



Review article

# State of the art and perspectives about non-thermal plasma applications for the removal of PFAS in water

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## ABSTRACT

The urgent need to remove emerging contaminants from wastewater before their discharge in the environment imposes - not only from an environmental point of view, but also soon from a cogent legislative one - the development and adoption of innovative tertiary treatments.

The technologies present on the market to the present day still do not reach the ideal features desirable for such processes especially for the removal of highly recalcitrant compounds such as the Perfluorinated Alkyl Substances (PFAS) which are poorly abated using “traditional” Advanced Oxidation Processes (AOPs).

The non-thermal plasma (NTP) treatment is a promising technology based on the production (in the water or immediately above the liquid) of a NTP capable of producing reactive species both in the liquid and gaseous phase. These species can react with stable and recalcitrant compounds (e.g. PFAS) up to their mineralization.

In this review, the NTP technology and its applications in wastewater treatment are reviewed, starting from the physics of the plasma, the different processes and reactors proposed in the literature, and the nature of the reactive species generated during the plasma process. Attention is dedicated to the applications of NTP for the abatement of Contaminants of Emerging Concern (CECs), with a focus on PFAS removal. Furthermore, the effects of the natural components of the waters, such as Natural Organic Matter (NOM), pH, and conductivity on the efficiency of NTP-based treatment are discussed.

Lastly, based on an overall vision of the published literature on this topic and of the technologies available on the market to the present day, some conclusions regarding the future of this technology have been drawn.

## 1. Introduction

World increasing population and the consequently increasing water demand have made clear that water reuse has become a primary necessity. Due to the rapid deterioration of the quality of water resources, often as a consequence of the ongoing climate change and of the continuous expansion of densely populated areas, the transition toward a circular economy of water represents an extremely challenging task. It has been estimated that only 52% of the global production of wastewater is submitted to water treatment processes while the remaining 48% is released into the environment untreated [1]. Furthermore, a great number of water contaminants of anthropogenic origin is not

completely removed in the traditional wastewater treatment plant and consequently they are released in natural water bodies [2,3]. Such compounds have been recently referred to as Contaminants of Emerging Concern or CECs and, despite belonging to very diverse classes of chemicals such as drugs, personal care products, agrochemicals, or compounds of industrial interest, they all share the characteristics of posing a significant risk to human health or to the environment and of being highly refractory to conventional wastewater treatment processes [4]. To cope with the problem of CECs and limit their concentration in surface waters, the EU has redacted in 2015, in support of European environmental legislation, the first watch list for emerging water contaminants. The list, that is regularly updated, includes a maximum of ten

**Abbreviations:** AOPs, Advanced Oxidation Processes; CD, Corona Discharge; CECs, Contaminants of Emerging Concern; DBD, Dielectric Barrier Discharge; NTP, Non-Thermal Plasma; PFAS, Perfluoroalkyl substances; PFBA, Perfluorobutanoic Acid; PFHpA, Perfluoroheptanoic Acid; PFHpS, Perfluoroheptanesulfonic acid; PFHxA, Perfluorohexanoic Acid; PFOA, Perfluorooctanoic Acid; PFOS, Perfluorooctanesulfonic Acid; PFPeA, Perfluoropentanoic Acid; ROS, Reactive Oxygen Species; RNS, Reactive Nitrogen Species.

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compounds (or classes of compounds) that, according to their toxicity and occurrence in the environment need to be prioritized with the aim to limit their release in the environment [5].

From a technological standpoint, Advanced Oxidation Processes (AOPs), relying on the production of highly oxidative species (e.g. hydroxyl and sulfate radicals), represent an excellent solution to the problem of CECs being able to degrade most of the compounds that are not abated with conventional treatments [4,6]. However, operational costs and technological requirements of AOPs have, up to date, strongly limited their large-scale application. In fact, while the use of ozone alone is largely applied for the treatment of civil wastewater, the use of AOPs such as the Fenton process is only limited to the treatment of heavily contaminated industrial wastewaters as in the case of tanneries (e.g. Santa Croce sull'Arno Plant in Italy) [7]. Furthermore, OH radicals are able to react with almost all the organic compounds, even if some classes of CECs have been proven to be scarcely abated with AOPs; this is the case of polyfluoroalkyl and perfluoroalkyl substances (PFAS).

PFAS are organic compounds having multiple fluorine atoms attached to an alkyl chain (typically from 4 to 16 atoms of carbon) terminated by a hydrophilic group such as a carboxylic, phosphonic, or sulphonic group. Due to their oil and water repellence and to their exceptional chemical and thermal stability, PFAS have encountered countless industrial applications and are commonly used in the production of food packaging, fire-fighting foams, textiles for waterproof clothing, and non-stick coatings [8]. Because of their stability however, PFAS are also extremely difficult to degrade (mainly because of the strength of the C–F bond) to the point that most AOPs are not able to remove them efficiently from treated water [9–11]. The inefficiency of current treatment technologies and unregulated discharge of contaminated wastewaters led, in some cases, to episodes of severe PFAS contamination of groundwater and drinking water such as for example the case of Veneto region (North-East of Italy) where the population has been exposed since the late 1960s via contaminated drinking water [12, 13]. The Stockholm convention has added PFAS to the list of Persistent Organic Pollutants (POPs) and highlighted the urge of banning (this is the case of the perfluorooctanoic acid, PFOA) as well as restricting (perfluorooctane sulfonic acid, PFOS) specific PFAS and the list is in continuous expansion [14].

The inadequacy of conventional AOPs to efficiently remove PFAS from water is pushing researchers to develop new technologies being able to efficiently remove this class of compounds. An ideal AOPs should satisfy several criteria: it should be highly efficient in the removal of all classes of water contaminants, have low operational and maintenance costs, and have limited environmental impact. Non-thermal plasma represents a very promising technology. A bibliometric analysis using the terms “non-thermal plasma”, “water”, and “treatment”, highlighted that the number of publications increased exponentially since the beginning of the 2000s reaching, in the last couple of years, over one thousand citations per year (Fig. 1).

Non-thermal plasmas in particular, have been studied with increasing interest in the last two decades and the results obtained in terms of both efficiency in CECs removal and versatility of treatment are contributing to their success. The efficiency of such technology relies on the simultaneous activation of several chemical and physical processes. The generation of high-energy electrical discharges (peak potential values are typically of the order of thousands of Volts) promotes the formation of radicals such as  $\text{HO}^\bullet$ ,  $\text{H}^\bullet$ ,  $\text{O}_2^{\bullet-}$ , as well as reactive species such as  $\text{H}_2\text{O}_2$ , ozone, singlet oxygen, and free electrons [15–18]. Furthermore, localized temperature increase in proximity of the discharge, the generation of shockwaves, and UV light emission, also take place inside the reactor. Since all these processes are activated by the plasma discharge itself, no addition of chemicals is required to perform the treatment resulting in an extremely green process (if the electricity is produced through carbon-neutral technologies). Preliminary data obtained with PFAS on a lab-scale level show that this technology can efficiently abate PFAS in different water matrices [15,19–21].

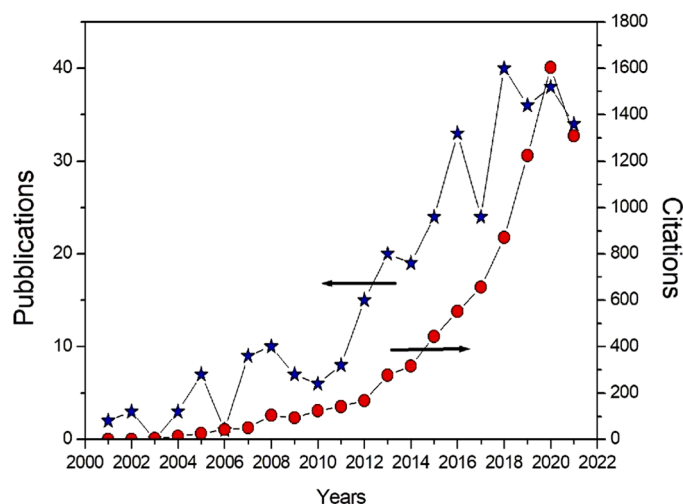


Fig. 1. Number of publications and citations on water treatment processes relying on non-thermal plasmas. Source: Own. Study based on the databases: Web of Science. Keywords: “non-thermal plasma” AND “water” AND “treatment”.

The goal of this review is to offer an overall vision of the various applications encountered of non-thermal plasma for PFAS removal from water. This was reached not only focusing on PFAS removal efficiency, but also on the mechanisms of degradation identifying the most important reactive species produced in the different systems. The effect of natural organic matter (NOM) on treatment performances, considering its ubiquitous presence in natural waters, is also considered.

## 2. Properties of plasma, reactors for NTP, non-catalytic vs (photo)catalytic processes

The term plasma is typically used to define the so called fourth state of matter characterized by an overall neutral ionized gas composed by free electrons, ions and photons formed as a consequence of an intense electric field. As a function of the properties of the plasma, the density of free charges changes in a wide range.

From a broad standpoint, the plasma can be divided in two main categories: Thermal Plasmas (TP) and Non-Thermal Plasmas (NTP). The formers are produced at high gas pressure when the collisions between the high energy electrons and the neutral species occur frequently. This implies that the electrons and the gas molecules reach a thermal equilibrium ( $T_g = T_e$ , where  $T_g$  and  $T_e$  are the temperatures of the gas molecules and the electrons, respectively) and the electron density in the NTP ranges in the  $10^{16}$ – $10^{19}$   $\text{cm}^{-3}$  [22]. In TP the temperature of both electrons and gaseous molecules are in the range of few electron volts (eV). An example of TP is the plasma torch employed in Inductively Coupled Plasma – Optical Emission Spectrophotometer (ICP-OES). At low pressure (e.g. at atmospheric pressure) the frequency of the collisions between the free electrons and the neutrals does not allow reaching the thermal equilibrium and consequently  $T_e$  remains in the few eV range, while  $T_g$  is close to room temperature. In this case the electron density falls down to  $10^8$ – $10^{14}$   $\text{cm}^{-3}$  [23]. NTP can be produced at atmospheric pressure in air or with supporting gasses, such as He, Ne, Ar,  $\text{O}_2$  and  $\text{N}_2$ . Despite of TP, to create and feed a NTP, few watts of power are needed.

The methods used to employ NTP in water treatments can be roughly divided in three: direct, indirect and bubbling methods. In direct methods the electrodes are immersed in the water solutions and the related sparks and streamers are created inside the bulk of the solution to be treated. On the contrary, in indirect methods the electrodes are placed above the surface of the water and consequently the reactive species generated from the plasma (vide infra) diffuse into the water

passing the plasma-water interface. Lastly, in the bubbling methods the plasma is produced inside bubbles that are injected into the solution. In this case the reactive species are formed inside the bubbles and easily dispersed in water.

