Interaction of plasma-generated reactive oxygen species with aqueous solutions

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Abstract: Reactive species, like atomic oxygen, produced by a cold atmospheric pressure plasma jet are effectively transported into aqueous solutions and react with the containing organic molecules. Especially the degradation of methylene blue molecules can be proven and the effect of atomic oxygen and ozone are studied.

Keywords: plasma-liquid interaction, reactive species.

1. Introduction

The treatment of aqueous solutions with atmospheric pressure plasma to generate so-called Plasma Treated Water (PTW) is nowadays getting large attention. The PTW shows a high reactivity with biological substrates due to the present reactive species [1, 2, 3]. However, the transport of these reactive species from gas-phase into the liquid-phase and the following aqueous reactions are for some cases still not well understood.

Other studies already showed that atomic oxygen, produced by an atmospheric pressure plasma, can be effectively transported into aqueous solutions [4] and plays a crucial role for the plasma-liquid interaction [5].

For this work an aqueous methylene blue solution was treated by the effluent of an atmospheric pressure plasma jet, the COST-jet [6], with He/O_2 gas mixture. This treatment leads to a degradation of the methylene blue molecule. Further, also other organic molecules dissolved in water will be used in this study. This might give an insight to the reaction mechanism and pathway of atomic oxygen. One important aspect will be whether the reactions of oxygen atoms are surface or volume dominant.

In these experiments, the atmospheric pressure plasma jet is used to dissociate O_2, used as gas admixture in the discharge, into two oxygen atoms, what is implied in figure 1. These oxygen atoms are present in the effluent of the jet and further transported into liquids. The density of the produced atomic oxygen is dependent on the admixture of molecular oxygen in plasma and the distance between liquid surface and jet exit [7].

Due to reactions of atomic oxygen with non-dissociated molecular oxygen ozone is formed. It can be shown, that the ozone formation directly corresponds to the O_2 admixture in plasma, while the maximum density of atomic oxygen is found at an O_2 admixture of 0.6 % [7]. Also the atomic oxygen density decreases with increasing distance to the jet while the density of ozone is increasing [7].

The distance and admixture dependent atomic oxygen and ozone densities can be used to study the separate effect of atomic oxygen in aqueous solutions.

2. Experimental setup

The used atmospheric pressure plasma jet, the COST-jet, consists of two parallel electrodes igniting an rf-plasma discharge at 13.56 MHz. In these experiments gas mixtures of He with 0-1 % O_2 admixtures are used. A scheme of the experimental setup is shown in figure 1.

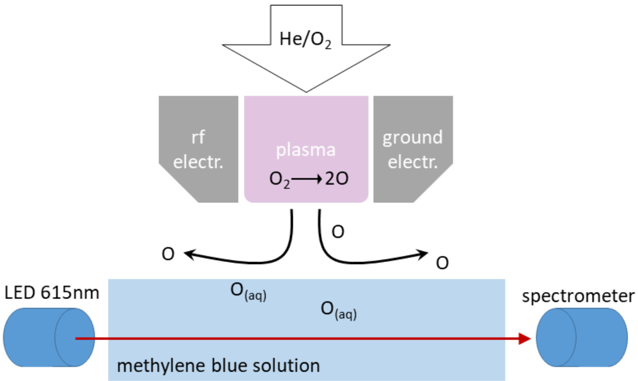

Fig. 1. Scheme of experimental set up. Absorption spectroscopy on plasma-treated aqueous solution.

With a distance of 4 mm underneath the jet exit an aqueous methylene blue solution is placed and treated by the effluent of the plasma jet. The treatment of this solution leads to a degradation of the methylene blue molecules.

To observe the degradation of methylene blue absorption spectroscopy with a LED source at 615 nm and a USB4000 spectrometer is used. The absorption spectrum of methylene blue and the spectrum of the LED source are shown in figure 2.

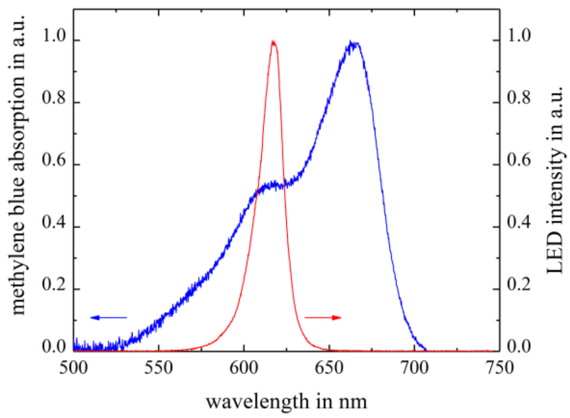

Fig. 2. Absorption spectrum of methylene blue (blue) and spectrum of the used LED source (red).

