Effectiveness of Non-Thermal Plasma Induced Degradation of Per- and Polyfluoroalkyl Substances from Water

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Abstract: Per- and polyfluoroalkyl substances (PFAS) are omnipresent synthetic chemicals. Due to their industrial importance and widespread use as a key component in various applications and a variety of products, these compounds can be found today in high concentrations (>1 µg/L) in surface and groundwater but also spread throughout the ecosystem, where they represent a serious threat to most living organisms. The removal or degradation of PFAS contaminants from water and soil is becoming a legal obligation in a growing number of countries around the globe. This, however, demands novel techniques for the degradation of PFAS since conventional water treatment techniques are either insufficient or extremely expensive due to the persistent nature of these compounds caused by their extraordinary chemical stability. The goal of this work was therefore to investigate the practical potential of the application-oriented use of atmospheric non-thermal plasma as a powerful advanced oxidation method for the purification of water contaminated with PFAS compounds. Special attention was devoted to the development of the concept that can be scaled up to the capacity level of approximately 100–200 m³ of water per hour, contaminated with PFAS and other contaminants including organic and inorganic material generally present in soil, and surface or groundwater. Our major research interest was to define the minimum required treatment time for optimal purification results, as well as to understand the influence of the initial concentration of PFAS in water and the potential presence of co-contaminants often present in situ on the efficiency of the degradation process. A chemical analysis of the treated samples demonstrated the ability of the atmospheric plasma to reduce more than 50% of the initial PFAS amount in the water samples in less than 300 s of treatment time. PFOA, however, showed more rigidity towards degradation, where a double treatment time was needed to reach similar degradation levels. The obtained results showed that the initial concentration level does not play a major role in the process. However, the PFAS degradation profiles for all tested concentrations show a strongly nonlinear behavior with time, characterized by the fast decrease of the process efficiency in the case of longer treatment times. For prolonged treatment times, a constant increase in the samples’ conductivity was measured, which might be the limiting factor for the degradation rate in the case of prolonged treatment times.

Keywords: non-thermal plasma; atmospheric plasma; electrical discharge; per-and polyfluoroalkyl substances; perfluorinated compounds; water treatment

1. Introduction

The synthetic chemicals PFAS were introduced in 1940, when USA company 3M developed a process to synthetize PFAS on a commercial level for different product applications, e.g., firefighting foams, paints, textiles, paper, etc. [1]. These long-chain organofluoride chemicals with a general formula F-(CF₂)n-R, include multiple carbon—fluorine
These are some of the strongest covalent bonds known in organic chemistry ($\Delta H = 450$ kJ/mol) [2]. The acronym PFAS covers over 6000 long- and short-chain organofluoride compounds having different chemical and physical properties and molecular weights but sharing common perfluoroalkyl moieties [3,4]. Perfluorooctanoic acid (PFOA) and perfluoroctane sulfonate (PFOS) are currently the most common PFAS contaminants detected in the environment. Both are classified as long-chain PFAS since they comprise, in the case of PFOA, a seven-carbon backbone that terminates with the carboxylate functional group ($\text{C}_7\text{F}_{15}\text{COOH}$) and, in the case of PFOS, an eight-carbon backbone that terminates with the sulfonate functional group ($\text{C}_8\text{F}_{17}\text{SO}_3\text{H}$) [5,6]. Due to the environmental impact of PFAS and their negative effects on human health, their further production was strongly disputed and since early 2000 the use of long-chain PFAS started phasing out. In most applications, the place of long-chain PFAS has now been taken over by short-chain PFAS [7]. Short-chain PFAS alternatives possess a similar structure to long-chain PFAS but one or more of the alkylether group are added into their short chains [8]. Apart from their production on a commercial scale, the degradation of long-chain PFAS also significantly contributes to their concentration in the environment. In addition, precursors such as perfluoroalkyl acids (PFAAs), bio-transform to PFOS and such precursors are being used as building blocks for different commercial products [9].

A closer look at the PFAS molecule reveals that it is composed of a hydrophobic C–F backbone attached to a hydrophilic functional group. Due to the high electronegativity of fluorine, the C–F bond is strongly polarized with the shared electrons on average closer to fluorine atoms. This contributes to the special physical properties of the PFAS such as their oleophobic and hydrophobic nature, non-wettability, high surface activity, high chemical, and thermal stability, etc. [10,11]. On the one hand, these extraordinary physical and chemical properties of PFAS compounds resulted in high demand and extensive industrial uses for the manufacturing of various products such as cookware, food packaging, stain and water-resistant fabrics, carpets, cleaning products, etc. On the other hand, these same properties initiate serious environmental concerns due to their persistent nature with long half-lives as well as the effects they have on human health.

