


Article

Nanobubble Technology Enhanced Ozonation Process for Ammonia Removal

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Abstract: Ozone (O₃) has been widely used for water and wastewater treatment due to its strong oxidation ability, however, the utilization efficiency of O₃ is constrained by its low solubility and short half-life during the treatment process. Thereby, an integrated approach using novel nanobubble technology and ozone oxidation method was studied in order to enhance the ozonation of ammonia. Artificial wastewater (AW) with an initial concentration of 1600 mg/L ammonia was used in this study. In the ozone-nanobubble treatment group, the concentration of nano-sized bubbles was 2.2×10^7 particles/mL, and the bubbles with <200 nm diameter were 14 times higher than those in the ozone-macrobubble treatment control group. Ozone aeration was operated for 5 min in both nanobubble treatment and control groups, however, the sampling and measurement were conducted for 30 min to compare the utilization of O₃ for ammonia oxidation. H⁺ was the by-product of the ammonia ozonation process, thus the pH decreased from 8 to 7 and 7.5 in nanobubble treatment and control groups, respectively, after 30 min of operation. The fast removal of ammonia was observed in both systems in the first 10 min, where the concentration of ammonia decreased from 1600 mg/L to 835 and 1110 mg/L in nanobubble treatment and control groups, respectively. In the nanobubble treatment group, ammonia concentrations kept the fast-decreasing trend and reached the final removal performance of 82.5% at the end of the experiment, which was significantly higher than that (44.2%) in the control group. Moreover, the first-order kinetic model could be used to describe the removal processes and revealed a significantly higher kinetic rate constant (0.064 min⁻¹) compared with that (0.017 min⁻¹) in the control group. With these results, our study highlights the viability of the proposed integrated approach to enhance the ozonation of a high level of ammonia in contaminated water.

Keywords: advanced oxidation process; ammonia oxidation; nanobubbles; water and wastewater treatment



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1. Introduction

Excessive ammonia in water is undesirable and usually causes environmental problems, such as surface water eutrophication and acute toxicity of aquatic biota [1,2]. Various approaches, such as biological denitrification [3], air stripping [4], ion exchange [5], breakpoint chlorination [6], and chemical oxidation [7], have been applied to the elimination of ammonia from wastewater. In industrial-based wastewater, the ammonia content may

achieve up to 1000 mg/L attributed to the sources of chemical fertilizer, coking, pharmaceutical, and petroleum refining [8]. The treatment of such high-strength ammonia wastewater is often challenging.

The biological process is sensitive to toxic loads (high initial ammonia level), and cold weather conditions, and requires a relatively long retention time and large footprint [9]. For the ion exchange treatment, an extremely low concentration of solids in the wastewater is required to prevent fouling [10]. To reach the chlorination breakpoint, sufficient chlorine must be added and resulting in high costs [11]. The air stripping process has been successfully used to treat higher ammonia concentrations (e.g., 1000 mg/L). The major drawback of ammonia stripping is that the lime used for raising the pH often results in unwanted calcium carbonate deposition fouling in the packed beds [10,12]. The use of ozone is another well-known method for the oxidation of ammonia. Molecular O₃ can not only directly oxidize ammonia but also acts as a precursor to generate the hydroxyl radical (•OH) that is even more reactive as a nonselective oxidant [13,14]. Moreover, in the presence of an advanced catalyst, such as MgO, CuO, and ZnO, ammonia can also be oxidized as gaseous nitrogen [15]. However, the intrinsic characteristics of ozone limited the efficiency of ozonation, such as low water solubility and half-life [16,17]. The low saturation in water leads to undesired reaction concentration and low utilization efficiency of ozone [18]. The half-life of ozone in water is less than 1 h (about 15 min at 298 K at pH = 7) which limits the distance of the reaction zone away from the ozone injection point [19]. Therefore, efficient techniques to enhance the ozonation process are especially desired for the treatment of strengthened ammonia-contaminated wastewater.

Nanobubbles (NBs) are tiny bubbles with diameters less than 1000 nm, which have increased attention due to special characteristics of high gas transfer efficiency and the long lifetime of the bubbles [20–22]. The application of NBs as a burgeoning industry valued by The Wall Street Journal at USD 10 billion in 2020 [23]. Previous evidence has shown that bubbles with radii of 150–200 nm can remain stable for two weeks [24]. The large surface area of NBs could enhance the mass transfer process between the liquid and gas phases, which helps to facilitate chemical reactions [25]. Hydroxyl radicals (•OH) generated during the collapse of the NBs are strong oxidants in aqueous solutions, reacting rapidly with a wide range of dissolved compounds [26]. The potential application of NBs is speeded to many sectors, including the mining industry, water and wastewater treatment [27], natural water restoration [28], surface cleaning [25], and agriculture [29]. Several recent studies revealed that ozone NBs can significantly increase the degradation efficiencies against a variety of organic contaminants, such as dye molecules in dyestuff wastewater [30], residual pesticides in vegetables [1], and trichloroethene in sands [31]. Currently, nanobubble technology in coupled ozonation treatment is mainly tested for the oxidation of recalcitrant pollutants [32]. Whether, in particular to what extent, this approach could contribute to other common pollutants, such as ammonia, still needs further investigation prior to the implementation.