Furthermore, NTP reactors and processes can be divided in categories as a function of *i*) the type of electric power supply (Direct Current (DC), Pulse, Alternating Current (AC), Radio Frequency (RF), Microwave Frequency (MW)...); *ii*) presence or absence of an additional dielectric between the electrode (different from the gas or the water to be treated); *iii*) reactor geometry; *iv*) polarity and *v*) feeding gas.

For the water treatment, among the numerous proposed plasma reactors, the most diffuse are the Dielectric Barrier Discharge (DBD) and the Corona Discharge (CD) reactors. In DBD reactors the two electrodes are separated by an insulating material that creates one or more insulating layers. In this case the temperature of the electrons can reach 10,000–100,000 K [24]. On the contrary, in the CD reactors no additional material separates the electrodes, the breaking of the dielectric layer (in this case usually air) is easier than in DBD and the electron temperature reaches lower temperatures as a consequence of the lower energy needed to ionize the gas between the electrodes.

Lastly, a plethora of different geometries have been proposed for the reactors where the discharge is in liquid (direct) or in contact with liquid (indirect or bubbling). Fig. 2 shows (without the intention to be comprehensive) the main proposed geometries for the different type of reactors.

As detailed below, the plasma produces not only reactive species inside the solution, but also reactive gaseous species. Ozone is one of the most interesting because it is a strong oxidant. As a function of the fate of the produced ozone we can divide the reactors in pure plasma reactors and in plasma-ozonation systems. In the former the gaseous generated from the plasma are considered wastes to move away from the reaction system. In the latter the ozone produced by the plasma is recycled and bubbled inside the reactor to increase the treatment efficiency. Often additional ozone is generated through an additional ozone generator

and added to that produced by the plasma to further increase the concentration of reactive species [26].

Lastly, the plasma processes can be divided in non-catalytic and catalytic processes. In non-catalytic ones no additional catalyst is placed inside the reactors, while in the catalytic plasma processes different catalysts can be employed to better exploit the species produced by the plasma discharge. As an example, heterogeneous photocatalysts (e.g.  $\text{TiO}_2$ ,  $\text{WO}_3$ , graphene, hybrid inorganic-organic materials...) can harvest the UV-photons release from the plasma activating the production of additional high oxidative species (e.g. adsorbed  $\cdot\text{OH}$ , holes in the valence band...) [27–30]. Alternatively, iron-based materials have been proposed to activate Fenton processes able to exploit the water peroxide that is cumulated inside the solution and consequently to boost the production of hydroxyl radicals [31,32]. An in-depth study of catalytic NTP technologies is far from the scope of the present review, to deepen this topic refer to the recent review by Russo et al. [22].

One of the more complex aspect related to the investigation of the plasma processes applied to the water treatment, is comparing the results obtained in different experimental conditions to highlight the most efficient and promising technologies. No standard methods have been proposed yet and consequently the comparison is often quite difficult because of the different experimental conditions adopted (different nature and concentration of the substrate to be removed, chemical composition of the solution, treatment time...). In this light, an excellent comparison among the major types of plasma reactors (in the absence of any catalyst) has been carried out by Malik in 2010 [33]. The author compared, on the basis of the Energy Yield  $G_{50}$  measured in the original works or computed on the basis of the reported experimental evidences, 27 different plasma systems (not only in terms of reactors, but also in terms of type of electrical power, type of atmosphere...) extracting some general conclusions regarding the plasma techniques applied to the abatement of organic pollutants. The Energy Yield  $G_{50}$  was computed as follows:

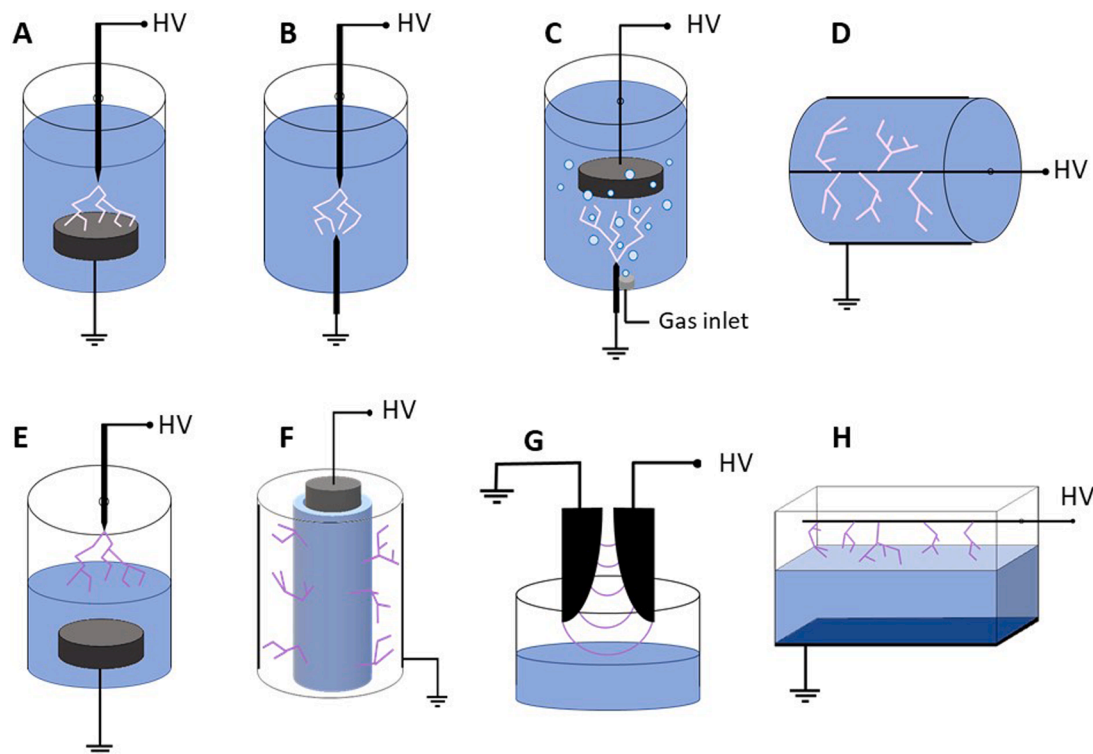


Fig. 2. Different reactor geometries for the generation of NTP inside the liquid(A–D): A) point-to-plate, B) point-to-point, C) point-to-plate with bubbling gas, D) wire-to-plate; different reactor geometries for the generation of NTP above the liquid (E–H): E) point-to-plate, F) DBD with falling liquid film, G) gliding arc above liquid, H) wire-to-plate. Adapted from Magureanu et al. [25].

$$G_{50} = 1.8 \times 10^6 \frac{C_0 V_0 M}{P t_{50}} \quad (1)$$

where  $C_0$  is the initial concentration of the pollutant in mol/dm<sup>3</sup>,  $V_0$  is the volume of the treated solution (dm<sup>3</sup>),  $M$  is the molecular weight of the substrate to be degraded (g/mol),  $P$  is the power of the reactor (W) and  $t_{50}$  is the time needed to halve the initial concentration (s). The main results obtained by Malik are summarized in Fig. 3 where the different techniques were compared on the basis of the Relative Energy Efficiency (REE) that is the value of  $G_{50}$  normalized on the  $G_{50}$  value of the pulsed corona discharge in water without bubbling gas (the most diffuse plasma technology), to this technology Malik assigned a REE 1. The energy yield to degrade toxic organic pollutants follows the orders: (i) power supply: pulsed DC > continuous DC or AC; (ii) type of reactor: pulsed corona discharge > pulsed dielectric barrier discharge > diaphragm discharge; (iii) place of the degradation: oxygen plasma > air plasma > liquid; (iv) treated solution as: fine droplets inside the plasma > thin film > deep layer = bulk. The most efficient technology was in the Malik's analysis the pulse powered reactors where the treated solutions are sprayed directly in the plasma zone.

### 3. Reactive species

Among the AOPs, the plasma processes are probably those in which the nature, from a qualitative point of view of the reactive species, is the most complex. The production of the plasma in the water or on the surface of the water to be treated, activates a plethora of high energetic processes that produce different primary species able not only to interact directly with the pollutant to be eliminated, but also to evolve in secondary (and often more stable) reactive species. Furthermore, species generated in the air over the aqueous solution (e.g. ozone and/or nitrogen oxides) can be efficiently recycled bubbling this gas inside the solution and consequently promoting alternative degradative processes. Furthermore, the coupling of the thermal processes with specific catalysts, as an example heterogeneous photocatalysts, can furtherly increase the complexity of the degradation process enlarging the number of the reactive species involved in the degradation process. Lastly, the

nature of the reactive species is strongly related to numerous experimental conditions that strongly affect the production of reactive species.

The investigation of the activated processes by electrical discharges inside water can be related to the first study of the nature of electricity by Michael Faraday in the first decades of XIX century [34]. The first report regarding the formation of radical species ( $\bullet\text{OH}$  and  $\bullet\text{H}$ ), oxygen atom (O) and hydrogen peroxide as a consequence of electrodeless discharges in water vapor was reported by Rodebush and Wahl in 1933 [35]. After this seminal work, the production of molecular oxygen (O<sub>2</sub>) and hydrogen (H<sub>2</sub>) [17,36] together with hydroperoxyl radical and other radicals have been proposed [37].

The plasma process results in the formation of initial high energetic species, often in the excited state (H<sub>2</sub>O\*,  $\bullet\text{OH}$ ,  $\bullet\text{H}$ , e<sub>(aq)</sub><sup>-</sup>...) that can either recombine to give more stable reactive species (H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>, O<sub>3</sub>...), or go back to a ground state dissipating the excess of energy through UV light emission. Furthermore, during the plasma discharge, shockwaves (able to create cavitation bubbles) and the formation of hot spots in the solution can also activate the pyrolytic degradation of organic substrates. The UV light can promote the direct photolysis of some pollutants - in this case the species to be degraded absorbs a quantum of light ( $h\nu$ ), goes in an excited state from which it dissipates energy through the homolytic or heterolytic cleavage of molecular bonds. Lastly, in the presence of semiconductors with energy gap  $E_g \leq h\nu$ , the photocatalytic degradation of the pollutants can be activated through the formation of high energetic species (e.g. highly oxidative valence band holes able to oxidize the substrate - adsorbed at the photocatalyst or in solution - through a direct or mediated electron transfer).

The plasma discharge happens inside a channel where high-energy electrons can interact with the water molecules by inelastic collision. As a function of the energy of these electrons, different processes can be activated, such as (i) the production of molecules in excited vibrational or rotational states, (ii) the dissociation of one or more molecular bonds, (iii) the ionization and (iv) the electron attachment. A not comprehensive selection of some primary reactions between the high energy-electrons produced in the plasma channels and ground water molecules are reported in Table 1 together with the related energy threshold needed to activate the process. Note that the energy of the electrons in pulsed electrical discharges falls in the 0.5–2 eV range (with often a wide distribution of the energy across the average value). From the comparison of the average energy of the electrons produced in plasma and the threshold reported in Table 1, it is manifest that the real effect of the inelastic collision between electrons and the solvent molecules (i.e. water) is the production of water in excited states, more than the cleavage of the covalent bonds of water. This is in agreement with the low degree of ionization of the water inside the streamer channels that has been proposed (< 1%) [38].

