中國環境工程學刊　第十五卷　第一期　（民國九十四年）
*Journal of the Chinese Institute of Environmental Engineering, Vol. 15, No. 1, pp. 37-45 (2005)*

# DYNAMIC MODEL OF BUBBLE AERATION OF VOLATILE ORGANIC COMPOUNDS

**Yi-Hung Chen,[1] Je-Lueng Shie,[2] Ching-Yuan Chang,[1,*] Ken-Hung Chen,[1] Chiung-Fen Chang,[3]**
**Chyow-San Chiou,[2] Chun-Yu Chiu,[4] We-Ling Su[1] and Pen-Chi Chiang[1]**

*[1]Graduate Institute of Environmental Engineering*
*National Taiwan University*
*Taipei 106, Taiwan*
*[2]Department of Environmental Engineering*
*National I-Lan University*
*I-Lan 260, Taiwan.*
*[3] Department of Environmental Science*
*Tunghai University*
*Taichung 407, Taiwan*
*[4]Department of Environmental Engineering*
*Lan-Yang Institute of Technology*
*I-Lan 261, Taiwan*

***Key Words :*** Bubble aeration, volatile organic compounds, dynamic models, mass transfer, water treatment.

## ABSTRACT

A refined model was developed to predict the variations of liquid ($C_{BLb}$) and gas ($C_{BGi}$) concentrations of volatile organic compound (VOC) during a bubble aeration process. As a bubble aeration process starts, the gas is introduced and dispersed into to the VOC containing solution. The VOC is then transferred from the liquid to the gas phase. Thus, the concentrations of $C_{BLb}$ and $C_{BGi}$ of VOC in the solution vary with time continuously. The removal efficiency of VOC depends on the values of Henry's constant, gas and liquid flow rates and gas-liquid mass transfer properties simultaneously. The previous models proposed for bubble aeration system usually neglected the effect of VOC concentration in the gas phase. The negligence would cause the significant deviation for the estimation of mass transfer coefficient ( $K^{0}_{LB}$ $a_e$) and concentration variation of VOC. Furthermore, most bubble aeration models for continuous system were developed for the steady state. Accordingly, the concentrations of VOC in the early stage of bubble aeration processes are usually not predicted, and the time required for the steady state establishment remains to be determined. Moreover, the concentration of VOC in the discharged gas ($C_{BGe}$) should consider the delayed effect due to the free space of the tank. The present model employed three equations to describe the dynamic variations of the VOC concentrations in the liquid, gas holdup and free space, respectively. A set of analytical solutions for the model were obtained and can be easily applied for the simulation of the continuous or semibatch bubble aeration system. The model results showed good agreement with the data of the bubble aeration experiments of naphthalene in the 1-butanol containing solution performed in this work. The validity of the model was also well demonstrated by comparing the predicted results with the bubble aeration process of toluene in the literature. Furthermore, the effects of system parameters on the performance of the bubble aeration process were investigated. Consequently, the present model is useful for the proper prediction of the variables of a bubble aeration system.

## INTRODUCTION

Volatile organic compounds (VOCs) such as benzene, naphthalene, toluene and chlorobenzene are consistently found in wastewater treatment plant influents [1]. Volatilization has been considered to be a viable mechanism for removal of VOCs from wastewater [2]. Quantification of the concentration

---

[*] To whom all correspondence should be addressed.
E-mail address: cychang3@ntu.edu.tw

variation of VOCs in the water is critical to the rational design and optimization operation of a bubble aeration system [3]. Moreover, VOCs in the off-gas that have been identified as being odorous, ozone precursors (like ethane, n-butane, and propene etc.) and potential air toxicants are considered harmful to the exposed human being [4]. Therefore, the assessment of VOC emissions to the atmosphere is also necessary for achieving good control of possible air pollution.

Certainly, the VOC concentrations in the gas phase should be considered during the bubble aeration process. However, the previous bubble aeration model employed for describing of the gas–liquid mass transfer of VOCs usually neglected the effect of the VOC concentrations in the gas phase [5, 6]. This deficiency may cause the significant deviation for estimating the mass transfer coefficients and the concentration variations of VOCs. Furthermore, there exists a temporary and unsteady period before the continuous bubble aeration system reaches steady state. Most models for the continuous bubble aeration process were developed for the steady state, for examples, Aeration System Analysis Program (ASAP) and the models of Matter-Müller et al. [7], Roberts et al. [8] and Namkung and Rittman [9]. Accordingly, the variations of VOC concentrations in the early stage of bubble aeration have been usually not predicted, and the time required for the steady state establishment remains to be determined. Moreover, the delayed effect due to the free space of the tank, which would influence the concentration profile of the discharged VOC, should be considered for the prediction of VOC concentration in the off gas. The delayed effect has been usually neglected in previous bubble aeration models.

The object of this study was to model and investigate the dynamic bubble aeration process in a semibatch or continuous system. The present model employed three simultaneous equations to describe the dynamic variations of VOC concentrations in the liquid ($C_{BLb}$), gas holdup ($C_{BGi}$) and free space ($C_{BGe}$), respectively. Furthermore, a set of analytic solutions for the model were obtained and applied for simulation. The bubble aeration experiments of naphthalene (NAP) in the 1-butanol containing solution were performed. NAP is one of the polycyclic aromatic hydrocarbons (PAHs) with relatively high volatility. The estimated values of the gas–liquid mass transfer coefficient for the bubble aeration processes of NAP showed the significant difference between the present and previous models indicating the necessity of this study. In addition, the validity of the model was demonstrated by the satisfactory agreement of predicted results compared with the experimental data of Dahlan et al. [6]. Consequently, the model proposed is useful for the proper prediction of the dynamic bubble aeration process of VOC.

