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Ozone Mass Transfer with Combined Effects of Ozone Decomposition and Reaction with Pollutants in a Semibatch Stirred Vessel

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Abstract—The mathematical models for a semibatch stirred gas-liquid contactor proposed by Anselmi et al. (1984, 1985) are extended to described the mass transfer of ozone absorption, decomposition and reaction with pollutants in aqueous solution with the decomposition and reaction rate expressions of general reaction orders (not necessarily integers) taking into consideration the effects of ozone decomposition and reactions on absorption. Four system equations are employed to describe the ozone (A) concentrations in the bulk liquid (C_{ALb}), the hold-up gas (C_{AGi}), and the outlet gas in the free volume above the liquid surface (C_{AGe}), and the pollutant (B) concentration in the bulk liquid (C_{BTLb}), respectively. The combined effects of ozone decomposition and reaction with pollutant on the mass transfer, which are reflected by the enhancement factor (E_r) defined as the ratio of mass absorbed per unit area in time t with chemical reactions to that without chemical reactions or of the purely physical absorption, are considered in the refined model. Furthermore, the model also takes into account the variation of E_r with C_{ALb} and C_{BTLb}, which vary with time during the course of gas-liquid contacting. Comparison of the predicted values of concentrations of the proposed model in simplified form with the experimental data of Anselmi et al. (1985) indicates good agreement. For ozonation systems with high reaction rates (for example, ozonation of o-cresol investigated by Beltran et al. (1990)), the enhancement factors are large and cause significant influence on the mass transfer of the ozone and pollutant.

Key Words : Ozone, Ozonation, Mass transfer, Enhancement factor

INTRODUCTION

Ozonation has been widely applied for the treatment of pollutants in water/wastewater treatment processes (Chen et al., 2002). Ozone mass transfer is of importance for the ozone utilization in a semibatch stirred gas-liquid contactor (Yocum, 1979; Anselmi et al., 1984). For such a semibatch stirred vessel, the model of Anselmi et al. (1984) has been extended to describe the mass transfer of ozone absorption with decomposition in the aqueous solution with a three-equation model by Chiu et al. (1997). The three-equation model described the variations of the ozone (A) concentrations in the bulk liquid (C_{ALb}), the hold-up gas (C_{AGi}), and the outlet gas in the free volume above the liquid surface (C_{AGe}), respectively. The effect of ozone decomposition on the mass transfer, which is reflected by E_r defined as the ratio of mass absorbed per unit area in time t with chemical reactions to that without chemical reactions or of the purely physical absorption (Danckwerts, 1970), was considered in the refined model. The inclusion of E_r helps the description of the mass transfer in combination with different reactions. The value of E_r

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increases with ozonation reaction rate, and changes continuously during ozone absorption. No such refined model has been available for the ozonation with pollutants.

An important feature of ozonation is the existence of two different reaction pathways. Ozone reacts directly with the pollutants or can produce highly reactive free radicals such as hydroxyl, hydroperoxyl, and other radicals, by ozone self-decomposition in aqueous solution, which then vigorously react with pollutants. Therefore, the combined effects of ozone and free radicals on the oxidation of pollutant must be considered in an ozonation system.

The model of Chiu et al. (1997) for ozone absorption with decomposition in a semibatch stirred gas-liquid contactor employed the ozone decomposition rate expression of general reaction orders (not necessarily integers). The model can be applicable for other kinetic expressions of ozone decomposition reported by many investigators (Weiss, 1935; Sheffer and Esterson, 1982; Sotelo et al., 1987; Nadezhdin, 1988; Farooq and Ahmed, 1989; Mehta et al., 1989; Ku et al., 1996). The present study extends the model of Chiu et al. (1997) to include the reaction of ozone with pollutants. In view of the works of Anselmi et al. (1985), Beltran et al. (1990), and Chang et al. (2001), the applicable overall rate expressions of ozone decomposition and reaction with pollutant (B) take the general form:

$$-\mathrm{d}[\mathrm{O_3}]/\mathrm{d}t = k_{Am}[\mathrm{O_3}]^m + k_{Bn}[\mathrm{O_3}]^n + k_R[\mathrm{O_3}]^a[B]^b, \qquad (1)$$

$$-\mathrm{d}[B]/\mathrm{d}t = \beta k_R[\mathrm{O_3}]^a[B]^b. \qquad (2)$$

In Eqs. (1) and (2), k_{Am}, k_{Bn} and k_R represent the acidic and basic decomposition reaction rate constants, and overall ozonation reaction rate constant, respectively. The exponents m, n, a and b represent the reaction orders of the acidic and basic decomposition reactions with respect to O_3, and of the ozonation reaction with respect to O_3 and pollutant B. The β is the stoichiometric coefficient of the ozonation reaction. Furthermore, the present model also takes into account the variation of E_r with the concentrations of ozone and pollutants in the bulk liquid solution, which vary with time during the course of gas-liquid contacting. All these factors would have to be taken into consideration for properly modeling the ozone mass transfer with combined effects of ozone decomposition and reaction with pollutants in a semibatch stirred vessel.

