Ozone formation by gaseous corona discharge generated above aqueous solution

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Production of ozone generated in oxygen by the gas phase discharge above aqueous solution was studied for different applied pulse high voltage and discharge gap heights between gas phase high voltage electrode and water surface. The ozone production increased with higher gap and higher applied voltage, while the efficiency decreased with higher voltage for fixed gap height and increased with higher gap height. The appearance of the gas phase discharge occurring above the water significantly differed with the change of discharge gap height. The formation of ozone was affected by the presence of water vapor formed through the vaporization of water surface by the gas phase discharge, which was in direct contact with aqueous solution.

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1 Introduction

Electrical treatment by applying pulsed high voltage discharges directly in the aqueous solution has been recently used to degrade a variety of organic compounds in water, e.g. [1]–[5], and also for sterilization [6] and modification of surface properties of polymeric materials [7]. It has been demonstrated that non–thermal plasma generated by these discharges initiate a variety of chemical and physical effects in water, such as intense ultraviolet radiation, overpressure shock waves, and, in particular, formation of chemically active species (OH•, H• and O• radicals, H2O2 etc.) [4]–[10]. It was shown that the principle reactive species involved in the breakdown process are hydroxyl radical and hydrogen peroxide [3]–[6]. Consequently, a number of studies have utilized gas phase discharge generated over the water surface to produce in the gas or at the gas–liquid interface strongly oxidative species, such as OH radicals, O atoms and their reaction products (O3, H2O2) that can dissolve into the water to initiate oxidation processes, e.g. [11],[12].

Hybrid gas–liquid phase electrical discharge reactors generating simultaneously gas phase non–thermal plasma formed above the water surface with the liquid phase corona discharge in water are of very recent interest for possible application in water treatment. Two types of configurations have been constructed: the hybrid–parallel and hybrid–series [13]. In the series configuration the high voltage point electrode is placed in the liquid phase and the electrode made from reticulated vitreous carbon (RVC) is placed in the gas phase above the liquid. The parallel configuration employs a high voltage RVC electrode in the gas phase and a high voltage needle–point electrode in the liquid phase with the ground electrode placed at the gas–liquid interface. The main advantage of these reactors include the production of the same chemical and physical effects as initiated in the individual gas and liquid phase reactors, which lead to enhancement of the overall efficiency of the corona
discharge process for the removal of pollutants from water and, in addition, by using only one power supply. Previous experiments have demonstrated the simultaneous formation of ozone in the gas phase and hydrogen peroxide and hydroxyl radicals in the liquid phase in these reactors [13]. Consequently, significantly enhanced degradation of nitrobenzene and phenol in the hybrid discharge reactors compared to their removal in the single-liquid phase discharge reactor was observed [14], [15].

However, further development of these reactors is needed due to only limited control of the gas phase discharge above the water surface in the current reactor arrangement. In order to optimize the power delivered into the discharges generated in the gas and the liquid and to effectively tune the power supply to the hybrid discharge reactor we have constructed the gas–liquid phase discharge reactor with separately charged electrodes in the gas and liquid phases using two pulse power supplies, which allow us an independent control of the gas and liquid phase discharges including variation of input power, voltage, and frequency. In this work, preliminary results on the measurement of the formation of gaseous ozone in such hybrid discharge reactor considering only the gas phase discharge over the water surface are presented. The effects of the pulse high voltage applied to the reactor and the gas phase discharge gap height on ozone production under oxygen atmosphere are discussed.

2 Experimental

A schematic diagram of the apparatus for generating pulsed electrical discharge simultaneously in the water and in the gas phase above the water surface is shown in Fig. 1. The reactor is a closed plexiglass wall box with outer dimensions of $200 \times 200 \times 200$ mm. It consists of a two separately charged high voltage electrodes placed in water and in the gas phase above the water separated by circular perforated plate made from stainless steel connected with the electrically grounded stainless steel tube of the inner diameter of 160 mm. The electrode system of needle–plate geometry is used in the liquid with the needle–plate distance of 28 mm. The high voltage needle electrode is made from mechanically sharpened tungsten wire placed along the axis of stainless steel tubular ground electrode. The gas phase high voltage electrode is made from RVC disk (diameter 50 mm × thickness 10 mm), which is attached to a stainless steel holder connected to the pulsed high voltage. The distance between RVC electrode and ground stainless steel plate submerged in water is fixed at 40 mm. The inner walls of the stainless steel tube above the plate are insulated to prevent discharging along the water surface to the walls of stainless steel tube. The gas phase discharge gap referred in this work is defined as a region between RVC electrode and the water surface and its height was varied by the volume of the aqueous solution used in the reactor.

