Removal of Perfluoroalkyl Substances (PFASs) in Industrial Runoff Water

By Subhash S. Rathnaweera, Eilen A. Vik, Lelum D. Manamperuma and Bjørn Rusten

Subhash S. Rathnaweera (Ph.D), *Eilen Arctander Vik* (Ph.D) *Lelum D. Manamperuma* (Ph.D) and *Bjørn Rusten* (Dr.ing.) are scientists at Aquateam COWI.

Sammendrag

Fjerning av Perfluoroalkyl substanser (PFAS) fra avløpsvann fra industri. Studien ble gjennomført for å undersøke fjerning av poly- og perfluoralkylstoffer (PFAS), en utbredt gruppe av miljøforurensninger, ved bruk av tre ulike adsorbenter. To typer granulær aktivt kull (GAC) viste bedre effekt sammenlignet med en testet mikroporøs polymertype. Isotermstudier avdekket at likevekt for PFAS-adsorpsjon kan oppnås etter 70 timers risting med GAC. Videre ble det funnet at prosentvis fjerning var høyere når testene ble gjennomført ved 20 °C sammenlignet med 10 °C. Langmuirs modell viste best korrelasjon for isotermtestene. Adsorpsjonskapasiteten for 110 og 55 mg tot-PFAS/kg GAC ble beregnet for henholdsvis 20 °C og 10 °C. Kolonnetester viste ingen betydelig forskjell for tester utført med ulike konsentrasjoner og empty bed-kontakttider (EBCT). Kolonnetestene bekreftet en gjennomsnittlig adsorpsjonskapasitet på 37 g tot-PFAS/tonn GAC før konsentrasjonen i utløpet nådde en grense på 1 µg/l ved 20 °C.

Summary

This study was conducted to explore the removal of poly- and perfluoroalkyl substances (PFAS), a widespread group of environmental contaminants, using three different adsorbents. Two types of granular activated carbon (GAC) showed better performance compared to the tested microporous polymer type. Isotherm studies revealed that equilibrium for PFAS adsorption can be achieved after 70 hours of shaking with GAC. Furthermore, the percentage removal was found to be higher when the tests were conducted at 20 °C as compared to 10 °C. Langmuir's model showed the best correlation for the isotherm tests. The adsorption capacities of 110 and 55 mg tot-PFAS/kg GAC were calculated for 20°C and 10°C, respectively. Column tests showed no significant difference for tests conducted with different concentrations and empty bed contact times (EBCT). The column tests confirmed an average adsorption capacity of 37 g tot-PFAS/ton GAC before the effluent concentration reached a 1µg/l limit at 20 °C.

Introduction

Per- and polyfluoroalkyl substances (PFAS) are a widespread group of environmental contaminants known as "forever chemicals", meaning that PFAS do not break down easily once released into the environment. PFASs are anthropogenic chemicals that have been used for over 80 years in industrial applications, household products, food packaging, firefighting foams, and many other products. One of the main concerns with PFAS is their persistence in the environment. The

persistent nature of PFAS leads to its accumulation in air, water, soils, as well as living organisms, including humans. The two most well-known and extensively studied PFAS are perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) (Espana *et al.*, 2015).

The major concerns associated with PFAS pollution are related to potential health effects (Fenton *et al.,* 2020). PFOA and PFOS have been linked to various adverse health outcomes in humans, including kidney and testicular cancer, liver damage, thyroid disorders, developmental issues in infants and children, and effects on the immune system. While most research has focused on PFOA and PFOS, there are thousands of different PFAS, and the health effects of many of them are not yet fully understood.

Addressing the PFAS pollution problem requires a multi-faceted approach. Governments and regulatory agencies are setting guidelines and standards for acceptable levels of PFAS in water and food, and efforts are underway to regulate and phase out certain PFAS and develop safer alternatives. Remediation of contaminated sites and water treatment technologies capable of removing PFAS are also being researched and implemented. The Norwegian Environmental Agency (NEA) has compiled a priority list of PFAS substances, which includes PFOS (2002), PFOA (2007), C9-PFCA to C14-PFCA (2014), PFHxS (2017), PFBS (2019), PHxA (2020), and HFPO-DA (GenX) (2020), as stated by the NEA in 2022.

In 2018, a waste management company (WMC) in Norway, which specialised in decommissioning of metal installations, discovered that its runoff water contained over 10 µg/l of PFAS. The NEA had recently implemented new emission limits for PFAS in wastewater and runoff water. In response, the company aimed to enhance its existing wastewater treatment plant by adding a new treatment process that targets the removal of PFAS from surface runoff water.

