An Investigation of Plasma-driven Decomposition of Per- and Polyfluoroalkyl Substances (PFAS) in Raw Contaminated Ground Water

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Abstract

Per- and polyfluoroalkyl substances are contaminants of emerging concern owing to their ability to bioaccumulate in the body and subsequently cause cancer. PFAS, while recalcitrant to advanced oxidation, can be degraded by plasma action. In this work, we investigate the efficacy of two plasma reactors on degrading PFAS in ground water derived from two different contaminated sites. The reactors included an array of underwater plasma jets and a dielectric barrier discharge with water dielectric barriers. While, both reactors showed effectiveness in removing PFAS, the DBD with water barriers was most efficient in regards to rate of degradation and power consumed. This better performance was attributed to the increased plasma-liquid contact area. Experiments indicate that air is a suitable working gas alternative to argon, and both AC and ns-pulsed power sources can generate the plasmas for these reactors. Furthermore, it was found that for both reactors, the removal rate for low and high PFAS concentration ground water was the same, suggesting the reactors are most efficient at treating heavily contaminated water. In this respect, a concentration step followed by plasma treatment may be a cost effective means to treat the PFAS contaminated water.

I. Introduction

Per-and polyfluoroalkyl substances (PFAS) are fluorinated organic compounds that are extensively used in industrial and public settings in items such as water and oil repellant surfaces, no-stick cooking surfaces, food packaging, in firefighting foams.[1] Many of the applications of these chemicals leverage the fact that they are heat resistant, hydrophobic and highly stable. In the case of the firefighting foams, PFAS floats on the surface of burning liquid fuel, thus smothering it and reducing heat transfer from the fire. The fact that PFAS coatings resist the formation of oil stains, its use has proliferated for packaging in the fast-food arena, for example pizza boxes. The substance's relative stability to decomposition, though an advantage for various commercial applications is however particularly problematic from an environmental standpoint. This stability is derived from the strength of the carbon fluorine bond, the highest in organic chemistry.[2] This stability combined with its high hydrophobicity makes it very difficult to decompose by conventional means. The substance therefore has the capacity to accumulate in the environment such as ground water. Invariably, uptake by humans is a consequence through the ingestion of water or seafood. Indeed, over 98 percent of all Americans have detectable levels of PFAS in their blood stream.[1] Accumulation pathways are illustrated in Figure 1 as discussed by Sunderland and colleagues. PFAS compounds can bioaccumulate in human tissue and typical have a long half-life in the body leading to long term health effects such as diabetes, cancer, thyroid hormone disruption, and low sperm activity to name a few.[3] Since its introduction in the 1940s, it was not until very recently that there has been the formulation of a comprehensive plan to address the substance's proliferation in the environment, particular ground water. The number of actual PFAS compounds numbers well over 4,000 thus giving some appreciation of the diversity of these recalcitrant compounds that have been introduced into the environment.[3] A chemical depiction of two PFAS compounds found in contaminated ground water include PFOA and PFOS shown in Figure 2.

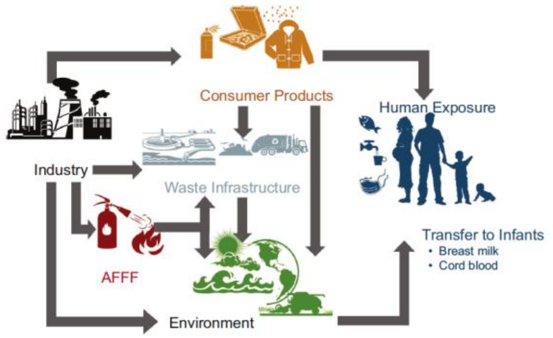

Figure 1. From Sunderland et al., pathways to contamination AFFF (aqueous film forming foams –firefighting foams).
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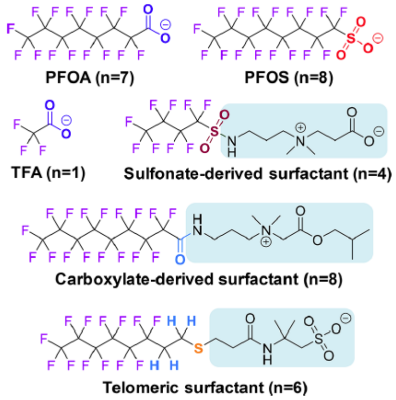

Figure 2. Example PFAS Structures, Bentel, 2019. Reproduced with permission from Environ. Sci. Technol. 53, 3718 (2019). Copyright 2019 American Chemical Society.

Which specific PFAS compounds are most prevalent in the ground water of a given region is highly dependent upon the nature of chemical exposure such as whether it is derived from industrial chemical processing, landfill leachates or regions near air bases where contamination is derived from extensive use of firefighting foam products.

The primary issue with novel compounds is inadequate study of the full chemical lifecycle; a comprehensive picture of how the substances enter the environment and are ultimately remediated is lacking. The EPA is currently reviewing alternatives to a class of PFAS compounds as well as developing a plan for stewardship and eventual elimination of these chemicals. While regulatory pressures will ultimately determine the trajectory of the phase out of these chemicals, the presence of the chemicals in the environment owing to extensive use needs to be addressed. The US EPA's current guidance (2020) on PFAS where remediation action is recommended is 70 ppt.[4] Recently state laws have also been passed with considerably lower remediation action concentration levels.[5] Because state laws have now established maximum contamination levels of PFAS compounds in waste water, the substance is officially regulated and compliance requires that treatment technologies be capable of removal. Unfortunately, the recalcitrant nature of these compounds makes removal and destruction difficult. The removal of this substance represents an important opportunity, particularly for the introduction of new water treatment technologies such as plasmas. Several treatment options are being explored. These methods which can be categorized by philosophy of approach include 1) collection and concentration and 2) decomposition.[6,7] Conventionally, one can use activated granular activated carbon, ion exchange membranes or reverse osmosis methods capture and thus remove PFAS compounds from waste streams. These technologies required water to be treated to be fairly polished to minimize modification to absorption surfaces or membranes by site occupancy or pore clogging. Additionally, the methods themselves generate highly contaminated PFAS contaminated waste streams in addition to purified water. While the contaminant is removed from the water, the filtered concentrate or loaded carbon powder must be further treated to eliminate the contaminant. In the case of activated carbon, the carbon is incinerated whereas in membrane processes the concentrate is sent to an evaporation pool where the residue can be then collected and incinerated. In these cases, the treatment methodology is multistep requiring additional expenditure of energy along with cost associated with complexity. Direct decomposition is desirable in that ideally it does not create an additional waste stream, rather the compound is disassembled chemically to harmless by-products. A key regarding PFAS treatment include: what is the fate of the shorter chains produced, and is the advanced method also appropriate to treat these shorter chains? Such questions have not been settled to date.[8]

In this work, plasma treatment is applied to the treatment of PFAS contaminated ground water. While plasma treatment is often thought of as an advanced oxidation method, it has been shown that oxidation is not effective in decomposing short chain PFAS compounds.[8] This is largely due the relative strength of the C-F bond and the high electronegativity of fluorine. The oxidation potential of fluorine is larger than that of OH, the chief radical in advanced oxidation. Reduction methods on the other hand have shown success at defluorinating and ultimately decomposing PFAS compounds.[9] These methods feature solvated electrons—a short lived, highly reactive complex that destabilizes PFAS compounds. Solvated electron destruction of PFAS compounds is facilitated by Hydrogen-Fluorine exchange and by chain shortening via bond breaking of C-C along with the cleaving of C-F bonds.[10] The exact decay paths for the complete decomposition of PFAS compounds via advanced reduction are still not well understood. What is known however is that advanced reduction of PFAS is most efficient in water at neutral to elevated pH to minimize hydrogen scavenging of the solvated electron, low nitrate concentration (another solvated electron scavenger), reduced dissolved organic media which compete with PFAS molecules for solvated electrons, and elevated temperature which increases the collision frequency for reactions.[10] Plasmas are also a source of free electrons which solvate when in contact with water and have been explored as a means to remove organic contaminants.[11] Plasmas have shown success at decomposing PFAS.[12–14] Here, we describe the effect of plasma and associated plasma-derived solvated electrons on PFAS compounds found in contaminated well water. The reactor featured in this work is the barrier discharge with liquid dielectrics.[15] This reactor separates the waste stream in to narrow jets of water, between which plasma is generated. The geometry maximizes plasma to liquid contact area, a key consideration in treating surfactant compounds like PFAS which tend to collect at the boundary of the gas liquid interface.

