

## Enhanced ozonation of textile wastewater by microbubbles

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### Abstract

In this paper the microbubble technology was employed to increase the mass transfer rate of ozone as well as to enhance the ozone oxidation. Experiments were performed using the microbubbles generator and the bubble contactor, which is commonly used in ozonation system, for the purpose of comparison. The microbubble generator produced a milky and high intensity microbubble solution in which the bubbles had a mean diameter of less than 58 microns, a numerical density of more than  $2.9 \times 10^4$  counts/mL, and a specific surface area of more than  $334 \text{ m}^{-1}$  at the gas flow rate of less than 0.5 L/min. Compared to the bubble contactor, the total mass transfer efficiency in the microbubble system were 1.6-2.7 times higher. During the ozonation of practical textile wastewater, the input ozone could be thoroughly utilized and the rate of decolourization and organic reduction were much faster by using the microbubble system. The time required for 80% removal of color was about 140 and 280 min by introducing ozone into the microbubble generator and bubble contactor, respectively. The COD removal efficiency was higher 20% by using the microbubble system. The results suggested that in addition to the enhancement of mass transfer, microbubbles, which had higher inner pressure, could accelerate the formation of hydroxyl radicals from the decomposition of ozone and hence improve the oxidation of dye molecules.

Keywords: ozonation, microbubble, mass transfer, textile wastewater

### 1. Introduction

Ozone has been widely used in the field of drinking water and wastewater treatment [1]. The ozonation process is a typical example of gas absorption with a chemical reaction where the total reaction rate can be affected by the reaction kinetics and mass transfer [2]. It has been determined that the rate-limiting step comes from the low gas-liquid mass transfer rate due to the low solubility of ozone [3]. The rate of ozone mass transfer depends on the mixing characteristics of the gas-liquid contactor used, the

kinetics of ozone decay in the water, and the number and size of the ozone bubbles produced [4-5]. The effectiveness of ozonation can be increased by a higher surface area of ozone through the generation of smaller bubble [6].

Microbubbles are defined as bubbles with diameters in the order of less than several tens of microns. Compared to conventional bubbles with diameters of several millimeters, microbubbles have a huge interfacial area and bubble density, low rising velocity in liquid phase and high inner pressure [7]. Microbubbles have shown promise due to their potential to be widely used in such fields as biomedical engineering, environmental engineering, drug reduction in shipbuilding, marine culture, mining and domestic bathes [7]. The application of microbubble technology in ozonation processes will provide a new approach to improving ozonation efficiency.

In this paper, the ozonation of practical textile wastewater was investigated by using a microbubbles generator and a bubble contactor, which is commonly used in ozonation system, for the purpose of comparison. The objectives of the study were to examine the enhanced mass transfer and the ozone oxidation of dyestuff wastewater by microbubble technology. The mechanism of enhanced degradation of the dye by ozone microbubbles was also analyzed.

## 2. Materials and methods

### 2.1. Experimental apparatus

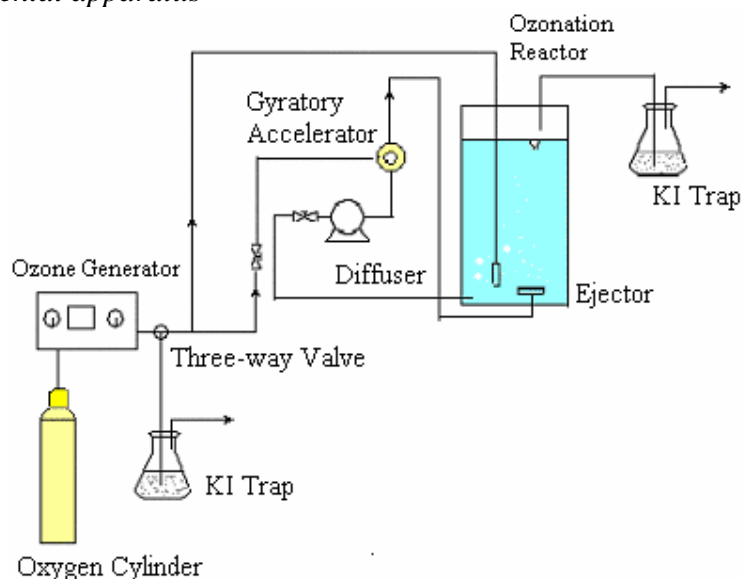


Fig. 1. Schematic diagram of the experimental set-up

The microbubble generator was made by Kyowa Engineering Co., Ltd. (Japan). It consisted of a recycling pump, a gyrotory accelerator and an injector (Fig. 1). The working volume of the Plexiglas reactor was 20 L. Ozone was produced from pure oxygen by an ozone generator (ED-OG-R4, Eco Design, Japan) and fed into the reactor by the microbubble system or a conventional gas diffuser, which was used for comparison. The titanic porous diffuser was cylindrical, with a pore size of 45  $\mu\text{m}$ . A

2% (w/v) potassium iodine solution was used to adsorb the ozone remaining in the off gas at the exit of the reactor.

