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Micro and nano-sized bubbles for sanitation and water reuse: from fundamentals to application

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HIGHLIGHTS

- MNBs can enhance other water purification methods.
- MNB technology is its ability to eliminate pathogens in water and wastewater sources.
- The stability or MNBs and oxygen transfer depend on the size of bubbles.
- Ozone-MNBs provide an efficient and cost-effective approach to wastewater treatment.

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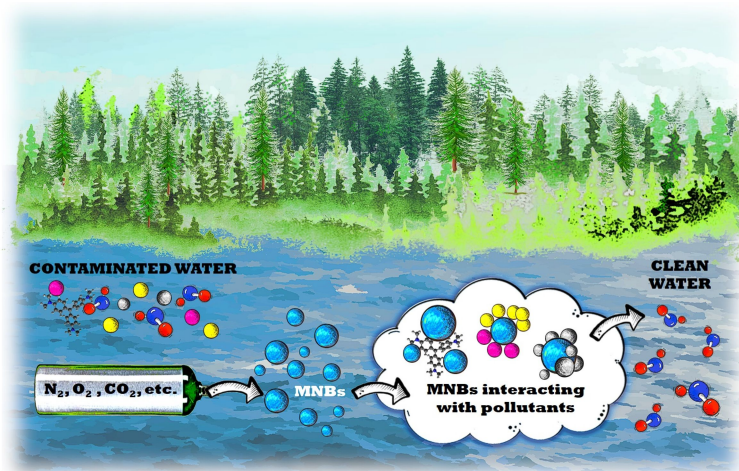
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GRAPHIC ABSTRACT



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ABSTRACT

The global scarcity of drinking water is an emerging problem associated with increasing pollution with many chemicals from industry and rapid microbial growth in aquatic systems. Despite the wide availability of conventional water and wastewater treatment methods, many limitations and challenges exist to overcome. Applying technology based on microbubbles (MBs) and nano-bubbles (NBs) offers ecological, fast, and cost-effective water treatment. All due to the high stability and long lifetime of the bubbles in the water, high gas transfer efficiency, free radical generation capacity, and large specific surface areas with interface potential of generated bubbles. MBs and NBs-based technology are attractive solutions in various application areas to improve existing water and wastewater treatment processes including industrial processes. In this paper, recent progress in NBs and MBs technology in water purification and wastewater treatment along with fundamentals, application, challenges, and future research were comprehensively discussed.

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1 Introduction

Given global environmental issues such as the deterioration of water resources and deficiency of drinking water, there is a growing demand for effective and low-cost, methods for water purification. Different conventional methods have been used for the treatment of sewage and wastewater from different sources to ensure that water is safe to drink and use for domestic activities. These methods have been discovered to be ineffective in removing toxic compounds, and elements; and generally, require more than one step to effectively remove some toxic compounds (Zhang et al., 2023). One of the most economical and green methods is the application of microbubbles (MBs) and nanobubbles (NBs) that can remove biofilms, toxic compounds, and sediments keeping clean water without using additional chemicals that could be secondary water contaminants (Wu et al., 2021b). NBs and MBs can be easily generated offering high stability (Alheshibri et al., 2016; Nirmalkar et al., 2018), charged surface (Parmar and Majumder, 2013; Gurung et al., 2016), large surface/volume ratio (Kim et al., 2019), and generation of free radicals and/or oxygen (Takahashi et al., 2021). Fujita et al. (2021) enabling fast and efficient catalytic degradation of chemicals, and improving water purification (Colic et al., 2007). MNBs technology has gained popularity over the last two decades (from 2000 to 2020) mainly in environmental studies including wastewater treatment for the facile generation of micro and nanobubbles, and their economical use in both laboratory and industrial scale, as well as higher effectiveness comparing to the classical aeration methods.

For example, Yao et al. (2016) investigated the effect of MBs on the gas-liquid mass transfer process and wastewater treatment. MBs increased the volumetric mass transfer coefficient compared to conventional bubbles at the same gas flow rate. The MBs used in wastewater containing aerobic-activated sludge enhanced the chemical oxygen demand (COD) degradation rate due to increased dissolved oxygen concentration. Similar results were observed in the wastewater treatment process using ozone (O_3), except that the COD degradation rate increased with increasing COD concentration by both MBs and conventional bubbles. The use of an MB generator for wastewater treatment processes requires careful consideration of its high power consumption and

enhanced mass transfer rate (Yao et al., 2016). Since then, there have been many other papers indicating the rapid growth trend of nanobubbles-based technology globally (Movahed and Sarmah, 2021).

Depending on the chemical composition of bubbles they cannot only be used for disinfection and chemical degradation but also can be used for aquafarming like the aeration described by Budhijanto et al. (2017) where authors investigated the effectiveness of a Micro Bubble Generator (MBG) aerator on the aquaculture of tilapia fish, compared to conventional aerator and control. The research found that aeration is a significant cost in aquaculture, and the MBG was a potentially affordable alternative that produced MBs to form high dissolved oxygen levels in the water. The study concluded that the fish exposed to MBs gained the most in length and weight compared to the fish in the classically aerated containers. Additionally, the high dissolved oxygen level delivered by the MBG did not differ significantly from the conventional aerator (Budhijanto et al., 2017).

Besides aquaculture applications, MNBs offer fast water recovery directly in the environment. Sun et al. (2018) featured the use of micro-nano bubble (MNB) and submerged resin floating bed composite technology (MBSR) to utilize two urban rivers from the water contamination presented as mildly black and stinking water bodies. By analyzing the physicochemical parameters they observed that the oxidation-reduction potential (ORP) changes at about a threefold increase in the two rivers after the use of the proposed method. The conductivity of one river reduced remarkably, leading to a decrease in the ionic strength of the river and the presence of heavy metal ions. The study also found that MBSR treatment affected the microbial activity related to the degradation of organic matter in the restoration process of the urban rivers. The relative abundance of the predominant phyla varied with physicochemical conditions, and some aerobic microorganisms responsible for pollutant degradation were stimulated in the process of MBSR remediation (Sun et al., 2018).

Despite the multifunctionality of MNBs technology, it becomes a powerful tool in water purification and disinfection when combined with other techniques. Many efforts have been made in recent years in this field. Harun and Zimmerman (2019) highlighted the importance of combining bubble-based technology with membrane

filtration approaches such as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis for wastewater treatment and waste recovery. As the Electrical Conductivity (EC) of the feed can change during the filtration process due to colloid breakdown and sedimentation of solid charged and non-charged residues onto the membrane, the application of MBs can increase the effectiveness of membrane cleaning and defouling. The fluidic oscillator-generated MBs resulted in a higher defouling efficiency of the filtration membrane and a change in transmembrane pressure drop (TMP). So based on the MBs the relationship between the fluidic oscillator and defouling rate was estimated. The study clearly indicated the potential of MNBs in fast and effective defouling of membranes during water filtration (Harun and Zimmerman, 2019).

Another work determined the optimal air-to-water ratio for MBs generation using three different sizes of venturi and applied MBs for wastewater treatment with different time of water flow rates and air suction rates. The demonstrated found that the mass of air in water decreases as the air-to-water ratio increases to 25%. The venturi with a throat diameter of 3 mm was found to be the most effective in reducing COD in the wastewater by 55%, 43.5%, and 29.5% for air-to-water ratios of 15%, 20%, and 25%, respectively (Vilaida et al., 2019).

In turn, the acoustic cavitation-assisted plasma (ACAP) process was combined with MNBs technology as an innovative tool for wastewater treatment demonstrating the promising effect of plasma discharge and acoustic cavitation in the production of reactive radicals and physical effect on wastewater, without mechanical stirring resulting in improved spark discharge due to acoustic cavitation bubbles (Fang et al., 2019).

A review published by Xiao et al. (2019) the MNBs technology was used for surface water purification, sewage water treatment, soil and groundwater remediation, and sludge treatment as a green technology with reduced chemicals use, economical operational costs, high utilization rate of oxidants such as ozone, and excellent effectiveness toward water purification. The study also hypothesized that the application MNB into absorbent could efficiently achieve high absorption rates of volatile organic compounds (VOC) and promising combining of MNBs technology combined with oxidation-absorption technology for flue gas pollutant removal pointing out an interesting topic worth exploring (Xiao et al., 2019). Nevertheless, further efforts are needed to promote MNBs technology applications in actual environmental pollution control processes, including the development of covariant response mechanisms for water quality, micro-nano aeration parameters, studies of bubble characteristics, optimization of synergistic processes with other oxidation methods, and development of lower energy consumption and more efficient MNBs generation devices.

Other work refers MNBs use in the seawater reverse osmosis (SWRO) membrane-based process to control calcium precipitates like CaSO_4 and CaCO_3 formation onto the membrane's surface as a chemical-free scaling mitigation method, where SWRO is widely developed due to limited access to fresh water sources globally. The study demonstrated higher effectiveness of the continuous use of MNBs than pulsed bubbles generation with inhibition of the formation of the precipitate onto membrane while reversed osmosis process showing the potential of MNBs to help achieve chemical-free SWRO operation, reducing the operational cost of the water purification process, and eliminating the negative impacts on the environment for the lack of chemical additives used in the process (Dayarathne et al., 2021).

In the other works, authors investigated the effectiveness of MNB in preventing concentration polarization layers and the MNBs effect on the permeate flux and solute rejection showing the permeate flux and solute rejection enhancement by 24.62% and 0.8%, respectively, and inhibition of concentration polarization layers formation (Dayarathne et al., 2017). The advantages of MNB over traditional bubble aeration make the application in water treatment processes versatile. According to the study, the maximum removal rates of COD, $\text{NH}_3\text{-N}$, Geosmin, and 2-methylisoborneol by MNBs were improved by 12%, 10%, 16%, and 12%, respectively compared to the ordinary aeration.

In 2020, Zhang et al. (2020a) defined MNBs as bubbles with a diameter ranging from 200 nm to 10 μm . MNBs were characterized by high mass transfer, generation of hydroxyl radicals, and high Zeta potential values at the interface (Zhang et al., 2020a). The study reported on the enhanced performance of ozone-based MNBs on simulated wastewater containing azo dyes, where the total mass transfer coefficient of O_3 and the removal rate of total organic carbon (TOC) were increased by 80% and 30%, respectively, compared to classical aeration (Zhang et al., 2020a).

Every year more and more work shows the high effectiveness of the use of this technology. For example, Wang et al. (2021) demonstrated the work on the catalytic generation of micro/nano-sized Nas-H_2 toward the reduction of Class 2A carcinogen-classified nitrate and nitrite (NO_x^-) pollution in water. In their work NO_x^- was removed using a Raney nickel (R-Ni) hydrogenation catalyst, generating Nas-H_2 bubbles and hydrogen adatoms H_{ads} to defeat nitrate-based water pollution. The study showed that the ReNi/Nas-H_2 hydrogenation system was more efficient in reducing NO_x^- than the ReNi -based commercial H_2 generation system. The study contributes to the research on NO_x^- pollution reduction and can help mitigate its negative impacts on the environment and human health just within the micro/nano-sized Nas-H_2 bubbles (Wang et al., 2021).

MNBs are also used to enhance the photocatalytic

degradation of water contaminants as they can increase dissolution of oxygen, colloidal stability, and dispersion of the nanocatalyst, and even offer interfacial photoelectric effect on nanocatalyst/MNBs suspension like the work demonstrated by [Fan et al. \(2021c\)](#) on the TiO_2 photocatalytic degradation of model pollutant combined with MNBs suspensions. The study highlights the importance of understanding how ultrafine MNBs interact with photocatalysts and light to influence photocatalysis and photocatalytic pollutant degradation. The results indicate that increasing the dissolved oxygen (DO) concentration significantly enhances the photocatalytic degradation (PCD) of methylene blue (MB). The study also shows that MNBs enrich the oxygen content in an aqueous solution and increase the light absorption of photocatalysts ([Fan et al., 2021b](#)).

