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Degradation of 2,4-dichlorophenoxyacetic acid in water by ozone-hydrogen peroxide process

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Abstract: This study reports an investigation into the degradation of 2,4-dichlorophenoxyacetic acid in bubble contactor column by O_3/H_2O_2 process, which is widely used as a principal advanced oxidation process. The degradation of 2,4-dichlorophenoxyacetic acid was studied under different H_2O_2/O_3 molar ratio and pH value. Meanwhile, TOC removal was investigated both in distilled water and tap water. The influences of ozone transfer and consumed hydrogen peroxide were also discussed. The degradation products and oxidation intermediates were identified by GC-MS and LC-MS. A possible reaction mechanism was thus proposed.
Keywords: 2,4-dichlorophenoxyacetic acid; ozone; hydrogen peroxide; advanced oxidation process

Introduction

At present, several types of organic pollutants referred to as environmental endocrine disruptors (ED) have been suggested to be associated with abnormal sexual development (Hu, 2000). It was reported that the ED led to the decline of reproductive ability of fish with their gonads becoming smaller (Arcand *et al.*, 1998; Harris *et al.*, 2001; Zhao and Yuan, 2001). Increases in breast cancer, testicular cancer, hypospadia, cryptorchidism, and drops in sperm count have all been reported (Colborn *et al.*, 1993). It has been hypothesized that those effects were caused by ED chemical exposures. The ED pollutants have been paid more and more attention in recent years. The USA and Japanese governments and the European Union are gathering information, funding large research efforts, and in some cases, enacting laws regulating EDs. In the USA, amendments to the Safe Drinking Water Act and the Food Quality Protection Act mandate testing of ED activities for chemicals found in water and food. Accordingly, the development of methods to remove the ED from the polluted water is urgently needed.

Recently, sixty-seven chemicals were promulgated in Japan as the possible environmental ED (Hu, 2000). Among them, 2,4-dichlorophenoxyacetic acid (also called 2,4-D) is widely used in many countries as herbicide, which has not been banned so far. At present, substantial research has been conducted to remove 2,4-D from the water. It was reported that electrochemically generated hydroxyl radicals were effective to remove 2,4-D. It was shown that more than 95% of 2,4-D and the oxidation intermediates such as 2,4-dichlorophenol, 2,4-dichlororesorcinol and 4,6-dichlororesorcinol generated during the electrolysis were mineralized (Oturan, 2000). In another paper, it was also reported that when photocatalysis was used in combination with ozonolysis to treat 2,4-D polluted waters, a long-living intermediate that was identified as 2,4-dichlorophenol was observed with better degradation efficiency and lower intermediate concentration (Muller *et al.*, 1999). The ozonation of 2,4-D was also studied in the presence of UV light and TiO_2, or in the presence of UV and Fe(II) (Piera *et al.*, 2000). However, the selection of oxidation process may depend upon many factors such as the degree of degradation, the by-products formed in the process, the total cost and the safety and reliability of the process. Advanced oxidation processes are attractive alternative technologies for destroying toxic organic contaminants. Advanced oxidation processes are studied in different combinations: ozone with ultraviolet radiation; ozone with hydrogen peroxide; ozone/hydrogen peroxide with ultraviolet radiation; hydrogen peroxide with ultraviolet radiation; ozone at high pH and so on. The common feature of advanced oxidation processes is the production of high concentration of HO· radical, which can non-selectively attack organic compounds 10^6—10^9 times faster than most of known oxidizing agents. It was reported that the second order rate constant of the direct attack of O_3 to 2,4-D had a value of 1—2.3 L/(mol·s), while more efficient removal of 2,4-D was achieved in presence of HO· ($K_{HO\cdot}$ = (4—5) $\times 10^9$ L/(mol·s)) (Yao and Haag, 1991; Haag and Yao, 1992). In this study, O_3/H_2O_2 process was selected to investigate the removal of 2,4-D in the water due to the fact that this process is a competitive method for applying in large-scale water treatment plants.

