Basic characteristics and application of micro-nano bubbles in water treatment

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Abstract. Recently, micro-nano bubbles (MNBs) have been widely used as a highly efficient and environmentally friendly gas-liquid phase treatment process in sewage and wastewater treatment, aquaculture agriculture, and water ecosystem restoration. In this article, the basic characteristics of MNBs with long residence time, high zeta potential at the interface, generation of hydroxyl radicals, and high mass transfer efficiency were introduced. Firstly, the methods of generating MNBs including hydraulic cavitation, particle cavitation, sonic explanation, electrochemical cavitation were emphasized. Then, the application status of MNBs in water oxygenation, pollutant degradation, and membrane cleaning were discussed. These reviews are expected to provide guidance for the theoretical research and practical application of MNBs.

1. Introduction

According to the classification criteria of bubble size, bubbles with a diameter of 200nm-10μm are defined as micro-nano bubbles (MNBs). The existence of MNBs at the liquid-solid interface has been proven by various techniques. Among them, atomic force microscope[1] shows that MNBs at the liquid-solid interface are similar to spherical caps, and their longitudinal height is generally several nanometers to several tens of nanometers, while the transverse diameter is between several tens to several hundreds of nanometers. Compared with traditional bubbles, MNBs show unique advantages in terms of size/size distribution, mass transfer efficiency, interface characteristics, and chemical properties, and thus are gradually used in varied scientific areas, especially in the control of environmental pollution. Laboratory-scale experiments have been carried out to investigate the practical potentials of the MNBs in water aeration, underground soil remediation, pollutant degradation, cleaning of polluted membranes, air flotation, etc. However, it is still unclear the effect of complex water bodies on the stability of MNBs in actual engineering applications, so the feasibility of MNB technology in practical applications needs to be further evaluated.

2. Basic characteristics of MNBs

MNBs have been highlighted due to their advantages, which include the small size, large specific surface area, long residence time in water, high mass transfer efficiency, high interface zeta potential, and the ability to generate hydroxyl radicals. These characteristics are significantly distinct over those of the traditional large bubbles.

According to the principle of buoyancy, the rising speed of bubbles in water declines with the decrease of the bubble sizes. Compared with ordinary bubbles, MNBs themself have smaller volume...
to bear less buoyancy and stronger surface which cause MNBs not to collapse easily. Studies have showed the rising speed of MNBs with size less than 1μm is much slower than that of Brownian motion, consequently MNBs appear to be stable in water during a long time[2]. Generally, the mass transfer rate of a gas largely depends on the mass transfer area of the gas-liquid phases, so that of MNBs is much higher. According to Henry's Law, the MNBs will undergo self-pressurization and dissolution[3], which can make the gas dissolution rate in water reach a supersaturated state, further improve the gas-liquid mass transfer efficiency.

The combination of ions adsorption on the surface of bubbles and the creation of counter ions on the inner surface causes high interface zeta potential of MNBs, which is similar to colloid particles. In most cases, due to the difference in enthalpy of hydration between OH− ions (−446.8kJ/mol) and H+ ions (−1104kJ/mol), the OH− groups are tend to adsorb at the interface of MNBs and dominate, resulting in a negative charge on the surface of MNBs. In pure water, the Zeta potentials of air MNBs, nitrogen MNBs, oxygen MNB are −45mV, −37mV, and −40mV, respectively[4]. The Zeta potential of MNBs is not only affected by the gas source, but also related to the characteristics of chemical reagent solution. After adding 0.001M dimethyldioctadecylammonium bromide, the Zeta potential of air MNBs changes from −22mV to 38mV[5].

Moreover, the collapse of MNBs in the absence of external stimuli could generate hydroxyl radicals, which has been experimentally demonstrated through electron spin resonance spectroscopy [6-7]. At the moment when the gas-liquid interface disappears by bubble collapsing, the extremely high concentration of charged ions accumulated on the interface through the process of MNBs self-pressurizing to dissolve will instantly release the chemical energy, which in turn releases hydroxyl radicals. The amount of hydroxyl radicals generated by collapsing MNBs is related to the type of bubbles and the pH values of solutions. Generally, oxygen MNBs are more inclined to the formation of hydroxyl radicals.