Similarly, [Chen et al. \(2022b\)](#) investigated the removal of tetracycline (TC) using a MNBs with H_2O_2 (MNBs/ H_2O_2) showing an enhanced effect of MNBs (increased by 92.43%) compared to classical H_2O_2 effectiveness for the higher radicals generation rate promoting the degradation of TC. Overall, the study suggests that the MNBs/ H_2O_2 use can be a powerful tool to degrade not only TC but also other antibiotic-based pollutants present in wastewater ([Chen et al., 2022b](#)).

Following that trend [Sakr et al. \(2022\)](#) described the advantages of using MNB technology in wastewater treatment providing a review of the characterization of MNBs, including bubble size, gas mass transfer, generation of free radicals, Zeta potential, and bubble stability. Demonstrated work highlights the effectiveness of MNBs for the small-size of bubbles, high surface area, slow rising up velocity, generation of free radicals, and high stability of bubbles in the aqueous media. The review also discusses several studies on ozonation and flotation processes that have confirmed the increase in mass transfer when using more stabilized small-sized bubbles. While the MNB technology shows great potential as a green way of wastewater treatment, there is still a need for additional examination of its effectiveness on emerging organic compounds and hazardous heavy metal ions present in wastewater ([Sakr et al., 2022](#)).

Hence, there are many papers including broad review articles published recently on the MNBs technology use for water purification, still, there is a need to deliver a concise overview providing data on the different ways of generating bubbles along with the fundamentals, and MNB-based or combined water treatment methods for environmental applications. Thus, we cover these topics including bubble generation methods and insights into potential improvements in water treatment performance, and provide robustness to process applications, considering a range of experiments and conditions. Future advances are required for large-scale application and understanding of mechanisms under specific conditions. We hope that this review will assist readers in their future

research.

Recent review papers on MNBs technology for water treatment provide information on the MNB's definition, water disinfection, flotation, aeration, and membrane filtration with MNBs separately focusing mainly on the particular feature. The same appeals to the details on the different ways of generating bubbles along with the fundamentals and mechanism as well as the description of the biological, filtration, coagulation and flocculation, disinfection, and advanced oxidation process applications pilot-scale treatment applications in water areas of MNB. Here, we deliver a concise review covering all the topics mentioned above and provide information on the use of MNB applications in the laboratory, at pilot scale, and in the field. We hope that this review will be useful for readers in their future research.

2 Definition for microbubbles and nanobubbles

Based on the size, water bubbles, which are gas-filled cavities in a liquid, bubbles can be classified into three categories: fine bubbles also called macrobubbles, MBs, and NBs ([Temesgen et al., 2017](#); [Khan et al., 2020](#)). Macrobubbles or large bubbles are defined as sized in the range of $> 100 \mu\text{m}$ that is large enough to rise rapidly in the aqueous media and burst upon arrival at the surface. Fine bubbles can be separated into MBs and NBs ([Fig. 1](#)). Microbubbles refer to very small bubbles, with minimum and maximum diameters within the range of $10\text{--}100 \mu\text{m}$ ([Temesgen et al., 2017](#)) that are associated with cloudy/milky solutions ([Yasui et al., 2016](#)), while NBs are extremely small in size, typically tens to hundreds of nanometres in radius ($< 100 \text{ nm}$) being undetectable by the naked eye, or employing standard optical microscopes ([Azevedo et al., 2016](#)). The identification of NBs is usually through laser beam scattering. The unique physical properties of MBs and NBs, which include a high surface area per unit volume, a high Zeta potential, long residence times in water, a high oxygen transfer efficiency, as well as high internal pressures, render them suitable for applications associated with sanitation, wastewater treatment, and water purification ([Weijs et al., 2012](#); [Azevedo et al., 2016](#); [Chaplin, 2019](#)). According to

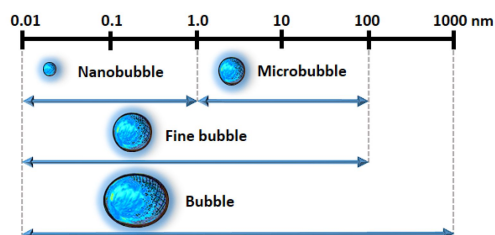


Fig. 1 Characterization of bubble based on size—schematic diagram prepared based on ISO-20480–1–2017.

the chemical composition, the micro and nano-sized bubbles can be made of air as well as other gases like O_2 , O_3 , N_2 , Ar, CO_2 , H_2 , volatile organic compounds (VOC), and many other compounds in the gaseous form (Chuenchart et al., 2021; Patel et al., 2021; Zhou et al., 2021).

2.1 Properties and physicochemical characterization techniques for MNBs

2.1.1 Size and distribution

The characteristics of bubbles, concerning shape and rising velocity in the solution, are determined by their size. For very small bubbles, the inertia force is far less than the surface tension (Weijs et al., 2012). Specifically, a smaller bubble size reduces the rising velocity and increases the surface area (Ramirez, 1979). Small well-distributed bubbles, with a slower rising velocity, will facilitate the adherence of pollutants to their surface, during the treatment of wastewater (Besagni and Inzoli, 2016).

The size as well as distribution, of MNBs, depends on the system design, and various operational conditions. For example, the size and distribution of MNBs, which are generated by depressurization of air-saturated water, are influenced by factors that include water and air saturation degree, as well as temperature (Besagni and Inzoli, 2016). Figure 2 shows a comparison between bubble size distribution, and bubble sizes measured for different flotation processes where the uniform bubble-size distribution can be achieved by way of the electrolytic process, with the bubble diameter at 100 μm , and the bubble rise rate at 0.5 cm/s.

Bubble size distribution is also influenced by bubble formation and breakup, where the increase of the distance from the column bottom affects the size of bubbles. Pressure changes across the nozzle system have a broad influence on the fraction and size of MBs. The increase in air density, brought about by greater pressure, serves to reduce the bubble size but the size of MBs remains constant at a pressure of 3.5 atm and above (Khan et al., 2020). For nanobubbles in liquids, while the rate of Brownian motion is not affected by particle density, it is

related to viscosity and temperature. The Stokes-Einstein equation was employed for the calculation of size, according to the particle movement rate. The size, of nanobubbles, is determined by factors which include the dimension and type of hose, as well as the pressure and sonic power levels.

The properties and physicochemical characterization techniques, to determine MBs and NBs size and distribution, including the photographic method (Besagni and Inzoli, 2016), the acoustic method (Kracht and Moraga, 2016), optical and light scattering (Hansen, 1985), the inverted funnel method (Vazquez et al., 2005), Phase doppler anemometry (PDA) (Meng et al., 2016), Bayesian magnetic resonance (Holland et al., 2012), Drift-flux analysis (Bhunia et al., 2017), and X-ray particle tracking velocimetry (PTV) (Lee and Kim, 2005). These methods come with their advantages and limitations. While the photographic method is frequently harnessed for bubble size estimation, its drawbacks include the requirement for a transparent wall (to facilitate image capture), the requirement for a low bubble concentration, a complicated experimental setup, and a process that is highly time-consuming (Pelssers et al., 1990).

The computation for bubble size, through the photographic method, represents a direct form of measurement and visualization process, which requires the use of a high-speed camera to capture the generated bubbles, as well as a light source to realize a clear picture of the bubbles. The high-speed camera employed in the photographic method comes with the capacity to capture more than 500 frames per second (fps) (Desai et al., 2019). The estimation of bubble size by way of the captured images can be achieved with the employment of image processing software, such as Octave, ImageJ, MATLAB, Mathematica, and LabVIEW (Desai et al., 2019). This technique, which entails the manual measurement of bubble size, is applicable for large bubble clusters, and can only capture bubbles located close to the column wall (Hansen, 1985). As the use of the photographic method is more suitable for single bubbles, it is deemed unreliable when it comes to overlapping and noncircular bubbles (Meng et al., 2016; Boucheron et al., 2018).

What is more, it is necessary to understand the

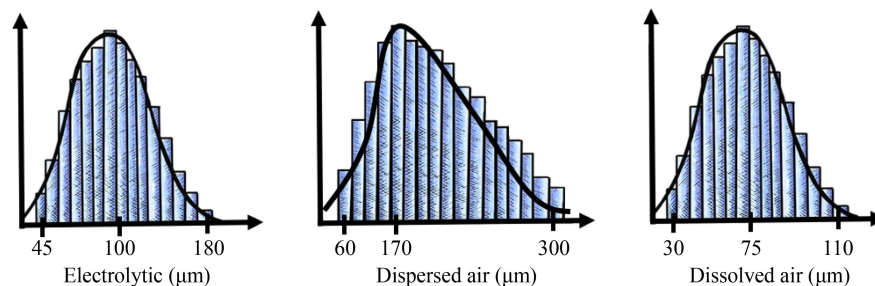


Fig. 2 Bubble size distribution measured in three different aeration systems. Schematic image prepared based on (Ramirez, 1979).

dynamics of the bubble in water, such as rising velocity and diameter variation, to get the perfect bubble size. Literature shows models used to predict the velocity of a spherical bubble, where the most common are Stoke's law, the Davies and Taylor equations, or the Hadmard-Rybczynski equation (Meng et al., 2016; Boucheron et al., 2018). These easy-to-use analytical equations were developed to establish the relationship between the specific diameter of the bubble and the terminal velocity under ideal conditions (uniform motion). Besides the sphericity and the motion description, the Epstein-Plesset theory (Meng et al., 2016; Boucheron et al., 2018) and the models proposed by Yasui et al. (2016) and Xue et al., (2022) can be used to describe gas diffusion, heat transfer, and energy conversion over time for dissolving bubbles in the liquid media. In addition, the computational fluid dynamics and population balance method (CFD-PBM) model was created, enabling the prediction of nanobubble size distributions. In the CFD-PBM coupled simulation, the multiphase flow problem in CFD simulation is solved by utilizing the transport equations of mass, momentum, and energy. Meanwhile, PBM can predict bubble evolution and dynamics by considering the effect of aggregation and breakage in the interface region between continuous fluid and dispersed bubbles (Meng et al., 2016; Boucheron et al., 2018).

The light scattering technique is an advanced process, for the measurement of bubble size and distribution. This approach is based on the principles of the Mie scattering theory, as well as the Rayleigh scattering theory for NBs (Pelssers et al., 1990; Bohren and Huffman, 1998). It involves the employment of a photomultiplier tube, to determine the intensity of the scattered light. The intensity, of the scattered light, is inversely proportional to the diameter of the bubble. The light scattering technique is suitable for the measurement of bubble size distribution, within the range of 0.02–2000 μm . On the other hand, the phase Doppler anemometry (PDA) technique, takes into consideration the size, concentration, and velocity of bubbles and droplets, in gases or liquid phases (Meng et al., 2016). This method is based on light scattering interferometry, which measures the size and velocity of each fluid particle simultaneously and delivers real-time data (Boucheron et al., 2018).

2.1.2 Stability and lifetime

The stability and lifetime, of MNBs, are measured by the length of time that they remain in the solution. Bubble stability is significant as it determines the period (ranging from 60 min to months) for gas mass transfer into the water. According to Meegoda et al. (2018), the formation of macrobubbles and MBs is governed by the Young-Laplace law. As depicted in Eq. (1) below, this entails an estimation, of the MNBs inner gas pressure:

$$\Delta P = \frac{2\gamma}{R}, \quad (1)$$

where ΔP is the difference in pressure, inside (vapor phase) and outside (liquid phase) of the bubble, γ is the surface tension, and R stands for the bubble radius.

