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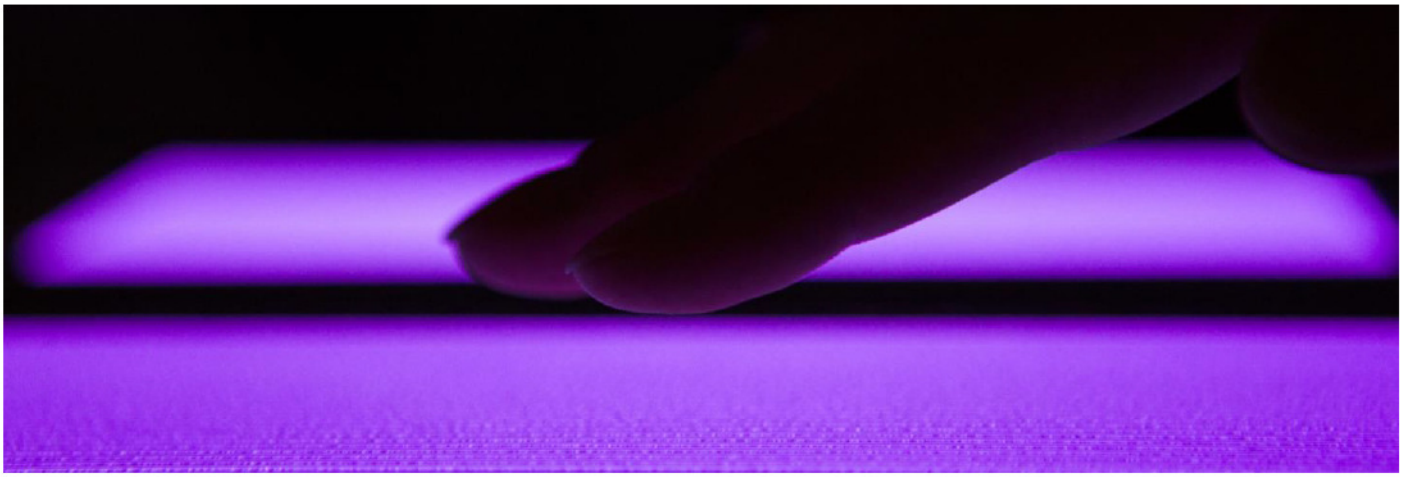
with joint COST TD1208 workshop Non-Equilibrium Plasmas with Liquids for Water and Surface Treatments



Book of Contributed Papers

Masaryk University

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PROPAGATION OF ARGON SURFACE DISCHARGE IN LONG TUBES AT ATMOSPHERIC PRESSURE, ITS BACTERICIDAL EFFECT AND THE EFFECT OF UV EMISSION

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The objective of the presented work is the bio-decontamination of small diameter long tubes by direct exposure of the tube inner surface to the plasma of a pulsed corona discharge in dry or humid argon. Bactericidal tests were conducted with *Escherichia coli* strain DH-1 for various exposure times. Up to ~5.5 $\log_{10}$ reduction was observed for *E. coli* exposed 44 cm away from the HV electrode, for a 20 minute treatment. The factors contributing to the observed bactericidal effect include desiccation, reactive oxygen species (OH), H_2O_2 accumulation in the liquid phase, and UV B (and possibly VUV) in dry argon.

Keywords: low-temperature plasma; bio-decontamination; UV emission; argon plasma; pulsed corona discharges

1 Introduction

In the domain of surface sterilization of thermally sensitive materials, the decontamination of the interior of small diameter tubes (e.g. catheters, endoscopes) is an important issue. In previous studies, the inner surfaces of tubes were exposed to different plasma processes at atmospheric pressure in direct [1-3] or remote exposure modes. For the remote exposure mode, a flowing post-discharge was passed through the tube inlet. The plasma source was either a pure nitrogen corona discharge producing an emissive afterglow [4], or a humid argon dielectric barrier discharge [5]. In the latter case, argon was preferred to air as a feed gas in order to avoid the formation of ozone and nitrogen oxides that may damage the treated surface. Furthermore, water dissociation in the argon discharge is much more efficient than in air or nitrogen [6].