In the sections that follow, we describe the experimental setup and approach followed by the test results. Here, we compare the performance of an underwater plasma jet with the barrier discharge with liquid dielectrics reactor to show the benefits of maximizing the plasma to surface contact area. We also describe implications of results and methods to improve overall conversion efficiency.

II. Experimental set up

A. Reactors

Two types of reactors were investigated for the decomposition of PFAS compounds contained in water extracted from heavily contaminated ground water sites. The first reactor is the underwater dielectric barrier discharge plasma jet (DBD-PJ), based on the configuration and construction by Foster et al.[16] The DBD-PJ reactor consists of a 1 L wide-mouth glass jar with a lid that has been adapted to allow three individual DBD plasma jets to be mounted with a common central ground electrode feedthrough. The lid was fitted with an exhaust port through which evolved gases could escape. The port was also used as a conduit to pass a thermocouple probe for monitoring the water temperature. The individual DBD plasma jets act as plasma applicators and each consisted of a 6.35 mm OD quartz tube enclosing the powered electrode. The ground lead consisted of a coil wrapped around the end of the quartz tube. Compression fitting tees are attached to the top of each quartz tube to allow for the passage of feed gas and the connection to the high voltage electrode. A single jet configuration is shown in Figure 3a.

All three jets could be powered at once to increase the plasma contact area; however, it was found that with increasing input power, it was difficult to maintain the same intensity of discharge to each tube simultaneously. To minimize the uncertainty in the plasma contact area due to discharge competition between the jets, this study reports on single and dual plasma jet configurations. The dual jet configuration was found to be more stable than the triple jet with discharge intensity similar for each when powered by a single power supply. Regardless of the number of tubes operated, the total gas flow was constant. Gas was sent through unpowered tubes to facilitate mixing. The DBD plasma jets were operated using two types of power supplies: 1) a low frequency sinusoidal AC (1-5 kHz) voltage source with step up transformer and 2) a repetitively pulsed (1-10 kHz) ns voltage source.

The two sources were chosen to understand the role of localized heating. Plasma gas temperatures can reach over 2,000 K when excited with the low frequency AC voltage source, whereas the gas remains close to room temperature in the ns-pulsed plasma.[17] This gas heating is a charge relaxation time effect. The relaxation time is on the order of 1 to 10 ns for the ground water samples, depending on the electrical conductivity of the water during treatment. The rise time of the ns-pulser is about 100 ns, while the rise time for the AC supply is about 10,000 ns. In this respect, the pulse rise time is long compared to the relaxation time, so current can build almost quasi arc-like since the liquid acts more like a conductor over these time scales. This effect can be observed in ns-pulsed discharges as well in salty solutions.[18] Since it has been shown that pyrolysis is effective in the treatment of PFAS, the higher temperature plasma generated by the AC power source is of potential interest as an additional pathway leading to decomposition.[19] The assumption therefore is that this hot discharge may have some benefit over the cooler ns-pulsed discharges.

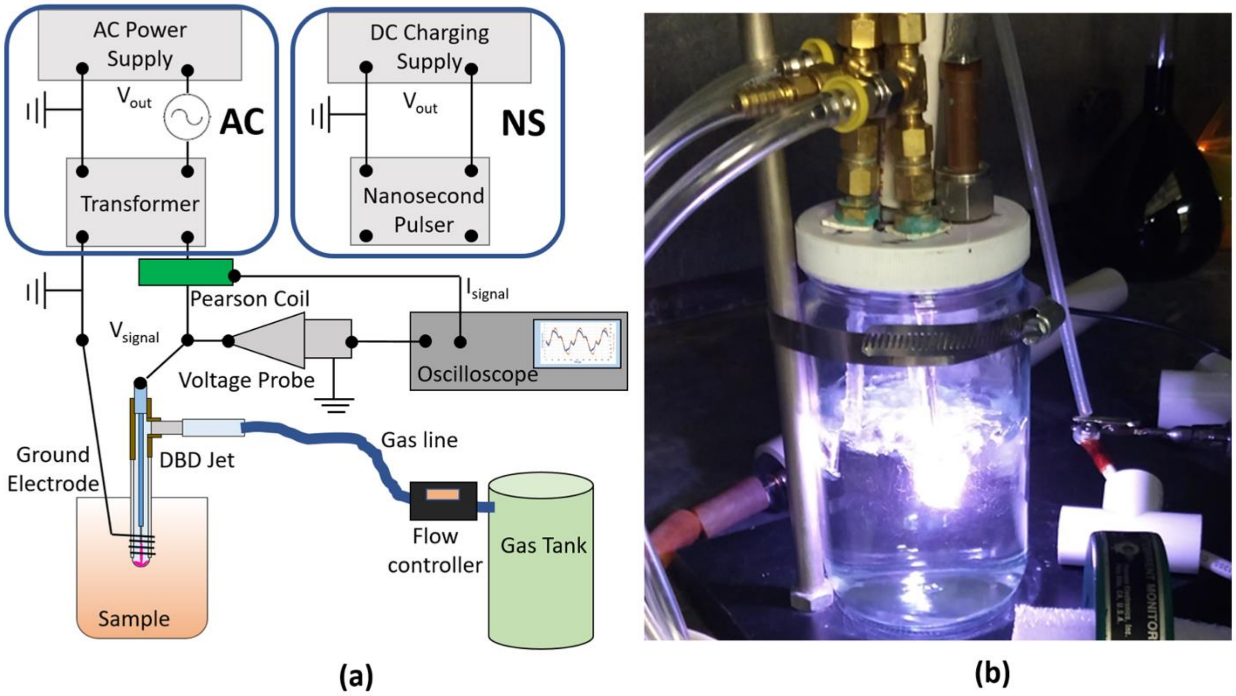

Figure 3. (a) Schematic of the DBD-PJ reactor setup, capable of being powered by AC or ns-pulsed power supplies. (b) Image of the DBD-PJ reactor operating in single-jet mode under ns-pulsed excitation.

