



*Citation for published version:*

Jia, M, Farid, MU, Kharraz, JA, Kumar, NM, Chopra, SS, Jang, A, Chew, J, Khanal, SK, Chen, G & An, A 2023, 'Nanobubbles in water and wastewater treatment systems: Small bubbles making big difference', *Water Research*, vol. 245, 120613. <https://doi.org/10.1016/j.watres.2023.120613>

*DOI:*

[10.1016/j.watres.2023.120613](https://doi.org/10.1016/j.watres.2023.120613)

*Publication date:*

2023

*Document Version*

Version created as part of publication process; publisher's layout; not normally made publicly available

[Link to publication](#)

## University of Bath

### Alternative formats

If you require this document in an alternative format, please contact:  
[openaccess@bath.ac.uk](mailto:openaccess@bath.ac.uk)

#### General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

#### Take down policy

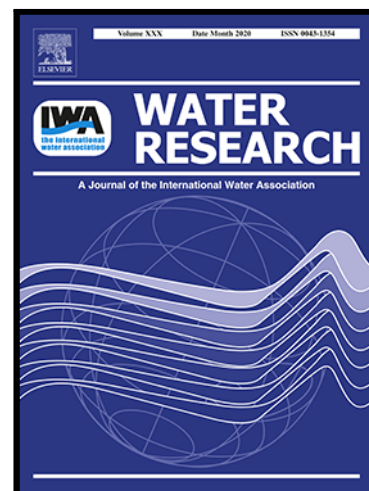
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

## Journal Pre-proof

Nanobubbles in water and wastewater treatment systems: small bubbles making a big difference

Mingyi Jia , Muhammad Usman Farid , Jehad A. Kharraz ,  
Nallapaneni Manoj Kumar , Shauhrat S. Chopra , Am Jang ,  
John Chew , Samir Kumar Khanal , Guanghao Chen ,  
Alicia Kyoungjin An

PII: S0043-1354(23)01053-9  
DOI: <https://doi.org/10.1016/j.watres.2023.120613>  
Reference: WR 120613



To appear in: *Water Research*

Received date: 19 April 2023  
Revised date: 22 July 2023  
Accepted date: 9 September 2023

Please cite this article as: Mingyi Jia , Muhammad Usman Farid , Jehad A. Kharraz , Nallapaneni Manoj Kumar , Shauhrat S. Chopra , Am Jang , John Chew , Samir Kumar Khanal , Guanghao Chen , Alicia Kyoungjin An , Nanobubbles in water and wastewater treatment systems: small bubbles making a big difference, *Water Research* (2023), doi: <https://doi.org/10.1016/j.watres.2023.120613>

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2023 Published by Elsevier Ltd.

## Highlights

- A comprehensive review on the application of NBs in water and wastewater treatment
- NBs' fundamental properties and their relevancy to water treatment
- Advancements in NB technology for water treatment processes beyond lab scale
- Existing controversies and inconsistencies in NBs literature
- Economic and environmental sustainability assessment of NB technology

Journal Pre-proof

## **Nanobubbles in water and wastewater treatment systems: small bubbles making a big difference**

Mingyi Jia <sup>a</sup>, Muhammad Usman Farid <sup>a,\*</sup>, Jehad A. Kharraz <sup>a</sup>, Nallapaneni Manoj Kumar <sup>a,b</sup>,  
Shauhrat S. Chopra <sup>a</sup>, Am Jang <sup>c</sup>, John Chew <sup>d</sup>, Samir Kumar Khanal <sup>e</sup>, Guanghao Chen <sup>f</sup>, and  
Alicia Kyoungjin An <sup>a,\*</sup>

<sup>a</sup> School of Energy and Environment, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong SAR

<sup>b</sup> Center for Circular Supplies, HICCER – Hariterde International Council of Circular Economy Research, Palakkad 678631, Kerala, India

<sup>c</sup> Department of Global Smart City, Sungkyunkwan University (SKKU), 2066, Seobu-ro, Jangan-gu, Suwon, Gyeonggi-do, 16419, Republic of Korea

<sup>d</sup> Department of Chemical Engineering, University of Bath, Bath BA2 7AY, UK

<sup>e</sup> Department of Molecular Biosciences and Bioengineering, University of Hawai'i at Manoa, 1955 East-West Road, Honolulu, Hawai'i 96822, United States

<sup>f</sup> Department of Civil and Environmental Engineering, Chinese National Engineering Research Center for Control & Treatment of Heavy Metal Pollution and Water Technology Center, The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, China

\* **Corresponding authors:** Dr. Alicia Kyoungjin An

Tel: +(852)-3442-9626, Fax: +(852)-3442-0688, E-mail: alicia.kjan@cityu.edu.hk (A.K. An)

*Dr. Muhammad Usman Farid; E-mail: mufarid@cityu.edu.hk*

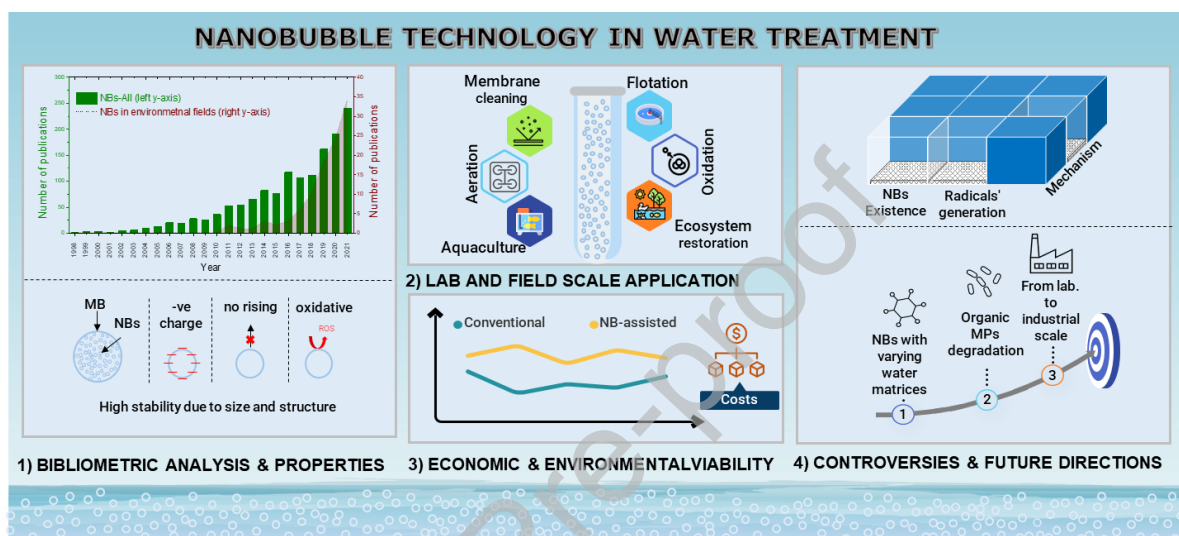
## **Abstract**

Since the discovery of nanobubbles (NBs) in 1994, NBs have been attracting growing attention for their fascinating properties and have been studied for application in various environmental fields, including water and wastewater treatment. However, despite the intensive research efforts on NBs' fundamental properties, especially in the past five years, controversies and disagreements in the published literature have hindered their practical implementation. So far, reviews of NB research have mainly focus on NBs' role in specific treatment processes or general applications, highlighting proof-of-concept and success stories primarily at the laboratory scale. As such, there lacks a rigorous review that authenticates NBs' potential beyond the bench scale. This review aims to provide a comprehensive and up-to-date analysis of the recent progress in NB research in the field of water and wastewater treatment at different scales, along with identifying and discussing the challenges and prospects of the technology. Herein, we systematically analyze 1) the fundamental properties of NBs and their relevancy to water treatment processes, 2) recent advances in NB applications for various treatment processes beyond the lab scale, including over 20 pilot and full-scale case studies, 3) a preliminary economic consideration of NB-integrated treatment processes (the case of NB-floatation), and 4) existing controversies in NBs research and the outlook for future research. This review is organized with the aim to provide readers with a step-by-step understanding of the subject matter while highlighting key insights as well as knowledge gaps requiring research to advance the use of NBs in the wastewater treatment industry.

## Keywords

Nanobubbles; Nanobubble technology; Water and wastewater treatment; Nanobubble floatation; Nanobubble aeration

## Graphical Abstract



## 1. Introduction

The threats to global water security have been increasing over the past decades. Global population growth and rapid industrialization have brought significant increases in municipal and industrial water consumption, along with emerging contaminants whose ubiquitous presence has adversely impacted the water environment and increased the complexity of urban and rural water systems. Conventional treatment processes have shown limitations in meeting the discharge needs in the face of these growing challenges, calling for the development of more effective treatment procedures. In this context, nanobubbles (NBs), with its many unique characteristics, have been receiving growing interest in various fields of application, as they offer great

opportunities to improve existing water and wastewater treatment processes in various dimensions.

NBs, also known as ultrafine bubbles, are defined by the International Standard Organization (ISO) as gas-filled cavities with a volume equivalent diameter of less than  $1\mu\text{m}$  (ISO, 2017). Macrobubbles (MaBs) and microbubbles (MBs), which are larger than NBs as their names suggest, have been widely applied in water treatment processes, including flotation (Chen et al., 2016), aeration (Thomas et al., 2021) and membrane cleaning (Qaisrani and Samhaber, 2011). However, these coarser bubbles disappear quickly in water, either rising up and collapsing at the surface or shrinking and dissolving in water, which limit their overall efficiency (Demangeat, 2015). NBs, on the other hand, are highly stable and can exist in water from a few hours to up to several months (Ghaani et al., 2020). Besides their high stability, NBs possess other distinctive properties, such as a high surface area-to-volume ratio, high negative zeta potential, low buoyancy, and the ability to generate radicals, which allow them to contribute to physical, chemical and biological water treatment processes in many ways (Takahashi et al., 2021). NB technology is regarded as a type of green nanotechnology for its potential to partially replace or enhance conventional technologies that require the extensive use of energy or chemicals and allow the transition towards cost-effective and chemical-free processes (Pal et al., 2022).

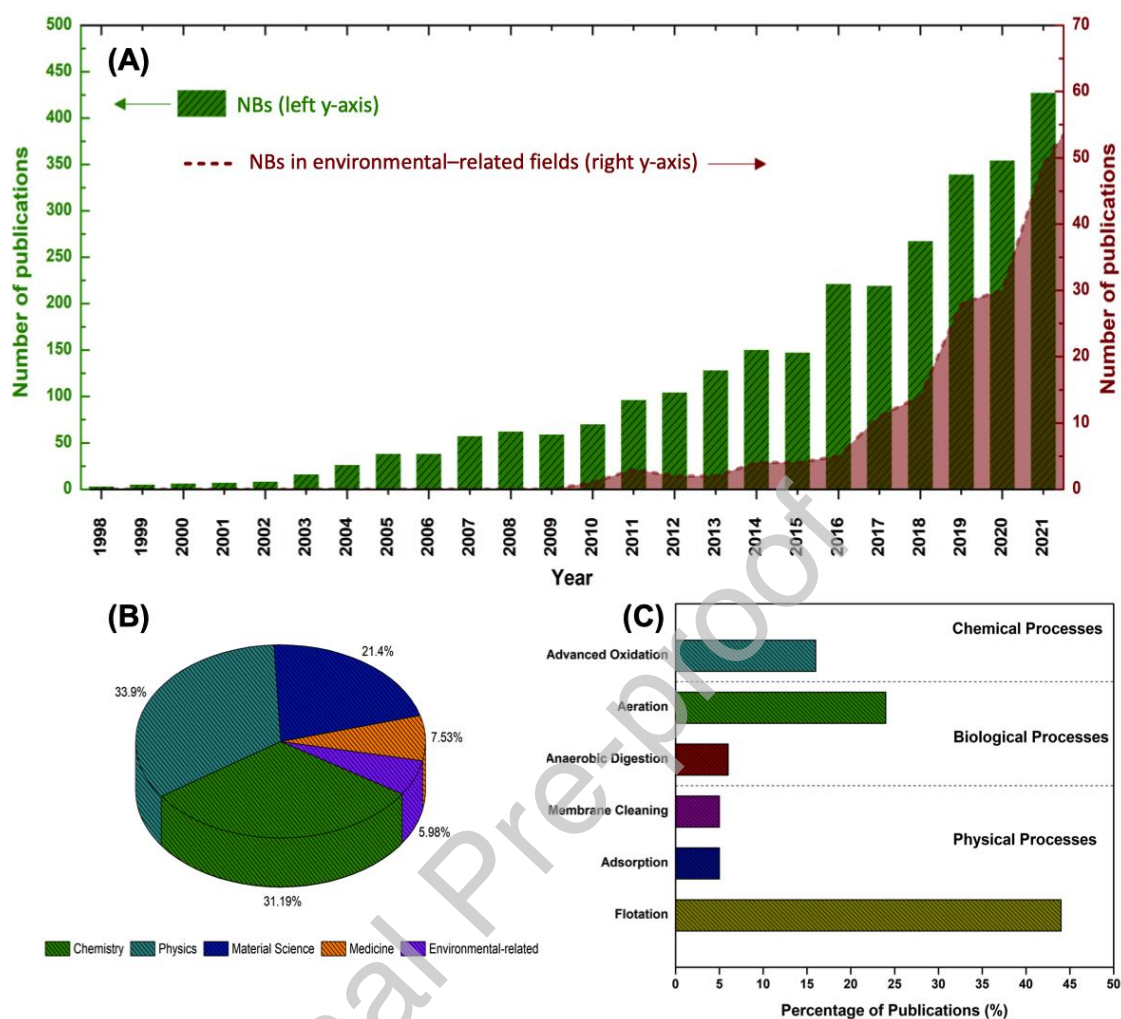
A comprehensive bibliometric analysis shows that NB research experience a rapid upsurge in recent years (**Figure 1**). Although studies exploring the physical and chemical properties of NBs still take up the largest portion of the 170 publications identified, an increasing number of works have been published on the application of NBs in environmental fields (**Figure 1(A, B)**). In particular, quite a few papers have covered the use of NBs in various water treatment processes

for water and wastewater purification (**Figure 1(C)**), which is the focus of this study. The detailed bibliometric analysis can be found in the **Supplementary Information (SI.1)**.

While the development of NB technology is still in the exploration stage, several review articles have shed light on the fundamental properties of NBs and their role in water treatment processes. Most of these articles have focused on the role of NBs in specific treatment processes, such as flotation (Kyzas et al., 2021), anaerobic digestion (Chuenchart et al., 2021), and groundwater remediation (Haris et al., 2020), or covered the applications of NBs in general water treatment processes (Atkinson et al., 2019). Limited efforts have been made on reviewing the progress made so far in understanding how NBs' properties change with varying water matrices or have outlined the underlying mechanisms of NBs in the process of treating water and wastewater. There also remain controversies and inconsistencies in the published literature on the existence, properties, and effectiveness of NBs.

Moreover, the existing literature also lacks two essential considerations regarding the use of NB technology in the water treatment industry, namely, the economic and environmental assessment of using NBs in conventional treatment systems and the potential for real-world applications of NB technology outside the laboratory. Hence, this review aims to provide a more comprehensive and realistic picture of the application of NBs at different scales. Herein, we identify and discuss the challenges and prospects of NB technology while shedding light on the recent advances of NB technology in different water treatment processes beyond the bench scale, including over twenty pilot and full-scale case studies. Furthermore, we provide a preliminary economic and environmental analysis of NB technology in wastewater treatment systems (the case of NB-floatation vs. conventional dissolved air floatation) to deliver insights into the sustainability of this technology for practical large-scale applications.





**Figure 1.** Bibliometric analysis of NB research. (A) Total number of publications on NBs and the number of publications on NBs in the field of environmental research from 1998 to 2021. (B) Distribution of NB-related publications in various fields of research. (C) Distribution of NB-related publications in the field of water and wastewater treatment.

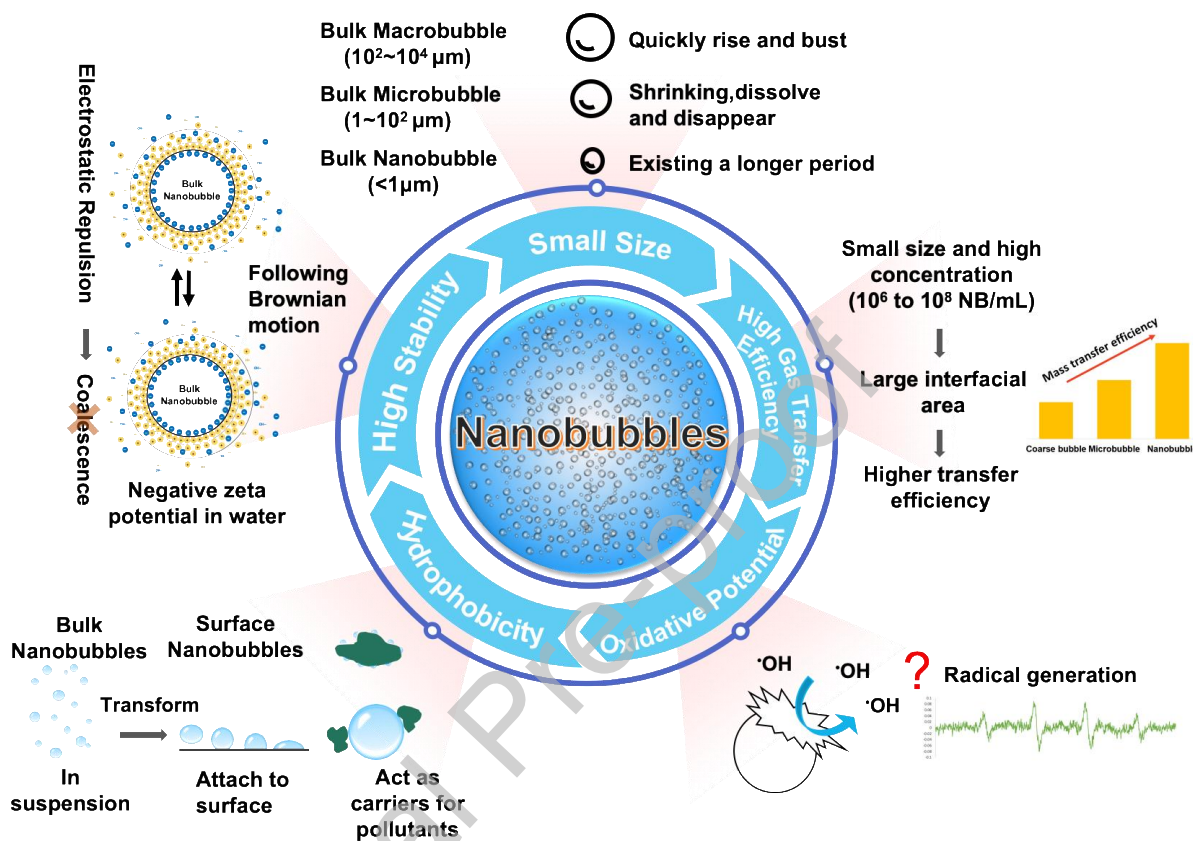
## 2. Fundamental characteristics of nanobubbles

### 2.1. Distinctive physiochemical properties

Gas bubbles are widely found in nature and in various industrial application processes. Compared with MaBs and MBs, which have already been extensively applied, NBs' unique properties have relatively recently come to researchers' attention (**Figure 2**). NBs can be further categorized into surface NBs and bulk NBs (BNBs), which mainly differ in terms of their mobility. Surface NBs are generated directly on a surface in the form of a spherical cap. Compared with BNBs, surface NBs have been investigated for a more extended period, especially in relation to froth flotation for mineral processing. However, their inherent immobility has limited their broader application. BNBs, on the other hand, are generated as freely suspended spherical bubbles, but they can also transform into surface NBs when they come into contact with a surface (Yasui et al., 2021). As the properties of surface NBs are well studied, BNBs will be the main focus of this review.

