

Generation of dissolved O₃ and OH radicals in water and O₃ gas with a submerged low-temperature dielectric barrier discharge plasma reactor

Young Sik Lee^{1*}, Hyoung Kyun Han¹ and Cheong-Jo Cheong²

¹Inland Aquaculture Research Center, National Fisheries Research and Development Institute, Changwon, Kyungnam 645-806, Korea

²Department of Environmental Engineering, Suncheon National University, Jeonnam, 540-950, Korea

*Corresponding Author's Email : namdu@korea.kr

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Abstract

Generation of O₃ and OH radicals in water and O₃ in air, using a low-temperature dielectric barrier plasma reactor was investigated to determine the optimal operating conditions of the plasma reactor in seawater and freshwater for fisheries. For seawater, increase in dissolved O₃ concentration at air flows < 3 l min⁻¹ was slow, while the rate increased rapidly at air flows > 4 l min⁻¹. For freshwater, O₃ concentration at air flows < 3 l min⁻¹ increased slightly after 1 min and then remained unchanged. O₃ concentrations were markedly higher at air flows of 5–7 l min⁻¹ relative to those at air flows < 3 l min⁻¹, but no further increase occurred after 4 min. The dissolved O₃ concentration for 5.00 ppt salinity increased to > 2.5 mg l⁻¹ for 20 min, while the concentration with added natural salt and refined salt increased to 0.6 mg l⁻¹ at 5 min and did not increase further. The maximum concentration of dissolved OH radicals in seawater was observed at air flow rates of 5–7 l min⁻¹, and the rate of OH radical production was affected much less by the air flow rate than O₃ generation. The formation of OH radicals was similar in freshwater and seawater. O₃ concentration in air increased more rapidly in freshwater than in seawater. An air flow rate of 3–4 l min⁻¹ appeared to be optimal for minimizing the generation of O₃ gas in air and maximizing the generation of OH radicals and O₃ for maximum bactericidal effect and water purification.

Key words

O₃ and OH radicals, Operating parameters, Plasma reactor

Introduction

Plasma, the fourth state of matter, is defined as a special state of ionized gas, and plasma technologies have been applied in a variety of industries (Chung *et al.*, 2010; Li *et al.*, 2009; Zhang *et al.*, 2008). Dielectric barrier discharge (DBD) plasma reactors, which insert a dielectric between a set of electrodes and generate plasma, have been used in the semiconductor industry and to treat air pollution (Feng *et al.*, 2012). Chemically active species, such as H, O, -OH, H₂O₂, and O₃, are formed via various physical and chemical reactions. In addition, ultraviolet light (UV) and shock waves occur when plasmas are generated in water. All of these phenomena, active species, UV radiation, and shock waves, can be applied in water purification systems to remove refractory materials and odors, decompose organic matter, and

change the color or clarity of water (Bruggeman and Schram 2010; Locke and Shih 2011; Magureanu *et al.*, 2013). Consequently, plasma treatments have emerged as a new water treatment technology because they are relatively simple, do not generate secondary pollution, and require fewer chemicals.

However, the conductivity of water makes underwater plasma generation very difficult. High pulsed power, high-frequency power, and coated membrane electrodes are used to avoid short pulses (Magureanu *et al.*, 2013; Penru *et al.*, 2012). Installing these units in a small aquarium is difficult because of their size and weight (Uhm, 2006). In addition, they are very expensive to maintain and consume large amounts of power. Techniques to discharge plasma in water using various dielectrics have been studied recently (Kim and Park, 2011). These studies

have revealed several persistent problems. Discharge efficiency decreases and stable discharges do not occur or short-circuits take place instead.

A submerged, low-temperature DBD plasma reactor using quartz dielectric, rod-type ground electrodes, and a constant air flow to prevent short circuits was designed and applied to treat wastewater (Kang, 2011). This low-temperature DBD plasma reactor has not been commercialized due to insufficient information about the generation of OH radicals and O₃ in water. And one essential issue regarding ozone processes is emission of unreacted ozone in atmosphere (Mok *et al.*, 2009). It is well known that exposure to ozone has direct adverse effects on human health like permanent lung injury and respiratory diseases.

Therefore, the current study was carried out to investigate the generation of OH radicals and O₃ in water and O₃ in air for operating a DBD plasma reactor in seawater and freshwater to maximize the generation of OH radicals and O₃ in water and minimize the O₃ generation in air. These OH radicals and O₃ in water play an important role in the decomposition of organic matter and neutralization of bacteria and O₃ in air has direct adverse effects on human health.

