Review

A Review on Ultrasonic Catalytic Microbubbles Ozonation Processes: Properties, Hydroxyl Radicals Generation Pathway and Potential in Application

Xingyao Xiong ¹, Bing Wang ^{1,2,*}, Wei Zhu ³, Kun Tian ¹ and Huan Zhang ¹

¹ School of Chemistry and Chemical Engineering, Southwest Petroleum University, Chengdu 610500, China; xiongxgy@stu.swpu.edu.cn (X.X.); tiankun@stu.swpu.edu.cn (K.T.); zhanghuan@stu.swpu.edu.cn (H.Z.)

² Sichuan Provincial Key Laboratory of Environmental Pollution Prevention on Oil and Gas Fields and Environmental Safety, Chengdu 610500, China

³ Department of Quality, Security and Environmental Protection, PetroChina Tarim Oilfield Company, Korla 841000, China; zhuwei-tlm@petrochina.com.cn

* Correspondence: wangb@swpu.edu.cn; Tel.: +86-028-83037300

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Abstract: Ozone-based advanced oxidant processes (AOPs) have attracted remarkable attention as an alternative and effective approach for mineralization of refractory organics to innocuous substances. Key issues for ozone-based AOPs mainly focused on how to enhance ozone mass transfer and improve the production of hydroxyl radicals. Unfortunately, great efforts have been made, though, the application of ozone-based AOPs still remained in the laboratory scale due to lack of understanding of mechanisms of these hybrid processes. Besides, obtaining the balance of economical-technical feasibility is a great challenge. Ultrasonic catalytic microbubbles ozonation could be considered as a promising method, despite that there are a few studies that addressed this potential technology. Therefore, in this review, summaries about ozone-based microbubbles process, ultrasonic catalytic ozonation process, and ultrasonic catalytic microbubbles ozonation process have been provided in order to give a novel prospective about these hybrid technologies. The main influential parameters, such as initial pH, ozone dosage, intake flow rate, operating temperature, bubble size distributions, ultrasonic frequency, ultrasonic power density, and natural water constituents have also been well discussed. We truly hope that this paper will bring convenience to researchers that are devoted in the field of application of ozone-based AOPs for mineralizing refractory organics in wastewater.

Keywords: ozonation; microbubbles; ultrasonic; mass transfer; hydroxyl radicals; catalytic ozonation

1. Introduction

Ozonation is one of the most attractive and mature advanced oxidant processes (AOPs), which has been widely applied in the water/wastewater treatment accomplished by the removing of non-biodegradable compounds as well as refractory organics [1–6]. Ozone molecule with an oxidation potential of 2.07 V is capable of disinfection, color removal, and pollutants degradation in one single unit process [7–9]. Besides, OH· (2.80 V) generated through ozone decomposition in liquid phase is one of the major advantages [10].

Ozonation as well as ozone-based AOPs could be achieved by two routes:

- direct oxidation based on O₃ molecule through electrophilic, nucleophilic and dipolar addition, all of which are comparatively slow and selective; and,

- indirect oxidation based on $\text{OH}\cdot$, which is capable of oxidizing refractory contaminants to CO_2 and H_2O in a fast and non-selective way.

In a single ozonation processes, the ozonation efficiencies were always confined by the relatively low mass transfer because of low solubility and stability of ozone in liquid phase [11,12]. With underused ozone existed in most processes, problems such as resource waste, a rather high treatment cost, and great harm to human health will emerge if ozone leakage occurs [13–16]. In addition, the selective reaction between ozone molecular and unsaturated bonds or amino groups in organics would lead to the formation of aldehydes and carboxylic acid, which is liable for the incomplete mineralization of pollutant [17–20]. For this reason, some modifications that could both/either enhance ozone mass transfer and/or promote $\text{OH}\cdot$ generation are imperative.

Ozonation always proceeds by aeration. In this process, the adsorption of ozone into the liquid phase is controlled by liquid-film because the diffusion resistance of ozone molecule mainly exists in liquid phase [16]. The ozone-liquid transport rate mostly depends upon the interfacial area of ozone-liquid [8,21,22]. Thus, a comparatively smaller bubble diameter should benefit ozone mass transfer [16,23,24]. Microbubbles technology that could provide small bubbles with a respective diameter of 10–50 μm has gained enormous attention [25,26]. Microbubbles are characterized by huge interfacial areas, low rising velocity and high inner pressure as compared with macrobubbles [24,25,27], which are widely used in intensifying gas mass transfer into liquid phase [28–30]. The combination of ozone and microbubbles would be a promising method to enhance ozone mass transfer and is followed by an increase of degradation efficiency of pollutants.