As could be expected, after several decades of intensive use and inappropriate disposal, most of the PFAS ended up in ground or seawater as the main environmental sink for all biologically non-degradable compounds. This ensured their current omnipresence around the globe, affecting our ecosystem everywhere. It is reported that generally, among all the PFAS contaminants of European groundwater, PFOA and PFOS are the major ones, with maximum reported shares reaching up to 66% and 48%, respectively [12]. Together with water, food such as fish, meat, eggs, and dairy products, are the major direct exposure pathways to PFAS for humans. The exposure to PFAS by humans leads to serious health concerns as was first noticed in 1961. [13] Since then, firm evidences have been introduced relating PFAS to serious health issues such as increased uric acid levels, reduced female fertility and sperm quality, pregnancy-related difficulties, birth defects, etc. [14]. Adverse effects such as the malfunctioning of the human immune system, metabolic dysfunction, and increased cancer rates were also reported [14,15]. Reported links between PFAS exposure and health were used to argue the need to limit or cease production of these chemicals. However, their wide use in a variety of products makes an immediate ban impractical. Consequently, a number of advisories and laws for both drinking and groundwater have been issued by health regulation authorities and disease control centers in different regions of the world [16–20]. In Germany and the European Union, for example, this level has been set at 0.10 $\mu$g/L for individual PFAS and 0.5 $\mu$g/L for combined PFAS [21]. In the USA, the health advisory for PFOA + PFOS set by the Environmental Protection Agency (EPA) is 70 ng/L [22].

Today, reaching permissible concentrations is a major challenge for conventional water-treatment technologies due to their limited effectiveness and the high costs involved in the removal/degradation of PFAS molecules. Traditional advanced oxidation processes (AOPs) that generate abundant amounts of $^\bullet$OH radicals and are widely used in water
treatment processes are mostly ineffective when it comes to strong C–F bonds and PFAS removal. The presence of inorganic ions or natural organic matter in groundwater additionally reduces the effectiveness of AOPs [23]. Alternative techniques recently reported in the literature include adsorptive materials (e.g., minerals, biomaterials, polymers, ion exchange resins, etc.), bioremediation, electrocoagulation, foam fractionation, sonolysis, photocatalysis, mechanochemical and electrochemical degradation, beams of electrons, etc. [24,25]. Among the major challenges, the complex operation, limited efficiencies, selectivity for different PFAS, and the release of toxic byproducts, are most commonly reported in connection with the alternative technologies.

Currently, the most widely used PFAS removal approach on the industrial scale is the ex situ adsorption on activated carbon. The extreme operational costs of this technology are related to the high costs for the activated carbon and its later incineration in the special facilities equipped with the systems for the chemical treatment of the combustion products (exhaust gas purification). The less frequently applied conventional alternatives to this technology are adsorption on ion-exchange resins [26], reverse osmosis, and nano-filtration [27]. Their use is commonly related to PFAS removal from groundwater. Taken with a certain reserve, common for all existing technologies in practical use today are high operational costs, a need for post treatments, and/or efficiency limitations due to the presence of co-contaminants. This indicates that there is a need and a large market for an alternative method that would partially reduce operating costs and increase the efficiency of the PFAS degradation process.

In this sense, non-thermal plasma (NTP)-assisted PFAS degradation is one of the interesting alternatives, capable of the in situ generation of high-energy species (e.g., radicals, reactive oxygen and nitrogen species, excited electrons and ions, and VUV and UV photons, etc.) for the direct degradation of the impurities present in water. The term “plasma” was introduced in 1929 by Irving Langmuir and defines the fourth state of matter, which is composed of ionized gas containing high-energy species. Those high-energy species enable the plasma to initiate chemical reactions or break strong chemical bonds, such as C–F or similar. One of the most general classifications distinguishes between a high-temperature or thermal (fusion) plasma and a non-thermal or low-temperature (gas discharges) plasma. In the case of thermal plasma, plasma gas reaches high temperatures of over 10,000 K at which time the electrons and bulk molecules are in a state of thermal equilibrium. Thermal plasma is commonly used in applications that require extensive heat generation, e.g., material processing, metal melting, welding, waste treatment, etc. [28–31]. In the case of non-thermal plasma, such an equilibrium is lacking as the bulk gas molecules have a far lower temperature than the electrons, thus resulting in the near-to-room temperature of the overall plasma.

Several researches on the non-thermal plasma treatment of PFAS-contaminated water are available, where PFAS were decomposed into less harmful products and, thus were eliminated from the environment. This approach is based on liquid-gas and liquid-phase reactions for which different reactor designs have been tested. The most recent overview of this topic was provided by Palma et al. [32].

The goal of this work was to investigate the practical potential of the application-oriented use of atmospheric non-thermal plasma as a powerful advanced oxidation method for the purification of water contaminated with PFAS compounds. Special attention was devoted to the development of a concept that can be scaled up to a capacity of approximately 100–200 m³ of water per hour, that has been contaminated with PFAS and other contaminants, including organic and inorganic material generally present in soil, or surface and ground water. Our major research interest was to define the minimum required treatment time for optimal purification results, as well as to understand the influence of the initial concentration of PFAS in water and the potential presence of co-contaminants often present in situ on the efficiency of the degradation process.
2. Materials and Methods

In the scope of this work, we investigated the effects of non-thermal plasma (NTP) treatment on distilled water samples mixed with a certain amount of PFAS to obtain different initial targeted concentrations of 0.1, 1.0, and 10.0 μg/L. Focus of the research was placed on the samples of distilled water mixed with PFOA, PFOS, and their mixture, as they are the most common PFAS contaminants in the environment. Analytical grade PFOA (99.99%) and PFOS (99.99%) were used in the research. All chemicals were purchased from Sigma Aldrich, Germany. Apart from the samples of distilled water selectively contaminated with controlled amounts of chemically pure PFOA and PFAS, tests were also conducted with samples of contaminated groundwater taken from one of the R&H Umwelt GmbH soil-sanitation sites in Bavaria in the south of Germany.

