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PFAS are persistent chemicals of concern and pose significant risk to human health and the environment. In this study, some advanced treatment technologies capable of commercialisation and generating less secondary waste were studied and compared for treating PFAS containing wastewater. This research provides a valuable reference for the employment of the existing technology in the PFAS contaminated water treatment.
Comparative study of PFAS treatment by UV, UV/ozone, and fractionations with air and ozonated air

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Abstract:

Per- and poly fluorinated alkyl substances (PFAS) and their derivatives are persistent organic chemicals, resulting in significant adverse human health and environmental effects. In this paper, UV, ozonated air fractionation, air fractionation and UV/ozone combined treatment for PFAS removal were studied and compared. The feed water was synthesised from the firefighting foam, which contained multiple per- and poly fluorinated alkyl substances. Combined UV and ozone equipment patented by EGL were used to compare the performance of different treatment methods, in which a two-unit rig was employed as a benchtop setup and a nine-unit rig using UV/ozone combined treatment was employed as a pilot rig. It was found from the benchtop tests that PFAS removal efficiency was improved with the increases of air and feed flowrates in the UV/ozone combined treatment. The highest PFAS removal efficiency achieved was 87% at an air flowrate of 30 L/min and feed flowrate of 1.4 L/min (10 min residence time). The different treatment techniques including UV only, ozonated air fractionation, and air fractionation were compared with the UV/ozone combined treatment at the residence time of 20 min. UV alone removed 16.8% PFAS, which showed the worst performance of all tests. 73% PFAS was destructed by the UV/ozone combined treatment. Air fractionation was able to achieve 81% PFAS removal. Ozonated air fractionation showed the best PFAS removal efficiency, which was more than 95%, as a result of the enriched OH radicals in the gas bubble. For the nine-unit pilot rig, the UV/ozone combined treatment achieved about 79% PFAS removal. However, foam fractionation occurred during the treatment, which led to approximately 4% removal of PFAS based on the mass balance. Therefore, the PFAS removal contributed by UV and ozone combined treatment was 75%, which was similar to the result of benchtop rig. All treatment resulted in a concentration increase of at least one type of short-chain PFAS. When foam fractionation with gas bubbles occurred in the treatment, it was easier to remove perfluoroalkyl sulfonate (PFSA) than perfluoroalkyl carboxylate (PFCA), because PFSA is more hydrophobic than PFCA, which makes it more affinity to gas bubbles. In addition, in comparison with long-chain PFAS it is much more difficult to remove the short-chain PFAS by fractionation technologies, due to the partition factor declining exponentially with the reduced carbon number.
1. Introduction

PFAS products have been used since 1940s, and their roles as synthetic pollutants emitted to the natural environment by various pathways were only scarcely considered by environmental chemists, toxicologists, or food chemists. The first observations of organic compounds containing fluorine in humans were made at the end of 1960s and did not attract great attention. At the beginning of 2000s, the works done by Moody and Field and Giesy and Kannan raise significant interest in these anthropogenic pollutants. They considered the environmental implications of the use of firefighting foam with PFAS and the global distribution of perfluorooctanoate in wildlife.

Australia’s national industrial chemicals assessment body concluded that perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are persistent, bioaccumulative, and toxic substances, which undergo long-range transport in water and air and transfer between different media. In 2017, the Australian Government Department of Health regulated the PFOS/perfluorohexane sulfonate (PFHxS) and PFOA concentrations of 0.07 µg/l and 0.56 µg/L in drinking water, respectively. In 2017, the USEPA proposed the unregulated reference concentrations of PFOA and PFOS to be 0.07 µg/L in drinking water.

The primary technologies for PFAS removal from water resources can be divided into two categories:

I. Separation of PFAS from treated water, and destruction of the concentrated PFAS in a separate process

II. Direct destruction of PFAS in-situ the treated water

At present, the technologies in Category I are widely applied in the large-scale water treatment plants, including membrane filtration, adsorption, ion exchange and foam fractionation. Membrane filtration such as reverse osmosis (RO) and nanofiltration (NF) can effectively remove PFAS. However, the treatment cost by filtration is considerable for plants treating large volumes of water. Furthermore, a PFAS concentrated stream (approximately 10% of the treated water volume) is produced from RO and NF processes and needs further treatment. Currently, adsorption is the most popular technology used by water utilities. Adsorbents include powdered activated carbon (PAC) and granulated activated carbon (GAC), which are not generally regenerated. The cost of incorporating these adsorbents into existing water treatment processes can be high, because a contact column is essential and the adsorbent needs to be continually purchased. The disposal of the adsorbents is also costly, usually requiring high-temperature incineration. Ion exchange resin can also remove PFAS efficiently. However, the exhausted ion exchange resin is difficult to be regenerated, since it produces high salinity PFAS containing wastewater. If no regeneration is undertaken, the considerable solid waste would be produced. Foam fractionation has also been used for separation of the PFAS from wastewater,
since PFAS also act as surfactants. The running cost of foam fractionation is low and produces only small amounts of highly concentrated PFAS containing water. However, the removal efficiency is about 80% and is not very effective when dealing with short-chain PFAS.