Materials and Methods

A plasma reactor, with a volume of approximately 3 l and equipped with a rod-type ground electrode made of quartz, was used in this study. Air flow was controlled by a flow gauge (Fig. 1). Seawater and freshwater, used in this study, were obtained from

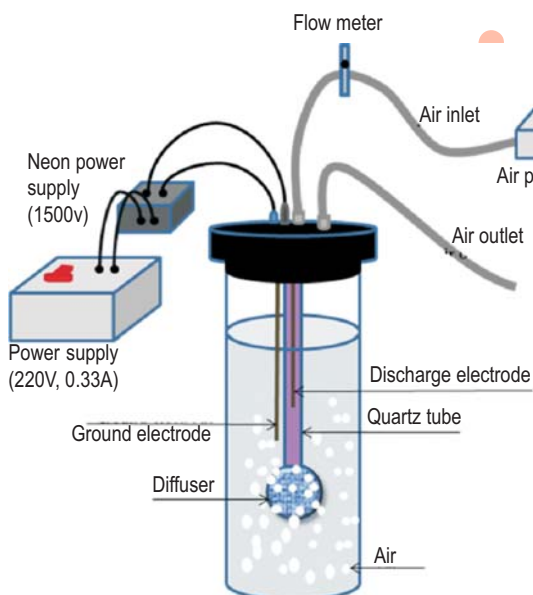


Fig. 1 : Schematic diagram of the experimental apparatus (Submerged low-temperature dielectric barrier discharge plasma reactor)

Chinhae Bay and tap water, respectively. Salinity was measured with a water-quality monitor (YSI 600XL; YSI Nanotech, Yellow Springs, OH, USA). Low salinity samples were prepared by mixing tap water. The dissolved O₃ concentration in water at 5 ppt salinity, adjusted using sun-dried or refined salt, was also measured to determine the effect of salt. Air flows were adjusted to 1, 2, 3, 4, 5, 6, or 7 l min⁻¹ to generate the dissolved O₃, and operating times were 0, 0.5, 1, 2, 3, 4, 5, 10, or 20 min. Variation in OH radical concentrations were examined using *N,N*-dimethyl-4-nitrosoaniline (RNO), which reacts selectively with OH radicals (Li *et al.*, 2009). The RNO concentration was determined by measuring the solution absorbance at 440 nm using a UV-visible spectrophotometer (Cary 1E; Varian, Palo Alto, CA, USA). The concentrations of O₃ in water were measured using a colorimeter (C105; Eutech Instruments, Singapore). O₃ concentrations in air were measured at air outlet that was connected with headspace in the plasma reactor using a detector tube (No. 18; Gastec, Tokyo, Japan) directly (Fig. 1). All tests were run three times and their average values were calculated.

Results and Discussion

Dissolved O₃ concentration in seawater increased slightly (0.1 mg l⁻¹) at air flows of 1~2 l min⁻¹ after 1 min but remained constant thereafter (Fig. 2A). At 3 l min⁻¹, the concentration of dissolved O₃ increased steadily (>0.2 mg l⁻¹). At air flows of 4~7 l min⁻¹, dissolved O₃ level increased more sharply. At an air flow of 4 l min⁻¹, the O₃ concentration was 2.5 mg l⁻¹ after 10 min. Lee *et al.* (2012) reported that using plasma reactor equipped with ring-type ground electrode, that dissolved O₃ concentration in seawater at air flow of 6 l min⁻¹, was 2.3 mg l⁻¹ after 5 min. This result seems to be similar to above result.

The dissolved O₃ concentrations in freshwater remained unchanged at an air flow of 1 l min⁻¹ (Fig. 2B). At 3 l min⁻¹, the O₃ concentration increased slightly up to 1 min and then remained constant. At air flows of 5~7 l min⁻¹, increase in O₃ concentration was greater than that measured at flows < 3 l min⁻¹ but remained stable after 4 min. O₃ concentration at flow rates of 5~7 l min⁻¹ remained below 0.5 mg l⁻¹. These data showed that increasing dissolved O₃ concentration was more effective in seawater than in freshwater. In addition, air flow appears to be an important factor in determining O₃ concentration in water.

