Review

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Generation Mechanism of Hydroxyl Radical In Micro Nano Bubbles Water and Its Prospect in Drinking Water

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Abstract: Micro nano bubbles (MNBs) can generate ·OH in situ, which provides a new idea for the safe and efficient removal of pollutants in water supply systems. However, the difficulty in obtaining stable MNBs causes the low efficiency of ·OH generation, which makes the inability to guarantee the removal efficiency of pollutants. This paper reviews the application research of MNBs technology in water security from three aspects: the generation process of MNBs in water, the generation rule of ·OH during MNBs collapse, and the control mechanism of MNBs on pollutants and biofilms. We found that MNBs generation methods are divided into chemical and mechanical (about 10 kinds) categories, and the instability of bubble size restricts the application of MNBs technology. The generation of ·OH by MNBs is affected by pH, gas source, bubble size, temperature, external stimulation. And pH and external stimulus have more influence on ·OH generation in situ than other factors. Adjusting pH to alkaline or acidic conditions and selecting ozone or oxygen as the gas source can promote the ·OH generation. MNBs' collapse also releases a large amount of energy, which the temperature and pressure can reach 3000K and 5Gpa respectively, making it efficient to remove ≈90 % of pollutants (i.e., trichloroethylene, benzene, and chlorobenzene). The biofilm can also be removed by physical, chemical, and thermal effect. MNBs technology also has great application potential in drinking water, which can be applied to improve water quality, optimize household water purifiers, and enhance the taste of bottled water. Under the premise of safety, let people of different ages taste, finding that compared with ordinary drinking water, 85.7 % of people think MNBs water is softer, 73.3 % of people think MNBs water is sweeter. This further proves that MNBs water has a great prospect in the drinking water application. This review provides innovative theoretical support for solving the problem of drinking water safety.

Keywords: micro nano bubbles; hydroxyl radical; drinking water security; pollutants; biofilm; engineering application

1. Introduction

Water is the source of life. Eight billion people in the world need to consume about 1.1375×10^{13} m^3 of fresh water resources every year, of which drinking water accounts for about 7.3×10^9 m^3 (Mekal et al., 2023). Therefore, ensuring the safety of drinking water quality is a notable prerequisite to the healthy survival of human society (Mekal et al., 2023). In recent years, due to population growth and urban expansion, the pollution and shrinkage of water sources and the deterioration of urban water supply network systems have significantly, grown inducing severe water supply system quality issues. Based on that, the existence of emerging and refractory pollutants can determine challenges to drinking water safety.

The challenges of drinking water safety mainly focus on water quality changes caused by the complexity of pipe network system, and the inability of traditional treatment technology to remove refractory pollutants in water. At the moment, many researchers have focused and established a suitable guide the layout of pipe network systems and predict the water quality problems that may

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occur in advance and solve them (not discussed in this paper) (Chang et al., 2022; Liu et al., 2016; Barton et al., 2019). For the refractory pollutants removal in drinking water, we found numerous researchers have developed and applied different methods for its treatment.

This paper reviews the drinking water treatment methods found in various investigations, summarizes, and literature (as shown in Table 1); These treatments can be divided into three categories (i.e., physical, chemical and biological methods). Physical processes (Kim et al., 2015; Yüksel et al., 2013; Zhang et al., 2021) (e.g., adsorption and filtration) are simple and feasible, separating the pollutants from the liquid phase, and the separated pollutants remain to be further treated. Chemical methods (Baig et al., 2001; Pera-Titus et al., 2004; Brillas et al., 2009; Moreira et al., 2013; Subramanian et al., 2021; Li et al., 2022; Xu et al., 2022) usually need to add some chemical reagents (e.g., ozone, Fenton's reagent, chlorine dioxide), which shall inevitably produce some toxic intermediate products during the reaction process, inducing secondary pollution. Biological methods (Kurniawan et al., 2010; Ilmasari et al., 2022) tend to be highly selective, and the toxicity and non-biological degradation of some organic pollutants require a longer time and complex equipment to be effectively removed. Due to that, it has shown a high importance of developing green, safe and efficient technologies for drinking water security assurance. Therefore, Micro nano bubbles (MNBs) used to generate hydroxyl radicals (·OH) with strong oxidation in situ can provide a new idea for the safe and efficient removal of pollutants in the water supply network.

Table 1. Summary of drinking water treatment methods.

Treatment Methods		Pollutants Removed from Drinking Water	Advantages	Disadvantages	References
Physico-chemical methods	Adsorption	Organic pollutants (Bisphenol A)	Simple and effective.	Adsorbent regeneration, high cost; The adsorption capacity of regenerated adsorbent decreases and the service life is short.	Kim et al., 2015
	Membrane separation technology	Particles, Sediments, Algae, Bacteria, Protozoa, Small colloid, Virus, Dissolved organics, Divalent ions Monovalent ions, COD	No secondary pollution.	High energy consumption, complex equipment, high intake water quality requirements; Membrane fouling.	Yüksel et al., 2013
	Coagulation/flocculation	Refractory organics	Economical and practical.	Produce secondary pollution.	Zhang et al., 2021
	Ultrasonic decomposition	Particles, Organic pollutants	Short reaction time, simple process facilities.	Relatively low efficiency.	Zhang,2013

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	Photocatalytic technology	Dissolved organic carbon (DOC), Bacteria	Semiconductors are cheap, can mineralize refractory compounds, clean and safe.	Still in the development stage and immature.	Pera-Titus et al., 2004
Chemical methods	Electrochemical advanced oxidation processes (EAOPs)	Organic micro-pollutants	Has the environmental compatibility, versatility, high efficiency, safety.	Relatively low efficiency. Formation of stable by-products.	Brillas et al., 2009; Moreira et al., 2013
	O_3 based oxidation process	Organic pollutants (chlorophenols), Bacteria	Economical and efficient, harmless to most organisms, no harmful by-products generation.	Harmful to human health; High energy demand.	Pera-Titus et al., 2004; Baig et al., 2001
	H_2O_2 based oxidation process	Organic pollutants (chlorophenols), Bacteria	Safe, efficient and easy to use; Widely used to prevent pollution and improve biodegradability.	The reaction process is affected by many factors, and the reaction time is long.	Pera-Titus et al., 2004
	Chlorine based oxidation process	Organic matter, Bacteria Micropollutants, Viruses	Chlorine remains in the water as residual chlorine, and the activity is persistent. High yield of active species, broad-spectrum, safe and effective.	Taste and smell are not ideal, forming more than 40 DBPs. Disinfection effect is not ideal, used for secondary disinfection.	Zhai et al., 2017; Li et al., 2022; Xu et al., 2022; Subramanian et al., 2021
Biological methods	Biological sand filtration (BSF)	Viruses, Bacteria, Heavy metals, Nitrogenous compounds, Pesticides, Organic chemicals, Dissolved organic carbon (DOC), NOM, etc.	Easy operation, efficient and reliable operation, low cost.	(i) Microorganisms have high selectivity to pollutants, and the biodegradation time is long and the equipment is complex.	Pokhrel et al., 2009; Schijven et al., 2013; Hedegaard et al., 2014; Cai et al., 2014; Pramanik et al., 2015
	Biological activated carbon (BAC)	Nitrogenous compounds, Organic carbon, Micropollutants.	The dual functions of adsorption and biodegradation improve the effectiveness of drinking water.	(ii) The uncontrolled growth of microorganisms may lead to health problems.	Li et al., 2012; Yapsakli et al., 2010; Zhang et al., 2010; McKie et al., 2016; Akcay et al., 2016
	Trickling filter (TF)	NH_3-N, Fe, Mn.	No external air supply required.	(iii) The application of biological sand	Tekerlekopoulou et al.,2007

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Biological aerated filter (BAF)	COD, $NH_4{+}$-N, Fe, Mn, Diclofenac.	Economical and effective.	filtration has high requirements on terrain and limited application scenarios.	Hasan et al., 2011; Han et al., 2013, 2016; He et al., 2014; Marsidi et al., 2018
Membrane bioreactor (MBR)	Nitrate, Total organic carbon (TOC), Deamination, Macro pollutants, Anionic micropollutants (perchlorate, bromate, nitrate)	Overcomes the problem of microbial contamination and supports the growth of selected microorganisms.		Buttiglieri et al., 2005; Li et al., 2003; Ricardo et al., 2012; Matos et al., 2008
Fluidized bed biofilm reactor (FBBR)	TOC, THM, Ammonia.	No backwash required, easy to manage.		Xie et al., 2006
Integrated/ combining technologies	Microorganism, Particle, Nitrate, Phosphate, Organic matter, Ammonium	Higher treatment efficiency. Improve the quality of treated water and reduce membrane pollution.		Tian et al., 2008; Tian et al., 2009

MNBs are bubbles with a respective diameter of greater than 1 μm and smaller than 1 μm (Haris et al., 2020). As a kind of tiny bubbles with diameters in the micrometer and nanometer scale, compared with ordinary bubbles (diameter≥1 mm), MNBs have the characteristics of small volume, large specific surface area, long existence time, good mass transfer efficiency, high surface potential, strong biological activity(Due to the high mass transfer efficiency of MNBs, the dissolved oxygen level in the water is increased, thus improving the biological activity), large adsorption capacity, and ·OH generation (Haris et al., 2020; Sakr et al., 2022). MNBs have been widely applied in different fields due to their superior characteristics, as shown in Table 2. For example, MNBs have strong adsorption performance due to their large specific surface area, which is extensively used in metal surface cleaning to remove oil stains on their surface (Tan et al., 2020). According to the high mass transfer efficiency (biochemistry field), MNBs can substantially increase the efficiency of oxygen use for microorganisms, and improve aerobic metabolism and microbial growth (Xiao et al., 2021). The high Zeta potential and high density of NBs may be conducive to nutrient transport and play a positive role in promoting the growth of probiotics, which can be provided using nanobubble water (NBW) to contribute to the production of probiotics (Guo et al., 2019). Over recent years, more and more attention has been paid to the removal process of organic pollutants, refractory pollutants and pathogenic microorganisms in sewage by MNBs. For example, MNBs has a worthwhile degradation effect on methylene blue in printing and dyeing wastewater, and ·OH generated during bubble collapse in water plays a significant role in the degradation process of methylene blue (Wang et al., 2018). Due to attributes of ·OH generation in micro nano bubble water (MNBW), it can significantly inhibit the proliferation of E. coli in sewage by 75 % under the MNBs treatment (Mezule et al., 2009).

Table 2. Application of MNBs in different fields.