The O_3/H_2O_2 process is a principal advanced oxidation process employed in water treatment to enhance the removal of refractory organic compounds. The pH and O_3/H_2O_2 ratio are the main factors affecting the oxidation (Paillard *et al.*, 1988; Duguet

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et al., 1990). An investigation on the oxidation of pharmaceuticals in water showed that O_3/H_2O_2 process led to the formation of HO·, which improved the degradation of all investigated compounds (Zwiener and Frimmel, 2000). It was reported that 80% of atrazine and >99% of some phenylureaherbicides could be degraded by O_3/H_2O_2 at pH 7.8 and at the H_2O_2/O_3 ratio of 3.7 g/g (Ijpelaar *et al.*, 2000). In particular, the O_3/H_2O_2 process is highly effective for enhancing the degradation of some compounds in solutions, which may exist in natural waters (Goncharuk and Vakulenko, 1998).

1 Materials and method

1.1 Materials and apparatus

The 2,4-D used in this study was purchased from Jiamusi Agricultural Chemical Factory (HPLC grade > 99%). The 2,4-D aqueous solution was prepared by dissolving 2,4-D with distilled or tap water. The other chemicals used are all analytical reagent grade.

A 3-L aqueous solution containing 30 mg 2,4-D was put into a bubble contactor column, which is made of stainless steel. The size of the reactor is 50 mm × 1850 mm. The ozone gas was introduced into the column, which could form small bubbles through the distributing plate equipped at the bottom of the column. Hydrogen peroxide was admitted to the water samples, concomitant to the application of ozone. Ozone was generated with high purity oxygen by an XZF-5 ozone generator. The experimental apparatus is shown in Fig.1.

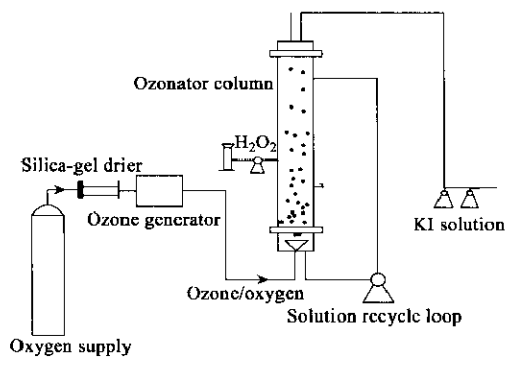


Fig.1 Schematic diagram of the laboratory ozonation apparatus

1.2 Analytical method

2,4-D was analyzed by high performance liquid chromatography (Shimadzu LC-10A$_{VP}$, Japan) with a HPLC column (ODS-C-18). Acetonitrile and water (70:30 in v/v) were used as the mobile phase, and the pH value of water had been adjusted to 3.0 by adding acetic acid before being used as the mobile phase. Separation was performed at a flow rate of 1 ml/min. The water sample was detected by a UV detector at 280 nm.

For GC-MS and LC-MS analysis, two kinds of methods were applied. In the first case, the ozonated water solution was reduced in volume by a factor of 500 with a rotary evaporator at a temperature 38℃. In the second case, the ozonated water solution was extracted with CH_2Cl_2, and then the extraction raffinate was reduced in volume with a rotary evaporator, and in consideration that the samples treated by the first method may lose some volatile organics during evaporation.

The identification of these degradation products and intermediates was performed by GC-MS (Shimadzu GCMS-QP5050A, Japan). The mass spectra were recorded at electron energy of 70 eV and scanned from 45 to 400 μ. Separation was carried out with a column of DB-5MS (30 m × 0.25 mm × 0.25 μm). The oven temperature was initially set at 40℃ and kept for 2 min. Then the temperature was increased to 120℃ at a rate of 6℃/min. Afterwards, the temperature was further increased to 280℃ at a rate of 20℃/min. Helium was used as carrier gas with a flow rate of 1.2 ml/min. The degradation products and intermediates were also identified by LC-MS (Agilent 1100 LC-MSD, USA). The mass spectrometer equipped with an electrospray interface (ESI) was operated in the negative ion mode in the *m/z* of 50—1500 range. The ESI temperature was set to 350℃ and the cone voltage was 70V. The chromatographic separation was carried out with a column (ODS-C-18) using gradient elution at a flow of 1 ml/min. The operating conditions were 30% acetonitrile and 70% water with a linear gradient to 99% acetonitrile in 3.5 min, and then kept for 15 min.

Residual hydrogen peroxide concentrations were determined with cobalt colorimetric method after introducing nitrogen continuously to the water sample for 6 min to drive residual ozone off (Belhateche and Symons, 1991). Ozone exhausted from the contactor column was determined with iodimetry method (Bader and Hoigne, 1981).