Unlike surface NBs, BNBs follow a Brownian motion in solutions, which make it difficult to experimentally verify or model their behaviors, thereby preventing the clear elucidation of their underlying mechanisms. Nevertheless, many efforts have been made to investigate BNB's fundamental properties, which will be discussed in the following section. Although this review refers to nano-sized bubbles as "NBs" in general, they are also frequently referred to as micro-nanobubbles (MNBs) in existing literature since BNBs are generated together with MBs. Thus, in the remainder of this review, nano-sized bubbles generated within a bulk solution will sometimes be referred to as MNBs if they are originally mentioned as such in the referenced

studies. Other similar terms, such as pico-bubble and submicron-bubble, appear in literature, but they will not be used due to their lack consistent definitions.



**Figure 2.** Fundamental physicochemical properties of nanobubbles.

### 2.1.1 Key features for gas-liquid phase operations: miniature size and high efficiency for mass transfer

Although the physicochemical properties of bubbles have been extensively investigated, they are classified rather simply into MaBs, MBs, and NBs based on their sizes and their stability under water (**Figure 2**). The nano-scale sizes of NBs endow them with a large surface area-to-volume ratio and the Brownian motion in liquid with negligible buoyant force. Besides, NBs, which are

generated in massive quantities ( $10^6$  to  $10^8$  NB/mL), are also expected to spread over a larger region and reach confined spaces more easily.

An efficient gas-liquid mass transfer is crucial in gas-liquid phase operations, such as air flotation, aeration, and aerobic processes for treating water. Several studies have demonstrated that NBs can significantly increase the efficiency of gas partitioning into water and thereby enhance the efficiency of these treatment processes. Xiao and Xu (2020) and Fan et al. (2021a) found that  $O_2$  NBs and  $O_3$  NBs have respectively 1.5 times and 4.7 times higher mass transfer efficiency than coarse bubbles, and Chen et al. (2022) found that MNBs showed a 52.6% lower oxygen decline rate than coarse bubble aeration.

### **2.1.2 Role as a carrier: high negative zeta potential and hydrophobicity of NBs**

NBs' surface properties dominate their behavior in liquid solutions and are critical for their application. As the surfaces of NBs are electrically charged, ions distribute around their surface and form an electrical double layer around the bubble. Zeta potential measures the electrical potential (i.e., the charge repulsion and attraction) at the boundary of the diffuse layer and is a critical parameter for determining bubble stability and bubble-particle interactions. The zeta potential of BNBs varies under different conditions but is typically in the range of -50 mV to -20 mV (Zhou et al., 2020). Several studies have proposed that the negative charge of NBs arises due to their small radius and the high polarity of hydroxyl ions, which lead to the adsorption of dissociated hydroxyl ions on the bubble surface, while hydrogen ions are easily hydrated and prefer to stay in the bulk liquid. A higher absolute zeta potential indicates higher stability, as the repulsive force generated by NBs' surfaces prevents them from merging with one another (Ushikubo et al., 2010).

Surface hydrophobicity is another essential property of NBs as it allows NBs to interact with other particles through hydrophobic attraction. BNBs can adsorb on hydrophobic particles and increase their mobility in the liquid, while attached NBs can promote particle-particle or particle-bubble interactions through capillary bridging effects that produce an attractive force between two surfaces (Hampton and Nguyen, 2010).

### **2.1.3 Long residence time in water: NBs' long-term stability**

Among the various characteristics NBs possess, the most astonishing is their longevity. Upon generation, bubbles generally maintain their diameters for a certain amount of time, after which the bubbles begin to grow and eventually dissolve in the solution. Experimental results have confirmed that NBs are able to exist in water from days to months. Nirmalkar et al. (2018b) monitored the temporal variation of NBs' mean diameters with different initial NB concentrations and observed no significant changes in their diameters for over 170 days. Similarly, Wang et al. (2019b) also found that N<sub>2</sub> and O<sub>2</sub> NBs were stable for 48 h, although CO<sub>2</sub> NBs were stable less than 48 h, primarily due to the higher density and gas solubility of CO<sub>2</sub>.

While the stability of NBs has been increasingly confirmed with the advancement of characterization technologies, which is discussed later in Section 3, the establishment of theoretical models to explain and describe the stability of NBs, particularly BNBs, in liquid solutions requires further research. Several theories and models have been developed to explain the unusual longevity of BNBs, with the most popular being the electrostatic repulsion model (Satpute and Earthman, 2021), as well as contamination models, which include skin model (Yasui et al., 2018) and the armored bubble model (Alheshibri and Craig, 2019). Recently,

researchers have applied molecular dynamics (MD) simulations in BNB research to unravel the underlying mechanisms of their stability. Gao et al. (2021) underscored the complexity of BNBs' stabilization mechanism using MD by revealing NBs' supersaturation, surface charge, interfacial molecular structure, and high inner density as contributing factors.

#### 2.1.4 NBs' oxidative potential: radical producer and scavenger

NBs' generation of free radicals is considered one of their most attractive properties, but the extent to which they do so is yet debatable due to the difficulty of detecting radical species. Several studies have reported the detection of free radicals in NB solutions, with the most frequent type being hydroxyl radicals ( $\bullet\text{OH}$ ). Notably, while other types of NBs were found to produce reactive oxygen species (ROS) as reported in **Table 1**,  $\text{H}_2$  NBs acted as radical scavengers, given the strong antioxidant effect of hydrogen. Liu et al. (2018) reported that  $\text{H}_2$  water with NBs showed better removal efficiencies for four types of ROS ( $\bullet\text{OH}$ ,  $\text{ClO}^-$ ,  $\text{ONOO}^-$ , and  $\text{O}_2\bullet^-$ ) than  $\text{H}_2$  water without NBs, implying NBs' ability to relieve oxidative stress. Liu et al. (2021) predicted that hydrogen NBs can produce hydrogen radicals ( $\text{H}\bullet$ ), but they failed to observe  $\text{H}\bullet$  using electron paramagnetic resonance (EPR), possibly due to slow  $\text{H}\bullet$  generation and the low concentration of  $\text{H}\bullet$  below the detection limit. Instead, they indirectly proved the existence of  $\text{H}\bullet$  by converting  $\text{H}\bullet$  to  $\bullet\text{OH}$  by adding  $\text{H}_2\text{O}_2$  and successfully observing  $\bullet\text{OH}$ . Despite ongoing research, it is still unknown how NBs generate free radicals (e.g., whether NBs self-collapse without dynamic stimuli to generate radicals). The existing debate and knowledge gaps regarding the generation of radicals by NBs will be further discussed in the outlook section.

*Table 1. Radicals detection methods in NB research.*

NB type	Detection method and conditions	Detection results	Reference
Air NBs & O <sub>2</sub> NBs	Electron paramagnetic resonance (EPR) with DMPO as the radical trapping agent	•OH and methyl radical (due to presence of organic contaminants) detected	(Michailidi et al., 2020)
O <sub>3</sub> NBs		•OH peak observed only when HCl was added as stimuli	(Takahashi et al., 2021)
Air & O <sub>2</sub> NBs	Terephthalic acid as probe compound (at 425 nm photoluminescence peak) using a fluorescence spectrophotometer; Ultrasonication applied as stimuli	Considerable amount of •OH observed when stimuli was applied	(Ahmed et al., 2018a)
CO <sub>2</sub> & N <sub>2</sub> NBs		Limited amount of •OH observed when stimuli was applied	
O <sub>3</sub> NBs	Formaldehyde capturing method using UV-vis	•OH: in rang of 0-32 ugL-1 H <sub>2</sub> O <sub>2</sub> : 0.37-0.66 ugL-1	(Fan et al., 2021a)
O <sub>2</sub> NBs	APF fluorescent probe (excitation 490 nm, emission 515 nm) using a fluorescence spectrophotometer	•OH detected in the submicromolar level	(Liu et al., 2016)
H <sub>2</sub> NBs	EPR with BMPO	No •H detected	(Zhang et al., 2022)
	APF fluorescent probe (excitation 490 nm, emission 515 nm) using a fluorescence spectrophotometer	•OH detected	

## 2.2. Variation of NBs' properties with water chemistry

Since the majority of existing studies on NB applications have been conducted by adding NB-enriched pure water into various processes, most reported NB characterizations and quantifications are only representative for NBs generated in deionized water. However, as NBs' properties could vary depending on the water chemistry of different processes, it is crucial to understand how they change under different bulk solution conditions to better predict their performance for practical applications and control the stability, size, and number density of NBs.

**Table 2** summarizes the progress of current research on the effects of changes in pH, temperature, surfactants, ions, natural organic matters (NOM) and chlorine on NBs. In general, studies show that these parameters can affect the stability and sizes of NBs to a certain extent. Notably, while NBs are generated with negative zeta potentials, their zeta potential can become

positive when multivalent ions are present. In fact, several studies have purposefully reversed NBs' zeta potential to achieve their removal targets (Nam et al., 2022). Nevertheless, as there has been limited research, contradictories exist in the reported findings. For example, inconsistent results have been reported for the effect of temperature on the zeta potential of NBs, where higher temperature either increased or decreased the negativity of NBs. Hence, more research is required to gain a comprehensive understanding of the relationship between the water matrix and NBs' properties.

Journal Pre-proof



**Table 2.** Effects of bulk solution chemistry on BNBs' properties.

	Zeta potential (ZP)	Bubble size & number density	Mechanism
<b>pH</b>	ZP became more negative when NBs were generated at a higher pH (Zhang et al., 2020; Zhou et al., 2021).	Average NB size became smaller with higher pH (Zhang et al., 2020).	As the solution became more alkaline, the concentration of OH ions increased, increasing surface charge, and allowing NBs to become more stable.
<b>Temperature</b>	The negative magnitude of ZP increased and then became stable with increased solution temperature (Li et al., 2021a); <b>Contradictory results:</b> ZP was less negative with increases in temperature (O <sub>2</sub> NBs, from 15 to 30, pH =7).	NBs' sizes decreased with increased temperature (from 6 to 40°C) (Farid et al., 2021; Li et al., 2021a); NB concentration decreased (Farid et al., 2021; Yurchenko et al., 2016) or remained unchanged (Li et al., 2021a) with increased temperature.	Adsorbed state of ions became unstable with increased temperature, so NBs lost their stability and vanished. Lower water surface tension at a higher temperature.
<b>Surfactants</b>	Anionic	More negative ZP.	Increased the magnitude of ZP's negative value due to an anionic group's adsorption.
	Cationic (Nirmalkar et al., 2018a)	ZP became less negative or positive when concentration was higher.	ZP became more positive as the cationic group adsorbed on NBs.
	Non-ionic (Nirmalkar et al., 2018a)	No effects.	N/A
<b>Ions</b> (Nirmalkar et al., 2018a; Yurchenko et al., 2016)	Monovalent	Less negative.	As a result of either specific cation ion adsorption or under high pH conditions, the cation hydroxides adsorb on the gas-liquid interface of the bubble.
	Multivalent	Increased valency can neutralize or completely reverse ZP to positive.	
<b>Natural Organic Matter (NOM)</b>	When added with hydrophilic NOM, the negative magnitude of ZP increased slightly (Soyluoglu et al., 2021) or had negligible change (Ahmed et al., 2018b).	No change in NB diameter range (Soyluoglu et al., 2021).	NOM can interact with NBs and impart a negative charge to NBs, increasing their overall surface potentials (Soyluoglu et al., 2021).
<b>Chlorine</b>	No effects (Soyluoglu et al., 2021).	No effects (Soyluoglu et al., 2021).	N/A

### 3. NBs generation, visualization, and characterization technique

The rising interest in applying NBs to industrial applications has led several studies to explore different methods for improving the efficiency of generating NBs. Commonly employed methods are hydrodynamic cavitation, acoustic cavitation, electrolysis, and solvent exchange, as listed in **Table SI.2**. A detailed discussion on NB generation methods and mechanisms is provided in **Section SI.2**.

Subsequent to NB generation, growing reports on NBs and their mysterious stability have led to speculations on whether the reported nano-entities are gas bubbles or, instead, supramolecular structures, solid nanoparticles, or nanodroplets. Hence, validating and characterizing the generated nano-entities became a crucial part of NB research. The list of the different approaches used to detect and characterize NBs is given in **Table 3**, along with their mechanisms and limitations. Light scattering methods, being one of the most frequently used method in NB research, can provide information on the sizes and concentrations of NBs. While this genre of methods cannot differentiate bubbles from other colloidal particles, it is usually sufficient for environmental research using a commercialized NBs generator. Visualization methods allows the direct observation of NBs, but high-resolution images usually entail expensive equipment that is not widely available at laboratories. Physical perturbation methods and other indicators listed in the table are all indirect detection methods, which, by themselves, cannot provide sufficient information on NBs, thus often requiring the combined use of light-scattering or visualization methods.

**Table 3. Methods to characterize and differentiate nanobubbles.**

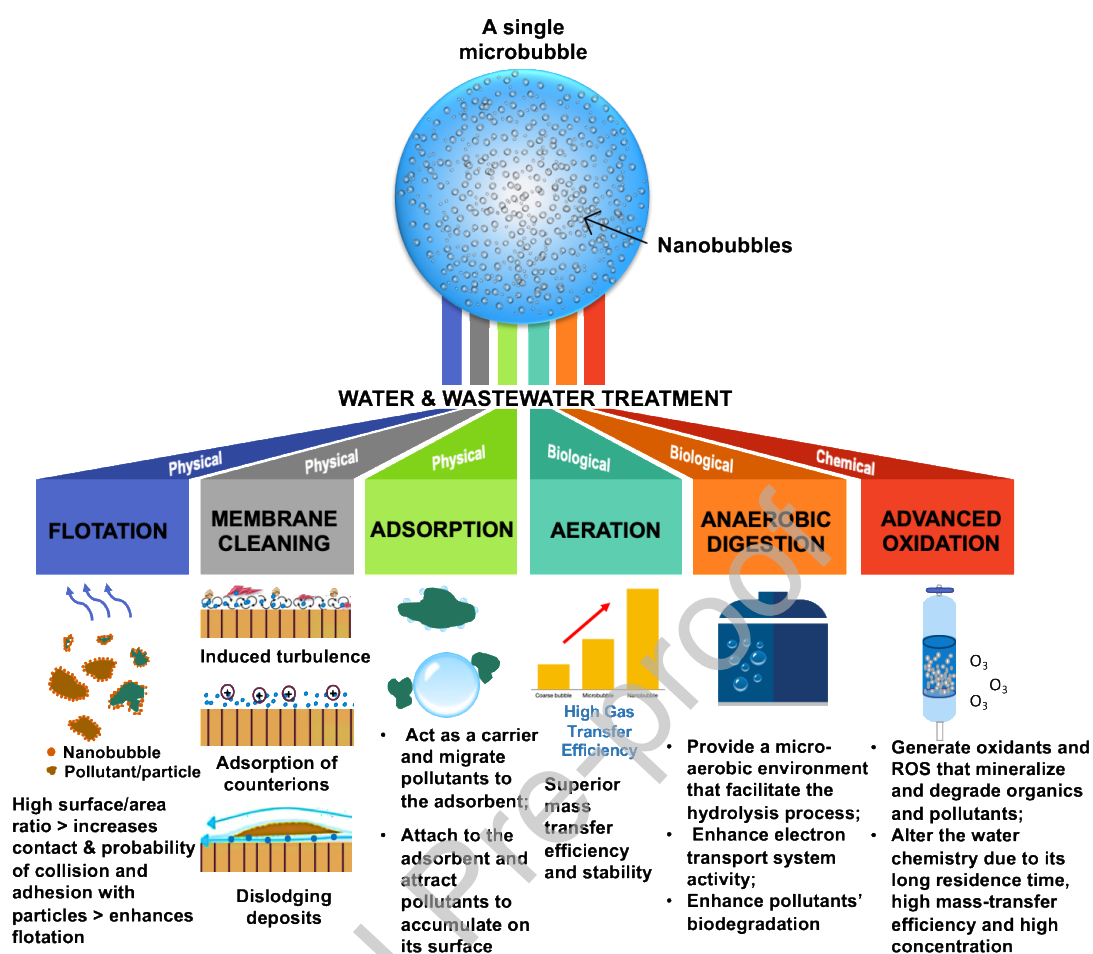
Methods	Mechanism and Limitations
<b>Light scattering method</b>	
Dynamic Light Scattering (DLS) (Nirmalkar et al., 2018b)	DLS, NTA, and Tyndall effect detect NBs based on light scattering. DLS and NTA can give the size distribution and number density of NBs. Tyndall effect can directly visualize whether colloidal particles exist in a liquid solution.
Nanoparticle-tracking analysis (NTA) (Nirmalkar et al., 2018b)	Nevertheless, the light scattering technique cannot differentiate between gas bubbles, solid particles, and liquid droplets, so it needs to be complemented with other methods (Eklund and Swenson, 2018).
Tyndall effect (Farid et al., 2022b; Li et al., 2021b)	
<b>Visualization method</b>	
Electron microscopy (EM) (Jadhav and Barigou, 2020; Ohgaki et al., 2010; Shin et al., 2015; White et al., 2011)	The high resolution of Cryo-SEM and TEM enable the direct detection and characterization of NBs. However, the method is limited by equipment availability.
Optical microscopy (Kim et al., 2019; Nirmalkar et al., 2018a)	Optical microscopy can verify the existence of NBs and accurately measure the size of a single bubble.
Atomic force microscopy (AFM) (Shi et al., 2021)	AFM is applied to measure the existence of NBs on solid surfaces, but it is not suitable for measuring NBs. Also, the equipment is expensive.
<b>Physical perturbation</b>	
Freeze and thaw (Agarwal et al., 2022; Jadhav and Barigou, 2020; Nirmalkar et al., 2018a; b)	After freezing and thawing, if nanobubble density drops, nano-entities are bubbles instead of solid particles/droplets. This method can be complemented with light scattering methods. However, aggregates maybe formed during this process.
Centrifugation (Sedlak and Rak, 2013)	Given the significant difference in density, centrifugation can separate buoyant colloids from sediment colloids. DLS and NTA should be done subsequently to observe any kinetic changes.
Vacuum treatment/degassing (Qiu et al., 2017)	Vacuum treatment can decrease the concentration of dissolved gas in the bulk solution. The bulk solution becomes undersaturated once the pressure normalizes, forcing gas bubbles to dissolve. If a considerable reduction in number density is found, the nano-entities are expected to be bubbles.
Pressurization (Tuziuti et al., 2017)	Exerting pressure onto an NB solution will compress the bubbles, which could cause them to collapse. The under-saturation of air while under pressure then forces them to dissolve, causing a decrease in bubble number density and an increase in diameter.
<b>Other indicators</b>	
Resonant mass measurement (RMM) (Hernandez et al., 2019; Tanaka et al., 2020)	Similar to the light scattering method, RMM can measure buoyant mass and estimate the density, size, and distribution of submicron particles in liquid solutions based on the Archimedes principle.
Ultrasound response (Hampton and Nguyen, 2010; Leroy and Norisuye, 2016)	By transmitting an ultrasonic signal through bulk solution, solid and gas colloid can be distinguished.
Detection of pollutants (Ferraro et al., 2020; Jadhav and Barigou, 2020; Li et al., 2021b)	GC-MS, ICP-MS, etc., can be used to analyze if organic/inorganic/trace metal contaminants exist in the bulk solution, which can further be validated using the light scattering method, i.e., if light scattering methods detect colloidal while no pollutant is observed, the existing nanoparticles should be nanobubbles.
Dissolve oxygen (DO) level (Eklund et al., 2021; Kim et al., 2019)	This method compares the DO levels of NB solutions under various conditions that can change NBs' volume concentration. A discrepancy would indicate the existence of NBs since NBs can slowly release oxygen. This is suitable for O <sub>2</sub> or air NBs and requires a considerably high-volume concentration.

