

Formation of hydroxyl radicals in a pulsed corona discharge in contact with liquid

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Abstract: The generation of hydroxyl (OH) radicals by a pulsed corona above water has been investigated. Production of OH is more energetically efficient for short discharge pulses. In a plasma-ozonation system with recycling the effluent gas from the plasma the reaction between plasma-generated ozone and hydrogen peroxide represents an important source of OH formation.

Keywords: pulsed corona, hydroxyl radicals, reactive oxygen species, water treatment.

1. Introduction

Research in the field of water treatment by advanced oxidation processes (AOPs) became more and more active due to the increasing concern regarding water pollution. All AOPs rely on the in-situ generation of oxidising species, especially hydroxyl radicals, which are among the strongest oxidizers and react non-selectively with most types of organic pollutants [1].

Plasma in liquid or gas-liquid environment also produces OH radicals, mainly by electron dissociation of water molecules, although other pathways can also be important, depending on plasma parameters [2]. The formation of OH in plasma has been evidenced by various spectroscopic techniques [3-6] and its presence in liquid samples exposed to plasma has been detected by chemical probes [7-9].

In the present work the formation of OH is investigated in a pulsed corona in oxygen, in contact with water. The influence of the pulse width has been addressed, in connection with the improved degradation efficiency of organic compounds obtained in previous studies by reducing pulse duration [10,11]. Previous results also showed greatly enhanced pollutants degradation in a plasma-ozonation system, based on recycling the ozone-rich effluent gas from the plasma, as compared to plasma alone [12]. Thus, the concentrations of OH radicals in the liquid have been compared for these two configurations (plasma alone and plasma-ozonation).

2. Experimental

A pulsed corona discharge above liquid in multi-wire to plate configuration has been used [10]. The experiments are performed in oxygen, flowing at 300 mL/min. The solution continuously circulates between the plasma reactor and a cylindrical reservoir (flow rate 160 mL/min). The effluent gas from the plasma, containing ozone, can be bubbled through the solution in the reservoir (plasma-ozonation configuration) or can be vented immediately after the plasma reactor (plasma alone configuration) [10,12].

High voltage pulses of negative polarity were generated using either capacitors of 2 nF and 6 nF discharged by a solid-state thyristor switch, or coaxial cables of 6 m and 10 m with a self-triggered spark-gap switch [11]. Thus, different pulse durations can be obtained, in the range 55-380 ns (FWHM). The voltage amplitude was kept constant at 17-18 kV and the pulse repetition rate was maintained at 25 Hz. The amplitude of the current pulses, the energy per pulse and the average power dissipated in the discharge are given in Table 1.

Table 1. Parameters of the discharge pulses: Δt – pulse width (FWHM), I – amplitude of the current pulses, E_p – energy per pulse, P – average power in the discharge

Δt – FWHM (ns)	380	250	110	55
I (A)	292	175	140	110
E_p (mJ)	1230	439	175	83
P (W)	29	10	4.4	2.1

The formation of OH radicals in solution was evaluated using a chemical probe, in particular from the reaction of OH with coumarin 3-carboxylic acid (3CCA) yielding the fluorescent product coumarin 7-hydroxy-3-carboxylic acid (7OH-3CCA) [9,12,13]. In most experiments the 3CCA solution (10^{-3} M) was prepared in distilled water, with NaCl used to adjust the conductivity to 350-400 $\mu\text{S/cm}$. In some experiments, synthetic water was used, prepared from distilled water with 25 mg/L $\text{Mg}(\text{NO}_3)_2$, 30 mg/L CaCl_2 and 270 mg/L NaHCO_3 , in order to be closer to the tap water conditions.

The detection of 7OH-3CCA and the consumption of the parent compound 3CCA were done by HPLC with a fluorescence detector (excitation wavelength 334 nm, emission wavelength 447 nm) and an UV-Vis DAD detector, respectively. A Zorbax SB-C18 column (4.6 mm x 250 mm) was used with a mobile phase of 75% of phosphate buffer 20 mM (pH 3) and 25% acetonitrile, at a flow rate of 1 mL/min.

3. Results and discussion

The concentration of 7OH-3CCA formed in the solution exposed to the corona discharge is shown in Fig. 1, as a function of treatment time (Fig. 1a) and input energy (Fig. 1b), for the plasma alone configuration with pulse durations in the investigated range (55-380 ns). The input energy represents the total energy introduced during the experiment, calculated by multiplying the average power with the treatment time.