2 Results and discussion

2.1 Effect of transferred H_2O_2/O_3 ratio

The results of the research work showed that ozone alone had very limited effectiveness on the degradation of 2,4-D. However, the presence of hydrogen peroxide highly enhanced the removal of 2,4-D from the water. Within a certain range, the removal efficiency increased with increasing H_2O_2/O_3 ratio when ozone dosage was kept constant. Similar results were found both in distilled water and tap water. The results are shown in Fig.2.

The mechanism of hydroxyl radicals production in O_3/H_2O_2 process is indicated in Eqs. (1)—(8) (Staehelin and Hoigne, 1982):

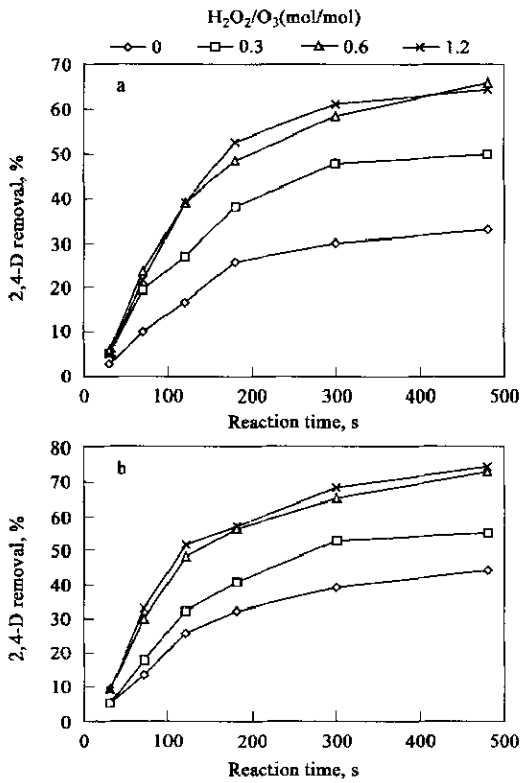


Fig.2 Removal efficiency of 2,4-D in distilled water (a) and tap water (b) with transferred H_2O_2/O_3 ratio
O_3 applied: 4.6 mg/L; H_2O_2 applied: 0, 1, 2, 4 mg/L

$$H_2O_2 \rightleftarrows H^+ \quad (1)$$

$$HO^- + O_3 \longrightarrow O_2 + HO_2^- \quad (2)$$

$$HO_2^- + O_3 \longrightarrow HO_2\cdot + O_3^{\cdot -} \quad (3)$$

$$HO_2\cdot \rightleftarrows H^+ + O_2^{\cdot -} \quad (4)$$

$$O_2^{\cdot -} + O_3 \longrightarrow O_2 + O_3^{\cdot -} \quad (5)$$

$$O_3^{\cdot -} + H^+ \longrightarrow HO_3\cdot \quad (6)$$

$$HO_3\cdot \longrightarrow HO\cdot + O_2 \quad (7)$$

$$HO\cdot + O_3 \longrightarrow HO_2\cdot + O_2 \quad (8)$$

and thus: $$2O_3 + H_2O_2 \longrightarrow 2HO\cdot + 3O_2 \quad (9)$$

It is indicated in Eq.(9) that the theoretical molar ratio of H_2O_2/O_3 is 0.5. Ozone cannot be transferred to hydroxyl radical effectively if H_2O_2/O_3 ratio is smaller than 0.5. However, too much H_2O_2 applied may cause the decrease of the concentration of hydroxyl radical in solution as H_2O_2 itself can also react with hydroxyl radicals rapidly. Actually, in practical investigation the proper H_2O_2/O_3 ratio may be different from the theory because of the influence of various operational parameters. It was found that the proper H_2O_2/O_3 ratio changed with different reactor and process adopted in the investigation (Glaze and Kang, 1989). In Duguets study the proper H_2O_2/O_3 ratio is 0.4 to remove chloronitrobenzene in water (Duguet *et al.*, 1990). Some paper showed that the proper H_2O_2/O_3 ratio is between 0.5—1.4 (Aieta *et al.*, 1998; Glaze and Kang, 1990). As shown in Fig.2, the proper H_2O_2/O_3 molar ratio under this experimental condition for the degradation of 2,4-D is around 0.6.

