ZeroPM

Zero pollution of Persistent, Mobile substances

Grant Agreement No. 101036756

Deliverable 7.1

February 2023

Ad-/desorption performance of IEX resins towards short chain PFAA

Work Package 7 – Technical Solutions, Method Development and Analysis

Deliverable Work Package Leader:
DVGW DEUTSCHER VEREIN DES GAS UND WASSERFACHES – TECHNISCH-WISSENSCHAFTLICHER VEREIN EV

Revision: 1 – Draft
Dissemination level: Public

Any dissemination of results must indicate that it reflects only the author's view and that the Agency is not responsible for any use that may be made of the information it contains.

The present document has not yet received final approval from the European Commission and may be subject to changes.

Note about contributors

Lead partner responsible for the deliverable: DVGW DEUTSCHER VEREIN DES GAS UND WASSERFACHES – TECHNISCH-WISSENSCHAFTLICHER VEREIN EV

Deliverable prepared by: Lukas Lesmeister, Marcel Riegel, Nicole Zumbülte, Nadine Löffler, Frank Thomas Lange

Partner responsible for quality control: Norwegian Geotechnical Institute

Deliverable reviewed by: Sarah Hale and Hans Peter Arp

Other contributors: Tim aus der Beek, IWW Water Centre, Andre Bannink, RIWA Association of River Water Works

Project information

Project partners:

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 monitoring and treatment methods such as a combination of granular activated carbon (GAC) filtration and ion exchange (IEX) resins to remove per- and polyfluorinated alkyl substances (PFAS) from drinking water. In this process, long chain perfluoroalkyl acids (PFAA) will be treated by GAC and short chain PFAA with earlier breakthroughs in the GAC filter will be treated using IEX which will be regenerated in aqueous solution. This is deliverable 7.1 which reports on the ad-/desorption performance of different IEX resins towards short chain PFAA. The aim of the work carried out in this regard is to find appropriate resins that: (i) have sufficient sorption capacity towards PFAS and (ii) can be regenerated in aqueous solution, without an organic solvent, for multiple use. The best materials will be tested in a pilot plant at a waterworks located in Rastatt, Germany, where the groundwater used for drinking water production is contaminated with PFAS.

The present report describes experiments with fifteen different anion exchange (AEX) resins from five manufacturers. Tested resins included weak base (WBA) and strong base (SBA) AEX resins. Among the SBA resins were also some PFAS-specific resins. The experiments conducted included adsorption in batches with different resins, regeneration of selected AEX in batches with different aqueous regenerating agents (e.g. NaOH, NaCl, Na_2SO_4, $NaNO_3$), column adsorption experiments which included a regeneration step, and adsorption and regeneration in multiple consecutive cycles.

After evaluating the results, two WBAs and two SBAs were considered promising. The two WBA (Lewatit® MP62 WS, Purelite® A111) are resins with exclusively tertiary amine functional groups which could be regenerated with regenerative agents based on sodium hydroxide (NaOH). The SBA that performed the best regarding adsorption and regeneration, Lewatit® MonoPlus M600, was a SBA type II (dimethylethanolammonium functional groups) which could be regenerated with 1 M $NaNO_3$. One of the two WBA will be tested in the pilot plant. The SBA type II will also be tested in the pilot plant, if available. Otherwise, the second-best alternative, Lewatit® K6362, a SBA type I resin will be used instead.

Complementing the results for the selection of AEX, the annex to this report contains the technical data sheets on the analytical methods for the determination of PM substances which fulfil Milestone M12 of the project "Analysis protocols and selection of anion exchangers".

Contents

Tables

Figures

Appendices

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 south west 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 the terminal degradation products perfluoroalkyl acids (PFAA), the PFAS 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 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 PFAA with shorter alkyl chain lengths can be much lower than for PFAA with longer alkyl chains leading to earlier breakthroughs in the filter for short-chain PFAA. The previous guide and orientation values (Leitwerte, Gesundheitliche Orientierungswerte) for some PFAA (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 value of 0.1 µg/L for the sum of 20 PFAS including short chain PFAA with more than three carbon atoms is achieved (Directive (EU) 2020/2184, 23.12.2020). This value is a considerate reduction of the threshold concentration, especially for the short chain PFAA which had higher guide and orientation values compared to long chain PFAA. 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: Leitwerte (LW), 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).

In order 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 PFAA are negatively charged under typical environmental pH values, they can undergo electrostatic interactions with an anion exchanger (AEX). In addition, it can be expected that the hydrophobic alkyl chain will also interact with the polymer structure of the AEX resin and the alkyl moieties of the amine functional groups of the resin via hydrophobic interactions and van der Waals interactions (Boyer et al. 2021). Within the proposed treatment, the GAC eliminates long-chain PFAA whereas the subsequently applied AEX removes short-chain PFAA. Thus, the AEX resin is supposed to adsorb all the short chain PFAA with early breakthroughs in the GAC filter and thus extent the operating time of the GAC filter again.
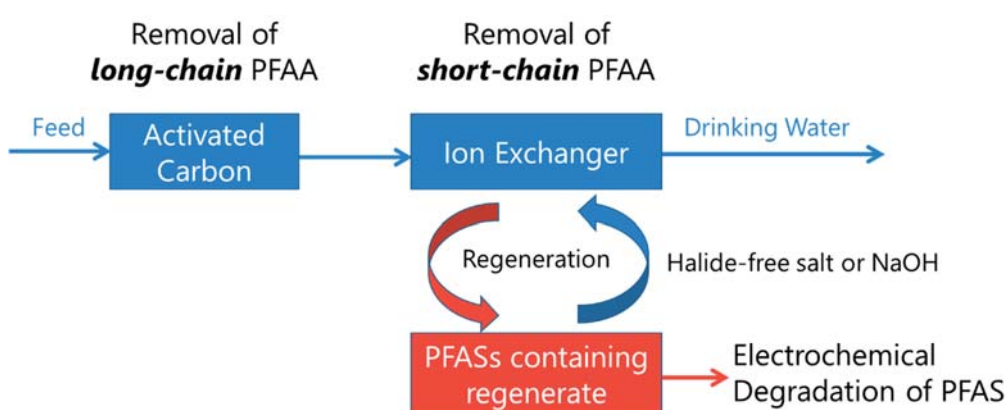
Figure 1-1: Proposed process to treat PFAS contaminated source water for drinking water production (treatment 1). The feed in is PFAS contaminated water.

To reduce material costs for the AEX, the resin should be regenerable. Regeneration is described as the process by which the resin's function as an adsorbent for the PFAA is restored. The mechanism by which regeneration takes place here is desorption of the

PFAA from the resin. Using a weak base anion exchanger (WBA), this can be achieved by increasing the pH to high alkaline values thus deprotonating the primary, secondary or tertiary amine functional groups. This removes the charge from the resin and is the reason why regeneration usually works best with WBA and when a hydroxide solution is used as the regenerative agent. Strong base anion exchangers (SBA) possess only quaternary amine functional groups and thus cannot be regenerated by altering the pH. In this case, regeneration works with a great excess of inorganic anions to shift the chemical equilibrium towards desorption of bound target compounds, in this case PFAA. A highly concentrated solution of an inorganic salt (e.g. NaCl) can be used as the regenerative agent in this case. WBA can also be regenerated using such a method, although increasing the pH usually is more effective.

To also reduce hydrophobic interactions between alkyl chains of the PFAA and the resin and thus increase the regeneration efficiency, organic solvents such as methanol or ethanol can be used. Despite increasing the regeneration efficiency, there are several disadvantages of applying these solvents for the regeneration process: they are harmful to the environment, they can promote microbiological growth on the resin hampering the filter function, their use in drinking water production is forbidden or restricted and on-site storage at the waterworks is difficult. Therefore, ZeroPM aims to apply only aqueous solutions for regeneration. Nevertheless, regeneration always creates a highly contaminated waste stream. In the proposed process, the regenerate is to be treated electrochemically to destroy the PFAA therein. The electrochemical treatment is the reason why the regenerative agent should be halide-free (Figure 1-1) to avoid the formation of toxic halogenated by-products during electrolysis. 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 of the AEX and the regeneration process. The electrochemical degradation will be part of a later deliverable.

2 Task definition

Treatment 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 PFAA whereas the subsequently applied AEX removes short-chain PFAA and other anionic contaminants from the water. In this process, the AEX should be regenerated without the use of an organic solvent (methanol, ethanol, etc.), halide-free and in a cost effective and environmentally feasible manner.

The experiments described in the present report aimed at (i) testing and comparing the adsorption performance of various AEX resins towards short-chain PFAA and (ii) testing and comparing possible ways to regenerate these resins, i.e. by investigating desorption performance with different regenerative agents (various aqueous inorganic

salt solutions) and various reaction times. The results should enable a selection of AEX resins combined with suitable regenerative agents that are most promising for a successful application within water treatment processes involving an operation in consecutive cycles of adsorption and regeneration. The best AEX resins based on adsorption and regeneration performance will be tested with the best performing regenerative agents at pilot scale. A pilot-scale treatment plant will be set up at a waterworks of the test site in Rastatt in 2023 as a follow-up to this deliverable.

This report presents the results of the experimental studies on adsorption and regeneration of tested AEX. The appendix contains the technical data sheets on the analytical methods for the determination of PM substances which fulfil Milestone M12 "Analysis protocols and selection of anion exchangers".

