Dynamic Model of Ozone Contacting Process with Oxygen Mass Transfer in Bubble Columns

Y. H. Chen¹; C. Y. Chang²; C. Y. Chiu³; W. H. Huang⁴; Y. H. Yu⁵; P. C. Chiang⁶; Y. Ku⁷; and J. N. Chen⁸

Abstract: The dynamic process of the dissolution of ozone in a countercurrent bubble column is studied for model establishment. Bubble columns have been used widely for ozone contacting in the plant and laboratory. Ozone is produced by oxygen-enriched gas through an ozone generator, and introduced into the bottom of the column equipped with the gas diffuser. The ozone contacting system proceeds for a temporary and unsteady period before reaching steady state. The available ozone dissolution models employed for the description of the dissolved ozone profiles were commonly developed for the steady state. Moreover, oxygen mass transfer is usually neglected in the preceding ozone dissolution models. However, this information is desirable for proper operation of ozone dissolution in a bubble column. Thus, the objective of this study is to model and investigate the dynamic ozone dissolution process in a bubble column.

The validity of the model is demonstrated by comparing the predicted results with the experimental data. The dynamic model of ozone dissolution is useful and referable for proper prediction of the variables of the contacting system in a bubble column.

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Introduction

Ozone is widely used as an oxidant applied in water treatment and disinfection. It is commonly produced by electrical discharge into pure oxygen or oxygen-enriched gas through an ozone generator. The mixture of gases composed of oxygen and ozone is transferred to water by bubbling it through the bulk solution. The efficiency of ozonation processes is usually dependent on the dissolved ozone concentration. Certainly, a quantification of the dissolved ozone concentration variation is critical to the rational design and optimization of the ozonation treatment.

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in bubble columns is still scarce. Accordingly, the prediction of the treating qualities of water such as the $C_t$ factor in the initial stage of ozone contacting is usually not available. Also, the required duration for steady-state establishment remains to be determined. The $C_t$ factor is defined as the product of the concentration of the dissolved ozone, $C$, in milligrams per liter, and the contact time, $t$, in minutes. The value of $C$ would be assumed to the value at the point in the column of concern, while $t$ would be assumed to the $t_{10}$ value, where $t_{10}$ is determined by the tracer test and equals the time necessary for 10% of the tracer mass to exit the column (Langlais et al. 1991). Furthermore, one of the advantages of ozone dissolution is its contribution to dissolved oxygen, which can be used in the biological process after the decomposition of ozone (McGhee 1991). The concentration of ozone is usually relatively low with respect to that of oxygen in the carrier gas. The oxygen mass transfer may affect the ozone concentrations of the liquid and off-gas. However, the description of the role of oxygen is usually not included in modeling the ozone dissolution. This would result not only in a lack of information of the dissolved oxygen concentration but also in an incomplete description of the ozone mass transfer during the ozone contacting processes.

The objective of this study is to model and investigate the dynamic ozone contacting process in a countercurrent bubble column with the oxygen mass transfer. Three major factors are included in the dynamic ozone contacting model: (1) hydrodynamic behavior; (2) gas–liquid mass transfer; and (3) ozone decomposition reaction kinetics. Note that the reaction kinetics of this model considers solely the decomposition of the dissolved ozone in water, which is applicable to the cases of the disinfection and oxidation with a relative small amount of impurity (Smith and Zhou 1994). For systems with a considerable amount of contaminants, the role of the contaminants should then be included in describing the ozonation kinetics and ozone consumption. This would be taken as our further work. Based on the dynamic axial dispersion model (DADM) proposed in this paper, the dynamic variations of the ozone and oxygen concentration profiles can be predicted. Further, the experimental data of the ozone dissolution in the bubble column are obtained for the model verification. Moreover, the effects of the simplified assumptions, which neglect the oxygen mass transfer or superficial gas velocity variation, on ozone dissolution simulation are examined. The validity of the model is demonstrated by the good agreement of the predicted results with the experimental data. The proposed model can provide useful information about the dynamic dissolution process of ozone in a bubble column.

**Theoretical Analysis**

Modeling of the dynamic processes of ozone dissolution in a bubble column requires quantification of the rates of the mass transfer and ozone decomposition reaction associated with the hydrodynamic condition of the system. Noting that the diffusivities of ozone and oxygen in the gas phase are about $10^4$ times higher than those in the liquid phase, this study assumes that the resistance of the mass transfer is solely contributed by the liquid phase. As the ozone is dissolved in water, it may be consumed via the self-decomposition reaction. For spontaneous ozone decomposition to oxygen in water, the overall reaction and the corresponding pseudo-first-order decomposition rate equation may be expressed in the following forms (Kuo and Huang 1995):

$$2O_3 \rightarrow 3O_2 \quad (1)$$

$$- \frac{dC_{O_2}}{dt} = 2 \frac{dC_{O_2}}{dt} = k_dC_{O_2} \quad (2)$$

It is noted that Eq. (1) is an overall expression. In fact, the ozone decomposition involves a rather complex mechanism. The hydrodynamic condition of the flow field affects the concentration profiles. A dynamic axial dispersion model is developed to describe the dynamic processes of ozone dissolution in a countercurrent bubble column. The derivation of the governing equations are shown in detail in the Appendix. The resulting equations in dimensionless forms are as follows.