For all treatment methods of Category I, the destruction of concentrated PFAS is still required. Plasma incineration followed by calcium hydroxide absorption is commonly used to convert PFAS to low hazard compounds.

Category II methods focus on the direct destruction of PFAS, avoiding the concentration step. However, perfluorinated surfactants do not exhibit the preferred reactive sites for reaction with •OH radicals generated during the advanced oxidation. The abstraction of fluorine from a carbon atom is thermodynamically unfavorable because the F-OH bond has a dissociation energy of at least 216 kJ/mol lower than that of the C-F bond (CF$_3$F 552 kJ/mol, R-CF$_2$-F 352 kJ/mol, R,R’-CF-F 508 kJ/mol). Furthermore, the electron density of the ionic head group (e.g., carboxylate and sulfonates) is reduced by perfluorination, hindering electron transfer reactions. The kinetic rate constant for the reaction of trifluoroacetic acid with •OH has been estimated to be less than 1×10$^{6}$ M$^{-1}$s$^{-1}$, indicating a slow rate of reaction with practically no reactivity of •OH towards trifluoroacetic acid. PFOS is resistant to different advanced oxidation treatment methods (Fenton, UV/H$_2$O$_2$, ozonation in alkaline solution, and peroxon process (O$_3$/H$_2$O$_2$) over 120 min at room temperature. Hori et al. found that the addition of hydrogen peroxide in UV treatment method has a detrimental effect on the degradation of PFOA, compared to direct UV-photolysis (radiation source: Xenon-doped mercury lamp), which supports the persistence of PFCs in the presence of •OH. It was reported that 83% PFOS was removed under the conditions of 5 h UV dosing with molecularly imprinted polymer-modified TiO$_2$ catalyst.

The combination of ozone and ultraviolet radiation (UV) could achieve better water treatment than the ozone alone, due to the promoted formation of hydroxyl radical intermediates. In the UV/O$_3$ process, the dissolved ozone will be split by UV irradiation ($\lambda < 300$ nm), and reacts with water to form a thermally excited H$_2$O$_2$ which decomposes into two •OH subsequently. Houston Research Inc. showed that ozone/UV enhances the oxidation of complexed cyanides, chlorinated solvents, pesticides that contribute to COD and BOD in many cases. In some reactions, the intermediate oxidation products remaining in the solution may be as toxic as or even more toxic than the initial compound. Completion of oxidation reactions, as well as oxidative destruction of compounds immune to unassisted ozone, can be achieved by supplementing the reaction with UV radiation. Many organic contaminants absorb UV energy in the range of 200 -300 nm and decompose due to direct photolysis or become excited and more reactive with chemical oxidants. Therefore, the combination of UV/ozone might be able to achieve effective PFAS removal.

However, Category II technologies are not favoured by most large-scale water treatment plants directly, because strong oxidants/radiation at high dose are required to decompose PFAS, and PFAS concentration in the wastewater is generally at PPB to PPT level.

Thus, it is necessary to combine both treatment methods in Categories I and II. Through the methods in Category I, the PFAS could be concentrated into a much smaller volume than the original PFAS, which will significantly reduce the load of the subsequent destruction treatments in the Category II. Therefore, minimising the total rejected volume (containing high...
concentration PFAS) from Category I would be critical to reducing the overall operation cost. A multifunctional rig patented by EGL was tested for PFAS removal. It can be used to treat the water by UV, ozonation, fractionation and their combinations. The performances of different treatments were also compared in this study.

