

Gas nanobubble technology in wastewater treatment and anaerobic digestion

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Abstract

Nanobubbles (NBs) are gas-filled cavities with diameters around 100 nm, exhibiting unique properties such as high surface area-to-volume ratios, negative zeta potential (ζ -potential), and prolonged stability in liquids. These attributes make NBs highly effective in enhancing gas transfer, microbial activity, and pollutant removal. This study aims to assess the impact of NBs on wastewater treatment and anaerobic digestion processes. In a wastewater treatment plant, NBs aeration increased dissolved oxygen levels by 35 % and improved organic matter breakdown. It was also found that nano-aeration could potentially reduce energy consumption compared to conventional aeration systems. The study also examines the effect of introducing oxygen NBs into the fermentation liquid on the concentration of hydrogen sulfide (H_2S) in biogas production. The results demonstrated that in a methane digestion plant, oxygen NBs reduced H_2S concentrations by over 90 %, while causing a slight increase in methane production. Despite these benefits, challenges such as limited sludge flotation and the need for enhanced oxygen delivery systems were identified. This research underscores the potential of NBs to enhance biogas production and wastewater treatment efficiency while highlighting operational challenges that warrant further exploration.

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Introduction

Water deficiency and environment pollution are pressing global issues, intensified by rapid industrialization and urbanization, which have overwhelmed conventional water treatment processes. In response, NBs have emerged as a promising technology for enhancing water treatment. Defined as gas-filled cavities with diameters around 100 nm, NBs possess unique characteristics such as high surface area-to-volume ratios, negative zeta potential, and long stability in liquids, making them highly effective in

applications like wastewater treatment and methane production (Alheshibri *et al.* 2016). Unlike conventional macro- and microbubbles, which quickly collapse, NBs persist in water, facilitating more efficient processes such as flotation, aeration, and chemical-free oxidation (Takahashi *et al.* 2021).

Due to the unique physical properties of NBs, such as enhanced gas solubility and high electrostatic interactions, which improve the removal of organic pollutants, heavy metals, and other contaminants,

nano-aeration techniques could represent a modern approach in wastewater treatment. Bulk NBs, in particular, have shown significant promise in treating various types of wastewaters, including oily, coke, and heavy metal-containing wastewater, without generating secondary pollution. Additionally, when combined with aerobic biological methods, NBs can enhance organic matter biodegradation, making them a powerful tool for improving the efficiency and sustainability of water treatment processes (Bui and Han 2020; Wu *et al.* 2021).

Although anaerobic digestion requires anaerobic conditions, recent research shows that micro-aeration and NBs can enhance methane production in anaerobic digestion. The improvement in biogas quality primarily results from enhanced solid-liquid interaction, accelerated hydrolysis and volatile fatty acid generation, as well as increased microbial activity, which leads to higher methane production, particularly important for high-lignocellulose feedstocks (Nguyen *et al.* 2019; Wang *et al.* 2020). Introducing oxygen or air NBs under controlled conditions also affects the levels of H₂S, sulfides, or elemental sulfur present in the fermented substrate. As a result of biochemical and chemical processes, the use of NB technology contributes to improving biogas quality by reducing or completely eliminating H₂S from the biogas through its oxidation to elemental sulfur or sulfates (Díaz *et al.* 2010).

However, there are notable challenges associated with NB technology. One key issue is the lack of understanding regarding how NBs behave in complex water matrices, which can affect their efficiency. Additionally, inconsistencies in the literature regarding the precise mechanisms of NBs, especially concerning their stability and effectiveness, pose challenges to their widespread adoption (Pal *et al.* 2022). Economic viability and large-scale environmental impacts also remain underexplored, raising concerns about their practical application beyond the laboratory setting (Haris *et al.* 2020).

This paper describes the unusual properties of gas NB's in water, selected methods for their production, and initial observations and conclusions drawn from the author's own research utilizing the mentioned technologies. The obtained

results and observations address both the advantages and challenges of applying NBs technology in wastewater treatment and anaerobic digestion, providing insights into future developments and potential solutions.