3 Experimental

The initial idea of the treatment process focusses on the use of a weak base AEX (WBA) resins and an aqueous sodium hydroxide (NaOH) solution as regenerative agent. This is because without an organic solvent, WBA are usually easier to regenerate (compared to strong base AEX (SBA)) and NaOH is usually among the best regenerative agents for WBA. Compared to alternative regenerative agents such as sodium chloride (NaCl), NaOH does not produce toxic by-products in the suggested electrochemical treatment process for the highly contaminated regenerate (task 7.3 of WP7). Nevertheless, in some cases, promising regeneration efficiencies have been achieved without an organic solvent for SBA (Boyer et al. 2021; Dixit et al. 2020, 2021), and because most regeneration studies have focussed on OH- and Cl-based regenerative agents, the use of alternative regenerative agents is a research gap. Exploring the performance of some alternatives such as sulphate- or nitrate-based salts will help to fill this gap. For these reasons, some SBA resins were included in the tests (Table 3-1) alongside the WBA. Furthermore, regeneration studies were conducted with different aqueous regenerative agents. In Table 3-1, the AEX names are shown with their trade names. For simplicity, trade names are omitted for the remainder of the report.

For all experiments, a 1:1-mixture of demineralized water and tap water from Karlsruhe has been used, resulting in a background matrix that has the physico-chemical properties displayed in Table 3-2. The concentration of the eight PFAA that were investigated in the subsequent experiments were also measured. All except trifluoroacetic acid (TFAA) were below the limit of quantification of 10 ng/L. The TFAA concentration (0.17 µg/L) was about ten times lower than the dosed concentration in the later experiments (1–2 µg/L). Hence it was assumed that there would be no influence of the concentration of TFAA in the demineralized water and tap water on the results here. The same assumption was made for the PFAA found below 10 ng/L as their concentration would be at least 100 times lower than the dosed concentration. Furthermore, the concentrations of these PFAA were also measured in the controls or influents after dosing in every experiment to have the exact concentrations. Other small PFAS recently reported in source water for drinking water production such as tris(pentafluoroethyl)trifluorophosphate and bis(trifluoromethylsulfonyl)imide

(Neuwald et al. 2022) were not investigated. However, relevant concentrations of unknown PFAS can be considered unlikely due to the overall low concentrations of the investigated PFAA in the mixture.

Table 3-1: AEX used in the experiments

Name	resin type	functional group	matrix	structure
Purolite® A111	WBA	tertiary amines	styrenic	macroporous
Lewatit® A365	WBA	tertiary amines	acrylic	macroporous
Lewatit® DW 630	SBA type I	quaternary amines	styrenic	macroporous
Lewatit® K6362	SBA type I	quaternary amines	styrenic	gel
Lewatit® MonoPlus M600	SBA type II	quaternary amines	styrenic	gel
Lewatit® MP62 WS	WBA	tertiary amines	styrenic	macroporous
Purofone® PFA694E	PFAS-specific	proprietary	styrenic	macroporous
Treverlite® XS141000	WBA	primary amines	styrenic	macroporous
Lewatit® TP 107	SBA type I	quaternary amines	acrylic	macroporous
Lewatit® TP 108 DW	PFAS-specific	proprietary	styrenic	gel
Jacobi-PFAS-WBA	WBA	proprietary	styrenic	macroporous
Jacobi-WBA2	WBA	tert. & quart. amines	styrenic	macroporous
AmberLite® HPR4100	SBA type II	quaternary amines	styrenic	gel
AmberLite® HPR6700	WBA	tertiary amines	acrylic	gel
AmberLite® HPR9700	WBA	tert. & quart. amines	styrenic	macroporous

Table 3-2: Water quality of the 1:1-mix of drinking water (from the tap) and demineralised water used for the laboratory tests.

Temperature at measurement	°C	14
Electr. conductivity at 25 °C	µS/cm	363
pH at measurement temperature	-	7.2
Acid capacity until pH = 4,3	mmol/L	2.82
Base capacity until pH = 8,2	mmol/L	0.4
Hardness	° dH	9.8
Calcite deposition capacity	mg/L	9
Calcium	mg/L	59
Magnesium	mg/L	6.8
Sodium	mg/L	7.1
Potassium	mg/L	1.2
Chloride	mg/L	15.2
Nitrate	mg/L	1.2
Sulphate	mg/L	33
TOC	mg/L	0.36
Trifluoroacetic acid (TFAA)	ng/L	176
Perfluoropropionic acid (PFPrA)	ng/L	< 10
Perfluorobutanoic acid (PFBA)	ng/L	< 10
Perfluoropentanoic acid (PFPeA)	ng/L	< 10
Perfluorohexanoic acid (PFHxA)	ng/L	< 10
Perfluorooctanoic acid (PFOA)	ng/L	< 10
Trifluoromethane sulfonic acid (TFMS)	ng/L	< 10
Perfluorobutane sulfonic acid (PFBS)	ng/L	< 10

Values from drinking water measurement on 5th September 2022.

The experimental solution was spiked with the following PFAA which were then quantified during the subsequent experiments: trifluoroacetic acid (TFAA), perfluoropropionic acid (PFPrA), perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOA), trifluoromethane sulfonic acid (TFMS) and perfluorobutane sulfonic acid (PFBS). Perfluoroheptanoic acid (PFHpA) was additionally added for later column experiments. All experiments were conducted in a mixed solution with all target compounds present at the same time to obtain information about competitive effects.

3.1   Batch experiments

Before using resins in batch experiments, the resins were washed and conditioned depending on resin type and experimental question. The resins were soaked in demineralized water for several hours and then put into a glass column (4.5–6 cm in diameter depending on the amount of resin) filled with demineralized water. At the bottom, the column outlet was connected to a gooseneck-shaped outlet to ensure a constant water level in the column. Approximately 10 bed volumes (BV) of chemical solutions and demineralized water were dripped from the top into the column in turn. The amount of used water varied as water was dripped through the column until the pH was constant (measured with test strips, Merck KGaA, Germany) or after a maximum

throughput of 20 L. The filtration velocity for the chemical solutions was set to be between 2 BV/h and 2.5 BV/h, the one for demineralized water to 5–10 BV/h.

After soaking in water, WBA resins were prepared as follows:

- Apply 10 BV of 1 M HCl (2–2.5 BV/h)
- Rinse with demineralized water until constant pH
- Apply 10 BV of 1 M NaOH (2–2.5 BV/h)
- Rinse with demineralized water until constant pH
- Optional: apply 10 BV of 1 M H_2SO_4, if the resin was to be investigated in sulphate form

After soaking in water, SBA resins were prepared as follows:

- Apply 10 BV of 1 M NaOH (2–2.5 BV/h)
- Rinse with demineralized water until constant pH
- Apply 10 BV of 1 M HCl (2–2.5 BV/h)
- Rinse with demineralized water until constant pH

3.1.1 Batch adsorption

Batch adsorption experiments were performed in 250 mL glass bottles with either 200 mL of spiked PFAS solution and 150 mg AEX material or 150 mL of spiked PFAS solution and 112.5 mg AEX. In both cases, the ratio between solution and resin was 1.3 L solution per 1 g resin. The initial concentration in the batch adsorption experiments was around 2 µg/L for each PFAA and experiments were conducted in a mixed solution with all target compounds present at the same time. The solution was additionally spiked with 0.05 M imidazole/HCl buffer and the pH was adjusted to be around 7 by adding 10% HCl. The bottles were shaken for 72 h on a horizontal laboratory shaker (GFL Orbital Shaker 3019, GFL, Germany) operated at 180 rpm. A control without resin was always included. After shaking, pH was measured in all bottles and a 50 mL aliquot was taken from the solution and analysed on PFAS by HPLC/MS/MS (see attachments for details). The adsorbed percentage was calculated with Equation 1.

Equation 1: $adsorbed\ percentage = 100\% * \frac{adsorbed\ mass}{initial\ mass\ in\ solution}$

The initial mass was obtained from the concentration and volume in the control without resin. The adsorbed mass was calculated by subtracting the residual mass in solution after 72 h (concentration times volume) from the initial mass in solution.

3.1.2 Batch regeneration

After usage in the batch adsorption experiments, the resins were separated from the treated solution by filtering through a 0.45 µm filter (Merck Millipore Ltd, Ireland). The separated resins were then transferred to a 50-mL glass bottle to which 10 mL regenerative agent was added. Not all resins were tested with every regenerative agent. The tested combinations can be seen together with results in Table 4-2. Tested regenerative agents included: 1 M NaOH, 0.1 M NaOH, 1 M Na_2SO_4, 0.1 M Na_2SO_4,

0.1 M NaOH + 0.1 M Na_2SO_4, 1 M $NaNO_3$, 1 M KNO_3, 1 M NH_4NO_3. The resins, together with the regenerative agent, were shaken again for 24 h before analysis for PFAA by HPLC/MS/MS. The regenerated percentage was calculated with Equation 2.

Equation 2: $\quad regenerated\ percentage_{batch} = 100\% * \frac{regenerated\ mass}{adsorbed\ mass}$

The adsorbed mass was calculated in the batch adsorption experiments as described. The regenerated mass was calculated from the product of the concentration found in the regenerative agent times the volume of the regenerative agent.