To address this knowledge gap, this study investigated the capability of ozone-nanobubble technology for ammonia removal from water. Firstly, the bubble size and distribution of ozone nanobubbles generated by a nanobubble generator were analyzed. Then, the water quality and the removal efficiency of ammonia in high-strength synthesized ammonia water were compared with the treatment of conventional ozone macrobubble. The findings from this study could provide further insights into the feasibility of using ozone nanobubbles, as an efficient and effective approach, for the removal of ammonia from wastewater.

2. Materials and Methods

2.1. Ozone-Nanobubble Solution Preparation

The ozonator (OZ-5) was purchased from MAT Filtration Technologies™, which can convert the oxygen to ozone by the corona-discharge method [33]. The output flow rate and concentration of ozone produced by OZ-5 were approximately 5 g/h and 5 L/min using

dried air as the gas source, respectively. In the nanobubble treatment group, the ozone was then injected into the nanobubble generator (KMT, Nikuni Co., Ltd., Kanagawa, Japan) and a ceramic diffuser, respectively, under the gas flow of 0.45 L/min. The nanobubble generator was operated by recirculation of artificial wastewater at a flow rate of 1000 L/h. The superficial liquid velocity in the column was 0.035 m/s, and the residence time in the system was approximately 2.1 min. For the ozone-macrobubble control group, the ozone, with the same inflow rate of 0.45 L/min, was passed through a ceramic diffuser for the treatment. The experimental setup is schematically shown in Figure 1.

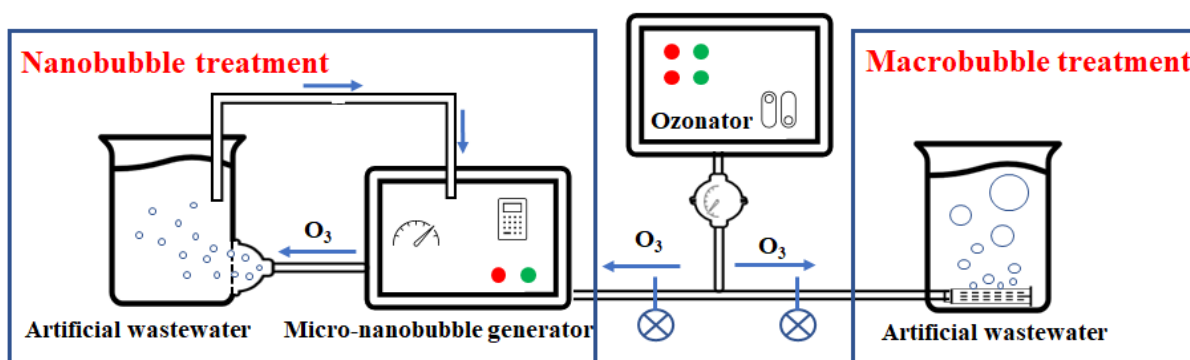


Figure 1. Schematic of the experimental setup.

2.2. Experimental Procedure

To simulate the high concentration of ammonia wastewater discharged from landfills, petrochemical industries, and piggeries, artificial wastewater (AW) was prepared by adding the chemical of NH_4Cl to tap water in order to obtain the final concentration of 1600 mg/L. The tap water used in this study was supplied by Severn Trent Water Ltd. (Coventry, UK), with ammonia ≤ 0.5 mg/L, chloride ≤ 250 mg/L, iron ≤ 200 $\mu\text{g/L}$, manganese ≤ 50 $\mu\text{g/L}$. The pH of AW was then adjusted to 8 by 0.1 mol NaOH. Ten liters of AW were then poured into the test (nanobubble treatment) and control (macrobubble treatment) systems at the beginning of the experiment. Both treatment systems were reaction statical for 30 min after the bubble generator running for 5 min. AW samples were collected at 0, 5, 10, 20, and 30 min for analysis. The experiment was set up at room temperature (25 ± 2 °C) and repeated three times.

2.3. Analytical Parameters Determination

The sizes and distributions of nanoscale bubbles (<1000 nm) in the 5 min AW samples were determined through nanoparticle tracking analysis by ZetaView PMX 120 (Particle Metrix, Meerbusch, Germany) and its corresponding software ZetaView 8.04.02. The pH and dissolved oxygen (DO) of all AW samples were measured by Hach's portable meters (Hach, America). The ammonia concentrations in AW samples were determined by an AQ400 nutrients autoanalyzer (Seal analytical, Southampton, UK) and subjected to the dilution according to the detection manual [34]. All the experiments were done in a fume hood with an ozone gas detector to ensure the environmental O_3 concentration was lower than 120 $\mu\text{g/m}^3$.

