Removal of per- and polyfluoroalkyl substances (PFASs) from tap water using heterogeneously catalyzed ozonation†

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1 Introduction

Rising concern exists over human exposure to per- and polyfluoroalkyl substances (PFASs). Their ubiquitous use in various commercial and industrial products has led to unintended human exposure incidents in the past when local drinking water was contaminated.1–4 Conventional drinking water treatment does generally not decrease PFAS concentrations.5–8 Municipalities in which raw water is contaminated therefore often apply granulated activated carbon (GAC) filters, which are capable of removing PFASs if freshly regenerated or newly replaced.8 In order to meet current drinking water guidelines, these filters however need to be changed often and are therefore a costly interim solution. Due to the substitution of fluorine for hydrogen in the alkyl carbon chain of PFASs, they are recalcitrant towards conventionally applied oxidation treatment.9,10 Fluorine has a reduction potential of $E^0 = 3.6$ (ref. 11) and is the strongest inorganic oxidant. Therefore it is thermodynamically unfavorable to oxidize fluorine in the oxidation state ($-1$) to its elemental state of $F_2(0)$ with any other one-electron oxidant.10 Nonetheless, the use of advanced oxidation processes (AOPs) has been discussed as a promising approach for the removal of PFASs on both laboratory and full-scales.12,13 AOPs describe a group of treatment techniques that are based on in situ generation of radicals. AOPs are widely applied in diverse combinations in
water treatment to degrade a large number of different organic pollutants with the help of ozone ($O_3$), hydrogen peroxide ($H_2O_2$), ultraviolet radiation (UV), persulfate ($S_2O_8^{2-}$) and other oxidizing agents. Different reaction conditions lead to the generation of highly reactive radicals like hydroxyl radicals ($OH$), sulfite radicals ($SO_3^-\) or peroxo radicals ($O_2^\cdot$) or carbonate radicals ($CO_3^-\). Molecular oxygen, which has a redox potential of $E^0 = 2.07 V$, and $OH^\cdot (E^0 = 2.8 V)$ have shown to be insufficient for the degradation of PFASs. Other oxygen containing radical species created by means of catalytic oxidation processes (e.g. Fenton’s reagent chemistry or catalyzed hydrogen peroxide) have on the other hand shown to degrade PFAS with various functional groups. Furthermore, several studies found that the application of sulfate radicals leads to efficient degradation of various organic micropollutants including perfluorooalkyl carboxylic acids (PFCAs; $C_nF_{2n+1}$COOH) found a substantial decrease of PFCA concentrations when treating contaminated water with photocatalytically activated persulfate while Wang et al. showed that $F^\cdot$, $CO_3^\cdot$, and small quantities of shorter chain PFCAs were the main reaction products in a similar experiment. Abu Anm et al. found an enhanced PFAS removal in landfill leachate for the combination of ozone and persulfate compared to a treatment with ozone only. Schröder et al. investigated PFAS destruction via a combination of ozone treatment and heterogeneous catalysis on celite and removal efficiencies of about 14% (PFOA), and 53% (PFOS) were reported. It should be noted that Schröder et al. hypothesized that various types of strong oxidizing agents including hydroxyl radicals led to perfluoroalkyl chain shortening, while later research showed that hydroxyl radicals do not transform perfluoroalkyl substances, as mentioned above. Until now, there is however a lack of understanding and knowledge about the use of ozone in combination with a catalyst and persulfate for the removal of PFASs.

In this study research on heterogeneously catalyzed ozone removal for the removal of PFASs from water was assessed in laboratory- and pilot-scale treatment. Ozone was applied in situ in combination with a heterogeneous iron-oxide based catalyst using ultrapure water on a laboratory scale as well as spiked drinking water on a pilot scale. The specific objectives of this study were i) to test the combinations of ozone, a catalyst and persulfate in terms of removal efficiency of PFASs in order to draw conclusions about the potential to improve the existing, commercially available treatment, ii) to investigate the treatment efficiency in pilot-scale treatment of contaminated drinking water, and finally iii) to evaluate treatment specific thermodynamic and kinetic aspects regarding PFAS removal and possible reaction mechanisms.