TOC removal of 2,4-D was also investigated both in distilled water and tap water. The results in Table 1 show that under such experimental condition O_3/H_2O_2 process had limited effectiveness on the TOC removal toward 2,4-D, especially for tap water background, although the concentration of 2,4-D is highly decreased. Large amounts of different organic acids with low molecular weight such as propane diacid, oxalic acid and acetic acid were found in the investigation of the degradation products through GC-MS and LC-MS. This explains the little TOC removal in our study. Most of the 2,4-D molecules might be oxidized to organic acids with low molecular weight instead of being mineralized completely. The TOC value of 2,4-D in tap water is much higher than in distilled water because some organic ingredients exist in it. O_3/H_2O_2 process showed less effectiveness toward TOC removal of 2,4-D in tap water compared with distilled water background.

Table 1 TOC removal of 2,4-D in distilled and tap water with different H_2O_2/O_3 ratio

H_2O_2/O_3 ratio, mol/mol	0.00	0.30	0.60	1.20
Original TOC in distilled water, mg/L	5.047	4.986	5.164	4.869
Final TOC in distilled water, mg/L	4.831	4.014	3.878	3.415
Original TOC in tap water, mg/L	9.057	8.984	9.381	8.916
Final TOC in tap water, mg/L	8.889	8.358	8.105	7.814

Notes: O_3 applied: 4.6 mg/L; H_2O_2 applied: 0, 1, 2, 4 mg/L; reaction time: 480 s

Different H_2O_2/O_3 ratio may also influence the transfer of ozone from gas to the liquid, as shown in Table 2. The ozone applied includes three parts: ozone exhausted, ozone remaining unreacted in solution and ozone consumed in the reaction. The difference between ozone applied and ozone exhausted is ozone transferred into the water solution. Hence, ozone transfer is calculated as follows:

$$O_3\ \text{transfer}(\%) = \frac{O_3\ \text{applied} - O_3\ \text{exhausted}}{O_3\ \text{applied}} \times 100$$

Table 2 shows that the addition of hyd rogen peroxide only slightly increased the ozone transfer into water solution. However, with the addition of hydrogen peroxide the removal of 2,4-D was highly

Table 2 Ozone transfer and consumed hydrogen peroxide with different H_2O_2/O_3 ratio

H_2O_2/O_3 ratio, mol/mol	0.00	0.30	0.60	1.20
O_3 transfer, %	41.12	41.05	43.38	44.73
Total dissolved O_3, mg/L	1.89	1.89	1.99	2.06
Applied H_2O_2 dose, mg/L	0.00	1.00	2.00	4.00
Residual H_2O_2, mg/L	0.08	0.68	1.44	3.06
H_2O_2 consumed, mg/L	-	0.32	0.56	0.94
H_2O_2 consumed, %	-	32.00	28.10	23.50

Notes: O_3 applied: 4.6 mg/L; H_2O_2 applied: 0, 1, 2, 4 mg/L; reaction time: 480 s; water background: distilled water

enhanced. The only reason for this is the increasing concentration of hydroxyl radical in solution, the same as the conclusion gained from Fig.2.

In the experiment it was found that most of hydrogen peroxide remained unreacted in water solution as residual. It should be noticed that ozone alone could also produce trace hydrogen peroxide. As mentioned in Eq.(2): ozone can react with hydroxide ion in the water to produce HO_2^-, which may combine with H^+ to produce hydrogen peroxide. This explains why trace hydrogen peroxide was detected in the oxidation process of ozone alone. A greater mass of hydrogen peroxide (around 60%—70%) remains as a residual in water solution with increasing mass applied. However, it was found that residual hydrogen peroxide concentrations in the water samples decreased with time, especially in tap water samples. It is deduced that residual hydrogen peroxide may have a continued reaction with the organics in water sample. Compared with distilled water the tap water contains more organics, which enhances the decreasing of hydrogen peroxide concentration.