2. Experimental

2.1. Benchtop rig tests

![Schematic diagram of the benchtop rig](image)

A schematic drawing of the benchtop UV/ozone rig (Environmental Group Limited, Australia) is shown in Figure 1. The benchtop rig consists of two reaction chambers connected to two ozone generators. There are one ozone bubbler stone connected to the ozone generator and two UV lamps ($\lambda = 254$ nm, Cnlight®, China) in the reaction chamber. The air from a compressor can be partially ozonated in the ozone generator by an ozone lamp ($\lambda = 185$ nm, Cnlight®, China) in the chamber before bubbling into the reaction chambers. A peristaltic pump was used to supply the feed into the benchtop rig. The total volume of the two reaction chambers was 14 L. The UV intensity was measured by UV intensity meters (210 - 280 nm, Run-Goal Technology Co. Ltd. China), which showed different readings for the same amount of UV radiation due to the difference of the distance to the UV lamps. The air flowrates were monitored by an air flowmeter (Siargo®, M5700 Series, China). The PFAS containing feed was synthesized by mixing waste firefighting foam (Cleanaway, Australia) containing about 6.3 mg/kg PFAS with tap water to achieve PFAS concentration between 3 to 10 µg/L.

2.1.1 Blank test

Blank tests were conducted with the tap water to achieve the operation baseline. The UV intensity and ozone residual were measured without the interference from the added PFAS containing firefight foam. The feed flowrates were set at 0.35 and 1.4 L/min to obtain residence...
times of 40 and 10 min, respectively. The air flowrates during the tests were varied at 10, 20, and 30 L/min, respectively.

2.1.2 System PFAS adsorption test

An adsorption test was firstly conducted to check whether PFAS will be absorbed in the benchtop testing rig. The original PFAS wastewater was pumped through the rig at a flowrate of 0.7 L/min (residence time = 20 min). The feed was sampled at the beginning of the test, and the effluent was sampled after one hour.

2.1.3. UV/ozone combined treatment for PFAS wastewater

In the UV/ozone combined PFAS wastewater treatment tests, both the ozone and UV lamps were set on. The feed flow rate was set at 0.35, 0.7 and 1.4 L/min to achieve the residence time of 40, 20 and 10 min, respectively. The air flowrate was varied in the range of 15 - 30 L/min.

2.1.4. Ozonated air fractionation, air fractionation and UV for PFAS wastewater treatment

As we can see from the schematic diagram of the benchtop rig in Figure 1, it is possible to have UV radiation, air fractionation and ozonated air fractionation/ozone oxidation involved in the treatment. Therefore, it is necessary to identify the dominant PFAS removal mechanism in the treatment. All the tests were conducted at the feed flow rate of 0.7 L/min (residence time of 20 min). The feed was sampled at the beginning of the test, and the effluent was sampled at the end of the test (after one hour).

In the UV test, only UV lamps were switched on, and there was no air bubbling into the reaction chambers.

In the air fractionation tests, only air was bubbled into the reaction chambers at an air flowrate of 20 L/min, and both the UV and ozone lamps were set off.

In the ozonated air fractionation tests, the ozone lamps were set on, and the UV lamps were set off. The air at a flowrate of 20 L/min was partially ozonated by the ozone lamps and bubbled into the reaction chambers.

2.2. Pilot UV/ozone rig test

The scale-up of the engineering process may result in great performance differences relative to the benchtop tests. Therefore, a pilot test was also conducted under the optimum conditions identified from the benchtop tests. In comparison with the benchtop rig, the pilot rig includes nine reaction chambers and sixteen ozone generators. All the reaction chambers were equipped with two UV lamps, but three of them were not connected to the ozone generators, which is different from the benchtop rig. The total volume of the pilot rig was 63 L. Therefore, the feed flowrate was set at 3.15 L/min to achieve a 20 min residence time. The feed was prepared by dissolving 100 g firefighting foam into 200 L water. The experiment lasted for one hour. The feed was sampled at the beginning of the test, and the effluent was sampled at the end of the test.

2.3. Analysis
The PFAS in the water was analysed by ALS, Australia with the LC-MS-MS method EP231X, and the detection limit is in the range of 0.01-0.1 µg/L. The total PFAS concentration is the sum of the concentration of 28 PFAS analytes, which are listed in Appendix 1.

The ozone residual in the reaction chamber was analysed by the Hach DR/800 with AccuVac® method. Triplicate measurements were conducted for the same tests, and the mean value was reported in this paper.