The formation of the primary reactive species is mainly due to process involving water at excited states, such as the following ones

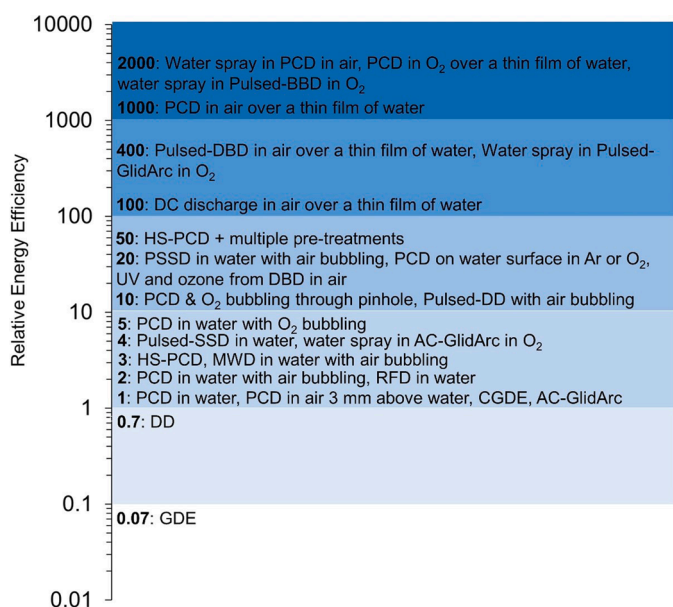


Fig. 3. Comparison of different plasma technologies on the basis of their relative energy efficiency (REE). DBD = Dielectric Barrier Discharge, PCD = Pulsed Corona Discharge, HS = Hybrid Series, PSSD = Pulsed Streamer and Spark Discharge, DD = Diaphragm Discharge, MWD = Microwave Discharge, RFD = Radio Frequency Discharge, CGDE = Contact Glow Discharge Electrolysis. Adapted from Malik [33].

Table 1

Selection of primary reactions between the high energy-electrons produced in the plasma channels and ground water molecules [39].

Type of reaction	Reaction	Threshold, eV
Rotational Excitation	$\text{H}_2\text{O}(J=0) + e^- \rightarrow \text{H}_2\text{O}^*(J=2) + e^-$	0.008
Rotational Excitation	$\text{H}_2\text{O}(J=0) + e^- \rightarrow \text{H}_2\text{O}^*(J=1) + e^-$	0.198
Vibrational Excitation	$\text{H}_2\text{O}(000) + e^- \rightarrow \text{H}_2\text{O}^*(010) + e^-$	0.453
Vibrational Excitation	$\text{H}_2\text{O}(000) + e^- \rightarrow \text{H}_2\text{O}^*(100) + e^-$	0.198
Dissociation	$\text{H}_2\text{O} + e^- \rightarrow \bullet\text{OH} + \text{H}(n=1) + e^-$	7.0
Dissociation	$\text{H}_2\text{O} + e^- \rightarrow \text{H}_2 + \text{O}^*(3^3\text{P}) + e^-$	17.0
Ionization	$\text{H}_2\text{O} + e^- \rightarrow \text{H}_2\text{O}^+ + 2e^-$	13.0
Ionization	$\text{H}_2\text{O} + e^- \rightarrow \text{OH}^+ + \text{H} + 2e^-$	15.0
Electron Attachment	$\text{H}_2\text{O} + e^- \rightarrow \text{OH}^- + \text{H}$	4.30
Electron Attachment	$\text{H}_2\text{O} + e^- \rightarrow \bullet\text{OH} + \text{H}^-$	4.36



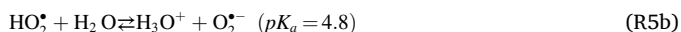
The same reactive species can be formed also directly through the inelastic interaction between high energy electrons and water molecules, but in the common water plasma systems the electrons have not enough energy to promote the direct production of these species.

As reported above the plasma discharge can generate high temperature points (2000–5000 K) where not only the pollutants to be degraded can be pyrolyzed, but where the thermal decomposition of water can be operational (R4). This process has been often reported as the basic step of the sonochemical decomposition of water pollutants. High temperatures reached during the plasma discharge has been also reported, e.g. Namihira et al. measured 15,000 K during the pulsed discharge plasma produced underwater through a magnetic pulse compressor (applied voltage 72–82 kV, output voltage approximately 3  $\mu\text{s}$ ) [40].

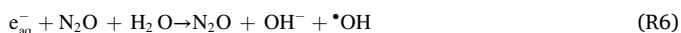


The direct observation of the produced radicals during the plasma discharge was carried by optical emission spectroscopy analyzing the most intense emission signals produced by the pulsed electrical discharge under water. The spectrum emitted by the process showed the signals related to the presence of the radicals  $\cdot\text{OH}$  (284 and 309 nm, for H),  $\text{H}^*$  (486 and 656 nm) and atomic oxygen O (777 and 844 nm) [41].

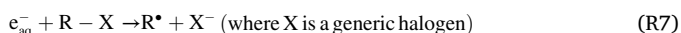
The radical  $\text{H}^*$  once produced can react with dissolved oxygen to give hydroperoxyl radical according to reaction R5. Hydroperoxyl is a weak acid characterized by  $\text{p}K_a = 4.8$  [42]. At pH higher than 4.8 the dominant species is the superoxide radical anion.



$\text{H}^*$  and  $\text{O}_2^{\bullet-}$  are not the only reductive species formed during the plasma discharge. The formation of aqueous electrons ( $e^-_{\text{aq}}$ ) has been largely reported as a consequence of the solvation of some electrons escaped from the plasma zone to the bulk solution. Gupta et al. proposed the formation of aqueous electron on the basis of the increased formation of  $\cdot\text{OH}$  in the presence of  $\text{N}_2\text{O}$ . This gas is well known to be reduced by  $e^-_{\text{aq}}$  to give molecular nitrogen and hydroxyl radical accordingly to reaction R6.



Interestingly, the very low reductive potential of  $e^-_{\text{aq}}$  ( $E^\circ \text{H}_2\text{O}/e^-_{\text{aq}} = -2.77 \text{ V}$  vs NHE) can be helpful to promote the reductive degradation of halogenated compounds (e.g. the very recalcitrant PFAS) according to the general reaction R7



As reported above, the primary radical species formed inside the plasma can diffuse outside the plasma channel where they can recombine to form more stable radicals or stable molecules. These secondary chemical reactions form a very complex scenario. These reactions can involve not only reactions with the solvent or the ubiquitous dissolved oxygen, but also species dissolved in the water solution, such as inorganic salts, low molecular weight organics or organic macromolecules (e.g. the natural dissolved organic matter). Furthermore, gaseous reactive species can be produced (e.g.  $\text{O}_3$  and  $\text{NO}_x$ , vide infra).

For a quite complete list of the formation and recombination reactions – with the related rate constants – involving the main radicals

formed during a plasma process please refer to Table 3 of the really rich review by Joshi and Thagard [39].

From the recombination of the most important primary radical ( $\cdot\text{OH}$ ,  $\text{H}^*$  and  $\text{O}$ ) molecular hydrogen, oxygen and hydrogen peroxide are produced. The accumulation of hydrogen peroxide has been widely reported and explained through the following reactions: the dismutation of the hydroperoxyl radical (R8), the dimerization of  $\cdot\text{OH}$  (R9) and the reaction of the hydroperoxyl radical with  $\text{H}_2$  (R10) or water (R11).



Regarding the production of reactive gaseous species, the formation of ozone and nitrogen oxides seems to be the most important processes. Ozone can be produced from the atomic oxygen in the presence of a third body able to dissipate the excess of energy R12, (13).



The produced ozone (high concentrations were measured especially in the case of underwater plasma discharge [15]) can be effectively used as additional oxidant in the plasma process being this molecule not only able to oxidize directly organic substrates (especially for addition to double bonds), but also to promote the formation of additional  $\cdot\text{OH}$  radicals especially in alkaline media according to the reaction R14, 15 [43], or through the reaction with the cumulated hydrogen peroxide (R16 [26]).



Lastly, when the plasma discharge is carried out in water in contact with air, the production of reactive nitrogen species (RNS) has been reported (R17–R21). The main nitrogen reactive species observed both in the gaseous and liquid phase are  $\text{NO}$ ,  $\text{NO}_2$ , nitrate, nitrite / nitrous acid and peroxyxynitrite ( $\text{ONOO}^-$ ) [44]. Despite of the reaction of organic compounds with ROS, that often gives less toxic compounds, the toxicity of the by-products formed for the reaction of the original pollutants with RNS must be carefully evaluated because often the formed nitro and nitroso compounds show higher toxicity than the parent compounds. Furthermore, the accumulation of nitrate and nitrite in solution can give a further source of hydroxyl radical because their UV photolysis is a well-known process able to produce hydroxyl radical in solution [45].



## 4. Matrix effect and interferences in NTP processes

### 4.1. pH

NTP treatments have been reported by other authors to cause acidification of treated solutions especially when working under air or

nitrogen atmosphere [20,46–50]. The degree of acidification strongly depends on the gas phase in contact with the plasma, on reactor geometry, and on the type of plasma that is generated and it is typically caused by the formation of reactive nitrogen species (RNS) such as  $\text{NO}_x$  that undergo hydrolysis. Therefore, both initial pH and pH evolution over treatment are important parameters to monitor in order to maintain the system under the desired chemical conditions. Bolouki et al. reported a strong acidification of solutions treated with a micro pulsed DBD plasma with pH values dropping from 7 to 2 after 12 min of treatment under air atmosphere [51]; when working under argon or oxygen atmosphere in the same system, acidification did not occur. The degradation of PFAS with NTP has been observed to be pH dependent by Jovicic et al. being strongly inhibited at acidic pH. Using an atmospheric plasma jet, they observed that the degradation of PFOA and PFOS (initial total PFAS concentration 0.932  $\mu\text{g/L}$ ) stopped after a few minutes of treatment. Simultaneously, pH values of treated solution dropped from 7 to around 2.5. When diluted PFAS solution having circumneutral pH were treated with the same system, PFAS concentration further decreased proving that samples acidification was acting as a barrier for PFAS degradation [46].