## THEORETICAL ANALYSIS

### Two-film Model of VOC Mass Transfer

For modeling the dynamic behavior of the bubble aeration process, it is necessary to quantify the gas–liquid mass transfer rate of VOC associated with the operation conditions of the contactor. The mass transfer rate of VOC (denoted as B) from the liquid to gas phase can be described by the two-film model [10]:

$$m_B = K^0_{LB} a_e V_L (C_{BLb} - C_{BGi}/H_B) \tag{1}$$

The relationship between the overall mass transfer coefficient ($K^0_{LB}$) and the liquid ($k^0_{LB}$) and gas ($k^0_{GB}$) mass transfer coefficients is expressed as Eq. (2).

$$1/K^0_{LB} = 1/k^0_{LB} + 1/(k^0_{GB} H_B) \tag{2}$$

The Henry's constant ($H_B$) is a ratio of a compound concentration in the air to its concentration in the water at equilibrium. The greater $H_B$ value represents the greater tendency for the volatilization of VOC from water to air phase. In the case of VOCs with $H_B > 0.1$, such as benzene, toluene and tetrachloroethylene, the values of $K^0_{LB}$ are close to those of $k^0_{LB}$ [7, 11].

### Bubble Aeration Model

A model for bubble aeration in a stirred tank would be developed based on the mass balance considerations. Some assumptions of the model are deemed properly as follows [6, 7, 12].

1.The VOC concentrations in the liquid and gas phases are homogeneous due to the complete mixing.

2.The gas holdup volume and mass transfer coefficient are constant.

3.Other effects of VOC accumulation are neglected.

Further, three governing equations expressed by Eqs. (3)–(5) are employed to describe the variations of the VOC concentrations in the liquid ($C_{BLb}$), gas holdup ($C_{BGi}$) and free space ($C_{BGe}$), respectively.

$$\begin{aligned} dC_{BLb}/dt = {} & Q_L(C_{BLb0} - C_{BLb})/V_L \\ & - K^0_{LB} a_e (C_{BLb} - C_{BGi}/H_B) \end{aligned} \tag{3}$$

$$\begin{aligned} dC_{BGi}/dt = {} & Q_G(C_{BGi0} - C_{BGi})/V_H \\ & + K^0_{LB} a_e V_L (C_{BLb} - C_{BGi}/H_B)/V_H \end{aligned} \tag{4}$$

$$dC_{BGe}/dt = Q_G(C_{BGi} - C_{BGe})/V_F \tag{5}$$

with the initial conditions:

$$t = 0,\ C_{BLb} = C_{BLb0},\ C_{BGi} = C_{BGe} = 0 \tag{6}$$

In Eqs. (3)–(5), the left-hand side terms represent the variations of the local VOC concentrations, while the right-hand side terms stand for the convection and gas–liquid mass transfer, respectively. Note that the gas bubbles that come out from the gas diffuser commonly have short dispersion and retention times [13]. Therefore, the VOC concentrations ($C_{BGi}$) in the gas bubbles at initial instant (t = 0) are relatively low and negligible [7].

Referring to the previous studies, the VOC concentration in the inlet gas is usually negligible ($C_{BGi0} = 0$). Introducing it into Eq. (4), one may accordingly obtain the analytic solutions of Eq. (7) from Eqs. (3)–(6). The VOC concentrations are in the dimensionless forms defined by Eq. (8).

$$\begin{bmatrix} \theta_{BLb} \\ \theta_{BGi} \\ \theta_{BGe} \end{bmatrix} = \begin{bmatrix} a_1 \\ a_2 \\ a_3 \end{bmatrix} \exp(x_1 t) + \begin{bmatrix} 1 - a_1 - a_5 \\ -a_2 - a_6 \\ a_4 \end{bmatrix} \exp(x_2 t) + \begin{bmatrix} 0 \\ 0 \\ -a_4 - a_3 - a_6 \end{bmatrix} \exp(-c_s t) + \begin{bmatrix} a_5 \\ a_6 \\ a_6 \end{bmatrix} \quad (7)$$

$\theta_{BLb} = C_{BLb} / C_{BLb0}$,

$\theta_{BGi} = C_{BGi} / (C_{BLb0} H_B)$,

$\theta_{BGe} = C_{BGe} / (C_{BLb0} H_B)$ (8)

In Eq. (7), the symbols signed as a, c and x are system constants as follows.

$a_1 = (x_2 + c_6 + a_5 x_2 + a_5 c_6 - a_6 c_2)/(x_2 - x_1)$,

$a_2 = (x_1 + c_6) a_1 / c_2$,

$a_3 = a_2 c_5 / (x_1 + c_5)$,

$a_4 = - c_5 (a_2 + a_6)/(x_2 + c_5)$,

$a_5 = c_1 c_7 / (c_6 c_7 - c_2 c_4)$,

$a_6 = c_1 c_4 / (c_6 c_7 - c_2 c_4)$,

$c_1 = Q_L / V_L$,

$c_2 = K^0_{LB} a_e$,

$c_3 = Q_G / V_H$,

$c_4 = K^0_{LB} a_e V_L / (V_H H_B)$,

$c_5 = Q_G / V_F$,

$c_6 = c_1 + c_2$,

$c_7 = c_3 + c_4$, $x_1$ and

$x_2 = [- (c_6 + c_7) \pm \sqrt{(c_6 + c_7)^2 - 4(c_6 c_7 - c_2 c_4)}\ ] / 2$. (9)

Firstly, the values of $c_1$ to $c_7$ are calculated based on the conditions of the bubble aeration system. The values of $x_1$, $x_2$ and $a_1$ to $a_6$ can be computed consequently from the known $c_1$ to $c_7$. Thus, one can then predict the variations of the VOC concentrations in a continuous bubble aeration system applicably by Eq. (7). It may be noted that the values of $a_5$ and $a_6$ represent the steady state values of dimensionless liquid and gas VOC concentrations, respectively. In addition, the instantaneous rate and accumulative amount of VOC discharged in the gas phase can be calculated as $Q_G C_{BLb0} H_B \theta_{BGi}$ and $\int_0^t Q_G C_{BLb0} H_B \theta_{BGi} dt$ [where $\int_0^t \theta_{BGi} dt = [a_2 \exp(x_1 t)]/x_1 - [(a_2 + a_6) \exp(x_2 t)]/x_2 + a_6 t$, respectively.

