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Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202302090

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Cold Plasma for Green Advanced Reduction/Oxidation Processes (AROPs) of Organic Pollutants in Water**

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Dedicated to Professor Maurizio Prato on the occasion of his 70th birthday

Cold plasma is gaining increasing attention as a novel tool to activate energy demanding chemical processes, including advanced reduction/oxidation processes (AROPs) of organic pollutants in water. The very complex milieu generated by discharges at the water/plasma interface comprises photons, strong oxidants and strong reductants which can be exploited for achieving the degradation of most any kind of pollutants. Despite the complexity of these systems, the powerful arsenal of mechanistic tools and chemical probes of physical organic chemists can be usefully applied to understand and develop plasma chemistry. Specifically, the added value of air plasma generated by *in situ* discharge with respect to ozonation (*ex situ* discharge) is demonstrated using phenol and various phenol derivatives and mechanistic evidence for the prevailing role of hydroxyl radicals in the initial attack is presented. On the reduction front, the impressive performance of cold plasma in inducing the degradation of recalcitrant perfluoroalkyl substances, which do not react with OH radicals but are attacked by electrons, is reported and discussed. The widely different reactivities of perfluorooctanoic acid (PFOA) and of perfluorobutanoic acid (PFBA) underline the crucial role played in these processes by the interface between plasma and solution and the surfactant properties of the treated pollutants.

Introduction

Plasma is an ionized gas and is often referred to as the fourth state of matter, the "fire" of Empedocle's classification of our world into four "roots", fire, air, water, earth. Plasma makes up for ca. 98% of the visible mass of the universe with temperatures of several million degrees.[1] This paper is about cold plasma, specifically about its application for the treatment of water contaminated by organic pollutants. Unlike stellar plasmas, cold plasmas are weakly ionized gases and non-equilibrium systems due to the presence of high energy electrons (typically with energies of a few tens eV corresponding to several tens of thousands degrees) in a gas at room temperature. Cold plasmas occur in nature (lightning, aurora borealis) and are readily produced artificially by the application of an electric discharge to a gas at atmospheric pressure and ambient temperature.[2] They are already widely used in the semiconductor and lightning industries and are being actively pursued in research to develop applications in many fields including medicine, space propulsion, energy production and environmental remediation, notably water decontamination treatments.[3]

The increasing demand for clean water and the diffusion of refractory pollutants, including pharmaceuticals, herbicides and pesticides, dyes, poly- and perfluoroalkyl substances (PFAS) and others, are raising great concern worldwide.[4] This is in turn stimulating the search for new purification methods of wide applicability, high efficiency, competitive costs and, ideally, no impact on the environment. The last two issues are in fact tightly intertwined, more stringent health and environmental concerns leading to stricter regulations which in turn enforce and justify higher costs. Among the new advanced reduction/oxidation processes (AROPs) being currently investigated and developed, those based on cold plasma are particularly enticing for a number of reasons including high efficiency and efficacy in the degradation of any kind of organic pollutants, no need for heat, pressure or vacuum, no need for added chemicals or catalysts, and short and facile switch on/off operations.[5] Thus, only energy is required and the possibility of utilizing green sources, specifically solar energy, to power the discharge is being currently pursued. Under this perspective, cold plasma qualifies as a novel promising green approach to water treatment.[6] The history of cold plasma based water treatment technology dates back to the invention of the first ozonizer by Siemens in 1857[7] and to the first ozone based

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[**] Maurizio Prato, to whom this paper is dedicated, and senior author C.P. were labmates as young researchers at the Centro Studio Meccanismi Reazioni Organiche of the Italian National Council of Research. The common background in physical organic chemistry and mechanistic studies built during that time sustained and leaved a trademark in the research of both, despite the very disparate ways they travelled.

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wastewater treatment plants in the early 1900s.[8,9] Ozone is indeed considered an "environmentally friendly oxidant"[10] and is recommended for the treatment of wastewaters because of its dual role as disinfectant and as oxidant.[8] Ozonizers come nowadays in all sizes for all kinds of applications, including very large setups for water potabilization plants. All apply discharges to dissociate molecular oxygen at room temperature and pressure and produce atomic oxygen which combines with O_2 to form ozone. With respect to traditional ozonation, in which ozone is produced remotely (discharge *ex situ*) and then brought in contact with the water to be treated, the new approach of applying the discharge *in situ*, i.e. in the gas directly in contact with the water to be treated, offers the promise of faster and more efficient degradation of most any organic pollutant due to the direct engagement of short-lived species which are way more reactive than ozone itself, including notably OH radicals but also free and hydrated electrons.[11] Cold plasmas are indeed complex redox milieux comprising electrons, photons, as well as both oxidizing and reducing species, and are thus capable of attacking virtually any organic pollutant. Specifically, as shown in this paper, *in situ* discharges succeed in degrading PFAS, compounds which do not react with either ozone or OH radicals, but are instead attacked by electrons. Based on this concept cold plasma is being exploited as a unique tool to promote advanced reduction/oxidation processes (AROPs) in aqueous media and develop novel water treatment technologies.[5]

Major goals of this paper are to alert the chemical community about the extraordinary potential of cold plasmas and, specifically, to show how the powerful arsenal of mechanistic tools and chemical probes of physical organic chemists can be most usefully applied to the understanding and development of plasma activated chemical processes. Original contributions from our laboratories will be used to illustrate this point.

Specifically, following a brief description of the plasma sources employed in research reported here and of their main features, in the first part of the paper we focus on the comparison of *in situ* discharge treatment and of ozonation, which we refer to as *ex situ* discharge. To this end, we carried out and compared the results of pairs of parallel experiments in which we treated organic compounds within the same reaction vessel with the same amount of ozone, obtained from two different sources. Specifically, ozone was produced in one case directly within the reaction vessel by a barrier discharge applied in the air above the water (*in situ* discharge), in the other case by a remote ozonizer and then transferred into the reaction vessel (*ex situ* discharge).The results clearly show the advantages of applying the discharge *in situ* with respect to ozonation (*ex situ* discharge). Furthermore, by applying Hammett correlation analysis and kinetic analysis we provide evidence supporting the conclusion that OH radicals are the major reactive species in these processes. In the second part of the paper we show that treatment with *in situ* discharge succeeds in degrading also very oxidation-resistant emerging organic pollutants, notably perfluoroalkyl carboxylic acids belonging to the PFAS family. In this case an experimental set-up suitably designed to maximize the plasma/liquid interface[12] was used to engage plasma electrons to attack PFAS and initiate their degradation.

