ZeroPM

Zero pollution of Persistent, Mobile substances

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Optimized elimination of residues arising from drinking water treatment

Work Package 7 – Technical Solutions, Method Development and Analysis

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Summary

The European research project ZeroPM – "Zero pollution of Persistent, Mobile substances" combines three interlinked strategies to tackle pollution with persistent and mobile (PM) substances: Prevent, Prioritize and Remove. Work Package 7 – "Technical Solutions, Method Development and Analysis" (WP7) is dedicated to the removal of PM substances. Among other things, WP7 will develop innovative treatment methods for residues arising from Anion Exchange Regenerates (AEX), which is also being developed in ZeroPM (see Deliverable 7.2). This deliverable reports on the experiments that have been performed to (i) investigate electrochemical oxidation for the elimination of PFAS in AEX regenerates, (ii) test suitable operating conditions for electrochemical PFAS elimination by 20 L scale electrolysis plant, (iii) evaluate degradation kinetics of singe PFAS and (iv) investigate the PFAS elimination of raw water from a contaminated site.

Previous studies concerning the AEX process (Deliverable 7.1) with selected adsorption resins showed the best PFAS adsorption and regeneration performance using 1 M NaOH. However, high salt concentrations in the regeneration solution hindered electrochemical oxidation, which improved when NaOH concentration was reduced to 0.002 M. Due to this limitation, the study shifted focus to direct PFAS elimination from raw water.

The LabSys pilot plant by CONDIAS proved effective in removing various PFAS, including PFOA and TFA, and is portable for on-site testing. Optimal pump performance was found at 40 %, beyond which no significant gains were observed. PFAS elimination efficiency depended on molecular structure, with sulfonic acids being more resistant than carboxylic acids. Kinetic studies supported first-order degradation behaviour for PFOA and PFBA.

Overall, electrochemical oxidation offers a promising alternative to traditional methods by not just concentrating but mineralizing PFAS. Its effectiveness is enhanced at higher PFAS concentrations and can be optimized further through enrichment techniques without increasing conductivity. Key outputs related to this deliverable will be used in future work in ZeroPM to compare the life cycle analysis (LCA) impacts of alternative water treatments (notably in the forthcoming Deliverable 2.6)

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1 Introduction

ZeroPM, which stands for Zero pollution of Persistent, Mobile substances, is a 5 year long European research project funded under the Horizon 2020 research and innovation program. ZeroPM will interlink and synergize three strategies to protect the environment and human health from persistent and mobile (PM) substances: Prevent, Prioritize and Remove. To do this, ZeroPM will develop an evidence-based multilevel framework. The framework will guide policy, technological and market incentives to minimize use, emissions and pollution of entire groups of PM substances.

Work Package 7 – "Technical Solutions, Method Development and Analysis" (WP7) has the overall objective to demonstrate how and if legacy and prioritized PM substance pollution can be remediated. WP7 investigates innovative treatment and monitoring methods for water (ground, surface, bank filtrate, waste) and sludge to protect water resources, provide safe drinking water and protect human health and the environment, with a focus on PM substances and media from three different test sites.

One of these test sites (test site 1) is located in the southwest of Germany ("Rastatt case"), where more than 600 ha of agricultural land is contaminated with per- and polyfluorinated alkyl substances (PFAS) (Goldenman *et al.* 2019). The most likely source is compost blended with paper fibre sludge from paper mill waste, which had been applied to acres in the area between 2005–2008 (Regierungspräsidium Karlsruhe 2022). The PFAS typically present at the site are polyfluorinated alkyl phosphate esters and perfluoroalkane sulfonylamidoethanol phosphate esters as well as their intermediate and terminal degradation products. More mobile than the parent compounds are the terminal degradation products, which are primarily perfluoroalkyl acids (PFAAs). The PFAAs present at the site contaminate the groundwater which is used for drinking water production. To protect the drinking water source, new installations had to be set up which cost the drinking water production company, Stadtwerke Rastatt, 3.6 million Euro at the end of 2017 (with costs only increasing since then) (Goldenman *et al.* 2019).

One of the new waterworks treats the PFAS contamination using activated carbon (AC) filters. The biggest part of the treatment costs is dependent on the frequency with which the activated carbon in the filters must be exchanged after exhaustion. In addition, it is also important to note that the sorption capacity for PFAS with shorter alkyl chain lengths can be much lower than for PFAS with longer alkyl chains leading to earlier breakthroughs in the filter for short-chain PFAS. The previous threshold values and health advisory values(in German: *Leitwerte*, *Gesundheitliche Orientierungswerte*) for some PFAS (Table 1-1) allowed operating times of up to 1.5 years for the activated carbon filters (90000 bed volumes (BV)) (Haist-Gulde *et al.* 2021). The revised EU drinking water directive now requires that a threshold concentration of 0.1 µg/L for the sum of 20 PFAS including short chain PFAS with more than three carbon atoms is achieved (Directive (EU) 2020/2184 2020). This value is a considerate reduction of the threshold concentration, especially for the short chain PFAS which had higher guide and orientation values compared to long chain PFAS. For perfluorobutanoic acid (PFBA) alone, this means a reduction of the allowed concentration by at least a factor of one hundred. Combined with the early breakthrough in the activated carbon filters, this reduces operating times of the carbon filters by more than 50% which leads to additional costs and material efforts (Haist-Gulde *et al.* 2021).

Table 1-1: Previous guide & orientation values: water quality threshold values - *Leitwerte (LW),* health advisory values - *Gesundheitliche Orientierungswerte (GOW) of five exemplary selected PFAS.*

Acronym	Substance	No. C-atoms	LW, µg/L	GOW, µg/L
PFBA	perfluorbutanoic acid	4	10	-
PFPeA	perfluoropentanoic acid	5	-	3.0
PFHxA	perfluorhexanoic acid	6	6	-
PFHpA	perfluorheptanoic acid	7	-	0.3
PFOA	perfluoroctanoic acid	8	0.1	-

Source: Drinking Water Commission of German Environment Agency (UBA / TWK 2017).

To address this clear knowledge and technical gap, ZeroPM is investigating a new hybrid process that will also be used in a pilot plant at the test site in a waterworks in Rastatt. The process consists of a treatment train with a granular activated carbon (GAC) filter followed by ion exchange (IEX) (Figure 1-1). Since PFAS are negatively charged under typical environmental pH values, they can undergo electrostatic interactions with an anion exchanger (AEX). Within the proposed treatment, the GAC eliminates long-chain PFAS whereas the subsequently applied AEX removes short-chain PFAS. After regeneration of the AEX, which was shown to be most efficient using 1M NaOH (as demonstrated in ZeroPM Seliverable 7.1), the short-chain PFAS are concentrated in the regenerate and must also be treated. Therefore, electrochemical oxidation was tested in different scales, to form the last step of the pilot plant as shown in Figure 1-1, and thus, to complete the treatment chain.

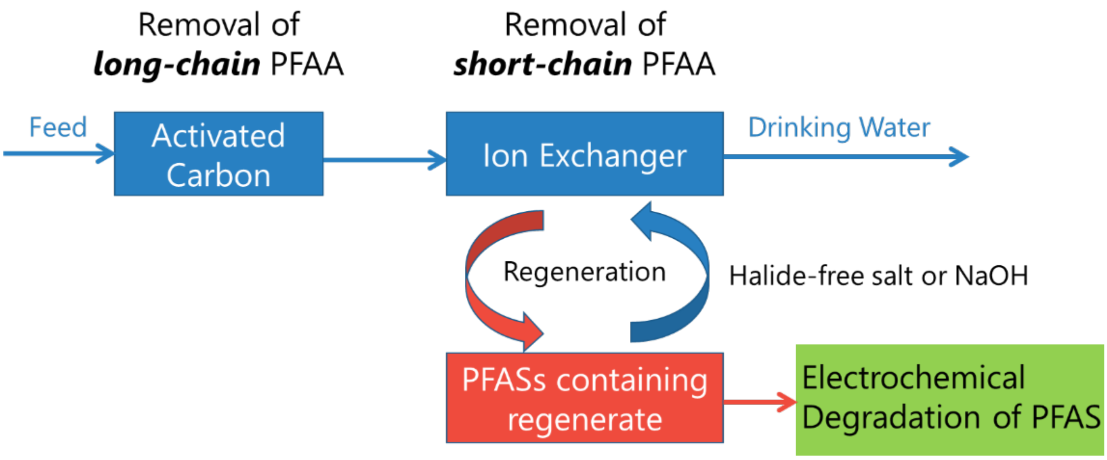

Figure 1-1: Proposed process to treat PFAS contaminated source water for drinking water production (treatment 1). The feed in is PFAS contaminated water.

In electrochemical oxidation processes, compounds that are difficult to degrade can be mineralised into inorganic compounds such as H_2O, CO_2 and salts. In this process, two electrodes are placed in a conductive liquid, the electrolyte, and a direct current is applied. The electrolyte is an ionic, liquid solution in which the application of the direct current causes current to flow due to the migration and discharge of the ions. The electrodes serve as solid conductors and have different roles and polarities. The positively charged anode and the negatively charged cathode conduct the electric current, with electrons being the charge carriers (Springborg 2020). An oxidation reaction takes place at the anode with the reactant present. During this reaction, negatively charged ions migrate to the anode and release electrons to the external circuit. This electron release reduces the electron deficiency of the anode and leads to the formation of positively charged ions or neutral molecules at the anode, which pass into the electrolyte. The reduction reaction takes place at the cathode. Here, the positively charged ions in the electrolyte take up electrons, which leads to a reduction in the excess electrons. The electrons are consequently reduced and negatively charged ions or neutral molecules are formed. The electrolyte serves as a medium for the flow of ions between the electrodes. The charge transfer via the electrolyte takes place at the phase interface between the electrodes and the electrolyte, which is also known as the electrolytic double layer.

