Ultrafine bubbles as an augmenting agent for ozone-based advanced oxidation

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ABSTRACT

In this study, the influence of nanobubbles (NBs) application in ozone (O\textsubscript{3}) based advanced oxidation processes (AOP) is investigated. The results demonstrate the potential of NBs application to O\textsubscript{3} – based AOP. It was observed that NBs suppress the negative influence of pH and operating temperatures on the efficiency of ozonation. In addition, the application of NBs tends to improve the solubility of O\textsubscript{3} and the rate of mass transfer under the influence of a broad range of temperature and pH conditions. The results of this research indicate that application of NBs minimized the reduction in concentration of dissolved O\textsubscript{3} with an increase in temperature. Furthermore, application of NBs highly improved the OH radical formation in acidic conditions. The results of this research depicted for first time that the application of NBs strongly encourages the initiation of reactions involving OH radicals. It was found by this research that NBs can boost the concentration of OH radicals up to 3.5 fold compared to equivalent MB-supported ozonation systems. This is assumed to improve the efficiency of currently existing conventional bubble supported O\textsubscript{3} – based AOP systems.

Key words: advanced oxidation, mass transfer, microbubbles, nanobubbles, ozone, ultrafine bubble

HIGHLIGHTS

- MB nanosizing reduces the negative influence of pH on the efficiency of ozonation.
- MB nanosizing reduces the negative influence of temperature on ozonation efficiency.
- Nanobubbles enhance 'OH concentration by up to 3.5 fold compared to microbubbles.
- Nanobubbles improve the mass transfer of O\textsubscript{3} during ozonation compared to MBs.

GRAPHICAL ABSTRACT

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1. INTRODUCTION

Ozone is a powerful oxidant, which reacts with a broad range of organic and inorganic compounds in water (Ouederni et al. 1987; Katsoyiannis et al. 2011; Khuntia et al. 2015). It has been applied to water treatment because of its high reactivity, ease of production, self-decomposition to oxygen, and ability to be used in combination with other conventional treatment methods as well as chemicals to enhance the efficiency of water treatment (Sano et al. 2007; Khuntia et al. 2015). The level of investment required, the operational costs related to energy use and off-gas treatment are the major challenges against the broad application of O₃-based treatment systems. However, these systems continued to attract attention because of the trend in enhanced energy efficiency improvement in O₃ generation technologies over the recent decades (Sievers 2011), formulation of stringent regulations in water treatment, increased water scarcity, and growing public awareness of the need for safe water (Loeb et al. 2012).

In O₃-based wastewater treatment, the oxidation of compounds occurs either by direct reaction with O₃ or indirect reaction with OH radicals (‘OH) formed from O₃ decomposition (Khuntia et al. 2015). The oxidation of contaminants by the latter is known as an advanced oxidation process (AOP). AOPs mineralize organic compounds to carbon dioxide, water, and mineral acids or salts. This process is enabled when an elevated number of radicals are generated in a system. The generation of radicals is achieved by (1) direct or physical processes, (2) the addition of oxidants, and (3) the use of solid catalysts (Sievers 2011). In AOPs using O₃ as an oxidant, the OH radicals are the predominant radical species that play the indirect oxidation role (Lucas et al. 2009, 2010; Sievers 2011). Substantial studies have been conducted to optimize the processes of both ozonation and AOPs by influencing operating conditions, such as pH, alkalinity, organic matter composition, concentration and temperature, as well as changing ozonation equipment design parameters (Glaze et al. 1993; Siddiqui & Amy 1993; von Gunten 2003). An increase in the pH of water or concentration of hydroxide ions (OH⁻) can accelerate the decomposition of O₃ (Tomiyasu et al. 1985; Sehested et al. 1991; von Gunten 2003). In conventional bubbling systems, the generation of OH⁻ is not detected for low pH wastewater (Takahashi et al. 2007a). Studies have revealed that the degradation of organic substances by O₃ treatment under an acidic pH is relatively low and slow (Poznyak et al. 2006; Lucas et al. 2009). This degradation is more accelerated under neutral and alkaline pH conditions through the rapid formation of ‘OH due to the scavenging of O₃ by OH⁻ (Poznyak et al. 2006; Lucas et al. 2009). To understand the effect of pH on these O₃ decomposition reactions, the governing reaction mechanisms for O₃ previously proposed by Tomiyasu et al. (1985) (Tomiyasu et al. 1985; Kim et al. 2007; Khuntia et al. 2015) are used for explanation (see S1 in Supplementary Information). In these proposed mechanisms for the decomposition of O₃, OH⁻ ions act as initiators of fast chain reactions in alkaline solutions, whereas in acidic solutions, this is not the case and decomposition of O₃ is slower than that of an alkaline solution (Kim et al. 2007).