Results and Discussion

Cold plasmas are produced by the application of a high potential difference across two electrodes in a gas at ambient pressure, the high voltage (HV) electrode and the grounded electrode. The ensuing discharges produce high energy electrons which interact with the gas itself leading to excitation, ionization and dissociation events to form excited species, ions and secondary electrons, atoms and radicals. Cold plasmas are not at thermal equilibrium (they are also called non-thermal plasmas) since the average energy of electrons is much higher than that of the massive species which remain virtually at room temperature.[2,13] Depending on the electrode's shapes, sizes and relative position as well as on the high power supply used, the number of possible plasma sources one can envision is virtually infinite.[14] Other most important variables are the gas in which the discharge occurs and the reactor design. Each plasma source produces a characteristic ensemble of reactive species which can be made available to activate chemical process within aqueous media in contact with the plasma.

A schematic representation of the electrode configurations used in the work described here to generate cold plasma in contact with water is shown in Figure 1. The main differences are: i) the presence of a dielectric layer (the bottom wall of the pyrex

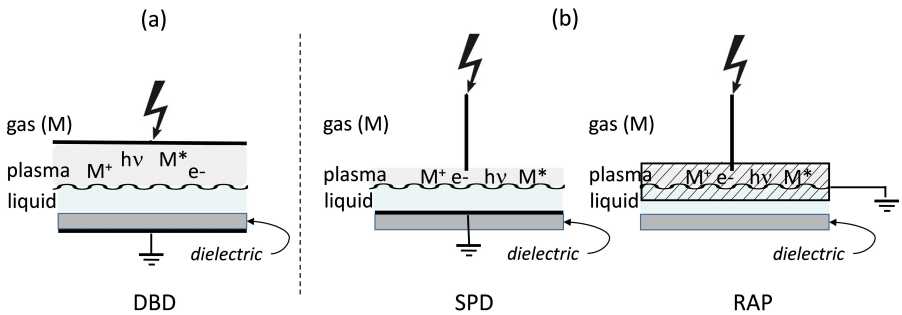

Figure 1. Schematic representation of electrode configurations and discharge types employed in this work. a) dielectric barrier discharge (DBD) and b) spark discharge used in the plasma–liquid contact reactors SPD (lefthand side) and RAP (righthand side). See the Experimental section for details. M was air or argon. When M is air, the above sketches representing the plasma reactive species are to be integrated, as detailed in the text, to take into account the dissociation of nitrogen and oxygen molecules and the consequent reactions of atomic nitrogen and oxygen to form O_3, NOx and RNS (reactive nitrogen species).

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glass or quartz reactor vessel) separating the two electrodes in the configuration shown in Figure 1(a), which is characteristic of dielectric barrier discharges (DBD) and ii) the high voltage electrode design and orientation with respect to the liquid surface (wires parallel to the surface in a) and needle orthogonal to the surface in b)). The arrangement schematized in Figure 1.a was adopted in developing DBD (dielectric barrier discharge) reactors,[15] whereas that in Figure 1(b) for the SPD (self-pulsed discharge) and the RAP (radial plasma)[12] reactors, hereafter called the plasma–liquid contact reactor, used to treat PFAS.

Cold plasma reactive species: hydroxyl radical and ozone

To promote advanced oxidation processes in water, air can be most conveniently used as gas to feed the plasma. When the discharge is applied in ambient (humid) air, many short-lived reactive species are formed including O atoms, OH and OOH radicals, $O_2^{-\bullet}$, $O_3^{-\bullet}$, and H_3O^+ ions as well as some nitrogen reactive species.[2,11] Secondary important reactive species in these systems include hydrogen peroxide, formed by OH radical recombination reaction, and, most importantly, ozone, formed by reaction of atomic oxygen with molecular oxygen.[2,11,16]

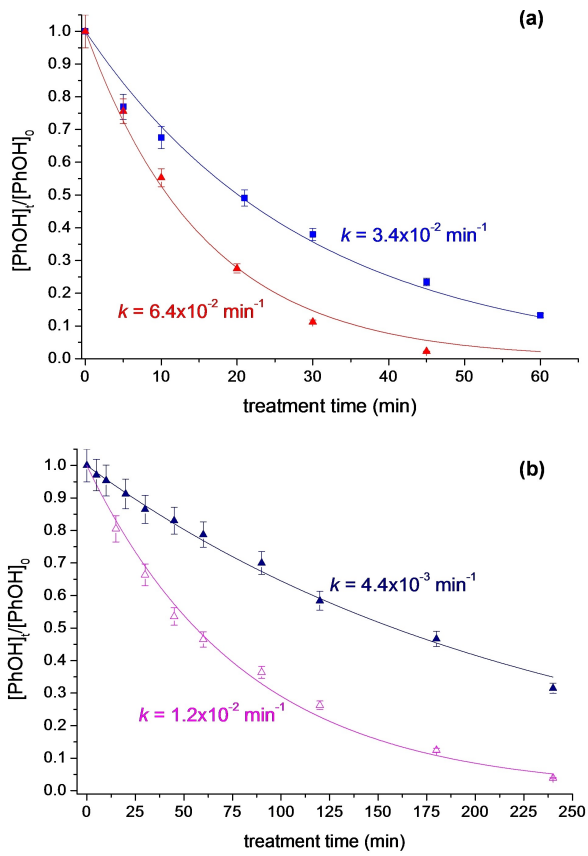

Figure 2. a) Decay of phenol (0.5 mM in aqueous phosphate buffer at pH 7) observed in experiments with discharge *ex situ* (ozonation, ■) and *in situ* (air plasma, ▲); b) decay of phenol (0.5 mM in milli-Q water) as single solute (Δ) and in the presence of a 100-fold molar excess t-butanol (▲).The reported rate constants were obtained by interpolation of the experimental data according to a first order exponential law.[15,18]

The results of experiments with phenol in the DBD reactor characterized by the electrode configuration shown in Figure 1(a) show, indeed, that the rate of *in situ* discharge is significantly higher than that of *ex situ* discharge (Figure 2a). Phenol was chosen for these experiments because it is a pollutant commonly used as a standard to test and compare AOPs.[17] Discharge and flow conditions were set so as to achieve in both experiments the same stable ozone concentration in the air flowing above the solution (1000 ppm, as determined by FT-IR. See Experimental Section).

