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PFAS are persistent chemical of concerns 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.

1 # Comparative study of PFAS treatment by UV, UV/ozone, and

2 # fractionations with air and ozonated air

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9

10 **Abstract:**

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

40 Key words: PFAS; advanced oxidation; UV; ozone; fractionation; wastewater treatment

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 [1]. At the beginning of 2000s, the works done by Moody and Field [2] and Giesy and Kannan [3], 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 [4]. In 2017, the USEPA proposed the unregulated reference concentrations of PFOA and PFOS to be 0.07 µg/L in drinking water [5].

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, include 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 [6], usually requiring high-temperature incineration. Ion exchange resin can also remove PFAS efficiently [7]. 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,

80 since PFAS also act as surfactants. The running cost of foam fractionation is low and produces
81 only small amounts of highly concentrated PFAS containing water. However, the removal
82 efficiency is about 80% and is not very effective when dealing with short-chain PFAS.

83 For all treatment methods of Category I, the destruction of concentrated PFAS is still required.
84 Plasma incineration followed by calcium hydroxide absorption is commonly used to convert
85 PFAS to low hazard compounds [8].

86 Category II methods focus on the direct destruction of PFAS, avoiding the concentration step.
87 However, perfluorinated surfactants do not exhibit the preferred reactive sites for reaction with
88 ·OH radicals generated during the advanced oxidation. The abstraction of fluorine from a
89 carbon atom is thermodynamically unfavorable because the F-OH bond has a dissociation
90 energy of at least 216 kJ/mol lower than that of the C-F bond (CF_3F 552 kJ/mol, $R\text{-}CF_2\text{-}F$ 352
91 kJ/mol, R,R'-CF-F 508 kJ/mol) [9]. Furthermore, the electron density of the ionic head group
92 (e.g., carboxylate and sulfonates) is reduced by perfluorination, hindering electron transfer
93 reactions. The kinetic rate constant for the reaction of trifluoroacetic acid with ·OH has been
94 estimated to be less than 1×10^6 $M^{-1}s^{-1}$ [10], indicating a slow rate of reaction with practically no
95 reactivity of ·OH towards trifluoroacetic acid. PFOS is resistant to different advanced oxidation
96 treatment methods (Fenton, UV/H_2O_2, ozonation in alkaline solution, and peroxon process
97 (O_3/H_2O_2)) over 120 min at room temperature [11]. Hori et al. [12] found that the addition of
98 hydrogen peroxide in UV treatment method has a detrimental effect on the degradation of
99 PFOA, compared to direct UV-photolysis (radiation source: Xenon-doped mercury lamp),
100 which supports the persistence of PFCs in the presence of ·OH. It was reported that 83% PFOS
101 was removed under the conditions of 5 h UV dosing with molecularly imprinted polymer-
102 modified TiO_2 catalyst [13].

103 The combination of ozone and ultraviolet radiation (UV) could achieve better water treatment
104 than the ozone alone, due to the promoted formation of hydroxyl radical intermediates [14, 15]. In
105 the UV/O_3 process, the dissolved ozone will be split by UV irradiation ($\lambda < 300$ nm), and reacts
106 with water to form a thermally excited H_2O_2 which decomposes into two ·OH subsequently [15].
107 Houston Research Inc. showed that ozone/UV enhances the oxidation of complexed cyanides,
108 chlorinated solvents, pesticides that contribute to COD and BOD [16-19]. In the
109 conventionalozonation, organic compounds are not completely oxidized to CO_2 and H_2O in
110 many cases [20]. In some reactions, the intermediate oxidation products remaining in the solution
111 may be as toxic as or even more toxic than the initial compound [21]. Completion of oxidation
112 reactions, as well as oxidative destruction of compounds immune to unassisted ozone, can be
113 achieved by supplementing the reaction with UV radiation. Many organic contaminants absorb
114 UV energy in the range of 200 -300 nm [22] and decompose due to direct photolysis or become
115 excited and more reactive with chemical oxidants. Therefore, the combination of UV/ozone
116 might be able to achieve effective PFAS removal.

117 However, Category II technologies are not favoured by most large-scale water treatment plants
118 directly, because strong oxidants/radiation at high dose are required to decompose PFAS, and
119 PFAS concentration in the wastewater is generally at PPB to PPT level [23, 24].

120 Thus, it is necessary to combine both treatment methods in Categories I and II. Through the
121 methods in Category I, the PFAS could be concentrated into a much smaller volume than the
122 original PFAS, which will significantly reduce the load of the subsequent destruction
123 treatments in the Category II. Therefore, minimising the total rejected volume (containing high

124   concentration PFAS) from Category I would be critical to reducing the overall operation cost.
125   A multifunctional rig patented by EGL was tested for PFAS removal.It can be used to treat the
126   water by UV, ozonation, fractionation and their combinations [25]. The performances of different
127   treatments were also compared in this study.