Temperature is the other operating condition that influences AOPs. An increase in operating temperature increases the O₃ depletion rate while not affecting ‘OH exposure (Elowitz & von Gunten 1999; Elowitz et al. 2000). Higher operating temperatures increase the formation of bromate as a byproduct of AOPs (Siddiqui & Amy 1993). Therefore, a rise in the process temperature has a dual negative effect of decreasing the solubility of O₃ and potential of increasing the AOP reaction rates.

The O₃ utilization and mass transfer can be improved by increasing the concentration of O₃ in the bulk liquid and reducing the amount of O₃ leaving as off gas. To understand the effects of different factors on improving mass transfer and utilization efficiency of O₃, researchers have studied parameters including agitation speed, gas flow velocity, and input gas pressure (Ouederni et al. 1987) for the generation of O₃ as well as the type of gas sparger and water characteristics (Zhou & Smith 2000). Intuitively, a reduction in bubble size may also be assumed to play an important role in improving the efficiency. However, limited studies exist that analyze the application of fine bubbles to improve ozonation efficiency (Takahashi et al. 2007b; Chu et al. 2008). There has been very limited discussion on the effect of bubble size for ozonation, especially on AOP mechanisms in particular. Zhang et al. (2013) reported that a reduction in bubble diameter for a given bubble column can be caused by an increase in the inlet O₃ concentration and increased solubility of O₃. Chu et al. (2008) studied mass transfer, chemical oxygen demand (COD) and color removal from textile industry wastewater using O₃ microbubbles (MBs) instead of conventional bubbles. They found that the COD removal efficiency improved and de-coloration time reduced when MBs are applied. Additionally, the pressure inside MBs was found to induce the decomposition of O₃ and formation of ‘OH, resulting in a reduction of COD by indirect oxidation. However, considering the stability of nanobubbles and expected high mass transfer rates, little research has been done on the effect of NBs on O₃-based AOPs. Therefore, this paper addresses the influence of bubble size reduction from MB to NB, on O₃-based AOPs. Moreover, the influence of bubble size reduction on AOP...
operating parameters, mainly temperature and pH, and the effect of size change on improvement of AOP mechanism as well as the potential for oxidation efficiency improvement is investigated by comparing MB and NB systems.

2. MATERIAL AND METHODS

2.1. Experimental setup
Gas-liquid mass transfer experiments for AOPs were conducted in a semi-batch reactor. A Plexiglas column with an internal diameter of 0.152 m, a height of 0.7 m and a working volume of 10 liter was fitted with a gas-tight lid to force off gas through an O₃ wash bottle before being released to a fume hood, shown in Figure 1 was used. The bubble generation system is fitted with a gas-water mixing variable speed pump having an outer saturator pipe of 8 mm in diameter with an effective length of 1 m connected at an outlet port. A hydrodynamic microbubble splitter with an interchangeable internal flow path length 'l' and flow diameter “d” was installed between the outlet port of the saturator pipe attached with the air-water mixing pump and the bubble column as shown in Figure 1. The flow channel in the splitter is designed to simulate a plug flow. The internal surface of the flow channel was constructed with a rough surface channel to reduce the size of bubbles created by cavitation from the mixing pump and saturation pipe. This system reduces the bubble size over the flow length by increasing hydrodynamic friction. As O₃ is reactive, O₂ was used as a surrogate gas to measure the change in bubble size for two flow path lengths at the same flow diameter d = 3 mm. Given the flow area of the splitter and bubble flow path lengths l₁ = 2 m and l₂ = 15 m, the bubble sizes generated were 58 μm and 897 nm, respectively, at a water flow rate of 1.2 l/min. For this research, the flow path length that generated the smaller bubble size was used to represent the application of NBs, whereas the other one was used to represent the MB system for comparison. The cumulative bubble size distribution for both systems is presented in Fig S2.

