

THE COMPARISON OF OXIDATION EFFICIENCY OF REACTIVE OXYGEN SPECIES (ROS): PILOT SCALE OF MICROBUBBLE TECHNOLOGIES WITH OXYGEN CONCENTRATION

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Received: July 26, 2023; Revised: August 16, 2023; Accepted: December 28, 2023

Abstract

The objective of this study is to assess and compare the effectiveness of an oxidizing agent. Within the field of advanced oxidation processes (AOPs), ozone, a highly reactive gas, generates reactive oxygen species (ROS) as byproducts through chemical reactions. The study employed a dielectric barrier discharge (DBD) plasma generator to produce ozone gas. This study was carried out under different gas source conditions, including both air and oxygen. Additionally, the ROS produced as byproducts from the interaction between ozone gas and water were measured using oxidation-reduction potential (ORP) values. The ORP values exhibit strong foundational attributes for both ozone dissolution and ROS oxidation efficiency. To extend the interaction duration between ozone gas and water, a stone diffuser was utilized to introduce ozone gas into the water. This mechanism resulted in the creation of ozone microbubbles through a process known as cavitation. The results illustrate a positive relationship between the flow rate and ozone yield. This trend reached its highpoint with the highest observed ozone concentrations approximately 14.11 mg/L for oxygen and 4.55 mg/L for air both achieved at a flow rate of 11 L/min. Furthermore, the highest ozone concentrations were recorded at 15.17 mg/L for oxygen and 12.59 mg/L for air after a 10 min discharge period. Interestingly, ozone generated from oxygen feed gas exhibited a higher concentration yield than that from air feed gas. Moreover, the ORP value displayed a continuous increase with longer treatment times, eventually stabilizing at around the 15 min. This pattern corresponded to the water reaching its highest the ORP values approximately 821 mV for oxygen and 569 mV for air. In summary, this study emphasizes the potential benefits of utilizing ozone as an effective oxidant in both gaseous (ozone gas) and liquid (ROS) phases. It especially emphasizes the essential role played by the generation of ozone and ROS from an oxygen-fed gas source. Moreover, it highlights the significance of maintaining an optimal flow rate of 11 L/min and

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a discharge duration of 10 min for achieving the highest ozone concentration. Similarly, a treatment time of 15 min for the liquid phase is recommended to maximize ORP values. Both of these values indicate the highest potential advantages for producing an effective oxidant.

Keywords: Advanced Oxidation Processes (AOPs); Oxidation-Reduction Potential (ORP); Ozone; Reactive Oxygen Species (ROS)

Introduction

Advanced oxidation processes (AOPs) encompass a wide range of highly effective methods utilized in wastewater treatment. These methods include ozone (O_3) treatment, Fenton reaction, hydrogen peroxide (H_2O_2) oxidation, ultraviolet (UV) radiation, wet air oxidation (WAO), sonication, and various combined processes such as peroxone (O_3/H_2O_2), ultraviolet light with peroxide (UV/ H_2O_2), peroxone in conjunction with ultraviolet light ($O_3/H_2O_2/UV$), O_3/TiO_2 /electron beam irradiation, and $O_3/TiO_2/H_2O_2$ systems (Malik *et al.*, 2020). These methods are considered advanced treatments, as they are capable of removing pollutants that cannot be effectively removed by conventional methods. AOPs produce reactive oxygen species (ROS), which are highly oxidizing radicals. These ROS include hydrogen peroxide (H_2O_2), superoxide anions (O_2^-), oxygen atoms (O), as well as hydroxyl ($\bullet OH$), perhydroxyl ($HO_2\bullet$), and oxygen ($\bullet O$) radicals which can effectively oxidize pollutants to harmless products (Luvita *et al.*, 2022). Among ozone-based AOPs, ozonation, O_3/UV , O_3/H_2O_2 , O_3 /catalysis, and O_3 /filtration have gained significant attention and are widely used in water treatment and reuse (Liu *et al.*, 2021). These processes utilize ozone as a strong oxidant to generate ROS, which can effectively oxidize pollutants in wastewater.

Ozone (O_3) has a high oxidation potential of about 2.07 V, which makes it widely favored for water disinfection and the degradation of organic pollutants. (Liu *et al.*, 2021). It has the unique advantage of not producing harmful byproducts. However, ozone is commonly characterized by its instability and low solubility, which impose limitations on its practical applications. To address this issue, mixing ozone with another gas can improve its stability. The half-life of ozone in water is considerably shorter compared to that in air, with durations of 15 min and 12 min at 25°C and 30°C, respectively. (Luvita *et al.*, 2022; Pal *et al.*, 2022).

