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A kinetic model of Ti(IV)-catalyzed H_2O_2/O_3 process in aqueous solution

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Abstract

To well describe the Ti(IV)-catalyzed H_2O_2/O_3 reaction in aqueous solution, a kinetic model was established based on its mechanism. This model was then validated by the experiments of acetic acid degradation in aqueous solution. It was found that the correlation coefficient of fittings was higher than 0.970. Three key operating factors affecting organic degradation in the Ti(IV)-catalyzed H_2O_2/O_3 process were studied, including Ti(IV) concentration, dissolved ozone concentration and initial H_2O_2 concentration. Furthermore, some experiments were conducted to determine the rate constant for dissolved ozone decomposition initiated by $Ti_2O_5^{2+}$. The rate constant measured is almost in accord with the data analyzed by this kinetic model. The goodness of fittings demonstrated that this model could well describe the kinetics of the Ti(IV)-catalyzed H_2O_2/O_3 reaction mathematically and chemically. Therefore, this kinetic model can provide some useful information to optimize the parameters in ozonation of water containing certain pollutants.

Key words: ozone; hydrogen peroxide; Ti(IV); kinetic model; acetic acid; degradation

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Introduction

Ozonation has been demonstrated to be an effective oxidation technology for oxidation of organic pollutants in water (Cooper and Burch, 1999; Wang et al., 2003; Einaga and Futamura, 2004). However, some organic compounds are resistant to conventional ozonation treatment (Esplugas et al., 2002; Nawrocki and Kasprzyk-Hordern, 2010). To enhance degradation efficiencies of these compounds, ozone-based advanced oxidation processes (AOPs-O_3) have been received increasing attention (Farré et al., 2005; Rosenfeldt et al., 2006; Cañizares et al., 2007; Rosal et al., 2009). The AOPs-O_3 are the processes involving hydroxyl radical, which reacts very quickly with many organic species, displaying kinetic constants in the range from 10^8 to 10^{10} L/(mol·sec) (Buxton et al., 1988; Haag and Yao, 1992).

In recent years, hydrogen peroxide/ozone (H_2O_2/O_3) is considered as an effective treatment process to achieve high degradation efficiencies for different contaminants (Ruppert et al., 1994; Gulyas et al., 1995; Hong et al., 1996; Qiang et al., 2010). However, to the authors' best knowledge, H_2O_2 can not effectively achieve the deprotonation reaction in acidic medium (especially when pH is less than 4.0), thus the oxidative efficiency of the H_2O_2/O_3 process is always very low under acid conditions (Kurniawan et al., 2006).

In our previous work, a Ti(IV)-catalyzed H_2O_2/O_3 (Ti(IV)/H_2O_2/O_3) process was developed to successfully degrade acetic acid in acid solutions (Li et al., 2010). The removal rate of total organic carbon (TOC) in the process was nearly the same as that of acetic acid, indicating that acetic acid was degraded completely to carbon dioxide and water. The process of Ti(IV)/H_2O_2/O_3 is a supplementary method to the H_2O_2/O_3 process and suitable for application in acid solutions, Combining the generally accepted hydroxyl radical-type mechanism for AOPs-O_3 and the results of our previous work (Gracia et al., 1996; Piera et al., 2000; Sauleda and Brillas, 2001; Li et al., 2010), it was considered to be the main cause for high oxidative efficiency of Ti(IV)/H_2O_2/O_3 that a yellow complex compound ($Ti_2O_5^{2+}$), generated from the reaction of Ti(IV) with H_2O_2, could initiate the decomposition of dissolved ozone to produce hydroxyl radicals (Cao et al., 1994; Li et al., 2010) .

The objective of this research was to establish a kinetic model for the Ti(IV)-catalyzed H_2O_2/O_3 reaction in acid solutions. Acetic acid was used as a model pollutant because it is very stable to ozone and always a final product of chemical oxidation. A series of acetic acid degradation experiments by the Ti(IV)-catalyzed H_2O_2/O_3 process were carried out to validate the established model.

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1 Experimental section

1.1 Materials and reagents

All chemicals used (acetic acid, hydrogen peroxide and titanium(IV) oxysulfate) were of analytical grade and used as received without further purification. All the glass wares used were first washed by soaking them in chromic acid and then rinsed with de-ionized water (II) before use.

1.2 Experiment setup

All experiments were performed in a semi-continuous process. Ozonation contactor was a 1.5-L cylindrical glass reactor (Fig. 1). Ozone was produced by a corona ozone generator (CFS-1A, Ozonia, Switzerland). The oxygen gas was dried and purified with silica gel prior to entering the ozone generator. Ozone concentration was regulated by varying the voltage and oxygen flow rate. The rate of gas flow was monitored by a rotor flowmeter. The flow rate of ozonized oxygen was always 0.86 L/min and the rate of ozone input was 8.60×10^{-4} mol/min without special illumination. Excess ozone was passed into two gas absorption bottles containing 2% KI solution.