Application fields	Main function	Gas type	Bubble size(nm)	Bubble concentration(one/mL)	Characteristics of applied MNBs	References
Biochemical process	Promote the growth of microalgae and increase the output of many high-value products.	air	<200	/	④	Zhu and Wakisaka, 2019; Choi et al., 2014
	Improve biofilm structure and promote aerobic metabolism; Improve COD and ammonia removal rate and reduce aeration.	air	<225	/	④	Xiao et al., 2021; Xiao and Xu, 2020
	Improve the production efficiency of probiotics through fermentation, mainly in the lag stage and logarithmic stage of strain growth.	air	180~220	$(3.59\pm1.14)\times10^7$	⑥	Guo et al.,2019
	Improve the production efficiency and recovery rate of yeast.	air	$\approx3\times10^5$	/	④	Hanotu et al., 2016
Groundwater remediation	Improve the mass transfer efficiency of O_3 and the in-situ remediation efficiency of organically contaminated groundwater.	O_3	10~1000	$(1\sim1000)\times10^6$	③， ④	Hu and Xia., 2018
Surface cleaning	Prevent and remove protein adsorbed on solid surface.	air	25~35	/	⑦	Wu et al., 2006; Wu et al., 2007
	Remove oil stain on metal surface.	air	$(2\sim6)\times10^4$	/	①， ②	Tan et al., 2020
Agronomy	Improve irrigation water use efficiency, crop yield and quality.	air	124~148	$(6\sim7)\times10^8$	④	Liu et al., 2019
	Improve plant growth; Purifying blue-green algae pollution.	air	200~2200	/	④	Nakashima et al., 2010
Soil environment	Change the redox conditions of submerged paddy soil to reduce methane emission.	O_2	128~242	$(6\sim8)\times10^7$	④	Minamikawa et al., 2020
	Remove metal pollutants from soil.	O_2	$<10^3$	/	④	Minamikawa et al., 2015
	Improve the availability of oxygen in clay or sandy soil and improve the soil anoxic environment.	O_2	190~210	$(0.5\sim1.5)\times10^9$	④	Baram et al., 2022
Marine animals and food	Significantly promote the growth of plants, fish and mice.	O_2 air	<200	/ /	④	Ebina et al., 2013
Water pollution treatment	Aeration to improve oxygen mass transfer efficiency.	air	$10^2\sim10^5$	/	④	Li et al., 2014
	Disinfect and can effectively remove bacteria and viruses.	O_3	$(3\sim6)\times10^4$	/	⑤	Sumikura et al., 2007
	Flotation to improve the treatment effect of printing and dyeing wastewater.	air	$<6\times10^4$	/	②,③,④,⑤	Liu et al., 2010
	Degradation of organic pollutants (see Table 4)					

Note: ①, small volume; ②, large specific surface area; ③, long existence time/good stability; ④, good mass transfer efficiency; ⑤, hydroxyl radical generation; ⑥, high Zeta potential and high NB density; ⑦, NBs occupy protein adsorption sites.

Advanced oxidation processes (AOPs) have recently caught the attention of numerous scientists because of their characteristics to degrade pollutants in water through the ·OH generation in the reaction. ·OH is significantly oxidizing (standard REDOX potential is higher at 2.85 V, second only to F_2), which can rapidly oxidize almost all organic matter until mineralization. The process to generate ·OH is complex by traditional advanced oxidation technologies (e.g., ozone oxidation, chemical oxidation, and electrochemical oxidation) due to the number of chemical agents or catalysts that need to be added to the reaction system. As a result of this reaction, a significant secondary pollution risk can be induced in the water treatment process. For instance, for the catalytic oxidation process of ozone, various dissolved metal catalysts (Zn^{2+}, Mn^{2+}, and Cu^{2+}) or solid metal catalysts (TiO_2, MnO_2, and Al_2O_3) need to be added to the reaction. These catalysts use not only increases the cost of water treatment but also has the possibility of metal leaching, which leads to certain risks and challenges to water treatment (Priyadarshini et al., 2022). Based on that, this method can be widely applied to sewage treatment. For drinking water, the essential standards, such as water quality and sensitivity, cannot be solved using the traditional AOP during its treatment. Therefore, generating ·OH safely, greenly, and efficiently has become a grave bottleneck problem that restricts the development of AOPs in drinking water treatment.

Compared with the traditional ·OH generation methods, ·OH can be generated by MNBs in the process of dissolution and collapse without adding any chemical agents or catalysts (Temesgen et al., 2017a), which has advantages of cleanliness, safety, and environmental protection. It is very suitable for ensuring the safety of drinking water with high water quality standard and high sensitivity. Therefore, MNBs technology has gradually shown potential in drinking water treatment application; however, its technology has barely been tested for the drinking water security field. The main reasons can be defined as follows: (i) It is difficult to obtain stable MNBs in water; (ii) It is low efficiency of ·OH generation by MNBW; (iii) The removal efficiency of pollutants cannot be guaranteed. In order to solve these issues, this paper focuses on reviewing the generation process and particle size characteristics of MNBs in water. Mostly, the process is to obtain stable and controllable MNBW by physical or chemical methods. Thus, we sort out the bubble collapse and ·OH in situ generation process and its influencing factors in MNBW that analyze its potential application for drinking water safety to combine the removal mechanism of pollutants and pipe wall biofilm. Based on this method, the MNB technology provides an innovative theoretical basis and technical support for solving the problem of drinking water safety.

2. Generation Process and Characteristics of MNBs in Water

2.1. The Generation Process of MNBs in Water

Continuous and stable generation of a large number of MNBs is the premise and basis for the broad application of its technology in various fields; hence, it is crucial to understand how to generate MNBs in water. In this section, we describe deeply the methods to produce MNBs in water. By comparing different occurrence conditions and equipment structures of MNBs, a suitable guide to carry on a stable generation of MNBs in the drinking water treatment process and improve the feasibility of its technology. Table 3 summarizes ten methods for generating MNBs in water and provides an overview of their advantages and disadvantages.

According to Table 3, the generation methods of MNBs can be summarized into two categories (i.e., mechanical and chemical). The mechanical methods are based on mixing up water and gas by increasing pressure. Then, applying high-speed rotation, impact, and cutting the water-gas mixture releases high-density MNBs in instantaneous dispersion, which can be obtained by pressurizing saturation, bubble shear, cracking, and mechanical stirring without any catalyst (Temesgen et al., 2017a). Chemical methods usually require chemical or electrolytic reactions to generate MNBs, which differ from mechanical processes due to their strong dependence on chemical reagents and catalysts. Moreover, this process produces uncontrollable by-products, which cause secondary pollution to the water quality environment if it is applied to the field of water purification. For practical cases, the mechanical way of simple operation, cleanness, and safety is often used to generate MNBs, finding that most methods include ultrasonic cavitation, hydrodynamic cavitation, pressurized dissolved gas release, and dispersed air method. Various investigations have further explored the influencing factors of the MNB process generated by different mechanical techniques. Such as the effects of ultrasonic time, ultrasonic cavitation times, and ultrasonic frequency increase the number of NBs generated using ultrasonic cavitation (Huang, 2016). By the pressurized dissolved gas release method, it was found that the diameter and quantity density of generated MBs depended on the cavitation mode of the nozzle, analyzing the liquid volume flow influence (decompression nozzle) and dissolved gas concentration upstream of the nozzle (Maeda et al., 2015).

Table 3. Summary of different micro nano bubbles generation methods.

Generation methods	**Generation process**	**Influence factor**	**Advantages**	**Disadvantages**	**References**
Hydrodynamic cavitation	When a large pressure difference is generated in the moving fluid, hydrodynamic cavitation will be observed, resulting in MNBs.	Pressure difference.	High efficiency and low energy consumption.	Bubble size is not easy to control.	Etchepare et al., 2017; Maeda et al., 2015; Huang et al., 2022; Sakr et al.,2022
Ultrasonic cavitation	Apply sound field to make the liquid generate tensile stress and negative pressure. If the pressure is too saturated, MBs will be generated.	Ultrasonic time, frequency.	The bubble size is small and uniform.	Complex operation for large-scale treatment.	
Optic cavitation	A certain wavelength of light is irradiated on the photocatalysis material, which makes the electrons transit, and MNBs precipitate.	Wavelength of light.	No secondary pollution.	High cost, not conducive to mass production.	
Jet dispersion method	The air-liquid mixture is formed after the air compressor is injected or inhaled by itself, and then injected at high speed, relying on the turbulence between the air and liquid to generate MNBs.	Air intake.	Rapid generation of MNBs with uniform size.	The air intake is difficult to control.	
Compressed air passing through diffusion plate method	The pressurized air enters the liquid phase through the micropores with a certain size on the special diffusion plate, and the gas forms MNBs under the shear of the micropores.	Size of micropore.	Relatively simple operation, easy to form MNBs.	Expensive device, pores are easy to block.	
Mechanical force high-speed shearing air method	The larger bubbles in the liquid are divided into MNBs by using the shear effect generated by the high-speed rotating impeller.	Impeller rotation.	Rapid generation of a large number of MNBs.	Unstable bubble size, high energy consumption.	
Dissolved gas release method	First, pressurize the gas to make it supersaturated and dissolved, and then decompress the gas to release, thus producing MNBs.	Pressure and nozzle cavitation mode.	Simple operation and low energy consumption.	Discontinuous gas dissolution and release, low efficiency.	

Aeration method	Directly use various micro nano bubble generators to aerate in water, producing MNBs.	MNBs generator type.	Easy to operate, non-toxic and residue free.	The instrument is expensive.
Chemical reaction method	Add chemical reagents to the solution to make it react violently, producing MNBs.	Type of reactant.	High bubble generation efficiency.	Bring secondary pollution
Electro-chemical method	Electrolyze water through electrode to form MNBs on the positive and negative plates.	Voltage size, electrolytic time .	The size of bubbles can be controlled.	High energy consumption and low efficiency.

MNB generation devices are based on the above mechanical methods, which have been industrialized for their application. Moreover, there are four types of mature generators: pressure dissolving type, vortex type, Venturi type, and jet type, which have different efficiencies in producing MNBs. Among them, the pressure dissolving type micro nano bubbles generator (MNBG) uses the principle of pressurized dissolved gas release method to generate MNBs. The production efficiency of MNBs is low due to the discontinuity of the gas-dissolved and released processes. Vortex type MNBG utilizes high-speed crushing and shear interactions between gas-liquid mixtures to form MNBs. Wu et al. (2022) reported the efficient generation of MNBs under low energy consumption conditions using the self-developed vortex type MNBG. According to numerous scientists, Venturi type MNBG is highly used due to its simple structure, high efficiency of bubble generation, and low energy consumption. Li et al. (2017) studied the influence of the main parameters of Venturi bubble generator, such as injection hole diameter, injection hole number and divergence angle, on the bubble generation process in water. The results showed that the divergence angle is the central parameter controlling bubble size, and the larger the divergence angle, the smaller the bubble size. Zhao et al. (2019) further studied the mechanism of the influence of divergence angle on bubble size, revealing that the bubble might experience a drastic deceleration in the divergence stage of the Venturi channel. Due to the large divergence angle, the bubble velocity shall decrease and extend the time of powerful interaction between gas and liquid phases, which makes it stretch and deform, causing the bubbles to burst and create more and smaller bubbles. The design of jet type MNBG takes advantage of Venturi effect. The fluid channel first converges and then expands. In the convergence stage, the fluid pressure energy is converted into velocity energy, creating a low-pressure area; thus, gas is self-aspirated from the highly reduced pressure point. The gas-liquid mixture enters the diffusion stage through the throat of the injector, reducing the velocity; afterward, the MNBs are generated by the turbulence and shear effect between the gas and liquid. Thus, using a liquid ejector instead of a traditional agitator, the vibration of the agitator can be avoided, which has the advantage of low equipment maintenance cost.