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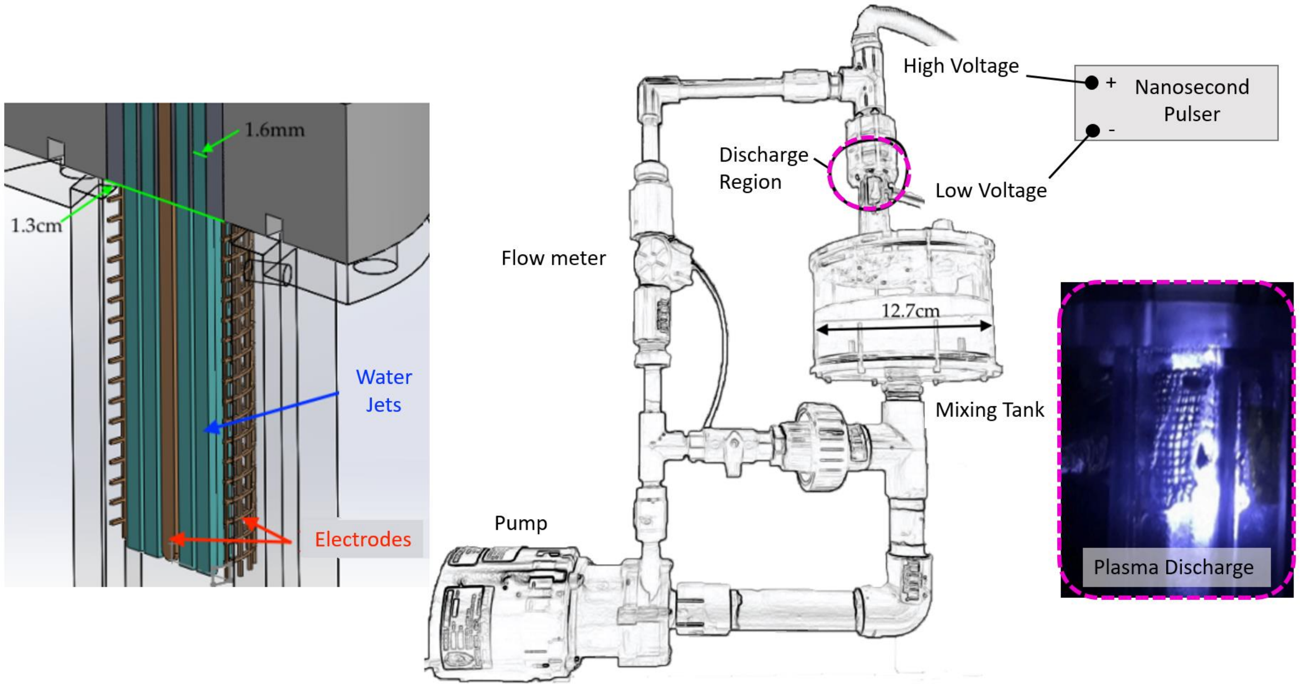
The second reactor investigated in this work was a DBD discharge with water dielectrics. Here the input water is disposed into a multitude of thin water jets symmetrically positioned about a centrally powered electrode as can be seen in Figure 4a. Application of voltage to the central electrode leads to plasma formation between the interstitial spaces of the water jets as well as the propagation of an ionization wave or surface plasma on the water jet.[15]**Error! Bookmark not defined.** Because the water acts as a barrier to appreciable current conduction – either as an insulator in the case of deionized water or as a resistive layer as in the case of water with finite conductivity, the arrangement is essentially a barrier discharge.[20] The water jets prevent the discharge from transitioning into a spark or arc discharge. The appeal of this arrangement is that it puts the liquid water in direct contact with high surface area to volume water streams. Since PFAS compounds are hydrophobic, this reactor arrangement assures plasma contact over a large surface area (associated with the water jets) and thereby circumvents the volume effect where treatment in the bulk would otherwise rely on the slow process of diffusion. As can be seen in Figure 4b, contaminated liquid from the reservoir is circulated through the plasma reactor, which functions to separate the liquid into thin spatially dispersed jet streams using a shower head applicator and bring the resulting streams into direct contact with plasma so that the solution is batch processed, though the reactor can be operated in a "once-thru" mode as well. By separating the water into thin streams, the approach is effectively a quasi- in-volume treatment approach. This reactor is referred to as a packed bed water reactor or PBR owing to similarities between the water jets and the dielectric aggregate of a packed bed reactor.



(a) (b)

Figure 4. (a) Schematic depiction of barrier discharge with water dielectrics. (b) Water circulator with discharge inset

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For both reactors, the voltage was measured using a P6015A high-voltage probe and the discharge current was measured with a Pearson 6585 coil current monitor. Waveforms were recorded and analyzed using a Tektronix MDO3024 oscilloscope with a bandwidth of 200 MHz. Typical current and voltage waveforms are provided in Figure 5. Using the time dependence of the voltage, $\boldsymbol{V(t)}$, and the current, $\boldsymbol{I(t)}$, the average power was obtained using equation 1:

$$\boldsymbol{P = \frac{1}{\tau} \times \int_0^{\tau_w} I(t) \times V(t)dt \quad (1)}$$

Where $\boldsymbol{\tau}$ is the reciprocal of the pulse frequency and $\boldsymbol{\tau_w}$ is the pulse width.

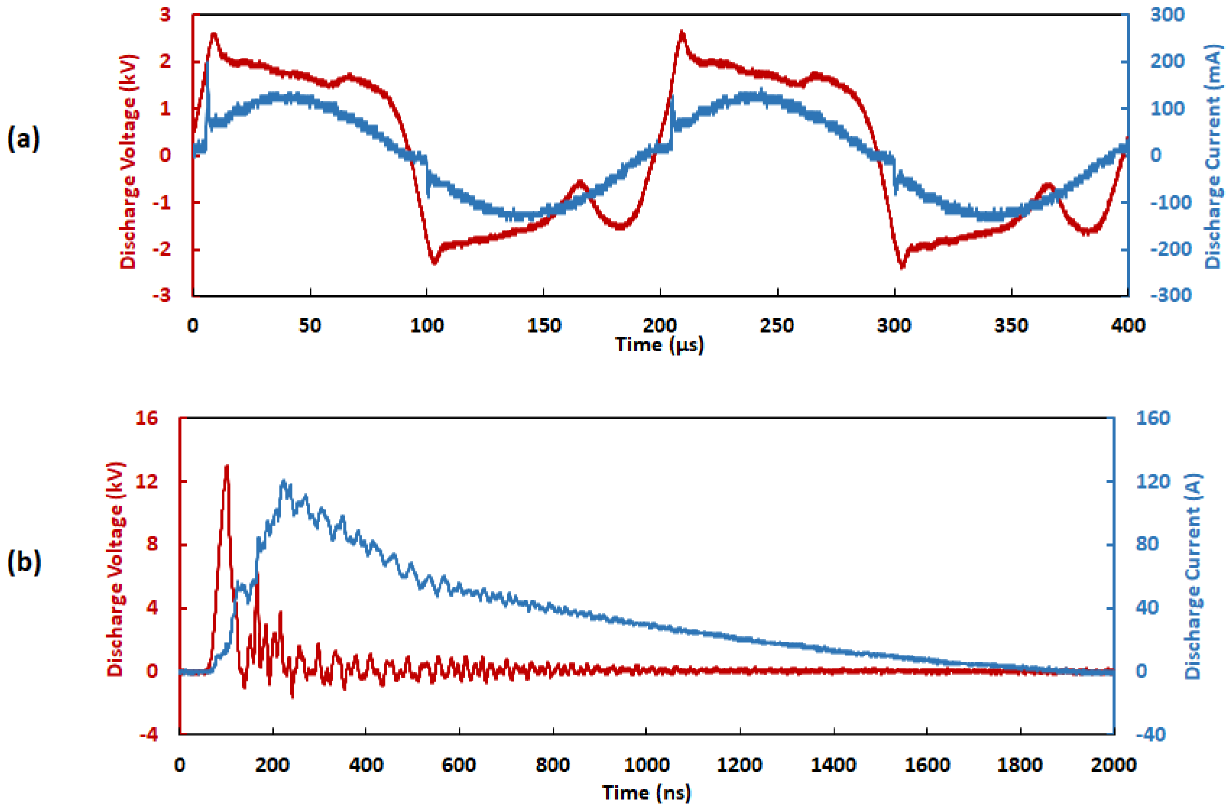

Figure 5. Typical voltage and current waveforms for: (a) the low frequency sinusoidal AC power supply operating at 5 kHz and (b) the repetitively pulsed ns voltage source.

B. Water samples

A goal of this work was to explore the efficacy of the aforementioned plasma sources for decomposing PFAS contaminants. The water samples tested in this work were derived from two legacy sites containing heavily PFAS-contaminated ground water at levels well above the regulatory limit. Site 2 had contamination levels ~100x that of site 1. This water is currently being treated by conventional methods. For this work, untreated samples as extracted from the ground water site used; that is, no pretreatment was carried out before plasma testing. Table 1 illustrates the relative abundance of PFAS compounds from the two sites. Of the many PFAS compounds present, PFOS and PFHxS were the most abundant. The concentrations of the contaminants were measured both at UM and at an independent chemical analysis laboratory. Both labs used the EPA Method 537.1 to determine concentration using Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS).[21] For each experimental run, 500 ml of the sample ground water was treated. Post-test treated solution temperature, pH and conductivity were measured. It should be pointed out that to assess potential leaching of PFAS from the reactor itself, test runs with deionized water were carried out. The level of PFAS in these sample runs were non-detect suggesting no measurable contamination is derived from the apparatus itself.

