18th International Symposium on Plasma Chemistry

Edited by
K. Tachibana, O. Takai, K. Ono, T. Shirafuji

August 26 - 31, 2007, Kyoto University, Japan

Bio-decontamination by DC Discharges in Atmospheric Air: Identification of Mechanisms by Emission Spectroscopy

Z. Machala[1], I. Jedlovský[2], K. Hensel[1]

[1] *Department of Astronomy, Earth Physics and Meteorology,*
[2] *Department of Nuclear Physics and Biophysics,*
Faculty of Mathematics, Physics and Informatics, Comenius University, Mlynská dolina, 84248 Bratislava, Slovakia

Abstract: Bio-decontamination by three types of DC electrical discharges in atmospheric air with one electrode in water (streamer corona, transient spark and glow discharge) were tested on bacteria in water solution both in a static and a flowing regime. The bacteria were killed most efficiently in the transient spark with ultra short high pulses. The emission spectroscopic analyses indicate a major role of radicals and active species among other bio-decontamination mechanisms.

Keywords: Bio-decontamination, atmospheric DC discharges, emission spectroscopy, radicals.

1. Introduction

Atmospheric pressure non-thermal plasmas are nowadays widely investigated for various biological (sterilization), medical, and environmental (flue gas and water cleaning) applications. [1-4] We investigate three types of DC atmospheric discharges and test their bio-decontamination effects on selected bacteria in water solutions. In bio-decontamination, it is very important to assess the role of various mechanisms involved. [1] We identify the dominant mechanisms by comparing the electrical characteristics of the investigated discharges, their emission spectra, and bio-decontamination effects.

2. Experiment

2.1. Experimental set-up

The experimental setup for investigations of the DC discharges was shown elsewhere. [5-6] The bio-decontamination effects of these discharges were tested in both static and flowing regime. Fig. 1 shows the experimental setup for the continual flowing water treatment. Five parallel discharges were operated in a transparent discharge tube. The stressed high voltage electrodes were hollow needles, opposite to the copper plate electrode submersed in a water stream, with the typical needle-water distance of 4 mm. The water flow rates, and thus the residence times in the discharge tube, were varied. In the static regime, we used one needle above a dish with a submersed copper electrode and a certain volume of water or physiologic solution (typically 5 ml) treated for a specific time.

The discharge voltage on each needle was measured by a high voltage probe Tektronix P6015A. The discharge current was measured: 1) mean DC current with milliamp meter; 2) time-dependent current waveform on a 50 Ω or 1 Ω resistor; and 3) by a Rogowski current monitor PEARSON 2877. The current and voltage signals were processed by a digitizing oscilloscope Tektronix TDS 2024 (200 MHz). The light emission from the discharges was detected by a two-channel spectrometer Ocean Optics SD2000 (200-1100 nm, resolution 0.6-1.2 nm).

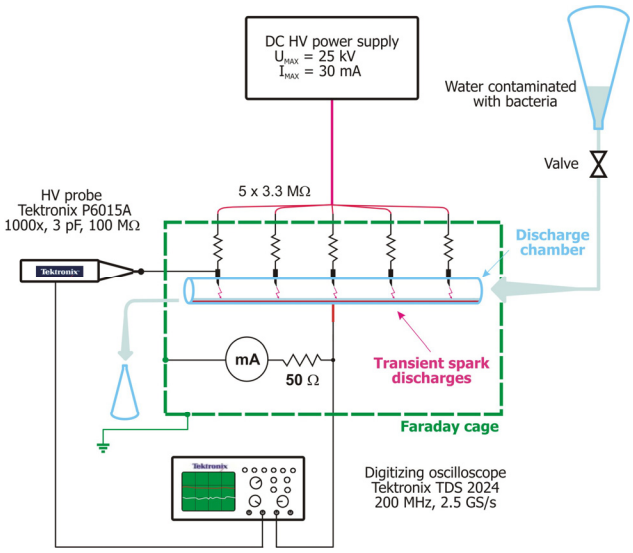
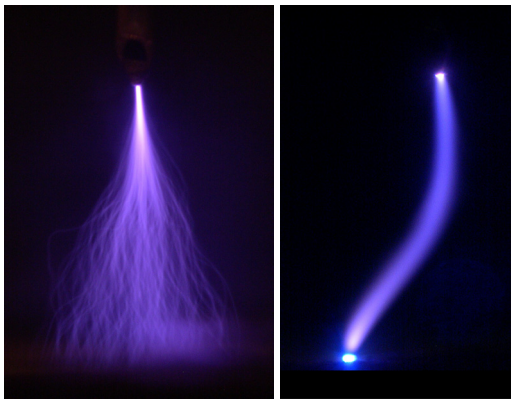


Fig. 1. Experimental set-up and a discharge tube with 5 parallel discharges for flowing regime water treatment.