During the electrochemical degradation of PFAS, the aim is to completely mineralise the PFAS to CO_2, H_2O and F^-. Depending on the time, the degradation of long-chain PFAS may not be complete until mineralisation and short-chain PFAS remain in the solution as a degradation product.

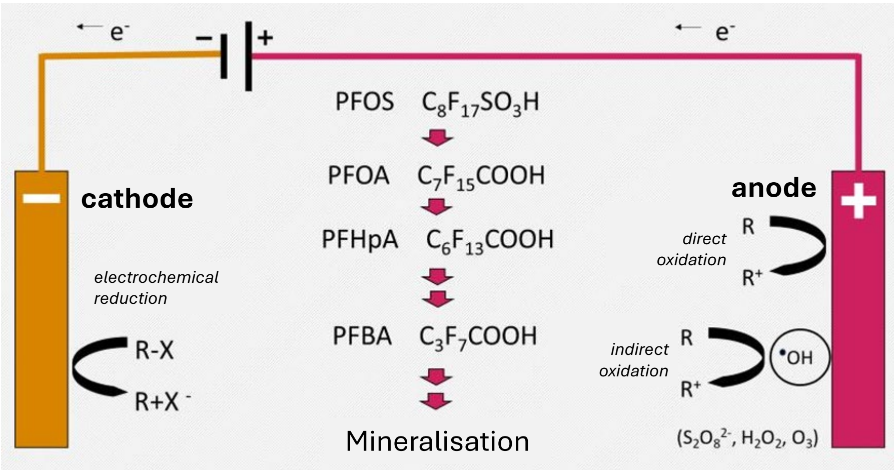

Figure 1-2 Principle of the electrochemical oxidation of PFAS (UBA 2020).

Using PFOA as an example, direct oxidation is described by (Lin *et al.* 2012) as follows:

$$\begin{aligned}
&Decarboxylation: && C_7F_{15}COOH \xrightarrow{-H^+} C_7F_{15}COO^- \xrightarrow{-e^-} C_7F_{15}COO\bullet \xrightarrow{-CO_2} C_7F_{15}\bullet \\
&Alcohol\ formation: && C_7F_{15}\bullet + OH\bullet \rightarrow C_7F_{15}OH \\
&Defluorination: && C_7F_{15}OH \rightarrow C_6F_{13}COF + HF \\
&Hydrolysis: && C_6F_{13}COF + H_2O \rightarrow C_6F_{13}COOH + H^+ + F^-
\end{aligned}$$

The degradation process of PFOA begins with the formation of a PFOA radical by the transfer of an electron to the anode. This is followed by the decarboxylation reaction in which the C_7F_{15} radical is formed. This radical can then react with other radical species, such as an OH radical, to form the alcohol $C_7F_{15}OH$. During defluorination, this undergoes F-elimination, whereby $C_6F_{13}COF$ is formed. The $C_6F_{13}COF$ can then be hydrolysed and PFHpA ($C_6F_{13}COOH$) is formed. In subsequent reactions, this degradation process is repeated and complete degradation to mineralisation can be achieved (Fang *et al.* 2017).

Using the example of PFOS, Zhuo *et al.* (2012) describe the degradation of perfluorinated sulfonic acids, in which the sulfonate group is split off and then replaced by a carboxyl group.

$$Electron\ transfer: \quad C_8HF_{17}SO_3 \xrightarrow{-H^+} C_8F_{17}SO_3^- \xrightarrow{-e^-} C_8F_{17}SO_3 \bullet$$

$$Hydrolysis: \quad C_8F_{17}SO_3 \bullet + H_2O \rightarrow C_8F_{17} \bullet + SO_4^{2-} + 2H^+$$

$$Alcohol\ formation: \quad C_8F_{17} \bullet + OH \bullet \rightarrow C_8F_{17}OH$$

$$Defluorination: \quad C_8F_{17}OH \rightarrow C_7F_{15}COF + HF$$

$$Hydrolysis: \quad C_7F_{15}COF + H_2O \rightarrow C_7F_{15}COOH + H^+ + F^-$$

First, electron transfer takes place at the BDD anode, then the resulting radical reacts with H_2O to form a C_8F_{17} radical, a sulphate ion and two protons. As with PFOA degradation, the C_8F_{17} radical formed reacts via alcohol formation, defluorination and hydrolysis to form PFOA, which can then be degraded.

Another phenomenon in the degradation of PFAS substances is that substances with the same carbon chain length but different functional head groups are degraded with different efficiency. As a rule, perfluorocarboxylic acids (PFCAs) with a boron-doped diamond electrode (BDD) as an anode are degraded better than pefluorosulfonic acids (PFSAs) with the same carbon number, as the functional group of PFSAs is more electrophilic than the carboxyl group of PFCAs, which hinders mass transfer at the electrode (Nzeribe *et al.* 2019; Zhuo *et al.* 2012).

After the electrochemical treatment, the PFAS-free regenerative agent can be reused for another regeneration cycle. By recycling the regenerative agent there is a reduction in materials and chemical agents needed.

The present report focuses on the performance electrochemical degradation process.

2 Task definition

Treatment method 1 of task 7.2 (“Treatment of groundwater (GW) and surface water for the production of safe drinking water (DW) and the protection of human health”) describes a hybrid process consisting of granular activated carbon (GAC) and ion exchange (IEX) resins, specifically anion exchange (AEX) resins (Figure 1-1). Within this treatment, the GAC eliminates long-chain PFAS whereas the subsequently applied AEX removes short-chain PFAS and other anionic contaminants from the water. More information on this was provided in Deliverable 7.2. In this deliverable, an optimized elimination of residues arising from such drinking water treatment processes is investigated.

The experiments described in this report aim at (i) testing the suitability of electrochemical degradation for the elimination of PFAS from AEX regenerates and (ii) evaluate the process of electrochemical oxidation for optimal operation parameters for the elimination of PFAS. A pilot-scale electrochemical treatment plant is available to be set up at a waterworks of the test site in Rastatt as a follow-up to this deliverable.

This report presents the results of the experimental studies on electrochemical degradation of PFAS from AEX regenerates and raw water. Key outputs related to this deliverable will be used in future work in ZeroPM to compare the life cycle analysis (LCA) impacts of alternative water treatments (notably in the forthcoming Deliverable 2.6)

3 Experimental

3.1 Set-up for electrochemical degradation

Two test set-ups were used for the electrochemical degradation tests. Tests were carried out in the CONDIACELL® SSZ-100 electrolysis cell and in a laboratory system (LabSys) from CONDIAS GmbH, in which larger volume flows could be treated. This chapter describes the two test setups, the experimental investigations carried out on them and the general data analysis of the electrochemical oxidation tests.

3.1.1 CONDIACELL® SSZ-100

Small-scale electrochemical oxidation was carried out using the CONDIACELL® SSZ-100 electrolytic cell from CONDIAS, consisting of a double-sided coated boron-doped diamond plate electrode (DIACHEM® electrode type 100 x 100 x 4 mm) as anode and a stainless steel housing that also acted as the cathode (Figure 3-1).

The electrolysis cell was continuously flowed through from bottom to top at different pump capacities. The pollutant-contaminated electrolyte was pumped from the storage tank in the circuit using a WPDC-06.7L-10M-24VDC pump from ROTEK Handels GmbH. A beaker with a maximum capacity of two litres was used as the storage tank. The electrolytic cell was operated in galvanostatic mode. The current was constantly regulated to 200 mA.

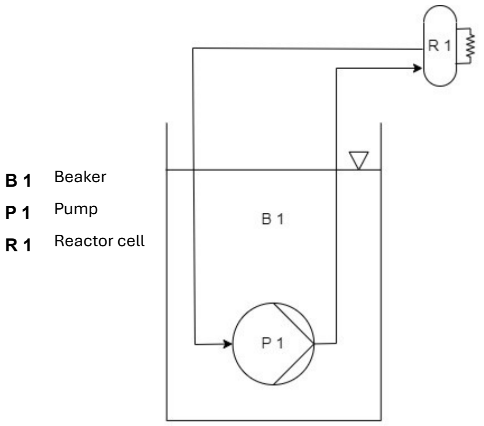

Figure 3-1 Scheme of CONDIACELL® SSZ-100.

3.1.2 CONDIAS Laboratory System (LabSys)

The electrolysis cell CONDIACELL® cell model ECWP D20x4P was used for pilot-scaled electrochemical degradation tests (Figure 3-2). The cell consists of four electrode packets with a packet spacing of 0.5 cm. Each packet consists of an anode and two cathodes (cathode-anode-cathode). Both the anode and cathode of the electrode package were perforated BDD electrodes (DIACHEM® from CONDIAS) with the electrode type Ø 20 x 1.5 d1.5. Compared to other electrodes where water is split into oxygen and hydrogen or hydrogen peroxide, BDD can also be used to form highly reactive hydroxyl radicals ($OH^{\cdot}$) (Debus 2004). The generation of this strong oxidising agent is due to the high overvoltage of 2.7 V to 2.9 V (vs. NHE) for oxygen evolution (Tröster *et al.* 2004). This enhances the degradation of substances with a high oxidation potential, such as persistent organic substances. In comparison to the plate electrode of the CONDIACELL® SSZ-100 electrolysis cell, which predominantly has a laminar flow at the electrode, the electrodes of the electrolysis system are also perforated and therefore enable hydrodynamic turbulence and thus higher current densities at the anode surfaces.

