A Review of Microbubble and its Applications in Ozonation

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Abstract.Ozonation has been demonstrated to be an effective technology for the oxidation of organic matters in water treatment. But the low solubility and low mass transfer efficiency limit the application. Microbubble technology has the potential of enhancing gas-liquid mass transfer efficiency, thus it can be applied in ozonation process. The applications of microbubble ozonation have shown advantages over macro bubble ozonation in mass transfer and reaction rate. Microbubble ozonation will be a promising treatment both in water and wastewater treatment.

1. Introduction

Water pollution remains a major issue to be addressed by improving wastewater treatments. Among all the different water treatment, oxidation technologies is almost the best method, especially in refractory wastewater treatment. Oxidation processes can achieve disinfection, color removal and degradation of organic pollutants in a single unit process.

Ozone is a well-known powerful oxidant. It has been widely used in water or wastewater treatment. However, it has been determined that the present ozonation process is limited by low gas-liquid mass transfer rate due to the low solubility in water [1]. Furthermore, ozone is not effective in the mineralization of organic substances. In many cases, ozonation cannot completely oxidize organic substances into carbon dioxide, leading to oxidation by-products [2]. To improve the efficiency of ozonation process, few novel techniques, for instance, catalytic ozonation have been tested. Undoubtedly, efficient technique for ozone transfer rate improving is especially desired for the treatment of wastewater containing high concentrations of organic pollutants.

In recent years, microbubble technologies have drawn great attention in water and waste water treatment due to its unique properties. Especially, microbubble technologies can improve gas-liquid mass transfer coefficient and increase solubility of gas. Thus, many experiment have been conducted to investigate the effect of combined technique of microbubble and ozonation [3-7]. In this paper, we will discuss about the unique properties of microbubble and its improvement of ozonation process.

2. Properties and generation of microbubble

2.1. Long stagnation under water
Microbubbles behave differently in water (liquid) with macrobubbles due to the extremely small diameter of microbubbles (10-50µm). Fig. 1 shows the main differences between normal macro bubbles and microbubbles.

![Figure 1. Behaviors of macro bubble and microbubble](image)

Normal macro bubbles rapidly rise and burst at the water surface, whereas microbubbles can exist for a long period under water surface. Microbubbles tend to gradually decrease in size and eventually disappear due to dissolution of the interior gas into surround water.

To further understand the behavior of microbubbles, surface charge is the key factors. It was reported that microbubbles can move towards the oppositely charged electrode in an electrophoresis cell. So the surface charge of microbubbles can be determined. In fact, due to the long stagnation of microbubbles, the zeta potential can be easily measured and in distilled water it is about -35 mV \[^9\]. Zeta potential is known as a key indicator of the stability of colloidal dispersions. For small particles, a high zeta potential will confer stability, i.e., the solution or dispersion will resist aggregation. Generally speaking, if the zeta potential of a colloidal particles ranges from ± 30 to ± 40, this system is considered as “moderate stability”.

2.2. High pressure inside microbubbles
Decrease in the diameter of bubble results in high internal pressure of gas inside the bubble. The relation between the diameter and pressure can be described by the Young-Laplace equation:

\[
P = P_1 + 4\delta/d\tag{1}
\]

Where \(P\) is the gas pressure, \(P_1\) is the liquid pressure, \(\delta\) is the surface tension of the liquid, \(d\) is the diameter of the bubble. For a microbubble with the diameter 1 µm, the internal gas pressure is about 390 kPa, which is almost three times higher than the atmospheric pressure. Interestingly, the area surrounding a microbubble has been shown to change its state in a pressure-temperature (P-T) diagram \[^10\].

As is shown in Fig.2, the gas pressure of a shrinking microbubble was increasing, and the amount of dissolved gas in the vicinity of the bubble was also increasing with the bubble pressure to near or over the supercooling limit (B-C) even though the whole system is not supercooled enough (A) for hydrate nucleation.

As mentioned before, microbubbles tend to gradually decrease in size and eventually disappear. So in the shrinkage, the interior gas pressure increases as the bubble becomes smaller; moreover, the rate of increase is inversely proportional to the bubble size. Therefore, a high-pressure spot might be created during the final stage of the collapse, as is shown in Fig.3. According to Henry’s law, the amount of dissolved gas surrounding a shrinking bubble increases with rising internal gas pressure. As
a consequence, the gas in microbubble can be dissolved in water during the process of shrinkage. The high interior gas pressure is one of the typical characteristic of microbubble.

