Plasma-liquid-interactions: chemistry and antimicrobial effects

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Résumé

Plasma-induced inactivation of bacteria in aqueous liquids is supported by acidic pH and accompanied by generation of detectable chemical species like nitrate, nitrite and hydrogen peroxide. To get more insight into mechanisms of change of liquid composition by plasma treatment as well as transmission of bactericidal plasma effects into aqueous liquids, plasma diagnostics and liquid analytics are combined with theoretical considerations to focus possible reaction channels of plasma-water interactions.

Introduction

At the present state of knowledge, inactivation of bacteria in aqueous liquids by atmospheric pressure plasma treatment is strongly dependent on acidification (Fig. 1). However, it was also demonstrated recently that acidification alone does not induce comparable bactericidal efficacy. Moreover, plasma treatment of aqueous liquids results in additional changes of liquid composition, e.g. by generation of nitrate (NO_3^-), nitrite (NO_2^-) and hydrogen peroxide (H_2O_2) [1-4]. Therefore, the aim of further work is to get more insight into possible mechanisms of both liquid chemistry and bactericidal efficacy.
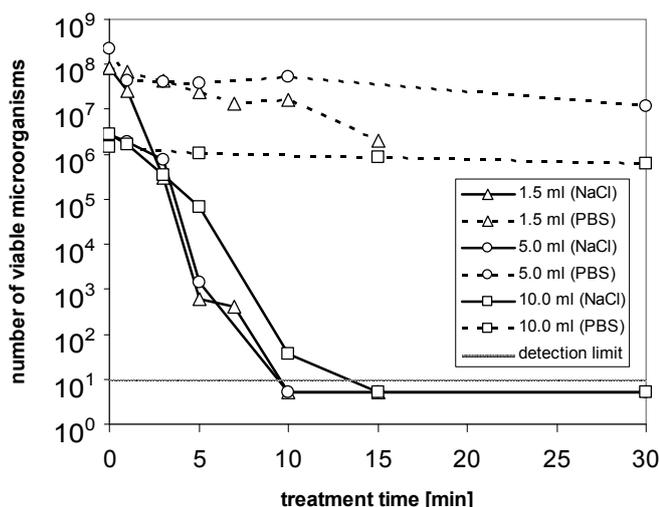
Fig. 1: Kinetics of inactivation of 1.5 ml (△), 5.0 ml (○) and 10.0 ml (□) *S. aureus* suspensions in physiological saline (NaCl; —) and phosphate-buffered saline (PBS; ---), respectively, by surface-DBD plasma (mean of n=2 each)

Experimental

Plasma treatment of aqueous liquids (distilled water, phosphate buffered saline, or physiological saline, respectively) was realized using a surface dielectric barrier discharge (surface-DBD) arrangement which was described in detail elsewhere [4]. Plasma is generated on the surface of an electrode array which was mounted by a special construction into the upper shell of a petri dish (60 mm diameter) in that way that a constant distance of 5 mm between the high-voltage electrode surface and the surface of a liquid sample in the lower shell of the petri dish (surface area 23.8 cm^2) can be adjusted. All experiments are performed at ambient air conditions using a pulsed sinusoidal voltage of 10 kV$_{peak}$ (20 kHz) with a 0.413/1.223 s plasma-on/plasma-off time. Energy of 2.4 mJ was dissipated into the plasma in each cycle of high voltage. The power is 0.25 W · cm^{-2}. Plasma diagnostics was realized using OES and FT-IR. For liquid analytics, UV/VIS spectrophotometer and semi-micro pH-electrode have been used. Detection of nitrite, nitrate and hydrogen peroxide in plasma treated water has been realized both by color forming reactions using chemical indicator substances and direct photometric analysis via total absorption spectra.

Results and discussion

Biological as well as chemical plasma effects in liquids must be a result of complex interactions at the plasma/gas-liquid interface and subsequent reactions in the liquid volume. To clarify possible mechanisms of chemical species generation as well as of microorganism inactivation in plasma-treated liquids, gas phase above the liquid surface was analyzed. Usually, direct or indirect actions of plasma-generated nitric oxide ($NO^\bullet$) or hydroxyl radicals ($HO^\bullet$) are considered to be mainly responsible for biological plasma effects. However, no $NO^\bullet$ was detected in the plasma/gas phase neither by OES via emission in the bactericidal effective UV-C range around 254 nm nor by FT-IR. Surprisingly there was also no emission of hydroxyl radicals ($HO^\bullet$) at 309 nm. This is in contrary to other studies [5] and could be explained by the low energy input realized with our discharge arrangement. Using FT-IR, stable molecules like nitrous oxide (N_2O), ozone (O_3), carbon dioxide (CO_2), and traces of nitric acid (HNO_3) and/or peroxynitrous acid ($ONOOH$) were measured. Reactions of these molecules from the plasma/gas phase with the aqueous liquid could result in acidification and generation of NO_3^-, NO_2^- and H_2O_2 via reactions which are associated with the occurrence of several more or less stable but biologically active chemical intermediates like $NO^\bullet$ or nitrogen dioxide ($NO_2^\bullet$). On the other hand, NO_3^-, NO_2^- and H_2O_2 could serve as starting reaction partners to generate $NO^\bullet$, $HO^\bullet$, $NO_2^\bullet$, $ONOOH$ and hydroxyl radicals ($HO^\bullet$) in the liquid (Fig. 2). Consequently, by treatment of aqueous liquids by atmospheric pressure plasma at ambient air conditions a very complex chemical reaction cascade is induced resulting in a multi-component biologically active liquid "cocktail" containing $NO^\bullet$ and $HO^\bullet$ even if these reactive species are not detectable directly within the plasma/gas phase.
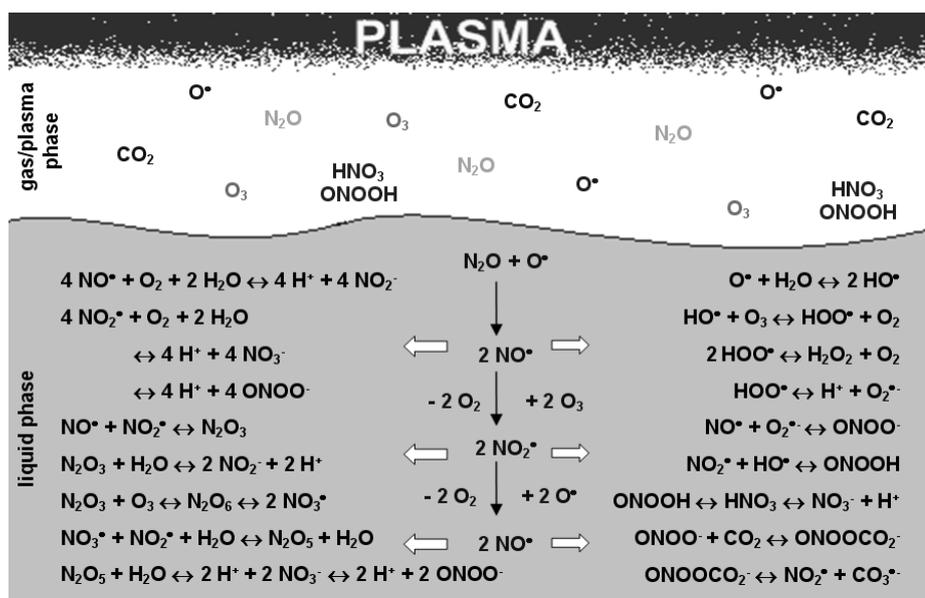
Fig. 2: Possible reaction channels of plasma/gas-liquid interactions

References

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