The contaminant-laden water was circularly pumped from the storage tank, which had a maximum capacity of 20 litres. As a result, the water continuously flowed through the electrode cell from bottom to top. A CSY-4081 pump from Speck Pumps was used, which could be operated in different performance ranges. The target current was set at 0.5-1.5 A. The experiments were thus operated galvanostatically.

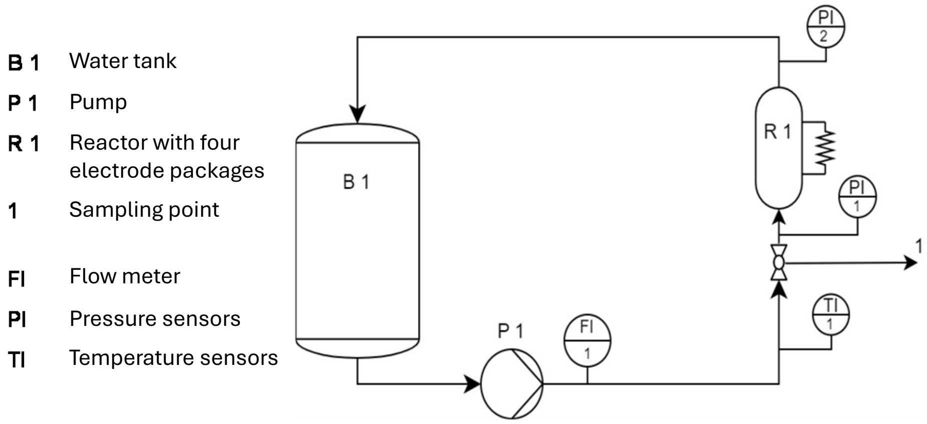

Figure 3-2 Scheme of CONDIACELL® cell model ECWP D20x4P.

3.2 Experiments performed

3.2.1 Electrochemical oxidation of AEX regenerate

In an initial step, a small-scale (1 L) elimination of PFAS from AEX regenerate, mainly loaded with 16 µg/L PFBA and 18 µg/L PFPeA, was electrolysed in the electrolysis cell at 200 mA current. Subsequently, this process was up scaled to the electrolysis plant (LabSys, volume of 20 L) and tested with two different pump intensities (40 and 70 %) and thus, flow velocities of ~5 to 8 L/min and ~11 to 14 L/min at a current of 2 A. To test the influence of electric conductivity/ regenerate concentration on the degradation of PFBA and PFPeA, these substances were spiked in 1 M and 2 mM NaOH solution with 50 µg/L each and treated in the LabSys plant with a pump rate of 90 %, meaning ~16-20 L/min.

The experiments were performed for 270 min (SSZ) and 240 min (LabSys) and samples for PFBA and PFPeA analysis were taken regularly during treatment.

Table 3-1: Experiments performed for treatment of AEX regenerate.

Exp.	Description	PFAS addition	Matrix and conc.
Reg 1	Small scale AEX regenerate (SSZ)	-	NaOH, ~ 1 M
Reg 2	Up-scale AEX regenerate (LabSys)	-	NaOH, ~ 1 M
Reg 3	Up-scale AEX regenerate – reduced flow velocity (LabSys)	-	NaOH, ~ 1 M
Reg 4	Up-scale artificial AEX regenerate (LabSys)	PFBA, PFPeA each 50 µg/L	NaOH, 1 M
Reg 5	Up-scale artificial AEX regenerate – reduced el. cond. (LabSys)	PFBA, PFPeA each 50 µg/L	NaOH, 2 mM

3.2.2 Testing suitable operating conditions and water hardness for electrochemical PFAS elimination

The operating conditions of the electrolysis plant LabSys were investigated to find optimum operating conditions for the elimination of PFCAs (PFOA, PFHpA, PFHxA, PFPeA, PFBA, PFPrA, TFA) and PFSAs (PFBS, TFMS). Therefore, different pump intensities were tested (40, 70 and 100 % pump rate): ~5 to 8, ~11 to 14 and ~16 to 20 L/min flow velocity (fluctuating flow rates are mainly due to the temperature, only with groundwater the flow rate decreases due to precipitation on the electrodes). As water matrix, an artificial drinking water was used, consisting of 0.3 mM $CaCl_2$ x 2 H_2O, 0.6 mM $MgSO_4$ x 7 H_2O, 2 mM $NaHCO_3$ and 1.6 mM $NaNO_3$ in ultrapure water.

To test the effect of the matrix hardness/ salt concentration on the electrochemical treatment of the PFAS mix, an artificial hard drinking water was used, consisting of 1.5 mM $CaCl_2$ x 2 H_2O, 2.1 mM $MgSO_4$ x 7 H_2O, 2 mM $NaHCO_3$ and 8.1 mM $NaNO_3$ in ultrapure water.

Table 3-2: Experiments performed for evaluation of good operational parameters for PFAS treatment.

Exp.	Description	PFAS addition	Matrix and conc.
PFAS 1	LabSys - Pump rate 40 %	PFAS mix*	Artificial drinking water
PFAS 2	LabSys - Pump rate 70 %	PFAS mix*	Artificial drinking water
PFAS 3	LabSys - Pump rate 100 %	PFAS mix*	Artificial drinking water
PFAS 4	LabSys – hard drinking water	PFAS mix*	Artificial hard drinking water

*PFAS mix: 100 µg/L each of PFOA, PFHpA, PFHxA, PFPeA, PFBA, PFPrA, TFA, PFBS, TFMS (pH 10)

3.2.3 Evaluation of degradation kinetics for single substances

To better understand the degradation kinetics of the relevant PFCAs and PFSAs (including formation of intermediary transformation products), single substances were electrolysed in the LabSys plant in 10 L of a good conductive aqueous matrix of 2.2 mM Na_2SO_4 at a current of 1.5 A. PFOA and TFA were investigated each in a triplicate and PFOS in a duplicate experiment.

To test the effect of the current on the degradation kinetics, experiments for PFOA and TFA were subsequently performed with a lowered current of 0.5 A.

Table 3-3: Experiments performed for evaluation of degradation kinetics for single PFCA and PFSA.

Exp.	Description	PFAS addition	Matrix and conc.
PFOA (triplicate)	Degradation kinetic single substance PFOA	PFOA 500 µg/L	2.2 mM Na_2SO_4
PFOS (duplicate)	Degradation kinetic single substance PFOS	PFOS 500 µg/L	2.2 mM Na_2SO_4
TFA (triplicate)	Degradation kinetic single substance TFA	TFA 500 µg/L	2.2 mM Na_2SO_4
PFOA - LC	Degradation kinetic single substance PFOA – lower current	PFOA 500 µg/L	2.2 mM Na_2SO_4
TFA - LC	Degradation kinetic single substance TFA – lower current	TFA 500 µg/L	2.2 mM Na_2SO_4

3.2.4 Electrochemical oxidation of Rastatt raw water

Raw water from the Rastatt pilot site was electrolysed in small scale (1 L, SSZ, pilot site 1 raw water) with a current of 200 mA and large scale (10 L, LabSys, pilot site 1 raw water 2) with a current of 500 mA. After reviewing all the results obtained so far and consulting with the manufacturer of the system, it was decided to use a lower current and a longer test duration for the raw water test. The PFAS concentration differed in the raw water, so one experiment was performed with raw water containing only low concentrations of TFA. In another raw water from the same site, the 9 PFASs (PFOA, PFHpA, PFHxA, PFPeA, PFBA, PFPrA, TFA, PFBS, TFMS) were added to obtain higher concentrations of ~100 µg/L each. The large-scale experiment with water from pilot site 1 raw water 2 contained low concentrations (<1 µg/L) of FOSAA, PFOA, PFHpA, PFHxA, PFPeA, PFBA, PFPrA, TFA, PFOS, PFHpS, PFHxS and PFBS.

Table 3-4 Experiments performed for electrochemical oxidation of Rastatt raw water.

Exp.	Description	PFAS addition	Matrix
Raw 1	Low concentration of PFAS (only TFA)	-	Raw water Pilot site 1
Raw 2	100x higher PFAS concentration	PFAS mix*	Raw water Pilot site 1
Raw 3	Low concentration of PFAS + FOSA		Raw water 2 Pilot site 1

*PFAS mix: 100 µg/L each of PFOA, PFHpA, PFHxA, PFPeA, PFBA, PFPrA, TFA, PFBS, TFMS (pH 10)

4 Results and Discussion

4.1.1 Electrochemical oxidation of AEX regenerate

The regenerate of the pilot AEX at the Rastatt model site was treated in a small-scale electrochemical batch experiment in the 1L SSZ (Figure 4-1). During the reaction time of 270 min, no reduction of either PFPeA, nor PFBA could be observed. Therefore, the experimental setup was scaled up to the CONDIAS LabSys.

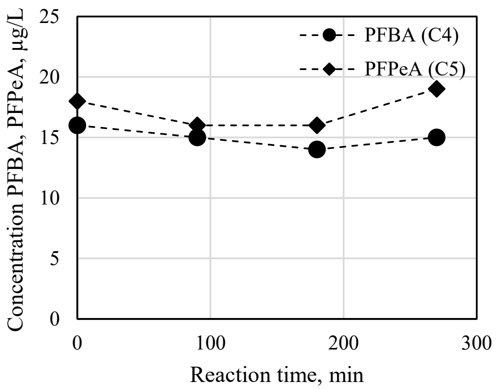

Figure 4-1 Electrochemical oxidation of AEX regenerate loaded with PFBA and PFPeA in 1 L scale (SSZ). Electrical conductivity of NaOH based regenerate was 154 mS/cm and solution was treated with 200 mA current and solution was pumped with 2.2 L/min (33 % pump rate).