Generation of $\text{OH}\cdot$ (or other reactive oxygen species) as much as possible is an alternative way to accelerate ozonation efficiency. Ozone decomposition in liquid phase is a pH dependent process and it is always facilitated by the high concentration of OH^- . $\text{OH}\cdot$ could be produced, even at acid medium in the presence of catalyst, which is defined as catalytic ozonation. Noteworthily, catalytic activity does not mean the formation of $\text{OH}\cdot$ [19,31]. It should be described as that the ozonation efficiency with a catalyst is higher than without the same catalyst at the same condition [31]. Catalytic ozonation could be categorized into two types in terms of catalyst: homogeneous (Mn(II) , Fe(II) , Fe(III) , Co(II) , Cu(II) , Zn(II) , and Cr(II) , et al.) and heterogeneous (metal oxides, metals on supports, activated carbon, et al.) modes [1,31]. Heterogeneous catalytic ozonation has been a hot issue of research in the last few years for the mineralization of recalcitrant. However, the mechanisms of these processes are still ambiguous, even controversial [17,32]. The exploitation of efficient catalysts is not a cost-effective process either. Disadvantages would limit the practical application of this technology. Hence, finding a modified ozonation process that possess both technical and economic feasibility is of important research challenge and obligatory.

The application of physical fields in ozonation process, such as Ultrasound/ O_3 and UV/ O_3 , could be assigned to homogeneous catalytic ozonation [33]. Amongst this, ultrasonic catalytic ozonation was considered as an attractive and promising AOP, because it conquers the major weaknesses of ozonation alone and ultrasound alone [34]. When compared with ultrasonic irradiation alone or ozonation alone process, additional $\text{OH}\cdot$ generation in these processes is almost due to ozone self-decomposition that occurred with energy transfer from physical fields to the liquid phase. The synergistic effect of ultrasound and ozone have been proved by many groups [35], and it exhibited superior advantages among other ozone-based AOPs, such as no need of adding any other agents and operation feasible. It could be speculated that the combination of ozonation, microbubbles, and ultrasonic process would possess extraordinary performance in the ozone mass transfer and in the generation of $\text{OH}\cdot$, thereby producing a better ozone utilization and a higher pollutant mineralization rate. Unfortunately, up to now, seldom efforts have been addressed in this field.

The main aims of this paper are to offer reviews on microbubbles, ultrasonic and ultrasonic catalytic ozonation process from the prospects of its mechanisms, and recent advances. Moreover, we focused on the combined technology-ultrasonic catalytic microbubbles ozonation from

the point of enhancement mechanism and essential operating parameters, in order to provide a new accessible approach for wastewater treatment at the industrial scale.

2. Ozonation-Based Microbubble Technology

2.1. Properties of Microbubble

Microbubbles are defined as tiny bubbles with diameters of 10 to 50 μm [25,36], which are capable of large gas-liquid interfacial area and relatively low rise velocity [28] (Figure 1) and they have exhibited superior properties of physical chemistry and size effects [26]. It has already been used in the fields of environmental engineering [37], biomedical engineering [38], and other industrial productions [39,40]. The efficacy of this technology depends on both diameter distribution and number density of microbubbles [28]. Thus, further understanding of microbubble generation mechanism to obtain better efficacy is important.

Figure 1. Compared schematic diagram of macrobubble and microbubble (reprinted with permission from (Free-Radical Generation from Collapsing Microbubbles in the Absence of a Dynamic Stimulus, [41]). Copyright (2019) Americam Chemical Society).

The most prominent property of microbubbles is that they could decrease in size and collapse liquid phase, while macrobubbles always burst at the surface [30]. High inner pressure, which is due to surface tension, is another key feature of microbubbles. The relationship between inner pressure and diameter could be described by the Young-Laplace equation:

$$P = P_l + \frac{4\delta}{d} \quad (1)$$

where P is inner pressure of microbubble, P_l is liquid pressure, δ is surface tension of liquid phase, and d is diameter of microbubble. Equation (1) indicates that the increased rate of inner pressure of microbubble could be inversely proportional to its diameter. The state of surrounding around microbubbles can be determined by a P-T diagram [30,42]. The formation process of hydrate nucleation is [30]: Firstly, microbubbles rise slowly in liquid phase, and shrinkage would occur at this point; and then, according to the Young-Laplace equation, inner pressure (P) increases with shrinking bubble, meanwhile more amounts of gas dissolved in the vicinity of microbubble due to Henry's law; finally, hydrate nucleation would appear if the shrinkage stage of microbubble is sustained until near or over the supercooling limit. All of the studies that focused on microbubbles technology (Table 1) suggested that microbubble technology possesses an excellent property for gas absorption. According to Katsuhiko Muroyama et al. [26], bubbles with diameters that were smaller than approximately 50 μm revealed extraordinary oxygen-absorption performance, and this could be

owing to the self-compression and shrinking of microbubbles. A similar result has been observed by Kangning Yao et al. [24] that K_La values for microbubbles and conventional bubbles were 0.02905 s^{-1} and 0.02191 s^{-1} , respectively, under a same operating condition.