Based on the above review, the present model is more appropriate than the usual models based on the assumption of constant C_{AGi} such as $C_{AGi} = C_{AGi}^0$ (for example, those of Gurol and Singer (1982), Huang and Shu (1995), Kageyama et al. (1996)). In fact, the difference between C_{AGi} and C_{AGi}^0 is enlarged with the mass transfer and ozonation reaction rates. Consequently, the variation of C_{AGi} should be considered for describing the ozonation systems in a stirred vessel of high ozonation rate and mass transfer coefficient. In addition, the effect of ozonation reactions on the mass transfer or the differentiation between the purely physical (k_L^0) and the chemical (k_L) mass transfer coefficients was also neglected in the usual models of Gurol and Singer (1982, 1983), Anselmi et al. (1985), Ikemizu et al. (1987), Huang and Sue (1995), and Kageyama et al. (1996). Moreover, most models except that of Anselmi et al. (1985) did not distinguish the difference between the gas concentrations of hold up (C_{AGi}) and free volume (C_{AGe}). The concentration commonly measured is C_{AGe}, since the measurement of C_{AGi} is very difficult if not impossible. Thus, for describing the concentration profiles of ozone and pollutants accurately, the refined model of this study is more adequate.

THEORETICAL ANALYSIS

Consider the mass transfer of ozone absorption, decomposition and reaction with pollutants in a semibatch stirred gas-liquid contactor with the reaction rate expressions of the general form as Eqs. (1) and (2). Referring to the work of Anselmi et al. (1984) which indicated that, owing to mechanical mixing, bubbles circulate in the reaction vessel randomly and break and coalesce continuously, one may assume that the liquid phase as well as gas phase are perfectly mixed as in continuous stirred tank reactors. Thus, the system equations in dimensionless forms describing the concentrations of ozone (A) in the bulk liquid (C_{ALb}), the hold-up gas (C_{AGi}), and the outlet gas in free volume above the liquid surface (C_{AGe}), and the pollutant (B) concentration in the bulk liquid (C_{BTLb}), which are derived from the mass balance and the absorption equilibrium, are as follows.

For ozone balance in liquid phase:

$$\underbrace{\mathrm{d}\theta_{ALb}/\mathrm{d}\tau}_{\text{rate of variation of dissolved } A} = \underbrace{E_r(\theta_{AH}-\theta_{ALb})}_{\text{rate of } A \text{ gained from gas-liquid mass transfer}} - \underbrace{[(m+1)/2]\,Sh\,M_{Am}\theta_{ALb}^{\,m}}_{\text{rate of } A \text{ lost by acidic decomposition reaction}}$$

$$-\underbrace{[(n+1)/2]\,Sh\,M_{Bn}\theta_{ALb}^{\,n}}_{\text{rate of } A \text{ lost by basic decomposition reaction}} - \underbrace{[(a+1)/2]\,Sh\,M_R\theta_{ALb}^{\,a}\,\theta_{BTLb}^{\,b}}_{\text{rate of } A \text{ consumed by ozonation reaction with } B}, \qquad (3)$$

For pollutant balance in liquid phase:

$$\underbrace{\mathrm{d}\theta_{BTLb}/\mathrm{d}\tau}_{\text{rate of variation of } B} = \underbrace{-\beta[(a+1)/2]\,Sh\,M_R\theta_{ALb}^{\,a}\,\theta_{BTLb}^{\,b}/k_q}_{\text{rate of } B \text{ removed by ozonation reaction with } A}, \qquad (4)$$

For ozone balance in holdup gas:

$$\underset{\text{rate of variation of } A \text{ in holdup gas}}{\mathrm{d}\theta_{AH}/\mathrm{d}\tau} = \underset{\text{rate of } A \text{ gained in holdup gas by convection}}{[Q_G V_L/(k_L^0 S_{GL} V_H)](1-\theta_{AH})}$$

$$\underset{\text{rate of } A \text{ lost in holdup gas by gas-liquid mass transfer}}{-[V_L/(He V_H)]\, E_r(\theta_{AH}-\theta_{ALb})}. \quad (5)$$

For ozone balance in free volume:

$$\underset{\text{rate of variation of } A \text{ in free volume}}{\mathrm{d}\theta_{AF}/\mathrm{d}\tau} = \underset{\text{rate of } A \text{ gained in free volume by convection}}{[Q_G V_L/(k_L^0 S_{GL} V_F)](\theta_{AH}-\theta_{AF})}. \quad (6)$$

Initial conditions of Eqs. (3)-(6) are:

$$\text{at } \tau = 0,\ \theta_{ALb} = 0,\ \theta_{BTLb} = 1,\ \theta_{AH} = 0,\ \theta_{AF} = 0. \quad (7)$$

The term E_r in the above equations represents the enhancement factor of mass transfer coefficient of absorption contributed by the ozonation reactions.

The system variables and parameters in dimensionless forms are defined as follows. Dimensionless concentrations of ozone in bulk solution, holdup and free volume are: $\theta_{ALb} = C_{ALb}/(C_{AGi}^0/He)$, $\theta_{AH} = C_{AGi}/C_{AGi}^0$, $\theta_{AF} = C_{AGe}/C_{AGi}^0$, where superscript "0" denotes the inlet condition, He = Henry's constant. Dimensionless concentration of pollutant (B) in bulk solution is: $\theta_{BTLb} = C_{BTLb} / C_{BTLb0}$, where subscript "0" denotes the initial condition. Dimensionless reaction rate parameters of the reactions of acidic and basic decompositions of ozone, and ozonation of pollutant are: $M_{Am}=2D_{AL}k_{Am}(C_{AGi}^0/He)^{m-1}/((m+1)(k_L^0)^2)$, $M_{Bn} = 2D_{AL}k_{Bn}(C_{AGi}^0/He)^{n-1}/((n+1)(k_L^0)^2)$, $M_R = 2D_{AL}k_R (C_{AGi}^0/He)^{a-1}C_{BTLb0}^{b}/[(a+1)(k_L^0)^2]$, where reaction rate constants (k_{Am}, k_{Bn}, k_R) and the reaction orders (m, n, a, b) are defined in Eqs. (1) and (2). Dimensionless concentration ratio of pollutant to ozone is: $k_q = C_{BTLb0}/(C_{AGi}^0/He)$. Dimensionless time is: $\tau = k_L^0 S_{GL} t/V_L$. Sherwood number is: $Sh = k_L^0 V_L/(D_{AL}S_{GL})$.