In a typical experiment of acetic acid degradation, the reactor was filled with a 500-mL acetic acid aqueous solution and the temperature was kept at room temperature (21 ± 0.5)°C in all cases. The required concentration of titanium ion and hydrogen peroxide prepared in advance were added to the reactor. The pH of the solution was kept at 2.8 during the whole reaction time. The sample was withdrawn for analysis at certain regular intervals, and dissolved ozone was removed by immediately bubbling nitrogen for 3 min after sampling to terminate oxidative reaction.

1.3 Analytical method

An ion chromatography (Dionex DX1500, USA) was used to determine the concentration of acetic acid (eluent: 3.5 mmol/L sodium carbonate and 1.0 mmol/L sodium bicarbonate, the flow rate was 1.0 mL/min). The concentration of ozone in gas was measured by the iodometric titration method (Birdsall et al., 1952). The concentration of ozone dissolved in aqueous solution was determined by a spectrophotometer using the indigo method (Bader and Hoigné, 1981). The concentration of H_2O_2 was determined by the spectrophotometric method using the dipotassium titanium oxide dioxalate method (Sellers, 1980). The comparison tests showed that the presence of H_2O_2 did not interfere with the determination of the concentrations of ozone and acetic acid. The pH value of the solution was recorded by a pH analyzer (PHS-3C, General Instrument Co., Ltd., Shanghai, China), and was controlled by adding 1 mol/L H_2SO_4 or NaOH. It was found the pH of the solution almost kept constant (2.8) during the whole reaction time.

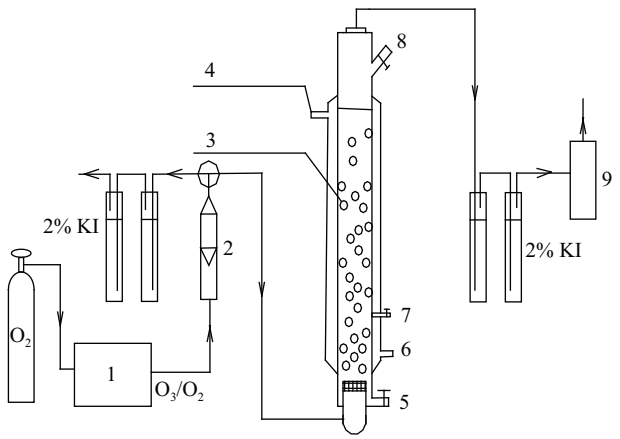

Fig. 1 Diagram of the experimental setup. (1) ozone generator; (2) flowmeter; (3) ozonation reactor; (4) outlet of circulation water; (5) outlet of solution; (6) inlet of circulation water; (7) sampling; (8) inlet of solution; (9) ozone destructor.

2 Results and discussion

2.1 Determination of the rate constant of ozone reaction with $Ti_2O_5^{2+}$

In general, ozonation always follows an electrophilic attack of electron rich sites of a target molecule (Gurol and Nekounaini, 1984; Luca et al., 2009). On the basis of the results of our previous work and the experiences of ozonation (Li et al., 2010; Beltrán et al., 2005), it can be inferred that the interaction of O_3 with $Ti_2O_5^{2+}$ leads to the production of reactive radical (O_3^-) (Reaction (1)).

$$O_3 + Ti_2O_5^{2+} \xrightarrow{k_1} O_3^- + Ti_2O_5^{3+} \quad (1)$$

To determine the rate constant for dissolved ozone reaction with $Ti_2O_5^{2+}$, the decomposition rate of ozone in water was monitored under suitable conditions (Tomiyasu et al., 1985; Ma et al., 2005; Benitez et al., 2007). At first, the ozonized oxygen was bubbled into the reactor continuously for 20 min to get an ozone-saturated solution. The solution was poured into a 500-mL beaker and a certain volume of solution containing $Ti_2O_5^{2+}$ was rapidly added to the beaker. After then, the concentration of the dissolved ozone was measured. Kinetics of a given compound reacting with dissolved ozone is always assumed to be second-order (first-order in the concentration of the dissolved ozone and the given compound). Without loss of generality, the rate law for dissolved ozone decomposition in this process can be formulated as:

$$-\frac{dC_{O_3}}{dt} = k_1 C_{O_3} C_{Ti_2O_5^{2+}} \quad (2)$$

where, k_1 is the second-order rate constant, t represents reaction time, C_{O_3} and $C_{Ti_2O_5^{2+}}$ represent dissolved ozone concentration and $Ti_2O_5^{2+}$ concentration in water at any time, respectively.