The better efficiency of *in situ* discharge processing with respect to ozonation is attributed to the action of short-lived reactive species present in air plasma or formed by its interaction with the liquid. Among these, most importantly the OH radical, which is formed by water dissociation due to interaction with electrons [Equation (1)] or by reaction of water with atomic oxygen [Equation (3)]. The latter, in turn, is formed via electron-induced dissociation of molecular oxygen [Equation (2)].[2] An ionic pathway is also available, initiated by charge exchange or direct electron ionization as outlined in Equations (4a) and (4b), where M is N_2 and Ar, depending on the gas used.

$$H_2O + e^- \rightarrow H^\bullet + {}^\bullet OH + e^- \quad (1)$$

$$O_2 + e^- \rightarrow 2O + e^- \quad (2)$$

$$O(^1D) + H_2O \rightarrow 2{}^\bullet OH \quad (3)$$

$$M^+(\text{or } e^-) + H_2O \rightarrow M\ (\text{or } 2e^-) + H_2O^{+\bullet} \quad (4a)$$

$$H_2O^+ + n\ H_2O \rightarrow H_3O^+(H_2O)_{n-1} + {}^\bullet OH \quad (4b)$$

Support for the prevalent role of hydroxyl radicals in the initial rate limiting attack is provided by the results of experiments in which phenol was treated by *in situ* discharge in the presence of a large excess of *t*-butanol, a known quencher of OH radicals.[10] Under these conditions the rate constant for phenol oxidation was drastically reduced (Figure 2b).

Since *t*-butanol reacts with OH radicals but is virtually unreactive with ozone[19] we used it also as a probe to investigate on the reactive species available in experiments of ozonation (*ex situ* discharge) and of air plasma treatment (*in situ* discharge). Results obtained at different pH values are summarized in Figure 3.

Ozonation (*ex situ* discharge) at pH 7 induced no appreciable reaction of *t*-butanol. This result is consistent with both, the known lack of reactivity of ozone towards *t*-butanol and the slow decomposition of ozone to produce OH radicals in neutral solutions.[20,21] In contrast, treatment with air plasma (*in situ* discharge) at pH 7 did afford the oxidation of *t*-butanol (Figure 3), supporting the concept that air plasma provides sources of OH radicals in addition to that available in ozonation.

In basic solution (pH 11), *t*-butanol was oxidized at a significant rate in ozonation experiments, due to its reaction with OH radicals formed by base induced ozone decomposition:[20,21] the observed rate constant (4.6×10^{-3} min^{-1})

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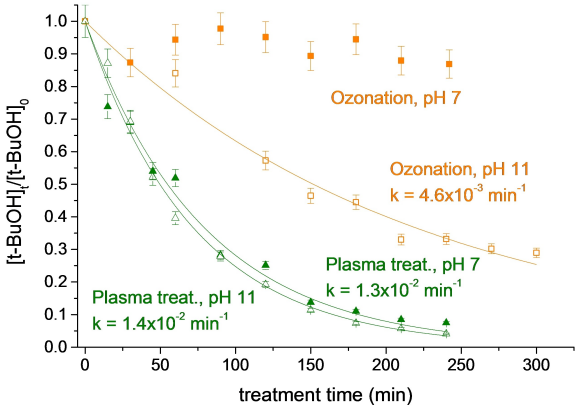

Figure 3. *t*-Butanol (0.5 mM initial concentration) decay in experiments of ozonation (*ex situ* discharge) and with plasma treatment (*in situ* discharge) in aqueous buffered solutions at pH 7 and at pH 11). Legend: ■ Ozonation, pH 7.0, □ Ozonation, pH 11, ▲ Plasma treatment, pH 7.0, Δ Plasma treatment, pH 11.0.

is, however, considerably lower than that (1.4×10^{-2} min^{-1}) of the process induced by *in situ* discharge at the same pH, again suggesting that more OH radicals are present when the solution is directly exposed to the plasma than to a flow of ozone produced *ex situ*. In contrast to what found for ozonation, the rate constants for *in situ* discharge induced oxidation of *t*-butanol at pH 7 and at pH 11 are nearly the same, 1.3×10^{-2} and 1.4×10^{-2} min^{-1}, respectively. These results suggest that OH radicals are primarily involved in *in situ* discharge experiments.

Structure/reactivity analysis is being extensively applied in the study of AOPs of organic pollutants.[22] In our work, support for the involvement of OH radicals in the initial step of air plasma induced oxidation of phenol was gained in a structure/reactivity correlation study. We performed this study with a series of monosubstituted derivatives of phenol. A reasonably linear Hammett correlation was obtained using resonance sigma substituent constants, σ+ and σ−,[23] yielding a slope (ρ) of −0.48 (Figure 4). The negative sign of ρ is consistent with rate determining electrophilic attack on an activated ring position; its very low absolute value is characteristic for reaction of OH, a highly reactive and poorly selective

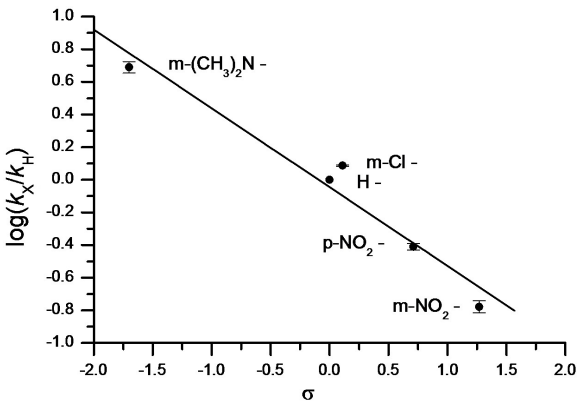

Figure 4. Hammett correlation for air plasma induced oxidation of phenols XC_6H_4OH (0.5 mM in milliQ water): X = m-$(CH_3)_2N$; H; m-Cl; p-NO_2; m-NO_2).

electrophile.[24] In the cited paper, dealing with OH attack on substituted benzenes, a ρ value of −0.41 is reported which is very similar to our finding of −0.48. In contrast, attack by ozone is much more sensitive to substituent effects, typical ρ values being around −3.[25–27]

Another important feature often observed in plasma activated reactions is the dependence of the reaction rate on the pollutant initial concentration, which usually entails that lower pollutants concentrations lead to faster processes. It can be easily appreciated how this phenomenon is most beneficial for the development and application of cold plasma based technologies for treatment of waters contaminated with micro-pollutants or other refractory pollutants, like PFAS, which are usually present in very low concentrations. Aside from practical implications, the dependence of the reaction rate on the pollutant concentration can also provide important mechanistic insight. The advanced oxidation reaction of phenol in our DBD reactor provides an interesting example[28] and serves as a case study here to test the value of a simple kinetic model in pinpointing the reactive species involved in the initial attack of the oxidation process. The model is an elaboration of the inhibition-by-products scheme published by Slater and Douglas-Hamilton many years ago and consisting of steps (5)–(7)[29]

$$G \rightarrow X \qquad S \quad (5)$$

$$X + OC \rightarrow I + \text{products} \qquad k_{OC} \quad (6)$$

$$X + I \rightarrow Z + \text{other products} \qquad k_I \quad (7)$$

$$X + Q \rightarrow I + \text{products} \qquad k_Q \quad (8)$$

where G is the gas-liquid system which, upon activation by the discharge, produces the reactive species X at a constant rate *S*; I is the first organic intermediate formed with rate constant k_{OC} by reaction of X with the original organic contaminant OC; intermediate I can in turn react with X, thus entering in competition with OC, to form Z, with rate constant k_I. Finally, we included in the model Equation (8), not considered by Slater and Douglas Hamilton,[29] to account for quenching of the reactive species X by one or more quenchers, cumulatively named Q. They are present in the system independently of OC and react with X with rate constant k_Q.

