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Kinetics and mechanism study of direct ozonation organics in aqueous solution

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Abstract

In this study, the kinetics and mechanism study of direct ozonation organics in aqueous solution was explored. Phenoxyacetic acid was selected as the model pollutant and ozonation experiments were performed in the bubble batch reactor in order to determine the rate constants for the direct reaction. Two kinetic methods were used for the determination of different kinetic rate constants (k_{app} and k_i). The first group of the results showed the degradation of phenoxyacetic acid followed the pseudo-first-order kinetics. A simplified model related to the operational parameters on phenoxyacetic acid degradation was derived and the apparent rate constant k_{app} was obtained. The reaction was proved in the slow kinetics of gas-liquid reaction and the kinetic constant k_i was built. The k_{app} and k_i influenced by the pH value, the O_3 dosage and the initial phenoxyacetic acid concentration were carefully analyzed.

Keyword: phenoxyacetic acid; direct ozonation; kinetic models; k_{app}; k_i

1. Introduction

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With the development of industrial productions, the amounts and categories of pharmaceuticals production increases in a geometric ratio. Some pharmaceuticals, such as antibiotics and pharmaceutical intermediates, are persisting organic pollutants and can hardly be well treated with the traditional biological technology if directly discharged into the environment[1-4]. Thus, sound way of pharmaceutical wastewater treatment is one of the focuses by both environmental workers and the government for the intolerable burden on the environment.[5-6]

To reduce the toxicity pharmaceutical wastewater, some effective efforts have been made, such as the advanced oxidation processes (AOPs).[9-11] As an AOP, ozonation is a useful water treatment technology because ozone is an oxidizing agent showing high reactivity with kinds of pharmaceuticals.[12-13] During the ozonation, ozone either reacts selectively with organic pollutant or decomposes in water to form free hydroxyl radical which is another stronger oxidizing agent for its high potential (2.80eV) leading to indirect reactions.[14]

The reaction of target pollutant B with molecular ozone (O_3) and hydroxyl radicals (• OH) during ozonation can be expressed in Eq. (1) and Eq. (2) parallel reactions as follows:[15]

$$\mathrm{B} + \mathrm{O}_3 \rightarrow \text{products} \qquad (1)$$

$$\mathrm{B} + \cdot\mathrm{OH} \rightarrow \text{products} \qquad (2)$$

Thus, for an ozone-reacting compound B, the chemical reaction rate r_B can be written as follows.

$$r_\mathrm{B} = -(zk_{\mathrm{O3}}[\mathrm{B}][\mathrm{O}_3] + k_{\mathrm{OH}\cdot}[\mathrm{B}][\cdot\mathrm{OH}]) \qquad (3)$$

The stoichiometric ratio z is the meaning of the number of moles of compound B consumed per mole of ozone consumed. k_{O3} is the second order rate constant between ozone and compound B, and $k_{OH\cdot}$ is the second order rate constant between hydroxyl radical and compound B. [B], [O_3] and [·OH] is the concentration of target compound B, ozone and hydroxyl radical, respectively.

Ozonation is a heterogeneous reactions and the kinetics of heterogeneous reactions are governed by absorption theories of gases in liquids along with chemical reactions.[16] So far, there are two most applied absorption theories are the film and surface renewal theories. Two-film theory is relatively mature and has been widely applied. The basis of the theory is mainly diffusion law and gas-liquid mass transfer model. Thus the main content of ozonation kinetics is to make sure of the mass transfer coefficients and the reaction rate constants. Eq. (4) represents the mass transfer of ozone from the gas to the liquid phase, and k_La is the volumetric mass transfer coefficient.

$$O_3(g) \xrightarrow{k_La} O_3(l) \tag{4}$$

In view of the competition of the ozone decomposition and the intermediates produced in the processes, absorption rate equations are unsuitable for irreversible second-order reactions.[17] The radical scavenger is necessary to add into the reactor to avoid the ozone decomposition. The ozone decomposition mechanism involves initiation reaction, propagation reaction and termination reaction. The free radical species are exactly formed in the initiation or propagation reactions of ozone with some agents like hydroxyl and hydroperoxide ion. Among these, the hydroxyl radical is the main responsible species.[18] Furthermore, tert-butyl alcohol (TBA) reacts with hydroxyl radicals quickly (k=5×10^8 $M^{-1}s^{-1}$) and slowly with O_3 (k=0.03 $M^{-1}s^{-1}$).[15,19] Therefore, TBA can be used as the hydroxyl radical scavenger.