Results of the NTP treatment in terms of concentration changes of targeted contaminants and their degradation products were analyzed in detail using combined mass spectroscopy and liquid chromatography (MS-LC) methods according to the German standard DIN 38,407 F42. Temperature, conductivity, and pH value of the samples were also measured before and after the plasma treatment.

2.1. Experimental Setup

Experiments were conducted using a laboratory-size prototype of a reactor, as shown in Figure 1. The setup consists of three main sections: (i) non-thermal, high voltage (HV), direct current (DC) plasma generator, (ii) cubical reactor, where the plasma discharges are generated above the water surface, and (iii) measurement and control system with an air supply unit.

![Figure 1. Experimental setup designed and used for NTP treatment of PFAS compounds in water.](image)

The core of the system is the batch reactor, designed as a 300 mm × 100 mm × 100 mm cubical vessel made of Polymethyl methacrylate (PMMA). During operation, the reactor is filled with 750 mL of PFAS-contaminated water. A high-voltage (HV) electrode is made of stainless steel in the form of a comb with eleven 30 mm high pins facing toward the water’s surface. The distance between the HV electrode pins and the steady water surface was 14 mm. Second, a plate-form ground electrode made of stainless steel in rectangular form with dimensions of 200 mm × 50 mm × 2 mm was placed 12 mm below the water’s surface, providing a total distance of 26 mm between the HV and the ground electrode. In order to increase the water surface exposed to the plasma discharges during the operation, dry air was continuously introduced into the reactor below the plate electrode in the form of dense air bubble flow, generated by two 100 mm long aquarium air stones (diffusers) placed at the bottom of the reactor.

In the described configuration, the plasma discharges in the gas phase of the reactor were produced by a high-voltage direct current (HV-DC) generator (PNC 60000-10) [33], operating at a voltage of 12 kV and a maximum current of 5 mA. This corresponds to the average power in the operation of approximately 60 W. A fast high-voltage switch (HTS 361-01-C) [34] was used to convert HV-DC to the high-voltage pulsed direct current.
(HV-PDC) required for the plasma generation in the reactor. The mass flow controller (MFC) was used to keep the supply of airflow to the air stones at a constant flow rate of 20 L/min and a constant temperature of 15 °C.

The described configuration enabled plasma generation in the form of a gas discharge directly above the surface of the water. Since the targeted PFAS molecules, due to their strong surfactant nature, tend to concentrate on the water’s surface, this brings them directly in contact with plasma-generated reactive species in the gas phase. Some of the generated high-energy species also disperse inside the water, thus initiating a set of reactions leading to the degradation of PFAS on the surface from the water side.

2.2. Measurement Plan

Focus of the research was to determine and quantify the influence of certain process parameters (presence of air bubbles in water, polarity of the HV electrode, total test time, etc.) and sample properties (type and concentration of the contaminants, presence of co-contaminants, etc.) on the effectiveness of PFAS degradation. Measurements were, therefore, divided into three main groups of experiments as schematically shown in Figure 2.

![Figure 2. Organigram of experimental tests with NTP under the following test conditions: volume of the water sample: V = 0.75 L, power of the NTP generator: p = 60 W, voltage between electrodes: U = 12 kV, and the test times: t = 1, 5, 10, 30, and 60 min.](image)

The first set of experiments was conducted with distilled water with and without air bubbling. The aim of the investigation was to observe the change in the water's pH, conductivity, and temperature during the plasma treatment. The second set of experiments was designed to investigate the influence of the applied HV electrode polarity (positive or negative HV) on the efficiency of plasma treatment of contaminated water, using the azo dyes as the marker for the changes. Characterization of the process efficiency was done based on the measurements of the values of the transmission and the absorbance index of the azo dye samples and their color degradation.

Thirdly, and the main part of this investigation, a set of experiments was conducted to determine and quantify the effects of plasma treatment on the degradation of PFAS in the water samples with and without other co-contaminants. In the first part of these experiments, solutions of PFOA, PFOS, and a mixture of 50% PFOA + 50% in concentrations of 0.1, 1.0, and 10 µg/L, with strictly controlled sample purity and composition, were experimentally treated under predefined conditions (airflow, positive polarity, etc.). In analyzing the changes in the samples before and after the test, the process of PFAS degradation was observed without the influence and effects caused by the organic and inorganic impurities commonly present in the water samples from the soil-sanitation sites.
inorganic impurities commonly present in the water samples from the soil-sanitation sites. After the experiments were completed under the strictly controlled conditions regarding the water sample purity and composition, another set of experiments was conducted using the samples of groundwater taken directly from the soil-sanitation sites. These tests were conducted in order to get a rough estimation of the influences of impurities in the water samples on the process of PFAS degradation.

