Ozone mass transfer in water treatment: hydrodynamics and mass transfer modeling of ozone bubble columns

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Abstract Most of the mathematical models that are employed to model the performance of bubble columns are based on the assumption that either plug flow or complete mixing conditions prevail in the liquid phase. Although due to the liquid-phase axial dispersion, the actual flow pattern in bubble columns is usually closer to being mixed flow rather than plug flow, but still not completely mixed flow. Therefore, the back flow cell model (BFCM), that hypothesises both back flow and exchange flow to characterise the liquid-phase axial dispersion, is presented as an alternative approach to describe the hydrodynamics and mass transfer of ozone bubble columns. BFCM is easy to formulate and solve. It is an accurate and reliable design model. Transient BFCM consists of $N_{BFCM}$ ordinary-first-order differential equations in which $N_{BFCM}$ unknowns ($Y_j$) are to be determined. That set of equations was solved numerically as $N_{BFCM}$ linear algebraic equations. Steady-state BFCM consists of $3 \times N_{BFCM}$ non-linear algebraic equations in which $3 \times N_{BFCM}$ unknowns ($Q_G, X_j$, and $Y_j$) are to be determined. Those non-linear algebraic equations were solved numerically using Newton–Raphson technique. Steady-state BFCM was initially tested using the pilot-scale experimental data of Zhou. BFCM provided excellent predictions of the dissolved ozone profiles under different operating conditions for both counter and co-current flow modes.

Keywords Back flow cell model; hydrodynamics; mass transfer; ozone bubble column; steady-state; transient

Introduction

Ozonation of water is usually conducted by dissolving the on-site generated ozone gas in the liquid phase. This is often achieved by using an ozone bubble column as the reacting chamber where ozone gas is bubbled through the liquid phase by utilising conventional bubble diffusers, turbine mixers, negative pressure gas ejectors, positive pressure gas injectors, etc. During ozonation, a number of processes occur simultaneously. Those processes are convection and backmixing of the liquid flowing through the contacting chamber, ozone gas mass transfer from the gas phase to the liquid phase, ozone auto-decomposition, and competitive reactivity of constituents in water with dissolved ozone (Zhou et al., 1994). The rates of individual phase transport and chemical transformation processes, contactor configuration, operating conditions, and water quality influence the overall performance of any ozonation system. Ozonation process relies in its effectiveness on the concentration of dissolved ozone. Quantifying the dissolved ozone is crucial to rational design and optimum operation of ozone contactors.

Mathematical models that are often applied to predict the dissolved ozone profiles along bubble columns are based on one of the following liquid-phase flow regime assumptions: (1) complete mixing or (2) plug flow (Alvarez-Cuenca et al., 1980; Alvarez-Cuenca et al., 1981; Chang et al., 1981; Laplanche et al., 1991; Hull et al., 1992; Lev et al., 1992). Applying such simplified models to describe the performance of ozone bubble columns will lead to unoptimised and unreliable designs and consequently poor performance of ozone contactors. The actual flow pattern in bubble columns is usually closer to being mixed flow rather than being plug flow, but still not completely mixed flow. Thus, it is essential to accurately characterise the fundamental processes and determine the variables that control and dictate the overall performance of any ozonation system.
This paper presents: (1) formulation of the transient and the steady-state BFCM for describing the hydrodynamics and quantifying the dissolved ozone profiles in bubble columns; and (2) initial testing of the steady-state BFCM using the pilot-scale experimental data of Zhou (1995).

