overview for the sum of the analysed PFAS components.

| | Initial concentration [ng/L] | Final concentration [ng/L] | Percentage removal [%] |
|-------------------------|------------------------------|----------------------------|------------------------|
| $\sum_{29} \text{PFAS}$ | 15747.37 | 17958.66 | -0.14 |

4 Conclusions and outlook

By increasing treatment duration and anode surface area higher concentrations of PFAS compounds will be oxidized. Precursors and other interfering components reduced the treatment efficiency considerably. Formation of PFAS during treatment is in most cases more than what is degraded.

Recommendations are to model a more efficient electrochemical cell and to invert the electrochemical process to clear out any scaling that occurs and to determine an efficient cleaning procedure for the system used in general to prevent cross contamination.

Appendix

A Additional data

A.1 General chemistry

Table 10: General chemistry of the treated and untreated water types.

| ELEMENT | SAMPLE | Shallow groundwater | | Deep groundwater 1 | | | Deep groundwater | |
|-------------------------------|-------------------------|---------------------|---------|--------------------|------------|------------|------------------|---------|
| | | Untreated | Treated | Untreated | Treated 3h | Treated 6h | Untreated | Treated |
| Ca, calcium | mg/L | 54.4 | 22.3 | 125 | 32.1 | 28.3 | 144 | 38.1 |
| Fe, iron | mg/L | 2.49 | 1.66 | 2.86 | 0.693 | 0.505 | 3.84 | 2.62 |
| K, potassium | mg/L | 7.53 | 7.52 | 52.4 | 49.6 | 51.6 | 20.3 | 20.4 |
| Mg, magnesium | mg/L | 8.84 | 2.56 | 23.7 | 11.1 | 3 | 32.8 | 23.8 |
| Mn, Mangan | µg/L | 125 | 28 | 721 | 314 | 81.3 | 382 | 232 |
| Na, sodium | mg/L | 442 | 435 | 185 | 176 | 181 | 109 | 109 |
| nitrite, NO ₂ | mg/L | 0.011 | 0.248 | 0.013 | 0.063 | 0.234 | <0.010 | 0.099 |
| Nitrite, NO ₂ -N | mg/L | 0.003 | 0.076 | 0.004 | 0.019 | 0.071 | <0.002 | 0.03 |
| chloride | mg/L | 308 | 50.7 | 337 | 36.5 | 1.6 | 253 | 10.4 |
| COD-Cr | mg/L | 338 | 415 | 18.8 | 1370 | 62.6 | 13.2 | 89.7 |
| fluoride | mg/L | 0.799 | 0.785 | 0.707 | 0.645 | 0.677 | 0.752 | 0.63 |
| ammonium NH ₄ | mg/L | 3.63 | 0.222 | <0.050 | <0.050 | 0.356 | <0.050 | <0.050 |
| ammonia- + NH ₄ -N | mg/L | 2.82 | 0.172 | <0.040 | <0.040 | 0.277 | <0.040 | <0.040 |
| nitrate, NO ₃ | mg/L | <2.00 | 9.24 | 6.32 | 3.05 | 3.78 | 16.8 | 4.49 |
| Nitrate, NO ₃ -N | mg/L | <0.500 | 2.09 | 1.43 | 0.688 | 0.854 | 3.8 | 1.01 |
| total phosphor, P | mg/L | 1.69 | 0.884 | 1.34 | 0.27 | 0.21 | 0.346 | 0.226 |
| Total nitrogen | mg/L | 7.2 | 6 | 1.7 | 1.1 | <1.0 | 3.5 | <1.0 |
| Chlorate | µg/L | <10 | 210000 | <10 | 182000 | 11700 | <10 | 26600 |
| turbidity | FNU | 13.1 | 14.2 | 32.8 | 13.5 | 11.7 | 84.6 | 50.8 |
| alkalinity | mg HCO ₃ -/L | 596 | 416 | 453 | 84.6 | 27 | 430 | 33.9 |
| TOC | mg/L | 112 | 146 | 8.86 | 373 | 2.78 | 6.09 | 10.3 |

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