## 4. Application of NBs in the water and wastewater treatment processes

### 4.1 Overview of NBs in different processes and their mechanisms

Equipped with a greater knowledge of NBs' properties and potential revealed by NB research over time, the research interest in NBs has started to steer toward the application of NBs in various industry sectors, including the agriculture, aquaculture, food processing, biomedical, mineral processing, and water treatment industries. From the bibliometric analysis (**Figure 1(C)**), the majority of the research on applying NBs to water treatment processes has been conducted on flotation and aeration, followed by advanced oxidation processes and anaerobic digestion, while NBs' role in membrane cleaning and adsorption have been less studied. These processes can be further categorized into the broader genres of physical processes (flotation, membrane cleaning, and adsorption), biological processes (aeration in bioreactor and ecosystem remediation, and anaerobic digestion), and chemical oxidation processes.

The aim of the section is to discuss the role of NBs in these processes based on current research, as well as the limitations and future directions. **Figure 3** and **Table 4** provide an overview of NBs' main contributions in each process based on existing studies. In general, the role of NBs can be summarized as followed: 1) the small size, high number density, and long-term stability of NBs enable their longer retention, thereby increasing water mobility and mass transfer efficiency; 2) the hydrophobicity of NBs allows them to act as particle carriers through hydrophobic attraction; and 3) the bursting of NBs generate ROS, although their contribution, as revealed so far, is minimal. Extended discussions of these mechanisms can be found in later sections.



*Figure 3. An overview of how NB technology can enhance water and wastewater treatment processes.*

*Table 4. Summary of the proposed main roles of NBs in water treatment processes.*

Water treatment processes	Commonly used NB types	Main roles of NBs in the processes			
		Increased water mobility	Increased mass transfer rates	Act as particle carrier	Generate radicals
Flotation	Air NBs	★ ★ ☆	☆ ☆ ☆	★ ★ ★	★ ☆ ☆
Membrane cleaning	Air NBs	★ ★ ★	☆ ☆ ☆	★ ★ ★	★ ☆ ☆
Adsorption	Air NBs	★ ★ ★	☆ ☆ ☆	★ ★ ★	☆ ☆ ☆
Aeration	Air/O <sub>2</sub> NBs	☆ ☆ ☆	★ ★ ★	☆ ☆ ☆	☆ ☆ ☆
Anaerobic digestion	Air/CO <sub>2</sub> /H <sub>2</sub> /O <sub>2</sub> NBs	★ ★ ☆	☆ ☆ ☆	★ ★ ★	★ ☆ ☆
Advanced oxidation	O <sub>3</sub> NBs	★ ☆ ☆	★ ★ ★	☆ ☆ ☆	★ ☆ ☆

Note: The number of stars indicate the level of NBs' contribution in water treatment processes in terms of the four mechanisms given; \*: low; \*\*: average; \*\*\*: high.

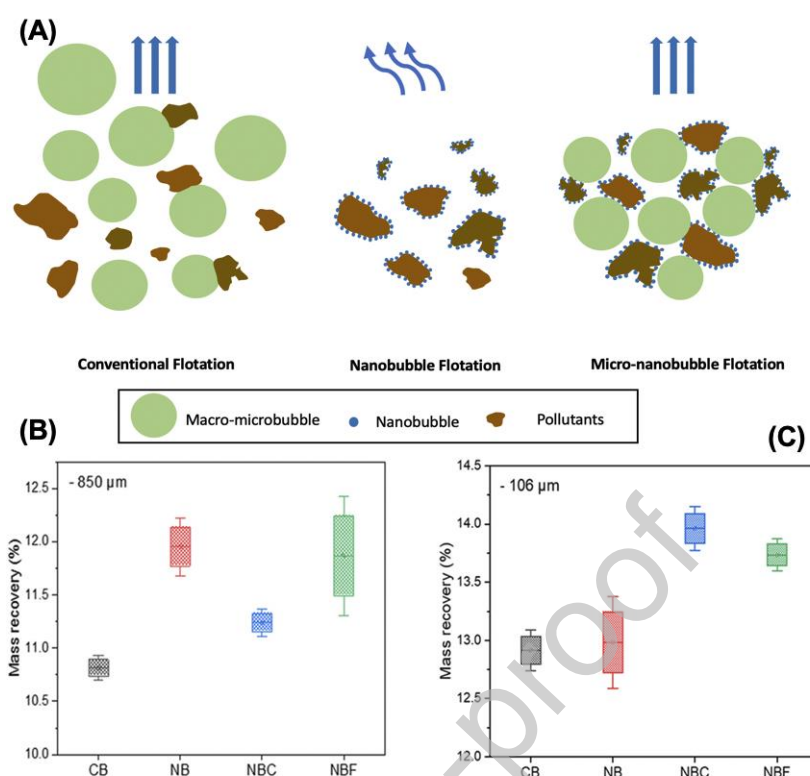
## 4.2 Nanobubble-assisted flotation

### 4.2.1 Role of NBs in flotation processes

Conventional flotation achieves high separation efficiency for particles ranging from 20  $\mu\text{m}$  to 150  $\mu\text{m}$  in size, while the recovery of coarse and fine particles outside this range remains as a challenge: the recovery of coarse particles is hindered by particle detachment, while it is difficult to remove fine particles due to low particle-bubble collision (Farrokhpay et al., 2021). Generally, the closer the size of particles/flocs is to that of bubbles, the higher the probability of collision and adhesion between them (Etchepare et al., 2017b). Thus, the probability of collision and adhesion with fine particles can be increased by applying NBs, which have higher surface-to-area ratios and are generated in larger quantities. Moreover, by attaching on coarse particles, NBs can increase the contact angles of both fine and coarse particles and reduce the probability of their detachment from bigger bubbles (Wang et al., 2020a). A schematic illustration comparing conventional and MNB flotation is provided in **Figure 4(A)**.

### 4.2.2 Existing research on NBs in flotation processes

Studies reporting the application of NBs in froth flotation have found that NBs can enhance the recovery of both fine and coarse particles outside the optimal recovery size range, mainly by increasing the contact angle of the particles (Chipakwe et al., 2021; Rosa and Rubio, 2018). An example of coarse apatite recovery with NBs is shown in **Figure 4(B, C)**. Compared with conventional flotation, tests with NBs consistently showed higher recovery of 850  $\mu\text{m}$  particles. For particles sized 106  $\mu\text{m}$ , NBs alone showed a similar removal rate but with a higher variation than the conventional test, while NBs with a collector and those with a frother showed significantly higher removal performances.



**Figure 4.** (A) Illustration of microbubble, nanobubble, and micro-nanobubble flotation. (B) Apatite flotation mass recovery for various tailings. CB—conventional test, NB—nanobubbles, NBC—nanobubbles with a collector, NBF—nanobubbles with a frother (Chipakwe et al., 2021).

Etchepare et al. (2017a) compared MNBs and isolated NBs for the removal of  $\text{Fe}^{3+}$  ions as  $\text{Fe}(\text{OH})_3$  precipitates and nanoparticles. The highest removal rate (>99%) was achieved with MNBs under a low saturation pressure of 2 bar, a condition that enables higher NB concentration. Isolated NBs also effectively removed a maximum of 77% of the nanoparticles and 91% of the precipitates. They also found that removal by NBs alone strongly depended on influent concentration, where higher feed concentration translated into higher removal. The same research group also compared the performance of MNBs and isolated NBs for separating emulsified oil in saline water. Flotation by MNBs achieved an oil separation

efficiency of >99% by flocculation with 5mg/L of Dismulgan, while isolated NBs also achieved 90%. Furthermore, by adding an extra step of floc conditioning using 1 and 3 mg/L of Dismulgan for isolated NBs improved the removal efficiency from 73% to 84% and 92% to 95%, respectively.

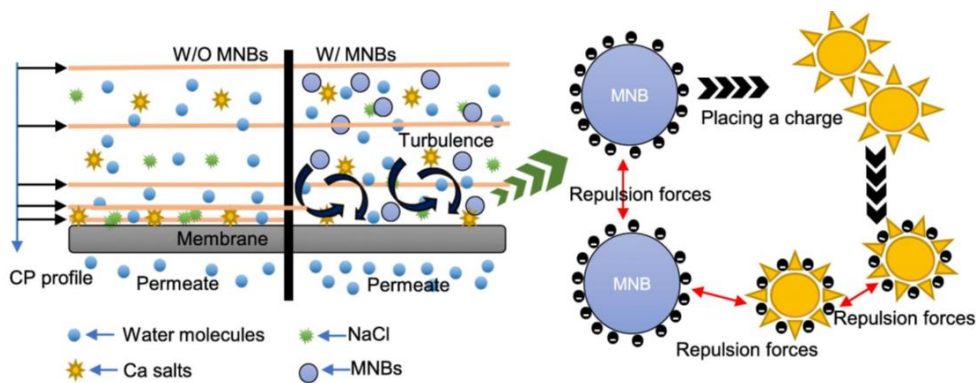
Although NBs possess several advantages over MBs, their low rising velocity and lifting power make it challenging for the application of NBs to be a stand-alone technique. Instead, several researchers have proposed that NBs can act as a ‘collector’ in combination with MBs to ensure a high overall efficiency (Rosa and Rubio, 2018; Zhang et al., 2021).

### **4.3 Membrane cleaning/defouling using NBs**

#### **4.3.1 Role of NBs in membrane cleaning/defouling processes**

Advanced membrane separation processes are highly efficient in separating pollutants from effluents, however, the occurrence of fouling during membrane operations largely compromises their performance efficiency (Kharraz et al., 2022a; Kharraz et al., 2022b). Various approaches have been proposed to alleviate the fouling problems (Farid et al., 2019; Lee et al., 2016). Among which, gas bubbling with coarse bubbles has been frequently used as a strategy for mitigating membrane fouling; however, due to the short lifespan of large bubbles, continuous or frequent intermittent bubble generation, which is energy-consuming, is required for efficient fouling control. In comparison, since NBs follow the Brownian motion when in large quantities and have a long lifespan, they are able to create constant turbidity that can help prevent particles from depositing and building up on the membrane. Besides, NBs’ hydrophobicity and negatively charged surface can carry away positively charged ions and prevent the binding of salts. The ROS generated by NBs is also believed to play a role in directly degrading organics (**Figure 5**).



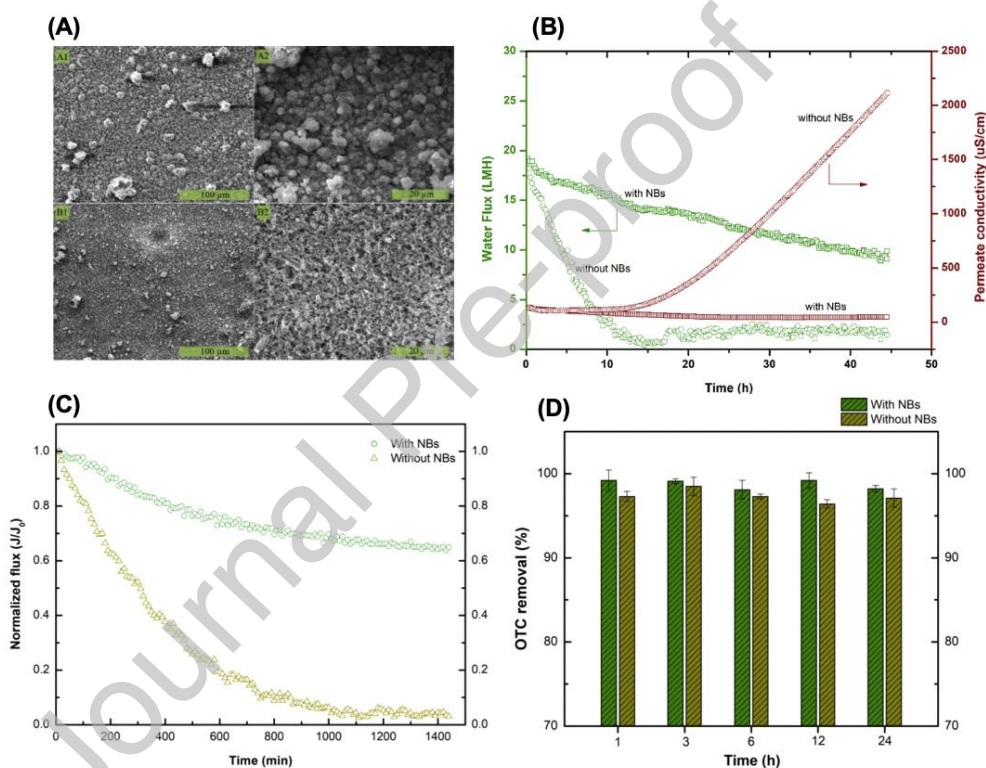


**Figure 5.** Main mechanisms behind membrane cleaning in reverse osmosis membrane processes (Dayarathne et al., 2019). W/O: without; W/: with. Reprinted with permission from Copyright 2019 Elsevier.

#### 4.3.2 Existing research on NBs in membrane cleaning/defouling processes

Several researchers have explored NBs' potential in mitigating membrane fouling/scaling and cleaning fouled/scaled membranes during various membrane processes. In both lab and pilot-scale experiments, MNBs were applied using the 'cleaning in place' method, which successfully improved the permeate flux and solute rejection rate (Dayarathne et al., 2017). Another study by Dayarathne et al. (2019) found that the continuous application of MNBs successfully inhibited calcium crystal formation on the membrane during the reverse osmosis (RO) process and achieved better scaling inhibition than the two commercially available antiscalants used in the study. However, intermittent MNBs application was less effective, since MNBs had a harder time removing calcium crystals after the formation of calcium scaling. Effect of NBs on scaling in membrane distillation (MD) was also investigated. Farid et al. (2022b) used feedwater with and without NBs to treat high salinity brine and found that after 13 h of operation, the flux reduced by 24% in the test with NBs, whereas the flux reached zero in the test without NBs. While after 98 h, operation with NBs showed a 63% reduction in flux and a 99.9% salt rejection throughout the test, indicating that pore wetting did not occur. SEM images of the direct-contact MD experiment results with DI water and

NB-DI water are shown in **Figure 6(A, B)**. Another study by Farid et al. (2022a) used NB-enriched feed water in a forward osmosis (FO) process and reported only a 23% reduction from the initial flux after a 24 h operation, compared to the significant reduction in permeate flux (-98%) observed using a feed without NBs (**Figure 6(C)**). Interestingly, they also found enhanced removal of oxytetracycline, a common antibiotic in aquaculture, by NBs through direct oxidation, although their contribution was relatively small: 11% by air NBs and 30% by O<sub>3</sub> NBs (**Figure 6(D)**).