Theoretical background

In bubble columns, non-ideal flow conditions affect the rate of absorption and concentration profiles of dissolved ozone in tubular bubble columns. The backmixing process involves the redistribution of material either by slippage due to shear forces or by turbulent eddies. Since, the redistribution process is repeated a large number of times during the flow of the fluid through the reactor, it was assumed that it is statistical in nature and a molecular diffusion-like process. Thus, the empirical Fick’s law is applied, replacing the molecular diffusion coefficient by an appropriate mixing parameter, the axial dispersion coefficient ($D_L$), which combines the effects of a non-uniform velocity profile (shear dispersion), molecular and eddy diffusivities:

$$ I = -D_L \frac{dC}{dx} \quad (1) $$

The mass transfer of ozone gas from the gas phase into the liquid phase can be described and quantified by the two-film model:

$$ \psi = k_L a (C_L^* - C_L) \quad (2) $$

where: $\psi$ = rate of absorption per unit volume, $k_L$ = local liquid mass transfer coefficient; $a$ = specific interfacial area; $C_L^*$ = concentration of dissolved gas in equilibrium with the bulk gas; and $C_L$ = concentration of the dissolved gas in the bulk liquid. Since the ozone gas diffuses much faster in the gas phase than in the liquid phase, the mass transfer in the liquid phase becomes a rate-controlling step and the overall mass transfer coefficient was considered to consist entirely of the local mass transfer coefficient in the liquid phase.

As ozone gas dissolves in water, it starts decaying through two pathways, auto-decomposition and oxidation of impurities in the liquid phase due to its extremely high oxidative properties (Hoigné, 1982). Two primary pathways involving those reactions have been proposed: direct oxidation and oxidation by the radical intermediates of ozone auto-decomposition products. Ozone auto-decomposition rate is usually dependent on water temperature and pH, organic and inorganic constituents in water, and the organic and inorganic initiators and inhibitors present in the water. Watt et al. (1989) observed that the overall decomposition rate was influenced by the concentration and the history of the ozonation process. A modified pseudo-first-order rate expression was proposed in which the reaction rate constant is replaced by a variable called the specific ozone utilisation rate constant ($k_w$) that accounts for the change of the water characteristics during ozonation:

$$ \frac{dC_L}{dr} = k_w C_L \quad (3) $$

Ozone auto-decomposition process affects the driving force of absorption and consequently the rate of mass transfer. Chemical reactions usually reduce the liquid-phase ozone concentration, causing the difference between the equilibrium and bulk liquid concentrations to be larger. If the chemical reactions are fast enough for the liquid-phase concentration in the liquid film to be depleted, a further enhancement of the local mass transfer coefficient ($k_L$) would result. For an irreversible first-order reaction, Danckwerts (1970) proposed a criterion for neglecting the effect of chemical reactions on the local mass transfer coeffi-
cient and hence, the gas absorption can be dealt with as pure physical absorption in which the dissolved gas diffuses from the surface to the bulk liquid without reacting on the way:

\[ H_a^2 = M = \frac{Dk_w}{k_L} \approx 1 \text{ (i.e., it reaches zero)} \]  

(4)

where: \( H_a = \sqrt{M} \) dimensionless Hatta number and \( D = \) molecular diffusivity of ozone. \( k_w \) was reported to be in the order of 0.167 min\(^{-1}\) for the raw surface water tested by Yurteri and Gurol (1988) and to be 0.028 min\(^{-1}\) for the de-ionised water tested by Zhou (1995). The diffusivity of ozone in water was determined by the Wilke-Chang formula as \( 1.74 \times 10^{-5} \) cm\(^2\) s\(^{-1}\) at 20°C. The most reliable value of \( k_L \) is in the order of \( 2 \times 10^{-3} \) to \( 3 \times 10^{-3} \) ms\(^{-1}\). Substituting those values into Equation 4, yields a squared Hatta number of \( 7.7 \times 10^{-7} \) and \( 1.3 \times 10^{-7} \) for the raw surface water and de-ionised water tested by Yurteri and Gurol (1988) and Zhou (1995), respectively. Therefore, it can be concluded that the occurrence of chemical reactions during the ozonation of water has negligible effect on the local mass transfer coefficient and hence Equation 2 can be applied for ozone absorption without modification.