2.2 Effect of pH value of water solution

As well known that it is the hydroxyl radical that improves the removal of refractory organics in the O_3/H_2O_2 process. In the reaction mechanism as shown in Eq.(1)—(9), OH^- ion is an important initiator. In the ozone decomposition mechanism the active species is the conjugate base HO_2^- whose concentration is strictly dependent on pH. Accordingly pH is an important factor for the reaction. It is also evident from this mechanism that the addition of hydrogen peroxide to the ozone aqueous solution will also enhance the ozone decomposition with production of hydroxyl radicals (Glaze and Kang, 1989). Both increasing the pH value and the addition of H_2O_2 to the aqueous ozone solution will thus result into the higher rates of hydroxyl radical's production and the attainment of higher steady-state concentrations of hydroxyl radicals in the radical chain decomposition process (Ma and Graham, 2001; Roberto *et al.*, 1999).

In our investigation, it was found that the variation of pH value of solution had significant influence on the oxidation. When the pH value varied from 3.65 to 9.87, the removal efficiency increased from 22.3% to 74.01%. Continually increasing the pH value of the solution to 11.83 would not lead to the obvious increase of 2,4-D removal efficiency. It is probably because that part of the HO_2^- can be further transferred to O_2^{2-} anion under conditions of higher pH. As a consequence, the decomposition of hydrogen peroxide was enhanced. The results of these experiments are shown in Fig.3.

Table 3 shows that the increasing of pH value of solution highly enhanced the ozone transfer from gas into water solution. This is also one of important

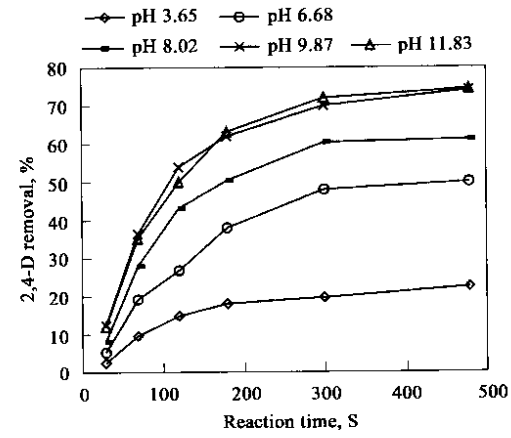


Fig.3 Removal efficiency of 2,4-D in distilled water with transferred pH value
Ozone applied: 4.6 mg/L; H_2O_2 applied: 1 mg/L

reasons of the obvious increase of 2,4-D removal efficiency with increasing pH value. And lower residual hydrogen peroxide occurred with the increasing of pH value of solution as OH^- ion could promote the decomposition of hydrogen peroxide. The consumed hydrogen peroxide reached 96% when the pH value of solution was 11.83.

Table 3 Ozone transfer and consumed hydrogen peroxide with different pH value

pH value	3.65	6.68	8.02	9.87	11.83
O_3 transfer, %	21.3	41.05	49.18	66.43	72.17
Total dissolved O_3, mg/L	0.98	1.89	2.26	3.05	3.32
Applied H_2O_2 dose, mg/L	1.00	1.00	1.00	1.00	1.00
Residual H_2O_2, mg/L	0.91	0.68	0.49	0.33	0.09
H_2O_2 consumed, mg/L	0.09	0.32	0.51	0.67	0.91
H_2O_2 consumed, %	9.00	32.00	51.00	67.00	91.00

