Absorption and decomposition of ozone in a three-phase split-rectangular airlift reactor under ultrasonic irradiation

Yin Xu, Xin Zhong and Hui Zhang

ABSTRACT

Ozone absorption was investigated in a three-phase split-rectangular airlift reactor under ultrasonic irradiation using \( \gamma \)-Al\(_2\)O\(_3\) as catalyst. The reactor consisted of a square column (50 \( \times \) 50 mm) with the height of 120 mm, divided into a riser and a downcomer by a baffle, 50 mm in width, 4 mm in thickness and 50 mm in total height. An absorption kinetic model was proposed to determine the volumetric mass transfer coefficient of ozone \( k_La \). The results showed that \( k_La \) increased from 0.409 to 0.712 min\(^{-1}\) as power density rose from 27.2 to 100.3 W L\(^{-1}\), comparing with 0.242 min\(^{-1}\) in the absence of ultrasonic irradiation. The increase in gas flow rate and catalyst loading also favored the increase of \( k_La \). The degassing effect due to ultrasonic irradiation could be ignored in the ozone absorption process.

INTRODUCTION

Over the past few years, heterogeneous catalytic ozonation has emerged as a powerful treatment method for the degradation of contaminants, especially for refractory organic pollutants, and high removal and mineralization can be achieved correspondingly (Restivo et al. 2012). The major advantage of the heterogeneous catalytic system is the ease of catalyst retrieval and, consequently, the reuse of catalyst. Various catalysts, including Al\(_2\)O\(_3\) (Lin et al. 2002), Fe\(_3\)O\(_4\) (Hou et al. 2013a), SiO\(_2\)-Al\(_2\)O\(_3\) (Lin et al. 2002), titanium oxide (Beltran et al. 2002; Rosal et al. 2006), zeolite and volcanic sand (Valdes et al. 2009), have been successfully used in catalytic ozonation. However, catalyst deactivation due to the accumulation of organic byproducts on the surface of the catalyst is still a great concern.

When ultrasound is introduced into the heterogeneous system, it will bring about many effects of cavitation phenomena, for instance, high temperature and pressure locally, acoustic streaming, the collapse of cavitation bubbles and so on. Of note, cavitational collapse near the catalyst surface will cause microjets to hit the surface and produce a non-symmetrical shock wave (Kumar et al. 2004; Chand et al. 2009; Gogate et al. 2011; Golash & Gogate 2012). This leads to the continuous cleaning of the catalyst surface. Moreover, the mechanical effects of ultrasound break the ozone gas bubbles, which results in a larger specific surface area and, consequently, a higher volumetric mass transfer coefficient of ozone. In the meantime, the ultrasound accelerates turbulence and subsequently increases the mass transfer of reactants and byproducts between the liquid bulk and the catalyst surface (Wang et al. 2011).

In our previous studies, a rectangular airlift reactor was employed for the catalytic ozonation combined with ultrasound (Wang et al. 2011; Hou et al. 2013a, 2013b). However, there is little systematic research on ozone mass transfer in the sono-catalytic ozonation system. Therefore, in this study, ozone absorption was investigated in a three-phase split-rectangular airlift reactor under ultrasonic irradiation. Mesoporous alumina (\( \gamma \)-Al\(_2\)O\(_3\)) was chosen as a catalyst due to its extensive use in catalytic ozonation. Catalytic ozone decomposition under ultrasonic irradiation was first performed at different power densities and catalyst dosages. Afterwards, the effect of power density, gas flow rate and catalyst dosage on ozone absorption was investigated. An absorption kinetic model was proposed to determine the volumetric mass transfer coefficient of ozone based on the ozone absorption and ozone decomposition data.

METHODS

The experimental set-up was similar to our previous study (Wang et al. 2011) and is illustrated in Figure 1. The rectangular
air-lift reactor consists of a square column (50 × 50 mm) with the height of 120 mm, divided into a riser and a downcomer section by a plexiglas baffle, 50 mm in width, 4 mm in thickness, and 50 mm in total height. The riser-to-downcomer cross-sectional area ratio is 1.3. The baffle is located at a distance of 12 mm from the bottom of the reactor. A gas distributor at the bottom of the riser was a perforated tube with six orifices of 1 mm diameter. The reactor was immersed into a water bath to maintain the temperature at 20 ± 2 °C.