2 Materials and methods

2.1 Chemicals

In total 18 target analytes were analyzed which included $C_nF_{2n+1}$, $C_{11}$-$C_{17}$, $C_{18}$-$C_{25}$, and $C_{17}$-$C_{28}$ PFCAs ($C_nF$, describing the amount of perfluorinated carbon atoms; PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTeDA, PFHxDA, and PFOS) and 10 mass labeled PFASs (C$_8$F$_{17}$SO$_2$NH$_2$. For quantification, 10 mass labeled PFASs were applied as internal standards (ISs); see Table A1 in the ESL†.

2.2 Experimental procedures

2.2.1 Kinetic experiments. For the kinetic adsorption experiments 0.1 g of the catalyst material and 40 mL tap water were added into a 50 mL PP-tube. After addition of 20 μL PFAS stock solution containing the 18 target analytes (20 000 μg mL$^{-1}$ per compound, in methanol), the tubes were put on a horizontal shaking machine at 150 rpm. Single 100 μL samples were taken after 1, 2, 5, 10, 15, 30, 75 and 100 min. The experiment was conducted in duplicate and the samples were analyzed the same day. Further, a positive blank test ($n = 2$) was conducted without a catalyst to evaluate PFAS adsorption to the tube material.

2.2.2 Adsorption isotherms. Adsorption isotherms for PFAS adsorption to the catalytic material were obtained for MilliQ water, tap water and dissolved organic carbon (DOC; 10.0 mg L$^{-1}$) containing water. DOC containing water was prepared by shaking 1.33 g uncontaminated soil with 150 mL Millipak MilliQ water (Millipak® Express 20, 0.22 μm filter, Merck Millipore) for 48 h at 50 rpm and subsequently centrifuging for 30 min at 3000 rpm. The supernatant was removed with 10 mL HSW NORM-JECT® syringes, pre-filtered through quantitative filter paper (Munktell Ahlstrom, Grade 00H, pore size: 0.45 μm) and filtered in a second step with syringe filters (VWR International, 0.45 μm pore size, nylon membrane). After diluting with MilliQ water, it had a DOC concentration of 10.0 mg L$^{-1}$.

For each trial, 40 mL of the respective water type, 0.1 g catalyst material and 20 μL of a respective PFAS mix (200, 1000, 2000, 10 000 or 20 000 μg L$^{-1}$) containing the 18 target analytes (in methanol) were added to 50 mL PP-tubes. The PP-tubes were shook horizontally for 100 h at 150 rpm. Experiments were conducted in duplicate for MilliQ, tap-, and DOC water each and the mean value was taken for further calculations. Experimental data obtained from the 100 h shaking experiment were evaluated regarding the fit to different adsorption isotherm models (i.e. Freundlich and Langmuir). Freundlich sorption parameters were calculated from eqn (1):

$$ln(Q_e) = ln(K_f) + \frac{1}{n}ln(C_e)$$
where \( Q_e \) represents the equilibrium adsorbate amount [mg g\(^{-1}\)] and \( C_e \) corresponds to the equilibrium concentration of the analyzed compounds [mg L\(^{-1}\)]. \( K_f \) [(\( \mu g \) g\(^{-1}\))(\( \mu g \) L\(^{-1}\))\(^{-n}\)] describes the adsorption capacity of the catalytic material and \( n \) [unitless] is the adsorption intensity for analyzed PFASs. Since positive blank experiments performed during the kinetic trials showed no significant change in concentrations after the first 10–20 min, these positive blank experiments were further used to account for losses during adsorption isotherm experiments.

