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Decomposition of alachlor by ozonation and its mechanism

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Abstract

Decomposition and corresponding mechanism of alachlor, an endocrine disruptor in water by ozonation were investigated. Results showed that alachlor could not be completely mineralized by ozone alone. Many intermediates and final products were formed during the process, including aromatic compounds, aliphatic carboxylic acids, and inorganic ions. In evoluting these products, some of them with weak polarity were qualitatively identified by GC-MS. The information of inorganic ions suggested that the dechlorination was the first and the fastest step in the ozonation of alachlor.

Key words: alachlor; ozonation; decomposition; mechanism

Introduction

The water treatment of environmental toxic compounds has become extremely important due to the increase of chemical contaminants such as pesticides in water system (Chun *et al*., 2003). Alachlor (2-chloro-2′,6′-diethyl-N-methoxymethylacetanilide), a herbicide and endocrine disruptor, has been classified as a carcinogen of B2 group by USEPA (Charizopoulos and Papadopoulou-Mourkidou, 1999). It has been found in groundwater and surface water in many places in North America (Thurman *et al*., 1996; Potter and Carpenter, 1995). In surface water, the residual levels ranged from 0.1 to 10 μg/L (Durand *et al*., 1992; Chiron *et al*., 1993; Pereira and Hostettler, 1993), while the maximum allowed concentration of alachlor is only 2 μg/L (Potter and Carpenter, 1995).

Ozone can be used to oxidize organic hazardous substances effectively from water during drinking water treatment (Rice *et al*., 1981). In reality, even though the destruction of pesticides by ozonation is often achieved successfully, a complete decomposition of these compounds into carbon dioxide is seldom obtained (Giuseppe *et al*., 2001). Therefore, the formation of several by-products or intermediates is usually expected in the form of secondary pollutants (Ku *et al*., 1998; Yao *et al*., 1998). Beltran *et al*. (1999) found that ozone effectively removed alachlor from drinking water, but many intermediates were produced during the ozonation. Furthermore, various chemical derivatives from alachlor were observed in groundwater from a cornfield (Potter and Carpenter, 1995). It is possible that these products are more difficult to be removed, and may possess is greater hazard to the environment than the original compound. Therefore, it is important to understand the possible ozonation pathway of alachlor in drinking water treatment as well as the potential of secondary contamination. Although ring cleavage probably enhanced the degradation of alachlor in ozonation (Cathleen *et al*., 1988), detailed information of the ozonation mechanism of alachlor is not clear.

This study was to investigate the reaction between ozone and alachlor to understand the ozonation process at acidic conditions. In addition to the identification of products, this study quantitatively monitored several main products during the ozonation using HPLC, GC, and ion chromatograph. GC-MS was also used to help establish the probable mechanism of ozonation.

1 Materials and methods

1.1 Materials

Alachlor (99%), which structure is shown in Fig.1, was from AccuStandard Inc. (USA), and the potassium indigotrisulfonate was from Acros Organics (New Jersey, USA). For high-performance liquid chromatography (HPLC), acetonitrile of HPLC grade was from Tedia Company, Inc. (USA). Other chemicals, including KI, H_2SO_4, ammonium acetate, and H_3PO_4, were of regent grade.

Synthetic raw stock water was prepared by dissolving

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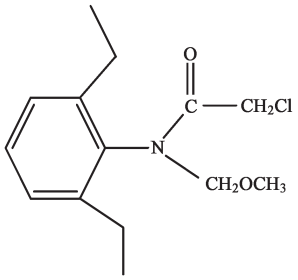

Fig. 1 Chemical structure of alachlor.

240 mg alachlor into 1000 ml ultra-pure water (18 MΩ) to afford a solution of 240 mg/L. The solution pH was 5.93. Alachlor solution of 10 mg/L was obtained by diluting the stock solution, and 1.2 L alachlor solution was used. For ozonation with high concentrations of alachlor, 500 ml raw water was utilized. The use of high concentration of alachlor solution eliminated the need for concentration steps, which may result in significant loss of by-products during the identification on HPLC. All the glassware used in the experiments was soaked in chromic acid, and then in 1% HNO_3 overnight. Except for the volumetric flasks, they were all muffled at 400°C for several hours after being rinsed by tap water and ultra-pure water.