#### 4.2. Water conductivity

Depending on the type of NTP reactor adopted and on the position of the plasma discharge with respect with the treated solution, water conductivity can highly influence treatment efficiency. In the case of immersed discharges, high conductivity hinders the formation of plasma discharges since water dielectric becomes more difficult to break. Palma et al. showed that conductivity was the main factor influencing the degradation of methylene blue solutions when working with underwater pulsed streamer discharge [15]. Liu et al. also observed that higher water conductivity values significantly lowered the degradation rate of aqueous aniline using non-thermal plasma generated in microbubbles [52].

#### 4.3. Nitrate concentration

Nitrate is an efficient scavenger of aqueous electrons that are formed in the NTP being easy to be reduced by  $e^-_{\text{aq}}$  (see above) [53]. Aqueous electrons are key reactants since they can directly react with water contaminants (reaction R7) but also participate in the formation of other reactive species (see Table 1 and reactions R6, R12, R17). Stratton et al. suggested that aqueous electrons are key reactants involved in the degradation of PFAS using NTP and demonstrated that the addition of  $\text{NaNO}_3$  10 mM suppressed the transformation of PFOA 20 mM almost entirely [20]. Despite such high concentrations of nitrate are not found in conventional wastewater effluents they could be easily reached in industrial wastewater. In such cases, the high nitrate concentration could represent a limit in the application of NTP for the removal of recalcitrant halogenated compounds such as PFAS.

#### 4.4. Dissolved organic matter

Dissolved organic matter (DOM) is ubiquitous in aqueous environments and thus in water supplies. Its amount and properties vary from one water source to another and depend on the biogeochemical cycles, season, amount of precipitation, and the human activities in the surrounding environment. From a chemical standpoint, DOM is a complex mixture of heterogeneous organic compounds typically divided into humic and non-humic fractions. The humic fraction contains high molecular weight mainly composed by polycondensed lignin-types compounds while the non-humic fraction regroups molecules of lower molecular weight such as proteins, carbohydrates, and organic acids [54].

During plasma-based water treatments, all these components can react with the reactive species produced in the discharge process, in

particular  $\bullet\text{OH}$  and  $\text{O}_3$ . Reaction rate constants of  $\bullet\text{OH}$  with DOM, measured in various natural water samples, typically lay within the range  $1\text{--}7 \times 10^4 \text{ s}^{-1} (\text{mg of C/L})^{-1}$  [55–58]. These values are in accordance with the second-order rate constant of  $\bullet\text{OH}$  with Suwannee River fulvic and humic acids (often taken as reference humic materials) equal to  $2.7 \times 10^4 \text{ s}^{-1} (\text{mg of C/L})^{-1}$  and  $1.9 \times 10^4 \text{ s}^{-1} (\text{mg of C/L})^{-1}$  respectively [58]. DOM also reacts efficiently with  $\text{O}_3$  with a reported first order rate constant of  $8.8 \times 10^{-3} \text{ s}^{-1}$  for a DOC of 3 mg C/L [56]. This reactivity of DOM with  $\bullet\text{OH}$  and  $\text{O}_3$  has as consequences that (i) the removal of DOM can be potentially achieved by the plasma-based water treatments and (ii) DOM can negatively affect the removal of contaminants.

Humic acids (HA), used as surrogates of the DOM contained in real surface waters, were reported to be removed by gas phase surface discharge plasma [59,60]. These studies investigated the chemical modifications of DOM under treatment and the mechanism of the reaction. UV-vis and fluorescence spectroscopies revealed that the molecular weight and the percentage of aromaticity of HA decreased during the treatment. Concerning the mechanism, the major role of  $\bullet\text{OH}$  radicals was demonstrated by the significant inhibiting effect of isopropanol ( $10^{-3} \text{ M}$ ), used as an  $\bullet\text{OH}$  radical quencher, on the HA removal [60]. Moreover, the formation of  $\bullet\text{OH}$  radicals via the reaction of dissolved ozone with  $\text{H}_2\text{O}_2$  was postulated based on two experimental results: the absence of HA removal with Ar as a gas carrier, although  $\bullet\text{OH}$  was present in the water droplets, and the better removal efficiency of plasma treatment with  $\text{O}_2$  as a gas carrier than ozonation [60]. Zhou et al. reported that both the percentage of HA removal and the rate of removal could be improved by coupling plasma discharge and activated carbon treatments [61]. To explain this synergistic effect, the authors postulated that the plasma process favors the adsorption of reactive species ( $\text{H}_2\text{O}_2$  and  $\text{O}_3$ ) generating OH radicals on the activated carbon and promote their interactions with HA.

Due to their  $\bullet\text{OH}$  radical scavenging capacity, DOM can also reduce the efficiency of plasma-based water treatments to remove pollutants. The inhibiting effect of DOM is however strongly dependent on the chosen experimental conditions. The degradation of microcystin-LR (2 mg/L) was poorly affected by HA until 150 mg/L [62] in a glow discharge plasma treatment taking place at the gas-solution interface in argon atmosphere. On the other hand, the removal of dimethylphthalate (30 mg/L) was slightly decreased by HA (10 mg/L) [63]. Based on a bimolecular rate constant of reaction between OH radical and dimethylphthalate of  $3.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$  [64] against  $1.9 \times 10^4 \text{ s}^{-1} (\text{mg of C/L})^{-1}$  for HA, one gets the inhibiting factor of 27% found experimentally.

### 5. NTP for the removal of CECs: a focus on the use of plasma technology for the abatement of PFAS

#### 5.1. Main features of the application of NTP for the PFAS removal

Different types of plasma discharges, reactor geometries, end electrodes configurations have been explored for CECs removal. One of the most common types of discharge used is the streamer discharge often produced with electrodes arranged in the so called point-to-plane configuration where a high voltage is applied to a pointy electrode while the large electrode is grounded [17,20,65–67]. Another popular type of discharge is the Dielectric Barrier Discharge (DBD), where a dielectric (glass is often used) is inserted between the electrodes, typically obtained in cylindrical glass reactor and metallic wires or plates used as electrodes [18,68–70]. NTPs have been successfully applied for the removal of a variety of water contaminants such as industrial dyes [27,28,71,72], pharmaceuticals [31,32,67], antibiotics [69], antibacterial and antimycotic compounds [29,30,73], surfactants [74], pesticides [75–79] and many others. Furthermore, NTPs has also been proven to be effective for water sterilization and bacterial inactivation [44,48,80–82]. It is however in the removal of PFAS that plasma-based water treatments are clearly outperforming other technologies; chlorination,

ozonation, and other AOPs have in fact been reported to be ineffective for PFAS removal [9].

Table 2 regroups data recently published in the literature on PFAS treatment using different types of non-thermal plasma reactors. Both artificial matrices such deionized water and real water matrices such as contaminated groundwater or landfill leachates have been included in the comparison. Initial PFAS concentration, their percentage of removal, and treatment time are reported together with absorbed power and energy yield calculated by the authors for the different plasma reactors. When available,  $G_{50}$  (see Eq. (1), [33,83]) are given; alternatively, energy requirements expressed in kWh/m<sup>3</sup> or in W/L are reported. Different types of plasma discharges and reactor configuration have been tested for PFAS removal with energy yields ranging from fractions

of mg/kWh to hundreds of mg/kWh and energy input ranging from 1.7 to 300 W. The most studied compounds, present in most of the reviewed literature, were PFOA and PFOS, often taken as model compounds in prepared solutions. In the case of PFAS contaminated samples, up to 14 PFAS were detected and treated simultaneously providing a wide scenario of the transformation phenomena taking place during plasma treatment [67,84,85].

As underlined above, PFAS is a complex family of compounds with a similar perfluorinated molecular skeleton and different polar moieties. This implies different reactivity towards the plethora of reactive species generated during the plasma discharge and consequently diverse% degradation and rate of transformation for different perfluorinated compounds subjected to the same NTP treatment. In general,

**Table 2**  
Comparison of NTP processes for PFAS removal encountered in the literature.

Discharge type	Matrix	Compound(C <sub>0</sub> )	Removal	Treatment time (min)	Energy input (energy yield)	Notes	Ref.
Pulsed streamer	MilliQ and tap water	PFOA (41.4 ppm)	84%	30	19 W (87.4 mg/kWh)	Faster degradation in tap water than in MilliQ water.	[65]
DBD ("Hollow electrode")	MilliQ	PFOA (41.4 ppm)	49%	30	7 W (78.0 mg/kWh)		
Corona discharge ("7 wires")	MilliQ	PFOA (41.4 ppm)	12%	300	10 W (0.23 mg/kWh)		
Pulsed corona discharge (O <sub>2</sub> )	Deionized water	PFOS (18.8 ppb)	80%	180	106 W (0.33 mg/kWh)	Higher formation of shorter PFAS and higher defluorination when working under O <sub>2</sub> . The addition of sulfobetaine surfactant led to an increase of 80–90% in PFOS degradation.	[88]
Pulsed corona discharge (Ar)	Deionized water	PFOS (0.75 ppm)	95%	180	103 W (22 mg/kWh)		
Pulsed corona discharge (Ar)	Deionized water	PFOS (10 ppm)		360	130 W (220 mg/kWh)		[18]
DBD (He)	Deionized water	PFOS (10 ppm)	97%	60	200 W (71 mg/kWh)		
Pulsed streamer (Ar)	Contaminated groundwater	Mix of 14 PFAS detected in 2 sites (total PFAS concentration of 15,100 ± 3800 and 27,500 ± 2300 ng/L)	>90% (long-chain PFAS) 0–95% (short-chain PFAS)	8.2–20 (depending on the flow rate)	9.2–31 kWh/m <sup>3</sup>	Better removal for long-chain PFASs. The addition of the cationic surfactant CTAB improved the removal of short-chain perfluoroalkyl acids.	[84]
Pulsed streamer (air)	MilliQ and groundwater	PFOS (1ppb) PFOA (1ppb) PFHxA (1ppb)	>99% 46% 38%	30 60 60	300 W (3–6 kWh/m <sup>3</sup> )	PFAS were treated both individually and in mixture obtaining comparable kinetics. Nitrate accumulation and H <sub>2</sub> O <sub>2</sub> during treatment were also measured.	[15]
Pulsed streamer	Deionized water	PFOA (8.3 ppm) PFOA (8.3 ppm)	90% 25%	30 30	76.5 W (54.6 W/L) 4.1 W (2.90 W/L)	Considerably faster PFOA degradation observed with negative polarity.	[20]
Pulsed streamer	Liquid investigation-derived waste	12 PFAS (up to 10 ppb)	–562%* - 100%	5–60 min	1.7–6.3 kWh/m <sup>3</sup>	Removal efficiencies were also higher for long-chain PFAAs than for short-chain PFAAs. PFASs were more rapidly removed than PFCAs of similar chain length.	[86]
Pulsed streamer (Ar)	landfill leachate	5 long-chain PFAS 6 short-chain PFAS 8 PFAS precursors	>99.9% 10–99.9% 44–99.9%	75 min 120 min 120 min	20 to 36 kWh/m <sup>3</sup> (calculated for PFOA and PFOS removal)	Short-chain PFAAs were not removed in the first 120 min of treatment. The addition of cationic surfactant CTAB resulted in the removal of 40–95% of the short-chain PFAAs.	[85]
DBD-Plasma jets	Contaminated groundwater	PFOS (900 ppt) PFHxS (200 ppt)	82% 56%	120 120	90 W (-)		[89]
DBD-water dielectrics	Contaminated groundwater	PFOS (1200 ppt) PFHxS (200 ppt)	96% 44%	90 90	70 W (93–196 kWh/m <sup>3</sup> for PFOS removal, ~45 kWh/m <sup>3</sup> for PFOA removal)	Better efficiency using nanosecond pulses rather than alternate current.	
Gliding arc plasma (air)	MilliQ	12 PFAS having initial concentration of ~100 mg/L each	40 - >99%	60	150 W (23.2 kWh/m <sup>3</sup> per order for PFOS, 213.4 kWh/m <sup>3</sup> per order for PFOA)	Better removal for long-chain PFASs. Better performances obtained using air as plasma feed gas than using N <sub>2</sub> or O <sub>2</sub> .	[21]