### 2.2.3 Laboratory-scale trials

Batch experiments were conducted at room temperature (22 °C) in 500 mL three-necked flasks under constant stirring at 500 rpm in a system schematically shown in Fig. 1a. A perforated 50 mL polypropylene (PP)-tube was placed in the flask and depending on the experiment, filled with 5 g catalyst material and/or an O\(_3\) gas diffuser. 500 mL MilliQ water (Millipak® Express 20, 0.22 \( \mu \)m filter, Merck Millipore) was spiked with 50 \( \mu \)L of a PFAS solution (PFBA, PFHxA, PFOA, PFDA, PFDoDA, PFTeDA, PFHxDA, PFBS, PFHxS, PFOS, 6:2 FTSA, 8:2 FTSA, and FOSA; containing 10 \( \mu \)gm L\(^{-1}\) per compound). After 10 min of balance adjustment, the first set of samples was taken and the ozone flow (300 mg ozone per h) was turned on and/or 187 mg ammonium persulfate (99.5%, Peroxy Chem, USA) (mole ratio PFASs/ammonium persulfate 1:50) was added, depending on the respective trial. Further 1 mL samples were taken after 5, 15, 30, 60, 90 and 120 min and immediately purged with nitrogen to remove dissolved ozone gas. All the samples were taken in duplicate. An overview over the conducted experiments on the laboratory scale is listed in Table 1. Both positive and negative blank experiments were conducted in the same manner as the actual trials with the same sampling intervals. Duplicate experiments were performed for all experiments and the mean value was taken for the discussion of results. Changes in PFAS concentrations for the positive blank tests (see Table 1) were within 0–15% and were considered in the calculations for deriving relative removal percentages in the laboratory-scale trials. Positive blank 2a was used for degradation trials using the catalyst, while positive blank 2b was used for trials not applying the catalyst. A correction factor was derived for each PFAS compound, where the deviation of the initial concentration in the positive blank samples was divided by the mean of the concentrations.

#### Table 1
Overview over the conducted laboratory-scale trials with the applied combinations of ozone (O\(_3\)), the catalyst (cat) and persulfate (PS); all trials were conducted in duplicate

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Persulfate</th>
<th>Ozone</th>
<th>Catalyst</th>
<th>Spike(^a)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Negative blank</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Contamination check</td>
</tr>
<tr>
<td>1</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Adsorption to: Laboratory materials and catalyst</td>
</tr>
<tr>
<td>Positive blanks</td>
<td>—</td>
<td>—</td>
<td>Yes</td>
<td>Yes</td>
<td>Treatment of PFASs through: Ozone</td>
</tr>
<tr>
<td>2a</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Yes</td>
<td>Ozone and catalyst</td>
</tr>
<tr>
<td>2b</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Persulfate</td>
</tr>
<tr>
<td>Degradation trials</td>
<td>T1: O(_3)</td>
<td>—</td>
<td>Yes</td>
<td>—</td>
<td>Ozone and persulfate</td>
</tr>
<tr>
<td>T2: O(_3)/cat</td>
<td>—</td>
<td>Yes</td>
<td>Yes</td>
<td>—</td>
<td>Persulfate and catalyst</td>
</tr>
<tr>
<td>T3: PS</td>
<td>Yes</td>
<td>—</td>
<td>—</td>
<td>Yes</td>
<td>Ozone, catalyst and persulfate</td>
</tr>
<tr>
<td>T4: O(_3)/PS</td>
<td>Yes</td>
<td>Yes</td>
<td>—</td>
<td>Yes</td>
<td>Persulfate and catalyst</td>
</tr>
<tr>
<td>T5: cat/PS</td>
<td>Yes</td>
<td>—</td>
<td>Yes</td>
<td>—</td>
<td>Persulfate and catalyst</td>
</tr>
<tr>
<td>T6: O(_3)/cat/PS</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>—</td>
<td>Persulfate and catalyst</td>
</tr>
</tbody>
</table>

\(^a\) The native PFAS stock solution contained 10 \( \mu \)g mL\(^{-1}\) per compound resulting in a concentration of 1 \( \mu \)g L\(^{-1}\) per compound in the flask.
measured during the remaining 120 min of the positive blank experiment.