It was found that PFAS spikes in WMC water did not occur regularly, and the source was uncertain. Figure 1 shows the quarterly average PFAS concentration (log scale) in water from the WMC yard between the years 2009 and 2021. It had been shown that the PFAS concentrations tended to rise in surface runoff during the reception and decommissioning of offshore process plants from the North Sea. One of the explanations for the PFAS contamination of offshore oil structures is the use of firefighting foams (Gallen *et al.,* 2018). Considerable amounts of firefighting foams are used on offshore platforms, both for training purposes and for firefighting purposes. Aqueous Film Forming Foam (AFFF) was one of the popular firefighting foam types commonly used on offshore structures (Hatton *et al.,* 2018). The offshore plants are now gradually discontinuing the use of AFFF firefighting foams due to their extremely high PFAS content. Furthermore, WMC operates a firefighting facility that employs fire foams containing PFAS. This can also contribute to the PFAS levels found in surface runoff water.

In 2020, the WMC obtained a discharge permit from the NEA that allows for a weekly average effluent concentration of no more than 4 µg/l and a maximum yearly emission of 0.6 kg of PFAS. According to Dale *et al.* (2022), in 2021, thirteen weekly water samples showed levels higher than the allowed concentration of 4 µg/l, and the yearly discharge was 1.1 kg, which exceeded the limit of 0.6 kg/year. Figure 1 (lower) shows the analysis with regard to 10 PFAS types in weekly samples during the year 2021.

Removing PFAS from water is a challenging task due to their chemical stability and resistance to degradation. There are several technologies available for PFAS removal from water, and the selection of the best available technology (BAT) depends on factors such as water quality, PFAS concentration, and treatment objectives. Moreover, BAT selection should consider site-specific factors and comply with local regulations and guidelines. Activated carbon adsorption, ion exchange, reverse osmosis (RO), advanced oxidation processes (use of chemical oxidants or UV light to degrade the compounds) and biological treatment are some of the most used technologies (Fulmer, 2016; Senevirathna *et al.*, 2010a, 2010b; Lindegren, 2015).
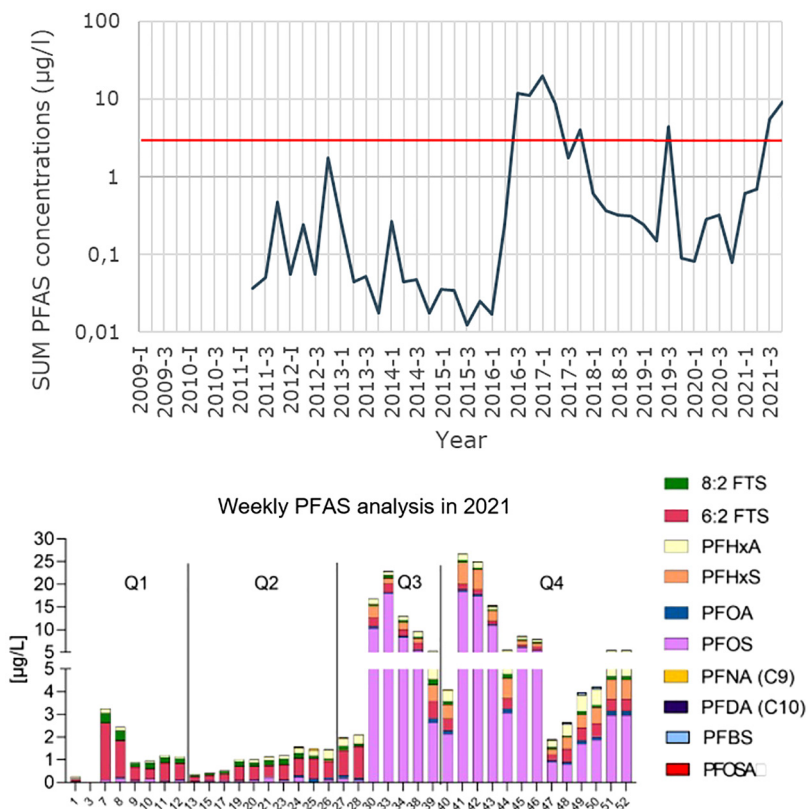
Figure 1. Quarterly average PFAS concentration (log scale) in effluent water from the WMC yard from 2009-2021(upper graph) and the weekly sample analysis in 2021 (lower graph) (from Dale et al., 2022).

A lab-scale experiment was conducted to evaluate the effectiveness of activated carbon adsorption as well as ion exchange in treating water from the WMC.