Ozone was produced by an ozone generator (XFZ-5BI, China) and the gaseous ozone concentration was determined by the iodometric method (Flamm 1971). Sonication was performed with a KS-250 ultrasonic generator (250 W, 20 kHz, Ningbo Kesheng Instrument Co., China) equipped with a titanium probe transducer. The tip of the probe was 1.0 cm in diameter and was inserted 1.5 cm into the liquid layer. The sonication was administered in a pulse mode of 2.5 s on and 2.1 s off. The acoustic power density $P$ was measured calorimetrically (Toru et al. 2005).

Mesoporous alumina ($\gamma$-Al$_2$O$_3$) was synthesized by using the surfactant-assisted sol-gel procedure, which involved the controlled hydrolysis of aluminum alkoxide precursor in the presence of Cetyl-trimethylammonium bromide (CTABr, (CH$_3$)$_2$(CH$_2$)$_{15}$N(CH$_3$)$_3$Br) (Li et al. 2014). The sample physical properties are summarized in Table 1.

In ozone decomposition experiments, an ozone solution was prepared by bubbling ozone-containing oxygen into the phosphate buffer solution (pH 6.7–6.8) with the presence of $\gamma$-Al$_2$O$_3$ until it was saturated. Then the gas stream was cut off, and ultrasound was introduced into the ozone solution. At pre-determined time intervals, samples were taken by a syringe and filtered through 0.45 μm membranes before the ozone concentrations were measured by the indigo method (Bader & Hoigné 1981).

In ozone absorption experiments, ozone was continuously bubbled into the rectangular airlift reactor containing 200 mL phosphate buffer solution with the presence of $\gamma$-Al$_2$O$_3$. The ultrasonic irradiation was applied during the whole experiment. The gas flow rate $Q$ was measured by a bubble flow meter and dissolved ozone was analyzed as described above.

## RESULTS AND DISCUSSION

### Ozone decomposition

Catalytic ozone decomposition usually occurs at the surface of the catalyst and in the bulk solution (Rosal et al. 2006). In the presence of ultrasound, the material balance of dissolved ozone can be expressed as follows:

$$\frac{d[O_3]}{dt} = \frac{-k_{homo} + k_{heter}}{k_L a_{D1}} \left( [O_3] - [O_3]^*_{de} \right)$$  \hspace{1cm} (1)

where $k_{homo}$ and $k_{heter}$ are ozone decomposition rate constants in the bulk solution and at the surface of the catalyst, respectively (min$^{-1}$); $k_L a_{D1}$ is the volumetric mass transfer coefficient of dissolved ozone desorbed into the degassing bubbles or air over the water level when no gas is bubbled (min$^{-1}$); $[O_3]$ is the dissolved ozone concentration at time $t$ (mg L$^{-1}$); $[O_3]^*_{de}$ is the ozone saturation concentration equilibrium with gaseous ozone concentration in the degassing bubbles or at the top of the reactor (mg L$^{-1}$); and $t$ is the time (min).

Defining $k_{tot} = k_{homo} + k_{heter}$, Equation (1) can be simplified as:

$$\frac{d[O_3]}{dt} = -k_{tot} [O_3] - k_L a_{D1} ([O_3] - [O_3]^*_{de})$$  \hspace{1cm} (2)

The above equation is integrated into the following equation by assuming $[O_3]^*_{de}$ is negligible (Zhang et al. 2007),

### Table 1  Surface area, pore size, pore volume and particle size of catalyst ($\gamma$-Al$_2$O$_3$)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET surface area (m$^2$ g$^{-1}$)</th>
<th>Pore size (nm)</th>
<th>Pore volume (cm$^3$ g$^{-1}$)</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$-Al$_2$O$_3$</td>
<td>531</td>
<td>6.1</td>
<td>1.2</td>
<td>200–800</td>
</tr>
</tbody>
</table>
ln \( \frac{[O_3]}{[O_3]_0} \) = -(k_{\text{tot}} + k_{LA}D_1)t \hspace{1cm} (3)

where \([O_3]_0\) is the initial ozone concentration (mg L\(^{-1}\)). The linear relationship between ln\(([O_3]/[O_3]_0)\) and \(t\) can be verified by the results as illustrated in Figure 2(a) and 2(b) when ozone decomposition was performed at different power densities and catalyst dosages.