Furthermore, the present model can be simplified to simulate the bubble aeration process in the semibatch system ($Q_L = 0$) as $a_5 = a_6 = c_1 = 0$. The previous model usually neglected the concentration of VOC in gas holdup to derive the expression as Eq. (10) in a semibatch bubble aeration system [5, 6].

$$\theta_{BLb} = \exp(-K^0_{LB} a_e t) \quad (10)$$

Eq. (10) signifies the variation of $\theta_{BLb}$ only depends on the value of $K^0_{LB}$ $a_e$ and bubble aeration time without considering the effects of $H_B$ and $\theta_{BGi}$. Comparing the present model with ASAP, which was developed by the Environmental Technologies Design Options Tools (ETDOTs), there are two main differences between these two models. One is the hydraulic assumption for the flow condition of gas phase that would affect the calculation of bubble aeration processes. The complete mixing and plug flow approaches are adopted for the gas phase in the present model and ASAP, respectively. However, in mechanically stirred tanks or reactors with low ratio of height to diameter, the actual situation of gas hydrodynamics is closer to the complete mixing [13]. Another difference is that ASAP is only applied for the steady state that may be a lack about the dynamic process of bubble aeration. Therefore, the present model can provide some additional information for predicting bubble aeration processes.

# EXPERIMENTAL METHODS

## Chemicals

The concentration of NAP as the target VOC was about 30 mg/L in the 1-butanol containing solution. The NAP with chemical formula as $C_{10}H_8$ has the molecular weight of 128.2, vapor pressure of 0.00011 atm, $H_B$ of 0.0197 and octanol-water partition coefficient ($K_{ow}$) of 2291 at 25 °C [11]. The 1-butanol was used as cosolvent with the concentration of 1% (V/V) prepared by deionized water. The volatilization of 1-butanol can be neglected during the bubble aeration processes according to the blank test.

## Experimental instrumentation and procedures

The airtight reactor of 17.2 cm inside diameter is made of Pyrex glass with an effective volume of 5.5 L, and equipped with water jacket to maintain a constant solution temperature at 25 °C in all experiments. The design of reactor was based on the criteria of the shape factors of a standard six-blade turbine [14]. The gas diffuser in cylindrical shape with pore size of 10 μm was located at the bottom of reactor. About 3.705 L solution was used in each experiment, while the total sampling volumes were within 5% of solution.

The stirred speed was as high as 800 rpm to ensure the complete mixing of liquid and gas phases according to previous tests [15].

Table 1. Summary of mass transfer properties at various superficial gas velocities ($u_{G0}$) for NAP bubble aeration.

| | $u_{G0}$ (mm/s) | | | correlation | $r^2$ |
|---|---|---|---|---|---|
| | 2.21 | 1.17 | 0.577 | | |
| $\varepsilon_G$ (-) | 0.0383 | 0.0339 | 0.0300 | $\varepsilon_G = 0.0331\ u_{G0}^{0.182}$ | 0.999 |
| $K^0_{LB}\ a_e^*$ ($s^{-1}$) | 0.00556 | 0.00266 | 0.00140 | $K^0_{LB}\ a_e^* = 2.39\times10^{-3}\ u_{G0}^{1.03}$ | 0.995 |
| $K^0_{LB}\ a_e$ ($s^{-1}$) | 0.000290 | 0.000128 | 0.0000707 | $K^0_{LB}\ a_e = 1.20\times10^{-4}\ u_{G0}^{1.05}$ | 0.985 |

* The values were obtained based on Eq. (7).

The values were obtained based on Eq. (10).

The stripping gas composed of pure oxygen from the oxygen cylinder was introduced into the reactor with various gas flow rates. The relative gas holdup ($\varepsilon_G$) is estimated by the volume-expanding method employing $\varepsilon_G = V_H / (V_H + V_L)$ while the gas stream starts. Samples were drawn out from the reactor at desired time intervals in the course of experiments. The residual concentrations of NAP were analyzed using the UV-spectrophotometer system at 276.3 nm (model UV/Visible Cintra 20 spectrometer, GBC, Dandenong, VIC, Australia). The injection volume of sample solution was 3-5 mL.

## RESULTS AND DISCUSSION

### Bubble Aeration of VOC in Semibatch Stirred Tank

The present model of Eq. (7) was applied to simulate the bubble aeration processes of NAP of this work and toluene of Dahlan et al. [6]. The variations of residual VOC concentration ($\theta_{BLb}$) in the solution were measured and compared with the prediction. Furthermore, the VOC concentrations in the holdup ($\theta_{BGi}$) and off ($\theta_{BGe}$) gases were predicted simultaneously. The values of relative gas holdup ($\varepsilon_G$) for the bubble aeration processes of NAP with various superficial gas velocities ($u_{G0}$) were estimated and listed in Table 1. Accordingly, the curves of the residual VOC concentration ($\theta_{BLb}$) variation can be well predicted based on Eq. (7) with the proper values of $K^0_{LB}\ a_e$ as shown in Fig. 1a. On the other hand, the values of $K^0_{LB}\ a_e$ were also estimated by Eq. (10) as listed in Table 1. Note that the determined parameters (such like $K^0_{LB}\ a_e$ and $\varepsilon_G$) from the laboratory equipment can be used to predict those in the plant scale based on geometrical, dynamic, and kinematic similarity [14]. It should be noted that the value of $K^0_{LB}\ a_e$ determined by Eq. (7) was about twenty times higher than that determined by Eq. (10). The difference was resulted from the negligence of the $\theta_{BGi}$ value in application of Eq. (10). In fact, the values of $\theta_{BGi}$ during the bubble aeration processes as predicted and shown in Fig. 1b should not be neglected compared with those of $\theta_{BLb}$. As a result in application of Eq. (10), the value of $K^0_{LB}\ a_e$ would be underestimated while the driving force of VOC concentration difference for the calculation of gas–liquid mass transfer rate was taken as $\theta_{BLb}$ instead of ($\theta_{BLb} - \theta_{BGi}$).