The effect of salinity on O₃ generation in water by plasma reactor was measured at a fixed air flow rate of 6 l min⁻¹ (Fig. 2C). At 0 ppt salinity, the dissolved O₃ concentration increased for 5 min and then stabilized. At 1 ppt, O₃ concentration increased slightly with time and increased rapidly at 5 ppt. This increase was proportional up to 10 ppt salinity (Fig. 3). At > 20 ppt salinity, O₃ concentration continued to increase but at a lesser rate. Variations in dissolved O₃ levels were determined using sun-dried or refined salt to adjust the salinity instead of seawater (Fig. 4). When the plasma reactor was operated for 3 min, dissolved O₃

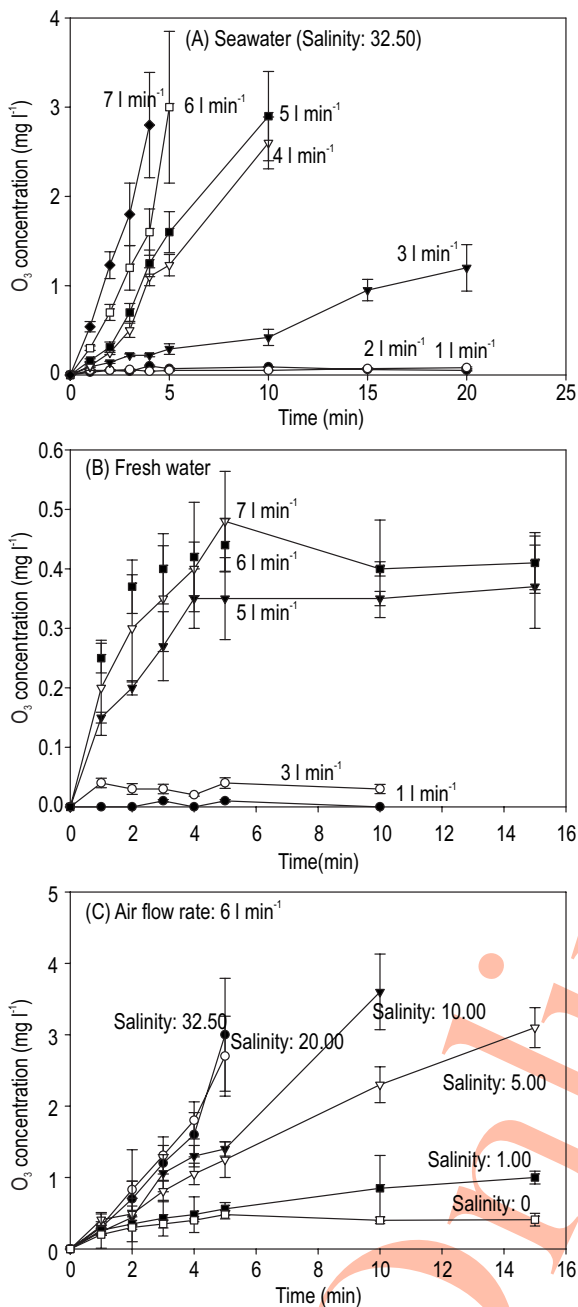


Fig. 2 : Variations of O₃ concentrations in solution at various air flow rate (A: seawater, B: Fresh water) and salinity (C) as a function of plasma operation time (n=3)

concentration was 0.5 mg l⁻¹ regardless of whether the salinity was adjusted with seawater, natural salt or refined salt. After 3 min, O₃ concentration in seawater increased with time, reaching > 2.5 mg l⁻¹ at 20 min. In contrast, with natural or refined salt, O₃

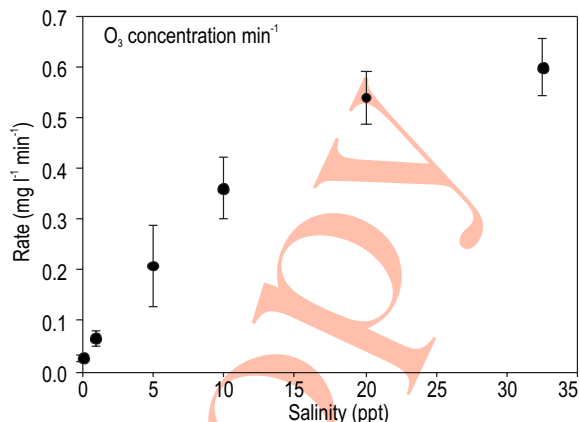


Fig. 3 : Increasing rate of O₃ concentrations in solution by salinity at various air flow rate (n=3)

concentration increased to 0.6 mg l⁻¹ at 5 min, peaked at 10 min, and then did not increase further. This result suggests that other minerals in seawater play a role in increasing the concentration of dissolved O₃.