128   **2. Experimental**

129   2.1. Benchtop rig tests

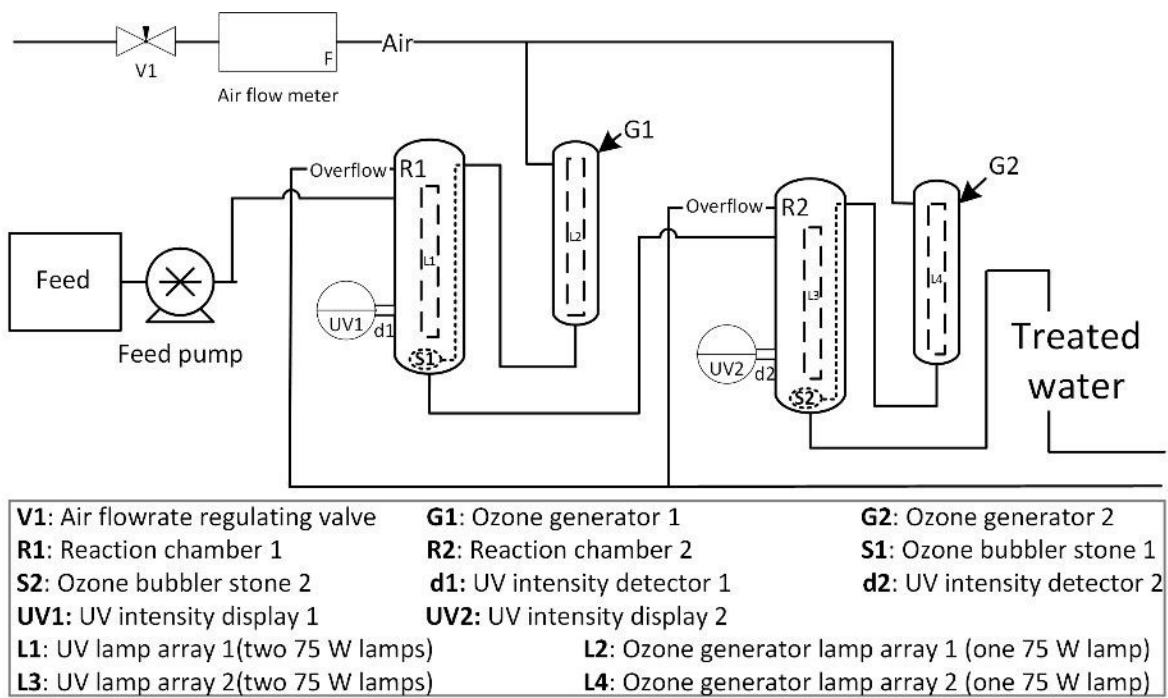|		
V1: Air flowrate regulating valve	**G1**: Ozone generator 1	**G2**: Ozone generator 2
R1: Reaction chamber 1	**R2**: Reaction chamber 2	**S1**: Ozone bubbler stone 1
S2: Ozone bubbler stone 2	**d1**: UV intensity detector 1	**d2**: UV intensity detector 2
UV1: UV intensity display 1	**UV2**: UV intensity display 2	
L1: UV lamp array 1(two 75 W lamps)	**L2**: Ozone generator lamp array 1 (one 75 W lamp)	
L3: UV lamp array 2(two 75 W lamps)	**L4**: Ozone generator lamp array 2 (one 75 W lamp)	

130

131   Figure 1. Schematic diagram of the benchtop rig

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

145   2.1.1 Blank test

146   Blank tests were conducted with the tap water to achieve the operation baseline. The UV
147   intensity and ozone residual were measured without the interference from the added PFAS
148   containing firefight foam. The feed flowrates were set at 0.35 and 1.4 L/min to obtain residence

149 times of 40 and 10 min, respectively. The air flowrates during the tests were varied at 10, 20
150 and 30 L/min, respectively.

151 2.1.2 System PFAS adsorption test

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

156 2.1.3. UV/ozone combined treatment for PFAS wastewater

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

160 2.1.4. Ozonated air fractionation, air fractionation and UV for PFAS wastewater treatment

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

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

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

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

174

175 2.2. Pilot UV/ozone rig test

176 The scale-up of the engineering process may result in great performance differences relative to
177 the benchtop tests [26]. Therefore, a pilot test was also conducted under the optimum conditions
178 identified from the benchtop tests. In comparison with the benchtop rig, the pilot rig includes
179 nine reaction chambers and sixteen ozone generators. All the reaction chambers were equipped
180 with two UV lamps, but three of them were not connected to the ozone generators, which is
181 different from the benchtop rig. The total volume of the pilot rig was 63 L. Therefore, the feed
182 flowrate was set at 3.15 L/min to achieve a 20 min residence time. The feed was prepared by
183 dissolving 100 g firefighting foam into 200 L water. The experiment lasted for one hour. The
184 feed was sampled at the beginning of the test, and the effluent was sampled at the end of the
185 test.