A gas-liquid mixture flow rate of Q = 0.8 l/min inside the bubble splitter was used for both AOP experiments. Oxygen (O₂, 99%) was supplied to a laboratory scale O₃ generator at a flow rate of 200 ml/min to generate an O₃-O₂ gas mixture. The concentration of the O₃ in the gas mixture leaving the ozone generator was measured using the modified indigo method (Chiou et al. 1995) and found to be 49.3 mg/l.

2.2. Chemicals
Potassium indigotrisulfonate (C₁₆H₇N₂O₁₁S₃K₃) and high purity p-Chlorobenzoic acid (pCBA, 99%) (Sigma Aldrich); high-performance liquid chromatography (HPLC) grade methanol (CH₃OH, >99.9%) (Fisher Chemical); Sodium dihydrogen phosphate dehydrate (NaH₂PO₄·H₂O) (Junsei Chemicals); and hydrochloric acid (HCl, >35%), phosphoric acid (H₃PO₄), 85%, and sodium hydroxide (NaOH) pellets (Daejung Chemicals) were purchased and used as received from the respective manufacturers for the experiments.

Figure. 1 | Schematic diagram for nanobubble generation apparatus.
2.3. Methods

In all experiments, deionized (DI) water (Millipore, Elix® Advantage System, USA) was used as the bulk water. The initial pH of the bulk water was adjusted using solutions of 0.1M HCl and 0.1M NaOH. The pH was measured using a pH meter (DKK-TOA, HM-31P, Japan).

In an aqueous solution, a dissolved O₃ concentration can be directly measured using an electrochemical method or optically using a colorimetric method. In this case, a standard indigo colorimetric method (APHA, AWWA, and WEF 2005) was used. The gaseous O₃ concentration was measured using the modified indigo method developed for gaseous ozone analysis by Chiou et al. (1995). Potassium indigotrisulfonate was used as an indicator, and the color change was analyzed using a UV spectrophotometer (Humas, model: HS 3300, Korea) at 600 nm wavelength. For this experiment, 20 ml of ozonated DI water was drawn from the middle of the bubble column through a sampling port every five minutes interval using a gastight syringe. The syringe was pre-filled with a sufficient predetermined amount of potassium indigotrisulfonate based on the initial pH of the bulk water. It automatically reacts with the O₃ in the solution. The solution was then analyzed with a spectrophotometer to determine the actual O₃ concentration.

The ⟨OH⟩ concentration was measured using pCBA as a probe (Elovitz & von Gunten 1999). The concentration of pCBA was determined by HPLC (YL instruments, YL9100, Korea) using a 55% methanol and 45% 10 mM phosphoric acid solution as the mobile phase mixture. A 50 μl sample was injected into a C18 column (Waters, SunFire, Ireland, C18, length = 150 mm, internal diameter = 4.6 mm, particle size = 5 μm) and pCBA was detected at a 234 nm wavelength. pCBA was particularly selected as the ‘OH-probe chemical as it has low reactivity with O₃ (k_{O_3/pCBA} < 0.15 M⁻¹s⁻¹ (David Yao & Haag 1991)) but readily reacts with ‘OH (k_{OH/pCBA} = 5 × 10⁹ M⁻¹s⁻¹) as reported by Elovitz & von Gunten (1999) quoting Neta & Dorfman (1968). For an indirect determination of ‘OH concentration, the 20 ml sample collected every 5 minutes was allowed to react with up to 250 μM of pCBA, pre-filled into the gas-tight syringe, depending on the initial pH. The resulting solution was analyzed using HPLC to detect the amount of unreacted pCBA to determine the ‘OH exposure. The off-gas containing O₃ from the bubble column was washed by passing it through an indigo solution in a gas washing bottle, as shown in Figure 1.

2.4. Determination and model development for the O₃ mass transfer coefficient

The dynamic measurement technique was used to determine the volumetric mass transfer coefficient for O₃. In this approach, O₃ bubbles are generated until saturation is reached (Fig S3. a). When saturation occurs, bubble generation is interrupted, and O₃ consumption by scavenging processes was done (Fig S3.b). The model for volumetric mass transfer coefficient (k_{La}) of O₃ gas in the bubble column is derived from a mass balance equation on the bulk liquid given by Equation (1).

\[
\frac{dc}{dt} = GTR - GCR \tag{1}
\]

where, dc/dt in (mg/l min) is the net O₃ mass transfer rate from the gas in the bubbles to the surrounding bulk liquid, GTR in (mg/l min) is the O₃ gas transfer rate to the bulk liquid given by equation S1, and GCR in (mg/l min) is the gas consumption rate of O₃ in the bulk liquid by O₃ scavenging reactions given by equation S2. Therefore, Equation (1) can be further expressed as:

\[
\frac{dC}{dt} = k_{La} * (C^* - C_L) - k_d * C_L \tag{2}
\]

where, C* in (mg/l) is the saturation concentration of O₃, C_L in (mg/l) is O₃ concentration at a given time t and k_{La} (min⁻¹) is volumetric mass transfer coefficient of O₃.