In this process, if the amount of H_2O_2 is in large excess, $Ti_2O_5^{2+}$ concentration can be considered to be a constant. Then the decomposition rate of the dissolved ozone can be assumed to be pseudo first-order (Eq. (3)).

$$-\frac{dC_{O_3}}{dt} = k_1' C_{O_3} \quad (3)$$

where, $k_1' = k_1 C_{Ti_2O_5^{2+}}$.

This expression can be integrated as follows:

$$\ln \frac{C_{O_3}^0}{C_{O_3}} = k_1' t \quad (4)$$

where, $C_{O_3}^0$ represents the initial concentration of the dissolved ozone.

The logarithmic plots of the concentration of the dissolved ozone exposure versus time at different $Ti_2O_5^{2+}$ concentrations are shown in Fig. 2, which indicates that the decomposition rate of the dissolved ozone follows a pseudo first-order law. Furthermore, the slope of the corresponding straight line was doubled when the concentration of $Ti_2O_5^{2+}$ increased one times, which confirms the reaction order with respect to $Ti_2O_5^{2+}$ is one. Therefore, the second-order rate constant (k_1) could be calculated to be 1.10×10^3 L/(mol·sec) by k_1' divided by the corresponding concentration of $Ti_2O_5^{2+}$.

2.2 Kinetic model of the Ti(IV)-catalyzed O_3/H_2O_2 process

The Ti(IV)-catalyzed H_2O_2/O_3 process should consist of three crucial reactions: (a) the decomposition of dissolved ozone initiated by $Ti_2O_5^{2+}$(Reaction (1)), (b) the generation of hydroxyl radicals (Reactions (5) and (6)), (c) the degradation of organic by HO· (Reaction (10)). Meanwhile, some other reactions (Reactions (7), (8) and (9)) coexist along with the crucial reactions as summarized below (Buxton et al., 1988; Cao et al., 1994; Haag and Yao, 1992; Li et al., 2010; Nöthe et al.,2009; Pérez et al.,2002; Staehelin and Hoigné, 1985; von Gunten, 2003):

$$O_3^- + H^+ \underset{k_{5-}}{\overset{k_{5+}}{\rightleftharpoons}} HO_3^\bullet \quad (5)$$

$$HO_3^\bullet \xrightarrow{k_6} HO^\bullet + O_2 \quad (6)$$

$$HO^\bullet + O_3 \xrightarrow{k_7} HO_2^\bullet + O_2 \quad (7)$$

$$H_2O_2 + HO^\bullet \xrightarrow{k_8} H_2O + HO_2^\bullet \quad (8)$$

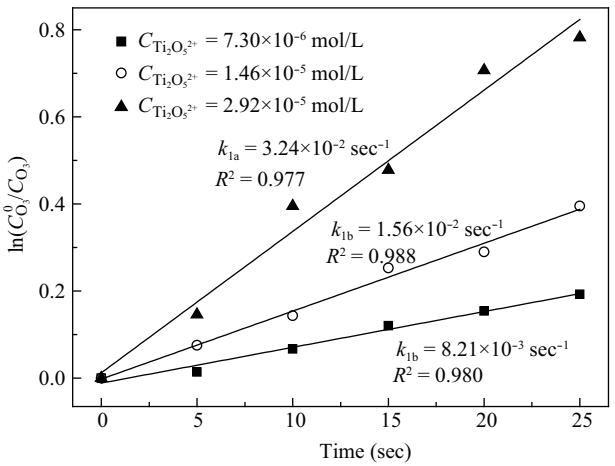

Fig. 2 Linear fittings of $\ln(C_{O_3}^0/C_{O_3})$ against time at different $Ti_2O_5^{2+}$ concentrations at pH 2.8.

$$Ti_2O_5^{2+} + HO^\bullet \xrightarrow{k_9} OH^- + Ti_2O_5^{3+} \quad (9)$$

$$\text{organic} + HO^\bullet \xrightarrow{k_{10}} \text{products} \quad (10)$$

To set up a kinetic model for representing the Ti(IV)-catalyzed H_2O_2/O_3 process, it is assumed that organic substance (S) is chiefly degraded by the hydroxyl radical and its decay rate (dC_S/dt) can be expressed by Eq. (11).

$$-\frac{dC_S}{dt} = k_{10} C_{HO\cdot} C_S \quad (11)$$

where, C_S and $C_{HO\cdot}$ represent the concentrations of organic compound and hydroxyl radical at any reaction time, respectively.

