

# Degradation of organic compounds in water by corona discharge combined with ozonation

M. Magureanu<sup>1</sup>, D. Dobrin<sup>1</sup>, C. Bradu<sup>2</sup>, B.M. Mandache<sup>1</sup>, V.I. Parvulescu<sup>2</sup>

<sup>1</sup>National Institute for Lasers, Plasma and Radiation Physics, Department of Plasma Physics and Nuclear Fusion, Atomistilor Str. 409, 077125 Magurele-Bucharest, Romania

<sup>2</sup>University of Bucharest, Department of Organic Chemistry, Biochemistry and Catalysis, Regina Elisabeta Blvd. 4-12, 030016 Bucharest, Romania

The degradation of methyl paraben in water was investigated using a pulsed corona discharge combined with ozonation. The efficient use of the ozone generated in high amounts in the plasma by passing it through the solution was beneficial for the oxidative degradation of the target organic compound. The role of ozone was evidenced by the comparison between the results obtained in the combined plasma + ozonation process and those achieved with ozone treatment alone.

## 1. Introduction

Non-thermal plasma generated in electrical discharges in liquid and gas-liquid environments has been investigated in the last years for the degradation of a wide variety of organic compounds in water [1,2]. Numerous chemically active species are formed in these discharges (hydroxyl radicals, ozone, hydrogen peroxide, peroxyxynitrite, etc.) [1], and promote the oxidative degradation of the target organic compounds.

It was suggested that the combination of plasma with ozone treatment may be beneficial from the point of view of degradation efficiency, especially when using the ozone generated in high amounts in the plasma [3,4].

In this work methyl paraben was chosen as target compound and its degradation was studied in a combined treatment consisting in a corona discharge above liquid + ozonation. Methyl paraben is the methyl ester of the p-hydroxybenzoic acid and has the chemical formula  $\text{CH}_3(\text{C}_6\text{H}_4(\text{OH})\text{COO})$ . Due to the antimicrobial properties, it is frequently used as preservative mostly in cosmetics and personal care products, in pharmaceuticals and even in food [5].

High amounts of parabens are released in wastewater and they were detected in river water [6-8]. Several recent studies noted weak estrogenic activity of parabens [9,10], which raised concern regarding their potential long-term effects on aquatic species.

The degradation of parabens in water has been investigated by several advanced oxidation processes, such as  $\text{TiO}_2$  photocatalysis [11,12], ozonation [13,14],  $\text{H}_2\text{O}_2$  + UV oxidation [15] and non-thermal plasma [16]. It was found that the photocatalytic degradation of parabens was a slow process, over 90% removal being achieved after 120

min treatment [11,12]. Faster removal was obtained with ozone treatment and in  $\text{H}_2\text{O}_2/\text{UV}$  experiments [13-15]. The advantage of non-thermal plasma is the operation without additives. Complete removal of methyl paraben in water was obtained after 10 min plasma exposure [16], with a higher rate than in ozonation and  $\text{H}_2\text{O}_2/\text{UV}$  oxidation.

In the present work methyl paraben (MeP) was degraded by a pulsed corona discharge generated above the solution combined with ozonation. The removal rate and mineralization degree were measured and compared with results obtained by ozone treatment alone. Several degradation products were identified. The formation of ozone ( $\text{O}_3$ ) in the gas phase was investigated in the absence and in the presence of MeP in solution.

## 2. Experimental

The experimental set-up is described in detail in [16] and is shown in Fig. 1.

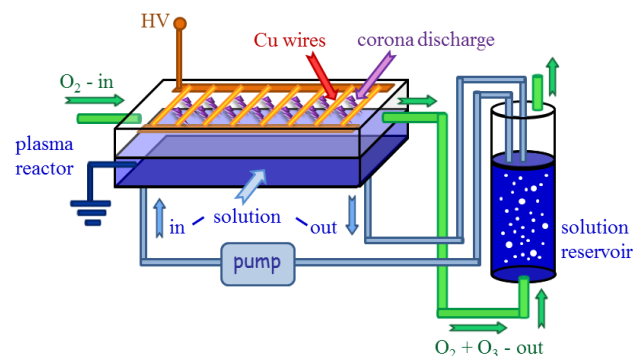


Fig. 1. Experimental set-up.

