Dielectric barrier discharge in contact with liquids: Diagnostics and Applications

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Progress in the chemical treatment of water led to the development of advanced oxidation processes (AOPs) which are based on in situ generation of strong oxygen-based oxidizers (hydroxyl radical, ozone, atomic oxygen, hydrogen peroxide, etc) which promote destruction and mineralization of the target pollutant. One of the efficient AOPs is based on discharges in contact with liquids, and one of the discharge realizations is a dielectric barrier discharge. In this lecture results of diagnostics and applications of one particular and efficient dielectric barrier discharge configuration for water treatment are presented.

1. Introduction

Non-thermal plasmas generated in contact with liquids have been extensively studied by non-thermal plasma community during the past decade. This is primarily due to the formation of reactive nitrogen species (RNS) and reactive oxygen species (ROS) in plasma treated liquids, such as highly reactive radicals (•OH, O_2^-•, NO•) and molecular species (O_3, H_2O_2, NO_3^-, NO_2^-). Their existence in a liquid exposed to plasma allows a wide range of applications, particularly bio-medical applications and degradation of pollutants in water. The generation of RNS and ROS in the considered liquid can be influenced by the reactor configuration, composition of the working gas and applied operating parameters.

2. Experiment and diagnostics

One of the realizations of non-thermal plasma above a liquid is water falling film dielectric barrier discharge (DBD) reactor in which DBD forms plasma above a thin film (< 0.5 mm) of falling water, see Fig. 1. To get a better insight into the plasma in the reactor and plasma-liquid interactions, distilled water was treated in different gas atmospheres: ambient air, nitrogen, oxygen, argon and helium. Gas flow rate was 5 L/min for all gases. The barrier discharge was generated within 4.5 mm gap between the inner and the outer glass tubes by applying voltage up to 20 kV at frequency of 300 Hz. Electric parameters were monitored by a digital oscilloscope and a high voltage probe. Lissajous figures (Q-U graphs) were used for determination of electric power dissipated in the plasma. The plasma characteristics were examined using spectroscopic methods in UV-Visible region using wide range spectrometer, while long-living species created in the gas plasma (effluents) were identified using FTIR spectroscopy. The most challenging task in characterizing the plasma-water interactions is the measurement of radicals like •OH radical, due to its non-selective reactivity and short lifetime. Its quantification is of crucial importance since it non-selectively reacts with pollutant

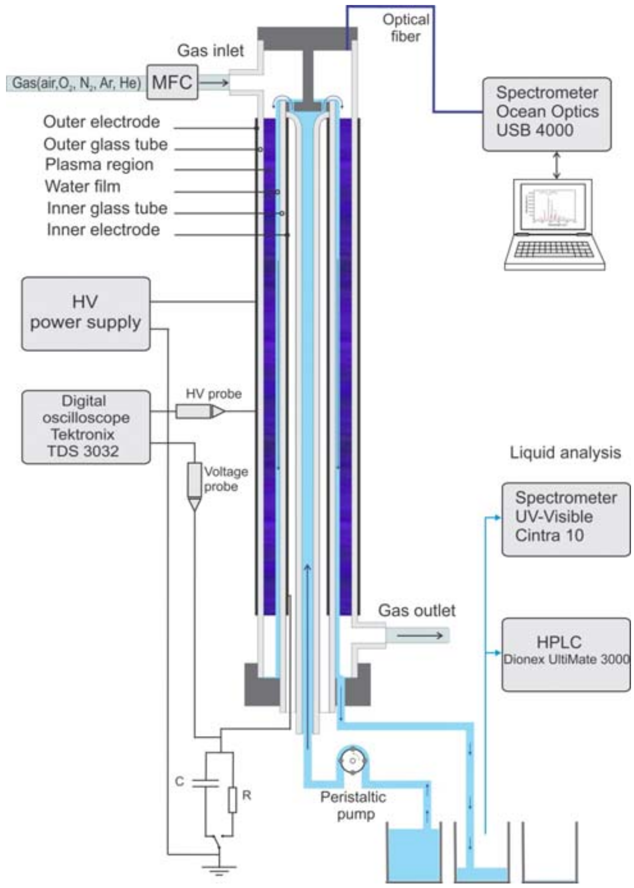

Figure 1. Schematic of the experimental set up.

molecules and it is considered to be the key molecule in water purification processes, and also has great impact on biological systems. We have used dimethyl sulfoxide (DMSO) as a chemical probe which quantitatively reacts with •OH to yield stable products which can then be quantified. In this paper we report on the study of the long-living species formation and production of short-living hydroxyl radical whose quantification is based on trapping reaction with DMSO. Here, the parameters such as pH and conductivity and concentrations of hydrogen peroxide (H_2O_2), nitrite (NO_2^-), nitrate (NO_3^-) and hydroxyl radical (•OH) were measured.

3. Applications

The DBD reactor was tested for treatment of water polluted with phenols, textile dyes, medicaments, herbicides and surfactants.

Treatment of phenols (phenol, 2-chlorophenol, 4-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol and 2,6-dichlorophenol) dissolved in bidistilled water and water from the river Danube was compared. Lower efficiency of phenol removal from river water was obtained, which is due to the shielding effect of fulvic and humic acids which also react with reactive species [1,2].

Studies on decoloration of four reactive textile dyes (using Fe^{2+} and H_2O_2 as catalysts) showed that treated solutions exhibit very similar decoloration kinetics [4]. As wastewater from the textile industries may contain appreciable levels of salts, which could impair the treatment processes, decoloration of a commercial reactive textile dye in a presence of inorganic salts (NaCl, Na_2SO_4 and Na_2CO_3) was studied. The results indicate that decoloration of the dyes was significantly limited in the presence of salts [4].

The article [5] is devoted to the comparison of two procedures for arsenic removal from potable water, one using a classical ozoniser and the second, using water falling film DBD reactor for primary oxidation.

The effect of different homogenous catalysts and their dosage on herbicide mesotrione degradation in DBD reactor was tested. Optimal conditions for four catalytic systems Mn^{2+}/DBD, Co^{2+}/DBD, Fe^{2+}/DBD, H_2O_2/DBD regarding the concentrations of catalyst and specific energy density (SED), as well as degradation products were found [6].

Degradation of two triketone herbicides, mesotrione and sulcotrione, was studied using four different advanced oxidation processes (AOPs): ozonation, DBD reactor, photocatalysis and Fenton reagent, in order to find differences in mechanism of degradation. Degradation products were identified by high performance liquid chromatography (HPLC–DAD) and UHPLC–Orbitrap–MS analyses. A simple mechanism of degradation for different AOPs was proposed. Similarity was observed between degradation mechanism of ozonation and DBD treatment [7].

Degradation of 4-chlorophenol was provided in the presence of homogeneous catalysts (Fe^2 and H_2O_2) and the rate of degradation and degradation products such as acetic, formic and oxalic acids were quantified using ion chromatography [8]. Due to the incomplete degradation, toxic intermediates can induce more severe effects than the parent compound, so toxicity studies are necessary. Brine shrimps *Artemia salina* and bioluminescence inhibition test (bacteria *Vibrio fischeri*) was used for the toxicity screening assay [8, 9].

Efficiency of the DBD reactor for ibuprofen removal from water solution was tasted by measuring ibuprofen degradation rate and identification of the degradation products [9].

Degradation of Triton X-100 (TX-100), non-ionic surfactant (widely used in detergents, emulsifiers, wetting agents…) in the same DBD reactor was studied using UV-VIS spectrophotometric methods with UHPLC–Orbitrap–MS. Finally, toxicity screening assay was provided [10].

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