From the Reactions (6)–(10), the variation of HO· concentration ($dC_{HO\cdot}/dt$) depends on its generation rate from $HO_3^\bullet$ decomposition, and its consumption rates reacting with O_3, H_2O_2, $Ti_2O_5^{2+}$ and organic substance (Eq. (12)).

$$-\frac{dC_{HO^\bullet}}{dt} = k_6 C_{HO_3^\bullet} - k_7 C_{HO^\bullet} C_{O_3} - k_8 C_{H_2O_2} C_{HO^\bullet} - k_9 C_{Ti_2O_5^{2+}} C_{HO^\bullet} - k_{10} C_S C_{HO^\bullet} \quad (12)$$

where, $C_{HO_3^\bullet}$ and $C_{H_2O_2}$ represent the concentrations of $HO_3^\bullet$ and H_2O_2 at any reaction time, respectively.

In addition, the change of $HO_3^\bullet$ concentration in solution relies on its generation rate (Forward Reaction (5)) and consumption rate (Backward Reaction (5) and Reaction (6)), which can be expressed by Eq. (13).

$$-\frac{dC_{HO_3^\bullet}}{dt} = k_{5+} C_{O_3^-} C_{H^+} - k_{5-} C_{HO_3^\bullet} - k_6 C_{HO_3^\bullet} \quad (13)$$

where, $C_{O_3^-}$ and C_{H^+} represent O_3^- concentration and H^+ concentration at any reaction time, and $k_{5+} = 5 \times 10^{10}$ L/(mol·sec), $k_{5-} = 3.3 \times 10^2$ sec^{-1}, $k_6 = 3.3 \times 10^5$ sec^{-1} (von Gunten, 2003). Since $k_6 \gg k_{5-}$, Eq. (13) can be simplified into Eq. (14).

$$-\frac{dC_{HO_3^\bullet}}{dt} = k_{5+} C_{O_3^-} C_{H^+} - k_6 C_{HO_3^\bullet} \quad (14)$$

Furthermore, the O_3^- concentration is determined by those of its generation rate (Reaction (1)) and its decay rate (Forward Reaction (5)) can be quantified by Eq. (15).

$$-\frac{dC_{O_3^-}}{dt} = k_1 C_{O_3} C_{Ti_2O_5^{2+}} - k_{5+} C_{O_3^-} C_{H^+} \quad (15)$$

Since HO•, $HO_3^\bullet$ and O_3^- are highly reactive free radicals with extremely short lifetimes (Staehelin and Hoigné, 1985; Liu et al., 1999, 2007), according to steady state approximation, their concentrations are generally considered to be constant but at very low levels (Eq. (16)).

$$\frac{dC_{HO^\bullet}}{dt} = \frac{dC_{HO_3^\bullet}}{dt} = \frac{dC_{O_3^-}}{dt} = 0 \quad (16)$$

On the basis of above equations, the $C_{HO^\bullet}$ can be expressed by the concentrations of O_3, $Ti_2O_5^{2+}$, S and H_2O_2 (Eq. (17)).

$$C_{HO^\bullet} = \frac{k_1 C_{O_3} C_{Ti_2O_5^{2+}}}{k_7 C_{O_3} + k_8 C_{H_2O_2} + k_9 C_{Ti_2O_5^{2+}} + k_{10} C_S} \quad (17)$$

Substituting Eq. (17) into Eq. (11), the rate of organic degradation can be expressed as follows:

$$-\frac{dC_S}{dt} = \frac{k_1 k_{10} C_{O_3} C_S C_{Ti_2O_5^{2+}}}{k_7 C_{O_3} + k_8 C_{H_2O_2} + k_9 C_{Ti_2O_5^{2+}} + k_{10} C_S} \quad (18)$$

Since k_8 (2.7×10^7 L/(mol·sec)) (Popiel et al., 2008) is two order smaller in magnitude than k_7 (1.0×10^9 L/(mol·sec)) (von Gunten, 2003) in acid solutions, it is fair enough to remove the item of $k_8 C_{H_2O_2}$ from Eq. (18) to simplify the integration. According to the mechanism of the Ti(IV)-catalyzed H_2O_2/O_3 reaction, low Ti(IV) concentration (always less than 6.70×10^{-5} mol/L) is enough to achieve high efficiency of organic (S) degradation. Therefore, the concentration of $Ti_2O_5^{2+}$ is about one order smaller in magnitude than the concentration of residual ozone C_{O_3} (usually between 1.04×10^{-4} mol/L and 2.50×10^{-4} mol/L) in this reaction. In addition, owing to the steric hindrance of $Ti_2O_5^{2+}$, k_9 is supposed to be smaller than k_{19} (7.5×10^9 L/(mol·sec), HO_2^--quenching reaction) (Beltrán, 2003). Thus, it is also appropriate to remove the item of $k_9 C_{Ti_2O_5^{2+}}$ from Eq. (18) (this assumption was approved by the results of acetic acid degradation). Finally, we get Eq. (20).