The pH values and temperatures during the tests were recorded with a pH meter device (QpH 70, VWR International GmbH, Darmstadt, Germany), whereas the conductivity was recorded using a conductivity meter set (Qcond 2200, VWR International, Darmstadt, Germany). For the transmission and absorbance index, a spectrometer, Spectronic 20 Genesys (Spectronic Unicam, Watertown, MA, USA), was used. The PFAS concentration after NTP was analyzed by combined liquid chromatography—mass spectroscopy (LC—MS), following the German Norm DIN 38,407 F42.

3. Results and Discussion

3.1. Effects of Forced Air Bubble Generation in the Water Samples

In the first set of experiments, distillate water was exposed to the NTP for different test times. In order to intensify mixing and increase the contact surface between a liquid and a gas phase within the reactor, air bubbles were generated at the bottom of the water tank below the lower NTP electrode. The goal of this set of experiments was to determine the effects of air bubble generation during the NTP treatment. Pure distillated water was used as a test sample in order to avoid the effects of the complex chemistry that takes place in the case of NTP treatment of contaminated water samples. The main parameters of interest in this set of measurements were the temperature of the water, its pH value, and its conductivity. These values were observed and recorded for different test intervals from 1 min to up to 60 min of treatment (Figure 3).

![Figure 3. Cont.](image-url)
The experiments revealed minor temperature changes of 1–2 °C during treatments shorter than 5 min. Longer exposure times result in further moderate increases in the water temperature. For the maximum tested treatment time of 60 min, the water temperature increased by 8–9 °C. The generation of air bubbles reduce temperature increases due to the cooling effect caused by the cold air bubbles. The measurement of the pH values revealed that due to the formation of nitrogen acids (Equation (1)), a significant reduction of the pH value of the treated water takes place already in the first 5 min of the experiment.

\[
\text{H}_2\text{O} + \text{N}_2 + \text{NO}_2 \rightarrow \text{HNO}_3 + \text{HNO}_2 \quad (1)
\]

In this time, the water’s pH value drops from initial pH = 7 to pH = 4.6. Longer treatment times of up to 60 min are related to a further, less-intensive decrease in pH values. The generation of air bubbles during the experiments limits further decreases in the pH value once it reaches a value of pH = 4. In the absence of air bubbles, this lower limit lies between pH = 2.5 and pH = 3.0. The main influence of the air bubble generation is, however, measurable in the case of water conductivity. In the first 5 min of treatment, the sample conductivities do not change significantly independently if the experiment is conducted with or without air bubbles in the water. Longer treatment times, on the other hand, lead to progressive increases in the sample conductivity, especially in the absence of air bubbles. The best illustration of the effect of air bubbles is visible after 60 min of treatment, where the conductivity of the water treated without air bubbles is 350% higher than the conductivity of the sample treated under the same conditions but with air bubbles in the water. Although all three diagrams in Figure 3 demonstrate the positive effects of the air bubble generation in the liquid phase, the most significant effect is the limitation in the increase in water conductivity during the treatment. As already indicated in the literature [35], a higher concentration of ions in water (i.e., higher electrical conductivity of the solution) reduces the contact area between the plasma species and the target molecules leading to decreased degradation rates. All further tests and results presented in this work are, therefore, provided for the tests where the air bubbles were continuously generated during the treatment time.

3.2. Effects of the Selected NTP Discharge Polarity and Type

The next point of interest relevant for the final design of this experimental set was the influence of the selected NTP discharge polarity and type on the properties of the water samples and the degradation of the targeted pollutant. In order to quantify these effects, four NTP discharge voltages were tested, namely pulsating and non-pulsating positive and negative DC. For the generation of the pulsating signals, an alternating signal of 60 Hz frequency was generated by the function generator and used as an input for the
fast high-voltage switch. The distillated water samples in this set of experiments were mixed with Procion Red MX-5B organic dye at a concentration of 0.001 g/L and treated for up to 60 min. In this phase, the use of dye instead of PFAS compounds as contaminants enabled detailed investigation with a large number of experiments due to the fast and cost-saving evaluation of the results in the case of the water samples contaminated with the dye.

The effect of NTP treatment generated by the pulsed and non-pulsed negative and positive polarity DC, on the degradation rate of the dye was observed and recorded through the change in the sample’s color. The temperature, pH, and conductivity values were also recorded, along with the absorption and the transmission values. In each experiment, air bubbles were generated below the lower electrode, according to the previous findings.

In general, there was no significant difference in the change of the water sample temperature and pH value during the test with regard to the tested discharge polarity (positive or negative) and type of discharge (pulsed or not). As for the effects of the tested parameters on the water conductivity, the experiments demonstrated certain advantages of the positive discharge voltage (Figure 4). This is especially noticeable in the comparison with the results of the negative and negative-pulsed discharge voltages where the water conductivity increased by 65% in comparison with the positive and positive-pulsed discharge voltages.

The measurements of the transmission and absorption coefficients of the water samples mixed with organic dye directly correlate to the efficiency of NTP in the degradation of the dye molecules. The transmission coefficient describes the amount of light that passes through the sample, thus corresponding to the clarity of the sample. The absorption coefficient corresponds to the amount of light that is absorbed by the sample, thus describing its opacity.