Furthermore, bubble rising speed and surface charge are crucial parameters that could affect the properties of microbubbles. It was reported that microbubbles move towards the oppositely charged electrode invariably in the electrophoresis cell. The zeta potential of bubbles could be easily examined because the long stagnation of microbubbles in the liquid phase, and value of -35 mV was obtained in distilled water [43]. This means that the microbubbles-distilled water was “moderate stability” [7]. According to Takahashi M [29], the zeta potential of microbubbles is almost independent of the diameter, and in the terms of shrinkage, the zeta potential value would increase. This suggests that the quantity of electrical charge per unit area at the gas-liquid interface is invariable. Besides, other researchers have found that microbubbles are always negatively charged under a wide range of pH [25].

2.2. Generation of Hydroxyl Radicals

Free radicals, especially $\text{OH}\cdot$, would be generated from collapsing microbubbles, which could non-selectively and quickly oxidize organics. The generation mechanism of free radicals has been studied by Takahashi M. and his group [44], they thought that the collapsing of microbubbles would take only tens of seconds, which is not sufficient to generate radical species by extremely high local temperature. Besides, the adiabatic compression would not happen in this condition. As the zeta potential increased during the process of bubble collapse, the possible pathway of the formation of free radicals has been proposed: first, some excess ions were trapped at the microbubble's interface; second, bubbles collapse leading to an abrupt disappear of gas-liquid interface, which allows for a drastic environmental change at this situ; finally, an instantaneous high density of ions occurred and free radicals generated. In this study, the presence of $\text{OH}\cdot$ has been confirmed by EPR (electron spin resonance) spectroscopy. A same has been observed by others in 2015 [41] that $\text{OH}\cdot$ existed in ozone-microbubbles, air-microbubbles, and ozone-macro-bubbles systems. According to Alexander W. et al. [45], the types of reactive species generated through the plasma microbubble reactor were dependent on the temperature of plasma and the power source duty cycle.

The types of free radicals could be affected by the composition of ions. Alkyl radicals were produced via the collapse of nitrogen-microbubbles, while $\text{OH}\cdot$ were generated via collapse of both air-microbubbles and oxygen-microbubbles [39].

2.3. Properties of Ozone-Based Microbubbles Technology

In the area of ozone-based microbubble process, the advantages are mainly reflected in two aspects: (I) the intensification of ozone mass transfer; (II) the production of a large amount of $\text{OH}\cdot$.

Ozone mass transfer in liquid phase can always be expressed by mass transfer coefficient, K_La , and could be described, as follows:

$$\ln \left[\frac{C_s}{C_s - C} \right] = K_L a t \quad (2)$$

where C_s is equilibrium concentration of ozone and C is dissolved ozone concentration. The K_La value is the slope of $\ln [C_s/(C_s - C)]$ versus t . Smaller bubbles could provide a larger gas-liquid contact area under a same input gas volume, resulting in a better mass transfer property. This has been confirmed by our previous study [46] that ozone microbubble with a smaller diameter would offer a higher ozone saturation concentration and a larger mass transfer coefficient.

Reactive oxygen species could be generated via two approaches:

- the shrinking and collapse of ozone microbubbles, which reactive oxygen species generated at interface of bubbles; and,
- the self-decomposition of ozone molecules, which occurs in bulk solution.

Table 1. Overview on wastewater treatment through microbubbles technology.

System	Wastewater/Organic/Simulated Wastewater	$K_L a$	Treatment Efficiency in Optimal Condition	Conditions	Reference
Air-microbubbles, Air-macrobubbles/conventional bubbles	Tap water	Air-macrobubbles: 0.02191 s^{-1} ; Air-microbubble: 0.02905 s^{-1}	-	Gas flow rate: 0.67 L min^{-1}	[24]
Air-microbubbles	Phenol	-	Phenol removal: 60% (2 h)	Initial temperature: $35 \text{ }^{\circ}\text{C}$; Gas flow rate: $0.5 \text{ dm}^3 \text{ min}^{-1}$; Initial pH: 2.3	[38]
Ozone-microbubbles, Ozone-macrobubbles	Acrylic fiber wastewater (e.g., alkanes, aromatic compounds, and other refractory/bio-refractory organic compounds, et al.)	Ozone-microbubbles: 0.3767 min^{-1} ; Ozone-macrobubbles: 0.1732 min^{-1}	Ozone-microbubbles: CODcr removal: 42%; $\text{NH}_3\text{-N}$ removal: 21%; UV_{254} removal: 42%; Ozone-macrobubbles: CODcr removal: 17%; $\text{NH}_3\text{-N}$ removal: 12%; UV_{254} removal: 7% FT removal: 35%;	Initial temperature: $20 \text{ }^{\circ}\text{C}$; ozone dosage: 5 g h^{-1}	[44]
Ozone-microbubbles	Fenitrothion (FT) pesticide residues	-	(cherry tomatoes were immersed into solution for 10 min)	Dissolve ozone concentration: 2.0 ppm	[47]
Ozone-microbubbles	Practical textile wastewater	$0.1072\text{--}0.4859 \text{ min}^{-1}$	Color removal: 80% (140 min); COD removal: 70% (200 min)	Initial temperature: $19 \text{ }^{\circ}\text{C}$; Gas flow rate: $0.5 \text{ dm}^3 \text{ min}^{-1}$; Input ozone concentration: 132 mg dm^{-3} ; Initial pH: 8.7	[48]
Ozone-microbubbles	dimethyl phthalate (DMP)	-	DMP removal: 99% (300 s, initial SMP concentration: 0.052 mol m^{-3}); 95% (1800 s, initial DMP concentration: 1.029 mol m^{-3})	Gas flow rate: 1.11 mg s^{-1} ; Initial pH: 9;	[49]