3.1.3 Multiple batch adsorption and regeneration cycles

Out of the resins with the highest adsorption capacity and the best regeneration yield in a single adsorption and regeneration cycle, two representative resins were selected and tested in a set up with multiple adsorption and regeneration cycles. Those selected were a pure WBA with tertiary functional amine groups (MP62 WS) and a type II SBA (MonoPlus M600). The regenerative agents used in these experiments were selected because they had led to the highest desorption of PFAA from these resins after the first single adsorption. For MP62 WS, these included 1 M NaOH, 0.1 M NaOH, 0.1 M NaOH + 0.1 M Na_2SO_4 and 1 M $NaNO_3$, for MonoPlus M600, it only was 1 M $NaNO_3$. After each batch regeneration, the resins were again separated from the liquid by filtering, washed with demineralized water, and again put into a 250-mL glass bottle for another batch adsorption cycle as described in section 3.1.1. This cycle was repeated four times.

3.2 Column experiments

In all the column experiments, applied resins were soaked in demineralized water for several hours before filling the columns. The columns were filled with the respective resin while a small column of water or a supernatant remained above the resin layer to avoid enclosed air bubbles within the resin layer. For monitoring adsorption and breakthrough, the water spiked with the eight/nine PFAA (c = 1 µg/L for each compound) was stored in an 800-L polypropylene (PP) tank from which the solution was pumped through the column in down-flow direction by a membrane pump (DDA 7.5-16 FCM-PV/T/C-F-31U2U2FG, GRUNDFOS, Denmark) applying a velocity of 10 BV/h. (Figure 3-1). The column effluent was collected in a 30-L PP tank, from which mixed samples were taken once a day (250 mL). After each sampling, the rest of the sample was poured onto a GAC filter and the effluent was emitted through appropriate infrastructure connected to the local sewer.
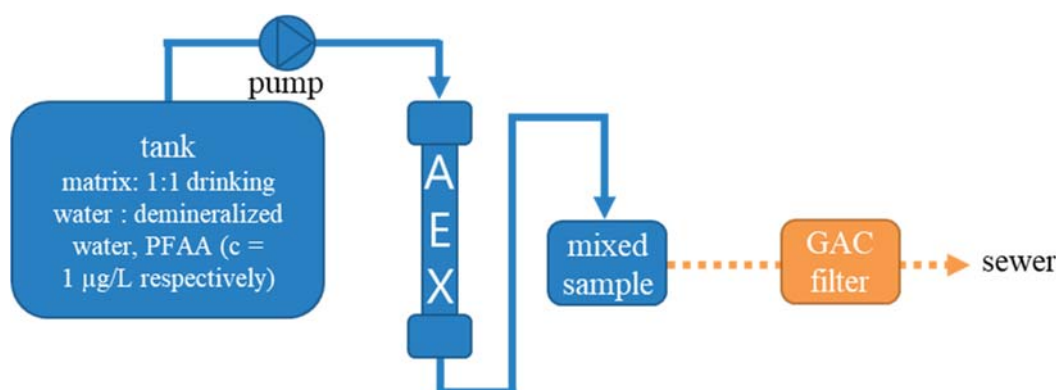
Figure 3-1: Schematic of the applied column set-up.

For the regeneration procedure, instead of the 800-L tank, the column influent was connected to a storage tank with regenerative agent. Regeneration was performed in down-flow direction with 10 BV of regenerative agent applying a velocity of 2.5 BV/h. Afterwards, the column was rinsed with 5 BV of demineralized water applying 10 BV/h. The column effluent was collected in a 2-L glass bottle and analysed as a mixed sample.

Regenerated percentages were calculated by Equation 3.

Equation 3: $$regenerated\ percentage_{column} = 100\% * \frac{adsorbed\ mass}{total\ mass\ in\ throughput}$$

The total mass in the throughput resulted from the product of the measured influent concentration and the volume of the throughput (measured by weighing the effluent). The adsorbed mass was the difference between the mass in the throughput and the mass measured in the effluent.

3.2.1 One-time adsorption and regeneration in 45-mL columns

One-time adsorption and regeneration was conducted in 45-mL columns with five different resins: A111, MP62 WS, A365, MonoPlus M600 and K6362. They were selected because they represent different resin characteristics as depicted in Table 3-3. As experimental results were promising for a first pure styrenic WBA resin, a second resin of the same type was included. The added PFAS solution contained the eight selected PFAA at a concentration of 1 µg/L for each compound.

Table 3-3: Resin characteristics of resins selected for one-time adsorption and regeneration experiment in 45-mL columns.

Resin	type	functional group	matrix	structure
A111	WBA	tertiary amines	styrenic	macroporous
MP62 WS	WBA	tertiary amines	styrenic	macroporous
A365	WBA	tertiary amines	acrylic	macroporous
K3662	SBA type I	quaternary amines	styrenic	gel
MonoPlus M600	SBA type II	quaternary amines including polar moiety	styrenic	gel

3.2.2 Multiple adsorption and regeneration in 70-mL column

A previous project with a similar set-up demonstrated that a WBA could be regenerated properly with the procedure described in the entrance section of 3.2, using 1 M NaOH as the regenerative agent (Riegel et al. 2022). For a SBA there was no previous experience. Thus, this experiment functioned as a first approach to apply a SBA that can be regenerated in aqueous solution in a column set-up with multiple consecutive adsorption and regeneration cycles. It can show whether such application is principally possible.

A 70-mL column (diameter = 2.1 cm, height = 20 cm) filled with MonoPlus M600 was operated with the same operating parameters for the adsorption operation as above. This laboratory column plant was operated until a total throughput of 5887 BV was achieved. Regeneration was done three times using 1 M $NaNO_3$ as the regenerative agent, each time after approximately one week or 1700 BV. For the regeneration procedure, the same parameters as the previously described ones were used for the first two cycles.

For the third regeneration, the procedure was changed. The amount of regenerative agent remained the same (10 BV), but instead of pumping it through the column with a velocity of 2.5 BV/h and then flushing it with demineralised water, the effluent regenerative agent was recycled to the tank and operated at 10 BV/h for 24 h. This increased the filter velocity from 0.5 m/h to 2 m/h while maintaining a long contact time, which should result in an improved film diffusion benefitting adsorption. This was done to maximize the regeneration effectiveness in case the regeneration was incomplete with the previous procedure. The maximum possible regeneration effectiveness is used as an orientation towards optimising the regeneration procedure in future experiments including the ones intended for the pilot plant.

4 Results and Discussion

In all adsorption experiments, there were several reoccurring trends:

- Adsorption or time until breakthrough (in column experiments) increased with increasing perfluoroalkyl chain length of the PFAA.
- Adsorption or time until breakthrough was comparably better for perfluorosulfonic acids (PFSA) than for perfluorocarboxylic acids (PFCA) of similar chain length, e.g. PFBS adsorbed better than PFPeA (both with 4 perfluorinated carbon atoms).
- For regeneration, the trend was the other way around and PFAA with shorter chain lengths desorbed better than PFAA with longer chain lengths regardless of the AEX and the regenerative agent used.

4.1 Batch experiments

4.1.1 Batch adsorption

For all eight tested PFAA, the best adsorption was achieved with the two PFAS-specific resins TP 108 DW and PFA694E, while TP 108 DW performed slightly better than PFA694E. Both resins possess modified quaternary amine functional groups whose specific characteristics are a company secret. The third best adsorption performance was achieved with a WBA resin from Jacobi, Jacobi-PFAS-WBA (name unavailable). According to the manufacturer, this resin was also developed with the treatment of PFAS pollution in mind. Its structure was also not available from the manufacturer. All three of these resins were able to achieve high adsorption with all tested compounds and were the only ones who could even adsorb more than 50% of TFAA. Good performances were also achieved by the two SBA K6362 and MonoPlus M600, both typical representatives of type I and type II SBA, respectively. In the performance ranking (see Table 4-1 for an example for PFBA), these two are directly followed by the two pure WBA with exclusive tertiary amine functional groups, A111 and MP62 WS. Both achieved higher adsorption percentages in their free base form (e.g. 68% ± 4%, 71% of PFBA) than the remaining SBA (DW 630 and TP 107) in their chloride form. For two of the tested resins, the WBA A365 and the SBA TP 107, no notable adsorption of any investigated PFAA could be determined.

Table 4-1: Tested AEX resins ranked according to their equilibrium adsorption performance in batch experiments (percentage of total dosed mass) for PFBA in mixed solution (c_0 = 2 µg/L; L/m = 1.3 L/g).

resin (*WBA in italics*)	form	substance	eq. Adsorption (batch) /%	deviation*	n
TP 108 DW	chloride	PFBA	96	4.9	3
PFA694E	chloride	PFBA	94	6.7	3
Jacobi-PFAS-WBA	free base	PFBA	91	0.63	2
Jacobi-PFAS-WBA	sulphate	PFBA	88	NA	1
MonoPlus M600	chloride	PFBA	77	0.8	5
K6362	chloride	PFBA	75	0.3	3
A111	free base	PFBA	71	NA	1
MP62 WS	free base	PFBA	68	3.85	6
DW 630	chloride	PFBA	65	NA	NA
MP62 WS	sulphate	PFBA	64	1.15	14
A111	sulphate	PFBA	62	NA	1
HPR9700	free-base	PFBA	61	4.3	6
MP62 WS	nitrate[1]	PFBA	58	0.2	2
MonoPlus M600	nitrate[1]	PFBA	56	NA	1
HPR4100 Cl	chloride	PFBA	36	4.2	6
XS141000	sulphate	PFBA	29	NA	1
XS141000	free base	PFBA	24	NA	1
TP 107	chloride	PFBA	< 10	NA	NA
A365	free base	PFBA	< 10	NA	NA
A365	sulphate	PFBA	< 10	NA	NA
HPR6700	free base	PFBA	< 10	NA	NA
Jacobi-WBA2	free base	PFBA	< 10	NA	NA

* for n ≥ 3, deviation = 95%-confidence interval; for n = 2, deviation = standard deviation.