The concentration of OH should be proportional to the concentration of 7OH-3CCA, under the assumption that this compound is not further decomposed during the experiments. For long plasma exposure time several other peaks appear in the chromatograms, therefore the experiment duration was limited to 40 minutes, in order to ensure results accuracy.

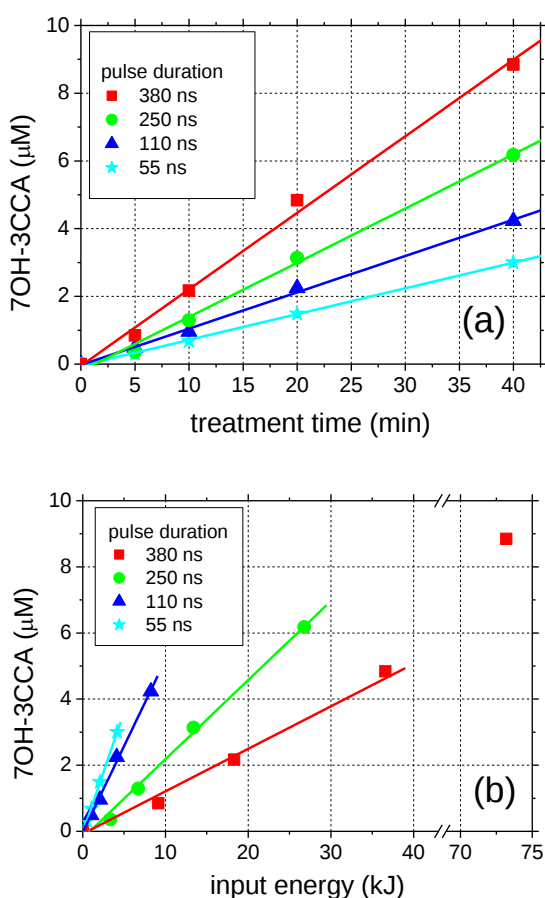


Fig. 1. Concentration of 7OH-3CCA formed in distilled water treated by the corona discharge with pulse durations in the range 55-380 ns as a function of (a) – treatment time, (b) – input energy.

The concentration of 7OH-3CCA increases linearly with plasma treatment time for all the pulse durations investigated (Fig. 1a). For longer pulses, larger amounts of 7OH-3CCA were detected: up to three times higher concentration for the 380 ns pulses as compared to the 55 ns pulses, after 40 minutes treatment. Newton and

Milligan reported a value of the yield for 7OH-3CCA formation from 3CCA of 4.7% per OH radical [13]. Thus, the maximum rate of OH generation under the present conditions amounts to approximately 80 nM/s.

Although longer pulses generate more OH radicals, short pulses produce them in a more energy efficient manner, as seen by plotting the data versus input energy (Fig. 1b). By dividing the concentration of 7OH-3CCA to the input energy, it is observed that the energy yield for OH formation was increased 6-7 times by reducing pulse duration within the investigated range.

Ono et al. also determined larger OH production with shortening the pulse width of a corona discharge in $H_2O/O_2/N_2$ mixtures [14]. The authors suggested that OH radicals are formed in the early part of the secondary streamer and their generation becomes inefficient in the later part, and thus explained the decrease in OH production efficiency when extending the duration of discharge pulses.

The larger concentration of OH present during longer pulses may favour recombination with formation of hydrogen peroxide (H_2O_2):



since the rate of reaction R1 increases with radical density. However, recombination of OH is not desirable from the viewpoint of water decontamination, since the generated H_2O_2 is much less reactive than OH, and therefore not as useful.

Measurements of H_2O_2 in the liquid show that its formation is independent on pulse duration and scales linearly with input energy (Fig. 2).

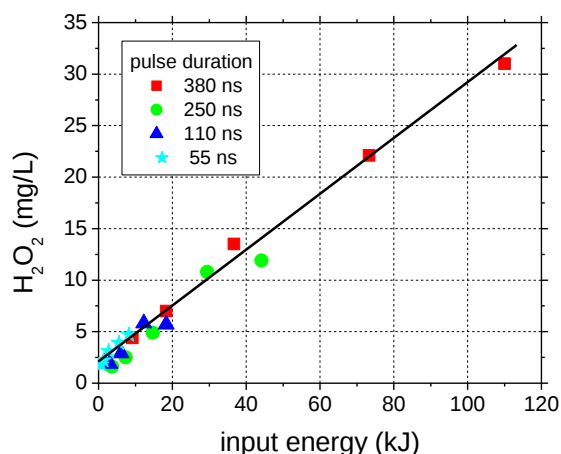


Fig. 2. Concentration of H_2O_2 formed in the plasma alone configuration, in tap water, as a function of input energy, for pulse durations in the range 55-380 ns