2.2. Applied DC Discharges

Three types of DC discharges of both polarities operating in atmospheric air with water were investigated: a well-known streamer corona, and relatively novel transient spark (TS) and glow discharge (GD). Their photographs are shown in Fig. 2. These discharges generate non-equilibrium plasmas inducing various chemical and biological effects that play role in bio-decontamination. Each discharge generates the plasma with specific properties, so each was studied separately.

We only describe TS and GD in more detail here. TS is a DC-driven pulsed discharge with high but short (~100 ns) current pulses, and repetitive frequency of about 0.5-5 kHz, as shown in Fig. 3. Due to very short pulse duration (given by a small internal capacity of the discharge chamber C_{int}), the plasma cannot reach LTE. On the other hand, a periodic streamer-to-spark transition provides non-equilibrium conditions with fast electrons, resulting in efficient chemical and biological cleaning. [5]



Transient spark (TS) *Glow discharge (GD)*

Fig. 2. Photo of TS and GD discharges above water, gap distance 4 mm.

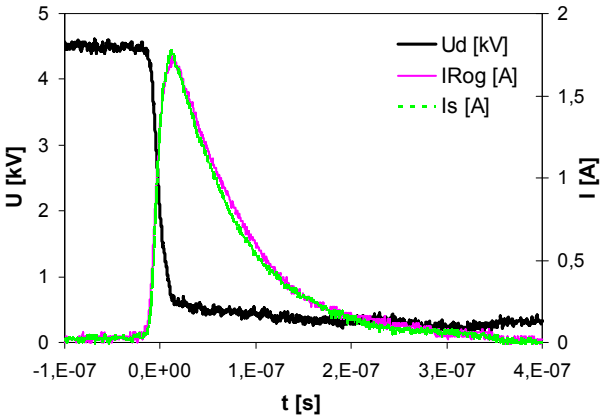


Fig. 3. Transient spark typical voltage (U_d), and current waveforms. (I_{Rog} - measured by the Rogowski monitor, I_s - measured on a 50 Ω resistor).

GD is typical with constant voltage and current (~1-10 mA), and a descending current-voltage characteristics. It is pulseless thanks to the appropriate series resistor that prevents its transition to spark but allows small current. Both TS and GD were also successfully for VOC abatement from flue gases. [7]

2.3. Treated bacteria

Biological effects of investigated DC discharges were tested on selected bacteria in water. The bacterial inactivation was examined by standard cultivation methods of a thermostatic growth on agar in Petri dishes, and was statistically evaluated. The following bacteria were treated:

1) *Salmonella typhimurium*, Gram-negative (G-) bacteria, (genetically modified strain TA 98): pathogen causing typhus diseases; its inactivation is important from the viewpoint of drinking water decontamination.

2) *Bacillus cereus*, Gram-positive (G+) bacteria: belongs to the same group as extremely hazardous *B. anthracis* (Anthrax precursor), which nowadays represents one of the highest bio-terrorism risks.

3. Results and discussion

3.1. Static regime treatment

The survival curves of *S. typhi* in water or physiologic solution treated in the static regime are shown in Fig. 4. The graph shows 2 experimental sets, starting at 7000 and 26 000 CFU/ml. The number of CFUs decreased with the treatment time in all discharges. We express the relative concentration decrease, i.e. the decontamination efficiency (Fig. 5). The typical discharge parameters were: streamer corona - repetitive frequency 26 kHz, current pulse amplitude I_{max}=25 mA; TS - 1 kHz, I_{max}=1.5 A; GD - I=6 mA. The highest efficiencies (72%) were obtained in the positive TS with 1 min treatment time, the lowest in the coronas; GD gives fairly high efficiencies as well.