2.4. Statistical Analyses

The first-order kinetics model (Equation (1): $\ln[C/C_0] = -kt$) was used to simulate the removal process of ammonia in both treatment systems. The non-parametric test (Mann-Whitney U test) was applied to compare the significance ($p < 0.05$) of the water quality and ammonia concentration in both systems at a certain sampling time.

$$\ln[C/C_0] = -kt \quad (1)$$

3. Results and Discussion

3.1. Characterisation of the Bubble Size and Distribution

The potential uses of nanobubbles have spread to high-value applications, which causes high efforts to develop generation methods [25]. Various methods have been developed to produce nanobubbles, such as ethanol–water exchange, direct immersion, temperature change, electrochemical reaction, and hydraulic cavitation [35]. Amongst them, the hydraulic cavitation method was deemed the most effective approach, in terms of nanobubble generation speed and stability, which was used in this study. The diameters of the nanobubbles mainly ranged from 45 to 400 nm (Figure 2). The concentration of nanobubbles was 4×10^6 particles/mL in the macrobubble treatment control system (Figure 2a), while a one-magnitude higher nanobubble concentration (2.2×10^7 particles/mL) was observed in the nanobubble treatment system after 5 min operation (Figure 2b). Over 87.1% of the bubbles could be categorized as bubbles sized <200 nm in the nanobubble treatment system, while only 33.3% in the control system. The results of the nanobubble size and distribution were similar to the previous study [36], where the ozone nanobubbles mainly ranged from 32 to 460 nm with a concentration of 4.55×10^7 bubbles/mL based on the hydraulic cavitation method.

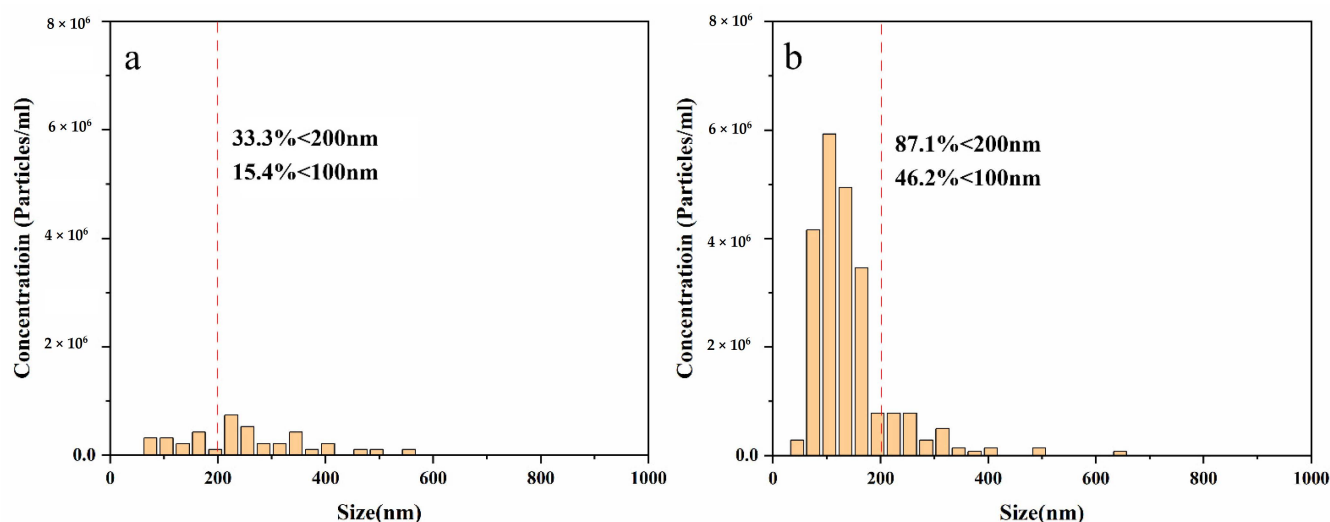


Figure 2. Nanoscale bubbles size and distribution in macrobubble treatment control system (a) and nanobubble treatment system (b).

3.2. The Changes in pH and Dissolved Oxygen (DO) during the Treatment

Previous studies have shown the efficiency of ozone oxidation of ammonia was higher in an alkali environment compared with that in neutral or acid conditions [5]. In this study, the initial pH of both systems was adjusted to 8, thus, the dissociation of NH_4Cl in water led to an equilibrium between the ammonium ion (NH_4^+) and free ammonia (NH_3), which can be expressed in Equation (2). The equilibrium between ammonium form and free ammonia depends on the pH of the solution. The ammonium form dominates at $\text{pH} < 7$, whereas the free ammonia increased at $\text{pH} > 7$. In the initial part of this study, the pH of AW was adjusted to 8 which facilitates the equilibrium tilt towards free ammonia [37]. As shown in Figure 3a, during the ammonia ozonation process, the pH of the reaction medium decreases with time due to the formation of H^+ ions (Equation (3)). However, the rate of pH descent in the nanobubble treatment system was faster than in the control system. At the end of the study (30 min), the pH achieved 7.00 ± 0.09 and 7.52 ± 0.04 in the nanobubble treatment and control systems, respectively.