186 2.3. Analysis

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

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

3. Results and discussion

193 **3. Results and discussion**

194 3.1. Benchtop UV/ozone combined tests

195 3.1.1. Blank tests with tap water for identification of the maximum UV radiation and ozone
196 residuals

197 Blank tests were carried out by using the tap water, which was used to dilute PFAS containing
198 firefighting foam. The purpose of these tests was to understand the baseline performance of the
199 combined UV/ozone system in the absence of PFAS. Besides, the blank tests also help to
200 identify the variations of ozone residuals and UV intensity with the feed and air flowrates, as
201 the reference for the following PFAS water treatment. Table 1 shows the ozone residual and
202 the UV intensity of the blank tests in reaction chambers R1 and R2 at feed flowrates of 1.4 and
203 0.35 L/min respectively, which are also the theoretical maximum value achievable for
204 following PFAS tests under the similar conditions. At the higher feed flowrate of 1.4 L/min
205 (10 min residence time), the total ozone residuals in R1 and R2 were almost the same and in
206 the range of 0.18 - 0.20 mg/L. This difference is in the error range. However, the UV intensity
207 declined about 17% in R1 as the air flowrate was increased to 30 L/min, due to enhanced
208 deflection/reflection of UV beams by increased air bubbles [27]. At the lower feed flowrate of
209 0.35 L/min (40 min residence time), the maximum total ozone residuals in R1 and R2 were 0.2
210 mg/L when the air flowrate was 20 L/min. The measured UV intensity also reduced to
211 approximately 12% at an air flowrate of 30 L/min, in comparison with that of an air flowrate
212 of 10 L/min in R1.

213 It is also worth mentioning that in general, the total ozone residuals at high feed flowrate were
214 higher than those at low feed flowrate. That is because of the high liquid turbulence at high
215 flowrate encouraging the ozone transfer from the gas phase to the liquid phase [28]. Furthermore,
216 in R1, the UV intensity was also higher at a feed flowrate of 1.4 L/min than that at 0.35 L/min
217 with the same air flowrate, because more and finer air bubbles created at higher feed flowrates
218 will produce more uniform UV scattering [29].

219 Table 1. Blank tests: Ozone residual and UV intensity

Feed flowrate (L/min)	Air flowrate (L/min)	UV Intensity (μW/cm^2)		Ozone residual (mg/L)		
		R1*	R2*	R1	R2	Total
1.4	12	100	44	0.08	0.12	0.20
1.4	20	100	45	0.11	0.08	0.19
1.4	30	83	43	0.09	0.09	0.18
0.35	10	84	43	0.07	0.06	0.13
0.35	20	80	43	0.14	0.06	0.20
0.35	30	74	44	0.06	0.04	0.10

220 * The different readings are due to the different installation distances to the UV lamps.

221   3.1.2. System PFAS adsorption test

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

225   Table 2. Analytical results for the system adsorption test

| Sample	PFPeS (μg/L)	PFHxS (μg/L)	PFHpS (μg/L)	PFOS (μg/L)	PFPeA (μg/L)	PFHxA (μg/L)	PFHpA (μg/L)	PFOA (μg/L)	PFAS (μg/L)
Feed	0.05	0.38	0.07	2.3	0.02	0.18	0.04	0.11	3.15
Effluent	0.04	0.37	0.08	2.4	0.02	0.14	0.04	0.10	3.19

226

227   3.1.3. UV/ozone combined treatment for PFAS wastewater

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

233   $$Re = (1 - \frac{C_t}{C_f}) \times 100\% \quad (1)$$

234   where Re is the percentage of PFAS removed from the treated water, C_t is the concentration
235   of PFAS in the treated water, and C_f is the PFAS concentration in the feed.