We also tested the inactivation of the G+ spore-forming *B. cereus* in the static regime. It was difficult to reasonably evaluate the survival curves with these bacteria because CFUs after incubation did not form typical easily countable dots but larger stains. Nevertheless, a decrease of their concentration is visually demonstrated in Fig. 6: initial concentration: 12 000 CFU/ml; TS (60 s): 160 CFU/ml, efficiency 98.7%.

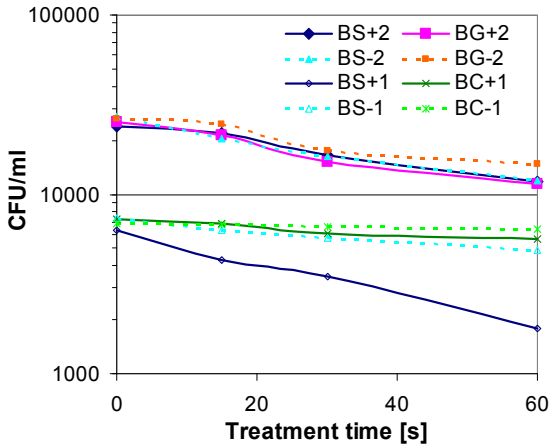


Fig. 4. S. typhi survival curves in semi-logarithmic scale. BS: transient spark, BG: glow discharge, BC: streamer corona, +: positive, -: negative polarity.

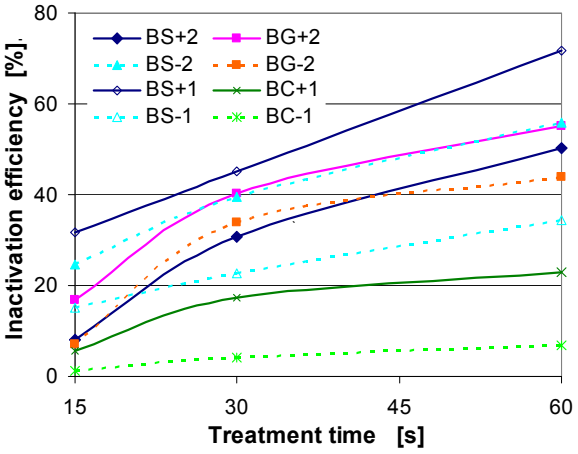


Fig. 5. S. typhi inactivation efficiency vs. treatment time. BS: transient spark, BG: glow discharge, BC: streamer corona, +: positive, -: negative polarity.

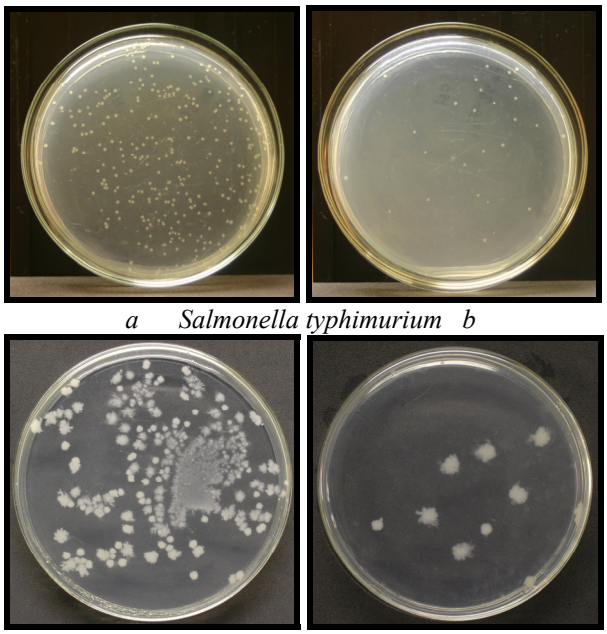


Fig. 6. Cultivated bacteria on Petri dishes. Reference *(a,c)* and after-treatment *(b,d)* samples.

3.2. Identification of mechanisms by Optical Emission Spectroscopy (OES)

OES in UV-VIS region is a powerful technique of plasma diagnostics, because it gives valuable information on excited atomic and molecular states, enables to determine the rotational and vibrational temperatures and thus the level of nonequilibrium in the plasma, and gives insight in ongoing plasma chemistry [6, 8]. Here, we employ OES, together with the comparison of the bio-effects of the three discharges to identify the dominant mechanisms involved in bio-decontamination.