In a study conducted by Meegoda et al. (2018), it was observed that upon generation, macrobubbles tend to rise rapidly to the surface and burst. Meanwhile, MBs rise at a slower rate, thus allowing more time for the transference of gas from bubble to liquid. The MBs shrink and disappear several hours after generation. Nanobubbles, on the other hand, were observed to shrink and disappear, several months after generation (Takahashi et al., 2007).

This is because whenever a moving small nanobubble collides with a large bubble, it can coagulate and coalesce with large bubbles, leading to the disappearance of the large bubbles and at this moment limiting their stability.

The findings, from this study, indicate that the stability of smaller bubbles is greater, as their movement is constrained by Brownian motion. The lower buoyancy of smaller bubbles contributes toward their extended period of suspension in liquids.

According to Azevedo et al. (2016), the stability of nanobubbles undergoes certain mechanisms. These mechanisms are described in the contamination theory, the gas density theory, the liquid height theory, the Knudsen gas theory, and the line tension theory. The stability of nanobubbles is also enhanced by the electrically charged liquid-gas interface, which stems from the repulsion forces that ward off bubble coalescence. Meegoda et al. (2019) opined that nanobubble stability is based on the electrostatic repulsion theory, wherein two types of surface forces, namely electrostatic repulsion and Van der Waals attraction, can be applied to determine the stability of any colloidal system. Colloidal stability can be explained by way of the Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory.

Kim et al. (2021) have confirmed through model simulations using a flotation model that nanobubbles can form aggregates, which means that they adjust their affinity for hydrophobic surfaces related to the stability of nanobubbles.

A study carried out by Zhou et al. (2021) showed that nanobubbles are more stable in deionized water than in salty water. This is because nanobubbles in salty water coalesced and increased in size (Zhou et al., 2021). As shown in Fig. 3, the large-sized bubbles eventually float to the surface and disappear.

2.1.3 Surface charge

Among the characteristics of MNBs, is the electrical charges on the bubble surface (Wu et al., 2012). The low electrical potential, generated by the charges on the surface of MNBs, can be associated with the physiologic activation in a living organism. These surface charges can

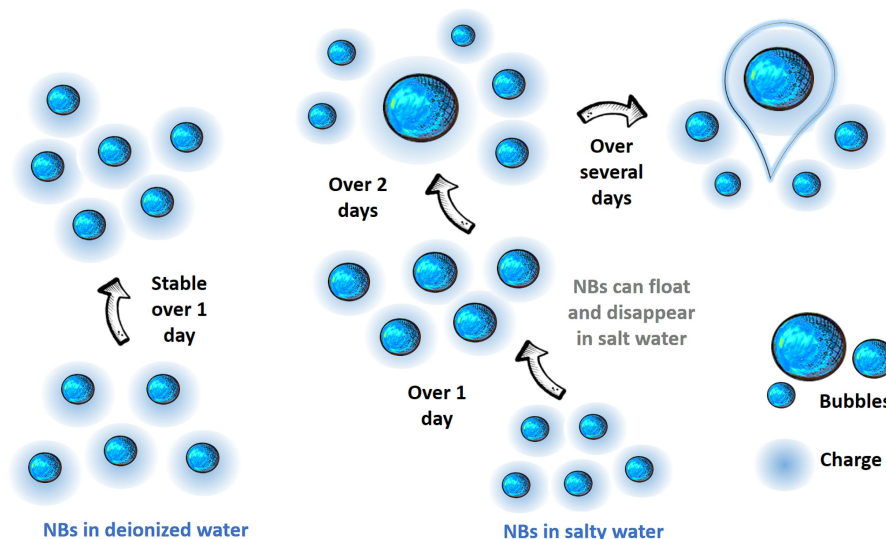


Fig. 3 Stability of nanobubbles in deionized and salty water.

be measured in terms of Zeta potential, which is defined as the electrical potential at the boundary layer, that separates the double layer, formed by the counter ions on the particle, and the bulk liquid (Ushikubo et al., 2010).

Ushikubo et al. (2010) measured the Zeta potential of different gases in water, following the generation of MNBs. The range of Zeta potential values for oxygen, air, nitrogen, carbon dioxide, and xenon bubbles were recorded as -45 to -34 mV, -20 to -17 mV, -35 to -29 mV, -27 to -20 mV, and -22 to -11 mV, respectively. These results are an indication that different gases have a different influence on bubble stability. Regardless of gas type, bubbles can have high Zeta potential values, if sufficient energy or pressure is made available, under controlled gas flow rates. It is notable that despite high Zeta potential values, a high flow rate, together with extensive bubble concentrations, can lead to the merging of bubbles, to produce larger unstable macrobubbles (Takahashi et al., 2007).

Other factors, that may affect the Zeta potential of MNBs, include viscosity, density of bulk liquid, temperature, pH, electrolyte types, concentration levels, and chemical surfactants (Meegoda et al., 2018). The summary of different findings on the effect of valency electrolytes on the surface charge of nanobubbles showed that nanobubbles are negatively charged in pure water, and the magnitude of its Zeta potential decreases with an increase in the concentration of the electrolyte. In the presence of monovalent electrolytes NBs were negatively charged, while as the cation valency increases, the Zeta potential becomes neutralized.

The MNB surface charge is associated with the OH^- ions, or less hydrated and more polarized anions, at the bubble gas-water interface. The addition of surfactants, or raising of the pH level, are among the methods used, to create a favorable environment, for the generation of OH^-

ions, or less hydrated and more polarized anions, at the gas-water interface. This will facilitate the generation of stable nanobubbles.

2.2 Generation of microbubbles and nanobubbles

2.2.1 Mechanical methods

The methods used, for the mechanical generation of MNBs, are influenced by internal and external factors. The device employed, for the mechanical generation of MNBs, consists mainly of a water pump, an air compressor, and a nozzle. From a water tank, a pump circulates water through a gas-dissolution tank, and bubbles are generated at the nozzle. Air is injected into the circulating water, on the suction side of the pump, and dissolved by way of a high-pressure system. MNBs are then generated, from the water supersaturated with air, due to the reduction in pressure at the nozzle. With this system, the generation of free radicals was reported, during the collapse of the MBs. This occurrence is attributed to the instantaneous development of high-density ions, at the surface of the collapsed MBs (Vogt, 1987). Figure 4 displays a schematic diagram of the MNB generator.

The cavitation process, for the mechanical generation of MNBs, involves the reliance on an external source, in the form of a probe or water bath. This process can be categorized as acoustic, hydrodynamic, optic, or particle-based. With this process, the formation of MNBs occurs, when the homogeneous liquid phase undergoes an alteration, due to a sudden drop in pressure, to below the critical value (Khan et al., 2020). Hydrodynamic cavitation involves the application of ultrasonic waves, or high pressure, in a running fluid (Vogt and Stephan, 2015). When the cavitation of bubbles undergoes an

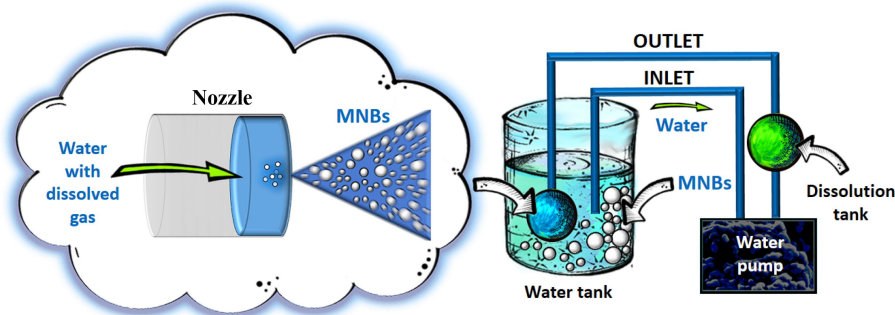


Fig. 4 Schematic diagram of the MNB generator. Adaptation of the image described by (Vogt, 1987).

asymmetrical implosion at the critical size, bubbles of a certain dimension can become unstable and collapse, causing a forceful micro-jet of liquid. A frequently applied hydrodynamic cavitation process is the venturi-type generator, which comes with an input flow, as well as a tubular and a tapered output flow (Blanco and Modestino, 2019). In this system, liquid and gas are transmitted simultaneously through the venturi tube for the generation of bubbles. When the pressurized liquid is injected into the tubular section, the flow of fluid into the cylinder throat becomes higher. Consequently, pressure is rendered lower than the input section, to bring about cavitation (Lim et al., 2014). Ahmadi and Khodadadi Darban (2013) generated nanobubbles within a range of 130–545 nm, through a venturi tube, by way of the hydrodynamic cavitation mechanism. A similar process was applied by Wu et al. (2012), to create nanobubbles with a size less than 500 nm.

2.2.2 Electrochemical method

Bubbles can also be generated electrochemically during many processes including fuel production, the splitting of chemicals in water, carbon dioxide electroreduction, organic electrosynthesis (Lim et al., 2014; Blanco and Modestino, 2019), the electrosynthesis of chloro-alkali and sodium chlorate, as well as aluminum production (Botte, 2014; Karlsson and Cornell, 2016). The electrochemical bubble generation involves the nucleation, growth, and detachment of the bubbles, from the gas-evolving electrode surface (Angulo et al., 2020; Ranaweera and Luo, 2020). The factors influencing bubble formation include the gas flow rate, mode of operation, flow/static condition of the liquid, as well as liquid density and viscosity (Kulkarni and Joshi, 2005; Zhang et al., 2006; Raman et al., 2023), while the bubbles generation can enhance the convection and the mass transfer rates (Dees and Tobias, 1987; Vogt, 1987; Vogt and Stephan, 2015).

In the context of wastewater treatment, when wastewater in the reactor cell is exposed to an electrical current, the electrical field established between the electrodes, brings about the nucleation of tiny hydrogen

and oxygen bubbles, on the cathode and anode electrodes. Bubble generation is also influenced by the applied potential and the current intensity applied to the working electrode. A current density that is too low will lead to the removal of the dissolved gas from the electrode in the direction of liquid bulk by molecular diffusion and by superposed liquid convection, without the formation of a gas phase. At a current density, that is not too low, a sufficient supersaturation of the liquid occurs adjacent to the electrode. When the current density is sufficiently high, bubbles will form at the predestined nucleation site (Vogt, 1987; Ahmed et al., 2024).

The growth behavior of nucleated bubbles is influenced by the viscosity, inertia, and interfacial forces including surface, hydrodynamic, and capillary forces, while also the following features affect the generation of the bubble including electrochemical conditions (e.g., potential applied to the electrode), type of media (e.g. aqueous system), composition of the solution. When the diameter of the bubbles increases, the mass transfer rate of dissolved gas from the liquid becomes predominant, and other forces are rendered secondary. As the concentration is non-uniform, at the liquid bulk surrounding the electrode, coalescence of bubbles may occur, due to the sliding of big bubbles upward along the electrode, while embodying small bubbles, in a sort of scavenging effect. The departure, of smaller bubbles from the electrodes, is replaced by the large bubbles formed through coalescence. The growing bubbles remain attached to the electrode surface until a sufficient size is attained for departure.