The high voltage electrode is an array of 20 copper wires (100  $\mu\text{m}$  diameter, 36 mm length, 6 mm distance between adjacent wires) and the ground electrode is a rectangular aluminium tape

(122 mm × 48 mm) placed on the bottom of the vessel.

The paraben solution was prepared in tap water and has the following characteristics: initial concentration of paraben 50 mg/L, conductivity 250  $\mu\text{S}/\text{cm}$ , pH 7.6, total volume 330 mL. The solution is continuously circulated by a peristaltic pump between the plasma reactor and the solution reservoir, with a flow rate of 160 mL/min. Under these conditions, the height of the liquid in the plasma reactor is  $\sim 5$  mm. The discharge is generated in the gas, between the wires and the solution surface, and the discharge gap is 4 mm. Oxygen is flown continuously through the reactor with a rate of 300 mL/min. The effluent gas which contains ozone formed in the plasma is bubbled through a porous ceramic into the solution reservoir.

The discharge is operated in pulsed mode, with high voltage pulses produced by discharging a 6 nF capacitor by means of a self-triggered spark-gap switch. The discharge voltage is measured with a Tektronix P6015 probe and the discharge current with a Tektronix TCP0150 probe, and are monitored by an oscilloscope (Tektronix DPO 2024). Voltage pulses with amplitude of 18 kV, rise rate of  $\sim 1$  kV/ns and width of 325 ns are used. The current pulses have 270 A amplitude. The energy per pulse is 1.1-1.2 J and the average power dissipated in the discharge is  $\sim 26$  W for the pulse frequency of 23 Hz used in the experiments.

The concentration of MeP in solution was measured by HPLC (High Performance Liquid Chromatography), using a Varian ProStar apparatus equipped with UV detector (at  $\lambda = 255$  nm) and an ODS-3 (250 × 4.6 mm) column at 40 °C.

The degree of mineralization of MeP was followed by TOC (Total Organic Carbon) analysis. TOC was calculated by subtracting from the value of the total carbon (TC) the value of the total inorganic carbon (TIC). TC and TIC measurements were performed using an analyzer based on carbon dioxide infrared absorption (HiPerTOC Thermo Electron).

The degradation products of MeP were detected by HPLC and GC-MS (Gas Chromatography - Mass Spectrometry), using a chromatograph (Agilent 6890-5973) equipped with SPME sampler and 19091S-433 HP-5MS capillary column (30 m × 0.25 mm × 0.25  $\mu\text{m}$ ).

The concentration of  $\text{O}_3$  in the gas phase was measured by an ozone detector (Ozomat MP, Anseros).

In the ozonation experiments in the absence of plasma the same set-up is used, and oxygen containing  $\text{O}_3$  is introduced from an external source at the inlet of the plasma reactor and then bubbled through the liquid in the solution reservoir, maintaining all other experimental conditions (gas and liquid flow rate,  $\text{O}_3$  concentration) identical as in plasma + ozonation experiments.

### 3. Results and discussion

Fig. 2 shows the removal of MeP as a function of treatment time for the plasma + ozonation system and for ozone treatment alone.

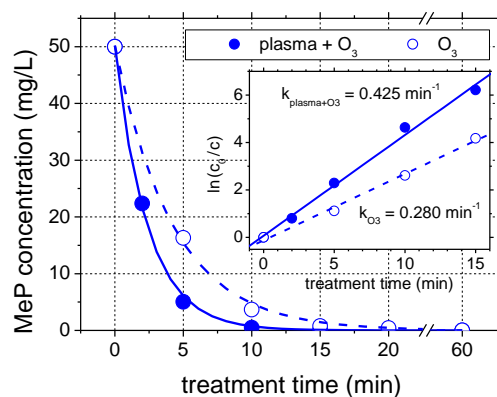


Fig. 2. Removal of MeP in water by plasma + ozonation and ozone treatment alone.

After 5 min plasma + ozonation treatment 90% of the initial MeP is degraded and complete removal is obtained within 10-12 min. Ozone treatment alone results in slower removal of the target compound, as seen in Fig. 2. The degradation obeys first order kinetics, with the rate constant  $0.425 \text{ min}^{-1}$  for plasma +  $\text{O}_3$  and  $0.280 \text{ min}^{-1}$  for ozone treatment. These values suggest that  $\text{O}_3$  has a significant contribution to the degradation of MeP in the combined process. Nevertheless, the other oxidants formed in the plasma also play an essential role, accounting for the higher degradation rate observed in the plasma +  $\text{O}_3$  system as compared to simple ozonation.