Key properties of nanobubbles

Nanobubbles exhibit unique physiochemical making them particularly interesting for a wide range of applications. Bulk nanobubbles, are dispersed throughout solutions and are less likely to adhere to surfaces. They are characterized by their high internal pressure, which is inversely proportional to their diameter. This results in a high internal pressure that prevents the gas inside the NBs from reaching equilibrium with its surroundings, leading to their persistence despite expectations of rapid dissolution (Duval *et al.* 2012). It was calculated that internal pressure for NBs with diameter of 10 nm is up to 144 atm (Akshith *et al.* 2024).

One of the most remarkable characteristics of NBs is their extraordinary stability in liquids, which is inconsistent with classical thermodynamic principles. Micro- or coarse bubbles collapse within seconds or minutes due to high internal pressure and gas dissolution into the liquid. However, NBs, due to their nanoscale size, remain stable in solution for extended periods ranging from days to months (Akshith *et al.* 2024). Nirmalkar *et al.* (2018) observed that NBs retained their size for over 170 days, with no significant change in diameter. This stability is partly due to the high zeta potential of NBs, which contributes to their ability to remain dispersed without merging (Ahmed *et al.* 2018a). Nanobubbles also serve as effective nucleation sites for crystal growth and can be loaded with surfactants to modify their interfaces (Ahmed *et al.* 2018b; Michalopoulou *et al.* 2020). Despite their small size, NBs exhibit high surface energy, which can lead to significant changes in response to fluctuations in concentration or temperature (Guo and Zhang 2019).

Due to small size and large surface area-to-volume ratio NBs are enabled to dissolve gases more effectively into liquid media. For instance, Xiao and Xu (2020) found that oxygen nanobubbles had 1.5 times the mass transfer efficiency of larger

bubbles. This property makes NBs highly beneficial for applications like water treatment, where efficient aeration is crucial.

It's worth mentioning that NBs possess the ability to generate hydroxyl radicals ($\bullet\text{OH}$), superoxide anion radicals ($\bullet\text{O}^{2-}$), and singlet oxygen ($^1\text{O}_2$). Mentioned reactive oxygen species are highly reactive and can degrade pollutants or natural complex polymers (e.g. lignin), which makes NBs useful for advanced oxidation processes. However, the exact mechanisms behind radical generation remain under investigation (Sakr *et al.* 2022).

Nanobubbles generation methods

The generation of NBs involves several methods, each influencing their properties and effectiveness for various applications. Common approaches for NB generation are based on hydrodynamic cavitation phenomenon, which induces rapid pressure changes in a liquid to form vapor-filled cavities. Hydrodynamic cavitation uses pressure drops and surface roughness to produce NBs, while acoustic cavitation relies on ultrasonic energy to create and collapse microscopic bubbles. The size and concentration of nanobubbles produced by these methods depend on factors such as the dissolved gas concentration and acoustic parameters (Nirmalkar *et al.* 2018; Lee *et al.* 2020). Venturi-type generators and ejector-type generators are specific implementations of cavitation techniques. Venturi-type generators accelerate a two-phase flow through a venturi tube, causing macrobubbles to shrink into microbubbles due to rapid pressure changes. This method is noted for its low energy consumption and compact design, yielding a high density of microbubbles (Yoshida *et al.* 2008). Ejector-type generators use stepwise shrinking and enlarging liquid flow channels to induce cavitation, leading to microbubble formation through self-suction of gas.

Other cavitation-based methods include gas–water circulation, where gas introduced into a vortex is converted into microbubbles by disrupting the vortex, and pressurization followed by decompression, which generates microbubbles from a supersaturated solution as gas escapes (Khuntia *et al.* 2012; Takahashi 2009).

Membrane or porous sintered material-based methods involve injecting gas through porous

materials to create NBs. By forcing gas through membranes with specific pore sizes, such as ceramic membranes with pores between 50 and 150 nm, a range of bubble sizes can be produced (Bari and Robinson 2013; Kukizaki and Goto 2006).

Electrolysis is another technique used to generate NBs through electrochemical reactions at electrodes. For example, alternating polarity electrolysis of water, using a Na_2SO_4 solution and specific electrode configurations, has been effective in producing bulk NBs with controlled sizes. Voltage pulses create NBs with initial sizes of 60 to 80 nm, which may increase to around 250 nm after the electrical pulses are stopped (Postnikov *et al.* 2018).

In conclusion, NBs hold considerable promise for advancing water treatment and anaerobic digestion due to their unique properties. In this context, mechanical cavitation methods and membrane-based techniques offer the most promising advantages due to their effectiveness and scalability. Therefore, these methods have been chosen for introduction to full-scale research.