The detachment of bubbles is governed by the dynamics of the surrounding liquid, as well as by the buoyancy, pressure, and adhesion forces. Following the departure of the bubbles from the electrode surface, the surplus gas remaining serves as a nucleus for the successive bubbles. Due to the mass transfer limitations in the direction of bulk, caused by the adhered bubbles, the concentration of dissolved gas reaches its maximum value, in the liquid adjacent to the electrode. In the application of the electrocoagulation method for wastewater treatment, upon the departure of bubbles from

the electrode surface, the subsequent steps in the electroflotation process are as follows (Shammas et al., 2010; Shammas and Bennett, 2010):

- Collision between the bubbles and suspended particles,
- Attachment of fine bubbles to the surface of the suspended particles,
- Collision between gas-attached suspended particles followed by agglomeration,
- Entrapment of more bubbles in the agglomerates,
- Upward rise of flocs by “sweep flocculation”.

3 Application of MNBs in wastewater treatment

3.1 Filtration processes

3.1.1 Membranes

One of the challenges with the membrane filtration process for water purification is fouling. This has led to high consumption of energy, waste of material, and high operational costs. The fouling can be reduced/eliminated with bubbles-based technology by inhibiting the adhesion of different types of pollutants on the membrane through the forming of “gas bridge” between the pollutants and the surface of membrane (Fan et al., 2022). Ghadimkhani et al. (2016) studied the utilization of MNBs wastewater treatment filtration process using ceramic membranes (CM). The study aimed to investigate the mechanisms of interactions between NBs and ceramic membranes and to explore the antifouling and defouling processes. Bench-scale ceramic membrane systems coupled with an NB generator were employed for experimental analysis. The results revealed that the CM’s permeate flux was unaffected by variations in temperature and pH. The highest permeate flow rate was observed at an applied pressure of 413.7 kPa, indicating optimal filtration efficiency. When humic acid was introduced, fouling of the CM surface occurred. However, the introduction of air NBs improved defouling without significant adverse effects. This approach offers a sustainable and innovative solution for membrane cleaning, reducing chemical use and enhancing the membrane’s lifespan, thereby contributing to a greener and more sustainable drinking water industry. The air NBs used with ceramic membranes can enhance water treatment, surpassing the limitations of classical thermodynamics theories (Ghadimkhani et al., 2016).

Tekile et al. (2017) presented the application of MNBs wastewater treatment filtration processes using membrane technology. The study focused on investigating the enhanced mass transfer of ozone O_3 and its oxidation ability in practical applications. The unique physicochemical properties of MNBs, including their small size,

large interfacial area, extended residence time, and high internal pressure, contribute to increased ozone mass transfer and utilization rate, leading to enhanced pollutant oxidation in water and wastewater. The research explored various applications of MNBs, including water disinfection, removal of organic and inorganic pollutants, and decoloration. The results demonstrated that MNBs improved disinfection efficiency by inactivating microorganisms and reducing the required ozone dosage. Moreover, MNBs were effective in the oxidation of organic and inorganic pollutants, including ammonia and arsenic. The enhanced removal efficiency of pollutants, color, and organic matter was observed, highlighting the potential of MNBs in wastewater treatment processes. However, further studies are needed to investigate the reduction in treatment facility size, formation of disinfection byproducts, and energy consumption associated with MNB generation for a comprehensive comparison of its practical application (Tekile et al., 2017).

3.1.2 Adsorption

Adsorption is a powerful tool in water purification, there are many works that combined this technology with other techniques including MNBs. Michailidi et al. (2019) provide an overview of the history, production, properties, and potential applications of NBs and MBs focusing on combining MNBs with other techniques like filtration and adsorption to treat wastewater. The authors discuss the generation of NBs through techniques such as sonication and electrolysis, as well as their impact on the physicochemical properties of the medium. The potential applications of NBs and MBs in flotation, water treatment, oil recovery, surface cleaning, and biological processes are explored. The research highlights the benefits of NBs in improving particle hydrophobicity, enhancing flotation efficiency, catalyzing chemical reactions for water treatment, and facilitating surface cleaning. The findings suggest that NBs and MBs have significant potential in various fields, but further research and standardization of production procedures are needed to fully understand their mechanisms and optimize their applications (Michailidi et al., 2019).

Kyzas et al. (2021) commented that although the incorporation of nanobubbles did not influence the adsorption capacity of lead ions, it accelerated the adsorption, and increased the number of adsorption-desorption cycles for reuse. This implies that in large-scale wastewater treatment where nanobubbles are incorporated, the whole process will be finalized much earlier, hereby saving energy/money. It was proposed that nanobubbles acted as carriers that transfer lead ions to the negatively charged surface and pores of the activated carbon (Kyzas et al., 2021). Figure 5 shows a schematic image of heavy metal ions transfer via MNBs into the porous material.

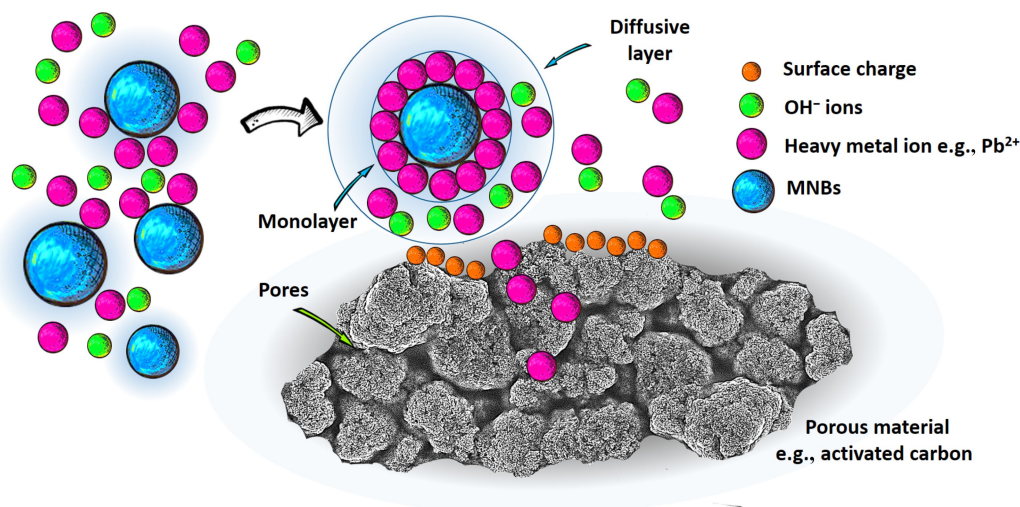


Fig. 5 Illustration of the effect of NBs on adsorption kinetics of heavy metal ions like Pb^{2+} by porous material like activated carbon (image inspired by Kyzas et al. (2021)).

3.2 Flotation

Likewise the other techniques of wastewater treatment, the flotation efficiency can be improved using MNBs technology (Wang et al., 2020; Li and Zhang, 2022; Tao, 2022). Kyzas et al. (2021) conducted a comprehensive review of the flotation process with a focus on MNBs technology for wastewater treatment. The study emphasized the wide range of applications for flotation, including the treatment of various contaminants such as bacteria, coal, clays, and heavy metal ions. The author discussed the fundamentals of bubble-particle interactions, Zeta potential measurements, and the impact of nanobubbles on flotation performance. The research highlighted the potential of nanobubbles to improve the recovery and grade of valuable minerals and the removal efficiency of contaminants. The findings indicated that the presence of nanobubbles enhanced the flotation performance by promoting bubble-particle attachment and altering the surface properties of target particles. The study also compared nanobubbles with dissolved-air flotation and emphasized the promising role of MNBs in water treatment applications. Overall, this research contributes to the understanding of the flotation process and highlights the potential of nanobubbles for efficient wastewater treatment and mineral recovery (Kyzas et al., 2021).

Zhang et al. (2020b) focused on the application of MNB wastewater treatment using flotation, where the characteristics of nanobubbles generated through hydrodynamic cavitation, including their size distribution, surface potential, and stability were studied. The effects of various factors such as frother dosage, solution pH value, liquid flow rate, air pressure, and air flow rate on the NBs properties were examined. The results demonstrated that NBs generated by hydrodynamic

cavitation had sizes ranging from 150 to 650 nm. The size of nanobubbles was influenced by frother concentration, liquid flow rate, pH value, air pressure, and air flow rate. Higher frother concentration, liquid flow rate, and pH value led to smaller nanobubble sizes. However, excessive air pressure resulted in hindered cavitation, leading to larger nanobubbles. Additionally, higher air flow rates increased the number of gas nuclei, but excessively violent cavitation reduced the cavitation intensity and resulted in larger nanobubbles. The findings provide valuable insights into the generation and control of nanobubbles for wastewater treatment using flotation processes (Zhang et al., 2020b; 2020c).

Sobhy and Tao (2013) enhanced the recovery of fine coal particles using a specially designed flotation column equipped with a hydrodynamic cavitation nanobubble generator. The study aimed to develop an innovative cavitation NBs flotation process by improving the fundamental understanding of NBs froth flotation. The results demonstrated that the generation of NBs through hydrodynamic cavitation was a selective process, favoring the attachment of hydrophobic particles. Application of nanobubbles to laboratory column coal flotation resulted in significant improvements in combustible recovery, reduced reagent and air consumption, and enhanced flotation efficiency. The recovery of fine coal increased by 5 to 50 absolute percentage points, depending on process conditions, while reducing the dosage of frother by one-third. The improved flotation performance was attributed to increased collision and attachment probabilities, along with a reduced probability of detachment. This study highlights the potential of nanobubbles in enhancing the coal flotation process and offers promising opportunities for efficient coal recovery and ash reduction (Sobhy and Tao, 2013).

3.3 Coagulation-flocculation processes

MNBs technology can be also used in coagulation-flocculation processes in environmental, agricultural, healthcare, chemical, industrial, and even energy sectors but its effectiveness depends on many experimental conditions.

Liu et al. (2012) emphasized the importance of Zeta potential in designing efficient coagulation-flotation systems, as the electrical charge interaction between particles and bubbles plays a vital role in particle-bubble attachment. Experimental comparisons based on three types of MBs and the stability of these bubbles were evaluated through drainage and oxygen diffusion models. The objective was to optimize the MB flotation process and enhance its effectiveness. The experimental setup involved mixing coke wastewater with a coagulant solution, followed by the introduction of a large number of MBs that adhered to the impurities and rose to the surface. The ozone MB system exhibited high absolute Zeta potential values, preventing bubble coalescence and promoting attractive interactions between bubbles and particles. Furthermore, the ozone MBs generated a significant amount of hydroxyl radicals, facilitating the degradation of organic materials in the wastewater. The study concludes that Zeta potential measurements effectively validated the optimum coagulation conditions, and the ozone MB flotation demonstrated superior performance. The ozone and oxygen MBs exhibited prolonged stability in water compared to air MBs, enhancing the efficiency of the flotation process (Liu et al., 2012).

Liu et al. (2010) presented the application of MNBs in coagulation-flocculation processes for the treatment of dyeing wastewater generated by the textile industry. The study highlights the extensive range of chemical substances present in textile mill effluents, including dyestuffs, auxiliaries, and agents used in various processes. Conventional treatment methods for dyeing wastewater often involve sedimentation followed by coagulation, which suffers from drawbacks such as high coagulant consumption, excessive sludge production, and lengthy treatment times. Experimental investigations were conducted using an MB flotation device, where a coagulant solution was mixed with the wastewater to facilitate reactions with impurities. The introduction of air MBs resulted in their adherence to the wastewater impurities, leading to their removal from the water surface. The findings demonstrated that the MB flotation technology significantly improved the removal efficiencies of COD, color, and oil by 30%, 110%, and 40% respectively, compared to conventional air bubble flotation. Furthermore, the coagulation MB flotation process exhibited remarkable removal efficiencies for oil (over 99%) and COD (over 85%) without the addition of electrolytes or surfactants. The study concludes that the implementation of MB flotation, with its prolonged

reservation time and large surface area-to-volume ratio, enhances the pretreatment efficiency of coagulation-flocculation for dyeing wastewater, requiring lower coagulant doses and shorter treatment times while achieving superior removal efficiencies (Liu et al., 2010).

