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Performance of water treatment systems for PFAS removal

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Performance of water treatment systems for PFAS removal

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ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) are a group of widely used man-made organic chemical substances. They contain alkyl groups on which all or many of the hydrogen atoms have been replaced with fluorine. As such, they contain at least one perfluoroalkyl moiety, $–(CF_2)_n–$. PFAS have been used because of their particular physicochemical properties: most are stable at high temperatures, recalcitrant to chemical oxidation and biological degradation (i.e., persistent), and act as a surfactant. Although beyond the scope of this report, as reported by the Australian Ministry of Defense[6], among others these properties mean there are a wide variety of PFAS-containing materials (e.g stain- resistant fabrics, nonstick cookware, polishes, personal care products, and fire-fighting foams), or materials where PFAS is used in the process (e.g. Mist suppression in metal plating or photography). Many such substances may also be bio-accumulative and toxic.

In this study several treatment technologies for PFAS removal were tested in the laboratory on both groundwater containing PFAS, and firefighting wastewater obtained from a firefighting training site where firefighting foam was applied. The treatment technologies assessed were performance of sorbents, coagulation/flocculation, nanofiltration, foam- and ozo fractionation technologies. In all cases the PFAS removal effectiveness was evaluated.

This report provides:

- Criteria and background information to select potential treatment technologies.
- Results of these performance tests of water treatment technologies for PFAS removal.
- Practicalities such as availability of the technology and experimental feasibility which are included in the evaluation.
- Recommendations for selection of treatment technologies for PFAS removal in practice for impacted groundwater and firefighting wastewater.

Experiments showed that all tested sorbents were able to remove PFAS from firefighting wastewater but the required sorbent dosages were in the g/L range. It is therefore concluded that groundwater containing PFAS can be treated with one of the tested sorbents directly, while for firefighting wastewater, which typically has higher PFAS concentrations as well as other contaminants, a treatment train approach is likely to be more efficient. An initial treatment, such as flocculation, nanofiltration or foam- / ozo fractionation that removes bulk PFAS load including co-contaminants followed by a polishing treatment (e.g. sorbents) that further reduces PFAS concentrations to acceptable levels is advised, unless a relative small fixed volume of firefighting wastewater needs to be treated.

This study provides a basis for readers of this publication to select, study and apply the best available technologies to mitigate risks associated with PFAS contamination.

KEYWORDS

PFAS (per- and polyfluoroalkyl substances), PFCA (per- and polyfluoroalkyl carboxylic acids), PFSA (per- and polyfluoroalkyl sulfonic acids), long-chain, short-chain, precursors, treatment technologies, PFAS impacted groundwater, firefighting wastewater, comparative evaluation, batch testing, pilot testing

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SUMMARY

Per- and polyfluoroalkyl substances (PFAS) are a group of widely used man-made organic chemicals. They contain one alkyl groups on which hydrogen atoms have been replaced with fluorine. As such, they contain at least one perfluoroalkyl moiety, $-(CF_2)_n-$. PFAS have been used because of their particular physicochemical properties: most are stable at high temperatures, recalcitrant to chemical oxidation and biological degradation (i.e. persistent), and act as a surfactant. Many of such substances may also be bioaccumulative and toxic. PFAS were first synthesised in the 1940's and commercialised in the 1950's in stain-resistant products. PFAS-containing fire-fighting foams were developed for military applications in the mid-1960's but became available for commercial fire-fighting uses in the late 1960's / early 1970's. The oil and gas industry is unlikely to have used PFAS-containing foams prior to circa 1970. In 2018, the OECD defined over 4,000 different CAS numbers representing chemicals that can be considered PFAS and this number is growing each year. Release of PFAS-foams to the environment may have occurred during:

- Firefighting incidents
- Firefighting practice and training
- Vapour suppression during hot work
- Firefighting foam storage, dispensing and handling
- Firefighting system testing

Uses of foam for firefighting lead to contamination of groundwater. They were commonly used at many industrial sites including petrochemical plants (and other sites with bulk fuel storage, such as military and civil aviation facilities) and at firefighting training sites co-located on petrochemical industry sites, or at third-party training facilities operated commercially or by public fire brigades. This report seeks to help Concawe members, and others, identify suitable technologies to treat PFAS from firefighting foams in groundwater, and mitigate new emissions by on-site treatment of firefighting wastewater residues. Within this study treatment technologies for both types of impacted waters have been studied. In addition the tested groundwater was spiked with benzene for selected experiments to study the effects of petrochemical co-contamination on the treatment performance.

This study contains two parts. First, a series of promising treatment technologies to separate PFAS from aqueous phases were tested in a laboratory setting using groundwater and wastewater obtained from a firefighting training site. Second, these technologies were also evaluated in a desk based assessment considering their practical application in the field, costs and potential production of waste. In addition information was gathered on costs, generation of waste, reuse possibilities and the physical footprint of such a technique, which can be a constraint when insufficient space is available.

The selected technologies were: treatment by a variety of sorbents in batch (bottle) and continuous (column) tests, coagulation/flocculation in batch tests and nanofiltration, foam- and ozo-fractionation in a continuous tests. In batch tests all tested sorbents are capable of removing over 85% total PFAS from both PFAS-impacted groundwater (with or without added benzene) as well as firefighting wastewater (FFWW). However, as concentrations of PFAS in the firefighting wastewater were roughly three orders of magnitude higher than in the groundwater, sorbent dosages in the g/L range were required to obtain PFAS removal. The tested

coagulant reduced PFAS concentrations at lower dosages as compared other sorbents for both firefighting wastewater and PFAS-impacted groundwater. However, PFAS levels did not fully drop below limits of detection at the highest dosages.

The tested foam fractionation with and without ozone separated 60 to 90% of the PFAS from the bulk water by concentrating it in a foam matrix. These removal rates were considered insufficient as a stand-alone treatment for the tested waters as PFAS concentrations were at µg/L level and mg/L level after treatment for groundwater and firefighting wastewater, respectively. Therefore additional treatment / polishing is advised. Similar results were observed for a nanofiltration membrane that was solely tested with the firefighting wastewater. Although the initial removal exceeded 95%, fouling occurred after several hours to a day of operation. Thus, the firefighting wastewater might require pre-treatment to prolong membrane service life. All in all this leads to the conclusion that all tested sorbents were able to remove PFAS from firefighting wastewater but the required sorbent dosages were very high. Therefore, a treatment train approach where an initial treatment, such as flocculation, nanofiltration or foam- / ozo- fractionation that removes bulk PFAS load including co-contaminants, and a second polishing treatment (e.g. sorbents) that further reduces PFAS concentrations to acceptable levels is likely to be more efficient for large volumes of firefighting wastewater.

Results were collected and summarized in the lookup table below. This table provides a basis for readers of this publication to select, study and apply the best available technologies to mitigate risks associated with PFAS present in groundwater and firewater.

Table I: Lookup table on advantages and disadvantages of treatment technologies. Colours ranging from red (-- very poor) via orange (-poor) and yellow (fair) to green (+, good and ++, very good); n.a. (grey) is not assessed, or the data is unknown.

	Removal mechanisms	Performance		Treatment strategy	Pre-treatment			Main treatment				Effects of temperature and pressure	Operational aspects				Costs	
		Short Chain PFAS	Long chain PFAS		Turbidity	Fn/Mn	TOC	Contact time	Hydraulic loading rate /filtration velocity	Contaminant loading rate	Bed lifetime		Energy use	Maintenance and personnel	Chemical use	Waste production	CAPEX	OPEX
Sorption																		
DESOTEC Granular Activated Carbon (GAC)	Hydrophobic, (pi-pi) electrostatic and ionic interactions	+	++	Fixed bed filtration, lag/lead configuration	-	-	-	20-30 min	10- 15 m/h	+	+	minimal	0	0	++	+	0	--
Rembind® (RB)	Hydrophobic- , electrostatic- and (an)ionic interactions	+ $^{2-3}$	+	2 options: 1: discontinuous batch with sedimentation 2: mixed media filter with sand	-	-	-	5-10 min, >80% sorption	unknown	+	+	unknown, expected minimal	0	0	+	+	0	unknown
Cyclopure DEXSORB+® (CP)	Hydrophobic- and electrostatic interactions	-	++	Fixed bed filtration, lag/lead configuration, with on-site regeneration possible	-	0	++	3-10 min	unknown, expected around 10 m/h	+	0	unknown, expected minimal	0	0 without regeneration - with regeneration	--	++	+	0
PolyQA-Osorb® (PQ)	Hydrophobic- and ionic interactions	0	+ (a)	not clear yet, possible fixed bed filtration with regeneration	-	--	--	1-5 min	unknown, expected around 10 m/h	0	n.a.	unknown, expected low. Possible pressure effects on swelling of material	0	0 without regeneration -1 with regeneration	--	+	+	0
FLUORO-SORB® Des+ (FS)	Hydrophobic and electrostatic interactions	+	++	Flow-through filter or batch treatment with sedimentation or floatation	-	-	0	2-10 min	up to >15 m/h	+	+	unknown, expected minimal	0	0	++	+	+	0
Flocculation																		
PerfluorAd (PFAD)	Hydrophobic- and electrostatic interactions	+ (b)	++ (b)	mixing tank, sedimentation, filtration	+	0	+	up to 60 min	for filtration up to 15 m/h	++	n.a.	unknown, expected better performance with increasing temperature	-	-	---	-	-	-
Other separation technologies																		
Nanofiltration (c)	Size exclusion	-	+	Filter units	0 (d)	0	0 (d)	n/a (short)	n/a	n.a.	n.a.	Increasing temperature has positive effects on operational aspects, increased pre-pressure reduces pump energy	-	-	--	---	--	--
Foam fractionation WITH OZONE	Surface active characteristics of PFAS	-	+	multiple contact tank(s) in series with compressed ozone bubbles	+	+	+	20-40 min	n/a	n.a.	n.a.	Unknown, but higher temperatures negatively affect gas transfer and saturation, this might have adverse effects	---	-	-	0	+	-
Foam fractionation WITHOUT OZONE	Surface active characteristics of PFAS	-	0	Discontinuous batch contact tank with compressed air bubbles	+	+	+	20-40 min	n/a	n.a.	n.a.	Unknown, but higher temperatures negatively affect gas transfer and saturation, this might have adverse effects	0	0	++	++	+	+

a) determination of sorption coefficients was complicated for GW
b) based on removal performance for firefighting wastewater
c) initial performance before fouling
d) suspended solids and TOC were higher than operational range stated by vendor

1. INTRODUCTION

1.1. PFAS

Per- and polyfluoroalkyl substances (PFAS) are a group of widely used man-made organic chemicals. They contain one alkyl groups on which hydrogen atoms have been replaced with fluorine. As such, they contain at least one perfluoroalkyl moiety, $-(CF_2)_n-$.[4] PFAS have been used because of their particular physicochemical properties: some are stable at high temperatures, recalcitrant to chemical oxidation and biological degradation, and act as a surfactant. Many also have one or more of the following properties: recalcitrant to degradation (i.e., persistent), subject to bioaccumulation, and toxic. These polyfluorinated compounds may transform into fully saturated perfluorinated compounds in the environment: polyfluorinated compounds can act as precursors to the perfluorinated molecules. In 2018, the OECD defined over 4,000 different CAS numbers representing chemicals that can be considered PFAS.[5]

Figure 1: PFAS applications / sources (kindly provided by the Australian Ministry of Defense)[6]

These substances act as surfactants and can reduce surface tension between aqueous and hydrophobic phases, which makes them water and oil repellent. PFAS are widely used, as illustrated in **Figure 1** and described further by Gluge, et al. [7]. Their properties benefit applications but are a potential risk for the environment. These properties potentially lead to persistence, bio-accumulation, and toxicity. Furthermore, the properties also complicate removal during water treatment such as remediation of impacted groundwater and treatment of residues from used firefighting foams. In firefighting (including within the petrochemical industry), PFAS-containing fire-fighting foams have been used to suppress flammable liquid fires or for firefighting training and spill control since about 1970. The composition of these firefighting foams changed over the past decades as a result of the development of new fluor-containing additives and regulations.

The potential persistence and toxicity of PFAS are reflected in water quality criteria and other regulatory thresholds down to the ng/L range for some PFAS [8-9]. This challenges PFAS-producers, PFAS-containing product manufacturers, and users of PFAS-containing products across society and industry, to reduce emissions to the environment and study the impact of this diverse group of compounds.

As a result of firefighting activities in a training setting or real situation, PFAS can be emitted. Firefighting initially results in large volumes of firefighting wastewater (FFWW), which can contaminate surface waters and groundwater (GW) when treatment and containment of the wastewater is not performed appropriately. Conventional treatment systems such as rapid sand filtration are not effective in removing PFAS from (waste) water. Activated carbon and ion exchange are generally applied to remove PFAS from water, but alternative treatment options are available. Therefore, Concawe seeks to understand the effectiveness of multiple treatment options for PFAS in firefighting foam-impacted GW and FFWW itself.

1.2. AIM

The aim of the report is to provide experimental results and criteria to support the selection of appropriate treatment technologies to remove PFAS from impacted water. This was done by experimental testing on lab scale to fill data gaps for these treatment technologies. Thereby, this report builds upon the German Water Centre (Technologiezentrum Wasser, TZW) review on treatment technologies for PFAS.[1] Furthermore, practical criteria such as availability of the technology and experimental feasibility are included in the evaluation. Thereby this report provides a basis for the selection and application of the best available technologies to mitigate PFAS contamination.

2. PART 1: TECHNOLOGY SELECTION

In this chapter an overview is given of the different treatment technologies for the removal of PFAS in water. These technologies are then evaluated against various criteria, and technologies are selected for experiments.

2.1. OVERVIEW OF TECHNOLOGY CONCEPTS

There are multiple PFAS-treatment technologies available on the market. TZW[1] (Technologiezentrum Wasser) evaluated a wide array of available technologies marketed by numerous suppliers. Conceptually, there are three treatment concepts. More details can be found in **Appendix 2**.

1. Sorption technologies: The PFAS will bind to sorption sites in or on the surface of the sorbent. The compound will distribute between the aqueous phase and the sorbent, to the energetically most favorable distribution. One can distinguish adsorption from absorption (extraction), where adsorption is the chemical interaction of a sorbate (e.g. PFAS) with a solid matrix (adsorbent) that retains the sorbate on the surface of the matrix. In comparison, absorption is the distribution of the sorbent into the porosity of a matrix where the compound is physically retained. Within this report we use the generic term sorption for the potential adsorption, ion exchange and complexation interactions together.

2. Physical separation techniques: liquid separation techniques separate the waste stream into two new streams. The first stream (concentrate) is typically small in volume and contains the majority of the contamination, while the second stream is much larger in volume and predominantly free of the contamination and has nearly all of the volume of water. The separation can be obtained by the use of a physical barrier such as a membrane. In addition, this separation can also be obtained by the addition of a complexing agent that interacts with PFAS by similar mechanisms as described in the sorption section and where the complexing agent coagulates and flocculates and is filtered in order to separate the water from the flocs containing the majority of the PFAS. Finally, the separation can also be obtained by injecting air or ozone to generate foam that pick up the PFAS from the water and concentrate them in or on the air bubble interface of the foam layer which is skimmed from the water surface.

3. Reactive degradation: these are (bio)chemical processes where the PFAS is degraded into intermediate products or completely mineralized. The effectiveness of the reactive degradation requires analytics that are able to determine parent chemicals as well as all transformation products formed during the reactions in order to define mass balances of the parents and the transformation products versus total mineralization. If the complete mineralization of the PFAS cannot be assessed, an additional polishing step is recommended. Further treatment may be required to remove transformation products. In case further treatment is necessary, sorption and/or separation technologies come into play.

2.2. SELECTING TECHNOLOGIES FOR TREATING PFAS IN GROUNDWATER AND FIREFIGHTING WASTEWATER

2.2.1. Preliminary criteria

The treatment of impacted aqueous streams require fit for purpose treatment technology. The suitability of any treatment technology is defined by many factors. The following factors should be mentioned:

- The composition of the water stream and in particular the presence of interfering components (the so-called matrix);
- The treatment efficiency for a wide array of PFAS (technology);
- Treatment costs (costs);
- Sustainability of the treatment (e.g., hazard-properties of the treatment products);
- Practical implementation on site or at a central location and the technology readiness level (practical application),
- Required reduction of contamination (target),
- Production of waste streams (waste management).

These criteria are interrelated, and as a result the following criteria have been used in this study:

- Technology Readiness Level (TRL) and viability to apply on full scale (if not applied on full scale yet);
- Single process or part of a treatment train;
- Removal efficiency;
- Inflow water quality requirements (pretreatment requirements);
- Waste produced;
- Formation of byproducts and post-treatment requirements;
- Use of chemicals;
- Energy consumption;
- Practical, full-scale applicability and robustness;
- Treatment of generated waste, regeneration or recovery of the sorbent;
- Costs, capital and operational expenditure (CAPEX, OPEX).

Furthermore, technologies can be combined which can improve efficiency or reduce costs or provide other advantages (waste reduction, logistics) of the full treatment train.

2.2.2. Selection of technologies for experimental testing

2.2.2.1. Sorption technologies

The different technologies are sorted based on the type of sorbent:

- Granular Activated Carbon (GAC);
- Surface Modified Clay-based (e.g. Matcare®, Rembind®, FLUORO-SORB®);

- Ion exchange resin based (Strong Base Anion resins);
- Biobased/Polymeric based (e.g., DEXSORB+®, PolyQA-Osorb®, CustoMem®/ Puraffinity CGM®).

From each of these type of sorbents, at least one product is tested except the ion exchange material.

The selection of the sorption material is based on:

- The cooperation of manufacturers to supply materials;
- The suitability of the product for the performance of bench- and/or column tests using relatively small volumes of GW or FFWW.

As stated, ion exchange material was not selected for testing. Both activated carbon and ion exchange resin are considered as proven and commonly used technologies by the Concawe STF33 experts. Activated carbon is however incorporated in the testing program for it is selected as the bench mark technology.

2.2.2.2. Physical separation technologies

Separation technologies are able to remove the bulk of the PFAS into a small amount of water, like:

- Membranes (Nanofiltration / Reverse Osmosis)
- Foam separation (foam-/ ozo fractionation)

Membranes require an intensive pretreatment if fed with FFWW to prevent suspended solids and organic material to foul or degrade membranes and thereby affect treatment. Recently capillary NF membranes were commercialized with a lower fouling tendency, likely to require less pretreatment. Therefore capillary NF are preferably be tested for treatment of FFWW.

Foam- and ozo fractionation produce a very limited amount of wastewater (compared to NF/RO). The IP for the technology has been developed by Evocra, a company based in Australia. Evocra has not only approved the testing of the technology, but also assisted KWR in executing the tests.

2.2.2.3. Reactive degradation

Reactive degradation technologies are not considered for testing in this phase of the project as they have a number of disadvantages:

- Testing them on lab scale is technically challenging due to the many different test conditions (proprietary knowledge) and the complexity of the necessary test equipment
- The formation of unknown transformation products
- The uncertainty to scale up to large installations for treating large volumes of water
- The anticipated high costs (Capex as well as Opex)

2.2.2.4. Selection of technologies

In **Table 1** an overview is given of the recommended technologies for experimental testing of PFAS removal. This table is based on the tables as presented by TZW (see **Appendix 8**), in which the TRL according to the EU Horizon 2020 programs[10] is used as a more quantifiable alternative for the "technical maturity" as used by TZW.

Table 1: *S*election of technologies for experimental testing, "Yes" indicates where a technology was selected, "No" that it was not.

Technology	TRL (EU H2020)	Preliminary evaluation and selection for testing	GW[1]	FFWW[2]	*Example* product/brand names
Granular Activated Carbon	9	Yes	Yes	Yes	e.g. Chemviron F300/F400, Desotec Organosorb 10AA, CABOT Hydrodarco 4000
Surface modified clay-based sorbents	5-6	Yes	Yes	Yes	e.g. Matcare®, Rembind®, FLUORO-SORB®
IEX without regeneration	9	No, because of high TRL, practical performance already largely known	No	No	SBA (strong base anion) resins, e.g. Purolite®, Lewatit®, Amberlite®, Dowex®
Biobased/polymeric based sorbent	5-6	Yes	Yes	Yes	e.g. Customem®, DEXSORB+®, PolyQA-Osorb®, PuraffinityCGM®
Flocculants	6-7	Yes	Yes	Yes	e.g. PerfluorAd®, InSite®
Nanofiltration/reverse osmosis	9	Yes for FFWW, No for GW because presumably concentrate volumes are still large	No	Yes	e.g. BWRO, DOW, Hydranautics
Foam- and ozo fractionation	7-8	Yes	Yes	Yes	e.g. OPEC systems, Evocra
IEX with regeneration	7	No, because practical performance already largely known, regeneration require research	No	No	WBA (Weak base anion) resins, e.g. Lewatit®, Amberlite®
Biobased/polymeric based sorbent with regeneration	4-6	No, first tests without regeneration	No	No	e.g. Customem®, DEXSORB+®, PolyQA-Osorb®, PuraffinityCGM®
Distillation	7-9	No based on costs for primary treatment	No	No	n.a.

3. PART 2: TECHNOLOGY TESTING

In this chapter the experimental evaluation and studies of the different technologies are described and the results are discussed.

3.1. PFAS IMPACTED WATER

This study focuses on the treatment of PFAS impacted GW and FFWW. The FFWW was collected from a firefighting training site in Hungary and the impacted GW was obtained from a site in Germany. The collected FFWW contains C6 telomers, while the impacted GW is impacted by historical contamination of PFAS origination from firefighting activities decades ago. The composition of PFAS in the GW is a product of the use of PFAS in the past, the hydrological conditions of the subsoil, the mobility of the different PFAS in the soil and potential transformation of PFAS (precursors) into other more stable PFAS during soil passage.

Table 2: Typical generalized characteristics of impacted groundwater (GW) and firefighting wastewater (FFWW)

	Impacted groundwater (GW)[1]	*Firefighting wastewater (FFWW)*[2]
Volumes and duration	Large volumes continuous or for longer periods	Smaller volume generated during emergency response
Concentration of PFAS	Generally (sub) µg/L range	Up to g/L range
Concentration of total organic carbon	Generally mg/L range	Variable mg/L - g/L range
Salt content	Generally low, levels typically found in freshwater and pristine groundwater	Variable

[1] (historically) impacted GW with PFAS near petrochemical plants often contains residues of petrochemicals such as BTEX.
[2] FFWW contains PFAS present and transformed during firefighting activities and petrochemical residues, and organic (soot) and mineral particles.

PFAS impacted GW was collected at a petrochemical site in Germany and transported to the University of Amsterdam (UvA), The Netherlands, by using 20 L jerry cans. The water was collected in July 2019 and January 2020, and was stored in the dark at 4°C until use. A single jerry can was used to perform all batch sorption studies except the complexant /coagulant PFAD that was supplied at a later stage. PFAS impacted GW from firefighting activities often coincides with petrochemical contamination, since PFAS-containing fire-fighting foams have been used to fight Class B liquid (hydrocarbon) fires. In order to study the effect of residues of BTEX on the treatment performance the collected GW sample spiked with 20 mg/L. The benzene concentration is based on measured BTEX levels in petrochemical impacted GW (personal communication with Concawe members). All batch experiments with benzene spiked GW and the PFAD study with and without benzene spike were performed with a second jerry can from the same batch.

FFWW was collected at a training site in Hungary and transported to the UvA in Amsterdam, The Netherlands, by using 20 L jerry cans in July 2019. A single jerry can was used to perform all batch sorption studies except the complexant /coagulant PFAD that was supplied at a later stage. For the column tests GW was collected at a petrochemical site in Germany and transported to KWR in Nieuwegein, The Netherlands, by using fifty 20 L jerry cans on the 18th of June 2020.

Here all water was mixed in a single container to be supplied to the columns. Details on sample preparation and analysis can be found in **Appendix 7**.

3.2. EXPERIMENTAL SET UP OF REMOVAL TESTS

Different treatment techniques have been tested by batch and pilot testing. The ultimate goal was to determine the performance of treatment methods to remove PFAS from different types of water, and define the conditions that can affect the performance. **Table 3** shows the technologies selected for testing.

Table 3: PFAS remediation technologies tested in this research.

Sorption technologies	
Granular activated carbon	DESOTEC Granular Activated Carbon (GAC)
Remediation and PFAS sorbents	Rembind® (RB), FLUORO-SORB® Des+ (FS)
Bio-based or polymeric based sorbent	Cyclopure DEXSORB+® (CP), PolyQA-Osorb® (PQ)
Coagulation /Flocculation	
Flocculant	PerfluorAd (PFAD)
Other separation technologies	
Nanofiltration[1]	NxFiltration (NF)
Foam- and ozo fractionation	Evocra Foam ozo fractionation (FOF)
Foam fractionation (FF)	Evocra Foam fractionation (FF)

[1] Only applied to FFWW

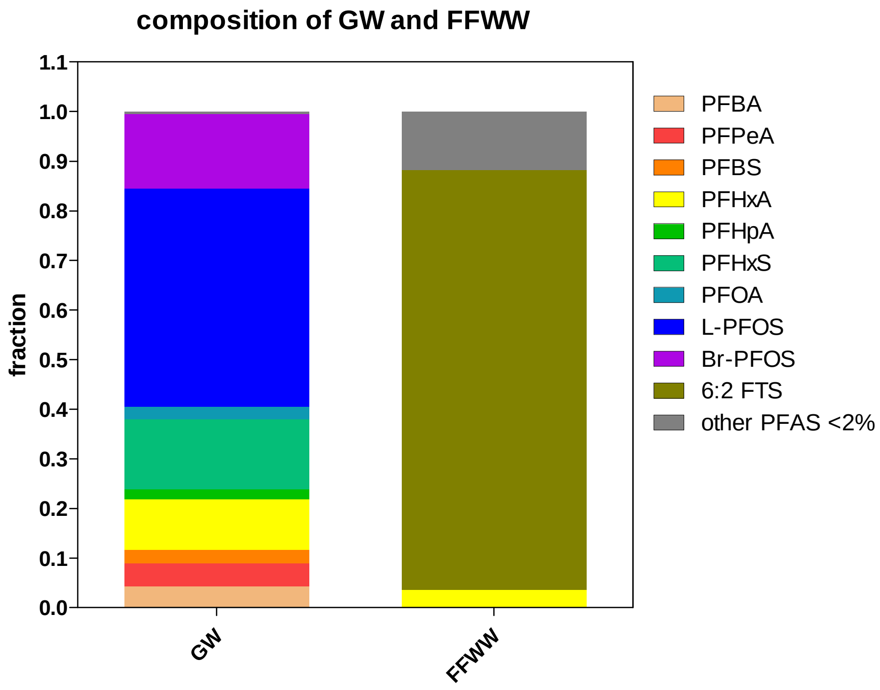
Details on the experimental set up of the batch sorption experiments with FFWW and GW for five sorbents and one flocculant can be found in **Appendix 3**. For foam- and ozo- fractionation experiments with FFWW and GW a pilot test set up consisting of a column with an air/ozone bubble supply at the bottom and an extraction mechanism for the foam fraction at the top is presented in **Appendix 4**. The nanofiltration treatment of FFWW is given in **Appendix 5** and the small scale columns experiments with GW can be found in **Appendix 6**.

3.3. RESULTS AND DISCUSSION

3.3.1. Results PFAS composition

This study tested treatment technologies for FFWW and impacted GW. The concentrations and composition of PFAS as well as other constituents differ between these two samples as the impacted GW contains historical PFAS contamination of infiltrated FFWW from times when PFOS and PFOA were not banned (or AFFF product specification changed to shorter chain PFAS compounds), and some firefighting foam contained large quantities of especially PFOS [11].

Figure 2: Relative composition of measured PFAS in impacted groundwater (GW) and firefighting wastewater (FFWW).

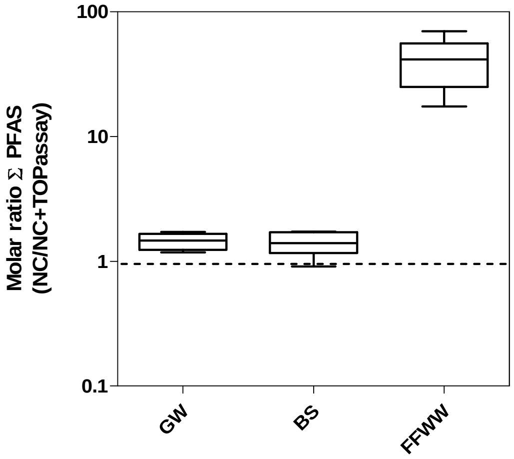


In **Figure 2** it can be observed that the composition of the FFWW and GW differ. FFWW is dominated by fluortelomer sulfonic acids, especially 6:2 FTS, while GW contains a wider share of perfluorinated sulfonic and carboxylic acids. The concentrations of the PFAS in the FFWW were three orders of magnitude higher than in the impacted GW. The bars represent the average of triplicate samples. The average total detected PFAS concentration in the impacted GW used for the sorbent tests was 13.4 µg/L (SD 1.7 µg/L, n=3). The average total detected PFAS concentration of the FFWW in the sorbent tests was: 9478 µg/L (SD 201 µg/L, n=3).

3.3.2. Results TOP assay

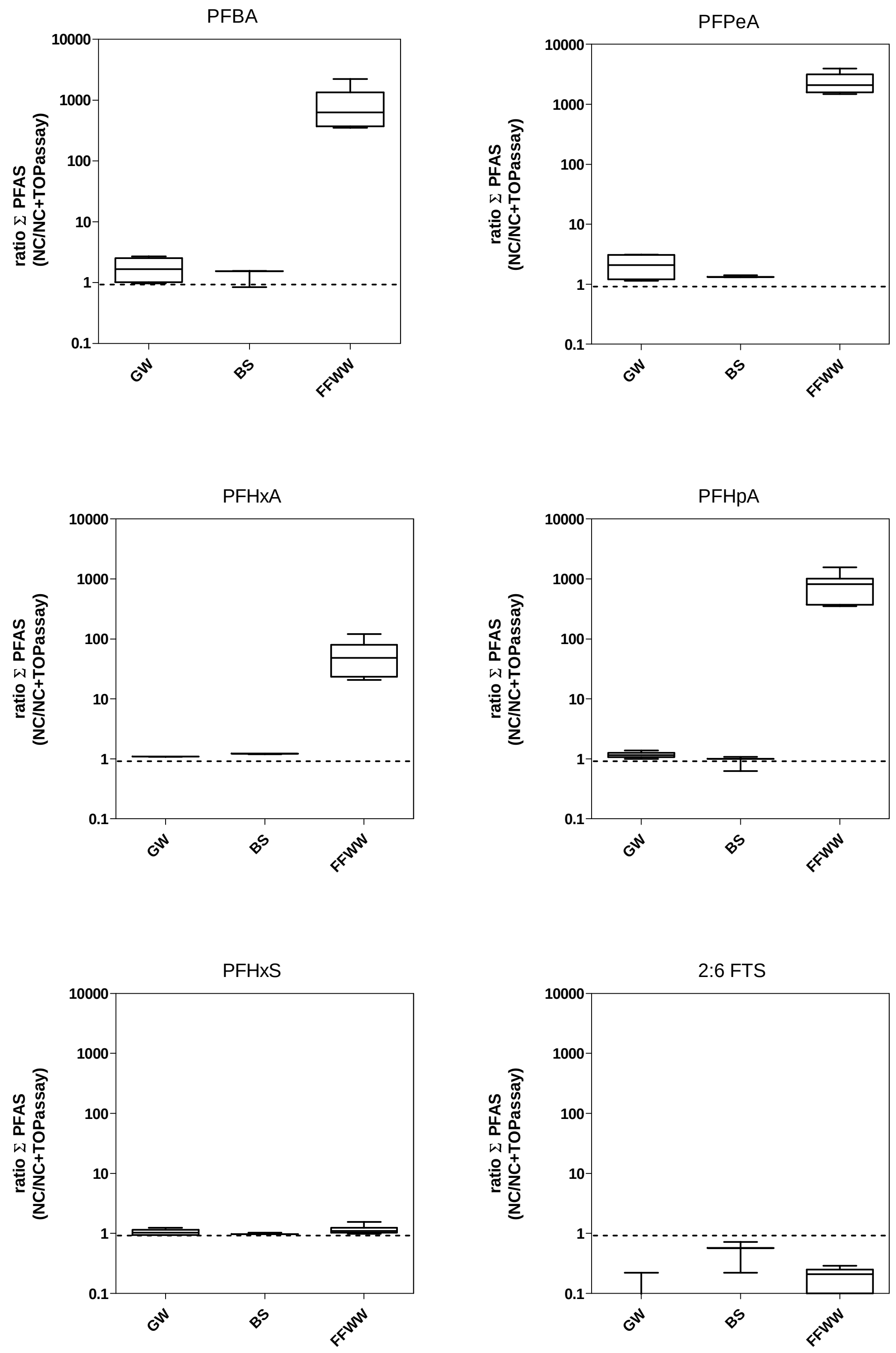
TOP Assay is a standardized pre-treatment of water samples or sample extracts designed to expose underlying PFAS not amenable to standard analysis. Perfluorinated carboxylates and sulfonates are stated to remain intact under the conditions of the assay. A large series of samples was oxidized according to the TOP assay as described in **Appendix 7** and by Houtz and Sedlack[12]. Below the transition of the composition of the samples are shown for all negative controls (NC) (**Figure** 3).

Figure 3: The ratio of total PFAS before and after TOP assay for groundwater (GW n=11)), benzene spiked (BS n=6)) and firefighting wastewater (FFWW n=6) in the negative controls (without sorbent/flocculant or before treatment).



For FFWW, the TOP analysis illustrates an average 41-fold increase based on Molar concentrations, with a 95% Confidence limit of ranging from 31 to 52 of total PFAS. The GW with and without benzene spike shows a small yet significant difference between the TOP treatment and the untreated samples with a 1.45 (95% CL 1.21-1.69) for GW and 1.40 (95% CL 1.07-1.73) for the benzene spiked GW.

Figure 4: The ratio of selected individual PFAS before and after TOP assay for groundwater (GW n=11)) benzene spiked (BS n=6)) and firefighting wastewater (FFWW n=6) in the negative controls (without sorbent/flocculant or before treatment).



