Kinetic Study of Pressurized Ozonation Reactor of Tap Water

Nien-Hsin Kao¹ and Ming-Chien Su²

¹Department of Environmental Engineering, Kun Shan University. 949, Da-Wan Road, Yun Kan, Tainan county 710, Taiwan. (E-mail: kaon@mail.ksu.edu.tw)
²Graduate Institute of Environmental Policy, National Dong Hwa University. No. 1, Sec. 2, Da Hsueh Rd., Shou-Feng, Hualien 974, Taiwan. (E-mail: mcsu@mail.ndhu.edu.tw)

Abstract: A developed pressurized pilot scale ozonation system with the volume of 28 L was designed to simulate the field operating condition by transferring premixed ozone and tap water into this system under the influence of three system pressure (1, 2 and 3 kgf/cm²), seven initial pH (5, 6, 6.5, 6.8, 8, 8.5, 9). The system was running in a continuous mode and with only initial pH adjustment to study the dissolution, self-decomposition and mass transfer of ozone in these conditions. The effects of the operating pressure and pH on ozone dissolution concentration, ozone decomposition rates and the liquid phase overall mass transfer coefficients (KLa) were determined quantitatively. The data show the calculated average ozone decomposition rates for pH increase from 5 to 9 are 9.01E-7 to 2.64 E-6 mol/L-min by using mole balance equation at the system pressure 2 kgf/cm². The calculated average of KLa at the pseudo-steady state are 0.039 min⁻¹ and 0.069 min⁻¹ for pH less 6.5 and greater than 6.8, respectively.

Keywords: overall mass transfer coefficient; ozone decomposition rate; pressurized ozonation reactor

INTRODUCTION

Ozone used as an oxidizing agent in treating wastewater was categorized as one of the AOPs (Advanced Oxidation Processes) at high pH conditions. Comparing to other AOPs, the ozone technology has its advantages, such as; it produces no sludge, has strong oxidizing ability, and can be produced on site. In water and wastewater treatment, ozonation reactors were operated primarily under normal pressure conditions. In those treatment works, traditional dissolution mechanisms were applied, such as bubble column diffuser (Lee et al., 1999). While there is few pilot scale pressurized ozonation system reported. Pressurized ozonation reactor has many advantages, such as increase the dissolved ozone concentration; reduce the consumption of source gas (oxygen) and the stability is acceptable if the reactor is well designed. There are also many reported modified ozonation systems that combine O₃, UV, H₂O₂ or sonication (Masten et al., 1994; Acero et al., 2000; Weavers et al., 2000). In these reaction systems, mass transfer parameters were reported most often by various researchers (Biñ A. K. 1995; Roustan et al., 1995; Sheffer et al., 1982; Beltrán et al., 1995, 1997; Qiu et al., 2001; Ting et al., 2001). Many previous researchers reported that there are numerous ways of ozone reactions in the water, they reported that initiator and promoter compounds such as hydroxide ion and organohydro (RH) are connected to the chain reaction of ozone decomposition, while those scavengers such as carbonate ions will terminate the chain reaction (Sotelo et al., 1987, 1989; Masten et al., 1994; Ellovitz et al., 1998). Other researchers also reported the ozone decomposition rate in the first or second order rate constants format for every studied condition or modeling results (Tomiyasu et al., 1985; Ting et al., 2001; Wu et al., 2001). Sotelo et al. (1987) reported a global ozone decomposition rate equation. They conducted a comprehensive bench scale study of ozone decomposition by using deionized distilled water under the conditions of buffered pH 2.5 to 9 and temperature controlled 10 to 40 °C and, they suggested that the dissolution of ozone in water follow through five chain reactions and the reported ozone decomposition rates at 20 °C at pH 2.5 to 9 were 9.77 E-9 to 5.5 E -7 mol/L-min, respectively. While there were few researchers reported the mass transfer coefficients and decomposition rates of ozonation in a pressurized pilot scale CSTR reactor, most of them studied the effects of pH, temperature under normal pressure and at lab-top batch experiments (Sheffer et al., 1982; Sotelo et al., 1987; Chang et al., 1996; Ting et al., 2001). Unlike bench scale reactor, when an operation is conducted in a field condition with large flow rate, it is not cost-effective to maintain temperature and pH continuously. Generally, in ozonation treatment, the adding of chemicals such as buffer agents might only increase the ionic capacity and impurities of water and thus decrease the treatment efficiency. Based on that, this system was using drinking water with only adjusted inflow pH to simulate a field operating condition. The objective of this research is to study the kinetic constants.
such as ozone dissolution and self-decomposition rates under the influence of pressure and temperature at various pH conditions by using the pilot scale pressurized ozonation system. This study applies the mole balance equation of this unbuffered pilot scale system to calculate ozone decomposition rate.