**Figure 6.** Comparison of scaling behaviors in feeds with and without NBs in different membrane processes. (A) SEM image of scaling behavior and salt deposition on a C-PVDF membrane when using a high-salinity feed solution in a DI water feed (A1–A2) and in a NB-DI water feed (B1–B2) in MD. (B) Water flux and permeate conductivity of a C-PVDF membrane with and without NBs in the feed (Farid et al., 2022b). Reprinted with permission from Copyright 2022 Elsevier. (C) Permeate flux comparing standard FO and NB-assisted

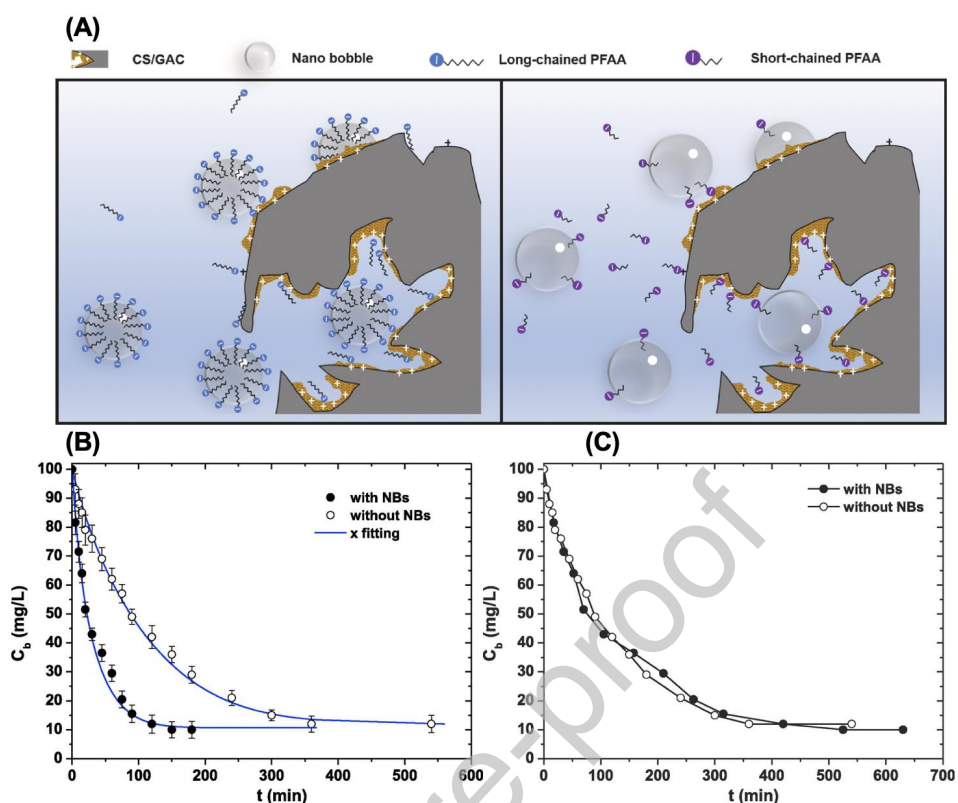
*FO processes. (D) OTC removal with and without NBs (Farid et al., 2022a). Reprinted with permission from Copyright 2022 Elsevier.*

While studies have used NBs for membrane cleaning in various membrane processes, including RO, FO, and MD, and obtained satisfactory results, most of them have experimented with a single type of pollutant in the influent and for a short operation time. Hence, further investigations are required on in-situ membrane cleaning with NBs in a long-term operation using influents with complex compositions.

#### **4.4. NB-assisted adsorptive removal of water contaminants**

##### 4.4.1 Role of NBs in adsorptive removal processes

Despite being less explored than other treatment processes, researchers have also investigated the role of NBs in adsorption processes. Existing studies have shown that NBs can promote adsorption in the following ways: 1) NBs dispersed in the solution act as a carrier and migrate the pollutant particles to the adsorbent, and 2) NBs attach to the adsorbent and attract pollutants to accumulate on their surface, which increases the adsorption site for pollutants.



**Figure 7.** (A) Schematic of the removal mechanism by nanobubbles combined with activated carbon using PFAA as a model pollutant (Liu et al., 2022). Reprinted with permission from Copyright 2022 Elsevier. (B) Enhanced adsorption of Pb(II) by 366% with NBs than without NBs. (C) Rescaled kinetic curve (multiplied by 3.66) to show that the shape of the kinetic curve is modified by NB presence (Kyzas et al., 2019). Reprinted with permission from Copyright 2019 Elsevier.

#### 4.4.2 Existing research on NBs in adsorptive removal process

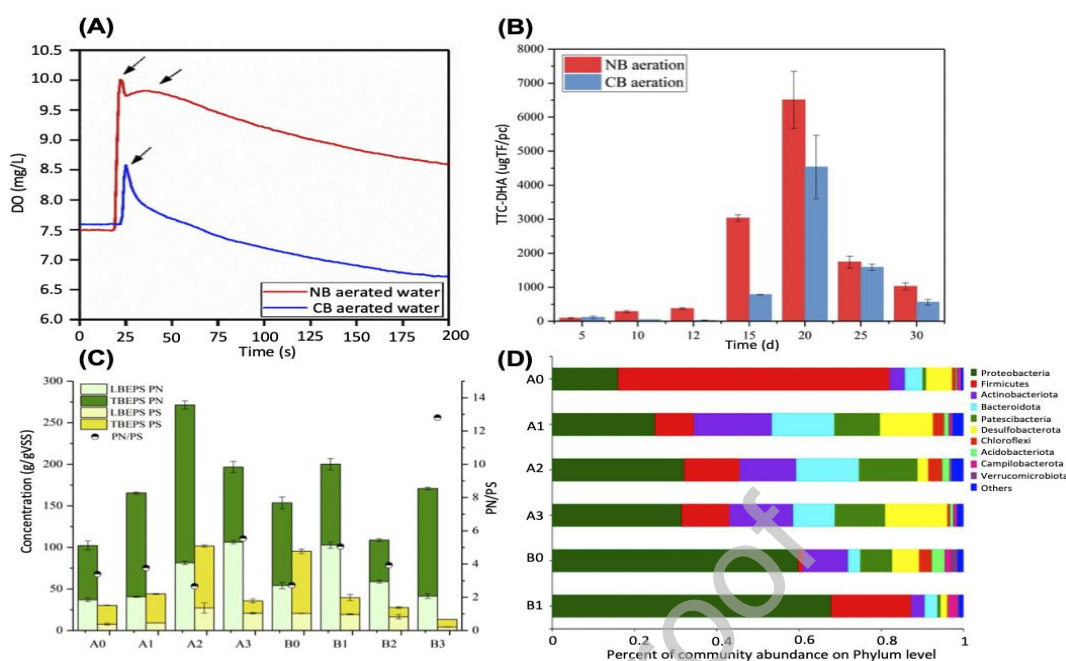
NBs was found to enhance the adsorption of per-and polyfluoroalkyl substances (PFAs) by graphene/activated carbon through modelling and simulation along with an aeration and degassing experiment. Jiang et al. (2021) found that PFA removal efficiency increased by 21-29.2% after aeration by NBs and decreased by 27.7% after vacuum degassing. The NBs' role

as carriers and their attachment to the adsorbent were both observed, the first being more important for hydrophilic adsorbents, and the second being more critical for hydrophobic adsorbents. The results suggested the combination of aeration and granular activated carbon as a potential solution to enhance PFA removal. Liu et al. (2022) found a positive relationship between NBs' concentration and PFAAs' removal efficiency. They also pointed out the difference between the removal mechanisms of short-chain and long-chain PFFAs (**Figure 7(A)**). Kyzas et al. (2019) used NBs to accelerate the adsorption process of Pb(II) onto activated carbon by 366%. They found that the adsorption capacity of activated carbon remained the same throughout the process, proving the role of NBs as carriers transferring Pb(II) to the negatively charged sites of activated carbon (**Figure 7(B, C)**). Later, the same research group also found that NBs can facilitate the batch adsorption process; without agitation, the batch with NBs increased the maximum adsorption capacity from 9 mg/g to 94 mg/g (Kyzas et al., 2020).

#### **4.5 NBs-assisted aeration in bioreactors**

##### 4.5.1 Role of NBs in bioreactor aeration

Aeration plays a vital role in oxygen delivery and can be an essential process in biological water and wastewater treatment and restoration. However, aeration is highly energy-consuming, accounting for 70–80% of the total energy consumption of water treatment processes (Sun et al., 2016). To improve aeration efficiency and reduce energy costs, aeration by NBs is considered a viable option in aerobic biosystems (e.g., biofilm reactors and activated sludge reactors) given the superior mass transfer efficiency and stability of NBs compared with coarse bubbles. NB-aerated biofilms were found to enhance homogeneity of dense extracellular polymeric substances and affect the spatial and microbial structure of microbial community.



**Figure 8.** (A) Dissolved oxygen results of dropwise injections of water aerated with NBs and coarse bubbles on the same biofilm at the same location (10th day of cultivation; depth = 500  $\mu\text{m}$ ). (B) Dehydrogenase activity of the NB- and coarse bubble-aerated biofilms (Xiao and Xu, 2020). Reprinted with permission from Copyright 2020 Elsevier. (C) quantification of the extracellular polymeric substance of biofilm. (D) Microbial community profiles of biofilm samples at the phyla level. A0-A3: NBs with different reflux ratios, B0: air bubbling, B1: air bubbling + NBs. (Xiao et al., 2021b)

#### 4.5.2 Existing research on NBs in bioreactor aeration

Xiao and Xu (2020) used air NBs in a biofilm system and found NBs to have around a 1.5 times higher oxygen diffusion coefficient than coarse bubbles, which shifted the microbial community and increased enzyme activity. Specifically, they observed up to a six-fold growth in dehydrogenase activity, which subsequently enhanced the removal of chemical oxygen demand (COD) and ammonium (**Figure 8(A, B)**). However, the enhancement of COD removal became insignificant with time due to the physical barrier created by the thickened biofilm, suggesting the importance of periodic backwash. A follow-up study further compared

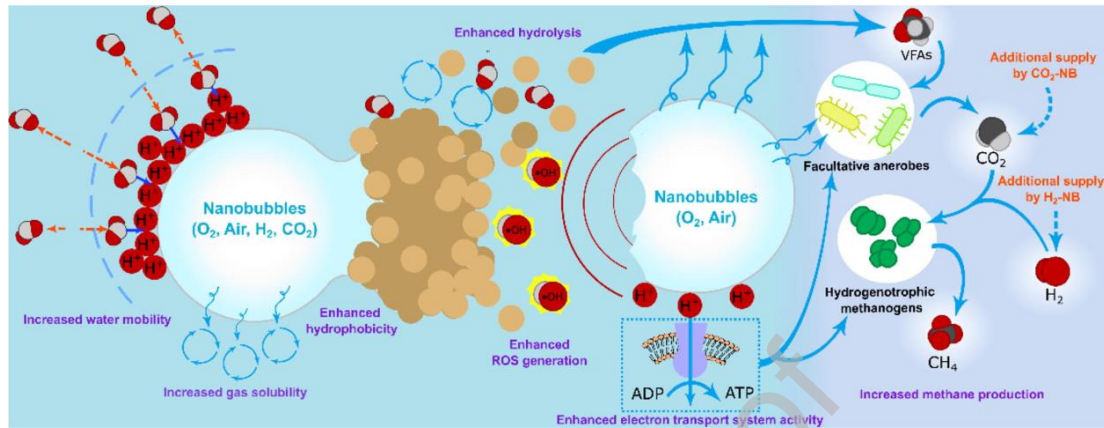
the effect of adding NBs to microbial aggregates in biofilm and activated sludge (Xiao et al., 2021a). The sizes and thicknesses of the activated sludge and biofilm were enlarged by 23.35% and 86.67%, respectively, which further contributed to the improvement of total nitrogen (TN) removal by as much as 10.58%. However, at the same time, they observed an irreversible sludge floating in the early stage, likely due to the increased floatability of sludge as NBs attached on them. A similar finding was also highlighted by Yaparathne et al. (2022). They found NB-aerated samples having a cloudier effluent than coarse-bubble aerated samples, which can be attributed to the large differences in number of filament bacteria. Another key concern of substituting conventional aeration with NB aeration is that NBs cannot provide sufficient shear stress, which can help split off the aged biofilm and guarantee suitable biofilm thickness (**Figure 8 (C, D)**). Hence, it is suggested that combining NB aeration with proper mechanical bubbling or reflux ratio is essential for achieving the desired removal efficiency.

#### **4.6 NB-enhanced anaerobic digestion process**

##### 4.6.1 Role of NBs in anaerobic digestion processes

Wasted activated sludge (WAS) generated from wastewater treatment plants contains rich organics matters and can become a secondary pollutant if not properly disposed of (Guo et al., 2021; Guo et al., 2020). As a widely employed green technology using WAS as substrates to produce renewable energy, anaerobic digestion is reported to have a higher production efficiency when NBs play a role (**Figure 9**). The role of NBs in anaerobic digestion proposed in existing research are as follows: 1) the small size and high zeta potential of NBs increase the water molecules' mobility, allowing the NBs to carry nutrients to the inner region of the biofilm and promote microorganisms and enzyme activities (Wang et al., 2020e); 2) the radicals generated by NBs can enhance the oxidative decomposition of substrates by microorganisms (Yang et al., 2020); 3) oxygen-containing NBs promote higher ATP

synthesis and metabolite transport (Wang et al., 2020d); and 4) CO<sub>2</sub> and H<sub>2</sub> NBs can serve as additional substrates for methanogens (Chuenchart et al., 2021).

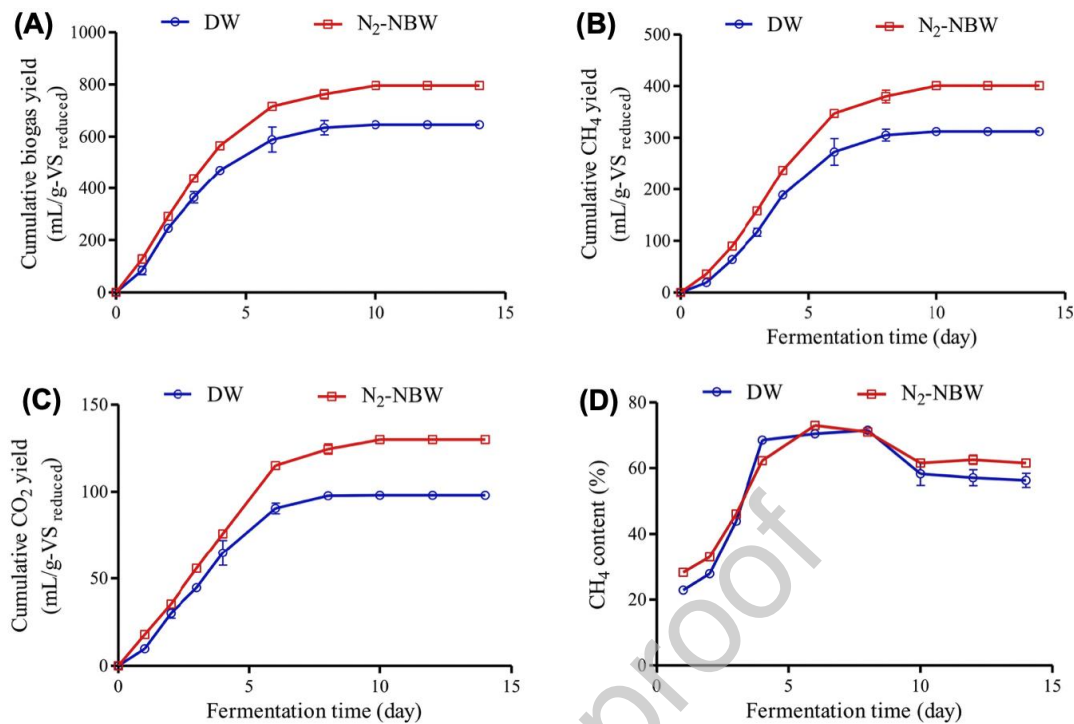


**Figure 9.** A schematic overview of the role of NBs in anaerobic digestion (Chuenchart et al., 2021). Reprinted with permission from Copyright 2021 Elsevier.

#### 4.6.2 Existing research on NBs anaerobic digestion processes

Wang et al. (2019a) found that NBs supplemented with gas species of H<sub>2</sub>, CO<sub>2</sub>, air, and N<sub>2</sub> can all enhance methane yields in anaerobic digestion using WAS as substrates by 21%, 20%, 18%, and 14% than a reactor with tap water and by 17%, 16%, 14%, 11% than a reactor with deionized water, respectively. In particular, the enhancement by air NBs suggested that the presence of a limited micro-aerobic environment can facilitate the hydrolysis process. Yang et al. (2019) added N<sub>2</sub> NB water in WAS and observed enhanced hydrolysis, which was attributed to the 14-17% increases found in four types of extracellular hydrolases activity (alkaline phosphatase (ALP), acid phosphatase (ACP),  $\alpha$ -glucosidase, and protease). Hence, N<sub>2</sub> NBs facilitated the conversion of macromolecules to volatile fatty acid (VFAs), thereby increasing the methane yield by 29% (**Figure 10**).





**Figure 10.** Effect of  $N_2$  NB water on (A) biogas, (B)  $CH_4$ , (C)  $CO_2$  production, and (D)  $CH_4$  content during 14 days of fermentation. All data are expressed as mean  $\pm$  SD of duplicate experiments (Yang et al., 2019). Reprinted with permission from Copyright 2019 Elsevier.

The degradation of recalcitrant components in substrates, such as lignocellulosic biomass, is one of the main challenges for enhancing anaerobic digestion. Wang et al. (2020d) applied with various types of NBs (i.e., air,  $N_2$ ,  $O_2$ , and artificial  $N_2/O_2$  gas mixture with different mixing ratios) to the anaerobic digestion of cellulose and reported an 8-14% increase in cellulose reduction and an 8-30% increase in methane yield compared with the control group using deionized water.  $O_2$  NBs achieved the highest efficiency among the tested gas types, as  $O_2$  acted as an electron acceptor in the electron transport system to enhancing NBs' activity. Yang et al. (2020) used  $N_2$  NBs in the co-digestion of WAS and alkaline lignin, which is a highly recalcitrant biofiber, and found that  $N_2$  NBs simultaneously enhanced methane production by 17% and lignin degradation by 10%. Higher volatile solid reduction rates were

also observed with the addition of N<sub>2</sub> NB water. The authors also proposed that the enhancement in lignin degradation could be due to •OH generated when bubbles collapse.

Although NBs have been reported to enhance methane production successfully, some of their underlying mechanisms have yet to be experimentally confirmed. For example, it has been reported that the enzyme activities increased after adding NBs, but the exact role of NBs in enhancing enzyme activities remains unknown.