Model development

Transient back flow cell model (TBFCM)

BFCM hypothesises both back flow and exchange flow to characterise the axial dispersion in the liquid phase. Figure 1 represents a BFCM schematic for co-current flow conditions in bubble columns, where the back flow ratio is equal to the exchange flow ratio, and both are constant along the column height. BFCM consists of two series of completely mixed cells, one series representing the liquid phase and the other representing the gas phase and each has a number of cells equalling \( N_{BFCM} \). The assumptions that govern the transient BFCM are: (1) back flow occurs only in the liquid phase; (2) back flow is negligible in the gas phase due to the large buoyancy of gas bubbles; (3) ozone bubble column is operated at constant liquid and gas flow rates; (4) gas hold-up and bubbles’ interfacial surface area are constant along the column height; and (5) no mass transfer and chemical decay should be considered for the inert tracer. To ensure that the gas phase flow conditions are as close as possible to plug flow conditions, the number of mixed cells has to be equal to or greater than 10. By employing the mass balance with respect to the inert tracer around cell number 1, the mathematical relationship for the TBFCM is as follows:

\[ Q_L C_0 + Q_g C_2 - (Q_L + Q_g) C_1 = \frac{dC_1}{dt} V_c \]  

(5)

where: \( V_c \) is the cell volume and is equal to the total volume of the bubble column (V) divided by the number of cells \( (N_{BFCM}) \). Dividing Equation 5 by where:

\[ C_0 = \frac{M}{V_c} = \frac{M}{V/N_{BFCM}} \]  

(6)

and \( M = \) volume of inert tracer, substituting in the resultant equation for:

\[ r = \frac{Q_g}{Q_L} \]  

(7)

where \( r \) is the back flow ratio, and rearranging, one can obtain:

\[ \frac{dY}{dt} = -\frac{1 + r}{\tau_{BFCM}} Y_1 + \frac{r}{\tau_{BFCM}} Y_2 \]  

(8)
Following the same procedure used to derive Equation 8, one can obtain the transient BFCM equations for the cells from $j = 2$ to $j = N_{\text{BFCM}}$ as follows. For $2 \leq j \leq N_{\text{BFCM}} - 1$:

$$\frac{dY_j}{dt} = \frac{1 + r}{\tau_{\text{BFCM}}} Y_{j-1} - \frac{1 + 2r}{\tau_{\text{BFCM}}} Y_j + \frac{r}{\tau_{\text{BFCM}}} Y_{j+1}$$

(10)

and for $j = N_{\text{BFCM}}$:

$$\frac{dY_{N_{\text{BFCM}}}}{dt} = \frac{1 + r}{\tau_{\text{BFCM}}} Y_{N_{\text{BFCM}} - 1} - \frac{1 + r}{\tau_{\text{BFCM}}} Y_{N_{\text{BFCM}}},$$

(11)

BFCM and ADM describe the backmixing of the liquid phase using different mixing parameters ($Pe_L$, $N_{\text{BFCM}}$, and $r$). Those parameters are interrelated by the following relationship:

$$r = \frac{N_{\text{BFCM}}}{Pe_L} - 0.5 = \frac{D_j N_{\text{BFCM}}}{u_L L} - 0.5$$

(12)

Equations 8, 10, and 11 are $N_{\text{BFCM}}$ first-order ordinary differential equations in $N_{\text{BFCM}}$ unknowns ($Y_j$). Those differential equations were solved numerically by applying an explicit technique for time discretisation to transform them into a system of linear algebraic equations which were then solved using a simple spreadsheet program. The initial conditions for that system of equations (for pulse-input tracer tests) are as follows, at $t = 0$: $Y_j = 1$ for $2 \leq j \leq N_{\text{BFCM}}$, $Y_j = 0$ for $2 \leq j \leq N_{\text{BFCM}}$.