For the overall mass balance of the gas phase, one may have a dimensionless governing equation such as Eq. (3) for the superficial gas velocity:

$$\frac{dU_G}{d\xi} = \frac{\alpha_p}{\beta_p} U_G - E_rASt_{GA} \frac{1}{\beta_p} y_A(\theta_{AGi} - \theta_{ALb})$$

$$- R_{fO} St_{GO} \frac{1}{\beta_p} y_O(\theta_{Ogi} - \theta_{OLb}) \quad (3)$$

for

$$0 \leq \xi \leq \frac{h^*_B}{U_G}$$

with boundary condition (BC):

$$\xi = 0 \quad U_G = 1 \quad (4)$$

For $h^*_B < \xi \leq 1$, $U_G = 0$. The dimensionless height of the gas bubbles ($h^*_B$), which can be calculated by Eq. (5), has the maximum value of unity:

$$\frac{dh^*_B}{d\tau} = R_{GL} U_{G,\xi} - h^*_B \quad (5)$$

with initial condition (IC):

$$\tau = 0 \quad h^*_B = 0 \quad (6)$$

The governing equations of ozone and oxygen in gas and liquid phases are as follows. For the hold-up gases,

$$\frac{\partial \theta_{AGi}}{\partial \tau} = R_{AGi} \left[ \frac{1}{P_G} \frac{\partial^2 \theta_{AGi}}{\partial \xi^2} - \frac{\partial (U_G \theta_{AGi})}{\partial \xi} - E_rASt_{GA}(\theta_{AGi} - \theta_{ALb}) \right] \quad (7)$$

$$\frac{\partial \theta_{Ogi}}{\partial \tau} = R_{AGi} \left[ \frac{1}{P_G} \frac{\partial^2 \theta_{Ogi}}{\partial \xi^2} - \frac{\partial (U_G \theta_{Ogi})}{\partial \xi} - R_{fO} St_{GO}(\theta_{Ogi} - \theta_{OLb}) \right] \quad (8)$$

For the liquid phase,

$$\frac{\partial \theta_{ALb}}{\partial \tau} = \frac{1}{P_L} \frac{\partial^2 \theta_{ALb}}{\partial \xi^2} + \frac{\partial \theta_{ALb}}{\partial \xi} + E_rASt_{LA}(\theta_{AGi} - \theta_{ALb}) - Da_\lambda \theta_{ALb} \quad (9)$$

$$\frac{\partial \theta_{OLb}}{\partial \tau} = \frac{1}{P_L} \frac{\partial^2 \theta_{OLb}}{\partial \xi^2} + \frac{\partial \theta_{OLb}}{\partial \xi} + R_{fO} St_{LO}(\theta_{Ogi} - \theta_{OLb}) + Da_\lambda \theta_{ALb} \quad (10)$$

For the gas ozone in the free volume in the column,
The validity of the DADM is verified by the experimental data by Letzel et al. (1999) of about 1–7 s and the retention time for examining the concentration variations of the effluent from the column.

At the top, the pressure transmitter (model 691, Huba, Würenlos, Switzerland) with a range of 0–30 kPa is employed to detect the pressure difference (ΔP) of two points [with hydrostatic height (h)] with and without aeration. The gas holdup (εG) is then estimated by the differential hydrostatic pressure method employing εG = ΔP/[(ρg - ρ0)gh].

All experimental solutions are prepared using deionized water without other buffers. The conductivity of the water used is less than 1 μS/cm. The measured value of pH during ozone contacting in the bubble column is about 6.3 ± 0.3. The initial dissolved oxygen concentration (C_{O2 bât}) in the experiments is close to the saturated value in equilibrium with air as θ_{O2 bât} = 0.21(P_{T} + α_{p}Y_{O2}). For example, 0.21[(P_{T} + α_{p}Y_{O2})/1.1 ] = 0.190; at P_{T} = 1 atm, Y_{O2} = 0.984, and α_{p} = 0.124, while the measured θ_{O2 bât} [= C_{O2 bât}/(C_{O2 bât}/H_{O2})] = 0.187 (C_{O2 bât} = 8.9 mg/L, C_{O2 bât} = 1,468 mg/L, H_{O2} = 30.81).

**Experimental Procedures**

There have been numerous studies about the mixing effect on the performance of bubble columns, for example, those of Levenspiel (1972), Deckwer et al. (1974), Rice et al. (1981), Shah et al. (1982), Langlais et al. (1991), Deckwer and Schumpe (1993), and...
Table 1. Summary of Hydrodynamic and Mass Transfer Properties at Various Superficial Gas (u_{G0}) and Liquid (u_L) Velocities; Inlet Gas: Pure Oxygen, L = 1.33 m, temp. = 294 K

