Diagnostic methods for fast estimation of NO_x concentrations in plasma treated water

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Abstract: The comparison of two diagnostic methods for NO_x concentrations in plasma treated water was performed. The first method uses the Debye-Huckel-Onsager law and is compared to the second method using calibrated absorption spectroscopy. Results of both diagnostic methods show linear growth of followed reactive oxygen and nitrogen species. This multi-diagnostic approach could contribute to the fundamental understanding of the chemistry in plasma-water interactions and offer fast and accurate results in industry applicable environments.

Keywords: Atmospheric Plasma, Plasma Water Treatments (PTW), PTW diagnostics

1. Introduction

Low temperature plasma has found its way into many applications from agriculture to medical fields [1]. Its vivid chemistry in interaction with different substrates offers a way to catalyse reactions [2] and introduce new chemical species and processes. Plasma water interactions have been studied for many years. The chemical processes that occur in the layer above the water surface lead to generation of reactive nitrogen and oxygen species, which are studied for their antimicrobial properties [3]. Diagnostics are being developed for both the plasma itself and the plasma treated water (PTW) to judge the efficiency of plasma treatment and the processes involved. Plasma induces acidification of water and an increase in its conductivity. Both acidity and conductivity are commonly followed parameters for fast estimation of NO_x⁻ concentrations [4].

Using the Debye-Huckel-Onsager law, conductivity and pH of PTW can be brought in connection with NO_x^- ions formed using plasma treatment, under the assumption that the main species are NO_x^- . Comparing this method to known and calibrated absorption spectroscopy [5] this method was validated as both fast and accurate. Measuring conductivity and pH requires less and cheaper equipment and sampling is easier compared to UV absorption spectroscopy.

2. Materials and methods

If the PTW is considered to be a solution of just nitrites and nitrates as negative ions and H^+ as positive ions [6], the conductivity of the solution, using Kohlrausch's law can be connected with the individual conductivities of the dissolved ions as:

$$\Lambda_0 = \sum_i \qquad \lambda_i. \tag{1}$$

Here Λ_0 is the limiting molar conductivity and λ_i is the limiting ionic conductivity for each ion present in the solution. Kohlrausch found that for an infinite dilution of any electrolyte solution the conductivity of electrolyte *K* itself is proportional to its molar concentration *C* with the limiting molar conductivity as a proportionality constant:

$$K = \Lambda_0 C \tag{2}$$

In case of a water solution the molar conductivity (3) decreases when salt is dissolved in it:

$$\Lambda(C) = \Lambda_0 - A\sqrt{C} \tag{3}$$

This theory was improved by Debye, Huckel and Onsager leading to their law [7] for strong electrolytes:

$$\Lambda_m = \Lambda_m^0 - (A + B\Lambda_m^0)\sqrt{C} \tag{4}$$

where A and B are constants that are temperature dependent [8].

3. Experimental setup

The plasma activated water used for the method validation was obtained using a plasma discharge in a pinto-plate configuration, as shown in Fig. 1. In this configuration the grounded electrode was submerged in a petri dish that was completely filled with 75 mL demi water, while the powered electrode was a needle placed above water surface. The gap size between the needle and the water surface was kept constant at 2 mm. An "Amazing1" power supply was used to apply 12 kV (peak-to-peak) AC voltage to the needle electrode.

After the water was treated for 10 min, it was stirred to achieve a more homogeneous sample and a better distribution of the reactive species. The measurements of



Fig.1.Schematic view of the pin-to plate setup used for water treatment.

both pH, conductivity and absorption spectra were taken 10 min after the sample was taken, to make sure plasma introduced radicals had time to react with water.

4. Results and conclusion

Debye-Huckel-Onsager law was used to derive a fast method to estimate the concentrations of reactive species in plasma activated water. The results show good agreement with standard UV-vis absorption spectroscopy method.

The chemical properties of studied PTW are similar to the ones previously found in literature [9]

This method offers fast and accurate estimate of NO_x^- concentrations, while removing the need for a spectrometer, lamp, cuvette etc., but cannot differentiate between NO_2^- and NO_3^- which remains significant advantage of absorption spectroscopy. The results obtained with both methods showed concentration of NO_x^- having linear growth with treatment time [9].

5. References

[1] I. Adamovich et al, Journal of Physics D: Applied Physics, 55(37), 9 2022.

[2] C. Yan, The Journal of Physical Chemistry C, 126 (23), 9611-9614, 2022.

[3] Z Machala et al, Journal of Physics D: Applied Physics, 52 034002, 2019.

[4] W.F.L.M. Hoeben et al, Plasma Chem Plasma Process 39, 597–626, 2019.

[5] Yibing Li et al, Journal of Spectroscopy, 9771245, 2021.

[6] D. C. Prieve et al, Advances in Colloid and Interface Science, 244:21–35,6, 2017.

[7] D. Fraenkel, Physical Chemistry Chemical Physics, 20(47):29896-29909.30474091, 2018.

[8] ISO 7888. International Standard Water quality Technical report, 1985.

[9] Z. Zhao et al, LWT, 147:111633, 7 2021.