The decomposition and ozonation reactions may affect the mass transfer rate of ozone. The influence is reflected by the enhancement factor E_r in Eqs. (3) and (5). Therefore, it is necessary to evaluate the E_r in advance for solving Eqs. (3)-(7).

According to the film model, one may describe the ozone absorption association with decomposition and ozonation reactions as follows.

$$\underset{\text{diffusion of } A \text{ in liquid film}}{\mathrm{d}^2\theta_{AL}/\mathrm{d}X^{*2}} = \underset{A \text{ lost by acidic decomposition reaction}}{[(m+1)/2]M_{Am}\theta_{AL}^{m}} + \underset{A \text{ lost by basic decomposition reaction}}{[(n+1)/2]M_{Bn}\theta_{AL}^{n}}$$

$$+ \underset{A \text{ consumed by ozonation reaction with } B}{[(a+1)/2]M_R\,\theta_{AL}^{a}\,\theta_{BTL}^{b}}, \quad (8)$$

$$\underset{\text{diffusion of } B \text{ in liquid film}}{\mathrm{d}^2\theta_{BTL}/\mathrm{d}X^{*2}} = \underset{B \text{ removed by ozonation reaction with } A}{\beta\,[(a+1)/2]M_R\theta_{AL}^{a}\,\theta_{BTL}^{b}/(D_{BA}k_q)}. \quad (9)$$

Boundary conditions of Eqs. (8)-(9) are:

$$\text{at}\quad X^* = 0,\ \theta_{AL} = \theta_{AH} = (C_{AGi}/He)/(C_{AGi}^0/He),$$

$$\mathrm{d}\theta_{BTL}/\mathrm{d}X^* = 0, \quad (10)$$

$$X^* = 1,\ \theta_{AL} = \theta_{ALb} = C_{ALb}/(C_{AGi}^0/He),$$

$$\theta_{BTL} = \theta_{BTLb} = C_{BTLb}/C_{BTLb0}, \quad (11)$$

where, $X^* = 0$ represents the gas-liquid (G-L) interface, $X^* = 1$ denotes the position at the edge of liquid film or in the bulk liquid. Equation (10) states that the gas and liquid are in equilibrium and the component B in liquid is not volatile at G-L interface ($X^* = 0$). Equation (11) represents the bulk condition ($X^* = 1$). The G-L mass transfer resistance of ozone is restricted in the liquid film of thickness x_M. Dimensionless concentrations of ozone and pollutant in the liquid film are: $\theta_{AL} = C_{AL}/(C_{AGi}^0/He)$, $\theta_{BTL} = C_{BTL} / C_{BTLb0}$. Dimensionless distance from the G-L interface into the liquid film is: $X^* = x/x_M = x\, k_L^0/D_{AL}$. Liquid diffusivity ratio of pollutant and ozone is: $D_{BA} = D_{BL}/D_{AL}$.

The mass fluxes of absorption of A with and without the chemical reactions, respectively, are :

$$N_{Ar} = -D_{AL}\,(\partial C_{AL}/\partial x)|_{x=0}$$

$$= -k_L^0\,(C_{AGi}^0/He)\,(\partial\theta_{AL}/\partial X^*)|_{X^*=0}. \quad (12)$$

$$N_A = k_L^0\,(C_{AGi}/He - C_{ALb})$$

$$= k_L^0\,(C_{AGi}^0/He)\,(\theta_{AH} - \theta_{ALb}). \quad (13)$$

According to the definition of enhancement factor E_r (Danckwerts, 1970) and combining Eqs. (12) and (13), one then has:

$$E_r = N_{Ar}/N_A = -(\partial\theta_{AL}/\partial X^*)|_{X^*=0}/(\theta_{AH} - \theta_{ALb}). \quad (14)$$

Computing the concentration distributions of ozone (A) and pollutant (B) in the film from Eqs. (8)-(11) by finite difference method to give the value of E_r from Eq. (14) and then solving for Eqs. (3)-(7) by the fourth order Runge-Kutta method, one can obtain the concentrations of A and B at successive absorption times for any specific case.