The rate constant obtained in these experiments is higher than the values reported for parabens removal by photocatalysis ( $0.018 \text{ min}^{-1}$ ) [11] and  $\text{H}_2\text{O}_2/\text{UV}$  oxidation ( $0.098 \text{ min}^{-1}$ ) [15]. This confirms that plasma may be a promising approach for the degradation of organic compounds in water.

The mineralization degree reflects the complete degradation of the target organic compound into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  and is shown by the TOC removal. The mineralization of MeP is shown in Fig. 3 in the plasma +  $\text{O}_3$  system and for simple ozonation.

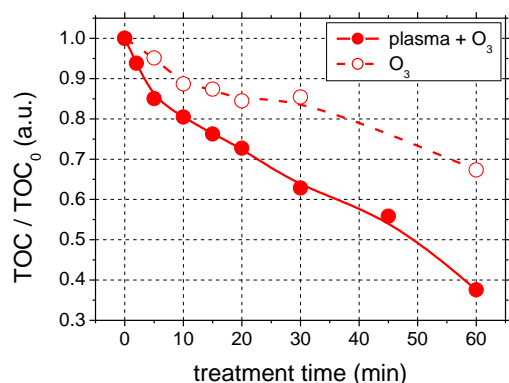


Fig. 3. TOC removal as a function of treatment time. Comparison between plasma combined with ozonation and ozone treatment alone.

As seen in the figure, mineralization is much slower than MeP removal, since the degradation process occurs gradually, leading first to the formation of organic intermediates, which are further decomposed and finally yield  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . After 60 min plasma +  $\text{O}_3$  treatment the TOC removal reached 62.4%, while with  $\text{O}_3$  alone it is approximately half this value (32.7%).

The evolution of ozone concentration in the effluent gas was followed during a 30 min experiment in the plasma +  $\text{O}_3$  system and is shown in Fig. 4.

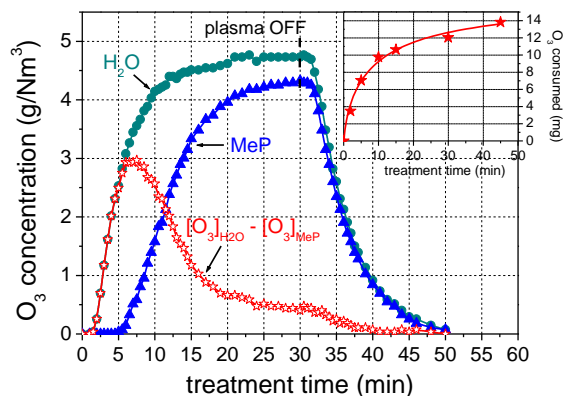


Fig. 4. Concentration of ozone in the effluent gas of the plasma + ozonation system operated with water (●) and with the MeP solution (▲). Inset: Ozone consumption as a function of treatment time.

Initially the  $\text{O}_3$  concentration is measured with water instead of the MeP solution, providing information on the  $\text{O}_3$  formed in the discharge which remains in the gas phase and is not transferred to the liquid. In the presence of the MeP solution, the  $\text{O}_3$  concentration in the gas is lower, especially in the beginning of the treatment. The difference between them (denoted in the figure with  $[\text{O}_3]_{\text{H}_2\text{O}} - [\text{O}_3]_{\text{MeP}}$ ) gives the ozone consumed in reactions with MeP

and its degradation products. The total amount of ozone consumed was calculated by integrating the concentration of  $\text{O}_3$  over the duration of experiment and multiplying with the gas flow rate, and is shown in the inset of Fig.4 as a function of treatment time.

The concentration of  $\text{O}_3$  measured for the discharge above water was 4.5-4.7  $\text{g/Nm}^3$ .  $\text{O}_3$  consumption in the presence of MeP in solution is substantial in the first minutes of treatment. During the first 5-6 min practically all ozone produced in the plasma is consumed in chemical reactions. After 6-8 min,  $\text{O}_3$  consumption rate starts to decline, so that for longer treatment times ( $> 20$  min) it remains around 0.5  $\text{g/Nm}^3$ . The global  $\text{O}_3$  consumption clearly illustrates this effect, displaying a steep initial increase (up to 10-15 min), followed by an increase at a much slower rate. Ozone consumption correlates well with the degradation of MeP, which occurs fast and is completed after 10-12 min.