[1] nitrate form was tested after regeneration with $NaNO_3$. The specific adsorption capacity may therefore not be directly comparable to the other tested forms.

4.1.2 Batch regeneration

Eight of the fifteen tested AEX were investigated in batch regeneration experiments. Results of regeneration percentages (percentage of previously adsorbed mass) per resin, form and regenerative agent are summarized in Table 4-2 for PFPeA as an example. Not all resins were tested with every regenerative agent. Some resins were only tested a few times to evaluate their regeneration potential.

The two most studied resins for regeneration were MP62 WS and MonoPlus M600. MP62 WS was picked because due to its structure (pure WBA), the regeneration percentage was expected to be high and studying different regenerative agents to optimise the regeneration procedure seemed promising. A111 with a similar structure was expected to behave similarly. MonoPlus M600 was picked for more detailed studies because regeneration is expected to be easier for a type II SBA than for SBA with different structures such as PFAS-specific resins or type I SBA. These two resins were also picked for experiments with multiple batch adsorption and regeneration cycles with different regenerative agents (section 4.1.3).

Table 4-2: Tested AEX resins ranked according to their equilibrium regeneration performance in batch experiments (percentage of total adsorbed mass) for PFPeA in mixed solution, n = 2.

resin	form	regen. Agent	equilibrium regeneration (batch) /%*	standard deviation
A111	sulphate	0.1 M NaOH + 0.1 M Na_2SO_4	163	
A111	free base	0.1 M NaOH + 0.1 M Na_2SO_4	155	
MP62 WS	free base	0.1 M NaOH + 0.1 M Na_2SO_4	99	2.2
MP62 WS	sulphate	0.1 M NaOH + 0.1 M Na_2SO_4	99	2.25
MP62 WS	sulphate	0.1 M NaOH	95	1.26
MonoPlus M600	nitrate	1 M $NaNO_3$	84	
MonoPlus M600	chloride	1 M $NaNO_3$	83	18
MP62 WS	sulphate	1 M $NaNO_3$	81	0.66
MonoPlus M600	chloride	1 M NH_4NO_3	75	4
MP62 WS	nitrate	1 M $NaNO_3$	74	1
MP62 WS	free base	0.1 M KOH + 0.1 M K_2SO_4	73	4.8
MP62 WS	sulphate	1 M NaOH	70	0.57
K6362	chloride	1 M $NaNO_3$	64	1
MonoPlus M600	chloride	1 M KNO_3	63	1
MonoPlus M600	chloride	0.5 M $NaNO_3$	63	0.2
XS141000	sulphate	0.1 M NaOH + 0.1 M Na_2SO_4	59	
MP62 WS	free base	1 M KNO_3	50	0.46
MP62 WS	free base	1 M $NaNO_3$	49	0.66
MP62 WS	free base	1 M NH_4NO_3	49	1.3
MonoPlus M600	chloride	2 M NaCl	40	
MonoPlus M600	chloride	0.1 M $NaNO_3$	34	0.4
XS141000	free base	0.1 M NaOH + 0.1 M Na_2SO_4	26	
Jacobi-PFAS-WBA	free base	0.1 M NaOH + 0.1 M Na_2SO_4	25	
MP62 WS	sulphate	2 M NaCl	20	3.68
MonoPlus M600	chloride	0.1 M Na_2SO_4	7	
MP62 WS	sulphate	0.1 M Na_2SO_4	6	0.12
K6362	chloride	1 M Na_2SO_4	4	3
MonoPlus M600	chloride	1 M Na_2SO_4	3	
MP62 WS	sulphate	1 M Na_2SO_4	3	0.17
PFA694E	chloride	1 M NaOH	1	0.4
TP 108 DW	chloride	1 M NaOH	1	0.5
Jacobi-PFAS-WBA	free base	1 M $NaNO_3$	0.4	
Jacobi-PFAS-WBA	sulphate	1 M $NaNO_3$	0.3	

*colouring: green = sufficient; orange = not sufficient but with some potential; red = not sufficient.

Speculative explanation for regeneration percentages above 100%: see text (last paragraph of this section).

The results in Table 4-2 show that NaOH-based regenerative agents work best for the WBA with only tertiary amine functional groups (deprotonation of amines due to pH shift to alkaline pH). Regardless of the form (sulphate, free base), regeneration effectiveness was at least 95%. At the same time, NaOH-based regeneration did not work well with SBA. However, the SBA MonoPlus M600 showed a promising regeneration effectiveness with 1 M $NaNO_3$ as the regenerative agent ($\geq$ 83%).

The calculated regeneration percentages of A111 were above 100%. These values indicate a high uncertainty of the determination. Although an uncontaminated resin was not used as a control, release of PFAA from the empty resins is highly unlikely. It is more likely that the high salt content in the regenerates represents a more complicated water matrix in which the PFAA are more difficult to analyse. Furthermore, the high salt and PFAA concentrations in the regenerates require a high dilution of the samples ($\geq$ 50-fold) creating a higher uncertainty of the resulting concentration. For this reason, the regenerated percentages shown in the table are only an indication for the quality of the regeneration. To confirm that the regeneration process was indeed successful and complete, the adsorbed percentage can be determined after regeneration by repeating the batch adsorption experiment as described in the next section.

4.1.3   Multiple batch adsorption and regeneration cycles

The most promising regenerative agents with MP62 WS and MonoPlus M600 after a first (one-time) adsorption and regeneration cycle were selected for a longer experiment consisting of 4 cycles. Each experimental combination of AEX and regenerative agent was carried out in duplicate. The regenerative agents used in these experiments were 1 M NaOH, 0.1 M NaOH, 0.1 M NaOH + 0.1 M Na_2SO_4 and 1 M $NaNO_3$ for the MP62 WS and 1 M $NaNO_3$ for MonoPlus M600.

Two decisive factors were investigated: (i) if and how the specific adsorption capacity changes with continuing cycles, and (ii) if and how the regenerated percentage changes with continuing cycles. As an example, the adsorbed percentage for the eight PFAA to MP62 WS when continuously regenerating with 0.1 M NaOH + 0.1 $NaSO_4$ are shown in Figure 4-1.
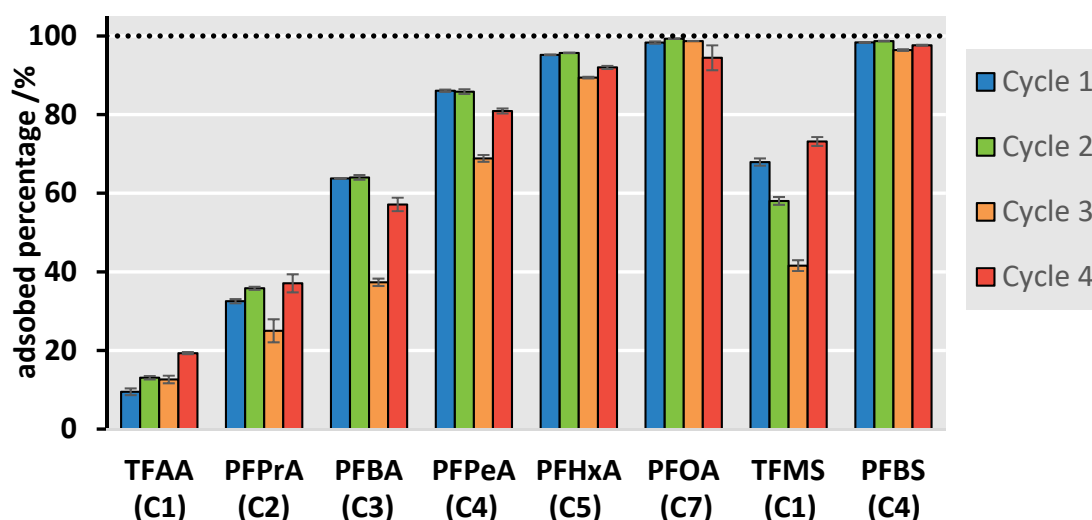

Figure 4-1: Adsorbed percentages of PFCA (C1–5, C7) and PFSA (C1, C4) in batch experiments using MP62 WS in 4 cycles of adsorption and regeneration with 0.1 M NaOH + 0.1 $NaSO_4$ as regenerative agent. Dotted line = 100% of dosed mass; error bars = standard deviation of duplicates. C = no. of perfluorinated alkyl carbon atoms in the PFAA molecule.

The figure clearly demonstrates an increasing adsorption affinity with increasing perfluoroalkyl chain length for both PFCA and PFSA and a better adsorption affinity for PFSA compared to PFCA with similar alkyl chain lengths (e. g TFAA vs. TFMS both with one perfluorinated alkyl carbon). Furthermore, throughout the four cycles, no significant decrease of the sorption capacity occurred. Therefore, it can be concluded from the figure that the regeneration process worked successfully.