236   The maximum total PFAS removal was 87% at an air flowrate of 30 L/min and feed flowrate
237   of 1.4 L/min. At the same air flowrate, better PFAS removal was achieved at higher feed
238   flowrate, owing to the higher UV intensity and ozone residual obtained at higher feed flowrate
239   in the blank tests as shown in Table 1. Therefore, it can be concluded that the high ozone
240   transfer rate and UV intensity are able to enhance the PFAS removal.
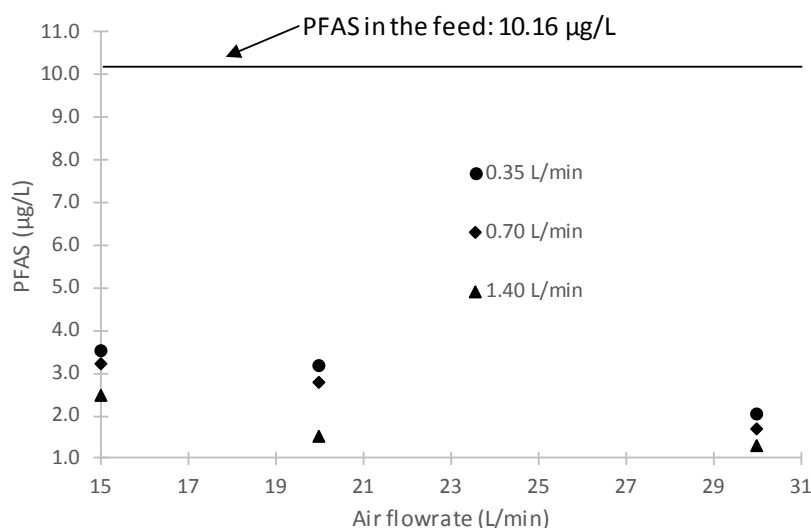
241
242   a. PFAS concentration in the treated water
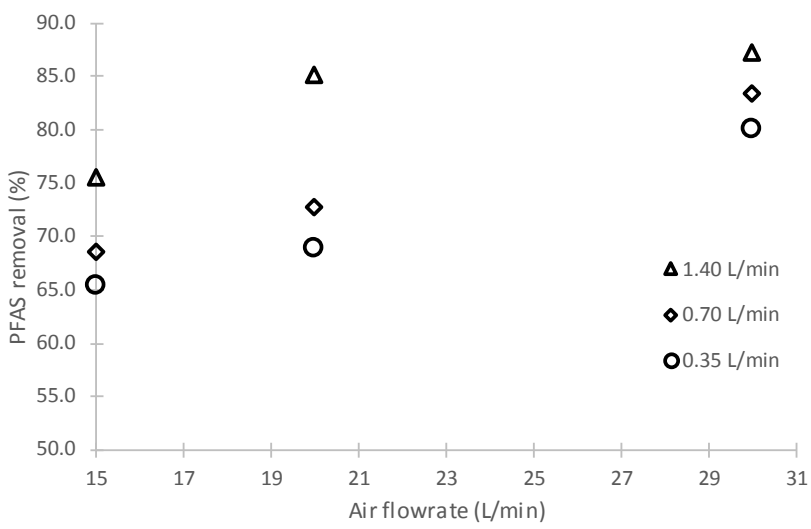
243
244   b. PFAS removal efficiency
245   Figure 2. Performance of treatment at different feed and air flowrate

246   Table 3 shows the concentrations of four major per- and poly-fluoroalkyl substances in the feed
247   and treated water. It can be seen that, after the ozone/UV combined treatment, all PFAS
248   concentrations reduced, except for perfluorohexanoic acid (PFHxA). Moreover, the increases
249   of feed and air flowrates could facilitate the PFOS and PFOA removals under all the operating
250   conditions. However, the feed and air flowrates had less influence on PFHxS removal. On the
251   other hand, PFHxA concentration increased under almost all the treatment conditions, and up
252   to a 50% increase of PFHxA was observed when 97.3% PFOA removal was achieved.
253   Therefore, it can be confirmed that the UV/ozone combined treatment could convert PFAS into
254   PFHxA [30]. It seems that PFHxS also could be generated from other PFAS sources in the
255   treatment process, but it could not be demonstrated unequivocally based on the available
256   analytical results. After the treatment under the optimum treatment conditions (air flowrate =
257   30 L/min, feed flowrate = 1.4 L/min), the total concentration of PFHxS (0.48 µg/L) and PFHxA
258   (0.22 µg/L) was 0.70 µg/L greater than the total concentration (0.60 µg/L) of PFOS (0.52 µg/L)
259   and PFOA (0.08 µg/L), although their total concentration in the feed was only one third of that
260   of the PFOS and PFOA. Therefore, to achieve high total PFAS removal, the PFHxA and
261   PFHxS concentrations should be considered, as they could not be easily removed by the
262   UV/ozone combined treatment and PFHxA appeared to be generated by the process.