Though some studies on the oxidation of relevant pharmaceuticals have addressed,[12] the developing kinetic aspects are still limited. In this study, phenoxyacetic acid (PAA) is selected as the model pollutant because it is an important pharmaceutical intermediate and widely applied in the pharmaceutical industry. It can be used as the parent molecule of herbicides, which is highly toxic compounds and applied in the agricultural fields. It can be also applied in the preparation of cefazolin, penicillin and meclofenoxate.

The aim of this study is to establish a database with kinetic rate constants for the direct reaction of PAA degradation. Two kinetic methods for the PAA degradation in ozonation system were utilized and the corresponding models were built. One relatively macroscopical kinetics model was established with the ozone dosage, the initial concentration of phenoxyacetic acid, and the pH value, which could be easily used in highly concentrated organic wastewater pollution treatment with ozonation. The other model studying the characteristics of the initial kinetic to reflect the reaction rate constant was also discussed. This paper can give basic data and kinetic reference for the ozonation of pharmaceutical wastewater.

2. Experimental

2.1 Materials and reagents

Phenoxyacetic acid was purchased from Shanghai J&K Scientific Ltd. (China), (purity 99%). Tert-butyl alcohol (TBA) was chosen as the radical scavenger and purchased from Shanghai Lingfeng Chemical Reagent (China) Co., Ltd.

All other chemicals used in the experimental process were analytical reagent or guaranteed reagent. Ultra-pure water was used as experimental water. The pH value of the solutions was adjusted with sodium hydroxide.

2.2 Apparatus and methods

Ozone was produced by an ozone generator (CFY-3) with high purity oxygen (99.999%). The experiments were carried out in a cylindrical Pyrex glass reactor (inner circulation) with a capacity of 1.5 L at room temperature. Samples connection was set on the top of the reactor. An aeration head was fixed at the center of the bottom of the reactor for gas distribution. At the beginning of the reaction, ozone became small bubbles in sufficient contact with the solution through the aeration head and thus resulted in forming the gas-liquid two-phase. Samples were withdrawn at fixed time, then filtered through 0.45 μm pore size membrane filters and finally analyzed.

2.3 Analytical methods

Phenoxyacetic acid (PAA) was detected by high performance liquid chromatography (1200, Agilent Technologies, USA) with a UV-detector at 210 nm using a C18 reversed phase column. The column temperature was 30 °C. The mobile phase was a mixture of ammonium biphosphate (pH=7, adjusted by ammonia water) and acetonitrile at 85:15 (v/v) at 0.8 $mL \cdot min^{-1}$ flow rate. The injection volume was 5 μL. The intermediates produced in ozonation/TBA system were detected through HPLC, IC and GC-MS technologies. The methods were performed as the previous work.[17]

3. Results and discussion

3.1 Effect of tert-butyl alcohol on PAA removal

Fig.1 shows the effect of the presence and absence of tert-butyl alcohol (TBA) in acid, neutral and alkaline conditions for PAA removal. The initial pH was investigated in the range of 3.0-11.0. It could be seen that the effect of pH from 3.0-7.0 on PAA removal was non-significant, but showed a rising trend in alkaline environment without the addition of TBA. While the presence of TBA involved a negative acceleration of PAA removal compared to the experiments carried out under the same operating condition in the absence of TBA. When pH is lower than 12.0, the ozone decomposition probably competes for the available ozone that reacts with pollutants.[18] 79.22% of PAA removal rate could be eliminated after 50 min at pH 3.0 without TBA, while 67.14% with TBA, it was evident of the competitive effect of ozone decomposition. In this case, the ozone decomposition can be stopped by the addition of scavengers of hydroxyl radicals (TBA).

Fig.1

The intermediates formed in ozonation/TBA were identified by HPLC, IC and GC-MS technologies. Compared with those products caused by ozonation alone, which have been detected in the previous article,[17] we found that TBA rarely affected the categories of intermediates.