3. Results and discussion

3.1. Benchtop UV/ozone combined tests

3.1.1. Blank tests with tap water for identification of the maximum UV radiation and ozone residuals

Blank tests were carried out by using the tap water, which was used to dilute PFAS containing firefighting foam. The purpose of these tests was to understand the baseline performance of the combined UV/ozone system in the absence of PFAS. Besides, the blank tests also help to identify the variations of ozone residuals and UV intensity with the feed and air flowrates, as the reference for the following PFAS water treatment. Table 1 shows the ozone residual and the UV intensity of the blank tests in reaction chambers R1 and R2 at feed flowrates of 1.4 and 0.35 L/min respectively, which are also the theoretical maximum value achievable for following PFAS tests under the similar conditions. At the higher feed flowrate of 1.4 L/min (10 min residence time), the total ozone residuals in R1 and R2 were almost the same and in the range of 0.18 - 0.20 mg/L. This difference is in the error range. However, the UV intensity declined about 17% in R1 as the air flowrate was increased to 30 L/min, due to enhanced deflection/reflection of UV beams by increased air bubbles. At the lower feed flowrate of 0.35 L/min (40 min residence time), the maximum total ozone residuals in R1 and R2 were 0.2 mg/L when the air flowrate was 20 L/min. The measured UV intensity also reduced to approximately 12% at an air flowrate of 30 L/min, in comparison with that of an air flowrate of 10 L/min in R1.

It is also worth mentioning that in general, the total ozone residuals at high feed flowrate were higher than those at low feed flowrate. That is because of the high liquid turbulence at high flowrate encouraging the ozone transfer from the gas phase to the liquid phase. Furthermore, in R1, the UV intensity was also higher at a feed flowrate of 1.4 L/min than that at 0.35 L/min with the same air flowrate, because more and finer air bubbles created at higher feed flowrates will produce more uniform UV scattering.

Table 1. Blank tests: Ozone residual and UV intensity

<table>
<thead>
<tr>
<th>Feed flowrate (L/min)</th>
<th>Air flowrate (L/min)</th>
<th>UV Intensity (µW/cm²)</th>
<th>Ozone residual (mg/L)</th>
<th>R1*</th>
<th>R2*</th>
<th>R1</th>
<th>R2</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>12</td>
<td>100</td>
<td>44</td>
<td>0.08</td>
<td>0.12</td>
<td>0.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4</td>
<td>20</td>
<td>100</td>
<td>45</td>
<td>0.11</td>
<td>0.08</td>
<td>0.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4</td>
<td>30</td>
<td>83</td>
<td>43</td>
<td>0.09</td>
<td>0.09</td>
<td>0.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.35</td>
<td>10</td>
<td>84</td>
<td>43</td>
<td>0.07</td>
<td>0.06</td>
<td>0.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.35</td>
<td>20</td>
<td>80</td>
<td>43</td>
<td>0.14</td>
<td>0.06</td>
<td>0.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.35</td>
<td>30</td>
<td>74</td>
<td>44</td>
<td>0.06</td>
<td>0.04</td>
<td>0.10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The different readings are due to the different installation distances to the UV lamps.
3.1.2. System PFAS adsorption test

All the detectable PFAS in the system adsorption test are shown in Table 2. It can be found that the PFAS concentrations in the effluent are almost the same as the feed. Thus, there is no detectable PFAS adsorption by the benchtop rig in our tests.

Table 2. Analytical results for the system adsorption test

<table>
<thead>
<tr>
<th>Sample</th>
<th>PFPeS (µg/L)</th>
<th>PFHxS (µg/L)</th>
<th>PFHpS (µg/L)</th>
<th>PFOS (µg/L)</th>
<th>PFPeA (µg/L)</th>
<th>PFHxA (µg/L)</th>
<th>PFHpA (µg/L)</th>
<th>PFOA (µg/L)</th>
<th>PFAS (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>0.05</td>
<td>0.38</td>
<td>0.07</td>
<td>2.3</td>
<td>0.02</td>
<td>0.18</td>
<td>0.04</td>
<td>0.11</td>
<td>3.15</td>
</tr>
<tr>
<td>Effluent</td>
<td>0.04</td>
<td>0.37</td>
<td>0.08</td>
<td>2.4</td>
<td>0.02</td>
<td>0.14</td>
<td>0.04</td>
<td>0.10</td>
<td>3.19</td>
</tr>
</tbody>
</table>

3.1.3. UV/ozone combined treatment for PFAS wastewater

In the UV/ozone combined tests, both UV and ozone lamps were set on, and the ozonated air was bubbled into the reaction chambers. Figure 2a and Figure 2b show the total PFAS concentration in the treated water and the total PFAS removal efficiency under different feed and air flowrates, respectively. Total PFAS removal efficiency is calculated by Equation (1) as below:

\[ Re = \left(1 - \frac{C_t}{C_f}\right) \times 100\% \quad (1) \]

where \( Re \) is the percentage of PFAS removed from the treated water, \( C_t \) is the concentration of PFAS in the treated water, and \( C_f \) is the PFAS concentration in the feed.