3.4 Biological processes

MNBs have the potential to be used also in the systems enhancing the extraction of biological compounds and/or growth of living organisms. Xia and Hu (2018) investigated the feasibility and efficiency of utilizing O₃ MNBs for the treatment of wastewater contaminated with organic pollutants. Organic contaminants, including dyes, petrochemicals, and agrochemicals, pose significant environmental and health risks. While various technologies have been developed for their degradation, physical adsorption is limited in complex wastewater, and biological processes are time-consuming and influenced by surrounding conditions. In this study, a spiral liquid flow-type MNB generator was used to produce ozone MNBs. The mass transfer efficiency of MNBs was found to be influenced by their quantity and size, with larger amounts and smaller bubble sizes enhancing mass transfer flux. The treatment efficiency of ozone MNBs was examined under different pH and salinity conditions using methyl orange as a representative contaminant. The results demonstrated that ozone MNBs exhibited a pseudo-first-order kinetics in the degradation of methyl orange, with optimal treatment efficiency observed at pH 5. Additionally, the presence of salt accelerated the treatment process, although the potential formation of chlorinated aromatic compounds should be monitored. This research concludes that ozone MNBs show promising potential for the removal of organic contaminants, even in wastewater with high salinity, with a significant reduction in COD observed after 14 h of treatment (Xia and Hu, 2018).

Wu et al. (2021a) focused on the application of MNBs in biological wastewater treatment processes. They found that bulk nanobubbles were effective in enhancing flotation efficiency for the removal of organic contaminants such as grease. Additionally, the presence of nanobubbles accelerated the oxygen mass transfer rate, benefiting microbial biodegradation processes. The collapse of bulk nanobubbles generated free radicals, promoting oxidation processes. The study demonstrated that NBs improved the oxygen utilization rate and mass transfer coefficient compared to conventional bubble aeration devices. Furthermore, the retention time for organic degradation in nanobubble-aerated systems was significantly reduced. The research highlighted the potential of NBs in enhancing various wastewater treatment pathways, including air flotation, aeration in biodegradation processes, and the oxidation of difficult-to-biodegrade compounds. The findings also emphasized

the importance of nanobubbles' unique characteristics, such as high stability, long lifetimes, and high mass transfer efficiency, in improving water treatment technologies. Further research is warranted to explore the production of active oxygen and the role of hydroxyl radicals ($\cdot\text{OH}$) during nanobubble application. Ultimately, the development of low-cost competitive devices with superior performance for practical engineering applications holds great significance (Wu et al., 2021a).

Patel et al. (2021) presented that nanobubble technology (NBT) holds great potential for wastewater treatment using biological processes. The unique properties of nanobubbles, such as longer stability, negative Zeta potential, and oxidation potential, make them suitable for various applications, including pathogen control, mineral scale prevention, and contaminant removal. The study explores the recent advancements in the generation techniques of nanobubbles and discusses their unique properties for broader applications in the growth of living organisms, production enhancement, and extraction of biological substances. The research highlights the stability of NBs as a crucial attribute for strategic application and examines the properties of NBs generated from different gases. Additionally, the study investigates the effects of NBs on marine and terrestrial animals, algal growth and metabolism, bacterial and yeast bioprocesses, microbial and pesticide removal, wastewater bioremediation, surface water, and sediment/land remediation, as well as nanoparticle generation and medicinal usage. The findings demonstrate the potential of NBs in various fields, including enhanced methane production, improved algal harvesting, reduction in pollutant release, and increased bacterial growth. Overall, the study concludes that NBs offer energy-efficient and versatile solutions for water and wastewater treatment, agricultural processes, and medical applications, with the potential for broader implementation in industrial bioprocesses (Patel et al., 2021).

3.4.1 Aeration of aquatic systems

Aeration of aquatic systems plays an important role in environmental studies. Khan et al. (2020) focused on the application of MNBs technology for wastewater treatment. It reviews important studies in this area and discusses the fundamental properties of MNBs, including their stability, generation methods, and chemical and physical features. The paper also provides an overview of the current status of MNBs application in water treatment processes such as flotation, aeration, and disinfection, as well as their uses in agriculture, aquaculture, medical, and industrial sectors. While the review highlights the promising role of MNBs in water-related applications, it also concludes that the current research has not fully realized their true potential and emphasizes the need to enhance their application on a broader scale likewise the

aeration of the aquatic systems (Khan and Carroll, 2020; Khan et al., 2020).

Das and Singh (2022) described wastewater treatment using MNBs technology in Aeration lagoons, with an emphasis on sustainability and high efficiency. The study highlights the limitations of conventional effluent treatment techniques, including energy-intensiveness, low output efficiency, and risks of secondary contamination. To address these challenges, the research suggests a paradigm shift in the process development and design of wastewater treatment plants. The chapter explores novel technology solutions such as integrated membrane separation, photocatalysis, and nanotechnology, which aim to achieve complete pollutant degradation without generating toxic residues while prioritizing eco-friendliness. The advantages and disadvantages of conventional effluent treatment plants are examined, along with their modifications in the modern era. Furthermore, the research delves into the emerging novel technology solutions, their potential applications, and the possibility of integrating them with existing separation techniques. The chapter concludes by discussing strategies such as waste valorization and process intensification in design, aiming to promote sustainable and cost-effective technology development for wastewater treatment (Das and Singh, 2022).

Chen et al. (2022a) argued that black odorous rivers (BOR) pose a significant environmental challenge in urban areas with high population density proposing a novel approach for BOR treatment by employing MNBs in an anoxic-oxic (AO) process with traditional activated sludge methods, facilitated by a specially designed reactor. The utilization of MNBs offers several advantages, including a high specific surface area, efficient oxygen transfer, extended retention time, and interface effects. The experimental results demonstrate the remarkable efficacy of MNBs in enhancing the removal of COD, NH_4^+-N , and total nitrogen (TN) from BOR water. Additionally, MNBs provide high levels of dissolved oxygen, promoting the transformation of floc sludge into biofilm. Through 16S rRNA amplicon sequencing, a significant distinction is observed between the microbial communities in MNBs and macro bubbles sludges, highlighting the enrichment of biofilm-forming bacteria through MNBs aeration. Functional predictions further indicate that MNBs promote nitrification and aerobic ammonia oxidation without adversely affecting denitrification. This study underscores the great potential of MNBs in combining activated sludge and biofilm processes for effective BOR treatment. The findings contribute valuable insights into sustainable approaches for addressing the challenges associated with contaminated rivers (Chen et al., 2022a).

Besides dealing with biofilms, NMBs technology has been developed also in aquaculture to improve aeration efficiency. Lim et al. (2021) compared the growth of

L. vannamei in MBs and NBs aerated conditions clearly indicating that MBs aeration has a significant effect on the growth of shrimps, similar to the work presented by Rizky et al. (2022). Another work described the effect of MBG aerator used on the enhancement of the degradation of the organic content in the water (Marbelia et al., 2020) and induced faster fish growth as measured by length and weight (Budhijanto et al., 2017), whereas Marcelino et al. showed the improvement of both nitrifications in hydroponic systems and plant field (Marcelino et al., 2023). However, the list of works describing the positive effect on the biological systems in the context of growth promotion in agriculture and marine animal farming is much longer confirming the benefits of the MNBs technology on a large scale.

3.5 Advanced oxidation processes assisted with MNBs

Thanks to the operational flexibility and high efficiency, advanced oxidation processes (AOPs) have many important applications in the treatment of refractory organic wastewater that cannot be treated by conventional methods (Chávez et al., 2019; Giannakis et al., 2021). AOPs are of great interest as one of the promising advanced technologies that enable the production of reactive oxygen species such as hydroxyl radicals in the amount required for the treatment of wastewater. The most commonly used AOPs are processes such as Fenton, electro-Fenton, and ultraviolet radiation. Recently, studies have focused on a MNBs-assisted oxidation technology for the efficient removal of resistant organic pollutants from waters, which will further enhance the effectiveness of AOPs. In addition to their advantage of producing OH^\cdot and increased gas mass transfer efficiency, macro-nano bubbles have limited oxidation ability. For this reason, it is stated that the combination of MNBs and AOPs can accelerate the degradation of pollutants.

3.5.1 Fenton processes

The Fenton technology is based on the use of Fe^{2+} ions along with hydrogen peroxide (H_2O_2) to produce OH^\cdot toward enhanced oxidization of organic pollutants to CO_2 and H_2O . However, Fenton oxidation has several shortcomings, including the narrow range of pH in its application, the consumption of large iron salts, and the separation and subsequent processing of large quantities of sludge. Therefore, thanks to the OH^\cdot radicals MNBs produced *in situ* by the Fenton reaction water, a positive relationship was observed between the concentration of OH^\cdot content and the removal of persistent pollutants. It has been reported that both MNBs and Fenton oxidation can produce OH^\cdot , which increases the oxidation ability of a waste treatment system. Ma et al. used the Fenton process combined with MNBs to degrade Congo red (CR) dye to facilitate the degradation process of organic

pollutants and reduce the cost of the process (Ma et al., 2023). Their results showed that CR decay could reach 94.4% using MNBs + Fenton. Additionally, while the conventional Fenton process was more efficient at acidic pH, the MNBs + Fenton combination was able to expand the pH range of the highly efficient oxidation reaction, achieving a high degradation rate under neutral conditions. Furthermore, a combination of MNBs and H_2O_2 was used for the treatment of tetracycline wastewater. The results showed that with MB/ H_2O_2 technology, the degradation rate of tetracycline hydrochloride could reach 92.43%. The authors also noted that in the MB/ H_2O_2 system, it was possible to activate H_2O_2 to obtain a greater quantity of reactive oxygen species due to the high temperature and high-pressure environment that is created when MB is broken down (Chen et al., 2022b). Bui and Han used three nanobubble systems (NB, ultrasonic NB, and NB/ H_2O_2) to break down dark green Rit dye. More than 90% of Rit dye removal was achieved within 30 min and 60 min respectively, when ultrasonic NB and NB/ H_2O_2 systems were used (Bui and Han, 2020). Apart from this, a Biocoal-based Fe-Ce bimetallic Fenton-like heterogeneous catalyst was prepared and applied in the degradation of wastewater produced during the synthesis of caprolactamine (wastewater-CPL) in the presence of MNBs. This resulted in the biochar-based catalyst + H_2O_2 + MNB system achieving the best purification effect where the COD removal rate could reach 93.26%. Additionally, it was stated that adding MNBs to the process affected the efficiency of treatment. The treatment effect of MNBs + H_2O_2 on wastewater was approximately 60% higher than that of H_2O_2 alone.