3.2 Kinetic model of pseudo first-order reaction

The ozonation experiments were performed in the presence of scavengers of hydroxyl radicals to guarantee the environment in direct ozonation, aimed at studying the kinetic models of direct ozone reactions between ozone and phenoxyacetic acid (PAA). Then the second term on the right side in Eq. (3) is negligible, under experimental conditions with ozone in great excess, it can be assumed.

$$r_{\mathrm{PAA}} = -k_{\mathrm{app}}[\mathrm{PAA}] \tag{5}$$

where k_{app} is the kinetic rate constant of pseudo first-order reaction.

Integration of the apparent rate constant leads to

$$\ln\left(\frac{[\mathrm{PAA}]}{[\mathrm{PAA}]_0}\right) = -k_{\mathrm{app}}\mathrm{t} \tag{6}$$

where $[\mathrm{PAA}]_0$ is the initial concentration of target compound PAA. The apparent rate constant k_{app} was used to reflect the effect of the ozone dosage, initial concentration of PAA and the pH value on PAA degradation in 50 min by ozonation. Table 1 shows the apparent rate constant k_{app} is well fitting the pseudo-first-order kinetics with the linear correlation coefficient (R^2) over 0.99 under various experimental conditions. The variation of the ozone dosage (16, 24, 32 and 40 $\mathrm{mg{\cdot}min^{-1}}$) resulted in k_{app} of 0.51×10^{-2}, 0.79×10^{-2}, 1.28×10^{-2} and 1.68×10^{-2}, respectively. Hence, the ozone dosage was proportional to the apparent rate constant k_{app}, while the initial concentration of PAA was inversely proportional. The pH value impeded the observation of any significant difference in the apparent rate constant k_{app}. Based on the optimization of operational factors, the apparent rate constant k_{app} is hypothesized to be related to ozone dosage (Q_{O3}), the initial concentration of PAA ($[\mathrm{PAA}]_0$), the pH value (OH^-) and the temperature (T).[20]

Table 1

If a relatively macroscopical kinetics is established with optimization of operational factors, it will be more convenient in control of the highly concentrated organic wastewater pollution by ozonation. Since dissolved ozone concentration is difficult to figure out, a relationship between k_{app} and O_3 dosage is supposed to be built. Therefore, an empirical equation forms as Dai et al[21] said

$$k_{\mathrm{app}} = \mathrm{A}\exp(\frac{-\mathrm{E}_a}{\mathrm{RT}})\mathrm{Q}_{\mathrm{O3}}{}^{\alpha}[\mathrm{PAA}]_0{}^{\beta}[\mathrm{OH}^-]^{\gamma} \tag{7}$$

Eq. (7) expressed in logarithmic form becomes

$$\ln k_{\mathrm{app}} = \ln\mathrm{A} - \frac{\mathrm{E}_a}{\mathrm{RT}} + \alpha\ln\mathrm{Q}_{\mathrm{O3}} + \beta\ln[\mathrm{PAA}]_0 + \gamma\ln[\mathrm{OH}^-] \tag{8}$$

The regression analysis between the first item and the O_3 dosage, the initial concentration of PAA and the pH value, respectively, was conducted. Corresponding α and β were equal to 1.3273 and -1.1816 from Fig. 2a and Fig. 2b with linear correlation coefficients of 0.9918 and 0.9948, respectively. Due to the nonlinear relationship between $\ln k_{app}$ and $\ln[OH^-]$, γ was regarded as 0 which could be viewed in Fig. 2c.

Thus Eq. (8) can be converted into

$$k_{\mathrm{app}} = \mathrm{A}\exp(\frac{-\mathrm{E}_a}{\mathrm{RT}})\mathrm{Q}_{\mathrm{O3}}{}^{1.3273}[\mathrm{PAA}]_0{}^{-1.1816} \tag{9}$$

Since the experiments were done at room temperature, $\mathrm{A}\exp(-\mathrm{E}_a/\mathrm{RT})$ was obtained from the substitution of all experimental data into Eq. (9). The result was equal to 0.51. Finally, the kinetic model turns into

$$[\mathrm{PAA}]_{\mathrm{t}} = [\mathrm{PAA}]_0\exp(-0.51\mathrm{Q}_{\mathrm{O3}}{}^{1.3273}[\mathrm{PAA}]_0{}^{-1.1816}\mathrm{t}) \tag{10}$$