263   Table 3.Operation parameters and analytical results

Sample	Feed flowrate (L/min)	Air flowrate (L/min)	PFHxS C (µg/L)	PFHxS Re (%)	PFOS C (µg/L)	PFOS Re (%)	PFHxA C (µg/L)	PFHxA Re (%)	PFOA C (µg/L)	PFOA Re (%)
Feed	/	/	2.40	/	5.40	/	0.16	/	2.20	/
S1	0.35	15	0.44	81.7	2.30	57.4	0.18	-12.5	0.60	72.7
S2	0.35	20	0.46	80.8	1.70	68.5	0.19	-18.8	0.80	63.6
S3	0.35	30	0.48	80.0	1.10	79.6	0.18	-12.5	0.26	88.2
S4	0.7	15	0.70	70.8	2.20	59.3	0.18	-12.5	0.12	94.5
S5	0.7	20	0.58	75.8	1.60	70.4	0.18	-12.5	0.40	81.8
S6	0.7	30	0.60	75.0	0.72	86.7	0.19	-18.8	0.18	91.8
S7	1.4	15	0.58	75.8	1.50	72.2	0.16	0.0	0.24	89.1
S8	1.4	20	0.92	61.7	0.28	94.8	0.24	-50.0	0.06	97.3
S9	1.4	30	0.48	80.0	0.52	90.4	0.22	-37.5	0.08	96.4

264

265 3.1.4. UV, air fractionation and ozonated air fractionation for PFAS wastewater treatment

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

269 Figure 3 shows images of the observation windows of the UV/ozone combined test, air
270 fractionation test, ozonated air fractionation test, and UV only test. It can be seen from Figures
271 3a and 3d that there was no foaming observed. However, in both fractionation processes where
272 air and ozonated air was bubbled through the reaction chambers, it can be seen from Figures
273 3b and 3c that foaming occurred. Since foaming in the reaction chambers is a sign of
274 fractionation due to existing surfactants (PFAS), no foam observed in the UV/ozone combined
275 and UV tests indicated that the PFAS removal in both processes was due to the destruction
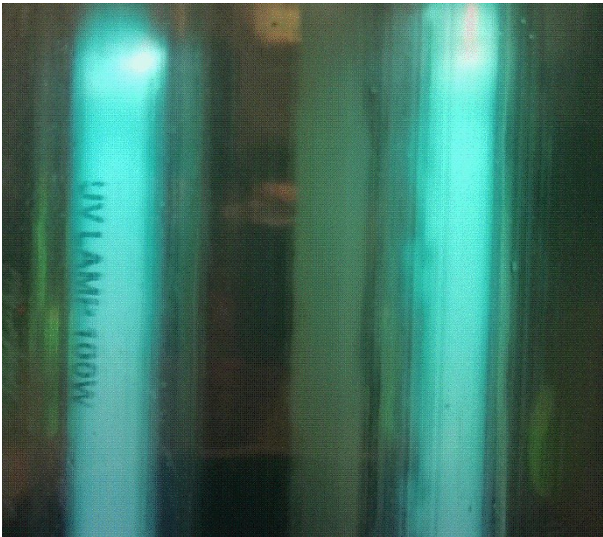276 rather than foam fractionation.

277

278 a. UV+Ozone

279
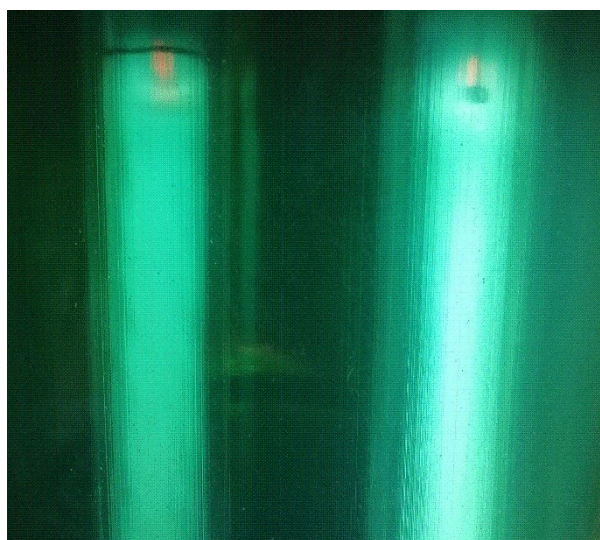
280 b. Air fractionation

281
282   c. ozonated air fractionation

283

284   d. UV only
285   Figure 3. Foaming at different operations

286   In Table 4, the analytical results from the various processes are shown. Feed 1 was used for
287   the air fractionation test, and S1 was the treated water by air fractionation. Feed 2 was used
288   for both UV and ozonated air fractionation tests, and S2 and S3 were the treated waters thereof.
289   The removal efficiencies of all detectable PFAS containing different carbon numbers are
290   shown in Figure 4. Since the detection limit was 0.02 µg/L for the perfluoropentane sulfonate
291   (PFPeS) and perfluoropentanoic acid (PFPeA) containing five carbons, it is impossible to make
292   a solid conclusion based on the analytical method, although some PFPeA removal was found
293   during the ozonated air fractionation. Therefore, the removal efficiency of the PFAS containing
294   five carbons is not shown in Figure 4. Furthermore, since some concentration changes after
295   treatment were less than the detection limit of 0.02 µg/L, those changes were considered in the
296   analytical error range and are not discussed further.

