

## Characterization of non-thermal atmospheric plasmas applied for the degradation of organic pollutants in air and in water with Optical Emission Spectroscopy (OES)

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Optical Emission Spectroscopy was used to characterize the plasma produced by DC or pulsed corona discharges in air at atmospheric pressure in a wire-cylinder reactor and in a Dielectric Barrier Discharge reactor. Non-thermal plasmas have been used to activate Advanced Oxidation Processes for the degradation of organic pollutants in air and in water. The results provide some important plasma parameters, such as electron temperature and density, and vibrational and rotational temperature of the bulk gas as a function of different plasma regimes. Moreover OES can identify the intermediate short-lived species involved in the oxidation process chain, giving some information on the favoured reactions and their mechanisms.

The advanced oxidation processes (AOPs) activated by non-thermal atmospheric plasmas seem to be one of the most promising and challenging approaches for air and water pollution abatement. In the last decades many reactors with different geometries have been developed, in order to investigate various types of discharges and to generate different plasma regimes; however, despite the advanced technological developments, the comprehension of the chemical and physical mechanisms, which are responsible for the decomposition of the organic pollutants, is far from being definitively reached.

Furthermore, research articles often report the main reactive species ( $\cdot\text{OH}$ ,  $\cdot\text{H}$ ,  $\cdot\text{O}$ ,  $\text{O}_2^-$ ,  $\cdot\text{HO}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$ ) [1], but do not investigate their role in the oxidation process chain.

It is well known that the chemical reactions involved in the pollutant decomposition, in air, liquid or hybrid-liquid phase discharges, are strongly dependent on the reactor characteristics, on the experimental conditions and on some fundamental plasma parameters. However, all these variables are generally not yet optimized.

In particular, electron temperature and density influence the plasma regime, since electrons are responsible for the ionization, excitation and dissociation processes of the bulk gas inside the reactor; so depending on the electron energy and then on the type of electric power provided to the system, some reactions are favoured with respect to others.

In this framework, the present work proposes a complete characterization of non-thermal atmospheric plasmas in corona regimes, in two different reactors, using Optical Emission Spectroscopy; this technique represents a powerful non-invasive and non-perturbing tool, allowing to investigate plasma under very different experimental conditions. The information provided by OE spectroscopy are useful for the determination of the chemical reactions involved, by means of the detection and the identification of the intermediate short-lived organic excited species in air and non-volatile soluble excited species in water, as a function of plasma parameters. The diagnostic system used for this purpose, a high resolution Czerny-Turner spectrometer, 500 mm focal length, equipped with two blazed/holographic gratings (2400 gr/mm UV-optimized and 1800 gr/mm 500 nm blazed) and a back-illuminated CCD camera as detector, has recently been installed. The spectral region investigated ranges from 300 nm (UV) to 850 nm (Visible range).

The first reactor, with a wire-cylinder configuration (60 cm long and 3.85 cm diameter), can produce a non-thermal plasma in corona regime at atmospheric pressure; it has been developed to study the mechanism of volatile organic compounds degradation in air, induced by different types of corona discharges. Using different VOCs (for example n-hexane) as contaminants, the products and the reactive intermediates both in dry and humid air, have been compared.

Depending on the characteristics of the corona regime, obtained by different power supplies, VOC decomposition is initiated by reactions with atoms, such as  $\text{O}(^3\text{P})$  in dry air, radicals, such as OH in humid air, ions and electrons [2, 3]. In order to better characterize the different plasma regimes produced in the corona discharge reactor, OES has been used to diagnose some excited neutral and

ionic species both in atomic and molecular form. By means of the proper interpretation of the vibrational and rotational bands of suitable molecules, their vibrational and rotational temperature which are related to the equilibrium temperature of the bulk gas, can be inferred. The electron temperature has been determined by the ratio of the band head intensities of the first negative system of  $N_2^+$  ( $B^2\Sigma_u^+ - X^2\Sigma_g^+$ ) at 391.4 nm and the second positive system of  $N_2$  ( $C^3\Pi_u^+ - B^3\Pi_g^+$ ) at 394.3 nm; the vibrational temperature can be measured from the nitrogen second positive system emission spectrum, considering a sequence of some first vibrational levels in the range between 360 and 395 nm, while the rotational temperature can be deduced by the comparison of a simulated nitrogen second positive system with the experimental rotational structure, choosing for example the band at 337.4 nm or 380.4 nm [4].

The second experimental system characterized by OES, is a novel Dielectric Barrier Discharge (DBD) reactor for the oxidative degradation of organic pollutants (as for example phenol) in water, where the discharge is applied above the surface of the aqueous solution (emerged discharges). DBD discharges are powered by an alternate high voltage supply and characterized by the presence of a layer of dielectric material covering one of the electrodes.

In our reactor [5], the dielectric barrier between the active electrode, two bare metal wires in air, and the ground electrode is constituted by the aqueous solution and by the glass bottom of the reactor. The advanced oxidation processes with this kind of geometry are based on the application of non-thermal discharges in air at atmospheric pressure. This method is particularly attractive, since it induces the production in situ of oxygen-based reactive species such as ozone ( $O_3$ ), suitable for the decomposition of organic pollutants.

One of the purposes of this second application is to demonstrate that the generation of the discharge in situ is advantageous with respect to the conventional process of ozonation, as it gives an improvement on the efficiency of pollutant decomposition. Indeed, the formation of the corona discharge directly in the inter-phase region between air and aqueous solution, has the advantage to produce other reactive species as the OH radicals, which contribute to the degradation of the contaminants.

For the first time OES has been applied to this novel system in order to characterize the plasma process both in the gaseous and aqueous phases, and to determine the important plasma parameters mentioned above, as for example the electron temperature. This is a fundamental parameter from the application point of view, in order to optimize the plasma efficiency treatment. By comparing the results obtained under different plasma conditions, it is possible to understand the relationship between the plasma species composition and the process efficiency. On the other hand the comparison of the reactive species observed with and without the presence of the organic pollutants gives indications about their role in the oxidation processes.

## References

- [1] H. Wang, J. Li, X. Quan, Y. Wu, *Appl. Cat. B: Environ.* **83** (2008) 72-77;
- [2] B. Zaniol, M. Schiorlin, E. Gazza, E. Marotta, X. Ren, M.E. Puiatti, M. Rea, P. Sonato, C. Paradisi, *Int. J. Plasma Env. Sci. Techn.* **2** Number 1 (2008) 65-71;
- [3] E. Marotta, A. Callea, X. Ren, M. Rea, C. Paradisi, *Plasma Process. Polym.* **5** (2008) 146-154;
- [4] N. Britun, M. Gaillard, A. Ricard, Y.M. Kim, J.G. Han, *J. Phys. D: Appl. Phys.* **40** (2006) 1022-1029;
- [5] E. Marotta, M. Schiorlin, X. Ren, M. Rea, C. Paradisi, *Plasma Process. Polym.* **8** (2011) 867-875.