Fig. 2

3.3 Kinetic model in initial stage

3.3.1 Validation of the reaction in the slow kinetic regime

Ha is the dimensionless Hatta number for an irreversible first-order reaction. For an irreversible first-order reaction, the mass transfer rate of the gas–liquid system is defined as follows:

$$Ha = \frac{\sqrt{k_{\mathrm{app}} \mathrm{D}_{\mathrm{O}_3}}}{k_{\mathrm{L}}} \qquad (11)$$

where *Ha* indicates the relative importance of chemical reaction and D_{O3} is the diffusion coefficient of O_3 in water. k_{L} is the individual mass transfer coefficient of ozone in the liquid phase. As a function of the Hatta number, the ozonation kinetic regimes can be classified as fast, moderate, and slow reactions. When *Ha* is more than 3, the reaction is in the fast kinetic regime. When *Ha* is between 0.3 and 3, it is in the moderate kinetic regime. The third regime is called the slow kinetic regime when *Ha* is less than 0.3.[22]

Some research[23-25] has been done to study D_{O3}. In the ozonation process, the empirical correlation of Johnson and Davis[25] is more available to determine D_{O3}:

$$\mathrm{D}_{\mathrm{O3}} = (5.9 \pm 0.04) \times 10^{-10}\, \mathrm{T} / \mu_s \qquad (12)$$

where μ_{s} = the viscosity of the solvent. Thus, the determination of D_{O3}, which was equal to 1.4×10^{-9} $m^2\cdot s^{-1}$, was obtained from the calculation result of Eq. (12).

The determination of the individual mass transfer coefficient k_{L} in liquid phase is up to the types of reactors. For the bubble batch reactor in the experiment, k_{L} could be determined by detecting the mass transfer of CO_2. Based on the absorption reaction of CO_2 in Na_2CO_3-$NaHCO_3$ system, hypochlorite ion and $NaAsO_2$ as the catalysts, k_{L}', the individual mass transfer coefficient of CO_2, could be got by the plot method of Roberts and Danckwerts.[26] The basic requirement was that the absorption reaction of CO_2 was the pseudo first-order reaction. The absorption rate is defined as follows:

$$N_{CO2} = [CO_2]^* a\sqrt{k_L'^2 + k_{CO2}D_{CO2}} \qquad (13)$$

where N_{CO2} is the absorption rate per unit volume, $[CO_2]^*$ is the saturated solubility of CO_2 at equilibrium in the buffer solution, D_{CO2} is the diffusion coefficient of CO_2 and k_{CO2} is the kinetic rate constant of pseudo first-order reaction of CO_2 in absorption system.

Then Eq. (13) can be converted into

$$(N_{CO2}/[CO_2]^*)^2 = (ak_L')^2 + a^2 k_{CO2} D_{CO2} \qquad (14)$$

From Eq. (14), it can be seen that $(N_{CO2}/[CO_2]^*)^2 \sim k_{CO2}D_{CO2}$ shows a linear relationship. k_L' could be attained by the variation of $k_{CO2}D_{CO2}$. D_{CO2} was equal to 1.58×10^{-9} $m^2\cdot s^{-1}$. Finally, k_L is determined by the calculation of Eq. (15).[27]

$$k_L = (\frac{D_{O3}}{D_{CO2}})k_L' \qquad (15)$$

k_{app}, D_{O3} and k_L measured in different conditions were taken into account Eq. (11) to the yield of *Ha* constant shown in Table 2. The calculated results indicated the reaction was in slow kinetic regime because all *Ha* constants were lower than 0.3 in the PAA degradation by ozonation and also indicated that the reaction of ozone decomposition took place in the bulk water.