Materials and Methods

Approximately one cubic meter of surface water was collected from the WMC yard for laboratory studies. As the PFAS concentrations in the water emissions from the WMC yards were not always high, collected water sample had relatively low PFAS concentrations. Therefore, the water had to be spiked with PFAS to prepare water for lab studies. A mixture of fluorotelomer sulfonate (FTS), PFOS, and PFOA, which were the main PFAS substances found in WMC discharge water, was prepared for this purpose. 40% PFOS solution and 95% PFOA powder were obtained from Merck Chemicals, but FTS

was not commercially available. Therefore, a stock solution of FTS was prepared using the firefighting foam referred to as AFFF. AFFF contains a mixture of water, hydrocarbon surfactants (which help the foam spread and adhere to surfaces), and PFAS. The PFAS are what give AFFF its unique properties, including its ability to form a stable foam blanket. The firefighting foam contains high concentrations of FTS as well as PFOS and PFOA (Hatton *et al.*, 2018).

Using the firefighting foam was challenging because it added high concentrations of organic carbon (TOC) to the solution. These other organic compounds competed with PFAS for the adsorption to the material tested for PFAS removal. To prevent the impact of TOC caused by firefighting foam, a laboratory-scale biological degradation treatment using an MBBR (Moving Bed Biofilm Reactor) was performed.
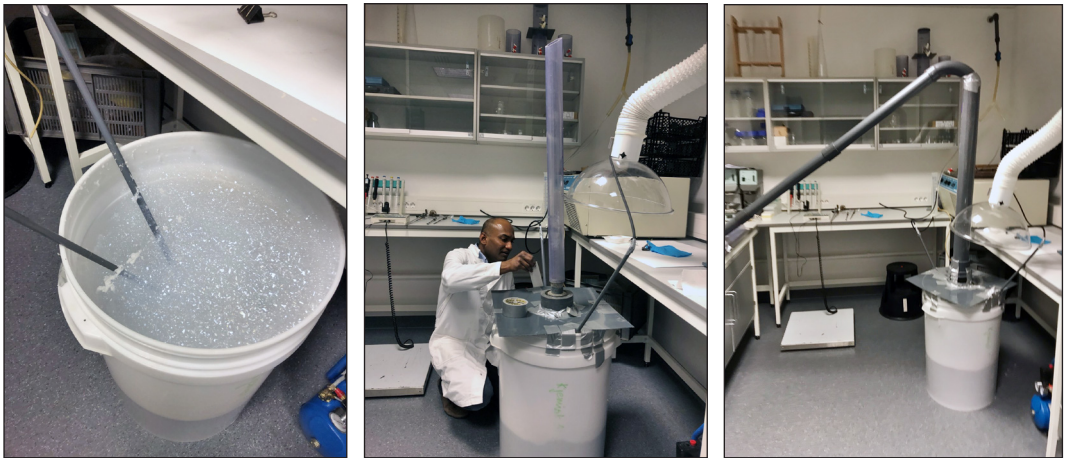
Figure 2. Biofilm reactor (MBBR) designed for removal of organic carbon (TOC) from AFFF firefighting foam. The structure was made to prevent losses due to foam formation.

Table 1. Properties of three adsorbent types

Adsorbent	Surface area (m²/g B.E.T)	Density (g/liter)	Iodine number (mg/g)	Grain size (mm)
N830	1100	500	950	0.6-2.4
F400	1050	540	1000	0.5-0.75
Amb	725	1080		0.1-1.4

Active biofilm carriers for the MBBR reactor were obtained from a wastewater treatment plant. The bioreactor was aerated to keep biofilm carriers in suspension and to make the dissolved oxygen concentration higher than 5 mg/l. Special precautions had to be taken to avoid problems due to the foam bubbles in the reactor. After ten days, the process proved to be efficient as it successfully removed 84% of TOC and 79% of chemical oxygen demand (COD). Pictures from the tests are shown in Figure 2.

Isotherm tests (IS) were conducted by employing two commercially available GAC types Filtrasorb 400 (F400) (obtained from Calgon Carbon) and Norit 830 (N830) (obtained from Cabot /Brenntag) and a synthetic macroporous polymer Amberlite ZAD4 (Amb) (obtained from Sigma Aldrich). Table 1 presents the properties of the three adsorbents.

The first IS test (IS-1) was carried out for screening and to compare the efficiency of the three adsorbent types. Three amounts (1g, 2g and 5g) of each adsorbent were each added to 1 l of PFAS solution (1mg/l) in bottles and shaken on a rotary shaker for 110 hours at room temperature (20 °C).

Only N830 was used for the second IS (IS-2) to investigate the influence of temperature on the adsorption capacity of GAC. IS-2 was conducted using a set amount of N830 (1 g) in different PFAS concentrations (0.0, 2.5, 5.0, 10, 20 and 50 mg/l) and shaken for 94 hours at two different temperatures (10 °C and 20 °C).