The maximum total PFAS removal was 87% at an air flowrate of 30 L/min and feed flowrate of 1.4 L/min. At the same air flowrate, better PFAS removal was achieved at higher feed flowrate, owing to the higher UV intensity and ozone residual obtained at higher feed flowrate in the blank tests as shown in Table 1. Therefore, it can be concluded that the high ozone transfer rate and UV intensity are able to enhance the PFAS removal.
Table 3 shows the concentrations of four major per- and poly-fluoroalkyl substances in the feed and treated water. It can be seen that, after the ozone/UV combined treatment, all PFAS concentrations reduced, except for perfluorohexanoic acid (PFHxA). Moreover, the increases of feed and air flowrates could facilitate the PFOS and PFOA removals under all the operating conditions. However, the feed and air flowrates had less influence on PFHxS removal. On the other hand, PFHxA concentration increased under almost all the treatment conditions, and up to a 50% increase of PFHxA was observed when 97.3% PFOA removal was achieved. Therefore, it can be confirmed that the UV/ozone combined treatment could convert PFAS into PFHxA. It seems that PFHxS also could be generated from other PFAS sources in the treatment process, but it could not be demonstrated unequivocally based on the available analytical results. After the treatment under the optimum treatment conditions (air flowrate = 30 L/min, feed flowrate = 1.4 L/min), the total concentration of PFHxS (0.48 µg/L) and PFHxA (0.22 µg/L) was 0.70 µg/L greater than the total concentration (0.60 µg/L) of PFOs (0.52 µg/L) and PFOA (0.08 µg/L), although their total concentration in the feed was only one third of that of the PFOS and PFOA. Therefore, to achieve high total PFAS removal, the PFHxA and PFHxS concentrations should be considered, as they could not be easily removed by the UV/ozone combined treatment and PFHxA appeared to be generated by the process.

Table 3. Operation parameters and analytical results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Feed flowrate (L/min)</th>
<th>Air flowrate (L/min)</th>
<th>PFHxS C (µg/L)</th>
<th>PFOS C (µg/L)</th>
<th>PFHxA C (µg/L)</th>
<th>PFOA C (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Re (%)</td>
<td>Re (%)</td>
<td>Re (%)</td>
<td>Re (%)</td>
</tr>
<tr>
<td>S1</td>
<td>0.35</td>
<td>15</td>
<td>0.44</td>
<td>2.30</td>
<td>0.18</td>
<td>-12.5</td>
</tr>
<tr>
<td>S2</td>
<td>0.35</td>
<td>20</td>
<td>0.46</td>
<td>1.70</td>
<td>0.19</td>
<td>-18.8</td>
</tr>
<tr>
<td>S3</td>
<td>0.35</td>
<td>30</td>
<td>0.48</td>
<td>1.10</td>
<td>0.18</td>
<td>-12.5</td>
</tr>
<tr>
<td>S4</td>
<td>0.7</td>
<td>15</td>
<td>0.70</td>
<td>2.20</td>
<td>0.18</td>
<td>-12.5</td>
</tr>
<tr>
<td>S5</td>
<td>0.7</td>
<td>20</td>
<td>0.58</td>
<td>1.60</td>
<td>0.18</td>
<td>-12.5</td>
</tr>
<tr>
<td>S6</td>
<td>0.7</td>
<td>30</td>
<td>0.60</td>
<td>0.72</td>
<td>0.19</td>
<td>-18.8</td>
</tr>
<tr>
<td>S7</td>
<td>1.4</td>
<td>15</td>
<td>0.58</td>
<td>1.50</td>
<td>0.16</td>
<td>0.24</td>
</tr>
<tr>
<td>S8</td>
<td>1.4</td>
<td>20</td>
<td>0.92</td>
<td>0.28</td>
<td>0.24</td>
<td>-50.0</td>
</tr>
<tr>
<td>S9</td>
<td>1.4</td>
<td>30</td>
<td>0.48</td>
<td>0.52</td>
<td>0.22</td>
<td>-37.5</td>
</tr>
</tbody>
</table>
3.1.4. UV, air fractionation and ozonated air fractionation for PFAS wastewater treatment

The purpose of the tests was to verify the overall PFAS removal efficiency and to identify the removal efficiency of specific types of PFAS under different treatment methods provided by the benchtop rig.

