Ozone Nanobubbles for Controlled Harmful Algal Blooms Mitigation in the Environment

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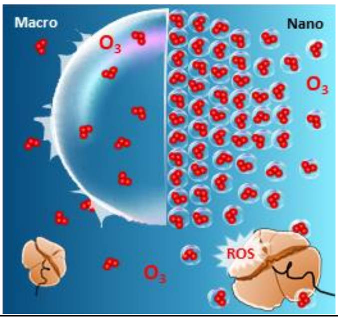

This study explores the integration of nanobubble (NB) technology as a novel strategy for controlling harmful algal blooms (HABs) in freshwater and saline environments. NBs, ultrafine gas domains with enhanced gas-liquid contact properties, enable rapid and precise delivery of ozone (O_3) for algal suppression. Our experiments demonstrate that NBs achieve desired O_3 concentrations more than 7 times faster than conventional bubbling. Moreover, NBs facilitate rapid oxygen release, crucial for maintaining healthy oxygen levels in the water and enabling aquatic life. These findings highlight the potential of NB technology to enhance water treatment efficiency, mitigate environmental impact, and safeguard aquatic ecosystems from HABs.

Introduction

Climate change and water eutrophication have raised a major environmental concern: harmful algal blooms (HABs). These blooms are massive phytoplankton growths mainly dominated by cyanobacteria (blue-green algae) in inland freshwaters and red tides algae in coastal marine waters [1]. They cause widespread death of aquatic animals due to oxygen depletion and exposure to toxins, posing serious risks to human and animal health, with an annual economic impact of billions of dollars. Therefore, there is an urgent need for rapid mitigation strategies that can be deployed directly in affected water bodies to reduce risk in the short term.

Among the various strategies proposed to control HABs, chemical approaches stand out for their effectiveness and speed. Green oxidants such as ozone (O_3) have been successfully used to treat algae-contaminated waters very effectively in water treatment plants. However, the use of ozonation in natural waters has been limited by the high inefficiency of gas delivery of conventional bubbling. In natural water, poor dosing control may cause undesirable effects on non-target species, as well as release high amounts of greenhouse gases into the atmosphere. This, coupled with the need for constant bubbling to treat vast quantities of water with rapidly changing dynamics, makes the application of these advanced oxidation processes (AOPs) in the environment unfeasible.

Recently, an innovative approach has emerged that promises to be a game changer for processes that rely on gas-liquid interfaces: Nanobubble (NBs) technology [2]. The NBs are ultrafine gas domains in liquids with 1,000 times more surface area than conventional bubbles. By reducing bubble size to the nanoscale (<300 nm), they become reliant on Brownian motion, enhancing gas-liquid contact and ensuring more even dispersion [3]. NBs exhibit remarkable resistance to buoyancy forces and coalescence, allowing them to remain suspended in solution without rising and releasing to the atmosphere. This conference paper aims to integrate NBs technology into AOPs to precisely control O_3 dosage and mitigate HABs in both freshwater and saline environments.

This work demonstrates the high efficacy of NBs in increasing dissolved oxygen (DO) and O_3 in water compared to conventional bubbling. Ozonated water was used to control two of the major harmful algal species of global concern: the cyanobacterium *Microcystis aeruginosa*, ubiquitous in freshwater; and *Karenia brevis*, a dinoflagellate that cause red tides and plagues the coasts of the Gulf of Mexico. The efficacy of O_3 in controlling these two species was compared with that of hydrogen peroxide (H_2O_2), an environmentally friendly oxidant with algae-killing capacity [4].

Material and Methods

M. aeruginosa UTEX LB 2385 and *K. brevis* CCMP718 were grown in artificial freshwater (BG11) and seawater (L1) media, respectively. Algae were grown under 12-hour day-night cycle (25-40 $\mu mol \cdot m^2 \cdot s^{-1}$). Ozone was generated from pure oxygen gas (>99% purity) using a ClearWater Tech CD12 generator (8 $g \cdot h^{-1}$) at 1 $L \cdot min^{-1}$ flow rate. It was injected into a 5 L pure water recirculation system via a venturi valve and a GAIA ultrafine bubble generator. Pure water was degassed with nitrogen gas before ozonation. Bubble size distribution was analyzed with a nanoparticle tracking analyzer (NTA, Malvern NanoSight). Experiments were performed by adding different doses of O_3 NBs (up to 1.5 $mg \cdot L^{-1}$), and H_2O_2 solution (30% w/w, Sigma-Aldrich) (up to 5 $mg \cdot L^{-1}$) to the algal culture to study cell viability. The results were compared with a control without NB and a treatment with water supersaturated with NB-oxygen (30 $mg \cdot L^{-1}$ DO). Experiments were conducted in triplicate. Algal cells were counted via fluorescence microscopy with *in vivo* chlorophyll-*a* autofluorescence visualization.