For the further verification, the bubble aeration process of toluene performed by Dahlan et al. [6] was studied. A set of their experimental conditions were : $C_{BLb0} = 500$ mg/L, $Q_G = 0.12$ L/min, $V_L = 0.4$ L, $V_H + V_F = 0.1$ L and T = 20 °C. Other data needed for simulation were obtained as follows. The $H_B$ value of toluene was reported as 0.237 [9]. The value of $V_H$ was assumed as 0.0147 L with $\varepsilon_G = 0.0356$, while the $\varepsilon_G$ within the range of 0.003 – 0.1 was tested of being insensitive to the predicted results. Accordingly, the satisfactory fitting of the data with Eq. (7) can be obtained with $K^0_{LB}\ a_e = 0.00513\ s^{-1}$ as shown in Fig. 2. On the other hand, the prediction of $\theta_{BLb}$ and $\theta_{BGe}$ would be overestimated by Eq. (7) if one used $K^0_{LB}\ a_e$ of $0.000855\ s^{-1}$ determined according to Eq. (10) (Fig. 2). Obviously, the application of Eq. (10) to estimate $K^0_{LB}\ a_e$ was not adequate because the values of $\theta_{BGe}$ compared with $\theta_{BLb}$ were noticeable. Moreover, $K^0_{LB}\ a_e$ also can be estimated by that of the reference compound (like $O_2$) or from the correlations. Certainly, the value of $K^0_{LB}\ a_e$ obtained by fitting the experimental data directly would be more accurate. It may be noted that the VOC concentration in the gas phase still need to be considered in the simulation, otherwise, the $C_{BLb}$ would be underestimated with the correlated $K^0_{LB}\ a_e$ value.

Comparing the profiles of $\theta_{BGi}$ and $\theta_{BGe}$ in Figs. 1b and 1c, the peaks of $\theta_{BGe}$ appeared later with values lower than those of $\theta_{BGi}$ due to the delayed effect of the free space. The maximal values of $\theta_{BGi}$ and $\theta_{BGe}$ as 0.95 and 0.91 spread from 1 to 200 and 100 to 1000 seconds, respectively. The peak of $\theta_{BGe}$ occurred earlier with higher gas flow rate as depicted in Fig. 1c. The delayed time would be increased with large volume of free space and low gas flow rate.

### Effect of Henry's Constant of VOC on Bubble Aeration

The variations of $\theta_{BLb}$ as the function of $H_B$ and $K^0_{LB}\ a_e t$ are shown in Fig. 3, while the other conditions are the same as case 1 in Fig. 1. The VOCs with small $H_B$ value require long bubble aeration time to achieve high removal efficiency. On the other hand, the $\theta_{BLb}$ value would decrease scarcely as the $H_B$ value increased from 10 to 100. The reason can be further illustrated by Fig. 4, which shows the variations of