3.5.2 Electro-Fenton processes

As an advanced electrochemical oxidation process, the electro-Fenton (EF) method has attracted great attention in recent years due to its versatility, high oxidation capacity, and compatibility (Deng et al., 2019; Deng et al., 2021; Zhu et al., 2021). EF is a process in which O_2 input is required to produce hydrogen peroxide for the treatment of resistant organic pollutants. The aeration step added to EF increases the dissolution of the oxygen bubbles in the solution and their stability, and therefore, the rate of degradation. Thus, in EF studies, MNB-assisted electrodes have been usually designed to increase the number of hydroxyl radicals in the medium and improve iron reduction. To simultaneously improve cathodic H_2O_2 deposition and Fe^{3+} reduction in the EF process, a MB-assisted rotary tubular titanium cathode (MRTTC) was designed for the first time. With this cathode, H_2O_2 deposition was increased by a factor of 4.05 compared to conventional EF treatment, resulting in a 200% increase in iron reduction. The MRTTC use degraded fully sulfamerazine organic pollutant, in just 3 h. A new and promising design was reported for

antibiotic wastewater treatment with a MB-assisted cathode (Qiu et al., 2022). Additionally, membrane ventilation with oxygen-supported MBs was used to degrade ciprofloxacin by EF, where the effects of the ventilation mode, applied current, membrane opening, ventilation rate, and ciprofloxacin concentration on the degradation rate were examined offering a degradation rate of 97% in 4 h and 10 min (Zhi et al., 2022). Zhu et al. (2022a; 2022b) built a new self-contained EF system in which newly manufactured Fe, N, and S jointly doped cathodes were ventilated through microporous ventilation, and a greater number of cathodes were used. They stated that the EF system, which was proposed to support MB aeration and oxygen mass transfer, enabled the improvement of the BOD/COD ratio in the treatment of real pharmaceutical wastewater. Following study shows the treatment of textile wastewater using EF and EC with the addition of sprinkled air was evaluated. Experiments were carried out in setups with and without sprinkling air (SA). According to the results, after 280 min of treatment, the rate of wastewater color change reached 100% in all processes, and COD removal rates were over 90.3% (Louhichi et al., 2022). Additionally, EF was performed using a new O₂ sprinkling electrochemical reactor for the decay of the reactive red 195. A dye concentration of 50 ppm at 2 mA/cm, an oxygen rate of 0.012 cm/s, and a contact time of 60 min resulted in the achievement of 100% color reduction and 96% COD removal efficiency. The advantages of the reactor they used compared to reactors used in previous studies were highlighted (Elbatea et al., 2021). Pirsaeheb et al. investigated the aeration of an aqueous solution of ciprofloxacin (CIP) and the elimination of ultrasonic irradiation by a nano zero valent iron (nZVI)-based Fenton reaction. It was stated that this process provided more effective antibiotic removal than conventional systems. The authors achieved an initial CIP concentration of 100 mg/L under a neutral pH condition with a CIP removal of 94% within 60 min (Pirsaeheb et al., 2020).

3.5.3 Photoelectrochemical treatment

The photoelectrocatalysis (PEC) process has the advantage of photocatalysis while increasing radical production efficiency through the combination of electrolytic reactions (Bessegato et al., 2015; Mousset and Dionysiou, 2020). Photocatalysis is one of the AOPs that have been extensively researched to mineralize a wide range of contaminants. PEC water separation has the potential to be an efficient and cost-effective method of producing hydrogen, where the photoelectrode in the PEC system absorbs sunlight and splits water directly into hydrogen and oxygen (Hu et al., 2020; Tang et al., 2021; Yang et al., 2021; Liccardo et al., 2022; Xiong et al., 2022). In photoelectrochemistry, oxygen bubbles develop in the photoelectrode, while hydrogen bubbles develop in

the cathode. The increased water separation efficiency of PEC is due to its improved photocatalytic activity and mass transfer near the photoelectrode surface (Hu et al., 2020). MNBs have attracted a wide range of attention thanks to their special properties such as high mass transfer efficiency, large specific surface area, and the production of reactive oxygen species (ROS), which allow MNBs to have potential applications in the PEC reaction. MNBs and PEC systems are combined to achieve efficient PEC water oxidation. Huang et al. (2022) showed that metal oxide photoanodes (TiO₂, BiVO₄, and WO₃) achieved a 10%–26% improvement in photocurrent density and showed significantly improved efficiency values in charge injection and separation in MNB electrolytes. Additionally, MNB-integrated processes with photocatalysis which are photoelectrochemical methods have been used to remove a large variety of organic pollutants. It was stated that this method improved the removal of COD and permanent organics by 27.52% and 14.38%, respectively (Fan et al., 2019). A visible light photocatalysis combined with MNB were proposed to improve the aqueous disinfection of bacterial spores. The inactivation efficiency of *Bacillus subtilis* spores in the system in which MNBs were present was significantly higher than in the system in which MNBs were absent. The presence of MNBs provided a sustainable source of O₂ by capturing photoelectrons (Fan et al., 2021a). Additionally, in a study conducted with TiO₂ photocatalysts and MNBs to ensure the degradation of dyes in wastewater, it was stated that the dye degradation efficiency was 100% (Rojviroon and Rojviroon, 2022).

3.5.4 Sonochemical treatment

Sonochemical reactors are finding a promising future in the field of wastewater treatment as advanced oxidation methods. Both sonochemical and ultrasound irradiation are very effective methods to remove debris from solid surfaces, and it is widely used in research and industry (Yamamoto et al., 2015). Studies are being conducted on the combination of ultrasonic irradiation and ventilation, regarding the extent to which air bubbles inside the reactor affect the sonochemistry. MNBs generation supports pollutant oxidation in combination with sonochemistry. The effect of micro air bubbles (20 and 70 µm, 0.1%–5.0% volume) on sonochemical activity was tested in a horn-type reactor (20 kHz). The results indicated that compared to the bubble-free state, 20 µm-sized bubbles improved sonochemistry at all concentrations, while 70 µm-sized bubbles inhibited sonochemistry at the highest concentration (5.0% by volume) (Xia et al., 2022). Additionally, a significant increase in sonochemical oxidation was observed with the constant sprinkling of air (Choi et al., 2019). Some research has indicated that MBs have an enhancing effect on sonochemistry, but they

may also have inhibitory effects (Gogate et al., 2015; Tuziuti, 2016; Choi et al., 2021).

3.6 Disinfection processes

Disinfection is an important process in water treatment to protect human health from waterborne diseases such as cholera, dysentery, leptospirosis, and many others. Common disinfection processes such as ozonation, chlorination, and antiseptic ultraviolet irradiation have been used and researched for the inactivation of bacteria (Szeto et al., 2020; Simpson and Mitch, 2022). MBs and NBs have been reported to be effective in ventilation, flotation, and disinfection processes (Fan et al., 2021a; 2021b; 2021c; Seridou and Kalogerakis, 2021).

3.6.1 Ozonating and chlorinating

Due to its strong oxidation activity, ozone (O_3) is widely used for the removal of persistent micropollutants from aqueous environments (Prasse et al., 2012; Xia and Hu, 2018; Zhang et al., 2020b; 2020c). However, the usage effectiveness of O_3 is limited due to its low solubility and short half-life during the refining process (Khan and Carroll, 2020). The impact of ozonation with MBs and NBs technology has been investigated in many areas of engineering and wastewater treatment (Khuntia et al., 2014; Temesgen et al., 2017; Li et al., 2018; Shangguan et al., 2018; Azevedo et al., 2019; Koda et al., 2019; Wu et al., 2019; Deng et al., 2021; Jabesa and Ghosh, 2021). Figure 6 showing the schematic diagram of MNBs use in the water pollutants treatment including the ozonation.

The combination of MNBs and O_3 in wastewater treatment not only prolongs the reaction activity but also increases the solubility of ozone, improving the mass transfer efficiency of ozone (Xia and Hu, 2018). The presence of MBs can accelerate the decomposition of hydroxyl radicals of ozone and greatly improve the mineralization efficiency of resistant organics (Xia and Hu, 2018; Nashmi et al., 2020; Zeng et al., 2021; Matsuura et al., 2022). Since MBs and NBs can remain in water for a long time, their treatment efficiency is high. Batagoda et al. (2018) proved this showing four times longer stability of generated nano-ozone bubbles than bubbles produced with a normal diffuser. Compared to conventional macro-bubble ozonation, the 4-chlorophenol removal can be almost 7 times higher using nano-ozone bubbles (Fan et al., 2021a; 2021c). Similarly, phenol and nitrobenzene (Wu et al., 2019), and ammonia can also be enhanced using ozone NBs (Wu et al., 2022). Chu et al. (2008) achieved 20% higher effectiveness using ozone MBs to treat high concentrations of textile wastewater compared to MBs, while Jabesa and Ghosh presented much higher removal of TOC and dimethyl sulfoxide (DMSO) using ozone MBs than using milli-bubbles (sized in the range from micron to millimeter) (Jabesa and Ghosh, 2021). In addition, ozone NBs combined with H_2O_2 improve the degradation of tetramethylammonium hydroxide (TMAH) in wastewater by increasing the mass transfer ratio of ozone (Kim et al., 2021). MB ozonation is also effective in removing carcinogenic disinfection by-products such as trihalomethanes (THMs) and haloacetic acids (HAAs) formed during chlorination (Qadafi et al., 2020).

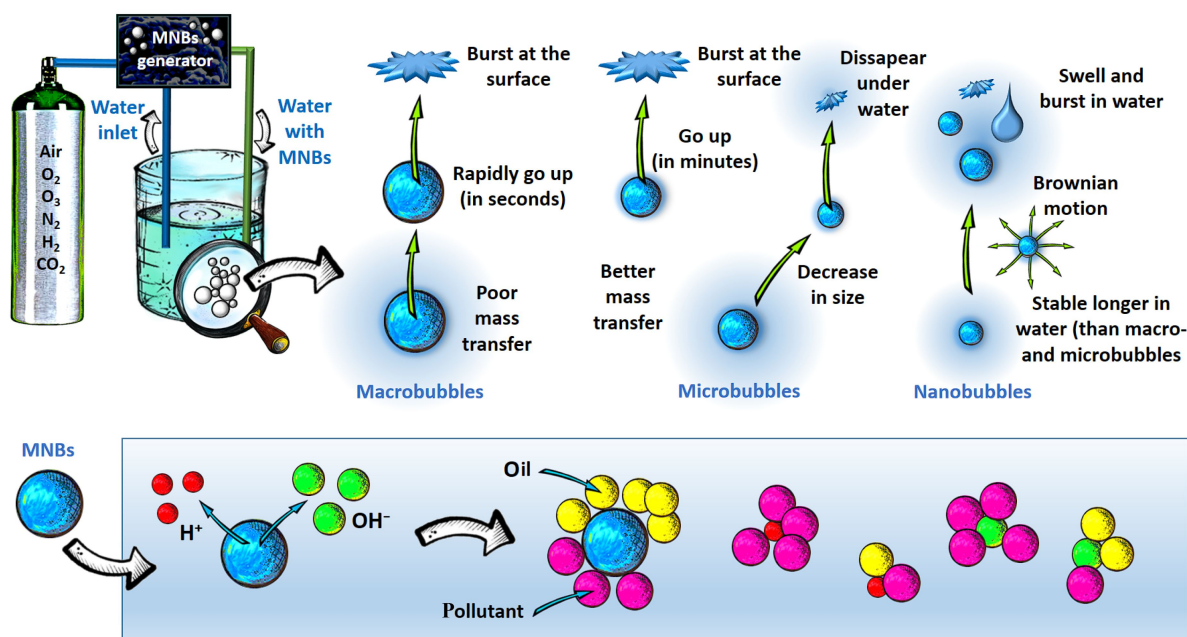


Fig. 6 Schematic diagram of MNBs behavior in water and interaction with water pollutants.

Other studies show the synergistic effects of MNBs and ozone/UV in the enhancement of decomposition, biodegradability, and discoloration of organic pollutants in water (Tasaki et al., 2009; Takahashi et al., 2012; Zheng et al., 2015). Wang and Wang (2023) studied an effective degradation of Basic Yellow 28 dye with different catalyst types and O₃/MBBs technology. Additionally, the effect of O₃-MNB doses on 2,4-D decay was studied. Only 39.0% of the 2,4-dichlorophenoxyacetic acid was removed 15 min after the addition of O₃-MNBs, and the removal efficiency increased from 59.0% to 89.0% as the dose of ozone and MNBs increased (Zhu et al., 2022a; 2022b). Ozone MNBs also show a significant effect on the removal of organic pollutants from high-salinity wastewater (COD removal rate above 63% after 14 h of treatment) (Xia and Hu, 2018). However, the ozone MNBs effectiveness also depends on the pH and salinity. Although the salts presence can accelerate the methyl orange removal with ozone MNBs, the potential formation of chlorinated aromatic compounds can occur (Xia and Hu, 2018).