IS-3 was conducted to study the adsorption kinetics of two GAC types. Six bottles were added one gram of N830 and one litre of PFAS mixture (50 mg/l). A further six bottles were added 1 g F400 and 1 litre of PFAS mixture (50 mg/l) water each. The bottles were shaken on a rotary shaker at a constant speed at room temperature (20 °C). Samples for analysis were taken after 2, 4, 6, 22, 70 and 94 hours of shaking.

Three column tests were performed with two initial PFAS concentrations and two empty bed contact times (EBCT). Three columns with 2.5 cm diameter and 40 cm height were filled with
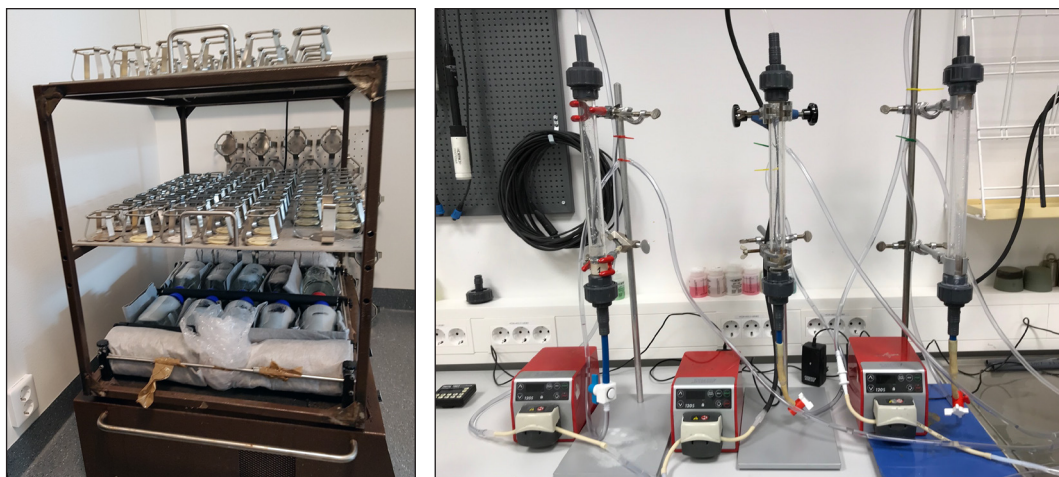
Figure 3. Lab-scale isotherm tests on rotary shaker (left) and in column tests (right).

10 g (20 ml) of N830 in each. Columns 1 and 2 were continuously fed with 8.7 µg/l PFAS solution at 2 ml/min and 1 ml/min, respectively, giving an EBCT of 10 and 20 minutes. Column 3 was fed with 6.1 µg/l PFAS solution at a rate of 2 ml/min (10 min EBCT). The columns were operated for 52 days, and 8 064 bed volumes were reached by the columns with 10 min EBCT and 4 032 bed volumes completed for the column with 20 min EBCT.

Figure 3 shows the IS tests on rotary shaker (left) and the test setup for column tests (right). All samples were analysed for 33 different PFAS substances.

Results and discussion
Isotherm experiments
The four graphs in Figure 4 show PFOS, PFOA, 6:2 FTS and total-PFAS (sum-PFAS) removal with 1, 2 and 5 grams of N830, Amb and F400. The tests showed 30% PFOS removal with 1 g N830, but the PFOS removal with 1 g Amb and 1 g F400 measured negative due to error either in sampling or analysis. With 2 and 5 grams N830 and F400 removed over 99% PFOS, while only 55% and 66% PFOS were removed with 2 and 5 g Amb. PFOA and 6:2 FTS removal with the three adsorbents also showed the same pattern as PFOS. Near 100% removal of PFOA and 6:2 FTS could be seen when employing 2

and 5 g N830 and F400. Maximum PFOA and 6:2 FTS removal for Amb were achieved with 5 g and the removals were 73% and 45% respectively.

Both GAC types displayed significantly better performance than the Amb, giving nearly 99 % sum-PFAS removal when employing 2 or 5 g. In contrast, the Amb polymer removed only about 45% sum-PFAS per 5 g Amb. Therefore, Amb was not considered for further investigations.

IS-2 was run at two temperatures, at ambient temperature of 20 °C and controlled room temperature of 10 °C. As shown in Figure 5, the percentage PFAS removal at two temperatures varied with increasing influent concentrations. Maximum removal at 10 °C was approximately 64% (27 mg tot-PFAS/g GAC) at an influent concentration of 42 mg tot-PFAS/l. At 20 °C, around 95% removal (40 mg tot-PFAS/g GAC) was reached with the same influent concentration. The lowest removal rate of the studied compounds was shown for PFOA at both temperatures.