$$HO^\bullet + HO_2^- \xrightarrow{k_{19}} HO_2^\bullet + OH^- \quad (19)$$

$$-\frac{dC_S}{dt} = \frac{k_1 k_{10} C_{O_3} C_S C_{Ti_2O_5^{2+}}}{k_7 C_{O_3} + k_{10} C_S} \quad (20)$$

After integration, the organic concentration C_S reduces from its original concentration C_S^0 at initiation time ($t = 0$) gradually as depicted in Eq. (21):

$$\ln(\frac{C_S^0}{C_S}) + \frac{k_{10}}{k_7 C_{O_3}}(C_S^0 - C_S) = \frac{k_1 k_{10} C_{Ti_2O_5^{2+}}}{k_7} t \quad (21)$$

If we let $a = k_{10}/k_7 C_{O_3}$, $b = k_1 k_{10} C_{Ti_2O_5^{2+}} / k_7$, Eq. (21) can be re-arranged in a simplified form as shown below (Eq. (22)).

$$\ln(\frac{C_S^0}{C_S}) + a(C_S^0 - C_S) = bt \quad (22)$$

In conclusion, Eq. (22) has been established as the prime kinetic model for the Ti(IV)-catalyzed H_2O_2/O_3 reaction in acid solutions.

2.3 Validation of the kinetic model

To validate this kinetic model for the Ti(IV)-catalyzed H_2O_2/O_3 process, three sets of experiments were carried out by varying three key factors of Ti(IV) concentration $C_{Ti(IV)}$, dissolved ozone concentration C_{O_3} and initial H_2O_2 concentration $C^0_{H_2O_2}$, respectively. In each experiment, the initial concentration of acetic acid $C^0_{CH_3COOH}$ was 1.67×10^{-3} mol/L and the pH of the solution was 2.8. Figure 3 presents the experimental results of acetic acid degradation at different concentrations of Ti(IV), which are also fitted by the model of $[\ln(C_S^0/C_S) + a(C_S^0 - C_S)]$ versus reaction time (t). It can be seen that the correlation coefficients at different concentrations of Ti(IV) are very high (> 0.970), which validate that this kinetic model can well explain the mechanism of the Ti(IV)-catalyzed H_2O_2/O_3 process. Furthermore, according to Eq. (21) and the slope value of the fitting line, the second-order rate constant of Reaction (1) (k_1) could be calculated to be 1.40×10^3 L/(mol·sec), which well agrees with the former data (1.10×10^3 L/(mol·sec)) obtained from the decomposition rate of the dissolved ozone.

The experimental data from the second set of experiments at different concentrations of dissolved ozone were fitted using this kinetic model (Fig. 4). It can be seen that the results of acetic acid degradation at different concentrations of dissolved ozone have high fitness with the stimulated curves ($R^2 > 0.990$). The results also showed that the efficiency of acetic acid degradation was found to significantly increase with the increase of dissolved ozone concentration for a given reaction time at first, and then a further increase of ozone concentration caused the decrease of acetic acid degradation. Consequently, higher ozone doses is an impetus to the reaction of the Ti(IV)-catalyzed H_2O_2/O_3 process, but excessive ozone would quench the hydroxyl radicals, thus lowering the degradation efficiency of organic.

In this Ti(IV)-catalyzed H_2O_2/O_3 reaction model, we omit the factor of initial H_2O_2 concentration to simplify the integration. In fact, the concentration of H_2O_2 plays

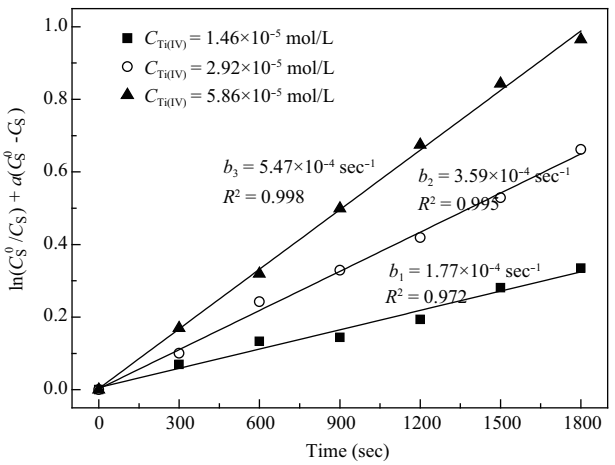

Fig. 3 Linear relationship of acetic acid degradation at different Ti(IV) concentrations fitted by the kinetic model. $C^0_{H_2O_2} = 2.73 \times 10^{-3}$ mol/L, $C^0_{CH_3COOH} = 1.66 \times 10^{-3}$ mol/L, flow rate of ozonized oxygen: 0.86 L/min, rate of ozone input: 8.60×10^{-4} mol/min and pH 2.8.