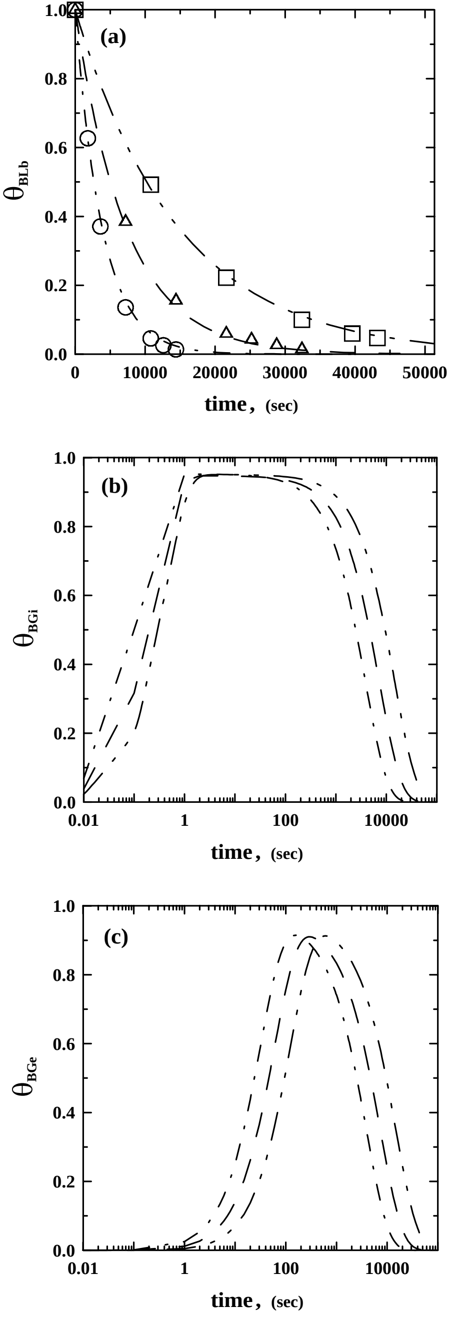

Fig. 1. Variations of VOC concentrations with time for NAP bubble aeration in semibatch stirred tank. $V_L$ = 3.705 L, $H_B$ = 0.0197, T = 25 °C. Symbols: experiments of this work; lines: prediction based on Eq. (7). ○ and— · —, △ and — —, □ and —· ·—, cases of 1, 2, 3. Case 1: $C_{BLb0}$ = 35.2 mg/L, $K^0_{LB}a_e$ = 0.00556 $s^{-1}$, $Q_G$ = 3.07 L/min, $u_{G0}$ = 2.21 mm/s, $V_F$ = 1.65 L, $V_H$ = 0.147 L. Case 2: $C_{BLb0}$ = 31.5 mg/L, $K^0_{LB}a_e$ = 0.00266 $s^{-1}$, $Q_G$ = 1.63 L/min, $u_{G0}$ = 1.17 mm/s, $V_F$ = 1.66 L, $V_H$ = 0.130 L. Case 3: $C_{BLb0}$ = 30.2 mg/L, $K^0_{LB}a_e$ = 0.00140 $s^{-1}$, $Q_G$ = 0.805 L/min, $u_{G0}$ = 0.577 mm/s, $V_F$ = 1.68 L, $V_H$ = 0.115 L. (a) $\theta_{BLb}$, (b) $\theta_{BGi}$, and (c) $\theta_{BGe}$.

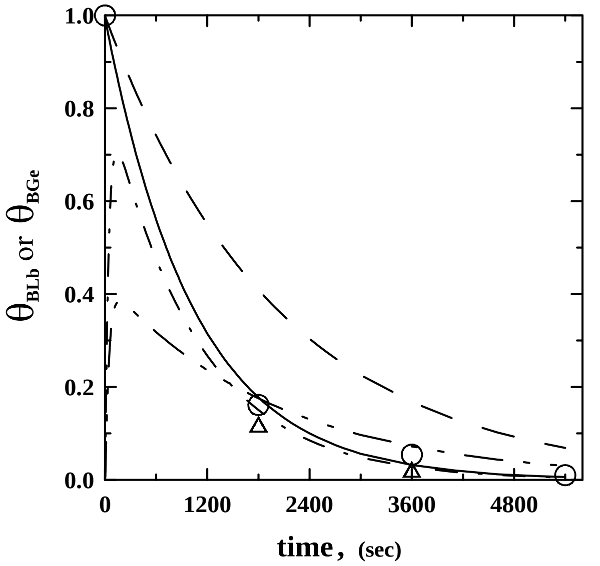

Fig. 2. Variations of $\theta_{BLb}$ and $\theta_{BGe}$ with time for toluene bubble aeration in semibatch stirred tank. $C_{BLb0}$ = 500 mg/L, $H_B$ = 0.237, $Q_G$ = 0.12 L/min, T = 20 °C, $V_F$ = 0.0853 L, $V_H$ = 0.0147 L, $V_L$ = 0.4 L. Symbols: experiments of Dahlan at al. (1999); lines: prediction based on Eq. (7). ○, △ : $\theta_{BLb}$, $\theta_{BGe}$, ——, — · —: $\theta_{BLb}$, $\theta_{BGe}$ with $K^0_{LB}a_e$ = 0.00513 $s^{-1}$. — —, —· ·—: $\theta_{BLb}$, $\theta_{BGe}$ with $K^0_{LB}a_e$ = 0.000855 $s^{-1}$.

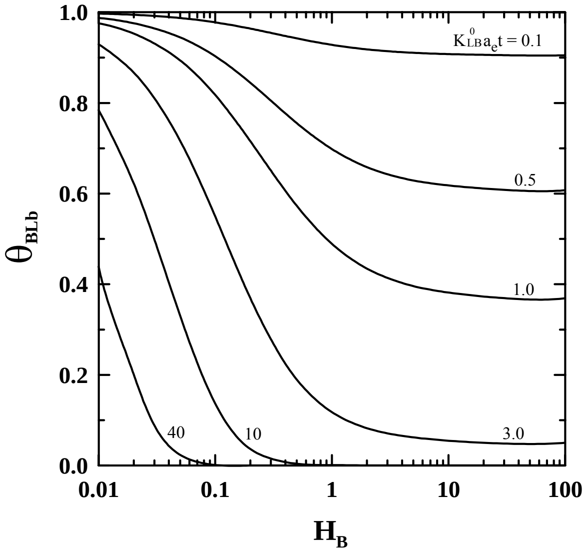

Fig. 3. Variations of $\theta_{BLb}$ with $H_B$ at various $K^0_{LB}a_e t$ for bubble aeration in semibatch stirred tank. Lines: prediction. The other conditions are the same as case 1 in Fig. 1.

$\theta_{BGi}$ with $K^0_{LB}$ $a_e t$ at various values of $H_B$. In the regime of $H_B < 1$, the inclusion of $\theta_{BGi}$ value [= $C_{BGi}/(C_{BLb0}H_B)$] is essential to estimate the gas–liquid mass transfer rate and apparently affected by the value of $H_B$. By contrast, the values of $\theta_{BGi}$ compared with those of $\theta_{BLb}$ would be insignificant while $H_B > 10$. Accordingly, one could estimate the main limiting factor of VOC gas–liquid mass transfer is the equilibrium condition in the regime of $H_B$ smaller than 1. However, the main limiting factor of VOC gas–liquid mass transfer would be the bubble aeration kinetics if the $H_B$ value is greater than 10. The statement can help to elucidate the results of Koziel et al. [16], who studied the emissions of five volatile chemicals with different $H_B$ values along small sewer reaches.