RESULTS AND DISCUSSION

The present model proposed for the ozonation system employs three chemical reaction forms of ozone as acidic decomposition, basic decomposition, and ozonation with pollutant in general reaction orders of m, n, a and b, respectively. The chemical reactions may affect the mass transfer rate of the ozone absorption process. The influence can be expressed

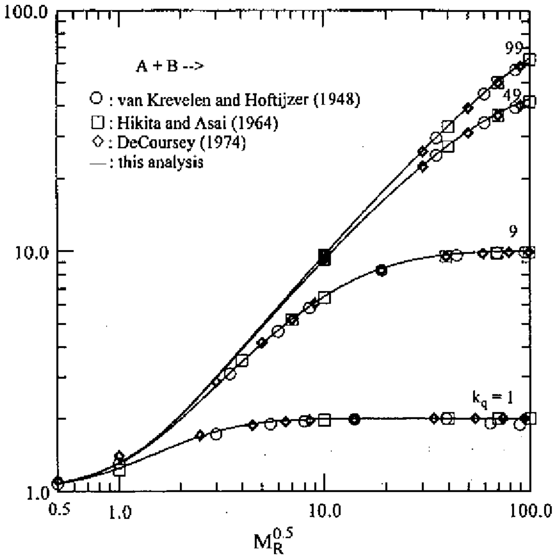

Fig. 1. Comparison of results of E_r vs. $M_R^{0.5}$ of the simplified model of this analysis (——) with those of others (○) van Krevelen and Hoftijzer (1948); (□) Hikita and Asai (1964); (◇) DeCoursey (1974)) at various k_q (= 1, 9, 49, 99) for $\beta = 1$, $M_{Am} = 0$, $M_{Bn} = 0$, $a = b = 1$.

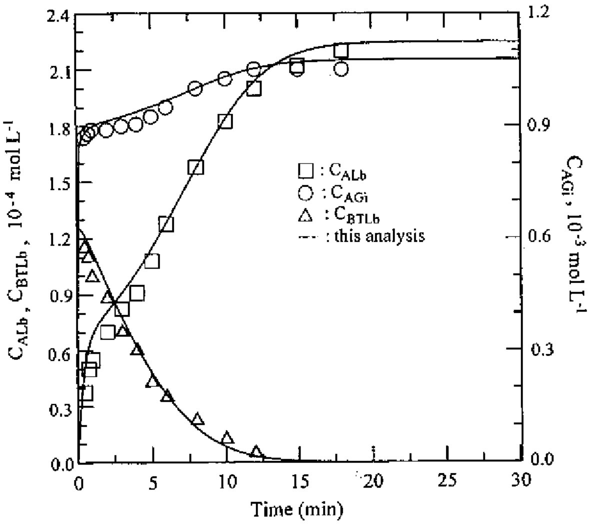

Fig. 2. Variations of ozone (C_{ALb}, C_{AGi}) and BSA (C_{BTLb}) concentrations with ozonation time in a semibatch stirred vessel. (——) : this analysis. (□) C_{ALb}; (○) C_{AGi}; (△) C_{BTLb} : experimental data of Anselmi et al. (1985). Conditions: T = 296 K, Q_G = 40 L·h^{-1}, N_r = 400 rpm, V_L = 1 L, V_H = 0.025 L, V_F = 0.075 L, He = 4.48, k_L^0 = 0.024 cm·s^{-1}, S_{GL} = 700 cm^2, C_{BTLb0} = 1.26×10^{-4} M, C_{AGi}^0 = 1.10×10^{-3} M, D_{AL} = 1.734×10^{-5} cm^2·s^{-1}, D_{BL} = 2.0×10^{-5} cm^2·s^{-1}, m = 1, a = b = 1, β = 1/6, k_{Am} = 1.16×10^{-3} s^{-1}, k_{Bn} = 0, k_R = 39 L·mol^{-1}·s^{-1}.

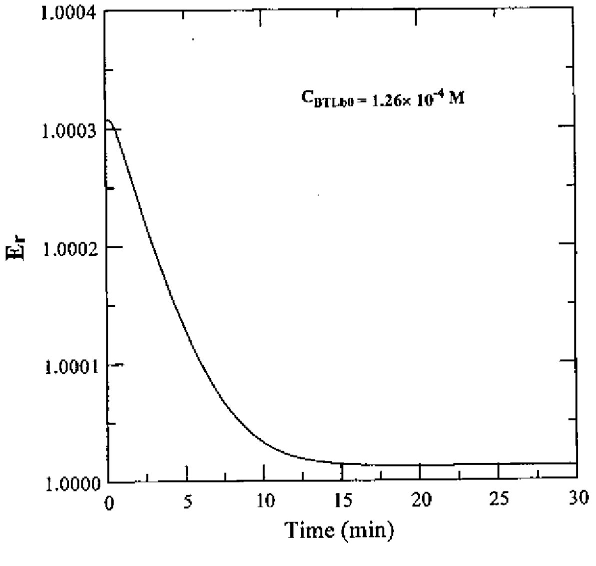

Fig. 3. Variations of enhancement factor (E_r) with ozonation time in a semibatch stirred vessel. The conditions are the same as those in Fig. 2.

in terms of the enhancement factor (E_r). The consideration of these factors and their time variations reveals the distinct contribution of the model.