The generation of reactive oxygen species at the interface of ozone-liquid via the collapse of ozone microbubbles could be expressed by Figure 2 [50]: H^+ and OH^- around microbubbles were trapped at microbubbles' surface in the process of shrinking; and, the diameter of bubbles continued to shrink until collapse; meanwhile, reactive oxygen species, especially $OH\cdot$, were produced due to the sudden disappear of the surface. Furthermore, self-decomposition of ozone molecules in liquid phase, triggering the formation of $OH\cdot$, has no difference with the conventional ozonation process. The extra $OH\cdot$ produced by microbubble collapse has a high benefit on the oxidation of refractory organic matters. The collapse of microbubbles also induces local turbulences, which could facilitate the contact between $O_3/OH\cdot$ and pollutants, and is followed by an intensification of organic mineralization.

Figure 2. Schematic diagram of ozone-microbubble in liquid phase.

Tianlong Zheng et al. [41] made a comparison between macrobubble-ozonation process and microbubble-ozonation process on the degradation of wet-spun acrylic fiber wastewater. The results showed that, when compared with microbubble ozonation, the microbubble could efficiently improve the removal efficiency of COD_{Cr}, NH₃-N, and UV₂₅₄ by 25%, 21%, and 42%, respectively. Biodegradability has also been improved. This phenomenon could be ascribed to the production of more $OH\cdot$, which has been measured by 3D-EEM (three-dimensional excitation-emission matrix fluorescence spectroscopy). According to H. Ikeura et al. [47], ozone-microbubbles also specialized in the removal of residual pesticides as compared with ozone-millibubbles. Li Pan et al. [51] found difference on DBPs (degradation by-products) generation between microbubbles ozonation and conventional bubbles ozonation and proved that most bromate formation was the result of O_3 molecular direct oxidation, which could be limited by the addition of ammonia. An enhanced color removal efficacy has also been observed [48,52]. According to literatures [45,53], a novel plasma dielectric barrier discharge (DBD) microbubble reactor was designed, and ozone-microbubbles that were produced by this reactor could effectively oxidize toxic cyanobacterial species to harmless productions and can also be used for the pretreatment of lignocellulosic biomass.

An indirect method for $OH\cdot$ measurement was firstly proposed by Elovitz M.S. and Gunten U.V. [54], where pCBA (*p*-chlorobenzoic acid) was selected as radical probe due to the low reaction activity with the O_3 molecule as compared to $OH\cdot$ for the rate constants between PCBA and O_3 molecule/ $OH\cdot$ are 0.15 and $5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively. In-depth research for measuring the amount of $OH\cdot$ in ozone microbubbles process has been conducted by Snigdha Khuntia et al. [10]. In this paper, O_3 exposure, $OH\cdot$ exposure, and Rct values which indicate the ratio of $OH\cdot$ —exposure and O_3 —exposure, were calculated, and the results showed that the values of O_3 exposure and $OH\cdot$ exposure in acid medium were higher than neutral/basic medium. However, a remarkable increase

was observed when pH value exceeds 10. It is a tremendous advantage for microbubbles ozonation process, because the amount of $\text{OH}\cdot$ in acid treated medium could be negligible in macrobubbles ozonation processes. The generation of $\text{OH}\cdot$ at pH 7 has been reported by Abdisa Jabesa [49], which was responsible for the degradation of DMP (dimethyl phthalate). This indicates that the application range of ozone-based AOPs would be expanded, because $\text{OH}\cdot$ can even be produced in the acid medium. In many cases, industrial effluents are usually acid liquid.