The IS results were evaluated using Langmuir's (Langmuir, 1916) and Freundlich's (Freundlich, 1906) models. The best correlation was obtained with the Langmuirs model with 99% correlation at both temperatures (Figure 6). Using Langmuir's model, adsorption capacities
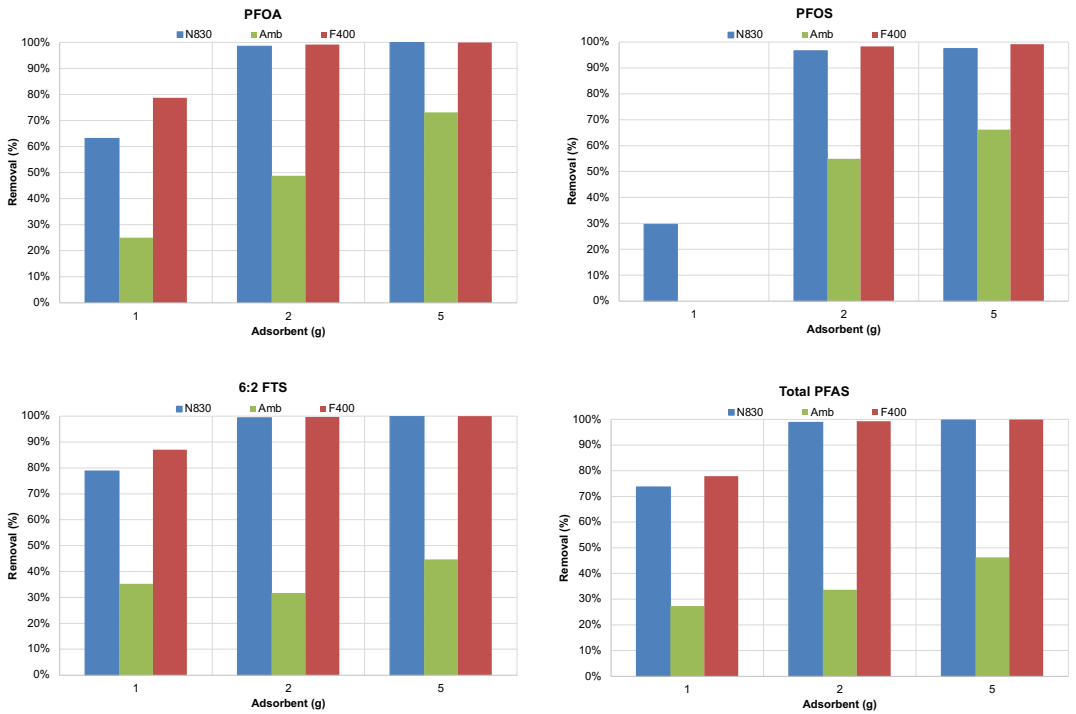
Figure 4. Total removal of PFOS, PFOA, 6:2 FTS and Sum PFAS using 1, 2 or 5g adsorbent, 110 hours (%).
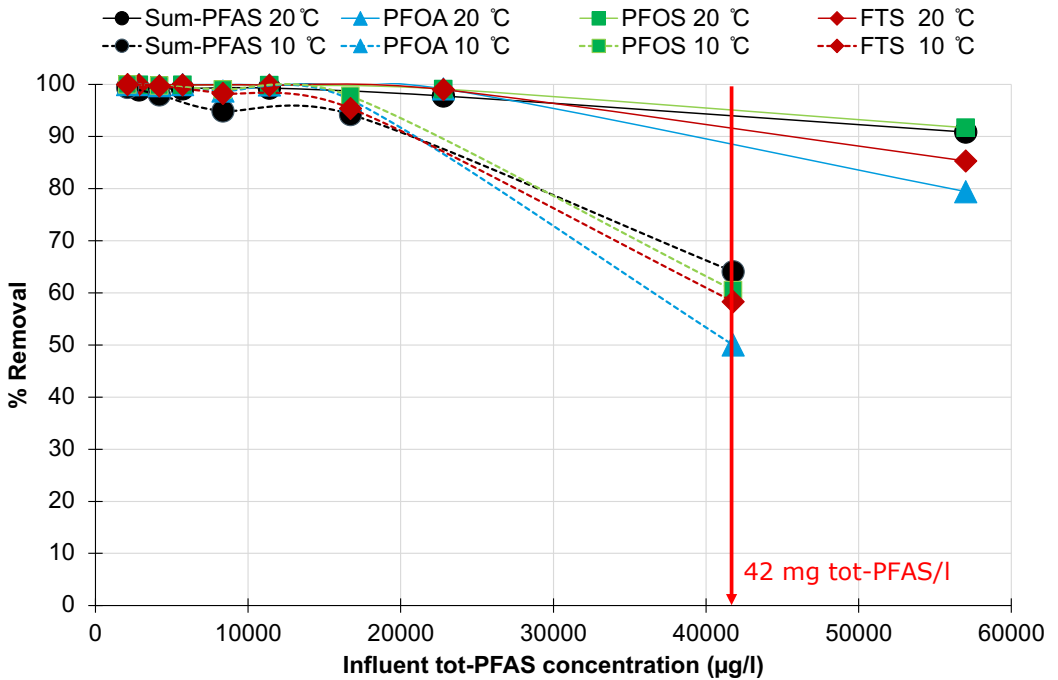