Experimental

Anaerobic digestion plant research

To address the high and fluctuating levels of H_2S caused by substrate variability, a micro-/nano-oxygenation method was applied in the biogas plant. The aim of this study was to evaluate the impact of introducing oxygen NBs into the fermentation liquid on the concentration of H_2S and the quality of the produced biogas.

The research was conducted at an agricultural biogas plant with a capacity of 0.99 MW, located in southeastern Poland. The biogas plant primarily processes natural waste, including agricultural residues, garden waste, waste produced by the food sector, and animal manure.

An injector with a specially designed ceramic sintered membrane was directly introduced into the fermentation mass mixing system. The membrane had a pore size of 200–500 nm. Oxygen was supplied to the membrane at a rate of 2–4 m^3/h . Biogas composition, including H_2S content, was monitored for one year.

Wastewater treatment plant research

The research was conducted at a small municipal wastewater treatment plant located in northern Poland. Due to significant seasonal fluctuations in wastewater volume and a decline in treatment efficiency, an NB oxygenation system was introduced. The aim of the study was to determine the impact of NB oxygenation on key wastewater parameters. The plant, equipped with a porous bed on which a bacterial film develops, is designed to treat domestic wastewater generated by a nearby tourist resort. Initially, the plant was equipped to handle a wastewater load expressed in terms of equivalent population (EP) not exceeding 75, with a maximum wastewater flow (Q_{max}) designed at 1.5 m³/h. Due to the continuous expansion of the resort and the increasing volume of wastewater, a significant deterioration in treated wastewater parameters was recorded, especially during the summer months. For this reason, the 2m³ Micro-Nano Bubble Generator (Qingdao Aozengnier Purification Equipment Co., Ltd) was implemented into the existing treatment plant infrastructure. The device could produce oxygen NBs smaller than 100 nm. The schematic of the NBs aeration system is shown in [Figure 1](#).

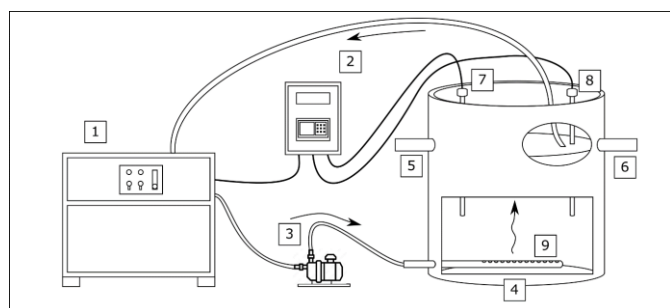


Figure 1. Nanoaeration system implemented in wastewater treatment plant: (1) – nanobubble generator, (2) – monitoring and control device, (3) – recirculation pump, (4) – bioreactor, (5) – wastewater inlet, (6) – wastewater outlet, (7) - pH, Red-Ox potential and dissolved oxygen probe, (8) – Red-Ox potential probe, (9) – aeration pipes.

In presented studies, the performance of the original aeration system was compared with the new nano-aeration system. Monitoring was conducted for parameters such as pH, Dissolved Oxygen (DO), and RedOx potential at the wastewater inlet to the reactor and the RedOx potential of the effluent leaving the aeration

chamber. Each aeration system was monitored for two days using the CX-804 controller (Elmetron, Poland) during the tourist peak season.

Results and discussion

Influence of nanoaeration on anaerobic digestion

While methane (CH₄) can serve as a valuable fuel, its production with use anaerobic digestion process is often accompanied by H₂S formation. Hydrogen sulfide not only inhibits CH₄ production but also requires removal to make the biogas suitable for applications like electricity generation or as a natural gas alternative. Traditional post-treatment methods for H₂S removal, such as biotrickling filtration and chemical scrubbing, are effective but costly and generate waste. Emerging strategies like substrate pretreatment and in-situ process regulation (e.g., microaeration) are more cost-effective, reducing H₂S formation and enhancing CH₄ production during anaerobic digestion ([Diaz et al. 2010](#)). In addition to the positive impact of NBs on H₂S concentration in biogas, they play a significant role in enhancing anaerobic digestion by facilitating nutrient delivery to biofilms and increasing microbial and enzyme activity ([Wang et al. 2020](#)).