3.3.3. Discussion TOP assay results

When looking at individual chemicals and their change in concentrations due to the TOP assay, it can be observed that the TOP assay did not completely transform the 6:2 FTS, suggesting that the TOP assay did not result in full oxidation of this PFAS. Despite the fact that the total PFAS concentration of (benzene spiked) GW was hardly affected, minor shifts in the composition of PFAS occurred, where the five and six carbon perfluorinated acids PFPeA and PFHeA, slightly increased, while the 6:2 FTS that was present at very low concentrations was reduced by the TOP treatment. The lowest removal was observed for the (benzene spiked) GW. One should note that the initial 6:2 FTS levels were very low in those samples, leading to higher deviation in the analytical results.

For the FFWW the individual chemicals show clear patterns. For 6:2 FTS the median removal was with 81% ranging from 71% to 100%. The FFWW is dominated by 6:2 FTS (**Figure 2**). As seen in **Figure 3** the TOP treatment resulted in a large increase in total PFAS concentration. This can be mainly attributed to the increase of the 4-7 carbon chain perfluorinated carboxylic acids, PFBA, PFPeA, PFHxA and PFHpA of which the median increases were a factor of 630, 1953, 49 and 852 respectively with variations below one order of magnitude. This illustrates the presence of 6:2 FTS and many other precursors are transformed into other compounds by the TOP treatment, resulting in the above mentioned 41 (31-52) fold increase in PFAS detectable with the applied target method.

TOP assay was also performed on all samples that underwent various treatments such as batch sorption studies, column studies, filtration, and foam fractionation. These treatments affected the composition of the PFAS in a different way than the TOP assay themselves. The impact of the treatment on the composition of the PFAS mixture and the impact of the TOP oxidation on the composition of the PFAS mixture could not be separated. Therefore the results of the negative controls and the untreated source waters were used to illustrate the sole impact of the TOP assay and thereby the composition of persistent and transformable (precursor) PFAS in the tested waters. Furthermore, the treatment itself might lead to transformation of precursors. For example the foam fractionation where the added ozone (or air) might also act as oxidant for precursors during treatment. This might affect the interpretation of the obtained results in the tests as oxidation processes of especially the FFWW treatment efficiency might be biased for some compounds in a positive manner (oxidizable PFAS like 6:2 FTS) and negatively by their products (e.g. PFBA, PFPeA, PFHxA and PFHpA).

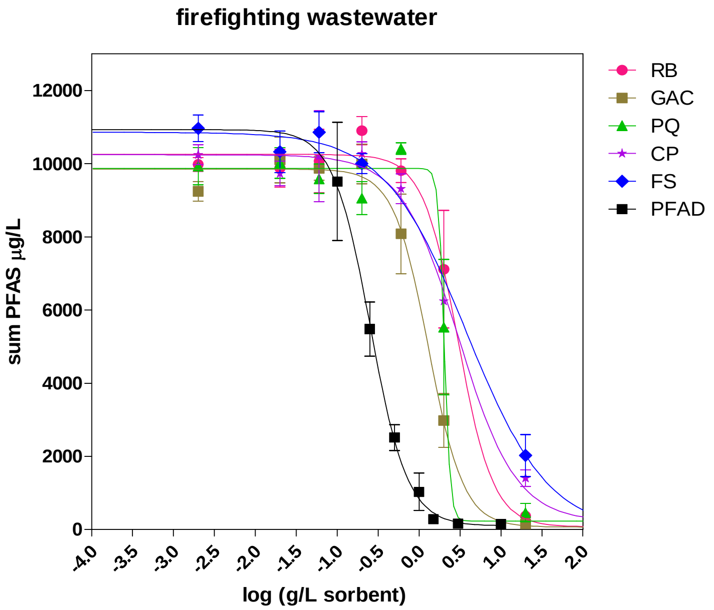
3.3.4. Other constituents in PFAS impacted waters

Analyses of other constituents of the studied water types (GW and FFWW) were performed by Al-West of the Agrolab group in Deventer, the Netherlands. The benzene spiked GW was not tested as the composition was identical to the GW with the exception of the benzene addition. In **Appendix 5** the analytical results are given. FFWW showed three orders of magnitude higher content of organic carbon measured as Total Organic Carbon (TOC) and Biological Oxygen Demand (BOD) and Chemical Oxygen demand (COD) than the GW. Inorganic salts were present at generally orders of magnitude higher levels in the FFWW. Only for inorganics that are at least partially of natural origin such as Ca, Fe, Mn, SiO_2 showed rather similar levels in both waters.

3.3.5. Results batch sorption and flocculation tests - firefighting wastewater

The total PFAS aqueous concentration of the FFWW was analysed for different treatments with a variety of loads the sorbents Rembind® (RB), Granulated Activated Carbon (GAC), PolyQA-Osorb® (PQ), Cyclopure (CP) and FLUORO-SORB® (FS) and the flocculant PerfluorAd (PFAD).

Figure 5: PFAS decrease from the FFWW as a function of sorbent dosing of the five selected sorbents and one flocculant, tested in batch sorption tests with 7 doses and a negative control, each in triplicate. The negative control is plotted as 0.0000001 mg/L sorbent in order to include the data in the graph, using a logarithmic X-axis. The tested sorbents were Rembind® (RB), Granulated Activated Carbon (GAC), PolyQA-Osorb® (PQ), Cyclopure (CP) and FLUORO-SORB® (FS) and the flocculant was PerfluorAd (PFAD).



In **Figure 5** it can be observed that PFAD is effective in reducing the sum of PFAS (dominated by 6:2 FTS) most rapidly, compared to the sorbents tested. This observation can be explained by the competition of large amounts of PFAS, oil residues and other organic contamination present in FFWW at levels up to mg/L level (**Table 23, Table 24, Table 25, Table 26** and **Table** 27, in **Appendix 5**). In conclusion, all sorbents require dosages in the range of grams sorbent per liter of treated water to render a relevant reduction of PFAS from the aqueous phase.

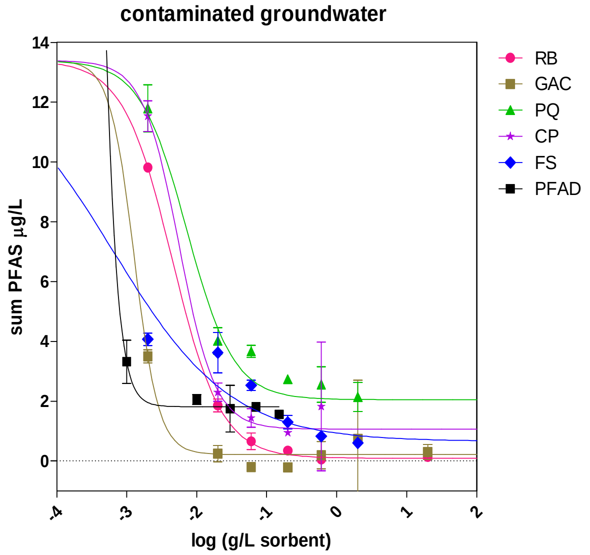
The fitted curves are logistic dose-response curves, the fit allows to determine the loading of the sorbent when 50% of the initial total measurable PFAS concentration in the treated water is reduced. The statistical evaluation also allows the calculation of 95% confidence limits of the fitted values. The loading rate where 50% of the initial concentration that was around 10 mg/L (10.000 µg/L) is reached and the rest of the detectable PFAS are sorbed to the sorbent in gram per kg sorbent is 21.4 (95%CL = 18.0-25.5) for PFAD, 3.8 (95%CL = 3.2-4.4) for GAC, 3.8 (95%CL = 3.2-4.4) for CP, 1.7 (95%CL = 1.2-2.5) for RB, 1.4 (95%CL = 0.8-2.5)for FS. For PQ data did not allow fitting of the confidence limits but the loading was estimated to be 2.4 g/kg sorbent.

As the FFWW contains much more undetected PFAS, the loading is potentially much higher. The loading rate of non-detected PFAS cannot be determined. However the TOP assay is indicative for part of the PFAS that were missed upon initial analysis, and if we presume that the precursors of the PFAS detected after the TOP analyses are sorbed to the sorbents in a similar manner as the PFAS that were detected, these loading rates can be multiplied by a factor of ~41 leading to loading rates ranging from 10 to over 500 (!) grams per kg sorbent. However, it should be noted that we do not know the sorption behaviour of these precursors that are detected as different compounds after oxidation. Nevertheless, this shows that the sorbents are able to remove relevant fractions of PFAS from water.

3.3.6. Results batch sorption and flocculation tests - impacted groundwater

The total aqueous PFAS concentration of the impacted GW was analysed for different treatments with a variety of loads the sorbents Rembind® (RB), Granulated Activated Carbon (GAC), PolyQA-Osorb® (PQ), Cyclopure (CP) and FLUORO-SORB® (FS) and the flocculant PerfluorAd (PFAD).

Figure 6: PFAS decrease from the impacted groundwater (GW) as a function of sorbent dosing of the five selected sorbents and one flocculant, tested in batch sorption tests with 7 doses and a negative control, each in triplicate. The negative control is plotted as 0.0000001 mg/L sorbent in order to include the data in the graph, using a logarithmic X-axis. The tested sorbents were Rembind® (RB), Granulated Activated Carbon (GAC), PolyQA-Osorb® (PQ), Cyclopure (CP) and FLUORO-SORB® (FS) and the flocculant was PerfluorAd (PFAD).

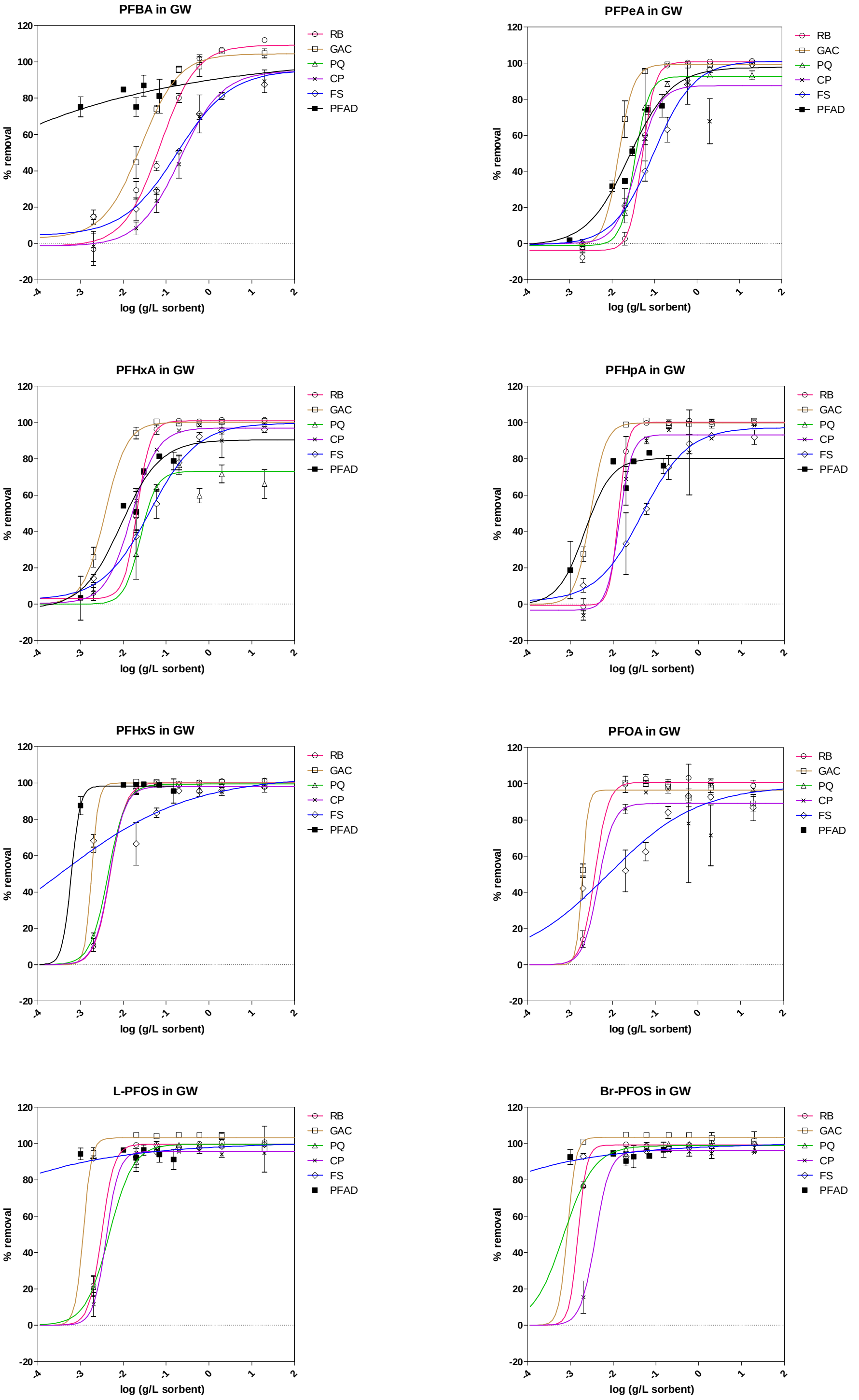


Note that the data for PFAD have a different offset as a different batch of GW was used that contained 3.6 times more PFAS than the experiments with the sorbents. In **Figure 6** it can be observed that GAC, RB, and FS show the highest removal of most PFAS, where can be observed that the GAC treatment results in a reduction down to PFAS concentrations near zero, while the other two sorbents some of the PFAS remains in the sampled aqueous phase, also at higher dosages of sorbent. PFAD also shows a steep decline at low dosages, but the residual PFAS (~2 µg/L) at higher dosages of PFAD. One has to note that the PFAD experiments were performed with a different batch of GW containing a higher initial PFAS concentration. It can be concluded that all sorbents are rather effective in removing PFAS from GW while the flocculant is very effective in reducing the PFAS concentrations but does not lead to (near) full removal. Sorbent dosages below 100 mg/L or even 10 mg/L appear to be sufficient to remove most of the PFAS from the aqueous phase (**Figure** 7).

The fitted curves are logistic dose-response curves, the fit allows to determine the loading of the sorbent when 50% of the initial total measurable PFAS concentration in the treated water is reduced. The statistical evaluation also allows the calculation of 95% confidence limits of the fitted values. The loading rate where 50% of the initial concentration is reached and the rest of the detectable PFAS are sorbed to the sorbent in gram per kg sorbent is calculated. The results in gram per kg sorbent are 61.5 (95%CL = not determinable) for PFAD, 10.5 (95%CL = 4.2-26.4) for FS, 5.2 (95%CL = 1.2-22.0) for GAC, 1.5 (95%CL = 1.4-1.6) for RB, 1.2 (95%CL = 0.8-1.9) for CP and 0.9 (95%CL = 0.6-1.4) for PQ. It can be observed that the confidence limits of these fitted values are often large. This is likely due to the fact that the lowest dose of sorbent already leads to a significant decrease of the dissolved concentration, which on its turn requires the extrapolation to obtain the sorbent dose were 50% of the aqueous concentration was sorbed. This results in a rather high uncertainty.

Potentially the GW contains additional PFAS that remained undetected with the method applied. However, the applied TOP assay did not result in a significant change of detectable PFAS, so the contribution of undetected precursor PFAS is presumed limited. Generally the loading rate of the sorbents ranges from 0.9 gram up to 61 gram of detectable PFAS per kg sorbent at aqueous concentrations of roughly 7 µg/L for the sorbents and 25 µg/L for the flocculant PFAD.

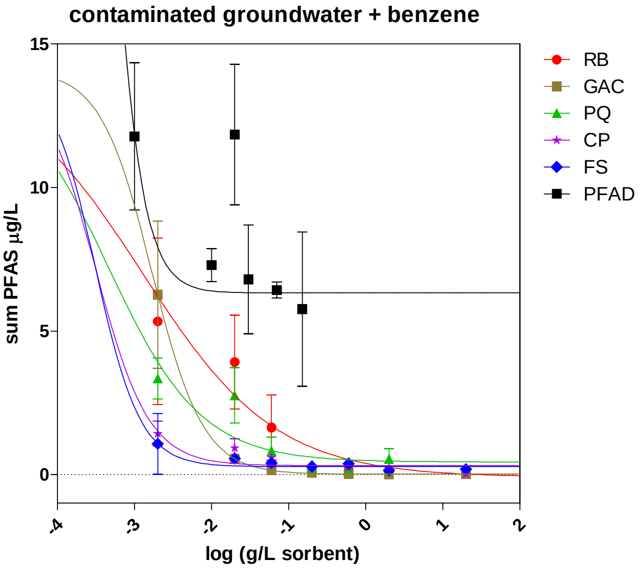
Figure 7: Removal of individual PFAS from the impacted and benzene spiked groundwater (GW) by five selected sorbents and one flocculant, tested in batch sorption tests with 7 doses and a negative control in triplicate. The negative control is plotted as 0.0000001 mg/L sorbent in order to include the data in the graph, using a logarithmic x-axis. The tested sorbents were Rembind® (RB), Granulated Activated Carbon (GAC), PolyQA-Osorb® (PQ), Cyclopure (CP) and FLUORO-SORB® (FS) and the flocculant was PerfluorAd (PFAD).



3.3.7. Results batch sorption and flocculation tests - Impacted groundwater spiked with benzene

PFAS impacted GW from firefighting activities can coincide with petrochemical contamination. In order to study the effect of residues of petrochemicals on treatment performance benzene was spiked to the impacted GW in a controlled manner. The selected concentration (20 mg/L) is based on measured benzene levels in petrochemical impacted GW (personal communication with Concawe members). These are orders of magnitude lower than the petrochemical residues found in the FFWW.

Figure 8: PFAS decrease from the impacted groundwater (GW) with 20 mg/L benzene spike as a function of sorbent dosing of the five selected sorbents and one flocculant, tested in batch sorption tests with 7 doses and a negative control, each in triplicate. The negative control is plotted as 0.00001 mg/L sorbent in order to include the data in the graph, using a logarithmic x-axis. The tested sorbents were Rembind® (RB), Granulated Activated Carbon (GAC), PolyQA-Osorb® (PQ), Cyclopure (CP) and FLUORO-SORB® (FS) and the flocculant was PerfluorAd (PFAD).



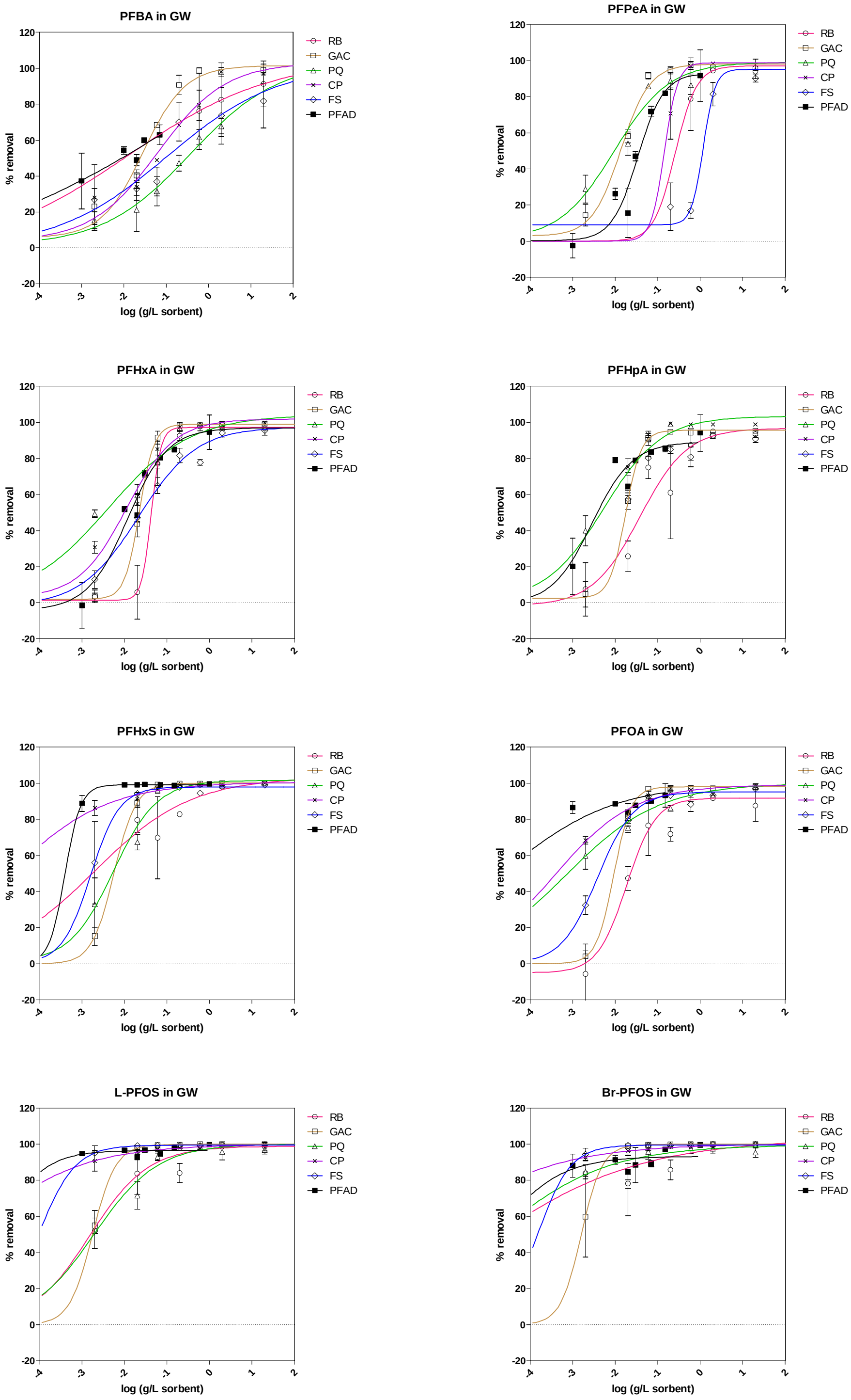
In **Figure 8**, it can be observed that GAC, FS show the highest removal of most PFAS. Furthermore, it can be observed that the GAC treatment results in a reduction down to PFAS concentrations near zero. PFAD also shows a steep decline at low dosages, but the residual PFAS (~6 µg/L) at higher dosages of PFAD. One has to note that the PFAD experiments were performed with a different batch of groundwater containing a higher initial PFAS concentration. It can be concluded that all sorbents are rather effective in removing PFAS from GW while the flocculant is very effective in reducing the bulk PFAS concentrations but does not lead to (near) full removal. Sorbent dosages below 100 mg/L or even 10 mg/L appear to be sufficient to remove most of the PFAS from the aqueous phase. Dosages around 10-100 mg/L appear to be sufficient to remove most of the PFAS from the aqueous phase for the best performing sorbents.

The fitted curves are logistic dose-response curves, the fit allows to determine the loading of the sorbent when 50% of the initial total measurable PFAS concentration in the treated water is reduced. The statistical evaluation also allows the calculation of 95% confidence limits of the fitted values. The loading rate where 50% of the initial concentration is reached and the rest of the detectable PFAS are sorbed to the sorbent in gram per kg sorbent is calculated. The results in gram per kg sorbent are 61.0 (95%CL = not determinable) for PFAD, 22.8 (95%CL = 6.2-83.0) for CP, 22.6 (95%CL = 2.3-226.0) for FS, 15.7 (95%CL = 6.9-35.6) for PQ, 5.5 (95%CL = 2.1-14.3) for RB and 4.2 (95%CL = 3.2-5.5) for GAC. It can be observed that the confidence limits of these fitted values are sometimes widely spread. This is likely due to the fact that the lowest dose of sorbent already leads to a significant decrease of the dissolved concentration, which requires the extrapolation to obtain the sorbent dose were 50% of the aqueous concentration was sorbed. This results in a rather high uncertainty.

Contrary to the experiment without benzene, the order of the most to least efficient sorbent changed but the range of the sorbent loading was similar to the treatment without benzene (4.2 gram up to 61 gram of detectable PFAS per kg sorbent at aqueous concentrations of roughly 7 µg/L for the sorbents and 25 µg/L for the flocculant PFAD).

When we compare these results of the FFWW and the (benzene spiked) impacted GW the following can be observed. The loading rates of the impacted GW fall roughly in the same range as the levels observed for the FFWW, when we take into account that a major part of the PFAS in the FFWW are missed by the detection method. As we cannot detect all PFAS we cannot compare the loading rates directly. Nevertheless observed loading rates are in the range of what is observed in literature (see chapter 4). Additional analysis is required to better cover the spectrum of PFAS present in (especially the) FFWW.

Figure 9: Removal of individual PFAS from benzene spiked groundwater (GW) by five selected sorbents and one flocculant, tested in batch sorption tests with 7 doses and a negative control in triplicate. The negative control is plotted as 0.0000001 mg/L sorbent in order to include the data in the graph, using a logarithmic x-axis. The tested sorbents were Rembind$^{®}$ (RB), Granulated Activated Carbon (GAC), PolyQA-Osorb$^{®}$ (PQ), Cyclopure (CP) and FLUORO-SORB$^{®}$ (FS) and the flocculant was PerfluorAd (PFAD).



PFBA in GW

PFPeA in GW

PFHxA in GW

PFHpA in GW

PFHxS in GW

PFOA in GW

L-PFOS in GW

Br-PFOS in GW

3.3.8. Discussion batch sorption and flocculant tests

When the removal of individual PFAS present in the impacted waters is studied, it can be observed that the longer the CF chain the more effective all sorbents become in removing the PFAS. This is not surprising as the length of (fluorinated) chains affects the aquatic solubility as well as the hydrophobicity of molecules. Similar trends are observed for both ionic and non-ionic surfactants that are not halogenated [13-15].

There are differences observed between the sorbents and flocculant and between the different treated waters. Generally the GAC shows the most robust *total* removal. PFAD seems to be most effective at the lowest dosages. This is especially true for the FFWW. FS performs similarly well in a situation with benzene spike. The performance of especially the flocculant PFAD but also to a lesser extent the bio-based or polymeric based sorbents PQ and CP are not able to remove *all* PFAS in the different treatments. This is hardly visible in the FFWW as initial concentrations were very high, but is more pronounced for PFAS impacted GW without and PFAS impacted GW spiked with benzene. Here, do not seem to reach a zero concentration at high dosages but tend to drop to 2-20% of the initial PFAS concentration even at extremely high dosages of sorbent / flocculant. This is most pronounced in the impacted GW tests with and without benzene spike. This observation is difficult to explain from a thermodynamic perspective of sorption and complexation processes [16-17]. Theoretically, the addition of sorbent leads to more available sorption sites that consequently leads to lower freely dissolved concentrations of the PFAS and presumably higher sorption coefficients when typical nonlinear Langmuir or Freundlich-like sorption isotherm are assumed. Therefore, the theory suggests an artefact such as incomplete separation of the flocculant or polymers and the aqueous phase at high dosages, leading to overestimation of the aqueous concentration and thereby underestimating the removal at higher sorbent or flocculant dosage. Interestingly, the addition of the benzene resulted in better performance of these polymer and bio-based sorbents and lower residual fractions in the sampled aqueous phase (**Figure 6** and **Figure 8)** while the flocculant PFAD performed poorer.

Optimizing the sorbent water separation in pilot or full size applications will likely result in larger removed fractions that can be brought close to 100%. Therefore, we consider these residual concentrations an artefact of the experimental set up for some of the sorbents and flocculant under certain test conditions.

3.3.9. Results foam fractionation with ozone and air

The foam fractionation experiments were executed with air and with ozone. Three types of water were used, being FFWW, impacted GW and impacted GW spiked with 20 mg/L benzene (GW-BS). The benzene is a surrogate for BTEX residues that can coincide with the PFAS contamination in GW underneath petrochemical plants and other contaminated sites. The results are presented in **Figure 10**.

Figure 10: Composition and concentrations of PFAS the treated water was sampled at the time that no foam was formed anymore (0h) and 1 hour (1h) of operation for the treatments with ambient air (Air) and ozone (O3). Firefighting wastewater = FFWW, groundwater = GW and benzene spiked groundwater = GW-BS, the feed water (negative control) = NC and the Concentrate (foam) = Conc. All treatments were performed in triplicate for GW-O3-Conc. and GW-BS-O3-0h one of the triplicates is excluded because that particular sample strongly deviated for all chemicals. * FFWW-air-1h is missing because the foam formation was too abundant and only one sample was collected during the test (FFWW-air-oh).

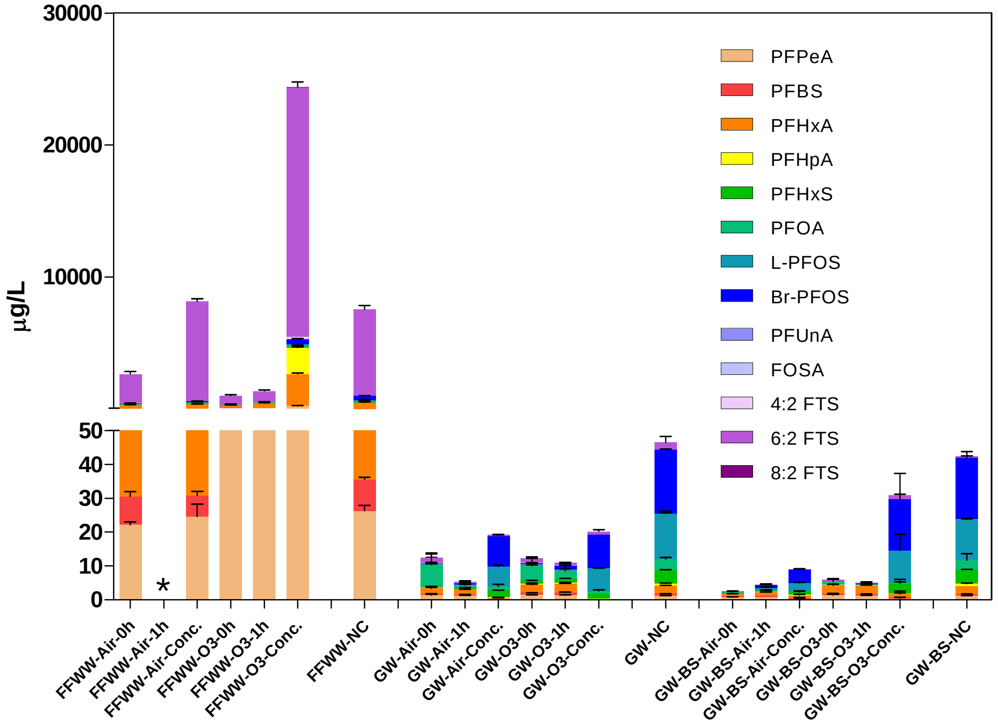


Figure 11 represents a picture of the untreated (left two bottles) and treated (right two bottles) water.

Figure 11: Firefighting training wastewater, untreated vs. treated colour.

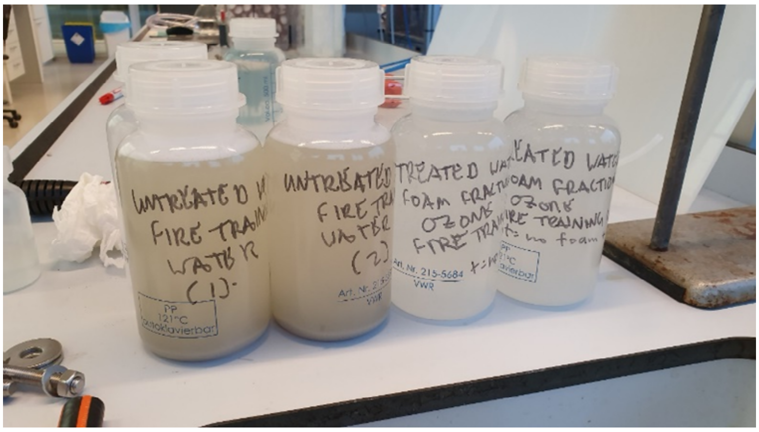


Table 4 lists the volume of the treated water and the collected concentrate. For the ambient air treatment the reduction after 1h operation could not be determined, while the ozone treatment lead to a factor 5 reduction for FFWW. For GW a factor 2.5 and 4 reduction was observed for air and ozone treatment, respectively, while BS treatment resulted in reduction of a factor 5 and 8, respectively. Together with the collected volumes of foam versus the volumes of treated water a concentration factor between the foam and the water can be determined for the sum of PFAS.

Table 4: Experimental conditions, PFAS fraction (%) remained in the treated water and the concentration factor of summed PFAS between foam and water for air and Ozo fractionation of groundwater (GW) benzene spiked (BS) and firefighting wastewater (FFWW) and additional experimental conditions.

Sample	pH	ORP (mV)	Treated volume (L)	Collected concentrate (L)	Sum PFAS not removed (1h treatment / negative control (%))	Sum PFAS Concentration factor [concentrate] / [treated water]
FFWW-air fractionation	n.a.[2]	n.a.[2]	6-7	0.100[1]	n.a.[2]	-
FFWW-Ozo fractionation	2.8	1090	6-7	n.a.[2]	18%	-
GW-air fractionation	8.2	235	7-8	0.150	41%	67-77
GW-Ozo fractionation	4.4[3]	1083	9-10	0.075	24%	380-422
BS-GW-air fractionation	-	-	7-8	0.100	21%	263-301
BS-GW-Ozo fractionation	4.2[3]	1075	12-13	0.075	12%	1173-1271

[1] Calculated with 0 hour water sample as the 1h treatment was corrupted by extensive foam formation

[2] Not applicable as no sample of the 1h treatment could be obtained

[3] adjusted pH

3.3.10. Discussion foam fractionation with ozone and air

Figure 10 and **Table 4** show the results of the air and ozo fractionation. The setup of foam fractionation is a delicate process of adjusting air (or ozone) flow, potentially adding chemicals to allow or reduce foam formation to be sufficiently stable for separation but also not too stable to enable collection of the foam. Currently, foam fractionation is mainly applied to impacted GW. Treating FFWW is currently very far out of the normal operation (personal communication Evocra).

The composition of impacted GW is different from water generated from firefighting activities (**Table 2**). The excessive foam formation illustrated that the initial settings and conditions of the pilot test system were not suitable for the FFWW. Subsequently, conditions required adaptation and iron chloride was added and the tested water was diluted in case of the air treatment to allow the collapsing of the formed foam for separation. Even these adaptations were not sufficient to fully solve the overproduction of foam. This was reflected in the omission of the samples and determination of the volume of the foam and water generated one hour after a stable foam layer was formed since the test was aborted to prevent the system from getting completely contaminated with the foam including filters and tubing. This illustrates the necessity to adapt and optimize the settings and conditions related to the treated matrix, which apparently require extensive studies when highly contaminated matrices such as FFWW are treated.