## 4.7 Ecosystem restoration using NBs

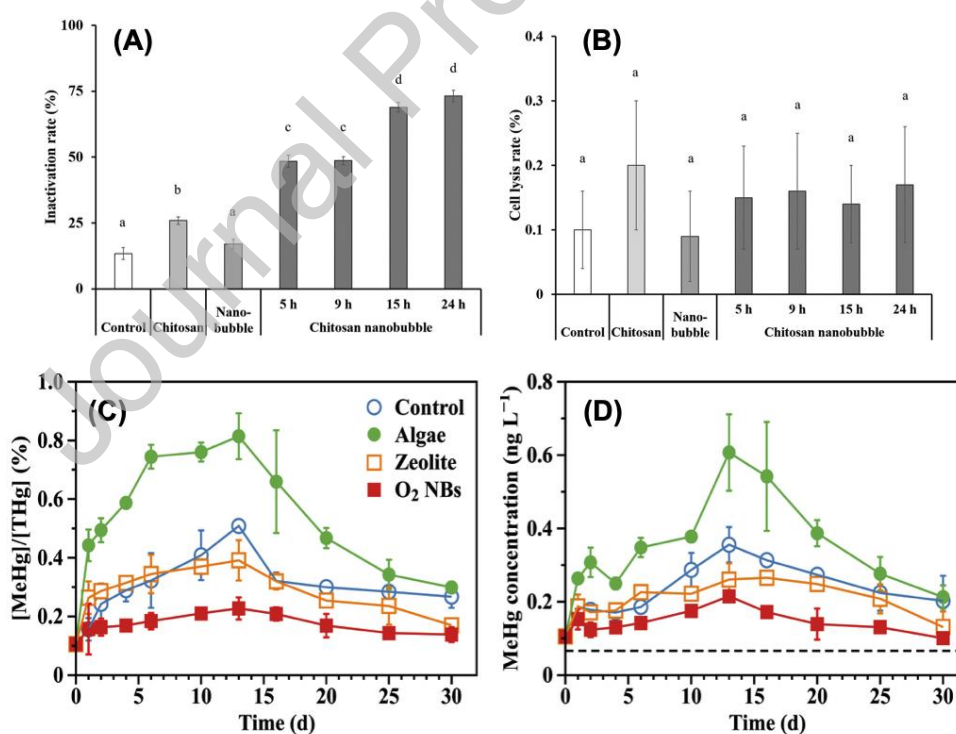
### 4.7.1 Role of NBs in ecosystem restoration

Eutrophication is a common phenomenon that occurs in various water bodies, leading to algal blooms and adverse effects on the ecosystem. Algal blooms can induce anoxia/hypoxia, intensify CH<sub>4</sub> emissions, and even aggravate the pollution problems in water bodies. Researchers have come up with various strategies for delivering oxygen to anoxic/hypoxic areas to combat this issue, but many of the techniques are energy-intensive. NB-generated hydroxyl radicals are believed to disrupt cell integrity and inactivate bacteria, making them a potential strategy for reducing algae growth, while aeration with O<sub>2</sub> NBs may be a greener alternative solution for delivering oxygen to anoxic/hypoxic areas.

### 4.7.2 Existing research on NBs in ecosystem restoration

Nam et al. (2022) attempted to use chitosan-modified NBs to inactivate cyanobacteria to prevent algal bloom. NBs are generated with negative zeta potentials, but the zeta potential of chitosan-modified NBs was found to be less negative, which enable them to produce more hydroxyl radicals to disrupt cell membrane integrity and inactivate *M.aeruginosa* with negligible cell lysis rate (**Figure 11(A, B)**). Shi et al. (2018) delivered O<sub>2</sub> surface NB-loaded

zeolites to anoxic sediments and successfully reversed the oxidation-reduction potential from  $-200$  mV to  $+189$  mV. The DO level was stable at around  $5.7$  mg/L, and  $\text{CH}_4$  emission was reduced by a factor of 3.2 compared to the control group. Ji et al. (2020) used  $\text{O}_2$  surface NBs-loaded zeolites and successfully decreased MeHg content in water and in sediments by 69% and 56%, respectively (**Figure 11(C, D)**). Similarly, zeolites loaded with  $\text{O}_2$ -loaded surface NBs were able to alleviate arsenic pollution in hypoxic water by reducing the level of dissolved arsenic from  $23.2$   $\mu\text{g/L}$  to less than  $10$   $\mu\text{g/L}$ , while, at the same time, stimulating the conversion to less toxic species. In comparison,  $\text{N}_2$  NB-loaded zeolites did not show obvious effects (Tang et al., 2021). Another study found that Geosmin and 2-methylisoborneol (MID) produced by cyanobacteria can also be controlled better through oxidation by mixing  $\text{O}_2$  MBs and NBs (Soyluoglu et al., 2022).



**Figure 11.** Application of NBs in ecosystem restoration. (A) Inactivation rate and (B) cell lysis rate by control, chitosan, nanobubble and chitosan-modified nanobubbles (Nam et al., 2022). Reprinted with permission from Copyright 2022 Elsevier. (C) Variations of %MeHg and (D) MeHg concentrations in the overlying water from four treatment groups during a 30 d incubation period.(Ji et al., 2020). Reprinted with permission from Copyright 2020 Elsevier.

Other than mitigating eutrophication, studies have also examined the effects of NBs at different initial concentrations for aquatic plant restoration. The findings show that an appropriate density of NBs can enhance plant growth, however, once the density level exceeds the threshold, NBs may inhibit plant growth and photosynthesis (Wang et al., 2020c). Liu et al. (2021) used H<sub>2</sub> NBs to alleviate heavy metal contamination in freshwater and demonstrated that H<sub>2</sub> NBs can relieve copper-induced toxicity in algae by protecting algae against copper uptake and reducing copper-induced endogenous ROS.

#### **4.8 Degradation and disinfection of pollutants by NBs during advanced oxidation processes**

##### **4.8.1 Role of NBs in advanced oxidation processes**

Advanced oxidation processes (AOP) for removing organic pollutants through degradation are powerful and effective, especially for eliminating pathogens and recalcitrant pollutants directly in aqueous phase. However, these processes are often limited by their cost-effectiveness, requiring further optimization and enhancement. Ozonation, which is a commonly employed AOP for water treatment (e.g., disinfecting drinking water or degrading pollutants in water bodies) is an energy-intensive process that is further hindered by the low dissolution and short half-life of O<sub>3</sub>. Several studies have shown that NBs can effectively prolong the reactivity of O<sub>3</sub> during ozonation by enhancing ozone dissolution and lifespan

(Seridou and Kalogerakis, 2021). For example, Fan et al. (2021a) found that NB aeration enhances the mass transfer coefficient and dissolved  $O_3$  concentration by 4.7 times and 1.7 times, respectively, than MaB aeration. Kim et al. (2021) found that the half-life of  $O_3$  NBs was 23 times longer than  $O_3$  MaBs. Moreover, Fan et al. (2021b) demonstrated that NBs can raise  $\bullet OH$  concentration two to three times higher than MBs, which further improved the removal performance of ozonation.

Besides ozonation, NBs have also been applied to assist and enhance other AOPs, e.g. photocatalysis, which is widely researched but suffers from limited application due to its low efficiency. The addition of MNBs in photocatalysis process was found to enrich oxygen in solution, enhance the light absorption of photocatalysts, stabilize and prevent settling of photocatalyst particles, as well as improve interfacial photoelectric effects of  $TiO_2$ /MNB suspensions (**Figure 12**) (Fan et al., 2021b).

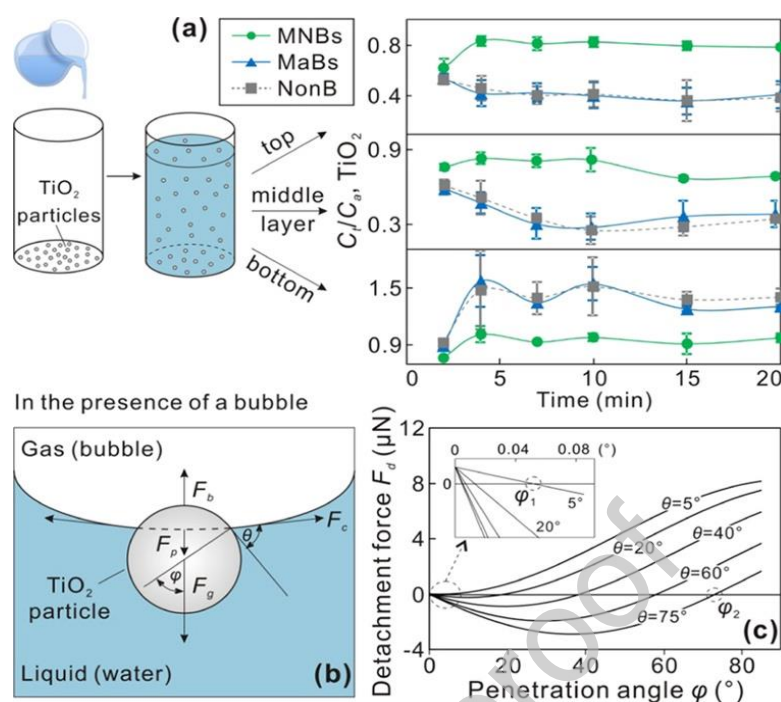
#### 4.8.2 Existing studies of NBs in AOP

Several studies have explored the removal ability of  $O_3$  MNBs. Xia and Hu (2019) used  $O_3$  MNBs to treat persistent pollutants in groundwater. After 30 min, 95% of benzene and chlorobenzene and 67% of nitrobenzene were removed despite their high initial concentrations (over 500 mg/L). However, the removal efficiency for P(o)-nitrochlorobenzene was relatively poor at 35%. The same study also applied  $O_3$  MNBs to treat industrial wastewater with high salinity and achieved a 63% removal of COD after 14 h of treatment. Also, because stable by-products formed during the treatment, they proposed using  $H_2O_2$  in combination to enhance the removal efficiency.

Another study tested the efficiencies of ozone MNBs,  $H_2O_2$ , and a combination of both at different mass ratios in treating trichloroethylene (TCE)-contaminated groundwater (Hu and

Xia, 2018).  $O_3$  MNBs were able to reduce TCE concentration from 14mg/L to 0mg/L in 20min, while  $H_2O_2$  decreased the concentration by 50% after 2 h of treatment. In comparison, the removal efficiency was enhanced threefold when using  $O_3$  MNBs and  $H_2O_2$  in combination at a mass ratio of 1:1. Based on the results, in-situ remediation was further tested with the 1:1  $O_3$  MNBs/ $H_2O_2$  combination for 6 days, which achieved an overall removal efficiency of 99%, indicating that  $O_3$  MNBs can be applied as a feasible technology for groundwater remediation.

Fan et al. (2021b) used MNBs together with  $TiO_2$  and UV irradiation to degrade methylene blue and compared with the performance of MaB. It was found that more than 92.25% of MB was removed after 20 min in the MaB-aerated solutions, while  $O_2$ -MNB aerated solutions achieved completed removal of MB within 5 min. Meanwhile, Yu et al. (2021) pointed out that  $O_2$  NBs alone, without photocatalysts or irradiation, cannot degrade methyl orange. Another study found that using  $O_2$  NBs with visible light can degrade 60% of OTC after 4 h, showing a better performance than MaBs, but the NBs failed to degrade OTC without irradiation (Wang et al., 2020b).



**Figure 12.** Photocatalyst particle stabilization by MNBs. (A) Concentration profiles of TiO<sub>2</sub> particles as a function of time in three different solutions: MNB suspension, MaB-aerated DI water, and DI water without aeration (labeled NonB). (B) Schematic illustrating the forces of a TiO<sub>2</sub> particle adhered to a bubble. (C) Detachment force ( $F_d$ ) of a TiO<sub>2</sub> particle. (Fan et al., 2021b). Reprinted with permission from Copyright 2021 American Chemical Society.

#### 4.9 NBs in water and wastewater treatment: case studies

NB technology has developed significantly over the last two decades and has demonstrated high efficiency in various environmental engineering applications. To date, the academic literature on NB applications in water treatment have mainly highlighted the technological proof of concept and success stories primarily at the laboratory scale, and evidence authenticating the potential of NB technology at the industrial or large pilot scale has not been rigorously reported. However, this has not stopped the industry from applying NB technology to their operations, and there have been numerous reports of successful field and industrial-

scale applications of NB technology especially over the last decade. **Table 5** summarizes the case studies of NB applications in water and wastewater treatment carried out worldwide using commercial NB generators from various leading companies. Specific applications of NB technology in the water and wastewater treatment industry include NB-based flotation of wastewater pollutants and recovery of fine particles; enhanced aeration for high DO levels in wastewater treatment; advanced oxidation of organics or disinfection of pathogens (including viruses) via NB-induced free radicals; ecosystem restoration of water bodies (lakes/ponds), including the suppression of algal blooms and odor control; drinking water treatment and disinfection; groundwater remediation; and oil-water separation.

These case studies provide substantial indication that NB technology can be successfully applied beyond the bench scale for environmental applications and demonstrate that NB generators are highly efficient and cost-effective as supplemental aeration systems that can be retrofitted into a wide range of treatment systems. Most importantly, they show that the installation of NB technology is quick and straightforward— a single NB generator unit can be installed within 2-3 hours without disrupting the overall system operation or needing to hire an external engineering firm. Moreover, according to the reports, the addition of NB technology to water and wastewater treatment processes enhanced DO levels and oxygen transfer while reducing BOD, total suspended solid (TSS), sludge, odor, bacteria, viruses, and algae levels in the treated waters. Nearly all cases also report a significant reduction in their annual energy consumption upon NB application, which increased their energy efficiency and annual energy savings.

As NB research is a nascent and expanding field, most fundamental studies are still conducted at the lab scale. Thus, field studies are primarily conducted by governmental agencies or the R&D departments at private companies, and as such, they provide limited information on operational parameters and conditions. The lack of comprehensive information makes it



difficult to make meaningful comparisons or draw definitive conclusions. Additionally, while comparisons between conventional and NB-assisted technology on their treatment performances are common in lab-scale studies, they are not well-documented in field testing (Kalogerakis et al., 2021). Therefore, suitable benchmarking should be performed with more field applications of NBs. Furthermore, the industrial applications of NB technology have mostly been limited to small-to-medium-sized operations, bodies of water, and treatment plants, rather than larger ones with much higher treatment loads. Further improvements in the capacity and efficiency of commercially available NB systems are required to enable their application to larger industrial processes and increase their market infiltration.

**Table 5.** Commercial applications of NBs in water and wastewater treatment industry.

Application/ Purpose	No.	Location	Generator Type	Conditions	Key Outcomes	Ref.
<b>NB assisted-dissolved air flotation</b>	1	Wastewater treatment facility at a plastics recycler, 7 Chino, California (USA)	50 XTB nanobubble generator; Moleaer Inc., USA	Treatment capacity: 10,000 gallons Bubble rise rates: 8-12 inches/min Pump power: 2 HP NB type: Air NBs	<u>Economic/energy savings:</u> Estimated annual energy savings of over \$8,500 ~90 % projected yearly savings of the centrifugal recirculating pump's maintenance and repair costs 87% reduction in power consumption	(Moleaer, 2017f)
	2	Wastewater treatment facility at F&A Dairy Products, Inc.	200 XTB nanobubble generator; Moleaer Inc., USA	Treatment capacity: 10,000 gallons Flow rates: 187,000 gallons per day (GPD) NB type: Air NBs	<u>Treatment performance:</u> 89.6% reduction in BOD5; 99.7% reduction in TSS <u>Economic/energy savings:</u> Energy usage from 275kw per day to 91kw Projected annual energy savings of over \$6,000	(Moleaer, 2017a)
	3	Wastewater treatment facility at Hershey's Creamery Company, USA	100 GPM nanobubble generator; Moleaer Inc., USA	Pump power: 3 HP NB type: Air NBs	<u>Treatment performance:</u> 37% reduction in BOD; 24% increase in TSS removal 70% reduction in HP; more uniform and smaller float sludge <u>Economic/energy savings:</u> ~\$100,000 projected yearly savings	(Moleaer, 2017d)
	4	Wastewater treatment facility at a meat processing plant, NSW, Australia	NBT's nanobubble generator; Nano Bubble Technologies (NBT), Australia	Treatment Capacity: >9kL/hr/day NB type: Air NBs	<u>Treatment performance:</u> Tripled dissolved air flotation (DAF) handling capacity Almost 4 times greater BOD removal in kg/hr More than 80% removal of TSS & Visibly better overall wastewater clarity <u>Economic/energy savings:</u> Up to 70% reduction in energy consumption	(NanobubbleTech nologies)

Application/ Purpose	No.	Location	Generator Type	Conditions	Key Outcomes	Ref.
NB assisted- dissolved air flotation	5	TerraHydroChem, New Braunfels, Texas, USA	200 XTB nanobubble generator; Moleaer Inc., USA	Treatment capacity: 2 million gallons NB gas type: O <sub>2</sub> NBs	<p><u>Treatment performance:</u> Increased DO levels to an unprecedented level of 5ppm for such oily wastewater</p> <p><u>Economic/energy savings:</u> Eliminate the need for additional horsepower (HP) to the system (traditional methods typically require the addition of at least a 25 HP blower)</p> <p>Reduced operational costs</p>	(Moleaer, 2017b)
	6	Dissolved air flotation system at a meat rendering plant, New Zealand	25 GPM nanobubble generator; Moleaer Inc., USA	NB gas type: Air NBs	<p><u>Treatment performance:</u> 71% oil &amp; grease reduction (90% improvement)</p> <p>30% reduction in BOD</p> <p>60% increase in TSS removal</p> <p>Thicker and more uniform sludge</p>	(Moleaer, 2017g)
	7	Wastewater treatment facility at Scheid Vineyards, USA	ClearBlu ultrafine bubble aerator; ClearBlu, USA	Flow rates: 110,000 GPD Treatment capacity: 2.36M gallons; 2.09M gallons, and 1.1M gallons. NB gas type: O <sub>2</sub> NBs	<p><u>Treatment performance:</u> Reduction in BOD levels</p> <p>30-40% sludge reduction</p> <p><u>Economic/energy savings:</u> Reduction in energy consumption by 326,268 kWh/yr Estimated annual savings of \$39,152</p>	(ClearBlu Environmental, 2010)
NB aeration	8	Wastewater treatment facility at a meat processing plant, Idaho, USA	200 XTB OPB nanobubble generator with centrifugal pump; Moleaer Inc., USA	Treatment capacity: 10,000 gallons feed EQ tanks; 10,000 gallons each in 4 aeration tanks; 10,000 gallons to DAF Flow rates: 20,000 GPD Retention time: 3 days NBs type: Air NBs	<p><u>Economic/energy savings:</u> 66% absolute energy reduction for the plant;</p> <p>Enhanced the removal of suspended solids and insoluble BOD from the wastewater</p>	(Moleaer, 2017e)