2.2.4 Pilot-scale trials. The experiment on the pilot-scale was separated into three parts: A) adsorption to the system walls (day 1), B) adsorption to the catalyst (days 2–5) and C) degradation experiment (day 6), as summarized in Table 2. The pilot-scale system (Fig. 1b) was filled with 50 L tap water and spiked with 0.1 mL, followed by 1 mL, respectively, of a PFAS mix containing the 18 target analytes (50 000 ng mL\(^{-1}\) per compound, in methanol), equal to a final concentration of 1.1 μg L\(^{-1}\) per compound. During the first test phase (A), the catalytic bed was excluded and the water circulated through the pipes of the system only, at a flow of 850 L h\(^{-1}\). The water was spiked with 0.1 mL of the PFAS mix in order to observe possible adsorption to the walls of the system. Samples were taken after 0.5, 1, 4, 9.5 and 23.5 h. On the next day, prior to the second spike, the catalytic bed was opened and further 10 L tap water was introduced into the system since the catalytic bed did not contain water. A second period of the water circulating through the system was awaited during days 2–5 and several samples were taken in order to monitor equilibrium adjustment during this period (see Table 2). Diverse ad- and desorption processes to and from the catalyst material were observed during the second test period (part B; see Table 2). The degradation trials (part C) investigated the effectiveness of the ozonation treatment in terms of PFAS removal and samples were collected at 0.5, 1, 2, 3, 4, 5, 6, 7 and 8 h during which ozone was applied to the system. Samples were taken in duplicate and the mean value was taken for calculations. For data analysis and better data comparability, each calculated concentration per analyzed compound and sampling time was normalized to the sample taken directly prior to turning on the ozone flow (S14 (0 h); Table 2). During the whole time of the experiment, the pH was kept constant at pH = 7.5 by automated sodium hydroxide (NaOH) or hydrochloric acid (HCl) addition. Additionally, the redox potential was constantly monitored.

2.3 Instrumental analysis

Samples for the adsorption isotherm experiments, kinetic experiments and laboratory-scale experiments T1, T2 and T3 were analyzed via direct injection by ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS; TSQ Quantiva, Thermo Fisher Scientific, San Jose, CA, USA) whilst on-line solid phase extraction (SPE) UHPLC-MS/MS was conducted for the pilot-scale experiment (LC/UPLC system; Thermo Scientific Dionex UltiMate 3000 Pumps; TSQ Quantiva, Thermo Fisher Scientific, San Jose, CA, USA). An Acquity UPLC BEH-C18 column (100 mm × 2.1 i.d., 1.7 μm particle size from Waters Corporation, Manchester, UK) was used as an analytical column. A Hypersil GOLD aQ column (20 mm × 2.1 mm i.d., 12 μm particles, from Thermo Fisher Scientific, San Jose, CA, USA) was used as an on-line SPE column. In order to distinguish signals due to mobile phase contamination from sample peaks, a trapping column was
applied after the mixing chamber (ACQUITY UPLC column reversed-phase 1.7 μm spherical hybrid, 3 mm × 30 mm from Waters Corporation, Manchester, UK). Both the trapping column and the analytical column were equipped with an ACQUITY UPLC BEH C18 VanGuard pre-column (130 Å, 1.7 μm, 2.1 mm × 5 mm from Waters Corporation, Manchester, UK). The injection volumes were 10 μL for direct injection samples and 1.0 mL for on-line SPE samples. Data were evaluated using TraceFinder™ 3.3 software (Thermo Fisher). A detailed overview of instrumental parameters as well as single reaction monitoring transitions can be found in Tables A3 to A5 in the ESI† respectively. Samples from laboratory-scale experiments T4, T5 and T6 were analyzed by direct injection HPLC-MS/MS (HPLC, Agilent Technologies 1200 Series, Palo Alto, CA, USA). The analysis was conducted according to a method described elsewhere.30

2.4 Quality control and quality assurance

Limits of detection (LODs) are defined as the concentrations found in the replicate negative blank samples plus three times the relative standard deviation (eqn A1 in the ESI†). Further, the limits of quantification (LOQs) are defined similarly, however by adding 10 times the relative standard deviation to blank concentrations (eqn A2 in the ESI†). In the case where no PFAS contamination was detected in the negative blank, the lowest calibration point at the same concentration with a signal to noise ratio of S/N > 10 was set as LOD and LOQ, respectively; see also Table A6 in the ESI†. Negative blank samples (n = 2) were retrieved by conducting experiments with unspiked water using the same procedure as for each respective experiment (Table A7 in the ESI†). For each experiment series performed in the laboratory positive blank experiments were conducted in duplicate. In the case where significant losses were observed, they were taken into consideration when calculating removal efficiencies or adsorption for the actual experiments. For this, a correction factor was calculated by dividing the concentration at time 0 min (sample size n = 2) by the mean concentrations across the full positive blank time series (n = 8 for kinetic and adsorption isotherm trials; n = 5 for laboratory-scale trials; for details see Table A8 in the ESI†). The recovery of the internal standards was on average 97% for the adsorption tests (n = 11), 81% for the pilot-scale test (n = 8) and 110% for the laboratory-scale test (n = 11); see also Table A9 in the ESI†.