## 2.2. Materials

The practical textile wastewater was from Beijing Guanghua Textile Plant. The textile wastewater is heavily coloured with a large variation in chemical composition, such as residual reactive azo dye, alkali, surfactants et al. Table 1 shows the practical wastewater characteristics.

Table 1 Practical wastewater characteristics

Items	Values
pH	6.9-8.7
SS (mg/L)	60-80
COD (mg/L)	530-600
BOD <sub>5</sub> (mg/L)	80-116
BOD <sub>5</sub> /COD (%)	15-22
Temperature (°C)	30 ± 3

## 2.3. Analysis

The concentration of ozone in the gas phase was analyzed by the iodometric method with KI solution [8]. The liquid-phase ozone concentration was measured using the indigo colorimetric methods [9]. Decolorization capacity was determined by integration method, which involved scanning the optical spectra of a sample from 200 nm to 800 nm by a UV-visible spectrometer (UV 757, Shanghai Cany Precision Instrument Co., Ltd., China) and integrating the area under the absorbance curve. The pH value was monitored by the pH meter (Model 828, ORION). COD was analyzed using the K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> oxidation method. A BOD analyzer (BOD Trak, HACH) was employed to analyze the BOD<sub>5</sub> concentration.

The size of the microbubbles was measured using a microscope (E600, Nikon, Japan) equipped with a CCD digital camera (SPOT RT SUPER, Diagnostic Instruments, Inc., USA). The recorded images were analyzed to determine the bubble sizes using *Image-Pro Plus* software (Media Cybernetics Incorporated, USA). After the produced microbubbles reached stability, 1 cm-long cells were filled with samples, and immediately closed. Microscopy was used to detect the sizes of the microbubbles. The preparation and observation were conducted immediately to ensure that there was no obvious change in the microbubble size inside the fully filled and closed cells. This method might not accurately reflect the distribution of the original bubble sizes because some large bubbles may have been broken during the sampling, but it did provide a rough idea of the features of the microbubble generator.

## 2.4. Experimental procedure

The experiments were divided into two parts. First, the enhancement of the mass transfer was studied. The temperature of the reactor was kept at 18 ± 2 °C. The ozone gas was absorbed into deionized water until the ozone in the reactor reached saturation. Because the self-decomposition constant ( $K_d$ ) of ozone is much lower than the total mass transfer coefficient ( $K_{La}$ ), the influence of  $K_d$  was not taken into account in the derivation of  $K_{La}$ . Consequently, the values of  $K_{La}$  could be determined by the following equation:

$$\frac{dC}{dt} = K_L a (C^* - C) \quad (1)$$

where  $C$  is the concentration of dissolved ozone in the bulk liquid phase (mg/L) and  $C^*$  is the concentration of saturated ozone in water (mg/L).

We assumed that  $K_L a$  and  $C^*$  were constant throughout the testing period. Equation 1 can be integrated to yield the following expression for  $C$  as a function of time,  $t$ :

$$C = C^* - (C^* - C_0) \exp(-K_L a t). \quad (2)$$

Secondly, the ozonation of dyestuff wastewater was studied. Prior to this experiment, a three-way-valve was used to bypass the ozone-containing gas into the KI solution, with a gas flow rate of 0.5 L/min, to determine the inlet ozone concentration and to ensure the stability of the gas. The input ozone concentration was approximately 132 mg/L. Then the ozone-containing gas was introduced into the reactor, which was operated in semi-batch mode by feeding the ozone-containing gas continuously. Samples were taken at appropriate time intervals to analyze the color, pH and COD. In addition, the ozone concentration in the off-gas was detected during the ozonation. The ozonation experiments were performed using both the microbubble generator and a conventional bubble contactor for comparison. All the experiments were repeated to ensure accuracy.

### 3. Results and Discussion

#### 3.1. Enhanced mass transfer of ozone by microbubbles

With the introduction of gas, the water in the reactor gradually became almost milky because many fine bubbles were formed. After gas feeding was stopped, the water remained milky and bubbly for 4-5 min, indicating the very low upward velocity of microbubbles. By observing more than 600 bubbles, the bubble size distribution in terms of count as a function of gas flow rates was obtained (see Fig. 2).