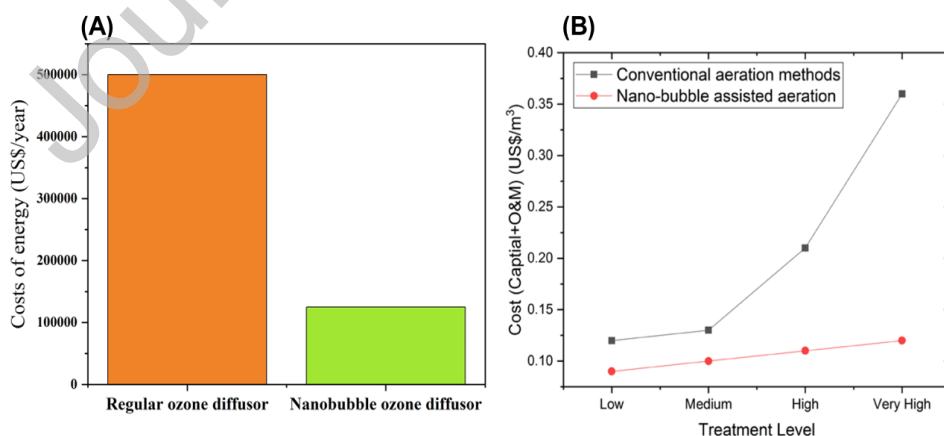
Application/ Purpose	No.	Location	Generator Type	Conditions	Key Outcomes	Ref.
	9	Golf Course Lake, Bonita Springs, Florida	200 GPM nanobubble generator; Moleaer Inc., USA	Water body size: 1.3-acre lake	<u>Treatment performance:</u> Increased DO levels by over 50%	(SolimudLake Management, 2019)
<b>NB aeration</b>	10	Fallbrook Public Utility District (FPUD) Wastewater Treatment Plant, California, USA	1800 GPM mobile nanobubble generator; Moleaer Inc., USA	Flow rates: 2,700,000 GPD Gas type: Air	<u>Treatment performance:</u> Upstream application of nanobubble generator in primary clarifiers Treated 1.4 MGD of wastewater; 60% more oxygen transferred <u>Economic/energy savings:</u> 45% potential energy savings	(Moleaer, 2021b)
<b>NBs aeration for Odor control</b>	11	Wastewater treatment facility at the Zirku Island, Abu Dhabi, UAE	XTB nanobubble generator; Moleaer Inc., USA	Treatment capacity: 1,717,000 gallons Flow rates: 1,585,000 GPD Retention time: 24hr	<u>Treatment performance:</u> DO levels rose to 7.0 ppm; more than 4x greater than normal pond conditions; BOD decreased from 110 mg/l to 45 mg/l; foul odors started to abate	(Moleaer, 2018b)
	12	Poriya Reservoir, Israel	Nanobubble Ozone system; Filtoflex	Water body size: 35 dunams Volume: 135,000 cubic meters Depth: 4 meters in average	<u>Treatment performance:</u> In 3 days, a separation of surfactants and lipids was observed In a week, the DO level was raised from 1.5ppm to 3.5ppm	(Filtoflex, 2022a)
<b>NB aeration in aerobic digestion</b>	13	Nevada Municipal Wastewater Treatment Plant, USA	200 XTB nanobubble generator; Moleaer Inc., USA	Treatment capacity: 772,000 gallons Flow rates: 650,000 GPD Pump power: 5HP; NB type: Air NBs	<u>Treatment performance:</u> Up to an 8-fold increase in DO levels than the normal range during aerobic digestion process	(Moleaer, 2018a)
					<u>Treatment performance:</u>	
<b>NB aeration in oxidation ditch</b>	14	3-ring oxidation ditch system in the Village of Warrens, Wisconsin, USA	200 XTB nanobubble generator with submersible pump; Moleaer Inc., USA	Treatment capacity: 207,000 gallons Flow rates: 209,000 GPD NB type: O <sub>2</sub> NBs	Outer ditch Middle ditch Center ditch	DO levels before XTB DO levels after XTB
					0.11 ppm 1.2 ppm 4 ppm	3.6 ppm 7 ppm 10 ppm
						(Moleaer, 2017c)

Application/ Purpose	No.	Location	Generator Type	Conditions	Key Outcomes	Ref.
<b>NB aeration in membrane bioreactor</b>	15	Wastewater treatment facility at Beer Republican Brewing Company, USA	2 x 200 GPM nanobubble generator; Moleaer Inc., USA	Treatment capacity: 36,000 gallons NB gas type: O <sub>2</sub> NBs	<p><u>Treatment performance:</u> Enhanced DO levels and oxygen transfer Increased BOD treatment capacity by more than 35%</p> <p><u>Economic/energy savings:</u> Reduced chemical (chemical defoamer) costs</p>	(Moleaer, 2021a)
<b>Irrigation water disinfection</b>	16	Water well at Rusgenot Farm, Pearl, South Africa	MK3 Ultra-fine bubble generator with ozone; Fine Bubble Technologies, South Africa	NB gas type: O <sub>3</sub> NBs	<p><u>Treatment performance:</u> Iron (Fe): within legal limits Faecal coliforms: 0 CFU 100% removal of bacteria, algae, amoeba, fungus &amp; virus Removed heavy metals, pesticides, and any bad taste and odor</p> <p><u>Economic/energy savings:</u> 90% reduction in operational and maintenance costs 100% chemical-free treatment</p>	(Kaloger akis et al., 2021)
<b>Drinking water disinfection</b>	17	Seaple water utility company, Puerto Vallarta, Mexico	Nanobubble Ozone system, Fitoflex	Flow rates: 40L/s NB types: O <sub>3</sub> NBs	<p><u>Treatment performance:</u> Reduce the iron and manganese from 5ppm and 5NTU to 0.3ppm and 0.45 NTU</p>	(Fitofle, 2022b)
<b>NBs for eco- restoration</b>	18	Xavage Water Park at Xcaret, a resort in Playa del Carmen, Mexico	2 x 200 GPM nanobubble generator; Moleaer Inc., USA	Water body size: 9.25 million gallons	<p><u>Treatment performance:</u> Increased DO levels; Eliminated odor Significantly improved water clarity and color Improved water clarity and quality</p> <p><u>Economic/energy savings:</u> Reduced chemical costs</p>	(Moleaer, 2019b)
Application/	No.	Location	Generator Type	Conditions	Key Outcomes	Ref.

Purpose						
19	Lakes and ponds at the Las Lomas golf club, Mexico	200 GPM nanobubble generator; Moleaer Inc., USA		Capacity: 264,000 gallons every 24hr NB water type: O <sub>2</sub> NBs	<u>Treatment performance:</u> Increased DO by 770% over 6 days Improved water clarity and quality <u>Economic energy savings:</u> Eliminated the need for chemical treatments	(Moleaer, 2019a)
20	Guruvayur temple pond, Kerala, India	Nanobubble system of Accelerated Cleaning systems Private limited, Mumbai, India	Pond size: 61 m × 60 m × 6 m NB gas types: O <sub>2</sub> NBs Ozone dosage: 1.0mg/L Time of treatment: 30days	<u>Treatment performance:</u> 91% reduction in BOD 89% reduction in TSS 82% reduction in turbidity 42% increment in DO level	(Pal et al., 2022)	
				<u>Treatment performance:</u> Increased DO level Removed unpleasant odor Restored water clarity from less than 0.3 m visibility to over 1 m visibility over 60 days Reduced harmful bacteria (Faecal coliforms and <i>E.coli</i> ) Restored natural balance of the pond		
21	Irrigation ponds at the Westlake Golf Club, South Africa	MK1 Bubble Africa	NanoBubbler; Fine South	Pond size: 2,640,000 gallons. NB gas types: O <sub>2</sub> NBs	<u>Treatment performance:</u> Increased DO level Removed unpleasant odor Restored water clarity from less than 0.3 m visibility to over 1 m visibility over 60 days Reduced harmful bacteria (Faecal coliforms and <i>E.coli</i> ) Restored natural balance of the pond	(Kalogerakis et al., 2021)

## 5. Preliminary assessment of NB technology's economic viability and potential for carbon mitigation over conventional DAF

The industrial case studies mentioned in Section 4.5 have demonstrated NB generators as highly efficient supplemental systems with the potential for cost-effectiveness that can be retrofitted into a wide range of water treatment processes, with nearly all stated case studies reporting higher performance efficiencies and significant reductions in annual energy consumption upon integrating NB technology. Although these case studies provide deeper insights into the technical performance of NB, they lack an understanding of economic viability and environmental sustainability, which are essential for determining whether NB technology is a viable and sustainable option for process integration option in water and wastewater treatment processes. In this regard, a couple of recent studies have conducted brief economic analyses on NB-assisted aeration and NB-assisted ozonation processes, which have shown that using NB-assisted processes is advantageous in reducing energy consumption and costs (Figure 13). However, their economic assessments lack comprehensiveness in the sense that they do not provide detailed data or only include simple cost components.



*Figure 13. Existing economic analyses on NB-assisted treatment processes. (A) Comparison between regular and nanobubble ozone diffusers on their yearly energy costs in a typical water plant. Adopted from Batagoda et al. (2019). (B) Comparison between conventional and nanobubble-assisted aeration in terms of their capital, operational and management costs at different treatment levels (English, 2022).*

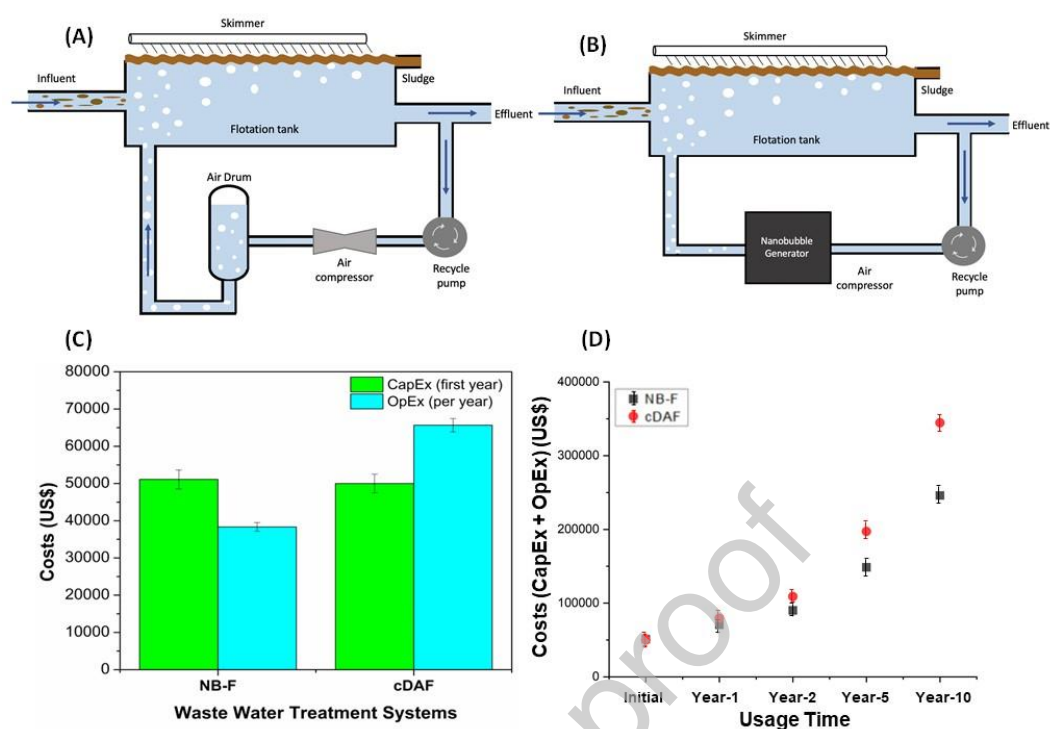
Thus, to better understand the feasibility of integrating NB technology with existing industrial-scale water treatment systems, a preliminary investigation on the economic and environmental aspects of NB-flotation (NB-F), which is one of the most frequently proposed NB-based water treatment systems based on our bibliometric analysis (**Figure 1(C)**), was performed by estimating cost parameters, energy requirements, and carbon mitigation potential through electricity reduction, and the results were compared with cDAF system (**Figure 14(A, B)**). For an accurate and fair comparison, the treatment capacity of NB-F and cDAF were both assumed to be 3000 m<sup>3</sup>/d and the influent and effluent quality were assumed to be the same for both techniques. Both systems involve two processes, pre-treatment and floatation, and the electricity consumption during these two processes was based on Hong Kong's electric grid.

Estimations of water treatment costs and the carbon mitigation potential are two important indicators that can provide sensible insights into NB technology's viability and sustainability. While capital expenditure (CapEx), which is the cost input during the implementation phase, accounts for a significant part of the overall cost of producing water in water treatment systems, the expenditure for operation and maintenance (OpEx) (e.g., energy, chemicals, and other materials) and the associated carbon dioxide (CO<sub>2</sub>) release are critical for determining viability and sustainability. For instance, the energy requirements associated with bubbling and aeration systems can be high in cDAF; as a result, there is a chance that the system is less sustainable from an energy consumption point of view if the energy is mainly supplied from



fossil fuels or a grid energy mix that is dominated with fossil fuels. In this case, the treatment process can be made more sustainable by adopting a new technology to improve the energy efficiency or changing the energy source to renewables. The application of NBs pertain to the former, in which the unique properties of NBs, especially their long retention time, helps reduce the overall consumption of energy significantly compared to traditional macro-bubbles aeration systems.

The estimated cost parameters of the NB-F and cDAF treatment plants are given in **Figure 14(C)**, including CapEx, OpEx, and replacement costs (i.e., costs for replacing equipment and parts, etc., during the use phase of the plant subject to repair and maintenance conditions) assumed at 10% CapEx. The data on operational expenses, such as electricity consumption and price and chemical requirements, were collected from manufacturers, published literature, and suppliers (e.g., Alibaba). The details of these cost parameters are given in **Table SI.3.1**. Our assessment shows that the CapEx of the NB-F system is slightly higher than the cDAF system, primarily due to the price difference of the air saturator component (while the other parts of the system remain the same). On the other hand, NB-F's OpEx is 20% lower than cDAF; this lower cost is directly related to the unique properties of NBs, particularly those that allow a single generation event to produce millions of NBs that stay in suspension for an extended time. Thus, NB-F does not need to supply bubbles as often as cDAF, which translates into less energy consumption. Moreover, the small size of NBs and their high efficiency, both in floating particles irrespective of size and in acting as a carrier for pollutants and flocs, reduces the need for chemicals (i.e., use of coagulants).

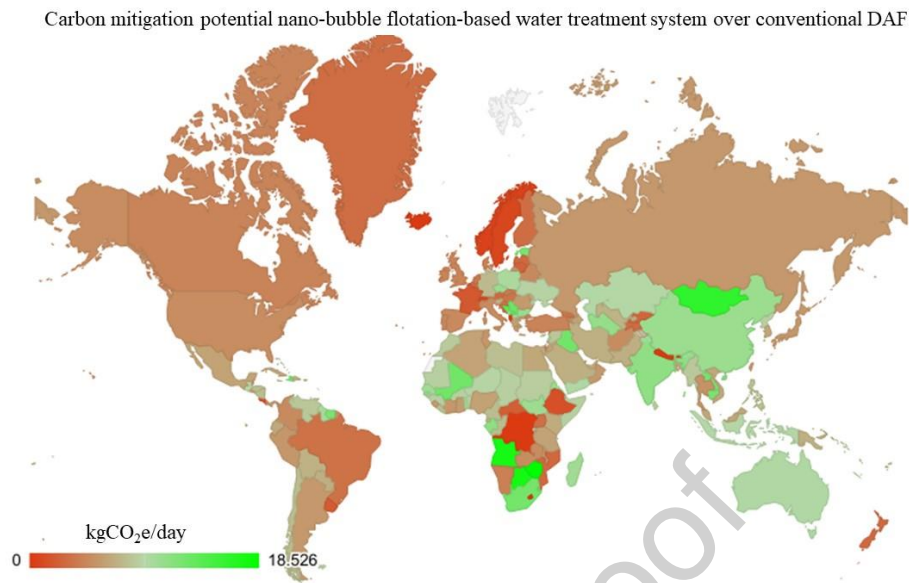


**Figure 14.** Schematic representation of the water treatment systems. (A) Conventional dissolved air flotation (cDAF) and (B) NB-based flotation (NB-F). (Adopted from MOLEAER White Paper). (C) Estimated first-year CapEx or initial investment and OpEx (per year) for the cDAF and NB-F systems. (D) The estimated total costs for operating the NB-F and cDAF systems over a 10-year period.

The advantage of the NB-F system's lower OpEx becomes more apparent in industrial-scale implementations and over the lifetime of the treatment plant. **Figure 14(D)** compares the estimated total costs of NB-F and cDAF over a ten-year period. The result shows that NB-F has a slightly higher cost (2% more) at the initial phase compared to cDAF; however, the costs of electricity and pre-treatment is vastly reduced due to NB-F's higher energy efficiency and lower chemical requirements during operation. As a result, compared to cDAF, NB-F's overall cost, including both CapEx and OpEx, becomes increasingly lower over time. After one year of implementation, the overall cost of cDAF is 13% higher than NB-F, while

the cost difference further increases to 40% after ten years, demonstrating the cost-effectiveness of NB technology integration. A detailed comparison of the unit annualized water treatment costs of NB-F and cDAF under varying interest rates that also consider the effects of water treatment levels and salvage costs also suggests NB-F to be viable in the long run, the details of which is provided as **Figure SI.3.1**.

Besides the economic viability, the assessment of carbon mitigation potential, which was performed using the methodology shown in the Supplementary Information (see **SI 3.2**), indicated that the integration of NB technology has a higher potential for carbon mitigation mainly due to the improvements it brings in the overall system's energy efficiency. For the Hong Kong region, the carbon mitigation potential of NB-F was observed to be ~51% with the present energy mix scenario. Considering this huge potential for CO<sub>2</sub> reduction, along with the cost-effectiveness of NBs in the long run, transitioning from cDAF to NB-F is a smart strategy for Hong Kong. Although our assessments were specific to Hong Kong, we expect that the transition from cDAF to NB-F across the nations would lower CO<sub>2</sub> emissions greatly worldwide. **Figure 15** presents the use-phase carbon mitigation potential if existing cDAF systems are globally replaced with NB-F. Green gradient colors indicate a higher potential for CO<sub>2</sub> reduction if using energy-efficient NB-F over cDAF. Notably, countries with a fossil fuel-dominant energy mix show the greatest potential to benefit from this transition. By continent, these countries include Mongolia, China (including special administrative territories), and India in Asia; Angola, Botswana, Zimbabwe, South Africa, and Mauritania in Africa continent; the United States, Canada, Guinea, and Suriname in the Americas; Bulgaria and Serbia in Europe; and Australia and New Zealand in Oceania. For these countries, transitioning from cDAF to NB-F is a highly viable and sustainable option from both cost and CO<sub>2</sub> reduction perspectives.



**Figure 15.** Use-phase carbon mitigation potential if existing cDAF systems are globally replaced with NB-F. The countries with green gradient colors indicate higher potential for carbon dioxide reduction if using energy-efficient NB-F over cDAF.

