

# PFAS removal performance of novel technologies for treatment of firefighting water and groundwater

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**Abstract:** Per- and polyfluoroalkyl substances (PFAS) are a group of widely used man-made organic chemical substances. PFAS have been used because of their particular physicochemical properties: most are stable at high temperatures, recalcitrant to chemical oxidation and biological degradation, and act as a surfactant. Many PFAS may also be bio-accumulative and toxic and there are concerns around their environmental effect.

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.

Experiments showed that all sorbents were able to remove PFAS from both groundwater containing PFAS as well as firefighting wastewater, but the latter required sorbent dosages in g/L range. It was therefore concluded that groundwater containing PFAS can be treated with one of the tested sorbents directly, while for firefighting wastewater, typically has higher PFAS concentrations as well as other contaminants, a treatment train approach is likely to be more efficient.

**Keywords:** PFAS (per- and polyfluoroalkyl substances), treatment technologies, PFAS impacted groundwater, firefighting wastewater, comparative evaluation.

## 1. Introduction

PFAS are a large family of thousands of synthetic chemicals. 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<sub>2</sub>)<sub>n</sub>–. Concern around the environmental effects of PFAS began when it was realised that, due to their resistance to biodegradation, perfluorooctane sulfonate

(PFOS) and perfluorooctanoic acid (PFOA) were ubiquitous and widely detected in various biological and environmental matrices [1]. Among the many uses of PFAS, they are ingredients (1 to 5 wt%) in many formulations of a aqueous film forming foams (AFFF) that are used to fight flammable liquids fires [2], and have been used at various sites, including airports, military establishments and sites that stored petroleum products in bulk (e.g., oil refineries, terminals, and depots) [3]. As a result, release of PFAS to the environment at oil refinery sites may occur as a consequence of accidental spillages, or more commonly during legitimate use of firefighting foams. These uses and releases may cause surface water, as well as soil and groundwater (GW) impacts that require risk assessment and management action [2, 3].

PFAS are a challenging family of compounds to treat due to their unique properties. There are multiple PFAS-treatment technologies available on the market, applying three different treatment concepts: A) Sorption technologies: PFAS bind to sorption sites in or on the surface of a sorbent material; B) Physical separation techniques: separation of wastewater stream into two. First stream (concentrate) small in volume and contains majority of PFAS. Second stream much larger volume and predominantly free of contamination; and C) Reactive degradation: (bio)chemical processes where PFAS is degraded into intermediate products or completely mineralized.

In 2020, Concawe produced a literature review of commercial and pilot-ready treatment systems capabilities and operating ranges, for both GW and firefighting wastewater (FFWW) containing PFAS [4]. The review identified several knowledge gaps on treatment performance, which Concawe has sought to address in subsequent experimental work of this study, which contained 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 considering their practical application in the field, costs and potential production of waste. This paper describes the first part of the study.

## 2. Materials and methods

PFAS-impacted GW and FFWW were sourced from two and four sites, respectively, to establish the experimental conditions in terms of presence and concentrations of different PFAS residuals in GW and FFWW, along with data on the other typical hydrocarbon constituents that were also present in those waters. Water analyses were carried out in triplicate using solid-phase extraction (SPE) and liquid chromatography tandem mass spectrometry (LC-MS<sup>2</sup>) at the University of Amsterdam (UvA). The PFAS analytical suite included 17 target PFAS, of which five were sulfonic acids, eleven were carboxylic acids and one sulfonamide. These substances were commonly applied in the past and/or are transformation products of various PFAS precursors that are currently in use [5]. In addition, three fluorotelomer sulfonates (4:2 FTS, 6:2 FTS and 8:2 FTS) and one were analysed, extending the analysis suite to 20 PFAS species in total (**Table 1**). The method used to analyse the PFAS is validated according to ISO standard ISO/IEC 17025. Furthermore, the amount of total oxidizable precursors (TOP) was analysed using the TOP-assay protocol [6]. After the pre-experimental analyses one GW and one FFWW sample were prepared for batch testing.

For both GW and FFWW treatment, novel adsorbent technologies (two surface modified clay-based (SMC 1 and 2) and two bio-based and polymeric based (BP 1 and BP 2) adsorbents) were tested and compared against granular activated carbon (GAC) as a benchmark. One of each sorption technology type was then selected for continuous testing in a small scale column based performances in batch tests and applicability of the material in columns. In addition, three novel physical separation techniques were tested; flocculation (FLOC), nanofiltration (NF), and foam- and ozo fractionation (FF & OF). Physical separation tests were either batch or continuous due to design and project constraints. NF was tested with FFWW only since GW treatment was assumed to give concentrate volumes which are large and impractical. Reactive degradation technologies were tested as these were considered as technically challenging to set up for small scale tests, would likely lead to unknown transformation products, and have uncertainties around to scale up and costs.