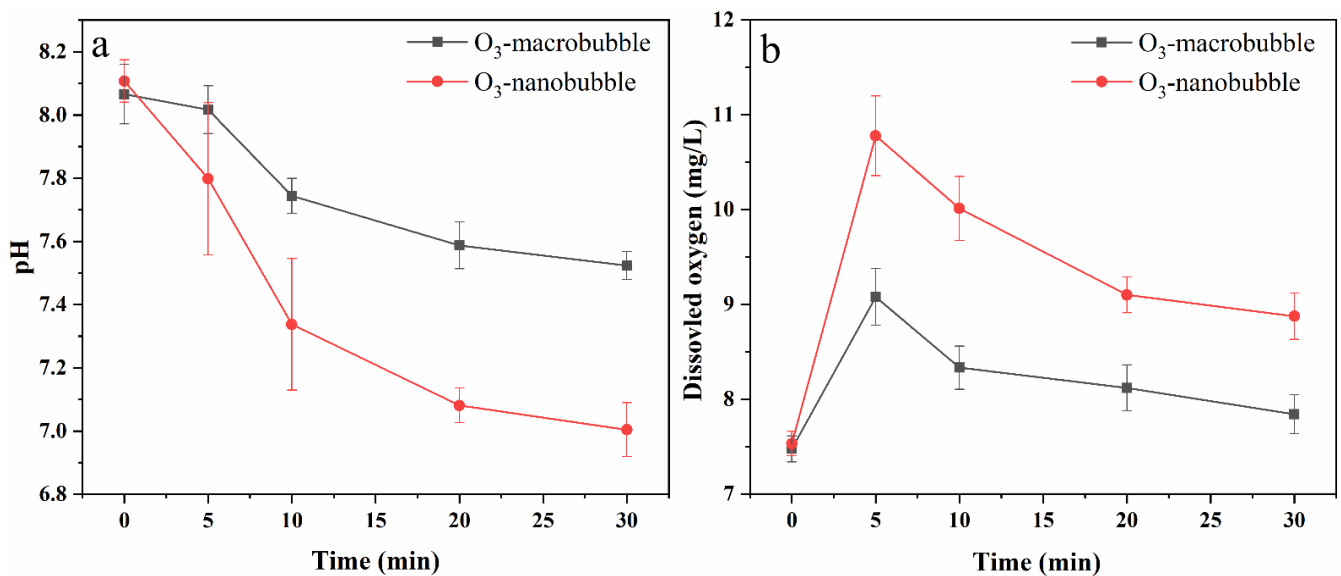


Figure 3. The dynamics of pH (a) and dissolved oxygen (b) in both treatment groups.

Although one-unit ammonia can consume four-unit ozone during the process of ammonia oxidation by ozone (Equation (3)), continuous aeration in both systems could deliver excess ozone into the solution and produce oxygen following the chemical reaction in Equation (4) [38]. Therefore, the DO concentrations increased from 7.5 ± 0.1 mg/L to 10.8 ± 0.4 and 9.1 ± 0.3 mg/L in nanobubble treatment and control systems after 5 min of operation (Figure 3b). It has been reported that the cavitation process for nanobubble generation could induce super-saturation of gas in water [39], which supported the significantly higher DO level in the nanobubble treatment group.

Previous studies have observed that nanobubbles in water can exist for up to several weeks [40]. Zhang et al. detected the heterogeneous pressures inside nanobubbles by atomic force microscopy (AFM), which was modeled in a molecular dynamics simulation as a high-gas-density state [41]. The gas (O_3 in this study) inside nanobubbles may exist as an aggregation rather than the phase of the dissolved state in the solution [42], and the diffusion of the O_3 inside nanobubbles is likely to be slow and to take place over a long period of time. Thus, the DO concentration decreased to 7.8 ± 0.2 mg/L, which was similar to the original DO level in the control group after 30 min (Figure 3b). On the contrary, the decrease in DO level in the nanobubble treatment group was much slower and kept a significantly higher value (8.9 ± 0.2 mg/L) than that in the control group. It demonstrated that the application of nanobubble aeration could potentially improve ammonia oxidation due to a higher O_3 utilization rate.

3.3. Ammonia Nitrogen Removal Performance and Kinetics

Ozonation has been applied to remediate organics, ammonia, and disinfection in water and wastewater treatment since the 1970s [43,44]. For high-strength ammonia wastewater, ozonation is also used to decompose the recalcitrant form of nitrogen and enhance the biodegradability of the wastewater [45]. In this study, the ammonia concentrations quickly decreased from 1600 mg/L to 1380 ± 270 and 1510 ± 157 mg/L in nanobubble treatment and control groups, respectively, at the first 5 min along with the operation of aeration (Figure 4a). Although the aeration was stopped after 5 min, the dissolved O_3 in both systems could still contribute to ammonia oxidation, which resulted in the concentrations of 835 ± 90 and 1110 ± 214 mg/L in nanobubble treatment and control groups, respectively, after 10 min.