As the MNBs are efficient in water purification (Chen, 2009), it is also used to treat bacteria like *Escherichia coli* (Sumikura et al., 2007; Mezule et al., 2009). In particular, a disinfection process that combines MNBs with ozone, which is an extremely cost-effective method, can increase efficiency further. NBs reduced the dose of ozone needed to achieve 2-log coliform inactivation by > 70% (Atkinson et al., 2019). Furuichi et al. (2013) reported that NBs of ozone neutralize both Gram-positive and Gram-negative bacteria. The combination of ozonation and hydrodynamic cavitation in the disinfection of *E. coli* was completed within 60 min, and the concentration of bacteria was reduced to zero with ozonation alone within 45 min (Karamah et al., 2018). Some researchers investigated the degradation of pharmaceutical compounds by a MB ozonation process and clearly saw that there could be an alternative option to conventional ozonation processes for the reduction of pharmaceutical compounds (Cruz and Flores, 2017; Lee et al., 2019). In a different study, the potential of ozonated NBs as a single process in treatment plants during the outbreak to eliminate persistent SARS-CoV-2 was investigated. Although effective disinfection was provided compared to conventional ozonation, SARS-CoV-2 was found to remain in several treated wastewater samples (Verinda et al., 2021).

Apart from laboratory-scale or pilot-scale water treatment, the use in open or closed water fields of MNBs has been effective in reducing water pollution. For water treatment in cooling towers and HVAC systems, for example, more ozone is often needed because the performance of the system cannot last for a long time (Choi et al., 2021). Using MNB technology, it was found that the process of ozonation in water treatment and groundwater reclamation could be financially supported

and economically improved. Field tests conducted in Japan on a site contaminated with trichloroethylene (TCE) show that six-day ozone MNB treatments of groundwater can remove even 99% of TCE in water (Xia and Hu, 2018). A different study was performed in ponds to deal with odor, where the water was treated with NB of ozone and cleaned removing 85% of TSS, 80-90% of BOD, and 55% of COD. Ozone NBs technology was also used to reduce algae in a freshwater pond in Hong Kong, China, leading to inactivation of about 68.2% in just 9 min (Ng et al., 2023).

Furthermore, a synthetic soil with grain size distribution similar to real river sediments was artificially contaminated with chromium, and ultrasound and ozone NBs were used to treat the deposits. The test results showed 97.54% chromium removal efficiency (Batagoda et al., 2019). NBG systems can improve water quality in lakes and ponds (Pal et al., 2022). Table 1 shows the application of ozone MNBs to be used in the wastewater treatment.

In conclusion, ozone-MNBs provide an efficient and cost-effective approach to wastewater treatment and water improvement. Studies on this issue continue increasingly. The main objective of the implementation of MNBs is to downsize plants, reduce the operating time, and lower the operating and maintenance costs of water treatment plants with a greater efficiency of contaminant removal (Wu et al., 2022).

Besides the ozonation, another method that is the most widely used disinfection process in the treatment of drinking water and wastewater is chlorination. Despite the broad use, it can be non-sufficient for wastewater treatment. Recent studies show that the effectiveness of chlorination can be enhanced by combining it with other methods. Sekhon et al. (2022) assessed the effects of adding gaseous (air, CO₂, or N₂) ultrafine bubbles to 100 and 200 ppm chlorine (Cl₂) solutions to inactivate fresh *Listeria monocytogenes* biofilms on stainless steel. Larger log reductions occurred in the air (5.0 log CFU/cm²) and CO₂ NBs (4.9 log CFU/cm²) at 100 ppm Cl₂ compared to non-gas ultrafine bubble Cl₂ dosing (3.7 log CFU/cm²) (Sekhon et al., 2022). The biocidal effect of ultrasound is in the form of acoustic cavitation, which involves the formation and collapse of MBs at intense temperatures (5000 K) and high pressures (1000 atm) (Mason, 1996). For this reason, ultrasound (US) and chlorine dioxide (ClO₂) have been combined to improve wastewater disinfection. With this combination, it was shown that *E. coli* and total coliform in raw wastewater were removed from the wastewater at a high level (Ayyildiz et al., 2011). Additionally, the activities of polyaluminum chloride (PAC) as a coagulant and cetyltrimethylammonium chloride (CTAC) as a cationic surfactant in the separation of emulsified palm oil by modified column flotation were examined by a MB process. MB purification with PAC and MB creation was found to be

Table 1 Applications of ozone-MNBs in wastewater treatment

References	Ozone application	Results	MNBs or NBs diameter
Batagoda et al. (2018)	Wastewater treatment	Effective drinking water purification with ozone retention in water for approximately four times longer at 1 h stabilization with a nano-diffuser	–
Fan et al. (2021a)	Wastewater treatment	1.7 times higher resolution of O ₃ , It increased the mass transfer coefficient 4.7 times, 6.9 times 4-chlorophenol removal	< 1 µm
Nashmi et al. (2020)	Wastewater treatment	Removal efficiency of Methylene orange 100% under conditions of pH 5.6	Average 32 µm
Wu et al. (2019)	Wastewater treatment	70% removal of nitrobenzene in pH 7	Less than 50 µm
Wu et al. (2022)	Wastewater treatment	Ozone NBs treatment (82.5%) is better ammonia removal than ozone-macrobubble treatment (44.2%)	< 200 nm
Chu et al. (2008)	Wastewater treatment	For 80% color removal in less time and 20% more COD removal rate with ozone MBs	Approximately a few mm
Jabesa and Ghosh (2021)	Wastewater treatment	Ozone was used 65%–79% in the conventional system, 21%–48% in the MBs system. TOC removal efficiency was the best in ozone MBs and hydrogen peroxide systems	80 µm
Kim et al. (2021)	Wastewater treatment	Reduction in acute (40-fold) and chronic (2-fold) toxicity after nano-ozone/H ₂ O ₂ processing into wastewater for the degradation of tetramethylammonium hydroxide	Average between 86.7 and 133.7 nm
Qadafi et al. (2020)	Wastewater treatment	At pH 7, the outlet total trihalomethanes concentration was 33.73 ± 0.40 µg/L and haloacetic acids were 49.89 ± 0.09 µg/L	Average 52 µm
Zhu et al. (2022a)	Wastewater treatment	As the 2,4-dichlorophenoxyacetic acid degradation ozone and MNB dose increased, the removal efficiency increased from 59.0% to 89.0%	The range of 10–300 nm
Xia and Hu (2018)	Wastewater treatment	The COD removal rate in high-salinity wastewater is over 63%	The range of 40–370 nm
Lee et al. (2019)	Wastewater treatment	Solubilization rate and the reactivity of O ₃ and OH radicals provided strong effects on the degradation of the pharmaceutical compounds	The range of 1–25 µm
Xia and Hu (2018)	Wastewater treatment	The site contained trichloroethylene (TCE) cleared	The range of 32–60 nm
Pal et al. (2022)	Wastewater treatment	TSS 85%, BOD 80%–90% and COD 55% reduction	< 5 µm
Ng et al. (2023)	Wastewater treatment	68.2% algae removal for 9 min	–
Wei et al. (2023)	Wastewater treatment	Effective degradation of Basic Yellow 28 dye	The range of 20–30 µm
Sumikura et al. (2007)	Disinfection	NBs reduced the ozone dose required to achieve 2 log of coliform inactivation by > 70%	The range of 30–60 nm
Mezule et al. (2009)	Disinfection	3 min of exposure inhibited 75% of <i>E. coli</i>	–
Karamah et al. (2018)	Disinfection	Both Gram-positive and Gram-negative bacteria were inactivated. <i>E. coli</i> reduced to zero within 60 and 45 min	–
Cruz and Flores (2017)	Disinfection	Achieving a reduction of total coliforms up to 100 CFU/100 mL (99.96%) and fecal coliforms up to 100 CFU/100 mL (99.92%)	–
Verinda et al. (2021)	Disinfection	Effective disinfection of SARS-CoV-2	–
Batagoda et al. (2019)	Soil pollution treatment	97.54% chromium removal in chromium-contaminated soil	–

more effective at removing oil oxidations than MB purification alone (Van Le et al., 2012). Nevertheless, despite the high effectiveness in water purification, the subsequent chlorination after the ozone MBs generation enhances the formation of disinfection bi-products (DBPs) that can be harmful to the aquatic system. The application of chlorination on the MBs-ozonated bromide-containing water can lead to the formation of bromo-organic DBPs that are more toxic than chlorinated DBPs making this method limited to non-halogenated contaminants treatment especially when it comes to the application in the field (Li et al., 2018).

As MNBs can reduce biological, chemical, and physical loads to reduce operating costs and improve the quality of treated water they can have versatile applications in environmental studies. Table 2 shows

advantages and disadvantages compared to other water treatment methods.

4 Future prospects, limitations, and challenges

The MNBs technology has not only shown its practicality in medicine (Helfield et al., 2021), agriculture (Marcelino et al., 2023), and industry (Kalogerakis et al., 2021) but also holds immense potential in revolutionizing broader industrial applications along with providing sustainable solutions to the environment. MNBT is considered an eco-friendly process because no additional chemicals are used to generate free radicals that promote the oxidation of organic compounds, disinfection of water, and control

Table 2 Advantages and disadvantages of the treatment methods of water and wastewater and MNBs

Treatment process	Advantages	Disadvantages
Membranes	Low sludge yield High effluent quality High process stability	Contamination, High energy consumption and material costs Low removal of COD
Adsorption	Easy operating conditions Applicable for a wide range of pH High metal binding capabilities	Cost of materials Low selectivity Generation of waste products
Flotation	Useful for pre-treatment Low retention time	High initial capital cost Energy costs Maintenance and operation costs are not negligible Selectivity is pH-dependent
Coagulation-flocculation processes	Process simplicity Effortless procedure	Possible undesired by-products, Operating costs Sludge production
Biological processes	Odour control, nitrogen management, and biodegradation of organic waste Pathogens inactivation and/or removal	Generation of biological sludge and uncontrolled degradation products Possible sludge bulking and foaming
Advanced oxidation processes	No sludge production Possibility of water recycle Simple, rapid, and efficient process	High capital and operational costs Not effective in the treatment of wastewater with high TSS
MNB technology	An eco-friendly process No additional chemicals Simple bubble generation Efficient collision Improved time-cost efficiency High mass transfer rate Free hydroxyl radical formation Reduction of operational cost Enhanced the degradation of the natural organic matter Ease of operation	Large-scale feasibility The use of ozone-corrosion-resistant pipelines The by-products formed from ozone and/or the halogens during chlorination, etc. MNBs generators that use high-power

of fouling. For the ease of bubble generation, enhanced time-cost efficiency, high mass transfer rate, drug loading capacity, free hydroxyl radical formation, and efficient collision, MBs and NBs-based technologies have the potential to become a future viable option for water and wastewater treatment via disinfection and floatation (Patel et al., 2021; Wang and Wang, 2023). NBs technology for the increase of the phase dissolved oxygen levels offers not only organics and pathogens treatment in environmental studies but also agriculture including aquaculture, horticulture, agronomy, aquaponics, and hydroponics; and environmental engineering including algal biomass production, fermentation, and anaeration (Marcelino et al., 2023).