Due to the self-decomposition of ozone, \(k_{LA}D_1\) cannot be determined directly. According to Higbie’s penetration theory, \(k_{LA}D_1\) can be calculated by the following equation,

\[
k_{LA}D_1 = k_{LA}D_2 \sqrt{\frac{D_{\text{ozone}}}{D_{\text{oxygen}}}}
\]

where \(k_{LA}D_2\) is the volumetric mass transfer coefficient of dissolved oxygen desorbed into the degassing bubbles or air over the water level when no gas is bubbled (min\(^{-1}\)), and \(D_{\text{ozone}}\) and \(D_{\text{oxygen}}\) are the molecular diffusion coefficients of ozone and oxygen, respectively (m\(^2\) s\(^{-1}\)). They are determined to be \(1.71 \times 10^{-9}\) m\(^2\) s\(^{-1}\) and \(2.37 \times 10^{-9}\) m\(^2\) s\(^{-1}\), respectively (Zhang et al. 2007).

To determine \(k_{LA}D_2\), the separate oxygen degassing experiments were performed like ozone decomposition experiments, except that ozone-containing oxygen was replaced by pure oxygen. Then, the material balance of dissolved oxygen can be expressed as follows:

\[
\frac{d[O_2]}{dt} = -k_{LA}D_2([O_2] - [O_2]^*)
\]

Figure 2 | Effect of power density (a) and catalyst dosage (b) on the ozone decomposition ([O\(_3\)]\(_0\) = 0.3 mg/L, line: simulated); effect of power density (c) and catalyst dosage (d) on the degassing of oxygen ([O\(_2\)]\(_0\) = 8.3 mg/L, line: simulated).
where $[O_2]$ and $[O_2]^*$ are dissolved oxygen concentration and oxygen saturation concentration, respectively (mg L$^{-1}$). Equation (5) can be integrated as:

$$\ln \left(\frac{[O_2] - [O_2]^*}{[O_2]_0 - [O_2]^*}\right) = -k_{L_a}D_{22}t$$  \hspace{1cm} (6)

where $[O_2]_0$ is the initial oxygen concentration (mg L$^{-1}$).

The calculated $k_{L_a}D_{22}$ values are illustrated in the insets of Figure 2(c) and 2(d). With the increase in power density, the degassing effect of ultrasound became more significant, and $k_{L_a}D_{22}$ increased accordingly. As indicated in the inset of Figure 2(c), $k_{L_a}D_{22}$ was only 0.027 min$^{-1}$ in the absence of ultrasonic irradiation, while it increased from 0.053 to 0.116 min$^{-1}$ when power density rose from 0.2 to 0.6 g L$^{-1}$. The existence of catalyst particles may promote the formation of cavitations since the cavitation threshold is lowered in the presence of trapped vapour-gas nuclei in the crevices of catalyst, and this promotion is achieved with the appropriate addition of particles (Toru et al. 2005). As can be seen in the inset of Figure 2(d), $k_{L_a}D_{22}$ increased from 0.054 to 0.101 min$^{-1}$ when the catalyst dosage rose from 0.2 to 0.4 g L$^{-1}$, but further increase in the catalyst dosage to 0.6 g L$^{-1}$ resulted in the drop of $k_{L_a}D_{22}$ to 0.083 min$^{-1}$.

After the determination of $k_{L_a}D_{22}$, the total ozone decomposition rate constant $k_{tot}$ can be obtained according to Equation (3), and the results are shown in the insets of Figure 2(a) and 2(b). Figure 2(a) shows the introduction of ultrasound enhanced ozone decomposition and the rate constant increased with power density. Specifically, $k_{tot}$ was only 0.035 min$^{-1}$ in the absence of ultrasonic irradiation, while it increased from 0.042 to 0.113 min$^{-1}$ when power density varied from 27.2 to 100.3 W L$^{-1}$. More active sites would be available at a higher catalyst dosage, and the ozone decomposition rate increased accordingly. As indicated in the inset of Figure 2(b), $k_{tot}$ increased from 0.052 to 0.122 min$^{-1}$ when the catalyst dosage rose from 0.2 to 0.6 g L$^{-1}$.