It can be observed that the ozone treatment appeared to be more effective than the air treatment for the GW and benzene spiked GW. However, within the current experiments the air and ozone flow differed due to the capacity of the ozone generator. Therefore, these differences between ozone and air treatment can be either attributed to the effect of ozone vs. air or simply the dose of these gasses that affects the formation and the structure of the foam. These two effects cannot be fully distinguished in the applied experimental setting, but give opportunities for further fine-tuning of the treatment.

The addition of benzene improved the removal of PFAS from impacted GW for both the air and ozone treatment. Potentially the solvent affected the foam formation or structure in such a way that PFAS removal was improved.

When the ozone treatment of FFWW was compared to GW with and without benzene the residual PFAS in the treated water rate appeared similar. However the unbiased comparison of the impacted GW and FFWW is hampered by multiple factors. First, the comparison of the removal is biased by the composition of PFAS that differs considerably between the impacted GW and the FFWW. The FFWW is dominated by 6:2 FTS while the impacted GW holds a wider spectrum of PFAS containing also more polar (shorter carbon chain) constituents. This argues for the comparison of PFAS removal for individual PFAS. However, the aeration and especially the ozone treatment might induce the transformation of less persistent PFAS into more persistent transformation product, as air and especially ozone will enhance oxidation. This affects the composition of PFAS in the system during the experiment and corrupts the analysis of removal of individual PFAS by the fractionation process. A close look at individual PFAS in the ozone treated FFWW illustrates that this is actually happening. PFPeA concentrations increased almost two-fold after treatment (1h sample) and PFHxA, PFHpA were hardly removed during treatment (between feed water and 1h sample) and appeared to increase 2 and 4 times between the 0h and 1h sample.

So while quantitative interpretation of the results of both the summed PFAS levels and individual PFAS levels for the FFWW is complicated, we can safely assume that the comparatively mild oxidation by ozo fractionation is not leading to relevant change in the summed PFAS in GW. Even the more aggressive TOP assay did not result in a significant change in total PFAS for impacted GW (**Figure 3**).

Despite of suboptimal foam fractionation conditions and potential biases of the oxidation of PFAS into other PFAS during treatment, the experiments show the potential of foam fractionation as a (pretreatment) technology. The treatment effectively lead to the concentration of PFAS in a small volume of foam and a significant reduction of PFAS in the treated water. With additional testing and optimizations applied, it is likely possible to improve the separation and removal of the impacted GW further and to treat the FFWW in stable operation. This potentially requires the following experimental steps:

- Optimizing gas inlet to minimize bubble formation at the start;
- Optimizing $FeCl_3$ dosing;
- Change pump settings.

3.3.11. Results nanofiltration tests

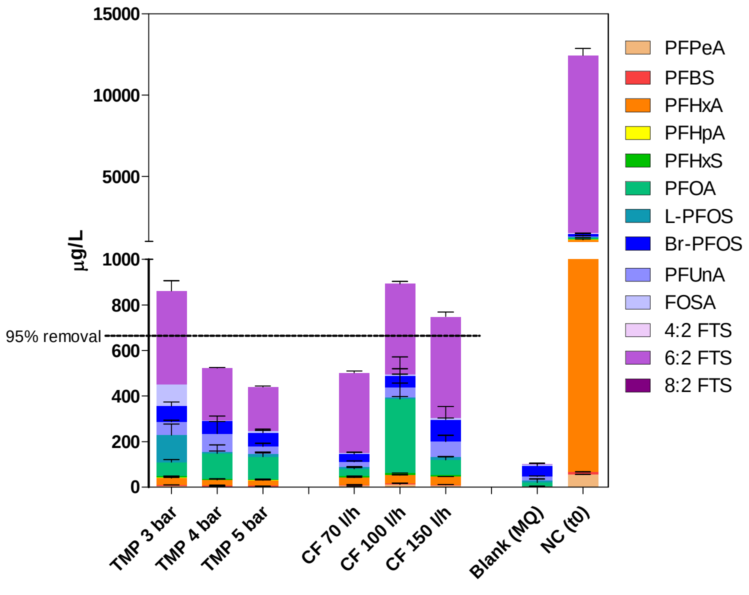
Membrane separation experiments

In the membrane filtration experiments, the pilot installation MexPlorer from NXFiltration was used. Three different experiments were performed with this installation using FFWW: transmembrane pressure, flow velocity and recovery tests as described in **Appendix 5**.

In the tests according protocol 1 of the Standard Test Protocol Nanofiltration Mexplorer (NXF-TR: 17-45-1C) of the technology provider the membrane was tested at feed pressures of 3, 4 and 5 bar. At increasing pressure the water flux through the membrane is increasing while the PFAS passage through the membrane is nearly equal. This results in lower PFAS concentrations in the permeate at higher feed pressures.

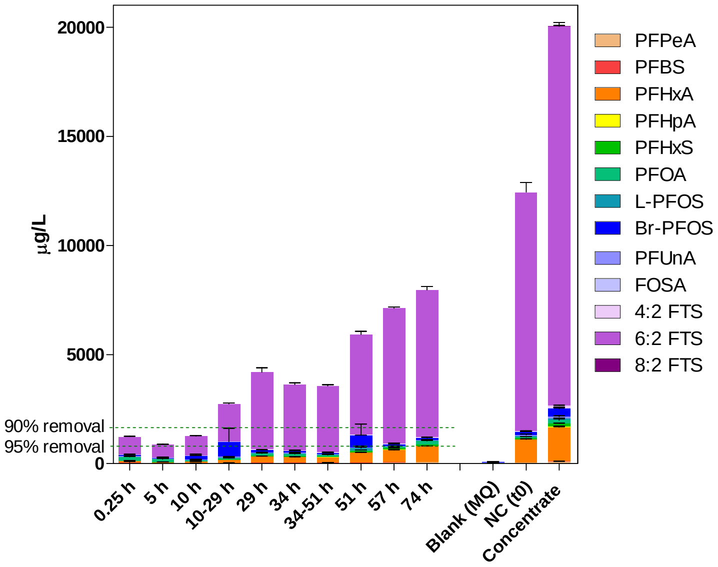
In the tests according to protocol 2 the membrane was tested at crossflow capacities of 70, 100 and 150 L/h. When retaining a solute in membrane filtration, the concentration of that solute significantly increases at the water/membrane separation layer interface. This is called concentration polarization, a phenomenon that happens almost immediately. High levels of concentration polarization will reduce the overall rejection of the solute. The magnitude of this concentration polarization can be reduced by actively transporting the higher solute concentrations away from the water/membrane interface. In hollow fibre filtration this is done by increasing the (tangential) crossflow velocity through the fibre. **Figure 12** illustrates the obtained results for the different treatments.

Figure 12: Composition and concentrations of PFAS in initial feed water (NC) and treated water permeate obtained from protocol 1 and protocol 2 (NXF-TR: 17-45-1C). Blank represents the results from milliQ water. The treated water (permeate) was sampled after 15 min of operation at a trans-membrane pressure (TMP) of 3, 4, and 5 bar or a cross-flow velocity (CF) of 70, 100 and 150 l/h without oxidation.



In addition an experiment was performed to obtain the removal efficiency for a preset recovery. As the permeate flow dropped during operation, reaching the recovered permeate volume required over 3 days. **Figure 13** illustrates the results. It can be observed that the long term operation leads to increasing amounts of PFAS in the treated water (permeate) slowly reaching towards the level of the feed water concentrations. This illustrates that the membrane is – with longer operation – not capable of separating the PFAS from the aqueous phase.

Figure 13: Composition and concentrations of PFAS in initial feed water (NC), the concentrate and treated water permeate obtained from firefighting wastewater (FFWW). Blank represents the results from miliQ water. The treated water (permeate) was sampled after a series of run times up to 74h. The bars indicated with two run times (10-29 and 34-51) are composite samples of overnight collection of the permeate between the two run times.



3.3.12. Discussion nanofiltration tests

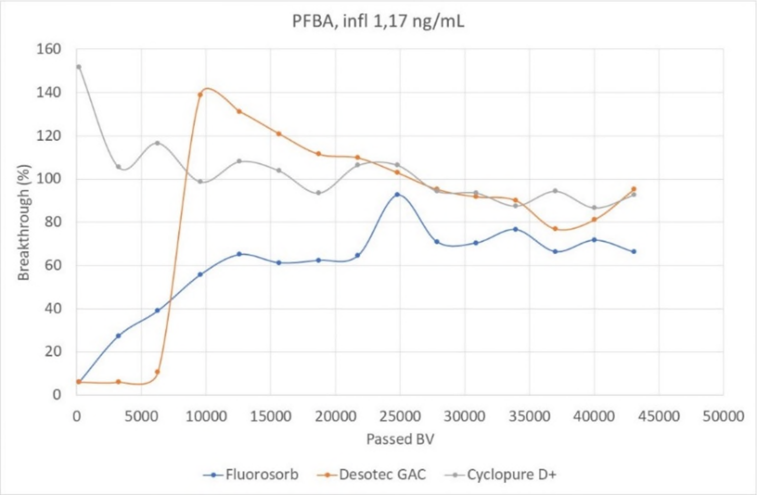
The nanofiltration experiments were applied under different pressures and transmembrane permeate flows (**Figure 12**). Furthermore the set up was operated for 74 hr. to obtain a preset permeate recovery (Figure 13). With longer operation of the membrane filtration the permeate flow dropped. This was likely due to the fact that the FFWW matrix contained particles that blocked the pores of the membrane hampering the water to pass the membrane. The nanofiltration experiments show that the applied membrane is able to remove the PFAS effectively during the first hours of operation (0.25 hr.-10 hr.), reaching removal rates of 90->95% (the membranes in **Figure 12** were all operated for 0.25 hr.). However, when the membrane was operated for a longer period trans membrane flows dropped and the passage of PFAS slowly increase to levels approaching concentrations in the feed-water (low removal). In addition, upon inspection, a penetrant “gasoline smell” could be recognized in the filtrate after longer operation, illustrating the permeability of the membrane for petrochemical residues as well. The transmembrane pressure increased sharply with longer operation.

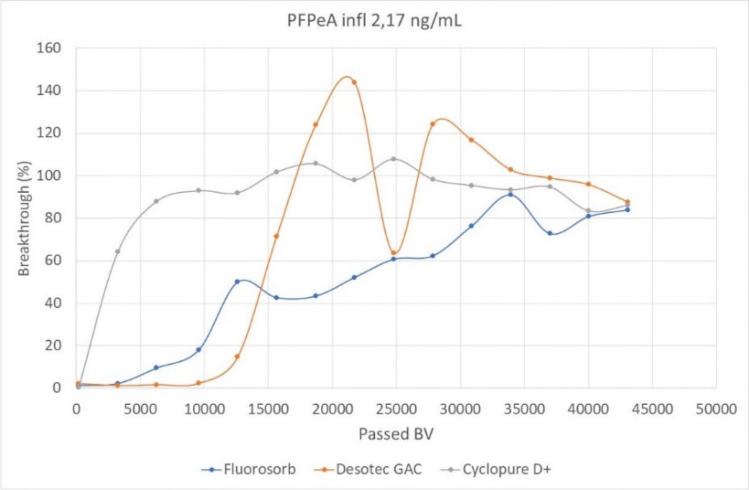
3.3.13. Results small-scale column tests

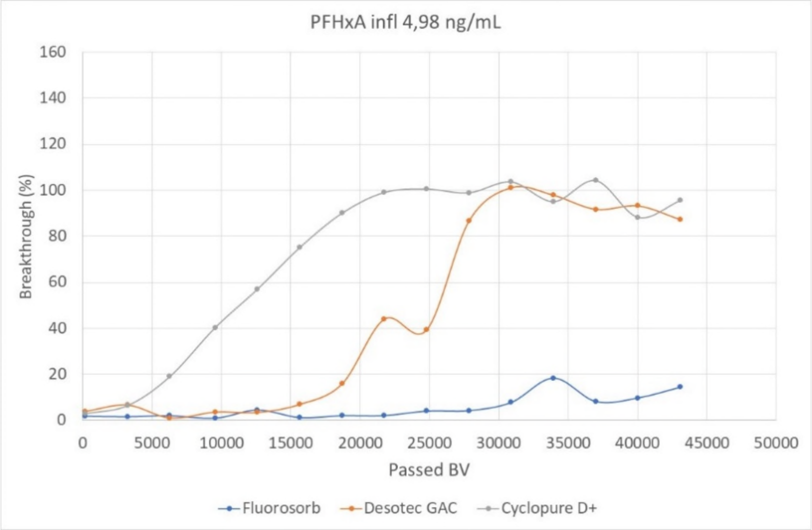
The small-scale column pilot studies were designed to obtain in breakthrough curves of the different PFAS present PFAS affected GW. These corves explores the individual PFAS concentrations is as the fraction of the concentration in the feed water. 20% breakthrough were defined and expressed in the bed volumes the column has been exposed to. This is indicative for the treatment capacity of the sorption material in the column for the different PFAS present in the water. More than 40,000 bed volumes were passed. Based on the results of the batch sorption experiments FLUORO-SORB® (FS) Cyclopure D+ (CP) and Desotec Granulated Activated Carbon (GAC) were selected for the column studies because of their observed performances in batch tests and the applicability of the material in columns.

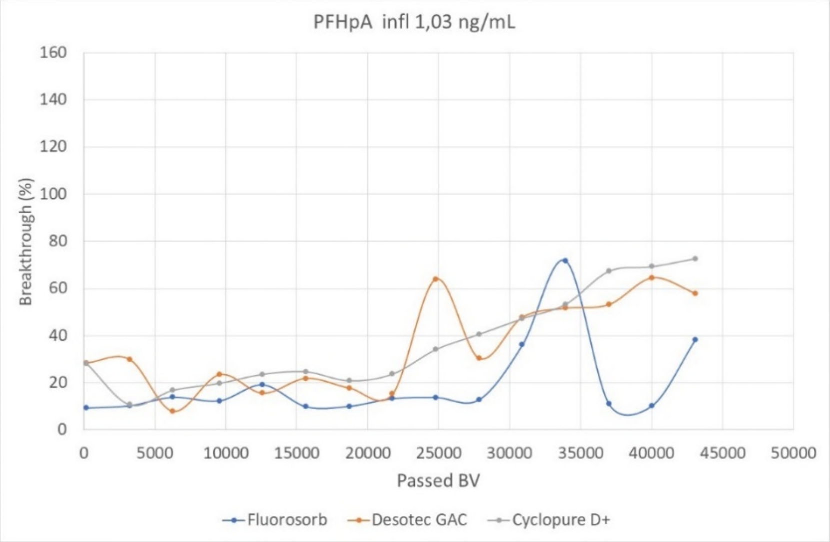
In **Figure 14** the results of the small-scale column tests are shown, it has to be noted that only results are shown of the compounds that showed relatively good interpretable results: not all compounds were present in the influent water or sometimes only at a concentration near the detection limit, which resulted in poorly interpretable breakthrough curves.

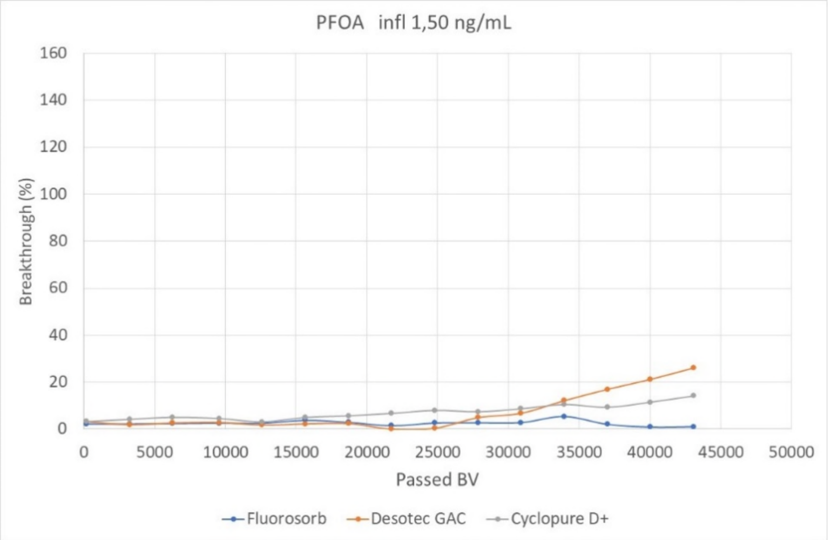
Figure 14: Breakthrough curves of respectively PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFBS, PFHxS and PFOS tested obtained with the small-scale column test.

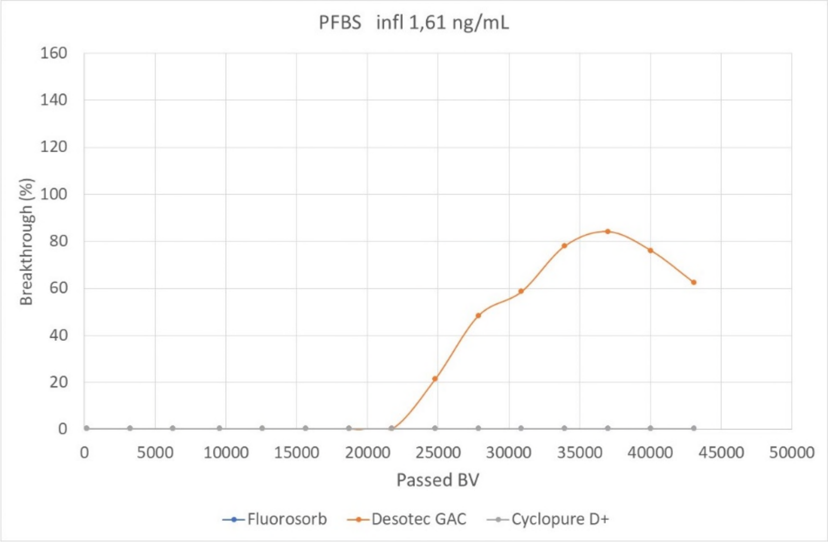


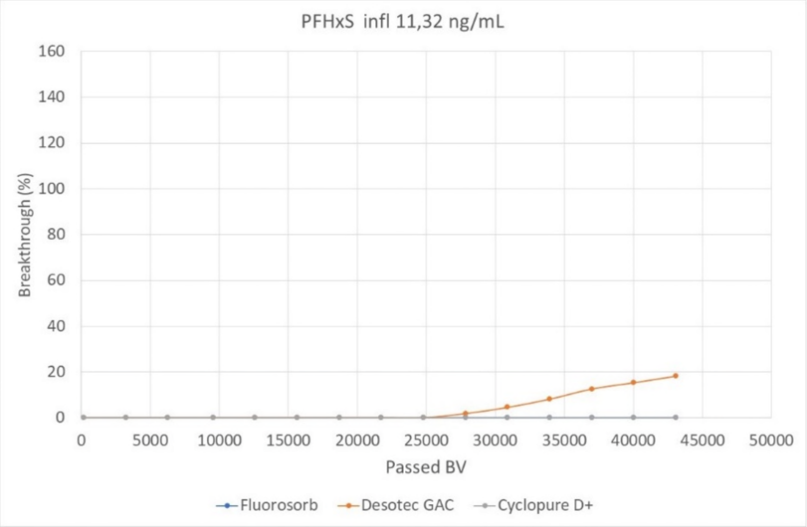


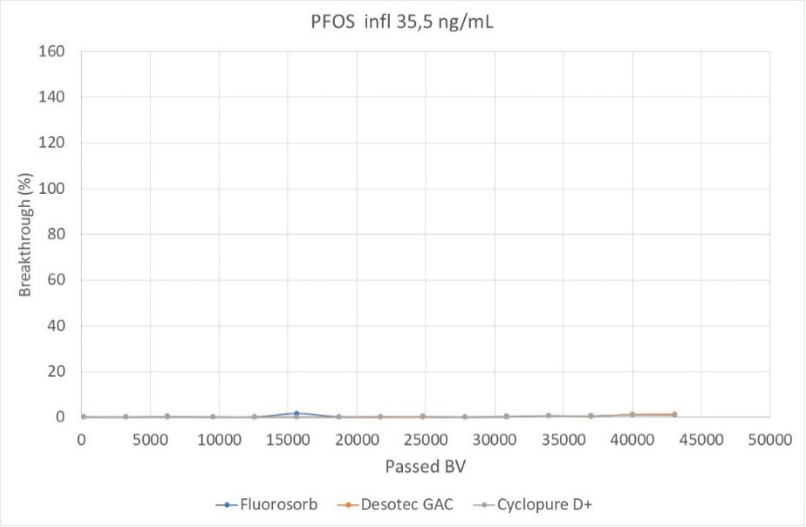

PFHxA infl 4,98 ng/mL
Breakthrough (%)
160
140
120
100
80
60
40
20
0
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
50000
Passed BV
Fluorosorb
Desotec GAC
Cyclopure D+


PFHpA infl 1,03 ng/mL
Breakthrough (%)
160
140
120
100
80
60
40
20
0
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
50000
Passed BV
Fluorosorb
Desotec GAC
Cyclopure D+


PFOA infl 1,50 ng/mL
Breakthrough (%)
160
140
120
100
80
60
40
20
0
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
50000
Passed BV
Fluorosorb
Desotec GAC
Cyclopure D+


PFBS infl 1,61 ng/mL
Breakthrough (%)
160
140
120
100
80
60
40
20
0
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
50000
Passed BV
Fluorosorb
Desotec GAC
Cyclopure D+


PFHxS infl 11,32 ng/mL
Breakthrough (%)
160
140
120
100
80
60
40
20
0
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
50000
Passed BV
Fluorosorb
Desotec GAC
Cyclopure D+


PFOS infl 35,5 ng/mL
Breakthrough (%)
160
140
120
100
80
60
40
20
0
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
50000
Passed BV
Fluorosorb
Desotec GAC
Cyclopure D+

In **Table 5**, estimations of breakthrough moments at 20 % breakthrough are given in passed BV, to be able to compare the used sorbents. It has to be noted that the choice for 20% breakthrough is debatable, but was selected as native PFAS concentrations did not always allow a lower threshold due to limits of quantification.

Table 5: Estimated breakthrough moments at 20 % breakthrough of the measured compounds in passed Bed Volumes (BV), obtained with the small-scale column test.

Compound	Influent concentration (µg/L)	Amount of passed BV at 20% breakthrough			Remarks/observations
		FLUORO-SORB®	Desotec GAC	Cyclopure D+	
PFBA	1.17	2,000	7,000	Immediate	Desotec GAC shows desorption profile after 7,000 BV
PFPeA	2.17	10,000	13,000	1,000	Desotec GAC shows desorption profile after 17,000 BV
PFHxA	4.98	> 40,000	19,000	7,000	
PFHpA	1.03	29,000	22,000	12,000	All show direct 10-20 % breakthrough
PFOA	1.5	> 40,000	40,000	> 40,000	
PFBS	1.61	> 40,000	25,000	> 40,000	
PFHxS	11.3	> 40,000	> 40,000	> 40,000	
PFOS	35.5	> 40,000	> 40,000	> 40,000	

With the small-scale column tests more than 40,000 BV were passed and the applied method made it possible to compare the three chosen sorbents applied in a column. It has to be noted however that the obtained breakthrough curves cannot be directly converted to estimations of breakthrough of compounds in larger practice situations using unground materials.

3.3.14. Discussion of small-scale column tests

All tested materials were capable in removing the longer chained PFAS molecules, no break though was observed after > 40,000 bed volumes. No difference between the sorbents was detected for the long chain PFAS molecules. They appear to be removed quite efficiently. The activated carbon based material (Desotec GAC) seemed to be a bit better capable of removing the shorter chained PFBA and PFPeA in comparison with FLUORO-SORB® and Cyclopure D+. However, Desotec GAC showed desorption of the shorter chained compounds PFBA and PFPeA after breakthrough started. This might be caused by better sorbing compounds that displace these shorter chained PFAS compounds. This indicates that these compounds are less strongly bound to the GAC material and can even be fully desorbed after a longer time of operation. The other materials did not show this phenomenon. For PFHxS Desotec GAC showed an earlier breakthrough compared with FLUORO-SORB® and Cyclopure D+. However the concentration remained below 20% of the initial concentration at up to 43,000 bed volumes that have been tested.

4. PART 3: TECHNOLOGY APPLICATION

This chapter focusses on application of the technologies, thus giving an overview of the known operating ranges and constraints of the technologies, along with identification of key design criteria for each treatment technology.

The basis for the chapter is the factual information from the previous report[1], along with the experimental results as described in previous chapters and additional information from suppliers. Unless otherwise specified, information is derived from this study.

Based on the information obtained from the technology-suppliers and the experiences gained during the experimental phase, this overview of the technologies provides input for the Concawe-members to evaluate the state of the art and the most recent operational knowledge of the technologies. This chapter gives insight into the potential cost-effectiveness of PFAS removal: high chemical- or energy costs related to very limited PFAS removal could be, for example, undesirable. The chapter finally identifies where knowledge and information is still lacking regarding practical applications and costs.

The findings in the report are condensed in the form of a look-up table to help Concawe members select the PFAS treatment technology conditions appropriate to their site-specific characteristics. This table allow the Concawe-members to quickly see the relevant technologies for specific treatment challenges and their available information, the main text body gives additional (background) information.

This chapter briefly describes the basics of each technologies, followed by the summary of the PFAS-removal performance based on Riegel, et al. [1] and the experimental results. Furthermore, key design criteria are discussed that form the basis for operational aspects and finally the costs for each technology. In order of appearance, the following technologies are described:

- Activated Carbon;
- Rembind®;
- DEXSORB+®;
- PolyQA-Osorb®;
- FLUORO-SORB®;
- PerfluorAd;
- Nanofiltration;
- Foam- and ozo fractionation.

Disclaimer for further reading

It has to be stated that a comparison of the technologies for the purpose of site specific application is far more complex than the intrinsic technology comparison provided in this study. Several factors are at play when properly comparing technologies and their applicability at specific locations and for specific purposes under specific conditions in depth. Mainly very local conditions play a key role in technology selection. The main influences are:

Location characteristics

A GW contamination with PFAS will have completely different characteristics that are related to the hydrology, geochemistry of the soil it is in, and the related aqueous chemistry of the GW (salt content, pH, DOC etc.). For example, GW contamination in peat or silty soils in deltas such as in the Rotterdam or Antwerp Harbour areas will affect the contamination plume differently than upstream locations along a river with higher flow velocity often coinciding with gravel / sandy soils with extremely high permeability and lower sorption capacity such as is found upstream in the Rhine and Meuse valley.

It can be expected that plume size, mobility and the rate of GW extraction in case of a GW remediation will be far less in a delta such as the Rotterdam area than upstream along the river Rhine. In addition, the location characteristics such as the positioning and dimensions of a location determine the physical space available for treatment as well as logistics and opportunities in the supply of materials used for treatment and opportunities to remove or reuse waste. Finally, legal requirements will also differ between locations depending on function (e.g. nature area, farmland, industrial area, GW protection zone, or residential area's) and between countries.

The selection of treatment technology will be dependent on all of these parameters:

In some cases, the available area on-site is limiting the footprint of a technology. This gives the preference to short EBCT sorption filters, since these have an inherent smaller footprint. For example in case the extraction rate needs to be very high, a sorbent with a short Empty Bed Contact Time is preferable over the use of a sorbent with a long EBCT. At extraction rates of approximately 100 m3/hr or more, the volume of sorbent for the water treatment will become significant in case of long EBCT's.

In case of gravelly soils the use of recirculation might be a viable and very economical option, particularly when the stand time of the sorbent could be prolonged by it.

(Geo)chemical conditions of the water

The (geo)chemical composition of the water is another important factor. As we have seen in the study, the presence of other organics and inorganics affect the efficiency of the processes for all presented technologies. It is vital that these effects are assessed for each case individually.

What we know from literature, this study and other projects is that some of the sorbents are less affected by increased levels or organic or inorganic constituents[1]. So dependent on the composition of the treated water, a selection for the sorbent (or the necessary pretreatment) might differ.

Local regulations

The legal requirement for discharge of water or processing of waste could severely influence the selection process for the treatment technology. The permitted discharge concentrations (if defined in local jurisdiction) differ for PFAS from site to site. This difference will affect the decision making process on whether a treatment facility is needed or on how the actual treatment will take place.

Equilibrium processes with regards to sorption

It is known that sorption is an equilibrium process, which means that the greater the incoming concentration, the greater the load on sorbent, e.g. activated carbon sorbs until a maximum loading is reached and the sorbent no longer is able to remove the compound of interest. When the treated water contains a mixture of contaminants, the affinity of the individual compounds will result in competition where compounds with a stronger affinity will replace compounds with lower affinity. Depending regulatory constraints for individual compounds, targets set by the user and requirements for potential reuse, the application of the technique is determined. This is typical for PFOS, a molecule with a significant sorption affinity on activated carbon. A sorption isotherm can be found in **Appendix 7**. The steeper the curve, the greater the sorption load. The greater the incoming concentration, the greater the contaminant loading rate on activated carbon. This also shows that the red curve (ORGANOSORB 10-AA) is much steeper than the green curve (ORGANOSORB 10) and thus gives the macroporous activated carbon the greatest load. Which we thus also observe in practice.

4.1. ACTIVATED CARBON

4.1.1. Introduction

Granular activated carbon, or activated carbon as a whole, is regarded as one of the benchmark technologies for (ground)water remediation. The technology has been widely applied many times from pilot to full-scale installations and has proven its effectiveness. Activated carbon is marketed by a large number of specialized vendors. Carbons specialized to remove PFAS are offered by various vendors such as DESOTEC, CABOT-NORIT and Chemviron, and applied for GW remediation.

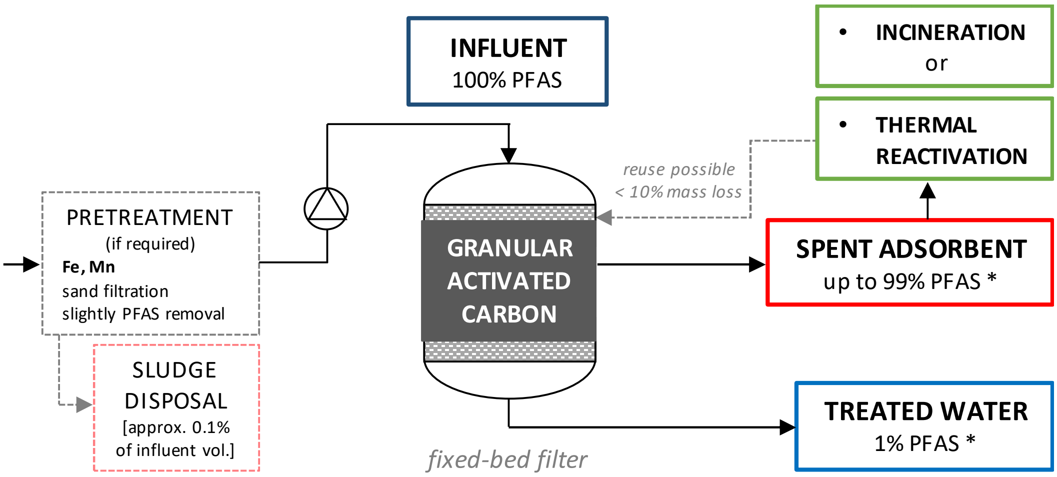
In general granular activated carbon sorbs all non-water soluble organic substances present in water streams.

There are numerous types of granular activated carbon that differ in effectiveness and in pricing, **Appendix 7**. The price difference between a high quality GAC and a low quality GAC ranges a factor 5 to 10. Price is mainly dependent on the sorption capacity of the activated carbon, which is dependent on the surface area, pore volume and pore size distribution.

The removal mechanism is sorption in the pores of the activated carbon, based on hydrophobic interactions between the (hydrophobic) fluorinated chain of the PFAS and the activated carbon surface. **Figure 15** below shows a flow diagram of a GAC system including potential pre-treatment and disposal routes of the spent material[1].

The working range for GAC for the treatment of impacted water is broad. Projects in e.g. the drinking water industry have shown the effectiveness of the sorbent even at very low concentrations (< 100 ng/L).

Figure 15: PFAS flow diagram for continuous adsorption filtration with GAC. Note that the values are indicative based on Riegel, et al. [1]; removal efficiency and target PFAS concentrations strongly depend on PFAS components to be removed and site-specific conditions (e.g. influent concentration, presence of competing substances, etc.).



4.1.2. Performance

Generally, the sulfonic acids (PFSAs, such as PFOS), are more effectively removed by activated carbon than the carboxylic acids (PFCAs such as PFOA). The main reason is the higher electrostatic interaction PFSA-compounds have with the carbon surface due to the three oxygen atoms comparing to the two oxygen atoms at PFCAs [1]. Similarly, long-chain PFAS are more readily removed than short-chained species due to greater hydrophobic interactions and increased confinement in the pores. Actual removal efficiency thus differs based on matrix and specific PFAS. Removal rates of >90% up to close to 100% are observed for some PFAS, whilst for some short-chained PFCA's removal of <50% is not uncommon in practical field experiences with field conditions.

As discussed in Paragraph 3.3 batch experiments of the tested GAC shows higher affinity for longer chain PFAS than for shorter chain PFAS. Below the sorption coefficients (K_{sw}) that were derived from these data by means of fitting Freundlich isotherms (**Appendix 6**), are listed in **Table 6** below. Within this table the sorption coefficients that are listed are the coefficients at an aqueous concentration of 1.0 µg/L. This normalisation at a concentration of 1.0 µg/L allows to compare compounds independent of the native concentrations. The slope of the isotherm indicates the linearity of the sorption with concentration. The sorption coefficient is independent of concentration when 1/n is (near) 1 and becomes lower with increasing concentrations when it is <1, values above 1 are not expected. The sorption of the sulfonic acids appears to be stronger than that of the carboxylic acids when compounds with the same fluorinated carbon chain length are compared. These observations coincide with observations in literature summarized in Riegel, et al. [1].

Table 6: Freundlich sorption characteristics of different PFAS compounds on activated carbon in impacted groundwater (GW).