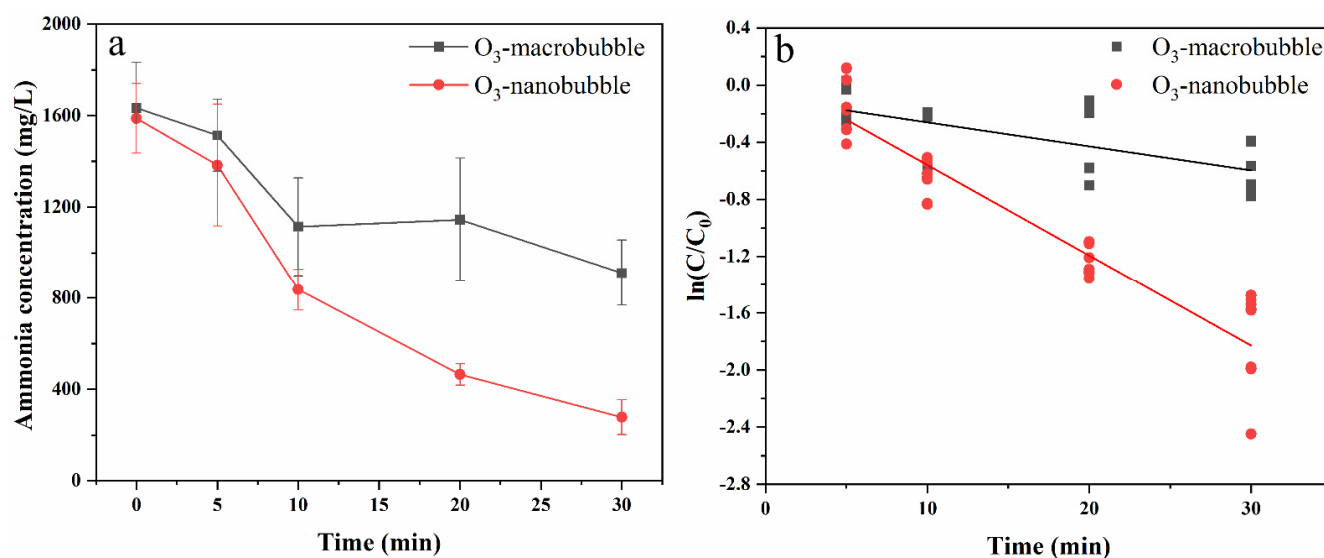


Figure 4. The concentration of ammonia remaining in the wastewater during the treatment, and the simulations of the first-order kinetics model of the ammonia removal.

It is well known that the ozone oxidation treatment was hindered by the low solubility and O₃ utilization efficiency in water [40]. The ammonia concentration in the control group with macrobubble treatment only slightly decreased to 910 ± 144 mg/L with the final removal efficiency of 44.2% at the end of the experiment. Due to the long lifespan of nanobubbles and the capability of slowly releasing the filled gas into the surrounding water (Figure 3b), the ammonia concentration in the nanobubble treatment group kept a fast-decreasing trend to 277 ± 76 mg/L with the final removal efficiency of 82.5% at 30 min (Figure 4a). Liu et al. reported the removal rate of ammonia by ozone could reach 80%, however, with the presence of MgO catalyst [46]. It is hypothesized that the combination of ozone-nanobubble treatment and the catalysis could achieve an even higher removal capability of the ammonia from contaminated water. When using the ozone aeration with the bubble sizes of micrometers, 99.1% of ammonia can be removed from the wastewater, however, with continuous aeration of 570 min [47]. Notably, these results were gained in a relatively lower initial concentration of ammonia in wastewater (50–100 mg/L). It supported that the aeration of nano-sized ozone bubbles is potentially more efficient and cost-effective for ammonia removal from water. Directly and indirectly, oxidation pathways were probably involved in the oxidation of ammonia by ozone nanobubbles. Firstly, owing to the long existence of the nano-sized ozone bubble in water, ozone could sustainably diffuse to the surrounding water, thus ammonia would directly oxidize to nitrate by ozone as shown in Equation (3) [5]. Secondly, the collapsing of ozone nanobubbles may deliver hydroxyl radicals, which could act on ammonia oxidation. However, the occurrence of hydroxyl radicals depends on the pH of the solution [48]. Takahashi et al. have shown that hydroxyl radicals are formed from ozone microbubbles under strongly acidic conditions in the presence of mineral acids [26]. As the pH decreased in our experiment, the mechanism of oxidation of ammonia by ozone nanobubbles can occur either by direct oxidation or via the hydroxyl radicals.

The removal dynamics of ammonia in both systems can be well described by the first-order kinetics model (Figure 4b), which was supported by previous studies [49]. The pseudo-first-order rate constant $k = 0.064 \text{ min}^{-1}$ was obtained for the slope of the regression line for the ozone-nanobubble treatment group, which was 3.78 times higher than the control group ($k = 0.017 \text{ min}^{-1}$). Overall, the result of the current study demonstrated the high potential of coupling novel nanobubble technology with the traditional ozone oxidation approach for strengthened ammonia-contaminated water treatment.

3.4. Implementation Potential

Ozone has a high oxidation potential and has been applied in water treatment for more than a century. In recent years, ozone has been increasingly applied for enhanced municipal wastewater treatment [50]. However, the lifetime of ozone in water is short and leads to low utilization efficiency of gaseous ozone and thus high operation costs [40]. The generation of macrobubble mainly relies on agitation-induced shear forces to the dispersion of the gaseous phases in water [51], which needs relevant lower energy input to compare with the nanobubble generation via hydraulic cavitation process [36]. However, large size bubbles have a much shorter lifetime and high buoyance that could lead to low gas transfer efficiency compared with nanobubble aeration during the ozonation treatment. It is estimated that the high utilization of the gas could compensate for the energy consumption for nanobubble generation. The current study demonstrated that nanobubbles significantly increase the efficiency of the ozonation process. Although the mechanisms have not been quantified in this study, the potential drivers could be concluded as the large gas-liquid interfacial area, the slow rising velocity with a longer lifetime, and a smaller amount of ozone required due to the generation of hydroxyl radicals responsible for the oxidation of pollutants [5,40]. The present study demonstrates the superior performance of ammonia ozonation by ozone nanobubble. It is expected that ozone nanobubbles can be also used to enhance the oxidation of organic micropollutants, e.g., pesticides, pharmaceuticals, and personal care products [13]. The ability to generate free radicals during bubble collapse potentially facilitates the degradation of a broad range of contaminants [27]. Nevertheless, given the complexity of pollutants and environment parameters, ozonation reactions and bubble dynamics in real wastewater bodies, further study on the impacts of background matrix and hydraulics on the efficiency of ozonation by ozone nanobubble to the successful application of ozone nanobubble in a water or wastewater treatment plant.