3. Ultrasonic Catalytic Ozonation

3.1. Ultrasonic Technology

Ultrasound has been widely used in waste water treatment for the removal of aromatic compounds, chlorinated aliphatic compounds, herbicides, pesticides, azo dyes, and bacteria, et al. [55–62]. This is due to the fact that ultrasound is able to yield $\text{OH}\cdot$ (Equation (3)) in the liquid phase by decomposing water molecule [63–65]. Other free radicals were produced simultaneously in this process such as $\text{H}\cdot$, $\text{HOO}\cdot$ (Equations (3) and (4)). Moreover, according to Fitzgerald, H_2O_2 (Equation (5)) would also be formed in this process [66]. The formation of H_2O_2 would also benefit pollution degradation. In short, this process could be described as follows [56]:

In addition, it is noteworthy that H_2O_2 could be decomposed to generate $\text{HO}\cdot$ in the presence of acoustic cavitation [67]:

The application of ultrasound in AOPs for enhancing the mass transfer efficiency and/or chemical reactions is defined as “sonochemistry” [68,69]. Sonochemistry is always performed accompanied by acoustic cavitation [70,71], which refers to the process of cavitation in bubbles formation, growth, and collapse [69,72]. It could be explained by the hot spot theory that when ultrasound applied in liquid phase, vibrations of molecules due to ultrasonic energy would result in a decreasing liquid static pressure, and cavitation bubbles arise until liquid pressure below the vapor pressure abruptly [59,69]. It should be emphasized that the shrinkage rate of cavitation bubbles is extremely quick than microbubbles [25]. The implosion of cavitation bubbles leading to an enormous concentration of energy conversion from liquid motion (kinetic energy) into bubble content (heating energy), resulting in a “hot spot”, where 5200 K in bubble gas phase and 1900 K in gas-liquid interface [73–75], followed by an extraordinary rapid cooling immediately, which allows for both chemical and physical effects [70,76–80]:

- chemical effect: this extreme circumstance would provide a specific pathway for chemical reactions happen; the generated $\text{OH}\cdot$ by pyrolysis inside the cavity and near the interface of the cavity would oxidize organic matters non-selectively; and,
- physical effect: the severe turbulence in liquid that is caused by cavitation bubbles could benefit the mixing of target organics and oxidizing agents/catalysts.

3.2. Properties of Ozone-Based Microbubbles Technology

Cavitation is an effective way to reduce ozone mass transfer resistance by causing turbulence in bulk solution and microcirculation surrounding cavitation bubbles, which is advantageous for ozone mass transfer, and is followed by an increased ozone dissolve concentration [46,78,81–83]. Meanwhile, molecular ozone was decomposed into oxygen molecule and oxygen atom in liquid phase under ultrasonic irradiation, and followed by $\text{OH}\cdot$ formation as a result of reaction between oxygen atom and water molecule. This process could be described as [70]:

In the ultrasonic catalytic ozonation process, $\text{OH}\cdot$ are expected to generated by approaches that (i) self-decomposition of O_3 (in basic medium); (ii) thermal decomposition of H_2O ; and, (iii) reaction between O (atomic) and H_2O .

The enhanced ozone mass transfer and production of large amount of $\text{OH}\cdot$ in bulk solution, indicating that the mineralization efficiency of recalcitrant organics could be further improved in a same operating condition as compared with ozonation alone or ultrasound alone. Zhiqiao He. et al. [84] reported the color decay of C.I. Reactive Black 5 by O_3 /Ultrasound, and results showed that this process followed pseudo-first-order kinetics. Another dye has been studied by Yongjun Shen et al. [85], and the degradation efficiency of active red X-3B by ozone, ultrasound, and ozone/ultrasound follow the order of O_3 /Ultrasound > O_3 > Ultrasound. Research conducted by Amna M. et al. [86] proved that this hybrid technology has a potential of water disinfection, which was in accordance with the literature provided by Jyoti K. K. et al. [72], and the optimal synergetic factor (E) reaches 1.42. A pilot scale study has been conducted by Guodong Ji et al., [87], of which the results showed that the value of kinetic rate constant has been improved from $1.1 \times 10^{-3} \text{ min}^{-1}$ (ozonation alone) to $49.9 \times 10^{-3} \text{ min}^{-1}$ (ultrasonic catalytic ozonation). The relationship between oxidation efficiency, $\text{OH}\cdot$, and ultrasonic fields was revealed by Lei Zhao et al. [34] that multiple-field of ultrasound (28 kHz) could intensify the removal efficiency of nitrobenzene and a positive correlation between the enhancement degree and the amount of ultrasound field, both of which could be ascribed to the enhanced ozone mass transfer and accelerated initiation $\text{OH}\cdot$ concentration. In most studies, additional $\text{OH}\cdot$ plays a major role in pollutants removal; however, according to WanQian Guo et al. [88], direct oxidation via ozone molecular was responsible for sulfamethoxazole degradation. The degradation efficiency of acephate and degradation products have also been studied [89].