Owing to the high uncertainties associated with the determination of the PFAA concentrations in the regenerates (see final paragraph of section 4.1.2), the regenerated percentages shown in Figure 4-2 represent an orientation rather than a display of absolute values. Moreover, measurements of the samples from the third and fourth cycle were repeated because high blank values in the analysis laboratory were suspected. However there was only marginal differences in the concentrations determined in the second analysis. Additionally, there was no isotopically labelled internal standard (IS) available for TFMS (see attachment), so matrix effects could not be accounted for. Though it can be noted from the figure that there seemed to be no decreasing trend overall regarding the regenerated percentages. This finding confirms the results from the consecutive adsorption cycles shown in Figure 4-1 indicating a successful regeneration throughout all four cycles with no decreasing sorption capacity for the PFAA.
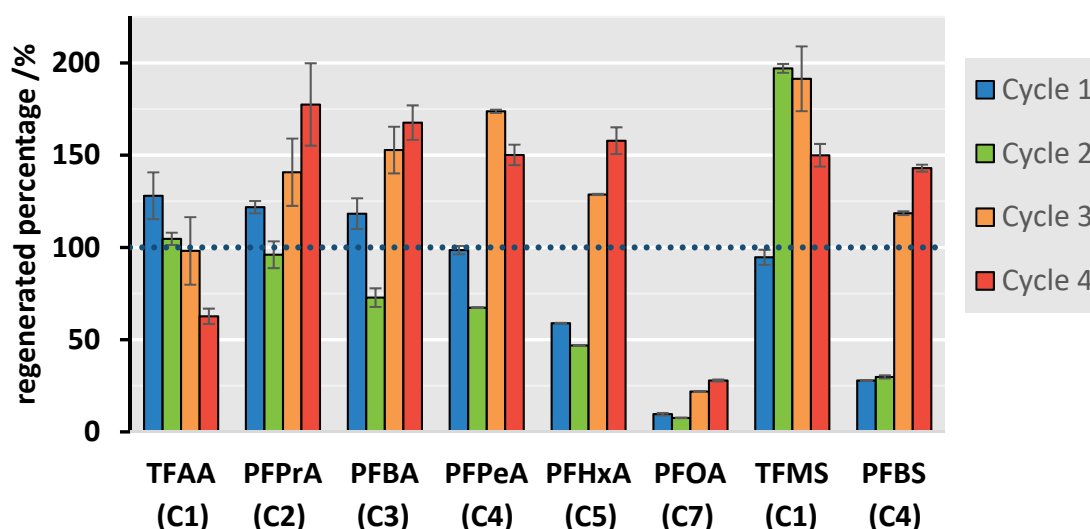

Figure 4-2: Regenerated percentages of PFCA (C1–5, C7) and PFSA (C1, C4) in batch experiments using MP62 WS in 4 cycles of adsorption and regeneration with 0.1 M NaOH + 0.1 NaSO$_4$ as the regenerative agent. Dotted line = 100% of adsorbed mass; error bars = standard deviation of duplicates. C = no. of perfluorinated alkyl carbon atoms in the PFAA molecule.

With the SBA MonoPlus M600, the adsorbed percentages for the well adsorbed compounds PFOA and PFBS remained close to 100% throughout all the cycles (Figure 4-3). For the PFCA with 1–5 perfluorinated alkyl carbons, there seemed to be a drop of the adsorption capacity after the first cycle. However, during the third and fourth cycle, the adsorbed percentages either remained similar or increased again compared to the second cycle. As the experiment was carried out using a single replicate it was not possible to say whether there was a significant change in the adsorption capacity for the

shorter-chained PFCA throughout the different cycles. The three values from the first cycle for PFHxA, PFOA and PFBS slightly surpass 100%. However, the values are still within typical measurement uncertainties (< 20%) of HPLC-MS/MS measurements in this concentration range. The value of 130% for TFMS from the second cycle is higher than that likely due to the concentration being determined without an IS. Overall, the adsorbed percentages indicate successful and complete regeneration without a loss of the sorption capacity for the well desorbable short chain PFAA (PFCA < C7, TFMS).
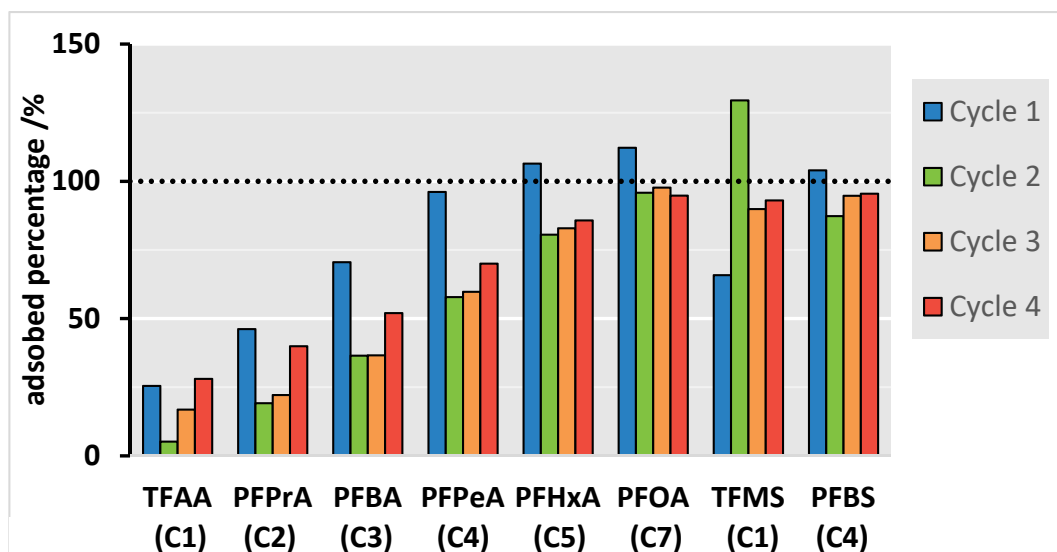

Figure 4-3: Adsorbed percentages of eight PFAA in batch experiments using MonoPLus M600 in 4 cycles of adsorption and regeneration with 1 M NaNO$_3$ as regenerative agent. Dotted line = 100% of dosed mass; n = 1. C = no. of perfluorinated alkyl carbon atoms in the PFAA molecule.

The regenerated percentages of the different PFAA from MonoPlus M600 with 1 M NaNO$_3$ throughout the four consecutive cycles are shown in Figure 4-4. They show that the regeneration effectiveness for the short-chain PFCA up to PFPeA was close to 100% in all four consecutive cycles. Even the percentages of PFHxA were between 62% and 99%. The long chain PFOA, however, only reached a maximum regeneration effectiveness of 25%. For the values above 100%, the same explanation as previously mentioned could be the reason.

The combined results of the adsorption and regeneration throughout the four consecutive cycles described in this section indicate that a continuous use of the tested AEX for the proposed drinking water treatment process is principally possible. The conditions for adsorption and regeneration in these batch experiments were set-up so that there was always enough time to reach sorption-desorption equilibrium. This condition and further details of this simple batch set-up do not necessarily reflect realistic operating conditions in a column set-up at technical scale at the test site. To address this, results from laboratory-scale column experiments have also been included as they provide a more realistic approach and can be used to support a decision regarding promising AEX materials for the pilot-scale application. Results of the column experiments are described below.
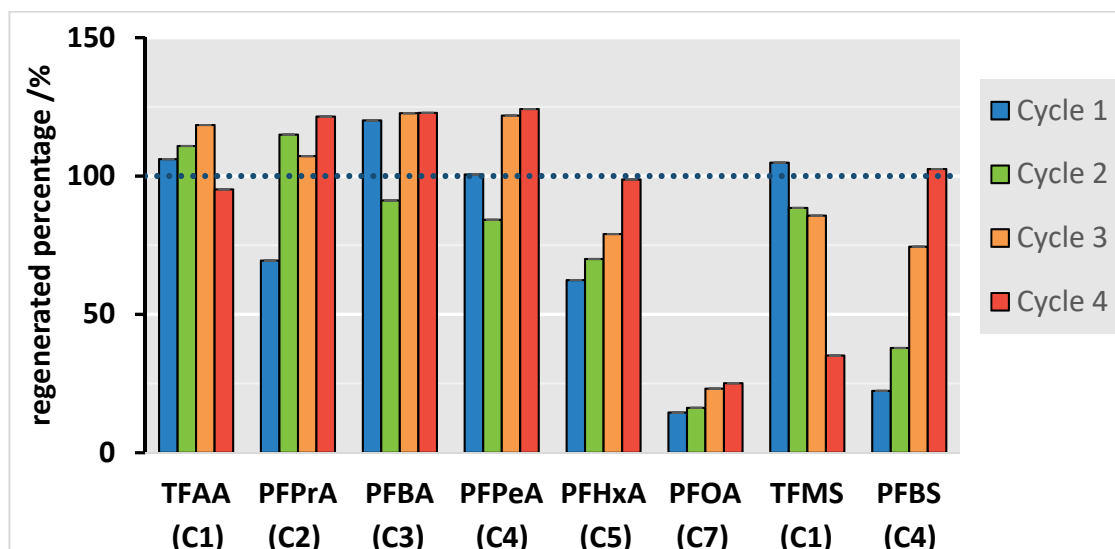
Figure 4-4: Regenerated percentages of eight PFAA in batch experiments using MonoPlus M600 in 4 cycles of adsorption and regeneration with 1 M NaNO₃ as regenerative agent. Dotted line = 100% of adsorbed mass; n = 1. C = no. of perfluorinated alkyl carbon atoms in the PFAA molecule.