The dependence in time of the concentrations of OC and of reactive species X are given by Equations (9) and (10), respectively.

$$d[OC]/dt = -k_{OC}[X][OC] \quad (9)$$

$$d[X]/dt = S - k_{OC}[X][OC] - k_I[X][I] - k_Q[X][Q] \quad (10)$$

Since the concentration of OC is experimentally found to decay in time according to a first order law [Equation (11)],

$$d[OC]/dt = -k[OC] \quad (11)$$

there follows that,

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$$k = k_{OC}[X] = \text{constant} \quad (12)$$

Assuming the steady state (ss) approximation for reactive species X, its constant concentration $[X]_{ss}$ is derived to be

$$[X]_{ss} = S/(k_{OC}[OC] + k_I[I] + k_{OC}[Q]) \quad (13)$$

Substituting in Equation (9) one obtains Equation (14)

$$\begin{aligned} &d[OC]/dt = -k[OC] = \\ &-k_{OC}[X]_{ss}[OC] = \\ &-k_{OC}\ [S/(k_{OC}[OC] + k_I[I] + k_Q[Q])]\ [OC] \end{aligned} \quad (14)$$

from which the observed first order decay constant of OC is derived as in Equation (15)

$$k = k_{OC}S/(k_{OC}[OC] + k_I[I] + k_Q[Q]) \quad (15)$$

the reciprocal of which is given in Equation (16)

$$1/k = (k_{OC}[OC] + k_I[I] + k_Q[Q])/k_{OC}\ S \quad (16)$$

If we assume that OC and I react with X at the same rate ($k_{OC} = k_I$) and that $[OC] + [I] = C_0$ where C_0 is the organic contaminant OC initial concentration, an approximation which is certainly valid at short reaction times, then Equation (16) simplifies into Equation (17)

$$1/k = (1/S)C_0 + k_Q[Q]/k_{OC}\ S \quad (17)$$

which predicts linear dependence of $1/k$ on C_0 and provides the rate of formation of reactive species X, S, as the reciprocal of the line slope.

Figure 5 shows that the plot of $1/k$ vs. C_0 data, where k is the observed first order rate constant of phenol degradation in our plasma reactor and C_0 is its initial concentration, is reasonably linear, with an R^2 of 0.9941. From the line slope, a rate of production of 1×10^{-5} M min^{-1} is derived for the kinetically relevant reactive species X.

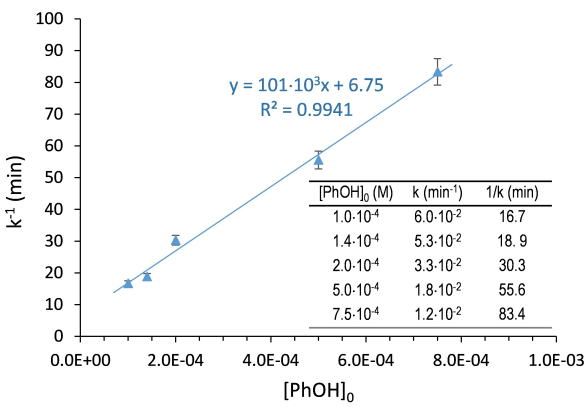

Figure 5. $1/k$ vs. C_0 data for plasma treatment of phenol in water. The data are taken from Ref. [28] and rielaborated.

Equation (17) also allows one to evaluate the lifetime of reactive species X, τ_X, defined as the reciprocal of the rate of X consumption by quenchers Q [Equation (18)]

$$\tau_X = 1/k_Q[Q] \quad (18)$$

Thus, considering the ratio slope/intercept of Equation (17) and substituting $1/k_Q[Q]$ by τ_X, one obtains Equation (19)

$$\text{Slope/intercept} = k_{OC} \cdot \tau_X = 1.5 \times 10^4\ M^{-1} \quad (19)$$

Under the hypothesis that X is the OH radical, one can substitute in Equation (19) the value of its rate constant for reaction with phenol, which is reported in the literature to be 1×10^{10} M^{-1} s^{-1},[26] and obtain a lifetime of OH radicals in solution of 1.5×10^{-6} s. This value is in full agreement with the conclusions of a recent study reporting a lifetime of microseconds for the OH radical plasma treated aqueous media.[30]

The experiments with t-BuOH also provide a means to estimate the OH radical stationary concentration and the relative contributions to its formation due to ozone degradation and to *in situ* reaction of short lived reactive species produced by the discharge [Equations (1)–(4)]. Considering that t-BuOH does not react with ozone and assuming that its degradation is exclusively due to attack by OH radicals, the observed first order exponential decay (Figure 3) for this degradation [Equation (20)]

$$\text{t-BuOH} + \text{OH} \rightarrow \text{products} \qquad v = k_{obs}\ [\text{t-BuOH}] \quad (20)$$

is consistent with the steady state approximation for the reactive species, the OH radical [Equation (21)].

$$k_{obs} = k_{OH}\ [OH]_{ss} \quad (21)$$

Thus, the OH radical steady state concentration ($[OH]_{ss}$) in each experiment is given by the k_{obs}/k_{OH} ratio, where k_{obs} is the experimentally determined degradation constant and k_{OH}, the second order rate constant for the reaction of t-butanol with the OH radical, which is reported to be equal to 6×10^8 M^{-1} s^{-1}.[31]

In ozonation experiments, the OH radical is only formed by the decomposition of ozone, whereas in plasma experiments it forms by ozone degradation as well as by other routes activated by the discharge [Equations (1)–(4)]. Therefore,

$$\text{in ozonation}: \ [OH]_{ss} = [OH]_{ozone} \ \text{in plasma}: \ [OH]_{ss} = [OH]_{ozone} + [OH]_{plasma}$$

Since in all experiments, both ozonation and *in situ* discharge, the same ozone concentration was present in the air flowing above the liquid surface, it is reasonable to assume that the amount of OH radicals produced by the dissociation of ozone in solution was also the same. It is therefore assumed that the term $[OH]_{ozone}$ had the same value for each pair of parallel experiments, ozonation and *in situ* discharge treatment,