According to the above criterion, there are various types of MNBs generation methods in water. Nevertheless, it is hard to obtain bubble water with stable particle size distribution either by mechanical or chemical methods; hence, the size distribution of bubbles in water is immense, ranging from tens of nanometers to tens of micrometers. Based on previous approaches, the bubble generation process is limited to the mechanical process of bubble cutting, and there is no scientific unified consensus on the stable generation and existence mechanism of bubbles. Therefore, the scientific community refers to this kind of water containing MBs and NBs as MNBW. It is worth mentioning that different generation methods and test conditions influence the MNBs' quantity and characteristics. And then affect the effectiveness of MNB technology in drinking water treatment applications. By exploring and optimizing the stable generation mechanism, the occurrence conditions and equipment structure of MNBs can guarantee the effective generation of MNBs, improving the quality and quantity of MNBs in drinking water treatment. The MNBs generation process in water is shown in Figure 1A.

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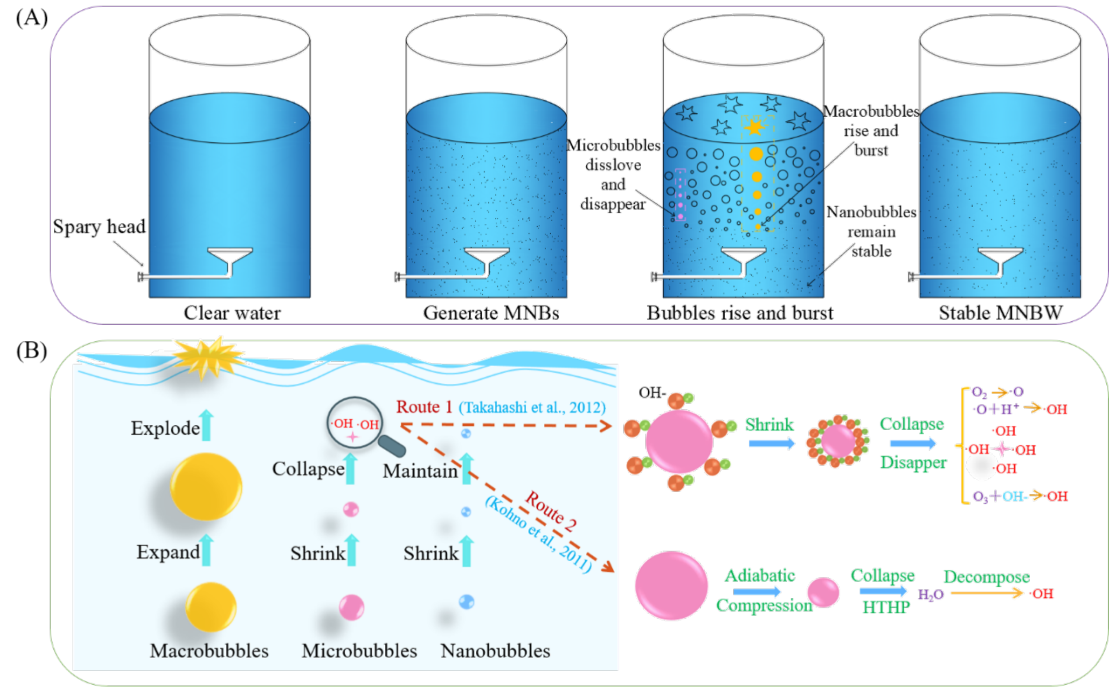
2.2. Characteristics of MNBs in Water

It is crucial to analyze the MNB characteristics, which have been widely used in various aspects. Compared with ordinary bubbles, MNBs have the characteristics of small volume, large specific surface area, long existence time, good mass transfer efficiency, high surface potential, strong biological activity, large adsorption capacity, and ability to generate ·OH, described in detail below.



(C)

	Macrobubbles	Microbubbles	Nanobubbles	References
Size	>100μm	1-100μm	<1μm	
Specific surface area	Small	Large	Larger	
Buoyancy force	Large	Small	Smaller	
Existence time	10^0~10^1s	10^1~10^2s	>10^5s	Temesgen et al.,2017a; Sakr et al., 2022
Rising velocity	>10^4μm/s	10^1~10^3μm/s	<10^0μm/s	
Mass transfer efficiency	Low	High	Higher	
Zeta potential	/	-50mv~10mv	<-50mv	
Formation of hydroxyl radicals	/	Yes	Yes	
Internal pressure	Low	High	Higher	
DO level	<10^0mg/L	10^0~10^1mg/L	>10^1mg/L	

Note: HTHP, high temperature and high pressure.

Figure 1. Differences among Microbubbles, microbubbles and nanobubbles. (A) The generation process of micro nano bubbles in water. (B) Mechanism of hydroxyl radical generation by micro nano bubbles. (C) The difference among macrobubbles, microbubbles, and nanobubbles.

(1) Long existence time. After generating ordinary bubbles (diameter ≥1 mm) in water, they can rapidly rise to the surface, rupture, and disappear, making their existence time very short in water. Compared with ordinary bubbles, the existence time of MNBs is significantly longer in water, and the process from generation to collapse usually lasts tens of seconds or even minutes (Takahashi et al., 2003). Moreover, for MBs, the smaller the volume is, the slower the rise rate in water is, and the longer the existence time is. For NBs (Azevedo et al., 2016), they can exist for several weeks after being generated in water, as shown in Figure 1.

The stability mechanism of NBs in water has played a crucial role in the existence of MNBs for a long time in water. Therefore, this paper summarized the mechanism and reasons for the stable existence of NBs in water. Firstly, MNBs' sizes are smaller, inducing their buoyancy in the water, which makes them rise very slowly and steadily through the water. For instance, for bubbles with a

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radius of 100 nm, the rising speed in water is around 20~30 nm/s (Chaplin, 2019; Seddon et al., 2012). MNBs with a diameter of less than 1 μm rise much slower in water than Brownian motion (Qiu et al., 2017). The inner density of bubbles at the nanoscale may be very high, even close to the liquid density of gas, which increases the NBs' life by four orders of magnitude (Zhang et al., 2007). It is worth pointing out that the density inside the bubble increases with the decrease in the bubble size, indicating more stability with a small size. By measuring the angle corresponding to the liquid phase adjacent to the NBs, is well known as the contact angle, it was found that compared with the macroscopic bubbles, the contact angle and radius of curvature of NBs are much larger, and the corresponding Laplace pressure driving bubble dissolution was reduced, which greatly improved the stability of the NBs in solution (Zhang et al., 2006). Strong hydrogen bond presence at the NBs interface in water further increases the stability of the NBs, whose structure is different from that of bulk water, and it can keep NBs stable at lower internal pressures (Nagayama et al., 2006; Seddon et al., 2012). To explore the bubble interface characteristics, it can be found that a large number of OH- ions accumulate on the surface of MNBs, inducing a high negative Zeta potential, and the repulsive force between negative charges prevents the merger between NBs (Ushikubo et al., 2010). The surface of NBs is partially covered by hydrophobic impurities (e.g., oil, fat, and carbon particles) that further aggravates the resistance of bubble merger (Yasui et al., 2016a, 2019). Thus, the nanoscale particle size and particular interfacial properties of the bubble allow NBs in water to show high stability and durability.

(2) Good mass transfer efficiency. As a terminal electron acceptor of microorganisms, dissolved oxygen (DO) plays an important role in aerobic biodegradation. Compared with ordinary bubbles, MNBs contributes to the increase of DO concentration in water due to its high mass transfer efficiency (Sakr et al., 2022). It was found that the mass transfer efficiency of MBs with an average particle size of 33 μm was much higher than that of ordinary bubbles with an initial particle size of 10 mm. The dissolved oxygen peak value (DOPV) and the average initial dissolved oxygen increase rate (AIDOIR) of oxygen MBs were 100 times and 2 times higher than those of ordinary oxygen bubbles, respectively. The DOPV and AIDOIR of air MBs were 35 times and 1.05 times higher than those of ordinary air bubbles, respectively (Li et al., 2014a). The DO mass transfer rate of oxygen MNBs was 125 times higher than that of ordinary air bubbles. Meanwhile, the highest DO peak was 3 times higher (Li et al., 2014b). The DO concentration produced by MBs aeration was 9.87 mg/L in 60 min. While the DO concentration produced by ordinary aeration was only 6.54 mg/L in 100 min under the same airflow condition (Tao et al., 2011). The oxygen utilization rate and volume mass transfer coefficient of the MNBs aeration system were about twice as high as that of the ordinary bubble aeration system (Temesgen, 2017b).

Generally, the mass transfer rate of gas depends on and is positively correlated with the mass transfer area of the gas-liquid phase; MNBs have shown a high mass transfer because of their large mass transfer area. According to Henry's law, when the bubble diameter is small, the surface tension makes the MBs shrink continuously due to undergoing self-compression and dissolution in water, making the dissolution rate of gas in water reach supersaturation, and improving the mass transfer efficiency (Zhang et al., 2020; Ljunggren and Eriksson, 1997). This statement can be explained by the Laplace equation, which is defined as follows:

$$\Delta P = 2\gamma / R \qquad (1)$$

where ΔP is the pressure difference between the inside and outside the bubble, γ is the surface tension of the interface between the bubble and the surrounding liquid, and R is the bubble radius. Interestingly, with a smaller bubble size, the internal pressure and specific surface increase significantly, permitting the gas to pass through the bubble interface and dissolve into water, which is conducive to gas-liquid mass transfer. Moreover, with a high difference in pressure between the inside and outside of the bubble, the mass exchange from the bubble to the water will be faster (Henry, 1832). Notably, when MNBs rise very slowly and have a stable existence in water and prolong the gas-liquid mass transfer time, the gas-liquid mass transfer might be elevated.

(3) Large adsorption capacity. MNBs have a large specific surface area due to their small volume; thus, the contact area with pollutants is also extensive, significantly improving the adhesion probability between contaminants and bubbles. These compounds (pollutants) are adsorbed on the interface of MNBs, where they are degraded by oxidants or rise to the water surface with MNBs. With a pH 8, due to the contact promotion between aromatic hydrocarbons and ·OH at the MNBs interface, the oxidation efficiency of ozone MNBW for aromatic hydrocarbons increased by 13.6 %~22.6 % compared with ozonized water (Shen et al., 2023). Compared with conventional macro bubbles, oil is easily adhered to the surface of MNBs due to the large specific surface area per unit volume of liquid, and due to the low density, oil can rise to the surface with MNBs by flotation for oil collection and oil-water separation (Jin et al., 2021). With the assistance of deionized water, MNBs successfully removed 80 %-90 % of the oil on the surface of metal parts, and had the advantages of low energy consumption, sustainability, efficiency, and green (Tan et al., 2020).

(4) Generation of ·OH. MNBs have been widely applied for water treatment due to their ·OH generation with powerful oxidizing capacity. Many studies have confirmed that free radicals, including ·OH, are generated in the MNBs collapse process. Recently, the mechanism of MNBs generating free radicals has not been deeply studied, which can be summarized into two theories. The ion accumulation theory and adiabatic compression theory induced by ultrasonic cavitation or hydrodynamic cavitation. With regard to the former, in the absence of dynamic stimulation, the high concentration of ions accumulated at the gas-liquid interface and the accumulated chemical energy play an important role in the generation of ·OH and alkyl radicals during the MBs collapse process (Takahashi et al., 2007b). By studying the degradation of methylene blue by MBs, it was also shown that in the absence of any dynamic stimulation, air MBs could continuously generate a large amount of ·OH, in which the decomposition of oxygen molecules caused by the rapid increase of the absolute value of the Zeta potential at the gas-liquid interface was the key to the generation of free radicals. And the higher air flow rate and lower pH were favorable to increase highly the ·OH generation (Wang et al., 2018; Takahashi et al., 2012). Ozone MBs reacted with OH- at the gas-liquid interface to generate ·OH (Takahashi et al., 2012). As shown in path 1 in Figure 1B, the above research reports all support the ion accumulation theory.