1.2 Experimental procedures

Ozone was generated by a laboratory ozonizer (Mitsubishi, Ozonizer series OS-1N, Japan). The average production of ozone was 1.68 mg/min, and the gas flow rate was controlled at 30 ml/min. The experiments were performed in a stainless reactor (300 mm high, 70 mm i.d.), and the reactor was equipped with a Ti porous plate (10 μm porous size) at its bottom to obtain smaller gas bubbles. Ozone flowed through the solution until a stationary state regime was attained. To absorb the excess ozone, effluent gas was introduced into a glass bottle containing 300 ml of 2% KI solution. During the reaction, 10 ml aliquot samples were collected at regular time periods. Then nitrogen was introduced to terminate the reaction to avoid very large peak appeared on the HPLC chart which influenced the intermediate identification with radical terminations such as Na_2SO_3 added.

1.3 Analytical methods

In this section, all the other parameters were measured directly in solution except for the identification of intermediates by GC-MS.

The concentrations of dissolved ozone were measured colormetrically by indigo method (Bader and Hoigne, 1981). Adsorption measurements were performed using a portable datalogging spectrophotometer (Model DR/2010, Hach, USA) at 600 nm. The amount of applied ozone was calculated by:

$$O_{3\ \text{applied}} = O_{3\ \text{introduced}} - (O_{3\ \text{off-gas}} + O_{3\ \text{residual}}).$$

The residual concentrations of alachlor were determined, and the polar intermediates were directly followed by HPLC (10A, Shimadzu, Japan) after the ozonation. Liquid chromatography was carried out on a ZORBAX Extend-C18 column (250 mm in length, 4.6 mm i.d. Agilent, USA) equipped with a SPD-M10A UV/Visible detector. Pure ACN (acctonitrile) (99.8%) and HPLC grade water with 50 mmol/L ammonium acetate were used as mobile phase. The linear gradient used for the mobile phase was ACN/H_2O (20%, v/v) at a flow rate of 1.0 ml/min at beginning and increased to ACN/H_2O (90%, v/v) over 15 min. The mobile phase was then kept at ACN/H_2O (90%, v/v)) for 12 min. Total run time was 27 min. Injection volume was 20 μl. The absorbance was detected at 215 nm, and quantified using a 5-point calibration curve.

The intermediates were identified by GC-MS. In this procedure, 10 mg/L alachlor was applied to obtain as many products as possible because some of them presented at a very low concentration. After being stripped by nitrogen, ozonated sample solution containing alachlor and its intermediates were extracted by solid-phase extraction (SPE). The cartridges filled with ODS-C18 (500 mg) were from Agilent Technologies (USA). The cartridges were washed by 5 ml of methanol and then 5 ml of distilled water before being used. Solution samples (each was 200 ml) were forced to pass through the cartridges at a flow rate of 2 ml/min by using a vacuum manifold. Most water was expelled by vacuuming for 1 min after the sample was passed through the cartridge. The residual water was removed by passing a gentle nitrogen stream through the cartridges for about 10 min. Then alachlor and its intermediates were eluted by passing through the trap with 5 ml of methylene chloride. The effluents were evaporated under a gentle nitrogen stream, and the final volume was made to 0.5 ml (*n*-hexane). GC-MS analysis was conducted on a DB5 MS (60 m length, 0.25 mm i.d. 0.33 μm film thickness) fused silica capillary column (HP, USA), and directly interfaced to the ion source through a transfer line heated to 280°C. One μl of a sample was injected into a splitless injector at 250°C. The operating conditions were as follows, carrier gas: helium, flow rate: 1 ml/min, initial temperature: 60°C, ramped at 4°C/min to 160°C, then 2°C/min to 280°C. EI mass spectra were obtained at 70 eV electron energy with the ion source at 180°C. The background-subtracted mass spectra were matched against those in the NIST mass spectra library, and interpreted on the basis of the observed fragmentation.

Aliphatic carboxylic acids (acetic acid, propionic acid and oxalic acid) produced during the ozonation were analyzed using an ion chromatographer (Dix-500, Dionex Co.) equipped with a conductivity detector and an AG9-HC guard column (Dionex Co.). The eluent was 9.0 mmol/L Na_2CO_3 solution.

UV scans were done on an Ultraviolet/vision spectrophotometer (U-3100, Hitachi Co. Japan) with samples diluted for 7.5 factors. The evolution of inorganic ions in the ozonation was measured using an ion chromatography of Dionex 4000i (Dionex, Sunnyvale, CA, USA) equipped with an AS4A-SC column (4 mm). TOC was determined using a Phoenix 8000 TOC analyzer (Tekmar-Dohrmann Co., USA) also with the samples diluted for 7.5 factors.