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run under the same pH conditions. Indeed, the relative contribution of $[OH]_{ozone}$ and $[OH]_{plasma}$ in plasma treatment depends on the solution pH. For example, since the rate of t-BuOH decay in ozonation at pH 7 is negligible (Figure 3) it is reasonably concluded that $[OH]_{ozone}$ is negligible and that reaction of t-butanol in plasma treatment at pH 7 is brought about by OH radicals formed exclusively by discharge pathways. So, one can derive that in experiments with plasma at pH 7, $[OH]_{ss} = [OH]_{plasma} = 3.7\times10^{-13}$ M. In contrast, at pH 11.3, ozone degradation does contribute significantly to the overall OH radical amount available in plasma treatment: under the assumption stated above, the contribution to $[OH]_{ss}$ due to $[OH]_{ozone}$ can be estimated as 1.4×10^{-13} M (Figure 3) which provides an estimate of 3.0×10^{-13} M for the $[OH]_{plasma}$ term (determined as the difference between $[OH]_{ss}$ and $[OH]_{ozone}$). If we now compare this value (3.0×10^{-13} M) with that determined for plasma treatment at pH 7 (3.7×10^{-13} M), the match is remarkable once the acid dissociation equilibrium of the OH radical is considered, Equation (22), converting it into the O^- species which is generally less reactive with organic compounds than the OH radical.[31] Thus, while at pH 7 the fraction of ionized OH radicals is negligible, at pH 11.3 it reaches the value of 0.8. There follows that in order to have a value of $3.0\cdot10^{-13}$ M for $[OH]_{plasma}$ the input of OH radicals by the plasma has to be equal to 3.7×10^{-13} M ($3.0\times10^{-13}/0.8$), that is exactly the value determined for the discharge *in situ* at pH 7.

$$^{\bullet}OH + H_2O \leftrightarrow O^{-\bullet} + H_3O^+ \qquad pK_a = 11.9 \quad (22)$$

A final note is due about the products formed in these processes. Obviously, products are an issue as important as kinetics not only in the elucidation of mechanistic aspects but also in the prospect of practical applications. The extent of mineralization achieved and the types and amounts of remaining organic residues are key criteria to assess the performance of plasma activated water treatments.

Although, as mentioned in the introduction, the exhaustive oxidation of all organic pollutants to CO_2 is not necessarily the goal of any water decontamination treatment, it is important to note that, thanks to the high efficiency of plasma induced oxidation, complete mineralization of organic pollutants can be achieved with no organic residue remaining in the treated water. This was proven in experiments with phenol[32] but also, most interestingly, with a few persistent organic pollutants which are presently a major environmental concern and a challenge for water purification treatments, including pharmaceuticals, herbicides and pesticides.[33] Interestingly, treatment of perfluoroalkyl compounds using the same reactors and experimental conditions used in these studies achieved very limited degradation.[34] We learned the reasons for this lack of reactivity and studied ways to promote plasma activated PFAS degradation in water, as described in the next paragraph.

Cold plasma reactive species: gaseous ions and free electrons

Although the large majority of organic compounds is readily attacked by hydroxyl radicals, there are notable exceptions including the important family of PFAS (per- and polyfluoroalkyl substances).[35] PFAS are manmade chemicals which are most useful in many applications for their exceptional chemical inertia. For the very same feature they are highly persistent pollutants once released in the environment and are presently found ubiquitously causing health hazards and posing a formidable challenge in the treatment of waste and potable waters.[36] PFAS do not react under typical AOP conditions so, it was not a surprise that PFOA (perfluoroalkyl octanoic acid), a most common PFAS often used as a prototypal model in fundamental and applied research, reacted very slowly when treated in the cold plasma reactor described above under conditions that were highly effective in oxidizing phenols and many other organic pollutants.[34] We note, incidentally, that failure of PFOA to react in this system is consistent with the conclusion that OH radicals are the major reactive species involved in these processes. Cold plasmas, however, offer more to be exploited than just ROS for activating pollutants degradation, notably gaseous ions and free electrons.[14,37] These are very short-lived species which can be taken advantage of in reactors designed in such a way as to maximize the contact between plasma and polluted water (Figure 1b). A few such designs have been developed and are described in the literature,[38,39] including the SPD reactor[34] and the RAP reactor[12] by our group. The remarkable results achieved with both SPD and RAP are attributed to the very extended plasma/liquid interface characterizing these discharges and to the matching surfactant properties of PFOA which accumulates at the liquid surface exposing the perfluorinated alkyl chain directly into the plasma.[12,34,37,38] The prevailing role of plasma electrons in attacking PFOA, thus initiating its degradation in the SPD reactor, is consistent with the results of a recent optical emission spectroscopy study which highlighted a correlation between the efficiency of PFOA degradation in solution and the density of electrons within the plasma at the liquid interface.[40] Hydroxyl radicals, however, do appear to be involved in subsequent steps of the complex process[40] which achieves the fast and complete degradation of PFOA with only trace amounts of organic carbon byproducts remaining in the treated solution. These byproducts are mainly perfluoroalkyl carboxylic acids homologues of reduced chain length, formed in an orderly sequence and in turn decomposed as sketched in Scheme 1.

A detailed mechanistic scheme was recently proposed to account for these intermediate products as well as for those of minor side reactions resulting in hydro-defluorination and hydroxy-defluorination of PFOA and of its lower homologues.[40] Interestingly, while complete degradation of perfluoroalkyl carboxylic acids from C8 to C5 could be achieved in both the SPD and RAP reactors, the shorter chain homologues including notably perfluorobutanoic acid (PFBA) appeared to be extremely refractory also to prolonged treatment. This behavior is evident in Figure 6(a) which reports the time evolution of

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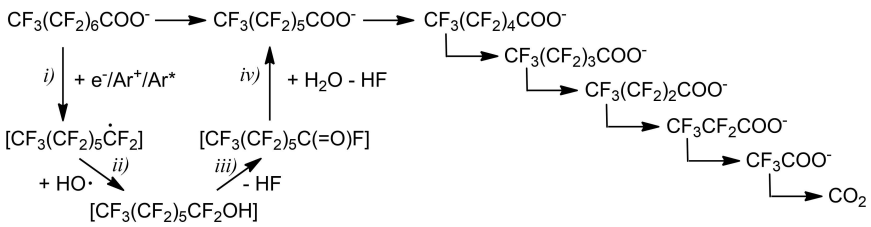

Scheme 1. Mechanism of PFOA plasma induced degradation.