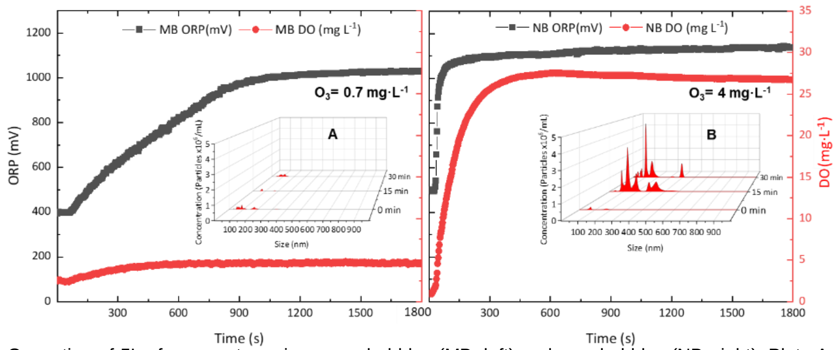

Figure 1. Ozonation of 5L of pure water using macrobubbles (MB, left) and nanobubbles (NB, right). Plots A and B inside show the distribution of nanoparticles (up to $5 \cdot 10^6$ particles$\cdot$mL^{-1}) after 15 min and 30 min of ozonation.

Results and Discussion

Results shown in Figure 1 illustrate the significant differences in the efficient transfer of O_3 and oxygen (using oxygen as gas inlet) when utilizing NBs compared to conventional macrobubbling under equivalent gas flow rate. Notably, conventional ozonation fails to achieve the maximum values of oxidoreduction potential (ORP) for water disinfection (>900 mV) until 15 minutes, whereas with NBs, the maximum ORP value is attained in less than 2 minutes (>7 time faster). At this time, NBs reached 4 mg$\cdot$L^{-1} of maximum O_3 concentration, while the macrobubbles did not exceed 0.6 mg$\cdot$L^{-1} of O_3 after 30 min. This rapid achievement of desired O_3 concentration underscores the advantage of using NBs in controlling appropriate dosages of O_3 in water treatment. Additionally, during O_3 generation, oxygen is concurrently released. The DO concentration reaches healthy water levels within seconds and is supersaturated at concentrations above 25 mg$\cdot$L^{-1} in 4 min with NBs, while conventional ozonation fails to exceed 5 mg$\cdot$L^{-1} even after 30 min. Translating these results to real water matrices, the rapid interaction of O_3 with dissolved organic matter may allow control of algae populations with minimal by-product generation and gas losses to the atmosphere. Simultaneously, the rapid co-release of oxygen would allow rapid saturation of DO, which would increase its availability to replenish aquatic life.

On the other hand, while much work has been done on ozonation in water treatment [5], not much is currently known about the specific mechanisms of nano-O_3 as a method for HAB control in nature. Only a few recent studies have proposed the use of air NBs, and more complex O_3 treatments in combination with coagulants for the control of HABs [6], [7]. Our findings confirm the effectiveness of AOPs in controlling both algae (Figure 2), with O_3 demonstrating particularly high efficiency against *K. brevis*. These results are in line with previous studies showing that higher doses of H_2O_2 (> 5 mg-L-1) are necessary to control *K. brevis* in seawater [8], with O_3 being a more suitable oxidant to control this species [9]. Interestingly, although H_2O_2 has been widely proposed to control *M. aeruginosa*-dominated HABs, at low doses (1 mg$\cdot$L^{-1}) only O_3 NBs achieved more than 25% cell removal in 24 hours. Oxygen did not decrease the number of cells in the algae tested.

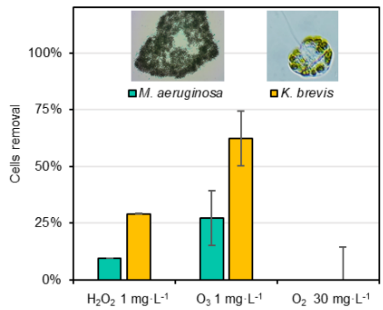

Figure 2. Effect of different AOPs on harmful algae control after 24h. The initial cell number of *M. aeruginosa* was ~10^6 cells$\cdot$mL^{-1}, and for *K. brevis,* it was ~10^4 cells$\cdot$mL^{-1}; *i.e.,* the typical cell number found in the environment.

Conclusions

Our study shows that NBs are highly effective in increasing DO and O_3 levels compared to conventional bubbling. This rapid oxygen release maintains crucial DO levels for aquatic life. NB-assisted O_3 treatment at low doses is effective against tested HAB species, underscoring its potential in environmental water treatment.

Acknowledgments

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References

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