After up-scaling to a 20 L batch and treatment with 2 A current, again no reduction of PFPeA or PFBA could be observed after 270 min (Figure 4-2). Reducing the pump rate from 70 to 40 %, to increase the contact time of the anions to the electrode surface, did not change this result.

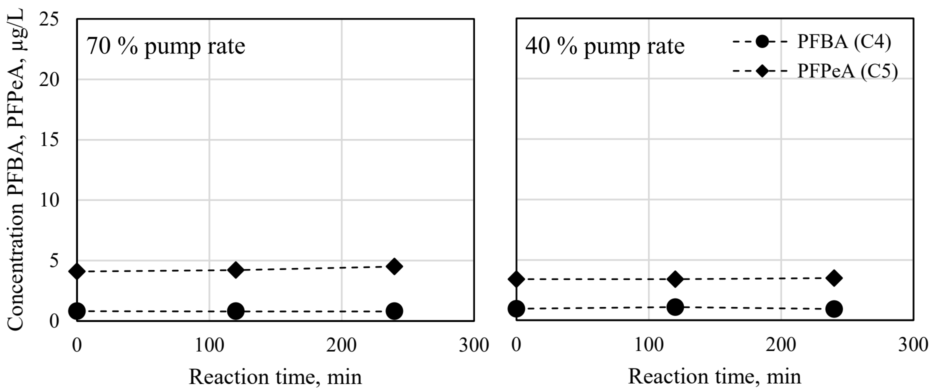

Figure 4-2 Electrochemical oxidation of AEX regenerate loaded with PFBA and PFPeA in 20 L scale (LabSys). Electrical conductivity of NaOH based regenerate was ~150 mS/cm. Solution was treated with 2 A current and pumped with 11-14 L/min (70 % pump rate) and 5-8 L/min (40% pump rate), respectively.

It was hypothesised that the high electrical conductivity of ~150 mS/cm plays a crucial role in inhibiting the electrochemical oxidation. Thus, experiments with artificial regenerate were performed to compare two different electrolyte concentrations.

By reducing the electrolyte concentration from 1000 to 2 mM, a reduction of the two main components of the artificial AEX regenerate was observed after 240 min of reaction time, even at high pump rate of 90 % (Figure 4-3).

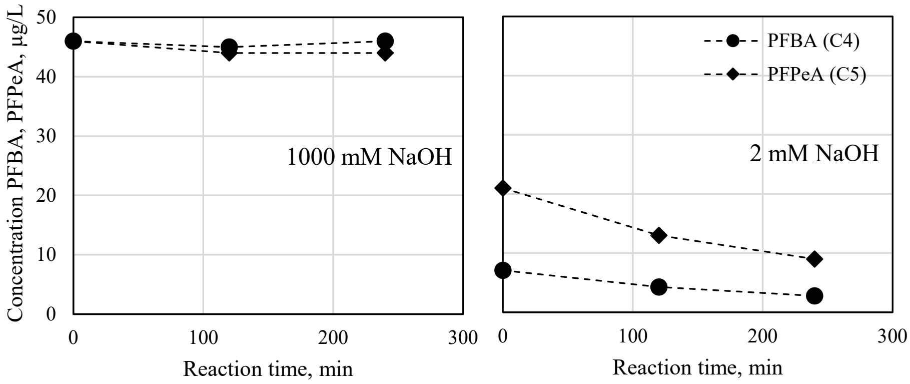

Figure 4-3 Electrochemical oxidation of artificial regenerate of AEX loaded with PFBA and PFPeA in 20L scale (LabSys). Electrical conductivity of NaOH based regenerate was ~175 mS/cm (1000 mM NaOH) and 0.4 mS/cm (2 mM NaOH), respectively. Solution was treated with 1 A current and pumped with 16-18 L/min (90 % pump rate).

The initial experiments showed that a direct subsequent on-site treatment of AEX regenerate is not practical, since the electric conductivity of the NaOH based regenerate is too high for treatment in an electrolysis reaction. However, reducing the NaOH concentration, and the successful treatment thereafter, showed a proof of principle, that an oxidation of both PFBA and PFPeA is possible in the pilot scale LabSys electrolysis plant.

This plant was kept in the laboratory for further experiments, being able to characterize the process of electrochemical oxidation in 10 to 20 L scales under controlled conditions.

4.1.2 Testing suitable operating conditions for electrochemical PFAS elimination

To find suitable operating conditions of electrochemical PFAS oxidation with the LabSys electrolysis plant, more experiments with a PFAS mixture in artificial and defined drinking water were carried out. Different pump rates and drinking water types were compared to see the effects on PFAS degradation, transformation product formation and complete mineralization (free fluoride formation).

In general it was observed that the strength of the elimination was dependent on the carbon chain length and the head group of the PFAS substances. Sulfonic acids were eliminated much more inefficiently compared to carbonic acids of equal chain length. This likely due to the extra and initial chemical reaction step, where the sulfonate group is replaced by a carboxyl group and the more electrophilic head group of sulfonic acids compared to the carboxyl group, hindering the mass transfer at the electrode. This effect is confirmed also by studies of Radjenovic *et al.* (2020), who observed PFCAs have a higher k_{obs} values than PFSAs.

Comparing different pump rates (40, 70 and 100 %, Figure 4-4), no consistent trends occurred for all PFAS. For TFA (33, 31, 37%), PFHpA (98, 100, 98 %) and PFOA (99, 100, 98%) no substantial difference was observed when comparing the elimination of at different pump capacities and lower pump rate was more promising for the sulphonic acids TFMS (20, 4, 12 %) and PFBS (52, 32, 38 %). The performance of the remaining PFCAs is marginally better at 100% and is therefore recommended.

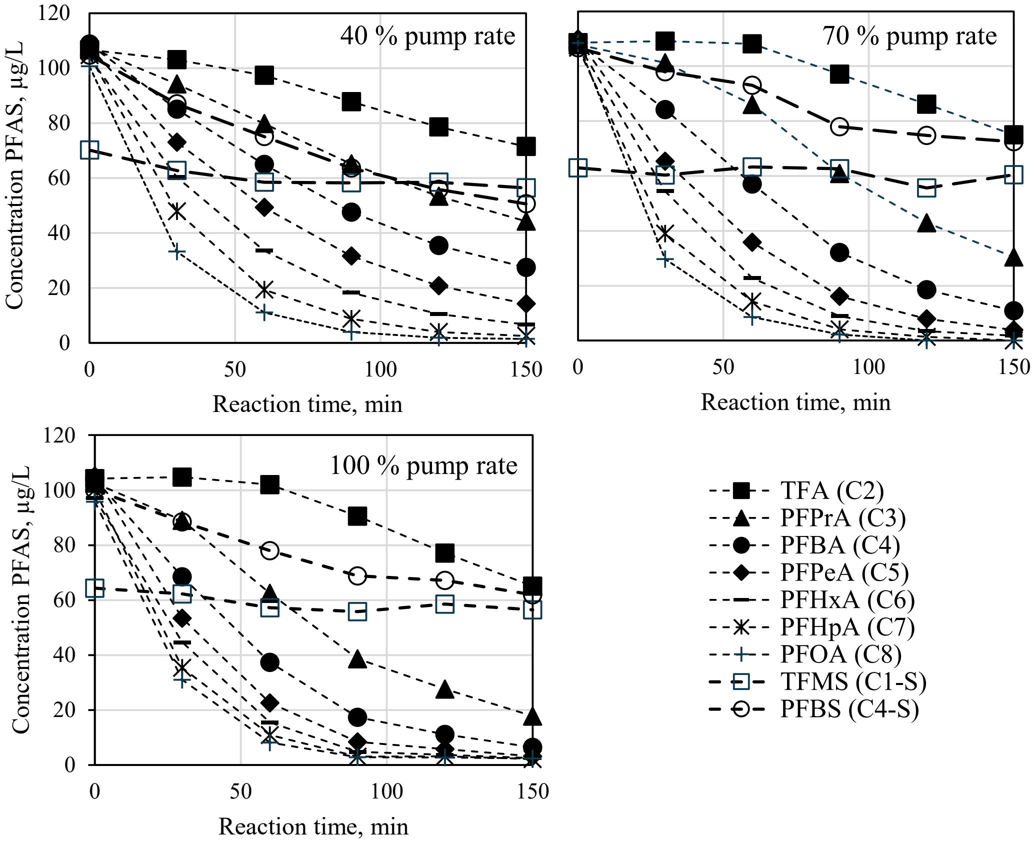

Figure 4-4 Electrochemical oxidation of PFAS mix in artificial drinking water loaded with 100 µg/L each of C2-C8 carbonic acids and C1 and C4 sulfonic acids in 10 L scale (LabSys). Electrical conductivity of the aquatic electrolyte solution was 350-590 µS/cm. Solution was treated with 1.5 A current and pumped with 5-8 L/min (40% pump rate), 11-14 L/min (70 % pump rate) and 18-20 L/min (100% pump rate), respectively.

The best elimination was achieved for most substances at full pump capacity of 100 %. This was probably because the material transport became more efficient because the medium in the electrolysis system circulates more frequently at high pump outputs and is therefore in contact with the electrodes more often. In addition, the increased flow through the perforated electrodes can create stronger turbulence, which is likely to have a positive effect on the electrochemical reaction mechanisms, as this increases the current density, improves mixing, better supplies the solution to the electrodes and removes degradation products better removed from the electrodes. This correlation between the degradation rate of organic contaminants and the flow rate during electrolytic water treatment has already been established in degradation tests of organic pollutants such as herbicides or substances from the textile industry (Basha *et al.* 2012; He *et al.* 2020; Pereira *et al.* 2012).