<table>
<thead>
<tr>
<th>u_{G0} (mm/s)</th>
<th>u_L (mm/s)</th>
<th>E_L (m^2/s)</th>
<th>t_g (s)</th>
<th>k_{L,OA}^0 (s^{-1})</th>
<th>e_G (—)</th>
<th>k_{L,OA} (s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.33</td>
<td>1.42</td>
<td>0.00855</td>
<td>934</td>
<td>0.00664</td>
<td>0.00435</td>
<td>0.00588</td>
</tr>
<tr>
<td>1.33</td>
<td>2.83</td>
<td>0.00856</td>
<td>467</td>
<td>0.00682</td>
<td>0.00419</td>
<td>0.00604</td>
</tr>
<tr>
<td>1.33</td>
<td>4.25</td>
<td>0.00852</td>
<td>311</td>
<td>0.00664</td>
<td>0.00437</td>
<td>0.00588</td>
</tr>
<tr>
<td>2.31</td>
<td>4.25</td>
<td>0.01254</td>
<td>310</td>
<td>0.00795</td>
<td>0.00863</td>
<td>0.00704</td>
</tr>
<tr>
<td>4.85</td>
<td>4.25</td>
<td>0.02334</td>
<td>307</td>
<td>0.01270</td>
<td>0.0184</td>
<td>0.01125</td>
</tr>
<tr>
<td>7.40</td>
<td>4.25</td>
<td>0.03261</td>
<td>304</td>
<td>0.01680</td>
<td>0.0285</td>
<td>0.01488</td>
</tr>
<tr>
<td>9.48</td>
<td>4.25</td>
<td>0.04120</td>
<td>302</td>
<td>0.01930</td>
<td>0.0349</td>
<td>0.01709</td>
</tr>
</tbody>
</table>

Zahradník and Fialová (1996). Their results indicate that the axial dispersion coefficient of liquid (E_L) is probably a function of u_{G0}, column diameter, solution properties, gas-diffuser design, etc. A pulse-input tracer test has been commonly conducted to examine the hydrodynamic behavior of the experimental apparatus employed. Sodium chloride (NaCl) is chosen as the liquid tracer in this work due to its low volatility and easy quantification.

Table 1. Oxygen, L = 1.33 m, temp. = 294 K

The results concerning the dynamic ozone dissolution in bubble columns include two parts: (1) the parameter determination of the ozone contacting system; and (2) ozone dissolution experiments associated with model verification. The system parameters, including E_L, k_{L,OA}, k_{d,OA}, k_d, and H_A, are estimated. The ozone dissolution experiments are carried out with different inlets u_{G0}, u_L, and x_G. The temporal concentration variations of the θ_{ALB}, θ_{OLB}, and θ_{AG}, are monitored in order to provide experimental data for model verification.

Ozone Dissolution Parameters Determination

The equation describing the concentration variation of the tracer (C_a = C_{OA}l_f/m_f) is similar to Eq. (9) with θ_{ALB} replaced by C_a without the third and fourth terms on the right-hand side of Eq. (9). The IC is C_a = 0 at t = 0. The BCs at the bottom and top of the column are similar to Eqs. (14) and (16) of θ_{ALB} plus a pulse-input δ(t) on the right-hand side of Eq. (16), respectively. E_L values are obtained from the effluent RTD of the tracer (Levenspiel 1972), as listed in Table 1. It is seen that E_L is dependent slightly on u_L and strongly on u_{G0}, respectively. This finding is consistent with the conclusions of previous studies (Deckwer et al. 1974; Deckwer and Schumpe 1993).

As for oxygen aeration, Eqs. (3)–(6), (8), and (10) and their corresponding ICs and BCs are applied to describe the θ_{OLB} in the column. The values of P_L obtained in the tracer tests are used. A comparison of θ_{OLB} from the model prediction to that from the experiments then gives the proper values of k_{L,OA}. The mass transfer properties (k_{L,OA}^0, k_{L,OA}, and e_G) along with hydrodynamic characteristics (E_L and t_g) of the bubble column at various u_{G0} and u_L are listed in Table 1.

From the above results, the parameters of E_L, k_{L,OA}, and k_{L,OA}^0 are mainly dependent on u_{G0}. The correlations derived from Table 1 can be expressed as: 

E_L = 1.696u_{G0}^{0.803} \times 5.168u_{G0}^{1.063}, \quad k_{L,OA}^0 = 0.2567u_{G0}^{0.560} .

The correlation of E_L shows E_L \approx u_{G0}^{0.803}, which is considered reasonable for the bubble flow regime (Rice et al. 1981). Deckwer et al. (1983) illustrated that the k_{L,OA}^0 values are not independent of the liquid velocity and are about the same for various bubble columns with u_L varied from 10 to 120 mm/s. The k_{L,OA}^0 values of 0.00664–0.0193 s^{-1} of this study in Table 1 are greater than 0.000843–0.00842 s^{-1} obtained from the correlation of Akita and Yoshida (1973). One may notice that the higher k_{L,OA}^0 values are attributed to the difference of the gas flow assumption of the gas phase.