By comparing the ratios between the concentration of H_2O_2 and that of 7OH-3CCA for the different pulses, it can be seen that the values are approximately two times higher for the 380 ns pulses than for the 55 ns ones. This confirms the assumption that for long pulses a larger proportion of the OH radicals recombine to form H_2O_2 , while in case of short pulses a more important part of the

plasma-generated OH remains available to react with the organic compounds present in the liquid.

In the experiments performed in synthetic tap water, the scavenging effect of carbonates leads to considerably smaller concentrations of OH: the detected amounts of 7OH-3CCA are more than one order of magnitude lower than the values obtained in distilled water. However, the dependence on pulse width is preserved even for these very low concentrations.

The concentrations of 7OH-3CCA detected in distilled water for plasma alone and plasma-ozonation are compared in Fig. 3 for 110 ns discharge pulses. A similar trend was obtained for the other pulse lengths.

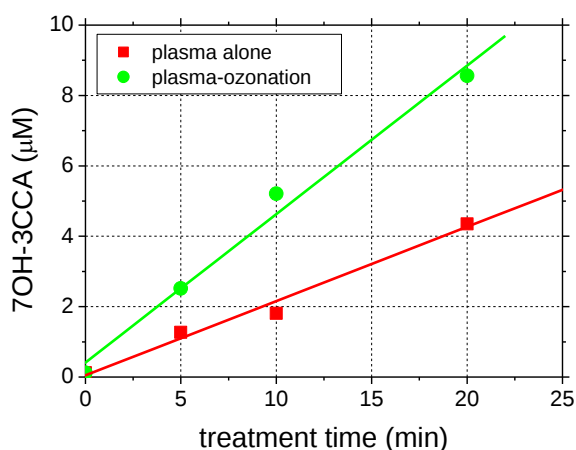
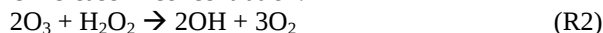


Fig. 3. Concentration of 7OH-3CCA formed in distilled water treated by plasma alone and in the plasma-ozonation system, for discharge pulses of 110 ns, as a function of treatment time

In the plasma-ozonation configuration, the OH concentration is approximately two times higher than in plasma alone, regardless of pulse duration. The plasma characteristics are the same in both configurations, therefore the higher level of OH obtained in plasma-ozonation experiments can only be explained by OH formation from another source besides electron impact on water molecules. The peroxone process, i.e. the decomposition of H_2O_2 by O_3 (reaction R2) resulting in OH formation is the most likely process responsible for this increase in concentration.



This argument is supported by the drop in O_3 and H_2O_2 concentration observed in plasma-ozonation experiments. In this case, regardless of pulse duration and treatment time, the concentration of H_2O_2 in water remains below 2 mg/L, as compared to the values up to 32 mg/L obtained with plasma alone. The O_3 concentration in the gas phase also decreases with approximately 25%.

From the viewpoint of water decontamination, the peroxone process is beneficial, since it (re)uses plasma-generated H_2O_2 and O_3 to produce highly reactive OH radicals available for reactions with the pollutant compounds.

4. Conclusions

It was observed that shortening the discharge pulses results in more efficient generation of hydroxyl radicals in water exposed to plasma. One of the reasons might be that formation of OH occurs relatively early during the pulse. Another possible cause of this effect might be the high reactivity of OH, leading to recombination with formation of hydrogen peroxide. This assumption is supported by H_2O_2 measurements, which confirm that for longer discharge pulses a larger proportion of OH react to yield H_2O_2 .

The plasma-ozonation configuration based on recycling of the ozone-rich effluent gas from the plasma appears beneficial from the point of view of OH production. In this case, besides the direct generation of OH in the plasma, an indirect route via the reaction between plasma-generated ozone and hydrogen peroxide represents an important source of OH formation. This is supported by the decline of O_3 and H_2O_2 concentrations in the plasma-ozonation system as compared to plasma alone, accompanied by a considerable increase in concentration of OH.

Based on these results, it appears that application of non-thermal plasma in water treatment can be optimised by careful tuning of the discharge pulse width and by proper recycling of the long-lived oxidising species generated in the plasma.

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5. References

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