3. Method for generating MNBs

3.1. Pressurized dissolved gas release method

The main principle of the pressurized dissolved gas release method[8] is to change the gas pressure. Under pressurized conditions, the air is dissolved in water to form an air supersaturated state, then the air is suddenly decompressed to precipitate out and released into the water as fine bubbles. Moreover, the decompression method can also prepare MNBs by performing a short-time pumping treatment on the aqueous solution. However, there are existing shortcomings of discontinuity of the gas dissolution and releasing processes and low efficiency of generating MNBs. To compensate for these defects, a method of generating MNBs by air flotation pump was later created, which is a combination of
impeller gas diffusion technology and pressurized dissolved gas release method. Compared with the former, the MNB generation rate is higher and the bubble size is smaller.

3.2. Dispersed air method
The main principle of the dispersed air method is to use various methods such as hydraulic shear, high-speed swirling, jet flow, microporous structure to form shearing forces and create an extreme condition under which air is repeatedly sheared and broken to mix with water to generate a large amount of MNBs. Oliveira et al[9] investigated the bubble dispersion parameters of the air NBs generated in a high-rate hydrodynamic cavitation tube, which showed NBs with average diameter of 220-280nm and concentration of $6.4 \times 10^8$ NBs mL$^{-1}$ when the gas-liquid volume ratio was 30%.

3.3. Electrochemical method
The electrochemical method can not only directly generate bulk MNBs in an aqueous solution, but also use a conductive substrate as an electrode to generate interface MNBs on its surface. The number and size of interfacial MNBs generated by electrolysis can be controlled by the magnitude of the applied voltage and the electrolysis time.

Yang et al[10] electrolyzed water to generate MNBs on the surface of highly oriented pyrolytic graphite(HOPG). When HOPG surface acted as a negative (positive) electrode, hydrogen (oxygen) MNBs were produced. Moreover, the yield of hydrogen MNBs was almost twice that of oxygen MNBs.

3.4. Ultrasonic cavitation
Ultrasonic cavitation is a process in which high-energy nuclei generated by ultrasonic energy grow uniformly in solution or heterogeneously on a hydrophobic surface and continuously accumulate sonic energy. When the energy reaches a certain threshold, the cavitation bubbles rapidly shrink and rupture. The effective diameter of the generated bubbles is related to the ultrasonic power and the sonication time. Vibra-Cell sonicator was used to sonicate the solution to produce MNBs with an effective diameter of 750-800nm, which increased with the increase of ultrasonic power and processing time[11]. The efficiency of generating MNBs by ultrasonic cavitation is not high and the size of the bubbles increases significantly due to the evaporation of volatile components as the ultrasonic treatment continues, which need to be further improved.

3.5. Solution replacement method
The solution replacement method requires a substrate and two solutions with different gas solubility can be mutually soluble. When a solution with high gas solubility is replaced with a solution with low gas solubility, excess gas will be deposited on the substrate surface to form MNBs. The commonly used method is ethanol-water exchange. Hu Jun et al[2] used this method to successfully generate MNBs with overage diameter range of 100-200 nm and the concentration of $4 \times 10^8$ per milliliter which were stable for more than 4.5 hours, under the optimal conditions of ethanol/water ratio of 1:12 and experiment temperature of 35 °C.

In addition, other technical methods such as high temperature, chemical reactions, photo/chemical catalysis and micro-pipes are also used to generate MNBs. Among them, the micro-pipe technology uses a micro-air pump to inject a trace amount of gas into a liquid through a micro-pipe, forming MBs in the liquid. The size of MBs is depended on the pressure and flow of the micro-pump.

4. Application of MNB technology in water treatment

4.1. Aeration in water
In water treatment, oxygen is not only an important part to maintain the life of aquatic organisms, but also a biochemical reaction substrate for degradation of oxidative pollutants, so it needs aeration to transport oxygen. However, conventional mechanical aeration requires a large amount of electrical
4. Degradation of organic pollutants and water disinfection

MNBS not only improve the utilization of chemicals by virtue of high mass transfer efficiency, but also can generate hydroxyl radicals when they collapse to directly non-selectively react with organic pollutants. It has been widely proven that MNBS generated by hydraulic cavitation can effectively promote the oxidative decomposition of refractory organic pollutants.

