Water Bio-decontamination in DC Discharges

Z. Machala[1], I. Jedlovský[2]

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

We tested bio-decontamination by three types of DC electrical discharges in atmospheric air with one electrode submerged in water, on selected bacteria (*S. typhi*, *B. cereus*) in water solution. The employed DC discharges were streamer corona, and two novel types: transient spark and glow discharge. They generate nonequilibrium plasmas with high concentrations of radicals and other active species, as detected by optical emission spectroscopy. A substantial decrease of bacterial concentration was observed both in the static and flowing treatment regime, especially with the transient spark. A study of the transient spark current pulse showed the largest efficiency with very short high pulses. Together with the comparison of the three discharge types used, this indicates a major role of radicals and active species among other decontamination mechanisms.

1. Introduction

Non-thermal plasmas at atmospheric pressure are nowadays widely investigated for various environmental (flue gas and water cleaning) and bio-decontamination (sterilization) applications. [1-3] We investigate three types of DC-driven 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. [2] We attempt to do so by comparing the electrical characteristics of the investigated discharges, their emission spectra, and their bio-decontamination effects.

2. Experiment

2.1. DC Discharges

Three types of DC discharges of both polarities operating in atmospheric air with water in the discharge chamber were investigated: a well known streamer corona, and relatively novel transient spark (TS) and glow discharge (GD). Their photographs are shown in Fig. 1. 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 one was studied separately [4-5].

Since transient spark provided the highest bio-decontamination efficiency, we describe this type in more detail here. TS is a DC-driven pulsed discharge with high but very short (~100 ns) current pulses, and repetitive frequency of about 0.5-5 kHz, as shown in Fig. 2. Due to very short pulse duration (given by a small internal capacity of the discharge chamber), the plasma cannot reach LTE conditions. On the other hand, the periodic streamer-to-spark transition provides non-equilibrium conditions with fast electrons, resulting in efficient chemical and biological cleaning. [4] GD is typical with constant voltage and current. Both TS and GD were also applied for VOC abatement from flue gases. [6]

Transient spark (TS) Glow discharge (GD)

Fig. 1. Photo of TS and GD discharges above water, gap distance 4 mm (aperture 4.8, exposure ¼ s).

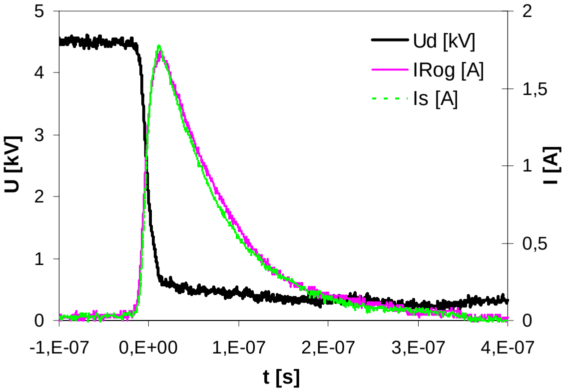


Fig. 2. Transient spark typical voltage (U_d), and current waveforms. (I_{Rog} - measured by the Rogowski monitor, I_s -measured on a 50 Ω resistor).

2.2. Experimental set-up

The experimental setup for investigations of the DC discharges was shown elsewhere [3-4]. The water bio-decontamination effects of these discharges were tested in both static and flowing regime. Fig. 3 shows the experimental setup for the flowing regime continual water treatment. In this case, 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 its residence time in the discharge tube, were varied. In the static regime, we used one needle above a Petri dish with a submersed copper electrode and a certain volume of water or physiologic solution (typically 5 ml) treated for a specific time, as shown in Fig. 4.

The discharge voltage on each needle was measured by a high voltage probe Tektronix P6015A. The discharge current was measured by: 1) total 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, 2.5 GS/s).

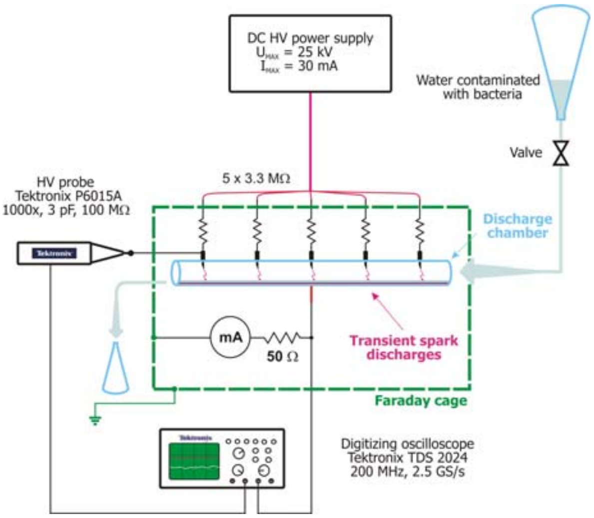


Fig. 3. Experimental set-up and discharge tube with 5 parallel discharges for flowing water treatment.

Fig. 4. Single needle – Petri dish discharge chamber for static water treatment

2.3. Bacteria

Biological effects of investigated DC discharges were tested on selected bacteria with standard cultivation method of thermostatic bacterial growth on agar on Petri dishes, and were statistically evaluated. The following bacteria were treated:

1) *Salmonella typhimurium*, Gram-negative (G-) bacteria, genetically modified strain TA 98,

2) *Bacillus cereus*, Gram-positive (G+) bacteria.