With these measurements, the reaction rate of methylene blue molecules can be calculated in respect of O_2 admixture or jet distance.

As treated liquid, 3 ml of a 10 µmol l^{-1} of an aqueous methylene blue solution were used.

3. Preliminary Results

The treatment of the aqueous methylene blue solution with the COST-jet using a He/O_2 gas mixture shows that methylene blue is efficiently degraded. The calculated reaction rate at different O_2 admixtures is shown in figure 3, which shows that the reaction rate seems to be stable for O_2 admixtures higher than 0.3 %. As the atomic oxygen density is expected to be at a maximum value with an O_2 admixture of 0.6 % (mass spectrometry results [7]) these behaviour of methylene blue degradation seems to be unexpected.

One explanation for the seeming stable reaction rate might be the limitation by diffusion time of methylene blue in water. While the concentration of the solution is small, also the amount of methylene blue molecules close to the liquid surface is small. If the diffusion time is long, the maximum reaction rate is limited by the amount of methylene blue in a certain water layer, which can be reached by atomic oxygen. This is a result of the limited lifetime of atomic oxygen due to reactions with dissolved O_2 ($\tau \sim 100$ µs).

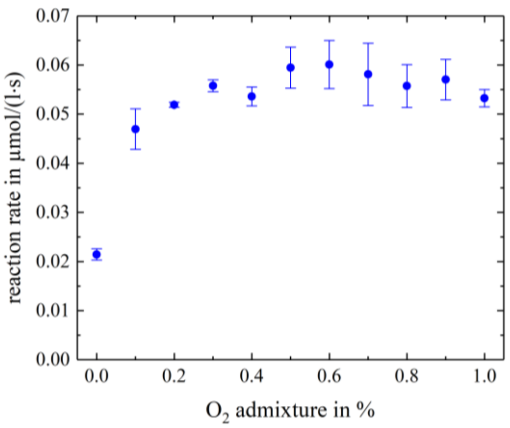

Fig. 3. Reaction rate of methylene blue degradation at different O_2 admixture in the COST-jet with He feed gas.

Furthermore, also other reactive species, like ozone, could degrade methylene blue molecules. As explained before, the ozone density corresponds directly with the O_2 admixture in the plasma jet. Even with decreasing density of atomic oxygen at higher O_2 admixtures than 0.6 % the increasing density of ozone might lead to a constant reaction rate.

To study the effect of ozone, the distance between jet exit and liquid surface can be varied, as the ozone density is increasing with increasing distance. Figure 4 shows the distance variation with an O_2 admixture of 0.6 %. A clear decrease of the reaction rate with increasing distance can be observed. Anyhow, even at distances of 50 mm where the density of atomic oxygen is negligible still a reaction rate is measurable. This strongly indicates the ozone contribution to the degradation of methylene blue.

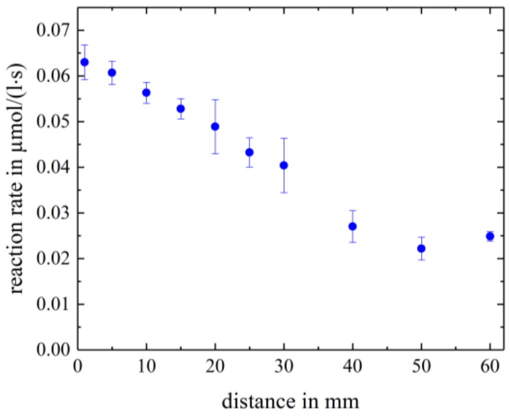

Fig. 4. Reaction rate in dependence of the distance to the jet exit with a gas mixture of He and 0.6 % O_2.

4. Conclusion and Outlook

It was shown that methylene blue can be degraded by the effluent of a cold atmospheric pressure plasma jet with He/O_2 gas mixture. This is given by the reaction with atomic oxygen and ozone. In addition, the reaction rate can be calculated and its behaviour with regard to the O_2 admixture compared with known densities of oxygen species in the effluent. The results of a seeming stable reaction rate also imply an effect of the limitation by diffusion of methylene blue molecules in water.

Additional studies will investigate the influence of this diffusion time of methylene blue molecules in detail by using higher methylene blue concentrations.

Furthermore, the experimental results will be combined with simulations of the transport of atomic oxygen in the gas-phase and the transport from gas into liquid-phase. Measurements with other organic compounds in aqueous solutions which react more selectively to atomic oxygen or ozone are planned as well.

5. Acknowledgements

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6. References

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