3.3.2 Kinetic rate constant in initial stage

In general, the ozone process presents two steps in series, involves the mass transfer of ozone through the film layer and the chemical reaction with phenoxyacetic acid in the bulk liquid. Considering the influence of mass transfer, the rate constant of the direct reaction between ozone and phenoxyacetic acid can also be written:

$$r_{PAA} = -zk_i[PAA]_b[O_3]_b \qquad (16)$$

where the subindex b refers to bulk phase. In fact, the meaning of the kinetic constant in the initial stage (k_i) is as the same as the rate constant (k_{O3}). Eq. (16) can be used if concentrations of phenoxyacetic acid and ozone are known with time. While ozone not only reacted with PAA, but also reacted with intermediates formed from the ozone-PAA direct reaction simultaneously.[17] To determine the kinetic constant will acquire more parameters taking into account. It is rather difficult. As a consequence, a method of studying the characteristics of the initial kinetic to reflect reaction rate is chosen to determine k_i, which was also applied in the kinetic study of the ozonation of fluorine.[28]

The presence of dissolved ozone in water is a symbol of the slow kinetic regime. For the slow kinetic regime, the reaction factor E (Eq. (17)) is 1, which is perceived as the ratio between the actual chemical absorption rate and that of physical absorption in gas-liquid reaction.[18]

$$\mathrm{E}=\frac{\mathrm{N}_{\mathrm{O3}}}{k_{\mathrm{L}}a([\mathrm{O}_3]^*-[\mathrm{O}_3]_{\mathrm{b}})}=1 \qquad (17)$$

where N_{O3} is the physical absorption rate of ozone, $[O_3]^*$ represents the concentration of ozone in the gas-liquid system at equilibrium, $[O_3]_b$ is the concentration of O_3 in the bulk of the liquid.

This method has a disadvantage that the value of the ozone concentration is vague. Actually, the concentration of dissolved ozone is theoretically zero at the beginning of reaction. Nonetheless, the application of the mass balance of ozone in water is well handled with this problem. This Eq. (18) in the case of a semi-batch reactor is as follows:[18]

$$k_{\mathrm{L}}a([\mathrm{O}_3]^*-[\mathrm{O}_3])=\sum_{\mathrm{i}}k_{\mathrm{j}}[\mathrm{J}]_{\mathrm{b}}[\mathrm{O}_3]_{\mathrm{b}}+k_{\mathrm{d}}[\mathrm{OH}^-][\mathrm{O}_3]_{\mathrm{b}}+k_{\mathrm{T}}[\mathrm{O}_3]+\frac{\mathrm{d}[\mathrm{O}_3]_{\mathrm{b}}}{\mathrm{dt}} \qquad (18)$$

where the subindex j in the right of the equation represents any compound j (PAA in the experiment) present in water that reacts with ozone directly and the k_j, k_d and k_T

are the rate constants of the ozone direct, hydroxyl-ion-initiated decomposition and other initiation reactions, respectively. The left of this equation represents the transport rate of transference from the gas phase to the liquid phase. At the beginning of ozonation, the ozone accumulation rate term d$[O_3]_b$/dt and intermediates reactions are regarded as negligible, so Eq. (18) reduces to

$$k_L a([O_3]^* - [O_3])\big|_{t=0} = k_i[PAA]_0[O_3]_b\big|_{t=0} = -\frac{r_{PAA0}}{z} \tag{19}$$

From the change of Eq. (19), the concentration of ozone in initial reaction is

$$[O_3]_b\Big|_{t=0} = \frac{k_L a[O_3]^*}{k_i[PAA]_0 + k_L a} \tag{20}$$

Combining Eq. (17) and (20) allows us to determine kinetic constant k_i in the initial stage:

$$k_i = \frac{-k_L a r_{PAA0}}{z[PAA]_0\left(k_L a[O_3]^* + \frac{r_{PAA0}}{z}\right)} \tag{21}$$

Table 2 shows some parameters, such as individual mass transfer coefficients and the Hatta number, are useful to determine kinetic constant k_i in the initial stage. The comparison of k_i with different parameters, such as pH value, the initial concentration of PAA and the ozone dosage is shown in Fig. 3. Fig. 3a describes the effect of different initial concentration of PAA ($[PAA]_0$) on k_i. The more initial concentration of PAA was, the less k_i was, which was as the same as the variation of k_{app} with the increasing of initial concentration of PAA. Fig. 3b shows the effect of the ozone dosage (Q_{O3}) on k_i. When the ozone dosage increased from 16 to 40 mg·L^{-1}, k_i could be regarded independent of the value of the stable ozone concentration in agreement with the opinion of Leitner et al.[29] It is obvious that the effect of the ozone dosage on k_{app} is larger than k_i. Fig. 3c shows the effect of pH on

k_i. Increasing the pH value from 3.0 to 11.0, the shifty amplitude of k_i was not evident which is almost identical to that of k_{app}. It explained directly that the main sites of reaction are due to molecular ozone only, namely the ozone decomposition was inhibited well by TBA. The results showed in Table 1 and Table 2 confirmed the relationship between k_{app} and k_i. k_{app} changed with the variation of k_i and the concentration of ozone.