S. typhi is a pathogen causing typhus diseases, and so its inactivation is important from the viewpoint of drinking water decontamination. *B. cereus* 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 water treatment

The survival curves of *S. typhi* in water or physiologic solution treated in the static regime are shown in Fig. 5. The graph shows 4 experiment 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. 6). 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. 7: initial concentration: 12 000 CFU/ml; TS (60 s): 160 CFU/ml, efficiency 98.7%.

3.2. Flowing water treatment

The tests of 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 always 0.1 l of contaminated water or physiologic solution and varied several 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 Petri dish.

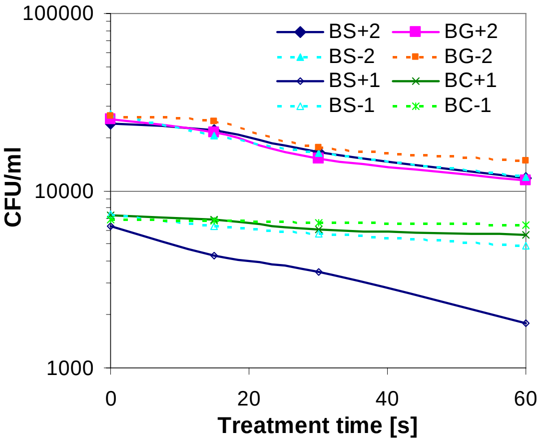


Fig. 5. *S. typhi* survival curves in semi-logarithmic scale. BS: transient spark, BG: glow discharge, BC: streamer corona, +: positive, -: negative polarity.

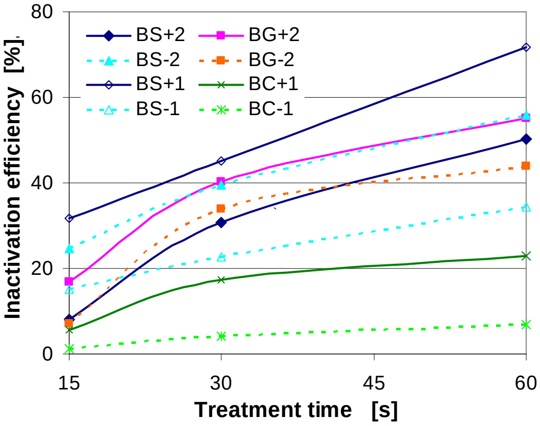
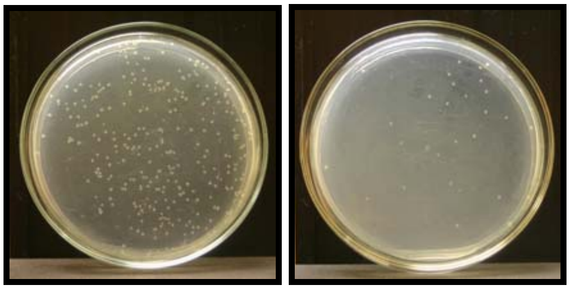


Fig. 6. *S. typhi* inactivation efficiency vs. treatment time. BS: transient spark, BG: glow discharge, BC: streamer corona, +: positive, -: negative polarity.

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 effect of the medium on bio-decontamination was observed, i.e. water vs. physiologic solution.



a Salmonella typhimurium b

c Bacillus cereus d

Fig. 7. Cultivated bacteria on Petri dishes. Reference *(a,c)* and after-treatment *(b,d)* samples.

Table 1. Bio-decontamination of *S. typhi* in 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
1500	phys. sol.	28	12750	5250	58,82

3.3. Pulse shape effect and involved mechanisms

With the TS discharge, we explored the effect of the pulse shape. As mentioned earlier, the TS pulse amplitude and duration is 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. 8. With increasing r, the pulse amplitude decreased but its duration extended. The amplitude decrease was due to lowering additional

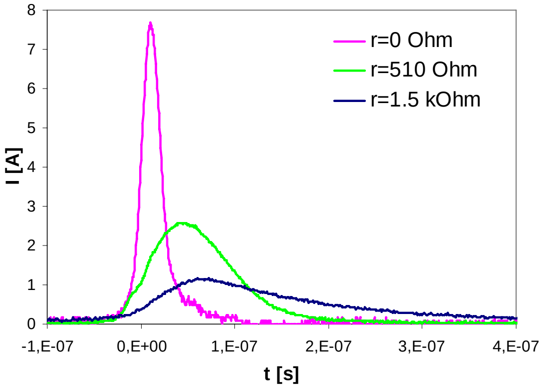


Fig. 8. Effect of the separating resistor r on the current pulse waveform.

capacities on C_{int}, and the duration extension due to larger time constant. The mean current (integrated I(t) waveform) was kept approximately constant.

Interestingly, the bio-decontamination tests with various r applied showed that larger 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. [4] Emission spectroscopic characteristics of the applied discharges described in detail in [5] 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 indicate that the role of radicals and other active species is very important.

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. It is hard to distinguish the temperature effect at this stage. Streamer corona was the least efficient discharge for bio-decontamination. This is partly because it is the least energetic and partly because the active region is in the proximity of the needle tip only, while most of the space is occupied by the drift region.

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, the flowing water was treated with 5 parallel transient sparks, and higher decontamination efficiencies were achieved in shorter treatment times. Spectroscopic discharge investigations indicated important bio-inactivation mechanisms, mainly the major role of radicals and active species.

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5. References

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