As degradation products of MeP, hydroxylated derivatives (namely hydroquinone and methyl 3,4-dihydroxybenzoate) were detected in the first minutes of treatment. They are subsequently degraded and carboxylic acids (maleic, tartaric, 2-hydroxypropionic, acetic, oxalic and formic acid) are formed by ring opening. The high  $\text{O}_3$  consumption in the first minutes of treatment suggests the significant contribution of  $\text{O}_3$  to the degradation of MeP and its aromatic intermediates. However, carboxylic acids formed as final by-products are much less susceptible to the attack of  $\text{O}_3$ , which may explain the low  $\text{O}_3$  consumption for long treatment time.

### 3. Summary and conclusions

A pulsed corona discharge above liquid combined with ozonation was successfully used for the oxidative degradation of methyl paraben in water. The target compound was removed fast (90% elimination within 5 minutes treatment) with a rate superior to other AOPs. The mineralization degree reached 62.4% after 60 minutes treatment. The comparison with ozonation results suggests that the role of ozone is important in the degradation, but the other chemically active species formed in the plasma also contribute essentially to the oxidation of MeP and its degradation products.

The identification of degradation intermediates indicates that hydroxylation of the aromatic ring, demethylation and decarboxylation represent the first step in the degradation of MeP, followed by ring opening with formation of carboxylic acids, and finally mineralization.

#### 4. References

- [1] P. Lukes, B.R. Locke, J.-L. Brisset, in *Plasma Chemistry and Catalysis in Gases and Liquids*, Eds. V.I. Parvulescu, M. Magureanu, P. Lukes, Wiley-VCH (2012) 243.
- [2] B. Jiang, J. Zheng, S. Qiu, M. Wu, Q. Zhang, Z. Yan, Q. Xue, *Chem. Eng. J.* **236** (2014) 348.
- [3] M. Magureanu, D. Piroi, N.B. Mandache, V. Parvulescu, *J. Appl. Phys.* **104** (2008) 103306.
- [4] D. Gerrity, B.D. Stanford, R.A. Trenholm, S.A. Snyder, *Water Res.* **44** (2010) 493.
- [5] M.G. Soni, I.G. Carabin, G.A. Burdock, *Food Chem. Toxicol.*, **43** (2005) 985.
- [6] I. Gonzalez-Marino, J.B. Quintana, I. Rodriguez, R. Cela, *Water Res.* **45** (2011) 6770.
- [7] B. Kasprzyk-Hordern, R.M. Dinsdale, A.J. Guwy, *Water Res.* **42** (2008) 3498.
- [8] M. Terasaki, Y. Takemura, M. Makino, *Environ. Chem. Lett.* **10** (2012) 401.
- [9] J. Boberg, C. Taxvig, S. Christiansen, U. Hass, *Reprod. Toxicol.* **30** (2010) 301.
- [10] M. Terasaki, R. Kamata, F. Shiraishi, M. Makino, *Environ. Toxicol. Chem.*, **28** (2009) 204.
- [11] Y. Lin, C. Ferronato, N. Deng, F. Wu, J.-M. Chovelon, *Appl. Catal. B: Environ.*, **88** (2009) 32.
- [12] H. Fang, Y. Gao, G. Li, J. An, P.-K. Wong, H. Fu, S. Yao, X. Nie, T. An, *Environ. Sci. Technol.* **47** (2013) 2704.
- [13] L. Hernandez-Leal, H. Temmink, G. Zeeman, C.J.N. Buisman, *Water Res.* **45** (2011) 2887.
- [14] K.S. Tay, N.A. Rahman, M.R. Bin Abas, *Chemosphere* **81** (2010) 1446.
- [15] D. Bledzka, D. Gryglik, M. Olak, J.L. Gebicki, J.S. Miller, *Radiat. Phys. Chem.*, **79** (2010) 409.
- [16] D. Dobrin, M. Magureanu, C. Bradu, N.B. Mandache, P. Ionita, V.I. Parvulescu, *Environ. Sci. Pollut. Res.* **21** (2014) 12190.