Oxygen aeration has often been applied to study the gas–liquid mass transfer coefficient by numerous investigators because the chemical reaction in the O_2–liquid system can be neglected and the dissolved oxygen concentration is easily measured (Alvarez-Cuenca and Nerenberg 1981; Hikita et al. 1981; Shah et al. 1982; Deckwer et al. 1983; Letzel et al. 1999). The variation of the effluent dissolved oxygen concentration (C_{OLB,OA}) is monitored in this study to obtain the k_{L,OA}^0 of oxygen in water. This approach considers the hydrodynamic condition. k_{L,OA}^0 of oxygen can then be corrected to obtain the k_{L,OA}^0 of ozone for the physical adsorption by k_{L,OA}^0(C_{OLB,OA}) = (D_O/D_A)_{0.5}^0, according to the surface renewal theory (Danckwerts 1970; Bín 1995). The values of D_O and D_A of 2.24×10^{-9} and 1.76×10^{-9} m^2/s at 21°C are calculated from Wilke and Chang’s formula (1955). Henry’s constant of oxygen (H_O) is 30.81 at 21°C in water (Sawyer et al. 1994).

The values of the ozone decomposition rate constant (k_d) and Henry’s constant (H_O) are obtained by batch and semibatch experiments, respectively. The temperature of the deionized water used in the stirred reactor is maintained at 21°C by a water jacket. The stirring speed is as high as 800 rpm to ensure the complete mixing of the liquid and gas phases according to previous tests. Ozone-containing gas is introduced into the reactor with a gas flow rate of 1.78 NLPM (L/min at 0°C, 1 atm). The detailed geometric size and operation conditions of the stirred reactor may be found elsewhere (Li et al. 2000; Chang et al. 2001).

Accordingly, ozone dissolution with distinct u_L, u_{G0}, and C_{AGG} in a countercurrent bubble column is performed for the model verification. Before starting the ozone dissolution experiments, the ozone-containing gas is bypassed to the photometric analyzer to assure stability and determine the ozone concentration. A portion of the gas stream at a preset flow rate is directed into the column when reaching the set conditions. All experiments performed to study the dynamic process of ozone dissolution are carried out using a flow rate of 1.78 NLPM and a stirring speed of 800 rpm to ensure the complete mixing of the liquid and gas phases according to previous tests. The stirring speed is as high as 800 rpm to ensure the complete mixing of the liquid and gas phases according to previous tests. The stirring speed is as high as 800 rpm to ensure the complete mixing of the liquid and gas phases according to previous tests. The stirring speed is as high as 800 rpm to ensure the complete mixing of the liquid and gas phases according to previous tests.
spargers used (Shah et al. 1982). The gas sparger of this study is porous with multiflores of mean pore size of 28 μm, while that of Akita and Yoshida (1973) is a single hole 5.0 mm in diameter.

The value of \( k_d \) is computed from Eq. (2) with \( \ln(C_{ALB}/C_{ALB0}) \) versus \( t \) in the batch reactor. The obtained value of \( k_d \) is 1.47 \times 10^{-4} \text{ s}^{-1}. The rate expression of ozone decomposition can then be expressed as \( \frac{dC_{ALB}}{dt} = k_d C_{ALB} = 1.47 \times 10^{-4} \text{ s}^{-1} C_{ALB} \) with \( R^2 = 0.998 \). The value of \( k_d \) of 1.47 \times 10^{-4} \text{ s}^{-1} \) is small due to the low ionic strength and moderate pH value (about 6.3) of the deionized water (Staehelin and Hoigné 1982). Therefore, \( E_{IA} \) and \( R_{GO} \) computed by Eqs. (19) and (20) are about 1–1.000002 and 1–0.999993 for the conditions studied in this work, respectively. These values of \( E_{IA} \) and \( R_{GO} \) are close to unity and thus can be deemed as unity for further use.

Considering the combined absorption and decomposition of ozone in a semibatch stirred gas–liquid reactor (sb), one obtains the mass balance equation, \( C_{AGe,ss}/H_{A} = [k_d + (k_{Ld}A)_{sb}/e_{L}] C_{ALB,ss}/e_{L} \), describing the steady-state condition in the reactor for the consumption of the ozone decomposition. The \( (k_{Ld}A)_{sb}/e_{L} \) of ozone is determined as 0.0186 \text{ s}^{-1} by conducting the oxygen aeration in the semibatch reactor and applying \( k_{Ld}^0 A/(k_{Ld}A)_{sb}/e_{L} = (D_{Al}/D_{A})^{0.5} \). With the available \( (k_{Ld}A)_{sb}/e_{L} \), one may perform a linear regression by plotting \( C_{AGe,ss} \) against \( [k_d + (k_{Ld}A)_{sb}/e_{L}] C_{ALB,ss}/e_{L} \) at various inlet gas ozone concentrations. The slope representing the \( H_{A} \) is obtained as 3.802. The value of \( H_{A} \) is close to 4.025 derived by Langlais et al. (1991) at the same temperature. The slight difference may be caused by the difference of the pH and ionic strength of the solutions used (Sotelo et al. 1989).

All the above obtained parameters \( (e_{L}, k_{Ld}^0 A, k_d, v_{G}, \text{ and } H_{A}) \) along with \( H_{G}(=30.81) \) are used for model prediction in bubble columns.