On the other hand, the adiabatic compression theory describes that when water is exposed to ultrasonic radiation, a higher number of tiny bubbles appear and burst violently, which is well-known as the acoustic cavitation phenomenon (Takahashi et al., 2007b). These tiny bubbles repeatedly expand and contract regarding the incident ultrasonic wave pressure oscillation. If the bubble contraction speed exceeds the speed of sound, the internal temperature of the bubble will rise sharply due to the adiabatic compression when it bursts. All of this can establish a high hot spot. As previously stated, the internal pressure of MNBs is inversely proportional to their particle size, indicating that a small particle size increases the internal pressure. Therefore, a high-pressure point will also form in the final stage of the contraction and collapse of MNBs. Under this extremely high temperature and pressure condition, MNB collapses, and ·OH is generated, as shown in path 2 in Figure 1B. When high-frequency (1650 kHz) ultrasonic waves were irradiated into water dissolved with different gas molecules, free radicals would be generated, and the generation mode of free radicals was determined by the dissolved gas molecules (Kohno et al., 2011).

Due to the strong oxidation capacity of ·OH, MNBs technology plays a crucial role in the removal process of refractory organic matter. We used MNBW to treat the phenol solution and found that the degradation rate of phenol was as high as 52.8 %. After adding tert-butyl alcohol to quench ·OH, the degradation rate of phenol was only 11.1 %. Moreover, the DMPO-OH was detected by electron spin method, which fully showed that ·OH was generated in MNBW, as shown in Figure 2A. Notably, the number and type of free radicals generated during the collapse of MNBs are also affected by diverse factors, such as gas type, pH value, temperature, bubble size, etc., which will be discussed in detail in Section 2.2.

(5) High Zeta potential. According to the theory of compressed electric double layer, the MNBs surface adsorbs negatively charged surface ions and positively charged countercharged ions due to the electrical attraction. Zeta potential is commonly used to characterize the potential difference of the surface charge formation of MNBs. Indicating that is essential to determine the interaction of bubbles during the merging process and the way of interaction between bubbles and other materials

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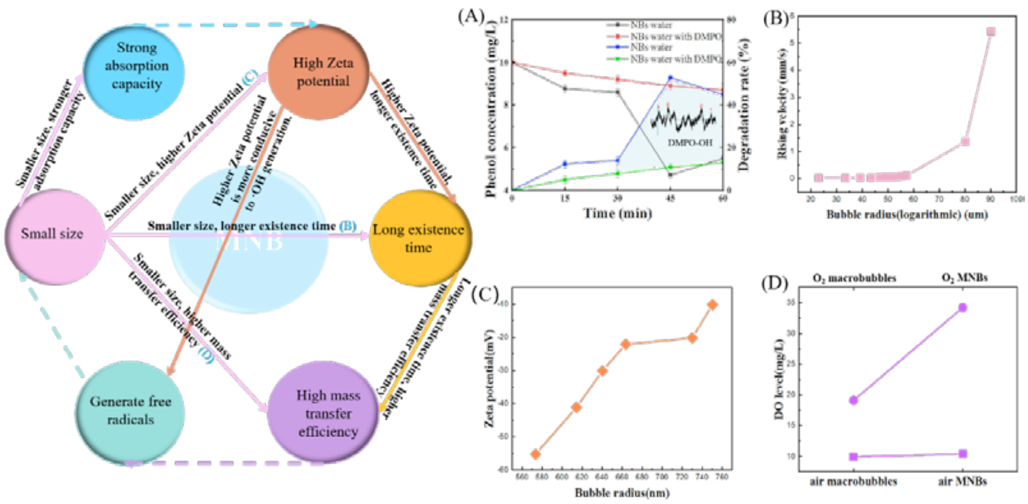
(Jia et al., 2013). When MBs contracts in water, the charged ions are rapidly concentrated and enriched at the very narrow bubble interface, inducing a significant increase in Zeta potential. Very high Zeta potential values can be produced at the interface before the bubble collapses (Takahashi et al., 2007b). Moreover, the smaller particle size of MNBs, the higher concentration of ions aggregated per unit area, and the higher Zeta potential is produced. Takahashi, (2005) reported the Zeta potential of MNBs surface in aqueous solution and found that MBs were negatively charged under a wide range of pH conditions, but positively charged only under strongly acidic conditions. For example, in distilled water at pH 5.8, air MBs were negatively charged with an average Zeta potential of about -35mv. With the increase of pH value, the absolute value of Zeta potential increased until to reach a stable value of about -110mV at pH 10. It was also proved that OH^- and H^+ were the key factors affecting the charge at the gas-water interface. In addition, many studies have confirmed that the Zeta potential of different MNBs is negative, but its absolute value changes with the type of gas in the MNBs, the pH of the solution, and the type and concentration of the electrolyte solution (Ushikubo et al., 2010; Khaled et al., 2018; Meegoda et al., 2018).

Based on that, it is worth noting that the various characteristics of MNBs are not unrelated, but consistent and co-dependent, as shown in Figure 2. With a smaller MNBs size, the adsorption capacity, the Zeta potential, and the existence in water is significantly elevated, which is more conducive to improve the gas-liquid mass transfer and the biological activity of MNBs (as shown in Figure 2B, C, and D). An increase of Zeta potential on the surface in MNBs plays a crucial role in the formation of ·OH during its collapse, besides, it is beneficial to the stable existence of MNBs in water. Analyzing the factors that affect the MNBs stability, the results showed that MNBs with high negative Zeta potential could be generated in a solution with high pH value, low salt concentration and low temperature. And the bubbles generated under alkaline conditions were smaller and more stable, while those generated under acidic conditions were larger and more unstable (Meegoda et al., 2018). Hamamoto et al. (2018) confirmed that MNBs were more stable under alkaline conditions. This can be explained by the fact that at higher pH and in the presence of higher OH^- concentration, the MNBs surface charge becomes more negative, the Zeta potential is higher, and the repulsion between bubbles is greater, hence, more stable. In particular, because of these closely related the MNBs characteristics that its technology shines brightly in different fields.



Note: Solid line means relationship, dotted line means relationship unknown. (i) TB means for tert-butanol, ·OH quencher. Experimental conditions: Temperature 15°C, pH 7.3, initial concentration of phenol 10 mg/L.

Figure 2. Relationships among the characteristics of MNBs. (A) Degradation of phenol by MNBW. (B) The relationship between bubble rising velocity and bubble radius indirectly reflects the relationship between bubble rising velocity and existence time. (C) The relationship between bubble Zeta potential and bubble radius. (D) The relationship between DO level and bubble radius indirectly reflects the relationship between bubble mass transfer efficiency and bubble radius (Source of original Data: (B), Li et al., 2014a; (C), Li, 2020; (D), Li et al., 2014b).

3. Characteristics of MNBs Collapse and Influencing Factors of Hydroxyl Radical Generation in MNBW

3.1. Characteristics of MNBs Collapse

The growth and collapse of MNBs is accompanied by changes in bubble morphology and surrounding micro-environment. A complete bubble period is divided into three phases: growth, collapse, and post-collapse (Yan et al., 2019). During the growth phase, the bubble slowly expands (lasting tens of milliseconds); During the collapse phase, the bubble rapidly shrinks (lasting more than ten microseconds). In the process of bubble growth and collapse, the bubble generates microjet and shear stress on the surrounding fluid, forming a local high temperature and pressure point, which induces the ·OH generation under extreme environments of high temperature and high pressure. In the post-collapse phase, the fluid gradually returns to its original state under the action of the previous two phases. Kroninger et al. (2010) analyzed the collapse process of MBs through high-speed photography, finding that the bubble expanded to a maximum radius of 750 μm at 70 μs, and collapsed for the first time at 140 μs. The team further used particle tracking velocimetry to study the influence of MBs collapse on the surrounding flow field, and found that shortly before the bubble collapsed, a ring vortex formed near the bubble wall, and a high-speed liquid jet was produced after the bubble collapsed. The discovery of this high-speed jet is consistent with the results of a 2007 study by Zwaan's team, which showed that bubbles expanded faster than they contracted. Meanwhile, high-speed jets were generated when bubbles collapsed at the scale of 100 microns near the wall (Zwaan et al., 2007).

To compensate for the uncertainty of the morphology test results, scientists promote using numerical simulation methods to quantitatively study the environmental conditions of the MNBs collapse, of which we are more concerned about the high-temperature and high-pressure points formed by the MNBs collapse. Yasui et al. (2016b，2019) proposed to use the bubble dynamics model to calculate the high-temperature and high-pressure points, and this model had been verified by the single-bubble sonoluminescence model and sonochemical studies (Yasui., 1997, 2005).

$$\frac{dn_i}{dt} = -4\pi R^2 D_i \frac{(c_{s,i} - c_{\infty,i})}{R} \tag{2}$$

Where n_i refers to the number of gas molecules in a bubble, t refers to time, R refers to the instantaneous radius of bubble, D_i refers to the diffusion coefficient of gas i in the liquid, $C_{S,i}$ refers to the saturation concentration of gas i in the liquid at the bubble wall, and $C_{\infty,i}$ refers to the concentration of gas i in the liquid away from the bubble, It is assumed that the bubble surface is clean and not covered by hydrophobic materials.

$$D_i = B_i e^{-\frac{\nabla E_i}{R_g T_{L,i}}} \tag{3}$$

where R_g is the gas constant, and $T_{L,i}$ represents the liquid temperature at the bubble wall.

$$c_{s,i} = \frac{10^3 \rho_{L,i} N_A P_g}{K_{H,i} M_{H_2O}} \left(\frac{n_i}{n_t}\right) \tag{4}$$

where $\rho_{L,i}$ refers to the instantaneous liquid density at the bubble wall, N_A represents Avogadro's constant, P_g refers to the instantaneous pressure inside the bubble, $K_{H,i}$ is the Henry's law constant of gas type i under the instantaneous liquid temperature ($T_{L,i}$) at the bubble wall, which is a function of temperature, M_{H_2O} expresses the molar mass of water, n_i is the instantaneous number of molecules of gas type i in the bubble, and n_t represents the instantaneous total number of molecules in the bubble.

Using numerical simulations, it was found that the oxygen NBs dissolved in water would generate ·OH due to the high temperature and pressure (2800 K and 4.5 GPa) in the moment. Moreover, ·OH might be generated when the temperature and pressure inside the air NBs increase

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to about 3000 K and 5 GPa, respectively (Yasui et al., 2019). Some investigations reported that in this process if the temperature rises to >5000 K, the water vapor and non-condensable gases (including air) in the bubble shall decompose and generate free radicals (such as ·OH) (Takahashi et al., 2007b). Wang et al. (2021) described that due to the inertia and compressibility of the bubble contents, an immense implosion force might be generated when the bubble collapses, causing local hot spots and releasing a large amount of energy, with a high temperature (500~15000 K) and pressure (100~5000 Pa). Sun et al. (2018) confirmed that the high hot spot temperature formed by bubble collapse ranged from 2000 to 6000 K. Recently, there is no consensus on the high-temperature and high-pressure points created by the collapse of MNBs, as shown in Table 4.