Figure 2. State change in the area surrounding a microbubble

Figure 3. Increase in the interior gas pressure of microbubbles during shrinkage

2.3. Radicals generation during collapse
Under specific circumstances, if the collapsing speed of tiny bubbles in the final stage of the collapse is fast enough, we can assume that this process is an adiabatic compression process. In this adiabatic process, no heat is transferred between microbubble and the surroundings. Hence, the temperature inside the bubble will drastically increase. In the acoustic cavitation, when water is irradiated by a strong ultrasonic wave, a large amount of tiny gas bubbles appear and disappear. These tiny bubbles repeatedly expand and shrink because of the pressure oscillation caused by the ultrasonic wave. The speed of the bubble collapse may be higher than the speed of sound velocity, so the temperature inside these bubbles can increase drastically due to adiabatic compression process. The temperature may even increase to higher than 5000 K during the collapse, then pyrolytic decomposition will take place within the collapsing bubbles, the free radicals (like ·OH radical) and shock waves can be generated at the gas-liquid interface\cite{8}. Such phenomenon also occurs in hydrodynamic cavitation.

Takahashi, et al. \cite{8} reported the generation of free radicals during the collapse of microbubbles. They also found that the solution pH has significant effect on the quantity of free radicals generated by the collapse of microbubbles, e.g. lowered pH enhanced generation of free radicals. However, the mechanism of radicals’ generation by microbubbles is not similar to that in cavitation bubbles. The shrinking rate of microbubbles was extremely slow, thus the shrinkage is not an adiabatic compression process. They proposed a hypothesis that the instantaneous high density of ions at the surface of the collapsed microbubble could potentially cause the phenomenon of free-radical generation, and the composition of the ions around the interface could affect the type of free radicals generated.

2.4. Methods for generation of microbubbles
At present, few methods have been developed to generate microbubbles. The most widely used method bases on decompression. For the decompression method, supersaturated water is created at high pressure, the supersaturated gas is highly unstable and will easily escape out from the water when pressure decrease. As a result, large number of microbubbles would be generated instantly. This kind of microbubble generation system usually contains a tank and a pump. The method Takahashi, et al. \cite{8} used is exactly this type.

Another widely used method bases on gas-water dispersion process using a certain medium. SPG membrane is a kind of porous glass membrane which has uniform-sized cylindrical, tortuous pores.
The numerous pores of SPG membrane together form a three-dimensional interconnected network which is beneficial to gas-water dispersion. During gas-water dispersion process, gas at high pressure is forced through the SPG membrane into the liquid to form microbubbles. The key advantage of SPG membrane method is that the size and void fraction of microbubbles are mainly determined by the membrane pore size and membrane area. So the size and void fraction of microbubbles can be optimized to fit various conditions [12].

3. Applications in ozone treatment

3.1. Conventional ozone treatment
Ozone has a high oxidation potential and has been widely used for disinfection and the removal of organics for water and wastewater treatment. It is well known that there are two pathways of ozonation: direct ozone molecular oxidation and indirect oxidation. Ozone is unstable in water and will easily self-decompose to oxygen. The decomposition of ozone leads to generation of hydroxyl radicals (·OH).

\[3O_3 + OH^- + H^+ \rightarrow 2OH + 4O_2 \] (2)

The oxidation capacity of ozone strongly depends on pH of the solution, under acid condition, decomposition of ozone will not generate hydroxyl radicals.

\[O_3 + 2e^- + 2H^+ \rightarrow O_2 + H_2O\] (3)

Reactions of ozone with organic matter usually lead to the formation of small organic molecules such as aldehydes and carboxylic acids, both of which do not react with ozone. So total mineralization of organic matter cannot achieved. This is one of the important limitation of ozone treatment. Koaska, et al [2] investigated the ozonation of six hydrazine compounds. By adding TBA, a hydroxyl radical scavenger, they determined that NDMA was formed mainly by ozone molecular reaction. However, in the absence of TBA, NDMA yield is still high.

Ozone can be conveniently generated through an electrical discharge using pure oxygen or air as the gas source. The ozone concentration in the gas mixture is about 6% when use pure oxygen as the gas source. The solubility of ozone is 570 mg/L at 20 degree, which is higher than oxygen. However, this solubility dramatically drops down at low ozone concentrations in the gas phase according to Henry’s law. Low concentration of ozone in water leads to low gas-liquid mass transfer rate, which is the other vital limitation of ozone treatment.

3.2. Promotion of mass transfer
Microbubble technology has the potential to enhance gas-liquid mass transfer due to its large interfacial area and high interior pressure. According to the ‘two-film theory’ of mass transfer, the gas-liquid interface lies between a gas film and a liquid film, and the mass transfer resistance exists in both film. It is accepted that gas phase mass transfer resistance is negligible. Also, for the sparingly soluble gas such as ozone, mass transfer resistance mainly exists in the liquid phase. Hence, the total mass transfer coefficient could be predicted by a series of equations (which are not listed in this paper).