EXPERIMENTAL METHOD

Apparatus and analysis
The schematic diagram of the pressurized ozonation system is given in Figure 1. The pressurized system is running in a continuous mode. The system includes a high-pressure pump, which pumps water and simultaneously draws ozone gas, blending it with the water. Thus, the completely mixed gas and water will then flow through an initial pressure tank (V=2L), which will maintain the mixed fluid at the operated system pressure, and finally the fluid emerges into a main reactor (V=28L) through a teflon disk diffuser (average pore size \( \phi = 2 \text{ mm} \)). The key function of the initial pressure tank is to increase and maintain the stability of main reactor. The operating pressure of initial tank and main reactor can be adjusted individually as required, but in this stage, pressure was maintained equal for these two containers. The ozone was generated from an ozonator (Model 300.5, Maximum concentration 45 g ozone/m\(^3\), Erwin sander, Germany) by using 99.9 % pure grade oxygen. Unbuffered tap water was used for the entire experiment runs. The system pressure was maintained by adjusting a backpressure valve, which is located in the effluent end of the main reactor. Valves and flow meters that are located in the ozonator and pipeline were used to adjust and quantify the gas and water flow rates; an additional flow meter (Aalborg Ins., USA) was used to maintain the gas flow rate. All piping, gauges and reactors that are in contact with ozone were coated with teflon or ozone proof materials, and for safety reasons, pressure relief valves were also installed in the top of reactor. This system is operated in continuous runs and the operating parameters are the inlet ozone gas flow rate (in L/min), water flow rate (in L/min) and system pressure (in kgf/cm\(^2\)).

Due to the role of the initial pressure tank is for adjusting and maintaining the stability of the system and then increase the dissolution and distribution of ozone within the main reactor. With the help of the initial pressure tank, the head space within the main reactor can be diminished and thus, the study focuses on the mass transfer of ozone diffuser within the main reactor with no head space. Under pressurized condition, the liquid and dissolved ozone gases were completely mixed within the main reactor and a white-form liquid phase can be seen at the moment of outlet from the reactor.

The water inflow rate was fixed at 1 L/min accompanied by an ozone-gas drawing rate of 0.5 L/min, thus, the HRT (Hydraulic Retention Time) was 28 min. Initially, ozone dissolution study was conducted at various system pressure (1, 2 and 3 kgf/cm\(^2\)) and pH conditions. Following that stage, a system pressure (2 kgf/cm\(^2\)) was chosen to extent the study of ozone decomposition under various pH (5, 6, 6.5, 6.8, 8, 8.5, 9) conditions. In these studies, due to the field operational scale reactor, it is impractical to control the reactor at a wanted temperature. Thus, during all runs, the temperature of reaction will increase from its’ initial temperature to a “pseudo-steady” state and will maintain in a certain value with a small variance. The increment of reaction temperature is due to the mechanical pumping frictions and the generated heat from ozonator. Initially, the reactor was filled with pH adjusted (with NaOH or H\(_3\)PO\(_4\)) tap water and then both ozone and pH adjusted water was pumped into the reactor. Each pH and pressure operation condition was run at least three times to justify the system’s stability. The reference of tap water quality was according to the governmental regulation of “Drinking Water Quality Standard” (Taiwan EPA, May, 2004), which regulated 55 kinds of water quality for the drinking water used in these experiments. The most concerned of listed water quality for this ozonation study may be the turbidity, chloride, total hardness as CaCO\(_3\), total dissolved solids and free residual chloride; and their standards are 2 NTU, 250 mg/L, 300 mg/L, 500 mg/L and 2.2-1.0 mg/L, respectively. The results of the study are shown in measured ozone dissolved concentration (mg/L), the calculated liquid phase overall mass transfer coefficient...
(K_{L.a, \text{ min}}^{-1}), and the calculated ozone decomposition rate (R_{O3}, \text{ mole/L-min}). During all experimental runs, the water quality parameters, dissolved ozone concentration (mg/L), pH and temperature (°C) were determined by using standard methods (4500-O₃ residual, AWWA, 1992), pH meter and thermometer, respectively. Inlet ozone gas concentration (mg/L) was monitored by on-line UV detector (Model Quantozon 2, Erwin sander, Germany). Inlet ozone gas concentration was found to be 7.44 ± 0.16 mg/L at system pressure of 2 kgf/cm² and which is used for calculation in the mole balance equation.