Steady-state back flow cell model (BFCM)

The assumptions that govern the application of the BFCM for modelling two-phase flows in ozone bubble columns are the same as the assumptions, 1 through 4, used to derive the TBFCM equations. In addition to those assumptions, further assumptions are needed.
Those include: (1) ozone mass transfer resistance for the ozone absorption is confined to the liquid side alone; (2) enhancement factor of the mass transfer due to the occurrence of chemical reactions was assumed to be 1.0 as the absorption of ozone in water could be considered in the slow chemical reaction regime; (3) steady-state isothermal operation; (4) Henry’s law applies; (5) air constituents are assumed to be inerts; (6) local mass transfer coefficient \( k_L \) is constant along the column height; (7) owing to the hydrostatic head, total pressure varies linearly with the column depth; (8) superficial gas velocity is variable due to ozone absorption, ozone gas depletion, and hydrostatic pressure decrease; and (9) ozone auto-decomposition, in the liquid phase, is described by a pseudo-first-order rate expression and is negligible in the gas phase.

For a co-current flow mode and by referring to Figure 1, the basic mass balance with respect to the dissolved ozone within each cell leads to the following equations, for \( j = 1, 2 \leq j \leq N_{\text{BFCM}}^{-1} \), and for \( j = N_{\text{BFCM}}^{-1} \) respectively:

\[
Q_L C_{L,0} + Q_B C_{L,2} + k_L a(C_{L,1}^* - C_{L,1}) \frac{V}{N_{\text{BFCM}}} - k_u C_{L,1} e_L \frac{V}{N_{\text{BFCM}}} - (Q_L + Q_B) C_{L,1} = 0
\]  

(13)

\[
(Q_L + Q_B) C_{L,j-3} + Q_B C_{L,j+1} + k_L a(C_{L,j}^* - C_{L,j}) \frac{V}{N_{\text{BFCM}}} - k_u C_{L,j} e_L \frac{V}{N_{\text{BFCM}}} - (Q_L + 2Q_B) C_{L,j} = 0,
\]  

(14)

\[
(Q_L + Q_B) C_{L,N_{\text{BFCM}}^{-1} - 1} + k_L a(C_{L,N_{\text{BFCM}}^{-1}}^* - C_{L,N_{\text{BFCM}}^{-1}}) \frac{V}{N_{\text{BFCM}}} - k_u C_{L,N_{\text{BFCM}}^{-1}} e_L \frac{V}{N_{\text{BFCM}}} - (Q_L + Q_B) C_{L,N_{\text{BFCM}}^{-1}} = 0
\]  

(15)

For cell number \( j \), and for the gaseous ozone and total gas respectively, the basic mass balance leads to the following equations:

\[
Q_{G,j-1} C_{G,j-1} - Q_{G,j} C_{G,j} - k_t a(C_{L,j}^* - C_{L,j}) \frac{V}{N_{\text{BFCM}}} = 0
\]  

(16)

\[
Q_{G,j-1} C_{T,j-1} - Q_{G,j} C_{T,j} - k_t a(C_{L,j}^* - C_{L,j}) \frac{V}{N_{\text{BFCM}}} = 0
\]  

(17)

The hydrostatic head \( P_j \) in the column decreases linearly with the depth \( l \) assuming that the change in the liquid hold-up is negligible, therefore:

\[
P_j = P_1 + \rho g e_L \left(1 - \frac{j - 0.5}{N_{\text{BFCM}}} \right) L = P_1 [1 + \alpha(j - 0.5)]
\]  

(18)

where \( \alpha \) is defined by Equation 22. The equilibrium concentration \( C_{L,j}^* \) is given by:

\[
C_{L,j}^* = \frac{P_j y_j}{H v_j}
\]  

(19)

The gaseous ozone concentration \( C_{G,j} \) and the total gas concentration \( C_{T,j} \) respectively, are given by:

\[
C_{G,j} = \frac{P_j y_j}{RT}
\]  

(20)

\[
C_{T,j} = \frac{P_j}{RT}
\]  

(21)

Introducing the following dimensionless terms into Equations 13 to 17:

\[
\alpha = -\rho g e_L L / N_{\text{BFCM}} P_0
\]  

(22)
and rearranging the resultant equations, yields the steady-state BFCM equations.

