AC-driven pin-to-liquid discharge: characterization and application

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Abstract: An AC-driven pin-to-liquid discharge configuration for plasma-treatment of up to 1 L water is presented. Electrical and optical investigations of the discharge for different kinds of treated water (tap water, saline solution, distilled and Milli-Q water) are discussed. The changes of the characteristics of the treated liquids are investigated. as well as the resulting antimicrobial properties.

Keywords: plasma activated water, pin-to-liquid discharge, inactivation of bacteria

1. Introduction

The treatment of bacteria in liquids with non-thermal plasma is well studied and reported [1-3]. Different bacteria like *E. coli, S. aureus* or *B. atropheus* were successfully inactivated. These investigations were performed with plasma in close vicinity or with direct contact to the surface of the liquids. Plasma jets were also found to be an effective technology for inactivation of bacteria in liquids [4]. In these reported experiments, the liquids already contained the bacteria to be treated. In [5] it is shown that plasma treated distilled water remains antibacterial for several days. This proves that bacteria to be treated do not have to be in contact with the plasma or the plasma generated gaseous species but can be efficiently inactivated just by treating with the plasma-activated water (PAW).

For the plasma treatment of liquids several discharge configurations and electrical operation modes are investigated up to now. In [6] a DC-driven pin-to-liquid configuration is presented, [7] reports of a pulsed powered multineedle-to-liquid discharge, and [8] used a low frequency AC-voltage driven plate-to-liquid configuration for plasma generation. Different discharge modes like filamentary or glow mode were observed. This variety provides a certain degree of freedom in designing an electrode configuration and electrical control. Research results of electrical discharges in and in contact with liquids have been summarized in [9] and [11].

The volumes of generated PAW in the experiments found in the literature were quite small (in the range of some millilitres). This is sufficient for the investigation of the chemical and biological properties of the treated liquid. In order to use the antimicrobial properties of PAW for cleaning of surfaces or storage of disinfected medical devices the need for large volumes of PAW (in the range of litres) raised. Thus, a portable device for the production of up to 1 L PAW was manufactured and characterized by means of electrical, optical and chemical investigations. Furthermore, the antimicrobial effectivity is demonstrated for different treatment times.

2. Experimental Setup and Procedure

The experimental setup as schematically shown in Figure 1 was used to investigate pin-to-liquid discharges. It mainly consisted of a beaker filled with the liquid to be plasma-treated. This beaker was positioned on a magnetic stirrer. On top of the beaker an electrode configuration was placed. The electrodes, made of stainless steel, were connected to a commercial high-voltage source (NeonPro 10000-30), providing two sinusoidal high-voltage outputs of up to 10 kV_{PP} at a frequency of around 30 kHz. The voltages are phase inverted to each other as depicted by the small diagrams in Figure 1. The discharges ignited between the metal electrodes and the water surface. By means of voltage probes (Tektronix P6015A) and current probes (Pearson 2877) the electrical data were measured and recorded with an oscilloscope (Tektronix DPO 7582A). For spectroscopic investigations an Ocean Optics HR 4000 fiber spectrometer was used. These measurements were performed with a modified beaker providing optical access to the discharge.

The treatment of up to 1 L of liquid was performed with an electrode configuration consisting of two of the above described configurations. Thus, four electrodes driven by two high-voltage sources were used. Again, the beaker was placed on a magnetic stirrer and the liquid was stirred permanently. The treated liquids were tap water, saline solution (0.85 % NaCl), distilled water, and Milli-Q water.

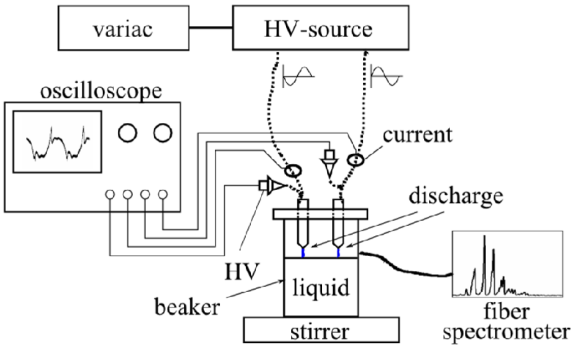

Figure 1: Experimental setup

For these liquids the pH-value, the temperature, and the conductivity were measured with a multiparameter meter (Hanna Instruments HI 9828). Additional tests (concentration of NO_2^-, NO_3^-, and H_2O_2) were performed with test stripes (MQuant).