The accuracy and applicability of this model in evaluating E_r by Eqs. (8)-(11) and (14) would be verified and checked with a number of available models. First, the present model is simplified to simulate the cases of previous studies. For $M_{Am} = 0$, $M_{Bn} = 0$, $a = b = 1$ and $\beta = 1$, as a second order bimolecular chemical reaction, Fig. 1 compares the results of E_r versus $M_R^{0.5}$ of the simplified model of the present analysis employing Eqs. (8)-(11) and (14) with those of others (e.g., van Krevelen and Hoftijzer, 1948; Hikita and Asai, 1964; DeCoursey, 1974) at various k_q values, indicating good agreement. These three previous models, which have the close form solutions based on the film theory (van Krevelen and Hoftijzer, 1948; Hikita and Asai, 1964) and penetration theory (DeCoursey, 1974), respectively, only consider the second order bimolecular chemical reaction. Furthermore, the present model can be reduced to the model proposed by Jhaveri (1969), which is limited to gas adsorption with two chemical reactions. For $M_{Am} = 10$, $M_{Bn} = 0$, $m = 1$, $a = b = 1$ and $\beta = 1$, as parallel chemical reactions, the comparison of the results also shows good agreement. Thus, Eqs. (8)-(11) and (14) of this analysis and the numerical methods employed compare favorably with the existing simple models. Therefore, the present model is more generalized for the ozone adsorption system with chemical reactions.

Figure 2 compares the predicted value of the proposed model employing Eqs. (3)-(11) and (14) to the experimental data of Anselmi et al. (1985) about the ozonation of benzenesulfonic acid (BSA) in a semibatch stirred vessel, also indicating good agreement. The variation of E_r is shown in Fig. 3. It is seen that the effect of chemical reaction on the absorption rate is not significant for the case study of

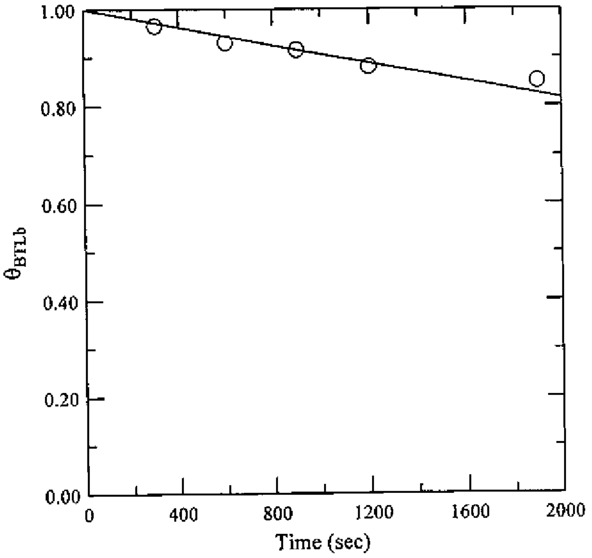

Fig. 4. Variations of o-cresol concentration (θ_{BTLb}) with ozonation time in a semibatch stirred vessel.(—) : this model, (○) : experimental data of Beltran et al. (1990). Conditions: $T = 293$ K, $Q_G = 50$ L·h^{-1}, $N_r = 300$ rpm, $V_L = 0.5$ L, $V_H = 0.01$ L, $V_F = 0.24$ L, $He = 5.0$, $k_L^0 = 0.0065$ cm·s^{-1}, $S_{GL} = 185$ cm^2, $C_{BTLb0} = 1.0\times10^{-3}$ M, $C_{AGi}^0 = 362.8$ Pa, $D_{AL} = 1.734\times10^{-5}$ cm^2·s^{-1}, $D_{BL} = 1.021\times10^{-5}$ cm^2·s^{-1}, pH = 2.0, $m = 1$, $a = b = 1$, $\beta = 1/2$, $k_{Am} = 2.4\times10^{-4}$ s^{-1}, $k_{Bn} = 0$, $k_R = 12000$ L·mol^{-1}·s^{-1}.

Anselmi et al. (1985). The applicable values of variables reported by Anselmi et al. (1985) for generating the results of Figs. 2 and 3 are : $T = 296$ K, $Q_G = 40$ L·h^{-1}, $N_r = 400$ rpm, $V_L = 1$ L, $V_H = 0.025$ L, $V_F = 0.075$ L, $He = 4.48$, $k_L^0 = 0.024$ cm·s^{-1}, $S_{GL} = 700$ cm^2, $C_{BTLb0} = 1.26\times10^{-4}$ M, $C_{AGi}^0 = 1.10\times10^{-3}$ M, $D_{AL} = 1.734\times10^{-5}$ cm^2·s^{-1}, $D_{BL} = 2.0\times10^{-5}$ cm^2·s^{-1}, $m = 1$, $a = b = 1$, $\beta = 1/6$, $k_{Am} = 1.16\times10^{-3}$ s^{-1}, $k_{Bn} = 0$, $k_R = 39$ L·mol^{-1}·s^{-1}. The above values were the experimental data measured or used by Anselmi et al. (1985), except that of D_{BL} which was retrieved from the literature.

Figure 4 also compares the predicted value of the present analysis employing Eqs. (3)-(11) and (14) to the experimental data of Beltran et al. (1990) for the ozonation of o-cresol in a semibatch stirred vessel, indicating good agreement. The variation of E_r with time is revealed in Fig. 5. It is seen that the effect of ozonation reaction on the absorption rate is significant with $E_r = 2.23$ to 1.00 for $t = 0$ to 15000 s. Thus for a large value of $M_R^{0.5}$, the variation of E_r with time during the course of gas-liquid contacting is of importance. The applicable values of variables given by Beltran et al. (1990) for simulating Figs. 4 and 5 are: $T = 293$ K, $Q_G = 50$ L·h^{-1}, $N_r = 300$ rpm, $V_L = 0.5$ L, $V_H = 0.01$ L, $V_F = 0.24$ L, $He = 5.0$, $k_L^0 = 0.0065$ cm·s^{-1}, $S_{GL} = 185$ cm^2, $C_{BTLb0} = 1.0\times10^{-3}$ M, $C_{AGi}^0 = 362.8$ Pa, $D_{AL} = 1.734\times10^{-5}$ cm^2·s^{-1}, $D_{BL} = 1.021\times10^{-5}$ cm^2·s^{-1}, pH = 2.0, $m = 1$, $a = b = 1$, $\beta = 1/2$, $k_{Am} = 2.4\times10^{-4}$ s^{-1}, $k_{Bn} = 0$, $k_R = 12000$ L·mol^{-1}·s^{-1}. Again, all the parameters and constants listed above for the model simulation were experimental data measured or used by Beltran et al. (1990).