All discharges emit N_2 (2^{nd} and 1^{st} positive system) and OH emission, thus indicating the presence of excited OH radicals formed from water molecules by dissociation. GD emits the strongest OH and also emits NO γ system. TS emits in addition N_2^+, and atomic lines of O, N and H radicals which signify high electron energy. The typical UV and VIS-NIR spectra are shown in Figs. 7-8.

Rotational, i.e. gas, and vibrational temperatures are evaluated by fitting experimental with simulated spectra using program SPECAIR [8]. SC and TS generate cold, nonequilibrium plasmas (300-550 K), GD plasma is hotter, yet nonequilibrium (1900 K). Electronic excitation temperature (9800 K) and OH radical concentration (3×10^{16} cm^{-3}) were estimated in GD assuming the Boltzmann distribution of excited states.

OES characteristics of the applied discharges described in detail in [6] showed that electrons with the highest energies are present in TS. These electrons initiate dissociations, ionizations and excitations of various species. Atomic O, N and H radicals, and the N_2^+ ions have only been detected in TS, and there were a lot of OH radicals. O radicals may react with air O_2 and form ozone O_3. These results synthesized with those of bacteria treatment indicate that the role of radicals and other active species is very important in bio-decontamination.

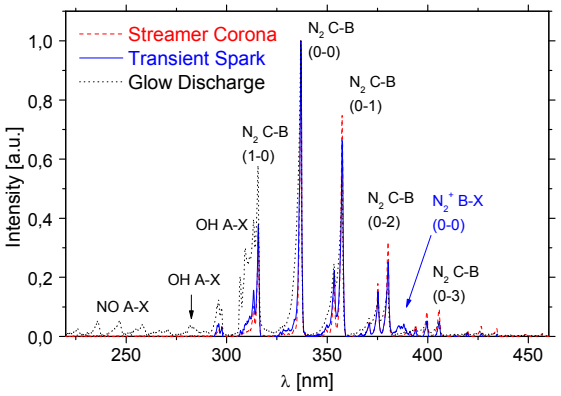


Fig. 7. Typical emission spectra of DC discharges in UV region. Gap: 4 mm; SC: 26 kHz, I_{max}=25 mA; TS: 1 kHz, I_{max}=1.5 A; GD: I=6 mA.

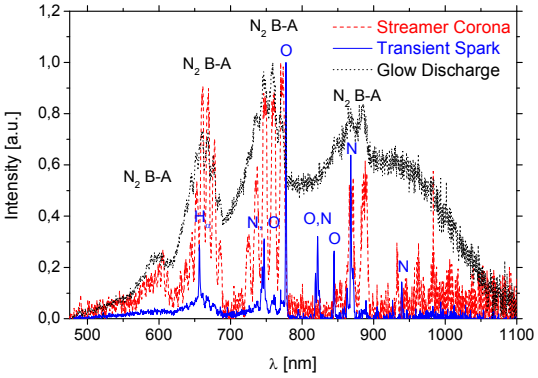


Fig. 8. Typical emission spectra of DC discharges in VIS-NIR region. Gap: 4 mm; SC: 26 kHz, I_{max}=25 mA; TS: 1 kHz, I_{max}=1.5 A; GD: I=6 mA.

High inactivation efficiencies were also reached in GD but at higher energy costs, due to the gas heating. The advantage of GD is a large amount of OH radicals forming by dissociation of the vaporized water. Streamer corona was the least efficient discharge for bio-decontamination. This is partly because it was the least energetic and partly because the active region was only in the proximity of the needle tip.

3.3. Flowing regime treatment

Bio-decontamination of *S. typhi* by positive TS in the 5-discharge tube in flowing regime gave better results than in the static regime. We treated 0.1 l of a contaminated water or a physiologic solution and varied the treatment times (15-28 min), i.e. flow rates (3-6 ml/min). The typical discharge parameters were: mean current 5 mA, U_d = 7 kV, f = 6 kHz. These results are viewed in Table 1. The decontamination efficiencies reached 99.25-100%, which is by 1-2 orders of magnitude larger than in the static regime, despite the residence time of the treated water in the discharge zone was shorter (10-20 s). This can be explained by much better 'volume efficiency,' i.e. the portion of water volume directly

treated by the discharge was substantially larger here than in the static dish.