4. Conclusions

This study investigated the integrated approach using novel nanobubble technology and the traditional ozone oxidation method for the treatment of high-strength ammonia wastewater. Due to its higher dissolution ability and longer ozone retention time properties, ozone-nanobubble treatment performed better removal of ammonia (82.5%) than that (44.2%) in the control group with the ozone-macrobubble treatment. The first-order kinetics model can be used to describe the removal of ammonia, and presented a significantly higher removal rate constant (k value) of 0.064 min^{-1} in the nanobubble treatment group compared with that (0.017 min^{-1}) in the control groups. The ozone nanobubble could remain in the water and slowly dissolve the gas and continually contribute to the ammonia oxidation, which could further potentially reduce the operation cost. Overall, the result suggests that ozone nanobubbles can be a more effective ozonation method for the treatment of heavily polluted wastewater.

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References

1. Ikeura, H.; Kobayashi, F.; Tamaki, M. Removal of residual pesticides in vegetables using ozone microbubbles. *J. Hazard. Mater.* **2011**, *186*, 956–959. [[CrossRef](#)] [[PubMed](#)]
2. Lyu, T.; Song, L.; Chen, Q.; Pan, G. Lake and River Restoration: Method, Evaluation and Management. *Water* **2020**, *12*, 977. [[CrossRef](#)]
3. Bejan, D.; Graham, T.; Bunce, N.J. Chemical methods for the remediation of ammonia in poultry rearing facilities: A review. *Biosyst. Eng.* **2013**, *115*, 230–243. [[CrossRef](#)]
4. Lyu, T.; He, K.; Dong, R.; Wu, S. The intensified constructed wetlands are promising for treatment of ammonia stripped effluent: Nitrogen transformations and removal pathways. *Environ. Pollut.* **2018**, *236*, 273–282. [[CrossRef](#)] [[PubMed](#)]
5. Khuntia, S.; Majumder, S.K.; Ghosh, P. Removal of ammonia from water by ozone microbubbles. *Ind. Eng. Chem. Res.* **2013**, *52*, 318–326. [[CrossRef](#)]
6. Karthik, N.B.; Krishna, B.K.C.; Sathasivan, A. Effectiveness of Breakpoint Chlorination and Rechlorination on Nitrified Chloraminated Water. In Proceedings of the International Conference on Environment, Resources and Energy Engineering (EREE), Bangkok, Thailand, 9–11 October 2020.
7. Liu, R.; Wang, H.; Liu, Z.; Tao, C. Electrokinetic remediation with solar powered for electrolytic manganese residue and researching on migration of ammonia nitrogen and manganese. *J. Water Process Eng.* **2020**, *38*, 101655. [[CrossRef](#)]
8. Adam, M.R.; Othman, M.H.D.; Abu Samah, R.; Puteh, M.H.; Ismail, A.F.; Mustafa, A.; Rahman, M.A.; Jaafar, J. Current trends and future prospects of ammonia removal in wastewater: A comprehensive review on adsorptive membrane development. *Sep. Purif. Technol.* **2019**, *213*, 114–132. [[CrossRef](#)]
9. Zhao, H.W.; Mavinic, D.S.; Oldham, W.K.; Koch, F.A. Controlling factors for simultaneous nitrification and denitrification in a two-stage intermittent aeration process treating domestic sewage. *Water Res.* **1999**, *33*, 961–970. [[CrossRef](#)]
10. Yuan, M.H.; Chen, Y.H.; Tsai, J.Y.; Chang, C.Y. Ammonia removal from ammonia-rich wastewater by air stripping using a rotating packed bed. *Process Saf. Environ. Prot.* **2016**, *102*, 777–785. [[CrossRef](#)]
11. Jafvert, C.T.; Valentine, R.L. Reaction scheme for the chlorination of ammoniacal water. *Environ. Sci. Technol.* **1992**, *26*, 577–586. [[CrossRef](#)]
12. Liu, B.X.; Giannis, A.; Zhang, J.F.; Chang, V.W.C.; Wang, J.Y. Air stripping process for ammonia recovery from source-separated urine: Modeling and optimization. *J. Chem. Technol. Biotechnol.* **2015**, *90*, 2208–2217. [[CrossRef](#)]