4. Ultrasonic Catalytic Microbubbles Ozonation Process

4.1. Properties of This Hybrid Technology and Generation Pathway of Hydroxyl Radicals

The hybrid technology of O_3 /Ultrasonic has been reported by several researchers (Table 2); however, only few studies have focused on the combined application of ultrasound and ozone-microbubbles (Table 3). The first attempt has been and made by Zheng Xu et al. [35], in which the 1, 4-Dioxane has been selected as target pollutant. According to this research, the synergistic effect on reaction rate constant could be owing to the formation of additional $\text{OH}\cdot$, the increasing ultrasonic input power, and the higher ozone concentration.

This hybrid technique employs the combination of ozonation, ultrasound, and microbubbles process, leading to both an improved ozone mass transfer and an increased level of $\text{OH}\cdot$ in the liquid phase, hence the pollutants removal rate would be significantly improved, especially refractory pollutants and biorefractory compounds. According to our previous study on ultrasonic catalytic microbubbles ozonation process [46], an increment of 0.194 min^{-1} of $K_L a$ value was observed after the application of ultrasonic power, and both the degradation and mineralization efficiency of SMP

(sulfonated phenolic resin) were intensified as expected, which could be ascribed to both an improved ozone mass transfer coefficient and the generation of extra $\text{OH}\cdot$.

Both the reduced ozone mass transfer resistance in virtue of acoustic cavitation and the final stage of microbubble shrinkage would make a contribution to the dissolution of more ozone, which may render higher ozone saturation concentrations. Furthermore, $\text{OH}\cdot$ could be produced via (i) ozone self-decomposition; (ii) water thermal decomposition; (iii) atomic O react with H_2O molecular; and, (iv) the collapse of microbubbles. This mutual promotion process exhibits some unique technology superiorities, such as reduced reaction time and elevated mineralization rate.

4.2. Typical Experimental Operating Parameters

4.2.1. Initial pH

The initial pH of reaction medium is usually considered as a prime parameter in ozone-based AOPs, because it could alter both ozone self-decomposition rate and ozonation pathway. As generally recognized, basic environment facilitates the mineralization of recalcitrant chemicals as a result of indirect oxidation via $\text{OH}\cdot$ in ozonation processes [90–93]. Whereas, acid medium always benefits the formation of $\text{OH}\cdot$ in microbubbles systems [25]. Hence, experiments must be conducted to clarify the kinetics and mechanism of ozone reactions and optimize pH to obtain $\text{OH}\cdot$ as much as possible.

4.2.2. Ozone Dosage

Ozone dosage could directly affect dissolved ozone concentration, ozone saturation concentration, and production of $\text{OH}\cdot$, and then affect ozone-liquid mass transfer, ozone utilization rate, and removal rate of contaminations. Ozone utilization rate could be calculated by equation:

$$\text{O}_3 \text{ utilization } [\%] = \frac{\text{O}_{3(\text{input})} [\text{mg/L}] - \text{O}_{3(\text{off gas})} [\text{mg/L}]}{\text{O}_{3(\text{input})} [\text{mg/L}]} \times 100 \quad (12)$$

This means that higher ozone-liquid mass transfer may not coincide with higher O_3 utilization rate, because $K_L a$ is a function of ozone saturated concentration and time, while ozone utilization rate is associated with other conditions (e.g., ozone-self decomposition rate). We could speculate that, in strong basic medium, $K_L a$ value is much lower than acid medium, but the O_3 utilization rate is just the reverse. This is because ozone is unstable in the presence of an ample amount of OH^- and could decomposed into $\text{OH}\cdot$ rapidly [92–94], which dramatically reduces ozone saturated concentration, and eventually, a decreased $K_L a$ value. However, the basic condition may result in higher ozone concentration gradient between gas and liquid phase, which is the main driving force for ozone mass transfer. Thus, more ozone molecular could be dissolved into liquid phase, consequently a higher O_3 utilization rate. Hence, it is necessary to take both the ozone mass transfer coefficient and O_3 utilization into consideration in practical application. To date, O_3 utilization has seldom been assessed. On the other hand, excessive ozone might impede organic mineralization [95]:

Table 2. Overview on wastewater treatment through ultrasonic catalytic ozonation process.