Dissolved ozone. For $j = 1, 2 \leq j \leq N_{\text{BFCM}} - 1$, and for $j = N_{\text{BFCM}}$, respectively:

\begin{align*}
X_0 - (1 + r + D_a + S_{L_0})X_1 + rX_2 + S_{L_0}\left(1 + \frac{\alpha}{2}\right)Y_1 &= 0 \\
(1 + r)X_{j-1} - (1 + 2r + D_a + S_{L_0})X_j + rX_{j+1} + S_{L_0}\left[1 + \alpha(j - 0.5)\right]Y_j &= 0 \\
(1 + r)X_{N_{\text{BFCM}} - 1} - (1 + r + D_a + S_{L_0})X_j + rX_{j+1} + S_{L_0}\left[1 + \alpha(N_{\text{BFCM}} - 0.5)\right]Y_{N_{\text{BFCM}}} &= 0
\end{align*}

Gaseous ozone. For cell number $j$:

\begin{align*}
(1 + \alpha(j - 1.5))q_{G,j-1}Y_{j-1} - (1 + \alpha(j - 0.5))q_{G,j}Y_j - S_{G,j}\left[(1 + \alpha(j - 0.5))Y_j - X_j\right] &= 0
\end{align*}

Total gas. For cell number $j$:

\begin{align*}
(1 + \alpha(j - 1.5))q_{G,j-1} - (1 + \alpha(j - 0.5))q_{G,j} - S_{G,j}\left[(1 + \alpha(j - 0.5))Y_j - X_j\right] &= 0
\end{align*}

A similar approach could be used to derive the equations for the counter-current flow mode.

Based on the definitions of variables (Equations 27 to 29), the zero-index variables are:

\begin{align*}
X_0 &= C_{L_0} / C^*_{L_0}, \quad Y_0 = 1, \quad \text{and} \quad q_{G,0} = 1
\end{align*}

Results and discussion

Transient back flow cell model (TBFCM)

The system of Equations 8, 10, and 11 was solved, for $N_{\text{BFCM}} = 10$ and $Pe_L$ ranging from 1 to 20, to examine the effect of $Pe_L$ or $r$ on the theoretical RTD. As shown in Figure (2-a), as $Pe_L$ increases, the RTD at the bottom port narrows as the liquid phase flow conditions are approaching plug flow. The effect of $Pe_L$ on RTD at the top sampling port is shown in Figure (2-b). As $Pe_L$ increases, the RTD narrows and becomes more symmetrical and the peak increases as well, suggesting that the liquid flow conditions are approaching plug flow.
Steady-state back flow cell model (BFCM)

The predictions of the steady-state BFCM were tested using the pilot-scale experimental data of Zhou (1995). The bubble column used in the experiments was a cylindrical glass column with an inside diameter of 100 mm and a height of 2000 mm. The water depth was kept constant at 1750 mm. The gas sparger used was a 25 mm spherical fused crystalline aluminium stone. The water samples were withdrawn from six bell-shaped sampling taps that were installed at equal intervals along the column height. The operating conditions for the co-current and counter-current flow modes are shown in Tables 1 and 2 respectively.

The number of mixed cells ($N_{\text{BFCM}}$) was set equal to 10. A pseudo-first-order specific ozone utilisation rate was assumed to equal 0.028 min$^{-1}$ for de-ionised water. Steady-state BFCM equations (Equations 30 to 34) were solved numerically using Newton–Raphson technique by utilising the TKSOLVER™ software. The program executed until a user-specified comparison tolerance of 10$^{-6}$ was satisfied. The program execution time ranged