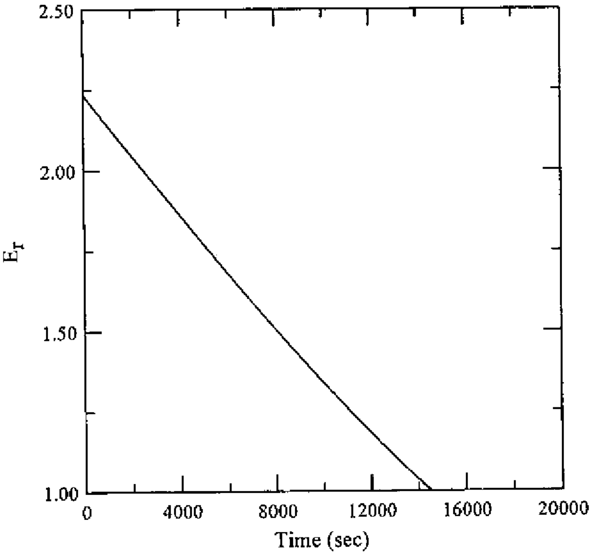

Fig. 5. Variations of enhancement factor (E_r) with ozonation time in a semibatch stirred vessel. (—) : prediction of this model. The conditions are the same as those in Fig. 4.

In summary, this study establishes the validity of the modeling approach through the comparisons of the predicted results of the present model with the available theoretical and experimental results. The accuracy of the numerical calculation of this analysis is verified by the comparison with the theoretical results of van Krevelen and Hoftijzer (1948), Hikita and Asai (1964), Jhaveri (1969) and DeCoursey (1974), showing good agreement. Further, the present model also well simulates the experimental results of the ozonation of BSA and o-cresol (Anselmi et al., 1985, Beltran et al., 1990).

Figure 6 illustrates the simulation results of this analysis with variable E_r, E_r of 1, and E_r estimated by the method of van Krevelen and Hoftijzer (1948). At the β_{BTLb} (= C_{BTLb} / C_{BTLb0}) of 0.3, the relative deviations of times employing the present model with constant E_r from that with variable E_r are about 80% and −19% for $E_r = 1$ and 2.23, respectively. The values of parameters for generating the results of Fig. 6 are the same as Figs. 4 and 5. Also from Fig. 6, it clearly indicates that the ozone concentration (θ_{ALb}) increases with time after most of the pollutants in the liquid bulk have been consumed. Thus, the time for starting the accumulation of the ozone concentration in the liquid bulk is earlier for the situation with the larger reaction rate. The variations of the concentrations of the hold-up gas (θ_{AH}) and the outlet gas in the free volume above the liquid surface (θ_{AF}) with

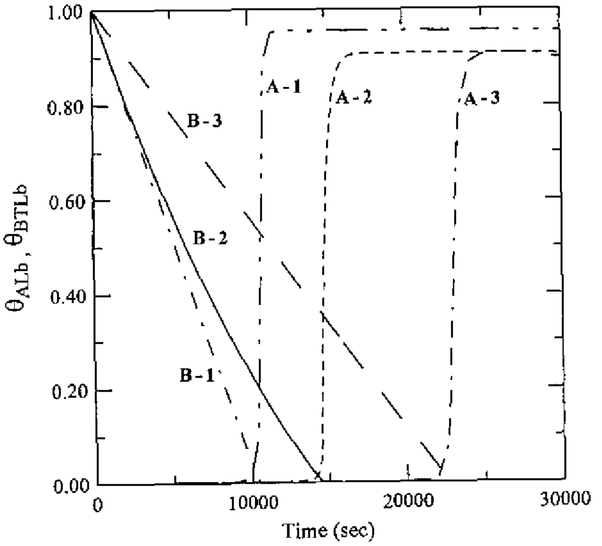

Fig. 6. Variations of θ_{ALb} and θ_{BTLb} with ozonation time in a semibatch stirred vessel with different estimations of E_r value. (------) A-2, (— · — — ·) A-3 and (— · · — · ·) A-1: θ_{ALb} with variable E_r (as indicated in Fig. 5), E_r = 1 and E_r = 2.23 (estimated by the method of van Krevelen and Hoftijzer, 1948). (——) B-2, (— —) B-3, and (- - - - - - -) B-1: θ_{BTLb} with variable E_r, E_r =1 and E_r = 2.23. The other conditions are the same as those in Fig. 4.

time during the course of gas-liquid contacting employing variable E_r, E_r of 1, and E_r of 2.23 can be examined as illustrated in Fig. 7. In general, the values of θ_{AH} and θ_{AF} increase with time during the course of gas-liquid contacting. The accumulation of θ_{AH} and θ_{AF} is faster for the case with higher reaction rate. For the ozonation systems with high reaction rates, the enhancement factors (E_r) are large and cause significant influence on the mass transfer of the ozone and pollutant (Huang et al., 2001). Moreover, the values of E_r may vary with time.