## 6. Outlook

### 6.1 Limitations and controversies in existing NB research

Despite the substantial research conducted so far on NBs, there remains many controversies and disagreements on their existence, properties, and effectiveness that need to be addressed before widespread industrial implementations of NB technology can be realized. The main disagreement over the existence of NBs centers on the contradictions between theoretical explanations and experimental observations. On the one hand, there have been a plethora of works on generating and observing stable and long-lasting NBs (Etchepare et al., 2017b; Farid et al., 2022a; Farid et al., 2022b), which have established the existence of NBs beyond question. On the other hand, the theoretical predictions of different models, such as the Epstein and Plesset's theory of bubble dissolution and growth and the Laplace Pressure Bubble Catastrophe, deny the existence of NBs, saying that they can only have a very short

lifetime ( $<0.02$  s) as a result of their small size or their rapid dissolution into the solution due to high Laplace pressure (Agarwal et al., 2011; Alheshibri et al., 2016; Epstein and Plesset, 1950; Ljunggren and Eriksson, 1997; Pyrgiotakis et al., 2014). However, it is worth noting that these models are best applied for larger MaBs, rather than NBs with their own unique properties. For instance, the electrostatic repulsion between two similarly charged bubbles prevent the coalescence of NBs, while the Brownian motion governing NBs' movements prevent their quick rise (Alheshibri et al., 2016), thus explaining their still and stable motion. New models need to be developed to align theory with the experimental observations and better define the existence and stability of NBs.

Another long-debated NB-related issue is the generation of free radicals, particularly ROS, which have been actively discussed in the field of water treatment as having great potential for replacing currently-used chemical, toxic, and energy-intensive methods for pathogen inactivation and pollutant removal and oxidation (Atkinson et al., 2019). While various studies have reported the presence of ROS (as described in Sections 3 and 5), there remain disagreements on how these free radicals are produced: whether they are associated with NB generation methods (e.g., hydrodynamic cavitation) or due to NBs' collapse. For instance, despite having very short lifetimes (e.g.,  $1 \times 10^{-9}$  s in the case of  $\bullet\text{OH}$ ), Liu et al. (2010) reported a continuous detection of ROS in NB water amid decreases in DO and NB concentration over time. Accordingly, they hypothesize that the disappearance of NBs (i.e., their collapse) causes the constant production of ROS in water. Under fluorescence microscopy, Jin et al. (2020) observed that  $\bullet\text{OH}$  radicals were mainly generated at the edges of NBs and thus concluded that  $\bullet\text{OH}$  radicals are produced when NBs collapse. However, Yasui et al. (2018) performed numerical simulations of the dissolution of air NBs into liquid water and concluded that no  $\bullet\text{OH}$  radicals are produced from dissolving NBs. Instead, they suggested that the experimentally detected signals originated from the  $\text{H}_2\text{O}_2$  produced during

the generation of bulk NBs (i.e., via hydrodynamic cavitation) and not from  $\bullet\text{OH}$  radicals. Later, Yasui et al. (2019) conducted another simulation on  $\text{O}_2$  NBs dissolution and estimated that although a few  $\bullet\text{OH}$  radical molecules could be produced by dissolving  $10^7$   $\text{O}_2$  NBs without dynamic stimuli, the productivity is still 13 magnitudes smaller than the productivity experimentally reported by Liu et al. (2016). Systematic studies are needed to evaluate the production of free radicals with different generation methods and the effect of used gas and other operational parameters. Additionally, continuous ROS measurement should be performed during NB-integrated operations.

Inconsistencies among the reports on NBs' fundamental aspects and characteristics present yet another limitation. Various methods have been used for generating NBs, but limited research has been done on how different methods and operational conditions lead to variations and sometimes contradictions in reported literature. For instance, improved treatment efficiencies after NB application are mainly attributed to the bubbles' sizes and concentrations; yet, the previously reported findings are heterogenous and inconsistent. Reports also vary regarding NBs' zeta potential, which is another important property that explains NBs' advantages based on bubble-pollutant charge attraction/repulsion, with significant inconsistencies in their values and point of zero charges. Additionally, although most NB generators generate heat, few studies have reported the effect of temperature on NBs' stability and characteristics despite the considerable impact it may have on the physical and chemical properties and stability of different matters and media.

Moreover, the underlying mechanisms of how NBs enhance water treatment processes remain largely unknown. Most studies have inferred possible mechanisms from similar phenomena observed using other techniques, such as improved flow hydrodynamics and electrostatic attractions, but they have not confirmed whether those mechanisms are truly at work through explicit characterizations or experimental testing.

## 6.2 Outlook on future research

The growing knowledge on the unique properties of NBs accumulated over the past decades has set high expectations for this promising technology to achieve remarkable improvements in reducing byproducts and achieving safer production of water in water treatment processes (Atkinson et al., 2019). Still, the application of NB technology in water treatment is relatively at an early stage of development. As emphasized already, despite the growing recognition of NBs' potential, most of the available research on NBs has been limited to lab-scale testing, which can sometimes be impractical and require theoretical assumptions for drawing conclusions. Testing these systems at pilot and full-scale levels is necessary to provide a realistic view of NBs' potential at the industrial scale and deal the associated upscaling issues. In addition, as explained so far, a number of aspects need to be addressed before the practical implementation of NBs can be realized. The existence and stability of NBs and the inconsistencies in the reported findings on NBs' fundamental aspects need to be verified through the development of new models that can explain experimental observations. NBs' generation of ROS and the relationship between the NB generation technique and the free radicals produced as a result may be studied through the live monitoring of free radicals' levels with continuous measurements of NBs' sizes and concentrations. The unique properties of NBs and their interactions with liquids should be characterized beyond the primarily studied attributes of size, concentration, and mass transfer. For example, heat transfer, viscosity, and hydraulic conductivity are essential characteristics that can affect performance and play a crucial role in pollution control (Haris et al., 2020). The inconsistencies in the reported features of NBs due to the employment of different characterization techniques and the absence of a controlled environment show the need for universal tools that can accurately and consistently provide reliable characterizations.

Furthermore, experimental proof of the mechanisms behind the improved water treatment efficiency of NBs-assisted systems is essential for promoting their greater application.

Another area demanding the attention of future research is the ability of NBs to enhance the removal or degradation efficiency of organic micropollutants (MPs), including pharmaceutical active compounds (PhACs), personal care products (PCPs), and endocrine disrupting chemicals (EDCs). Several studies have shown the beneficial effects of NBs on the removal of several pollutants from water and wastewater, such as organics and inorganics (Cheng et al., 2018; Menendez and Valverde Flores, 2018; Xia and Hu, 2018), bacteria and fungi (Cruz and Valverde Flores, 2017; Reyes and Valverde Flores, 2017), total phosphorous and total nitrogen (Wang and Zhang, 2017; Zhang et al., 2013), heavy metals (Garcia and Valverde Flores, 2017; Vicente and Valverde Flores, 2018), dye and color (Zhang et al., 2018), and oil (R. Etchepare et al., 2017; Li et al., 2016; Liu et al., 2010). However, other persistent pollutants that hold potential risk and toxicity to humans, such as organic MPs and other hazardous heavy metals, should also be explored (Sakr et al., 2022).

Meanwhile, most of the published studies have tested NBs in distilled or synthetic waters, thus pointing to the need to perform tests with natural water/wastewater to understand how their diverse constituents, such as organics, salts, suspended solids, nutrients, and other contaminants, affect the NBs' characteristics and manipulate their interactions. Differentiating these constituents from NBs will become trickier, which may affect the ability to measure NBs' different characteristics accurately. Thus, upgraded characterization techniques should be considered to deal with these complexities.

Lastly, the economic feasibility and environmental aspects of NB applications in different water treatment areas also require address by future research. Despite their numerous advantages in achieving improved water treatment efficiencies, it will not be possible to adopt NBs quickly for industrial implementations if they come with a high price tag. While



some reports claim that employing NBs leads to lower costs compared to other conventional techniques (Rizaldi et al., 2019), there still lacks a detailed study that thoroughly investigates the various cost-determining factors. In this regard, this review has initiated the roadmap by providing a preliminary assessment of the viability and sustainability of a typical NB-assisted process (i.e., NB-F), compared to a cDAF systems. A detailed cost-benefit analysis may provide a systematic quantification of total costs that compares the expected benefits of NB-assisted processes against traditional approaches and enable the determination of the best approach for achieve the desired performance at the minimal cost. Additionally, a life cycle analysis, including social and environmental aspects, should be considered to complement the cost-benefit analysis and provide a holistic view of NB technology's potential in the water industry.

### **Acknowledgements**

This work was supported by ECF - Environmental and Conservation Fund (05/2020), Marine Conservation Enhancement Fund (MCEF20017), and the Research Grants Council of the Hong Kong Special Administrative Region, China through (Project Nos. RFS2223-1S04, 11218122, and 11209421).

### **Conflict of interest**

The authors declare no competing financial interests.

### **References**

- Agarwal, K., Trivedi, M. and Nirmalkar, N. 2022. Does salting-out effect nucleate nanobubbles in water: Spontaneous nucleation? *Ultrason Sonochem* 82, 105869.
- Ahmed, A., Shi, X.N., Zhang, W. and Marhaba, T. 2018a. Influences of air, oxygen, nitrogen, and carbon dioxide nanobubbles on seeds germination and plants growth. *Abstr Pap Am Chem S* 256.
- Ahmed, A.K.A., Sun, C.Z., Hua, L.K., Zhang, Z.B., Zhang, Y.H., Marhaba, T. and Zhang, W. 2018b. Colloidal Properties of Air, Oxygen, and Nitrogen Nanobubbles in Water: Effects of Ionic Strength, Natural Organic Matters, and Surfactants. *Environ Eng Sci* 35(7), 720-727.
- Alheshibri, M. and Craig, V.S. 2019. Armoured nanobubbles; ultrasound contrast agents under pressure. *J Colloid Interf Sci* 537, 123-131.

- Alheshibri, M., Qian, J., Jehannin, M. and Craig, V.S.J. 2016. A History of Nanobubbles. *Langmuir* 32(43), 11086-11100.
- Atkinson, A.J., Apul, O.G., Schneider, O., Garcia-Segura, S. and Westerhoff, P. 2019. Nanobubble Technologies Offer Opportunities To Improve Water Treatment. *Accounts Chem Res* 52(5), 1196-1205.
- Batagoda, J.H., Hewage, S.D.A. and Meegoda, J.N. 2019. Nano-ozone bubbles for drinking water treatment. *J Environ Eng Sci* 14(2), 57-66.
- Chen, B., Zhou, S.N., Zhang, N., Liang, H.Y., Sun, L.P., Zhao, X., Guo, J.Y. and Lu, H. 2022. Micro and nano bubbles promoted biofilm formation with strengthen of COD and TN removal synchronously in a blackened and odorous water. *Sci Total Environ* 837.
- Chen, K.Y., Zhang, X.B. and Li, J. 2016. Advanced treatment of oilfield production wastewater by an integration of coagulation/flotation, catalytic ozonation and biological processes. *Environ Technol* 37(19), 2536-2544.
- Chipakwe, V., Jolstera, R. and Chelgani, S.C. 2021. Nanobubble-Assisted Flotation of Apatite Tailings: Insights on Beneficiation Options. *Acs Omega* 6(21), 13888-13894.
- Chuenchart, W., Karki, R., Shitanaka, T., Marcelino, K.R., Lu, H. and Khanal, S.K. 2021. Nanobubble technology in anaerobic digestion: A review. *Bioresource Technol* 329.
- ClearBluEnvironmental 2010 Wastewater treatment-Scheid Vineyards.
- Dayarathne, H.N.P., Choi, J. and Jang, A. 2017. Enhancement of cleaning-in-place (CIP) of a reverse osmosis desalination process with air micro-nano bubbles. *Desalination* 422, 1-4.
- Dayarathne, H.N.P., Jeong, S. and Jang, A. 2019. Chemical-free scale inhibition method for seawater reverse osmosis membrane process: Air micro-nano bubbles. *Desalination* 461, 1-9.
- Demangeat, J.-L. 2015. Gas nanobubbles and aqueous nanostructures: the crucial role of dynamization. *Homeopathy* 104(2), 101-115.
- Eklund, F., Alheshibri, M. and Swenson, J. 2021. Differentiating bulk nanobubbles from nanodroplets and nanoparticles. *Curr Opin Colloid In* 53.
- Eklund, F. and Swenson, J. 2018. Stable Air Nanobubbles in Water: the Importance of Organic Contaminants. *Langmuir* 34(37), 11003-11009.
- English, N.J. 2022. Environmental Exploration of Ultra-Dense Nanobubbles: Rethinking Sustainability. *Environments* 9(3).
- Etchepare, R., Azevedo, A., Calgaroto, S. and Rubio, J. 2017a. Removal of ferric hydroxide by flotation with micro and nanobubbles. *Sep Purif Technol* 184, 347-353.
- Etchepare, R., Oliveira, H., Nicknig, M., Azevedo, A. and Rubio, J. 2017b. Nanobubbles: Generation using a multiphase pump, properties and features in flotation. *Miner Eng* 112, 19-26.
- Fan, W., An, W.G., Huo, M.X., Xiao, D., Lyu, T. and Cui, J.Y. 2021a. An integrated approach using ozone nanobubble and cyclodextrin inclusion complexation to enhance the removal of micropollutants. *Water Research* 196.
- Fan, W., Li, Y.H., Wang, C.L., Duan, Y.T., Huo, Y., Januszewski, B., Sun, M., Huo, M.X. and Elimelech, M. 2021b. Enhanced Photocatalytic Water Decontamination by Micro-Nano Bubbles: Measurements and Mechanisms. *Environmental Science & Technology* 55(10), 7025-7033.
- Farid, M.U., Choi, P.J., Kharraz, J.A., Lao, J.Y., St-Hilaire, S., Ruan, Y., Lam, P.K.S. and An, A.K. 2022a. Hybrid nanobubble-forward osmosis system for aquaculture wastewater treatment and rescue. *Chem Eng J* 435, 135164.
- Farid, M.U., Khanzada, N.K. and An, A.K. 2019. Understanding fouling dynamics on functionalized CNT-based membranes: Mechanisms and reversibility. *Desalination*

- 456, 74-84.
- Farid, M.U., Kharraz, J.A., Lee, C.H., Fang, J.K., St-Hilaire, S. and An, A.K. 2021. Nanobubble-assisted scaling inhibition in membrane distillation for the treatment of high-salinity brine. *Water Res* 209, 117954.
- Farid, M.U., Kharraz, J.A., Lee, C.H., Fang, J.K.H., St-Hilaire, S. and An, A.K. 2022b. Nanobubble-assisted scaling inhibition in membrane distillation for the treatment of high-salinity brine. *Water Research* 209.
- Farrokhpay, S., Filippov, L. and Fornasiero, D. 2021. Flotation of Fine Particles: A Review. *Min Proc Ext Met Rev* 42(7), 473-483.
- Ferraro, G., Jadhav, A.J. and Barigou, M. 2020. A Henry's law method for generating bulk nanobubbles. *Nanoscale* 12(29), 15869-15879.
- Filtofle 2022a Case study at Poriya Reservoir, <https://filtoflex.com/case-study/poriya-reservoir/>.
- Filtofle 2022b Case study in Seaple, Puerto Vallarta, Mexico, <https://filtoflex.com/case-study/seaple-puerto-vallarta-mexico/>.
- Gao, Z., Wu, W.X., Sun, W.T. and Wang, B. 2021. Understanding the Stabilization of a Bulk Nanobubble: A Molecular Dynamics Analysis. *Langmuir* 37(38), 11281-11291.
- Ghaani, M.R., Kusalik, P.G. and English, N.J. 2020. Massive generation of metastable bulk nanobubbles in water by external electric fields. *Sci Adv* 6(14).
- Guo, H., Oosterkamp, M.J., Tonin, F., Hendriks, A., Nair, R., van Lier, J.B. and de Kreuk, M. 2021. Reconsidering hydrolysis kinetics for anaerobic digestion of waste activated sludge applying cascade reactors with ultra-short residence times. *Water Research* 202, 117398.
- Guo, H., van Lier, J.B. and de Kreuk, M. 2020. Digestibility of waste aerobic granular sludge from a full-scale municipal wastewater treatment system. *Water research* 173, 115617.
- Hampton, M.A. and Nguyen, A.V. 2010. Nanobubbles and the nanobubble bridging capillary force. *Adv Colloid Interfac* 154(1-2), 30-55.
- Haris, S., Qiu, X.B., Klammler, H. and Mohamed, M.M.A. 2020. The use of micro-nano bubbles in groundwater remediation: A comprehensive review. *Groundwater Sust Dev* 11.
- Hernandez, C., Abenojar, E.C., Hadley, J., Coyne, R., Perera, R., Gopalakrishnan, R., Basilion, J.P., Kolios, M.C. and Exner, A.A. 2019. Sink or float? Characterization of shell-stabilized bulk nanobubbles using a resonant mass measurement technique. *Nanoscale* 11(3), 851-855.
- Hu, L.M. and Xia, Z.R. 2018. Application of ozone micro-nano-bubbles to groundwater remediation. *Journal of Hazardous Materials* 342, 446-453.
- ISO 2017 Fine bubble technology — General principles for usage and measurement of fine bubbles
- Jadhav, A.J. and Barigou, M. 2020. Bulk Nanobubbles or Not Nanobubbles: That is the Question. *Langmuir* 36(7), 1699-1708.
- Ji, X.N., Liu, C.B., Zhang, M.Y., Yin, Y.G. and Pan, G. 2020. Mitigation of methylmercury production in eutrophic waters by interfacial oxygen nanobubbles. *Water Research* 173.
- Jiang, X.Z., Wang, W., Yu, G. and Deng, S.B. 2021. Contribution of Nanobubbles for PFAS Adsorption on Graphene and OH- and NH<sub>2</sub>-Functionalized Graphene: Comparing Simulations with Experimental Results. *Environmental Science & Technology* 55(19), 13254-13263.
- Jin, J., Wang, R., Tang, J., Yang, L., Feng, Z.Q., Xu, C.X., Yang, F. and Gu, N. 2020. Dynamic tracking of bulk nanobubbles from microbubbles shrinkage to collapse.