**Ozone absorption**

In the presence of ultrasound, when ozone was continuously bubbled into the rectangular airlift reactor, material balance of ozone in aqueous phase can be expressed as follows:

$$\frac{d[O_3]}{dt} = k_{L_a}A[O_3]_g - (k_{L_a}A + k_{tot} + k_{L_a}D_3)[O_3]$$  \hspace{1cm} (8)

Solving Equation (8) with initial condition of $[O_3] = 0$ at $t = 0$, we obtain:

$$[O_3] = \frac{k_{L_a}A[O_3]_g}{k_{tot} + k_{L_a}D_3 + k_{L_a}A} \left(1 - \exp(-(k_{tot} + k_{L_a}D_3 + k_{L_a}A)t)\right)$$  \hspace{1cm} (9)

Defining $A = k_{L_a}A$ and $B = k_{tot} + k_{L_a}D_3 + k_{L_a}A$, Equation (9) could be simplified as:

$$[O_3] = \frac{A}{B} \left(1 - \exp(-Bt)\right)$$  \hspace{1cm} (10)

$A$ and $B$ can be determined according to the data of $[O_3]$ versus time as illustrated in Figure 3. Then $k_{L_a}A$ and $k_{L_a}D_3$ can be calculated from Equations (11) and (12), respectively:

$$k_{L_a}A = \frac{A}{[O_3]_0}$$  \hspace{1cm} (11)

$$k_{L_a}D_3 = B - k_{tot} - k_{L_a}A$$  \hspace{1cm} (12)

As indicated in Table 2, the presence of ultrasound enhanced ozone mass transfer from gas phase to aqueous phase, and $k_{L_a}A$ increased with the increase of power density. The absorption of ozone is controlled by liquid film due to the low solubility of ozone. When $O_3/O_2$ bubbles enter the rectangular airlift reactor, the great mixing due to ultrasonic irradiation leads to turbulence, which reduces the liquid film thickness $\delta_L$ (Zhang et al. 2007). Based on the two-film theory, the liquid side mass transfer coefficient $k_L$ is inversely proportional to $\delta_L$. The decrease in $\delta_L$ leads to
the increase of $k_L$. Moreover, the mechanical effects of ultrasound give rise to the break-up of $O_3/O_2$ bubbles and, consequently, the larger specific surface area $a_A$ (Wang et al. 2014). As a result, the volumetric mass transfer coefficient $k_La_A$ would increase in the presence of ultrasonic irradiation. Moreover, the increase in power density would increase turbulence and enhance the mechanical effects to break up $O_3/O_2$ bubbles which would increase the mass transfer rate of ozone from gas phase to aqueous phase.

Table 2 shows the $k_La_A$ s was only 0.242 min\(^{-1}\) in the absence of ultrasonic irradiation, while it increased from 0.409 to 0.712 min\(^{-1}\) as power density rose from 27.2 to 100.3 W L\(^{-1}\).

With the increase of power density from 27.2 to 100.3 W L\(^{-1}\), $k_La_A$ increased from 0.532 to 0.794 min\(^{-1}\). It may result from two factors (Rosal et al. 2006). On the one hand, catalyst particles may concentrate at the interface and enhance the mass transfer due to the chemical reaction (ozone decomposition in this case). On the other hand, the enhancement of ozone absorption by catalyst particles is attributed to the adsorption of the transferred component (ozone) on the particles located near the gas–liquid interface via the mechanism called ‘grazing’ or ‘shuttle’ effect (Kars et al. 1979).

As indicated in Table 2, the ultrasonic degassing coefficient $k_La_{D3}$ could be negligible in comparison with the volumetric mass transfer coefficient of ozone absorption $k_La_A$. It can be concluded that the degassing effect of ultrasound was not pronounced in the sparging system in which ozone was continuously bubbled. This is consistent with the results observed by Weavers & Hoffmann (1998) and our previous study (Zhang et al. 2007).

### CONCLUSIONS

The catalytic ozone decomposition was enhanced by ultrasound. The ozone decomposition rate constant increased with the increasing power density and catalyst dosage. The absorption kinetic model could be used to determine the volumetric mass transfer coefficient of ozone $k_La_A$ when ozone absorption was performed in a three-phase split-rectangular airlift reactor under ultrasonic irradiation. The result obtained in this study may provide insight into the
enhancing mass transfer mechanism in sono-catalytic ozonation process.

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