\*negative removal values indicate the formation of the monitored compound during treatment.

perfluoroalkyl sulfonates (PFASs) are more rapidly removed than perfluorocarboxylic acids (PFCAs) characterized by similar chain length (and clearly at the same initial concentrations) [20]. This has been also observed by Palma et al. who reported that during the plasma treatment of a mixture of PFOS, PFOA and PFHxA (perfluorohexanoic acid) in both ultrapure water and groundwater, PFOS was no longer detected after 30 min, PFOA was removed for around 46% after 1 h in both matrices and PFHxA was the most recalcitrant compound with 29% and 38% of removal in ultrapure water and in groundwater, respectively [15]. Furthermore, removal are usually higher for long chain PFAAs than for short-chain PFAAs [20] and this could give the accumulation of transformation products up to significant concentration level as observed by Singh et al. during the plasma treatment of 13 PFAS contaminated groundwaters where the accumulation of some short-chain PFAS (e.g. Perfluoropentanoic Acid (PFPeA), Perfluorobutanoic Acid (PFBA)) and some PFAS precursors (e.g. 10:2 FTS, EtFOSAA, MeFOSA) was observed [86].

In our opinion, among the limits of the use of NTP for the removal of PFAS there are not only the medium-high energy demand of this technology - especially if compared with advanced treatment processes that use strong oxidants (e.g.  $O_3$ ,  $H_2O_2$ , persulfate, chlorine...) which have scarce energetic requirement, but that are not able to remove efficiently the PFAS - but also the limited comprehension of the main mechanisms operative during the transformation of these pollutants with NTP, both in term of reactive species involved and in term of the pathways of transformation of the PFAS (in this case the excellent article by Singh et al. [87] is an exception) with the identification and quantification of the main transformation products and of their toxicity.

## 5.2. PFAS degradation products

Due the limited amount of information actually available on PFAS degradation products in NTP treatments, an exhaustive picture of PFAS breakdown pathways in such systems cannot be drawn. However, from the study of the published literature appears that the formation of shorter-chained PFAS is commonly observed and both the % conversion and the nature of the formed by-products depend on the experimental parameters such as the gas atmosphere and the type of plasma discharge created.

Singh et al. carried out a detailed study on the degradation products of PFOA and PFOS formed both in the aqueous and in the liquid phase working with a pulsed streamer discharge [87]. In the liquid phase, they observed that shorter perfluoroalkyl-acids such as perfluoroheptanoic acid (PFHpA), perfluorohexanoic acid (PFHxA), perfluoropentanoic acid (PFPeA), and perfluorobutanoic acid (PFBA) represented the main degradation products of both PFOA and PFOS. The authors suggested that the first transformation step for PFOS is indeed its conversion to PFOA initiated by the attack of the aqueous electron on the C-S bond resulting in the release of the  $SO_3^-$  group and in the formation of the  $\bullet C_8F_{17}$  radical that is eventually oxidized to carboxylic acid. Short-chain PFAS originate from the subsequent electrons attack to the newly formed acids resulting in their iterative decarboxylation. In the gas phase, the authors observed the formation of cyclic perfluoroalkanes in the C4-C8 range such as perfluorocyclobutane and perfluorocyclohexane and the highest concentration of gaseous by-products was observed after 30 min of treatment. The total concentration of detected gaseous products was two order of magnitudes lower than that of the aqueous ones [87].

Aziz et al. also observed the formation of PFOA, PFHpA, PFHxA, PFPeA, and PFBA when treating aqueous solutions of PFOS with a pulsed corona discharge [88]. The authors also observed that both the rate of by-products formation and the rate of defluorination changed significantly with the gas atmosphere. In particular, they observed that the concentration of PFOA, PFHpA, PFHxA and PFPeA and the concentration of fluoride were much higher when working under  $O_2$  atmosphere than under He or Ar atmosphere and that the nature of formed

by-products was different as well [88].

In the study conducted by Lewis et al. the authors observed the formation of PFHpA, PFHxA, and PFBA when degrading aqueous PFOA in a gliding arc plasma reactor, but also the formation of perfluoroheptanesulfonic acid (PFHpS) and perfluorohexanesulfonic acid (PFHxS) when degrading PFOS in the same system. In this case, the detection of shorter-chained perfluorosulfonic acids, highlighted other possible degradation pathways for PFOS that did not involve the loss of  $SO_3^-$  in the first step [21].

In agreement with this hypothesis, Mahyar et al. also suggested that the desulfonation of PFOS in their DBD reactor would not occur in the first step of the degradation pathway [18]. The authors observed in fact that the desulfonation rate was lower than the defluorination rate and made the hypothesis that the first attack would rather take place on the more hydrophobic perfluoroalkyl chain pointing towards the gas phase.

## 6. Scientific knowledge and technology readiness level of the NTP technology

Despite an exhaustive comprehension of the fundamental phenomena taking place in the NTP has not been reached yet, the application of NTP for water treatment applications has been intensively studied in the last 10 years and we are now observing the transition from lab-scale setups to marketable solutions. However, to the best of our knowledge a very limited number of commercial solutions using NTP for water treatment have been encountered on the web. Among them we find the *Flowrox Plasma Oxidizer*<sup>TM</sup>, a NTP unit designed for the treatment of industrial wastewater. The manufacturer declares that the treatment of phenol solutions having initial concentration of 100 mg/L requires an energy yield of 88 g/kWh when working under air and 138 g/kWh working under oxygen enriched atmosphere. When performing the degradation of furfural at the concentration of 500 mg/L, reported energy yield is 133 g/kWh working in basic solution and 182 g/kWh in acidic solution [90].

Another NTP generator is the one proposed by *PlasmaLeap Technologies* that relies on the formation of DBDs assisted by air bubbles. The degradation of the antibiotic cefixime at the concentration of 100 mg/L led to a removal of 95% in 30 min of treatment with an energy yield of 1.5 g/kWh and declared discharge power of 6.3 W [91,92].

WAPULEC proposed a different solution: an NTP reactor in which pulsed corona discharges are obtained in gas medium (air or oxygen) in which water is showered in droplets, films, or jets. Phenol at the concentration of 100 mg/L was removed with an energy yield of 70 – 110 g/kWh. High removal efficiency was also achieved for the removal of lignin, furfural, pesticides, and in the treatment of pharmaceutical industry wastes [93]. The manufacturer states that their technology is suitable for a wide range of applications such as water potabilization, wastewater treatment, and water reuse.

Despite exhibiting high removal efficiencies for a wide range of organic water contaminants, none of the above-mentioned technologies was, to our knowledge, tested in respect of PFAS removal.

## 7. Conclusions

NTP treatments are proving to be a promising technology for the removal of recalcitrant pollutants from the aqueous phase. A specific feature of this kind of treatments is the ability to produce a plethora of different reactive species having both oxidative ( $\bullet OH$ ,  $HO_2\bullet/O_2\bullet^-$ ) and reductive ( $H\bullet$ ,  $e_{aq}^-$ ) properties. Furthermore, NTP technology can activate the direct photolysis of photochemically labile compounds (by the UV emission during the plasma discharge) as well as the direct pyrolysis of the compounds in the plasma-generated hot spots. This multiple reaction mechanism allows the degradation of those compounds that are poorly abated by other more conventional AOPs and this is undoubtedly the most important feature of the NTP-based water treatments. The most relevant example is represented by the perfluorinated compounds. The



degradation of PFAS parent compounds have generally been reported to take place with good efficiencies often reaching complete removal in relatively short treatment times. However, the removal of long-chain PFAS usually produces shorter-chain PFAS as intermediates and the degradation involves not only the hydrophilic moieties of PFAS (e.g. carboxylic or sulfo groups), but also the degradation of the perfluorinated methyl group with cleavage of the C–F bond. The formation of low molecular weight PFAS during the NTP treatments must be carefully evaluated because these compounds could have similar toxicity with respect to their parent compounds. PFAS tend to accumulate at the liquid-air interface and in the case of NTP treatment their degradation rate is increased in the presence of surfactants. The decrease of the surface tension helps the surface transport phenomena and consequently increases the PFAS transformation rate.

The comparison between the NTP technologies and the other AOPs from the viewpoint of energy consumption (evaluated in term of electrical energy per order values -  $E_{EO}$ ), classifies the NTP processes in a central zone with median energy consumptions in the 1–100 kWh/m<sup>3</sup> range, at the same level of photo-Fenton and pure electrolytic AOPs. On the contrary, processes relying on the use of strong oxidants (e.g. O<sub>3</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>/UV, UV/H<sub>2</sub>O<sub>2</sub>, UV/persulfate, UV/chlorine), but also the electron beam technology, have significantly lower  $E_{EO}$  values (<1 kWh/m<sup>3</sup>); on the other hand, UV-based photocatalysis, ultrasound, and microwave-based AOPs have significantly higher energy request (>100 kWh/m<sup>3</sup>) [94]. As clearly highlighted in Fig. 3, the energy demand for the NTP technologies is strongly affected by the nature of the plasma adopted and by the reactor type, spreading the  $G_{50}$  values on a range larger than 3 order of magnitude. From the point of view of the energy requirements, the NTP technologies are very promising, but it is crucial (i) to increase the energy efficiency with the aim of reaching  $E_{EO}$  values < 1 kWh/m<sup>3</sup> and (ii) to carefully choose the most efficient solution according to the target pollutant to be removed.

The NTP technologies have been employed for the transformation of natural organic matter (up to its mineralization) and significant rates of degradation were observed. This suggests that the NOM can play a competitive role for the reactive species generated by NTP with an overall decrement of the transformation rate of recalcitrant pollutants in the presence of dissolved organic matter. This aspect is crucial to consider when treating water matrices containing NOM such as natural waters.