	Carboxylic acids					Sulfonic acids			
Length of fluorinated chain	**4**	**5**	**6**	**7**	**8**	**4**	**6**	**8**	**6**
solute	**PFBA**	**PFPeA**	**PFHxA**	**PFHpA**	**PFOA**	**PFBS**	**PFHxS**	**PFOS**	**6:2 FTS**
GAC K_{SW}[1] (95% Confidence Limits)	21038 (13868 to 31842)	51523 (32885 to 80910)	1013911 (177011 to 5807644)	57016 (38726 to 84140)	430527 (248886 to 744732)	n.a.[4]	n.a.[4]	2500345 (2426610 to 2576321)	n.a[4]
GAC slope[6] (95% Confidence Limits)	0.54 (0.38 to 0.70)	0.50 (0.38 to 0.61)	1.12 (0.69 to 1.55)	0.27 (0.17 to 0.37)	0.85 (0.67 to 1.03)			-0.06 (n.a.[4])	

[1] Sorption coefficient ([PFAS] µg/kg sorbent / [PFAS] µg/L water) defined (extrapolated) at an aqueous concentration of 1 µg/L based on sorption isotherms listed in the **Appendix 6**). In most cases this concentration is at the high end of just outside the concentration range tested, so it can be considered a worst case sorption coefficient, as sorption coefficients generally increased with decreasing concentrations.
[2] Number of bed volumes where a break-through of 20% of the initial concentration was observed.
[4] Not applicable; data did not reveal clear sorption isotherms.
[6] The slope of the sorption isotherm (log concentration on sorbent (µg/kg) vs. log concentration in aqueous phase (µg/L)

As discussed in paragraph 3.3.8 sorptive treatment is able to remove PFAS from both the relatively clean matrix of impacted GW and the more heavily impacted matrices such as FFWW. But the application to heavily contaminated matrices with a wide variety of co-contaminants such as oil residues is not ideal as concentrations are very high leading to relevant residues in the effluent. This argues that treatment of FFWW requires pre-treatment in order to reduce the sorbent loading and thereby allowing longer sorbent life higher bed volumes and lower concentrations PFAS in the effluent.

4.1.3. Key Design criteria

Treatment strategy/treatment concept

Most commonly, a granulated activated carbon filter is used in a fixed-bed set up. The impacted water will flow downward through the filter where sorption takes place. Contact time can be easily managed this way. GAC-filters in a serial configuration using lag/lead filters (pseudo moving bed) is very common: the first filter is removing the bulk of the PFAS, the second is used for polishing. When the first reaches breakthrough, the second filter becomes first in line, whilst the first is replaced. This newly replaced filter starts out as polishing filter and thus the cycle continues. This method reduces the overall activated carbon consumption.

Pre-treatment

There are a few reasons to pre-treat water before treatment with a granular activated carbon filter:

Activated carbon possesses affinity for most hydrophobic organic compounds (e.g. BTEX, aromatic hydrocarbons, oil/petroleum). These substances are in (direct) competition with PFAS for sorption sites and thus have negative effects on the lifetime of the filter bed, so depending on the concentration of these compounds, pre-treatment might be cost effective. There are no general rule-of-thumb values available from which concentrations upward this becomes effective. Additionally, low concentrations of multivalent ions, like iron and manganese, can cause filter blocking/scaling. These compounds generally don't compete with PFAS for sorption sites, however they can pose a challenge for continued, reliable operation. Similarly, particulate matter can cause filter blocking and pressure loss during filtration resulting in frequent filter rinsing. Sand filtration is a common option to remove suspended solids and a fraction of organic matter. For suspended particles, a turbidity of 1.5 FTU/NTU/FAU or higher is a rule-of-thumb threshold for applying pre-treatment.

Contact time

The main design parameter for an activated carbon filter is the Empty Bed Contact Time (EBCT [min]), it defines the contact time of the water with the complete filter that includes voids. Typically, this varies between 20 and 30 minutes of EBCT, indiscriminate of the flow, but could be up to 60 minutes. A general rule-of-thumb is 20 minutes. EBCT's practically translate to total required filter volume: a flow of 150 m^3/h with an EBCT of 20 minutes results in 50 m^3 GAC* (wet and packed volume), whilst an EBCT of 1 hour requires 150 m^3. Generally, both contaminant loading rate and thus the bed lifetime increase with increasing the EBCT.

Hydraulic loading rate/filter velocity

The filter velocity, or hydraulic loading rate, is expressed as the 'speed' of the water through a filter. Typical filter hydraulic loading rates during operation vary between 5 and 15 m^3 per m^2 filter surface per hour, expressed as filter velocity (vF, [m/h]). A general rule-of-thumb is 10 m/h. According to literature[18], taller activated carbon filters might increase overall removal efficiency. The loading rate is important because it influences the mass transfer from the bulk solution to the carbon granules. A too low loading rate increased mass transfer resistance. The filter velocity should be designed in tandem with the EBCT and thus the bed volume to ensure enough contact time for sorption.

Contaminant loading rate

The contaminant loading rate is the amount of contaminant a certain amount of carbon can sorb [mg_{PFAS}/kg_{Carbon}]. Through sorption isotherm experiments, the loading capacity of a chosen type of GAC can be determined. Typical loading rates range between 10 to 60 mg PFAS/kg GAC. Generally, both contaminant loading rate and thus the bed lifetime increase with increasing the EBCT. These values vary strongly depending on the presence of compounds competing for sorption in the water matrix and the characteristics of the chosen GAC, so a generic rule-of-thumb value is not given.

Within this study contaminant loading rates were orders of magnitude higher with 4.2 (95% Confidence Level = 3.2-5.5) and 1.5 (95%CL = 1.4-1.6) g PFAS/kg sorbent for the GW without and with benzene spike respectively, and 3.8 (95%CL = 3.2-4.4) for FFWW. However, these loading rates were obtained at rather high aqueous concentrations of the detectable PFAS (~7 µg/L, for GW and around 5.000 µg/L for FFWW).

The observed loading rates are not representative for loading rates that lead to high removal percentages or acceptable effluent concentrations (sub µg/L-range) and low sorbent dosages. For ~99% reduction of PFAS concentrations from GW probably typically one to two orders of magnitude higher sorbent dosages are required, which automatically results in lower dosing rates. Such loading rates fall in the same range as observed in literature.

Bed lifetime

A sorptive filter needs replacement when the target compound(s) are breaking through. Normally this means that the treated water concentration is approaching the treatment target concentration. Continuing filtration would mean that the target concentration would be exceeded soon. The volume of water a filter can treat before reaching this target concentration is called the bed lifetime. It is expressed as the amount of Bed Volumes being the number of reactor volumes the filter has treated (abbreviated to BV). Values range from several thousands to several tens of thousands BV till breakthrough begins. These values vary strongly depending on the properties of the PFAS, presence of compounds competing for sorption in the water matrix, the desired removal rate and the characteristics of the chosen GAC. A generic rule-of-thumb value cannot be given. Within the small scale column studies, as shown in the table below, GAC showed > 40.000 bed volumes without breakthrough for PFHxA, PFOA, PFHxS and PFOS, while PFBA, PFPeA, PFHpA, and PFBS showed (20%) breakthrough at lower bed volumes (**Table** 7). This correlates with the obtained sorption coefficients from the PFAS also listed in the table. And with the generic trend that the shorter the fluorinated chain is, the lower the affinity of the sorbent is.

In order to make best use of the potential of the sorbent to sorb contaminant, it is best to make use of a lead and a lag vessel. The stand time of the lead vessel can be prolonged because of the of a second security (lag) vessel.

Table 7: Bed volumes treated at 20% breakthrough in column testing with impacted groundwater (GW).

	Carboxylic acids					Sulfonic acids			
Length of fluor chain	**4**	**5**	**6**	**7**	**8**	**4**	**6**	**8**	**6**
solute	**PFBA**	**PFPeA**	**PFHxA**	**PFHpA**	**PFOA**	**PFBS**	**PFHxS**	**PFOS**	**6:2 FTS**
GAC (20%)[2]	7.000	13.000	19.000	22.000	40.000	25.000	>40.000	>40.000	n.a.[5]

[2] Number of bed volumes where a break-through of 20% of the initial concentration was observed.

[5] Not applicable; concentrations were too low to assess sufficient reduction of 6:2 FTS in the treated water

Effect of temperature and pressure

Activated carbon filters can be constructed as gravity or pressurized filter units, depending on the requirements of the client. Temperature has some effect, but these effects are minimal compared to matrix effects and changes in contact time of the carbon bed.

4.1.4. Operational aspects

Energy use

The dominant primary energy use in an activated carbon filter are the feed pumps. Dependent on influent characteristics and treatment strategy, backwashing pumps might be applied as well. Energy use is directly linked to the treated water flow (m^3/h), the hydraulic head of the filter and the filter configuration and should be detailed on a case-by-case basis. Depending on the applied method for energy calculation, one might take transportation energy as well as the energy requirement for the off-site regeneration or disposal of the carbon into consideration. As a rule of thumb, for large-scale activated carbon filters an energy use of maximum 0.1 kWh/m^3 treated can be assumed based on van Nieuwenhuijzen, et al. [19]. This includes both feed- and backwash pumps with a hydraulic head of 6-8 m, and excludes energy related to transport and regeneration/disposal.

Maintenance and personnel

An activated carbon filter typically runs without intensive operation- and maintenance efforts and can be fully automated. The average time spent should typically not exceed 0.5 day per week assuming a plant of up to 25 m^3/h, depending on the exact filtration set up and water composition.

Chemical use

GAC-filtration does not apply any chemicals, besides the activated carbon itself. The need to buy new- or regenerated carbon is discussed above in the sections on bed lifetime and contaminant loading rate. Since the lifetime of a filter bed varies widely depending on several factors, there is no rule-of-thumb value for GAC-use.

Waste production

The main waste produced from an activated carbon filter is the spent carbon. Activated Carbon vendors typically offer management options for their spent sorbent. The price of processing the spent carbon is generally included in the costs for the carbon. Spent carbon can be either (thermally) reactivated or incinerated off-site. Several providers are able to regenerate the activated carbon. In this process the activated carbon is heated up to 900 degrees C, where a significant portion of the PFAS become volatile, thus removing (practically) all PFAS constituents from the GAC. The off-gas from this process needs to be treated further to ensure complete removal. Regeneration is restricted to certain types of GAC and to a certain level of contamination. The regenerated activated carbon is cheaper to use. Its performance could be similar to virgin GAC. As with chemical use, waste production is directly linked to several factors and thus a rule-of-thumb of waste production is not available. A relevant part to mention is the CO_2-footprint/emission of this process. By (re)activating/regenerating the carbon the energy intensive production of virgin activated carbon is avoided, resulting in a large CO_2-footprint reduction for reactivated carbon.

4.1.5. Costs

Capital costs

Capital costs are relatively low as these systems are relatively simple. Most vessels operate under atmospheric conditions and the technology is mature. Depending on the matrix some more extensive pre-treatment can be required, increasing the capital costs. If, for example, a sand filter is required, the capital costs can more or less double, so a general rule-of-thumb value for CAPEX is not available.

Operational costs

Operational costs are based on the abovementioned operational aspects. A major factor is the costs of the carbon itself, often the costs for management of the spent carbon is included in this price. Carbon is available in a wide price range, for PFAS-specific carbons, a typical value of around EUR 3/kg is to be expected for high quality virgin activated carbon, and around EUR 2/kg for high quality reactivated carbon [1]. Depending on water matrix, desired treatment efficiency etcetera, costs are estimated in the range of EUR 0.04 to EUR 0.20 per m^3 treated. The lower range is based on long chain PFAS-removal with higher bed lifetimes, whereas the higher range corresponds to short-chain PFAS removal with shorter bed lifetimes [1]. Besides these price estimates, there is no more accurate translation available to a cost of EUR/m^3 treated.

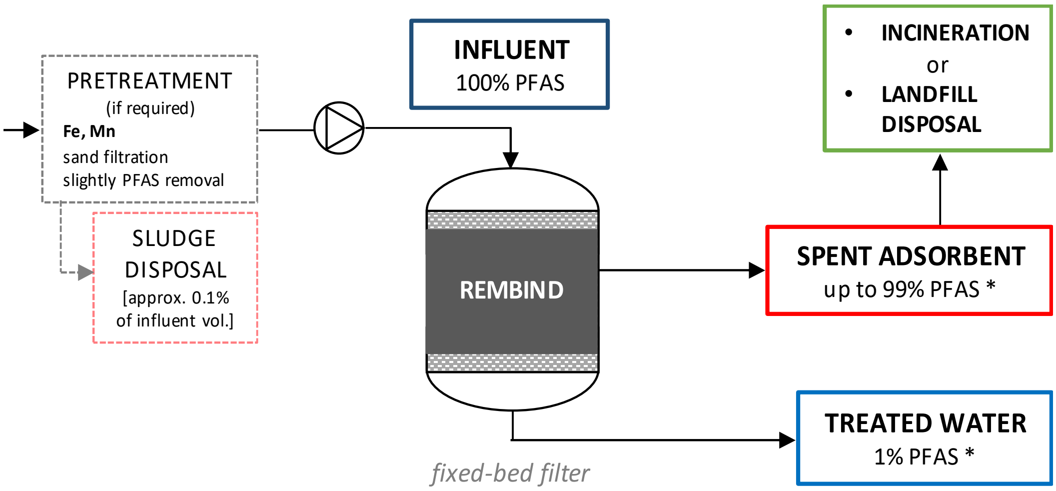
4.2. REMBIND®

4.2.1. Introduction

Rembind® is a (proprietary) sorbent, based on a mixture of amongst others amorphous aluminium hydroxide, activated carbon, organic matter and kaolinite. The product is marketed by the RemBind Pty Ltd Company. Rembind® is originally designed for soil treatment (immobilization), but a variation of the product can be used for water treatment.

The removal relies on a combination of three mechanisms: electrostatic interaction due to the surface charge of the mineral component, the binding of organic matter to anionic functional groups of PFAS and the hydrophobic interactions from the activated carbon component of Rembind®.

Figure 16: PFAS flow diagram for continuous sorption filtration with Rembind® sorbent in a mixed fixed bed. Note that the values are indicative based on Riegel, et al. [1]; removal efficiency and target PFAS concentrations strongly depend on PFAS components to be removed and site-specific conditions (e.g. influent concentration, presence of competing substances, etc.).



4.2.2. Performance

The reported performance in Riegel, et al. [1] is mainly based on laboratory-, bench- and pilot scale experiments. These experiments indicate removal of both short- and long chain PFAS. High removal has been reported (>99%), however, this was based on short contact times and Riegel, et al. [1] expressed doubt about the validity of the tests. Rembind® was only tested in Batch experiments in the current study, see **Table 8**. As discussed in Paragraph 3.3 batch experiments of Rembind® showed higher affinity for longer chain PFAS than for shorter chain PFAS. Below the sorption coefficients that were derived from these data by means of fitting Freundlich isotherms (**Appendix 10**). Within this table the sorption coefficients that are listed are the coefficients at an aqueous concentration of 1.0 µg/L. This normalisation at a concentration of 1.0 µg/L allows to compare compounds independent of the native concentrations. The slope of the isotherm indicates the linearity of the sorption with concentration. The sorption coefficient is independent of concentration when 1/n is (near) 1 and becomes lower with increasing concentrations when it is <1, values above 1 are not expected. Especially for the sulfonic acids no sorption coefficients could be accurately derived from the batch sorption tests.

Table 8: Sorption characteristics of the sorbent in batch tests with impacted groundwater (GW)

	Carboxylic acids					Sulfonic acids			
Length of fluor chain	**4**	**5**	**6**	**7**	**8**	**4**	**6**	**8**	**6**
sorbent	**PFBA**	**PFPeA**	**PFHxA**	**PFHpA**	**PFOA**	**PFBS**	**PFHxS**	**PFOS**	**6:2 FTS**
RB K_{SW}[1] (95% Confidence Limits)	13646 (7278 to 25586)	7447 (4267 to 12972)	33420 (25468 to 43853)	27990 (3945 to 198609)	63680 (11858 to 342768)	n.a.[4]	n.a.[4]	493174 (295801 to 820352)	n.a.[4]
RB 1/n ((95% Confidence Limits)	0.83 (0.42 to 1.24)	0.17 (0.02 to 0.32)	0.14 (0.01 to 0.26)	0.30 (-0.17 to 0.77)	0.65 (0.15 to 1.14)			0.22 (-0.07 to 0.50)	

[1] Sorption coefficient ([PFAS] µg/kg sorbent / [PFAS] µg/L water) defined (extrapolated) at an aqueous concentration of 1 µg/L based on sorption isotherms listed in the **Appendix 6**). In most cases this concentration is at the high end of just outside the concentration range tested, so it can be considered a worst case sorption coefficient, as sorption coefficients generally increased with decreasing concentrations.

[2] Number of bed volumes where a break-through of 20% of the initial concentration was observed.

[4] Not applicable; data did not reveal clear sorption isotherms.

[6] The slope of the sorption isotherm (log concentration on sorbent (µg/kg) vs. log concentration in aqueous phase (µg/L)

4.2.3. Key Design criteria

Treatment strategy/treatment concept

The Rembind® sorbent has two different treatment options: either a discontinuous batch reactor followed by sedimentation of sorbent and decantation of treated water or continuously in a mixed fixed-bed filter, applying sand to reduce pressure loss. Below, both systems are described where applicable.

Pre-treatment

Rembind® exhibits similar sensitivities to organic compounds as activated carbon, so similar pre-treatment options are available. There is currently no exact organics-threshold value available. A total petroleum hydrocarbon content (TPH) of <15 mg/L is considered acceptable, if the total petroleum exceeds this, additional treatment is required. A recent study by Kabiri and McLaughlin [2] showed that the sorption of PFAS by RemBind® is not influenced significantly by humic acids, competing ions or pH values at levels expected to be found in the environment.

Contact time

The supplier indicates that recent experiments have shown that a contact time of 5-10 minutes is sufficient to sorb >80% of PFAS. Hydraulic loading rate/filter velocity. For both the discontinuous- as well as the continuous system, there is no information available regarding hydraulic loading rate/filter velocity.

Contaminant loading rate

Within this study loading rates could be derived at aqueous concentrations that were half of the concentrations of the impacted GW (~7 µg/L) and FFWW (~5.000 µg/L). The contaminant loading rates where 1.5 (95%CL = 1.4-1.6) and 5.5 (95%CL = 2.1-14.3) g PFAS/kg sorbent for the GW without and with benzene spike, respectively, and 1.7 (95%CL = 1.2-2.5) for FFWW. These loading rates were obtained at rather high aqueous concentrations of ~7 µg/L for impacted GW and

5000 µg/L for FFWW. Interestingly, the loading rate of the benzene spiked GW appeared to be higher than the one without benzene spike. Comparison of loading rates of impacted GW and FFWW is not directly possible as the PFAS composition strongly differs (**Figure 2**) and the fraction of undetected PFAS in especially FFWW (**Figure 3)** is not accounted for.

The observed loading rates are not representative for loading rates that lead to high removal percentages or acceptable effluent concentrations (sub µg/L-range) and low sorbent dosages. For ~99% reduction of PFAS concentrations from GW probably typically one to two orders of magnitude higher sorbent dosages are required, which automatically results in lower dosing rates.

Bed lifetime

The supplier states that recent experiments by RemBind® show that the bed lifetime is similar to high grade activated carbon.

Effect of temperature and pressure

There is no information available regarding the effects of temperature and pressure of the continuous system. The effects are expected to be similar to activated carbon, so one could assume that effects are negligible. A recent study by Kabiri and McLaughlin [2] showed that a freeze/thaw cycle had no effect on PFAS binding to Rembind®.

4.2.4. Operational aspects

Energy use

The dominant primary energy use in a continuous filter are the feed pumps. Dependent on influent characteristics and treatment strategy, backwashing pumps might be applied as well, however this option is not mentioned in Riegel, et al. [1]. Energy use is directly linked to the treated water flow (m^3/h), the hydraulic head of the filter and the filter configuration and should be detailed on a case-by-case basis. Depending on the applied method for energy calculation, one might take transportation energy as well as the energy requirement for the off-site disposal of the material into consideration. As a rule of thumb, for large-scale filters, comparable to activated carbon filters, an energy use of maximum 0.1 kWh/m^3 treated can be assumed based on expert judgment. This includes both feed- and backwash pumps with a hydraulic head of 6-8 m, and excludes energy related to transport and disposal.

For the discontinuous powder application with a stirred contact tank and a sedimentation tank, the major energy users are the feed pumps and the mixing devices. Generally, these systems have a lower hydraulic head compared to continuous packed bed filters and mixing devices as well as settlers require very little energy compared to feed- and backwash pumps. The overall energy use can thus be expected to be less than that of continuous systems.

Maintenance and personnel

Since the continuous system is comparable to an activated carbon filter (benchmark system), the average time spent should not exceed 0.5 day per week, depending on the exact filtration set up and water composition. For a discontinuous system, there is no reason to assume it would be significantly higher or lower than the continuous variety.

Chemical use

The main chemical use is the sorbent. In continuous filtration, this is the only chemical that is applied. Based on current available data, the exact chemical use per m^3 treated is unknown. In discontinuous systems, additional chemical dosing can be implemented to increase the settling of the sorbent in the sedimentation step. The supplier specified that no chemicals are required for the RemBind® system. Spent material in a batch reactor is separated using filtration or centrifugation.

Waste production

Spent sorbent is dealt with similarly to activated carbon and needs to be incinerated or disposed. As it contains also inorganic material (aluminium oxide and kaolin), there will also be some of ashes after incineration but according to a leading landfill in Germany this ash content is not significant in terms of costs as stated by the supplier. Overall, the cost of RemBind® including disposal for spent RemBind® is similar to the cost of carbon including regeneration, according to the supplier. As with chemical use, waste production is directly linked to several factors and thus a rule-of-thumb of waste production is not available.

4.2.5. Costs

Capital costs

For continuous systems, the capital costs can be relatively low as these systems are relatively simple, comparable to activated carbon. The vessels operate under atmospheric condition. Depending on the matrix some more extensive pre-treatment can be required, increasing the capital costs. If, for example, a sand filter is required, the capital costs can more or less double. A major unknown factor is the EBCT, which largely determines the required volume of the system. A general rule-of-thumb value for CAPEX is not available.

Operational costs

Operational costs are based on the abovementioned operational aspects. A major factor is the costs of the sorbent itself as well as the disposal of the material. There is no accurate cost estimate available to determine EUR/m^3 treated.

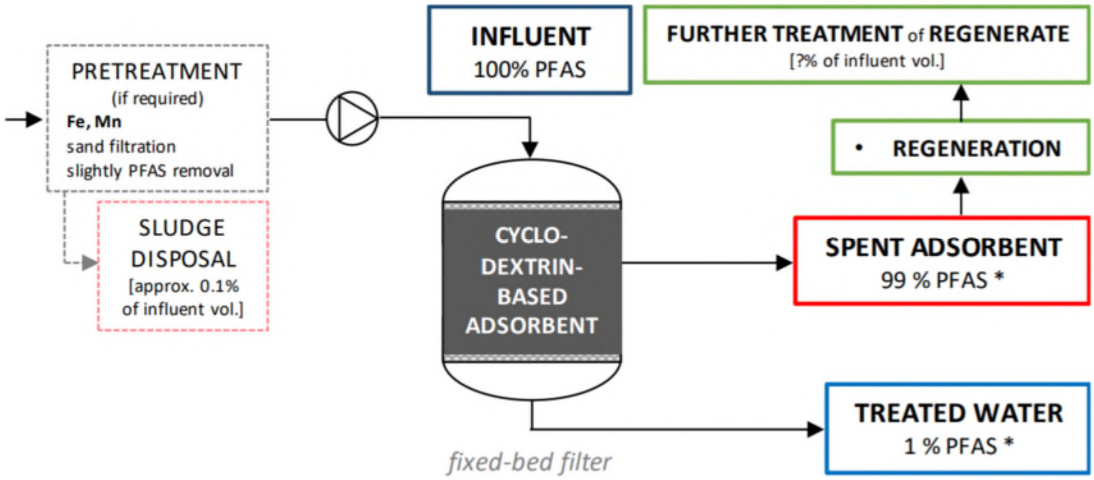
4.3. DEXSORB+®

4.3.1. Introduction

DEXSORB+® is a cyclodextrin-based sorbent derived from cornstarch. DEXSORB+® is currently brought to market by CycloPure (USA). Cyclodextrin-based sorbents are made by cross-linking of “cup-shaped” cyclodextrin molecules into porous polymers. During this process, functional groups can be added to make the removal more targeted towards for example PFAS. The sorbent is currently available as powder or in granular form. Based on supplier contact, the granular form seems most promising for water treatment application.

The removal mechanism relies on hydrophobic interactions between the inner part of the cyclodextrin molecules and the carbon chains of PFAS as well as on electrostatic interactions between the positively charged units and the anionic head groups of the PFAS molecules.

Figure 17: PFAS flow diagram for sorption filtration with cyclodextrin-based sorbent. Note that the values are indicative based on Riegel, et al. [1]; removal efficiency and target PFAS concentrations strongly depend on PFAS components to be removed and site-specific conditions (e.g. influent concentration, presence of competing substances, etc.). According to the supplier < 0.01% of influent volume needs further treatment of regenerate.



4.3.2. Performance

The reported performance in Riegel, et al. [1] is mainly based on laboratory- and bench scale experiments. Pilot tests are currently being performed, but results are not publicly available at the time of writing. The data suggest that both long-chain and short-chain PFAS can be removed with faster sorption kinetics than activated carbon. Removal efficiencies for FFWW up of 90-99% have been reported, and Riegel, et al. [1] describe the performances as “showing potential” for these applications. Breakthrough of different PFAS have been described, ranging from ~6.500 BV to >55.000 BV, depending on the matrix.

As discussed in Paragraph 3.3 batch experiments of the tested sorbent shows higher affinity for longer chain PFAS than for shorter chain PFAS. Below some sorption coefficients that were derived from these data by means of fitting Freundlich isotherms (**Appendix 10**) and are listed in **Table 9**. Within this table the sorption coefficients that are listed are the coefficients at an aqueous concentration of 1.0 µg/L. This normalisation at a concentration of 1.0 µg/L allows to compare compounds independent of the native concentrations. The slope of the isotherm indicates the linearity of the sorption with concentration. The sorption coefficient is independent of concentration when 1/n is (near) 1 and becomes lower with increasing concentrations when it is <1, values above 1 are not expected. The sorption of the sulfonic acid PFOS is stronger than that of PFOA (with the same carbon chain length) and any of the other carboxylic acids. The breakthrough curves even more explicitly show the difference between the removal of the sulfonic and carboxylic acids as the shorter chain carboxylic acids except PFOA all break through within 40.000 bed volumes while even the shorter chain sulfonic acids don’t (>40.000 BV). Results are in line with literature findings listed in the previous paragraph, except for PFBA and PFPeA that showed almost immediately or direct breakthrough.

Table 9: Sorption and break through characteristics of the sorbent in batch and column testing with impacted groundwater (GW).

	Carboxylic acids					Sulfonic acids			
Length of fluor chain	**4**	**5**	**6**	**7**	**8**	**4**	**6**	**8**	**6**
sorbent	**PFBA**	**PFPeA**	**PFHxA**	**PFHpA**	**PFOA**	**PFBS**	**PFHxS**	**PFOS**	**6:2 FTS**
CP K_{SW}[1] (95% Confidence Limits)	4613 (2472 to 8610)	16749 (13804 to 20324)	66681 (51286 to 86497)	116950 (57544 to 237684)	71614 (23659 to 216272)	n.a.[4]	n.a.[4]	314775 (221820 to 446684)	n.a.[4]
CP 1/n (95% Confidence Limits)	1.07 (0.51 to 1.62)	0.78 (0.71 to 0.86)	0.84 (0.73 to 0.95)	0.98 (0.80 to 1.16)	0.85 (0.67 to 1.03)			0.11 (-0.13 to 0.36)	
CP (20%)[2]	0[3]	1.000	7.000	12.000	>40.000	>40.000	>40.000	>40.000	n.a.[5]

[1] Sorption coefficient ([PFAS] µg/kg sorbent / [PFAS] µg/L water) defined (extrapolated) at an aqueous concentration of 1 µg/L based on sorption isotherms listed in the **Appendix 6**. In most cases this concentration is at the high end of just outside the concentration range tested, so it can be considered a worst case sorption coefficient, as sorption coefficients generally increased with decreasing concentrations.

[2] Number of bed volumes where a break-through of 20% of the initial concentration was observed.

[3] Direct break through, no significant retention

[4] Not applicable; data did not reveal clear sorption isotherms.

[5] Not applicable; concentrations were too low to assess sufficient reduction of 6:2 FTS in the treated water

[6] The slope of the sorption isotherm (log concentration on sorbent (µg/kg) vs. log concentration in aqueous phase (µg/L)

4.3.3. Key Design criteria

Treatment strategy/treatment concept

As mentioned above, DEXSORB+® is available as powder or in granular form. Currently, the supplier is testing granular-based applications for water treatment. The process flow diagram, as showed in **Figure 17**, accurately depicts the basic principle, comparable to activated carbon, a granular media DEXSORB+® filter will likely consists of either parallel or serial filters (lag-lead configuration). Regeneration, which is unique to DEXSORB+® with respect to activated carbon, can take place either in-line (on-site), or one of the filters can be taken out of the plant and regenerated at a central facility off-site. This is dependent on the total installation size and the economics that go along with transport and regeneration: if multiple sites in a close proximity are applying this technology, a central regeneration unit might be profitable. An exact tipping point for this application of economy of scale is not known yet.

Pre-treatment

Similar to activated carbon, pre-treatment for iron and manganese might be necessary. The benefit of DEXSORB+® is its resistance to fouling from complex matrices: due to its physical characteristics only low-molecular weight organics directly compete with PFAS, larger molecules such as NOM or DOC, pose less of a hindrance to DEXSORB+®. No pH effects have been expected, so also pH corrections are not required.

Contact time

Empty bed contact time in the DEXSORB+® filter vessel is substantially shorter than activated carbon. Whereas activated carbon requires contact times ranging from 15 minutes up to several hours, the vendor indicates that contact times of several minutes (3 to 5, up to a maximum of 10) should be sufficient for high removal.

Hydraulic loading rate/filter velocity

Filtration velocity is not known, based on kinetics and required contact time, one could assume that a faster velocity must be achieved to overcome mass transfer limitations than e.g. activated carbon, i.e. >10 m/h.

Contaminant loading rate

This data is not available from Riegel, et al. [1]. Experimental results from this study show that loading rates were 1.2 (95%CL = 0.8-1.9) and 22.8 (95%CL = 6.2-83.0) g PFAS/kg sorbent for the GW without and with benzene spike respectively, and 3.8 (95%CL = 3.2-4.4) for FFWW. However, these loading rates were obtained at rather high aqueous concentrations of the detectable PFAS (~7 µg/L, for GW and around 5000 µg/L for FFWW). Interestingly, the loading rate of the benzene spiked GW appeared to be remarkably higher than the one without benzene spike. Comparison of loading rates of impacted GW and FFWW is not directly possible as the PFAS composition strongly differs (**Figure 2**) and the fraction of undetected PFAS in especially FFWW (**Figure 4**) is not accounted for.

The observed loading rates are not representative for loading rates that lead to high removal percentages or acceptable effluent concentrations (sub µg/L-range) and low sorbent dosages. For ~99% reduction of PFAS concentrations from GW probably typically one to two orders of magnitude higher sorbent dosages are required, which automatically results in lower dosing rates.

Bed lifetime

Bed lifetime varies strongly based on desired removal rate and the composition of the wastewater. Literature reported bed lifetimes varying between 6.300 and >55.000 [1]. The supplier has additionally reported bed lifetimes up to and over 150.000 BV. The small scale column studies showed > 40.000 bed volumes without breakthrough for PFOA, and all sulfonic acids, while PFBA, PFpeA, PFHxA, PFHpA showed (20%) breakthrough at lower bed volumes ranging from 0 to 12.000 BV (**Table 9**) with the generic trend that the shorter the fluorinated chain is, the lower the affinity of the sorbent is. This is in line with data reported by Riegel, et al. [1], and lower than what was reported by the supplier. However this seeming contradiction might also be a result of the selection of test chemicals or matrix composition used in the various experiments.

Effect of temperature and pressure

There is no information available regarding the effects of temperature and pressure. The system applies ambient pressures and ambient temperatures, tests with elevated temperatures have not been conducted.

4.3.4. Operational aspects

Energy use

The main primary energy use for the DEXSORB+® system is the feed pumps. There are no other significant energy consumers. For a system with on-site regeneration, additional, smaller pumps for regeneration are required. For off-site regeneration, transportation energy might be taken into account, as well as the energy requirement for the off-site regeneration system. Exact energy use is thus dependent on pump energy, and with that directly related to the hydraulic head and the flow that is to be treated, and thus comparable to activated carbon (<0.1 kWh/m^3).

Maintenance and personnel

The DEXSORB+® system should be comparable to an activated carbon filter, which requires relatively little maintenance and upkeep. With an on-site automated regeneration system, longer bed lifetimes should be achievable, thus lowering re-filling frequencies of the sorbent media. Depending on the chosen regenerant fluid, one might require some more regular inspection and maintenance, since e.g. methanol is a flammable liquid. The supplier is currently looking into alternative regenerants that are more user-friendly. Overall maximum staffing of approximately 0.5-1 day per week should be expected.

Chemical use

Besides the sorbent itself, the DEXSORB+® system requires, if desired, the regenerant. As mentioned above, regeneration can be done by flushing the system with a methanol-salt solution, comparable to how some ion-exchange systems for PFAS-removal are regenerated. Exact dosing ratios and chemical consumption is not known.

Waste production

The DEXSORB+® system creates two waste streams: the spent sorbent and the regenerant. The supplier claims that the sorbent can be infinitely regenerated to a high degree. It is realistic to assume that a certain amount has to be replaced and thus disposed of. This material can then be treated comparable to other spent sorbent media, by for example incineration. The loaded regenerant fluid can be concentrated further, re-used and/or disposed similar to residues from ion exchange materials [1]. At this moment, the amount of waste produced is not known.

4.3.5. Costs

Capital costs

Capital costs are relatively low, comparable to activated carbon if no regeneration is applied and compared to an ion exchange system with regeneration. The vessels can operate under atmospheric conditions. Depending on the chosen regenerant fluid, one might have to take fire-safety into account, which will add to the costs of the installation and is a potential drawback of this system. Exact cost calculations for full-scale systems are not available.