Assuming that the O₃ concentration in the liquid phase is much lower than the scavenger (mainly OH⁻) concentrations reacting in the bulk DI water, the O₃ gas reaction rate (GCR) can be approximated by a pseudo-first order equation with respect to the O₃ concentration in equation S2. The pseudo-first order O₃ reaction constant, k_{d}, is found by determining the slope of the curve fitted to the normalized O₃ concentration vs. time graph (Fig S3. b). By integrating Equation (2) and using the constant k_{d} value determined from the previous assumption (refer to S6) Equation (3) can be developed as
the final model.

$$\frac{C_L}{C^*} = \frac{k_L a}{k_L a + k_d} (1 - e^{(-k_L a + k_d)t})$$ (3)

Using Equation (3), the $k_L a$ value can be determined by curve fitting the normalized O3 concentration vs. time graph for the bubbling time. But the circulation of water in the system results in an increased system temperature, therefore the $k_L a$ value determined from Equation (3) was corrected to a value at $T = 20 °C$ for a comparison purpose using Equation (4) (Stenstrom & Gilbert 1981).

$$kla_{20} = \frac{kla(T)}{1.024^{(T-20)}}$$ (4)

3. RESULTS AND DISCUSSION

3.1. Effect of nanobubbles on pH and O3 residual

The effect of pH on the O3 residual concentration has been well studied. The O3 reaction with $OH^-$ ions as a scavenger can be better explained with the rapid reduction of the O3 residual with an increase in the pH of DI water. The pH effect reduces the efficiency of the selective or direct reactions with O3 because of an increase in the competitive reactions with scavengers that reduce the O3 concentration in the bulk liquid. In this study, experiments done using both MB and NB as the O3 delivery system showed a similar trend to previous studies (Chu et al. 2008; Li et al. 2009). For the application of both bubble types, an increase in the residual O3 concentration was observed when the initial pH of the DI water was reduced (Figure 2). Moreover, the effect of the bubble size reduction for a specific pH was compared for three different pH values to observe the influence of pH on the O3 residual concentration (Figure 3).

During the bubble generation, there was a temperature increment, due to friction in the splitter for both MBs and NBs. This temperature increment was higher for the formation of NBs, and its effect is discussed in the next section. This temperature increment was intended to reduce the solubility of O3 in the NB system, compared to the MB system. However, the residual O3 concentration measured for all pH values shows that the application of NBs slightly increased the concentration of O3 residual in the bulk water compared to the MB system. This demonstrates the potential of NBs to improve the solubility or mass transfer from the gas phase to the bulk liquid when compared with larger bubbles. For the same volume of O3 gas supplied, an increase in the residence time and surface area to volume ratio for NBs in the bulk liquid compared to MBs may be the reason for an increase in the residual concentration of O3 during the application of NBs. Therefore, from the observed incremental rise in the residual O3 concentration due to the application of NBs, it can be assumed that there is a potential to improve the O3 disinfection efficiency by reducing the bubble size and also reducing the amount of O3 off-gas through retaining more in the bulk liquid. The sudden drops in Figure 3, a and c at the 30th and 15th min respectively, are assumed to be the result of measuring technique accuracy and are considered as outliers of the data collected.