\[ \frac{dC}{dt} = \frac{F_{O3i} - F_{O3} - V \times R_{O3}}{V_{NR}V_{QC}Q_{CQC}Q_{FF} \times = \frac{dC}{dt}} \]

\[ \frac{dC}{dt} = \frac{(Q_L \times C_{Lo}) + Q_g \times C_g}{} - (Q_L \times C_L) - V \times R_{O3} = N = V \times \frac{dC}{dt} \]  

\[ \frac{dC}{dt} = \frac{(Q_g \times C_g) - (Q_L \times C_L) - V \times R_{O3}}{N} = V \times \frac{dC}{dt} \]  

Here F_{O3i}, F_{O3}, V are the rates (calculated in mg/min) of ozone flow into, flow out of system and volume of reactor, respectively. C_{Lo} is the inflow liquid ozone concentration which is zero. Q_L, Q_g, C_g and C_L are the liquid inflow/outflow rate (L/min), ozone gas inflow rate (L/min), inlet

**Figure 1:** Pilot scale apparatus of pressurized ozonation reactor system.

**Rate analysis**

The general mole balance equation for this system can be expressed by the Equation (1):

\[ \frac{dC}{dt} = \frac{F_{O3i} - F_{O3} - V \times R_{O3}}{V_{NR}V_{QC}Q_{CQC}Q_{FF} \times = \frac{dC}{dt}} \]

\[ \frac{dC}{dt} = \frac{(Q_L \times C_{Lo}) + Q_g \times C_g}{} - (Q_L \times C_L) - V \times R_{O3} = N = V \times \frac{dC}{dt} \]  

\[ \frac{dC}{dt} = \frac{(Q_g \times C_g) - (Q_L \times C_L) - V \times R_{O3}}{N} = V \times \frac{dC}{dt} \]  

Here F_{O3i}, F_{O3}, V are the rates (calculated in mg/min) of ozone flow into, flow out of system and volume of reactor, respectively. C_{Lo} is the inflow liquid ozone concentration which is zero. Q_L, Q_g, C_g and C_L are the liquid inflow/outflow rate (L/min), ozone gas inflow rate (L/min), inlet
ozone gas concentration (mg/L) and dissolved ozone concentration (mg/L) in the effluent, respectively. Where \( R_{O_3} \) is the rate of ozone decomposition and \( N \) is rate of ozone transfer within the main reactor (mg/L-min), \( C \) is time dependent dissolved ozone concentration (mg/L). In this study, to analyse the rates of mass transfer and ozone decomposition, following calculations and assumptions are applied: (1) Only the mass transfer of the bubble diffuser within the main reactor is considered and which is expressed by liquid phase overall mass transfer coefficients (\( K_{L_a} \)). (2) Due to the fact it is impossible to monitor the ozone decomposition within the CSTR reactor, thus, mole balance equation was rearranged to calculate the ozone decomposition rate after the \( K_{L_a} \) was found. The theoretical equation of liquid phase mass transfer is shown in Equation (2) and which is used to calculate the liquid phase overall mass transfer coefficients (\( K_{L_a} \)) at the pseudo-steady state of each run. Beside that, a curve fitting equation that expresses an exponential growth curve which gradually reach maximum as shown in Equation (3) is also used to explain the data. Thus, by rearranging Equation (2) and compare with the curve fitting Equation (3) with maximum iteration number 100 and tolerance is set as 0.0001. Therefore, when plotting dissolved ozone concentration \( (y) \) verses reaction time \( (t) \), two parameters \( a, b \) can be found by curve fitting regression, which are corresponding to theoretical \( C^* \) and \( K_{L_a} \), respectively.

\[
\frac{dC}{dt} = K_{L_a} \times \left( C^* - C \right) = \int_{0}^{t} K_{L_a} \, dt
\]

\[
C = C^* \times \left( 1 - e^{-K_{L_a} \cdot t} \right)
\]

Here \( N \) is rate of ozone transfer (mg/L-min), \( C, C_0 \) and \( C^* \) are time dependent, initial and pseudo-steady state dissolved ozone concentration (mg/L), respectively. \( K_{L_a} \) is liquid phase overall mass transfer coefficient (min\(^{-1}\)). Finally, \( a \) and \( b \) are regression parameters. After the \( K_{L_a} \) and \( C^* \) are found, they were fit back into rearranged mole balance Equation (4) and thus the ozone decomposition rates within the main reactor can be calculated.