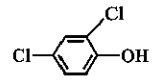
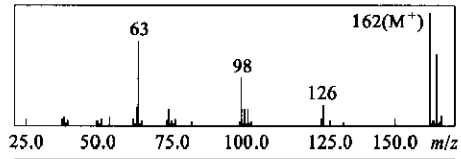
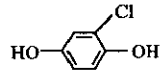
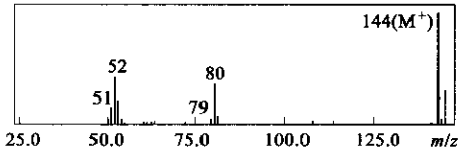
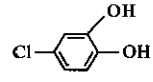
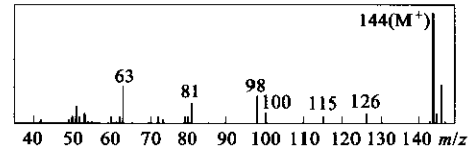
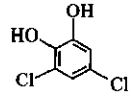
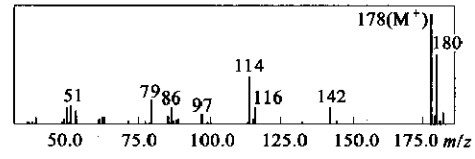
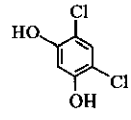
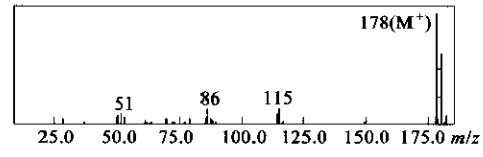
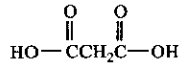
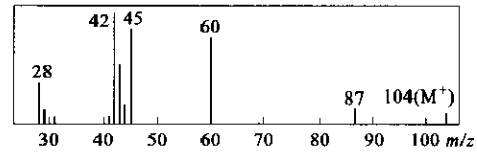
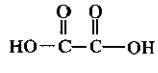
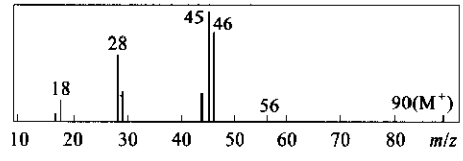
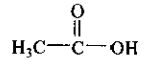
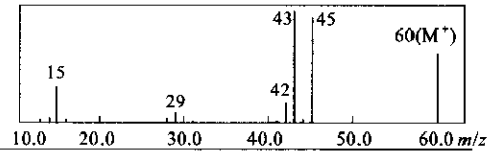
Notes: O_3 applied: 4.6 mg/L; reaction time: 480 s

2.3 Degradation products and possible reaction mechanism of 2,4-D oxidized by O_3/H_2O_2 process

The degradation intermediates and products of 2,4-D were identified by LC-MS and GC-MS. The MS results are shown in Table 4. It was found that 2,4-dichlorophenol was first identified as an important oxidation intermediates. This indicates that the degradation of 2,4-D begins from the destroying of alkoxy bond. It is suggested that 2,4-D is attacked by hydroxyl radical to give an unstable radical intermediate (a) that can combine with hydroxyl radical rapidly to give a hydroxy-acid (b). The carbon-oxygen bond of intermediate (b) is easy to be broken to produce 2,4-dichlorophenol as stable intermediate. Chlorohydroquinone, 4-chlorocatechol, 3,5-dichlorocatechol and 4,6-dichlororesorcinol are also found as the oxidation intermediates of 2,4-D in O_3/H_2O_2 process. It is deduced that 2,4-dichlorophenol can be directly transferred to chlorohydroquinone, 4-chlorocatechol, 3,5-dichlorocatechol and 4,6-

dichlororesorcinol respectively through hydroxyl radicals attacking different positions of its benzene ring. All these intermediates above and their possible producing pathway have been shown in Table 5.

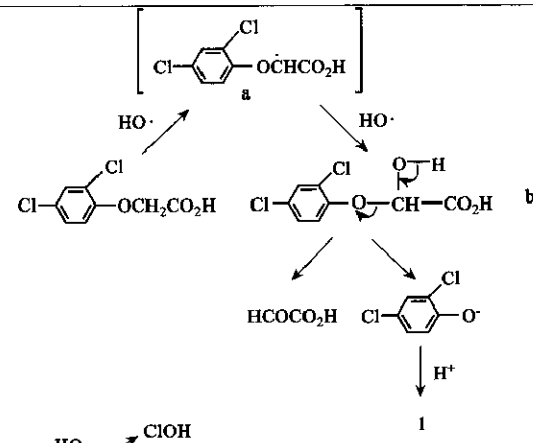
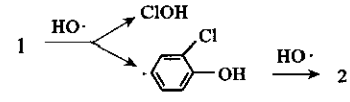
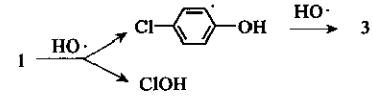
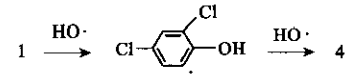
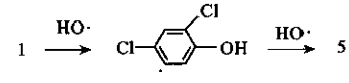
Table 4 Oxidation intermediates and degradation products of 2,4-D

	Compound	Chemical structure	MS spectra
1	2,4-Dichlorophenol		
2	Chlorohydroquinone		
3	4-Chlorocatechol		
4	3,5-Dichlorocatechol		
5	4,6-Dichlororesorcinol		
6	Propane diacid		
7	Oxalic acid		
8	Acetic acid		

At the same time high concentration propane diacid, acetic acid and oxalic acid were identified as the stable degradation products in the oxidation process as shown in Table 4. The further broken of benzene rings both in 2,4-dichlorophenol and its oxidation intermediates can give the acids above as the stable degradation products.

