Non-Thermal Plasma induced degradation of organic perfluoroalkyl substances (PFAS) in water

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Abstract: An overview will be given on recent advancements in this area of research and specifically on the steps we are taking in our laboratory to move towards an efficient and viable NTP-based process for the degradation of perfluorocompounds in water. Our approach puts major emphasis on the knowledge of mechanistic aspects, NTP generated reactive species, kinetics, intermediates and products. This knowledge is a powerful tool to guide the design and development of NTP sources and reactors and for process optimization.

Keywords: Perfluorocompounds, non-thermal plasma, water treatment, reactive species

1. Background

Perfluoroalkyl substances (PFAS) are anthropogenic compounds, designed, synthesized and used in the preparation of many products including stain- and water-repellent fabrics, nonstick materials such as Teflon, polishes, waxes, paints, cleaning products, fire-fighting foams. PFAS are lipophilic compounds characterized by exceptional chemical, photochemical and thermal stability. These very properties which make PFAS so fit for the above mentioned applications, are also responsible for their persistence in the environment and bioaccumulation. Thus, PFAS have become ubiquitous and are found in human serum, in groundwater and in the tissues of wildlife including fish, birds and marine mammals. In northern Italy, for example, the Po river basin, which is impacted by relevant industrial activities, is heavily affected by PFAS contamination [1]. This worrisome scenario is stimulating research along major lines including the development of sensitive and selective analytical methodologies for the quantitative determination of PFAS and metabolites, toxicological studies to identify and assess their effects in living organisms and the search for novel treatment processes for their removal from water [2].

Traditional methods for wastewater treatment are not able to remove PFAS and, owing to the presence of highly stable carbon−fluorine bonds, also advanced oxidation processes (AOPs), employing hydroxyl radical ($\cdot$OH) as the main oxidant species, have shown limited or null efficacy in the mineralization of these compounds [3]. Among the new approaches being pursued for removing PFAS, the application of atmospheric plasma has been gaining much attention in the last few years [4-8]. Among the advantages offered by atmospheric plasma for water treatment, are flexibility, *in situ* generation of very reactive species (OH, O, H, O_3, H_2O_2, superoxide, hydrated electrons and RNS) and no requirement for added chemicals, advantages that envision atmospheric plasma as a green technology [9].

2. Objectives

The objective of this study was to contribute to the development of non-thermal plasma based technologies for PFAS degradation in water. To achieve this goal the following steps were undertaken: i) exploratory experiments with the reactors already available in our laboratory [10-12]; ii) critical evaluation of the results achieved with these reactors and those reported in the relatively few literature papers dealing with the topic; iii) identification of conditions (type of discharge, gas in which the discharge is produced, solution pH and composition and others) leading to the best results in terms of conversion of the primary pollutant, extent of mineralization, duration of the treatment and energy yield; iv) identification of the intermediates and byproducts of PFAS degradation to obtain hints on the mechanisms involved and on the plasma generated reactive species possibly involved in the process; v) determination of the major reactive species generated by plasma under the various experimental conditions tested, and identification of that/those which are more likely involved in the degradation of PFAS; vi) modification of the available reactors and/or implementation of new ones to maximize the production of useful reactive species.

3. Results

The present study was carried out with AC and DC driven plasma reactors using perfluorooctanoic acid (PFOA) as a model compound. PFOA is one of the main PFAS used in industry, nowadays phased out in some countries but still persistent in the environment. Different reactor configurations were used, allowing us to generate plasma in gas bubbles produced inside the liquid, plasma streamers over the liquid surface with gas bubbling and streamers over a thin film of the solution. For each configuration plasma was produced in different gases (air or argon) and characterized by the measurement of discharge current and voltage. Optical emission spectroscopy experiments were also carried out to characterize the plasma (electron temperature, vibrational temperature, electron density). The decomposition rate of PFOA and the energy efficiency of the process were evaluated by measuring the residual PFOA as a function of treatment time and input energy.

A significant enhancement of the removal process is observed when the streamers are produced over a thin film of the solution, while the use of tap water or the increase of the solution conductivity do not affect significantly the degradation rate of PFOA with respect to that observed in pure water regardless the electrode and type of discharge used (Figure 1).

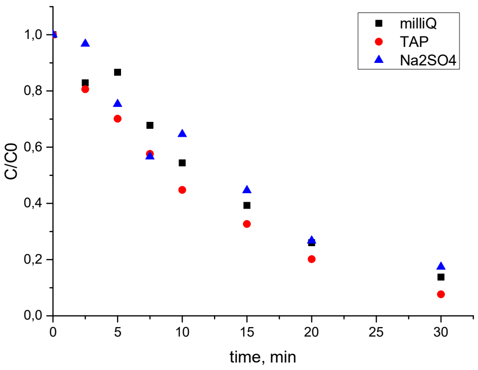

Fig. 1. Conversion of perfluorooctanoic acid as a function of treatment time. Comparison of different solvent media: milliQ water, tap water and Na_2SO_4 solution in milliQ water with the same conductivity as that of tap water.

Analysis of the solution, performed by means of HPLC-MS, also yielded the time profile for the various PFOA degradation intermediates as a function of treatment time and input energy. Interestingly, although most degradation intermediates are the same when either air or argon are used as process gas, a few appear to be specific of air treatment. The mineralization yield achieved in the experiments was assessed by TOC analysis of the residual organic carbon and by ion chromatographic determination of the fluoride released in solution. The results obtained with different reactor configurations and power supplies will be compared and discussed. Possible mechanisms for PFAS degradation will be critically examined also with reference to literature data.

4. References

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