297   It can be found that the UV treatment could remove 16.8% PFAS in total (Figure 4), which
298   was mainly associated with PFOS removal (Table 4). After the UV treatment, 25% PFOS was
299   removed from 2.8 to 2.1 µg/L in the treated water, but the PFOA concentration did not change.

300 However, the PFHxS concentration increased by approximately 33% from 0.3 to 0.4 µg/L.
301 Since only PFOS and/or PFOA was used in the firefighting foam and the variation of
302 perfluoroheptane sulfonate (PFHpS) from 0.06 to 0.05 µg/L is in the range of the detection
303 limit and is negligible, it can be concluded that the newly formed PFHxS was mainly from
304 PFOS degradation.

305 Based on research from Vecitis et al., perfluoroalkyl carboxylate (PFCA) should have a faster
306 photolytic degradation than perfluoroalkyl sulfonate (PFSA) [31] However, it can also be seen in
307 Table 4 that PFCA such as PFOA, PFHxA or PFHpA did not show obvious change after the
308 UV treatment, in comparison of the degradation of PFOS (PFSA). Yamamoto, etal. found that
309 one of the photodegradation pathways of PFOS is to transform into PFCA [30]. It also can be
310 found that 80% of the total PFAS in the feed is in form of PFOS as shown in Table 4. Therefore,
311 even if the PFCA degrades faster than PFSA, it could be possibly repenlished by the
312 photodegradation of the PFOS in this study. Thus, it would not be possible to make any
313 conclusion whether the PFCA had been destroyed by UV treatement in our study.

314 Table 4. Analytical results for the feed and treated water

Sample	Operation	PFPeS (µg/L)	PFHxS (µg/L)	PFHpS (µg/L)	PFOS (µg/L)	PFPeA (µg/L)	PFHxA (µg/L)	PFHpA (µg/L)	PFOA (µg/L)	PFAS (µg/L)
Feed 1	/	0.05	0.38	0.07	2.3	0.02	0.18	0.04	0.11	3.15
S1	Air fractionation	0.03	0.06	<0.02	0.3	0.02	0.15	0.02	0.01	0.59
Feed 2	/	0.04	0.3	0.06	2.8	0.02	0.16	0.04	0.09	3.51
S2	UV	0.05	0.4	0.05	2.1	0.02	0.16	0.04	0.1	2.92
S3	Ozonated air fractionation	0.03	<0.05	<0.02	<0.04	<0.02	0.14	<0.02	<0.01	0.17

315

316 From Figure 4, it can be found that air fractionation removed about 81.3% PFAS in total, and
317 80% PFHxS, approximately 100% PFHpS, 87.0% PFOS, 16.7% PFHxA, 50.0% PFHpA, and
318 91% PFOA were removed from the treated water. Since air is not a strong oxidant, foam
319 fractionation should be the dominant separation mechanism for the PFAS removal. For the
320 PFSA, the removal efficiency did not show a clear relationship to the molecular weight.
321 However, the removal efficiency for PFCA declined more than 80% as the carbon number
322 reduced from 8 to 6, because the lower lipophilicity of the shorter alkyl chain PFCA leads to
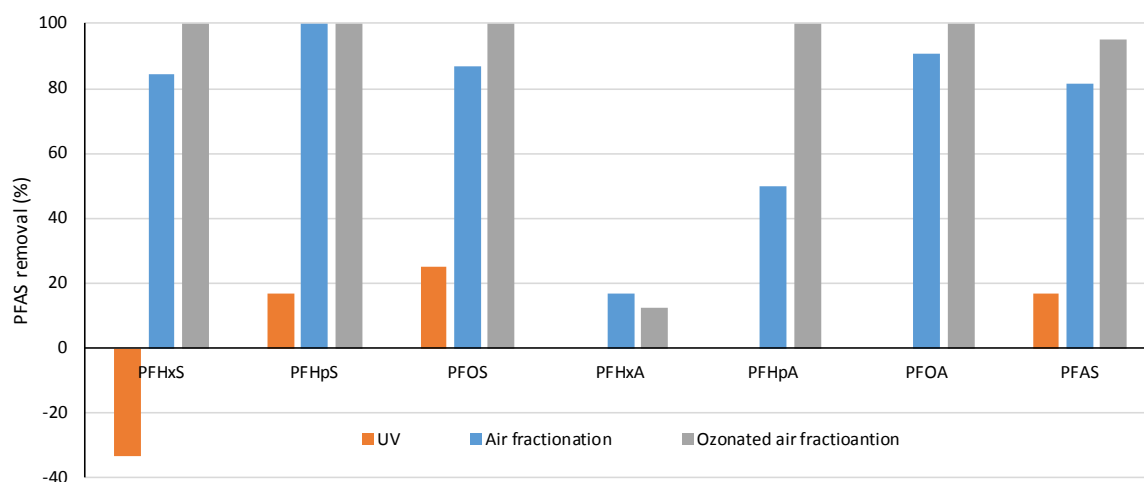323 its lower affinity to the air bubbles [32, 33].