\[
\begin{align*}
\therefore (Q_g \times C_g) - (Q_L \times C_L) - V \times R_{O_3} &= V \times K_{L_a} \times (C^* - C) \\
\therefore \frac{1}{V} \left[ (Q_g \times C_g) - (Q_L \times C_L) \right] - K_{L_a} \times (C^* - C) &= R_{O_3}
\end{align*}
\]

RESULTS AND DISCUSSION

Ozone dissolution and estimation of \( K_{L_a} \)

Figure 2 shows the dissolved ozone concentrations and estimated \( K_{L_a} \) at various operating system pressures and pre-adjusted \( pH \) around \( pH \) 7. Figure 2 indicates the dissolved ozone increases as system pressure is increased from 1, 2 and 3 kgf/cm\(^2\) for initial \( pH \) of 6.9 to 7.2, 6.8 and 6.9 to 7.9, respectively. Adopting Equation (2) and (3), Table 1 lists these regression parameters, it shows the theoretical steady state saturated ozone concentration \( C^* \) increases from 0.58 to 0.79 mg/L when system pressure increases from 1 to 3 kgf/cm\(^2\). The results show that it is practical to increase pressure of reactor, may be up to 3 kgf/cm\(^2\) or more in field operation, to achieve an increment of dissolved ozone with no additional generation gas (oxygen) consumed. Table 1 and Figure 2 also shown the regression results of each curve, which indicated most of the regression coefficients \( R^2 \) are greater than 0.8 and the estimated parameter \( b \) that is \( K_{L_a} \) is around 0.06 min\(^{-1}\) at these \( pH \) and pressure conditions.
Effects of pH for ozone dissolution and $K_{La}$

Based on previously results, the system pressure of 2 kgf/cm$^2$ was chosen as a fixed operation pressure to study the effects of pH to the rates of ozone decomposition and mass transfer. Figures 3 and 4 show the results of curve fitting for seven initial adjusted pH conditions (pH 5, 6, 6.5, 6.8, 8, 8.5, 9). Table 1 and Figure 3 indicated the theoretical saturated concentration of ozone ($C^*$) at initial pH 5 to 6.5 can reaches about 2.5 mg/L and the estimated $K_{La}$ is only about 0.04 min$^{-1}$. Comparing with higher pH condition, Table 1 and Figure 4 show that $C^*$ decreases from 0.64 mg/L to 0.15 mg/L as pH increases from 6.8 to 9, and the $K_{La}$ is about 0.07 min$^{-1}$. These results indicated the pH did affect the chain reactions of ozone dissolution reaction and the mass transfer rates will
Table 1: Estimated $K_La$ and theoretical saturated ozone concentration for various pressure and pH conditions.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>a or C*</th>
<th>b or $K_La$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>At Similar pH Conditions</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 kgf/cm²</td>
<td>0.5782</td>
<td>0.0597</td>
<td>0.84</td>
</tr>
<tr>
<td>2 kgf/cm²</td>
<td>0.6368</td>
<td>0.0629</td>
<td>0.93</td>
</tr>
<tr>
<td>3 kgf/cm²</td>
<td>0.7887</td>
<td>0.0604</td>
<td>0.88</td>
</tr>
<tr>
<td><strong>At Set 2 kgf/cm² Conditions</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 5</td>
<td>2.4060</td>
<td>0.0420</td>
<td>0.87</td>
</tr>
<tr>
<td>pH 6</td>
<td>2.5702</td>
<td>0.0374</td>
<td>0.80</td>
</tr>
<tr>
<td>pH 6.5</td>
<td>2.4810</td>
<td>0.0361</td>
<td>0.85</td>
</tr>
<tr>
<td>pH 6.8</td>
<td>0.6368</td>
<td>0.0629</td>
<td>0.93</td>
</tr>
<tr>
<td>pH 8</td>
<td>0.2995</td>
<td>0.0789</td>
<td>0.80</td>
</tr>
<tr>
<td>pH 8.5</td>
<td>0.2388</td>
<td>0.0699</td>
<td>0.76</td>
</tr>
<tr>
<td>pH 9</td>
<td>0.1501</td>
<td>0.0641</td>
<td>0.81</td>
</tr>
</tbody>
</table>

Note: C* is pseudo-steady state saturated $O_3(aq)$ (mg/L)
$K_La$ is liquid phase overall mass transfer coefficient (min⁻¹)
a, b are regression parameters.