III. Results and Discussion

The pre-test PFAS analysis of ground water samples from Site 1 and Site 2 are provided in Table 1. The concentrations of 24 different PFAS compounds were quantified in duplicate using an independent test laboratory and an in-house analytical mass spectrometer. This was done to validate measurements made in-house at the University of Michigan. The results were found to be in general agreement between both labs, with PFOS and PFHxS being the most prevalent PFAS compounds found at both sites. Water from Site 1 and Site 2 are heavily contaminated. For reference, the Michigan Department of Environment, Great Lakes, and Energy has set concentration limits for PFHxS and PFOS at 51 ng/L and 16 ng/L, respectively.[5] It should be emphasized that the extracted ground water samples were not modified, but rather collected from actual contaminated sites, thus demonstrating treatment of representative water matrix.

Compound	Site 1 Concentration (ppt)		Site 2 Concentration (ppt)	
	UofM**	Independent**	UofM***	Independent***
PFBA	NM*	54	NM	<100
PFPeA	NM	91	NM	280
PFHxA	40	74	<200	1,500
PFBS	46	12	370	220
4:2FTS	<1	<10	<200	<100
PFHpA	22	18	<200	250
PFPeS	51	18	630	450
PFOA	26	30	560	690
PFHxS	**240**	**180**	**16,000**	**10,000**
6:2FTS	11	46	<200	<100
PFNA	84	52	<200	<100
PFHpS	8	<10	620	470
FOSA	<1	<10	<200	<100
PFDA	<1	<10	<200	<100
PFOS	**270**	**330**	**33,000**	**43,000**
8:2FTS	<1	<10	<200	<100
PFUdA	<1	<10	<200	<100
PFNS	<1	<10	<200	<100
N-MeFOSAA	<1	<10	<200	<100
N-EtFOSAA	<1	<10	430	<100
PFDoA	<1	<10	<200	<100
PFDS	<1	<10	<200	<100
PFTrDA	<1	<10	<200	<100
PFTeDA	<1	<10	<200	<100

*NM = Not measured, UofM did not have Standard Curves for PFBA an PFPeA

**Independent diluted Site 1 samples 2x and UofM did not dilute Site 1 samples, with reporting limits of ±10 ppt and ±1 ppt respectively

***Independent diluted Site 2 samples 20x and UofM diluted Site 2 samples 200x, with reporting limits of ±100 ppt and ±200 ppt respectively

Table 1. PFAS concentrations (ppt) in the raw ground water samples, measured in-house at University of Michigan (UofM) and by an independent test laboratory.

Water samples from each site were processed by the plasma reactors and the concentrations of PFAS were quantified as described in Section II. Results from the Site 1 PFAS degradation experiments are listed in Table 2. Since PFOS and PFHxS were identified to have the highest initial concentrations in the ground water samples, these two compounds were used primarily to assess the contaminant removal. Four experiments were performed for the Site 1 ground water using the single jet DBD-PJ reactor operating for half an hour. The feed gas was varied between air and argon, and two different power supplies were tested with each feed gas. PFOS removal percentage was slightly greater for argon compared to air, with an additional 15% removal using the AC power source and an additional 11% removal using the ns-pulse source. The difference between applying AC power versus ns-pulsed was even less, as the AC source yielded an additional 8% for argon feed gas and 4% for air. The negative percent removal values observed for PFHxS indicate an increase in concentration. This result suggests that the longer chain PFOS is being decomposed into smaller chain PFAS, including PFHxS in agreement with Singh et al.[22] In this regard, additional treatment time is necessary to process these smaller chains.

Reactor	Power Source	Feed Gas	Reaction Time [hr]	PFOS*		PFHxS*	
				[ppt]	[% Removal]**	[ppt]	[% Removal]**
Single Jet	Alternating Current	Air	0.5	200	22%	260	-27%
Single Jet	Alternating Current	Argon	0.5	160	37%	270	-32%
Single Jet	Nanosecond Pulse	Air	0.5	210	18%	310	-51%
Single Jet	Nanosecond Pulse	Argon	0.5	180	29%	330	-61%
*Pretreated concentrations of PFOS and PFHxS were 255 ppt and 205 ppt, respectively							
**Negative values indicate an increase in concentration							

Table 2. PFOS and PFHxS removal data for Site 1 experiments using the single jet DBD-PJ reactor.

The same set of experiments were conducted for the Site 2 ground water, along with two tests with the dual jet reactor, and one test with the packed bed reactor. The results are shown in Table 3, and the same trends can be seen as in Table 2 regarding the effect of feed gas and power source for the single jet experiments. Using argon as the feed gas provides a slight increase in percent removal of PFOS over air, as does using the AC power source compared to the ns-pulse source. The increase in performance with the AC source is attributed to the higher overall gas temperature which can lead to thermal decomposition in contrast to the reduced gas temperature associated with ns-pulse operation. The advantage of argon over air is most likely due to the increased plasma density owing to the lack of loss mechanisms such as attachment and inelastic losses that would otherwise be incurred in air via the excitation of vibro-rotational modes.

Reactor	Power Source	Feed Gas	Reaction Time [hr]	PFOS*		PFHxS*	
				[ppt]	[% Removal]**	[ppt]	[% Removal]**
Single Jet	Alternating Current	Air	0.5	26,000	21%	14,000	15%
Single Jet	Alternating Current	Argon	0.5	22,000	33%	13,000	21%
Single Jet	Nanosecond Pulse	Air	0.5	27,000	18%	15,000	9%
Single Jet	Nanosecond Pulse	Argon	0.5	26,000	21%	15,000	9%
Dual Jet	Nanosecond Pulse	Argon	0.5	18,000	45%	18,000	-9%
Dual Jet	Nanosecond Pulse	Argon	2	5,900	82%	7,200	56%
Packed Bed	Nanosecond Pulse	Air	1.5	1,200	96%	9,200	44%
*Pretreated concentrations of PFOS and PFHxS were 33,000 ppt and 16,500 ppt, respectively							
**Negative values indicate an increase in concentration							

Table 3. PFOS and PFHxS removal data for Site 2 experiments.

The dual jet experiments were both performed with the ns-pulse power source and argon as the feed gas. When comparing the half hour treatment time to the single jet, ns-pulsed argon test, the dual jet doubles the percent removal of PFOS. This is attributed to the approximately doubled plasma contact area (surface area for electron reduction activity) that the dual jet provides. When the reaction time for the dual jet is increased to two hours, the reduction is consistent with exponential decay with a decay constant of 0.85, although more data points are needed to properly evaluate the decay behavior. Lastly, the packed bed reactor demonstrated 96% removal of PFOS for a 1.5-hour treatment time with water circulating at a flow rate of 4.5 L/min, while the dual jet achieved 82% removal over a 2-hour treatment time. In both cases significant decomposition of PFHxS was observed suggesting serial degradation proceeding from the precursor to the daughter byproducts. It should be noted that the average power and treatment time for the packed bed reactor was smaller than the dual jet operating on argon (70 W for 1.5 hours vs. 90 W for 2 hours, respectively), suggesting greater efficiency for the packed bed reactor. This greater efficiency is attributed to the higher plasma liquid contact area which occurs along the entire length of the water stream in contrast to the localized plasma attachments of the jets. In either case, it is clear at least at these power levels that the level of contaminant removal is dependent on treatment time. These plasma reactors should be capable of breaking down most, if not all the remaining PFAS, but the energy requirements to do so must be investigated.