Table 2

Fig. 3

4. Conclusions

The kinetic models about the PAA degradation by ozonation were discussed and two rate constants k_{app} and k_i were carefully explored. The apparent rate constant k_{app} was supposed to be related to the pH value, the initial concentration of PAA, the O_3 dosage and the temperature. The kinetics model was proposed as an exponential function of $[\mathrm{PAA}]_t = [\mathrm{PAA}]_0 \exp(-0.51 Q_{O3}{}^{1.3273} [\mathrm{PAA}]_0{}^{-1.1816} t)$.

The calculated results showed all *Ha* constants are lower than 0.3 in the PAA degradation by ozonation, so the reaction was proved to be in the slow kinetic regime of gas-liquid reaction. In kinetics study of the initial stage, the establishment of the mass balance equation of ozone and PAA in water determines the kinetic constant k_i.

$$k_i = \frac{-k_L a r_{\mathrm{PAA0}}}{z[\mathrm{PAA}]_0 \left(k_L a [O_3]^* + \frac{r_{\mathrm{PAA0}}}{z} \right)}$$

Compared the k_i and k_{app} in different conditions, the results implied that the effect of PAA initial concentration on k_{app} and k_{i} was apparent and followed the same trend. The ozone dosage didn't make any difference on k_{i}, but did on k_{app}. Increasing the pH value from 3.0 to 11.0, the shifty amplitude of k_{i} was not evident which is almost identical to that of k_{app} and proved ozone decomposition was inhibited well by TBA. The mathematical models are able to reproduce the experimental observations concerning the reaction rate of direct ozonation. This paper can give basic data and kinetic reference for the ozonation of pharmaceutical wastewater.

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Table 1 Apparent rate constant based on experimental results

Table 2 Factors of kinetic rate constants equation in the primary stage

Table 1 Apparent rate constant based on experimental results

No.	T / K	pH	$[PAA]_0$/ mg·L^{-1}	TBA/mmol·L^{-1}	Q_{O3}/mg·min^{-1}	R^2	k_{app}/ min^{-1}
1	298	3	200	50	40	0.9915	9.68×10^{-2}
2	298	3	500	50	40	0.9939	3.64×10^{-2}
3	298	3	1000	50	40	0.9934	1.68×10^{-2}
4	298	3	2000	50	40	0.9962	0.62×10^{-2}
5	298	3	1000	50	16	0.9970	0.51×10^{-2}
6	298	3	1000	50	24	0.9971	0.79×10^{-2}
7	298	3	1000	50	32	0.9976	1.28×10^{-2}
8	298	5	1000	50	40	0.9952	1.75×10^{-2}
9	298	7	1000	50	40	0.9973	1.61×10^{-2}
10	298	9	1000	50	40	0.9967	1.70×10^{-2}
11	298	11	1000	50	40	0.9952	1.70×10^{-2}

Table 2 Factors of kinetic rate constants equation in the primary stage

No.	T / K	pH	$[PAA]_0$/ mg·L^{-1}	Q_{O3}/mg·min^{-1}	k_L/ m·s^{-1}	*a*	*Ha* number
1	298	3	200	40	8.10×10^{-5}	95.3	1.86×10^{-2}
2	298	3	500	40	8.10×10^{-5}	95.3	1.14×10^{-2}
3	298	3	1000	40	8.10×10^{-5}	95.3	0.77×10^{-2}
4	298	3	2000	40	8.10×10^{-5}	95.3	0.47×10^{-2}
5	298	3	1000	16	6.90×10^{-5}	50.2	0.50×10^{-2}
6	298	3	1000	24	7.20×10^{-5}	62.8	0.60×10^{-2}
7	298	3	1000	32	7.60×10^{-5}	87.4	0.72×10^{-2}
8	298	5	1000	40	8.10×10^{-5}	95.3	0.79×10^{-2}
9	298	7	1000	40	8.10×10^{-5}	95.3	0.76×10^{-2}
10	298	9	1000	40	8.10×10^{-5}	95.3	0.78×10^{-2}
11	298	11	1000	40	8.10×10^{-5}	95.3	0.78×10^{-2}