Fig. 4 depicts the relation between theoretical mass transfer coefficient and diameter of bubble. It is obvious that theoretical mass transfer coefficient increase with the decrease in bubble diameter, especially when diameter is smaller than 100µm.

Yao [13] determined the volumetric mass transfer coefficient of microbubbles and macro bubbles to examine the enhanced mass transfer effect of the microbubble technology. In the study, air was introduced into the reactor by two different bubble generators. Oxygen dissolved into water continuously until the concentration of dissolved oxygen reached saturation. Fig. 5 shows variation of the dissolved oxygen concentrations with time in the two systems.

Clearly, the final steady value of microbubbles was higher than macro bubbles. The mass balance of oxygen in liquid can be describe as follows:

\[\frac{dC}{dt} = K_La \left(C_s - C\right)\] (4)
where \( C_S \) is the saturated concentration of oxygen, \( C \) is the practical concentration of oxygen in water, \( K_{La} \) is the volumetric mass-transfer coefficient. When integrated, equation (3) becomes:

\[
\ln(C_S - C) = -K_{La}t + \text{constant}
\]  

(5)

Based on equation (4), the volumetric mass-transfer coefficient of macro bubbles and microbubbles are 0.02191 s\(^{-1}\) and 0.02905 s\(^{-1}\), respectively. Which means the mass transfer rate was improved 32.59% by microbubbles.

3.3. Applications in ozonation

Due to the significant enhancement of mass transfer by microbubble technology, microbubble assisted ozonation has been successfully applied in simulated or practical wastewater treatment.

The ozonation of synthetic wastewater containing azo dye, Reactive Black 5, was investigated using a microbubble generator and a macro bubble contactor by Chu, et al [3]. The mass transfer coefficient of microbubble is 1.8 times higher than macro bubble, while the pseudo-first order rate constant is 3.2-3.6 times higher. Also, TOC removal is about 1.3 times higher per g ozone consumed. The addition of terephthalic acid as a hydroxyl radicals probe indicate that more hydroxyl radicals were produced in the microbubble system, which also contributed to the degradation of the dye molecules. Then, Chu, et al [4] investigated the efficiency of ozonation in practical textile wastewater using a microbubble generator and macro bubble contactor. During the ozonation, the input ozone could be almost completely utilized in the microbubble system. The time required for 80% removal of color was about 140 and 280 minutes by microbubble and macro bubbles, respectively. Also, the efficiency of COD removal was 20% higher in the microbubble system. These results revealed that microbubble ozonation is a promising process in wastewater treatment.

Zheng, et al [5] used microbubble ozonation process for advance treatment of wastewater from acrylic fiber manufacturing industry. COD, \( \text{NH}_3 \)-N, and \( \text{UV}_{254} \) of the wastewater were removed by 42\%, 21\%, and 42\%, respectively in the microbubble ozonation, while these removal rates by macro bubble ozonation were 17\%, 12\% and 7\% in the same ozone dose. The gas holdup of ozone microbubbles rapidly increased to saturation (15.1\%) within 7min. In contrast, the saturated gas holdup of ozone macro bubble was only 2.3\%, 6.6 times lower than microbubble ozonation. Moreover, the average ozone utilization in microbubble ozonation is 1.5 times higher than it in macro bubble ozonation. A combined microbubble ozonation/ultraviolet irradiation process has a higher performance in acrylic fiber wastewater treatment due to photolysis of ozone [6].

Ozone is effective in inactivating bacteria, viruses and certain algae. Ozone microbubbles have been used for disinfection against fungi and bacteria. Kabayshi et al [7] have investigated the disinfectant ability of ozone microbubbles against \( \text{Fusarium xysporum} \) f. sp. \( \text{melonis} \) and \( \text{Pectobacterium carotovorum} \) subsp. \( \text{carotovorum} \). The microbubbles remained in the water for a
longer period than the millibubbles, resulting in extremely high disinfecting activity against both phytopathogens.

4. Summary
Microbubbles have been widely used in many fields due to the unique properties. Ozone is a strong oxidant and is a routine process in water or wastewater treatment though the efficiency is limited by low gas-liquid mass transfer. It has been proven that microbubbles can significantly enhance gas-liquid mass transfer process. Several groups of researchers have investigated the applications of microbubbles in ozonation. Mass transfer coefficient, TOC removal and reaction rate constant were all enhanced. Undoubtedly, microbubble ozonation is a promising method in water or wastewater treatment.

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