Operational costs

Operational costs is based on the abovementioned operational aspects. A major factor is the costs of the sorbent itself and the costs of the regenerant fluid. Current estimates from the supplier is that the material will cost between EUR 15-20 per kg. Currently EUR 20 is achievable on lab-scale, but once scaled-up to industrial production, prices are expected to drop to <15 EUR. Regenerant can be a large cost factor, methanol, for example, is commercially available for around EUR 300-500 EUR/ton. Besides these price estimates, there is no translation available to a cost of EUR/m^3 treated.

4.4. POLYQA-OSORB®

4.4.1. Introduction

PolyQA-Osorb® is a sorbent based on organosilica, also known as swellable organically modified silica's (SOMS). PolyQA-Osorb® is marketed by ABS Materials (USA). PolyQA-Osorb® was not discussed in Riegel, et al. [1] since it was too new and no (peer-reviewed) literature was available, however during the technology selection phase for this study it was deemed promising. This chapter thus diverts from the rest of the previous chapters. Note that the available literature is generally on small lab-scale tests, so the validity needs to be proven by peer-reviewed studies and larger scale (pilot) tests.

The removal mechanism is a combination of hydrophobic and ionic interactions. The SOMS are highly hydrophobic, thus attracting the PFAS carbon tail. The SOMS are treated with a cationic quaternary amine (QA) polymer, creating the PolyQA-Osorb® as described here. This QA-polymer attracts the hydrophilic, ionic head of the PFAS. The sorbent swells as it sorbs more molecules, up to 2-3 times its original size, allowing for higher sorption capacities. The supplier notes the regenerative capacity as one of the most promising. By flushing the SOMS with solvent, PFAS can be pulled out of the matrix. Doing so fully regenerates the sorbent, according to the supplier.

4.4.2. Performance

For demineralized water, PolyQA-Osorb® removed >80% for a group of PFAS, with the majority being removed for >90%, up to 99%. Short chain PFAS are removed to a lower extent (PFBA, PFBS), however also some longer chain PFAS perform relatively poorly (PFDA, PFOSaAm). Overall, performance for short-chain PFAS is significantly higher than that of activated carbon. The PFCS slightly outperform their PFCA counterparts. In treatment tests of GW, >99% removal can be achieved for several short- and long chain PFAS. **Table 10** shows sorption coefficients derived from batch sorption experiments by means of fitting Freundlich isotherms (**Appendix 8**). Within this table the sorption coefficients that are listed are the coefficients at an aqueous concentration of 1.0 µg/L. This normalisation at a concentration of 1.0 µg/L allows to compare compounds independent of the native concentrations. The slope of the isotherm indicates the linearity of the sorption with concentration. The sorption coefficient is independent of concentration when 1/n is (near) 1 and becomes lower with increasing concentrations when it is <1, values above 1 are not expected. The tested sorbent did not allow fitting of removal curves for many of the native PFAS in GW. Therefore the relation with carbon chain-length or sulfonic vs. carboxylic acid is difficult to derive. No column studies were performed with PolyQA-Osorb®.

Table 10: Sorption characteristics of the sorbent in batch tests with impacted groundwater (GW).

	Carboxylic acids					**Sulfonic acids**			
Length of fluor chain	**4**	**5**	**6**	**7**	**8**	**4**	**6**	**8**	**6**
sorbent	**PFBA**	**PFPeA**	**PFHxA**	**PFHpA**	**PFOA**	**PFBS**	**PFHxS**	**PFOS**	**6:2 FTS**
PQ K_{SW}[1] (95% Confidence Limits)	n.a.[4]	7762 (4276 to 12972)	29376 (15276 to 56624)	n.a.[4]	n.a.[4]	n.a.[4]	n.a.[4]	306196 (260016 to 361410)	n.a.[4]
PQ slope (95% Confidence Limits)	n.a.[4]	0.3569 0.1048 to 0.6090	1.333 0.5891 to 2.077	n.a.[4]	n.a.[4]	n.a.[4]	n.a.[4]	0.5117 0.4082 to 0.6151	n.a.[4]

[1] Sorption coefficient ([PFAS] µg/kg sorbent / [PFAS] µg/L water) defined (extrapolated) at an aqueous concentration of 1 µg/L based on sorption isotherms listed in the **Appendix 6**. In most cases this concentration is at the high end of just outside the concentration range tested, so it can be considered a worst case sorption coefficient, as sorption coefficients generally increased with decreasing concentrations.

[2] Number of bed volumes where a break-through of 20% of the initial concentration was observed.

[4] Not applicable; data did not reveal clear sorption isotherms.

[6] The slope of the sorption isotherm (log concentration on sorbent (µg/kg) vs. log concentration in aqueous phase (µg/L)

4.4.3. Key Design criteria

Treatment strategy/treatment concept

Currently, the material application has not been clearly chosen by the supplier, although it seems likely that it is applied in a similar manner to Ion exchange or DEXSORB+®. PolyQA-Osorb®, like these two technologies, has the capacity to be regenerated with high recovery. It is thus likely that the treatment concept will consists of (several) filter vessels with regeneration possibility. How the swelling of the material will affect this and how to overcome the operational drawbacks of the swelling is not yet known.

Pre-treatment

There is no information available regarding pre-treatment, although based on its characteristics, it is expected that PolyQA-Osorb® has interference with both hydrophobic (organic) molecules as well as cationic interactions. Based on experiences in the US, this interference seems to be worse compared to the interferences experienced by activated carbon.

Contact time

The supplier states that an EBCT of 1 minute is sufficient for treatment.[20] This has not been tested during this lab research, so some caution is advised with this contact time since it seems rather optimistic based on expert judgement from other sorption systems.

Hydraulic loading rate/filter velocity

There is no exact information available regarding pre-treatment, although based on the EBCT it can be expected that the filter velocity is higher than that of an activated carbon filter, thus exceeding 10 m/h.

Contaminant loading rate

In literature, based on lab-scale tests contaminant loading rates of 5-50 mg_{PFAS}/g have been observed, depending on the target PFAS. This indicates significantly higher loading rates than e.g. GAC, which has loading rates in the order of mg/kg magnitude. Experimental results from this study show that loading rates were 0.9 (95%CL = 0.6-1.4) and 15.7 (95%CL = 6.9-35.6) g PFAS/kg sorbent for the GW without and with benzene spike, respectively. However, these loading rates were obtained at rather high aqueous concentrations of the detectable PFAS (~7 µg/L). Interestingly, similar to DEXSORB+® the loading rate of the benzene spiked GW appeared to be remarkably higher than the one without benzene spike.

Data of the experiment with FFWW showed 2.4 g PFAS/kg at very high aqueous concentrations of the detectable PFAS (~5000 µg/L). The data did not allow to calculate confidence limits. The observed loading rates are not representative for loading rates that lead to high removal percentages or acceptable effluent concentrations (sub µg/L-range) and low sorbent dosages. For ~99% reduction of PFAS concentrations from GW probably typically one to two orders of magnitude higher sorbent dosages are required, which automatically results in lower dosing rates. Subsequently, loading rates from literature seem to be over one order of magnitude higher than in our observations. Furthermore, the presumed difference with GAC mentioned above was not observed within our study.

Bed lifetime

Based on lab research, breakthrough of long-chain PFAS (PFOA, PFOS) occurs between 20.000-30.000 BV, where breakthrough is defined here as C/C_0 of 0.3. Shorter chain PFAS see much faster breakthroughs, PFBA is the first to reach breakthrough at 5.000 BV. The supplier states that for relevant scale application, they're expecting 500.000-750.000 BV, however this is not substantiated with calculations or measurements.[20] No column studies were performed, to either support or reject the supplier's claims, but the results of the sorption studies do not give indications in that direction, but rather align with other lab scale results.

Effect of temperature and pressure

There is no information available regarding the effects of temperature and pressure. It can be expected that elevated pressures have some adverse effect on swelling sorbents, by for example causing blocking or reducing the swelling capacity of the material, potentially leading to lower maximal contaminant loading rates on the filter as a whole, because the porosity decreases. A lower porosity requires, theoretically, longer EBCT's for sufficient diffusion and thus removal. At similar EBCT's, with a swollen bed, lower removal will be achieved. The actual effect is not known.

4.4.4. Operational aspects

Energy use

The main primary energy use for the PolyQA-Osorb® system is the feed pumps. There are no other significant energy consumers expected. For a system with on-site regeneration, additional, smaller pumps for regeneration are required. Exact energy use is thus dependent on pump energy, and with that directly related to the hydraulic head and the flow that is to be treated, and thus comparable to activated carbon (<0.1 kWh/m^3).

Maintenance and personnel

The PolyQA-Osorb® system should be comparable to an activated carbon filter, which requires relatively little maintenance and upkeep. With an on-site automated regeneration system, longer bed lifetimes should be achievable, thus lowering re-filling frequencies of the sorbent media. Depending on the chosen regenerant fluid, one might require some more regular inspection and maintenance, since e.g. methanol is a flammable liquid. Overall maximum staffing of approximately 0.5-1 day per week should be expected.

Chemical use

Besides the sorbent itself, the PolyQA-Osorb® system requires the regenerant. As mentioned above, regeneration can be done by flushing the system with methanol solution, comparable to how some ion-exchange systems for PFAS-removal are regenerated. Exact dosing ratios and chemical consumption is not known.

Waste production

The PolyQA-Osorb® system creates two waste streams: the spent sorbent and the regenerant. The supplier claims that the sorbent can be indefinitely regenerated to a high degree. It is realistic to assume that a certain amount has to be replaced and thus disposed of. This material can then be treated comparable to other spent sorbent media, by for example incineration. The loaded regenerant fluid can be concentrated further and/or disposed similar to residues from ion exchange materials[1] . At this moment, the amount of waste produced is not known.

4.4.5. Costs

Capital costs

Capital costs are relatively low, comparable to an ion exchange system. The vessels can operate under atmospheric conditions. With the current regenerant (i.e. methanol), fire-safety has to be taken into account, which adds to the costs of the installation and is a potential drawback of this system. Exact cost calculations for full-scale systems are not available.

Operational costs

Operational costs is based on the abovementioned operational aspects. A major factor is the costs of the sorbent itself and the costs of the regenerant fluid. Currently, exact material costs are unknown, although the supplier mentions that the material is more expensive per kg than activated carbon or ion exchange resin. How much more expensive is not known exactly, but currently the price for small amounts of material far exceeds other sorbents. Regenerant can be a large cost factor, methanol is commercially available for around EUR 300-500 EUR/ton. The supplier notes that they expect the system to be overall cheaper than activated carbon or ion exchange, but gives no actual values.

4.5. FLUORO-SORB®

4.5.1. Introduction

FLUORO-SORB® is a surface treated mineral (bentonite based). It is commercialized by Cetco (USA). FLUORO-SORB® was not discussed in Riegel, et al. [1] since it was too new and no (peer-reviewed) literature was available, but was deemed promising during the technology selection phase of this study. The mineral itself has a very high surface area >200 m^2/gram. The surface treatment is hydrophobic and attracts the PFAS molecules. The material is expandable and can accommodate a maximum sorption capacity of > 15 mg/g for commonly regulated PFAS compounds.

This chapter diverts from the rest of the previous chapters. The removal mechanism is not clearly described by the supplier, other than that it is a proprietary sorbent.

4.5.2. Performance

There is no prior information available regarding treatment performance. **Table 11** shows sorption coefficients derived from batch sorption experiments by means of fitting Freundlich isotherms (**Appendix 6**). Within this table the sorption coefficients that are listed are the coefficients at an aqueous concentration of 1.0 µg/L. This normalisation at a concentration of 1.0 µg/L allows to compare compounds independent of the native concentrations. The slope of the isotherm indicates the linearity of the sorption with concentration. The sorption coefficient is independent of concentration when 1/n is (near) 1 and becomes lower with increasing concentrations when it is <1, values above 1 are not expected. The sorption of the sulfonic acid PFOS is much stronger than that of PFOA (with the same carbon chain length) or any of the other carboxylic acids. The breakthrough curves even more explicitly show the difference between the removal of the sulfonic and carboxylic acids as PFBA, PFPeA and PFHpA break through within 40.000 bed volumes while even the shorter chain sulfonic acids don’t.

Table 11: Sorption and break through characteristics of the sorbent in batch and column testing with impacted groundwater (GW).

	Carboxylic acids					Sulfonic acids			
Length of fluor chain	**4**	**5**	**6**	**7**	**8**	**4**	**6**	**8**	**6**
sorbent	**PFBA**	**PFPeA**	**PFHxA**	**PFHpA**	**PFOA**	**PFBS**	**PFHxS**	**PFOS**	**6:2 FTS**
FS K_{SW}[1] (95% Confidence Limits)	15136 (6471 to 35481)	10186 (6310 to 16444)	23174 (15849 to 33963)	99770 (41687 to 238781)	66069 (10914 to 399025)	n.a.[4]	n.a.[4]	16865530 (1782379 to 159587915)	n.a.[4]
FS slope 1/n (95% Confidence Limits)	1.34 (0.69 to 1.99)	0.78 (0.60 to 0.95)	1.02 (0.72 to 1.32)	1.62 (1.32 to 1.92)	1.16 (0.50 to 1.82)			3.66 (1.80 to 5.50)	
FS (20%)[2]	2.000	10.000	>40.000	29.000	>40.000	>40.000	>40.000	>40.000	n.a.[5]

[1] Sorption coefficient ([PFAS] µg/kg sorbent / [PFAS] µg/L water) defined (extrapolated) at an aqueous concentration of 1 µg/L based on sorption isotherms listed in the **Appendix 6**. In most cases this concentration is at the high end of just outside the concentration range tested, so it can be considered a worst case sorption coefficient, as sorption coefficients generally increased with decreasing concentrations.

[2] Number of bed volumes where a break-through of 20% of the initial concentration was observed.

[3] Direct break through, no significant retention

[4] Not applicable; data did not reveal clear sorption isotherms.

[5] Not applicable; concentrations were too low to assess sufficient reduction of 6:2 FTS in the treated water

[6] The slope of the sorption isotherm (log concentration on sorbent (µg/kg) vs. log concentration in aqueous phase (µg/L)

4.5.3. Key Design criteria

Treatment strategy/treatment concept

FLUORO-SORB® is, according to the vendor, versatile in its deployment. For water treatment, the most likely concept is in *a flow-through filtration* system, similar to a fixed bed activated carbon filter. Due to short expected EBCT's, a large filter can be used for optimal removal.

4.5.4. Pre-treatment

There is not a substantial amount of information available regarding required pre-treatment. Based on contact with the suppliers, a similar pre-treatment regime is required as for GAC. As for all filter application, particle removal can always be an option if too much solids are going into the system. According to the vendor, FLUORO-SORB® is less affected by co-contaminants, showing high removal rates in the presence of diesel, dioxane, BTEX and TCE. Natural organic matter seems to have a negative effect on the removal of PFAS, although recent testing suggest lower competition with total organic carbon compared to GAC.

Contact time

The vendor claims an EBCT of 2-5 minutes is sufficient for high removal, no more details are given. Recent tests suggest an 8 minute EBCT is required when using a 200 grade material. A shorter EBCT thus means smaller filters.

Hydraulic loading rate/filter velocity

There is no information available regarding the hydraulic loading rate. Recent tests (using material Gen1 FS200/FS400) and Gen 2, suggest a hydraulic loading of 6 gal/minute per square foot, which translates to approximately 15 m/h hydraulic loading rate.

Contaminant loading rate

There is no factual information available regarding the contaminant loading rate. The supplier claims a loading rate between 0.5 and 1.75 mg/g, however this is not further substantiated with data. This indicates significantly higher loading rates than e.g. GAC, which has loading rates in the order of mg/kg magnitude. Contact with the supplier suggests a loading rate of the Gen1 (FS200/FS400) material, which is 4 times higher than bituminous GAC, depending on matrix effects and PFAS-composition. Contact with the supplier suggests a maximum sorption capacity of >15 mg/g, with breakthrough at an average sorption capacity of 0.2 mg/g with an EBCT of 10 minutes. Currently the supplier is working on a Gen2 version, which is supposed to have 4x higher loading rates compared to Gen1, with improved removal for short chain and carboxylic acid PFAS. Experimental results from this study show that loading rates were 10.5 (95%CL = 4.2-26.4) and 22.6 (95%CL = 2.3-226.0) g PFAS/kg sorbent for the GW without and with benzene spike respectively while data of the experiment with FFWW resulted in a loading rate of 1.4 (95%CL = 0.8-2.5). These loading rates were obtained at rather high aqueous concentrations of the detectable PFAS (~7 µg/L for impacted GW and even ~5.000 for FFWW). Interestingly the loading rate obtained for impacted GW is remarkably similar to the producers claim of maximum sorption capacity (>15 g/kg).

The observed loading rates are not representative for loading rates that lead to high removal percentages or acceptable effluent concentrations (sub µg/L-range) and low sorbent dosages. For ~99% reduction of PFAS concentrations from GW probably typically one to two orders of magnitude higher sorbent dosages are required, which automatically results in lower dosing rates. These levels are in line with the claimed loading rates of 0.5-1.75 g/kg and break though loading rate of 0.2 g/kg by to the supplier.

Bed lifetime

There is no information available regarding the bed lifetime. The column studies illustrate that the small scale column studies showed > 40.000 bed volumes without breakthrough for PFHxA, PFOA, and all sulfonic acids, while PFBA, PFpeA, and PFHpA showed (20%) break though at lower bed volumes ranging from 2.000 to 29.000 BV (**Table 11**) with the generic trend that the shorter the fluorinated chain is, the lower the affinity of the sorbent is. This is in line with data reported by Riegel, et al. [1].

Effect of temperature and pressure

There is no information available regarding the effects of temperature and pressure. Higher temperatures and pressures should not result in a degradation of performance.

4.5.5. Operational aspects

Energy use

The main primary energy use for the FLUORO-SORB® system is the feed pumps. There are no other significant energy consumers expected. Exact energy use is thus dependent on pump energy, and with that directly related to the hydraulic head and the flow that is to be treated, and thus comparable to activated carbon (<0,1 kWh/m^3).

Maintenance and personnel

The FLUORO-SORB® system should be comparable to an activated carbon filter, which requires relatively little maintenance and upkeep and should thus not exceed 0.5-1 day per week.

Chemical use

Based on current available information, the FLUORO-SORB® system requires no other chemicals then the sorbent itself.

Waste production

The FLUORO-SORB® system creates one waste stream: the spent sorbent. This material can then be treated comparable to other spent sorbent media, by for example incineration or landfilling. At this moment, the amount of waste produced is not known. The supplier states that they are investigating the commercial viability of regeneration process for FLUORO-SORB®.

4.5.6. Costs

Capital costs

Capital costs are expected to be relatively low, comparable to an activated carbon filter. The vessels can operate under atmospheric conditions. Exact cost calculations for full-scale systems are not available.

Operational costs

Operational costs are based on the abovementioned operational aspects. Contact with the supplier suggests material costs between EUR 2,500 and 3,000 per ton of material. The supplier notes that they expect the system to be overall cheaper than activated carbon or ion exchange, but gives no actual values.

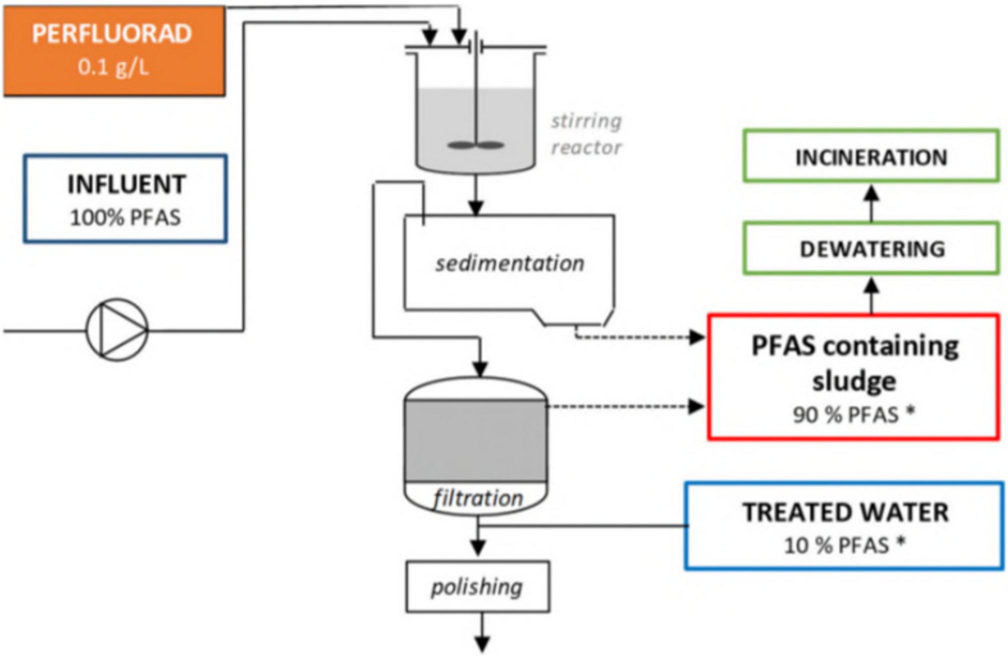
4.6. PERFLUORAD

4.6.1. Introduction

PerfluorAd is a flocculation technology that applies a proprietary liquid reactant to remove the bulk PFAS from the water. PerfluorAd is marketed by Cornelsen Umwelttechnologie GmbH (Germany).

The removal mechanism is based on both electrostatic and hydrophobic interactions between the reactant and the PFAS. Generally, PerfluorAd is applied for higher PFAS concentrations, from 0.3 µg/L onwards. The reactant is dosed in a stirred reactor, where the coagulation/flocculation takes place, followed by the removal of the PFAS-containing flocs, either by sedimentation, filtration or a combination thereof. Finally, polishing is used to obtain desired PFAS-levels. Generally, this is done with a sorptive technology like activated carbon or ion exchange resin.

Figure 18: PFAS flow diagram for treatment with PerfluorAd. Note that the values are indicative based on Riegel, et al. [1], applying 0.1 g/L flocculant dosage. Removal efficiency and target PFAS concentrations strongly depend on PFAS components to be removed and site-specific conditions (e.g. influent concentration, presence of competing substances, etc.).



4.6.2. Performance

Based on Riegel, et al. [1], the performance of PerfluorAd varies depending on dosage of the reactant and the target PFAS. Removal rates of up to 90% have been observed for some PFAS, others were only removed up to 60% at higher dosages, so no universally applied rule-of-thumb for removal can be given. It is noted that the goal of PerfluorAd is not to achieve low effluent values, since it is designed as a bulk-removal, followed by a polishing step that will reduce the PFAS to the desired concentration. The batch experiments with PerfluorAd illustrated high loading (complexation) rates. Loading rates were 61.5 (95%CL = not determinable) and 61.0 (95%CL = not determinable) g PFAS/kg sorbent for the GW without and with benzene spike respectively. The lack of the confidence limit was not necessarily a problem of poor data but rather of the result that even very low dosing of the flocculant lead to significant reduction of the PFAS with the result that no accurate CL could be determined. For FFWW the loading rate of determinable PFAS was 21.4 (95%CL = 18.0-25.5). These loading rates were obtained at rather high aqueous concentrations of the detectable PFAS (~7 µg/L for impacted GW and even 5.000 µg/L PFAS of the FFWW), such high dosages are exactly what this material is designed for (removal of bulk PFAS, rather than polishing). These observed loading rates are not representative for loading rates that lead to high removal percentages or acceptable effluent concentrations (sub µg/L-range). Probably an additional polishing step is required to reach such levels for this particular material.

4.6.3. Key Design criteria

Treatment strategy/treatment concept

PerfluorAd is applied as a pre-treatment for bulk PFAS removal, followed by a polishing step. The PerfluorAd system relies on mixing a fluid reagent with the PFAS-containing water in a stirred tank, where flocs are formed. These flocs are removed via either sedimentation, filtration or a combination of both. Generally, PerfluorAd is applied for higher PFAS concentrations, from 0.3 µg/L onwards.

Pre-treatment

The PerfluorAd itself does not require significant pre-treatment, however, it may be required to deal with some matrix effects if the following polishing step is negatively impacted. PerfluorAd removes iron, colour and particles to some extent, so less pre-treatment might be required. However there is no removal of manganese or DOC expected with the PerfluorAd system.

Contact time

There is no information available regarding the contact time in the stirred tank. Depending on the flocs and the chosen separation unit, sedimentation can take up to 40 minutes, whilst a (sand)filter for floc-separation generally has a contact time of 5-10 minutes. Depending on the chosen polishing step and its specific design criteria, an additional contact time of 2-20 minutes has to be taken into account.

Hydraulic loading rate/filter velocity

There is no information available regarding the hydraulic loading rate of the stirred tank. For flocculation, the characteristics of the flocs are not known, so loading rate is not known. Generally, depending on floc integrity and strength, for filtering through a sand filter, a filter velocity of 10-15 m/h can be assumed. Depending on the chosen polishing step and its specific design criteria, the filter velocity for this step is expected to be between 5-15 m/h.

Need for sedimentation vessel

The vendor mentions that sedimentation vessels are not always required. If a filtration stage for separation iron and/or solids is already in place, only the stirred tank is needed. It is not clear when a sedimentation vessel is required, but it stands to reason that this step is added when the flocs cause rapid blocking of the filter media, yielding a (too) high backwash frequency. At low suspended solids rates, a direct in-line coagulation can be possible.

Effect of temperature and pressure

There is no information available regarding the effects of temperature and pressure. However, with increasing temperature coagulation can be expected to perform better and with lower mixing energy, due to the decreased viscosity of the water. How relevant this effect is with regards to PFAS removal is unknown.

4.6.4. Operational aspects

Energy use

The primary energy use for the PerfluorAd system depends on the system boundaries. If a filter is already present and only the mixing vessel is required, energy use is expected to be very low. A stirring motor requires a low amount of energy compared to feed- and backwash pumps of filters. In this case, the backwash pumps will have to be used more often, so there's an increase in energy use. If there's no filter available, the feed- and backwash pumps of the filter are expected to be the largest energy consumers. This is expected to be similar to a sand- or activated carbon filter. Depending on the desire to dewater the PFAS-sludge, a dewatering installation also needs to be installed and powered. The energy use depends on the chosen dewatering technology and thus a generic rule of thumb is not available. Finally, PerfluorAd requires a polishing step, which brings along its own energy use. This is not described here.

Maintenance and personnel

There's no explicit data available on maintenance and personnel, however, based on the technology description, it is expected that it does not require significant amounts of attention. Coagulation/flocculation followed by filtration and/or sedimentation, combined with dewatering is always more demanding than just filtration. The exact time needed is not known.

Chemical use

The vendor claims that the reactant can be tailor-made for precipitation of specific PFAS. Dosing of the reagents lies between 25 to 2,000 mg/L, depending on the matrix and the desired removal rate. A higher dosing yields a higher removal rate, especially for short-chain PFAS. Exact use is thus highly dependent on matrix and desired yield and therefore no rule-of-thumb values can be given. The batch experiments are in line with the vendors dosing range, as FFWW as well as impacted GW show significant removal at PFAD dosages as low as 10 mg/L for impacted GW (**Figure 6**) and 1,000 mg/L for FFWW (**Figure 5**).

Waste production

The primary waste stream is the PFAS-containing sludge. The amount of waste directly correlates to the dosing ratio, the amount of co-precipitated contaminants (iron, colour, particles) and the ability to dewater the sludge. Exact waste production is thus highly dependent on matrix and desired yield and therefor no rule-of-thumb values can be given. The vendor claims that the active ingredients of PerfluorAd are biodegradable, however PFAS-containing sludge will highly likely have to be dewatered and subsequently dealt with according to local regulations, for example incineration.

4.6.5. Costs

Capital costs

There are no cost calculations available, however, compared to a stand-alone sorptive media filter, capital costs are expected to be at least double since two filter units are required, along with the mixing vessel, storage for the reagent and a dewatering step for the sludge.

Operational costs

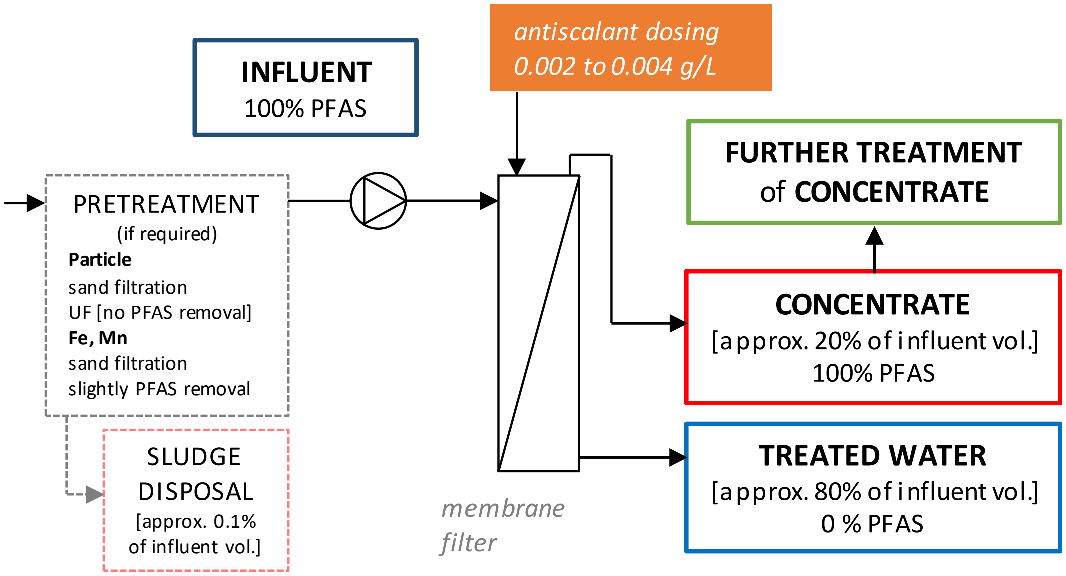
There are no cost calculations available. The main goal of PerfluorAd, however, is to decrease the operational costs of PFAS treatment by strongly concentrating the bulk of the PFAS in the sludge, so that the (expensive) sorbent has a longer lifetime.

4.7. NANOFILTRATION

4.7.1. Introduction

Nanofiltration is a pressure based separation technology that applies dense membranes. This technology is not supplier-specific, several different technology providers have their own variation of these membranes available. The removal mechanism is the non-target removal via physical separation based on molecular weight/size, along with chemical interactions with the membrane material. The technology yields two water streams: the concentrate and the treated water, as will be discussed below.

Figure 19: PFAS flow diagram for treatment with nanofiltration. Note that the values are indicative based on Riegel, et al. [1]. Removal efficiency and target PFAS concentrations strongly depend on PFAS components to be removed and site-specific conditions (e.g. influent concentration, presence of competing substances, etc.).



4.7.2. Performance

NF membranes will reject solutes such as PFAS while water permeates through the membrane. The rejections depends on the molecular weight cut-off of the membrane and other membrane characteristics such as surface charge. Generally, >90% of the PFAS can be removed, for many >99% is attainable. Within the experiments initial removal was indeed 90%-95% but with longer operation, the removal dropped to the point where the permeate nearly reached the concentration in the feed water. While the membrane started fouling and the transmembrane flow also dropped. Apparently the FFWW contained particulate material that corrupted membrane functioning and separation.

4.7.3. Key Design criteria

Treatment strategy/treatment concept

Generally, the treatment concept is quite simple: a feed pump pre-pressurizes water that is fed to the membrane units. Besides the membrane unit itself, extensive pre-treatment is required (discussed below). Membrane cleaning is also an important aspect. The concentrate stream, approximately 10-20% of the original water flow, generally needs further treatment, since it’s still a relatively diluted, watery volume.

Pre-treatment

Even though some membranes are more resistant to particulate matter, a general rule of thumb is that the water needs to be free of particles, iron and manganese to levels of <1 FTU turbidity, <0.05 mg/L iron and <0.02 mg/L manganese. Sand filtration is a common-pretreatment, as well as micro- or ultrafiltration. These steps do not retain PFAS, so the backwash water can be discharged safely. Acid and/or antiscalant dosing might be required to prevent scaling of sparingly soluble salts like $CaCO_3$, $CaSO_4$ or $BaSO_4$.

Filter type

There are several options available for membrane units that can be applied depending on the water matrix and the operating philosophy of the client. The most well-known examples are tubular, spiral-wound and hollow fiber membranes. Tubular membranes can handle viscous liquids with relatively high suspended solids and can be cleaned both mechanically or chemically. Spiral wound membranes are known for their space-efficiency and small footprint that can handle large throughputs. Downside of this is that these membranes lose robustness and thus require more careful pre-treatment. Hollow fiber membranes provide benefits of both: relatively small footprint that can be cleaned relatively easily and that can handle particles better than spiral wound. Downside of hollow fiber is that these are maxed out at a TMP of 2 bar. Furthermore, different materials can be used. Ceramic and polymer are the most common materials. Ceramic is more suitable for hostile environments (solvents, wide pH ranges etc.), otherwise polymeric membranes are the standard.

Pore size

Nanofiltration has pore sizes ranging from 0.5 to 2 nm. Increasing the pore-size yields lower removal, since smaller molecules can pass through, but decreases energy use. Pore size can, alternatively, be defined as the amount of Dalton to be filtered. Dalton is a molecule weight measurement, corresponding to the molecular weight [g/mol] and should be rounded down generously. Commonly occurring PFAS are ranging from 200 to 700 g/mol. For example, PFOS and PFOA have molecular weights of 500 and 414 g/mol, respectively. If a water is impacted with both short and long chain PFAS, one should consider a pore size of 200 Dalton. This lowest molecular weight, thus the aimed size of the pores, is called the molecular cut off weight.

Permeate flux

Another key design criterion is the permeate flux. This is a parameter defined as the amount of liquid transported through one unit of membrane surface per unit of time [L/m^2.hr]. The permeate flux and the ratio of the main treated water with respect to the concentrate depends on the chosen membrane, the water matrix and the transmembrane pressure. This ratio is also known as the recovery [%]. Maximum recovery is 90%, usually 80% recovery is a safer rule of thumb for proper treatment. Initial transmembrane flow and removal were acceptable, but with longer operation in order to reach sufficient recovery (~80%) membrane started fouling and the transmembrane flow also dropped resulting in very long operation (>3 days) in the pilot experiment, while also the PFAS removal dropped. Apparently the FFWW contained particulate material that corrupted membrane functioning and separation, suggesting that membrane treatment require some pretreatment step to remove the constituents that corrupt membrane functioning.