Ozone-based technologies have been recognized as effective water treatment methods for taste and odor control, killing a wide range of pathogens in drinking and waste water (Tawabini and Zubair, 2011). Itoh *et al.* (1997) and Oh *et al.* (1999) showed that more than 99.9% of *Vibrio anguillarum* and fish pathogenic bacteria were sterilized in low oxidant concentrations (0.1 mg l⁻¹) for <2 min. Therefore, the plasma reactor should be operated with an air flow of at least >3 l min⁻¹ in seawater and >5 l min⁻¹ in freshwater to attain sterilization. And, adding a small amount of salt in sewage would possibly increase the effectiveness of sterilization when using a plasma reactor.

OH radicals are important in waste treatments because they are a strong oxidizer with disinfection potential (Glaze *et al.*, 1987; Kim and Park, 2009). In this study, RNO concentration was measured in order to monitor the production of dissolved OH radicals in seawater and to evaluate the performance of a low-temperature DBD plasma reactor.

In seawater, almost no changes in RNO levels were observed at air flows < 2 l min⁻¹, indicating minimal production of OH radicals (Fig. 5A). RNO concentration decreased rapidly at an air flow rate of 3 l min⁻¹ and decreased further as the air flow was increased. RNO concentrations were similar at air flows of 5–7 l min⁻¹. As noted above, the dissolved O₃ concentration increased rapidly at 4 l min⁻¹, much as the generation of OH radicals increased rapidly at 3 l min⁻¹.

As observed in seawater, almost no changes in RNO concentrations were observed at air flows < 2 l min⁻¹ and increased sharply at 3 l min⁻¹ in freshwater. RNO levels decreased

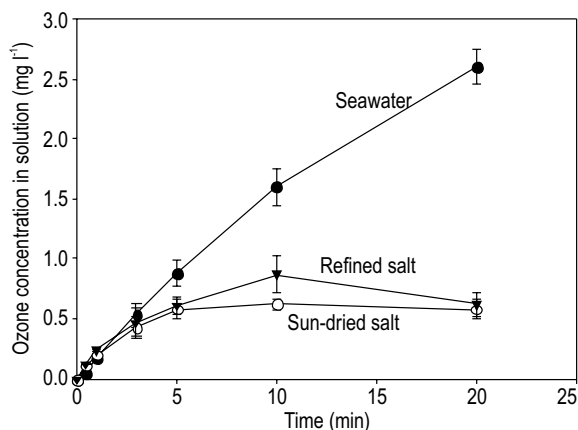


Fig. 4 : Variations of O_3 concentrations in solution by seawater, sun-dried salt and refined salt (salinity: 5.00, air flow rate: 6 l min^{-1}) as a function of plasma operation time ($n=3$)

with increasing air flows, reaching a maximum degradation rate at $6\text{--}7 \text{ l min}^{-1}$ (Fig. 5 B). According to Kim and Park (2011), although water did not flow into the quartz tube at 1 l min^{-1} , the RNO degradation rate was low. And RNO degradation increased rapidly at an air flow of 3 l min^{-1} in freshwater and optimum air flow rate was 4 l min^{-1} . These results are almost consistent with the findings of the present study. But in this study, optimum air flow rate was $6\text{--}7 \text{ l min}^{-1}$. These results seem to be due to experiment conditions such as distance of electrodes and ground electrode shape (rod and spring) and so on. To understand more clearly the effect of salt on the formation of OH radicals, RNO concentrations were checked at various salinity levels (Fig. 5C). Reduction in RNO levels were similar regardless of salinity at a flow rate of 7 l min^{-1} , as shown in Fig. 5C. Therefore, unlike O_3 generation in water, formation of OH radicals did not differ markedly between freshwater and seawater.

Ozone emission into the atmosphere causes air pollution and can have direct adverse effects on human health including permanent lung injury and respiratory diseases (Mok *et al.*, 2009). Thus, it is important to know the characteristics of O_3 gas generation in a plasma reactor. In this study, low level ($< 1 \text{ mg l}^{-1}$) of O_3 gas was detected in air at flow rates $< 2 \text{ l min}^{-1}$ (Fig. 6). At an air flow of 3 l min^{-1} , the concentration of O_3 gas emitted in seawater and freshwater were 80 and 220 mg l^{-1} , respectively. At a flow rate of 5 l min^{-1} , the concentration originating in seawater and freshwater were > 360 and $> 600 \text{ mg l}^{-1}$, respectively. In other words, O_3 concentration in air increased with air flow rate, but the increased rate was more rapid in freshwater than in seawater.