For the evaluation of the antimicrobial properties of the plasma-treated liquids *Escherichia coli* K-12 (NCTC 10538/DSM 11250) was used as test microorganism. Therefore, 100 µL of bacteria suspension were mixed with 5 mL of plasma-treated liquid. The total viable count was determined by spiral plate method (Spiral Plater: Eddy Jet 2, IUL, Barcelona, Spain) and the plates were incubated for 24 h at 37 °C. Afterwards, the number of surviving microorganisms was counted using an automated colony counter.

3. Electrical Discharge Characterization

In Figure 2 the voltages driving the discharges ignited on saline solution are shown. It is visible that the sinusoidal voltages collapse when the discharges occur. This is the typical behaviour of leak transformers with limited secondary current. It is also to be seen that the voltage

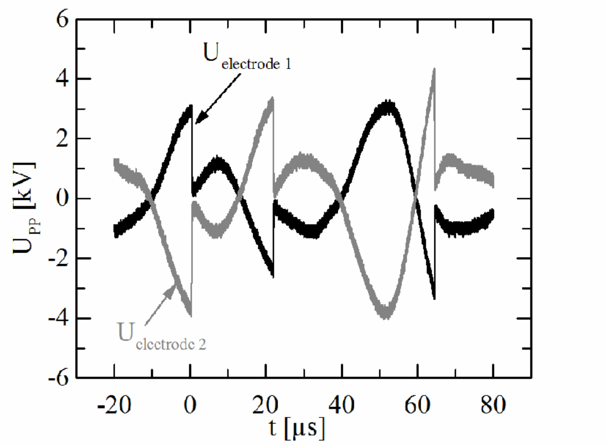

Figure 2: Overview oscillogram of voltage (left scale) and current (right scale), saline solution

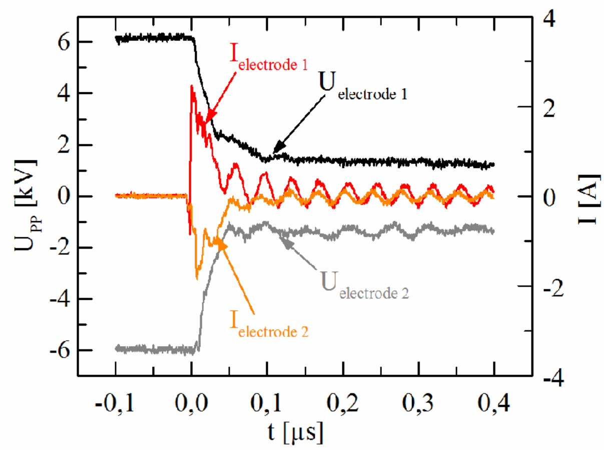

Figure 3: Single discharge oscillogram of voltage (left scale) and current (right scale), saline solution

curves are not exactly symmetrical indicating different electrical characteristics of the discharges. Moreover, the oscillogram shows that the discharges on both electrodes occur simultaneously. This is in detail shown in Figure 3. Because there is no grounded electrode connected to the liquid, discharges must occur on both electrodes simultaneously to permit current flowing from one electrode to the other. Operating the electrode configuration on tap water delivers very similar results as the presented results obtained with saline solution. Exchanging the liquid with distilled or Milli-Q water reveals the occurence of weaker discharges. The current peaks and the voltage drops at breakdown are smaller (data not shown). This is likely due to the different conductivities of the liquids (~16 mS/cm for saline solution and 3 µS/cm for Milli-Q water).