Trans-membrane pressure

Due to the small pores of the membranes, a high pressure of about 4 to 10 bars has to be applied to treat drinking water with these technologies. Generally, the range will be closer to 2-4 bar, 10 bar is on the higher end. The pressure drop (loss in pressure at the end of the filter) is usually around 0.5 to 1.5 bar. When operating in series, the pressure drop is the sum of all filters. When working in parallel, only one pressure drop can be accounted for. Pumps and piping should be chosen adequately considering these pressures.

Effect of temperature and pressure

There is no quantified information available regarding the effects of temperature and pressure on PFAS removal. However, increasing temperatures decrease the viscosity of the water which in turn has positive effects on the membrane flux and requires less transmembrane pressure for treatment. This results in a lower pre-pressure, resulting in lower energy use. Water that is already pressurized can, depending on the pressure, reduce energy use of pre-pressuring the filters. If the pressure of the water exceeds the maximum pressure of the chosen membrane a pressure release or pressure reduction step has to be implemented.

4.7.4. Operational aspects

Energy use

The major factor for energy use is the pumps. This is also the major cost factor (see below). Riegel, et al. [1] gives an energy use for NF of 0.4 kWh/m^3. Additionally, pre-treatment and concentrate treatment also require energy, depending on the choices that are made there.

Maintenance and personnel

If set up correctly, membranes should be able to run relatively easily, although they always require significantly more attention than media filtration. One should account for 2-5 days per week (0.5-1 FTE) to keep a membrane unit up and running.

Chemical use

Depending on the chosen membrane and the matrix, cleaning with water as backwash could be sufficient, or more extensive cleaning programs are required such as chemically enhanced backwashing and/or dosing of anti-scalant. The exact amounts also depend on the matrix. For anti-scalant a dosing of 0.002-0.004 g/L is a good starting point.

Waste production and concentrate treatment

There is no waste in the traditional sense of solid waste, however, the concentrate does need to be treated further. This is a significant volume, up to 20% of the original volume. There are several options available for this treatment, e.g. reverse osmosis membranes that concentrate the PFAS into a smaller volume, or one could use coagulant/flocculant based treatment on the concentrate stream. Eventually, the PFAS has to be disposed of. Concentrate treatment is a significant part of NF operations, but due to the varying options is not further discussed here.

4.7.5. Costs

Capital costs

Membrane installations are generally significantly more expensive with regards to filtration units. As mentioned, membrane units already require media filtration as pre-treatment. Exact costs are strongly dependent on the amount of pre-treatment required and the chosen membrane units. Generally, it can be expected that a full NF train has capital costs of 2 to 5 times that of a general (activated carbon) media filter.

Operational costs

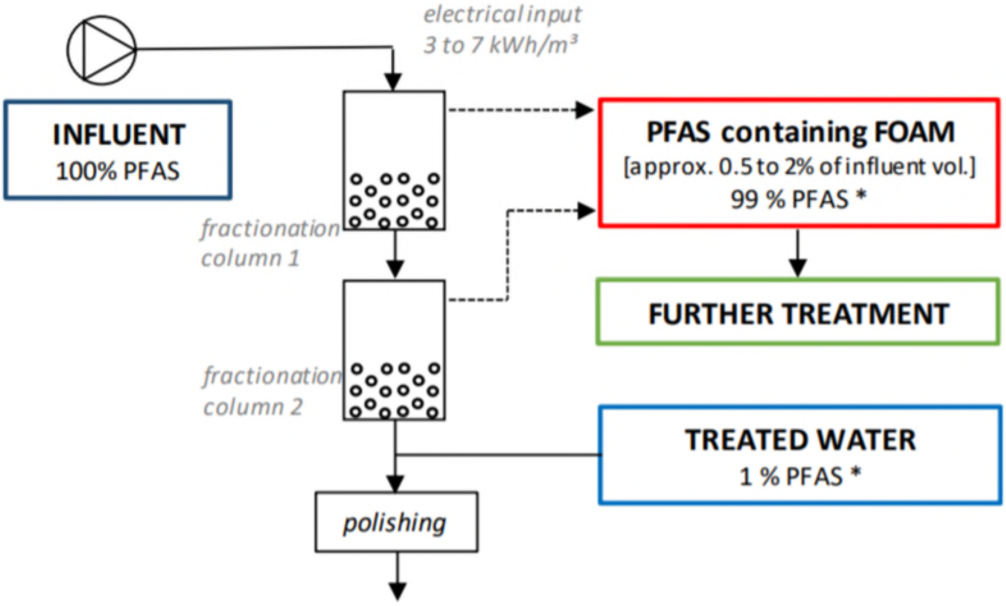
As mentioned, energy costs are a major factor in membrane filtration. For energy alone this amounts to about EUR 0.05-0.10 per m^3 treated, depending on energy use and local energy prices. Furthermore the membranes have to be replaced. Replacement frequency depends on operational regime and water matrix. The waste/concentrate has to be handled, which can be a significant cost factor depending on the chosen downstream processing. Based on this, there is no clear-cut rule-of-thumb cost for treatment with NF.

4.8. FOAM- AND OZO FRACTIONATION

4.8.1. Introduction

Foam fractionation applies injection of compressed air (foam fractionation) or ozone (ozo fractionation), which leads to the formation of bubbles into the water. The PFAS surfactants adhere to the bubble walls and the PFAS-enriched foam is collected at the aqueous surface for further (destruction-based) treatment. Foam fractionation is marketed by OPEC systems (AUS) under tradename SAFF (Surface Active Foam fractionation). Ozo fractionation is marketed by EVOCRA under tradename OCRA (ozofractionative catalyzed reagent addition). In both cases, the removal mechanism relies on the foam-forming/surfactant qualities of the PFAS. PFAS tend to favour air-water interfaces, due to their hydrophobic per- and polyfluorinated carbon chains and the hydrophilic functional groups.

Figure 20: PFAS flow diagram for treatment with foam fractionation. Note that this scheme is generic for both SAFF and OCRA. The values are indicative based on Riegel, et al. [1]. Removal efficiency and target PFAS concentrations strongly depend on PFAS components to be removed, chosen system and site-specific conditions (e.g. influent concentration, presence of competing substances, etc.).



4.8.2. Performance

Both SAFF and OCRA showed high removal rates in field-trials. Removal of 99-100% removal were observed for both systems without polishing step. SAFF was able to remove precursors and short-chain PFAS to some extent as well. OCRA has the added effect of oxidizing some oxidizable precursors into persistent PFAS. Especially when considering the addition of a polishing step, both systems can handle very high influent concentrations and still yield >99.9% removal overall. Within the pilot experiments such high removal rates were not obtained. Rather ~60-90% were observed. The formation and stabilization of the foam seemed to be rather tricky, especially with the heavily impacted FFWW, so potentially the experimental set up was not optimal to fully enable PFAS removal.

4.8.3. Key Design criteria

Treatment strategy/treatment concept

SAFF applies a main primary contactor where water is treated and the foam is removed. This primary contactor treats water in batches, thus for continuous operation multiple parallel contactors are required. A second and (optional) third step can be added to concentrate the foam further to reduce the amount of waste. The primary water flow can be polished if desired/required. OCRA applies a serial treatment with two or three consecutive treatment steps, followed by a polishing step.

Pre-treatment

For both foam- and ozo fractionation, significant effects of the matrix or co-contaminants on PFAS removal are not to be expected. If a polishing filter is applied, some more attention to pre-treatment can be beneficial, for example to remove iron, manganese or suspended solids to a further extent. Foam fractionation showed an effect of salinity increase, yielding higher amounts of non-PFAS surfactants in the foam. Ozo fractionation has some impact from high levels of organic compounds. The PFAS-removal is not affected according to Riegel, et al. [1], because ozone depletion is not critical for the main treatment mechanism. The presence of oxidisable compounds do increase the ozone use and thus the operational costs. This oxidation yields a cleaner effluent, which is an added benefit of the OCRA system.

Contact time

Exact contact times for both systems are not publicly available at the time of writing. Based on contact with the vendors, a contact time of approximately 30-45 minutes seems a good rule-of-thumb. As mentioned the foam fractionation system works as (sequencing) batch, whilst ozo fractionation is more geared towards a continuous system.

Hydraulic loading rate

For both systems, hydraulic loading rate is not defined.

Bubble size

Bubble size is an important design parameter that can be influenced by amongst others gas choice (ozone yields slightly smaller bubbles then air), type of aeration system (spargers, recirculation with side stream injection) and the water matrix. Generally speaking, the smaller the bubbles, the larger the air-water interface and thus a better removal. Smaller bubbles tend to have lower upward velocity and with that increase the required contact time. For both foam- and ozo fractionation, bubble sizes are in the micro-/nanobubble range, varying from tens of nanometers to tens of micrometers.

Concentration factor

Concentration factor is a dominant cost-determining parameter, since the PFAS-containing concentrate has to be treated downstream. The smaller this flow, the lower the waste costs are. Foam fractionation with the SAFF system with a three-stage treatment/concentrator set up is designed to reach 0.0025% concentrate in volume. The vendor claims that further concentration factors can be reached in the (near) future. Ozo fractionation in the current two-stage process reaches 0.5 to 2%.

Effect of temperature and pressure

There is no information available regarding the effects of temperature and pressure, however, elevated temperatures result in lower gas transfer rates and lower saturation levels. This can have an adverse effect on the bubble size and stability. Higher pressures could result in a higher solubility of gas, thus decreasing the amount of bubbles with a negative effect.

4.8.4. Operational aspects

Energy use

Energy use varies between the two systems. Generally, the air injection is comparable per contactor step: pump energy is required to feed the contactors and a recirculation pump or a compressor is required to feed the gas to the liquid phase. Exact energy consumption figures for foam fractionation are not known, however since it is only applying pumps and compressors, it is expected not to significantly exceed an activated carbon filter, so energy use of approximately 0.1 kWh/m^3 treated should be attainable. Ozo fractionation requires an additional energy consumption due to the production of ozone either from ambient air or liquid oxygen. This is a significant energy user. Overall, the vendor estimates energy consumption at 3 to 7 kWh/m^3 treated.

Maintenance and personnel

The foam fractionation system is relatively simple and mostly automated. The high concentration factor means very little handling of waste streams. Exact maintenance and personnel values are not known, but it is expected not to significantly exceed an activated carbon filter, so this should not exceed 1 day per week. Ozo fractionation is, as mentioned, very similar to foam fractionation with the difference that the ozone system requires attention and maintenance and the waste needs to be handled more often. These are not expected to be more than double that of foam fractionation, so between 1-2 days per week.

Chemical use

Foam fractionation does not require the addition of chemicals, since it applies ambient air. Ozo fractionation requires the use of ozone. Ozone has to be made on-site, either from ambient air via e.g. pressure swing sorption or from liquid oxygen. The ozone use is not known and thus the amount of liquid oxygen is not known.

Waste production

As mentioned in the subchapter on concentration factor, foam fractionation produces 0.0025% of the influent water as concentrated waste. Ozo fractionation produces 0.5-2%. Besides this, spent sorbent from the polishing step is a waste production that both systems share but is not specified further, as well as pre-treatment waste sludge from e.g. solids removal.

4.8.5. Costs

Capital costs

Capital costs for the contactor systems are relatively low as these are relatively simple. The vessels operate under atmospheric conditions. However, a general rule-of-thumb value for CAPEX is not available. For the ozo fractionation system, it should be noted that the production- and application of ozone is capital intensive, besides the ozone production step, additional safety measures have to be implemented, increasing the CAPEX. CAPEX for the ozone system depends partially on scale: small-scale ozone units generally apply pressure swing sorption, which increases CAPEX but results in a lower OPEX because liquid oxygen is not required. Liquid oxygen, however, increases ozone production efficiency, so has its own advantages. The efficiency balance tends to favor ozone production from liquid oxygen for larger scale systems. The ozo fractionation system is expected to be significantly more expensive than the foam fractionation system, however how much more expensive is difficult to predict and thus no general rule-of-thumb costs are available.

Operational costs

Energy use is a common cost factor for both foam fractionation and ozo fractionation. For pumps and aeration, this is roughly similar, however ozo fractionation requires significantly more energy due to the production of ozone. Exact energy uses varies from 0.1 kWh/m^3 for foam fractionation and 3-7 kWh/m^3 for ozo fractionation. At energy prices of 0.1 EUR/kWh, this yields 0.01 EUR/m^3 and 0.3-0.7 EUR/m^3 respectively. Waste handling is another significant cost. Based on the concentration factors and incineration costs of 1,000 EUR/m^3, based on price point 2019/2020 for incineration of PFAS-containing waste in the Netherlands, some insight can be given into the OPEX. For foam fractionation with a concentration factor of 0.0025%, this means that per m^3 treated, 0.025 L of waste is produced, costing EUR 0.025 to treat. Waste treatment costs thus come down to EUR 0.025/m^3 treated. For ozo fractionation, with 0.5-2%, this comes down to EUR 5-20 per m^3 treated. Further operational costs, like personnel and chemical use for the ozo fractionation are not known, so a more detailed breakdown of operational costs is not available.

5. DISCUSSION AND CONCLUSIONS

5.1. DISCUSSION

This chapter is the integrated discussion of the experimental research and evaluation of treatment technologies to remove PFAS from PFAS impacted GW and FFWW.

Within this study two types of contaminated water were studied. One being PFAS impacted GW and the other FFWW. Impacted GW and FFWW might be considered at both ends of the spectrum of PFAS contamination. The concentration of (detectable) PFAS differed almost by three orders of magnitude, with GW PFAS concentration in the µg/L range and FFWW PFAS concentration in the mg/L range. When samples were oxidized by a TOP analysis, the detectable PFAS concentration in the FFWW increased with over an order of magnitude, while the concentration in the impacted GW was not affected significantly. In addition to the PFAS concentration, the PFAS composition also differed. The FFWW was dominated by 6:2 FTS, while the impacted GW contained various PFAS such as PFOS and PFOA. Finally, the FFWW contained much more aromatic and mineral oil residues, metals and organic and inorganic particles of undefined composition than the impacted GW. The impacted GW and FFWW are therefore considered to provide the width of the application range and are therefore very suitable to test treatment technologies.

The differences in the two types of PFAS impacted waters lead to different treatment results. By design and removal mechanism, physical separation techniques such as foam fractionation appeared to be more suitable to (pre) treat heavily contaminated while sorption techniques with the various tested sorbents were more suitable to treat (polish) cleaner matrices. The table below give a very generic overview of the applied treatment techniques and materials with some notes on the applicability of the technique for the tested waters.

5.1.1. Sorption

The overview illustrates that the sorbents were capable of treating both types of water, but to remove PFAS from heavily contaminated firefighting water clearly requires much higher sorbent dosages. As initial concentrations are very high, such reductions are not sufficient to reduce PFAS concentrations to acceptable levels [8]. Therefore, it is not advisable to apply the tested sorptive techniques to FFWW as a single step treatment, while merely sorption techniques application could effectively treat PFAS impacted GW. Therefore only impacted GW was used in the column studies with GAC, FS and CP, while the FFWW was not treated in the column tests.

Bench top flocculation and membrane studies are conceptually very similar to their full scale treatment application while batch sorption tests the intrinsic sorption capacity of the tested sorbents but the test set up is conceptually different from their full scale treatment application Therefore batch sorption experiment cannot directly predict the performance in column studies. In addition, one should be careful in over-interpreting batch sorption and small-scale column studies. Small-scale column studies are not directly translatable to larger columns or full scale applications since the smaller grain size of the sorbent and shorter hydraulic retention might affect sorption kinetics and surface characteristics. Nevertheless, the results can be considered useful as determination of differences between sorbents in a relative manner, and are therefore functional in selecting the sorbent for pilot / full scale testing.

5.1.2. Flocculation

The flocculant appeared to be more effective in (pre)treating FFWW than the sorbents when compared on the basis of the sorbent/reagent mass per L water. The observed doses that resulted in significant reduction of PFAS concentrations were in the range of 10 mg/L for impacted GW and 1,000 mg/L for FFWW. In general, the flocculation appears to be able to efficiently (pre)treat the heavily contaminated FFWW, while the impacted GW with lower PFAS loads showed incomplete removal. Potentially this is due to the incomplete flocculation or the incomplete sedimentation and separation of the flocs, which leads to residues of PFAS in the aqueous samples. Therefore, floc formation and separation of water and precipitated material requires extra attention in future testing and full scale application to optimize performance. Nevertheless the techniques seems to be suitable to (pre)treat heavily contaminated water such as FFWW, but requires optimization to reduce aqueous concentrations from less contaminated water to levels near zero.

5.1.3. Separation by foam or membrane filtration

Two non-sorptive separation strategies were applied, being foam fractionation (with air and ozone) and membrane separation. Both impacted GW, benzene spiked GW and FFWW were applied in foam fractionation pilot set up, while only FFWW was treated by membrane filtration. Similarities and differences were observed between these techniques. Both techniques had difficulty in treating FFWW, although due to different reasons. The membrane treatment resulted in membrane fouling and low transmembrane flow and poorer removal after longer operation, while the foam fractionation (initially) led to excessive foam formation, hampering separation. Both these complications were not surprising as the heavily contaminated FFWW contained high loads of particles and surfactants that lead to these respective complications.

Separation techniques can be evaluated by two parameters, the removal efficiency and the recovery. The membrane separation showed 90-95% good initial removal before fouling but removal dropped significantly with longer operation. The foam fractionation resulted in removal of 60-90%. When looking at the recovery as permeate or as treated water, the foam fractionation enables to recover around 98-99% of the treated water while the recovery of the membrane treatment was lower (~80%), took several days and resulted in dropping treatment performance with increasing recovered volume.

The membrane treatment leads to a concentrate and treated water. Since the experiments show that the concentration ratio of filtrate and feed water decreases to marginal differences with longer operation to reach preset recoveries. The membrane treatment might not be suitable to treat such dirty matrices such as the FFWW and result in acceptable removal, recovered water fractions within a short time. This suggests that some form of pretreatment is required to optimize the performance.

The treatment performance of foam fractionation was not strongly affected by the treated matrix, and even seemed to perform slightly better for benzene spiked impacted GW when compared with the impacted GW without benzene, suggesting that organic solvents might enhance the foam formation or constitution and thereby enhancing removal. FFWW showed similar to higher removal rates than impacted GW, but the difference in the PFAS between the water (and potential oxidation of precursor PFAS during treatment of FFWW) does not allow direct comparison of the two types of water. Nevertheless, the results of the benzene spiked GW, and performance of the FFWW suggest that the foam fractionation is able to cope with heavily contaminated water sources, but requires optimization for the matrix it is applied to.

For both separation techniques applied to FFWW, the removal is insufficient to obtain PFAS concentrations that are acceptable for emission, as residues are still in the (low) mg/L range. The separation treatments are suitable as a pre-treatment step, but additional treatment is advisable.

5.1.4. PFAS removal in relation to matrix composition and physicochemical characteristics of the PFAS

Impacted GW contained a series of PFAS. The detected PFAS have carboxylic acid and sulfonic acid head groups and their carbon chain length varies between 4 and 8. Throughout the experiments it can be observed that (generally) the shorter the PFAS chain, the lower the removal. In addition, the carboxylic acids often show lower removal than their sulfonic acid counterparts with the same carbon chain length. This was for example observed in the batch sorption tests and column studies (**Figure 7**, **Figure 9**) and also, although a little less explicitly presented, in the membrane study and the batch experiment with flocculant (**Figure 10**, **Figure** 12).

It is known that environmental waters contain even shorter chain PFAS, that were not analysed in this study [21]. These compounds will be challenging for all treatment technologies tested, as they have lower sorption affinities and are better water soluble. It is expected that they also permeate more easily through membranes due to their smaller sizes and shorter hydrophobic tails. Furthermore, they are less likely fully accumulating in foam layers and are more easily out competed by BTEX and other petrochemicals. We therefore strongly recommend to study a wide spectrum of PFAS when assessing treatment efficiency in field or in pilot tests in future, as most likely not the long chain but the short chain PFAS will be the bottleneck for the treatment efficiency.

5.1.5. Evaluating and combining techniques towards practical application

The results with the different sorption materials, the flocculation tests, the membrane treatment and the foam separation indicate that their performance varies under different conditions. We have seen that the sorbents are generally more effective in rather clean matrices such as impacted GW, while the foam fractionation and the flocculant appear to be suitable (as well) for more heavily contaminated matrices. The membrane treatment was not tested for impacted GW, but results of the FFWW indicate that membrane fouling is a risk, suggesting that cleaner matrices are preferred (i.e. pre-treatment is preferred). We therefore can conclude that impacted GW can be treated with one of the sorbents directly, while the FFWW requires a multi-barrier approach, as the sorbents were able to remove PFAS but required excessive sorbent dosages (g/L treated water). This is, technically feasible, but often not desirable from a financial (OPEX) or environmental (CO_2-footprint) point of view, yielding high sorbent uses per year.

Therefore, likely a multi-barrier approach is interesting for some sites and specific matrices. This means that a general solution is not available and a case-by-case assessment must be made. An initial treatment removes bulk contamination including co-contaminants and a polishing treatment that reduces PFAS loads to acceptable concentrations. Among the techniques applied, presumably either a combination of foam fractionation and sorbent or flocculant and sorbent appear to be the most promising for further experimentation, and potential application.

Furthermore, reactive treatment technologies were not tested in this study. However in combined treatment systems these technologies may prove attractive as well. The optimal (combination of) treatment technologies is therefore dependent on the treated matrix and the wishes of the end user. In order to remove PFAS from impacted aqueous phases both effectively (sufficient removal) and efficiently (costs, practical issues) requires not only the selection of the most suitable treatment technologies, but also the optimization of treatment conditions.

5.1.6. Lookup table

To get an idea of the advantages and drawbacks of each of the technologies, as discussed in the previous paragraph, a lookup table has been constructed. This table gives the advantages and disadvantages of each technology along with the marked differences and key design parameters and can be used to get an overview of the findings in this study (**Table 12**). The table provides a basis to select and apply the best available treatment technologies to mitigate (further) PFAS contamination. One should note that the interpretation is based on various experiments and literature data, in some cases performance of techniques differed between the tested contaminated waters, so performance was averaged. This table should support the considerations of technologies, but additional information is required to enable a balanced evaluation for each specific situation.

Table 12: Lookup table on advantages and disadvantages of treatment technologies. Colours ranging from red (-- very poor) via orange (-poor) and yellow (fair) to green (+, good and ++, very good); n.a. (grey) is not assessed, or the data is unknown.

	Removal mechanisms	Performance		Treatment strategy	Pre-treatment			Main treatment				Effects of temperature and pressure	Operational aspects				Costs	
		Short Chain PFAS	Long chain PFAS		Turbidity	Fn/Mn	TOC	Contact time	Hydraulic loading rate /filtration velocity	Contaminant loading rate	Bed lifetime		Energy use	Maintenance and personnel	Chemical use	Waste production	CAPEX	OPEX
Sorption																		
DESOTEC Granular Activated Carbon (GAC)	Hydrophobic, (pi-pi) electrostatic and ionic interactions	+	++	Fixed bed filtration, lag/lead configuration	-	-	-	20-30 min	10- 15 m/h	+	+	minimal	0	0	++	+	0	--
Rembind® (RB)	Hydrophobic- , electrostatic- and (an)ionic interactions	+ $^{2-3}$	+	2 options: 1: discontinuous batch with sedimentation 2: mixed media filter with sand	-	-	-	5-10 min, >80% sorption	unknown	+	+	unknown, expected minimal	0	0	+	+	0	unknown
Cyclopure DEXSORB+® (CP)	Hydrophobic- and electrostatic interactions	-	++	Fixed bed filtration, lag/lead configuration, with on-site regeneration possible	-	0	++	3-10 min	unknown, expected around 10 m/h	+	0	unknown, expected minimal	0	0 without regeneration - with regeneration	--	++	+	0
PolyQA-Osorb® (PQ)	Hydrophobic- and ionic interactions	0	+ (a)	not clear yet, possible fixed bed filtration with regeneration	-	--	--	1-5 min	unknown, expected around 10 m/h	0	n.a.	unknown, expected low. Possible pressure effects on swelling of material	0	0 without regeneration -1 with regeneration	--	+	+	0
FLUORO-SORB® Des+ (FS)	Hydrophobic and electrostatic interactions	+	++	Flow-through filter or batch treatment with sedimentation or floatation	-	-	0	2-10 min	up to >15 m/h	+	+	unknown, expected minimal	0	0	++	+	+	0
Flocculation																		
PerfluorAd (PFAD)	Hydrophobic- and electrostatic interactions	+ (b)	++ (b)	mixing tank, sedimentation, filtration	+	0	+	up to 60 min	for filtration up to 15 m/h	++	n.a.	unknown, expected better performance with increasing temperature	-	-	---	-	-	-
Other separation technologies																		
Nanofiltration (c)	Size exclusion	-	+	Filter units	0 (d)	0	0 (d)	n/a (short)	n/a	n.a.	n.a.	Increasing temperature has positive effects on operational aspects, increased pre-pressure reduces pump energy	-	-	--	---	--	--
Foam fractionation WITH OZONE	Surface active characteristics of PFAS	-	+	multiple contact tank(s) in series with compressed ozone bubbles	+	+	+	20-40 min	n/a	n.a.	n.a.	Unknown, but higher temperatures negatively affect gas transfer and saturation, this might have adverse effects	---	-	-	0	+	-
Foam fractionation WITHOUT OZONE	Surface active characteristics of PFAS	-	0	Discontinuous batch contact tank with compressed air bubbles	+	+	+	20-40 min	n/a	n.a.	n.a.	Unknown, but higher temperatures negatively affect gas transfer and saturation, this might have adverse effects	0	0	++	++	+	+

n.a. not assessed
a) determination of adsorption coefficients was complicated for GW
b) based on removal performance for FFWW
c) initial performance before fouling
d) suspended solids and TOC were higher than operational range stated by vendor

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7. GLOSSARY

BOD	Biological Oxygen Demand
BS	Benzene Spiked
BV	Bed Volumes
C	Carbon
CAS	CAS Registry Number
CF	crossflows
CL	Confidence Limit
COD	Chemical Oxygen Demand
CP	Cyclopure DEXSORB+®
EBCT	Empty Bed Contact Time
F	Fluor
FAU	Formazin Attenuation Units
$FeCl_3$	Iron(III)chloride
FF	Foam fractionation
FFWW	Firefighting Wastewater
FS	FLUORO-SORB® Des+
FTS	Fluorotelomere sulfonic acid
FTU	Formazine turbidity unit
GAC	Granular Activated Carbon
GW	Groundwater
H	Hydrogen
HDPE	High Density Poly Ethylene
IEX	Ion Exchange
K_{sw}	Sorption coefficient
KWR	KWR Water Research Institute
LC	Liquid Chromatography
LC-MS^2	Liquid Chromatography Tandem Mass Spectrometry
MeOH	Methanol
MRM	Multiple Reaction Monitoring
NC	Negative Control
NF	NxFiltration
NH_4OH	Ammonium hydroxide
NOM	Natural Organic Matter
NTU	Nephelometric Turbidity Units
OCRA	Ozofractionative Catalyzed Reagent Addition

OECD	Organisation for Economic Co-operation and Development
ORP	Oxidation-Reduction Potential
PFAD	PerfluorAd
PFAS	Poly/Per-Fluoroalkyl Substances
PFCAs	Perfluorocarboxylic acids
PFOS	Perfluorooctanesulfonic acid
PFSAs	Perfluorosulfonic acids
PP	Polypropylene
PQ	PolyQA-Osorb®
PSU	Pressure Swing Unit
PTFE	Polytetrafluoroethylene
QA	Quaternary Amine
RB	Rembind®
RO	Reverse Osmosis
SAFF	Surface Active Foam fractionation
SOMS	Swellable Organically Modified Silica's
SPE	Solid-Phase Extraction
TCE	Trichloroethene
TMP	Transmembrane Pressure
TOC	Total Organic Carbon
TOP assay	Total Oxidizable Precursor assay
TPs	Transformation Products
TRL	Technology Readiness Level
TZW	DVGW-Technologiezentrum Wasser
UvA	University of Amsterdam

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APPENDIX 1: SAMPLE PREPARATION AND CHEMICAL ANALYSIS OF PFAS

This appendix provides details of applied analytical methods and data analysis. ***Table 14*** *lists PFAS included in various analysis protocols and regulatory lists. Currently, methods and protocols are improved and regulation is evolving quickly due to the attention in society for this group of chemicals.*

Sample treatment

Firefighting wastewater (FFWW) and PFAS impacted groundwater (GW) were collected from the 20 L containers for analysis or use in experiments. The aqueous phase was sampled at least 1 day after delivery and storage at 4°C in the dark in order to let solid residues precipitate at the bottom of the container and stabilize the floating oil layer on the surface of the water. Maximum storage time was 4 months. The GW samples were used as received, the FFWW samples were diluted 100-fold with solvent after extraction to enable analysis of high contaminant loads that were otherwise outside (linear) calibration curves and reduce potential matrix effects.

For the continuously operated column studies, the impacted GW was filtered at KWR one day after arrival (Friday 19th of June 2020) by a 1 µm cartridge filter to remove particles that could block the small scale columns, as shown in **Figure 21**. The filtrated water was stored in a 550 L stainless steel tank at 20℃, connected to the small scale columns set up.

Figure 21: 1 µm cartridge filters used (top) and unused (bottom) to filtrate the water

Selected samples were oxidized according to the TOP assay according to Houtz and Sedlak [12]. TOP assay is a standardized pre-treatment of water samples or sample extracts designed to expose underlying PFAS not amenable to standard analysis, see **Appendix 7**). This assay illustrates the potential transformation products that are formed from the PFAS contamination after long residence times in the environment (under oxic conditions) and is indicative for the fractions of PFAS that are missed by measuring a selected set of PFAS. Perfluorinated carboxylates and sulfonates are stated to remain intact under the conditions of the assay [22].

Chemical analysis

Within this study, 20 PFAS were selected based on their use and related potential environmental relevance, their diversity in their physicochemical properties and the available sensitive and robust analytical techniques at UvA. **Table 13** lists the test substances.

Table 13: The 20 selected PFAS test substances

Substance	Abbreviation	Internal standard[1]
PFSAs		
Perfluorobutane sulfonate	L-PFBS	$^{18}O_2$ PFHxS
Perfluorohexane sulfonate	L-PFHxS	
Perfluorooctane sulfonate (linear)	L-PFOS	$^{13}C_8$ PFOS
Perfluorooctane sulfonate (branched)	Br-PFOS	$^{13}C_8$ PFOS
Perfluorodecane sulfonate	L-PFDS	$^{13}C_8$ PFOS
PFCAs		
Perfluorobutanoic acid	PFBA	$^{13}C_4$ PFBA
Perfluoropentanoic acid	PFPeA	$^{13}C_2$ PFPeA
Perfluorohexanoic acid	PFHxA	$^{13}C_2$ PFHxA
Perfluoroheptanoic acid	PFHpA	$^{13}C_4$ PFHpA
Perfluorooctanoic acid	PFOA	$^{13}C_8$ PFOA
Perfluorononanoic acid	PFNA	$^{13}C_9$ PFNA
Perfluorodecanoic acid	PFDA	$^{13}C_6$ PFDA
Perfluoroundacanoic acid	PFUnA	$^{13}C_7$ PFUnA
Perfluorododecanoic acid	PFDoA	$^{13}C_2$ PFDoA
Perfluorotridecanoic acid	PFTrA	$^{13}C_2$ PFTrA
Perfluorotetradecanoic acid	PFTeA	$^{13}C_2$ PFTeA
PF Sulfonamide		
Perfluorooctane sulfonamide	PFOSA	$^{13}C_2$ PFOSA
Fluorotelomer sulfonates		
4:2 Fluorotelomer sulfonate	4:2 FTS	$^{13}C_2$ 4:2 FTS
6:2 Fluorotelomer sulfonate	6:2 FTS	$^{13}C_2$ 6:2 FTS
8:2 Fluorotelomer sulfonate	8:2 FTS	$^{13}C_2$ 8:2 FTS

[1] Recoveries were automatically corrected with the appointed internal standard

Preventing cross contamination

Because of the ubiquitous presence of PFAS, care is taken to work in clean (surfactant-free) lab conditions. Polytetrafluoroethylene (PTFE) materials are not being used in the lab materials and instruments. Even clothes of the researcher in the lab are selected in order to prevent cross contamination by, for example, Gore, Gore-Tex fabrics and dirt repelling sprays used to shield clothing and shoes. Furthermore, due to the tendency of PFAS to sorb to glass surfaces, high density poly ethylene (HDPE) bottles and tubes are used to handle the PFAS containing samples and minimize losses by sorption to lab materials.

Details of sample preparation and analysis procedure

50 mL of samples stemming from GW and FFWW (tests) were extracted in triplicate using solid-phase extraction (SPE) using weak anion-exchange (WAX) SPE cartridges containing 60 mg of sorbent. The cartridges were eluted with 1.2 ml MeOH (0.1% NH_4OH). In every batch a procedural blank, ultrapure water spiked with ~1 ng mass labelled internal standards, was added. Before SPE elution, deuterated internal standards were added to the eluent to account for matrix effects during analysis. A volume of 0.5 mL of each extract was diluted with 0.5 mL 0.1% acetic acid and transferred to polypropylene vials for liquid chromatography analysis (PP-LC vials). Analysis was performed with high performance liquid chromatography coupled to tandem mass spectrometry (HPLC-MS/MS) (Shimadzu Prominence 20 XR-AB Sciex 4000 QTrap), with Kinetex C18 Evo column (100x2.1mm x 2.6 µm) + C18 Evo guard column to protect the separation column. The chromatographic separation was performed using H_2O (2 mM ammonium acetate) and MeOH (2 mM ammonium acetate) as mobile phases. Analytical blanks and standards were injected in-between (roughly every 12 samples) and at the end of the sequence. The method was validated for all analysed PFAS with the exception of the perfluorotelomers that were later added to the analytical method according to the standard NEN 7777+C1 of the Dutch Royal Normalisation institute. Further. Quantifications were performed with 15 point calibration lines, standards with accuracies outside 75-125% were removed from the calibration lines to obtain a minimal linearity R^2 of ≥ 0.99. The first mass transition (multiple reaction monitoring (MRM)) were used for quantification, the second mass range transition for confirmation of the identity of the chemical.