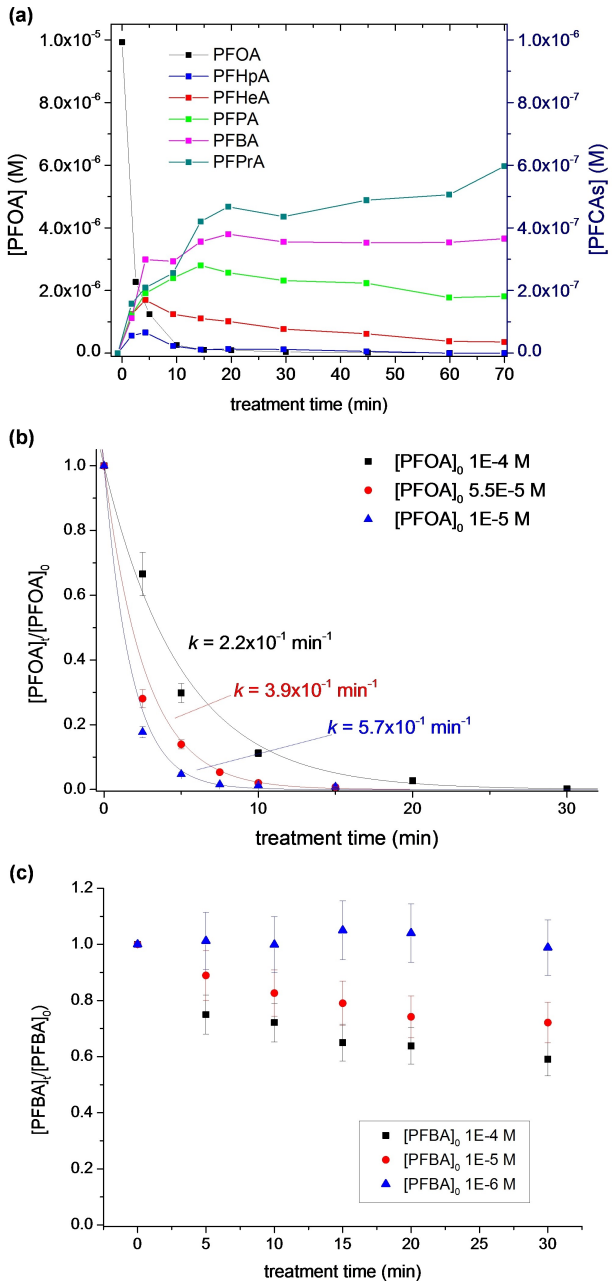

Figure 6. Concentration vs time profiles during treatment in the RAP reactor of: a) a 1.0×10^{-5} M PFOA solution in tap water. The right hand side scale of the ordinate axis is to be used for the intermediate degradation products, which are shorter chain perfluorocarboxylic acids (PFCAs): perfluoroheptanoic acid (PFHpA), perfluorohexanoic acid (PFHxA), perfluoropentanoic acid (PFPeA), perfluorobutanoic acid (PFBA) and perfluoropropanoic acid (PFPrA); b) decay profiles of PFOA at different initial concentrations in tap water; c) decay profiles of PFBA at different initial concentrations in tap water.

reactant and intermediate products in an experiment in which a 1×10^{-5} M PFOA solution was treated in the RAP reactor. The RAP reactor was used here because in the case of PFOA degradation proved to be more efficient than the SPD reactor.[12,34] It is seen (Figure 6a) that PFOA degradation is complete within a little over 10 min and that intermediate acids C7, C6 and C5 form and in turn decay at somewhat longer treatment times. This does not seem to be the case for C4 and C3. Notably, C4, perfluorobutanoic acid (PFBA), reaches a plateau concentration which, albeit very low appears to be persistent in time. If one is interested in obtaining PFAS free water this outcome is unsatisfactory. Moreover, the reason for this unusual behavior was puzzling and prompted an investigation of the behavior of PFBA under the experimental conditions used to treat PFOA. Indeed, the degradation of PFBA turned out to be very slow under conditions which are instead quite effective in bringing about the degradation of PFOA. In addition, while with PFOA the "normal" concentration effect described above, is observed, i.e. the rate increased as C_0 was decreased (Figure 6b), the opposite trend was found with PFBA (Figure 6c). Thus, at the lowest tested concentration (1×10^{-6} M) there appeared to be no reaction at all over 30 min treatment, whereas *ca.* 40% conversion was achieved under the same conditions in experiments run with an initial PFBA concentration of 1×10^{-4} M. In trying to rationalize these results the following facts should be considered: i) PFOA has surface active properties whereas PFBA has not, and ii) both PFOA and PFBA do not react with OH radicals but do react with electrons (free, i.e., plasma electrons, and hydrated electrons). Specifically, the rate constants for reaction of PFOA and of PFBA with hydrated electrons in aqueous solution are about the same.[41]

The poor reactivity of PFBA suggests that the reactive species capable of initiating its degradation, notably hydrated electrons,[41] are not available in sufficient amount within the bulk solution and that reaction only occurs at the liquid/plasma interface where plasma electrons and positive ions are available. This explains why PFOA, which is a surfactant and concentrates at the liquid/plasma interface, undergoes very fast reaction whereas PFBA, with no surfactant properties, does not. These conclusions are supported by the results of experiments run with PFBA at different initial concentrations (Figure 6c). It is seen that the rate of decay of PFBA increases with increasing initial concentration, in contrast with the opposite trend usually observed in plasma activated reactions of organic compounds. The peculiar behavior of PFBA is fully consistent with the hypothesis that reaction occurs at the liquid/plasma interface

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and with its physicochemical properties. Indeed, PFBA is not a surfactant and is therefore homogeneously distributed within the liquid phase. Thus, higher nominal concentrations are expected to be matched by correspondingly higher concentrations at the solution surface. Higher surface PFBA concentrations will in turn lead to a more efficient use of plasma electrons and ions. This contrasts and thus limits quenching losses of these reactive species. An important parameter for reaction efficiency under these conditions is the surface/volume ratio, which was quite high in the experiments reported in this paper and the effect of which is the focus of ongoing research. It is also important to note that the conclusions drawn for PFBA might lead to the wrong deduction that the RAP reactor is only effective in treating surfactants.[12] This is not true since organic compounds with no surface-active properties but with the ability to react with OH radicals do react in the RAP reactor and in these reactions the "normal" concentration effect is observed (k increases with $1/C_0$). This is the case, for example, of phenol, the most common standard used to test the performance of AOPs. The results of experiments run in the RAP reactor at two different initial concentrations (Figure 7) show that indeed phenol is degraded and that the rate of reaction depends inversely on its initial concentration as observed previously for its reaction in the DBD reactor described above. It is therefore reasonable to conclude that, likewise, OH radicals are the major species responsible for the initial attack leading to phenol degradation also in the RAP reactor. The presence of OH radicals in solution, however, is not useful to initiate the degradation of dissolved perfluoro compounds, like PFBA, which lack proper reactive sites, notably C–H and C–C π bonds.