Sorption coefficients ( $K_{sw} = [\text{PFAS}] \mu\text{g/kg sorbent} / [\text{PFAS}] \mu\text{g/L water}$ ) were derived from the data by fitting Freundlich isotherms defined (extrapolated) at an aqueous concentration of 1  $\mu\text{g/L}$  based on sorption isotherms.

## 3. Results and discussion

For the 20 species analysed for the sum of PFAS concentrations in sourced GW was about 13  $\mu\text{g/L}$ , and a

factor 730 lower than the sourced FFWW (about 9500  $\mu\text{g/L}$ ). In addition, the TOP-assay performed on the FFWW showed a big increase in PFAS concentration, ranging from 80 000 to 320 000  $\mu\text{g/L}$ , indicating the importance of assessing PFAS precursor substances. PFAS composition in the GW was dominated by L- and Br-PFOS, PFHxS, PFHxA and PFBS, whereas the PFAS composition of FFWW were dominated by 6:2 FTS (85%) and PFHxA (4%) while all others were individually <2% and account for 11% when combined. Many PFAS had concentrations close to the limit of quantification, which complicated determination of removal effectiveness.

In GW batch sorption and flocculation tests, GAC and SMC1 showed highest removal of sum (measurable) PFAS (**Figure 1**) and for most individual PFAS. Sorbent dosages below 100 mg/L or even 10 mg/L appear to be sufficient. Apparent loading rates were determined at 50% of initial concentration and showed that BP 1, BP 2 and SMC1 gave lowest loading (0.9-1.5 [g PFAS removed] / [kg material loaded]) whereas GAC showed ca 5 times higher loading. FLOC was observed to be most effective at the lowest dosages but did not achieve (near) full PFAS removal. For the removal of individual PFAS present, it was observed that the longer the C-F chain the more effective all sorbents become in removing the PFAS as the length of (fluorinated) chains affects the aquatic solubility as well as the hydrophobicity of molecules. Highest observed average  $K_{sw}$  values per PFAS type were for GAC (PFBA =  $2.1 \times 10^4$  L/kg; PFPeA =  $5.2 \times 10^4$  L/kg; PFHxA =  $1.0 \times 10^5$  L/kg; PFOA =  $4.3 \times 10^5$  L/kg), BP 1 (PGHpA =  $1.2 \times 10^5$  L/kg) and SMC 2 (PFOS =  $1.6 \times 10^7$  L/kg).

Based on the GW batch tests, SMC 2, GAC and BP 1 were selected for column studies to estimate breakthrough moments of the measured compounds in passed Bed Volumes (BV). 20% breakthrough was selected as individual PFAS concentrations did not always allow a lower threshold due to limit of quantification restrictions. For all sorbents no breakthrough was observed after > 40,000 BV for longer chained PFAS ( $F \geq 8$ ), whereas GAC seemed to be a bit more capable of removing the shorter chained PFBA and PFPeA (**Table 2**). GAC showed desorption of PFBA and PFPeA after breakthrough started, which was not observed for the others, which suggested that compounds with higher sorption affinity displaced shorter chained PFAS. For GW treatment tests overall, GAC appeared most robust in the batch and continuous lab tests, while all tested sorbents (batch and continuous) were capable of removing over 85% of sum PFAS from impacted GW and FLOC showed incomplete removal.

In FFWW batch sorption and flocculation tests GAC, SMC 1, BP 2 and FLOC were the most effective in reducing sum of PFAS (dominated by 6:2 FTS). FLOC was the most effective at the lowest dosages. All sorbents required dosages in range of g sorbent per L of treated water for relevant PFAS reduction. Therefore, FLOC appeared to be able to efficiently (pre)treat FFWW, whereas for sorbents direct FFWW treatment is not advisable due to high sorbent loading required and incomplete PFAS removal.

For FF with ozone and air, full process optimisation was not feasible due to excessive foam formation. Further, treatment affected PFAS composition during the experiment (oxidation of precursors leading to 2-fold increase of PFPeA during treatment with ozone) which made analysis for individual PFAS removal not possible. Despite suboptimal operating conditions and potential biases of oxidation during treatment, FF effectively lead to the concentration of PFAS in a small volume and significant reduction of PFAS in the treated water; for GW treated with ozone 9-10L was able to remove 76% of sum (measurable) PFAS, and giving a concentrate volume of 0.075 L with a PFAS concentration factor of 3.8-4.2. Thus, FF showed potential as a pretreatment technology.