In the present study, it was found that after one year of introducing oxygen in the form of micro-/nano-bubbles, the H₂S concentration in biogas was significantly reduced. The H₂S concentration measurement data is presented in [Figure 2](#). Regardless of seasonal substrate variations, H₂S levels dropped from peaks of 700–900 ppmv to values below 100 ppmv. This reduction significantly improved biogas quality, which can extend the lifespan of gas engines used for electricity generation in biogas plants ([Stanuch et al. 2020](#)).

It is worth noting that during the introduction of nano-oxygenation, an increase in methane content in the biogas by approximately 3 % (annual average) was recorded. It was also observed that the fermentation mass dewatered more effectively after the process. These aspects result from the generation of radicals, which improve the oxidative decomposition of substrates by microorganisms ([Yang et al. 2020](#)).

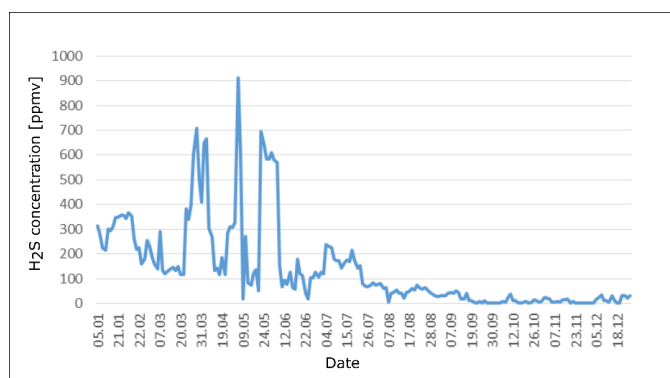


Figure 2. Changes in H₂S content in biogas after introducing nano-aeration into the fermentation chamber.

While nanobubbles offer promising benefits for anaerobic digestion, they come with certain challenges. One major challenge is the cost and complexity of nanobubble generation systems, which require specialized equipment and monitoring systems that can be expensive, potentially offsetting some of the cost savings from improved biogas yields. Moreover, excessive oxygen from nanobubbles could disrupt anaerobic conditions if not carefully controlled, potentially inhibiting methane production.

Wastewater treatment

Aeration is crucial for delivering oxygen in wastewater treatment processes, though it accounts for 70–80 % of the total energy consumption (Sun *et al.* 2016). The efficiency of aeration depends heavily on dissolved oxygen (DO) levels, which influence biological activity. Traditional aeration methods include shearing the liquid surface with mixers or turbines and releasing air through various materials (Puig *et al.* 2006). Nanobubbles present a promising alternative due to their superior mass transfer efficiency and stability compared to conventional coarse bubbles. They can improve aeration efficiency and reduce energy costs in aerobic biological systems, such as biofilm and activated sludge reactors. Research by Xiao and Xu (2020) demonstrated that air NBs have approximately 1.5 times higher oxygen diffusion coefficients than coarse bubbles, enhancing microbial community dynamics and enzyme activity (Xiao and Xu 2020). In comparison to conventional fine bubble aeration, NBs result in higher oxygen concentrations, lower sludge production, and improved organic matter

decomposition (Ahmadi *et al.* 2018). Fine bubbles, combined with deep subsurface infiltration systems, improve nitrogen and phosphorus removal, while NBs show superior performance in removing suspended solids and nitrogen compared to bottom aeration (Wang and Zhang 2017; Zhou *et al.* 2014).

In the current study, a traditional aeration system generating coarse bubbles in the aeration chamber was compared with a NB oxygenation system. Figure 3 illustrates changes in RedOx potential at the inflow and outflow of the aeration chamber over time when using the original blower installed at the treatment plant. Figure 4 presents changes in DO and pH values during a 4-day experiment. The red line in Figures 3 and 4 indicates the point at which conventional aeration was switched to nanobubble aeration.