2 Material and methods

2.1 Plasma device

Pulsed corona discharges were propagated on the inner surfaces of a quartz tube (8 mm inner diameter, 49 cm long), in which argon (3.9 slm) or humid argon (4.7 slm, 760 ppm water vapor/argon mixture) was flowing at atmospheric pressure, from a tungsten needle connected to a pulsed high voltage power supply placed at the tube inlet to a grounded counter electrode located at its outlet (Fig. 1). A voltage probe (Tektronix P6015A) connected to the needle electrode and a current transformer (Tektronix CT-2) connected to the counter electrode were used for voltage and current measurements respectively. Signals were recorded using a LeCroy WaveRunner 62 Xi digital oscilloscope. For all bactericidal tests, the plasma was generated with a 2-2.2 µs voltage pulse at 500 pulses/s with a 20.6-27.9 kV peak voltage depending on the sample and the gas humidity.

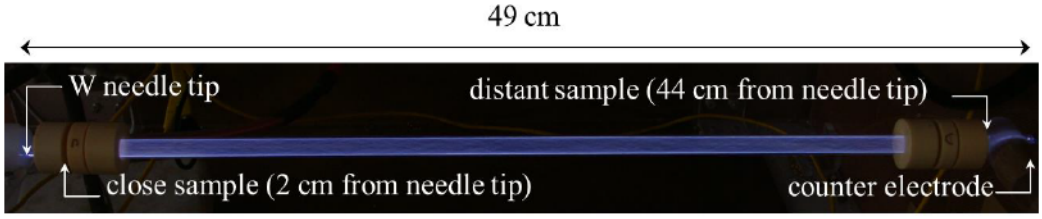

Fig. 1: The pulsed corona discharge propagating in argon gas inside an 8 mm inner diameter quartz tube over 49 cm. The bacterial sample locations at 2 and 44 cm are indicated.

2.2 Optical emission spectroscopy

OES was performed in the 250–850 nm range using an Acton Standard Series SP-2758 imaging spectrograph of a focal length 750 mm. Two ruled gratings were used in the measurements; a 2400 gr/mm blazed at 240 nm and a 300 gr/mm blazed at 300 nm. This spectrograph was coupled to a Princeton Instruments PI-MAX4:1024f-RB intensified CCD. For all spectroscopic measurements, a fiber optic cable with a collimator adjusted to collect light from a 1cm diameter disk centered on the tube axis was pointed perpendicularly at the tube from a distance of 38 cm. This fiber was moved along the tube's length in order to collect light from different positions.

2.3 Bacterial sample and test conditions

Escherichia coli strain DH-1 was used for all experiments. The culture in stationary phase was frozen with 20% (v/v) glycerol in 20 µl aliquots tittered at ~10^9 colony forming units (CFU)/ml. Before experiment aliquots were thawed and resuspended in 110 µl 1/3X LB. Droplets of 10 µl volume were placed inside or outside the quartz tube (to evaluate the UV B effect on bacteria viability), and either immediately treated as droplets (liquid) or dried at room temperature (2 – 4 h). Samples were positioned 44 cm from the needle electrode (Fig. 1) and treated by the plasma up to 20 min, samples exposed for the same duration to the argon flow alone were included as controls. Bacterial cells were recovered with rinsing of the inner or outer quartz tube surface with 100 µl sterile distilled water and resuspended in 1/3X LB. Recovered samples were serially diluted, plated on LB agar, incubated at 37°C overnight, and quantified by colony counting.

3 Results and Discussion

3.1 Optical emission spectroscopy

Optical emission spectra of the pulsed corona discharge plasma in dry and humid argon (Fig. 2) showed the presence of emissive OH radicals. In the presence of water (even traces, as it is for "dry" Ar condition), the argon plasma generates ultraviolet (UV B, 280–315 nm) emission through the de-excitation of OH^* [$A^2\Sigma^+$ - $X^2\Pi$] radicals (305–311 nm), mainly produced by a water dissociation mechanism involving Ar^*: Ar^* (4p) + H_2O → Ar (3p) + OH^* ($A^2\Sigma^+$) + H

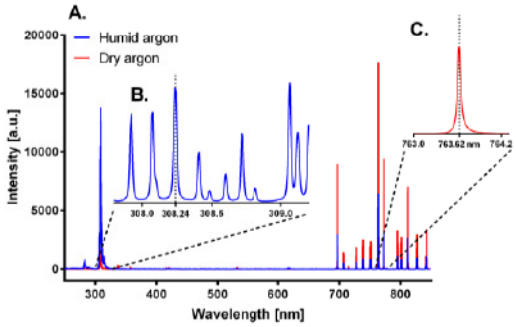

Fig. 2: A) Optical emission spectra of the pulsed corona discharge in and humid argon acquired at 5 cm from the HV electrode. Detector integration time 600 ns, grating 300 lines/mm. B) Spectrum of the rotational bands of OH [A^2S^+ - X^2P] measured in humid argon (760 ppm water vapor), grating 2400 gr/mm. C) Ar emission line in dry argon, grating 1800 gr/mm.

