Plasma agents in water and surface decontamination

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Résumé

Bio-decontamination of water and surfaces contaminated by bacteria (*Salmonella typhimurium, Bacillus cereus, Escherichia coli*) was investigated in two types of positive DC discharges in atmospheric pressure air, in needle-to-plane geometry: the streamer corona and the transient spark with short high current pulses of limited energy. Both generate cold non-equilibrium plasma. Electro-spraying of the treated water through the needle electrode resulted in fast bio-decontamination. Experiments providing separation of various biocidal plasma agents, the emission spectra, oxidation stress measurements in the cell membranes, and chemical changes induced in the treated water helped better understanding of the plasma agents responsible for microbial inactivation. Radicals and reactive oxygen species seem to be dominant biocidal agents, although understanding plasma-induced water chemistry requires further research.

Introduction

In bio-decontamination by plasma, it is crucial to understand the role of various mechanisms involved. The significant mechanisms depend on the plasma composition (gas), temperature, treated microorganisms and the environment (air, water, surfaces, etc.). In atmospheric pressure plasmas, the major role is typically attributed to radicals and reactive oxygen species (ROS, e.g. OH, O, O_3) and to charged particles, especially O_2^- affecting the cell membranes. UV radiation plays a role only if photons in UV C germicide region (220-280 nm) or in vacuum UV are produced. In cold air discharges (corona, DBDs, pulsed discharges), UV C or VUV are usually not generated, so radicals and ROS are identified as the dominant bio-inactivation agents.

Results and discussion

We investigated the biocidal effects of two plasma sources in atmospheric air with water: positive DC streamer corona (SC) and a novel regime transient spark (TS). Despite DC applied voltage, these discharges have a pulsed character with nanosecond repetitive pulses and generate cold plasma. Their electrical parameters and emission spectra were documented in detail in our previous works [1-3].

The contaminated water flew directly through the stressed hollow needle electrode, and so through the plasma active zone in its proximity (Fig. 1), which substantially improved the volume efficiency compared to our previous set-ups for water treatment [3]. The effect of electrostatic spraying occurred when the high voltage was applied on the needle electrode. The temperature of the treated water did not change in SC and was increased by maximum 10 K in TS. The lethal heat effect to bacteria can be excluded.

We focused on the identification of the dominant plasma agents in bio-inactivation by coupling the electrical discharge characteristics (oscilloscopic measurements), their emission spectra (time-integrated and time-resolved), the chemical effects induced in water (measurements of pH, conductivity, H_2O_2, NO_2^- and NO_3^-) and their biocidal effects (thermostatic growth plate count method).

Depending on the initial conductivity of the treated water (we tested 1, 500, 1000 μS/cm, and physiologic solution ~14 mS/cm) and the plasma parameters (SC or TS, power, water flow rate, etc.), we observed a pH decrease from 5-7 down to 3-5 and an increase of conductivity (from 1 up to 1000, from 500 up to 1300 μS/cm). Nitrates (NO_3^-) reached concentration up to 2.5 mM, nitrites (NO_2^-) up to 116 μM and peroxides (H_2O_2) up to 500 μM. pH decrease is probably due to nitric acid formation, as is evident from high concentrations of the produced nitrates. However, additional tests showed that the nitric acid solution of the same pH does not lead to the same biocidal effects. In agreement with [5], it seems that acid environment in synergy with plasma agents leads to bacterial inactivation. In addition, we suppose an interaction of nitrites and peroxides at lowered pH; this has to be further studied with using buffers.

Unlike in [5], our preliminary tests show that even with PBS buffer that holds pH at 6.8 we obtain decontamination comparable to non-buffered plasma treatment.

Measurements of the oxidative stress induced in microbial cells (TBARS method [3-4]) enabled to further indicate their respective roles. TBARS concentration gain representing the oxidative stress induced in the cell membranes correlated with the bio-decontamination efficiency of SC and TS applied to the electro-sprayed water. The same samples were irradiated by biocidal UV C radiation (Hg lamp, 254 nm) for comparison. UV C induced almost no oxidative stress despite its efficiency was very high. This indicates that oxidations of cell membranes by ROS are important in microbial inactivation in SC and TS discharges. More ROS is linked with the higher efficiency [4].

Comparing direct with indirect plasma effects enables separation of various biocidal plasma agents. We compared direct SC and TS plasma treatment with 2 types of indirect exposure of contaminated agar surfaces: 1) through a grounded metal mesh letting but neutral active species to the agar; 2) through a quartz or MgF_2 windows allowing but UV radiation generated in the plasma to the agar. Interestingly, there was very little difference between the direct and the through-mesh indirect plasma treatment with both discharges, even at very treatment times as short as 5 s. This indicates that neutral reactive species are crucial even in the direct exposure. Exposure to the UV light only demonstrated no visible decontamination. This correlates with the emission spectra of SC and TS lacking any UV C or VUV. Similar effects of direct and indirect plasma treatment agree with the emission spectra, oxidation stress measurements and our previous findings [3-4].

Conclusion

Radicals and ROS were found the dominant biocidal agents in atmospheric air SC and TS discharges. However, plasma-induced water chemistry and its relation to bio-decontamination still arise many questions and so require further research.

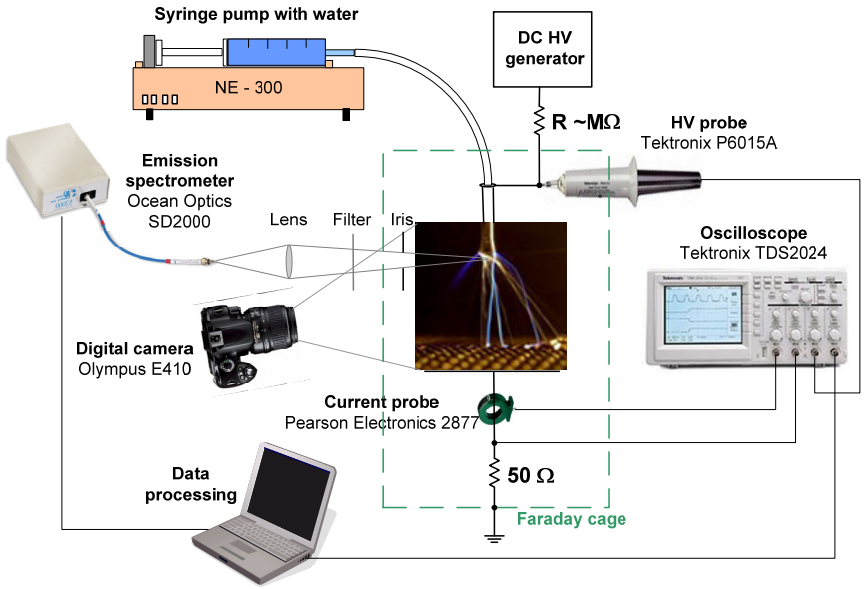

Fig. 1: Experimental set-up for DC discharges, with a high voltage hollow needle electrode enabling water flowing through the discharge zone and a plane or mesh electrode.

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