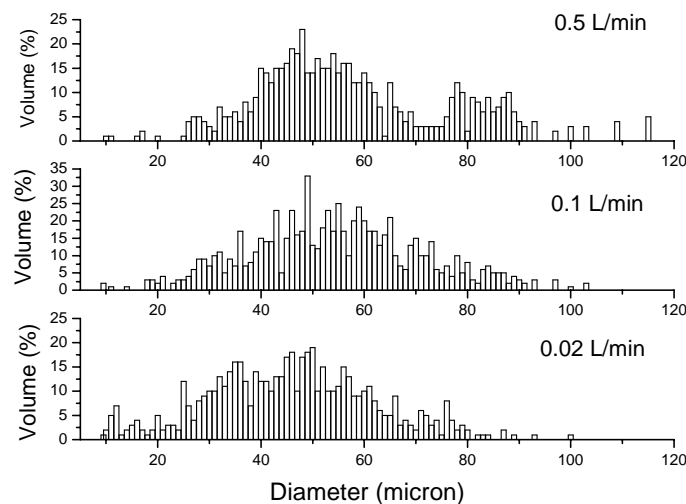


Fig. 2. Typical plots of microbubble size distribution  
Count mean diameter,  $d_c$ , is calculated according to the following equation:

$$d_c = \frac{\sum n_i d_i}{\sum n_i} \quad (3)$$

where  $n_i$  is the counted gas bubbles having diameter  $d_i$  and  $d_i$  is the individual bubble diameter ( $\mu\text{m}$ ).

The gas bubble concentrations are calculated based on the gas holdup:

$$N = \frac{\varepsilon_g}{\frac{\pi}{6} \left( \frac{\sum n_i d_i^3}{\sum n_i} \right)} \quad (4)$$

where  $N$  is the total number of gas bubbles per volume ( $\text{counts}/\text{m}^3$ ).

From the resultant bubble concentrations, the specific surface area  $a$  ( $\text{m}^2/\text{m}^3$ ) for the mass transfer was thus calculated as

$$a = N \frac{\sum n_i \pi d_i^2}{\sum n_i}. \quad (5)$$

Table S1 lists the calculated results.

Table 1 Results of bubble size measurement

Flow rate (L/min)	0.02	0.1	0.5
Count mean diameter ( $\mu\text{m}$ )	46	54	58
Bubble conc. ( $\text{counts}/\text{mL}$ )	$4.9 \times 10^4$	$3.4 \times 10^4$	$2.9 \times 10^4$
Specific surface area ( $\text{m}^2/\text{m}^3$ )	363	344	334

As shown, a mean diameter of less than  $58 \mu\text{m}$ , numerical density of more than  $2.9 \times 10^4 \text{ counts}/\text{mL}$  and specific surface area of more than  $334 \text{ m}^2/\text{m}^3$  were obtained at a gas flow rate of less than  $0.5 \text{ L}/\text{min}$ . With the increase of the gas flow rate, more bubbles with larger sizes were observed. Accordingly, the bubble density and the surface area-to-volume ratio decreased. The obtained high bubble concentration and large specific surface area demonstrated the high intensity of microbubble generation.

The total mass transfer coefficient in the two systems was compared in Table 2. As can be seen, the values of  $K_L a$  increased as the gas flow rate increased due to the increased quantity of ozone being available for transfer per liter of water entering the system. The  $K_L a$  was 1.6-2.7 times for the microbubble system than that for the bubble contactor. This is consistent with the expectation that smaller bubbles will result in higher rates of mass transfer of ozone from the bubbles by maximizing the surface area-to-volume ratio.

Table 2 Comparison of mass transfer efficiency

Flow rate ( $\text{L} \cdot \text{min}^{-1}$ )	Mass transfer coefficient $K_L a$ ( $\text{min}^{-1}$ )		
	0.5	1.0	1.5
Microbubble system	0.2215	0.2924	0.311
Bubble contactor	0.0962	0.1083	0.194

### 3.2. Enhanced ozonation of textile wastewater by microbubbles

As the ozonation progressed, the color of the textile wastewater gradually bleached from black, to brown, and then to light yellow. The performance of the two systems in

terms of decolorization, COD removal, output ozone concentration and pH was compared (see Fig. 3). The pH value decreased during the ozonation, which indicated the production of the intermediates containing acid substances. As demonstrated in Fig. 3, the color removal initially occurred rapidly, and slowed down, finally reaching 90%. The rate of decolorization was obviously faster in the microbubble system. The time required for 80% removal of color was about 140 min after introduction of ozone into the microbubble generator, compared to 280 min for the bubble contactor.