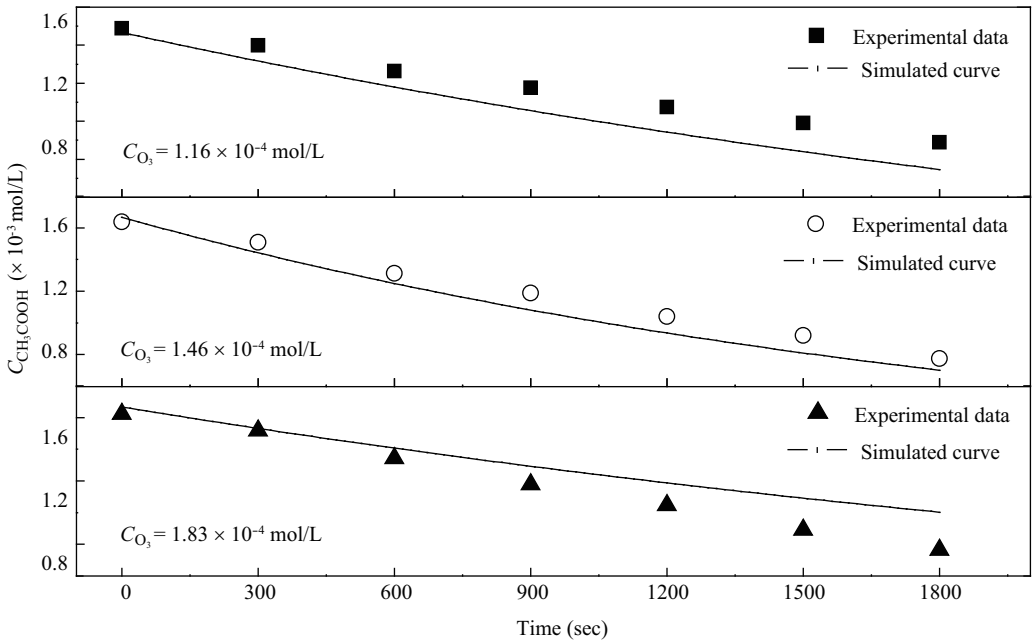

Fig. 4 Acetic acid degradation at different concentrations of dissolved ozone fitted by the kinetic model. $C^0_{H_2O_2}$ = 2.73 × 10^{-3} mol/L, $C_{Ti(IV)}$ = 5.86 × 10^{-5} mol/L, $C^0_{CH_3COOH}$ = 1.66 × 10^{-3} mol/L and pH 2.8.

an important role in this process. On one hand, suitable concentration of H_2O_2 can assure the effective generation of $Ti_2O_5^{2+}$ (Cao et al., 1994); on the other hand, too high concentration of H_2O_2 will quench hydroxyl radicals generated in the solution (Reaction (8)). The effect of different initial concentrations of H_2O_2 on the oxidative efficiency of the Ti(IV)-catalyzed H_2O_2/O_3 process for acetic acid degradation is shown in Fig. 5. It is found that too high H_2O_2 concentration was disadvantage to acetic acid degradation because H_2O_2 could partly quench the generated hydroxyl radicals. However, when initial H_2O_2 concentration was too low, the initiator of $Ti_2O_5^{2+}$ could not be produced effectively, thus leading to low efficiency of acetic acid degradation. Therefore, there must exist a proper initial H_2O_2 concentration range, in which Ti(IV)-catalyzed H_2O_2/O_3 process has high oxidation efficiency. After optimization, it was found that the Ti(IV)-catalyzed

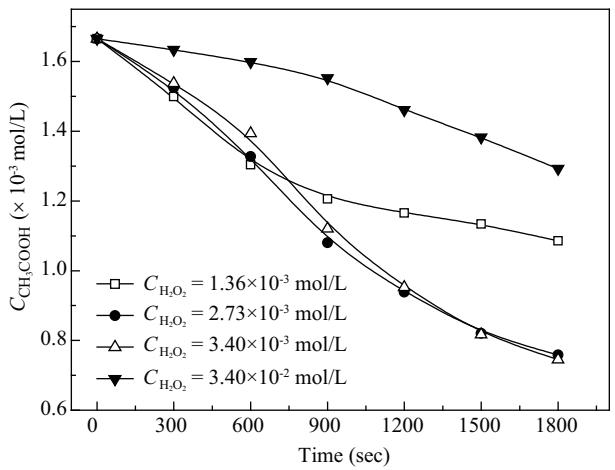

Fig. 5 Acetic acid degradation at different initial concentrations of H_2O_2. $C_{Ti(IV)}$ = 5.86 × 10^{-5} mol/L, $C^0_{CH_3COOH}$ = 1.66 × 10^{-3} mol/L, flow rate of ozonized oxygen: 0.86 L/min, rate of ozone input: 8.60 × 10^{-4} mol/min and pH 2.8.