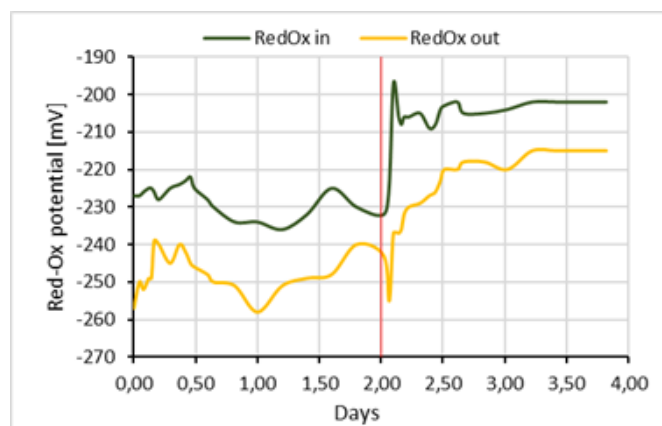


Figure 3. Changes in RedOx potential during a 4-day experiment. The moment of switching aeration systems is marked with a red line.

It was observed that the reactor was heavily loaded with organic matter, as indicated by the low RedOx potential at the outflow and low DO levels. After introducing the nanobubble aeration system, both RedOx potential and DO levels increased almost immediately. Notably, the NB system increased DO by an average of 35 %.

It is worth noting that the original blower consumed about 60 m³/h of air, while the NB generator required only 0.3 m³/h, with comparable energy consumption. This confirms that mass transfer efficiency with NBs is significantly higher. However, to meet the oxygen demand for an effective treatment process at the treatment plant under study, a more powerful NB generator would be necessary.

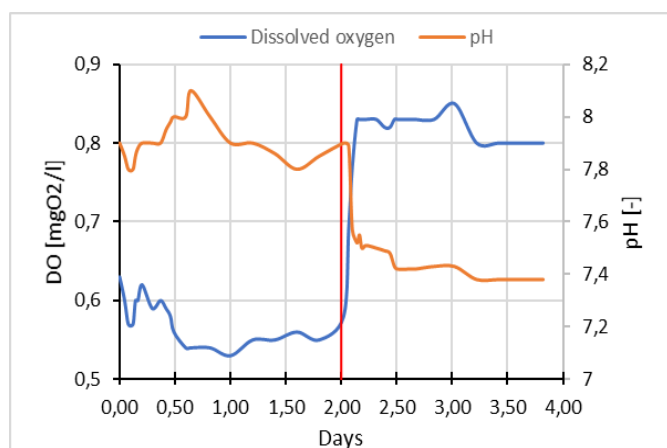


Figure 4. Changes in RedOx potential, pH, and DO during a 4-day experiment. The moment of switching aeration systems is marked with a red line.

In comparison, literature studies have shown that air micro-nano bubbles are effective in treating wastewater from various sources, for example, in sugar industry wastewater, air NBs reduced chemical OD by 85 %, total suspended solids by 79 %, and removed 66.21 % of total coliforms (Leyva and Flores 2018; Reyes and Flores 2017). Xiao *et al.* (2021) found that NBs increased the size and thickness of activated sludge and biofilm by 23.35 % and 86.67 %, respectively, improving total nitrogen removal by 10.58 % (Xiao *et al.* 2021).

Despite the mentioned benefits, the introduction of a nanoaeration system has certain drawbacks. Irreversible sludge flotation and a cloudier effluent, resulting from the proliferation of filamentous bacteria, were observed, as noted by Yaparathne *et al.* (2022). Additionally, NBs alone cannot provide the necessary shear stress to control biofilm thickness, which is crucial for the proper functioning of an aeration chamber with an immersed porous bed. This suggests that combining NB aeration with mechanical bubbling or optimizing reflux ratios is essential for achieving optimal performance.

Conclusions

Nanobubble technology presents significant advantages in both anaerobic digestion and wastewater treatment, primarily through enhanced gas transfer, improved microbial activity, and greater pollutant removal efficiency. The introduction of micro-/nanobubbles in anaerobic

digestion effectively reduced H_2S levels and can increase CH_4 production, offering a promising alternative to traditional H_2S removal methods. In wastewater treatment, NBs aeration demonstrated superior oxygen transfer efficiency, reducing energy consumption while improving water quality parameters. However, challenges such as maintaining the anaerobic environment in methane digesters and managing biofilm growth in wastewater treatment systems were observed. Addressing these challenges requires optimizing NB generator designs and aeration methods to fully realize the benefits of this technology in large-scale applications. Further research is needed to explore the long-term economic viability and scalability of NB's for widespread industrial use.

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Conflict of interest

Conflict of Interest: The authors declare that they have no conflict of interest

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