Based on the above, MNBs produce an extreme environment of high temperature and high pressure when they collapse, generating ·OH in these conditions. The author believes that ·OH generation should involve substances containing two elements of hydrogen and oxygen in water, such as water molecules, hydroxide ions or organic compounds containing hydrogen and oxygen bonds. The chemical bond related to hydrogen and oxygen in the substance is broken under high temperature and pressure to generate ·OH, even though this speculation needs further studies to confirm.

Table 4. Temperature and pressure at the time of MNBs collapse.

Bubble type	T	P	Reference
MNBs	＞5000K	/	Takahashi et al., 2007b
Air NBs	3000K	5GPa	Yasui et al., 2019
Oxygen NBs	2800K	4.5GPa	
MNBs	500~15000 K	100~5000 Pa	Wang et al., 2021
MNBs	2000–6000 K	/	Sun et al., 2018

3.2. Influencing Factors of ·OH Generation in MNBW

Existing conventional advanced oxidation techniques generate free radicals with the risk of catalyst dependence and disinfection by-products. Applying to sewage treatment is acceptable, but for drinking water quality, the standard is high and sensitive for water quality. The presence of catalysts and disinfection by-products shall aggravate the water quality sensitivity and threaten the water quality health. Although the MNB technology is green and safe, the free radical generation efficiency is low, and its utilization in drinking water is still limited to a certain extent. Therefore, we require deeply exploring the free radical generation mechanism and its influencing factors in MNBW, which improves the generation efficiency of ·OH and replace other advanced oxidation technologies in water treatment. The mechanism of ·OH generation by MNBs has been discussed in the above sections. To enhance ·OH generation by MNBs, it is essential to understand factors that affect the concentration of ·OH in MNBW. Existing studies have discussed the effects of pH, gas type, bubble size, temperature, and external stimuli on the production of ·OH by MNBs, as shown in Figure 3 A.

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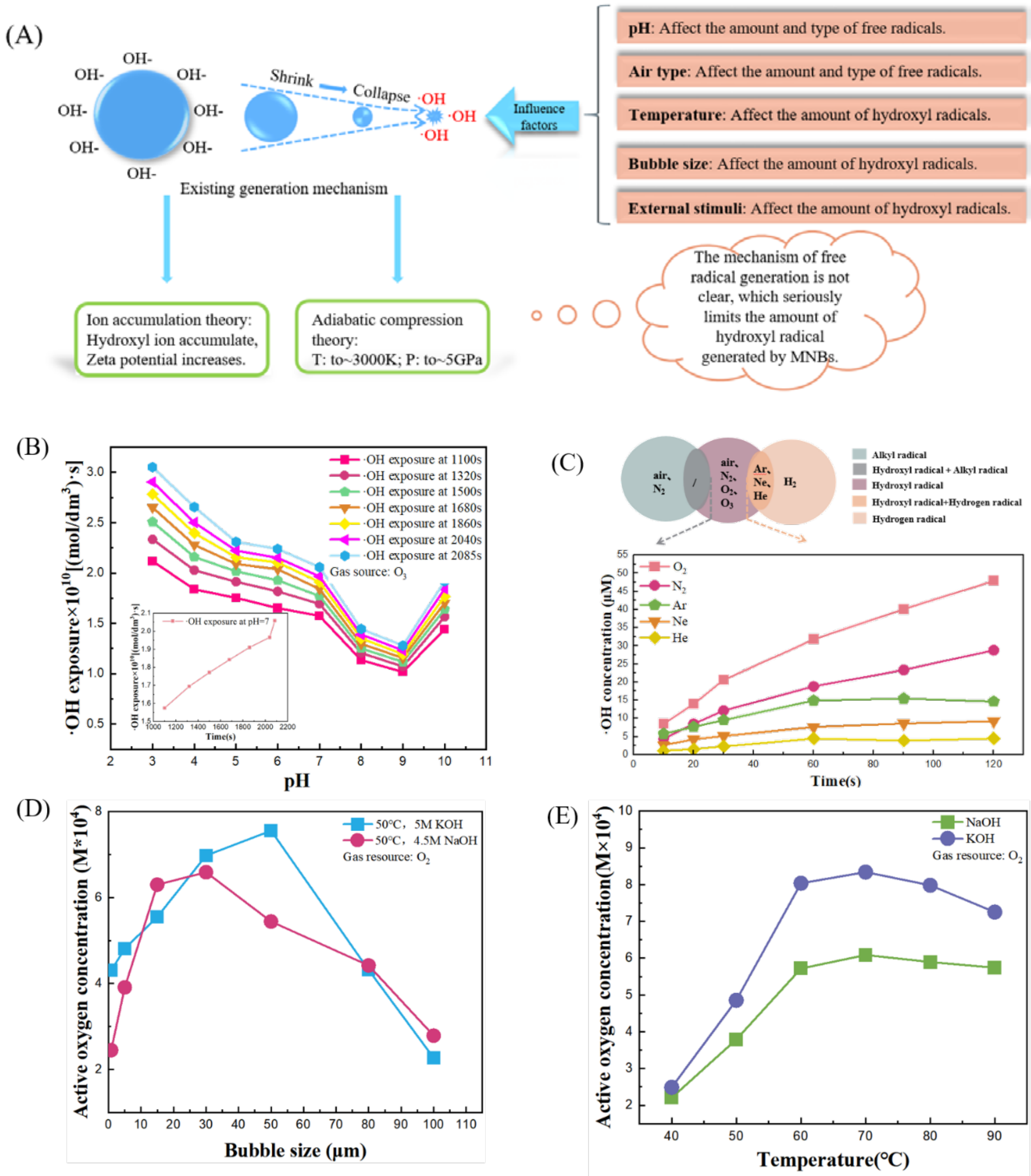

Figure 3. Influence of different factors on the generation of ·OH by MNBs. (A) Factors affecting the generation of ·OH by MNBs. (B) Effect of pH on ·OH exposure. (C) Effect of gas source type on the generation of free radicals by MNBs. (D) Relationship between active oxygen concentration and bubble size. (E) Relationship between active oxygen concentration and temperature. (Source of original Data, (B): (Khuntia et al., 2015); (C): (Kohno et al., 2011); (D): (Yu et al., 2017); (E): (Yu et al., 2017)).

(1) pH. pH affects the generation of free radicals by MNBs from two aspects; The type of free radicals generated by MNBs and the amount of ·OH generated by MNBs. First, we reviewed the current research on the effect of pH value on the type of free radicals generated by MNBs. Takahashi et al. (2007b) found that MNBs in distilled water could generate alkyl radicals during the rupture process, which may be caused by the presence of trace organic pollutants in the water using electron spin resonance spectroscopy and a DMPO spin capture agent. ·OH might be observed under strongly acidic conditions because pH impacts the charge of the gas-water interface, where the Zeta potential of the MNBs changed from negative to positive. The type of ions accumulated at the interface during collapse may be related to the type of radicals generated. Li et al. (2009a) tested the electron spin resonance to study the free radicals type generated by MNBs collapse. By that method, it was found that the presence of trace organic pollutants in distilled water containing nitrogen MNBs may induce the generation of alkyl free radicals. When the pH was reduced to 2.3, ·OH was generated in solutions containing either nitrogen or oxygen MBs. The above studies indicate that pH can affect the type of free radicals generated by MNBs.

Second, pH affects the amount of ·OH generated by MNBs. It is generally accepted that the increase of hydroxide ions at high pH, which is beneficial for ·OH generation. For ozone MNBs aqueous solution (Takahashi et al., 2007a), ·OH was assumed to be generated by the interaction between ozone and hydroxide ions gathered at the bubble interface during the collapse of MBs. Hence, a higher pH value and hydroxide ions concentration induce more favorable conditions for generation of ·OH. Similarly, it has been suggested that the free radical chain generating ·OH is stimulated by chemical reactions between ozone and hydroxide ions. Thus, high pH conditions induce the ·OH generation in ozone systems (Gottschalk et al., 2009). However, in the absence of an accepted explanation, various experiments have also shown the opposite effect of favoring ·OH generation under strongly acidic conditions induced by the addition of hydrochloric, sulfuric, and nitric acids. Takahashi et al. (2007a) used electron spin resonance spectroscopy to show that a large amount of ·OH might be generated when ozone MBs burst in strongly acidic aqueous solutions. Using the spectral characteristics of DMPO-OH formed by DMPO and ·OH, it was concluded that oxygen MBs generated more ·OH under acidic conditions (Li et al., 2009). The experiment of phenol degradation by MNBs and the remarkable improvement of phenol degradation rate under acidic conditions also proved this. It has been reported that ·OH is formed after the reaction between oxygen atoms produced by the decomposition of oxygen molecules and protons, so high oxygen concentration or low pH is conducive to the generation of ·OH (Wang et al., 2018). Khuntia et al. (2015) tested p-chlorobenoic acid (PCBA) as the probe compound to quantify and predict the ·OH generated by ozone MBs. The results showed that the exposure value of ·OH decreased with the increase of pH from 3 to 9, but increased at pH 10 due to the increase of hydroxide ion concentration in the solution, and continued to increase with time, as we can see in Figure 3B.

(2) Type of gas source. Similarly to pH, the type of gas source also affects the kind of free radicals and the amount of ·OH generated by MNBs，as shown in Figure 3 C. Regarding the former, Kohno et al. (2011) used electron spin resonance spectroscopy and DMPO as spin trapping agent to study the free radicals generated by ultrasonic cavitation of water samples dissolved with different gases. Finding that the generation of free radicals was related to the type of gas in MNBs, and only ·OH was generated during oxygen MBs collapse. In addition, only hydrogen free radicals were generated during hydrogen MBs collapse, while ·OH and hydrogen free radicals were generated during nitrogen MBs collapse. For noble gas MBs, ·OH and hydrogen free radicals were generated during the collapse process, which indicated that the type of free radical generated by MNBs was related to the type of gas. Furthermore, the results showed that the oxygen MBs generated more ·OH than nitrogen MBs. The number of hydrogen radicals and ·OH generated by the noble gas MBs increased in the order of Ar>Ne>He (Kohno et al., 2011). These findings are consistent with their earlier report (Kondo et al., 1988) on the noble gas MBs. The amount of ·OH generated during the collapse process increased in the following order: Xe>Kr>Ar>Ne>He. They interpreted these results as the generation of ·OH increased as the thermal conductivity of the noble gas decreased, and as the final temperature of the collapsed cavitation bubble increased. Li et al. (2009) analyzed the effect of changing the type of gas supplied to the microbubble generator on phenol degradation. It was found that during the two-hour treatment, the degradation rate of phenol increased in the following order: nitrogen < air < oxygen, 36%, 59% and 83%, respectively. Moreover, the detection by electron spin resonance spectroscopy showed that ·OH was generated by oxygen MBs collapse, and the decomposition of oxygen was the key to free radicals generation. While ·OH was generated by air and nitrogen MBs only under acidic conditions. Therefore, oxygen MBs are the most conducive to the generation of ·OH, followed by air MBs and nitrogen MBs. Since ozone is involved in the reaction of ·OH generation during MNBs collapse, the ozone MNBs can be considered to promote ·OH generation. Hu et al. (2018) applied MNBs to degrade methyl orange, and the results showed that the degradation rate of

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methyl orange by ozone MNBs was much higher than that by oxygen MNBs, indicating that ozone MBs was more conducive to the generation of ·OH than oxygen MBs.