To extend the contact time between ozone and pollutants, microbubble (MB) and nanobubble (NB) technologies have been developed. These technologies involve injecting ozone gas into water or wastewater, where it is poorly soluble. Passing the

gas through water in bubbles allows for longer contact time between ozone and pollutants (Luvita *et al.*, 2022; Verinda *et al.*, 2022).

This approach is particularly useful for producing ozone-based AOPs. Overall, ozone is an effective and natural oxidant, and these new technologies have made it easier to use in water treatment and reuse. The aim of this study is to assess and compare the oxidation efficiency of an oxidizing agent generated from ozone gas with those produced from different feed gases (air and oxygen) under varying flow rates and discharge times. Furthermore, this research aims to explore the fundamental properties of ozone dissolution in water including the concentration of highly oxidizing radicals known as ROS.

Materials and Methods

Ozone gas was generated using a dielectric barrier discharge (DBD) plasma generator, comprising electrodes positioned within a Pyrex glass tube and linked to a high-voltage supply through a cylindrical reactor. The optimal conditions for ozone production were achieved by utilizing air and oxygen as the feed gases, with adjustments made by controlling various flow rates: 2, 5, 8, 11, and 14 L/min. After reaching the optimized flow rate conditions, these were employed in the discharge process, which involved varying discharge times of 1, 5, 10, and 15 min.

The concentration of ozone generated by the DBD plasma generator was determined using the iodometric titration method, as described in previous reports. (Verinda *et al.*, 2022). In brief, 2.5 g of KI was added to 100 mL of distilled water in a 250 mL volumetric flask, followed by 1.0 mL of sulfuric acid (H_2SO_4) to acidify the solution. After mixing, the ozone gas generated was bubbled into the KI solution. The injected ozone oxidized I^- ions to I_2 molecules, which gave a brownish-yellow color to the originally clear KI solution. Next, a starch indicator solution was added to the solution, resulting in a dark blue coloration. The ozonated KI solution was then titrated with

$\text{Na}_2\text{S}_2\text{O}_3$ solution (0.158 M) until the solution became clear again (Verinda *et al.*, 2022). The ozone concentration was determined based on the calculated moles of sodium thiosulfate in the water solution and calculated using the following equation.

$$O_3 \left(\frac{\text{mg}}{\text{L}} \right) = O_3 \left(\frac{\text{mol}}{\text{L}} \right) \times M_O \left(\frac{\text{mg}}{\text{mol}} \right) \times 1000 \quad (1)$$

where

M_O is the molar mass of ozone (O_3)

To compare the oxidation efficiency of ROS, we conducted experiments using ozone microbubbles was assembled in the laboratory as shown in Figure 1. The ozone gas generated by the DBD plasma generator was injected into a stone diffuser to produce ozone microbubbles through the cavitation phenomenon. To measure the ability of the solution to accept or release electrons in a chemical reaction, and determined the oxidation-reduction potential (ORP) using an ORP meter. The ORP value with measured using an ORP meter, is an indication of the presence of highly reactive oxygen-containing molecules, was measured every 5 min. A positive ORP value suggests that the solution has an oxidizing tendency.

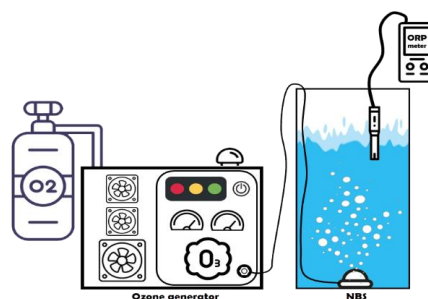


Figure 1. System for producing the ROS

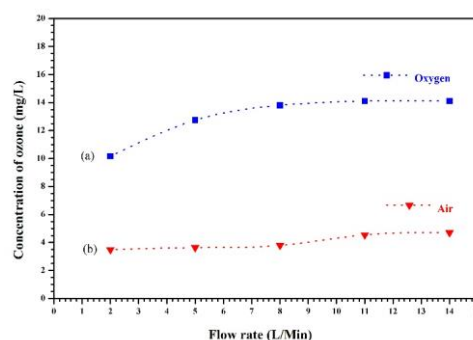


Figure 2. The relationship between ozone concentration and flow rate of the feed gas (a) oxygen and (b) air

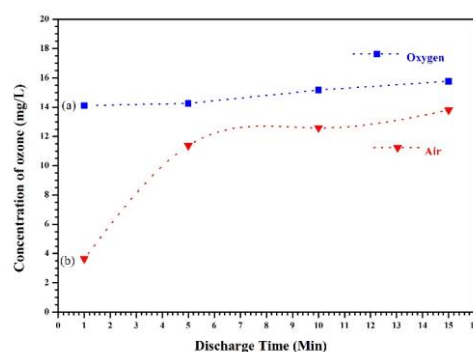


Figure 3. The relationship between ozone concentration and discharge times of the feed gas (a) oxygen and (b) air