4.2 Column experiments

4.2.1 One-time adsorption and regeneration in 45-mL columns

Figure 4-5 shows results from the column adsorption studies in which breakthrough curves were monitored per PFAA and for each AEX, respectively. The throughput is depicted as bed volumes (BV) and the effluent concentrations of the respective PFAA are depicted as percentage of the constant influent concentration (1 µg/L). Two WBA are shown in the top row of the figure and two of the tested SBA are shown in the bottom row. Another WBA was investigated with this set-up, A111. A111, like MP62 WS, is a styrenic, macroporous, pure WBA with tertiary amine functional groups and performed almost identical to MP62 WS for adsorption and regeneration. Owing to the similarity in performance A111 is not shown in the figure.

The effluent concentration for the column with the acrylic WBA, A365, was similar to the influent concentration in all samples, indicating that there was no significant adsorption of the PFAA to the material. This was similar to the results from the batch experiments with this AEX (section 4.1.1) and these findings suggest that this material is not suitable to treat PFAS in drinking water. Thus, it was not studied further. In the other three cases, the breakthrough curves for the different PFAA appeared to be ordered according to their alkyl chain lengths and PFSA had later breakthroughs (i.e., after more BV) than PFCA with similar chain lengths. For example, TFAA showed a 10%-breakthrough at < 250 BV with the WBA and between 750 BV and 1000 BV with the two SBA, while TFMS showed 10%-breakthroughs within the ranges 1000–1200 BV with the WBA and > 1500 BV with the SBA. Thus, the breakthrough of the sulfonic acid TFMS (C1) was comparable to the breakthrough of the carboxylic acid PFBA (C3). More importantly, these results also demonstrate that the two SBA possess a significantly higher specific sorption capacity for PFAA than the WBA (MP62 WS and

A111). For example, 10%-breakthrough of PFBA occurred at around 800 BV (3–4 days) with the WBA but with both of the SBA, the time until 10%-breakthrough was twice as long and occurred at around 1600 BV (6–7 days).
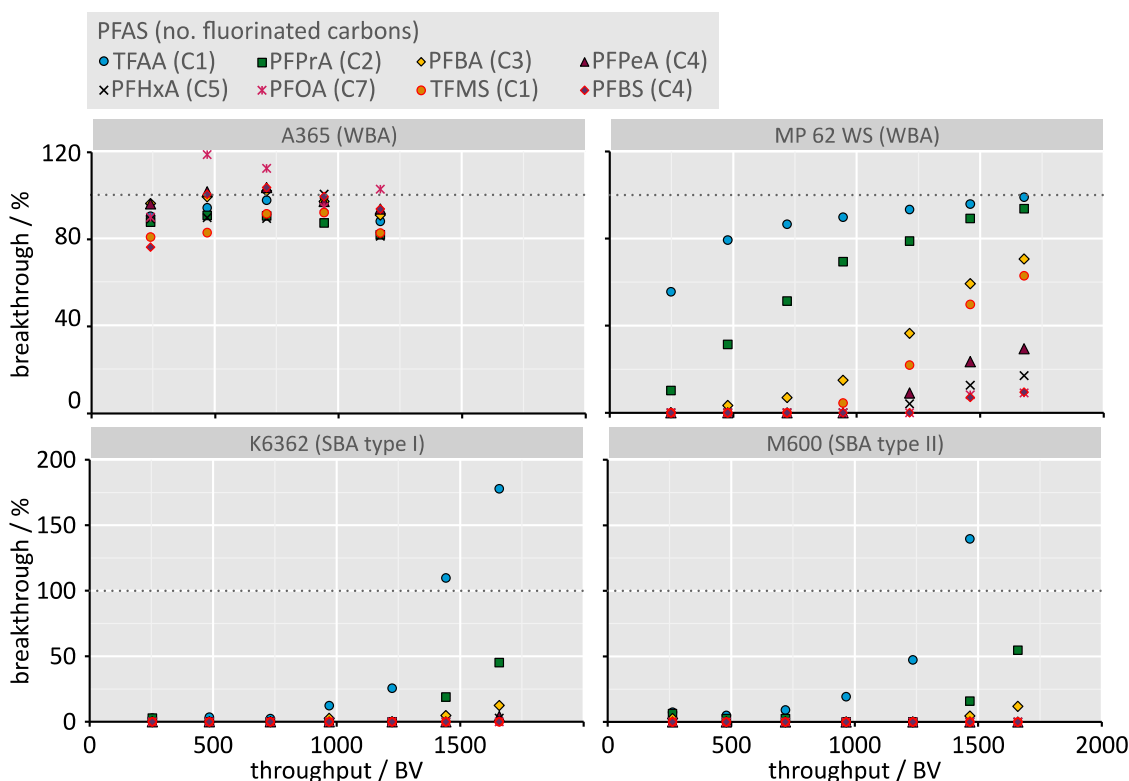

Figure 4-5: Breakthrough curves of eight spiked PFAA for four AEX in 45-mL columns. C_0 = 1 µg/L for each PFAA; water = demineralized water : drinking water in 1:1; Q = 10 BV/h. C = no. of perfluorinated alkyl carbon atoms in the PFAA molecule.

Since the batch experiments investigating the optimization of the regenerative agents were carried out in parallel or after these first column experiments, all resins that showed feasible PFAA adsorption were regenerated using 1 M NaOH as the regenerative agent. The calculated mass balances were promising for the regenerated WBA for short chain PFCA up to PFPeA and TFMS (Table 4-3). The A111 resin had promising regenerated percentages up to PFHxA, but in certain cases percentages were much higher than 100%. The previously described uncertainties with the analyses of the regenerates also apply here. The low values for TFAA and PFPrA with MP62 WS could have been expected to be higher, because it is unlikely that PFAA with shorter alkyl chains desorb to a lesser extent than PFAA with longer alkyl chains. As the values for A111 are likely too high and the ones for MP62 WS too low, and in addition that both resins are expected to behave similarly due to their similar structure, the real values can be expected to be somewhere between the two. Nevertheless, these results show that the regeneration procedure is feasible for the WBA. Further verification will be obtained by carrying out multiple adsorption and regeneration cycles and this will be done in the planned pilot plant.

With the two SBA, NaOH as a regenerative agent worked very poorly and is thus is not considered as a feasible option. However, both resins showed promising regeneration effectiveness with $NaNO_3$ in the batch experiments. MonoPlus M600 was therefore employed in a second laboratory column experiment with three adsorption and regeneration cycles and $NaNO_3$ was used as the regenerative agent (section 4.2.2).

Table 4-3: Regenerated percentages (% of adsorbed mass) of PFAA in 45-mL columns, regenerated with 1 M NaOH.

AEX/PFAA	TFAA (C1)	PFPrA (C2)	PFBA (C3)	PFPeA (C4)	PFHxA (C5)	PFOA (C7)	TFMS (C1)	PFBS (C4)
A111 (WBA)	168	160	124	112	101	27	180	73
MP62 WS (WBA)	59	80	93	75	18	2	139	10
K6362 (SBA type I)	20	4	1	0.4	0.5	0.4	NA	0.1
M600 (SBA type II)	28	12	4	1	1	1	NA	0.1

C = no. perfluorinated alkyl carbons; colouring: green = sufficient; orange = not sufficient but with some potential; red = not sufficient

4.2.2 Multiple adsorption and regeneration in 70-mL column

The purpose of this experiment was mainly to test if MonoPlus M600 could be regenerated using 1 M $NaNO_3$ as the regenerative agent in a column set-up. The aim was not to test its maximum adsorption capacity for different PFAA and monitor their breakthrough. For this reason, the operating time until regeneration was set to 1 week or 1700 BV regardless of potential breakthroughs. The effluent concentration curves in Figure 4-6 show that PFCA with longer chain lengths than PFPeA were still below 10 ng/L at the end of the first two (all) and the third (except PFHxA) cycle and thus did not show a beginning breakthrough. The same is true for PFBS.

Figure 4-6: Breakthrough curves of nine spiked PFAA in 70-mL column filled with MonoPLus M600. C_0 = 1 µg/L for each PFAA; Q = 10 BV/h; vertical dotted lines = regeneration with 1 M $NaNO_3$; 1st & 2nd regeneration with 10 BV, 2.5 BV/h; 3rd regeneration with 10 BV, 10 BV/h as circular regeneration; water = demineralized water: drinking water in 1:1, after third regeneration: flushing with demineralized water.