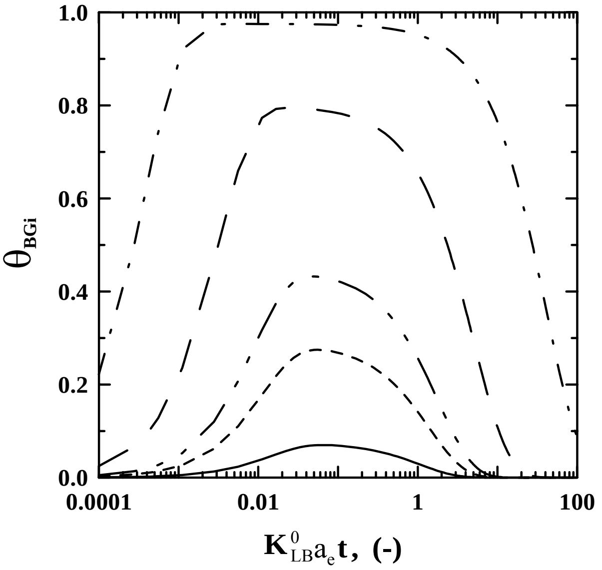

Fig. 4. Variations of $\theta_{BGi}$ with $K^0_{LB}a_e t$ at various values of $H_B$ for bubble aeration in semibatch stirred tank. The other conditions are the same as case 1 in Fig. 1. Lines: prediction. — · —, — —, —· · —, --- and —— : $H_B$ = 0.01, 0.1, 0.5, 1.0 and 5.0.

Moreover, the volatilization of 1-butanol that has very small $H_B$ value of 0.00046 also could be demonstrated negligible according to Fig. 3. Further, it should be remarked that the assumption of Eq. (10) is only practicable under the condition of Henry's constant value greater than 10 such as the deoxygenating process. Note that the values of $H_B$ for most VOCs are smaller than 1 [11]. Consequently, the variations of both VOC concentrations in gas and liquid phases should be considered simultaneously for the modeling of bubble aeration processes as demonstrated in this study.

## Simulation of Continuous Bubble Aeration Processes

To show the effects of operating parameters on the performance in the continuous bubble aeration system, the concerned variables at steady state with various levels of $Q_L$, $H_B$ and $Q_G$ are investigated respectively. The basic conditions are the same as case 1 in Fig. 1 and $Q_L$ = 0.124 L/min ($t_L$ = 30 min). After the introduction of stripping gas, the value of $\theta_{BLb}$ would decrease with time monotonically until reaching the steady state value ($\theta_{BLb,ss}$). The value of $\theta_{BGi}$ increased to the maximum value ($\theta_{BGi,max}$) in a short time denoted as $t_{max}$, then decreased to approach the steady state value ($\theta_{BGi,ss}$). The driving force of VOC stripping expressed as concentration difference of $\theta_{BLb} - \theta_{BGi}$ had the initial value of unit and decreased with time to reach the constant value of $Q_L(1 - \theta_{BLb,ss})/(K^0_{LB} a_e V_L)$.

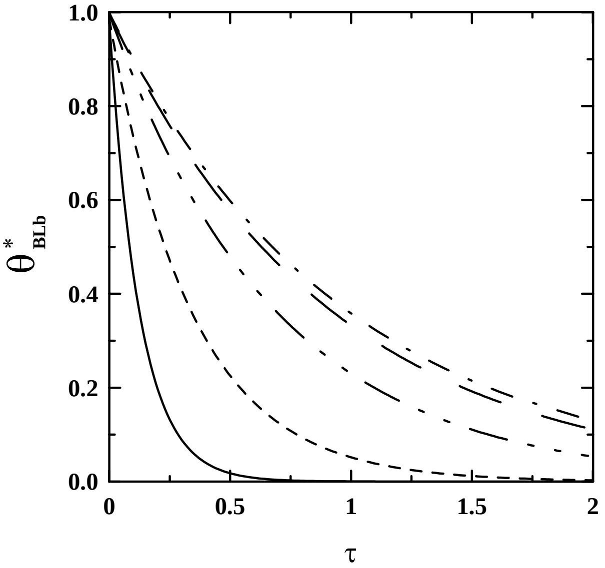

Fig. 5. Variations of $\theta^*_{BLb}$ with τ at various values of $H_B$ for bubble aeration in continuous stirred tank. $Q_L$ = 0.124 L/min. The other conditions are the same as case 1 in Fig. 1. Lines: prediction. — · —, — —, —· ·—, - - and ——: $H_B$ = 0.001, 0.004, 0.0197, 0.1 and 1.0.

As the $Q_L$ increased, the values of $\theta_{BLb,ss}$, $\theta_{BGi,ss}$ and $t_{max}$ increased while the $\theta_{BGi,max}$ remained constant. It means that the removal efficiency of VOC (= 1 – $\theta_{BLb}$) decreased as the $Q_L$ increased, although the rate of gas–liquid mass transfer (= $Q_L C_{BLb0}(1 - \theta_{BLb})$) may increase. Regarding the variation of $H_B$, it remarkably affects all system variables. The values of $\theta_{BLb,ss}$, $\theta_{BGi,ss}$ and $\theta_{BGi,max}$ decreased while the $t_{max}$ increased as the $H_B$ value became larger. The results of the predicted tendency are consistent with the studies of Namkung and Rittmann [9] and Bell et al. [17] who compared the bubble aeration removal efficiencies of different VOCs in full-scale wastewater treatment plants. Accordingly, the volatility of VOC is an important factor for assessing the treatment efficiency of a bubble aeration system. In addition, the values of $\theta_{BLb,ss}$, $\theta_{BGi,ss}$ and $t_{max}$ decreased while the $\theta_{BGi,max}$

varied slightly as the $Q_G$ increased. Consequently, high $Q_G/Q_L$ ratio and $H_B$ value would enhance the removal efficiency of VOCs in a bubble aeration process.