3 Results and discussion

3.1 Sorption behaviour of PFASs to the catalyst

A kinetic study was performed in the laboratory to gain information on the adsorption velocity of PFASs to the catalytic material. All evaluated PFASs reached equilibrium concentrations within the first 10 min (data not shown). Small changes in concentration during the remaining time of the sorption experiment of 100 h were observed for PFHxS, PFOS, and FOSA, however not significant.

Adsorption isotherms showed a fit according to the Freundlich adsorption model for all the evaluated PFASs in all three water types (MilliQ, tap water and DOC water); see Table A10 in the ESI†. The adsorption intensity n was found to be ≥ 1 for all PFASs and water types suggesting that the adsorption is a physical process rather than a process involving chemical binding.31−33 Kf describes the loading of the adsorbent with the adsorbate and was found to vary between 3.75 × 10−6 (μg g−1)(μg L−1)n (PFOS, DOC water) and 1.36 × 10−3 (μg g−1)(μg L−1)n (PFDoDA, tap water); see Table A10 in the ESI†. A linear relationship between ln(Kf) and the number of perfluorocarbon atoms was found for PFASs and most PFCAs in MilliQ water (see Fig. A1 in the ESI†). This observation was also found in previous studies investigating the adsorption of PFBS and PFOS on diverse types of GAC, powdered activated carbon (PAC) and three activated carbon fibers34 and for various PFASs.35 According to Tang et al.,36 it can be assumed that the observed increase in ln(Kf) for longer chain PFCAs (Fig. A1 in the ESI†) is an indication of increasing hydrophobic interactions between the catalyst surface and PFASs with increasing chain lengths. An increase in ln(Kf) for shorter chain PFASs (PFBA, PFBS) in tap water suggests increasing electrostatic interactions with decreasing chain lengths. The present study found lower ln(Kf) values for PFASs compared to PFCAs with the same perfluorocarbon chain length in MilliQ and DOC water (Fig. A1 in the ESI†), suggesting that the PFA adsorption strength to the catalyst material is slightly weaker than that of PFCAs with respect to the same perfluorocarbon chain length. Hansen et al.37 found that PFASs adsorb more strongly to GAC and PAC compared to PFCAs, and the increase of the Kf is more pronounced with a higher perfluorocarbon chain length. In contrast to GAC, the catalyst material used in this study is an inorganic material. The inverted behavior of the functional groups could be due to the weak ligand properties of the slightly larger PFSA molecules compared to those of PFCAs.38 The adsorption isotherm data for tap water showed the independence of the PFAS functional group and the ln(Kf) values of all the compounds seemed to depend on the perfluorocarbon chain length only (Fig. A1 in the ESI†).