### Table 1

operating conditions for the co-current flow mode

<table>
<thead>
<tr>
<th>Case #</th>
<th>$N_{\text{BFCM}}$</th>
<th>$P_{\text{in}}$</th>
<th>$r$</th>
<th>$\alpha$</th>
<th>$S_{\text{L}}$</th>
<th>$S_{\text{L}}$</th>
<th>$D_{\alpha}$</th>
<th>$y_{0}$</th>
<th>$C_{\text{L,0}}$* (mg/L)</th>
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</thead>
<tbody>
<tr>
<td>DW4</td>
<td>10</td>
<td>34.48</td>
<td>-0.21</td>
<td>-0.014</td>
<td>0.024</td>
<td>0.125</td>
<td>0.006</td>
<td>0.013</td>
<td>7.20</td>
</tr>
<tr>
<td>DW5</td>
<td>10</td>
<td>17.86</td>
<td>0.06</td>
<td>-0.014</td>
<td>0.176</td>
<td>0.126</td>
<td>0.006</td>
<td>0.002</td>
<td>0.92</td>
</tr>
<tr>
<td>DW9</td>
<td>10</td>
<td>4.63</td>
<td>1.66</td>
<td>-0.014</td>
<td>0.024</td>
<td>0.008</td>
<td>0.014</td>
<td>0.88</td>
<td></td>
</tr>
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</table>

### Table 2

operating conditions for the counter-current flow mode

<table>
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<tr>
<th>Case #</th>
<th>$N_{\text{BFCM}}$</th>
<th>$P_{\text{in}}$</th>
<th>$r$</th>
<th>$\alpha$</th>
<th>$S_{\text{L}}$</th>
<th>$S_{\text{L}}$</th>
<th>$D_{\alpha}$</th>
<th>$y_{0}$</th>
<th>$C_{\text{L,0}}$* (mg/L)</th>
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<tr>
<td>DW17</td>
<td>10</td>
<td>10.53</td>
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<td>0.112</td>
<td>0.014</td>
<td>0.010</td>
<td>5.56</td>
</tr>
<tr>
<td>DW18</td>
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<td>5.35</td>
<td>1.37</td>
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<td>0.379</td>
<td>0.130</td>
<td>0.014</td>
<td>0.002</td>
<td>0.92</td>
</tr>
</tbody>
</table>

Figure 2 (a) Theoretical RTD at the bottom sampling port and (b) theoretical RTD at the top sampling port

Figure 3 (a) Steady-state BFCM testing for co-current flow mode and (b) Steady-state BFCM testing for counter-current flow mode
from 0.11 to 0.22 s using a 366 MHz processor. Figures (3-a) and (3-b) illustrate the applicability of the steady-state BFCM to describe the performance of an ozone bubble column that utilises diffusers as the gas spargers in the co and counter-current flow modes, respectively. As shown, there was an excellent agreement between the experimental dissolved ozone profiles and the predicted ozone profiles, except for a few data points, where there was small deviation between the measured and the predicted dissolved ozone concentrations.

Conclusions
Transient BFCM can adequately describe the backmixing in the liquid phase in bubble columns at a wide range of operating conditions and for any given boundary conditions while the traditionally used ADM equations are not applicable for all the boundary conditions specially for closed-closed boundary conditions which is usually the case for ozone contactors. The main advantages of using TBFCM to describe the hydrodynamics of ozone bubble columns are: (1) TBFCM is easy to formulate; and (2) it can be solved using a spreadsheet program. For adequate predictions of the TBFCM, the number of cells in-series to be considered for model simulations should be carefully chosen depending on the ozone contactor configuration. TBFCM should be extended to account for variable backmixing along the column height as is often the case in bubble columns.

Steady-state BFCM has been proven to provide excellent predictions of the performance of pilot-scale ozone bubble columns. The model predictions should be further tested for different designs and scales of ozone contactors and under different operating conditions. Also, the model should be further extended to account for variable mass transfer coefficient along the contactor’s height for special contactor designs where the mass transfer process is enhanced near the entrance of the contactor rather than along the entire contactor height.

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References