System	Wastewater/Organic/Simulated Wastewater	$K_L a$	Treatment Efficiency in Optimal Condition	Conditions	Reference
O ₃ /Ultrasound	Nitrobenzene	O ₃ /Ultrasound: 0.24–0.43 min ^{−1} ; O ₃ : 0.20 min ^{−1}	Nitrobenzene removal: 60.9%; TOC removal: 88.8% (30 min, initial concentration: 50 µg L ^{−1})	Initial temperature: 20 °C; Total applied ozone: 1.2 mg L ^{−1} ; Initial pH: 6.85; Ultrasonic power density: 38.5 W L ^{−1} ; Ultrasonic power frequency: 28 kHz; Ultrasonic fields: 4	[34]
O ₃ /Ultrasound	Triazophos	-	Triazophos removal: 52.4% (90 min, initial concentration: 20 ppm)	Initial temperature: 37 °C; Ozone intake flow rate: 400 mg h ^{−1} ; Initial pH: 3.2; Ultrasonic power: 1500 W; Ultrasonic power frequency: 40 kHz; Initial temperature: 25 °C;	[62]
O ₃ /Ultrasound	Benzophenone-3	-	-	Ozone intake flow rate: 3500 mg h ^{−1} ; Ultrasonic power: 50 W; Ultrasonic power frequency: 160 kHz	[65]
O ₃ /Ultrasound	C.I. Reactive Black 5	-	Color removal: 100% (4 min, initial concentration: 100 mg L ^{−1}); 82% (4 min, 500 mg L ^{−1})	Initial temperature: 35 °C; Ozone concentration: 1 mg L ^{−1} ; Ultrasonic power density: 88 W L ^{−1}	[84]
O ₃ /Ultrasound	Reactive red X-3B dye	0.43 min ^{−1}	Dye removal: 99.2% (6 min)	Initial concentration: 100 mg L ^{−1} ; Ozone flux: 40 L h ^{−1} ; Initial pH: 6.52; Ultrasonic power density: 200 W L ^{−1}	[85]
O ₃ /Ultrasound	Bacteria	-	Reduction of live cells: 99% (4 min)	Initial temperature: 25 °C; Ozone dosage: g h ^{−1} ; Ultrasonic power: 100 Watt each Ultrasonic power frequency: 612 kHz	[86]
O ₃ /Ultrasound	Sulfamethoxazole (SMX)	-	SMX removal: 100%	Ozone dosage: 3 g h ^{−1} ; Initial pH: 9; Ultrasonic power density: 600 W L ^{−1} ; Initial temperature: 25 °C;	[88]
O ₃ /Ultrasound	Acephate	-	Acephate removal: 87.6% (60 min)	Ozone intake flow rate: 3500 mg h ^{−1} ; Ultrasonic power: 50 W; Ultrasonic power frequency: 160 kHz	[89]
O ₃ /Ultrasound	potassium ferrocyanide (KFC)	-	KFC removal: 82.41% (90 min, 200 ppm)	Initial temperature: 35 °C; Ozone dosage: 400 mg h ^{−1} ; Ultrasonic power: 1 kW; Ultrasonic power frequency: 25 kHz	[96]

Table 3. Overview on wastewater treatment through ultrasonic catalytic microbubbles ozonation process.

System	Wastewater/Organic/Simulated Wastewater	$K_L a$	Treatment Efficiency in Optimal Condition	Conditions	Reference
Ozone-microbubbles/Ultrasound	1, 4-Dioxane	-	Reaction rate constant: ozone-microbubbles/Ultrasound process: $6.3 \times 10^{-3} \text{ min}^{-1}$;	Ozone dosage: 101.5 mg L^{-1} ; Ultrasonic power: 150 W; Ultrasonic power frequency: 490 kHz Initial temperature: room temperature	[35]
Ozone-microbubbles/Ultrasound	Sulfonated phenolic resin (SMP)	Ozone-microbubbles: 0.438 min^{-1} Ozone-microbubbles/Ultrasound: 0.632 min^{-1}	SMP removal: 50% (5 min) TOC removal: 75% (120 min)	Ozone intake flow rate: 300 L h^{-1} ; Ultrasonic power: 1000 W; Ultrasonic power frequency: 20 kHz;	[46]

4.2.3. Intake Flow Rate

Ozone intake flow rate is related with state of liquid phase, bubble size distributions, and bubble rise velocity. An increasing gas intake flow rate would lead to severe turbulence of the liquid phase and less coalescence of small bubbles, which could expedite ozone-liquid mass transfer. However, the faster bubble rise velocity indicates the shorter ozone-liquid contact time, resulting in a lower mass transfer eventually. An appropriate intake flow rate should to obtain maximum utilization of ozone is crucial.