Generally, TFAA and PFPrA behaved as expected. They had the earliest breakthroughs with 10%-breakthroughs between approximately 500–880 BV (TFAA) and 500–1400 BV (PFPrA). After each regeneration with 1 M $NaNO_3$, their concentration in the column effluents dropped to levels below or close to the LOQ (Figure 4-7).
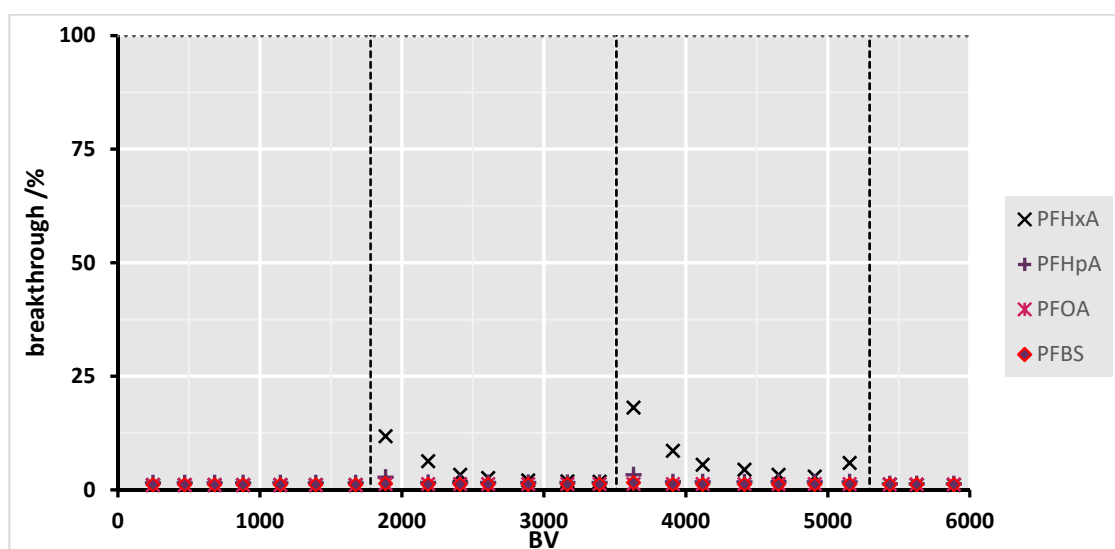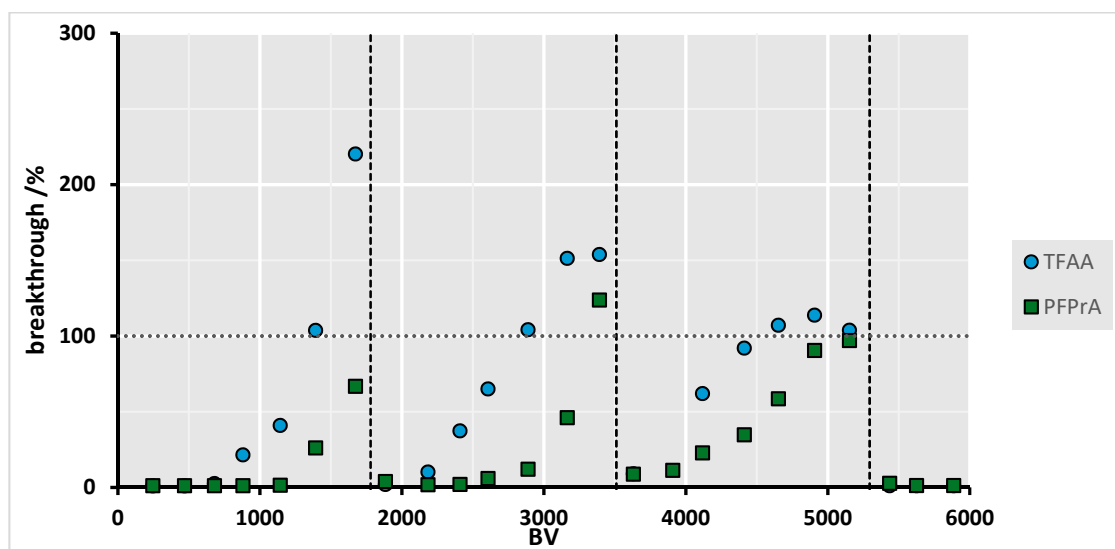

Figure 4-7: Breakthrough curves of TFAA and PFPrA in 70-mL column filled with MonoPLus M600. $C_0 = 1$ µg/L for each PFAA; Q = 10 BV/h; vertical dotted lines = regeneration with 1 M $NaNO_3$; 1st & 2nd regeneration with 10 BV, 2.5 BV/h; 3rd regeneration with 10 BV, 10 BV/h as circular regeneration; water = demineralised water: drinking water in 1:1, after third regeneration: flushing with demineralised water.

Moreover, the TFAA values show a chromatography effect that seems to become lesser from the first to the third cycle. However, the time until breakthrough also seems to decrease from the first to the third cycle. This is especially notable with PFPrA, for which 10%-breakthrough decreases from < 1400 BV to around 500 BV. Potential reasons for this will be discussed by including the results for PFBA, PFPeA and TFMS (Figure 4-8).

When the regeneration procedure works properly, all PFAA concentrations are below the limit of quantification right after the regeneration. This was the case for TFAA and PFPrA. When the regeneration procedure fails completely, the breakthroughs move forward regardless of the regeneration. The effluent concentrations of PFBA and PFPeA after the first and second regeneration were higher than before regenerating. However, effluent concentrations decreased from the first to the fourth sample after regeneration before they increased slightly again towards the end of a cycle. This indicates an incomplete flush out of the regenerated percentage. It could mean that the amount of regenerating agent, that the contact time was insufficient or that residual regenerating agent remained in the system and was only flushed out over time, causing extreme tailing. The latter was also indicated by the effluent nitrate concentration that showed a similar progression (data not shown). Still, the fact that effluent concentrations decreased at some point after each regeneration demonstrates that the regeneration works in principle.
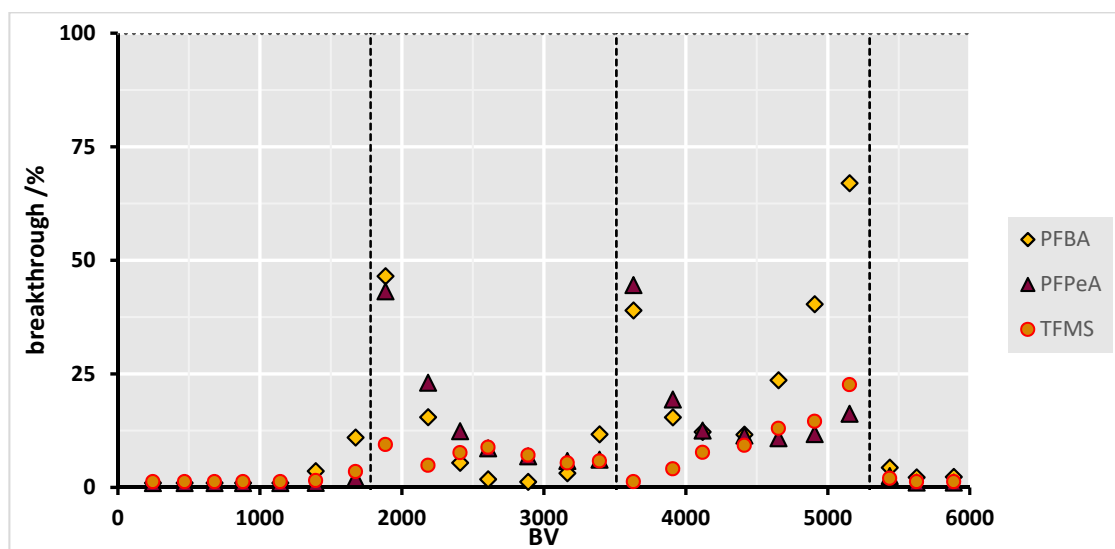
Figure 4-8: Breakthrough curves of PFBA, PFPeA and TFMS in 70-mL column filled with MonoPLus M600. $C_0 = 1$ μg/L for each PFAA; Q = 10 BV/h; vertical dotted lines = regeneration with 1 M NaNO₃; 1st & 2nd regeneration with 10 BV, 2.5 BV/h; 3rd regeneration with 10 BV, 10 BV/h as circular regeneration; water = demineralised. water : drinking water in 1:1, after third regeneration: flushing with demineralised. water.

Nonetheless, there are several indications that regeneration was incomplete with the applied procedure at the first and the second attempt. First, times until breakthrough decreased not only for TFAA and PFPrA, but also for PFBA, PFPeA and TFMS. An easy way to observe this is by comparing the respective concentrations right before regeneration. This fact alone does not necessarily mean incomplete regeneration of these short chain PFAA, because earlier breakthrough could also result from the fact that there are less sorption sites available on the resin with every further cycle. The sites may be occupied by PFAA with longer alkyl chain lengths that do not desorb from the resin during regeneration. However, the calculated regenerated percentages also indicate that incomplete regeneration is at least partly responsible for the decreased capacities (Table 4-1).

Table 4-1 Regenerated percentages (regenerated mass in % of adsorbed mass) of nine PFAAs in three cycles of adsorption and regeneration using MonoPLus M600.

Regeneration	TFAA	PFPrA	PFBA	PFPeA	PFHxA	PFHpA	PFOA	TFMS	PFBS
1st	98	97	71	33	10	2	1	31	1
2nd	107	74	73	42	15	2	1	21	1
3rd (circular)	-122	64	94	86	40	27	10	27	7

While the regenerated percentages of the first and second cycle are comparable, the values for the third cycle were notably higher for seven PFAA and were closer to the ones found in the batch experiments. This is still true when the masses from the first four samples after regeneration (the ones with the heavy tailing), are included in the mass balance calculation. In this case, the mass balances are 79% and 49% for the first regeneration, and 83% and 54% for the second regeneration for PFBA and PFPeA,

respectively. During the regeneration process for the third cycle, the contact time between resin and regenerative agent was much longer. Furthermore, during the subsequent flushing step between 5300 BV and 6000 BV, all PFAA concentrations were close to or lower than the LOQ. There was no peak and long tailing as seen after the first two regeneration steps. On the one hand, this indicates that the third regeneration was working, but on the other hand, it suggests that regeneration at the first and second time where incomplete. This needs to be considered for the planning of the regeneration procedure for the pilot plant.