13. Fan, W.; An, W.; Huo, M.; Xiao, D.; Lyu, T.; Cui, J. An integrated approach using ozone nanobubble and cyclodextrin inclusion complexation to enhance the removal of micropollutants. *Water Res.* **2021**, *196*, 117039. [[CrossRef](#)] [[PubMed](#)]
14. Zhang, H.G.; Lyu, T.; Bi, L.; Tempero, G.; Hamilton, D.P.; Pan, G. Combating hypoxia/anoxia at sediment-water interfaces: A preliminary study of oxygen nanobubble modified clay materials. *Sci. Total Environ.* **2018**, *637*, 550–560. [[CrossRef](#)] [[PubMed](#)]
15. Zhang, Z.; Ai, H.; Fu, M.-L.; Hu, Y.-B.; Liu, J.; Ji, Y.; Vasanthakumar, V.; Yuan, B. A new insight into catalytic ozonation of ammonia by MgO/Co₃O₄ composite: The effects, reaction kinetics and mechanism. *Chem. Eng. J.* **2021**, *418*, 129461. [[CrossRef](#)]
16. Dettmer, A.; Ball, R.; Boving, T.B.; Khan, N.A.; Schaub, T.; Sudasinghe, N.; Fernandez, C.A.; Carroll, K.C. Stabilization and prolonged reactivity of aqueous-phase ozone with cyclodextrin. *J. Contam. Hydrol.* **2016**, *196*, 1–9. [[CrossRef](#)]
17. Kim, J.; Choi, H. Modeling in situ ozonation for the remediation of nonvolatile PAH-contaminated unsaturated soils. *J. Contam. Hydrol.* **2002**, *55*, 261–285. [[CrossRef](#)]
18. Khan, N.A.; Carroll, K.C. Natural attenuation method for contaminant remediation reagent delivery assessment for in situ chemical oxidation using aqueous ozone. *Chemosphere* **2020**, *247*, 125848. [[CrossRef](#)]
19. Rakness, K.L. *Ozone in Drinking Water Treatment: Process Design, Operation, and Optimization*; American Water Works Association: Denver, CO, USA, 2005.
20. Pan, G.; He, G.; Zhang, M.; Zhou, Q.; Tyliczszak, T.; Tai, R.; Guo, J.; Bi, L.; Wang, L.; Zhang, H. Nanobubbles at Hydrophilic Particle-Water Interfaces. *Langmuir* **2016**, *32*, 11133–11137. [[CrossRef](#)]
21. Lyu, T.; Wu, S.; Mortimer, R.; Pan, G. Nanobubble Technology in Environmental Engineering: Revolutionization Potential and Challenges. *Environ. Ence Technol.* **2019**, *53*, 7175–7176. [[CrossRef](#)]
22. Wang, L.; Miao, X.J.; Ali, J.; Lyu, T.; Pan, G. Quantification of Oxygen Nanobubbles in Particulate Matters and Potential Applications in Remediation of Anaerobic Environment. *ACS Omega* **2018**, *3*, 10624–10630. [[CrossRef](#)]
23. Tan, B.H.; An, H.; Ohl, C.D. Stability of surface and bulk nanobubbles. *Curr. Opin. Colloid Interface Sci.* **2021**, *53*, 101428. [[CrossRef](#)]
24. Azevedo, A.; Etchepare, R.; Calgaroto, S.; Rubio, J. Aqueous dispersions of nanobubbles: Generation, properties and features. *Miner. Eng.* **2016**, *94*, 29–37. [[CrossRef](#)]
25. Favvas, E.P.; Kyzas, G.Z.; Efthimiadou, E.K.; Mitropoulos, A.C. Bulk nanobubbles, generation methods and potential applications. *Curr. Opin. Colloid Interface Sci.* **2021**, *54*, 101455. [[CrossRef](#)]
26. Takahashi, M.; Chiba, K.; Li, P. Formation of Hydroxyl Radicals by Collapsing Ozone Microbubbles under Strongly Acidic Conditions. *J. Phys. Chem. B* **2007**, *111*, 11443–11446. [[CrossRef](#)]
27. Fan, W.; Cui, J.; Li, Q.; Huo, Y.; Xiao, D.; Yang, X.; Yu, H.; Wang, C.; Jarvis, P.; Lyu, T.; et al. Bactericidal efficiency and photochemical mechanisms of micro/nano bubble-enhanced visible light photocatalytic water disinfection. *Water Res.* **2021**, *203*, 117531. [[CrossRef](#)]
28. Zhang, H.; Lyu, T.; Liu, L.; Hu, Z.; Chen, J.; Su, B.; Yu, J.; Pan, G. Exploring a multifunctional geoengineering material for eutrophication remediation: Simultaneously control internal nutrient load and tackle hypoxia. *Chem. Eng. J.* **2021**, *406*, 127206. [[CrossRef](#)]