In the next step of the investigation, water samples mixed with the Procion Red MX-5B organic dye were exposed to the different NTP discharge voltage polarities (positive and negative DC) and types (pulsed and non-pulsating). The results indicate that the water samples exposed to the NTP produced by the non-pulsating positive DC, have the highest final levels of red dye degradation in comparison with the other test cases seen in Figure 5.
Since the positive, non-pulsing DC polarity of the generated NTP has demonstrated the best performance for the selected reactor geometry and concept, this type and polarity of NTP discharge voltage was selected for all further investigations presented in this work. However, the selection of the polarity and type of the NTP discharge voltage should be tested for each individual concept since there are certain indications in the literature (e.g., [36,37]), which identify a negative DC plasma discharge polarity as being more effective in certain cases of the degradation of the water treatment.

### 3.3. Effects of NTP Treatment of PFAS in Distilled Water

The core of this study was the investigation of the influence and effects of NTP on the degradation of PFAS compounds in groundwater samples. However, groundwater samples can be chemically complex mixtures contaminated with different PFAS compounds, but also containing a variety of other organic and inorganic compounds. The exposure of such a complex mixture to NTP leads to a large number of interactions that can take place between the present contaminants, their precursors, and other co-contaminants. In order to isolate the effects of NTP treatment to specific PFAS components, in the initial sets of experiments solutions with only specific contaminants in the distillated water were prepared in defined concentrations and exposed to NTP. In this way, the effects of the complex interactions between different contaminants were avoided in order to first understand the effects of NTP on selected contaminants of interest in this work (PFOA, PFOS, and their mixture).

For this purpose, three solutions containing PFOA, PFOS, and their (50%/50%) mixture, with concentrations of 0.1, 1.0, and 10.0 µg/L, respectively, were prepared using distillated water. A later analysis of the untreated samples showed that the actual concentrations of the pollutants were slightly offset from the targeted values. For the clarity of the presentation, we refer to those samples by their targeted concentrations throughout this work. The related results, however, are represented by the actual confirmed concentrations measured during the sample analysis. The generated PFAS solutions were exposed to NTP for different treatment times of 1, 5, 10, 30, and 60 min. In all the test cases and based on the previous findings, NTP was generated using the positive DC high voltage. Air bubbles were generated below the bottom electrode with an airflow of 20 L/min in order to intensify mixing and increase the gas/liquid contact surface area. The repeatability of the obtained results was determined in the set of five repeated experiments and the standard deviation was found to be below 10%.

In Section 3.4, the results of the second set of experiments are presented, where the groundwater samples and all their organic and inorganic contaminants, taken from the PFAS soil-sanitation site in central Bavaria, Germany, were treated in a lab using the NTP.
3.3.1. NTP Treatment of PFOA in Distillated Water

Due to the low concentrations of PFOA in the water of \( \leq 10 \, \mu\text{g/L} \), the obtained results for the temperature, pH value, and conductivity of the samples after the NTP treatment were quite similar to the results obtained for the distilled water (Figure 3). The minimum pH value of 3.5 was reached after 60 min of NTP treatment, i.e., the same as the maximum values of the water sample conductivities, which were in the range of 210–240 \( \mu\text{S/m} \).

The reduction rate of the PFOA concentration is not so strongly dependent on the initial PFOA concentration as much as on the NTP treatment duration. An overview of the results is given in Figure 6, where all three sets of measurements are shown in the same diagram. Since the initial concentrations span over two orders of magnitudes, in order to present the results in the same diagram two different resolutions of PFOA concentrations were used. The left y-axis covers the range of PFOA concentrations from 0 to 10 \( \mu\text{g/L} \) and corresponds to the results of the tests with an initial PFOA concentration of 10 \( \mu\text{g/L} \) (blue line). On the other hand, the right y-axis covers the range of PFOA concentrations from 0 to 1.0 \( \mu\text{g/L} \) and corresponds to the results of the tests with initial PFOA concentrations of 0.1 and 1.0 \( \mu\text{g/L} \) (red lines).

![Figure 6](image_url)

**Figure 6.** Degradation of PFOA as a function of the NTP treatment time for three different initial concentrations.

The results demonstrate the high level of efficiency of NTP treatment in the first ten minutes of treatment, independent of the initial PFOA concentration. It is important to note that the PFOA degradation rate is nonlinear and that more than 50% of the PFOA degradation takes place during the first ten minutes of the NTP treatment for all initial PFOA concentrations. After the first ten minutes, the degradation rate is reduced so that for a degradation of 70% of the initial values, the NTP treatment time needs to be 30 min and for a degradation level of 90% of the initial concentration of PFOA, the NTP treatment time rises to 60 min for all test cases.

3.3.2. NTP Treatment of PFOS in Distillated Water

As with the previously mentioned case, the initial concentrations of PFOS in the test samples were quite low for all test cases (\( \leq 10 \, \mu\text{g/L} \)). As a result, the measured temperature changes, pH values, and changes in the samples’ conductivities after NTP treatments, do not differ significantly from the results obtained with the pure distilled water (Figure 3). The minimum pH value of 3.9 was measured in the experiments with a PFOS degradation
after 60 min of NTP treatment. For the same test time, the maximum values of the water sample conductivities were in the range of 180–190 µS/m.