Thus, the gas type can affect the free radicals generated by MNBs. For the impact on the amount of ·OH generated by MNBs, the production of ·OH generated by the collapse of noble gas MNBs increases in the order of Xe>Kr>Ar>Ne>He. The production of ·OH generated by the collapse of non-noble gas MNBs increases in the order of ozone > oxygen > air > nitrogen.

The pH value and gas type have a crucial effect on the generation of ·OH by MNBs, which are closely related and can also be considered together.

(3) Bubble size. Bubble size also plays a crucial role in the generation of ·OH by MNBs. Yu et al. (2017) reported that based on titanium microporous filters to control the size of MNBs to study the effect of their size on the concentration of reactive oxygen species (ROS). The results showed that the dependence of ROS concentration on the size of microporous filters induced a quasi-parabolic change. This is because with the increase of MNBs size, the stability of bubbles is reduced, and the bubbles are more likely to collapse, which is conducive to the formation of ROS; While the surface charge density of bubbles is reduced, it is not conducive to the formation of ROS. Therefore, the dependence of ROS formation on bubble size is a balance between bubble surface charge density and bubble stability, as we see in Figure 3D. Fan et al. (2023) obtained from the calibration model that in the range of water depth from 0.5 to 10 m, the particle size range was easy to generate free radicals from 42 to 194 μm for air MNBs, and 127 to 470 μm for oxygen MNBs.

(4) Temperature. Temperature also has a role in the ·OH generation by MNBs. Yu et al. (2017) explained that in alkaline MNB solution, the ROS concentration first increased and then decreased with the temperature rise. By this effect, it was shown that a parabolic trend, the ROS concentration reached its maximum at 65℃ (Figure 3E). They attributed this phenomenon to the combined effect of temperature on oxygen reactivity, diffusion coefficient, and dissolved oxygen concentration (where ROS and ·OH change in the same trend). Wang et al. (2008) described the effect of temperature on the degradation of rhodamine B by cavitation-induced and rotating jets. The results showed that the degradation efficiency of rhodamine B increased when the temperature increased from 20 ℃ to 40 ℃, and decreased when the temperature further increased from 40℃ to 60 ℃. Correspondingly, Wang et al. (2009a) studied the effect of temperature on the degradation of alachlor by hydrodynamic cavitation, finding that the degradation rate of alachlor increased when the temperature increased from 30 ℃ to 40 ℃. However, it decreased when the temperature reached from 40 ℃ to 60 ℃. These findings also prove that the temperature has a dual effect on the ·OH generation by MNBs. Due to the increase of equilibrium vapor pressure, the rise of temperature promotes the formation of MNBs, which is favorable to the generation of ·OH and the degradation of organic matter. However, if the temperature is too high, water vapor will fill the cavitation bubbles and alleviate the bubble collapse, which is not conducive to the generation of ·OH and degradation of organic matter (Thompson et al., 1999; Frontistis et al., 2012). It is worth noting that the temperature influences other test conditions, which should be comprehensively considered to the actual conditions.

(5) External stimulus. MNBs can generate ·OH, but the amount generated does not meet the needs of practical engineering applications. External conditions are also required to promote the generation of ·OH by MNBs, such as ultrasonic stimulation, catalysts addition, ultraviolet irradiation, etc. Thus, the role of these external stimuli in the process of ·OH generation by MNBs cannot be ignored. It has been noticed that ultrasonic cavitation is one of the methods to generate MNBs, and diverse ultrasonic frequencies play a crucial role in the ·OH generation by MNBs. Masuda et al. (2015) described the effect of ultrasound frequency on ·OH generation by MNBs. The results showed that ultrasound at 45 kHz promoted ·OH generation in MNB solution, while ultrasound at 28 kHz and 100 kHz inhibited ·OH generation. This may be influenced by the ultrasound at 45 kHz that interacts with MNBs with a diameter of about 1 μm and form new diminutive cavitation bubbles; hence, it is suitable for the ·OH generation (Makuta et al., 2013). MBs interfered with the standing wave sound field established by the ultrasonic transducer and reduced the hot spot generated by the cavitation bubble collapse. This indicated that frequencies of 28kHz and 100kHz ultrasound were not conducive to ·OH generation (Makuta et al., 2013). The influence mechanism of ultrasonic frequency on the generation of ·OH by MNBs remains to be further analyzed. Various investigations have shown that the content of ·OH generated by MNBs is proportional to the ultrasonic time and power under a condition of less than 225w (Li, 2020). Through electron spin resonance spectroscopy, it was found that copper as a catalyst could significantly enhance ·OH generated by the collapse of oxygen or air MNBs under acidic conditions. This may be related to the environmental changes inside the ruptured MBs (Li et al., 2009). Tasaki et al. (2009) studied the degradation of methyl orange by MNBs under the irradiation of low-pressure mercury lamp, indicating that ultraviolet irradiation with a wavelength of 185nm promoted the generation of ·OH by MNBs and improved the decolorization efficiency of methyl orange. Gao et al. (2019) used fluorescent probe method to determine ·OH, and found that under ultraviolet irradiation, the content of ·OH generated by ozone MNBs increased by 2~6 times.

Based on the above, it was noticed that the generation of ·OH by MNBs can be more or less affected by various internal or external factors. And pH and external stimulus have more influence on ·OH generation in situ than other factors. To make MNBW generate a high concentration of ·OH as much as possible, under the conditions of selecting a favorable air source (oxygen or ozone), maintaining a better pH and temperature, and controlling the bubble size within a certain range, the generation of ·OH can be further enhanced by ultrasonic stimulation, ultraviolet irradiation, or the addition of catalysts.

4. Effect Mechanism of MNBs on Pollutants and Biofilms in Water

4.1. MNBs Remove Pollutants from Water

Due to the superior characteristics of MNBs, broad application value in the pollutants removal in water has been developed. On the one hand, MNBs have a strong adsorption capacity and can adsorb pollutants to the MNBs interface; besides, the collapse of MNBs generates ·OH, which can effectively oxidize and degrade pollutants. And at the same time of bubble collapse, it also has a certain impact on the pollutants, which intensifies the removal efficiency. In addition, MNBs have high mass transfer efficiency that can increase the level of dissolved oxygen in water, which improves microbial activity and contribute to the biodegradation of pollutants. Therefore, MNBs technology is widely used to remove pollutants from water.

Lu et al. (2022) confirmed the application of MNB coagulation technology in drinking water treatment, reporting that the MNBs coagulation process could significantly improve the humic acid removal efficiency (DOC removal efficiency increased by 27.9%), which had potent practical application potential in drinking water treatment. Hu and Xia (2018) studied ozone MNBs application to repair groundwater contaminated by organic matter and evaluated field tests on trichloroethylene-contaminated sites, showing that the total removal rate of trichloroethylene reached 99% after six days of treatment. Xia and Hu. (2018) conducted an experiment using ozone MNBs to treat groundwater containing complex persistent organic pollutants, showing that after 30 minutes of treatment, most benzene and chlorobenzene were effectively removed with more than 95% removal efficiency. Moreover, they used ozone MNBs to degrade methyl orange in surface water and groundwater, which achieved a remarkable treatment effect (Xia and Hu, 2016). Achar et al. (2020) reported the removal effect of ozone MNBs on butylated hydroxytoluene, and the result showed that compared with the traditional ozone-based process, ozone MNBs could effectively degrade butylated hydroxytoluene and reduce its toxicity, in which ·OH played a key role. Li et al. (2009) used MNBs to degrade phenol and found that the removal rate of phenol by oxygen MBs reached 83% after two hours of treatment. MNBs can also effectively degrade a variety of organic pollutants, and the degradation of organic matter follows pseudo-first-order kinetics, as we can see in Table 5.

Table 5. Organic pollutants degraded by MNBs.

Pollutants	Generation of MNBs	Type of air source	Reaction time(min)	Initial concentration/(mg/L)	pH	Temperature	Degradation rate constant/degradation rate/lnc/c_0	References
Alachlor	Swirling jet-induced cavitation.	air	100	50	5.9	40°C	$4.90\times10^{-2}min^{-1}$	Wang and Zhang, 2009
Rhodamine B	Swirling jet-induced cavitation.	air	180	5	5.4	40°C	62%/$5.13\times10^{-3}min^{-1}$	Wang et al., 2008
Diethyl phthalate	Aeration method	O_3	30	222	9	25°C	98%	Jabesa et al., 2016
Phenol	Dissolved gas release method.	O_2	120	18.8	2.3	35°C	83%/$2.67\times10^{-2}min^{-1}$	Li et al., 2009b
	Dissolved gas release method.	air	180	/	<7	<50°C	30%	Takahashi et al., 2007
	Micro bubble ozonation reactor.	O_3+$Ga(OH)_2$	40	450	/	25°C	99%	Cheng et al., 2018
Methyl orange	Spiral liquid flow coupled pressurized dissolution	O_3	30	10	/	20°C	96%	Xia and Hu, 2016
	Aeration method	O_3	30	50	3~11	20°C	>90%	Xia and Hu., 2018
	Spiral liquid flow-type.	O_3	30	10	/	/	98%	Hu and Xia, 2018
Photoresist	Dissolved gas release method.	O_3	9.6	/	/	22°C	100%	Takahashi et al., 2012
Butylated hydroxy toluene	Aeration method	O_3	0.5	<2	7	/	97%	Achar et al., 2020
Dimethyl Sulfoxide	Aeration method	O_3	/	/	/	/	7.0×10^{-4}-$1.9\times10^{-3}s^{-1}$	Li et al., 2009c
P-chlorophenol	Ultrasonic cavitation.	air	120	/	/	38°C	$0.00899min^{-1}$/-0.83	Teo et al., 2001
P-nitrophenol	Jet cavitation reactor.	air	90	8	3.5	/	50%	Kalumuck and Chahine, 2000
Trichloroethylene	Aeration method	O_3	20	14	/	/	100%	Xia et al., 2018
Polyvinyl alcohol	Dissolved gas release method.	O_3	120	/	<7	<35°C	30%	Takahashi et al., 2007

Benzothiophene	Ultrasonic cavitation.	air	60	/	5	25°C	0.0492min^{-1}	Kim et al., 2005

Notably, the degradation of organic pollutants by MNBs has a certain relationship with pH. The investigation results show that the acid condition is effective in the degradation of the pollutants by MNBs; on the contrary, other research results show that the alkaline environment is suitable for the degradation of pollutants by MNBs. For instance, methyl orange (Xia and Hu, 2018a), phenol (Li et al., 2009) and rhodamine B (Wang et al., 2008) were best degraded by MNBs under acidic conditions. Nevertheless, the alachlor (Wang and Zhang., 2009), benzothiophene (BT) (Kim et al., 2005), and diethyl phthalate (Jabesa et al., 2016) degradation by MNBs were capable under alkaline conditions (Figure 4). This is because pH affects the free radicals generated by MNBs and the physical and chemical properties of the pollutant itself. Therefore, the degradation of organic pollutants by MNBs indicates the dual action of the above two aspects, and we should take comprehensive consideration.