In terms of mineralization of the textile wastewater, the COD removal efficiency could be increased markedly by using microbubble technology. The COD removal efficiency of the microbubble generator reached 70% (at 200 min); it was only 50% (at 360 min) for the bubble contactor.

The concentration of off-gas ozone of the microbubble system (0.04-2.5 mg/L) was significantly lower than that for the bubble contactor (0.08-74.3 mg/L), which demonstrated the very high ozone utilization of the microbubble system. Considering the high COD removal efficiency in the microbubble system described above, we propose that the microbubble technology can enhance the ozone oxidation as well as the mass transfer. In general, ozone oxidation pathways include direct ozone attack or free radical attacks. Since the oxidation potential of hydroxyl radicals is much higher than that of ozone molecules, direct oxidation is slower than radical oxidation. Microbubbles with higher inner pressure could induce the decomposition of ozone and contribute to the production of hydroxyl radicals.

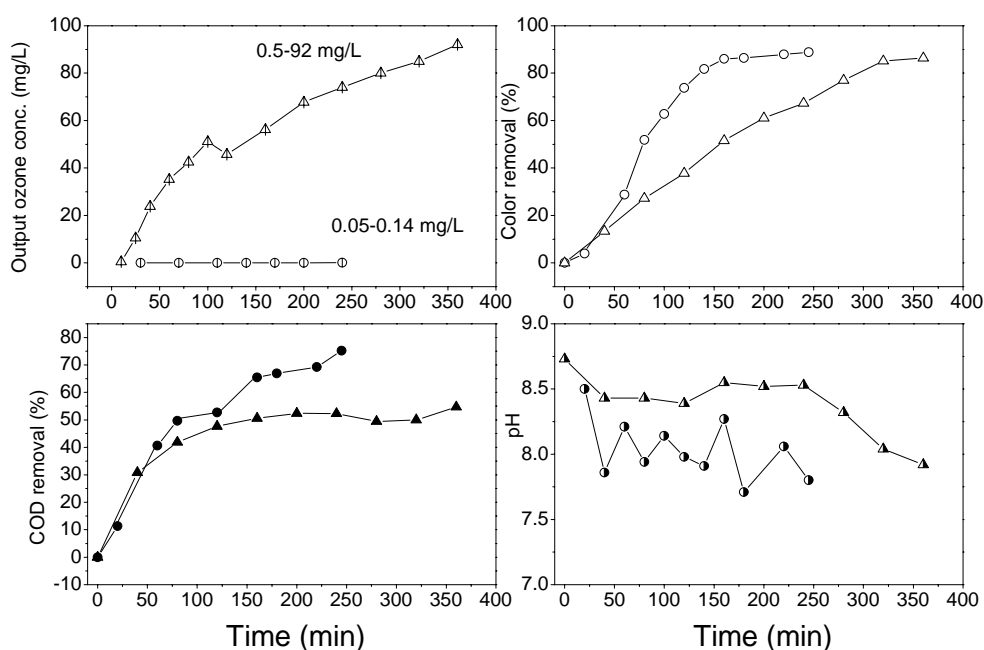


Fig. 3 Performance of practical textile wastewater treatment  
 Symbols: Circles – microbubble generator; Triangles – bubble contactor

#### 4. Conclusions

A microbubble technology was applied to increase the mass transfer rate of ozone as well as to enhance the ozone oxidation of practical textile wastewater in this paper. Experiments were performed using both the microbubbles generator and the bubble contactor, which is commonly used in ozonation systems, for the purpose of comparison. Main conclusions obtained are as follows:

- (1) The microbubble generator produced a milky and high intensity microbubble solution in which the bubbles had a mean diameter of less than 58  $\mu\text{m}$ , a numerical density of more than  $2.9 \times 10^4$  counts/mL, and a specific surface area of more than  $334 \text{ m}^{-1}$  at a gas flow rate of less than 0.5 L/min.
- (2) Compared with the bubble contactor, the total mass transfer coefficient was 1.6-2.7 times higher at the gas flow rate of 0.5-1.5 L/min.
- (3) For treating textile wastewater the decolorization rate was faster and the COD removal efficiency was higher by 20% in the microbubble system.
- (4) According to the results of mass transfer, decolorization, mineralization and ozone accumulation for treating practical dyestuff wastewater, the microbubble system is a promising process for enhancing both mass transfer and oxidation of ozone.

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