Figure 5. The percentage removal of tot-PFAS, FTS, PFOS and PFOA by GAC-adsorption using 1g N830 related to increased PFAS concentrations at 10 and 20 ºC - IS2.
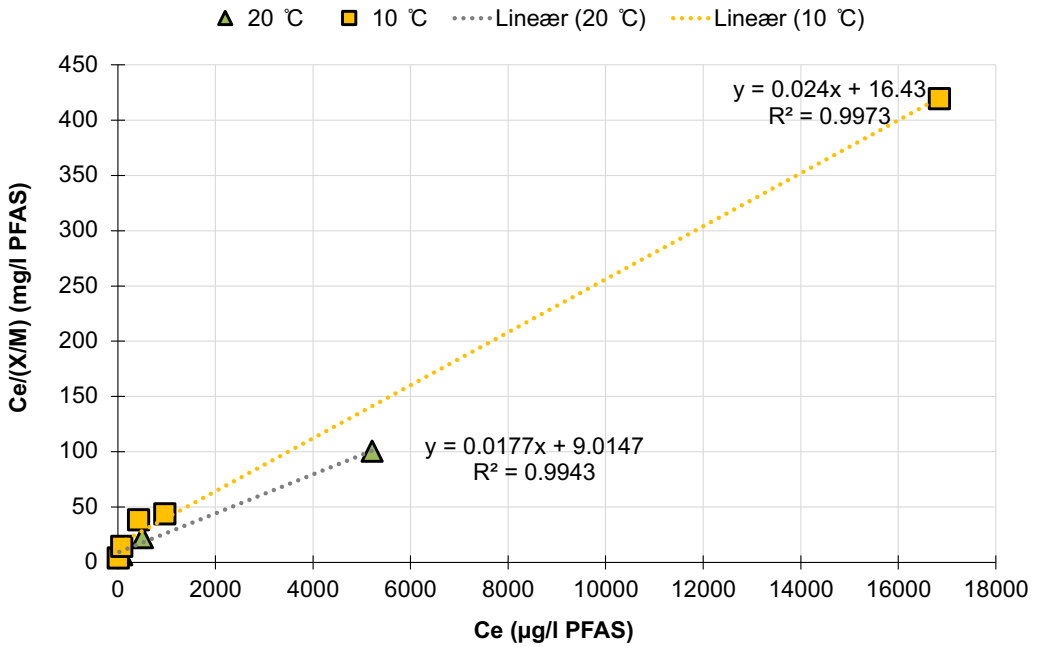
Figure 6. Langmuir isotherm curves (Sum-PFAS) for tests at 10 and 20 ºC. Sampling after 94 hours.

The legend of Figure 6 reads: △ 20 ℃   □ 10 ℃   ⋯⋯ Lineær (20 ℃)   ⋯⋯ Lineær (10 ℃)

Equations shown on Figure 6:

$$y = 0.024x + 16.43$$
$$R^2 = 0.9973$$

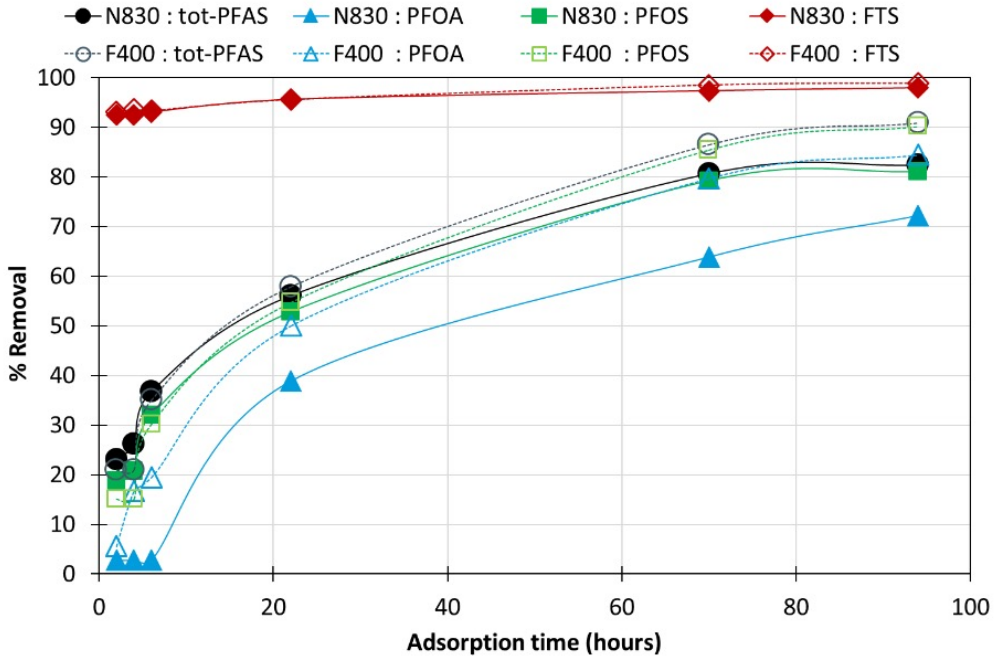$$y = 0.0177x + 9.0147$$
$$R^2 = 0.9943$$

Figure 7. Percentage removal of tot-PFAS, FTS, PFOS and PFOA versus adsorption time -IS3

of 110 and 55 mg tot-PFAS/kg GAC were found, for 20 and 10 °C respectively, at an effluent concentration of 1 µg/l.

Figure 7 shows the results of the IS-3. It took about 70 hrs for both GAC types to reach equilibrium concentration. Maximum removal after

96 hours (assuming equilibrium) with F400 was 51 mg sum-PFAS/l (91% removal) while removal with N830 was 46 mg sum-PFAS/l (81% removal). The 5 mg/l difference between the two GAC types should not be given weight, due to uncertainty in PFAS analysis, which was higher than 20%.

Column experiments

Three column tests with two initial PFAS concentrations (8.7 and 6.1 µg sum-PFAS /l) and two EBCTs (10 and 20 min) were performed. All three columns showed almost the same results, as can be seen in the breakthrough curves (Figure 8). Considering 90% removal as the breakthrough limit, the "unsaturated", "partially saturated" and "saturated" phases of the columns were identified as shown in the figure. There were approximately 1800 bed volumes in the unsaturated phase. Between 1800 and 9000 bed volumes was the partially saturated phase. GAC was saturated with over 9000 bed volumes.

Estimating these phases is required when designing adsorption filters with lead/lag configurations. In the context of adsorption filters, lead/lag configuration refers to the arrangement of multiple filters in a system to optimize their efficiency and effectiveness. The lead filter is the first stage in the adsorption filter system. Its primary purpose is to capture the bulk of the contaminants and pollutants present in the fluid stream. When the fluid stream passes through the lead filter, a significant portion of the impurities is adsorbed onto the filter media. The lag filter(s) follow the lead filter in the adsorption filter system. These filters complement the lead filter's function by further removing any remaining contaminants and pollutants from the fluid stream. This configuration allows the lead filter to be used until it is saturated, before consuming the unsaturated phase of the lag filter.

The effluent concentration of 1 µg/l was exceeded after 2000, 2100 and 2250 bed volumes of columns 1, 2 and 3, respectively (Figure 9).
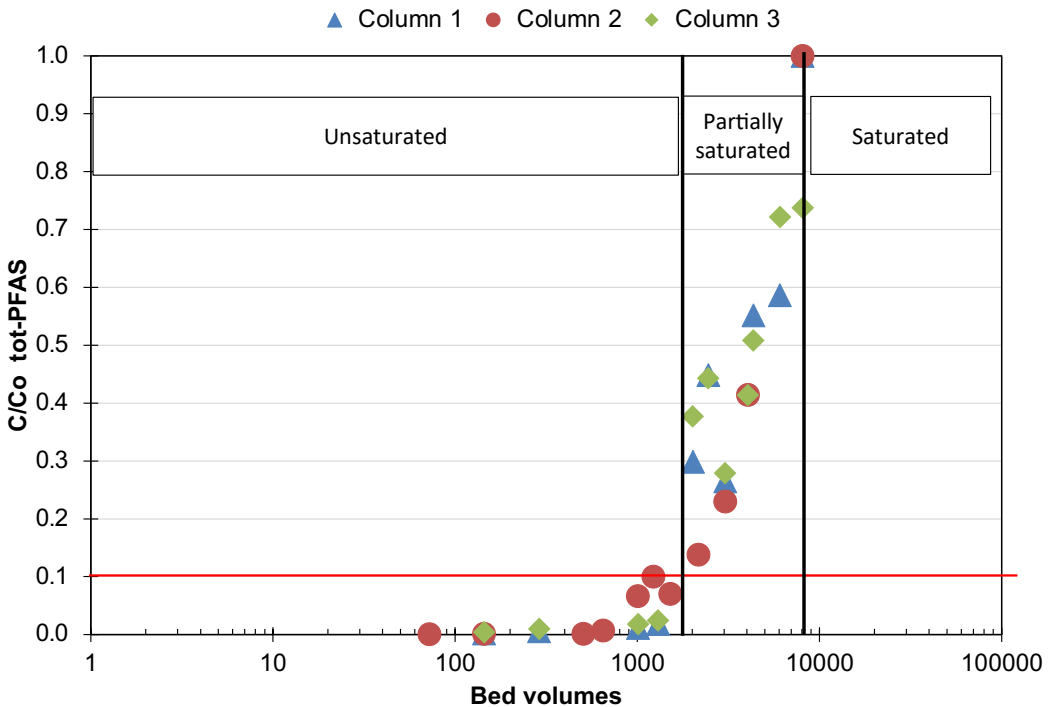