Results and Discussion

To identify the optimal conditions for achieving the highest ozone yield, this study considered both the flow rate and discharge times, using both oxygen and air as the feed gas. The results are presented in Figure 2. The finding depicted in Figure 2 indicate that using oxygen as the feed gas produces a higher ozone concentration than using air. Specifically, the ozone concentration reaches 14.11 mg/L at a flow rate of 11 L/min. Moreover, as the flow rate increases, the ozone yield at a flow rate of 11 L/min reaches a saturation point or even exhibits a slight decrease. This consists with the findings of Prasetyaningrum *et al.* (2019), which suggest that ozone concentration increases with higher ozone gas flow rates. However, an excessively high flow rate can decrease the ozone concentration due to the shorter residence time of ozone in the system. In contrast, when air is used as the working gas, the ozone concentration shows a slight increase as the flow rate increases from 2 to 14 L/min. Subsequently, at a flow rate of 11 L/min, the ozone concentration stabilizes at 4.70 mg/L. These observations are consistent with those of Cuong *et al.* (2019), who proposed that the amount of oxygen in the ozone reactor acts as

a limiting factor for ozone production. Therefore, a flow rate of 11 L/min can be regarded as the optimal condition.

Furthermore, the impact of various discharge times on ozone production was examined under the optimized flow rate conditions (11 L/min), as depicted in Figure 3. The results indicate that the highest ozone production rate of 15.17 mg/L is observed when oxygen is used as the feed gas,

and this occurs at a discharge time of 10 min. Similarly, when air is used as the feed gas, the highest ozone production rate of 12.59 mg/L is achieved at an optimal discharge time of 10 min. These observations are consistent with the findings of Panta *et al.* (2021), who proposed that an increase in non-elastic collisions with oxygen molecules results in a higher concentration of plasma formation.

When ozone gas is introduced into water through a stone diffuser, it reacts with water molecules to generate highly reactive oxidizing radicals, including hydrogen peroxide (H_2O_2), superoxide anions (O_2^-), oxygen atoms (O), as well as hydroxyl ($\bullet\text{OH}$), perhydroxyl ($\text{HO}_2\bullet$), and oxygen ($\bullet\text{O}$) radicals. These radicals possess high oxidation potential. This reaction can lead to an increase in the ORP value in the water. The experimental results shown in Figure 4 indicate that the initial ORP value of the water was 123 mV and increased after ozone gas was introduced through a stone diffuser, signifying an augmentation in the water's oxidation potential. Consequently, the ORP values increased with contact time, reaching a maximum before stabilizing after 15 min. The highest ORP value of 821 mV was observed when oxygen was employed as the feed gas, whereas the highest ORP value of 569 mV was observed when air was used as the feed gas. Hence, the ozone concentration plays a crucial role in enhancing the availability and reinforcement of dissolved ozone in water, resulting in an increase in the concentration of highly oxidizing radicals known as ROS.

Conclusions

From the experimental results, it is evident that the ozone concentration tends to stabilize or exhibit minor fluctuations under optimal conditions. Additionally, the ozone concentration increases, reaching its peak yield at the optimal working gas flow rate of 11 L/min and with a 10-min discharge time.

Under all experimental conditions, the ozone concentration in the oxygen feed gas was consistently higher than in the air feed gas. This difference suggests a greater ozone yield from oxygen compared to air.

The oxidation efficiency of ROS was assessed by evaluating the ORP value. This process revealed that injecting ozone gas into water through a stone diffuser resulted in the formation of microbubbles, consequently leading to an increase in the ORP value. The observed rise in the water's oxidation potential indicates enhanced oxidative capabilities after a treatment time of approximately 15 min.

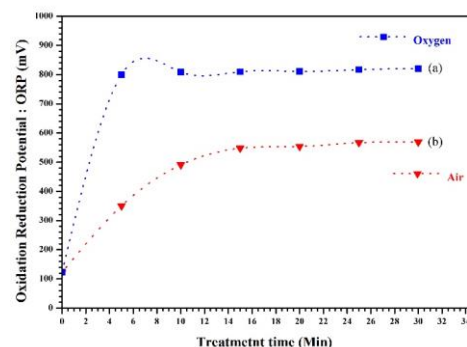


Figure 4. The relationship between the ORP value and the duration of ozone microbubble generation using the feed gas as (a) oxygen and (b) air

Furthermore, utilizing oxygen as the feed gas resulted in a higher oxidation potential compared to air, as evidenced by the increased concentration of ozone and ROS.

Acknowledgement

The authors would like to thank Faculty of Science at Si Racha, Kasetsart University, Si Racha campus, Thailand and Faculty of Science and Graduate School, Burapha University, Thailand.

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