From the analysis of the quite rich literature related to the use of NTP for the abatement of water contaminants, two general concluding remarks emerge. The first one is related to the variety of terms used for the description of NTP devices that is often a confounding element, especially when someone approaches this technology for the first time. A normalization of the terminology used to describe the NTP devices, reactors and processes is in this light desirable. The second point is related to the absence of recognized standardized methods to test NTP devices (especially in terms of nature and concentration of the substrates to be used and the matrix composition). This lack of standard procedures often hinders the direct comparison between published data creating difficulties in the identification of the best solutions. The explicit reporting of the  $G_{50}$  value of the investigated devices is suggested as the first step to ease the comparison between different NTP technologies. Furthermore, from the critical revision of the literature related to the application of the NTP technology as water treatment tool, it is possible to underline some key knowledge gaps and the related research directions essential to boost the use of these technologies up to real diffuse applications. The main important lacks are related to the absence of systematic investigations regarding the industrial scale-up of the more promising NTP technologies for the treatment of waste waters. In particular, there is a limited number of critical studies on the now-on-the-market technologies especially if one considers studies carried out by scientists without any relation with the producers of NTP plants. Additionally, there are very few studies regarding the application of NTP at large/industrial scale for the treatment of waters polluted by PFAS

that is probably the most promising field of application of NTP. This hinders an overall evaluation of the benefits and limits of this technology not only in terms of productivity (treated water per unit time, removal efficiency in real applicative scenarios and robustness/durability of the adopted tools), but also from the economic and energetic point of view.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## References

- [1] E.R. Jones, M.T.H. van Vliet, M. Qadir, M.F.P. Bierkens, Country-level and gridded estimates of wastewater production, collection, treatment and reuse, *Earth Syst. Sci. Data*. 13 (2021) 237–254, <https://doi.org/10.5194/essd-13-237-2021>.
- [2] M. Biel-Maeso, C. Corada-Fernández, P.A. Lara-Martín, Removal of personal care products (PCPs) in wastewater and sludge treatment and their occurrence in receiving soils, *Water Res.* 150 (2019) 129–139, <https://doi.org/10.1016/j.watres.2018.11.045>.
- [3] M. Clara, B. Strenn, O. Gans, E. Martinez, N. Kreuzinger, H. Kroiss, Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants, *Water Res.* 39 (2005) 4797–4807, <https://doi.org/10.1016/j.watres.2005.09.015>.
- [4] S.O. Ganiyu, E.D. van Hullebusch, M. Cretin, G. Esposito, M.A. Oturan, Coupling of membrane filtration and advanced oxidation processes for removal of pharmaceutical residues: a critical review, *Sep. Purif. Technol. Part. 3* (2015) 891–914, <https://doi.org/10.1016/j.seppur.2015.09.059>.
- [5] Institute for the Protection and Security of the Citizen (Joint Research Centre), L. Ceriani, T. Lettieri, R.N. Carvalho, A. Ippolito, Development of the First Watch List Under the Environmental Quality Standards Directive, Publications Office of the European Union, LU, 2015. <https://data.europa.eu/doi/10.2788/101376>, accessed August 30, 2021.
- [6] I.M.F. Cardoso, R.M.F. Cardoso, J.C.G. Esteves da Silva, Advanced oxidation processes coupled with nanomaterials for water treatment, *Nanomaterials*. 11 (2021), <https://doi.org/10.3390/nano11082045>.
- [7] <http://www.depuratoreaquareno.it/en-US/activities/wastewater-processing/industrial-wastewater-section>, (n.d.). <http://www.depuratoreaquareno.it/en-US/activities/wastewater-processing/industrial-wastewater-section> (accessed September 1, 2021).
- [8] M. Kotthoff, J. Müller, H. Jüring, M. Schlummer, D. Fiedler, Perfluoroalkyl and polyfluoroalkyl substances in consumer products, *Environ. Sci. Pollut. Res.* 22 (2015) 14546–14559, <https://doi.org/10.1007/s11356-015-4202-7>.
- [9] M.F. Rahman, S. Peldszus, W.B. Anderson, Behaviour and fate of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in drinking water treatment: a review, *Water Res.* 50 (2014) 318–340, <https://doi.org/10.1016/j.watres.2013.10.045>.
- [10] T. Anumol, S. Dagnino, D.R. Vandervort, S.A. Snyder, Transformation of Polyfluorinated compounds in natural waters by advanced oxidation processes, *Chemosphere*. 144 (2016) 1780–1787, <https://doi.org/10.1016/j.chemosphere.2015.10.070>.
- [11] C.D. Vecitis, H. Park, J. Cheng, B.T. Mader, M.R. Hoffmann, Treatment technologies for aqueous perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA), *Front. Environ. Sci. Eng. China*. 3 (2009) 129–151, <https://doi.org/10.1007/s11783-009-0022-7>.
- [12] G. Pitter, R.F. Da, C. Canova, G. Barbieri, J.M. Zare, à F. Dapr, F. Manea, R. Zolin, A.M. Bettega, G. Stopazzolo, S. Vittorii, L. Zambelli, M. Martuzzi, D. Mantoan, F. Russo, Serum levels of perfluoroalkyl substances (PFAS) in adolescents and young adults exposed to contaminated drinking water in the Veneto Region, Italy: a cross-sectional study based on a health surveillance program, *Environ. Health Perspect.* 128 (2009), 027007, <https://doi.org/10.1289/EHP5337> n.d.
- [13] T. Dalla Zuanna, D.A. Savitz, G. Barbieri, G. Pitter, M. Zare Jeddì, F. Daprà, A.S. C. Fabricio, F. Russo, T. Fletcher, C. Canova, The association between perfluoroalkyl substances and lipid profile in exposed pregnant women in the Veneto region, Italy, *Ecotoxicol. Environ. Saf.* 209 (2021), 111805, <https://doi.org/10.1016/j.ecoenv.2020.111805>.
- [14] Listing of POPs in the Stockholm Convention, (n.d.). <http://chm.pops.int/TheConvention/ThePOPs/AllPOPs/tabid/2509/Default.aspx> (accessed September 1, 2021).
- [15] D. Palma, D. Papagiannaki, M. Lai, R. Binetti, M. Sleiman, M. Minella, C. Richard, PFAS degradation in ultrapure and groundwater using non-thermal plasma, *Molecules*. 26 (2021), <https://doi.org/10.3390/molecules26040924>.