29. Wu, Y.; Tao, L.; Yue, B.; Tonoli, E.; Pan, G. Enhancement of tomato plant growth and productivity in organic farming by agri-nanotechnology using nanobubble oxygation. *J. Agric. Food Chem.* **2019**, *67*, 10823–11083. [[CrossRef](#)]
30. Chu, L.B.; Xing, X.H.; Yu, A.; Zhou, Y.N.; Sun, X.L.; Jurcik, B. Enhanced ozonation of simulated dyestuff wastewater by microbubbles. *Chemosphere* **2007**, *68*, 1854–1860. [[CrossRef](#)]
31. Sung, M.; Teng, C.H.; Yang, T.H. Dissolution enhancement and mathematical modeling of removal of residual trichloroethene in sands by ozonation during flushing with micro-nano-bubble solution. *J. Contam. Hydrol.* **2017**, *202*, 1–10. [[CrossRef](#)]
32. Aluthgun Hewage, S.; Batagoda, J.H.; Meegoda, J.N. In situ remediation of sediments contaminated with organic pollutants using ultrasound and ozone nanobubbles. *Environ. Eng. Sci.* **2020**, *37*, 521–534. [[CrossRef](#)]
33. John, A.; Carra, I.; Jefferson, B.; Jodkowska, M.; Brookes, A.; Jarvis, P. Are microbubbles magic or just small? a direct comparison of hydroxyl radical generation between microbubble and conventional bubble ozonation under typical operational conditions. *Chem. Eng. J.* **2022**, *435*, 134854. [[CrossRef](#)]
34. Gallagher, M.T.; Reisinger, A.J. Effects of ciprofloxacin on metabolic activity and algal biomass of urban stream biofilms. *Sci. Total Environ.* **2019**, *706*, 135728. [[CrossRef](#)] [[PubMed](#)]
35. Mo, C.-R.; Wang, J.; Fang, Z.; Zhou, L.-M.; Zhang, L.-J.; Hu, J. Formation and stability of ultrasonic generated bulk nanobubbles. *Chin. Phys. B* **2018**, *27*, 118104. [[CrossRef](#)]
36. Hu, L.M.; Xia, Z.R. Application of ozone micro-nano-bubbles to groundwater remediation. *J. Hazard. Mater.* **2018**, *342*, 446–453. [[CrossRef](#)] [[PubMed](#)]
37. Lin, S.H.; Yen, Y.L. Ammonia and nitrite removal from sea water by ozonation. *Environ. Technol.* **1997**, *18*, 65–73. [[CrossRef](#)]
38. Bavasso, I.; Montanaro, D.; Di Palma, L.; Petrucci, E. Electrochemically assisted decomposition of ozone for degradation and mineralization of Diuron. *Electrochim. Acta* **2020**, *331*, 135423. [[CrossRef](#)]
39. Zheng, T.; Wang, Q.; Zhang, T.; Shi, Z.; Tian, Y.; Shi, S.; Smale, N.; Wang, J. Microbubble enhanced ozonation process for advanced treatment of wastewater produced in acrylic fiber manufacturing industry. *J. Hazard. Mater.* **2015**, *287*, 412–420. [[CrossRef](#)]
40. Tang, Y.; Zhang, M.; Zhang, J.; Tao, L.; Cooper, M.; Pan, G. Reducing arsenic toxicity using the interfacial oxygen nanobubble technology for sediment remediation. *Water Res.* **2021**, *205*, 117657. [[CrossRef](#)]
41. Zhang, X.H.; Maeda, N.; Craig, V.S.J. Physical properties of nanobubbles on hydrophobic surfaces in water and aqueous solutions. *Langmuir* **2006**, *22*, 5025–5035. [[CrossRef](#)]
42. Wang, S.; Liu, Y.; Lyu, T.; Pan, G.; Li, P. Aquatic Macrophytes in Morphological and Physiological Responses to the Nanobubble Technology Application for Water Restoration. *ACS EST Water* **2021**, *1*, 376–387. [[CrossRef](#)]
43. Fan, W.; An, W.G.; Huo, M.X.; Yang, W.; Zhu, S.Y.; Lin, S.S. Solubilization and stabilization for prolonged reactivity of ozone using micro-nano bubbles and ozone-saturated solvent: A promising enhancement for ozonation. *Sep. Purif. Technol.* **2020**, *238*, 116484. [[CrossRef](#)]
44. Ruffino, B.; Zanetti, M. Orthophosphate vs. bicarbonate used as a buffering substance for optimizing the bromide-enhanced ozonation process for ammonia nitrogen removal. *Sci. Total Environ.* **2019**, *692*, 1191–1200. [[CrossRef](#)] [[PubMed](#)]
45. Almaguer, M.A.; Cruz, Y.R.; da Fonseca, F.V. Combination of Advanced Oxidation Processes and Microalgae Aiming at Recalcitrant Wastewater Treatment and Algal Biomass Production: A Review. *Environ. Processes* **2021**, *8*, 483–509. [[CrossRef](#)]
46. Liu, H.; Chen, L.; Ji, L. Ozonation of ammonia at low temperature in the absence and presence of MgO. *J. Hazard. Mater.* **2019**, *376*, 125–132. [[CrossRef](#)] [[PubMed](#)]
47. Ryskie, S.; Gonzalez-Merchan, C.; Neculita, C.M.; Genty, T. Efficiency of ozone microbubbles for ammonia removal from mine effluents. *Miner. Eng.* **2020**, *145*, 106071. [[CrossRef](#)]
48. Hoigné, J.; Bader, H. Ozonation of Water: Role of Hydroxyl Radicals as Oxidizing Intermediates. *Science* **1975**, *190*, 782–784. [[CrossRef](#)]
49. Lin, S.H.; Yen, Y.L. Ozonation kinetics of ammonia and nitrite removal from aqueous solution. *J. Environ. Sci. Health* **1996**, *31*, 797–809. [[CrossRef](#)]
50. Lim, S.; Shi, J.L.; von Gunten, U.; McCurry, D.L. Ozonation of Organic Compounds in Water and Wastewater: A Critical Review. *Water Res.* **2022**, *213*, 118053. [[CrossRef](#)]
51. Thomas, B.; Ohde, D.; Matthes, S.; Engelmann, C.; Bubenheim, P.; Terasaka, K.; Schluter, M.; Liese, A. Comparative investigation of fine bubble and macrobubble aeration on gas utility and biotransformation productivity. *Biotechnol. Bioeng.* **2021**, *118*, 130–141. [[CrossRef](#)]