Notably, despite Site 2 containing significantly higher initial concentrations of PFOS, the percent removal achieved is roughly the same for both sites' waters. For example, the single jet with ns-pulsed argon yielded 18% removal for both Site 1 and Site 2 waters. In this case, 45 ng/L were removed from the Site 1 water, whereas 6,000 ng/L was removed from Site 2 water. Since the volume in these experiments was 500 mL, that means about 23 ng PFOS was removed at Site 1 compared to 3,000 ng PFOS at Site 2, while approximately the same energy was spent in the treatment process. Therefore, when considering the mass removal efficiency, these plasma reactors are more efficient at treating high concentration PFAS waters because they can remove more mass of PFAS for a given energy input. This finding could play an important role when implementing these plasma reactors into a practical treatment train for decomposing PFAS contaminated waters.

Of particular interest is the concentration evolution during treatment for PFAS compounds. In addition to the ground water sample tests, a spiked test was also carried out. Here the goal was to assess the time evolution of PFAS decay. To investigate the decay behavior, deionized water samples were spiked with PFOA to achieve a concentration of approximately 5.7 mg/L. The high concentration affords one the opportunity to speculate on the effect of intermediates. PFOA was treated with the packed bed reactor and the residual PFOA concentrations were measured as a function of treatment time. The concentration was reduced by just over 90 percent for a 1-hour treatment time at a power level of approximately 25 W with air as the working gas. Interestingly, the data seem to show two types of rate behavior as can be seen in Figure 6. At early times there is a steep drop off in PFOA concentration (60%) followed by a more gradual decay. Compared to the relatively dilute solutions discussed previously in the ppb range, here the role of interfering intermediates may play a larger role in scavenging reactive species such as solvated electrons and AOPs. Future work will involve a full analysis of intermediates formed and their associated scavenging capacity. For comparison, Figure 7 illustrates the degradation of PFOA via a number of advanced oxidation processes.[23] While advanced oxidation is driven in the packed bed reactor as well, the differences in removal over time suggests that plasma effects such as the solvation of the free electrons lead to the significant increases in the removal rate of PFOA.

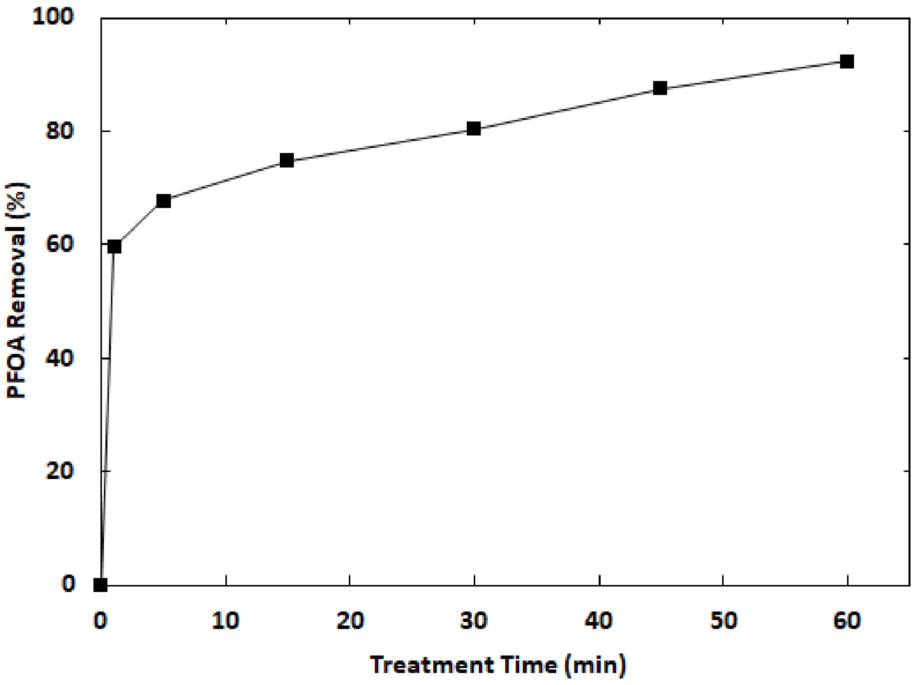

Figure 6. PFOA Removal (%) vs. treatment time using the PBR with ns-pulse voltage source.

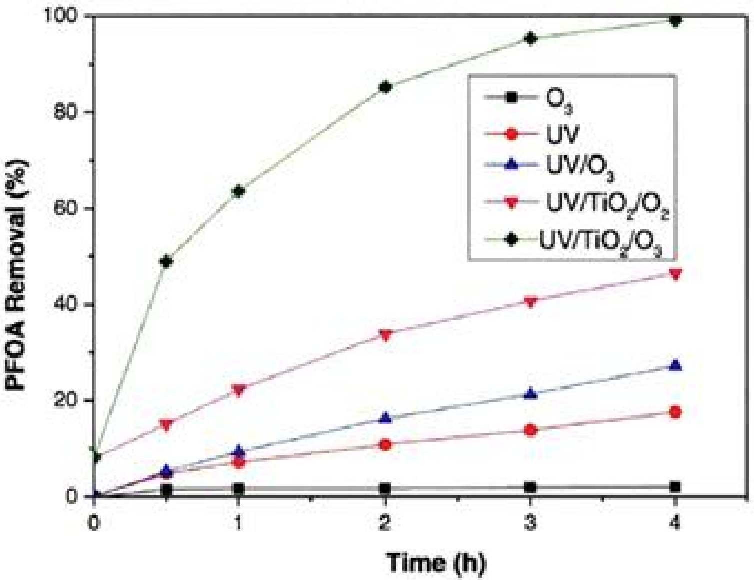

Figure 7. Advanced oxidation of PFOA (Trojanwicz et al.). Reproduced with permission from Chem. Eng. J. 336, 170 (2018). Copyright 2018 Elsevier.

Water treatment systems such as advanced oxidation treatment trains featuring for example, photolysis via UV, UV-Ozone, or UV-hydrogen peroxide utilize predominantly electrical power to drive decomposition. A figure of merit that describes the decomposition efficiency of these systems is the electrical energy per order.[24] The use of this parameter allows for direct comparison between this work and other PFAS studies featuring advanced reduction or advanced oxidation driven by electrical means including plasma methods. The approach is particularly appropriate in assessing the power cost of treating dilute contaminant streams such as the ones explored in this work where the decomposition can be modeled as an effective first order reaction. In short, the parameter is a measure of the power required to reduce the contaminant level one order of magnitude. The electrical energy per order (kWh/m^3) was calculated for the removal of PFOA based on the data in Figure 6 using equation 2:

$$\boldsymbol{E_{EO}} = \frac{\boldsymbol{P \times t \times 1000}}{\boldsymbol{V \times 60 \times log\left(\frac{C_i}{C_f}\right)}} \quad (2)$$

Where P in this case is the power discharged into the plasma (kW) calculated using equation 1, t is the treatment time (min), V is the treated volume of water (L), and C_i and C_f are the initial and final pollutant concentrations, respectively. In this case, the concentrations refer to the amount of PFOA in the water (ppt). Based on the waveform analysis, a treated volume of 0.5 L, and the 92.3% removal of PFOA over the hour-long treatment time, the E_{EO} was estimated to be approximately 45 kWh/m^3. This value is of similar magnitude as those reported in literature elsewhere.[14,25] The values of E_{EO} for the removal of PFOS from the ground water samples treated with the nanosecond pulse power supply ranged from 93 to 196 kWh/m^3. The values of E_{EO} are higher than for the de-ionized water spiked with PFOA due to the presence of multiple co-contaminants and other scavengers of plasma-derived reactive species present in the ground waters extracted from Site 1 and Site 2. Additionally, none of the tests presented here were optimized in terms of E_{EO}, so far. Future work will involve power matching as well as the development of a comparative figure of merit which will include considerations such as plasma density and gas temperature, which are measures of how well power is being transferred to the plasma in the form of charged species production and losses to the gas via heating.

One of the challenges with calculating E_{EO} for plasma-based systems is that the waveforms can be difficult to interpret due to reflected power causing nonphysical voltage peaks and oscillations. This uncertainty in the way the power supply quenches the applied pulse leads to some uncertainty in the discharge power calculation, and thus the E_{EO} estimation. Further studies are needed to account for these nonphysical waveforms structures and to achieve more accurate estimates of the discharge power and E_{EO} value of the plasma treatment process.