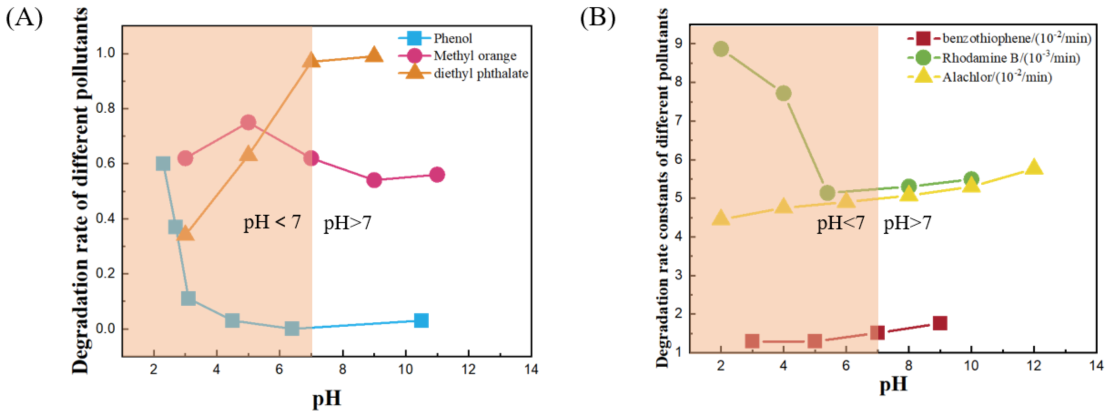

Figure 4. Effect of pH on the degradation of organic pollutants by MNBs. (A) Degradation rates of different pollutants by MNBs. (B) Degradation rate constants of different pollutants by MNBs (Data source: (Kim et al., 2005), (Wang and Zhang., 2009), (Wang et al., 2008), (Xia and Hu, 2018a), (Li et al., 2009), (Jabesa et al., 2016)).

4.2. Control Mechanism of MNBs on Pipe Biofilm Growth

The existence of microorganisms seriously affects the water quality safety in pipelines and threatens human health. A wide use of traditional disinfection methods has unsatisfactory effects on biofilm control and produces disinfection by-products, inducing secondary pollution. In recent years, as a clean, safe and efficient disinfection method, MNBs technology has shown great potential in alleviating biofilm by generating decisive oxidative ·OH in situ. As seen in Figure 6, MNBs can inhibit biofilms from physical, chemical, and thermal effects. In terms of physical results, the micromotor drive test (Yan et al., 2019) and cavitation erosion phenomenon (Hu et al., 2004) indicate that MNBs induce microjet, shock wave and shear stress in the surrounding liquid during collapse, and release a large amount of energy. Based on these effects, it breaks microorganism cell membrane/cell wall and drives the microbial attachment site to move, disturbing the biofilm to fall off. For chemical effects, firstly, ·OH can degrade organic matter in water, reduce the food source of microorganisms, and inhibit the metabolism and activity of microorganisms. Secondly, ·OH can directly kill microorganisms in water and reduce the total amount of microorganisms (The mechanism of ·OH inactivating microorganisms can be attributed to two aspects (Lakretz et al., 2011): i. Oxidation and destruction of the cell wall and membrane of microorganisms. ii. ·OH diffusion into the cell interior inactivates enzymes, damages intracellular components, interferes with protein synthesis and DNA structure, etc.). For thermal effects, the local high temperature generated by the surrounding liquid when MNBs collapses promotes the thermal inactivation of microorganisms. Therefore, MNBs can inhibit biofilm formation from physical, chemical and thermal effects, and their damage to microorganisms combined the above three results (Gogate et al., 2009; Sun et al., 2018) (Figure 5).

Physically, microflows generated by stable cavitation have been shown to have stresses sufficient to destroy cell membranes (Gogate et al., 2009), and are widely used to destroy microbial

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cells to obtain intracellular derivatives. Based on the mechanism of microbial cell destruction in high-speed and high-pressure homogeneous reactors, it was found that cavitation collapse and the resulting pressure pulse played a crucial role in the cell destruction process (Shirgaonkar et al., 1998). Mason et al. (2003) explained that the shear stress and liquid jet generated by the collapse of MNBs might cause physical damage to the cell wall/membrane of microorganisms, and the jet might cause significant pressure on microbial species, thus contributing to sterilization. Chemically, some studies have reported the application of MNBs in the physical-chemical-biological composite fouling of plugging irrigator. Tan et al. (2022) examined the alleviating effect of NBs on the composite clogging of the irrigator of the biogas slurry dripper system. The results indicated that the EPS content in dirt under the NBs treatment was significantly reduced by 29 % ~ 53 % compared with the control group. The experimental results were consistent with the research results (Wang, 2020), which showed that the mass of EPS in the irrigator was reduced by 29 % ~ 53 % under the treatment of oxygen MNBs. The investigation described that MNBs aeration declined the diversity and richness of microbial community in the adhesive blockage of the irrigator and reduced the number of core bacteria that affected the blockage of the irrigator (Li, 2020). Guo et al. (2019) reported that the strong oxidizing ·OH generated by NBs during the collapse process played an essential role in the microorganisms' removal in water. MNBs technology is widely applied in controlling membrane pollution, which can reduce the occurrence of membrane pollution by reducing EPS content. Agarwal et al. (2013) found that NBs treatment could effectively alleviate membrane pollution caused by biofilm attachment. In addition, ·OH generated by MNBs is used in water disinfection treatment, which can effectively remove bacteria, yeast and viruses in water (Khadre et al., 2001). Thermally, the study showed that the collapse of oxygen NBs might induce the liquid temperature at the bubble wall to rise to 94 °C, and the collapse of air NBs might induce the liquid temperature at the bubble wall to rise to 85°C (Yasui et al., 2019). Sun et al. (2018) employed the new hydrodynamic cavitation reactor to generate MNBs for disinfection. Within 14 minutes, the collapse of MNBs induced the surrounding water temperature to rise to 65.7 °C, and achieved 100 % removal of Escherichia coli in water samples.

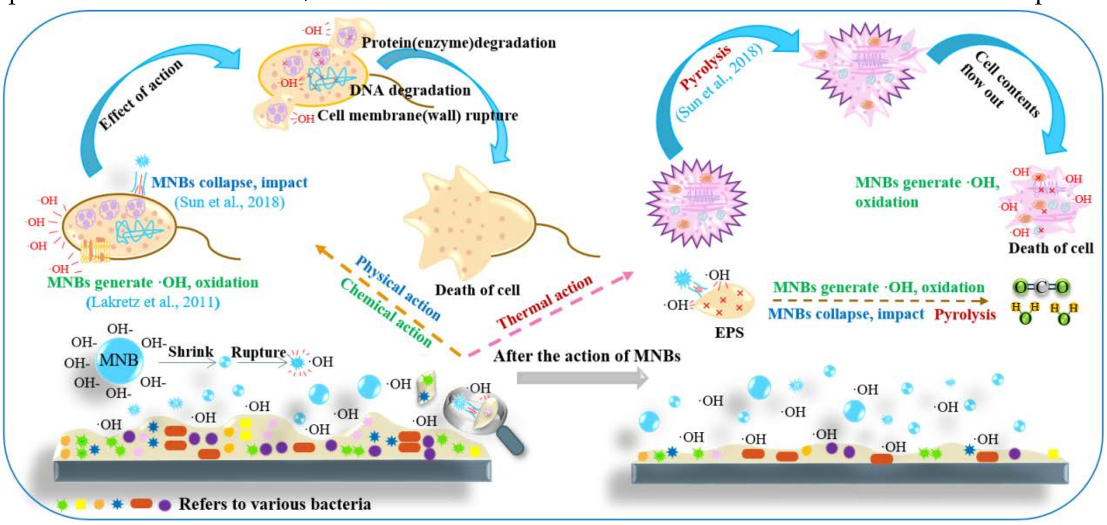

Figure 5. Control mechanism of physical, chemical and thermal effects of MNBs on biofilm.

5. Application Prospect of MNBs in Drinking Water

Human beings need to consume 2-3 Liters (L) of drinking water every day, and the quality of drinking water is crucial to human health. Ensuring the safety of drinking water quality is the premise and basis for improving human health and people's well-being. Drinking water quality safety mainly involves two aspects: chemical safety and biological safety. The existence of various organic pollutants and pathogenic microorganisms in drinking water brings potential risks to human health and reduces the chemical and biological safety of drinking water. Therefore, the problem of drinking water quality safety mainly relies on the removal of organic matter and microorganisms in water. Traditional drinking water treatment technologies often depend on catalysts and chemical reagents, leading to secondary pollution along the purifying water. Nevertheless, the emerging MNBs technology generates potent oxidizing ·OH in the process of bubble collapse, which is green and clean, having great potential in improving the chemical and biological characteristics of drinking water, being safe and efficient. Application prospects of MNBs in drinking water are shown in Figure 6.

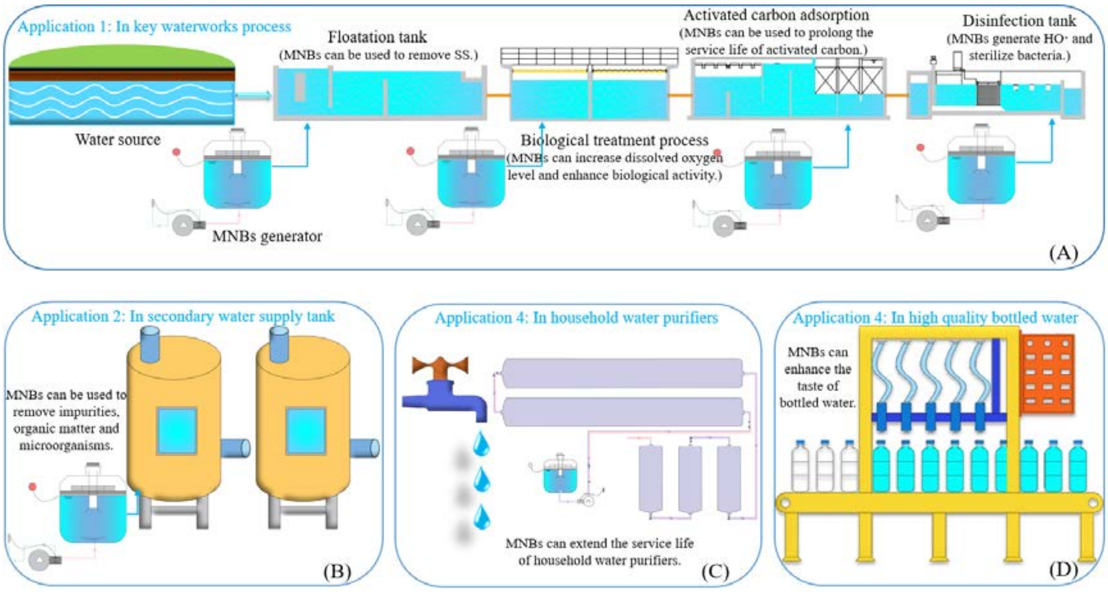

Figure 6. Application prospects of MNBs in drinking water.