It was noticeable that operation at 40% pump rate was the most promising for the sulphonic acids TFMS and PFBS, however always depending on water matrix and PFAS composition. This suggests that the longer residence time due to the lower flow rate at the electrodes is more favourable for the sulfonic acids, as the substance is in contact with the electrodes for longer and the probability of degradation of the substance by electrochemical reactions is increased.

During the test, it was also noticed that the temperatures of the water matrix were strongly influenced by the pump performance. The system manufacturer's maximum media temperature of 60 °C was reached during full load operation, which led to an emergency shutdown of the system. This means that a large proportion of the pump's mechanical energy was converted into heat and the system had to be cooled externally in further tests at full load.

Since the degradation test in low to medium load operation (40- 70% pump capacity) showed a lower temperature rise of the medium of 20 °C compared to the test in full load operation (ΔT = 35 °C) and a satisfactory degradation result was already achieved in the tests with the different load operations at 40 - 70°% pump capacity, it is assumed that the medium load operation is the most favourable operation in terms of energy for a future mode of operation of the system, which also achieves promising elimination results. As mostly TFA is formed and is mineralized comparably slow, and energy loss is lowest, 40 % was seen as the most practical pump rate for operation.

In terms of mineralisation efficiency, the fluorine mass fraction (Figure 4-5) shows a slight increase of mineralization rate with increasing pump rate, from 4024 µg free fluoride for 40% after 150 min to 4359 µg for 70% and 4620 µ for 100%, respectively.

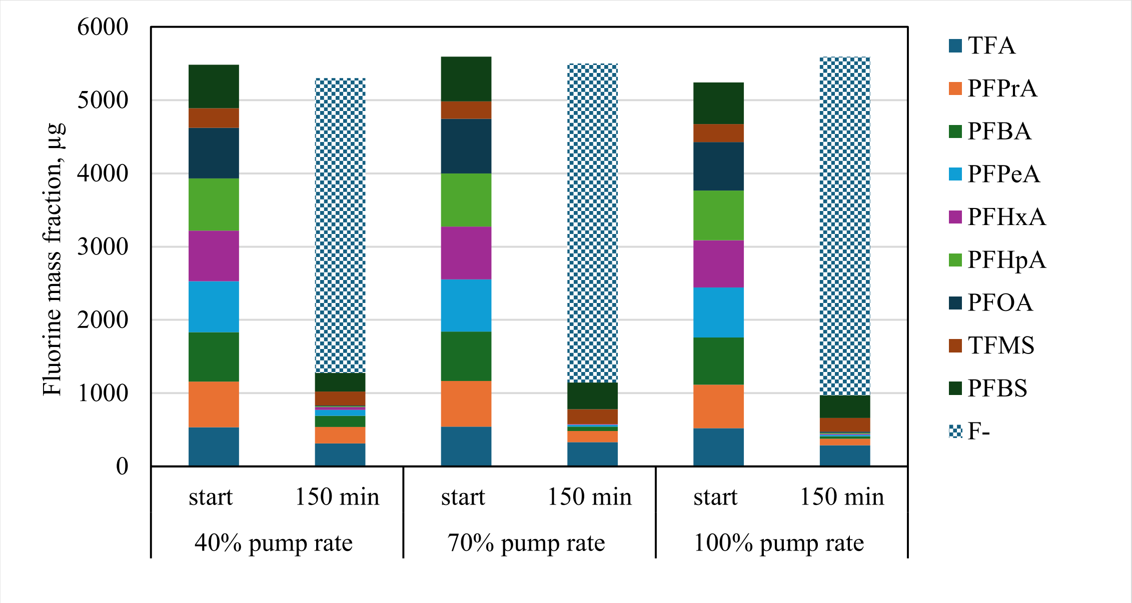

Figure 4-5 Fluorine mass fraction of analysed PFAS and transformation products at the start and after 150 min of electrochemical oxidation of PFAS mix in artificial drinking water loaded with 100 µg/L each of C2-C8 carbonic acids and C1 and C4 sulfonic acids in 10 L scale (LabSys). Electrical conductivity of the aquatic electrolyte solution was 350-590 µS/cm. Solution was treated with 1.5 A current and pumped with 5-8 L/min (40% pump rate), 11-14 L/min (70 % pump rate) and 18-20 L/min (100% pump rate), respectively.

4.1.3 Testing the influence of water hardness electrochemical PFAS elimination

The influence of water hardness was analysed, since water matrices in drinking water works differ and electrochemical oxidation with the LabSys plant might not be a suitable technique for all water types. Therefore, a soft and hard water matrix were compared, where the hard matrix had a three times higher electrical conductivity compared to the soft matrix (Figure 4-6).

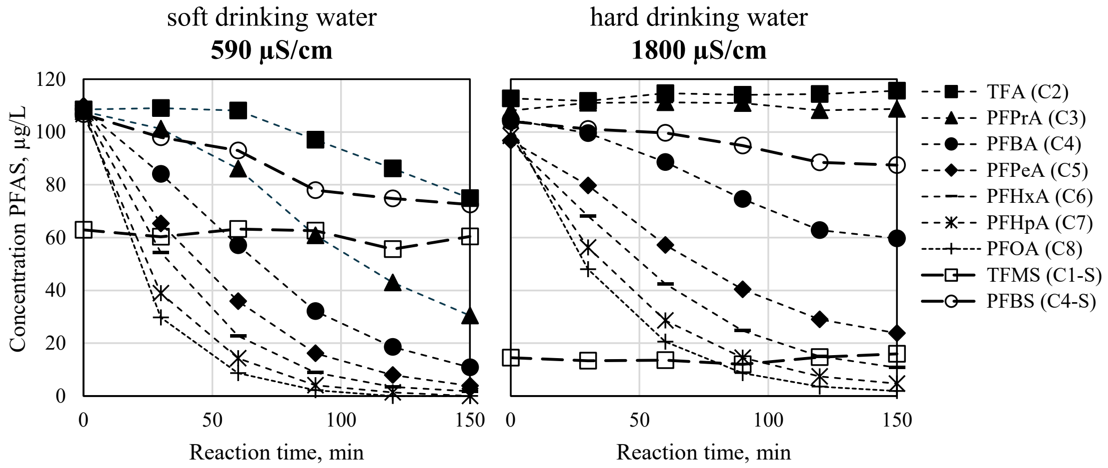

Figure 4-6 Electrochemical oxidation of PFAS mix in artificial soft vs. hard drinking water loaded with 100 µg/L each of C2-C8 carbonic acids and C1 and C4 sulfonic acids in 10 L scale (LabSys). Electrical conductivity of the aquatic electrolyte solution was 590 and 1800 µS/cm. Solution was treated with 1.5 A current and pumped with 11-14 L/min (70 % pump rate).

Looking at the elimination curves for hard model drinking water, a very good elimination of 98.3 % can be achieved for PFOA at the end of the test (Figure 4-6). The same effect also occurred for PFHpA. In the soft model drinking water matrix, PFPrA was eliminated at a rate of 46 %. In the hard matrix, on the other hand, the PFPrA concentration increased by approximately 11% compared to the initial concentration.

It was noticeable that PFBA degradation was significantly lower in the hard than in the soft model drinking water matrix. If the elimination is compared here using a specific charge of 1500 As/L as an example, an elimination of 40 % is achieved in the soft model drinking water. In contrast, a value of less than 10 % is achieved in the hard model drinking water with the same specific charge. As with TFA, this could be because PFBA is formed as a degradation product from the PFAS substances in the mixture with a longer chain length. In addition, the higher conductivity of the hard model drinking water could also be a reason for this, as the higher ion content means that more competitive reactions can take place in the oxidation processes.

Also, for both sulphonic acids TFMS and PFBS slightly more efficient elimination results were achieved in the soft model drinking water, with 4 % for TFMS and 32 % for PFBS, than in the hard water matrix, with no elimination for TFMS and 16 % for PFBS.

To assess the degree of mineralisation of the two tests, a fluorine balance is shown in Figure 4-7.

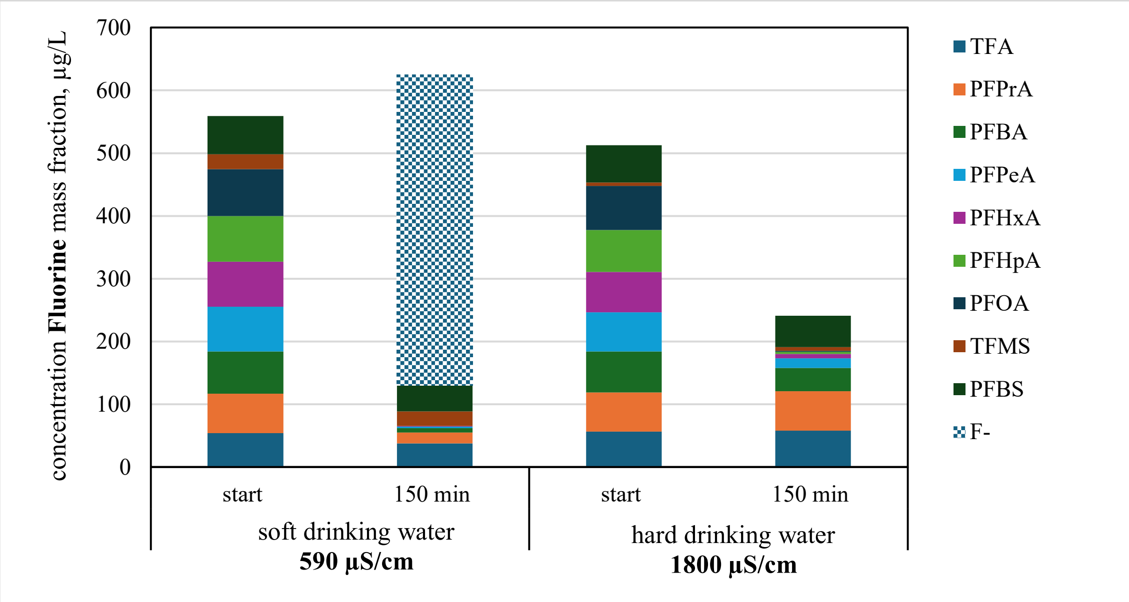

Figure 4-7 Fluorine mass fraction of analysed PFAS and transformation products at the start and after 150 min of electrochemical oxidation of PFAS mix in artificial soft vs. hard drinking water loaded with 100 µg/L each of C2-C8 carbonic acids and C1 and C4 sulfonic acids in 10 L scale (LabSys). Electrical conductivity of the aquatic electrolyte solution was 590 and 1800 µS/cm. Solution was treated with 1.5 A current and pumped with 11-14 L/min (70 % pump rate).