3.2 Laboratory-scale trials combining the catalyst, ozone and persulfate

Fig. 2a) shows a summary of removal of all evaluated PFASs after 120 min of treatment on the laboratory-scale for the ozone applying trials as a function of perfluorocarbon chain length. Significant removal of several PFASs was observed for the experiments using ozone in combination with the catalyst (T2: O3/cat, which was also used on the pilot-scale, see section 3.3), ozone in combination with persulfate (T4: O3/PS), ozone in combination with the catalyst and persulfate (T6: O3/cat/PS) and applying ozone only (T1: O3); see also Table A11 in the ESI†. In contrast to that, for all other possible treatment combinations described in Table 1 (i.e. T3: PS and T5: cat/PS) no significant PFAS removal was found, indicating that the
catalyst did not activate persulfate into sulfate radicals for transformation of PFASs. It was noted that i) the removal increased with increasing perfluorocarbon chain length and ii) the removal did not show a general trend regarding the PFAS functional group (Fig. 2). The observed trend of increasing removal with increasing perfluorocarbon chain length was consistent within a set of PFASs with the same functional group with the exception of PFBA in experiments T2 (O3/cat), T4 (O3/PS) and T6 (O3/cat/PS) for which the removal was larger than that for some longer chain PFCAs. No significant trend was found for the difference in removal between linear (L) and branched (B) isomers (p-value < 0.05, Fig. 2 and Table A11 in the ESI†). The treatment with ozone only (T1) showed the worst performance in comparison to the other three ozone applying treatment approaches (T2, T4, T6). This was expected, as other authors have reported that ozone alone does not have a significant impact on PFAS concentrations. The average removal efficiencies for the different experiments increased in the order T1 (O3): 22% average removal efficiency < T4 (O3/PS): 24% < T2 (O3/cat): 26% < T6 (O3/cat/PS): 47%. Compared to the combination used in the pilot-scale treatment (O3/cat, see section 3.3), the combination of all three parameters (O3/cat/PS) was found to improve the removal efficiency for many of the spiked PFASs significantly: +18% (PFBA), +14% (PFBS), +19% (linear PFHxS; L-PFHxS), +77% (branched PFHxS; B-PFHxS), +43% (L-PFOS), +15% (B-PFOS) and +15% (6:2 FTSA). An improved oxidizing ability for the combination of ozone and persulfate was previously reported by Abu Amr et al., 2014 (ref. 28) and Yang et al., 2016. It is argued that persulfate can be activated to form SO₄²⁻ in the presence of OH⁻:

\[ \text{S}_2\text{O}_8^{2-} + \text{OH}^{-} \rightarrow \text{HSO}_4^{-} + \text{SO}_4^{2-} + \frac{1}{2} \text{O}_2 \]  

Other authors have assumed the presence of other reactive radical species like superoxide to play an important role in catalyzed persulfate systems, as reviewed by Waclawek et al. Therefore, it can be assumed that an additional application of the catalyst material further increases the amount of radicals and thereby leads to increased PFAS transformation as observed in T6 (O3/cat/PS). The conductivity increased for all ozone applying trials, with the exception of T1 (ozone only); see also Fig. 2b). This further indicates the formation of charged species, such as radical species described above and possible activation of persulfate. It should be noted that a decrease of the initial pH from pH = 6–7 to a final value of pH = 3 was observed for all trials in which ozone was applied (see Fig. A2 in the ESI†). During the treatment with no ozone, the observed changes in pH were within less than one pH unit (see Fig. A3 in the ESI†). Curiously, a similar decrease in pH was observed for the blank trial, applying only the catalyst without ozone. As repeated blank trials of the same kind did not show a decrease in pH (data not shown), the observed drop in pH might be due to a faulty pH meter, and thus cannot be evaluated further. The observed removal of the long-chain PFASs during the laboratory-scale trials could be a result of the existence of these PFASs at the gas–water interface of introduced ozone bubbles, leading to an underestimation of PFASs over time. As all ozone applying trials however were run under the very same conditions, the trials can still be considered comparable to each other and the reasoning for the discussion points given above applies.

3.3 Removal efficiency of ozone and catalyst treatment on pilot-scale

The concentrations after the first spike (part A, see also Table 2) remained almost constant indicating that adsorption to walls of the pilot-scale system was negligible even at low
concentrations of 100 ng L$^{-1}$ for individual PFASs (Fig. A4 in the ESI†). As can be seen in Fig. 3 a rapid decrease of $>50\%$ for $\Sigma$PFAS concentrations was observed during the first 30 min of the ozonation experiment. After 1 h and 2 h, the removal of PFASs slowed down and stagnated at ca. 70% after 3 h with remaining amounts of 38% (1 h), 29% (2 h) and 26% (3 h) of $\Sigma$PFASs, respectively. The decrease in concentration was significant (two sample $t$-test, one sided) with a $p$-value $<0.05$ for PFPeA and $p < 0.01$ for all other analyzed PFASs from the moment when the ozonation started until the end of the trial. PFCAs with the longest evaluated perfluorocarbon chain length PFHxDA ($C_{13}^F$) and PFOcDA ($C_{12}^F$) showed an increase in concentrations in the first 30 min of the experiment. This can most likely be explained by desorption from the catalyst after disturbing the system by the introduction of ozone. Removal was observed for PFHxDA and PFOcDA after 30 min of ozone introduction.