IV. Conclusion

Water samples with PFAS contamination were collected from two legacy sites and treated with plasma reactors. The percent removal was evaluated by quantifying the concentrations of PFAS before and after treatment, and the impacts of certain reactor control variables were assessed. There was little difference in PFAS removal percentage between the AC and ns-pulse power supplies, although the ns-pulse power supply deposits less power into the discharge by about a factor of 10 in the single jet experiments. In this sense, the ns-pulse power source may be considered more energy efficient, but it is worth noting that the AC power source can achieve similar percent removal of PFOS for the same treatment time and may be a more cost-effective power source for practical use. Regarding the feed gas, argon achieved slightly greater removal percentages of PFOS compared to air in the case of the plasma jets. Still, the fact that ambient air can be used in these reactors to remove significant amounts of PFAS is an important result, as it eliminates the need to transport and store argon as a consumable in the treatment process.

While the type of power source and feed gas had relatively minor impacts on the percent removal of PFOS, the plasma-liquid contact area was shown to be a significant variable. The dual jet configuration achieved approximately double the removal percentage of a single jet, commensurate with the additional contact area for solvated electron mediated reduction processes. The packed bed reactor further enhanced the contact area and achieved even greater PFOS removal percentage than the dual jet reactor. Lastly, similar removal percentages were achieved for both waters, despite the higher starting PFAS concentrations in the Site 2 water, indicating an increase in mass removal efficiency when treating waters with high initial concentrations of PFAS with these plasma reactors. With this insight, plasma-induced breakdown of PFAS may be more effectively implemented into a practical treatment train in which the PFAS is first concentrated.

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Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

[1] E.M. Sunderland, X.C. Hu, C. Dassuncao, A.K. Tokranov, C.C. Wagner, and J.G. Allen, J. Expo. Sci. Environ. Epidemiol. **29**, 131 (2019).
[2] D. O'hagan, Chem. Soc. Rev. **37**, 308 (2008).
[3] J.L. Domingo and M. Nadal, Environ. Res. **177**, 108648 (2019).
[4] U.S.E.P.A. (EPA), *EPA PFAS Action Plan: Program Update, February 2020* (2020).
[5] Michigan PFAS Action Response Team, https://www.michigan.gov/pfasresponse/0,9038,7-365-95571_99970---,00.html, (2019).
[6] M.J. Bentel, Y. Yu, L. Xu, Z. Li, B.M. Wong, Y. Men, and J. Liu, Environ. Sci. Technol. **53**, 3718 (2019).
[7] I. Ross, J. McDonough, J. Miles, P. Storch, P. Thelakkat Kochunarayanan, E. Kalve, J. Hurst, S. S. Dasgupta, and J. Burdick, Remediation **28**, 101 (2018).
[8] H.N. Phong Vo, H.H. Ngo, W. Guo, T.M. Hong Nguyen, J. Li, H. Liang, L. Deng, Z. Chen, and T.A. Hang Nguyen, J. Water Process Eng. **36**, 101393 (2020).
[9] H. Park, C.D. Vecitis, J. Cheng, W. Choi, B.T. Mader, and M.R. Hoffmann, J. Phys. Chem. A **113**, 690 (2009).
[10] J. Cui, P. Gao, and Y. Deng, Environ. Sci. Technol. **54**, 3752 (2020).
[11] J.E. Foster, Phys. Plasmas **24**, (2017).
[12] M. Saleem, O. Biondo, G. Sretenović, G. Tomei, M. Magarotto, D. Pavarin, E. Marotta, and C. Paradisi, Chem. Eng. J. **382**, 123031 (2020).
[13] R.K. Singh, N. Multari, C. Nau-Hix, S. Woodard, M. Nickelsen, S.M. Thagard, and T.M. Holsen, Cite This Environ. Sci. Technol **54**, (2020).
[14] R.K. Singh, N. Multari, C. Nau-Hix, R.H. Anderson, S.D. Richardson, T.M. Holsen, and S. Mededovic Thagard, Environ. Sci. Technol. (2019).
[15] J.E. Foster, S. Mujovic, J. Groele, and I.M. Blankson, J. Phys. D. Appl. Phys. **51**, 293001 (2018).
[16] J.E. Foster, B. Weatherford, E. Gillman, and B. Yee, Plasma Sources Sci. Technol. **19**, 25001 (2010).
[17] J. Foster, B. Sommers, B. Weatherford, B. Yee, and M. Gupta, Plasma Sources Sci. Technol. **20**, (2011).
[18] J. Lai and J.E. Foster, J. Phys. D. Appl. Phys. **53**, 025206 (2020).
[19] N. Merino, Y. Qu, R.A. Deeb, E.L. Hawley, M.R. Hoffmann, and S. Mahendra, Environ. Eng. Sci. **33**, 615 (2016).
[20] R. Brandenburg, Plasma Sources Sci. Technol. **26**, (2017).

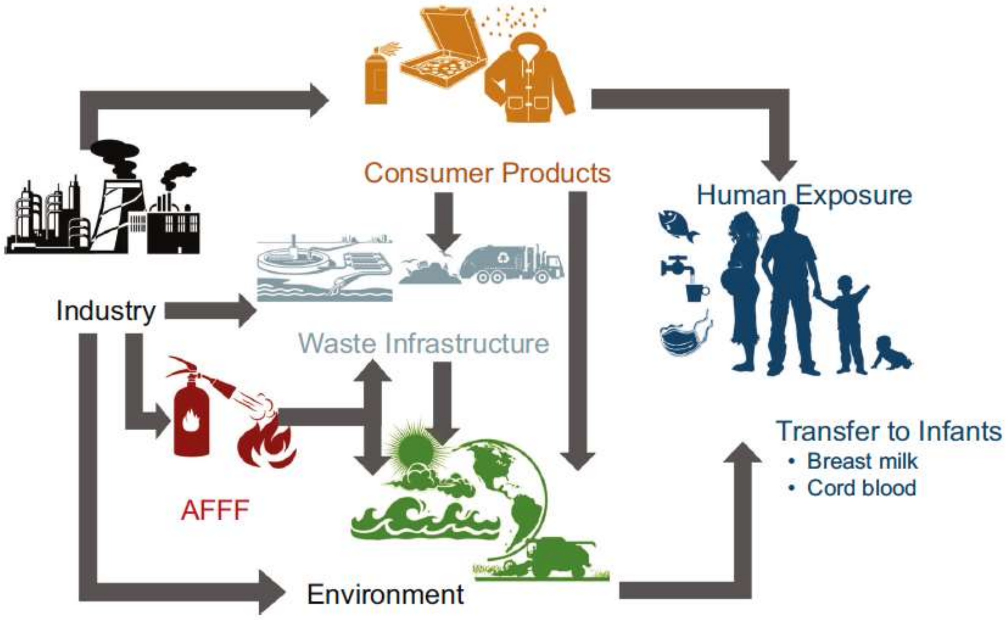
[21] S. J. and T. D., *Method 537.1: Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)* (Washington DC, 2018).

[22] R.K. Singh, S. Fernando, S.F. Baygi, N. Multari, S.M. Thagard, and T.M. Holsen, Environ. Sci. Technol. **53**, 2731 (2019).

[23] M. Trojanowicz, A. Bojanowska-Czajka, I. Bartosiewicz, and K. Kulisa, Chem. Eng. J. **336**, 170 (2018).

[24] J.R. Bolton, K.G. Bircher, W. Tumas, and C.A. Tolman, Pure Appl. Chem. **73**, 627 (2001).

[25] C. Nau-Hix, N. Multari, R.K. Singh, S. Richardson, P. Kulkarni, R.H. Anderson, T.M. Holsen, and S. Mededovic Thagard, ACS ES&T Water (2021).