No complete mineralisation was achieved in both drinking water matrices during a reaction time of 150 min. The balance at the start of the experiment is comparable with the balance at the end for soft drinking water. For the hard drinking water, no free fluoride was detected in the end. This is not supposed to be because of a lack in mineralization but probably due to precipitation of poorly soluble CaF_2). This could not be proven yet but will be verified analytically at a later stage.

To sum up, the highest possible pump rate with lowest relative increase of operation temperature would be most suitable for an efficient PFAS elimination by electrochemical oxidation with the LabSys plant., Additionally, a water matrix with relatively low ion content and thus, electric conductivity should also be considered for efficient elimination.

4.1.4 Evaluation of degradation kinetics for single substances

After determining suitable operational conditions for the LabSys plant, the degradation kinetics and transformation product patterns were studied for selected single substances, namely PFOA, PFOS and TFA.

During the reaction time of 270 min, PFOA was completely transformed into shorter chained PFAS and fluoride, as demonstrated in Figure 4-8. From 0 to 60 minutes an increase of several transformation products was observed, followed by a decrease of almost all transformation products, except TFA. The fluoride formation stagnated from 90 min to the end of the experiment, indication only transformation at the end of the experiment, but no further mineralization.

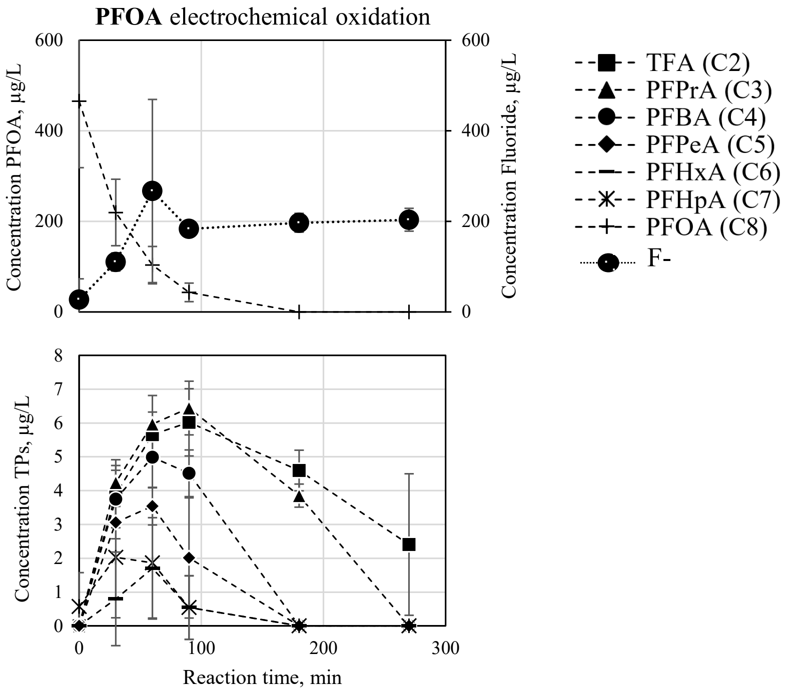

Figure 4-8 Electrochemical oxidation of 500 µg/L PFOA in 2.2 mM Na_2SO_4 in 10 L scale (LabSys) in triplicate experiment. Mean electrical conductivity of the electrolyte solution was 636 µS/cm. Solution was treated with 1.5 A current and pumped with 5-8 L/min (40 % pump rate). Top graph is showing PFOA reduction and parallel free fluoride formation, while transformation product (TP) formation is shown in the bottom graph.

In the absence of other concerning PFAS substances, PFOS can be degraded efficiently during 270 min reaction time (Figure 4-9). Among all analytes, only PFHpS, PFPrA and TFA could be detected as transformation products, and were mainly formed within the first 60 min and subsequently degraded again further. TFA was completely mineralized during this experiment.

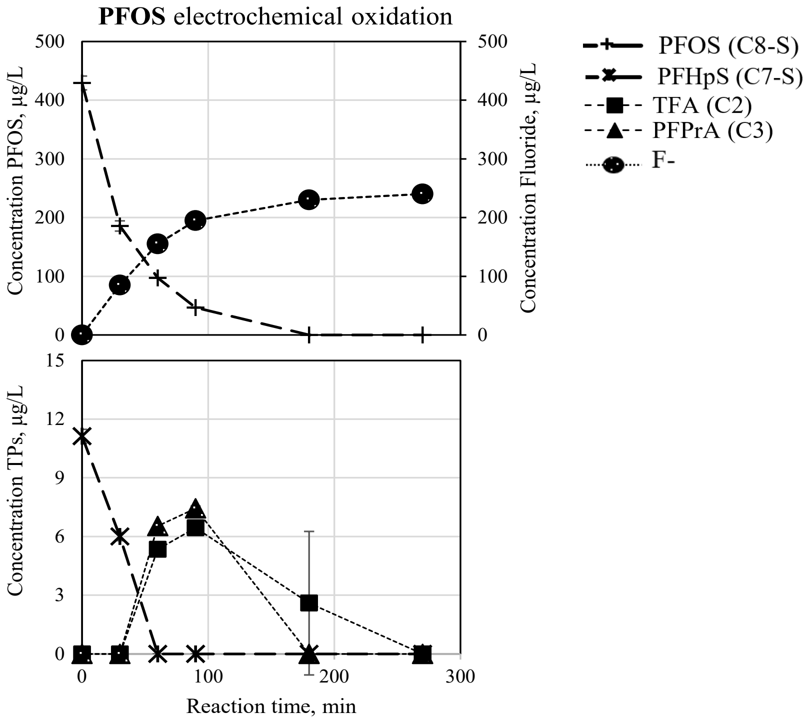

Figure 4-9 Electrochemical oxidation of 500 µg/L PFOS in 2.2 mM Na_2SO_4 in 10 L scale (LabSys) in duplicate experiment. Mean electrical conductivity of the electrolyte solution was 660 µS/cm. Solution was treated with 1.5 A current and pumped with 5-8 L/min (40 % pump rate). Top graph is showing PFOS reduction and parallel free fluoride formation, while transformation product (TP) formation is shown in the bottom graph. All other short and ultra short chained PFCAs(C2-C8) and PFSAs (C1-C6) were analysed but below LOQ.

TFA could not be degraded completely after 270 min, probably because of the small molecule size leading to a less efficient contact with the electrode surfaces (see Figure 4-10). Still, it is assumed that a longer treatment would have achieved also a complete TFA degradation.

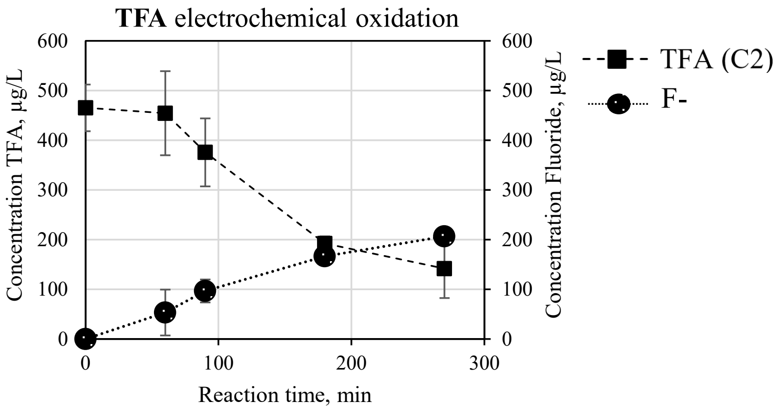

Figure 4-10 Electrochemical oxidation of 500 µg/L TFA in 2.2 mM Na_2SO_4 in 10 L scale (LabSys) in triplicate experiment. Mean electrical conductivity of the electrolyte solution was 642 µS/cm. Solution was treated with 1.5 A current and pumped with 5-8 L/min (40 % pump rate). The graph is showing TFA reduction and parallel free fluoride formation.