The measurements of the PFOS concentrations’ decrease over time (Figure 7), showed similar tendencies as in the case of the PFOA solutions (Figure 7). Under the same test conditions, however, NTP treatment results in a more efficient degradation of the PFOS compound in comparison with the degradation rates of the PFOA compound. For example, more than 85% of PFOS is degraded within the first 10 min of NTP treatment. In general, the efficiency of NTP treatment is on average 35% higher in the case of PFOS than PFOA contamination.

![Figure 7. Degradation of PFOS as a function of the NTP treatment time for three different initial concentrations.](image)

### 3.3.3. NTP Treatment of Mixed PFOA/PFOS in Distilled Water

The experiments demonstrated certain differences in the degradation rates of PFOA and PFOS due to their different responses to NTP treatment. In order to investigate the effects of NTP treatment in cases where both main PFAS pollutant compounds (PFOA and PFOS) are present in the solution another set of measurements was conducted. For this purpose, solutions with a mixture of PFOA and PFOS (50 mass% each) in distilled water were prepared in concentrations of 0.1, 1.0, and 10 mg/L and exposed to NTP. The treatment time was varied in the range from 1 to 60 min, as in the previous tests. The goal of this experiment was to determine the mutual influence of PFOA and PFOS on their degradation rates in the absence of other co-contaminants.

The temperatures, pH values, and conductivities of the PFOA/PFOS mixed solutions after the treatment did not vary significantly from the results obtained with the pure distilled water. The minimum recorded pH value of 3.7 was reached in the experiments after 60 min of NTP treatment. The maximum values of the water sample conductivities were in the range of 200–220 µS/m and were also reached after 60 min of treatment.

The results, summarized in Figure 6 for PFOA degradation and in Figure 7 for PFOS degradation, indicate the differences in the degradation rates of these two compounds under the same process conditions. It was, therefore, expected that the total concentration of the PFOA/PFOS mixture in the solution would decrease in accordance with the arithmetic middle line of the values from the separate PFOA and PFOS treatment tests.

However, the results of the tests summarized in Figure 8 indicate that the dynamics of the degradation of the PFOA/PFOS mixture during the NTP treatment are constrained by the presence of PFOA to a certain extent. The measured values for the final level of...
PFOA/PFOS concentrations for the different test times correspond to the results of the PFOA degradation summarized in Figure 6. For example, after a test time of 30 min, the total concentration of PFOA and PFOS compounds was reduced by around 70%, which corresponds to the results of the PFOA degradation after the same amount of time. This means that the overall degradation rate of a mixture of PFAS after NTP treatment depends on the concentration of the PFOA compound present in the test sample.

Figure 8. Degradation of PFOA and PFOS compounds in a solution of PFOA/PFOS mixture in distilled water as a function of the NTP treatment time for three different initial concentrations.

3.4. NTP Treatment of PFAS-Contaminated Groundwater Samples

The results of the NTP treatment of the distilled water solution with only two PFAS compounds demonstrate the importance and also the complexity of the internal chemical interactions between the compounds, their precursors, and the chemical species contained within the NTP. The influence of those interactions on the outcome of the NTP treatment, as previously shown, can be significant for the outcome of the NTP treatment. Considering the huge variety of potential organic and inorganic co-contaminants present in the real groundwater samples, it would be difficult to analyze the mutual interactions between each one of these compounds in the presence of highly ionized NTP. We have, therefore, focused on the determination of the general behavior of the real samples of contaminated groundwater. An additional set of experiments was conducted using the samples taken from the PFAS soil-sanitation site in central Bavaria, Germany. These samples were exposed to the NTP under the same conditions and for the same treatment times as the samples created by mixing the PFAS compounds with the distilled water.

Apart from the other organic and inorganic contaminants in the samples, the untreated groundwater sample analysis revealed a variety of different PFAS compounds as listed in Table 1.

Table 1. PFAS compounds contained in the groundwater sample from the sanitation site.

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Acronym</th>
<th>Concentration [µg/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfluorooctanesulfonic acid</td>
<td>PFOS</td>
<td>0.350</td>
</tr>
<tr>
<td>Perfluorooctanoic acid</td>
<td>PFOA</td>
<td>0.011</td>
</tr>
<tr>
<td>Perfluorohexanesulfonic acid</td>
<td>PFHxS</td>
<td>0.091</td>
</tr>
<tr>
<td>Perfluorohexanoic acid</td>
<td>PFHxA</td>
<td>0.026</td>
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<td>PFBA</td>
<td>0.011</td>
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<tr>
<td>Perfluoropentanoic acid</td>
<td>PFPeA</td>
<td>0.031</td>
</tr>
<tr>
<td><strong>Total:</strong></td>
<td><strong>PFAS</strong></td>
<td><strong>0.520</strong></td>
</tr>
</tbody>
</table>
A low total concentration of PFAS in the groundwater sample is typical for the process
of the sanitation of PFAS-contaminated soil. In this process, large amounts of clean water
(in average 200 m³/h) are used to wash out the PFAS contaminants from the soil. Due to the
large amount of water used in this process, the average concentration of PFAS compounds
in the water at the end of this stage is rather low. However, in the next step of the process,
this low-concentration PFAS mixture must be degraded or separated from the water, e.g.,
in active carbon filters, which then have to be incinerated in special facilities equipped with
chemical exhaust gas-cleaning systems.