![Figure 2](https://iwaponline.com/wst/article-pdf/84/12/3705/979495/wst084123705.pdf)

**Figure 2** | Effect of pH on the O3 residual concentration for two different bubble types (a) MB (b) NB.
3.2. Effect of NBs on the influence of temperature

It is known that an increase in process temperature reduces the solubility of gaseous O₃ in the bulk liquid. A similar result was observed for all experiments performed in this research for the same bubble types (Figure 4 and S4). For all experiments done, the O₃ concentration in the bulk liquid decreased when the process temperature increased from 10 to 20 °C for the same bubble type and pH value. However, because of the water circulation through the bubble splitter, the water temperature gradually increased throughout the entire bubble formation process. This temperature increment is due to the friction inside the splitter. For the formation of MBs and NB systems at the initial temperature of 20 °C a sample temperature increment change for MB and NB generation is shown in Figure 5(a). Similarly, the residual O₃ concentration for the two bubble type processes at different pH values under the influence of these changes in temperature is shown in Figure 5(b)–5(d). Due to the higher temperature increment for NB system compared to MB system, the solubility of O₃ gas to bulk liquids are expected to be less for NB system. Moreover, an increase in the surface area to volume ratio from the MB to NB system due to bubble size reduction is expected to increase the rate of scavenging reactions, which in turn will result in a reduction of the O₃ concentration in the bulk liquid. Furthermore, a higher temperature increment is also expected to favor the forward reaction of O₃ with the scavengers, which is expected to contribute to a reduction in the O₃ concentration in the bulk liquid. Despite these expectations, the measured dissolved O₃ concentration in the bulk liquid showed a slightly higher concentration for NB system for all pH values compared to the MB system. Conventionally an increase in temperature reduces the solubility of gases in an aqueous system. But in this research, the solubility of O₃ in the NB supported system showed increment while the temperature in the system increased from 19 °C to 25 °C. This result demonstrates that the amount of O₃ gas transferred by NBs is higher than that for MBs, despite an expected higher consumption of O₃ by scavenging reactions for the NB system. The same trends were observed for a process having an initial temperature of 10 °C (Fig S5). From these results, it is observed that the application of NBs can suppress the negative influence of temperature which reduces the solubility of O₃ residual concentration in the bulk liquid. Therefore, this favors an improved operating efficiency for O₃ based water treatment systems under a wide range of operating temperature. This is because of the mass transfer improvement potential of NBs resulting from a high persistence and high surface area to volume ratio compared to MBs.
3.3. Impact of bubble size on the net mass transfer of O₃

The net O₃ mass transfer equation (Equation (3)) was used to determine the volumetric mass transfer coefficient \( (k_{la}) \) of both systems at different pH values using the dynamic technique. The \( k_{la} \) showed an increment with pH for both bubble types. This may be due to the enhancement effect of reactions with scavengers.

For a pH of 4 and 7 the system with NBs showed a slightly better \( k_{la} \) most likely because O₃ mass transfer is a rate limiting process and the reaction with scavengers occurs relatively slowly in the bulk liquid close to the liquid film boundary. The gap between the \( k_{la} \) values for MB and NB systems reduces as pH increases (Figure 6). This is because of an increase in \( \text{OH}^- \) ion concentration, which helps as an initiator of rapid radical reactions. These reactions could occur instantaneously in the liquid film close to the gas liquid interface. As a result, the liquid film thickness is assumed to decrease and the film mass transfer resistance ‘1/\( k_l \)’ approaches an extent at which the resistance of the liquid film to mass transfer can no longer determines the rate. Therefore, for high pH operation, where fast radical reactions by scavengers occur, the liquid film mass transfer is no longer the rate controlling parameter of the overall process. Moreover, the value of the O₃ consumption rate constant \( k_d \), shows an increment with pH (Figure 7). This is may be due to an increase in the \( \text{OH}^- \) ion concentration, which improves the consumption rate of O₃ in scavenging reactions.

At a pH of 4 and 7, the value of \( k_d \) shows an increased value for the NB system in comparison to MB system for the same pH (Figure 7). This confirms that at low and neutral pH values, where radical reaction initiators (\( \text{OH}^- \) ions) are low in concentration, the higher mass transfer surface area to volume ratio and expected longer residence time of NBs in the bulk liquid contributes to an increase in the dissolved O₃ concentration. Therefore, this shifts the equilibrium towards O₃ reactions with scavengers. Similarly, the surface properties of fine bubbles contribute towards the initiation of scavenging reactions. Takahashi et al. (2015) reported that O₃ MBs tend to collect \( \text{OH}^- \) ions at the surface even at low pH values in a way that it almost simulates the situation in the high pH case. For a given inlet volume of O₃, further reduction of bubble size by
splitting of MBs to NBs increase in the bubble surface at which more OH\(^-\) ions collect and by that it avails more reaction surfaces with O\(_3\). For a high pH, the effect of bubble size between a MB and NB did not show observed difference for \(k_d\). This may be because of the rapid reactions occurring close to surface of the gas-liquid interface that makes the measurement difficult.