- [16] E.S.M. Mouele, J.O. Tijani, K.O. Badmus, O. Pereao, O. Babajide, O.O. Fatoba, C. Zhang, T. Shao, E. Sosnin, V. Tarasenko, K. Laatikainen, L.F. Petrik, A critical review on ozone and co-species, generation and reaction mechanisms in plasma induced by dielectric barrier discharge technologies for wastewater remediation, *J. Environ. Chem. Eng.* 9 (2021), <https://doi.org/10.1016/j.jece.2021.105758>.
- [17] M.J. Kirkpatrick, B.R. Locke, Hydrogen, oxygen, and hydrogen peroxide formation in aqueous phase pulsed corona electrical discharge, *Ind. Eng. Chem. Res.* 44 (2005) 4243–4248, <https://doi.org/10.1021/ie048807d>.
- [18] A. Mahyar, H. Miessner, S. Mueller, K.H. Hama Aziz, D. Kalass, D. Moeller, K. Kretschmer, S. Robles Manuel, J. Noack, Development and application of different non-thermal plasma reactors for the removal of perfluorosurfactants in water: a comparative study, *Plasma Chem. Plasma Process.* 39 (2019) 531–544, <https://doi.org/10.1007/s11090-019-09977-6>.
- [19] S. Garg, J. Wang, P. Kumar, V. Mishra, H. Arafat, R.S. Sharma, L.F. Dumée, Remediation of water from per-/poly-fluoroalkyl substances (PFAS) – challenges and perspectives, *J. Environ. Chem. Eng.* 9 (2021), 105784, <https://doi.org/10.1016/j.jece.2021.105784>.
- [20] G.R. Stratton, F. Dai, C.L. Bellona, T.M. Holsen, E.R.V. Dickenson, S. Mededovic Thagard, Plasma-based water treatment: efficient transformation of perfluoroalkyl substances in prepared solutions and contaminated groundwater, *Environ. Sci. Technol.* 51 (2017) 1643–1648, <https://doi.org/10.1021/acs.est.6b04215>.
- [21] A.J. Lewis, T. Joyce, M. Hadaya, F. Ebrahimi, I. Dragiev, N. Giardetti, J. Yang, G. Fridman, A. Rabinovich, A.A. Fridman, E.R. McKenzie, C.M. Sales, Rapid degradation of PFAS in aqueous solutions by reverse vortex flow gliding arc plasma, *Environ. Sci. Water Res. Technol.* 6 (2020) 1044–1057, <https://doi.org/10.1039/c9ew01050e>.
- [22] M. Russo, G. Iervolino, V. Vaiano, V. Palma, Non-thermal plasma coupled with catalyst for the degradation of water pollutants: a review, *Catalysts*. 10 (2020) 1438, <https://doi.org/10.3390/catal10121438>.
- [23] Y. Setsuhara, Low-temperature atmospheric-pressure plasma sources for plasma medicine, *Arch. Biochem. Biophys.* 605 (2016) 3–10, <https://doi.org/10.1016/j.abb.2016.04.009>.
- [24] K. Zhang, G. Zhang, X. Liu, A.N. Phan, K. Luo, A study on CO<sub>2</sub> decomposition to CO and O<sub>2</sub> by the combination of catalysis and dielectric-barrier discharges at low temperatures and ambient pressure, *Ind. Eng. Chem. Res.* 56 (2017) 3204–3216, <https://doi.org/10.1021/acs.iecr.6b04570>.
- [25] M. Magureanu, C. Bradu, V. Parvulescu, Plasma processes for the treatment of water contaminated with harmful organic compounds, *J. Phys. Appl. Phys.* 51 (2018), <https://doi.org/10.1088/1361-6463/aacd9c>.
- [26] M. Magureanu, D. Dobrin, C. Bradu, F. Gherendi, N.B. Mandache, V.I. Parvulescu, New evidence on the formation of oxidizing species in corona discharge in contact with liquid and their reactions with organic compounds, *Chemosphere*. 165 (2016) 507–514, <https://doi.org/10.1016/j.chemosphere.2016.09.073>.
- [27] G. Mouffok Redouane, F. Abdelmalek, N. Benderdouche, A. Addou, Enhancement of the bleaching and degradation of textile wastewaters by gliding arc discharge plasma in the presence of TiO<sub>2</sub> catalyst, *J. Hazard. Mater.* 164 (2008) 1266–1274, <https://doi.org/10.1016/j.jhazmat.2008.09.060>.
- [28] M.Y. Naz, S. Shukrullah, S.U. Rehman, Y. Khan, A.A. Al-Arainy, R. Meer, Optical characterization of non-thermal plasma jet energy carriers for effective catalytic processing of industrial wastewaters, *Sci. Rep.* 11 (2021) 2896, <https://doi.org/10.1038/s41598-021-82019-4>.
- [29] P. Nian, L. Peng, J. Feng, X. Han, B. Cui, S. Lu, J. Zhang, Q. Liu, A. Zhang, Aqueous methylparaben degradation by dielectric barrier discharge induced non-thermal plasma combined with ZnO-rGO nanosheets, *Sep. Purif. Technol.* 211 (2019) 832–842, <https://doi.org/10.1016/j.seppur.2018.10.048>.
- [30] J. Feng, P. Nian, L. Peng, A. Zhang, Y. Sun, Degradation of aqueous methylparaben by non-thermal plasma combined with ZnFe<sub>2</sub>O<sub>4</sub>-rGO nanocomposites: performance, multi-catalytic mechanism, influencing factors and degradation pathways, *Chemosphere*. 271 (2021), 129575, <https://doi.org/10.1016/j.chemosphere.2021.129575>.
- [31] M. Marković, M. Jović, D. Stanković, V. Kovačević, G. Roglić, G. Gojčić-Cvijović, D. Manojlović, Application of non-thermal plasma reactor and Fenton reaction for degradation of ibuprofen, *Sci. Total Environ.* 505 (2015) 1148–1155, <https://doi.org/10.1016/j.scitotenv.2014.11.017>.
- [32] N. Korichi, O. Aubry, H. Rabat, B. Cagnon, D. Hong, Paracetamol degradation by catalyst enhanced non-thermal plasma process for a drastic increase in the mineralization rate, *Catalysts*. 10 (2020) 959, <https://doi.org/10.3390/catal10090959>.
- [33] M.A. Malik, Water purification by plasmas: which reactors are most energy efficient? *Plasma Chem. Plasma Process.* 30 (2010) 21–31, <https://doi.org/10.1007/s11090-009-9202-2>.
- [34] M. Faraday, *Experimental Researches in Electricity: Reprinted from the Philosophical Transactions of 1831-1843, 1846-1852, R. and J.E. Taylor, 1839.*
- [35] W.H. Rodebush, M.H. Wahl, The reactions of the hydroxyl radical in the electrodeless discharge in water vapor, *J. Chem. Phys.* 1 (1933) 696–702, <https://doi.org/10.1063/1.1749229>.
- [36] M. Tezuka, Anodic hydrogen evolution in contact glow-discharge electrolysis of sulfuric acid solution, *Denki Kagaku*. 61 (1993) 794–795, <https://doi.org/10.5796/electrochemistry.61.794>.
- [37] C. Js, H. A., S. M., S. B., Non-uniform pulse discharge-induced radical production in distilled water, *J. Electrostat.* 43 (1998) 115–126.
- [38] S.B. Gupta, H. Bluhm, The potential of pulsed underwater streamer discharges as a disinfection technique, *IEEE Trans. Plasma Sci.* 36 (2008) 1621–1632, <https://doi.org/10.1109/TPS.2008.2001231>.
- [39] R.P. Joshi, S.M. Thagard, Streamer-like electrical discharges in water: part II. Environmental applications, *Plasma Chem. Plasma Process.* 33 (2013) 17–49, <https://doi.org/10.1007/s11090-013-9436-x>.
- [40] T. Namihira, S. Sakai, T. Yamaguchi, K. Yamamoto, C. Yamada, T. Kiyan, T. Sakugawa, S. Katsuki, H. Akiyama, Electron temperature and electron density of underwater pulsed discharge plasma produced by solid-state pulsed-power generator, *IEEE Trans. Plasma Sci.* 35 (2007) 614–618, <https://doi.org/10.1109/TPS.2007.896965>.
- [41] K. Shih, B. Locke, Optical and electrical diagnostics of the effects of conductivity on liquid phase electrical discharge, *IEEE Trans. Plasma Sci.* (2011). 10.1109/TPS.2010.2098052.
- [42] B.H.J. Bielski, D.E. Cabelli, R.L. Arudi, A.B. Ross, Reactivity of HO<sub>2</sub>/O<sup>-</sup> radicals in aqueous solution, *J. Phys. Chem. Ref. Data*. 14 (1985) 1041–1100, <https://doi.org/10.1063/1.555739>.
- [43] Johannes Staehelin, Juerg Hoigne, Decomposition of ozone in water: rate of initiation by hydroxide ions and hydrogen peroxide, *Environ. Sci. Technol.* 16 (1982) 676–681, <https://doi.org/10.1021/es00104a009>.
- [44] P. Lukes, E. Dolezalova, I. Sisrova, M. Clupek, Aqueous-phase chemistry and bactericidal effects from an air discharge plasma in contact with water: evidence for the formation of peroxyxynitrite through a pseudo-second-order post-discharge reaction of H<sub>2</sub>O<sub>2</sub> and HNO<sub>2</sub>, *Plasma Sources Sci. Technol.* 23 (2014), 015019, <https://doi.org/10.1088/0963-0252/23/1/015019>.
- [45] D. Vione, M. Minella, V. Maurino, C. Minero, Indirect Photochemistry in sunlight surface waters: photoinduced production of reactive transient species, *Chem. – Eur. J.* 20 (2014) 10590–10606, <https://doi.org/10.1002/chem.201400413>.
- [46] V. Jovicic, M.J. Khan, A. Zbogar-Rasic, N. Fedorova, A. Poser, P. Swoboda, A. Delgado, Degradation of low concentrated perfluorinated compounds (PFCs) from water samples using non-thermal atmospheric plasma (NTAP), *Energies*. 11 (2018) 1290, <https://doi.org/10.3390/en11051290>.
- [47] R.G.T. Kalavendan, A. Mishra, G. Eazhumalai, U.S. Annappure, Effect of atmospheric pressure non-thermal pin to plate plasma on the functional, rheological, thermal, and morphological properties of mango seed kernel starch, *Int. J. Biol. Macromol.* 196 (2022) 63–71, <https://doi.org/10.1016/j.ijbiomac.2021.12.013>.
- [48] A.L. Vieira Cubas, M. de M. Machado, J.R. dos Santos, J.J. Zanco, D.H. Baggio Ribeiro, A.S. Andre, N.A. Debacher, E.H. Siegel Moecke, Effect of chemical species generated by different geometries of air and argon non-thermal plasma reactors on bacteria inactivation in water, *Sep. Purif. Technol.* 222 (2019) 68–74, <https://doi.org/10.1016/j.seppur.2019.03.057>.
- [49] N. Korichi, O. Aubry, H. Rabat, B. Cagnon, D. Hong, Paracetamol degradation by catalyst enhanced non-thermal plasma process for a drastic increase in the mineralization rate, *Catalysts*. 10 (2020) 959, <https://doi.org/10.3390/catal10090959>.
- [50] M. Saleem, O. Biondo, G. Sretenović, G. Tomei, M. Magarotto, D. Pavarin, E. Marotta, C. Paradisi, Comparative performance assessment of plasma reactors for the treatment of PFOA: reactor design, kinetics, mineralization and energy yield, *Chem. Eng. J.* 382 (2020), 123031, <https://doi.org/10.1016/j.cej.2019.123031>.
- [51] N. Bolouki, W.-H. Kuan, Y.-Y. Huang, J.-H. Hsieh, Characterizations of a plasma-water system generated by repetitive microsecond pulsed discharge with air, nitrogen, oxygen, and argon gases species, *Appl. Sci. Switz.* 11 (2021), <https://doi.org/10.3390/app11136158>.
- [52] Y. Liu, H. Zhang, J. Sun, J. Liu, X. Shen, J. Zhan, A. Zhang, S. Ognier, S. Cavadias, P. Li, Degradation of aniline in aqueous solution using non-thermal plasma generated in microbubbles, *Chem. Eng. J.* 345 (2018) 679–687, <https://doi.org/10.1016/j.cej.2018.01.057>.
- [53] P. Rumbach, D.M. Bartels, R.M. Sankaran, D.B. Go, The solvation of electrons by an atmospheric-pressure plasma, *Nat. Commun.* 6 (2015) 7248, <https://doi.org/10.1038/ncomms8248>.
- [54] J.A. Leenheer, J.-P. Croué, Peer reviewed: characterizing aquatic dissolved organic matter, *Environ. Sci. Technol.* 37 (2003) 18A–26A, <https://doi.org/10.1021/es032333c>.
- [55] P.L. Brezonik, J. Fulkerson-Brekken, Nitrate-induced photolysis in natural waters: controls on concentrations of hydroxyl radical photo-intermediates by natural scavenging agents, *Environ. Sci. Technol.* 32 (1998) 3004–3010, <https://doi.org/10.1021/es9802908>.
- [56] P. Westerhoff, G. Aiken, G. Amy, J. Debroux, Relationships between the structure of natural organic matter and its reactivity towards molecular ozone and hydroxyl radicals, *Water Res.* 33 (1999) 2265–2276, [https://doi.org/10.1016/S0043-1354\(98\)00447-3](https://doi.org/10.1016/S0043-1354(98)00447-3).
- [57] R.G. Zepp, Juerg Hoigne, Heinz Bader, Nitrate-induced photooxidation of trace organic chemicals in water, *Environ. Sci. Technol.* 21 (1987) 443–450, <https://doi.org/10.1021/es00159a004>.
- [58] J.V. Goldstone, M.J. Pullin, S. Bertilsson, B.M. Voelker, Reactions of hydroxyl radical with humic substances: bleaching, mineralization, and production of bioavailable carbon substrates, *Environ. Sci. Technol.* 36 (2002) 364–372, <https://doi.org/10.1021/es010964e>.
- [59] Y. Li, G. Qu, L. Zhang, T. Wang, Q. Sun, D. Liang, S. Hu, Humic acid removal from micro-polluted source water using gas phase surface discharge plasma at different grounding modes, *Sep. Purif. Technol.* 180 (2017) 36–43, <https://doi.org/10.1016/j.seppur.2017.02.046>.
- [60] Y. Cui, J. Yu, M. Su, Z. Jia, T. Liu, G. Oinuma, T. Yamauchi, Humic acid removal by gas-liquid interface discharge plasma: performance, mechanism and comparison to ozonation, *Environ. Sci. Water Res. Technol.* 5 (2019) 152–160, <https://doi.org/10.1039/c8ew00520f>.