The challenge is therefore to find conditions to make plasma treatment effective in the degradation also of short chain PFAAs and other PFAS with no surfactant properties. One approach which is being suggested in the literature[42] involves addition of surfactants to bring PFAS to the liquid surface where reaction can occur. More appealing are approaches based on the complementary alternative which does not require use of additives, that is, instead of concentrating the PFAS to the plasma/liquid interface, extending the plasma/liquid interface so as to reach larger fractions of PFAS which are uniformly dissolved in the bulk liquid. This can be done in principle by injecting plasma into the liquid in the form of microbubbles or by exposing to the plasma a thin film of liquid.[43]

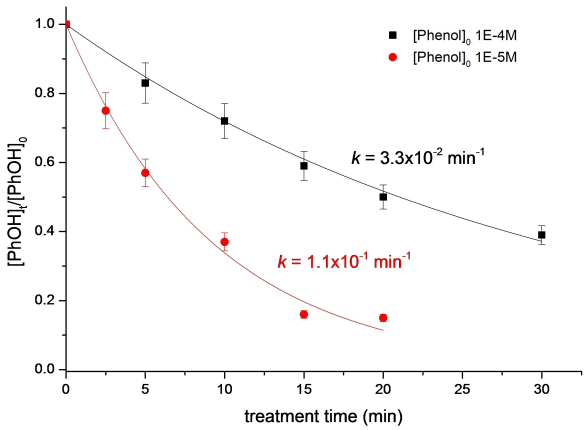

Figure 7. Plasma induced phenol degradation in the RAP reactor, at two different initial concentrations in tap water.

Conclusions

There is evidently a great potential in plasma activation to be exploited to bring about energy demanding chemical processes, like water decontamination treatments. This approach is especially attractive for the degradation of challenging water pollutants such as recalcitrant organic compounds including, notably, many PFAS for which there are few/no viable alternatives. The complexity of these heterogeneous systems composed of plasma/gas/liquid poses challenges in understanding the underlying reactions and in learning therefrom how to harness their exceptional reactivity to achieve the desired target. The results reported and discussed in this paper are a contribution towards reaching this goal. The case studies considered here (phenolic compounds, t-butanol, one long-chain and one short-chain perfluoroalkyl carboxylic acid) were selected purposedly to highlight the importance of identifying the reactive species which prevail in initiating the pollutant degradation. Specifically, the DBD reactor, a good source of OH radicals, fails in degrading PFAS whereas the RAP reactor, a good source of electrons, achieves the efficient degradation of perfluorooctanoic acid, a surfactant which accumulates at the liquid/plasma interface, but not of perfluorobutanoic acid which is uniformly dissolved in solution. These findings identify the need for a suitable discharge/reactor design capable of injecting electrons into the solution to attack PFAS with no surfactant properties. In conclusion, mechanistic insight and characterization of the discharge are necessary elements which suitably intertwined can guide the development and optimization of the experimental apparatus in terms of costs and efficiency. The perspective of developing this approach into applicable technologies is promising in view of the rather simple and robust apparatus required, the fast switch on/off operation with no need for vacuum or pressure, nor of heating. The only cost is electrical energy, as no additives or catalysts are required. Therefore, insofar as green energy sources are used, cold plasma-based technology is a prototypal green technology. To this end, one important focus of applied research in this field is nowadays the possibility to power these processes with green energy.

Experimental Section

Materials. Phenol, m-dimethylaminophenol, m-chlorophenol, m-nitrophenol, p-nitrophenol, and t-butanol were reagent grade products of Sigma-Aldrich and Fluka with purity $\geq$99%. Perfluorooctanoic acid (PFOA, purity $\geq$96%), perfluoroheptanoic acid (PFHpA, purity 99%), perfluorohexanoic acid (PFHxA, purity $\geq$98%), perfluoropentanoic acid (PFPA, purity $\geq$98%), and perfluorobutanoic acid (PFBA, purity $\geq$98%) were purchased from Sigma-Aldrich. Methanol (HPLC PLUS grade 99.9%) was purchased from Sigma-

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Aldrich, ammonium acetate (reagent grade purity ≥98%) was obtained from Fluka. Air used in the experiments was a synthetic mixture of 80% nitrogen and 20% oxygen purchased from Air Liquide with specified impurities of H_2O (<3 ppmv) and C_nH_m (< 0.5 ppmv). Argon was purchased from Air Liquide with specified impurities of H_2O (<0.5 ppm), H_2 (<0.1 ppm), O_2 (<0.5 ppm), CO_2 (<0.5 ppm), CO (<0.1 ppm) and THC (<0.1 ppm).

Plasma reactors and experimental procedures.

The DBD 2-wires reactor. The reactor and the experimental and analytical protocols for performing and monitoring *in situ* discharge experiments were described in detail previously.[15] Briefly, the reactor is a glass box vessel (95×75×60 mm) capped by a Teflon cover which supports the high voltage electrode (two parallel stainless-steel wires, C in Figure 8) to which an AC voltage of 18 kV at 50 Hz was applied. A mixture of 80% N_2 and 20% O_2 (synthetic air) was flown through the reactor at 30 mL min^{-1}. The gas at the outlet was analyzed by FT-IR on a Nicolet 5700 spectrometer using a 10 cm long flow cell. The concentration of ozone was determined by integration of the IR absorption bands at 1000–1070 cm^{-1}. Calibration of the instrument response was performed by iodometric titration of ozone as described previously.[15] The same experimental set-up was used for *ex situ* discharge experiments except that power supply A was switched off and remote ozonizer B was instead turned on (Figure 8a). In both types of experiments the solution (70 mL) was maintained under stirring during the treatment. Aliquots of the solution were withdrawn at different treatment times through a septum-sealed port in the cover using a syringe and analyzed by HPLC-UV and LC-ESI-MS/MS to determine the residual fraction of the organic pollutant and its oxidation intermediates and products. Details are given below.

The RAP reactor. The RAdial Plasma (RAP) discharge reactor and its characterization were described previously.[12] Briefly, it consists of a cylindrical Pyrex vessel (128 mm high with a diameter of 43 mm) fitted with an airtight Plexiglas cover and with a fritted glass diffuser fixed 17.5 mm above the cylinder base, through which argon is bubbled into the liquid at a flowrate of 100 mL/min (Figure 8b). The high voltage electrode, a pointed tungsten needle (2.5 mm in diameter), is positioned so that its tip reaches 6 mm above the liquid surface. The counter electrode is a stainless-steel ring (39 mm in diameter) held partially submerged into the liquid. Details about the power supply, electrical measurements and discharge characterization are found in the previous publication.[12] The input power was 4 W. In this reactor numerous random radial discharges develop in contact with the liquid surface, covering the entire area encircled by the grounded electrode and hence providing a dense and most effective plasma-liquid interface.