Consequently, the value of E_r, which varies with time, should be estimated properly for the accurate prediction of the fast ozonation system. According to Figs. 6 and 7, the comparisons indicate that the mass transfer rate of ozone would be underestimated remarkably when the value of E_r is taken as one. The concentration of dissolved ozone (θ_{ALb}) and the decomposition of pollutant are underestimated, while the concentrations of ozone in the hold up gas (θ_{AH}) and free volume (θ_{AF}) are overestimated simultaneously before certain ozonation time. Otherwise, the mass transfer rate of ozone would be overestimated, when the value of E_r is calculated based on the initial condition of the ozonation system (van Krevelen and Hoftijzer, 1948). The actual value of E_r decreases with ozonation time. Thus, with the overestimated E_r, the θ_{ALb} and the decomposition of pollutant are overestimated, while the θ_{AH} and θ_{AF} are underestimated before certain ozonation time. Hence, the model of present analysis is more rigorous and appropriate to describe the mass transfer of ozone absorption, decomposition, and reaction with pollutants in a semibatch stirred vessel with large E_r which varies with time but is usually assumed to be constant or simply set equal to one by previous investigators (Anselmi et al., 1985; Beltran et al., 1990).

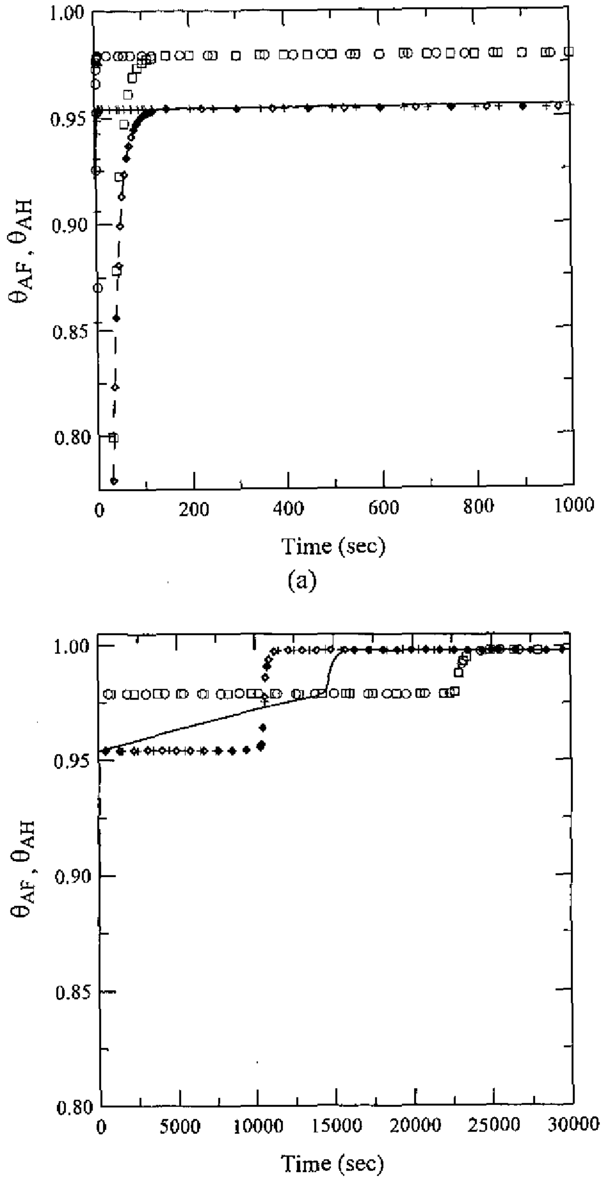

Fig. 7. Variations of θ_{AF} and θ_{AH} with ozonation time in a semibatch stirred vessel with different estimations of E_r value. (------) , (□) and (◇): θ_{AF} with variable E_r (as indicated in Fig. 5), E_r = 1 and E_r = 2.23 (estimated by the method of van Krevelen and Hoftijzer, 1948). (——) , (○), and (+): θ_{AH} with variable E_r, E_r =1 and E_r = 2.23. (a) Time = 0 to 1000 s; (b) Time=0 to 30000 s. The other conditions are the same as those in Fig. 4.

CONCLUSION

The ozone decomposition and reaction rates, and the enhancement factor (E_r) should be included in the system equations describing the mass transfer of ozone with absorption, decomposition, and reaction with pollutants in a semibatch stirred vessel. The model with variable E_r and considering the ozone (A) concentrations in the bulk liquid (C_{ALb}), the hold-up gas (C_{AGi}), and the outlet gas in the free volume above the liquid surface (C_{AGe}), and the pollutant (B) concentration in the bulk liquid (C_{BTLb}) is more rigorous and adequate to describe the system performance. For the ozonation systems with high reaction rates, the enhancement factors are large and have significant influence on the mass transfer of ozone and pollutant.