Fig.1 The effect of TBA in its presence and absence on the degradation of phenoxyacetic acid: Experimental conditions: $[PAA]_0$=1000 mg·L^{-1}, the ozone dosage=40 mg·min^{-1}

Fig.2 The pseudo first-order plots of PAA as a function of different parameters on the logarithmic scale: (a) $\ln k_{app}$ versus $\ln Q_{O3}$, fitted curve; (b) $\ln k_{app}$ versus $\ln[PAA]_0$, fitted curve; (c) $\ln k_{app}$ versus $\ln[OH^-]$, fitted curve

Fig.3 The initial kinetic constant k_i as a function of different parameters: (a) Tendency chart of k_i with initial PAA concentration; (b) Tendency chart of k_i with different O_3 dosage; (c) Tendency chart of k_i at different pH

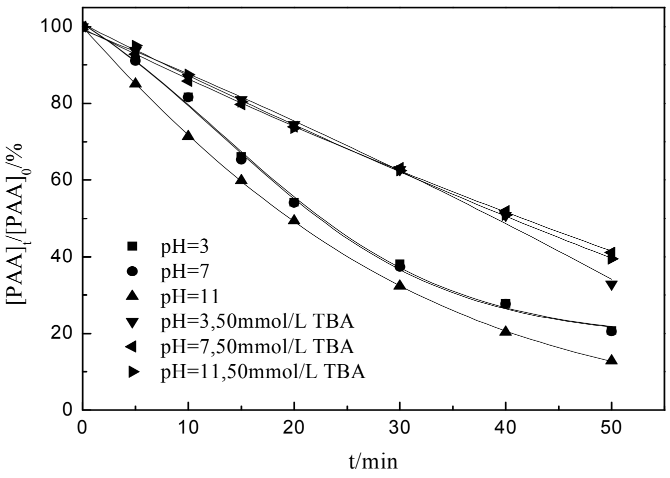

Fig.1 The effect of TBA in its presence and absence on the degradation of phenoxyacetic acid:

Experimental conditions: $[PAA]_0$=1000 mg·L^{-1}, the ozone dosage=40 mg·min^{-1}.