Figure 3: Estimated overall mass transfer coefficient at system pressure 2 kgf/cm² for pH 5 to 6.5.

Also be affected. Figures 3, 4 and Table 1 illustrate an “O₃ jump” between pH 6.5 and 6.8, it shows that when pH greater than 6.8 and small than 6.5, the C* increases from about 0.63 mg/L to 2.48 mg/L, respectively. Figure 5 shows the background information of reaction temperature and
pH conditions during these runs, it shows that initially, there was only 0.3 pH unit and less than 1 °C of temperature difference between pH 6.5 and 6.8, but a greater gap appeared by the end of runs. Based on the data of dissolved ozone concentration and pH changes, this indicates that water quality might have affected the ozone dissolution between pH 6.5 and 6.8. Figure 5 also shows the pH alteration during each run with different initially adjusted pH and it shows the trend of pH will increases for initial pH 6.8, 6.5, 5, and decreases for initial pH 8 and above. These conditions indicated that within the ozone chain reaction, the ozone decomposition were faster in higher pH range and thus, might be the hydroxyl ions consumption rate was higher than those in low pH conditions.

**Effects of pH for ozone decomposition rates**

By using Equations (4), the calculated ozone decomposition rates by using mole balance equation were determined as shown in Table 2. The table shows the calculated data where were measured from each sampling time for each respected operating conditions as shown in Figures 3 and 4. Table 2 lists the average ozone decomposition rates for pH increase from 5 to 9 are 9.01E-7 to 2.64E-6 mol/L-min which are similar with the results reported by Sotelo et al. Thus, for the studied unbuffered pH pilot scale system, the results by using mole balance show that ozone decomposition rate increases as pH increases. This indicates the increased concentration of hydroxyl ions, the initiator of chain reaction did affect the ozone decomposition as reported by previous researchers.

![Figure 4: Estimated overall mass transfer coefficient at system pressure 2 kgf/cm² for pH 6.8 to 9.](https://iwaponline.com/wpt/article-pdf/4/3/wpt2009047/384166/47.pdf)
Table 2: Estimated ozone decomposition rates at system pressure 2 kgf/cm$^2$ and various pH conditions.

<table>
<thead>
<tr>
<th>pH</th>
<th>Averaged (mol/L-min)</th>
<th>Standard deviation</th>
<th>n (sample size)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>9.01E-07</td>
<td>1.25E-08</td>
<td>54</td>
</tr>
<tr>
<td>6.5</td>
<td>9.16E-07</td>
<td>8.35E-08</td>
<td>54</td>
</tr>
<tr>
<td>6.8</td>
<td>2.24E-06</td>
<td>1.12E-08</td>
<td>53</td>
</tr>
<tr>
<td>8</td>
<td>2.50E-06</td>
<td>1.24E-08</td>
<td>51</td>
</tr>
<tr>
<td>8.5</td>
<td>2.57E-06</td>
<td>6.00E-09</td>
<td>52</td>
</tr>
<tr>
<td>9</td>
<td>2.64E-06</td>
<td>2.58E-09</td>
<td>69</td>
</tr>
</tbody>
</table>

Figure 5: Temperature and pH variations at each initial pH condition for system pressure 2 kgf/cm$^2$. 
CONCLUSIONS

The study of pilot scale continuous mode pressurized ozonation reactor that the dissolved ozone concentration increase as pressure is increased which indicates that pressurized reactor is practicable for field operation and can reduce the amount of oxygen consumption. The data also show the estimated $K_{L}a$ is around 0.06 min$^{-1}$ for system pressure 1 to 3 kgf/cm$^2$ at similar pH conditions. At set 2 kgf/cm$^2$ pressure condition, the average $K_{L}a$ are 0.039 min$^{-1}$ and 0.069 min$^{-1}$ for pH less 6.5 and greater than 6.8, respectively. The data show that there is a dissolved ozone concentration gap between pH 6.5 and pH 6.8 which might be due to the ionic concentration within the drinking water. The comparison calculation of ozone decomposition rates for the pilot scale and a bench scale study shows that it might be appropriated to using the concept of curve fitting techniques and mole balance equation to evaluate these values. The ozone decomposition rates in this pilot scale condition are between 9.01E-7 to 2.64 E-6 mol/L-min for pH increases from 5 to 9, respectively. These calculated decomposition rates are also close to previous reported values.

REFERENCES


Standard Methods for the Examination of Water and Wastewater 18th Ed., 4500-O$_3$ residual, 1992, AWWA.