- Colloid Surface A 589.
- Kalogerakis, N., Kalogerakis, G.C. and Botha, Q.P. 2021. Environmental applications of nanobubble technology: Field testing at industrial scale. *Can J Chem Eng* 99(11), 2345-2354.
- Kharraz, J.A., Farid, M.U., Jassby, D. and An, A.K. 2022a. A systematic study on the impact of feed composition and substrate wettability on wetting and fouling of omniphobic and janus membranes in membrane distillation. *Journal of Membrane Science* 641.
- Kharraz, J.A., Khanzada, N.K., Farid, M.U., Kim, J., Jeong, S. and An, A.K. 2022b. Membrane distillation bioreactor (MDBR) for wastewater treatment, water reuse, and resource recovery: A review. *J Water Process Eng* 47.
- Kim, S., Kim, H., Han, M. and Kim, T. 2019. Generation of sub-micron (nano) bubbles and characterization of their fundamental properties. *Environ Eng Res* 24(3), 382-388.
- Kim, T.K., Kim, T., Lee, I., Choi, K. and Zoh, K.D. 2021. Removal of tetramethylammonium hydroxide (TMAH) in semiconductor wastewater using the nano-ozone H<sub>2</sub>O<sub>2</sub> process. *Journal of Hazardous Materials* 409.
- Kyzas, G.Z., Bomis, G., Kosheleva, R.I., Efthimiadou, E.K., Favvas, E.P., Kostoglou, M. and Mitropoulos, A.C. 2019. Nanobubbles effect on heavy metal ions adsorption by activated carbon. *Chem Eng J* 356, 91-97.
- Kyzas, G.Z., Favvas, E.P., Kostoglou, M. and Mitropoulos, A.C. 2020. Effect of agitation on batch adsorption process facilitated by using nanobubbles. *Colloid Surface A* 607.
- Kyzas, G.Z., Mitropoulos, A.C. and Matis, K.A. 2021. From Microbubbles to Nanobubbles: Effect on Flotation. *Processes* 9(8).
- Lee, E.-J., An, A.K., Hadi, P. and Yan, D.Y. 2016. Characterizing flat sheet membrane resistance fraction of chemically enhanced backflush. *Chem Eng J* 284, 61-67.
- Lee, J. and Kim, J. 2022. Role of anionic surfactant in the generation of bulk nanobubbles by ultrasonication. *Colloid and Interface Science Communications* 46, 100578.
- Leroy, V. and Norisuye, T. 2016. Investigating the Existence of Bulk Nanobubbles with Ultrasound. *Chemphyschem* 17(18), 2787-2790.
- Li, M.B., Ma, X.T., Eisener, J., Pfeiffer, P., Ohl, C.D. and Sun, C. 2021a. How bulk nanobubbles are stable over a wide range of temperatures. *J Colloid Interf Sci* 596, 184-198.
- Li, T., Cui, Z., Sun, J., Jiang, C. and Li, G.Y. 2021b. Generation of Bulk Nanobubbles by Self-Developed Venturi-Type Circulation Hydrodynamic Cavitation Device. *Langmuir* 37(44), 12952-12960.
- Liu, S., Li, J.Y., Oshita, S., Kamruzzaman, M., Cui, M.M. and Fan, W.H. 2021. Formation of a Hydrogen Radical in Hydrogen Nanobubble Water and Its Effect on Copper Toxicity in *Chlorella*. *Acs Sustain Chem Eng* 9(33), 11100-11109.
- Liu, S., Oshita, S., Kawabata, S., Makino, Y. and Yoshimoto, T. 2016. Identification of ROS Produced by Nanobubbles and Their Positive and Negative Effects on Vegetable Seed Germination. *Langmuir* 32(43), 11295-11302.
- Liu, S., Oshita, S., Thuyet, D.Q., Saito, M. and Yoshimoto, T. 2018. Antioxidant Activity of Hydrogen Nanobubbles in Water with Different Reactive Oxygen Species both in Vivo and in Vitro. *Langmuir* 34(39), 11878-11885.
- Liu, W., Lin, T., Zhang, X., Jiang, F.C., Yan, X.S. and Chen, H. 2022. Adsorption of perfluoroalkyl acids on granular activated carbon supported chitosan: Role of nanobubbles. *Chemosphere* 309.
- Michailidi, E.D., Bomis, G., Varoutoglou, A., Kyzas, G.Z., Mitrikas, G., Mitropoulos, A.C., Efthimiadou, E.K. and Favvas, E.P. 2020. Bulk nanobubbles: Production and investigation of their formation/stability mechanism. *J Colloid Interf Sci* 564, 371-380.

- Moleaer 2017a F&A dairy upgrade daf with clean and efficient nanobubble generator. [www.moleaer.com](http://www.moleaer.com). Accessed on 3 July, 2023.
- Moleaer 2017b Moleaer 200 xtb lowers cost of treating oily wastewater. [www.moleaer.com](http://www.moleaer.com). Accessed on 3 July, 2023.
- Moleaer 2017c Moleaer boosts efficiency of municipal wastewater treatment system.
- Moleaer 2017d Moleaer boosts hershey creamery daf performance with nanobubble technology. [www.moleaer.com](http://www.moleaer.com). Accessed on 3 July, 2023.
- Moleaer 2017e Moleaer delivers exceptional cost savings to meat processing plant. [www.moleaer.com](http://www.moleaer.com). Accessed on 3 July, 2023.
- Moleaer 2017f Moleaer goes beyond typical aeration for dissolved air flotation systems. [www.moleaer.com](http://www.moleaer.com). Accessed on 3 July, 2023.
- Moleaer 2017g Moleaer improves dissolved air flotation performance at new zealand rendering plant. Accessed on 3 July, 2023.
- Moleaer 2018a Moleaer boosts dissolved oxygen levels at small municipal treatment system. [www.moleaer.com](http://www.moleaer.com). Accessed on 3 July, 2023.
- Moleaer 2018b Moleaer enhances and eliminates odors in lagoon-based treatment system. [www.moleaer.com](http://www.moleaer.com). Accessed on 3 July, 2023.
- Moleaer 2019a Mexican golf course improves water quality and clarity with Moleaer's innovative nanobubble solution. [www.moleaer.com](http://www.moleaer.com). Accessed on 3 July, 2023.
- Moleaer 2019b Water park solves algae issue with nanobubble technology. [www.moleaer.com](http://www.moleaer.com). Accessed on 3 July, 2023.
- Moleaer 2021a Moleaer enhances brewery membrane bioreactor system. [www.moleaer.com](http://www.moleaer.com). Accessed on 3 July, 2023.
- Moleaer 2021b Moleaer's nanobubbles improve wastewater treatment process performance. [www.moleaer.com](http://www.moleaer.com). Accessed on 3 July, 2023.
- Nam, G., Mohamed, M.M. and Jung, J. 2022. Novel treatment of *Microcystis aeruginosa* using chitosan-modified nanobubbles. *Environ Pollut* 292.
- NanobubbleTechnologies NBT's improvised DAF system, <https://www.nanobubble.com.au/case-study-daf/>. Accessed on 3 July, 2023.
- Nirmalkar, N., Pacek, A.W. and Barigou, M. 2018a. Interpreting the interfacial and colloidal stability of bulk nanobubbles. *Soft Matter* 14(47), 9643-9656.
- Nirmalkar, N., Pacek, A.W. and Barigou, M. 2018b. On the Existence and Stability of Bulk Nanobubbles. *Langmuir* 34(37), 10964-10973.
- Ohgaki, K., Khanh, N.Q., Joden, Y., Tsuji, A. and Nakagawa, T. 2010. Physicochemical approach to nanobubble solutions. *Chem Eng Sci* 65(3), 1296-1300.
- Pal, P., Joshi, A. and Anantharaman, H. 2022. Nanobubble ozonation for waterbody rejuvenation at different locations in India: A holistic and sustainable approach. *Results Eng* 16.
- Qaisrani, T.M. and Samhaber, W.M. 2011. Impact of gas bubbling and backflushing on fouling control and membrane cleaning. *Desalination* 266(1-3), 154-161.
- Qiu, J., Zou, Z.L., Wang, S., Wang, X.Y., Wang, L., Dong, Y.M., Zhao, H.W., Zhang, L.J. and Hu, J. 2017. Formation and Stability of Bulk Nanobubbles Generated by Ethanol-Water Exchange. *Chemphyschem* 18(10), 1345-1350.
- Rizaldi, M.I., Rahman, A., Deendarlianto, Prihantini, N.B. and Nasruddin 2019 Generation of microbubbles through single loop and double loop fluid oscillator for photobioreactor aeration, pp. 1446-1452.
- Rosa, A.F. and Rubio, J. 2018. On the role of nanobubbles in particle-bubble adhesion for the flotation of quartz and apatitic minerals. *Miner Eng* 127, 178-184.
- Sakr, M.A., Mohamed, M.M.A., Maraqa, M.A., Hamouda, M.A., Hassan, A.A., Ali, J. and

- Jung, J. 2022. A critical review of the recent developments in micro-nano bubbles applications for domestic and industrial wastewater treatment. *Alex Eng J* 61(8), 6591-6612.
- Satpute, P.A. and Earthman, J.C. 2021. Hydroxyl ion stabilization of bulk nanobubbles resulting from microbubble shrinkage. *J Colloid Interf Sci* 584, 449-455.
- Sedlak, M. and Rak, D. 2013. Large-Scale Inhomogeneities in Solutions of Low Molar Mass Compounds and Mixtures of Liquids: Supramolecular Structures or Nanobubbles? *J Phys Chem B* 117(8), 2495-2504.
- Shi, W.Q., Pan, G., Chen, Q.W., Song, L.R., Zhu, L. and Ji, X.N. 2018. Hypoxia Remediation and Methane Emission Manipulation Using Surface Oxygen Nanobubbles. *Environmental Science & Technology* 52(15), 8712-8717.
- Shi, X.N., Xue, S., Marhaba, T. and Zhang, W. 2021. Probing Internal Pressures and Long-Term Stability of Nanobubbles in Water. *Langmuir* 37(7), 2514-2522.
- Shin, D.H., Park, J.B., Kim, Y.J., Kim, S.J., Kang, J.H., Lee, B., Cho, S.P., Hong, B.H. and Novoselov, K.S. 2015. Growth dynamics and gas transport mechanism of nanobubbles in graphene liquid cells. *Nat Commun* 6.
- SolitudeLakeManagement 2019 Case Study: Nanobubbles Transform a Golf Course Lake in FL, <https://www.solitudelakemanagement.com/blog/case-study-nanobubble-aeration-florida-lake/>.
- Soyluoglu, M., Kim, D., Zaker, Y. and Karanfil, T. 2021. Stability of Oxygen Nanobubbles under Freshwater Conditions. *Water Res* 206, 117749.
- Soyluoglu, M., Kim, D., Zaker, Y. and Karanfil, T. 2022. Removal Mechanisms of Geosmin and MIB by Oxygen Nanobubbles during Water Treatment. *Chem Eng J*, 136535.
- Sun, J.Y., Liang, P., Yan, X.X., Zuo, K.C., Xiao, K., Xia, J.L., Qiu, Y., Wu, Q., Wu, S.J., Huang, X., Qi, M. and Wen, X.H. 2016. Reducing aeration energy consumption in a large-scale membrane bioreactor: Process simulation and engineering application. *Water Research* 93, 205-213.
- Takahashi, M., Shirai, Y. and Sugawa, S. 2021. Free-Radical Generation from Bulk Nanobubbles in Aqueous Electrolyte Solutions: ESR Spin-Trap Observation of Microbubble-Treated Water. *Langmuir* 37(16), 5005-5011.
- Tanaka, S., Naruse, Y., Terasaka, K. and Fujioka, S. 2020. Concentration and Dilution of Ultrafine Bubbles in Water. *Colloid Interfac* 4(4).
- Tang, Y., Zhang, M.Y., Zhang, J., Lyu, T., Cooper, M. and Pan, G. 2021. Reducing arsenic toxicity using the interfacial oxygen nanobubble technology for sediment remediation. *Water Research* 205.
- Thomas, B., Ohde, D., Matthes, S., Engelmann, C., Bubenheim, P., Terasaka, K., Schluter, M. and Liese, A. 2021. Comparative investigation of fine bubble and macrobubble aeration on gas utility and biotransformation productivity. *Biotechnol Bioeng* 118(1), 130-141.
- Tuziuti, T., Yasui, K. and Kanematsu, W. 2017. Influence of increase in static pressure on bulk nanobubbles. *Ultrason Sonochem* 38, 347-350.
- Ushikubo, F.Y., Furukawa, T., Nakagawa, R., Enari, M., Makino, Y., Kawagoe, Y., Shiina, T. and Oshita, S. 2010. Evidence of the existence and the stability of nano-bubbles in water. *Colloid Surface A* 361(1-3), 31-37.
- Wang, D., Yang, X.J., Tian, C.X., Lei, Z.F., Kobayashi, N., Kobayashi, M., Adachi, Y., Shimizu, K. and Zhang, Z.Y. 2019a. Characteristics of ultra-fine bubble water and its trials on enhanced methane production from waste activated sludge. *Bioresource Technol* 273, 63-69.
- Wang, H.N., Yang, W.Q., Yan, X.K., Wang, L.J., Wang, Y.T. and Zhang, H.J. 2020a. Regulation of bubble size in flotation: A review. *J Environ Chem Eng* 8(5).

- Wang, L., Ali, J., Wang, Z.B., Oladoja, N.A., Cheng, R., Zhang, C.B., Mailhot, G. and Pan, G. 2020b. Oxygen nanobubbles enhanced photodegradation of oxytetracycline under visible light: Synergistic effect and mechanism. *Chem Eng J* 388.
- Wang, Q.Z., Zhao, H., Qi, N., Qin, Y., Zhang, X.J. and Li, Y. 2019b. Generation and Stability of Size-Adjustable Bulk Nanobubbles Based on Periodic Pressure Change. *Sci Rep-Uk* 9.
- Wang, S., Liu, Y., Lyu, T., Pan, G. and Li, P. 2020c. Aquatic macrophytes in morphological and physiological responses to the nanobubble technology application for water restoration. *ACS ES&T Water* 1(2), 376-387.
- Wang, X., Yuan, T., Lei, Z., Kobayashi, M., Adachi, Y., Shimizu, K., Lee, D.-J. and Zhang, Z. 2020d. Supplementation of O<sub>2</sub>-containing gas nanobubble water to enhance methane production from anaerobic digestion of cellulose. *Chem Eng J* 398, 125652.
- Wang, X.Z., Yuan, T., Guo, Z.T., Han, H.L., Lei, Z.F., Shimizu, K., Zhang, Z.Y. and Lee, D.J. 2020e. Enhanced hydrolysis and acidification of cellulose at high loading for methane production via anaerobic digestion supplemented with high mobility nanobubble water. *Bioresource Technol* 297.
- White, E.R., Mecklenburg, M., Singer, S.B., Aloni, S. and Regan, B.C. 2011. Imaging Nanobubbles in Water with Scanning Transmission Electron Microscopy. *Appl Phys Express* 4(5).
- Xia, Z.R. and Hu, L.M. 2019. Treatment of Organics Contaminated Wastewater by Ozone Micro-Nano-Bubbles. *Water-Sui* 11(1).
- Xiao, W., Xu, G. and Li, G. 2021a. Effect of nanobubble application on performance and structural characteristics of microbial aggregates. *Sci Total Environ* 765, 142725.
- Xiao, W., Xu, G. and Li, G. 2021b. Role of shear stress in biological aerated filter with nanobubble aeration: Performance, biofilm structure and microbial community. *Bioresource Technol* 325, 124714.
- Xiao, W.T. and Xu, G.R. 2020. Mass transfer of nanobubble aeration and its effect on biofilm growth: Microbial activity and structural properties. *Sci Total Environ* 703.
- Yang, X., Nie, J., Wei, Y., Zhao, Z., Shimizu, K., Lei, Z. and Zhang, Z. 2020. Simultaneous enhancement on lignin degradation and methane production from anaerobic co-digestion of waste activated sludge and alkaline lignin supplemented with N<sub>2</sub>-nanobubble water. *Bioresource Technology Reports* 11, 100470.
- Yang, X.J., Nie, J.M., Wang, D., Zhao, Z.W., Kobayashi, M., Adachi, Y., Shimizu, K., Lei, Z.F. and Zhang, Z.Y. 2019. Enhanced hydrolysis of waste activated sludge for methane production via anaerobic digestion under N<sub>2</sub>-nanobubble water addition. *Sci Total Environ* 693.
- Yaparadne, S., Doherty, Z.E., Magdaleno, A.L., Matula, E.E., MacRae, J.D., Garcia-Segura, S. and Apul, O.G. 2022. Effect of air nanobubbles on oxygen transfer, oxygen uptake, and diversity of aerobic microbial consortium in activated sludge reactors. *Bioresource Technol* 351.
- Yasui, K., Tuziuti, T. and Kanematsu, W. 2018. Mysteries of bulk nanobubbles (ultrafine bubbles); stability and radical formation. *Ultrason Sonochem* 48, 259-266.
- Yasui, K., Tuziuti, T. and Kanematsu, W. 2019. High temperature and pressure inside a dissolving oxygen nanobubble. *Ultrason Sonochem* 55, 308-312.
- Yasui, K., Tuziuti, T. and Kanematsu, W. 2021. Interaction of Bulk Nanobubbles (Ultrafine Bubbles) with a Solid Surface. *Langmuir* 37(5), 1674-1681.
- Yu, W.J., Chen, J.Y., Ateia, M., Cates, E.L. and Johnson, M.S. 2021. Do Gas Nanobubbles Enhance Aqueous Photocatalysis? Experiment and Analysis of Mechanism. *Catalysts* 11(4).
- Yurchenko, S.O., Shkirin, A.V., Ninham, B.W., Sychev, A.A., Babenko, V.A., Penkov, N.V.,

- Kryuchkov, N.P. and Bunkin, N.F. 2016. Ion-Specific and Thermal Effects in the Stabilization of the Gas Nanobubble Phase in Bulk Aqueous Electrolyte Solutions. *Langmuir* 32(43), 11245-11255.
- Zhang, F.F., Sun, L.J., Yang, H.C., Gui, X.H., Schonherr, H., Kappl, M., Cao, Y.J. and Xing, Y.W. 2021. Recent advances for understanding the role of nanobubbles in particles flotation. *Adv Colloid Interfac* 291.
- Zhang, J., Fan, S.k., Zhang, M.h., Grieneisen, M.L. and Zhang, J.f. 2018 Aliphatic hydrocarbons recovered in vegetables from soils based on their in-situ distribution in various soil humus fractions using a successive extraction method, pp. 10-18, Elsevier B.V.
- Zhang, X.Y., Wang, Q.S., Wu, Z.X. and Tao, D.P. 2020. An experimental study on size distribution and zeta potential of bulk cavitation nanobubbles. *Int J Min Met Mater* 27(2), 152-161.
- Zhang, Y., Fan, W.H., Li, X.M., Wang, W.X. and Liu, S. 2022. Enhanced Removal of Free Radicals by Aqueous Hydrogen Nanobubbles and Their Role in Oxidative Stress. *Environmental Science & Technology*.
- Zhou, W.G., Liu, L.M., Zhou, B.N., Weng, L., Li, J.G., Liu, C., Yang, S.Y., Wu, C.N. and Liu, K. 2020. Electrokinetic potential reduction of fine particles induced by gas nucleation. *Ultrason Sonochem* 67.
- Zhou, Y.L., Han, Z.Y., He, C.L., Feng, Q., Wang, K.T., Wang, Y.B., Luo, N.N., Dodbiba, G., Wei, Y.Z., Otsuki, A. and Fujita, T. 2021. Long-Term Stability of Different Kinds of Gas Nanobubbles in Deionized and Salt Water. *Materials* 14(7).