Based on the analysis a possible reaction mechanism is proposed for the oxidation of 2.4-D by O_3/H_2O_2 process (Fig.4). It is concluded that alkoxy bond of 2,4-D is first destroyed to produce 2,4-dichlorophenol and aldehydic acid. The aldehydic acid can be further oxidized to oxalic acid, while 2,4-dichlorophenol must be oxidized to chlorohydroquinone, 4-chlorocatechol, 3,5-dichlorocatechol or 4,6-dichlororesorcinol as intermediates. Then these unstable intermediates may be oxidized to propane diacid through polyhydroxybenzene step. Through decarboxylating, propane diacid can be transferred to acetic acid, which can be further oxidized to oxalic

Table 5 Possible producing pathway of oxidation intermediates through HO· process

Oxidation intermediate	Producing pathway through HO· oxidation process
1 2,4-Dichlorophenol	
2 Chlorohydroquinone	
3 4-Chlorocatechol	
4 3,5-Dichlorocatechol	
5 4,6-Dichlorocatechol	

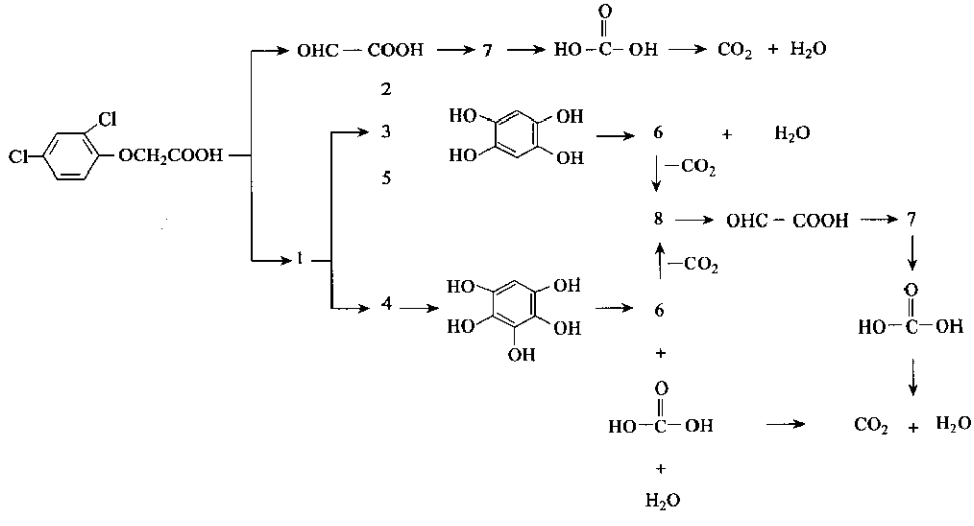


Fig.4 Possible oxidation mechanism of 2,4-D by HO· process
Arabic numerals represent the corresponding chemicals in Table 4

acid through an aldehydic acid pathway. At last, oxalic acid can be mineralized to carbon dioxide and water. The proposed intermediates aldehydic acid, polyhydroxybenzene were not found by GC-LS or LC-MS. It is believed that further oxidation may process rapidly because of their extreme instability.

3 Conclusions

The investigation of 2,4-D degradation by O_3/H_2O_2 process showed that hydrogen peroxide highly enhanced the oxidation of 2,4-D by ozone. The removal efficiency was highly improved with the increasing of H_2O_2/O_3 ratio and pH value of the 2,4-D solution within certain range. It is suggested that the oxidation of 2,4-D by O_3/H_2O_2 follows the radical

mechanism, which is also supported by the experimental results of ozone and hydrogen peroxide. Accordingly, the reaction mechanism of 2,4-D oxidized by O_3/H_2O_2 process is proposed: 2,4-D is oxidized to 2,4-dichlorophenol first and then converted to various polyhydroxylbenzene. These polyhydroxylbenzenes are oxidized to different organic acids with low molecular weight that can be finally mineralized by hydroxyl radicals.

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