Consumer Products
Human Exposure
Industry
Waste Infrastructure
AFFF
Transfer to Infants
• Breast milk
• Cord blood
Environment

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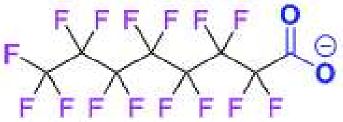
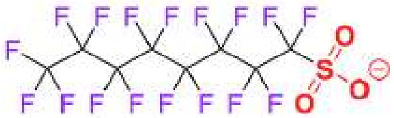


PFOA (n=7)



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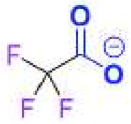

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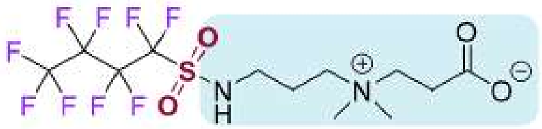
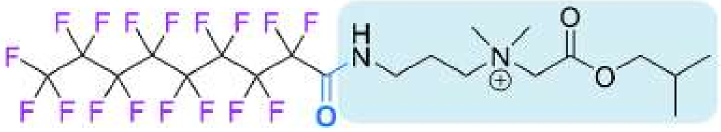
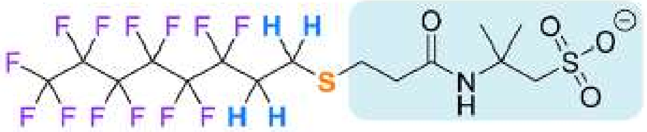


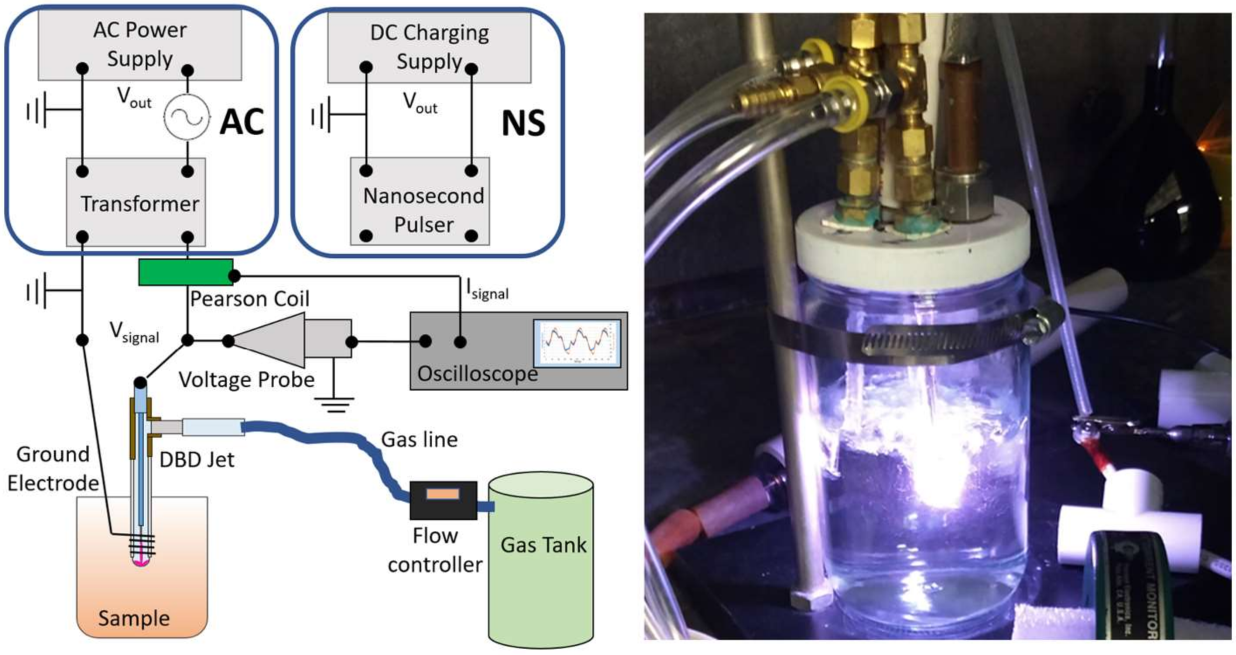
Sulfonate-derived surfactant (n=4)



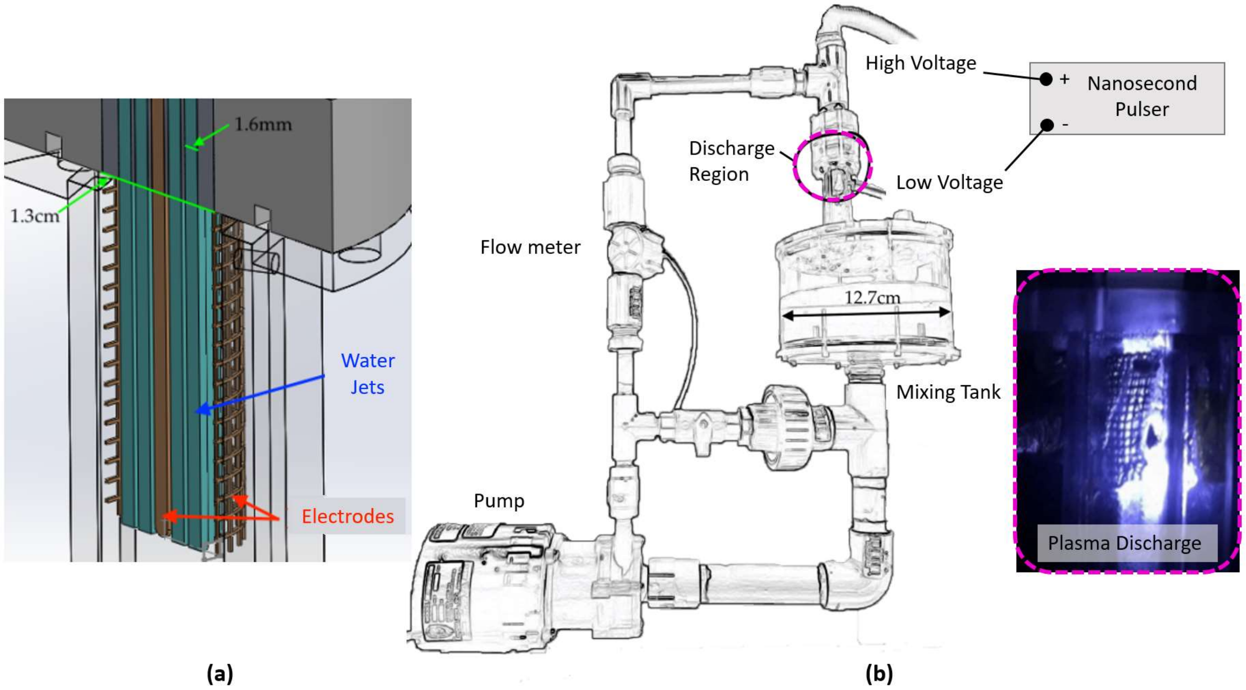
Carboxylate-derived surfactant (n=8)