The free radicals generated from MNBT have the future scope to improve other water treatment methods such as ozone. Integration of MNBT with ozone empowers ozone's low solubility and mass transfer while reducing the operational cost and formation of recalcitrant side products (Khan et al., 2020). Specifically, ozone MNBs enhance the degradation of the natural organic matter (NOM) and result in the destruction of organic molecules and color in wastewater via effective hydroxyl radical formation (Liu and Tang, 2019). Besides that, one of the greatest advantages of the MNB technology is its ability to affect pathogens in water and wastewater. Considering its high effectiveness, ease of operation, and eco-friendliness, MNB use can be beneficial for developing countries to strengthen their existing water quality and treatment methods (Moussavi et al., 2022; 2023).

A comprehensive understanding of the physical

interactions of MB/NBs with pathogens could improve process parameters for better wastewater treatment (Zhou et al., 2022). Therefore, it is needed to investigate the detailed interactions between the microbes/pathogens with the generated reactive oxygen species (ROS) from MBs and NBs and determine how ROS results in cell lysis along with comprehension of the effect of released cellular contents on sludge reduction. Additionally, the longevity of ROS in the aqueous media needs to be further explored due to the fact that ROS ($O_2^{\cdot-}$ and singlet oxygen 1O_2) can be active on the aqueous media only for a few seconds, while NBs can last for months. A reliable technology utilizing The correlation between the NB size and concentration along with the presence of ROS needs mechanistic understanding, especially when it comes to antimicrobial activity. Moreover, little is known about the disinfection capacity of the MNBs technology involving seawater treatment which possesses various salts, including sodium chloride, bromides, etc. (Seridou and Kalogerakis, 2021). As sodium chloride can also help to defeat pathogens (Li et al., 2013), the interaction of ozone and many different salts that can be present in water and wastewater including metal ions need further research to determine the broader applicability and efficiency of the MNBT technology.

Additionally, further research is needed to address the safety concerns associated with ozone, including the use of ozone corrosion-resistant pipelines and a comprehensive understanding of the formation of by-products. Furthermore, current MNBs generators require an application of high energy, so the novel solutions

reducing the energy consumption should be optimized likewise fluidic oscillation techniques that can improve bubble dispersion and lower ozone doses (Tekile et al., 2017).

The potential of MNB technology goes beyond ozone as other gases can be employed to improve the overall efficiency of the MNB technology. Previous reports have suggested that a combination of gas mixture and dosing ratio would be critical to building a future customized nanobubble-based treatment option. In such treatment options, the future NB technology will select a particular gas that can generate sufficient amounts of highly reactive radicals to kill pathogens; thus, future studies mainly focusing on application-oriented characterization of gaseous nanobubbles would be needed (Patel et al., 2021). Figure 7 shows the exemplary image on the on-fields application of the MNBs technology.

Although the MB/NB technology has shown immense potential for wastewater treatment, its large-scale feasibility has been challenging. Extensive studies over a longer period are needed to fully comprehend the process parameters that affect efficiency and overall performance. Prior to scale-up studies, simulation studies focusing on MB/NB interactions with contaminants are encouraged which significantly reduce the operation cost while improving overall performance; however, such studies are limited. To some extent, models are available to provide insight into the stability of MBs and mass transfer; however, these models do not take into account microbial interactions with MBs and organic contaminants. These studies are likely to provide a benefit for the optimal design of efficient systems retrofitted with MB/NB technologies. While the mass transfer efficiency of the MB/NB technology has been explored to a greater extent in several publications, heat transfer has been poorly studied. Heat is an important factor that is often generated during the process and heat could support the energetics of the treatment. This area requires further investigations to improve the efficiency of wastewater treatment by MB/NB (Nair et al., 2022). In summary, while the MNBT technology is unlikely to transform sewage into potable

water, it could purify it to a level where its safe disposal is possible.

MNBs can enhance the flotation process, a method employed to eliminate suspended solids, oils, and various other contaminants from water. Due to their diminutive size and extensive surface area, MNBs facilitate the adherence of contaminants to the bubbles, resulting in more efficient separation and removal. They may also increase the efficiency of the dissolved air flotation systems that can be applied in wastewater treatment. Thus, the small size of the bubbles improves the separation of fine particles, leading to higher clarity and quality of treated water. Another application field is connected with the food and beverage industry for disinfecting equipment, containers, and surfaces. MNBs can also be applied in the sanitation of medical instruments and hospital environments (Akbar et al., 2021). Moreover, in the textile sector, MNBs play a crucial role in eliminating dyes and chemicals from wastewater. They improve the flotation process of dye particles, resulting in cleaner discharge and a lower environmental footprint. MNBs are also utilized in mining flotation processes to separate valuable minerals from ores (Hilson, 2020; Yadav et al., 2022). Their ability to attach to vesicular particles enhances the efficiency of mineral recovery. Figure 8 shows schematic diagram of the AI use in MNBs technology.

5 Artificial Intelligence-based support

Artificial Intelligence (AI) is currently transforming various fields, including environmental sciences, by offering innovative tools and methodologies for understanding, monitoring, and addressing complex ecological challenges. With its capacity to swiftly analyze large data sets and create predictive models, AI opens up new possibilities for developing effective strategies in environmental conservation and sustainability (Qaddoori et al., 2023; Kim et al., 2024; Jaffari et al., 2024). One of the interesting AI applications is the support of micro and nano-sized bubble technologies in sanitation and water reuse processes (Nishu and Kumar, 2023). For example, Qaddoori et al. (2023) delivered the classifier for bubbles in which the sets of images of bubbles were analyzed based on the Convolution Neural Network (CNN) as part of the deep learning concept. As a result, the CNN containing 15 layers was being trained based on the input images to detect the bubble pattern and in fact, analyze the size of the bubbles. In this way, AI can help choose the most effective size and concentration, i.e. optimize the bubble production process in the context of selecting optimal parameters such as pressure, temperature, and gas composition (Hassanloo and Wang, 2024). In turn, in Hessenkemper et al. (2022), CNN architecture known as UNet was applied to the bubbles segmentation. This kind

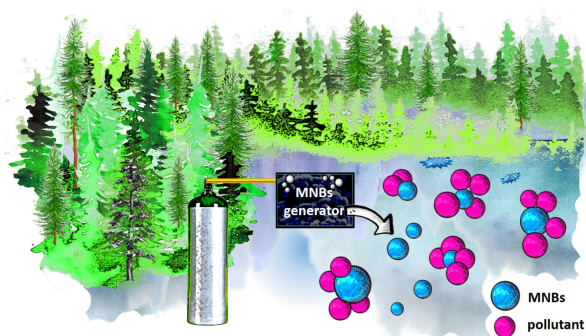


Fig. 7 Schematic diagram on the aqueous pollution treatment by MNBs in the field.

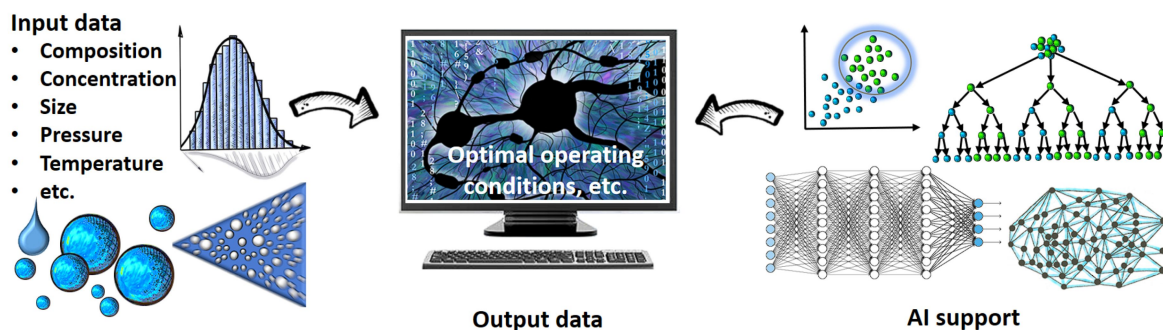


Fig. 8 Schematic image of AI application in MNBs use.

of architecture is specifically designed for pixel-level predictions, making it highly effective for segmentation tasks, such as identifying cell structures and analyzing medical images. The encoder reduces the array's spatial dimensions while increasing its depth (channels) to extract image features. Conversely, the decoder restores the spatial dimensions to capture detailed local information from the image (Wu et al., 2021b). Another approach based on a basic statistical Machine Learning model was shown in (Wu et al., 2021b). Namely, the TEM images were segmented with the Gaussian Mixture Model (GMM). This approach offers enhanced flexibility and accuracy in modeling and extracting the fundamental statistics of sample data. Consequently, it is widely utilized in tasks such as object recognition and classification. Another study presents the analysis of the MB image data set to measure their performance with AI-based algorithms. It turned out that single-stage and two-stage CNN models performed better in MB detection compared to Deformable Convolutional Network (DCN) and transformer-based models (Srisaeng et al., 2023). Moreover, the You-Only-Look-Once algorithm (YOLO) version 7 achieved the highest accuracy and effectiveness in detecting MBs when considering multiple evaluation metrics. An interesting approach was also shown in (Zhai et al., 2022). The Deep Neural Network (DNN) was applied to forecast the physical characteristics of bubbly flow.

Another potential application field for AI is the ability to provide real-time feedback on the performance of bubble-based sanitation systems (Muhammad et al., 2024). Another possibility of incorporating AI with this application is predicting when elements of bubble production and distribution systems may fail or require maintenance. This can reduce downtime and ensure the continuous operation of sanitation and water reuse systems. AI can also help identify opportunities to reduce energy consumption without compromising the efficiency of sanitation and water reuse processes. In AI-based algorithm (Özdemir et al., 2024), namely the Levenberg–Marquardt backpropagation algorithm was applied to predict the cleaning efficiency based on the degree of removal of oil/grease, organic substances, and

suspended solids with high accuracy. Moreover, AI can facilitate the scalability and adaptability of micro and nano-sized bubble systems across different environments and scales.

Thus, integrating AI with micro and nano-sized bubbles for sanitation and water reuse has the potential to significantly improve this process. It offers numerous benefits, including improved efficiency, real-time monitoring, predictive maintenance, and enhanced contaminant removal. In fact, the combination of AI and bubbles has the huge potential to make water treatment processes more effective and sustainable. However, AI applications have several limitations, including data dependency, interpretability issues, data biases, as well as access to data and computational resources.

6 Conclusions

This paper provides a concise overview of the latest trends in the application of micro and nano-sized bubbles (MNBs), covering their definition, fundamental properties, generation techniques, and their use in wastewater treatment. Water bubbles, which are gas-filled cavities in liquid, can be classified into three size-based categories: microbubbles, which are larger, visible bubbles that rise quickly and burst upon reaching the surface. MBs and NBs are fine bubbles, with minimum and maximum diameters ranging from 10–100 μm , high surface area per volume, and high Zeta potential values. These fine bubbles have unique physical properties, long residence times in water, high oxygen transfer efficiency as well as high internal pressures making them suitable for applications related to sanitation, wastewater treatment, and water treatment. The stability and lifespan of MNBs are measured by the length of time they remain in solution. MNBs are produced by different mechanical and electrochemical methods. MNBs can be effectively applied in wastewater treatment. The solubility of ozone can be increased using MNBs in wastewater treatment. Mass transfer efficiency improves with the increase in the solubility of ozone. Ozone-MNBs provide an efficient and cost-effective approach to wastewater treatment,

groundwater, and water reclamation. Numerous challenges and limitations for future research include technical complexity and the high cost of generating stable MNBs, the energy-intensive nature of MNB production, and scalability.

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