5   Conclusion

AEX selection for pilot plant

Fifteen different AEX resins from five manufacturers were tested in various adsorption and regeneration experiments to evaluate their feasibility for application in the proposed GAC-AEX hybrid-process. From the materials that are considered suitable, at least two will be used in a pilot plant at ZeroPM test site 1 (see chapter 1, Introduction). After evaluating the results from the experiments conducted in the specific water matrix, two WBA and two SBA are considered promising: MP62 WS, A111, MonoPlus M600, and K6362.

- ▼ MP62 WS and A111 were among the best WBA regarding their adsorption capacity of PFAA while being well regenerable with NaOH-based regenerative agents as the best option. Both performed very similarly and only one of them will be selected for the pilot study, depending on availability.
- ▼ MonoPlus M600 and K6362 had the best adsorption performance of the tested SBAs (except for the tested PFAS-specific resins with bad regeneration efficiency) and both show good regeneration with $NaNO_3$ as regenerative agent. In this work, MonoPlus M600 has been more thoroughly tested. Both SBAs had comparable performances, yet MonoPlus M600 could have slightly better regeneration efficiencies. For this reason, MonoPlus M600 would be the first choice and K6362 will be used if MonoPlus M600 is not available.

Further considerations

A technical and economic evaluation of the proposed hybrid process should include, though not be limited to the following considerations:

- ▼ Operating time until regeneration (e. g WBA vs. SBA)
- ▼ Effort of the regeneration procedure (how long, how much regenerative agent needed etc.)
- ▼ Treatment costs (carried out by project partner Chalmers University in ZeroPM's work package 2 "Alternatives Assessment")

The above points are important to compare the different AEX. However, it is also important to compare the hybrid system, regardless of which specific AEX is used, to alternatives. These alternatives include membrane treatment such as nano-filtration and reverse osmosis. For both, comparative laboratory tests will be conducted at a later stage

of the project. Economic considerations can also be taken into consideration by including the technical process used in a second waterworks at test site 1 which uses reverse osmosis to reduce PFAS concentrations in drinking water. Another alternative that will be easiest to compare to the hybrid treatment, is simply to exchange the GAC in the filters more frequently and thus negating the need for the subsequent AEX. Furthermore, the use of an AEX (or other adsorption media) which cannot be regenerated at all or regenerated without an organic solvent, but at the same time has a very high specific adsorption capacity towards PFAS, meaning a PFAS-specific resin, could be considered. Such an AEX could either replace the GAC completely or function as back up after the GAC such as in the proposed hybrid process.

To compare different approaches, the pilot plant will most likely be set up with the following treatment lanes:

- ▼ GAC + WBA with regeneration
- ▼ GAC + SBA with regeneration
- ▼ GAC (optional as pre-treatment) + PFAS-specific AEX without regeneration

A definitive set-up and experimental plan will be made in March – April 2023. Assuming there will not be delays, the pilot plant with at least two of the four presented AEX resins will start operating during the first half of 2023. Sampling will be carried out in collaboration with other partners in WP7 and in discussion with those investigating the full life cycle impact assessment of the treatments.

The appendix of this document contains the technical data sheets on the analytical methods for the determination of PM substances which fulfil Milestone M12 "Analysis protocols and selection of anion exchangers".

6 Acknowledgements

7 References

Boyer, Treavor H.; Fang, Yida; Ellis, Anderson; Dietz, Rebecca; Choi, Youn Jeong; Schaefer, Charles E. et al. (2021): Anion exchange resin removal of per- and polyfluoroalkyl substances (PFAS) from impacted water. A critical review. In: *Water research* 200, S. 117244. DOI: 10.1016/j.watres.2021.117244.

Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption (recast) (OJ L 435, 23.12.2020, pp. 1-62)

Dixit, Fuhar; Barbeau, Benoit; Mostafavi, Shadan Ghavam; Mohseni, Madjid (2020): Removal of legacy PFAS and other fluorotelomers. Optimized regeneration strategies in DOM-rich waters. In: *Water research* 183, S. 116098. DOI: 10.1016/j.watres.2020.116098.

Dixit, Fuhar; Barbeau, Benoit; Mostafavi, Shadan Ghavam; Mohseni, Madjid (2021): PFAS and DOM removal using an organic scavenger and PFAS-specific resin. Trade-off between regeneration and faster kinetics. In: *The Science of the total environment* 754, S. 142107. DOI: 10.1016/j.scitotenv.2020.142107.

Goldenman, Gretta; Fernandes, Meena; Holland, Michael; Tugran, Tugce; Nordin, Amanda; Schoumacher, Cindy et al. (2019): The cost of inaction: A socioeconomic analysis of environmental and health impacts linked to exposure to PFAS. Nordic Council of Ministers. DOI:10.6027/TN2019-516

Haist-Gulde, Brigitte; Hesse, Sebastian; Riegel, Marcel; Sturm, Sebastian (2021): Auswirkungen von PFAS-Parameterwerten auf das Aktivkohlemanagement am Beispiel des Wasserwerks Rauental. In: *energie / wasser-praxis* (10), S. 22–27.

Neuwald, Isabelle J.; Hübner, Daniel; Wiegand, Hanna L.; Valkov, Vassil; Borchers, Ulrich; Nödler, Karsten et al. (2022): Ultra-Short-Chain PFASs in the Sources of German Drinking Water. Prevalent, Overlooked, Difficult to Remove, and Unregulated. In: *Environmental science & technology* 56 (10), S. 6380–6390. DOI: 10.1021/acs.est.1c07949.

Regierungspräsidium Karlsruhe (2022): Überblick PFAS-Problematik in Mittelbaden und Mannheim. On: website of regional council of Karlsruhe, https://rp.baden-wuerttemberg.de/rpk/abt5/ref541/stabsstelle-pfc/pfc-problematik-mittelbaden-mannheim (last access 17th February 2023).

Riegel, Marcel; Schmid, Julian; Schell, Heico (2022) Wissenschaftliche Untersuchungen zur Entfernung von kurzkettigen PFAS. Abschlussbericht, Forschungsprojekt K 16567, promoted by Regierungspräsidium Karlsruhe and Stadtwerke Rastatt.

UBA / TWK (2017): Fortschreibung der vorläufigen Bewertung von per- und polyfluorierten Chemikalien (PFC) im Trinkwasser. Empfehlung des Umweltbundesamtes nach Anhörung der Trinkwasserkommission. On: https://link.springer.com/article/10.1007/s00103-016-2508-3 (last access 17th February 2023).

8 Appendix

Fact sheet 1: PFAS measurements of AEX resin adsorption and regeneration experiments 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 8-1: 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 8-2: 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

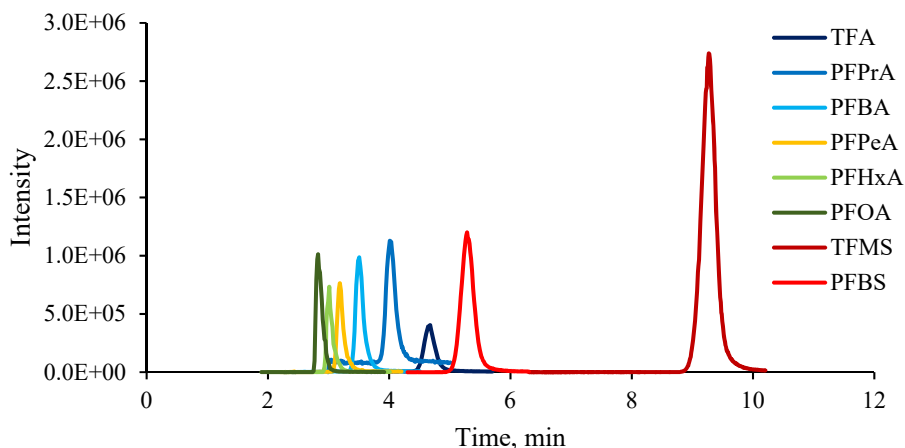[*] additionally added in later column experiments

Figure 8-1: 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 of AEX resin adsorption and experiments 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 8-3: 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

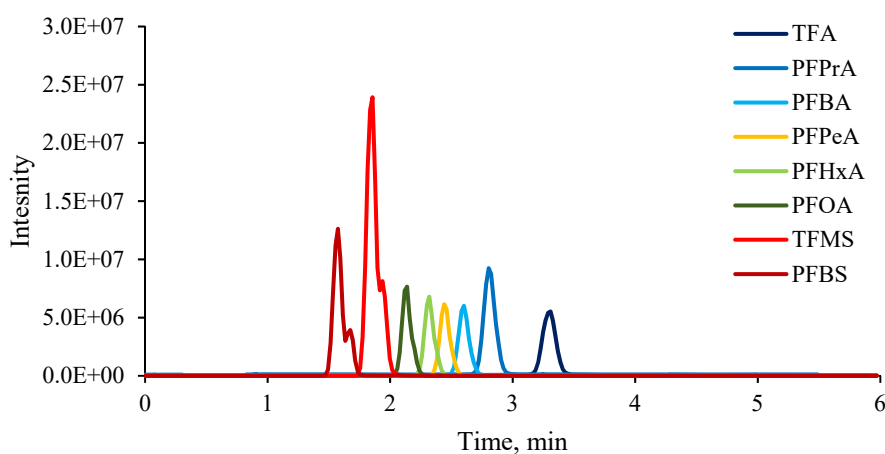* additionally added in later column experiments

Figure 8-2: Exemplary chromatograms showing the elution order of PFAS measured for resin adsorption and regeneration experiments. Measured in ultrapure water. Chromatographic separation with Raptor column.