In the case of the groundwater sample used in this work, the dominant PFAS com-
 pound is PFOS. With an initial concentration of 0.350 µg/L, it contributes more than 67% of
the total PFAS contamination of the sample. On the other hand, the concentration of PFOA
in the water samples from the soil-sanitation site is quite low and at 0.011 µg/L it is just
slightly above the detection limit of the measurement system (0.010 µg/L).

The described groundwater samples were treated with NTP for different test times
of up to 60 min, as with the samples in the previous experiments. The obtained results
revealed significant differences in the behavior of the ground water sample and the solu-
tions of distillated water contaminated with PFOA and/or PFOS compounds. The only
similar results were slight linear temperature increases of 9 °C within the 60 min test time,
which corresponds to all previous cases. On the other hand, the effects on the pH value
(Figure 9) of the test sample and its conductivity after the NTP treatment show significantly
different trends.

![Figure 9. Dependency of the pH value of the groundwater sample during NTP treatment on the
treatment time.](image)

The change in the pH value of the groundwater sample during NTP treatment indicates
a completely opposite trend than was observed in the previous tests with the PFOA and/or
PFOS solutions in the distillated water and pure distillated water (Figure 3b). Starting from
the initial pH value of 7.7, NTP treatment of the groundwater sample leads to an increase in
the pH value, probably due to the presence of calcium and potassium in the sample, which
generates basic products. Although this increase is not significant (maximum pH value
reached almost 8.6), it is the first test case of NTP water treatment where the pH value
tends to increase. It should be noted that the behavior of the pH value during the NTP
treatment depends not only on the selected test time but also on the specific composition
and concentrations of compounds found in the groundwater samples at the specific site.

The changes in the sample conductivity during the NTP treatment is also significantly
different from the results of the previous tests presented in Figure 3c. Since in this case
the water sample is not based on the distillated water, the conductivity has a certain initial
value, which is two orders of magnitude higher than in the case of the samples based on the
distilled water. Furthermore, all previously tested samples show a linear increase in water conductivity over time. This corresponds to the conductivity increase of 150–250 μS/m within the 60 min test, similar to the case of the bubble-assisted NTP treatment in Figure 3c. Due to the higher level of the chemical complexity of the groundwater sample, it also shows more complex changes in the conductivity over time (Figure 10).

On the other hand, this change took place within the narrow range of only 30 μS/m in 60 min of treatment. It is assumed that this behavior is related to the conversion of higher mobility and molar conductivity ions (H⁺ and OH⁻) [38] to basic compounds by the calcium and potassium present in the groundwater. Although out of the scope of this particular research, further investigation of the exact chemical mechanisms could reveal more precise reaction pathways.

The results of the degradation rate of PFOS or the sum of PFOS and PFOA during NTP treatment of the groundwater are summarized in Figure 11. The trend lines of those degradation rates correspond qualitatively to the trend lines of the degradation rates of PFOA (Figure 6), PFOS (Figure 7), and the mixture of PFOA/PFOS (Figure 8) solutions in distilled water at any tested initial concentration. However, careful observations and comparisons of the absolute values of the contaminant concentrations after the NTP treatments define the main difference between the behavior of the distilled water solutions and the groundwater samples, i.e., the efficiency of the contaminant degradation with NTP treatment. In other words, the main difference is how much the NTP treatment is capable of reducing the initial concentration of the contaminant in the sample. In the case of the distilled water solution, the process efficiency in the case of the 60 min test time is always in the range of 90–100% for all tested contaminants and for each tested initial concentration. In the case of the groundwater sample from the soil-sanitation site, the process efficiency after 60 min is slightly over 70% due to the inhibiting effects of the co-contaminants present in the groundwater sample and the high initial conductivity, which is two orders of magnitude higher in the case of the groundwater samples. A similar comparison of the process efficiencies can also be made for the other (shorter) treatment times.

![Figure 10. Dependency of the conductivity of the groundwater sample during NTP treatment on the treatment time.](image)
The obtained results also demonstrate an approximately 50% PFAS-degradation rate in the groundwater samples during the 10 min NTP treatment time. Using this, a rough estimation of the required energy input and treatment cost per m³ of groundwater with a comparable composition can be made. Taking into account that the HV NTP generator has an input power of around 0.06 kW and that the amount of water in the reactor during the test is 0.75 L, the specific energy requirement ‘e’ for the treatment of 1 L of groundwater with 50% PFAS degradation rate can be calculated as:

\[ e = \frac{P \cdot t}{V} \rightarrow e = 0.013 \text{ kWh/L} \]  

With a specific electric energy consumption of 0.013 kWh/L or 13 kWh/m³ and a current price of electric energy of approximately 0.25 €/kWh, the energy costs for the NTP treatment of water with 50% PFAS degradation rate would be around 3.25 €/m³. According to the German federal environmental agency (Umweltbundesamt), the operational, material, and investment costs for a PFAS water cleaning facility based on active carbon would be around 3.10 €/m³. However, this does not include the high costs of incineration with exhaust gas post-processing of active carbon at very high temperatures for the complete degradation of PFAS. Therefore, the costs of NTP water treatment should not be an obstacle to the competitiveness of this technology on the market. Process optimization and appropriate scaling of the NTP treatment facility can further reduce theses costs.