Table 14: PFAS target compounds of the UvA method and compounds listed by other Concawe analyses (STF-33, Analytik PFC & Lastfire) as well as potentially relevant regulatory lists such as the proposed Drinking Water PFAS list and the Groundwater Watch list.

type	Abbrev.	UvA [1]	STF-33 [2]	Analytik PFC [3]	Lastfire [4]	DWD [5]	GW-Watch [6]
Sulfonic acids							
C4	PFBS	X	X	x	X		X
C5	PFPeS						
C6	PFHxS	X	X	x	X	x	X
C7	PFHpS		X		X	X	
C8	PFOS	X	X	x	X	x	X
C9	PFNS				X	X	
C10	PFDS	X	X		X	x	
Carboxylic acids							
C4	PFBA	X	X	x	X		X
C5	PFPeA	X	X	x	X		X
C6	PFHxA	X	X	x	X	X	X
C7	PFHpA	X	X		X	X	X
C8	PFOA	X	X	x	X	x	X
C9	PFNA	X	X	x	X	x	X
C10	PFDA	X	X		X	X	X
C11	PFUnA	X	X		X		
C12	PFDoA	X	X		X		
C13	PFTrA	X			X		
C14	PFTeA	X			X		
Fluorotelomers							
C>>	4:2 FTS	X			X		
C>>	6:2 FTS	X			X		
C>>	8:2 FTS	X			X		
Perfluoroalkane sulfonamides							
C>>	PFOSA	X	X		X		
C>>	N-EtFOSA				X		
C>>	N-MeFOSA				X		
C>>	N-EtFOSAA				X		
C>>	N-MeFOSAA				X		
C>>	N-EtFOSE				X		
C>>	N-MeFOSE				X		

This method is comparable to the EPA 537 method, but has an extended list of target PFAS.

[5] In draft version of revised Drinking Water Directive as "list of Sum of PFAS" (most recent version we are aware of as of 3rd July 2019).

[6] Groundwater Watch List – "List Facilitating" (https://circabc.europa.eu/d/d/workspace/SpacesStore/b746afc1-3169-4135-95ec-312a4359676f/First%20List%20facilitating%20Annex%20I%20and%20II%20review%20process%20of%20the%20Groundwater%20Directive%20(Endorsed%20V2.1%20-June%202019).pdf)

In gray, PFAS are presented that are not part of the validated method, but can be determined semi-quantitative.

Dilution

The FFWW samples are suspected to contain high levels of PFAS residuals and furthermore are probably heavily contaminated with soot, hydrocarbons and other AFFF constituents and contain a substantial fraction of sand. Thus, these samples constitute a complex, multiple-phase matrix. Therefore, the aqueous phase in between particle residues on the bottom of the vessel and potential floating layers of petrochemical substances will be used for testing, to reflect the water treated after sedimentation and removal of floating layers. Because of the potential high concentrations of perfluorinated compounds, as observed during preliminary analysis, a dilution step is proposed in order to reduce matrix effects, improve the elution rate during extraction and to prevent the analytes from saturating the detector of the MS^2 system. The amount of dilution will depend on the concentrations of PFAS found in FFWW samples by screening analyses and Total Oxidizable Precursor (TOP)-assays. A most probable dilution range will be up to 3 orders of magnitude.

Extraction

In order to analyse the PFAS concentrations in the FFWW and GW samples using LC-MS^2 an extraction and purification procedure has to be followed. This procedure makes use of a SPE column with a weak ion exchange sorbent (WAX) (see **Table 15**). A blank sample containing only ultrapure water and a control sample with a reference material (local tap water) is also included in the procedure. Triplicates will be used throughout the extraction method. Before the SPE each tested sample is spiked with a ^{13}C internal standard and left overnight to equilibrate at room temperature. In addition, the control sample is spiked with a ^{12}C spike mix. Subsequently, the SPE manifold is loaded with the SPE cartridges and conditioned with 4 mL 0.1% NH_4OH in methanol without vacuum. Then the cartridges will be equilibrated using 4 mL ultrapure water (Milli-Q, Merck) after which the sample is loaded into the cartridge and vacuum (<20 In Hg) will be applied. After elution of the sample the vacuum pressure will be relieved. Subsequently, the cartridge will be washed with 2 mL 25 mM acetate buffer with a pH of 4 and 2 mL of methanol. Then, the cartridge will be dried under vacuum for at least 5 minutes, after which a sample rack with a 1.5 mL HPLC vial is placed in the manifold and a 0.2 µm filter is connected between the cartridge and manifold. Extraction takes place using 2 x 600 µL 0.1% NH_4OH in methanol. The captured extract will be diluted 1:1 with 0.1% acetic acid in water after which it is stored at 4 ^0C until analysis.

Table 15: Used SPE materials

Cartridge	Oasis WAX (Waters), 60mg, 3cc
Manifold	20 cartridge positions (Waters)
Sample	50 mL FF water
Conditioning	4 mL 0.1% NH_4OH in MeOH
Equilibrating	4 mL ultrapure water (Milli-Q)
Wash	2 mL 25 mM acetate buffer ($NH_4CH_3CO_2/CH_3COOH$) pH 4 & 2 mL MeOH
Elution	2 x 500 µL 0.1% NH_4OH in MeOH
Dilution of extract	0.1 % CH_3COOH in water

TOP-Assay

The PFAS impacted water is suspected to contain various precursors to PFCAs and PFSAs. Therefore, the concentrations of various perfluorinated precursors will be analysed following the total oxidizable precursor (TOP) assay. For this assay, the protocol of Houtz & Sedlak, 2012 will be followed, where the PFAS containing water is subjected to oxidation by adding $K_2S_2O_8$ and heating in a basic pH environment. This assay relies on hydroxyl radicals (OH), which are formed with the thermolysis of persulfate in basic pH and which transform the precursors to PFCAs and PFSAs of related chain lengths. PFCAs and PFSAs themselves remain stable in these conditions. Thus, the amount of oxidizable precursors could be established by assessing the difference in PFCA and PFSA concentrations between persulfate amended and un-amended samples. Furthermore, the transformation of FOSA in a spiked blank sample could be used in order to verify the conversion of PFAS by the TOP-Assay. In order to complete the TOP-Assay and to obtain reliable results, it is important that the samples are not contaminated with high loads of organic matter or contain high concentrations of PFAS, that both can hamper the oxidation. For that reason, the FFWWs are diluted ~2500x to reduce such matrix effects and prevent incomplete of the substances of interest.

For the TOP-assay, 0.8 g of K_2S2O_8 and 760 µL of 10N NaOH is added to the 50 mL diluted sample (60 mM & 150 mM respectively). Subsequently, the samples are placed in a water bath under constant shaking at 85 ºC for six hours, after which they are neutralized using HCl. After the TOP-assay the samples will be subjected to the aforementioned SPE protocol.

LC-MS^2 method

The quantification and detection of the target PFAS substances will be achieved by performing liquid chromatography tandem mass spectrometry (LC-MS^2). Characteristics of the LC-MS^2 system and method can be found in **Table 16**. A previously validated (following the Dutch NEN7777+C1 guideline) method which has been used in an investigation on PFAS in surface water for the Dutch Department of Waterways and Public Works (Rijkswaterstaat) will be used to detect and quantify the PFAS in the samples. Furthermore, quality control of this method has been performed following the NEN 6603 norm. The mobile phase gradient curve and the analytical characteristics of the target substances can be found in **Figure 22** and **Table 17** respectively.

Table 16: LC-MS^2 set up.

HPLC	Shimadzu LC20-AD
MS^2	AB Sciex 4000 QTRAP
Column	Phenomenex Kinetex C18 Evo (2.6 µm, 100 x 2.1 mm)
Guard column	Phenomenex C18 Evo
Ion source	Turbo spray
Eluent A	Ultrapure water (Milli-Q), 2% $NH_4CH_3CO_2$
Eluent B	Methanol, 2% $NH_4CH_3CO_2$
Acquisition	MRM mode, negative ESI
Injection volume	5-50 µL
Flow rate	0.3 mL/min
Column Tx	35 ºC

Figure 22: Liquid chromatography mobile phase gradient.

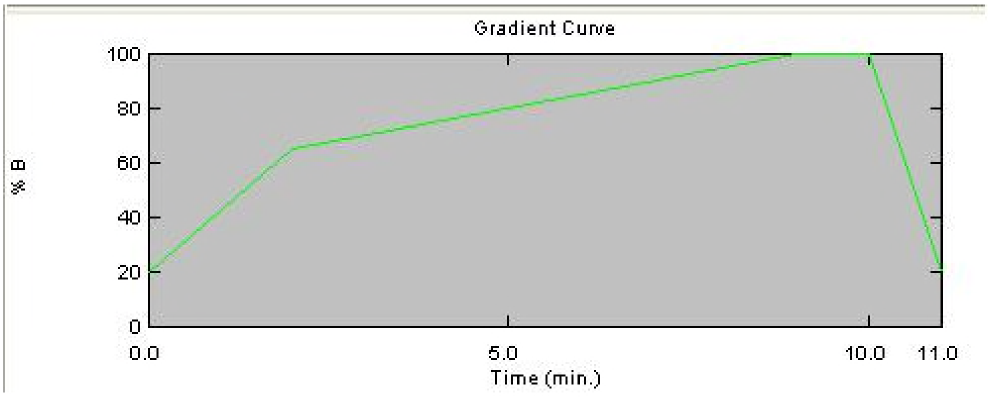


Table 17: **Analytical characteristics PFAS, quantifier (Q3)** in bold. **Q1 is the parent molecule mass and Q3 gives the masses of fragments that are used for identification and quantification.**

PFAS	***Retention time***	***Q1***	***Q3 (tr1/tr2)***	***Reporting limit (pg/L)***
PFBA	2.6	213	169	145
PFPeA	3.5	313	219	47.6
PFHxA	3.9	315	269/119	58.7
PFHpA	4.3	363	**319**/169	27.1
PFOA	4.7	413	**369**/169	18.3
PFNA	5.3	463	**419**/219	11.1
PFDA	5.7	513	**469**/219	21.3
PFUnA	6.3	563	**519**/269	20.2
PFDoA	6.8	613	**569**/319	23.7
PFTrA	7.3	663	**619**/369	24.4
PFTeA	7.7	713	**669**/369	40.1
PFOSA	6.4	498	**78**/169	25.0
L-PFBS	3.6	299	80/**99**	12.0
L-PFHxS	4.3	399	**80**/99	23.3
L-PFOS	5.2	499	**80**/99	21.2
Br-PFOS	5.1	499	**80**/99	20.7
L-PFDS	6.2	599	**80**/99	9.51

QA/QC

- All samples will be extracted and injected once.
- After each 18 injections a Method Blank sample is injected to evaluate carry over and potential drift in response and separation.
- Method Blanks should show no contamination for all compounds analyzed.
- In every batch a Procedure Control Sample will be included that is subjected to the same extraction procedures and sample treatment in order to obtain the impact of sample preparation.
- The results of the Procedure Control Samples will be monitored in a Shewart chart.
- Quantification of all measurements will be performed with a linear ten point calibration line (with $r^2 > 0.98$ for all analytes).
- Samples will all be quantified within the linear dynamic range (0.07 to 140 pg absolute injected) of the calibration line.
- Analyte concentrations will be corrected for total procedural recovery of the mass labeled internal standards.
- The (method) LOQ is defined as the lowest validated spike level meeting the method performance acceptability criteria (mean recoveries for each representative commodity in the range 50-130% for the mass labeled internal standards (and 60-130% for the native compounds) and with a RSD ≤ 20%).

- Calibration levels will be used only when complying with the following criterion:
    - (i) The nominal concentration of the different levels and the corresponding concentrations calculated with the linear calibration line (by the HPLC software: Analyst v1.5.1) of the levels does not deviate more than 40%. Analytes will be identified and quantified using the additional criteria:
    - (ii) Analyte peak area of the sample should be higher than that of the lowest calibration level (defined by criterion (i)).
    - (iii) Analyte peak area of the sample should be lower than that of the highest calibration level.
    - (iv) The peak area ratio of mass transitions 1 and 2 of the analyte in the sample does not deviate more than ±30% of the average ratio of the same mass transitions determined for the calibration levels.
- Branched PFOS is quantified using branched PFOS levels with linear PFOS as internal standard due to the limited availability of a ^{13}C labeled standard for branched PFOS.
- ^{13}C spike injections for each 10 sample injections will be used to check if sensitivity of the analysis changed during the course of measuring.

Data analysis of sorption and flocculation tests

Assuming equal volumes, temperature, pressure and sufficient contact time, an equilibrium exists between the amount of sorbent/flocculant and the concentration of PFAS in the liquid. The main output variable of batch sorption test will therefore be the concentration of PFAS per volume of liquid in the sample. These equilibrium values (Ce) could be used to calculate the equilibrium sorption capacity (qe) of the sorbent by the following calculation:

$$q_e = \frac{V(C_0 - C_e)}{m}$$

In which V is the volume of liquid, C_0 the original concentration in water and m the mass of sorbent/flocculant. Sorption isotherms are given by the relation between the equilibrium water concentration (C_e) and the equilibrium sorption capacity (q_e). Therefore, the tested parameter will be m, the mass of used sorbent. The original concentrations (C_0) of PFAS in the matrices will be established by sampling and analysis of the FFWW, and GW. The PFAS mass sorbed in the sorbent will not be measured. Therefore, the measurement of the sorbent mass must be very accurate. In case of PFAS that are not part of the standard series, C_0-C_e can be replaced with the responses of the chemical before and after treatment for a semi quantitative analysis of the q_e.

Foam fractionation

For foam fractionation the concentration of PFAS in the liquid before and foam and liquid after fractionation will be analyzed. There are multiple variables which could be tested for this technique which still depend on the development of a lab-scale test set up. These variables could include the operating time or the total volume of treated water.

Nanofiltration

In the nanofiltration set up, the concentration of PFAS before (similar to C_0) and after passing the membrane will be analyzed. In nanofiltration systems, the main parameter is flux (J), which in the proposed set up will be given by the total volume of treated water (membrane pore area will be constant). As in the following equation:

$$J = \frac{m^3}{m^2\ s}$$

Therefore, the test variable in the experiment will be volume of treated water, from which the flux can be calculated. A relationship between flux and solute concentration after passing the membrane will be established.

APPENDIX 2: DETAILS OF TREATMENT CONCEPTS

Sorption technologies

In sorption technologies the PFAS will bind to sorption sites on the surface of the sorbent. The compound will distribute between the aqueous phase and the sorbent, to the energetically most favorable distribution. One can distinguish adsorption and extraction (absorption), where the first is based on a solid matrix that adsorbs compounds on a surface and the second is based on a non-aqueous liquid matrix where the compound dissolves in.

Examples of sorbents where the interaction of the sorbent and sorbate is on the material surface are:

- Activated carbon, a carbon based material with a very large surface area, capable of adsorbing contaminants. Activated carbon is commonly applied to treat water. It is not a very specific adsorbent and can be considered as the benchmark technology.
- Ion exchange material, in most cases a chemical based sorbent (resin) containing functional groups. These functional groups can specifically bind negatively or positively charged contaminants.
- Complexing agents are sorbents (resins) containing functional groups or pockets that bind chemicals with specific size, structure and composition.

All these sorbents are limited in the number of sites on the surface. Upon use the material becomes saturated and at the end of the life-time of the sorbent, PFAS can be desorbed by competition with other sorbates (e.g. ions, other organic molecules, other PFAS).

The rate of saturation is dependent on multiple parameters. Below some of these influences:

- Flow and contact time;
- The number and concentrations of the PFAS present in the water stream;
- The presence of competing substances (amongst others other contaminants, natural organic material, iron and manganese);
- Biological activity.

Depending on the structure of the sorption material (surface-volume ratio and pore size), sorption processes require a certain contact time which determines the dimensions of the treatment system. Generally, sorption materials are most effective in rather clean matrices, where competition and fouling are limited. The surfactant properties of the PFAS lead to concentration on the interface of water and sorbent of absorbents, instead of dissolving in the sorbent [14, 23]. The smaller (short chain) PFAS are more aqueous soluble and have a lower tendency to sorb and are easily out-competed on sorbents [24].

Saturated (spent) sorption materials either have to be disposed as waste or need regeneration procedures to be reused.

Physical separation technologies

Liquid separation technologies

Liquid separation techniques separate the waste stream in two new streams. The first stream (concentrate) is preferably very small in volume and contains all (or most) of the contamination while the second stream is much larger in volume (almost) free of the contamination and has nearly all of the volume of water. The separation can be obtained by the use of a physical barrier such as a membrane or by another treatment concept that provides two phases that differ in contaminant load.

Most common technologies are the membrane based technologies like reversed osmosis and ultrafiltration. Less known are the ozo fractionation and air fractionation. The latter technologies are based on the formation of microbubbles that pick up the PFAS from the water stream which are then concentrated in the produced foam layer. As mentioned above complexation, flocculation and subsequent coagulation and filtration might also considered phase separation techniques.

The separated and concentrated waste stream needs further treatment by means incineration or reactive degradation.

Flocculation technologies

Flocculation is a technology where flocs are formed by agglomeration of suspended solids and precipitation of coagulants. The primary process is a sorption/complex forming process that might be classified as a form of sorption while the secondary process the complexes coagulate and are separated from the bulk aqueous phase by filtration or precipitation. The generated waste (the separated flocs) needs further treatment by means incineration or reactive degradation.

Reactive degradation technologies

The most common degradation technology for the degradation of PFAS is high temperature incineration. PFAS containing waste streams (spent resin, separated concentrates) are in most cases sent to certified processors. Saturated activated carbon, suited for regeneration is heat treated at 900 degrees C, the off-gases (containing the PFAS) are treated at higher temperatures. Several new reactive degradation technologies are under development for the water based streams. Electrochemical oxidation and sonochemical oxidation are good examples of these developments, whereas electrochemical oxidation is based on the degradation of PFAS using specific electrodes. Sonochemical oxidation is based on ultrasound degradation technology. So far these technologies cannot be considered as ready to market because upscaling and commercial issues but should be considered as promising.

APPENDIX 3: DETAILS OF EXPERIMENTAL SET UP BATCH SORPTION EXPERIMENTS WITH ADSSORBENTS AND FLOCCULANT

Sorption behaviour of native PFAS present in FFWW and GW was studied measuring sorption isotherms for five sorbents and removal with one flocculant. The sorbents and flocculants were added at a wide range of dosages, the dosage window for the flocculant was smaller than for the sorbents. The range was selected around the recommended dose by the supplier (**Table 18**).

Table 18: Sorbent and flocculant dosage in batch sorption studies

Sorbent/flocculant (abbreviation)	Groundwater (GW)	Groundwater benzene spike (GW-BS) (>>mg/L)	Firefighting wastewater (FFWW)
	Dosage sorbent (mg/L)		
Desotec Granular Activated carbon (GAC) Rembind® (RB) FLUORO-SORB® (FS) PolyQA-Osorb® (PQ) Cyclopure D+ (CP)	0, 2, 20, 60, 200, 600, 2000, 20000		
PerfluorAd (PFAD)	0, 1, 10, 20, 30, 70, 150, 1000		0, 100, 250, 500, 1000, 1500, 3000, 10000

For all tested sorption and flocculation technologies batch experiments were performed using 250 mL HDPE bottles containing 200 mL of (benzene spiked) GW or FFWW sample. For the sorption technologies, a dosing range of seven points covering four orders of magnitude around the 200 mg/L dosing was set up. All seven doses were tested in triplicate. For the flocculation experiments, also seven-point dosing ranges was set up, with a triplicate for each dose. For all sorbents and flocculant negative controls containing the water sample with no sorbent and blanks containing the sorbent in ultrapure water were tested.

Here, a well-mixed quantity of flocculant was pipetted in 200 mL of the treated water sample. The flocculation dosing was adapted to the PFAS concentrations of the tested matrix. This was necessary because increasing the dosage of flocculants affected coagulation and further separation of water and the coagulated flocs.

For the sorbents the samples were shaken at 90 rpm for seven days on a heavy-duty shaker in a dark incubation room with a stable temperature of 21 ˚C. For the flocculant the samples were shaken for at least 30 minutes, after which a small dose (10µL) of ferrous chloride solution (40% $FeCl_3$) was added in order to further stimulate flocculation and coagulation. After treatment, the flocs were separated from the matrix by filtration with Whatman 595 1/2 filter paper (4-7 µm). The filtrate was captured and stored in a refrigerator at 4˚C until SPE and analysis.

Subsequently, for all FFWW samples with high PFAS concentrations aliquots of 1.5 mL were pipetted into Eppendorf tubes. These were centrifuged in an Eppendorf centrifuge for 10 minutes at 12000 rpm, after which 500 µL of supernatant was pipetted into 50 mL of ultrapure water. The resulting samples were stored in a refrigerator at 4˚C until SPE and analysis.

For the GW and benzene spiked GW samples, aliquots of 50 mL were taken in 50 mL centrifuge tubes. Subsequently, these aliquots were centrifuged for 30 minutes at 4000 rpm in a Hettich benchtop centrifuge. After this, the supernatant was transferred to another 50 mL centrifuge tube and stored in a refrigerator at 4 ˚C until SPE and analysis.

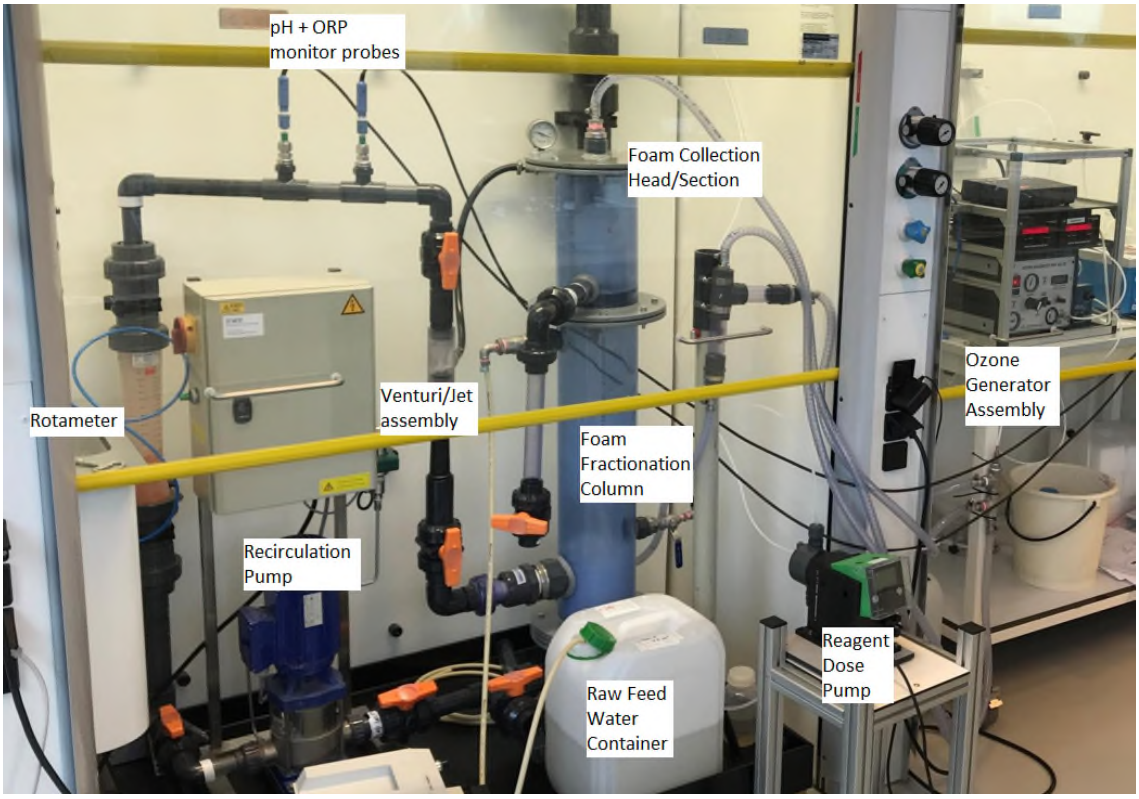
For the determination of the sorption capacity of the sorbents and flocculant, treatments (dosages) were selected that resulted in a significant reduction concentrations as compared to the control (no sorbent).

APPENDIX 4: DETAILS OF EXPERIMENTAL SET UP FOAM FRACTIONATION WITH FIREFIGHTING WASTEWATER

For foam- and ozo- fractionation, a pilot test set up consisting of a column with an air/ozone bubble supply at the bottom and an extraction mechanism for the foam fraction at the top was obtained from Evocra and set up at KWR. The water to be treated was recirculated through the bottom part of the column (volume approx. 16 L), while air or ozone was introduced to the recirculating water through a venturi tube, in line with the recirculating water. The foam was collected in the top part of the column, where it collapsed and the concentrate was collected in a separate sample collector. Foam- and ozo fractionation is a process that requires some experimentation of operational conditions (recirculation flow speed, air pressure, setting height of the foam collection tower, total liquid hold up (height of foam/liquid interface)) in order to obtain stable operation.

Feed water was fed into the top of the column via a peristaltic feed pump. Liquid flow rate was determined by estimating volume per time run at certain settings, and estimated drop in raw feed water container volume. Recirculation of water within the column is achieved by a centrifugal pump, allowing for the measurement of pH and ORP (Oxidation-Reduction Potential) parameters, as well as the production of vacuum to inject air or ozone into the stream, and subsequently the column.

Figure 23: Evocra OCRA Foam-and ozo fractionation column assembly with ozone generator



Due to the inherent restrictions of overall gas flow of the provided ozone generator, there appeared to be a restriction in overall gas injection when compared to air trials. This may have contributed to the larger amount of liquid able to be fed into the column for the GW tests, as the foam layer within the column was much smaller in comparison to the air-only test. This may have potentially reduced contaminant removal by having a coarser foam (lower surface area) for contaminant removal.

The ozone generator was set at 80% PSU, as there was no significant increase in ozone concentration above this point. Typical concentration of ozone produced varied from 20 – 25 g/Nm^3, with concentrations usually hovering around 22 g/Nm^3. ORP target levels for all tests were as high as possible as this typically allows for the highest removal efficiency.

For the experiments, pH was not adjusted during air only trials as prior experience indicated no improvement in performance. Ozone trials pH was adjusted by the addition of 90% w/w acetic acid, intended to create smaller bubbles to increase the contact surface, down to a target pH of 4.5, however as the reagent dose pump had to be manually controlled this was not always possible.

The column was flushed in between trials with demineralized water until no foam was generated and observed in rinse water by visual inspection during recirculation and air injection.

The aqueous phase was sampled as follows. All samples were analysed in triplicate:

- The feed water before treatment (negative control);
- The treated water at the time that no foam was formed anymore (t = 0 = no foam formation);
- The treated water at time + 1 hour that no foam was formed anymore (t = 1 = no foam + 1 hr);
- The concentrated foam (concentrate) was sampled once at the end of the tests.

Note that the subsequent trials with the column are generally considered the first step in optimizing the equipment for scale up. Further optimization for continuous operation is required and there is the potential for increased efficiency in both removal and waste volume reduction.

Groundwater without benzene spike

At the start of the foam fractionation test (air only) the column was fed with approximately 7 - 8 L of GW. The frequency drive of the recirculation pump was set at 50 Hz, resulting in a recirculation flow of approximately 2.5 m^3/h. The air was injected freely through the venturi. At the start of the ozo fractionation test (Ozone) the column was fed with approximately 9 - 10 L of GW. Here also the frequency drive of the recirculation pump was set at 50 Hz, resulting in a recirculation flow of approximately 2.5 m^3/h. The ozone injection was restricted by the capacity of the ozone destruction device. Therefore, air treatment produced a larger foam layer in the column when compared to ozone fed trials. During both trials the t = no foam sample, and t = no foam + 1 hr sample could be obtained.

Groundwater with benzene spike

At the start of the foam fractionation test (air only) the column was fed with approximately 7 - 8 L of GW. The frequency drive of the recirculation pump was set at 50 Hz, resulting in a recirculation flow of approximately 2.5 m^3/h. The air was injected freely through the venturi. At the start of the ozo fractionation test (Ozone) the column was fed with approximately 12 - 13 L of GW. Here also the frequency drive of the recirculation pump was set at 50 Hz, resulting in a recirculation flow of approximately 2.5 m^3/h. The ozone injection was restricted by the capacity of the ozone destruction device. Therefore, air treatment produced a larger foam layer in the column when compared to ozone fed trials. During both trials the t = no foam sample, and t = no foam + 1 hr sample could be obtained.

Firefighting wastewater

Foam fractionation of FFWW was complicated with air as well as ozone as the matrix resulted in excessive foam formation. Details on the development of the method can be found in **Appendix 3**.

This lead to the following adapted procedure for the foam fractionation test (air only). At the start of the ozo fractionation test the column was fed with approximately 6 - 7 L of FFWW.

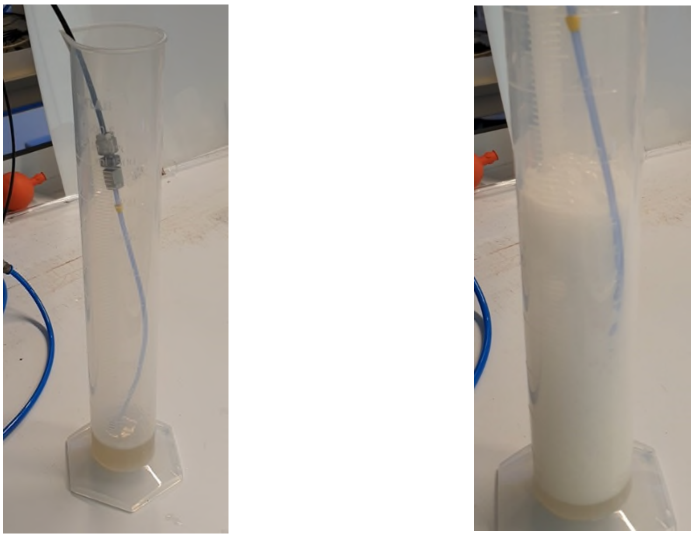
To control foam formation the FFWW was dosed with $FeCl_3$ to a concentration of 250 mg/L and diluted a factor 2 with tap water. Additionally, the frequency drive of the recirculation pump was reduced to 25 Hz. Despite these adaptations only one sample could be obtained (t = no foam sample) as longer operation resulted in excessive foam formation hampering further sampling.

With the lessons learned of the air only test, the ozo fractionation (Ozone) test was performed as follows. At the start of the ozo fractionation test the column was fed with approximately 6 - 7 L of FFWW. To control foam formation the FFWW was dosed with 250 mg/L $FeCl_3$. Additionally, the frequency drive of the recirculation pump was reduced to 20 Hz. The inherent restriction on the ozone gas inflow into the column reduced the amount of foaming within the column and potentially aided the trial. After an additional hour, the t = no foam + 1 hr sample could be obtained, but the volume of formed foam could not be determined accurately.

Background information and rationale for experimental set up

Foam fractionation for the FFWW was complicated. The first experiment showed to be a very strong foaming water by a benchtop test. This test involved 10 mL of FFWW and an air stone placed in a tall 100 mL cylinder and observing the foam produced when air is introduced via the air stone. The air stone was able to convert approximately 10 mL of FFWW into a structural foam that does not readily collapse.

Figure 24: Firefighting wastewater before air stone bubble test (1) and after air stone bubble test for 40 sec air flow (2)



(1) (2)

To control foam formation to acceptable structure and volumes, the FFWW was treated with 250 mg/L $FeCl_3$. As foaming was still very strong the FFWW was diluted with 1:1 ratio of tap water (rendering $FeCl_3$ concentration 125 mg/L). This dilution was also to expand the available volume of water for the ozone trial as there was potential to exhaust all available water.

Figure 25: FFWW with $FeCl_3$ dosed, continuous air feed by air stone, limited structural foam accumulation

At the start of the second foam fractionation test the column was fed with approximately 6 - 7 L of FFWW. The frequency drive of the recirculation pump was set at 25 Hz, resulting in a recirculation flow unable to be detected by the rotameter. Between the second and third attempt, the head was rinsed to remove the foam within and to allow for more foam to be generated, this foam was not collected as it would be diluted with water. Before the third attempt an additional dose of $FeCl_3$ was added to bring the concentration of $FeCl_3$ to 250 mg/L the FFWW again. The conditions were the same as for the second attempt. At the end of this attempt, the recirculation pump was started for a brief amount of time to collect a single treated water sample. At time of sample, ORP and pH were not observed as the recirculation pump was unable to run long enough for probes to stabilize, however are expected to not deviate significantly from untreated/raw water values. pH was not adjusted, as further stabilization of foam (if possible) was not desired. During the last trial only one sample could be obtained due to excessive foam formation.

Figure 26: Firefighting training wastewater, air foam fractionation, column full of structural foam

Ozo fractionation of firefighting wastewater

Using the lessons from the air foam fractionation tests, the pump frequency was lowered to 20 Hz, and the test was started with a 250 mg/L $FeCl_3$ concentration in the feed water. In addition the inherent restriction on the ozone gas inflow into the column reduced the amount of foaming within the column and potentially aided the trial.

At the start of the ozo fractionation test the column was fed with approximately 6 - 7 L of FFWW. The frequency drive of the recirculation pump was set at 20 Hz, resulting in a recirculation flow unable to be detected by the rotameter. The rotameter and recirculation line was also full of foam, and as such the gas-liquid mixture would not be an accurate representation of flow. After starting the recirculation pump, it was noticed that the foam formed was less stable. This might be due to the higher $FeCl_3$ concentration (250 vs. 125 mg/L) and/or the use of ozone instead of air as the ozone might oxidize part of the organic chemicals (carbohydrate surfactants) that would have given the foam its strength and stability. Similar structural foam entered the concentrate collection head, the first attempt had to be stopped to protect the ozone destruct catalyst.

Figure 27: Firefighting training wastewater, ozo fractionation, structural foam present in foam collection head

Foam destabilization was much faster than previous air test and 30 - 60 minutes was waited in between before starting the second attempt.