4. Optical discharge characterization

Overview emission spectra of discharges operated on saline solution and Milli-Q water are presented in Figure 4. The spectra are dominated by the emissions of molecular nitrogen between 300 and 400 nm. Furthermore, small emissions of nitrogen monoxide (NO) between 240 and 280 nm are detected. In the spectrum recorded with saline solution significant emission at 589 nm is found, which is related to sodium (Na) [10]. The appearance of this line is supposed to be due to sodium atoms evaporated from the NaCl-containing saline solution. This line is also present in the spectrum recorded with Milli-Q water but much weaker. Because Milli-Q water is supposed to be free of salts this is most likely due to impurities in the experimental setup. The line at 777 nm (atomic oxygen (O) [10]) found in the spectrum related to saline solution treatment does not appear in the spectrum

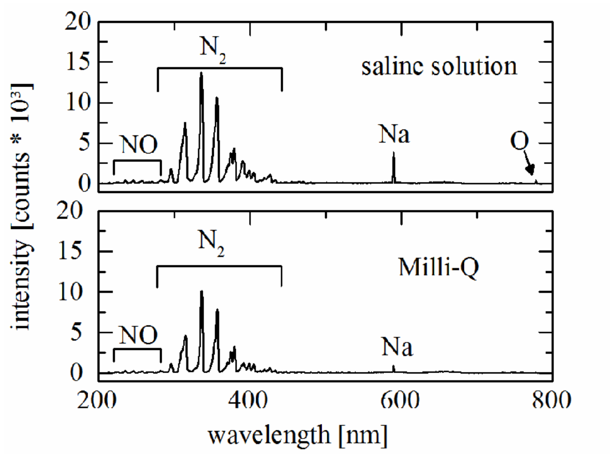

Figure 4: Overview spectra of discharges operated on saline solution (top) and Milli-Q water (bottom)

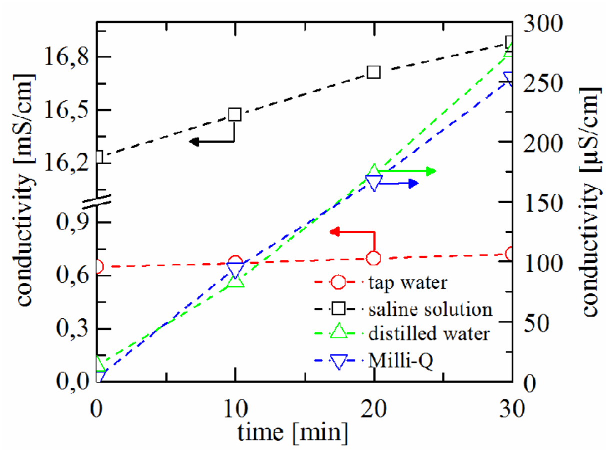

Figure 5: Conductivity of the plasma-treated liquids with respect to treatment time

related to Milli-Q water treatment. This, as well as the weaker intensity of the N_2-emission, is supposed to be due to the weaker discharge. As found in the electrical characterization the results for tap water and saline solution are comparable as well as the results for distilled and Milli-Q water.

5. Characterization of treated liquids

The treatment of the liquids with plasma changed various parameters of the liquid, e.g. pH-value, conductivity, temperature, and chemical composition. According to the literature, especially the pH-value plays a significant role for the antimicrobial activity [2]. In the experiments reported in this contribution an influence of the conductivity on the discharge current and the voltage drop is found. For all treated liquids, except tap water, an increase of the conductivity of some hundred µS/cm after 30 minutes of treatment is observed (Figure 5). In case of tap water the increase of the conductivity remains around 50µS/cm. The influence of the conductivity on parameters like breakdown voltage or discharge appearance is discussed in detail in [11].

The behaviour of pH-value is shown for all treated liquids in Figure 6. Again, for all liquids except tap water a significant decrease of the pH-value is found. It is supposed that tap water with a very high hardness as used in this study contains sufficient buffering components like carbonate, which prevents from acidification. Therefore, the pH-value keeps constant. Additional measurements with test stripes revealed significant production of nitrite (NO_2^- up to 80 mg/L) and nitrate (NO_3^- up to 500 mg/L). As shown in Figure 4, emissions from nitrogen monoxide (NO) are found in the spectra. This gives reason to assume that the nitration of the liquid is due to the input of nitrogen species from the gas by the discharge. Test stripes were also used to evaluate the generation of hydrogen peroxide (H_2O_2). In all investigated liquids the concentration of H_2O_2 after 30 minutes of plasma-treatment is almost negligible (around 1 mg/L).

6. Antimicrobial properties of treated liquids

The antimicrobial properties were evaluated by counting of the surviving bacteria after treatment with plasma-activated liquid. As an example, Figure 7 shows bacteria colonies after plating on agar before (left image) and after 30 minutes of treatment (right image) with plasma-activated saline solution. In this case, the liquid was plasma-treated for 20 minutes. The decrease of the number of surviving bacteria is clearly visible (the asterisk marked dot is a flaw of the Petri dish). For quantitative analysis the number of bacteria was counted with an automated colony counter.