2 Results and discussion

2.1 Removal efficiency of alachlor by ozonation

Table 1 shows the removal of alachlor and the corresponding TOC during ozonation process. It demonstrated that ozone was very effective in removing alachlor with degradation percentage of 94% after 30 min of ozonation. However, only 24.5% of TOC was removed after 180 min ozonation. This implied that under these reaction conditions, ozone was not able to completely mineralize alachlor into CO_2 and H_2O, and some persistent intermediates were still predominant in the solution. Furthermore, these intermediates appeared to be not very reactive to ozone at acidic conditions.

Table 1 Removal percentage of TOC and alachlor at different ozonation time

Ozonation time (min)	10	30	60	120	180
Alachlor (%)	55.7	91.2	93.4	95.8	95.9
TOC (%)	5.5	8.3	16.7	23.2	24.5

Initial alachlor: 120 mg/L; ozone applied: 1.17 mg/(L·min); ozone flow rate: 30 ml/min; temperature: 20°C.

2.2 Dechlorination and denitrification of alachlor

Side chain reactions happened at the initial stages of ozonation, producing inorganic ions in reaction solution. Table 2 depicts the formation of Cl^-, NO_2^- and NO_3^- from the mineralization of organic chlorine and nitrogen compounds, which are linked to alachlor molecule in the ozonation process. Ozonation might have induced the denitrification and cleavage of aromatic ring. The amount of the chloride anion increased rapidly at the initial stage of the ozonation process, and then stayed as constant when alachlor was completely degraded. However, the amount of nitrite ion increased continually throughout the entire ozonation process, and a small amount of nitrate ion was also detected. Interestingly, 80.8% of chlorine was converted into Cl^- after ozonized for 180 min, while only 25.8% of nitrogen was converted into nitrites and nitrates. These indicated that, at acidic reaction condition, ozone could effectively remove chlorine, and dechlorination was probably the first step in the ozonation of alachlor. Ring cleavage might not be the main mechanism. This also suggested that these chlorine and nitrogen compounds were still present in the reaction solution.

Table 2 Inorganic ions produced in the ozonation process of alachlor

Ozonation time (min)	10	30	60	120	180
Cl^- (mg/L)	2.207	4.654	7.635	12.63	12.8
NO_2^- (mg/L)	0.5	2.071	2.518	3.625	4.618
NO_3^- (mg/L)	0.176	0.235	0.471	0.686	0.902

Initial alachlor: 120 mg/L; ozone applied: 1.17 mg/(L·min); ozone flow rate: 30 ml/min; temperature: 20°C.

Because of the dechlorination reactions, the construction of the alachlor molecule changed dramatically during the ozonation process. This could be verified by the remarkable variation of UV spectra of the alachlor solution throughout the ozonation process (Fig.2). Fig.2 shows that the diagnostic absorption of alachlor disappeared almost completely after ozonated for 30 min, suggesting a drastic destruction of alachlor molecules. Nevertheless, a weak absorption in the range of 230–290 nm was observed although absorbance decreased eventually, implying that new compounds with conjugated structure might have been produced.

2.3 Polar aromatic intermediates formed in the ozonation process

Several kinds of intermediates were formed in the ozonation. Some of them appeared to have polar characteristics, and they were directly determined in the solution by HPLC. According to Fig.3, fourteen types of aromatic intermediates were detected by HPLC with a UV detector. Twelve of them had shorter retention time than that of alachlor, indicating that they were more polar compounds than alachlor. The aromatic structure must have been maintained because they were UV detectable. In addition, two of intermediates possessed weaker polarity than alachlor. Fig.4 shows the evolution of these intermediates with ozonation time. Most of them were quickly accumulated to the maximum concentrations initially, and then decreased