**Ozone Dissolution in Bubble Column**

The dynamic variations of the ozone and oxygen concentration profiles are predicted by solving for Eqs. (3)–(16). All input values of the modeling parameters can be obtained from the preceding results associated with the operation conditions. The simulated results of interest, including \( \theta_{ALB,eff} \), \( \theta_{ALB} \), \( \theta_{AGe} \), and \( U_{G,z=1} \), would be verified with the ozone dissolution experiments. Comparative analysis is also performed to elucidate the effect of the simplified assumptions used by different investigators on the simulation results of the dynamic ozone contacting processes. The predicted results of the DADM are compared with the experimental data of the ozone dissolution from the beginning to steady state.

The experimental results of \( \theta_{ALB,eff} \) and \( \theta_{AGe} \) versus \( \tau \) with \( u_{L}=1.42 \text{ mm/s}, u_{GO}=1.33 \text{ mm/s}, \) and various \( y_{A} \) are shown in Fig. 1 along with the model predictions of three cases. Case 1 considers (1) oxygen mass transfer, and (2) superficial gas velocity; case 2 neglects (1) while considering (2); and case 3 neglects both (1) and (2). The influence of \( y_{A} \) on the model predictions is found to be negligible. Both the model predictions and experimental data of \( \theta_{ALB,eff} \) and \( \theta_{AGe} \) approach the steady-state values as \( \tau \) is greater than 1.5. For a short time, say \( \tau < 0.3 \), the model predictions of the three cases are close. However, as \( \tau \) becomes large, the model predictions of case 3 overestimate about 4–10% of \( \theta_{ALB,eff} \) and \( \theta_{AGe} \). The difference between the predictions of cases 1 and 2 being within 2% seems insignificant. In addition, the prediction of case 2 compared with the experimental data has an error within 4.5%. For other operation conditions, the error scales due to neglect may be different depending on the geometry, flow, mixing, and reactive regime. However, an examination of previous studies (Zhou et al. 1994; Huang et al. 1998) indicates that the prediction of the dissolved ozone concentration profile at steady state without considering the oxygen mass transfer is satisfactorily close to the experimental data. One may propose that the oxygen mass transfer may be neglected for simulation of the ozone concentration with respect to engineering applications. Note that the dissolved oxygen concentrations cannot be obtained from cases 2 and 3 assuming oxygen as an inert gas. There is a time lag of about 0.051 \text{ s} for \( \theta_{AGe} \) between the experimental data and model predictions due to the model assumption of the free volume. The results indicate that the variation of the superficial gas velocity had better be considered, while the oxygen mass transfer may be neglected for the ozone concentration estimation.

\[
U_{G,z=1}
\]

represents the amount of the off-gas that can be used for computing the ozone transfer efficiency \( (\eta_{OTE}) \) and specific transferred ozone dosage \( (m_{STOD}) \). \( \eta_{OTE} \) is defined as the percentage of inlet ozone transferred into target water.

\[
\eta_{OTE} = \frac{\mu_{GO} \cdot C_{AGe,0} \cdot U_{G,z=1}}{\mu_{GO} \cdot C_{AGe,0}} = 1 - U_{G,z=1} \cdot \theta_{AGe,0} \cdot \tau_{1}
\]

(17)

\( m_{STOD} \) is defined as the ratio of transferred ozone, in moles or milligrams, to the target water volume, in cubic meters and liters. That is,
Fig. 2. $U_{G,\xi=1}$ versus $u_{G0}$ at steady state for ozone dissolution in countercurrent bubble column. $u_L=4.25$ mm/s, $\gamma_A=0.020$. Symbols: experiments; lines: prediction. ---, ---, ---: DADM with cases 1, 2, and 3 as specified in Fig. 1.

$$m_{STOD} = m_{SAOD} \times \eta_{OTE} = \frac{u_{G0}C_{AG0}}{u_L} \left(1 - U_{G,\xi=1}\theta_{AG,\xi=1}\right)$$

(18)

where $m_{SAOD}$ = specific applied ozone dosage $= C_{AG0} \times u_{G0} \times A/I(u_1 \times \Delta)$. Note that the values of $\eta_{OTE}$ and $m_{STOD}$ decrease with the ozone contacting time until reaching steady state due to variations of $U_{G,\xi=1}$ and $\theta_{AG,\xi=1}$. The steady-state values of $U_{G,\xi=1}$ predicted by the model simulations for the three cases are compared with the experimental data, as shown in Fig. 2. It is seen that the prediction of case 1 indicates a good agreement. The value of $U_{G,\xi=1}$ increases with $u_{G0}$ and approaches a constant at high $u_{G0}$. In contrast, cases 2 and 3 overestimate and underestimate the values of $U_{G,\xi=1}$, respectively. Consequently, consideration of the oxygen mass transfer and superficial gas velocity variation gives an accurate computation of $U_{G,\xi=1}$.

Further investigations were carried out to show the effects of various dimensionless parameters on the dynamic process of the ozone dissolution in a countercurrent bubble column, Figs. 5–7 depict the time variations of $\theta_{AL,b,eff}$, $\theta_{AG,e}$, and $(\theta_{OL,b,eff}-\theta_{OL,0})/(1-\theta_{OL,0})$ versus $t$ for ozone dissolution in countercurrent bubble column. $u_L=1.42$ mm/s. Symbols: experiments; lines: prediction. ○, △, ■: $y_A=0.00428$, 0.0115, and 0.0191 at $u_{G0}=1.33$ mm/s. ▲: $y_A=0.0192$ at $u_{G0}=4.85$ mm/s. ▲: $y_A=0.0162$ at $u_{G0}=9.48$ mm/s. (a) $\theta_{AL,b,eff}$, (b) $\theta_{AG,e}$, and (c) $(\theta_{OL,b,eff}-\theta_{OL,0})/(1-\theta_{OL,0})$.