4.2.4. Operating Temperature

Temperature is another important factor that can influence the ozone solubility, ozone self-decomposition rate, kinetics between oxidants (O_3 and/or $OH\cdot$) and organics in liquid phase, and vapor content in cavitation bubble. The increase of temperature could decrease ozone solubility (Equation (15)) [95,97,98] and $OH\cdot$ production, which are based on the implosion of cavitation bubble through increased bubble vapor content and declined collapse pressure [99,100]. Meanwhile, a rising operating temperature expedites the conversion of O_3 to $OH\cdot$ and then the degradation rate of pollutants increased [101,102]. Those contradictory results above indicate that the optimal temperature for ozone mass transfer and ozone utilization in practical application should be measured to obtain a better understanding of this hybrid process. In most studies, room temperature (25 °C) was found to be the best choice [95].

$$\log\left(\frac{H_{O_3}}{kPa \cdot m^3 \cdot mol^{-1}}\right) = 5.12 - \frac{1230}{T(K)} \quad (15)$$

4.2.5. Bubbles Size Distribution

The measurement of diameter distribution of microbubbles is indispensable as gas-liquid interface area plays a vital role in ozone mass transfer. The peak of bubble diameter distribution curve located in a smaller value, which indicates a smaller mean diameter of bubbles, moreover, a wider peak width reveals a larger proportion of small diameter bubbles, both of which advances ozone mass transfer due to a larger ozone-liquid contact area with the same ozone volume. According to Young-Laplace equation (Equation (1)), the internal pressure of a bubble with diameter of 1 μm is four times higher than atmospheric pressure [25].

4.2.6. Ultrasonic Frequency

Ultrasonic performance is closely associated with ultrasonic frequency. According to literature [103,104], as compared with high ultrasonic frequency, low frequency creates strong shear and mechanical forces that are conducive to the sonochemistry effect and followed with a better degradation efficacy of pollutant. 20–40 kHz frequencies were widely used according to report [104].

4.2.7. Ultrasonic Power Density

Ultrasound input power density (W/L or W/cm^2) is an important parameter in deciding the number of cavitation bubbles [105] and evaluating energy consumption [106]. An increase in ultrasonic power density always leads to a higher ozone saturation concentration, ozone mass transfer efficiency, and degradation efficacy of organics [106–109]. According to our previous study [46], the $K_L a$ value dropped with excessive evaluated ultrasonic density, and this phenomenon could be ascribed to increased coalescence odds of ozone bubbles and temperature. On the other hand, excessive power density would result in the augmentation of overall costs, which is sensitive in practical application.

4.2.8. Natural Water Constituents

Natural water constituents refer to anions (e.g., Cl^- , HCO_3^- , CO_3^{2-} , SO_4^{2-} , and PO_4^{3-}), cations (e.g., Ca^{2+} , Mg^{2+}) and natural organic matter (NOM). Effects of those ions on pollutants removal

in ozone-based AOPs are of great value to investigate. In basic medium, HCO_3^- and CO_3^{2-} acting as radical scavengers that can react with $\text{OH}\cdot$ (Equations (16) and (17)), which significantly hindered mineralization of pollutants. Phosphates present different forms at different pHs, such as H_3PO_4 , H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-} . The presence of phosphate ions in bulk solution would inhibit the production of free radicals via occupied active site on surface of heterogenous catalyst [17,110].

5. Conclusions

The instability and low solubility of ozone molecular in liquid phase impedes the further application of ozone and ozone-based technology in the field of wastewater treatment. Several achievements in ozone-based AOPs fields have been undertaken by researchers to obtain an improved ozone utilization rate. The ultrasonic catalytic microbubbles ozonation process can be considered as an appropriate way for improving ozone mass transfer and the conversion of ozone to $\text{OH}\cdot$, which results in an increased degradation of recalcitrant contaminant in bulk solution. The oxidation performance of this hybrid process is affected by several typical parameters; thus, if the operating conditions are properly selected and optimized based on experiments, a complete mineralization of pollutant with receptive ozone consumption would be accomplished. Receptive ozone consumption means high ozone utilization, including high ozone transfer and a large amount of $\text{OH}\cdot$ production.

This technology characterized by simplicity, lower expenses, ease of operation, and no reservoir pollutant has potential in the treatment of real wastewater and industrial application. However, the subject of ultrasonic catalytic microbubble ozonation is still a long way from the laboratory scale to industrial application. Some scale up strategies are given, as follows:

1. the economic feasibility of ultrasonic-assisted microbubble ozonation process at industrial scale should be verified;
2. enhancement mechanism of this technology is still unclear. Therefore, in-depth studies should be conducted. To accelerate degradation efficacy and improve ozone utilization in the field of ozone-based AOPs, parameters such as: ozone mass transfer efficiency, ozone utilization, ozone decay rate, amount of $\text{OH}\cdot$, COD removal, TOC removal and BOD removal, et al., ought to be measured at certain given times;
3. microelements/trace elements that exist in natural water can be chosen as target substances. A point must be emphasized here is that initial concentration of target substance in treatment of simulated wastewater should on basis of original concentration; and,
4. real wastewater with complex components and high COD value ($> 1000 \text{ mg/L}$) can be selected as the treatment object, as it is the fundamental aim of academic research. Initial properties of effluents should be characterized before studies undertaken.

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