Recent advances on plasma-based water treatment for the degradation of perfluoroalkyl substances

E. Marotta[1], G. Tomei[1], M. Saleem[1], M. Bortolussi[1], G.B. Sretenović[2]
[1]*Department of Chemical Sciences, University of Padova, Padova, Italy*
[2]*University of Belgrade, Faculty of Physics, Belgrade, Serbia*

Abstract: In this contribution, we report on the development of a combined process for the degradation of poly-and perfluoroalkyl substances (PFAS) dissolved in water based on the application of atmospheric plasma and the use of UV-sensitive additives (sulfite, iodide, nitrate).

1. Introduction

Plasma-based water treatment turned out to be particularly promising for the degradation of perfluoroalkyl substances (PFAS),[1,2,3] a class of contaminants highly persistent in the environment and refractory to remediation techniques primarily due to the strength of C-F bonds and to the absence of C-H bonds and of C-C π systems which can be attacked by OH radical.

However, the degradation of short-chain PFAS, which do not have surfactant properties and therefore do not concentrate at the plasma-liquid interface, still represents a challenge in the application of plasma in the treatment of PFAS-contaminated water.[4,5]

We thus investigated the combination of radial plasma (RAP) discharge with the addition of UV-sensitive additives in water to produce solvated electrons (from sulfite and iodide) or reactive radicals (from nitrate) in the solution bulk exploiting the radiation emitted by plasma. The sequential process in which atmospheric plasma treatment is followed by the water processing with UV-sensitive additives activated by an external lamp was, moreover, considered and compared.

2. Methods

A radial plasma discharge (RAP) reactor, characterized by a pointed tip high voltage electrode and a grounded ring partially submerged in water[2] (Figure 1), was used for the treatment of solutions of perfluorooctanoic acid (PFOA) and perfluorobutanoic acid (PFBA) at different pH and containing the selected additive (sulfite, iodide or nitrate) at the desired concentration (0-20 mM). Emission spectra in the UV range produced by the RAP discharge were recorded by means of an Ocean Optics QE65000 Spectrometer.

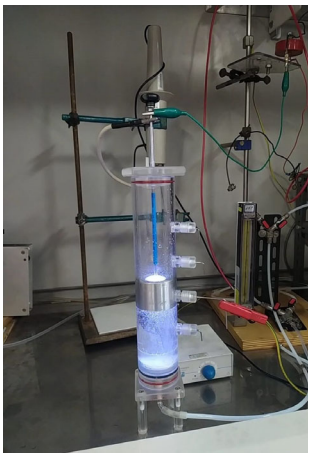

Fig. 1. Radial plasma discharge (RAP) reactor

A photoreactor equipped with an UV lamp (254 nm, HSGL OF 357 (Helios quartz) was used for the treatment of PFAS-contaminated water containing the selected UV-sensitive additive. Chemical analysis of the solutions was performed by means of a fluoride ion selective electrode (Mettler-Toledo perfectION comb F) and by liquid chromatography coupled with mass spectrometry using electrospray ionization (LC/ESI-MS, Thermo Scientific Ultimate 3000 and LTQ XL).

3. Results and Discussion

The optical emission spectra produced by the RAP discharge in argon and in argon containing various percentages of other gases were analyzed to maximize the emission needed to activate the UV-sensitive selected additive dissolved in water. Solutions of PFBA $1 \cdot 10^{-5}$ M were thus treated and the effect of pH and of the additive concentration was investigated. Sulfite activation was also performed through an UV lamp with λ_{max} = 254 nm and under these conditions PFBA was rapidly decomposed. A sequential process in which PFOA was degraded in the RAP reactor while the decomposition of its short-chain degradation products was performed through the treatment with UV/sulfite was thus developed to optimize the treatment time. Particular attention was given to the analysis of the obtained products, performed by LC/ESI-MS.

4. Conclusion

The combination of atmospheric plasma treatment with photodegradation mediated by UV sensitive additives is a promising approach to obtain the complete mineralization of perfluorocarboxylic acids.

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