In addition, the effects of the above parameters on the time required for the establishment of steady state were further examined. It was found that the bubble aeration processes reached steady state faster with higher values of $H_B$ and $Q_G$. For instance, the variation of $\theta^*_{BLb}$ [$= (C_{BLb} - C_{BLb,ss})/(C_{BLb0} - C_{BLb,ss})$], which has the initial value of unit and the steady state value of zero, with $\tau$ at various values of $H_B$ are shown in Fig. 5. The value of $\theta^*_{BLb}$ with lower $H_B$ value took longer time to reach zero. The processes under the conditions of this study were allowed to stabilize for about 1 to 4 hydraulic retention times ($t_L$) after the gas was introduced. Therefore, the time required for reaching the steady state need to be considered. The concentrations of VOCs in both gas and liquid phases are greater than the expected values (steady state values) during the transient period. That may cause the problems on the surrounding environment and treating quality. It could be designed to shorten the time required to reach the steady state for the bubble aeration processes based on the present model. The validity of the present model cases has been confirmed with the data of this work and Dahlan et al. [6]. As for a further comparison of the model prediction with experimental data, some further experiments of bubble aeration about $\theta_{BGe}$ measurement would be helpful.

## CONCLUSIONS

The present bubble aeration model is useful to predict the dynamic variations of volatile organic compound (VOC) concentrations in the gas and liquid phases from the beginning to steady state. Moreover, the model can be applied to better understand the properties of system parameters in a bubble aeration process.

1. After the gas was introduced, the residual concentration of VOC in the liquid phase decreases monotonically with time, while the concentration of VOC in gas holdup increases to a maximum value in a short time and then decreases with time. The peak concentration of VOC in the off-gas appears later with value lower than that in the gas holdup due to the delayed effect.
2. The gas concentration of VOC should not be neglected for calculating the gas–liquid mass transfer rate. The main limiting factor of VOC mass transfer in the regime of $H_B$ smaller than 1 would be the equilibrium condition. For the regime of $H_B$ greater than 10, the main limiting factor of VOC mass transfer is the bubble aeration kinetics.
3. The bubble aeration system with higher values of $Q_G/Q_L$ and $H_B$ is favorable for the removal of VOC. Furthermore, the time required for the establishment of steady state decreases with increased values of $H_B$ and $Q_G$. The continuous bubble aeration processes are allowed to stabilize for about 1 to 4 hydraulic retention times in this study.

## NOMENCULTURE

The following symbols are used in this paper:

| | |
|---|---|
| $a_e$ | specific gas–liquid interfacial area based on the volume of liquid (1/m) |
| $a_1$ to $a_6$ | system constants defined in Eq. (9) |
| $C_{BGi}$<br>$C_{BGi0}$ | gas concentrations of VOC of holdup and inlet gases (M or mg/L) |
| $C_{BGe}$ | gas concentration of VOC in free volume (M or mg/L) |
| $C_{BLb}$ | liquid concentration of VOC in bulk liquid (M or mg/L) |
| $C_{BLb,ss}$ | steady state value of $C_{BLb}$ (M or mg/L) |
| $C_{BLb0}$ | initial or inlet concentration of VOC in bulk liquid (M or mg/L) |
| $c_1$ to $c_7$ | system constants defined in Eq. (9) |
| $K^0_{LB}$ | overall mass transfer coefficient of VOC (m/s) |
| $k^0_{GB}$, $k^0_{LB}$ | gas and liquid mass transfer coefficients of VOC (m/s) |
| $H_B$ | Henry's constant of VOC (M M$^{-1}$),<br>$= C_{BGi}/C_{BLb}$ at equilibrium |
| $m_B$ | gas–liquid mass transfer rate of VOC (mole/s or mg/s) |
| NAP | naphthalene |
| $Q_G$ | gas flow rate (L/s or L/min) |
| $Q_L$ | liquid flow rate (L/s or L/min) |
| $r^2$ | correlation coefficient |
| t | time (s) |
| $t_{max}$ | time for $\theta_{BGi,max}$ (s) |
| $t_L$ | hydraulic retention time,<br>$= V_L/Q_L$ (s or min) |
| T | temperature (℃) |
| $u_{G0}$ | superficial gas velocity (mm/s) |
| $V_F$ | volume of free space (L) |
| $V_H$ | volume of gas holdup (L) |
| $V_L$ | volume of liquid (L) |
| $x_1$, $x_2$ | system constants defined in Eq. (9) |
| $\varepsilon_G$ | relative gas holdup, $= V_H/(V_L + V_H)$ |
| $\theta_{BGi}$ | dimensionless gas concentration of VOC in gas holdup, $= C_{BGi}/(C_{BLb0}H_B)$ |
| $\theta_{BGi,max}$ | maximum value of $\theta_{BGi}$ |
| $\theta_{BGi,ss}$ | steady state value of $\theta_{BGi}$ |
| $\theta_{BGe}$ | dimensionless gas concentration of VOC in free volume,<br>$= C_{BGe}/(C_{BLb0}H_B)$ |

| | |
|---|---|
| $\theta_{BLb}$ | dimensionless liquid concentration of VOC in bulk liquid, = $C_{BLb}/C_{BLb0}$ |
| $\theta_{BLb,ss}$ | steady state value of $\theta_{BLb}$ |
| $\theta^*_{BLb}$ | $(C_{BLb} - C_{BLb,ss})/(C_{BLb0} - C_{BLb,ss})$ |
| $\tau$ | dimensionless time, = $t/t_L$ |