H_2O_2/O_3 process had an excellent oxidation performance when the ratio of H_2O_2 concentration to Ti(IV) concentration was in the range of 30 to 50, in which the concentration of H_2O_2 well satisfy the requirement for simplifying Eq. (18). Thus in spite of omitting the concentration of H_2O_2, this kinetic model still can well describe the mechanism of Ti(IV)-catalyzed H_2O_2/O_3 process under the optimum conditions.

It is obvious that our new model can coincide quite well with the kinetic description of such a Ti(IV)-catalyzed O_3/H_2O_2 reaction in both mathematical and chemical ways.

3 Conclusions

In this study, a kinetic model for the Ti(IV)-catalyzed H_2O_2/O_3 reaction in aqueous solution was established mathematically. During the degradation of acetic acid by the Ti(IV)-catalyzed H_2O_2/O_3 process, it was found that the results of acetic acid degradation fitted well with the kinetic model. In addition, the effects of three key factors of initial H_2O_2 concentration, Ti(IV) concentration and dissolved ozone concentration, on the efficiency of the process were explored. The rate constant for the reaction of ozone with $Ti_2O_5^{2+}$ obtained by this kinetic model (1.40 × 10^3 L/(mol·sec)) agreed well with the data (1.10 × 10^3 L/(mol·sec)) analyzed by monitoring the decomposition rate of dissolved ozone. However, this kinetic model was only validated by the experiments of acetic acid degradation so far. Further studies to apply this kinetic model in degradation of other organics become necessary.

Acknowledgment

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References

Bader H, Hoigné J, 1981. Determination of ozone in water by the indigo method. *Water Research*, 15(4): 449–456.

Beltrán F J, 2003. Ozone Reaction Kinetics for Water and Wastewater Systems. CRC Press, Washington. 17–18.

Benitez F J, Real F J, Acero J L, Garcia C, 2007. Kinetics of the transformation of phenyl-urea herbicides during ozonation of natural waters: Rate constants and model predictions. *Water Research*, 41(18): 4073– 4084.

Beltrán F J, Rivas F J, Montero-de-Espinosa R, 2005. Iron type catalysts for the ozonation of oxalic acid in water. *Water Research*, 39(15): 3553–3564.

Birdsall C M, Jenkins A C, Spadinger E, 1952. Iodometric determination of ozone. *Analytical Chemistry*, 24(4): 662–664.

Buxton G V, Greenstock C L, Helman W P, Rose A B, 1988. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (middot OH/ middot O^-) in aqueous solution. *Journal of Physical and Chemical Reference Data*, 17(2): 513–886.

Cañizares P, Lobato J, Paz R, Rodrigo M A, Sáez C, 2007. Advanced oxidation processes for the treatment of olive-oil mills wastewater. *Chemosphere*, 67(4): 832–838.

Cao X Z, Song T Y, Wang X Q, 1994. Inorganic Chemistry (3th ed.) Higher Education Press, Beijing. 939–940.

Cooper C, Burch R M, 1999. An investigation of catalytic ozonation for the oxidation of halocarbons in drinking water preparation. *Water Research*, 33(18): 3695–3700.

Einaga H, Futamura S, 2004. Catalytic oxidation of benzene with ozone over alumina-supported manganese oxides. *Journal of Catalysis*, 227(2): 304–312.

Esplugas S, Giménez J, Contreras S, Pascual E, Rodríguez M, 2002. Comparison of different advanced oxidation processes for phenol degradation. *Water Research*, 36(4): 1034–1042.

Farré M J, Franch M I, Malato S, Ayllón J A, Peral J, Doménech X, 2005. Degradation of some biorecalcitrant pesticides by homogeneous and heterogeneous photocatalytic ozonation. *Chemosphere*, 58(8): 1127–1133.

Gracia R, Aragues J L, Ovelleiro J L, 1996. Study of the catalytic ozonation of humic substances in water and their ozonation byproducts. *Ozone Science and Engineering*, 18(3): 195–208.

Gulyas H, von Bismarck R, Hemmerling L, 1995. Treatment of industrial wastewaters with ozone/hydrogen peroxide. *Water Science and Technology*, 32(7): 127–134.

Gurol M D, Nekounaini S, 1984. Kinetic behavior of ozone in aqueous solutions of substituted phenols. *Industry and Engineering Chemistry Fundamentals*, 23(1): 54–60.

Haag W R, Yao C C D, 1992. Rate constants for reaction of hydroxyl radicals with several drinking water contaminants. *Environmental Science and Technology*, 26(5): 1005–1013.

Hong A, Zappi M E, Kuo C H, Hill D, 1996. Modeling kinetics of illuminated and dark advanced oxidation processes. *Journal of Environmental Engineering*, 122(1): 58–62.