Figure 28: Firefighting wastewater, ozo fractionation, foam section breaking away from liquid interface

Foam within the column collapsed considerably, however foam within the foam collection head was very stable, but not cleaned out, so this was done manually. Additional foam collected into the foam collection head, which did not collapse into readily collectible water, and large sections of foam rose and fell throughout the column and were unable to enter into the foam collection head. Approximately 1 L of additional water was fed into the column during this test. After 1 hr, and a large section of foam sticking to the top of the column, and another moving up and down, a t = no foam sample was collected and a 1 hr timer started. After an additional hour, the t = no foam + 1 hr sample could be obtained, but the volume of formed foam could not be determined.

APPENDIX 5: DETAILS OF EXPERIMENTAL SET UP MEMBRANE SEPARATION WITH FIREFIGHTING WASTEWATER

The nanofiltration treatment of FFWW was tested using a Mexplorer test kit of NXFiltration with an MP pilot module type Mexfil MP025 dNF40. The Mexfil MP025 dNF40 test module is a small module that contains approximately 100 membrane fibres. Each fibre has an effective length of approximately 23 cm and an internal diameter of 0.7 mm. The total membrane area of the test module is 0.05 m^2.

Figure 29: Mexplorer Portable test unit

The Standard Test Protocol Nanofiltration Mexplorer (NXF-TR: 17-45-1C) of the technology provider was followed for the operation of the pilot. The impacted FFWW was fed into the membrane in crossflow mode. The system was tested using different protocols in order to see the performance under different membrane setting:

- Protocol 1 - dNF Membrane Evaluation: measurement of the retention of the PFAS at three different permeate fluxes. This has been done with short lasting tests at a transmembrane pressure (TMP) of 3, 4 and 5 bar with a crossflow of 80 L/h. The produced permeate and concentrate were recirculated to the feed tank to represent longer operation periods;
- Protocol 2 – Influence of crossflow velocity: this has been done with short lasting tests at crossflows (CF) of 70, 100 and 150 l/h with a TMP of 3 bar. The produced permeate and concentrate were recirculated to the feed tank to represent longer operation periods;
- Protocol 3 – Influence of Recovery: A single long term test was done at a TMP of initially 3 bar and a CF of 80 L/h. As the flux decreased due to increasing osmotic pressure the TMP was increased after 34 hours of operation to 5 bar. The total test ran for 74 hours. The produced concentrate was recirculated to the feed tank and the produced permeate was discharged. This resulted in a decrease in the volume of the feed water simulating the increase in recovery.

To obtain a stable operation after each change in test conditions the pilot ran at least 15 minutes at the specified setting before sampling. Samples of 40 mL were taken for PFAS analyses.

The test conditions and measured parameters during the protocols are given in **Table 19, Table 20** and **Table 21**.

Table 19: Operating conditions during protocol 1 tests

Feed Pressure (bar)	Crossflow (L/h)	Crossflow velocity (m/s)	Permeate Flux (L/m²·h)	Permeate conductivity (µS/cm)
3	80	0.58	6.9	3.11
4	80	0.58	9.6	3.62
5	80	0.58	16.0	3.4

Table 20: Operating conditions during protocol 2 tests

Crossflow (L/h)	Crossflow velocity (m/s)	Feed Pressure (bar)	Permeate Flux (l/m²·h)	Permeate conductivity (µS/cm)
70	0.51	3	6.9	3.39
100	0.72	3	6.9	3.76
150	1.08	3	6.9	3.89

Table 21: Operating conditions during protocol 3 test

Time (h)	Crossflow velocity (m/s)	Feed Pressure (bar)	Permeate Flux l/m²·h	Volume feed tank (L)	Simulated Recovery (%)
0	0.58	3	6.9	10	0
0.25	0.58	3	6.9	10	0
5	0.58	3	6.9	8	20
10	0.58	3	4.8	7	30
29	0.58	3	2.2	4	60
34	0.58	5	n.d.	3.7	63
51	0.58	5	n.d.	2.5	75
57	0.58	5	n.d.	2.2	78
74	0.58	5	n.d.	1.8	82

n.d. = not determined

APPENDIX 6: DETAILS ON SET UP SMALL SCALE COLUMN EXPERIMENTS

Three small scale columns with an internal diameter of 6.5 mm were used to simulate a contact time of 25.2 minutes using the RSSCTs particle size independent diffusion model. To fill the small scale columns, the 3 different types of sorbents were collected and rinsed over the 90 µm sieve with ultrapure water (Veolia Elga Corus Analytic) with most of the dust being washed away. The sieved fraction with particle size 90-106 µm was then transferred to a 1 litre glass beaker and rinsed several times with ultrapure water to remove the remaining part of the dust.

The following sorbents were used for the column experiments with GW containing PFAS compounds:

- Desotec Granulated Activated Carbon (GAC);
- FLUORO-SORB® Des2 (FS);
- Cyclopure DEXSORB+® (CP).

All three sorbents were delivered grinded and sieved to a fraction of 90-180 µm. Because of a possible dry sieving by the supplier, the materials possessed a high amount of dust defined as particles < 90 µm. After wet sieving and thorough washing a usable amount of 90-180 µm fraction was collected. For the GAC however, an extra milling and sieving was necessary to obtain enough material to fill the mini column. Stainless steel tubes were used for the small scale columns (Figure 30) with an internal diameter 6.5 mm and length up to 20 cm. The sorbent was kept in the column by means of a stainless steel screen on both sides of the column. By means of vacuum suction on the bottom of the column, the small scale columns were filled with the 90-106 µm sorbent, which was poured into the column as a slurry. The small scale column was filled with sorbent to 15.8 cm column height (5.24 mL). To prevent the sorbents from settling at the column during the experiment, the remaining part (4.8 cm) was filled with inert sand. After this, the columns were placed in the set-up and rinsed upwards with demineralized water at 2 L/h for approximately 2 h. The effluent was visually checked to see e.g. wash out of the sorbent.

Figure 30: Set up with the small scale columns and flow control

The column studies result in breakthrough curves of the different PFAS present in the tested water. In these curves the concentration is expressed as the fraction of the concentration in the feed water. The 20% breakthroughs were defined and expressed as the bed volumes the column has been exposed to. This is indicative for the treatment capacity of the sorption material in the column for the different PFAS present in the water.

Background information

Table 22 lists the modelling data of the small scale columns after conversion from large column to a small scale column, EBCT stands for Empty Bed Contact Time.

Table 22: Conversion of 25.2 min contact time to the small scale column.

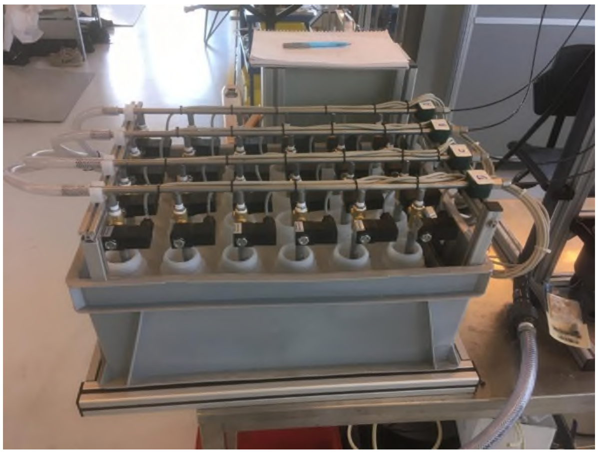
Parameter	**Large column**	**Small column**
Diameter particles (mm)	1.24	0.098 (0.090-0.106)
Height column (mm)	2,000	158
Diameter column (mm)	500	6.5
Water flow (L/h)	935	2.0
Filtration rate (m/h)	2.0	60.3
EBCT (min)	25.2	0.16
Bed volume (L)	393	0.00524

The experiment started the 22nd of June at 14:45h and was stopped the 29th of June at 8:00h, 2020. The small scale columns were fed with the desired flow by means of constant flow regulators. A constant pre-pressure of approximately 3.5 bar was used for the regulators. This pressure was necessary to guarantee a constant flow even with a pressure build up in time. In front of the columns, interchangeable stainless steel 2 µm filters were used to prevent fouling of the small scale columns. These filters were replaced once during the experiment. The flow rate of all columns was manually checked daily and adjusted when necessary, but was rather constant in time. In Figure 31 an overview of the setup is given, with in front a part of the jerry cans used to transport the water. In Figure 32 a close-up of the sample collector is given.

Figure 31: Overview photos of the mini column set up with the jerry cans, stainless steel tank, pump and small scale columns

The samples were collected every 4 h by using a sample collector (type KWR v1), see Figure 32. On a daily base, the samples were removed and stored at 4 ℃ in a cooling chamber. 1 L HDPE bottles were used to collect and store the water.

Figure 32: The sample collector, manufactured by KWR



Influent samples were taken before and after the filtration step, at the beginning and the end of the sorption experiment and every day after passing a blank (empty) small scale column. The experiment lasted for approximately 7 days to reach > 40.000 BV (Bed Volumes). In total 29 samples of 1 L per column were taken, with the first one after 1 h, and for a part analyzed at the Institute for Biodiversity and Ecosystem Dynamics (IBED) laboratory of the University of Amsterdam. From the 1L delivered samples, 50 mL was collected and spiked with ~1 ng (absolute) mass labelled internal standards. From every series of samples from the three sorbents the odd numbered samples were chosen for analysis and all the blanks. The samples were extracted and analysed as described in **Appendix 7**.

APPENDIX 7: ANALYTICAL METHODS AND RESULTS OF OTHER CONSTITUENTS

Methods used:

- GW: Heavy metals (NEN 5740), incl. Barium and filtration, (AS3000) (volatile) mineral oil, volatile chlorinated hydrocarbons, (NEN-EN-ISO 17294-2 (2004)) Ca, Fe, Mg, Mn, Na, potassium, (NEN-ISO 15923-1) Cl, NH4, NO2, (AS3100) NO3, SO4, (NEN-EN-ISO 17294-2 (2004)) dH, (AS 3100) EC, pH, (NEN-ISO 15923-1) phosphate, (NEN 6578) fluoride, (NEN-EN-ISO 9963-1) bicarbonate, (NEN 6541) silicate, (NEN-EN 1484) TOC, (NEN-EN 872) TSS, (NEN-EN 1899-1) BOD, (NEN 6633+A1 (2006)) COD.
- FFWW: Heavy metals (NEN6953 (ont.cfNEN6961, with ISO17294-2(2004)) incl. filtration, (NEN-EN-ISO 10301) mineral oil, volatile chlorinated hydrocarbons, (cf NEN6953(ont.cfNEN6961, with.cf ISO17294-2 (2004))) Ca, Fe, Mg, Mn, Na, potassium, (AS 3100) Cl, NO3, SO4, (NEN-ISO 15923-1) phosphate, (NEN 6578) fluoride, (NEN-EN-ISO 9963-1) bicarbonate, (NEN 6541) silicate, (NEN-EN 1484) TOC, (NEN 6621) TSS, BOD, (NEN 6633+A1 (2006)) COD.

Results of constituents of impacted GW and FFWW:

In **Table 23** the analytical results of generic water characteristics are summarized. Some compounds of the FFWW were not measured (given as n.m.). Only the liquid phase was analysed, so any solids, when present in the water, were not analysed.

Table 23: Analytical results of common parameters for the studied groundwater and firefighting wastewater.

Parameter common	Groundwater (GW)	Firefighting wastewater (FFWW)
Conductivity (25°C) (µS/cm)	652	n.m.
pH	7.8	n.m.
Temperature (°C)	19	n.m.
Carbonate (mg/L)	<6	< 6
Hydrogen carbonate (mg/L)	230	58
Fluoride [F] (mg/L)	0.14	14
Ammonia-N (mg/L)	<0.1	n.m.
Chloride (Cl) (mg/L)	62	390
Nitrate-N (mg/L)	0.5	< 3.0
Nitrite-N (mg/L)	0.01	n.m.
Ortho-phosphate (P) (mg/L)	0.05	510
Silicate (SiO2) (mg/L)	10	5.2
Sulphate (mg/L)	63	2,900
Total alkalinity (mmol/L)	2.6	n.m.
Total alkalinity (°dH)	15	n.m.
BOD 5 days (mg/L)	<1	370
COD (mg/L)	<5	4,500
Suspended solids (NEN-EN 872) (mg/L)	2.3	25
TOC (mg C/L)	1.6	1,500
Calcium (Ca) (µg/l)	86,000	77,000
Ferric (Fe) (µg/L)	< 5.0	8,000
Potassium (K) (µg/L)	4,700	6,300
Magnesium (Mg) (µg/L)	12,000	55,000
Manganese (Mn) (µg/L)	2,100	870
Sodium (Na) (µg/L)	32.000	260.000

In **Table 24** the analytical results of heavy metals are given of the studied water types. It is shown that the FFWW contained up to several orders of magnitude higher concentrations of most heavy metals, the only exception is barium (Ba), which is of natural origin. In most cases levels in GW were below detection limits so accurate ratios between the two water types could not be determined.

Table 24: Analytical results of heavy metals for the studied groundwater and firefighting wastewater.

Parameter aromatics	**Groundwater (GW)**	**Firefighting wastewater (FFWW)**
Barium (Ba) (µg/L)	120	57
Cadmium (Cd) (µg/L)	< 0.20	1.3
Cobalt (Co) (µg/L)	< 2.0	6.8
Copper (Cu) (µg/L)	< 2.0	64
Mercury (Hg) (µg/L)	< 0.05	< 0.05
Lead (Pb) (µg/L)	< 2.0	12
Molybdenum (Mo) (µg/L)	< 2.0	4,2
Nickel (Ni) (µg/L)	< 3.0	46
Zinc (Zn) (µg/L)	< 10	6.700

In **Table 25** the analytical results of aromatics in the studied types of water are given. FFWW contained at least two orders of magnitude higher amounts of aromatic compounds in comparison to GW. In most cases levels in GW were below detection limits so accurate ratios between the two water types could not be determined.

Table 25: Analytical results of aromatics for the studied groundwater and firefighting wastewater.

Parameter aromatics	**Groundwater (GW)**	**Firefighting wastewater (FFWW)**
Benzene (µg/L)	< 0.20	89
Toluene (µg/L)	< 0.20	110
Ethylbenzene (µg/L)	< 0.20	12
m,p-Xylene (µg/L)	< 0.20	31
ortho-Xylene (µg/L)	< 0.10	96
Sum Xylenes (µg/L)	0.21	130
Naphthalene (µg/L)	< 0.020	< 1.0
Styrene (µg/L)	< 0.20	89

In **Table 26** the analytical results of chlorinated hydrocarbons and volatile compounds are given. As can be seen, both water types contained residues of chlorinated hydrocarbons. Levels in FFWW were 1 to two orders of magnitude higher than in GW. For volatile compounds the difference was even larger with a difference of 3 or more orders of magnitude between FFWW and GW. In case of volatile compounds, levels in GW were below detection limits so an accurate ratio between the two water types could not be determined.

Table 26: Analytical results of several organic contaminants for the studied groundwater and firefighting wastewater.

Parameter organic contaminants	Groundwater (GW)	Firefighting wastewater (FFWW)
Dichloromethane (µg/L)	0.4	< 2.0
Sum cis/trans-1,2-Dichloroethene (µg/L)	0.14	1.4
Sum Dichloroethene (µg/L)	0.21	2.1
Sum Dichloropropanes (µg/L)	0.42	45
Volatile compounds C6-C10 (µg/L)	< 10	5.800

Finally, in **Table 27** the analytical results are given of mineral oil fractions present in the studied water types. As can be seen, FFWW contained all measured mineral oil fractions while GW did not contain any of these fractions above limits of quantification. Since levels in GW were below detection limits no accurate ratio between the two water types could not be determined.

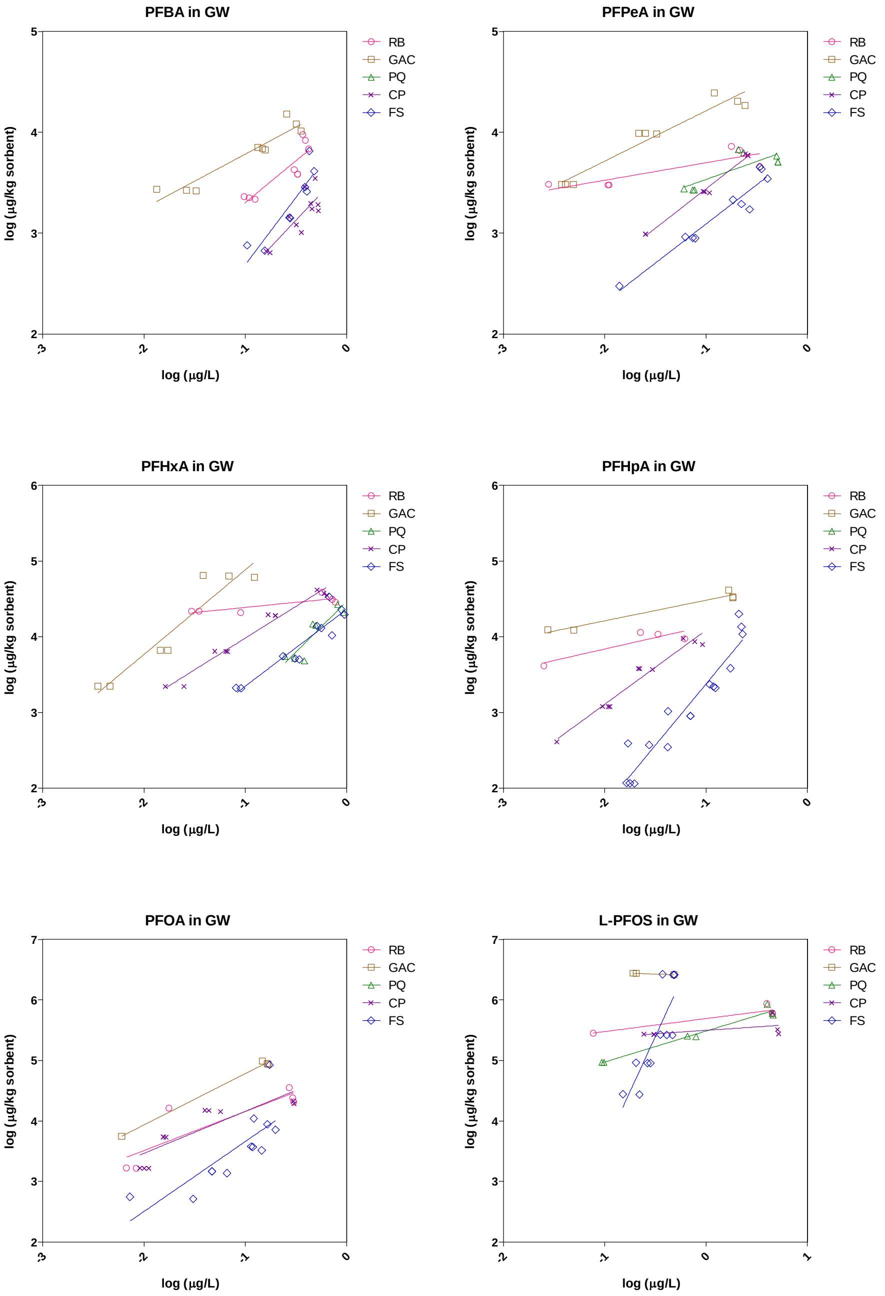
Table 27: Analytical results of mineral oil fractions for the studied groundwater and firefighting wastewater.

Parameter mineral oil fractions	Groundwater (GW)	Firefighting wastewater (FFWW)
Hydrocarbon fraction C10-C40 (µg/L)	< 50	640
Hydrocarbon fraction C10-C12 (µg/L)	< 10	35
Hydrocarbon fraction C12-C16 (µg/L)	< 10	67
Hydrocarbon fraction C16-C20 (µg/L)	< 5.0	78
Hydrocarbon fraction C20-C24 (µg/L)	< 5.0	120
Hydrocarbon fraction C24-C28 (µg/L)	< 5.0	110
Hydrocarbon fraction C28-C32 (µg/L)	< 5.0	120
Hydrocarbon fraction C32-C36 (µg/L)	< 5.0	81
Hydrocarbon fraction C36-C40 (µg/L)	< 5.0	34

APPENDIX 8: SORPTION ISOTHERMS OF BATCH SORPTION TESTS WITH GROUNDWATER

This appendix provides figures of the sorption isotherms of six PFAS derived from the sorption experiments of the five sorbents exposed to impacted groundwater (GW). No isotherms for other constituents are presented as the removal was too high to obtain trustworthy aqueous concentrations and derived concentrations on the sorbent.

Figure 33: Sorption isotherms of batch sorption studies performed with impacted groundwater. The presented sorbents were Rembind® (RB), Granulated Activated Carbon (GAC), PolyQA-Osorb® (PQ), Cyclopure (CP) and FLUORO-SORB® (FS)



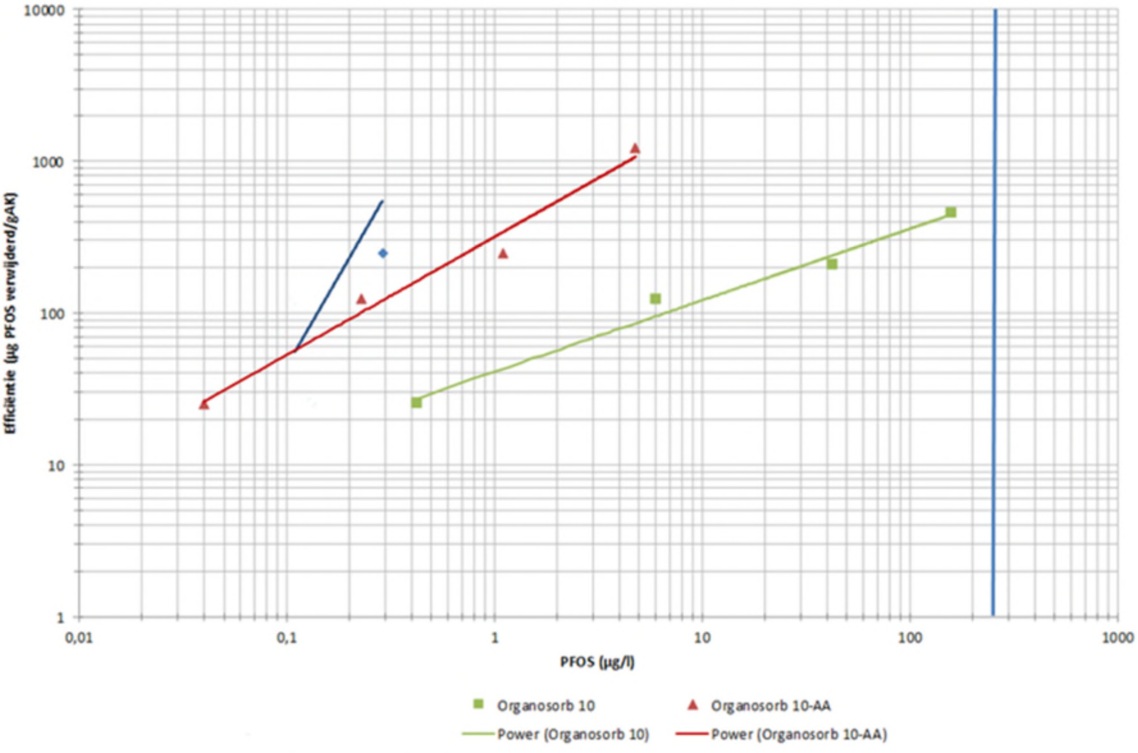
APPENDIX 9: SORBENT LOADING RATES

In the batch sorption experiments the sorbents reach high loads of PFAS in the tests. The levels of detectable PFAS for GW and benzene spiked GW at a 50% reduction of the initial aqueous concentration fall in the range of 1-60 g/kg sorbent. For FFWW the loading rate is more difficult to determine since a large fraction of the PFAS in the FFWW is not detectable with the applied analytical technique. Nevertheless the detectable PFAS sorbed fall within the same range, and if we assume that a relevant fraction of the PFAS is missed, the loading rate is presumably even higher. This can be expected since the concentration in the FFWW is, even when non-detected PFAS are excluded, almost two orders of magnitude higher. The presence of the artificially spiked benzene does not affect the loading rate of the sorbent by a large extent. The effect of the complex mixture of other contaminants in the FFWW cannot be quantified since the PFAS concentrations and the co-contaminants are at a different order of magnitude than for GW. When the effect of the addition of benzene is studied more carefully, it can be observed that the effect on the sorption coefficients of the large PFAS is marginal while for the smaller PFAS (especially PFBA and PFPeA) the sorption seems to be slightly reduced and the relation between the sorbent dose and the removal seems to flatten (PFBA). Although this was not clearly reflected in the figures for the total PFAS removal, the reduction of removal and flattening of curve suggests the following. Benzene competes for sorption sites with the smaller PFAS while larger PFAS are presumably better sorbed and experience less competition from a small organic chemical such as benzene.

APPENDIX 10: STRUCTURE OF ACTIVATED CARBON AND PFAS SORPTION

All types of activated carbon can be characterized in three categories (or combinations of these categories). These three categories are defined by pore size. The IUPAC (International Union of Pure and Applied Chemistry) defined three types of pores present in activated carbon: Macropores: > 50 nm, Mesopores: 2-50 nm and Micropores: < 2 nm. The final pore distribution of the granular activated carbon is determined by the product (e.g. coal, coconut) used for the production of the granular activated carbon and the activation conditions. The pore distribution with sorption sites determines the sorption capacity, where smaller pores have more sorption surface area and more capacity. The accessibility of the sorption surface is higher when there are more macropores that enable diffusion of molecules inside the material. So the optimal structure is a mixture of pore sizes with sufficient sorption sites. For PFAS constituents like PFOS, PFOA or Gen-X, the use of macro porous granular activated carbon is recommended. This phenomena is clearly visible in Figure 34 (provided by Desotec) where the sorption isotherm for a macropore granular activated carbon Organosorb 10AA) is compared with a micropore granular activated carbon (Organosorb 10).

Figure 34: Examples of sorption isotherms for PFOS on activated carbon.



APPENDIX 11: OVERVIEW OF TREATMENT TECHNOLOGIES FOR GROUNDWATER AND FIREFIGHTING WASTEWATER [1]

Evaluation matrix for treatment of groundwater

	Technical maturity	Reliability of data	Technical complexity	Reaching threshold values for long-chain PFAS	No need for pre-treatment for Fe / Mn	No need for pre-treatment for turbidity	Impact of high organic matter content	Tolerance of high salt content	Impact of high Petroleum substances content	Mass removal effectiveness for Short-chain PFAS	Mass removal effectiveness for Long-chain PFAS	No use of chemicals	No by-products	Key treatment parameter	Treatment costs
+ positive				**-** negative				**o** neutral							
Sorption technologies:														Operating time (PFOS)	
Activated Carbon	*Full-scale*	Many peer reviewed data	+	+	-	+	-	+	-	-	+	+	+	40,000 BV	+
MatCare	*Pilot-scale*	Single peer reviewed data	+	+	-	+	-	+	-	*No data*	+	+	+	*No data*	*No data*
Rembind®	*Pilot-scale*	Single peer reviewed data	+	+	-	+	-	+	-	*No data*	+	+	+	*No data*	*No data*
IEX without regeneration	*Full-scale*	Many peer reviewed data	+	+	-	+	-	-	-	+	+	+	+	150,000 BV	+
CustoMem without regeneration	*Lab-scale*	*Vendor-Information*	+	*No data*	-	+	-	+	-	*No data*	+	+	+	*No data*	*No data*
Cyclodextrin-based sorbent	*Pilot-scale*	*Vendor-Information*	+	+	-	+	-	+	-	+	+	+	+	6,300 - >55,000 BV	*No data*
Flocculation technologies:														Flocculent dosage / removal efficiency	
PerfluorAd	*Full-scale*	Single peer reviewed data	O	+ / -	+ / -	+	-	+	-	+	+	-	+	100 mg/L / 90%	*No data*
InSite	*Pilot-scale*	*Vendor-Information*	O	-	+ / -	+	-	+	-	*No data*	+	-	+	2 g/L / 99%	*No data*

	Technical maturity	Reliability of data	Technical complexity	Reaching threshold values	No Fe / Mn pre-treatment	No pre-treatment for turbidity	High organic matter	High salt content	Petroleum substances	Short-chain PFAS	Long-chain PFAS	No use of chemicals	No by-products	Key treatment parameter	Treatment costs
+ positive - negative **o** neutral															
Liquid-liquid separation technologies:														Energy demand / separation factor	
Nanofiltration, reverse osmosis	*Full-scale*	Many peer reviewed data	-	+	-	-	+	+	+	+	+	-	+	0.4 kWh/m^3 / 20%	o
Foam fractionation	*Pilot-scale*	*Vendor-Information*	-	+	-	+	+	+	+	+	+	+	+ / -	3 – 7 kWh/m^3 / < 2%	o
IEX with regeneration	*Pilot-scale*	*Single peer reviewed*	O	+	-	+	-	-	-	+	+	-	+	0.01 kWh/m^3 / 0.01 - 0.1 %	+
CustoMem with regeneration	*Lab-scale*	*Vendor-Information*	O	*No data*	-	+	-	+	-	*No data*	+	-	+	0.01 kWh/m^3 / 0.01 %	+
Cyclodextrin-based sorbent	*Pilot-scale*	*Vendor-Information*	O	+	-	+	-	+	-	+	+	-	+	0.01 kWh/m^3 / No data	*No data*
Distillation	*Pilot-scale*	*Vendor-Information*	-	*No data*	-	+	+	+	+	+	+	+	+	50 kWh/m^3 20%	-
Destruction technologies:														Energy demand for PFAS destruction	
Electrochemical degradation	*Lab-scale*	*Single peer reviewed*	+	+	-	+	O	+	+	+	+	+	-	50 kWh/m^3	+
Oxidation	*Lab-scale*	*Single peer reviewed*	+	-	-	+	-	+	-	+	+	-	-	*No data*	*No data*
Sonochemistry	*Lab-scale*	*Single peer reviewed*	+	+	-	+	+	+	-	+	+	+	+	100 kWh/m^3	o
UV radiation	*Lab-scale*	*Single peer reviewed*	+	-	-	-	-	+	*No data*	+	+	+	+	*No data*	*No data*
Distillation & Plasma	*Pilot-scale*	*Vendor-Information*	-	+	-	+	+	+	+	+	+	+	*No data*	4,500 kWh/m^3	-
Nanoscale zerovalent iron	*Lab-scale*	*Single peer reviewed*	-	-	-	+	*No data*	*No data*	*No data*	*No data*	+	+	+	*No data*	*No data*
Water Incineration	*Full-scale*	*Single peer reviewed*	-	+	+	+	+	+	+	+	+	+	+	700-2000 €/m^3	-

Evaluation matrix for treatment of firefighting wastewater (+: positive, -: negative, o: neutral)

	Technical maturity	Reliability of data	Technical complexity	Reaching threshold values	No pre-treatment for turbidity	Petroleum substances	Short-chain PFAS	Long-chain PFAS	No by-products	Key treatment parameter	Treatment costs
				+ positive		- negative		o neutral			
Sorption technologies:										Throughput	
Activated Carbon	*Full-scale*	*Single peer reviewed data*	+	+	+	-	-	+	+	*No data*	*No data*
MatCare	*Lab-scale*	*Single peer reviewed data*	+	*No data*	+	-	*No data*	+	+	*No data*	*No data*
Rembind®	*Pilot-scale*	*Single peer reviewed data*	+	+	+	-	+	+	+	*No data*	*No data*
IEX without regeneration	*No data*	*No data*	+	*No data*	+	-	o	-	+	*No data*	*No data*
CustoMem without regeneration	*No data*	*No data*	+	*No data*	+	-	*No data*	+	+	*No data*	*No data*
Cyclodextrin-based sorbent	*Pilot-scale*	*Vendor-Information*	+	+	+	-	+	+	+	*No data*	*No data*
Flocculation technologies:										Flocculent dosage / removal efficiency	
PerfluorAd	*Pilot-scale*	*Vendor-Information*	O	+ / -	+	-	+	+	+	*No data*	*No data*
InSite	*Pilot-scale*	*Vendor-Information*	O	-	+	-	*No data*	+	+	2 g/L / 99%	*No data*

	Technical maturity	Reliability of data	Technical complexity	Reaching threshold values	No pre-treatment for turbidity	Petroleum substances	Short-chain PFAS	Long-chain PFAS	No by-products	Key treatment parameter	Treatment costs
+ positive - negative **o** neutral											
Liquid-liquid separation technologies										Energy demand / separation factor	
Nanofiltration, reverse osmosis	*Pilot-scale*	Single peer reviewed data	-	*No data*	-	+	+	+	+	*No data*	*No data*
Foam fractionation	*Pilot-scale*	*Vendor-Information*	-	+	+	+	+	+	+ / -	3 - 7 kWh/m^3 / < 2%	**O**
IEX with regeneration	*No data*	*No data*	**O**	*No data*	+	-	o	-	+	0.01 kWh/m^3 / *No data*	*No data*
CustoMem with regeneration	*No data*	*No data*	**O**	*No data*	+	-	*No data*	+	+	0.01 kWh/m^3 / *No data*	*No data*
Cyclodextrin-based sorbent	*Lab-scale*	*Single peer reviewed data*	**O**	+	+	-	+	+	+	0.01 kWh/m^3 / *No data*	*No data*
Distillation	*Pilot-scale*	*Vendor-Information*	-	*No data*	+	+	+	+	+	50 kWh/m^3 20%	-
Destruction technologies:										Energy demand for PFAS destruction	
Electrochemical degradation	*Lab-scale*	*Single peer reviewed data*	+	+	+	+	+	+	-	250 kWh/m^3	+
Oxidation	*Lab-scale*	*Single peer reviewed data*	+	-	+	-	+	+	-	*No data*	*No data*
Sonochemistry	*Lab-scale*	*Single peer reviewed data*	+	+	+	-	+	+	+	300 kWh/m^3	+
UV radiation	*Lab-scale*	*Single peer reviewed data*	+	-	-	*No data*	+	+	+	*No data*	*No data*
Distillation & Plasma treatment	*Pilot-scale*	*Vendor-Information*	-	+	+	+	+	+	*No data*	4,500 kWh/m^3	-
Nanoscale zerovalent iron	*Lab-scale*	*Single peer reviewed data*	-	-	+	*No data*	*No data*	+	+	*No data*	*No data*
Water Incineration	*Full-scale*	*Single peer reviewed data*	-	+	+	+	+	+	+	700-2,000 €/m^3	-

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