$P_L$, $Da_0$, and $k_{L0,AG}$. As $P_L$ increases, the system approaches plug flow and has a higher axial gradient of $\theta_{AL,b}$ and driving force of the concentration difference. This is favorable to the gas–liquid mass transfer. Further, the values of $\theta_{AL,b}$ at steady state decrease as $Da_0$ increase. The higher decomposition rate of ozone is thus advantageous to reaching steady state. Moreover, an increase of the mass transfer rate of ozone associated with an increase of $k_{L0,AG}$, which is proportional to $k_{L0,AG}$, results in an increase of $\theta_{AL,b}$ accelerating the establishment of the steady state. These results demonstrate that the DADM proposed in this study is useful and referable for the prediction and illustration of dynamic ozone contacting processes.

Conclusions

1. The model proposed considers the oxygen mass transfer as well as the superficial gas velocity ($U_L$) variation. The dynamic variations of the oxygen and ozone concentrations during ozone dissolution in a countercurrent bubble column can be well predicted from the beginning to steady state.

2. For engineering application, the oxygen mass transfer may be neglected for simulation of ozone concentrations. The corresponding errors compared with experimental data are found < 4.5% in this study. However, correction of $U_G$ associated with the hydraulic pressure should be considered. Otherwise, 4–10% of overestimation would result.

Fig. 4. $\theta_{Alb}$ versus $\zeta$ for ozone dissolution in countercurrent bubble column. $u_G = 4.25$ mm/s, $y_A = 0.0115$. Lines: prediction. $\cdots$, $\cdot \cdot \cdot$, $\cdots$, and $\cdots$, $\tau = 0.2$, 0.5, and 1.0, and steady state. (a) $u_{GO} = 1.33$ mm/s; and (b) $u_{GO} = 9.48$ mm/s.

3. Both the oxygen mass transfer and $U_G$ variation should be considered for accurate estimation of the amount of off-gas, which is related to the computation of the ozone transfer efficiency and specific transferred ozone dosage.

4. The higher value of $U_G$ increases the saturation concentrations of the dissolved ozone and oxygen and the rate of the steady-state establishment owing to the higher mass transfer coefficients. On the contrary, the ozone transfer efficiency decreases with $U_G$. Further, the dissolved ozone concentration near the bottom of the column approaches the steady state faster.

5. The ozone contacting process in countercurrent bubble columns reaches the steady state faster with higher values of the Peclet number, ozone decomposition rate, and mass transfer rate.

Fig. 5. $\theta_{Alb}/\theta_{Alb,ss}$ of effluent versus $\tau$ at various $P_f$ for ozone dissolution in countercurrent bubble column. Lines: prediction. $\cdots$, $\cdots$, $\cdots$, $\cdots$, $\cdots$, and $\cdots$, $P_f = 0.01$, 0.667, 2.5, 10, and 100 (with $\theta_{Alb,ss} = 0.462$, 0.501, 0.559, 0.619, and 0.653).

Fig. 6. $\theta_{Alb}/\theta_{Alb,ss}$ of effluent versus $\tau$ at various $Da_o$ for ozone dissolution in countercurrent bubble column. Lines: prediction. $\cdots$, $\cdots$, $\cdots$, $\cdots$, $\cdots$, $\cdots$, $\cdots$, $\cdots$, and $\cdots$, $Da_o = 0.0458$, 0.5, 1.0, 2.5, and 5.0 (with $\theta_{Alb,ss} = 0.619$, 0.523, 0.448, 0.314, and 0.211).

Fig. 7. $\theta_{Alb}/\theta_{Alb,ss}$ of effluent versus $\tau$ at various $k_{LO}^0$ for ozone dissolution in countercurrent bubble column. Lines: prediction. $\cdots$, $\cdots$, $\cdots$, $\cdots$, and $\cdots$, $k_{LO}^0 = 0.001^*$, 0.003$, 0.00664$, 0.01$, 0.02$ (with $\theta_{Alb,ss} = 0.203$, 0.431, 0.619, 0.702, and 0.808). (a) $k_{LO}^0 = 0.000886$, $St_{GO} = 0.0325$, $St_{LO} = 0.313$, $St_{GA} = 0.233$, $St_{LA} = 0.277$. (b) $k_{LO}^0 = 0.00266$, $St_{GO} = 0.0975$, $St_{LO} = 0.939$, $St_{GA} = 0.699$, $St_{LA} = 0.832$. (c) $k_{LO}^0 = 0.00589$, $St_{GO} = 0.216$, $St_{LO} = 2.08$, $St_{GA} = 1.55$, $St_{LA} = 1.84$. (d) $k_{LO}^0 = 0.00886$, $St_{GO} = 0.325$, $St_{LO} = 3.13$, $St_{GA} = 2.33$, $St_{LA} = 2.77$. (e) $k_{LO}^0 = 0.0177$, $St_{GO} = 0.649$, $St_{LO} = 6.26$, $St_{GA} = 4.66$, $St_{LA} = 5.55$. 