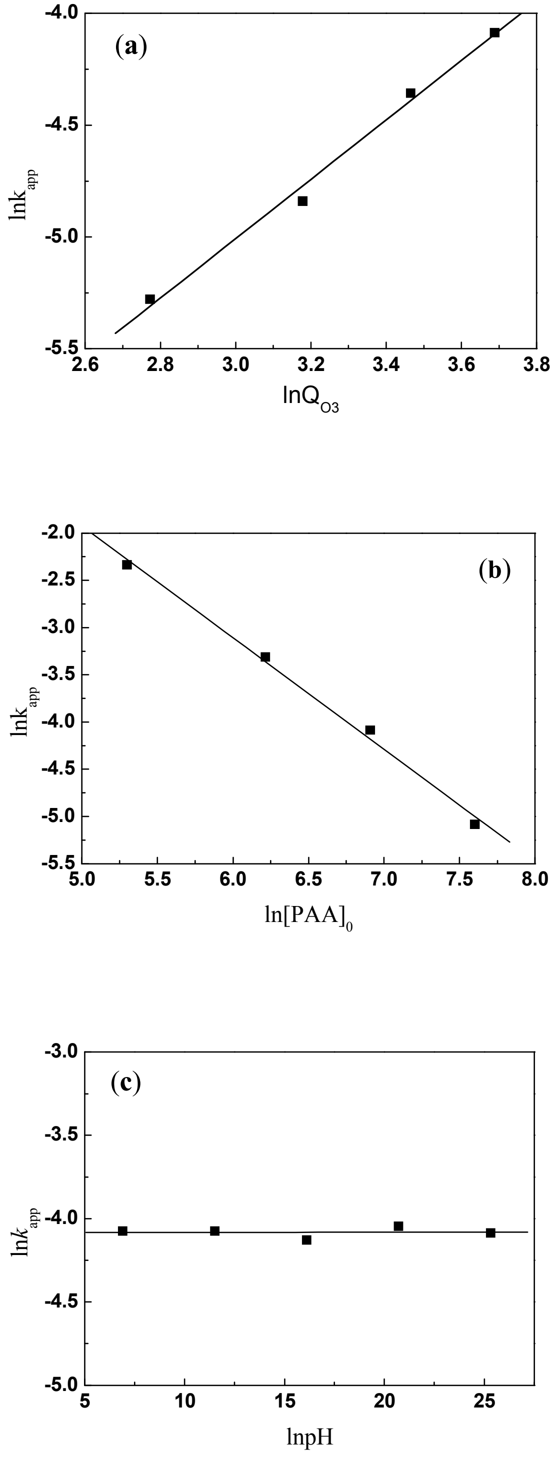

Fig.2 The pseudo first-order plots of PAA versus different parameters on the logarithmic scale: (a) lnk_{app} versus lnQ_{O3}, fitted curve; (b) lnk_{app} versus ln$[PAA]_0$, fitted curve; (c) lnk_{app} versus ln$[OH^-]$, fitted curve.

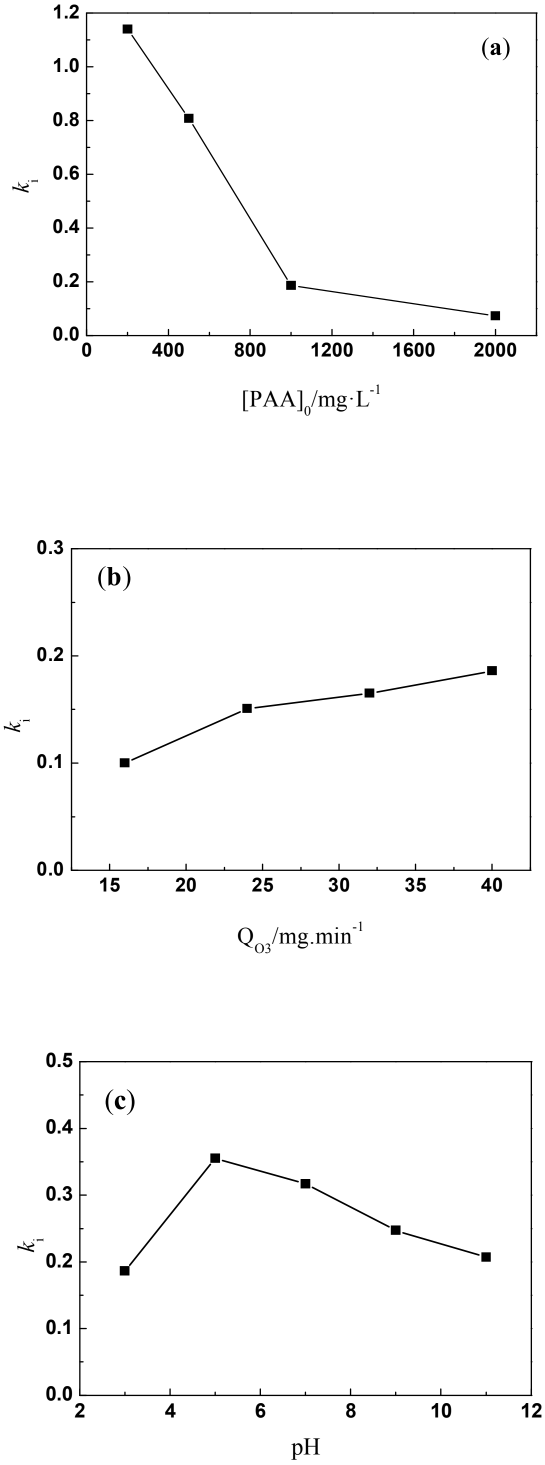

Fig.3 The initial kinetic constant k_i as a function of different parameters:(a) Tendency chart of k_i with initial PAA concentration; (b) Tendency chart of k_i with different O_3 dosage; (c) Tendency chart of k_i at different pH.