The pH in the pilot-scale system decreased as soon as ozone was introduced (see Fig. A5 in the ESI†) and needed to be stabilized by adding NaOH, as described in section 2.2.4. A drop in pH during ozonation can commonly be observed if organic matter containing double bonds is present in the treated water matrix, which can be the case for tap water. Ozonation leads to the formation of lower molecular weight organic acids, causing the pH to drop significantly.$^{43,44}$ Next to a thesis published in 2016,$^{45}$ the present study is one of the first to report removal of PFASs by a catalytic ozonation treatment on a pilot scale. Other studies evaluating pilot or full-scale ozone treatments found no significant PFAS removal.$^{7,46-48}$ Ozonation studies reporting PFAS degradation are on the other hand limited to laboratory-scale experiments.$^{9,21,49}$

### 3.4 Impact of the perfluorocarbon chain length and functional group

A removal efficiency of more than 98% was found for PFASs with a chain length of seven to eleven perfluorocarbon atoms ($C_{9}^F-C_{11}^F$) independent of the functional group in the pilot-scale ozonation trial, as shown in Fig. 4a. PFASs with $C_{9}^F-C_{11}^F$ showed the lowest average removal efficiency (33% on average) compared to $C_{12}^F-C_{14}^F$ (64%) and $C_{15}^F-C_{17}^F$ (99%). The outstanding removal efficiencies for $C_{12}^F-C_{14}^F$ PFASs were observed for both partially (i.e. 6:2 FTSA and 8:2 FTSA) and fully fluorinated PFASs (i.e. PFOA, PFNA, PFDA, PFUnDA, PFOS, and FOSA). Short chain PCFs, such as PFPeA, PFHxA and PFHpA, showed a slight increase of 11%, 21% and 25%, respectively (significant with $p$-value $<0.05$, two sample $t$-test, one sided), in concentration after 3 h while longer chain congeners, $C_{12}^F-C_{17}^F$ showed continued removal at that point. This may indicate step-wise unzipping of the perfluoroalkyl carbon chain through splitting-off of a $-CF_2$ moiety followed by hydrolysis, as proposed previously for the reaction of PFASs with superoxide radicals that can be created in AOPs.$^{22,51}$ The removal reactions for all analyzed PFASs followed second order reaction rates (Fig. 4b). Interestingly, these reaction rates showed a similar trend to the maximal removal efficiencies in terms of chain-length dependence observed during the 8 h treatment, see Fig. 4a. This indicates that the treatment is highly efficient (removal efficiency $>99\%$ in less than 3 h of treatment) for $C_{7}^F-C_{11}^F$ PFASs independent of the functional group.

Overall, a correlation between the adsorption strength and PFAS removal efficiency was not found. This means that the removal mechanism cannot be predicted from the adsorption strength of PFASs to the catalyst. Previous studies found that the degradation efficiency of PFASs in water by means of uncatalyzed ozonation on a laboratory-scale as well as on an industrial scale is low.$^{7,10,46}$ This was confirmed in the laboratory-scale experiments conducted in this study. For several AOP approaches, it is argued that hydroxyl radicals are not responsible for PFAS degradation.$^{22}$ Mitchell et al. found that non-hydroxyl radical reactive oxygen species or low concentrations of other reducing species (superoxide radical anions, perhydroxyl radicals, and/or hydroperoxide
decreased in tap water with an overall maximum removal of 77%. In the pilot-scale ozonation treatment, the removal performance of PFASs from water, especially for PFASs with a perfluorocarbon chain length of six to eleven, ozone can be created, applied and destroyed safely on-site. The evaluated system is a commercially available treatment method, and also available as a mobile system, and could therefore easily be applied in water treatment or in pump-and-treat processes for the treatment of contaminated water. Further research should investigate the production of degradation products and potentially unwanted by-products, monitor the occurrence of compounds in the gas-phase and prove the effectiveness of the treatment for other types of contaminants and application on different water types.

Conflicts of interest

There are no conflicts to declare.

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