The treated water (or physiological solution) had slightly increased temperature (from 22 to 31 ºC), conductivity (from 0.52 to 0.8-1.2 mS/cm for water and 15.2 to 16.4 mS/cm for physiologic solution), and decreased pH (from 7.4 to 3). The temperature increase is negligible from the point of view of bacterial survival, but the effects of increased conductivity and especially reduced pH may be important. They will be subjected to further analyses. No significant effect of the medium (water vs. physiologic solution) was observed.

Table 1. Bio-decontamination of *S. typhi* in the flowing regime, 5 parallel TS in the discharge tube.

r [Ω]	Medium	Treat. time [min]	Init. conc. [CFU/ml]	Final conc. [CFU/ml]	Effic-iency [%]
0	water	15	6650	20	99.70
0	water	28	17300	115	99.34
0	phys. sol.	18	12450	0	100
0	phys. sol.	25	13300	100	99.25
510	water	16.5	34700	4900	85.88
510	phys. sol.	14.5	25050	12450	50.30
1500	water	27.5	29800	7900	73.49
1500	phys. sol.	28	12750	5250	58.82

3.4. TS Pulse shape effect

With the TS discharge, we explored the effect of the pulse shape. As mentioned earlier, the TS pulse amplitude and duration are given by the repetitively discharging internal capacity of the chamber (C_{int} ~ 1-10 pF). When a high voltage probe and a high voltage cable were used, they added their own capacities to this C_{int}. To prevent this effect, we separated the discharge chamber by a small resistor *r* in order to minimize the capacity discharging in the spark pulse. We tested $r = 0$ (no resistor), 510 Ω, and 1.5 kΩ. Of course, a correction of the measured voltage on this *r* was then done. The pulse shape changed dramatically with various *r* tested, as demonstrated in Fig. 9. With increasing *r*, the pulse amplitude decreased but its duration extended. The amplitude decrease was due to the lowering capacities additional to C_{int}, and the duration extension due to larger time constant. The mean current was kept approximately constant.

Interestingly, the bio-decontamination tests with various *r* applied showed that substantially higher efficiencies were obtained with no *r*, i.e. strong and short pulses (~8 A, ~50 ns), see Table 1. Such pulses result in strong plasma nonequilibrium and generation of radicals and other active species, and low energy losses by gas heating. Similar effect was observed when comparing electrical properties, emission spectra and bio-decontamination effects of TS and GD, as described in section 3.2.

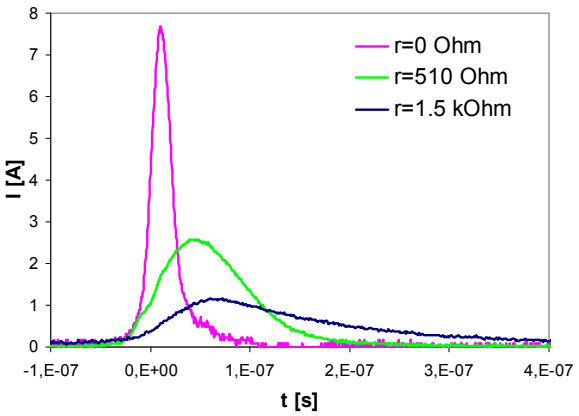


Fig. 9. Effect of the separating resistor *r* on the current pulse waveform.

4. Conclusions

We investigated bio-decontamination of water on selected bacteria (*S. typhi* and *B. cereus*) by three types of DC electrical discharges in atmospheric pressure air, with one electrode submerged in water: streamer corona and two novel types: transient spark and glow discharge. The discharges generate non-thermal plasmas with various gas temperatures and properties. Satisfactory results were obtained in the static regime, with the highest efficiency in the transient spark. In the flowing regime treatment by 5 parallel transient sparks, higher decontamination efficiencies were achieved in shorter treatment times. Spectroscopic and electric discharge investigations indicated important bio-inactivation mechanisms, mainly the major role of radicals and active species, generated especially in TS with high short pulses.

Bio-decontamination of spores, biofilms and surfaces is envisaged in near future, together with comparing the effects of a direct vs. remote plasma exposure.

This work was supported by NATO EAP.RIG 981194, Slovak Grant Agency VEGA 1/2013/05, and Slovak Research and Development Agency APVT-20-03240.

5. References

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