3.5. Dynamics of the Transformation of PFOA and PFOS into Short-Chain PFAS Compounds

In order to better understand the NTP degradation of long-chain PFOA and PFOS compounds in water samples, it is important to understand the dynamics of their dechlorination into the various short-chain (≤C7) PFAS species on the way to their complete mineralization. Short-chain PFAS species have a lower environmental impact but they can act as precursors under certain circumstances, leading to the reformation of long-chain PFAS compounds.

In the case of the distillated water-based samples, more than 90% of PFOA and PFOS degraded within 60 min, independent of the initial concentration. More than 50% of PFOA and PFOS degradation took place during the first five-to-ten minutes of the NTP treatment. In this degradation process, Perfluorohexanesulfonate (PFHxS), Perfluorohexanoic acid (PFHxA), Perfluorobutanoic acid (PFBA), Perfluorooctanesulfonic acid (PFHxS), Perfluorooctanoic acid (PFHxOAc), and Perfluoropentanoic acid (PFPeOAc) are common byproducts of both PFOA and PFOS degradation.
The results in Figure 12 demonstrate the dynamics of the transformation of long-chain PFOA and PFOS compounds into short-chain PFAS species during the NTP treatment of three different concentrations of PFOA/PFOS mixtures in distilled water. Similar results are also obtained for the tests with the pure PFOA and pure PFOS solutions in distilled water at different concentrations. In the PFOA and PFOS cases, the step-by-step chain degradation occurs starting from PFOA (C7) and PFOS (C8) to PFHpA (C7), PFHxA (C6), PFPeA (C5), and PFBA (C4). It is important to note that in all those cases, the total amount of PFAS species in the sample is constantly reducing during the NTP treatment. This means that NTP treatment not only leads to the simple transformation of PFOA and PFOS long-chain compounds into short-chain PFAS species, but also completely degrades most of the initial PFAS present in the samples.

![Figure 12](image_url)

**Figure 12.** Dynamics of transformation of PFOA and PFOS into short-chain PFAS compounds for three different initial concentrations and different NTP test times.

A more complex situation occurs in the case of the groundwater samples from the soil-sanitation sites, which initially contained different long-chain and short-chain PFAS compounds and also a variety of other organic and inorganic co-contaminants.

The analysis of the groundwater samples (Figure 13) reveals the presence of short-chain PFAS in the samples before NTP treatment and also different dynamics of the transformation of long-chain to short-chain PFAS compounds for different treatment times. In general, in the groundwater samples different NTP treatment times result in lower total levels of degradation and also in a significantly higher variety of short-chain PFAS compared to the PFOA/PFOS solutions in the distilled water.
1. The presence of the air bubble stream in the treated water significantly limits the water. However, and as an outlook of this work, the future scaling of this technology can investigate these challenges in more details.

2. The NTP treatment of PFOA compounds in distilled water demonstrated a high level of efficiency with a more than 50% degradation of the contaminant in the first ten minutes, a 70% degradation after 30 min, and a 90% degradation within 60 min of treatment, independent of the initial PFOA concentration. The treatment time is the main influence on the level of PFAS degradation and also on the overall cost of the treatment. Effects such as intensive mixing (bubbling) or electrode confirmation, etc., play a certain role and should be optimized in order to reduce the required treatment time in practical applications.

3. NTP was found to be even more effective in the degradation of PFOS compounds in distilled water. Compared to the case with PFOA contamination, the NTP treatment of PFOS-contaminated water was 35% more efficient, with close-to-zero concentrations reached after 30 min of treatment time, independent of the initial PFOS concentration in the sample.

4. The tests with the distilled water contaminated with a mixture of PFOA and PFOS compounds indicated that the dynamics of the degradation of the PFOA/PFOS mixture during the NTP treatment were constrained by the presence of PFOA.

5. The lowest NTP treatment efficiency was detected in the case of the groundwater samples from the soil-sanitation site. In this case, the process efficiency after 10 min of treatment time was approximately 50% and after 60 min of NTP treatment the value reached slightly over 70%.

6. An analysis of the dynamics of long-chain PFAS compounds’ degradation through the partial transformation into short-chain PFAS compounds indicated that although there are certain transformations of long-chain into short-chain compounds, most PFAS are completely degraded in the process and not just transformed into short-chain PFAS compounds.

NTP treatment shows potential for the successful removal of PFAS from contaminated water. However, and as an outlook of this work, the future scaling of this technology can be challenging in many ways, especially concerning process efficiency, costs, and control. Furthermore, the chemical and physical properties of the PFAS-contaminated groundwater can vary greatly compared to the cleaning sites in close proximity. In the next phase of this research, the aim is to design and produce a prototype reactor for in situ field tests and to investigate these challenges in more details.

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