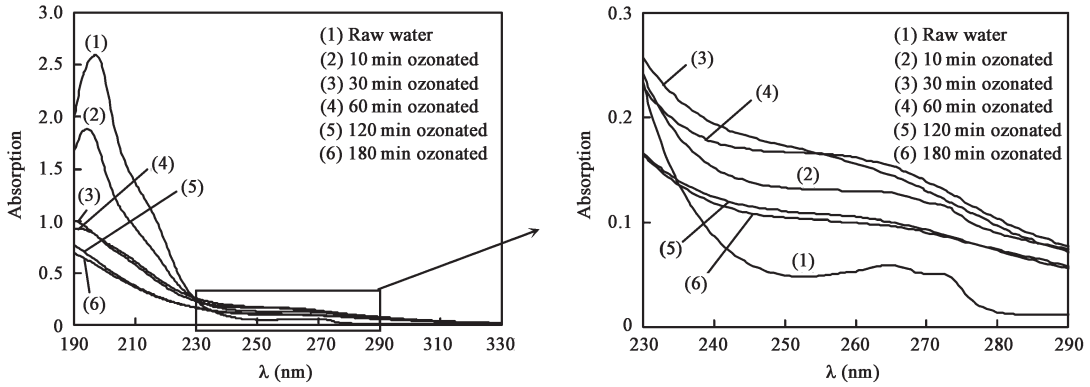

Fig. 2 Comparison of UV spectra of alachlor solution before and after ozonation. Initial alachlor: 120 mg/L; ozone applied: 1.17 mg/(L·min); ozone flow rate: 30 ml/min; temperature: 20°C.

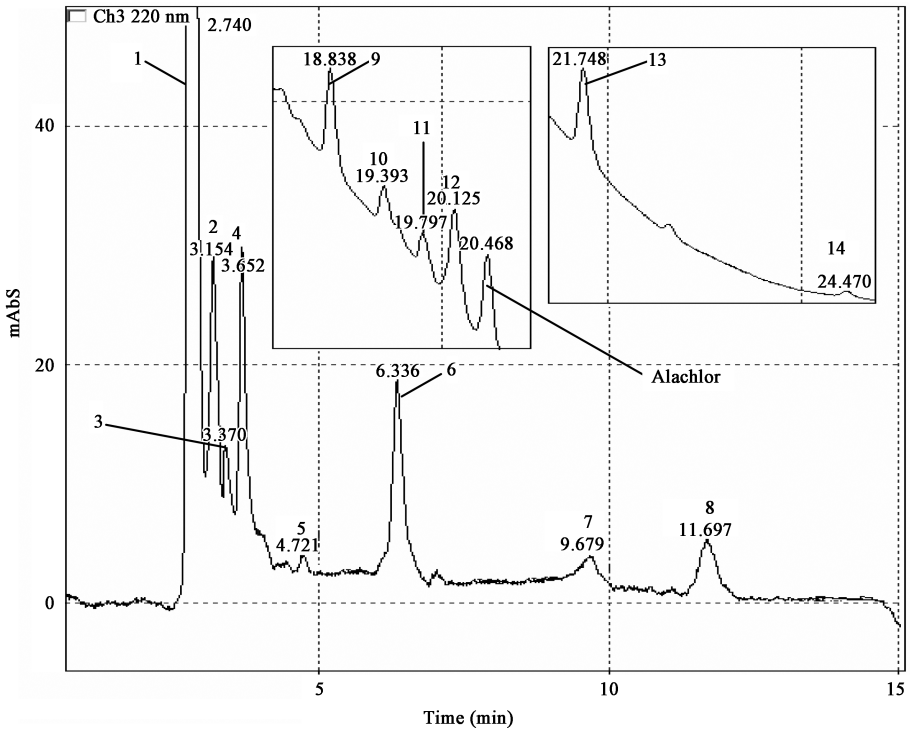

Fig. 3 HPLC-UV chromatogram of alachlor by-products after 30 min of ozonation. Initial alachlor: 120 mg/L; ozone applied: 1.17 mg/(L·min); ozone flow rate: 30 ml/min; temperature: 20°C.