324

325 Figure 4. PFAS removal by air fractionation, UV and ozonated air fractionation (residence time
326 = 20 min)

327 The total PFAS removal efficiency was about 95% by the ozonated air fractionation, as shown
328 in Figure 4, which is the highest among all the tested treatment methods. After the treatment,
329 no PFSA, PFOA and PFHpA was detected in the treated water. However, only 12.5% PFHxA
330 was removed from the treated water. Based on the blank tests, the maximum total ozone
331 residuals in both reaction chambers were 0.2 mg/L, which could not oxidise the PFAS in a
332 contact time of 20 min based on bond energy theory [11]. Therefore, the dominant PFAS removal
333 mechanism should be ozone-boosted foam fractionation. When ozone is dosed into water,
334 hydroxyl radicals are generated, which are strong electron binders [34, 35]. As shown in Figure 5,
335 there will be an OH radical rich layer around the interface of the gas bubbles, due to the ozone
336 diffusion from gas phase into the water phase. Since strong hydroxyl radical electron binders
337 could bind onto the negatively charged hydrophilic SO_3^-/COO^- ends of the PFOS/PFOA based
338 on affinity theory [36-39], more PFAS will concentrate around the interface of the gas bubbles, in
339 comparison with air fractionation. Therefore, the ozonated air fractionation can achieve higher
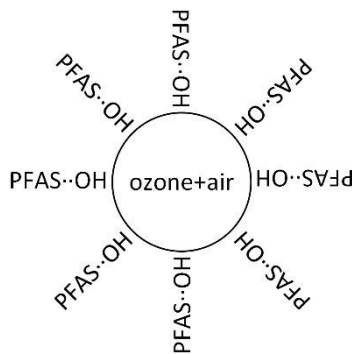340 PFAS separation efficiency than the air fractionation.

341

342   Figure 5. Schematic diagram of the proposed PFAS affinity to the gas bubble

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

352 3.2. Pilot-scale UV/ozone combined tests

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

356 From Table 5, after UV/ozone combined treatment, the mass of all short-chain PFCA increased,
357 while the mass of all short-chain PFSA decreased. The 6:2 Fluorotelomer sulfonic acid (6:2
358 FTS) that was not detected in both the feed and effluent was found in the foam. Therefore, it

359 can be concluded that the advanced oxidation could facilitate the formation of short-chain
360 PFAS.

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

363 $$D_{pfas} = \left(1 - \frac{C_{foam} \times V_{foam} + C_e \times V_e}{C_f \times V_f}\right) \times 100\% \qquad (2)$$

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

367

368   Figure 6. Foaming in the pilot rig

369 Table 5. PFAS concentration in the feed, treated water and foam

Sample	PFPeS (µg/L)	PFHxS (µg/L)	PFHpS (µg/L)	PFOS (µg/L)	PFPeA (µg/L)	PFHxA (µg/L)	PFHpA (µg/L)	PFOA (µg/L)	6:2 FTS (µg/L)	PFAS (µg/L)
Feed	0.04	0.24	0.03	1.20	<0.02	0.14	0.03	0.07	<0.05	1.75
Effluent	0.02	0.09	<0.02	0.05	0.02	0.15	0.03	0.01	<0.05	0.37
Foam	0.09	0.90	0.13	4.10	0.03	0.23	0.13	0.30	0.06	5.97

370

371 It can be seen from Figure 7 that about 79% PFAS in total was removed from the treated water
372 (effluent), in which 75% was destroyed by the UV/ozone combined treatment similar to the
373 result achieved by the benchtop at the same residence time. Meanwhile, with the same carbon
374 number, it is easier to remove the PFSA than the PFCA from the feed by either destruction or
375 fractionation, which is attributed to the hydrophobicity or lipophilicity difference between the
376 PFCA and PFSA. With the same alkyl chain length, PFCAs are more hydrophilic than PFSAs
377 [32, 33]. Therefore, the affinity of the PFSA molecule to the water-bubble interface is higher than

378   that of the PFCA molecule [41]. As a result, it would be easier for the PFSA to access the oxidant

379   in the bubble and to partition into the foam compared to PFCA. Furthermore, the concentration

380   of the short-chain PFCA including PFHxA and PFHpA increased due to the UV/ozone