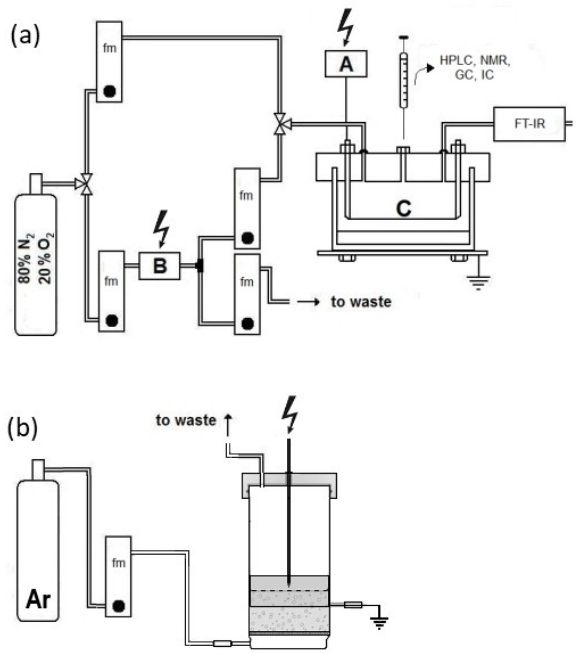

Figure 8. Schematics of a) DBD reactor and experimental set-up used for *in situ* and *ex situ* (ozonation) discharge experiments and of b) RAP reactor and gas line.

Batch experiments were performed by treating 30 mL aliquots of the prepared solutions for the desired time to build plots of residual concentration vs treatment time. The treated aliquots were then analysed by LC-ESI/MS to determine the residual pollutant concentration and those of its degradation products as described in the following section.

Chromatographic analyses

HPLC/UV. Solutions of phenol before and after the plasma treatment were analyzed by HPLC/UV using a Thermo Separation Products instrument with a P2000 Spectra System pump and a diode array detector UV6000LP or an Agilent 1260 Infinity series II instrument with a variable wavelength detector. The column was an Agilent Technologies Zorbax Sb–Aq 4.6×150 mm 3.5 μm with eluents A: water with 0.1% HCOOH and B: acetonitrile with 0.1% HCOOH. Gradient for B was: 10% for 2 min, to 30% in 5 min, to 100% in 14 min and 100% for 2 min. The flow rate was set at 1 mL/min and the injection volume was 20 μL. Elution was followed at 270 nm.

GC/FID. Solutions of *tert*-butanol (t-BuOH) before and after the plasma treatment were analyzed by a Hewlett Packard 6890 GC with FID detector, set at 300 °C. The column was an EC-1000 Alltech (30 m, 0.25 μm, i.d. 0.25 mm), the carrier gas was He flowed at 2 mL/min, the injected volume was 1 μL with a split ratio 1:5 and the injector temperature 220 °C. The oven temperature was 100 °C for 2 min, was then increased at 15 °C/min until 200 °C and left at 200 °C for 5 min.

LC/MS. PFOA and PFBA solutions before and after the plasma treatment were analysed by an HPLC Agilent 1200 series chromatograph coupled with a Thermo Scientific LTQ XL mass spectrometer equipped with an electrospray source and a linear ion trap analyser. The chromatographic separation was performed using an InfinityLab Poroshell 120 EC–C18 2.1×100 mm 2.7 μm column (Agilent Technologies) with the following eluents: ammonium acetate 5 mM in Milli-Q water (A) and methanol (B). During the elution, eluent B increased from 30% to 100% in 13 minutes and was then isocratic at 100% for 8 minutes. The flow rate was set at 0.3 mL/min and the injection volume was 10 μL. Samples ionization was performed in negative mode (ESI–), with a spray of 2.5 kV and a source temperature of 300 °C. Optimized values for auxiliary gas flows were the following: Sheath gas = 35 a.u., Auxiliary gas = 10 a.u., Sweep gas = 0 a.u. The quantification of PFOA ($[M–H]^-$, m/z 413), PFHpA ($[M–H]^-$, m/z 363), PFHxA ($[M–H]^-$, m/z 313), PFPA ($[M–H]^-$, m/z 263), and PFPrA ($[M–H]^-$, m/z 163) was carried out in Full Scan mode, while PFBA was quantified through Selected Reaction Monitoring mode (transition from $[M–H]^-$, m/z 213, to $[M–H–CO_2]^-$, m/z 169). In all cases perfluorononanoic acid (PFNA) was used as the internal standard and calibration curves were built considering the ratio of the signals of the analyte and PFNA.

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Acknowledgements

We thank Dr. Volodymyr Shapoval and dr. Matteo Beria for performing some of the experiments and Prof. Lino Conte, University of Padova for lending us the ozonizer used in this work. Financial support by the University of Padova is acknowledged (P-DiSC#06BIRD2019-UNIPD). LC-ESI/MS analyses were performed with a Thermo Scientific LTQ XL mass spectrometer funded by the "Dipartimenti di Eccellenza" Grant "NExuS", awarded to the Department of Chemical Sciences of University of Padova by the Italian Ministry for Education, University and Research (MIUR). The stimulating environment provided by COST Action 19110 is also gratefully acknowledged.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

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

Keywords: OH radical · ozone · non-thermal plasma · PFAS · water treatment

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Manuscript received: June 30, 2023
Accepted manuscript online: August 24, 2023

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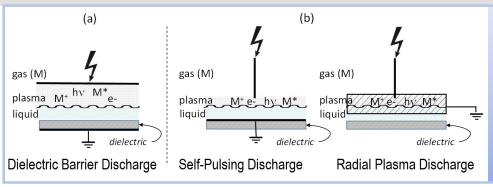

Cold plasma in contact with water activates efficient oxidation/reduction processes involving ROS, electrons, ions and excited species.

Plasma activation: These extremely reactive milieux attack any organic compound, including the most refractory environmental pollutants, leading to their mineralization. Depending on the specific target, suitable plasma sources can be developed for best performance. Cold plasmas offer the promise of novel technologies for PFAS degradation in water under ambient conditions using only (green) energy.

G. Tomei, Dr. M. Saleem, Dr. E. Ceriani, A. Pinton, Prof. E. Marotta, Prof. C. Paradisi**

1 – 11

Cold Plasma for Green Advanced Reduction/Oxidation Processes (AROPs) of Organic Pollutants in Water

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