The separate charging of the liquid phase needle electrode and gas phase RVC electrode is provided by two pulse power supplies, which are identical to the power supply used in our previous work [2]–[4]. Both systems consist of variable voltage 0÷50 kV DC source, rotating double spark gap giving the maximum pulse repetition frequency of 100 Hz and storage capacitor of 7 nF and 2 nF used for charging of the liquid and gas phase discharge,
respectively. In this work one power supply was used to generate only the gas phase discharge above the aqueous solution, i.e. no discharge was generated in the liquid phase. The pulsed high voltage of positive polarity in the range of 15–30 kV with fixed pulse repetition frequency of 50 Hz was used. The electrical power $P$ applied to the reactor was calculated from applied voltage $U$, charging capacity $C$ and pulse repetition frequency $f$ as $P = \frac{1}{2} C f U^2$. The water was circulated through the reactor by the peristaltic pump with circulation rate of 0.4 L/min and cooled to maintain constant temperature of ~ 12°C. The solution of NaH$_2$PO$_4$ (7.7 mmol/L) of the initial conductivity of 500 µS/cm was used in each case. Oxygen flowed continuously through the reactor at atmospheric pressure and ambient temperature at the flow rate of 2.5 L/min, fed into it via inlet port at the reactor wall. The concentration of ozone in the output gas was determined with the iodometric method by running the reactor outlet stream through a gas wash bottle containing the KI solution.

### 3 Results and discussion

Fig. 2 shows the dependence of (a) ozone concentration and (b) production efficiency on the applied voltage for different discharge gap heights between high voltage RVC electrode and water surface. Reported ozone concentrations are steady state values of volume
fractions of ozone in the output gas, in terms of parts per million.

It is apparent that the ozone concentration increased with the higher gap and higher applied voltage, while the efficiency decreased with higher voltage for fixed gap height and increased with higher gap height. For fixed gap length a higher applied voltage implies higher electric field and power density in the discharge. Increase of electric field results in decreasing the average density of the low-energy electrons, which decompose the gener-

![Graphs showing ozone concentration and efficiency as functions of applied voltage for different gap heights.](image)

Fig. 2. (a) Ozone concentration and (b) production efficiency measured in O\textsubscript{2} as a function of the applied voltage to the reactor for different discharge gap heights. Flow rate 2.5 L/min, \(C = 2\) nF, \(f = 50\) Hz, gap heights: ♦, 2.5 mm; ♣, 5.0 mm; ▲, 7.5 mm; ■, 10.0 mm.
ated ozone [16]. Thus, the higher electric field indirectly increases the production of atomic oxygen formed through electron impact dissociation of oxygen and this results in a larger generation of ozone. At the same time, decrease of ozone efficiency with higher applied voltage indicates that the increase in power density results in a higher power consumption in heat dissipation than in the ozone formation.

With higher gap, however, in addition to the effects of the decreasing electric field and power density on the ozone formation the change of appearance of the gas phase discharge occurring above the water has to be also mentioned. In small gaps (≤ 5 mm) very thin blue discharge filaments were formed during each pulse, which homogenously filled the discharge gap above the water. With larger discharge gaps less and brighter discharge filaments were formed in each pulse and in the discharge gap of 10 mm only single bright discharge channels were formed per each pulse. Therefore, as the number of plasma channels decreases with the increasing discharge gap, the charge transferred per each channel increases for the same applied voltage. This results in an increase of electron density delivered per each microdischarge and higher heat dissipation, which significantly influences the ozone formation similarly to the effects discussed above.

In addition, a detrimental effect of water vapor on ozone formation by the gas phase discharge generated above the water should be also taken into account. Since plasma channels formed in the gas are in direct contact with the water surface, the solution can be locally heated and vaporized by the action of the discharge. Typically, the concentrations of water measured in the output gas were 1.5±2.0 vol.% compared to less than 0.1 vol.% in the inlet gas but even higher concentrations can be expected in the region of the gas phase discharge above the water surface. Thus, the water vapor can absorb a substantial part of electronic energy of the discharge that could otherwise be used in the ozone formation process. H and OH radicals can be formed from water vapor and, consequently, cause reactions that destroy ozone molecules. In addition, O atoms formed through electron dissociation of oxygen can combine with water molecules and their products, preventing ozone formation [17]. The presence of water vapor can partly explain relatively low ozone production efficiencies determined in this work (~ 10 g/kWh) compared to the yields reported for ozone production using corona discharge in dry oxygen, e.g. (~ 50 g/kWh) [18]. However, although a high efficiency of O₃ production is an important factor in development of hybrid discharge reactors, the formation of OH radicals in water vapor or at gas-liquid phase interface is also desired since they significantly contribute in degradation of organic compounds dissolved in water as it was shown in [11], [15]. Therefore, the compromise between production of ozone and OH radicals by the gas phase discharge over water has to be always considered in the further development of hybrid gas–liquid discharge reactors.

4 Conclusions

Production of ozone generated in oxygen by the gas phase discharge above aqueous solution in hybrid gas–liquid phase electrical discharge reactor was studied for different pulse high voltage applied to the reactor and discharge gap heights between gas phase high voltage electrode and water surface. The ozone production increased with higher gap and higher applied voltage, while the efficiency decreased with higher voltage for fixed gap
height and increased with higher gap height. The appearance of the gas phase discharge occurring above the water significantly differed with the change of discharge gap height. The formation of ozone was affected by the presence of water vapor formed through the vaporization of water surface by the gas phase discharge, which was in direct contact with aqueous solution.

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