Kurniawan T A, Lo W H, Chan G Y S, 2006. Radicals-catalyzed oxidation reactions for degradation of recalcitrant compounds from landfill leachate. *Chemical Engineering Journal*, 125(1): 35–57.

Li W W, Liu P P, Zhang H, Shi R, Tong S P, Ma C A, 2010. Degradation of acetic acid by Ti(IV)-catalyzed H_2O_2/O_3. *Journal of Chemical Industry and Engineering*, 61(7): 1790–1795.

Liu D X, Liu J, Wen J, 1999. Elevation of hydrogen peroxide after spinal cord injury detected by using the Fenton reaction. *Free Radical Biology and Medicine*, 27(3-4): 478–482.

Liu H, Li X Z, Leng, Y J, Wang C, 2007. Kinetic modeling of electro-Fenton reaction in aqueous solution. *Water Research*, 41(5): 1161–1167.

Lucas M S, Peres J A, Lan B Y, Puma G L, 2009. Ozonation kinetics of winery wastewater in a pilot-scale bubble column reactor. *Water Research*, 43(6): 1523–1532.

Ma J, Zhang T, Chen Z L, Sui M H, Li X Y, 2005. Pathway of aqueous ferric hydroxide catalyzed ozone decomposition and ozonation of trace nitrobenzene. *Environmental Science*, 26(2): 78–82.

Nawrocki J, Kasprzyk-Hordern B, 2010. The efficiency and mechanisms of catalytic ozonation. *Applied Catalysis B: Environmental*, 99(1-2): 27–42.

Nöthe T, Fahlenkamp H, von Sonntag C, 2009. Ozonation of wastewater: rate of ozone consumption and hydroxyl radical yield. *Environmental Science and Technology*, 43(15): 5990–5995.

Pérez M, Torrades F, Domènech X, Peral J, 2002. Fenton and photo-Fenton oxidation of textile effluents. *Water Research*, 36(11): 2703–2710.

Piera E, Calpe J C, Brillas E, Domènech X, Peral J, 2000. 2, 4-Dichlorophenoxyacetic acid degradation by catalyzed ozonation: $TiO_2/UVA/O_3$ and $Fe(II)/UVA/O_3$ systems. *Applied Catalysis B: Environmental*, 27(3): 169–177.

Popiel S, Witkiewicz Z, Chrzanowski M, 2008. Sulfur mustard destruction using ozone, UV, hydrogen peroxide and their combination. *Journal of Hazardous Materials*, 153(1-2): 37–43.

Qiang Z M, Liu C, Dong B Z, Zhang Y L, 2010. Degradation mechanism of alachlor during direct ozonation and O_3/H_2O_2 advanced oxidation process. *Chemosphere*, 78(5): 517–526.

Rosal R, Gonzalo M S, Rodríguez A, García-Calvo E, 2009. Ozonation of clofibric acid catalyzed by titanium dioxide. *Journal of Hazardous Materials*, 169(1-3): 411–418.

Rosenfeldt E J, Linden K G, Canonica S, von Gunten U, 2006. Comparison of the efficiency of ·OH radical formation during ozonation and the advanced oxidation processes O_3/H_2O_2 and UV/H_2O_2. *Water Research*, 40(20): 3695–3704.

Ruppert G, Bauer R, Heisler G, 1994. UV-O_3, UV-H_2O_2, UV-TiO_2 and the photo-Fenton reaction – Comparison of advanced oxidation processes for wastewater treatment. *Chemosphere*, 28(8): 1447–1454.

Sauleda R, Brillas E, 2001. Mineralization of aniline and 4-chlorophenol in acidic solution by ozonation catalyzed with Fe^{2+} and UVA light. *Applied Catalysis B: Environmental*, 29(2): 135–145.

Sellers R M, 1980. Spectrophotometric determination of hydrogen peroxide using potassium titanium(IV) oxalate. *Analyst*, 105(1255): 950–954.

Staehelin J, Hoigné J, 1985. Decomposition of ozone in water in the presence of organic solutes acting as promoters and inhibitors of radical chain reactions. *Environmental Science and Technology*, 19(12):1206–1213.

Tomiyasu H, Fukutomi H, Gordon G, 1985. Kinetics and mechanism of ozone decomposition in basic aqueous solution. *Inorganic Chemistry*, 24(19): 2962–2966.

von Gunten U, 2003. Ozonation of drinking water: Part I. Oxidation kinetics and product formation. *Water Research*, 37(7): 1443–1467.

Wang C X, Yediler A, Linert D, Wang Z J, Kettrup A, 2003. Ozonation of an azo dye C.I. Remazol Black 5 and toxicological assessment of its oxidation products. *Chemosphere*, 52(7): 1225–1232.