Figure 8. Breakthrough curves (C/Co vs bed volumes) of three columns. The red horizontal line is the breakthrough at C/Co=0.1.
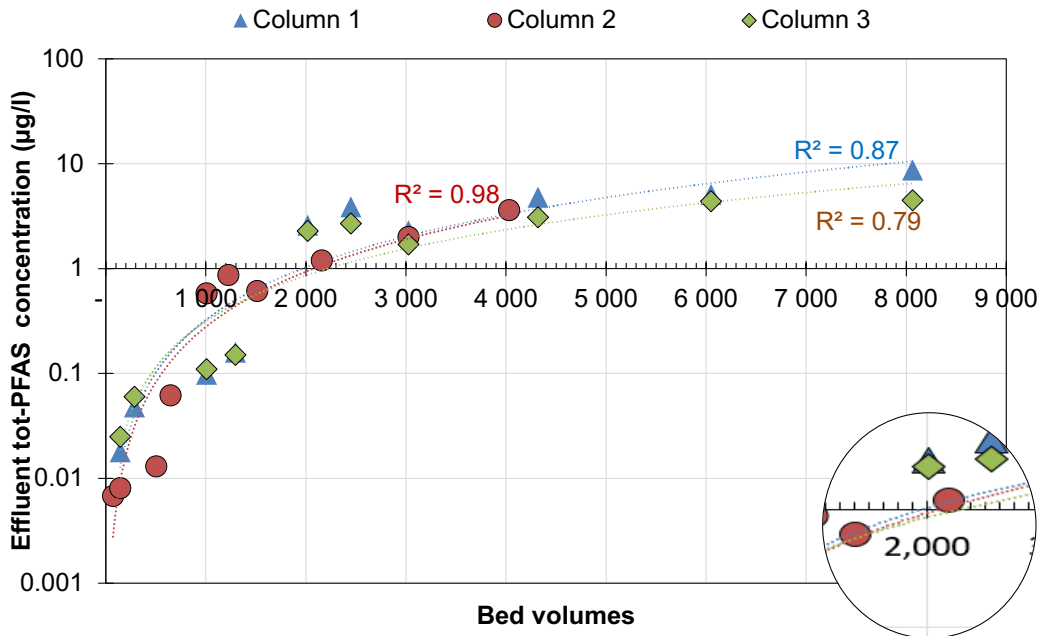
Figure 9. The effluent concentration of sum-PFAS as a function of the number of bed volumes.

This corresponds to an average adsorption capacity of 37 g tot-PFAS/ton GAC before the effluent concentration reaches the 1µg/l limit at 20 °C.

The results of these experiments were used as the basis for designing a full-scale PFAS treatment unit for the WMC yard. The existing treatment plant of the WMC yard includes chemical precipitation with iron chloride and separation in Dynasand filters. The proposed design includes a lead/lag configuration of two GAC filters (Dynasand) as the final treatment step, and it is recommended to carry out pilot scale experiments to ensure proper design.

Conclusions

The study shows that a proper PFAS removal system can be in place at the WMC yard. Design criteria for PFAS removal from the WMC yard showed >90 % removal of PFOS and PFOA using granular activated carbon (GAC) (NORIT 830 and Filtrasorb 400). Total PFAS emissions can be reduced by 80-85% when GAC is used. It is, however, important to ensure proper pretreatment (removal of DOC). Meeting the new discharge permits can still be a challenge. There-

fore, it is important to understand the causes of PFAS contamination to be able to select the best cost/benfit solution for the plant. If the source is firefighting foam, understanding the impacts of alternative firefighting foams on the analyses is also of importance.

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