The potential for improving the AOP efficiency in a given O\(_3\) based water treatment unit depends primarily on the rate of the \(^\cdot\)OH exposure. However, it is very difficult to directly measure the concentration of \(^\cdot\)OH. Therefore, \(pCBA\) is used as a

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**Figure 5** | (a) Change in bubble column process temperature for different bubble generation systems at an initial temperature of 20 °C, (b–d) the effect of bubble size on the dissolved O\(_3\) concentration at 20 °C, for different initial pH values of DI water.

**Figure 6** | Influence of pH and bubble size on \(k_a\) of O\(_3\).
probe compound, and the degradation reaction is modelled as a second-order reaction (\( k_\text{OH}/p\text{CBA} = 5 \times 10^9 M^{-1}s^{-1} \) (Elovitz & von Gunten 1999; Elovitz et al. 2000)) with the reaction rate equation expressed by Equation (4). Integrating this equation to determine the \( \cdot\text{OH} \) exposure (\( [\cdot\text{OH}] \cdot t \)) results in Equation (5), which is plotted in Figure 8.

\[
-\frac{dp\text{CBA}}{dt} = k_{\text{OH},p\text{CBA}}[\text{OH}][p\text{CBA}]
\]

(5)

\[
-\ln \left( \frac{p\text{CBA}}{p\text{CBA}_0} \right) = k_{\text{OH},p\text{CBA}}[\text{OH}]t
\]

(6)

The result shows that an increase in pH increases the \( \cdot\text{OH} \) exposure for both MB and NB systems as expected. However, the \( \cdot\text{OH} \) exposure is very high for NB systems compared to MB systems at the same pH. This supports the conclusions from previous sections, which suggest that NBs facilitate forward reactions for radical chain reactions. It is reported that \( \cdot\text{OH} \) are produced at higher pH conditions for MBs than conventional systems (Tomiyasu et al. 1985). Furthermore, the surface property of MBs in \( \text{OH}^- \) ion collection may help with the initiation of \( \cdot\text{OH} \) chain reactions even for low pH bulk liquid. Similarly, as shown in Figure 8, this research also confirms the potential of \( \cdot\text{OH} \) formation in acidic conditions by using O\(_3\) MBs as well as NBs. The new finding of this research shows that further reduction in bubble size to NBs have a tendency to improve the concentration of \( \cdot\text{OH} \) by at least 3.5 fold compared to the MB systems even for low pH values. After a longer time of operation, the effect of the forward reactions tends to produce different radicals and the \( \cdot\text{OH} \) concentration tends to decrease due to the scavenging of \( \cdot\text{OH} \) by the forward reactions. In the NB system at a pH of 10, the amount of \( \cdot\text{OH} \) increased to a maximum between 300 and 600 s before decreasing to zero. This may be because of relatively rapid initiation of the forward radical chain reactions or fast scavenging of \( \cdot\text{OH} \) by \( \text{OH}^- \) ions in the forward reactions. In higher pH, the high concentration of \( \text{OH}^- \) ions and the application of NBs resulted in rapid forward reactions compared to the MB system. This subsequently favors the rapid reduction of \( \cdot\text{OH} \) in the NB system. This phenomenon can be supported by the possibility of the reaction
zone shifting closer to gas-liquid interface where the mass transfer rate becomes less determinant as a rate determining process. Since an increase in $\cdot OH$ is directly related to an increase in the AOP efficiency, it can be concluded from the outcome of this research that reduction in bubble size to NB size can further improve the efficiency of O$_3$ based AOP systems.

4. CONCLUSION

In this article, the influence of bubble size reduction from MB to NB on O$_3$ based AOP was investigated. The results showed the promising possibility of NB application for the improvement of future ozonation systems. The main findings of this research are summarized as follows:

- In the NB-supported system, the solubility of O$_3$ increased while the temperature in the system was increasing. This showed that application of NBs in ozonation reduced the effect of an increase in temperature on the reduction of O$_3$ gas solubility in an aqueous system.
- The application of NBs showed an improved efficiency of ozonation in acidic aqueous media by improving the formation of $\cdot OH$ which facilitates the indirect oxidation route of ozonation in acidic waste streams.
- The use of NBs in ozonation systems improved the $\cdot OH$ initiation reactions by up to 3.5 fold compared to that of an MB-based ozonation system.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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