The relative intensity of the OH band depends on the humidity present in the feed gas and it is greater in argon with 760 ppm of water vapor than in dry argon [7]. This water vapor concentration is slightly below the optimum value, above which increasing the water vapor content does not lead to a further increase in the OH line intensity, but on the contrary leads to its decrease. This result was previously observed and was found to be caused by quenching mechanisms that become the dominant phenomena in high water vapor concentration conditions [7, 8] as per: OH^* ($A^2\Sigma^+$) + H_2O → OH ($X^2\Pi$) + H_2O. The presence of humidity in the feed gas has thus a dual benefit of producing both reactive OH radicals and UV B emission.

3.2 Bio-decontamination efficiency of the discharge and its UV B emission

We investigated the decontamination efficiency of the pulsed corona atmospheric pressure argon plasma at the inner and outer surfaces of the quartz tube 44 cm from the HV needle electrode. The water content (in argon gas or at the sample level) was shown to be a key parameter that strongly influenced the generation of reactive species [9]. Two extreme combinations are presented in Fig. 3 - combination with the highest water content of humid argon gas and liquid bacterial samples and dry argon gas with dried samples as dried combination. The bactericidal effect of the treatment is presented in terms of "reduction factor", defined as: $log_{10}(N_0/N)$ where N_0 is the control sample CFU and N the sample after plasma treatment CFU.

The biocidal activity of emission at 308 nm is cumulative, and the decontamination efficiency tends to increase with treatment time in all conditions, reaching a maximum efficiency of 1.24 reduction factor for 20 min treatment of a liquid sample with a humid argon feed gas at 44 cm (Fig 3.). The discharge in humid argon with a liquid sample, while not the most efficient when

looking at the decontamination efficiency of the overall plasma treatment process inside the tube (In), generated the best efficiency of decontamination for UV B radiation alone outside the tube (Out). In the case of dry argon/dry sample inside the tube, VUV can have high contribution to the decontamination efficiency. For the outside samples this is not the case because the quartz does not allow VUV to pass, although we still have the effect, probably of residual humidity, that produces UV B. In the case of humid argon/liquid sample, the inside samples are exposed to higher VU B emission, OH radical production, and there is accumulation of H_2O_2 in the liquid of sample. Outside samples are exposed to higher doses of UV B originated also from sample evaporation, therefore there is higher decontamination efficiency. In the case of liquid samples, there is a dilution of the reactive species and so a delay in the bactericidal effect compared to the dried samples.

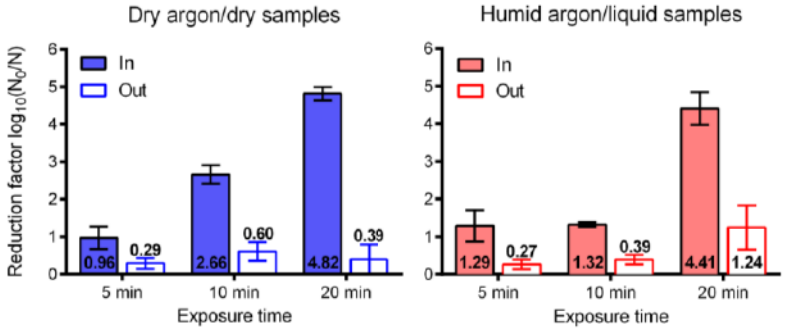

Fig. 3: Reduction factor measured after the argon plasma treatment (In) and the argon plasma-generated UV B radiation (Out) for increasing exposure times at 44 cm in humid and dry argon with liquid and dried samples. Assays were carried out in triplicates. Graphed: mean ± SEM.

4 Conclusion

We report biocidal results obtained with and atmospheric pressure non-thermal pulsed corona discharge source adapted for inner surfaces of long narrow tubes. Within 20 min exposure time 5 $\log_{10}$ reduction of bacterial population was reached at the end of the quartz tube. We showed that the UV B emission played important role in discharge bio-decontamination efficiency.

Acknowledgement

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