Figure 3 shows images of the observation windows of the UV/ozone combined test, air fractionation test, ozonated air fractionation test, and UV only test. It can be seen from Figures 3a and 3d that there was no foaming observed. However, in both fractionation processes where air and ozonated air was bubbled through the reaction chambers, it can be seen from Figures 3b and 3c that foaming occurred. Since foaming in the reaction chambers is a sign of fractionation due to existing surfactants (PFAS), no foam observed in the UV/ozone combined and UV tests indicated that the PFAS removal in both processes was due to the destruction rather than foam fractionation.
In Table 4, the analytical results from the various processes are shown. Feed 1 was used for the air fractionation test, and S1 was the treated water by air fractionation. Feed 2 was used for both UV and ozonated air fractionation tests, and S2 and S3 were the treated waters thereof. The removal efficiencies of all detectable PFAS containing different carbon numbers are shown in Figure 4. Since the detection limit was 0.02 µg/L for the perfluoropentane sulfonate (PFPeS) and perfluoropentanoic acid (PFPeA) containing five carbons, it is impossible to make a solid conclusion based on the analytical method, although some PFPeA removal was found during the ozonated air fractionation. Therefore, the removal efficiency of the PFAS containing five carbons is not shown in Figure 4. Furthermore, since some concentration changes after treatment were less than the detection limit of 0.02 µg/L, those changes were considered in the analytical error range and are not discussed further.

It can be found that the UV treatment could remove 16.8% PFAS in total (Figure 4), which was mainly associated with PFOS removal (Table 4). After the UV treatment, 25% PFOS was removed from 2.8 to 2.1 µg/L in the treated water, but the PFOA concentration did not change.
However, the PFHxS concentration increased by approximately 33% from 0.3 to 0.4 µg/L. Since only PFOS and/or PFOA was used in the firefighting foam and the variation of perfluorohexane sulfonate (PFHpS) from 0.06 to 0.05 µg/L is in the range of the detection limit and is negligible, it can be concluded that the newly formed PFHxS was mainly from PFOS degradation.

Based on research from Vecitis et al., perfluoralkyl carboxylate (PFCA) should have a faster photolytic degradation than perfluoralkyl sulfonate (PFSA). However, it can also be seen in Table 4 that PFCA such as PFOA, PFHxA or PFHpA did not show obvious change after the UV treatment, in comparison of the degradation of PFOS (PFSA). Yamamoto, et al. found that one of the photodegradation pathways of PFOS is to transform into PFCA. It also can be found that 80% of the total PFAS in the feed is in form of PFOS as shown in Table 4. Therefore, even if the PFCA degrades faster than PFSA, it could be possibly replenished by the photodegradation of the PFOS in this study. Thus, it would not be possible to make any conclusion whether the PFCA had been destroyed by UV treatment in our study.

Table 4. Analytical results for the feed and treated water

<table>
<thead>
<tr>
<th>Sample</th>
<th>Operation</th>
<th>PFPeS (µg/L)</th>
<th>PFHxS (µg/L)</th>
<th>PFHpS (µg/L)</th>
<th>PFOS (µg/L)</th>
<th>PFPeA (µg/L)</th>
<th>PFHxA (µg/L)</th>
<th>PFHpA (µg/L)</th>
<th>PFOA (µg/L)</th>
<th>PFAS (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed 1</td>
<td></td>
<td>0.05</td>
<td>0.38</td>
<td>0.07</td>
<td>2.3</td>
<td>0.02</td>
<td>0.18</td>
<td>0.04</td>
<td>0.11</td>
<td>3.15</td>
</tr>
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<td>0.06</td>
<td>&lt;0.02</td>
<td>0.3</td>
<td>0.02</td>
<td>0.15</td>
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<td>0.04</td>
<td>0.3</td>
<td>0.06</td>
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<td>0.04</td>
<td>0.09</td>
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<td>0.4</td>
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<tr>
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<td>Ozonated air fractionation</td>
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From Figure 4, it can be found that air fractionation removed about 81.3% PFAS in total, and 80% PFHxS, approximately 100% PFHpS, 87.0% PFOS, 16.7% PFHxA, 50.0% PFHpA, and 91% PFOA were removed from the treated water. Since air is not a strong oxidant, foam fractionation should be the dominant separation mechanism for the PFAS removal. For the PFSA, the removal efficiency did not show a clear relationship to the molecular weight. However, the removal efficiency for PFCA declined more than 80% as the carbon number reduced from 8 to 6, because the lower lipophilicity of the shorter alkyl chain PFCA leads to its lower affinity to the air bubbles.
Figure 4. PFAS removal by air fractionation, UV and ozonated air fractionation (residence time = 20 min)