For NF, the NF membrane was able to remove the PFAS from FFWW effectively during the first hours of operation (0.25-10 h), reaching removals of 90-95%. When operated for a longer period trans-membrane flows dropped and the passage of PFAS slowly increase to levels approaching concentrations in the feed-water. Therefore, FFWW may require pre-treatment to prolong membrane service life.

#### 4. Conclusions and outlook

Physical separation techniques such as flocculation and FF appeared to be more suitable to (pre)treat heavily contaminated matrices (e.g. FFWW) while sorption techniques were more suitable to treat (polish) cleaner

matrices (e.g. GW). A general solution is not available and a case-by-case assessment must be made. Likely, a multi-barrier approach is most appropriate for some sites and specific matrices; i.e. have an initial step to remove bulk contamination (incl. co-contaminants) and subsequent polishing step to reduce PFAS loads to acceptable levels.

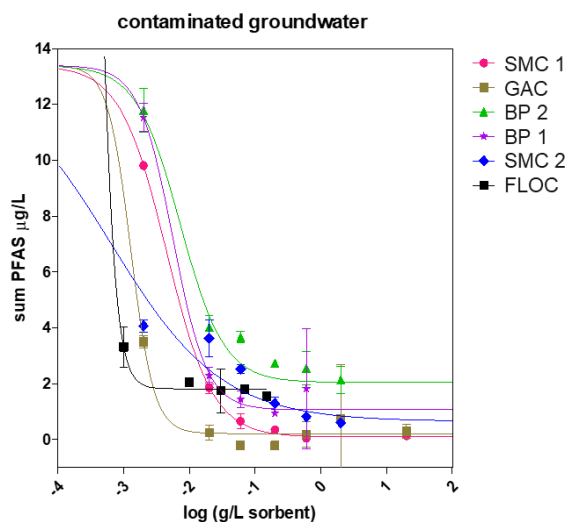
Environmental waters may contain even shorter chain PFAS not analysed in this study. These will be challenging for all treatment technologies tested here as these PFAS have lower sorption affinities and are more water soluble. It is recommended to study a wide spectrum of PFAS when assessing treatment efficiency in field or in pilot tests, as short chain PFAS will likely be the bottleneck for the treatment efficiency. It should also be noted that reactive treatment technologies were not tested in this study. However, in combined treatment systems these technologies may prove attractive as well.

**Disclaimer** - Conclusions resulting from this particular study, should not be interpreted as any official endorsement

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**Table 1:** PFAS analytical suite

Substance	Abbreviation
<i>Sulfonic acids (PFSA)</i>	
Perfluorobutane sulfonate	L-PFBS
Perfluorohexane sulfonate	L-PFHxS
Perfluorooctane sulfonate (linear)	L-PFOS
Perfluorooctane sulfonate (branched)	Br-PFOS
Perfluorodecane sulfonate	L-PFDS
<i>Carboxylic acids (PFCA)</i>	
Perfluorobutanoic acid	PFBA
Perfluoropentanoic acid	PFPeA
Perfluorohexanoic acid	PFHxA
Perfluoroheptanoic acid	PFHpA
Perfluorooctanoic acid	PFOA
Perfluorononanoic acid	PFNA
Perfluorodecanoic acid	PFDA
Perfluoroundecanoic acid	PFUnA
Perfluorododecanoic acid	PFDoA
Perfluorotridecanoic acid	PFTTrA
Perfluorotetradecanoic acid	PFTeA
<i>Perfluorinated Sulfonamide</i>	
Perfluorooctane sulfonamide	PFOSA
<i>Fluorotelomer sulfonates</i>	
4:2 Fluorotelomer sulfonate	4:2 FTS
6:2 Fluorotelomer sulfonate	6:2 FTS
8:2 Fluorotelomer sulfonate	8:2 FTS



**Figure 1:** PFAS decrease from the impacted groundwater 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.

**Table 2:** 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 %			Remarks/ observations
		SMC 2	GAC	BP 1	
PFBA	1.17	2,000	7,000	Immediate	GAC showed desorption profiler after 7,000 BV
PFPeA	2.17	10,000	13,000	1,000	GAC showed desorption profiler after 17,000 BV
PFH <sub>x</sub> A	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	
PFH <sub>x</sub> S	11.3	> 40,000	> 40,000	> 40,000	
PFOS	35.5	> 40,000	> 40,000	> 40,000	

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