A lower current of 500 mA instead of 1500 mA was tested for PFOA and TFA to see the effect on mineralization efficiency (Figure 4-11). This decrease in current had no substantial effect on PFOA transformation, as PFOA was already below the LOQ after a similar time. However, the whole transformation products, including formation and again transformation of the intermediate products PFPeA, PFBA, PFPrA and TFA was extended over a longer period of over 600 min. A complete mineralization could not be achieved during 810 min. For TFA, the degradation was slightly lower at 500 mA current, but a constant decrease accompanied by a constant increase of fluoride was observed. Complete mineralization was not achieved even at extended reaction time of 810 min, but would be with an even longer reaction time

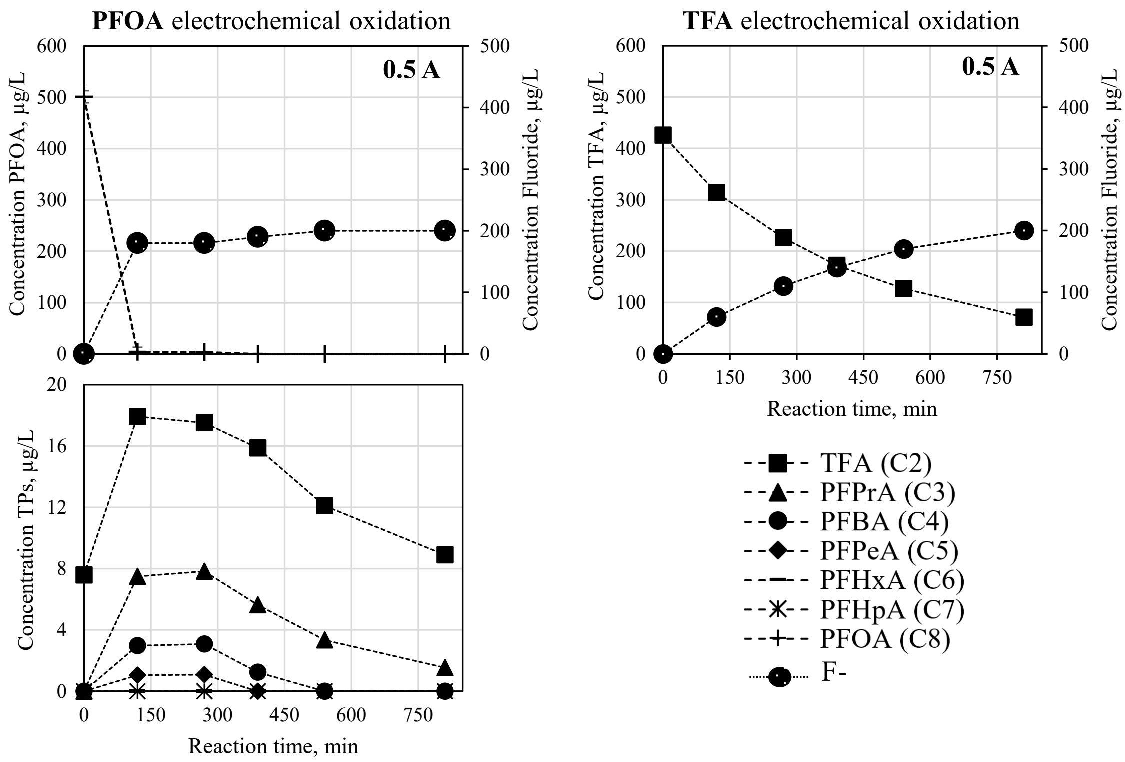

Figure 4-11 Low current electrochemical oxidation of 500 µg/L PFOA (left) and 500 µg/L TFA (right) in 2.2 mM Na_2SO_4 in 10 L scale (LabSys). Electrical conductivity of the electrolyte solution was 636 µS/cm for PFOA and 648 µS/cm for TFA experiment. Solution was treated with 0.5 A current and pumped with 5-8 L/min (40 % pump rate). Top graph is showing PFOA/ TFA reduction and parallel free fluoride formation, while transformation product (TP) formation of PFOA oxidation is shown in the bottom graph.

4.1.5 Electrochemical oxidation of Rastatt raw water

The utilization of the electrolysis method was focused on an application for PFAS contaminated raw water directly, without concentrating on an AEX regenerate in small scale SSZ experiments (Figure 4-12).

When only low concentrations of TFA was present in the raw water (ground water/influent to DWTP), the reduction of TFA within 270 min of reaction time was constant but incomplete. With a 100 x higher burden of PFAS substances, including not only TFA, but also PFOA, PFHpA, PFHxA, PFPeA, PFBA, PFPrA and the sulfonic acids PFBS and TFMS, a reduction of all carbonic acids was observed during 270 min. However, also here, especially the short and ultra-short chained substances PFPrA and TFA remained in the solution after the end of the experiment. A degradation of sulfonic acids could only slightly be observed for PFBS and not at all for TFMS. This again shows that the method is not suitable for sulfonic acid oxidation when too many PFAS with carbonyl head groups are present.

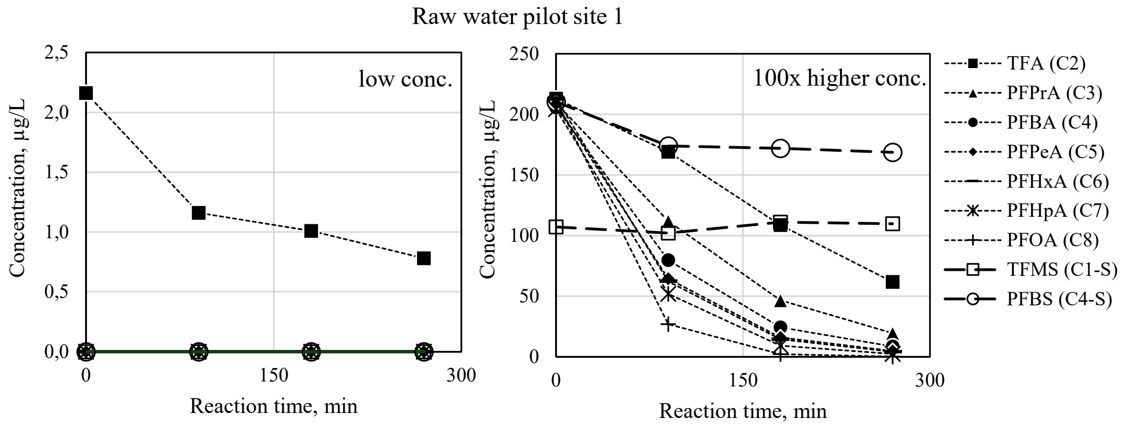

Figure 4-12 Electrochemical oxidation of pilot site 1 raw water with low PFAS concentrations (left) and and 100 x higher initial concentrations (right) in 1 L scale (SSZ). Electrical conductivity of the raw water was 304 µS/cm for low conc. and 307 µS/cm for 100x higher conc. experiment. Solution was treated with 200 mA current and pumped with 4.2 L/min (63 % pump rate).

Another raw water from a second well at the ZeroPM test site in Rastatt with PFAS contaminated groundwater was treated in the LabSys plant for 810 min at low current of 500 mA and low pump rate of 40%. The x-axis scale in Figure 4-13 is given logarithmically to make all transformation product formations visible, despite the low concentrations of formed products.

FOSAA and all short chained PFCAs and PFSAs (from C8 and lower) were present in the groundwater. FOSAA was degraded immediately and was already below the LOQ after 120 min. Therefore, PFHpS, PFPeS and PFBS increased constantly until the end of the experiment. These were probably the direct transformation products of FOSAA and PFOS. Except for TFA, also all PFCAs constantly decreased over time, again clearly showing the dependency of oxidation efficiency on the PFAS chain length.

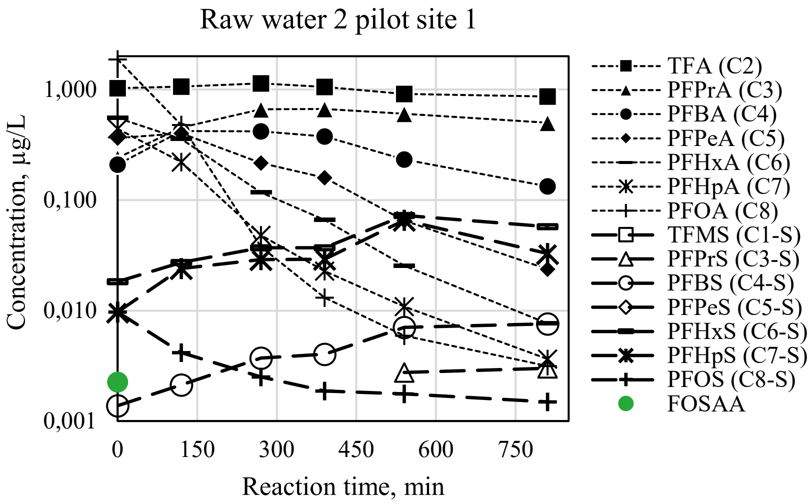

Figure 4-13 Low current electrochemical oxidation of pilot site1 raw water 2 with low PFAS concentrations in 10 L scale (LabSys). Electrical conductivity of the raw water was 339 µS/cm. Solution was treated with 0.5 A current and pumped with 5-8 L/min (40 % pump rate). Scale is given logarithmic to show the dynamics of low concentrated PFASs.

The TFA concentration remained near constant during the full reaction time, demonstrating how this substance is accumulation in water, when PFAS are oxidized. The formation of smaller PFAS from larger PFAS is expected based on the previous investigations of electrolysis pathways (Radjenovic *et al.* 2020; Smith *et al.* 2023). Even with electrochemical oxidation processes, which was shown in this deliverable to be very efficient to mineralize many short-chained PFAS, this ultra short-chained compound cannot be mineralized within the test conditions, showing that research focus on short chained and ultra short chained PFAS elimination should be included in future studies, such as through modelling work that may indicate further optimisation.

