# Mineralization of 2,4-dichlorophenoxyacetic acid by plasma-ozonation

M. Magureanu[1], C. Bradu[2], V.I. Parvulescu[3]

[1] *Department of Plasma Physics and Nuclear Fusion, National Institute for Lasers, Plasma and Radiation Physics, Magurele-Bucharest, Romania*
[2] *Department of Systems Ecology and Sustainability, Faculty of Biology, University of Bucharest, Romania*
[3] *Department of Organic Chemistry, Biochemistry and Catalysis, Faculty of Chemistry, University of Bucharest, Bucharest, Romania*

A pulsed corona discharge in contact with liquid combined with ozonation was investigated for the degradation of 2,4 dichlorophenoxyacetic acid (2,4-D), a widely used herbicide. The target compound was completely eliminated after 30 min treatment. The reaction rate constant for 2,4-D removal by plasma-ozonation was 194.5 x $10^{-3}$ $min^{-1}$, more than twice the value obtained by ozonation alone. Within 60 min over 90% mineralization was obtained, which represents a significant improvement as compared to $O_3$ alone. The chlorine balance demonstrates the absence of chlorinated by-products after 30 min treatment. An attempt to improve energy efficiency revealed the beneficial effect of shortening discharge pulse duration.

Pesticides are commonly detected in various water bodies and thus threaten aquatic species [1]. Various advanced oxidation processes are studied for elimination of these chemicals, and among them ozonation is considered one of the most promising, but the main drawback is poor mineralization [2,3].

In this work, non-thermal plasma generated in a pulsed corona discharge above liquid is combined with ozonation, with $O_3$ produced in the discharge. This combination proved efficient for the removal of other chemical compounds from water [4]. The target compound chosen for this study is 2,4-D, a widely used herbicide, often detected in surface and ground water and sometimes in drinking water [5].

The experiments were carried out using a pulsed corona discharge above liquid (multiwire-plate geometry) in series with a cylindrical ozonation reactor [4]. The 2,4-D solution (25 mg/L, 330 mL) was continuously circulated between the two reactors and the effluent gas from the plasma was bubbled into the solution contained in the cylinder.

The removal of 2,4-D is completed after 30 min treatment in the plasma-$O_3$ system (Fig. 1a) and the rate constant (194.5x$10^{-3}$ $min^{-1}$) is more than twice the value obtained for $O_3$ treatment alone (88.2x$10^{-3}$ $min^{-1}$). The mineralization degree is assessed from the elimination of TOC (total organic carbon). TOC removal reaches over 90% after 60 min plasma+$O_3$ treatment, much superior to the mineralization by $O_3$ alone (56%) (Fig. 1b). The results prove the major role played by other plasma-generated oxidants, besides $O_3$, in the degradation of 2,4-D.

Reducing discharge power by shortening the pulse duration did not affect the degradation, and thus results in lower energy costs.

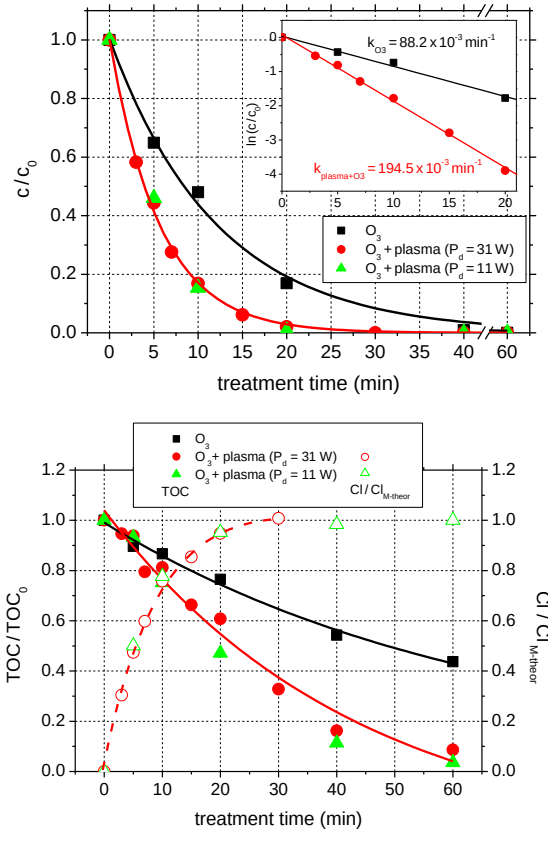


Fig. 1. a: Degradation of 2,4-D; b: Mineralization and dechlorination of 2,4-D solution during ozonation and plasma+$O_3$ treatment with plasma powers of 11 and 31 W

[1] L.H. Nowell et al., Sci. Total Environ. **476–477** (2014) 144

[2] K. Ikehata and M.G. El-Din, Ozone: Sci. Eng. **27** (2005) 83

[3] S. Chiron et al., Water Res. **34** (2000) 366

[4] M. Magureanu et al., Chemosphere **165** (2016) 507

[5] D.B. Donald et al., Environ. Health Perspect. **115** (2007) 1183