- [61] X.-F. Zhou, J.-P. Liang, Z.-L. Zhao, H. Yuan, J.-J. Qiao, Q.-N. Xu, H.-L. Wang, W.-C. Wang, D.-Z. Yang, Ultra-high synergetic intensity for humic acid removal by coupling bubble discharge with activated carbon, *J. Hazard. Mater.* 403 (2021), 123626, <https://doi.org/10.1016/j.jhazmat.2020.123626>.
- [62] H. Zhang, Q. Huang, Z. Ke, L. Yang, X. Wang, Z. Yu, Degradation of microcystin-LR in water by glow discharge plasma oxidation at the gas-solution interface and its safety evaluation, *Water Res.* 46 (2012) 6554–6562, <https://doi.org/10.1016/j.watres.2012.09.041>.
- [63] T. Wang, G. Qu, X. Yin, Q. Sun, D. Liang, X. Guo, H. Jia, Dimethyl phthalate elimination from micro-polluted source water by surface discharge plasma: performance, active species roles and mechanisms, *J. Hazard. Mater.* 357 (2018) 279–288, <https://doi.org/10.1016/j.jhazmat.2018.06.014>.
- [64] T. An, Y. Gao, G. Li, P.V. Kamat, J. Peller, M.V. Joyce, Kinetics and mechanism of •OH mediated degradation of dimethyl phthalate in aqueous solution: experimental and theoretical studies, *Environ. Sci. Technol.* 48 (2014) 641–648, <https://doi.org/10.1021/es404453v>.
- [65] M. Saleem, O. Biondo, G. Sretenović, G. Tomei, M. Magarotto, D. Pavarin, E. Marotta, C. Paradisi, Comparative performance assessment of plasma reactors for the treatment of PFOA; reactor design, kinetics, mineralization and energy yield, *Chem. Eng. J.* 382 (2020), 123031, <https://doi.org/10.1016/j.cej.2019.123031>.
- [66] J. Fan, H. Wu, R. Liu, L. Meng, Z. Fang, F. Liu, Y. Xu, Non-thermal plasma combined with zeolites to remove ammonia nitrogen from wastewater, *J. Hazard. Mater.* 401 (2021), <https://doi.org/10.1016/j.jhazmat.2020.123627>.
- [67] R.K. Singh, L. Philip, S. Ramanujam, Rapid degradation, mineralization and detoxification of pharmaceutically active compounds in aqueous solution during pulsed corona discharge treatment, *Water Res.* 121 (2017) 20–36, <https://doi.org/10.1016/j.watres.2017.05.006>.
- [68] S. Tang, D. Yuan, Y. Rao, N. Li, J. Qi, T. Cheng, Z. Sun, J. Gu, H. Huang, Persulfate activation in gas phase surface discharge plasma for synergetic removal of antibiotic in water, *Chem. Eng. J.* 337 (2018) 446–454, <https://doi.org/10.1016/j.cej.2017.12.117>.
- [69] M. Magureanu, D. Piroi, N.B. Mandache, V. David, A. Medvedovici, C. Bradu, V. I. Parvulescu, Degradation of antibiotics in water by non-thermal plasma treatment, *Water Res.* 45 (2011) 3407–3416, <https://doi.org/10.1016/j.watres.2011.03.057>.
- [70] G. Iervolino, V. Vaiano, V. Palma, Enhanced removal of water pollutants by dielectric barrier discharge non-thermal plasma reactor, *Sep. Purif. Technol.* 215 (2019) 155–162, <https://doi.org/10.1016/j.seppur.2019.01.007>.
- [71] G. Iervolino, V. Vaiano, G. Pepe, P. Campiglia, V. Palma, Degradation of acid orange 7 azo dye in aqueous solution by a catalytic-assisted, non-thermal plasma process, *Catalysts*. 10 (2020) 1–18, <https://doi.org/10.3390/catal10080888>.
- [72] S. Ma, S. Lee, K. Kim, J. Im, H. Jeon, Purification of organic pollutants in cationic thiazine and azo dye solutions using plasma-based advanced oxidation process via submerged multi-hole dielectric barrier discharge, *Sep. Purif. Technol.* 255 (2021), <https://doi.org/10.1016/j.seppur.2020.117715>.
- [73] K. Ma, L. Zhou, Y. Bai, Y. Xin, M. Chen, H. Li, C. Bao, Y. Zhou, Degradation and mechanism analysis of chloroxylenol in aqueous solution by gas-liquid discharge plasma combined with ozonation, *RSC Adv.* 11 (2021) 12907–12914, <https://doi.org/10.1039/d1ra01886h>.
- [74] T. Lee, U. Park, P. Puligundla, C. Mok, Corona discharge plasma-based degradation of simulated residual linear alkylbenzene sulphonate and dodecyl benzene sulphonate surfactants, *Int. J. Environ. Sci. Technol.* 17 (2020) 1171–1178, <https://doi.org/10.1007/s13762-019-02534-w>.
- [75] T. Mitrovic, S. Lazovic, B. Nastasijevic, I.A. Pasti, V. Vasic, T. Lazarevic-Pasti, Non-thermal plasma needle as an effective tool in dimethoate removal from water, *J. Environ. Manag.* 246 (2019) 63–70, <https://doi.org/10.1016/j.jenvman.2019.05.143>.
- [76] A. Giardina, F. Tampieri, O. Biondo, E. Marotta, C. Paradisi, Air non-thermal plasma treatment of the herbicides mesotrione and metolachlor in water, *Chem. Eng. J.* 372 (2019) 171–180, <https://doi.org/10.1016/j.cej.2019.04.098>.
- [77] N. Wardenier, Y. Gorbanev, I. Van Moer, A. Nikiforov, S.W.H. Van Hulle, P. Surmont, F. Lynen, C. Leys, A. Bogaerts, P. Vanraes, Removal of alachlor in water by non-thermal plasma: reactive species and pathways in batch and continuous process, *Water Res.* 161 (2019) 549–559, <https://doi.org/10.1016/j.watres.2019.06.022>.
- [78] P.M.K. Reddy, S. Mahammadunnisa, C. Subrahmanyam, Catalytic non-thermal plasma reactor for mineralization of endosulfan in aqueous medium: a green approach for the treatment of pesticide contaminated water, *Chem. Eng. J.* 238 (2014) 157–163, <https://doi.org/10.1016/j.cej.2013.08.087>.
- [79] N. Wardenier, P. Vanraes, A. Nikiforov, S.W.H. Van Hulle, C. Leys, Removal of micropollutants from water in a continuous-flow electrical discharge reactor, *J. Hazard. Mater.* 362 (2019) 238–245, <https://doi.org/10.1016/j.jhazmat.2018.08.095>.
- [80] A. Barjasteh, Z. Dehghani, P. Lamichhane, N. Kaushik, E.H. Choi, N.K. Kaushik, Recent progress in applications of non-thermal plasma for water purification, bio-sterilization, and decontamination, *Appl. Sci. Switz.* 11 (2021), <https://doi.org/10.3390/app11083372>.
- [81] T. Czapka, I. Maliszewska, J. Olesiak-Banska, Influence of atmospheric pressure non-thermal plasma on inactivation of biofilm cells, *Plasma Chem. Plasma Process.* 38 (2018) 1181–1197, <https://doi.org/10.1007/s11090-018-9925-z>.
- [82] D.C. Johnson, J.P. Bzdek, C.R. Fahrenbruck, J.C. Chandler, B. Bisha, L. D. Goodridge, B.M. Hybertson, An innovative non-thermal plasma reactor to eliminate microorganisms in water, *Desalination Water Treat.* 57 (2016) 8097–8108, <https://doi.org/10.1080/19443994.2015.1024752>.
- [83] G.R. Stratton, C.L. Bellona, F. Dai, T.M. Holsen, S.M. Thagard, Plasma-based water treatment: conception and application of a new general principle for reactor design, *Chem. Eng. J.* 273 (2015) 543–550, <https://doi.org/10.1016/j.cej.2015.03.059>.
- [84] C. Nau-Hix, N. Multari, R.K. Singh, S. Richardson, P. Kulkarni, R.H. Anderson, T. M. Holsen, S.M. Thagard, Field demonstration of a pilot-scale plasma reactor for the rapid removal of poly- and perfluoroalkyl substances in groundwater, *ACS Est Water.* 1 (2021) 680–687, <https://doi.org/10.1021/acsestwater.0c00170>.
- [85] R.K. Singh, E. Brown, S. Mededovic Thagard, T.M. Holsen, Treatment of PFAS-containing landfill leachate using an enhanced contact plasma reactor, *J. Hazard. Mater.* 408 (2021), <https://doi.org/10.1016/j.jhazmat.2020.124452>.
- [86] R.K. Singh, N. Multari, C. Nau-Hix, R.H. Anderson, S.D. Richardson, T.M. Holsen, S. Mededovic Thagard, Rapid removal of poly- and perfluorinated compounds from investigation-derived waste (IDW) in a pilot-scale plasma reactor, *Environ. Sci. Technol.* 53 (2019) 11375–11382, <https://doi.org/10.1021/acs.est.9b02964>.
- [87] R.K. Singh, S. Fernando, S.F. Baygi, N. Multari, S.M. Thagard, T.M. Holsen, Breakdown products from perfluorinated alkyl substances (PFAS) degradation in a plasma-based water treatment process, *Environ. Sci. Technol.* 53 (2019) 2731–2738, <https://doi.org/10.1021/acs.est.8b07031>.
- [88] K.H.H. Aziz, H. Miessner, A. Mahyar, S. Mueller, D. Moeller, F. Mustafa, K. M. Omer, Degradation of perfluorosurfactant in aqueous solution using non-thermal plasma generated by nano-second pulse corona discharge reactor, *Arab. J. Chem.* 14 (2021), 103366, <https://doi.org/10.1016/j.arabj.2021.103366>.
- [89] J.R. Groele, N. Sculley, T.M. Olson, J.E. Foster, An investigation of plasma-driven decomposition of per- and polyfluoroalkyl substances (PFAS) in raw contaminated ground water, *J. Appl. Phys.* 130 (2021), <https://doi.org/10.1063/5.0039264>.
- [90] Flowrox - Plasma Water Treatment Technology Overview, Flowrox. (n.d.). <https://flowrox.com/article/plasma-water-treatment/> (accessed October 14, 2021).
- [91] PlasmaLeap Technologies - Water Treatment, PlasmaLeap. (n.d.). <https://www.plasmaleap.com/water-treatment> (accessed October 14, 2021).
- [92] T. Zhang, R. Zhou, P. Wang, A. Mai-Prochnow, R. McConchie, W. Li, R. Zhou, E. W. Thompson, K. (Ken) Ostrikov, P.J. Cullen, Degradation of cefixime antibiotic in water by atmospheric plasma bubbles: performance, degradation pathways and toxicity evaluation, *Chem. Eng. J.* 421 (2021), 127730, <https://doi.org/10.1016/j.cej.2020.127730>.
- [93] Wapulec - advanced oxidation technology of water treatment using pulsed corona discharge plasma, (n.d.). <http://www.wapulec.com/index.html> (accessed October 14, 2021).
- [94] D.B. Miklos, C. Remy, M. Jekel, K.G. Linden, J.E. Drewes, U. Hübner, Evaluation of advanced oxidation processes for water and wastewater treatment - a critical review, *Water Res.* 139 (2018) 118–131, <https://doi.org/10.1016/j.watres.2018.03.042>.