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NOMENCLATURE

A	ozone species
a	reaction order with respect to O_3 in kinetic expression of Eq.(1)
B	species B, or pollutant
b	reaction order with respect to pollutant in kinetic expression of Eq. (1)
C_{AGe}	gas concentration of A in free volume, M
C_{AGi}	concentration of A in hold up gas, M
C_{AGi}^{0}	concentration of A of inlet gas, M or Pa
C_{AL}	concentration of A in film according to film model, M
C_{ALb}	concentration of A in bulk liquid, M
C_{BTL}	concentration of B in film according to film model, M
C_{BTLb}	concentration of B or pollutant in bulk liquid, M
C_{BTLb0}	initial concentration of B or pollutant in bulk liquid, M
D_{AL}	liquid diffusivity of A, $cm^2 \cdot s^{-1}$
D_{BA}	D_{BL} / D_{AL}
D_{BL}	liquid diffusivity of B, $cm^2 \cdot s^{-1}$
E_r	enhancement factor with effect of chemical reaction (ozone self-decomposition and reaction with pollutant), N_{Ar}/N_A
He	Henry's law constant, C_{AGi}/C_{AL} at gas-liquid interface
k_{Am}, k_{Bn}	acidic and basic decomposition rate constants in kinetic expression of Eq. (1), $M^{1-m} \cdot s^{-1}$, $M^{1-n} \cdot s^{-1}$
k_L	chemical liquid-phase mass transfer coefficient, $cm \cdot s^{-1}$
k_L^{0}	purely physical liquid-phase mass transfer coefficient, $cm \cdot s^{-1}$
k_q	$C_{BTLb0}/(C_{AGi}^{0}/He)$
k_R	reaction rate constant (Eq. (1)) of ozonation reaction, $M^{1-(a+b)} \cdot s^{-1}$
M_{Am}	dimensionless acidic decomposition reaction rate parameter, $[2D_{AL}k_{Am}(C_{AGi}^{0}/He)^{m-1}/(m+1)]/(k_L^{0})^2$
M_{Bn}	dimensionless basic decomposition reaction rate parameter, $[2D_{AL}k_{Bn}(C_{AGi}^{0}/He)^{n-1}/(n+1)]/(k_L^{0})^2$
M_R	dimensionless reaction rate parameter , $[2D_{AL}k_R(C_{AGi}^{0}/He)^{a-1}C_{BTLb0}^{b}/(a+1)]/(k_L^{0})^2$
N_A	mass flux of purely physical mass transfer, $k_L^{0}((C_{AGi}/He) - C_{ALb})$ according to film model, $M \cdot cm \cdot s^{-1}$
N_{Ar}	N_A with chemical reactions (ozone self-decomposition and reaction with pollutant) (r), $D_{AL}dC_{AL}/dx$ at $x = 0$, $M \cdot cm \cdot s^{-1}$
N_r	agitation speed, rpm
m, n	acidic and basic decomposition reaction orders with respect to O_3 in kinetic expression of Eq. (1)
P_{O_3}	ozone partial pressure, Pa
$P_{O_3}^{0}$	ozone partial pressure of inlet gas, Pa
Q_G	gas flow rate, $L\ h^{-1}$
S_{GL}	mass transfer area, cm^2
Sh	Sherwood number , $k_L^{0}V_L/(D_{AL}S_{GL})$
T	temperature, K
t	time, min or s
V_F	free volume above liquid surface, L
V_H	gas hold up volume, L
V_L	liquid volume, L
X^*	dimensionless x, x/x_M
x	distance from gas-liquid interface into liquid film, cm
x_M	thickness of liquid film representing liquid-phase mass transfer resistance, D_{AL}/k_L^{0}, cm

Greek symbols

β	stoichiometric ratio of reaction
θ_{AF}	dimensionless C_{AGe}, C_{AGe}/C_{AGi}^{0}
θ_{AH}	dimensionless C_{AGi}, C_{AGi}/C_{AGi}^{0}
θ_{AL}	dimensionless C_{AL}, $C_{AL}/(C_{AGi}^{0}/He)$
θ_{ALb}	dimensionless C_{ALb} , $C_{ALb}/(C_{AGi}^{0}/He)$
θ_{BTL}	dimensionless C_{BTL}, C_{BTL}/C_{BTLb0}
θ_{BTLb}	dimensionless C_{BTLb} , C_{BTLb}/C_{BTLb0}
τ	dimensionless time, $k_L^{0} S_{GL} t / V_L$

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攪拌槽中包含有臭氧自解及其與污染物反應的質量傳送

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摘要

本研究修改並延伸 Anselmi et al. (1984, 1985) 對於半批次氣-液攪拌槽所提出的數學模式，用來描述臭氧在水溶液中包含有吸收、臭氧自解及臭氧與污染物反應的質量傳送行為，且其中臭氧的自解速率式及臭氧與污染物反應的速率式可以用任意階反應式來表示(即其反應級數不一定為整數)。模式中共有四個系統方程式來描述臭氧在溶液中的濃度(C_{ALb})、污染物在溶液中的濃度(C_{BTLb})、臭氧在氣體滯留相中的濃度(C_{AGi})、及臭氧在液面上剩餘空間的濃度(C_{AGe})。同時模式中也考慮增進因子(E_r)的影響。利用本模式可以計算 E_r 和 C_{ALb} 與 C_{BTLb} 的關係。此動態系統之 E_r、C_{ALb} 和 C_{BTLb} 在氣-液接觸裝置中均會隨接觸時間而改變。將本模式簡化後，模擬 Anselmi et al. (1985)（苯磺酸與臭氧反應）和 Beltran et al. (1990)（甲酚與臭氧反應）的實驗條件並與其實驗數據作比較，結果顯示均相當吻合。因此足以證明本模式的有效性。