5 Conclusion

Optimization of electrochemical PFAS oxidation

To apply electrochemical oxidation following an optimized AEX process at the ZeroPM test site at the waterworks in Rastatt, initial experiments were carried out at the laboratory scale to provide proof of the principle under controlled conditions. As stated in Deliverable 7.1, for AEX, MP62, WS and A111 were among the best weak base anion exchange resins regarding their adsorption capacity of PFAS in addition to them being well regenerable with 1M NaOH-based regenerative agents. This rendered them the best option. The initial electrochemical oxidation tests revealed the following insights:

- Electrochemical oxidation can be very efficient at eliminating short-chain PFAS present at high concentrations. However, the water matrix is a decisive factor in the process. Matrices with high electric conductivities (those with a high salt content), such as 1 M NaOH, hinder the oxidation of the substances at the electrode. This was clearly demonstrated by lowering the concentration of the NaOH solution to 0.002 M, where oxidation processes were observed.

The regenerate, which was optimised for AEX regeneration at the pilot site, was not amenable for subsequent electrochemical PFAS elimination due to its high conductivity. External recycling of the regenerate and subsequent electrolysis at reduced conductivity could be helpful and should be examined as a follow-up. The focus of this study was shifted to direct elimination of PFAS in raw waters. By evaluating optimal operation conditions and testing different water matrices (soft and hard drinking waters), the following results could be achieved:

- The pilot plant LabSys by CONDIAS is an efficient ready-to-use system, which can eliminate PFOA, shorter chained transformation products and even TFA from raw and drinking water. Due to its easy transportability, it can be transferred to any test site for batch testing of PFAS elimination.
- The degree of elimination as well as the mineralisation to free fluoride correlated with an increased pump performance for individual PFAS substances, whereas no significant optimization was observed above 40% of the pump performance. Therefore, this pump performance is recommended for on-site applications of PFAS elimination and was used in most of the following experiments performed within this ZeroPM task.
- It was also shown that the strength of the elimination was dependent on the carbon chain length and the head group of the PFAS substances. Sulfonic acids were eliminated much more inefficiently compared to carbonic acids of equal chain lengths, probably due to the extra and initial chemical reaction step, where the sulfonate group is replaced by a carboxyl group, and because the sulfonic head group is more hydrophilic than the carboxyl group, hindering the mass transfer at the electrode.
- In the kinetic analysis of the degradation behaviour of the PFAS substances PFOA and PFBA, the assumption of first-order reaction kinetics was promising and could be confirmed by literature.

In summary, electrochemical oxidation processes are promising to eliminate PFAS from water. Electrochemical oxidation has a great advantage over most of the currently applied techniques, where PFAS are not mineralized but only concentrated by adsorption processes like AEX and AC filtration Electrochemical oxidation is more efficient for higher PFAS concentrations so that enrichment without increasing conductivity by e.g. electrosorption/desorption, could be advantageous.
The presented and further data will be used to develop a comprehensive model to explain and predict elimination of long chain PFAS and formation rates of shorter chain PFAS in collaboration with S.J. Smith from TU Delft (Smith *et al.* 2023).

6 Acknowledgements

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A Appendix

Fact sheet 1: PFAS measurements with ion-exchange chromatography

Matrices:	Water samples and regenerates of resin adsorption and regeneration experiments
Sample preparation:	Dilution with ultrapure water, variable dilution factors
HPLC:	Agilent Infinity II 1290 HPLC
MS:	Sciex Qtrap 6500+
Chromatographic method:	Ion-exchange chromatography
Analytical column:	Dionex IonPac AS17-C 2 x 250 mm, manufactured by Thermo Scientific
Guard column:	Dionex IonPac AG17-C 2 x 50 mm, manufactured by Thermo Scientific
Temperature:	35°C
Flow rate:	0.23 mL/min
Injection volume:	5-100 µL depending on sample
Eluent A:	Ultrapure water with 20 % methanol and 100 mM ammonium hydrogen carbonate
Eluent B:	Methanol

Table A-1: Gradient of HPLC with ion-exchange column.

Time, min	Eluent A, %	Eluent B, %
0	15	85
1.5	17	83
5.5	35	65
8.5	50	50
9	95	5
14.9	95	5
15	15	85
20	15	85

Table A-2: Precursor ion, product ion, corresponding internal standards, chromatographic retention times and limit of quantification for selected PFAS.

Substance	Internal standard	Retention time, min	Precursor ion, m/z	Product ion, m/z	LOQ (reporting limit), µg/L
TFA	TFA-13C2	4.7	112.9	68.9	0.05
PFPrA	PFBA-13C4	4.1	163.0	119.0	0.05
PFBA	PFBA-13C4	3.6	212.9	168.9	0.05
PFPeA	PFPeA-13C5	3.3	262.8	219.0	0.05
PFHxA	PFHxA-13C2	3.1	312.8	269.0	0.05
PFHpA*	PFHpA-13C4	3.0	362.8	319.0	0.05
PFOA	PFOA-13C4	2.9	412.9	368.9	0.05
TFMS	NA	9.2	148.9	79.9	0.05
PFBS	PFBS-13C3	5.4	298.8	80.0	0.05

* additionally added in later column experiments

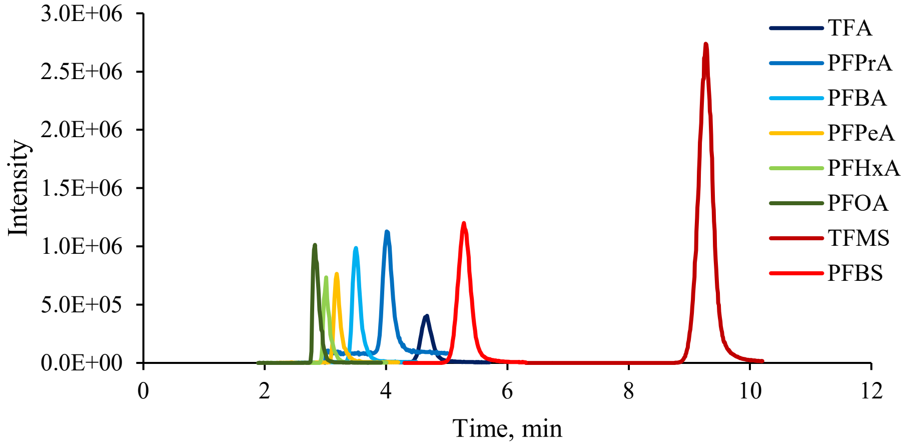

Figure A-1: Exemplary chromatograms showing the elution order of PFAS measured for resin adsorption and regeneration experiments. Measured in ultrapure water. Chromatographic separation with ion-exchange column.

Fact sheet 2: PFAS measurements using Raptor column

Matrices:	Water samples and regenerates of resin adsorption and regeneration experiments
Sample preparation:	Solvent exchange
HPLC:	Agilent Infinity II 1290 HPLC
MS:	Sciex Qtrap 6500+
Chromatographic method:	Combination of hydrophilic interaction and ion-exchange chromatography
Analytical column:	Raptor Polar 2.1 x 100 mm, particle size 2.7 µm, manufactured by Restek
Temperature:	30°C
Flow rate:	0.5 mL/min
Injection volume:	5-100 µL depending on sample
Eluent A:	Ultrapure water with 10 mM ammonium formate and 0.05% formic acid
Eluent B:	60 % acetonitrile and 40 % methanol with 0.05 % formic acid
Gradient:	Isocratic conditions, 15 % of Eluent A and 85 % of Eluent B for the run duration of 6 min

Table A-3: Precursor ion, product ion, corresponding internal standards, chromatographic retention times and limit of quantification for selected PFAS.

Substance	Internal standard	Retention time, min	Precursor ion, m/z	Product ion, m/z	LOQ (reporting limit), µg/L
TFA	TFA-13C2	3.4	112.9	68.9	0.05
PFPrA	PFBA-13C4	2.9	163.0	119.0	0.05
PFBA	PFBA-13C4	2.6	212.9	168.9	0.05
PFPeA	PFPeA-13C5	2.4	262.8	219.0	0.05
PFHxA	PFHxA-13C2	2.3	312.8	269.0	0.05
PFHpA*	PFHpA-13C4	2.2	362.8	319.0	0.05
PFOA	PFOA-13C4	2.1	412.9	368.9	0.05
TFMS	NA	1.8	148.9	79.9	0.05
PFBS	PFBS-13C3	1.4	298.8	80.0	0.05

* additionally added in later column experiments

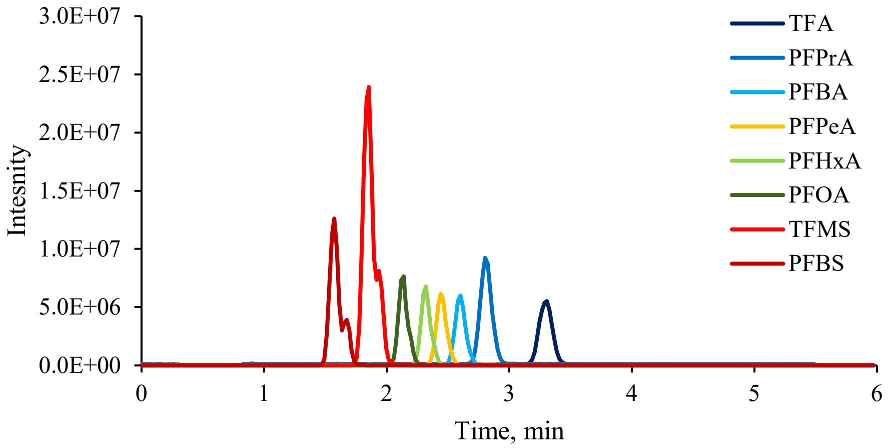

Figure A-2: Exemplary chromatograms showing the elution order of PFAS measured for resin adsorption and regeneration experiments. Measured in ultrapure water. Chromatographic separation with Raptor column.