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Appendix: Mathematical Model and Derivation

With the decomposition of ozone and formation of oxygen, the mass transfer rates of ozone (A) and oxygen (O) may be enhanced and retarded, respectively. The ratios of the mass transfer rates when mass transfer rates of ozone under Grant No. NSC 90-2211-E-002-039.

The common cases of the ozone self-decomposition. Should the phase may be described by Eq. 21. The left-hand-side term represents the variation of the local gas concentration, while the right-hand-side terms stand for the dispersion effect, convection, and ozone and oxygen mass transfers, respectively.

Applying the ideal gas equation and noting that the hydrostatic pressure (P) decreases linearly with the axial coordinate from the bottom of the column, one has

\[ C_G = \frac{P}{RT} = \frac{P + \varepsilon L G (L - z)/f_p}{RT} = \frac{P \beta_p}{RT} \]  

with \( \beta_p = 1 + \alpha_p (1 - z/L) \), and \( \alpha_p = \varepsilon L G L / (f_p P T) \).

Substituting Eq. (22) into Eq. (21), and putting in dimensionless forms, one may obtain Eq. (3) of the dimensionless superficial gas velocity (U_G) and the related Eqs. (4)–(6). While the bubbles rise along the axial coordinate of the column, the liquid height (L) also increases due to the accumulation of the gas holdup. The increased L tends to be constant as the gas bubbles reach the liquid surface. Steady state L is considered to be equal to \( L_0/(1 - \varepsilon_G) \), where \( L_0 \) is the liquid height with no gas holdup.

Further, the gas phase governing equations of ozone (C_AG) and oxygen (C_OG) can be expressed in dimensionless forms (7) and (8). The liquid phase governing the equations of ozone (C_AL) and oxygen (C_OL) should consider ozone decomposition terms according to Eq. (2) to give Eqs. (9) and (10). The gas ozone concentration (C_AG) in the free volume (V_f) in a bubble column can be described by Eq. (11) with the complete mixing assumption. The dimensionless variables and parameter groups in the system equations are defined in the Notation. Note that the Peclet numbers represent the flow condition. As the values of Peclet numbers become large, the system tends to approach plug flow. For small values of the Peclet numbers, the flow would behave as in complete mixing. Furthermore, the Stanton and Damköhler numbers stand for the significance of the mass transfer and chemical reaction, respectively.

Notation

The following symbols are used in this paper:

- A = cross section area of column (m²);
- a = specific gas–liquid interfacial area based on volume of liquid and gas (1/m);
- C_AG, C_AG,ss, C_AG,0 = gas concentration of ozone in free volume and its steady-state value (M or mg/L);
- C_AL, C_AL,ss, C_AL,i = gas concentrations of ozone of holdup and inlet gases (M or mg/L);
- C_OG, C_OG,0 = dissolved ozone concentrations in bulk and effluent liquids (M or mg/L);
- C_OL, C_OL,ss = steady-state value of C_OL (M or mg/L);
- C_e, C_e = experimental concentration data and its average value (M or mg/L);
- C_G = total gas concentration in gas phase (M or mg/L);
- C_OG, C_OG,0 = dissolved oxygen concentrations of oxygen of holdup and inlet gases (M or mg/L);
$C_{OL}$ = dissolved oxygen concentration of liquid at gas–liquid interface (M or mg/L);

$C_p$ = predicted concentration values (M or mg/L);

$C_i$ = tracer concentration (mg/L);

$C_0$ = dimensionless concentration of tracer $=$ $C_{Q(t)}$ $\tau_i$ $/$ $m$;

$D_A$, $D_o$ = molecular liquid diffusion coefficients of ozone and oxygen (m$^2$/s);

$D_{A0}$, $D_{00}$ = Damköhler numbers of ozone $=$ $k_d$ $L$ $C_{A0}$ $/ (2u_l C_{A0} (H_1))$ and oxygen $=$ $3 k_d$ $L$ $C_{A0}$ $/ (2u_l C_{A0} (H_1))$;

$E_G$, $E_L$ = gas and liquid axial dispersion coefficients (m$^2$/s);

$E_{IA}$ = enhancement factor of ozone defined as in Eq. (19);

$f_p$ = unit converted factor of pressure $=$ 101.325 Pa (atm)$^{-1}$;

$g$ = standard acceleration of gravity $=$ 9.8 m/s$^2$;

$H_A$, $H_0$ = Henry’s law constants of ozone $=$ $C_{A1}/(C_{A1} L)$ and oxygen $=$ $C_{O1}/(C_{OL} L)$ (M M$^{-1}$);

$H_{A1}$ = dimensionless Hatta number, $= \sqrt{k_d L A}$

$h_B$, $h_B^0$ = dimensional (m) and dimensionless ($h_B^0$) heights of rising gas bubbles at time $t$;

$h_{ss}$ = hydrostatic height of two different positions for estimating $e_G$, $e_G = \Delta P / [(p_L - p_G) g h_{ss}]$;