The total PFAS removal efficiency was about 95% by the ozonated air fractionation, as shown in Figure 4, which is the highest among all the tested treatment methods. After the treatment, no PFSA, PFOA and PFHpA was detected in the treated water. However, only 12.5% PFHxA was removed from the treated water. Based on the blank tests, the maximum total ozone residuals in both reaction chambers were 0.2 mg/L, which could not oxidise the PFAS in a contact time of 20 min based on bond energy theory \(^{11}\). Therefore, the dominant PFAS removal mechanism should be ozone-boosted foam fractionation. When ozone is dosed into water, hydroxyl radicals are generated, which are strong electron binders \(^{34, 35}\). As shown in Figure 5, there will be an OH radical rich layer around the interface of the gas bubbles, due to the ozone diffusion from gas phase into the water phase. Since strong hydroxyl radical electron binders could bind onto the negatively charged hydrophilic \(\text{SO}_3^-/\text{COO}^-\) ends of the PFOS/PFOA based on affinity theory \(^{36-39}\), more PFAS will concentrate around the interface of the gas bubbles, in comparison with air fractionation. Therefore, the ozonated air fractionation can achieve higher PFAS separation efficiency than the air fractionation.

![Figure 5. Schematic diagram of the proposed PFAS affinity to the gas bubble](image)

PFHxA is highly persistent and mobile in the environment as a short-chain PFAS \(^{40}\). Based on the results, it can be seen that none of the tested methods can remove PFHxA as effectively as other PFAS substances. The UV/ozone combined treatment method even caused an increase of the PFHxA concentration in the treated water, when PFOA was presented in the feed water. Therefore, ozone enhanced fractionation or air fractionation could be used to lower the PFOA concentration before applying the UV and ozone combined technology to destroy any PFAS passing fractionation treatment. Although the possibility exists that UV and ozone combined technology could destroy the PFHxA, it could not be confirmed based on our test results and further research is necessary to determine if it is possible and at what rate it might occur.

3.2. Pilot-scale UV/ozone combined tests

It can be found in Figure 6 that the foaming only occurred in the last two reaction chambers. During the 1 h experimental period, 189 L water was treated, and 2.5 L of water was collected from the overflow line due to the foaming in the last two reaction chambers.

From Table 5, after UV/ozone combined treatment, the mass of all short-chain PFCA increased, while the mass of all short-chain PFSA decreased. The 6:2 Fluorotelomer sulfonic acid (6:2 FTS) that was not detected in both the feed and effluent was found in the foam. Therefore, it
can be concluded that the advanced oxidation could facilitate the formation of short-chain PFAS.

In Figure 7, the removal efficiency of PFAS during the pilot rig operation by the UV/ozone combined treatment was calculated using Equation (2).

\[
D_{\text{pfas}} = \left(1 - \frac{C_{\text{foam}} \times V_{\text{foam}} + C_e \times V_e}{C_f \times V_f} \right) \times 100%
\]

(2)

where \( D_{\text{pfas}} \) is the percentage of PFAS destroyed by UV and ozone combined treatment; \( C_{\text{foam}} \) and \( C_e \) are the PFAS concentrations in the foam and treated water (effluent), respectively; and \( V_{\text{foam}}, V_e \) and \( V_f \) are the volumes of foam, effluent and feed, respectively.

It can be seen from Figure 7 that about 79% PFAS in total was removed from the treated water (effluent), in which 75% was destroyed by the UV/ozone combined treatment similar to the result achieved by the benchtop at the same residence time. Meanwhile, with the same carbon number, it is easier to remove the PFSA than the PFCA from the feed by either destruction or fractionation, which is attributed to the hydrophobicity or lipophilicity difference between the PFCA and PFSA. With the same alkyl chain length, PFCAs are more hydrophilic than PFSA. Therefore, the affinity of the PFSA molecule to the water-bubble interface is higher than...
that of the PFCA molecule. As a result, it would be easier for the PFSA to access the oxidant in the bubble and to partition into the foam compared to PFCA. Furthermore, the concentration of the short-chain PFCA including PFHxA and PFHpA increased due to the UV/ozone combined destruction, consistent with the benchtop results.