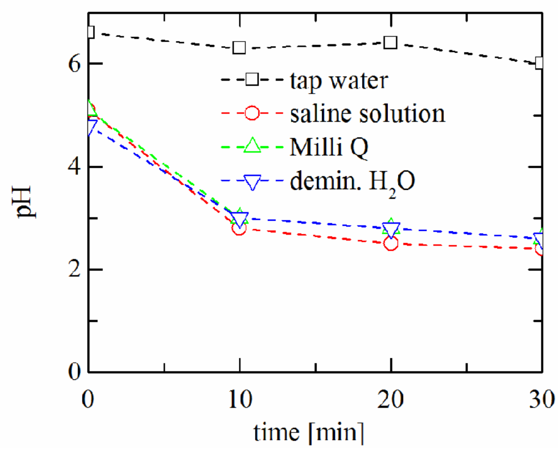

Figure 6: pH-value of plasma-treated liquids with respect to treatment time

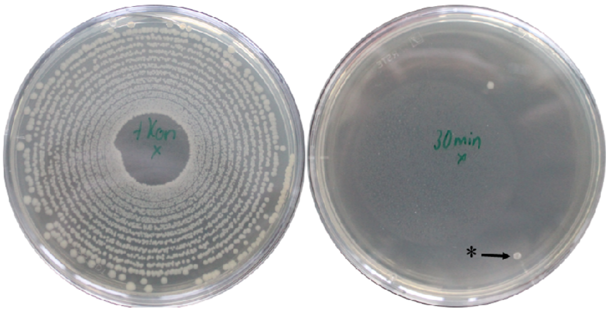

Figure 7: Image of agar plates for the determination of total viable count before (left) and after30 minutes treatment (right) with PAW (20 minutes activated), asterisk marked dot: flaw of petri dish

The results for saline solution, which was plasma treated for 10 minutes and for 30 minutes, respectively, are shown in Figure 8. The exposure time was up to 60 minutes. Both PAWs inactivated all bacteria in the sample but with the solution plasma-treated for 30 minutes the complete inactivation is achieved much faster than with the solution treated for 10 minutes.

7. Summary and conclusion

In this contribution, a mobile and easy-to-use system for the generation of plasma-activated water (PAW) was presented. Different kinds of water were treated and the influence of the water on the discharge was investigated. It was found that liquids with lower conductivity decrease the discharge current and the voltage drop at breakdown. Because of the treatment, the liquids changed their properties like conductivity and pH-value. The antimicrobial properties of the liquids were analyzed. As an example, it was shown that saline solution plasma-treated for 30 minutes reduces the number of surviving bacteria by 5 orders of magnitude.

It could be shown that also large volumes of liquid (up to 1 L) can be plasma-activated in reasonable time. Thus, the use of these liquids for antibacterial applications becomes feasible. For the identification of upcoming applications also the effect of PAW on other microorganisms than presented in this contribution has to be investigated as well as the long term activity for investigations of storability.

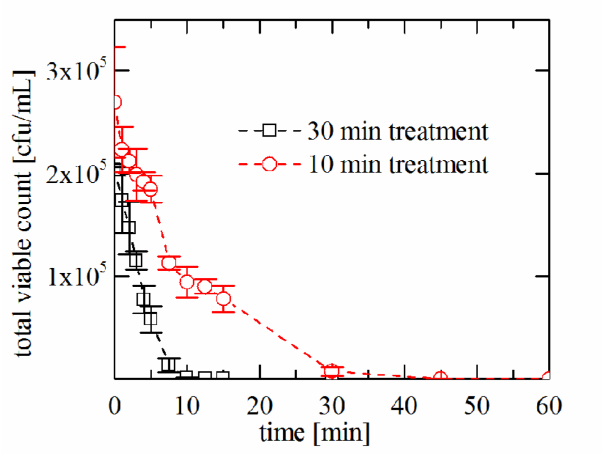

Figure 8: Total viable count [cfu/mL - colony forming units/mL] after treatment with saline solution activated for 10 and 30 minutes

8. Acknowledgements

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