Chu et al. [13] studied the enhanced performance of MNBS on ozone oxidation with azo dye simulated wastewater, which showed that the total mass transfer coefficient of ozone and the removal rate of TOC were increased by 80% and 30%, respectively. Li Pan et al. [7] selected phenol and nitrobenzene as model organic pollutants to study their degradation mechanism using MBs generated by cavitation, which found that the ozone mass transfer rate of MBs is 1.3-1.5 times higher than that of traditional bubble aeration, and removing about 70% of nitrobenzene by MB aeration requires only 50% of the ozone required for conventional bubbling. While the overall degradation of phenol is consistent with first-order kinetics, the apparent reaction rate constant of MBs is increased by 1.8–4.3 times compared to conventional bubbles. Furthermore, researches in the effects of MBs on intestinal pathogens showed that hydroxyl radicals and shock waves generated by MBs collapse were considered to be the main reasons for inactivation of coliform bacteria.

4.3. Flotation with MNBS

Air flotation as an efficient solid-liquid separation technology has been widely used in the field of micro-polluted water and industrial wastewater treatment. The main principle of the air flotation process is to use highly dispersed micro-bubbles precipitated from the water as a carrier to adhere to pollutants in the wastewater, using buoyancy to transfer the generated floc. Compared with ordinary bubbles, MNBS promote longer contact time and higher adhesion efficiency of bubbles and suspended solids due to their unique advantages of large specific surface area, high zeta potential, and long residence time in water [14], thus achieving solid-liquid efficient separation. Liu et al. [15] used air flotation technology of traditional bubbles and MNBS to conduct printing and dyeing wastewater treatment experiments, which showed that air flotation technology of MB increased the pretreatment rate and effectively reduced the amount of flocculant. In terms of removal rates of oil, COD, and chroma, they are 40%, 30%, and 110% higher than those of air flotation process using traditional bubble, respectively.

4.4. Membrane cleaning

As environmentally friendly and non-chemical cleaning agents, MNBS are used to prevent surface fouling and remove surface contamination, such as preventing the adsorption of bovine serum albumin on the surface of mica, and helping to remove organic pollutants on HOPG. Moreover, the combination of high-frequency, low-power ultrasound and MNBS has been proven to have great potential for controlling the adhesion of bacteria and algae on solid surfaces.

Dayarathne et al. [16] conducted laboratory-scale and pilot-scale cross-flow filtration experiments to evaluate the effect of air MNBS on permeate flux, TMP (transmembrane pressure) and solute rejection using reverse osmosis membranes. The results showed that MNBS effectively removed and/or
prevented the construction of concentration polarization layers, and thus the permeate flux and solute rejection were enhanced by 24.62% and 0.8%, respectively. Moreover, the membrane permeate flux recovery rate could reach to 100% by a simple physical cleaning.

Hu Jun et al[17] observed through AFM that the bovine serum albumin (BSA) adsorption rate on HOPG surface modified by MNBs generated by electrochemical treatment for 20 seconds was 66% - 74%, which was 26% -34% lower than that of HOPG surface modified without MNBs, see figure 3(b). Further, when BSA completely adsorbed on the surface of HOPG, BSA coverage was reduced to 82% after 50 seconds of electrochemical treatment, see figure 3(d). By observing the generation of NBs in situ, it was speculated that the NBs formed between HOPG and BSA layer forced the adsorbed proteins to be transferred from the solid-liquid interface to the liquid-air interface due to the advancing three-phase line, so the protein instability at the liquid-air interface is significantly removed by low shear water flow.

5. Conclusion
The advantages of MNBs over traditional bubble make the application of bubbles no longer being limited to enhancing the efficiency of dissolved oxygen in water. MNBs are characterized by high mass transfer, generation hydroxyl radicals by MNB collapse, high zeta potential at the interface, and thus can improve the reaction efficiency of chemicals and pollutants and degrade organic substances that are difficult to degrade under normal circumstances. As a new process without secondary pollution, MNB technology has favorable application prospects, even though there are challenges of the higher cost and energy consumption of MNB generators than ordinary bubble generation devices. Moreover, the stability of the generated bubbles is susceptible to the multiple factors of electrolyte, pH, water temperature, structure and principle of the generator, which need to be improved in practical engineering. Accordingly, great attentions should be paid to reduce the cost and energy consumption, simultaneously ensure the stability and production of MNBs, and further expand the application of MNBs, such as the combination with traditional oxidation technology.

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