## REFERENCES

1. Suschka, J., B. Mrowiec and G. Kuszmider, "Volatile Organic Compounds (VOC) at Some Sewage Treatment Plants in Poland," *Water Sci. Technol.*, 33(12), 273–276 (1996).
2. Speece, R. E., N. Nirmalakhandan and Y. H. Lee, "Nomograph for Air Stripping of VOC from Water," *J. Environ. Eng.*, 113(2), 434–443 (1987).
3. Dvorak, B. I., C. J. Herbeck, C. P. Meurer, D. F. Lawler and G. E. Jr. Speitel, "Selection among Aqueous and Off–gas Treatment Technologies for Synthetic Organic Chemicals," *J. Environ. Eng.*, 122(7), 571–580 (1996).
4. Wark, K., C. F. Warner and W. T. Davis, *Air Pollution Its Original and Control*, 3rd Ed., Addison Wesley Longman, Inc., Menlo Park, CA, USA (1998).
5. Truong, K. N. and J. W. Blackburn, "The Stripping of Organic Chemicals in Biological Treatment Process," *Environ. Progress*, 3, 143–152 (1984).
6. Dahlan, M. H., X. H. Xing, Y. Yoshikawa and K. Matsumoto, "Analysis of a Simple Biodegradation Process for the Removal of Volatile Organic Chemicals for Wastewater based on a Gas Stripping Principle," *J. Biosci. Bioeng.*, 87(4), 519–524 (1999).
7. Matter-müller, C., W. Gujer and W. Giger, "Transfer of Volatile Substance form Water to the Atmosphere," *Water Research*, 15, 1271–1279 (1981).
8. Robert, P. V., C. Munz and P. Dändliker, "Modeling Volatile Organic Solute Removal by Surface and Bubble Aeration," *J. Water Pollut. Control Fed.*, 56(2), 157-163 (1984).
9. Namkung, E. and B. R. Rittmann, "Estimating Volatile Organic Compound Emission from Publicly Owned Treatment Works," *J. Water Pollut. Control Fed.*, 59(7), 670–678 (1987).
10. Danckwerts, P. V., *Gas–liquid reactions*, 1st Ed., McGraw-Hill, New York, NY, USA, 1970.
11. Schwarzenbach, R. P., P. M. Gschwend and D. M. Imboden, *Environmental Organic Chemistry*, 1st Ed., John Wiley and Sons, New York, NY, USA (1993).
12. Munz, C. and P. V. Roberts, "Gas– and Liquid-phase Mass Transfer Resistance of Organic Compounds during Mechanical Surface Aeration," *Water Research*, 23(5), 589–601 (1989).
13. Kaštánek F., J. Zahradník, J. Kratochvíl and J. Čermák, *Chemical Reactors for Gas-liquid Systems*. 1st Ed., Ellis Horwood, New York, NY, UAS (1993).
14. McCabe, W. L., J. C. Smith and P. Harriott, *Unit Operations of Chemical Engineering*, 5th Ed., McGraw-Hill, New York, NY, USA (1993).
15. Chang, C. Y., Y. H. Chen, H. Li, C. Y. Chiu, Y. H. Yu, P. C. Chiang, Y. Ku and J. N. Chen, "Kinetics of Decomposition of Polyethylene Glycol in Electroplating Solution by Ozonation with UV Radiation," *J. Environ. Eng.*, 127(10), 908–915 (2001).
16. Koziel, J. A., R. L. Corsi and D. F. Lawler, "Gas–liquid Mass Transfer along Small Sewer Reaches," *J. Environ. Eng.*, 127(5), 430–437 (2001).
17. Bell, J., H. Melcer, H. Monteith, I. Osinga and P. Steel, "Stripping of Volatile Organic Compounds at Full-scale Municipal Wastewater Treatment Plants," *Water Environ. Research*, 65, 708–716 (1993).

---

Discussions of this paper may appear in the discussion section of a future issue. All discussions should be submitted to the Editor-in-chief within six months.

***Manuscript Received: August 12, 2004***
***Revision Received: November 5, 2004***
***and Accepted: November 12, 2004***

# 揮發性有機化合物之氣泡曝氣動態模式

陳奕宏[1] 謝哲隆[2] 張慶源[1,*] 陳庚鴻[1] 張瓊芬[3] 邱求三[2] 邱浚祐[4] 蘇維翎[1] 蔣本基[1]

[1]國立台灣大學環境工程學研究所
[2]國立宜蘭大學環境工程系
[3]東海大學環境科學系
[4]蘭陽技術學院環境工程系

關鍵詞：氣泡曝氣、揮發性有機化合物、動態模式、質量傳送、水處理

## 摘　要

本研究提出一動態模式來預測氣、液相中揮發性有機化合物，在氣泡曝氣程序中的濃度變化。當氣泡曝氣程序開始時，氣體被導入及分散於含有揮發性有機化合物的水溶液，揮發性有機化合物會從液相傳輸至氣相，因此氣相與液相的揮發性有機化合物濃度會隨著曝氣時間變化，揮發性有機化合物的去除效率與化合物之亨利常數、氣液流量、與氣液質量傳送特性有關。先前的氣泡曝氣模式大多忽略氣相中揮發性有機化合物濃度的影響，而在估算氣液質傳係數( $K^{0}_{LB}\,a_e$)與揮發性有機化合物濃度時會造成顯著誤差。此外，大多氣泡曝氣模式都只適用於穩定狀態，氣泡曝氣操作初期的濃度變化與達到穩定態所需的時間就無法估算。另外，對於排氣部分需考慮曝氣槽上方空間造成之延遲效應。本研究之動態模式應用三個控制方程式去描述液相、氣泡中、及槽中上方空間的揮發性有機化合物濃度，並提出一解析解可以很容易應用於描述連續流或半批次式的氣泡曝氣系統。結果顯示奈在含有丁醇的水溶液之曝氣實驗與本模式之預測結果有良好的符合度，另外也將模式應用於模擬文獻中含甲苯水溶液之曝氣程序，並探討曝氣系統的相關參數對於氣泡曝氣程序效率之影響。故本研究模式可以用於預測與描述揮發性有機化合物之氣泡曝氣程序。