$k_d$ = decomposition rate constant of ozone (1/s);

$k_{L0}$, $k_{L0}^0$ = physical liquid-phase mass transfer coefficients of ozone and oxygen (m/s);

$(k_{L0})_{sl}$ = value of $k_{L0}^0$ in semibatch reactor (1/s);

$L$, $L_0$ = liquid heights at steady state, or with no gas holdup (m);

$m_{SA0}$ = specific applied ozone dosage, $= C_{A0}$ $/ (u_{G0} L)$ (mg/L);

$m_{ST0}$ = specific transferred ozone dosage defined as (18) (mg/L);

$m_i$ = injection tracer mass (mg);

$N_{LPM}$ = L/min at 0°C, 1 atm;

$P$ = hydrostatic pressure as function of location of column in Eq. (22) (atm);

$P_T$ = gas pressure at free space (atm or kPa);

$P_{zm}$ = $P$ at position $z_m$ (kPa);

$P_G$, $P_L$ = Pecllet numbers of gas $= u_{G0} L / (E_G R_G)$ and liquid $= u_{L0} L / (E_L R_L)$ phases;

$Q_L$ = liquid flow rate (L/s);

$R$ = gas constant, $= 0.082$ atm L K$^{-1}$ mol$^{-1}$;

$R_{fo}$ = retarding factor of oxygen defined as in Eq. (20);

$R_{EL}$ = ratio of modified volume of liquid to free space, $= A_{L0} L / u_{L0} (V_{G0} / u_{G0})$;

$R_{ug0}$ = gas–liquid velocity ratio, $= u_{G0} L / (u_{G0} E_G)$;

$R^2$ = correlation coefficient, $= \pm \sqrt{\Sigma (C_i - C_{i0})^2 / \Sigma (C_i - \bar{C}_i)}^2$;

$r_{s}$ = correlation coefficient;

$S_{GA}$, $S_{GO}$ = gas Stanton numbers of ozone $= L k_d^0 / (u_{G0} (H_1))$ and oxygen $= L k_d^0 / (u_{G0} (H_1))$;

$S_{LA}$, $S_{LO}$ = liquid Stanton numbers of ozone $= L k_d^0 / (u_{L0} L)$ and oxygen $= L k_d^0 / (u_{L0} L)$;

$T$ = temperature (K);

$t$, $t_c$ = time (s), and contact time (min or s);

$t_{s}$ = mean liquid phase residence time, $= L e_{L} / u_{L}$ (min or s);

$t_{10}$ = time for 10% of tracer mass to exit column (min or s);

$U_G$, $U_{G,1}$, $U_{G,1,ss}$ = $u_{G0}/u_{G0}$, $u_{G,1}/u_{G0}$, and $u_{G,1,ss}$ at steady state;

$u_{G0}$, $u_L$ = superficial gas and liquid velocities (m/s or mm/s);

$u_{G,1}/u_{G0}$, $u_{G,1,ss}$ = outlet and inlet superficial gas velocities (m/s or mm/s);

$V_F$ = volume of free space (m$^3$ or L);

$\alpha_p$ = pressure ratio, $= E_{1} D_{1} L / (f_p P_T)$;

$\beta_p$ = local variable, $= 1 + \alpha_p (1 - z/L)$;

$\delta(\tau)$ = Dirac delta function to represent discontinuous pulse;

$\Delta P$ = pressure difference between two positions with and without aeration of hydrostatic height $h_{ss}$ for estimating $e_G$, $e_G = \Delta P / [(p_L - p_G) g h_{ss}]$ (Pa);

$e_G$, $e_L$ = relative gas and liquid holdups;

$\eta_{ote}$ = ozone transfer efficiency defined as in Eq. (17);

$\theta_{AG}$, $\theta_{AGe}$ = $C_{A1}/(C_{A1} L)$, $C_{AG1}/C_{AG1}$;

$\theta_{ALb}$, $\theta_{ALbs}$$\theta_{ALb}$ = $C_{ALb}/(C_{A1} (H_1))$; $C_{ALb,ss}$ = $C_{ALb}/(C_{A1} (H_1))$, and steady-state value of $\theta_{ALb}$;

$\theta_{OGi}$, $\theta_{OGi}$ = dimensionless $C_{og1}/C_{og1}$;

$\theta_{OLb}$, $\theta_{OLb}$ $\theta_{OLb}$ = $C_{OLb}/(C_{A1} (H_1))$, $C_{OLb,ss}$ = $C_{OLb}/(C_{A1} (H_1))$, and $C_{OLb,ss}$ = $C_{OLb}/(C_{A1} (H_1))$;

$\mu_L$ = liquid viscosity (kg m$^{-1}$ s$^{-1}$);

$P_G$, $P_L$ = gas and liquid densities (kg/m$^3$);

$\sigma_L$ = liquid surface tension (N/m);

$\tau$ = dimensionless time, $= t/t_{s}$; and

$\zeta$ = dimensionless axial coordinate of column from bottom, $= z/L$.

Subscripts:

$sb$ = semibatch stirred reactor; and

$ss$ = steady state.

References