381   combined destruction, consistent with the benchtop results.
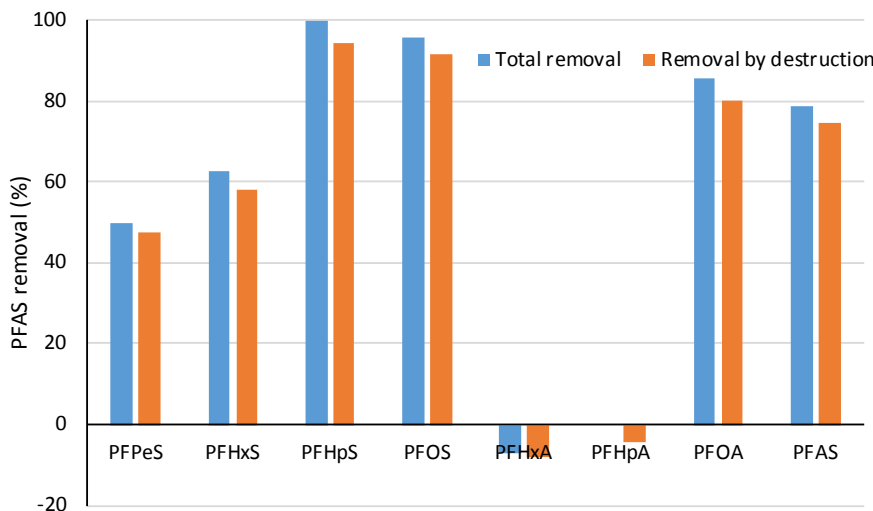

382

383   Figure 7. Percentage of PFAS removed from the effluent and PFAS destroyed by UV and ozone

384   combined treatment (residence time = 20 min, air flowrate = 160 L/min)

385   To assess the influence of carbon number on the foam fractionation, the partition factors of the

386   PFAS with different carbon numbers are calculated by Equation (3) using data in Table 5 and

387   shown in Figure 8.

388    $$\lambda = \frac{C_{foam}}{C_e} \qquad\qquad\qquad (3)$$

389   where λ is the partition factor between the effluent and the foam.

390   It can be found that the partition factor has an nearly exponential relationship with the PFAS

391   carbon number, due to the octanol-water and air-water partition coefficients increasing

392   exponentially with perfluorinated chain length [42]. Therefore, partitioning the shorter-chain

393   PFAS from the bulky feed into the foam would be more difficult than that of the long-chain
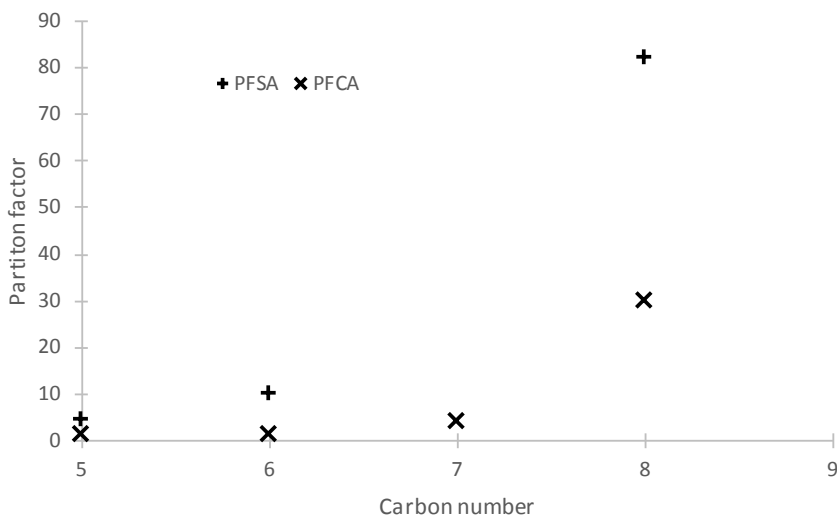
394   PFAS by the ozonated air fractionation treatment.

395

396   Figure 8. Distribution factors vs PFAS carbon number

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 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 redcuing carbon number of the PFAS.

Acknowledgement

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524

525

526

527 # 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 (PFDoDA)
PFAS - Perfluorotridecanoic acid (PFTrDA)
PFAS - Perfluorotetradecanoic acid (PFTeDA)
PFAS - Perfluorooctane sulfonamide (FOSA)
PFAS - N-Methyl perfluorooctane sulfonamide (MeFOSA)
PFAS - N-Ethyl perfluorooctane sulfonamide (EtFOSA)
PFAS - N-Methyl perfluorooctane sulfonamidoethanol
PFAS - N-Ethyl perfluorooctane sulfonamidoethanol
PFAS - N-Methyl perfluorooctane sulfonamidoacetic acid
PFAS - N-Ethyl perfluorooctane 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)

528

Conducted by a multifunctional equipment, the comparative study showed a 95% PFAS removal achieved by the ozonated air fractionation.