Thus, more care is required to treat O_3 gas in air leaking into the atmosphere in freshwater than in seawater. Discussed above, the dissolved O_3 concentration in seawater increased more sharply than in freshwater (Fig. 2). Therefore, ozone

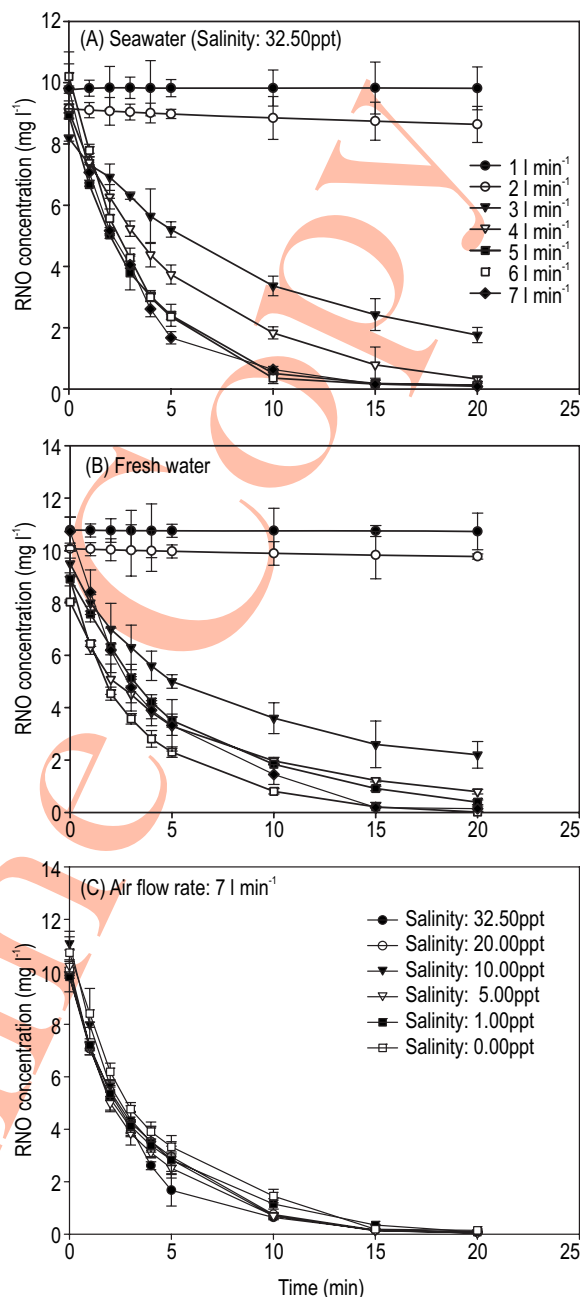


Fig. 5 : Variations of RNO concentration at various air flow rate (A) Seawater, (B) Fresh water and (C) salinity as a function of plasma operation time ($n=3$)

generated by the plasma reactor in freshwater seems to be less soluble than in seawater. An air flow rate of $3\text{--}4 \text{ l min}^{-1}$ appeared to be optimal for maximizing the generation of OH radicals and O_3 in water for maximum bacterial effect and water purification.

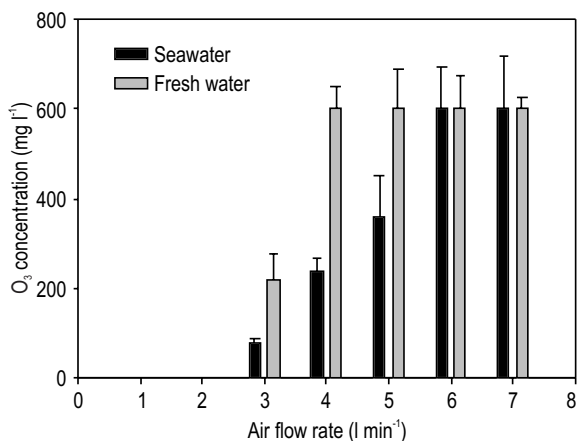


Fig. 6 : Variations of O₃ concentrations in air as a function of air flow rate when reactor was operated for 5 min (n=3)

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