Figure 7. Percentage of PFAS removed from the effluent and PFAS destroyed by UV and ozone combined treatment (residence time = 20 min, air flowrate = 160 L/min)

To assess the influence of carbon number on the foam fractionation, the partition factors of the PFAS with different carbon numbers are calculated by Equation (3) using data in Table 5 and shown in Figure 8.

\[ \lambda = \frac{c_{\text{foam}}}{c_{\text{e}}} \]  

where \( \lambda \) is the partition factor between the effluent and the foam.

It can be found that the partition factor has an nearly exponential relationship with the PFAS carbon number, due to the octanol-water and air-water partition coefficients increasing exponentially with perfluorinated chain length. Therefore, partitioning the shorter-chain PFAS from the bulky feed into the foam would be more difficult than that of the long-chain PFAS by the ozonated air fractionation treatment.
4. Conclusions

The performance of ozonated air fractionation, air fractionation, UV, and UV/ozone combined treatments on PFAS removal were studied and compared. The benchtop tests were conducted at a hydraulic residence time of 20 min and air flowrate of 20 L/min, and the conclusions were obtained as follow:

- ozonated air fractionation achieved the best performance, in which about 95% PFAS was removed from the treated water,
- UV showed the worst performance of 17% PFAS removal,
- air fractionation removed 81% of PFAS, and
- UV/ozone combined treatment achieved 73% removal of PFAS at a residence time of 20 min, which was also confirmed in the pilot rig test.

In comparison with the air fractionation, the ozonated air fractionation has higher PFAS removal efficiency, because of the affinity of OH radical to the negatively charged hydrophilic $\text{SO}_3^-$/COO- ends of the PFOS/PFOA.

It is relatively easier to remove PFSA than PFCA by both the air and ozonated air fractionations and the UV/ozone combined treatment, attributing to the involvement of gas bubbles and the greater lipophilicity of PFSA.

When PFAS destruction treatment is involved, the short-chain PFAS concentration will generally increase after the treatment. Both the air and ozonated air fractionations could not effectively partition the short-chain PFAS from the contaminated water into the foam, due to the exponential decline of the partition factor with the reducing carbon number of the PFAS.

Acknowledgement

Funding from the Environmental Group Limited and Australian Department of Industry, Innovation and Science are gratefully acknowledged. Pilot and benchtop testing rigs were supplied by the Environmental Group Limited. All Intellectual Property relating to this project and equipment design are covered by the EGL’s existing Patent.

Reference:


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**Appendix 1**

| PFAS - Perfluorobutane sulfonic acid (PFBS) |
| PFAS - Perfluoropentane sulfonic acid (PFPeS) |
| PFAS - Perfluorohexane sulfonic acid (PFHxS) |
| PFAS - Perfluoroheptane sulfonic acid (PFHpS) |
| PFAS - Perfluorooctane sulfonic acid (PFOS) |
| PFAS - Perfluorodecane sulfonic acid (PFDS) |
| PFAS - Perfluorobutanoic acid (PFBA) |
| PFAS - Perfluoropentanoic acid (PFPeA) |
| PFAS - Perfluorohexanoic acid (PFHxA) |
| PFAS - Perfluoroheptanoic acid (PFHpA) |
| PFAS - Perfluorooctanoic acid (PFOA) |
| PFAS - Perfluorononanoic acid (PFNA) |
| PFAS - Perfluorodecanoic acid (PFDA) |
| PFAS - Perfluoroundecanoic acid (PFUnDA) |
| PFAS - Perfluorododecanoic acid (PFDaDA) |
| PFAS - Perfluorotridecanoic acid (PFTrDA) |
| PFAS - Perfluorotetradecanoic acid (PFTeDA) |
| PFAS - Perfluoroctane sulfonamide (FOSA) |
| PFAS - N-Methyl perfluoroctane sulfonamide (MeFOSA) |
| PFAS - N-Ethyl perfluoroctane sulfonamide (EtFOSA) |
| PFAS - N-Methyl perfluoroctane sulfonamidoethanol |
| PFAS - N-Ethyl perfluoroctane sulfonamidoethanol |
| PFAS - N-Methyl perfluoroctane sulfonamidoacetic acid |
| PFAS - N-Ethyl perfluoroctane sulfonamidoacetic acid |
| PFAS - 4:2 Fluorotelomer sulfonic acid (4:2 FTS) |
| PFAS - 6:2 Fluorotelomer sulfonic acid (6:2 FTS) |
| PFAS - 8:2 Fluorotelomer sulfonic acid (8:2 FTS) |
| PFAS - 10:2 Fluorotelomer sulfonic acid (10:2 FTS) |
Conducted by a multifunctional equipment, the comparative study showed a 95% PFAS removal achieved by the ozonated air fractionation.