(1) Removal of organic matter from drinking water. Drinking water system includes source water, waterworks, water supply pipeline network and tap water, etc. Surface water (i.e., rivers, reservoirs, and lakes) and groundwater are vital drinking water sources; hence, ensuring their safety and cleanliness is highly required. With the aggravation of environmental pollution, a variety of emerging pollutants and refractory organic compounds (e.g., persistent organic contaminants, endocrine disrupters, pharmaceuticals, personal care products, and microplastics) have seriously contaminated the drinking water system and triggered harm to the drinking water safety and human health. Compared with conventional pollutants, these emerging pollutants have the characteristics of low concentration (ng/L~μg/L), difficult biodegradation, easy migration and transformation, easy bioenrichment, high toxicity, and long life. These characteristics make their control and removal a prominent challenge in the environment. Over recent years, advanced oxidation technologies based on ·OH have been widely used in various organic pollutants reduction, but they usually need to add chemicals or consume energy to generate ·OH, which has certain limitations. On the one hand, drinking water has very high requirements for water quality, which is sensitive, and traditional water purification methods may pose specific threats to drinking water quality; on the other hand, compared with other water purification methods, MNBs generate ·OH during its collapse process, which is green and clean and does not produce any secondary pollution. Therefore, MNBs technology is very suitable for use in drinking water. Moreover, we described in Part 3.1 that the practical application of MNBs in water sources with more complex water quality than drinking water indicates a potential application prospect in drinking water treatment. The use of MNBs technology to remove emerging pollutants and refractory organic matter in drinking water is bound to become a very effective method and means.

(2) Remove biofilm from water supply pipeline network. In drinking water distribution systems, microorganisms can be present in bulk water (such as planktonic bacteria) or attached to pipes (such as biofilms or loose sediments) (Zhu et al., 2020), where the biomass present in biofilms accounts for about 95 % (Zhu et al., 2020; Bimakr et al., 2018). Contrasted with the microorganisms in the bulk water, the microorganisms in the biofilm have higher density and biological activity, which is more difficult to inactivate, causes pipe corrosion, and directly brings a variety of water-borne

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diseases (e.g., cholera, diarrhea, dysentery, polio (Zhu et al., 2022)). Therefore, ensuring the biosafety of drinking water is mainly about reducing biofilm growth in the water supply pipeline. As mentioned in Part 3.2, MNBs can remove microorganisms from three aspects: thermal, physical and chemical effects, and MNB technology is widely applied in microbial cell destruction, control of physical-chemical-biological composite fouling, membrane biological contamination, disinfection and sterilization, both in terms of experimental phenomenon and mechanism. Based on the experimental phenomenon and mechanism, MNBs have shown a promising alternative to control biofilms. Based on that, MNBs technology is expected to be a reliable method to control the biofilm formation of water supply network, inducing a capable application prospect in the water supply pipeline network biofilm control.

(3) Application of MNBs in practical engineering. MNBs can generate ·OH and shear stress to degrade pollutants and sterilize bacteria. Consequently, MNBs technology can be applied to water sources to remove organic pollutants and microorganisms. In waterworks process, for instance, MNBs are used in the floatation tank to remove SS due to their strong adsorption ability; in the biological treatment process to improve the DO level and biological activity of water due to their high mass transfer efficiency, and in the disinfection tank to kill microorganisms due to their ·OH generation characteristic. Used in secondary water supply tank, inhibit the growth of biofilm in the tank, remove the rust impurities and organic pollutants mixed in the process of water flow in the pipeline. Used in household water purifier to ensure water quality safety and extend the service life of filter element, as shown in Figure 6. Moreover, this paper focuses on applying this technology to the bottled water preparation for the first time. Under the condition of safety, 15 young people aged 20 to 30 years old were asked to taste water. It was found that compared with ordinary drinking water, 85.7 % of people thought that MNBs water was soft or softer, and 73.3 % of people thought that MNBs water was sweet or sweeter. For that reason, MNBs technology can be applied to the bottled water production line to produce high quality bottled water containing MNBs, as shown in Figure 7. To sum up, MNBs technology has a very broad prospect in drinking water, and we should shift the research purpose to the application of MNB technology in drinking water.

(A)

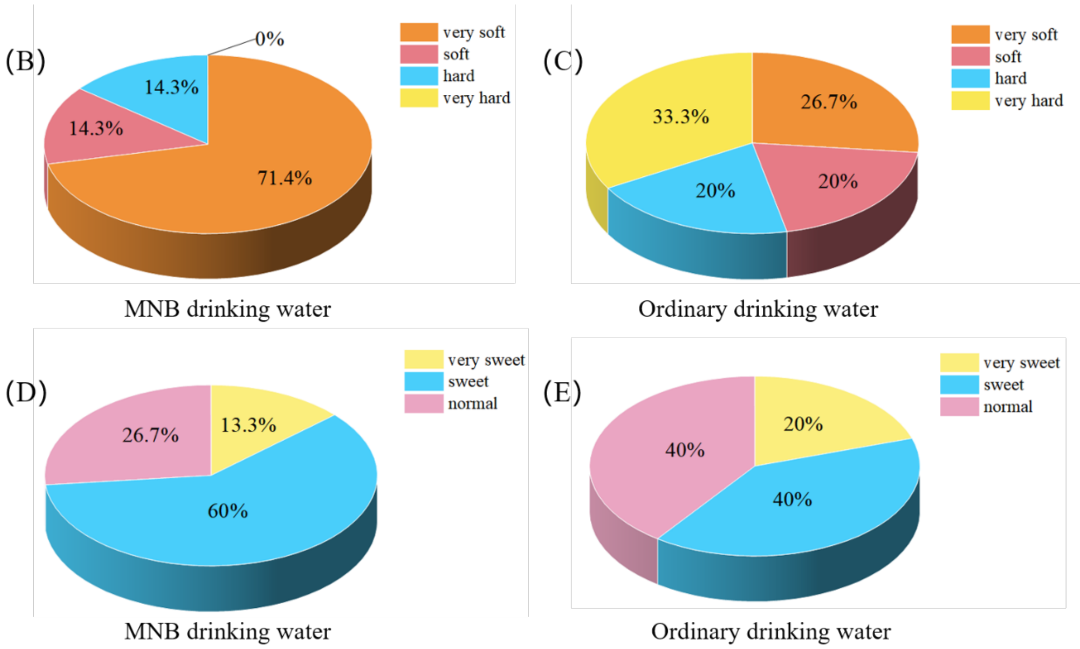

Figure 7. Survey results of MNB drinking water and ordinary drinking water. (A) MNBs drinking water and ordinary drinking water. (B) Investigation result of hardness of MNBs drinking water. (C) Investigation result of hardness of ordinary drinking water. (D) Investigation result of sweetness of MNBs drinking water. (E) Investigation result of sweetness of ordinary drinking water.

6. Limitations and Prospects of MNBs

Although MNBs technology has been applied in various fields, the MNBs investigation has not been deeply explored yet; therefore, there are still blind spots that require our attention. As an example of possible gaps found in this study, are described as follows:

1. The long-term stable existence of MNBs in water and the ·OH generation mechanism are highly controversial. Existing studies on the above two aspects remain at the surface and speculation level; hence, further discussion is needed.
2. The relationship between synergistic and antagonistic effects of MNBs on microorganisms remains unclear. Because the MNBs can generate substantial oxidizing ·OH to destroy microorganisms and provide great potential for water disinfection. Moreover, due to high mass transfer efficiency, MNBs have good biological activity and can promote the biological purification function of water. These two statements are contradictory. Therefore, to better apply MNBs technology, it is required to explore under what circumstances, which side of the synergistic and antagonistic effects of MNBs on microorganisms is more dominant.
3. It is difficult to quantitatively determine ·OH generated by MNBs. Recently, the detection methods of ·OH are all indirect methods, which are complicated in operation, and are inevitably interfered by many factors in the detection process, resulting in considerable errors. Future research should focus on direct detection of ·OH to reduce unnecessary interference items.
4. MNBs generates a limited amount of ·OH. The ability of MNBs to generate free radicals is only one of its many outstanding properties, and the ·OH generated is only one of the many free radical products. At present, studies on the influence of various factors on the generation of ·OH by MNBs are relatively simple. It should continue to explore how to promote the generation of ·OH by MNBs, and simultaneously control the factors that affect ·OH generation under optimal conditions.
5. NBs generation devices are expensive. NBs are superior to MBs in all aspects, but due to the high energy consumption and high price of NB generation devices, the application of NBs in various fields is limited to a certain extent. Hence, developing practical NB generation devices with low energy consumption, low cost, excellent performance and easy promotion is also a new direction of current research.

6. The study of MNBs characteristics is not comprehensive enough. At present, the research on the characteristics of MNBs mainly focuses on the well-known aspects of free radical generation and high mass transfer efficiency. Other characteristics of MNBs, such as heat transfer and viscosity, are unknown and require more analysis.

Although the current research on MNBs is not mature, the outstanding characteristics of MNBs have gradually applied and promoted in various fields. In particular, in the environmental domain, it plays a crucial role in the drinking water treatment application. It is assumed that with additional research on MNBs, it will become an indispensable technology in engineering applications.

7. Conclusions

This review analyzed ten methods for generating MNBs in water. Whether mechanical or chemical, the size distribution of MNBs generated ranges from tens of nanometers to tens of micrometers, and the size distribution is uneven. In addition, different generation methods are affected by the conditions of the method itself, instrument parameters, etc., so we need to coordinate control to get stable MNBW. In contrast with ordinary bubbles, MNBs have the advantages of good stability, high mass transfer efficiency and high Zeta potential. We focus on the characteristics that MNBs can generate ·OH and discuss the influence of various factors on the generation of ·OH. Among them, pH and type of gas source affect the kind of free radicals and the amount of ·OH generated by MNBs. Bubble size and temperature affect the amount of ·OH generated by MNBs, and the amount of ·OH varies with the two factors in a parabolic shape. Ultrasonic, ultraviolet, and catalyst can be used to promote the ·OH generation by MNBs. However, no consensus has been reached on the mechanism of the generation ·OH by MNBs.

There are two main theories (i.e., ion accumulation theory and adiabatic compression theory), mentioning that the high Zeta potential at the MNBs interface plays a crucial role in the ·OH generation or that the high temperature and pressure during the collapse of MNBs induce the ·OH generation. This review focuses on the application of MNBs in the water treatment field due to their characteristics of ·OH generation, shear stress, and microjets generated by the surrounding environment during the collapse. It can be extended to remove pollutants in drinking water and inhibit biofilm formation in the water supply network. It indicates that contrasted to other techniques, MNBs technology possesses the advantages of being green, safe, clean, and efficient. Nevertheless, the removal mechanism of MNBs on organic matter and microorganisms is still unclear and has not been deeply analyzed and studied; hence, it requires our attention in the future. In practical projects, MNBs technology can be used for secondary water supply tanks and household water purifiers to purify water quality and extend the service life of the filter element. Based on the survey conducted, compared with ordinary drinking water, 85.7 % of people think that MNBs drinking water is soft or softer, 73.3 % of people think that MNBs water is sweet or sweeter; therefore, MNBs can also be used in bottled water production lines to enhance the taste of drinking water. We expect that in the future, we all can explore more new investigations and potential applications of MNBs in various research fields.

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