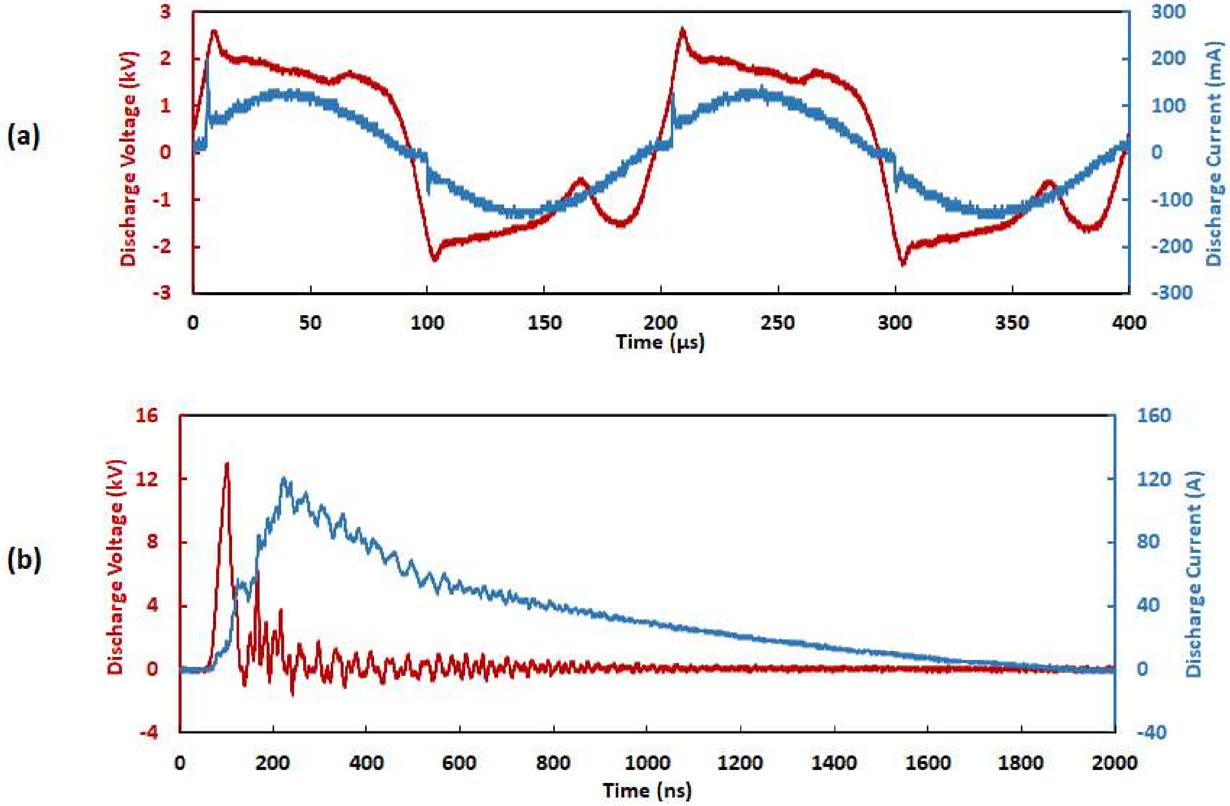


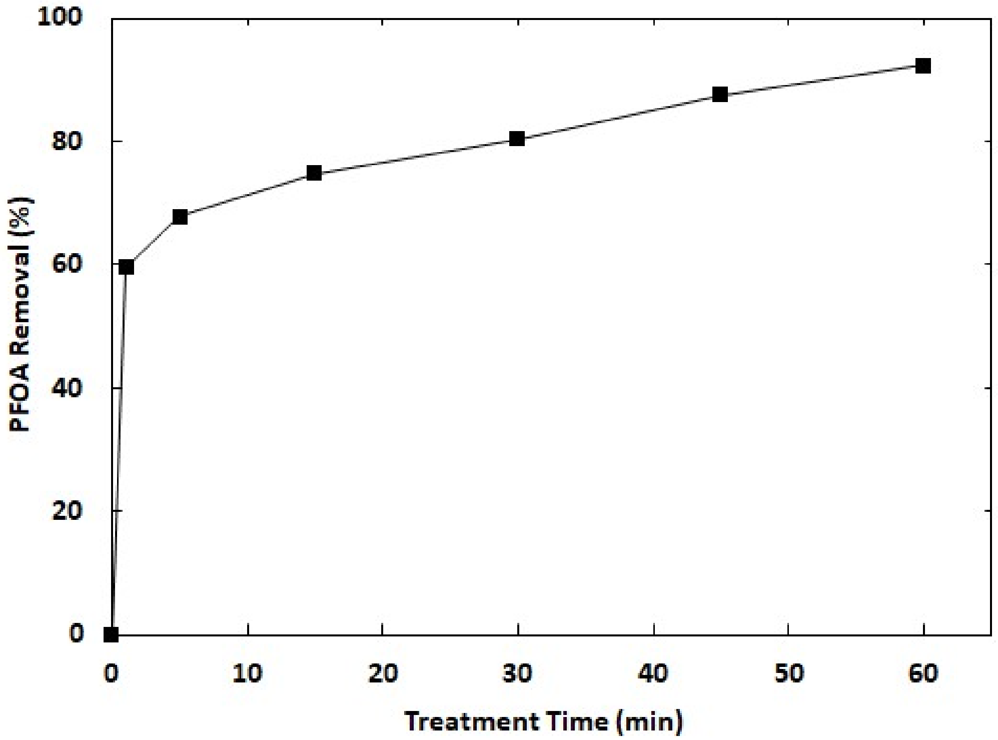
Telomeric surfactant (n=6)

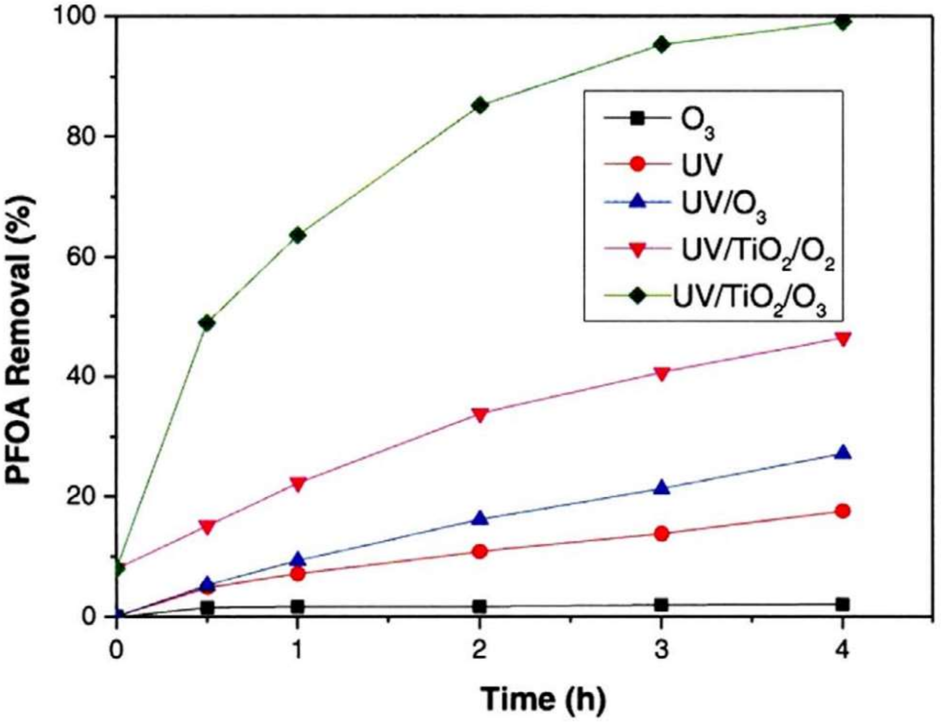

AC Power Supply
V_{out}
AC
Transformer
DC Charging Supply
V_{out}
NS
Nanosecond Pulser
Pearson Coil
I_{signal}
V_{signal}
Voltage Probe
Oscilloscope
Ground Electrode
DBD Jet
Gas line
Flow controller
Gas Tank
Sample

(a) (b)


1.6mm
1.3cm
Water Jets
Electrodes
(a)
High Voltage
+
Nanosecond Pulser
-
Discharge Region
Low Voltage
Flow meter
12.7cm
Mixing Tank
Pump
Plasma Discharge
(b)


(a)
Discharge Voltage (kV)
3
2
1
0
-1
-2
-3
Discharge Current (mA)
300
200
100
0
-100
-200
-300
0
50
100
150
200
250
300
350
400
Time (µs)
(b)
Discharge Voltage (kV)
16
12
8
4
0
-4
Discharge Current (A)
160
120
80
40
0
-40
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Time (ns)


100
80
60
40
20
0
PFOA Removal (%)
0
10
20
30
40
50
60
Treatment Time (min)


PFOA Removal (%)
0
20
40
60
80
100
Time (h)
0
1
2
3
4
O$_3$
UV
UV/O$_3$
UV/TiO$_2$/O$_2$
UV/TiO$_2$/O$_3$