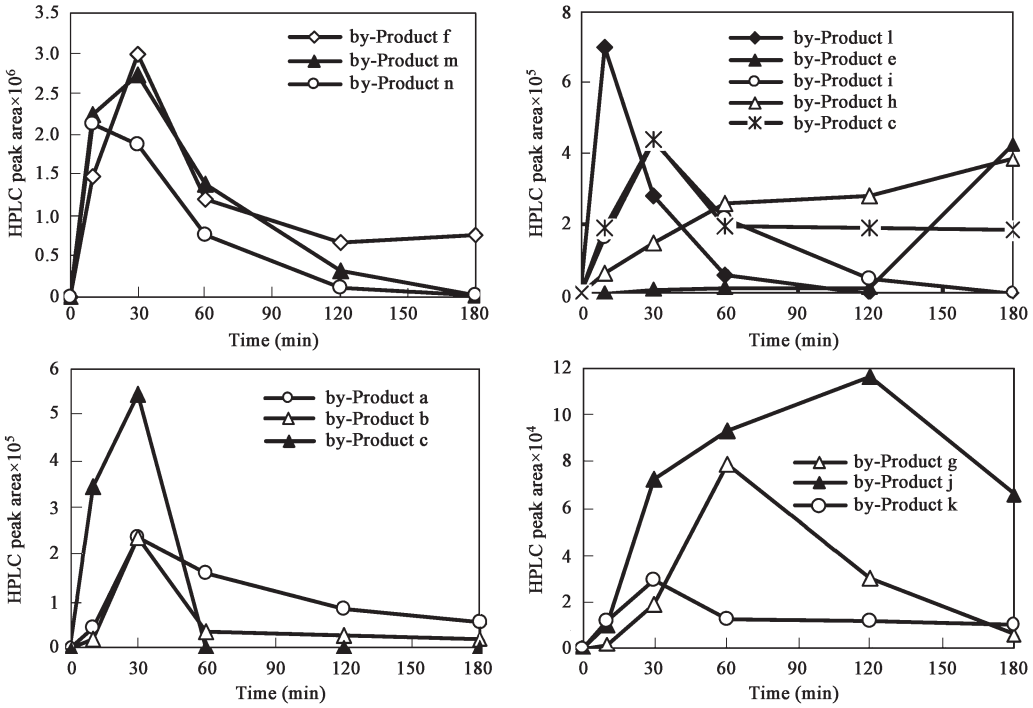

Fig. 4 Evolution of alachlor by-products in the ozonation process followed by HPLC. Initial alachlor: 120 mg/L; ozone applied: 1.17 mg/(L·min); ozone flow rate: 30 ml/min; temperature: 20°C. a–n are corresponding the peaks 1–14 in Fig.3.

to very low concentration levels as ozonation proceeded. However, there still were several intermediates that were resistant to ozone, and remained in the reaction solution to some extent.

2.4 Probable ozonation mechanism of alachlor at acidic condition

Many aromatic intermediate products were formed with a drastic change of the structure of alachlor. To identify

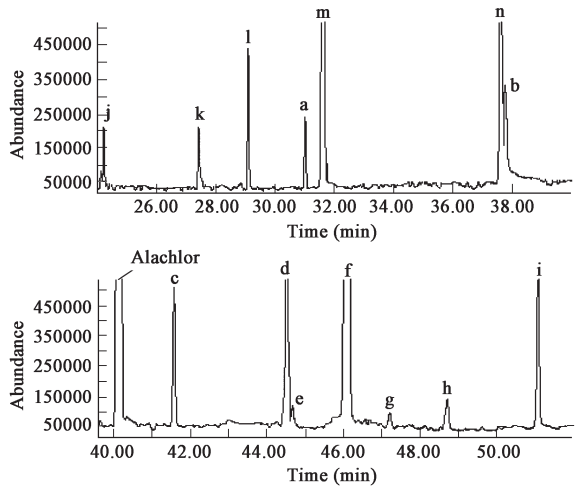

Fig. 5 Intermediates produced in the ozonation identified by GC-MS. Initial alachlor: 10 mg/L; ozone applied: 1.17 mg/(L·min); ozone flow rate: 30 ml/min; ozonation time: 30 min; temperature: 20°C.

these intermediates, GC-MS was applied. As presented in Fig.5 and Table 3, these compounds were characterized by substitution of chlorine by hydroxyl and replacement of aether by methyl or hydroxyl or acetyl by ketone. Five of the intermediates were not qualitatively identified, and the further study is still ongoing. From the information obtained so far, a possible ozonation pathway of alachlor at acidic conditions is proposed as Fig.6.

2.5 Product of ring cleavage reaction–carboxylic acids

The ozonation of alachlor had resulted in the formation of several organic aromatic intermediates, which were the earliest intermediate products. Then, they underwent further oxidation to more refractory and short-chain mono- and di-carboxylic acids such as acetic acid, propionic acid and oxalic acid (Fig.7), which resulted in a decrease of pH of the reaction solution from 5.93 to 3.76. One important thing need to point out is that degraded precursors of carboxylic acids were not identified because the sample was not derived for experimental reasons. As shown in Fig.7, when the solution was ozonated for 180 min, the concentrations of acetic, propionic and oxalic acids reached 40.0, 11.10 and 6.85 mg/L, respectively, and no further decrease trend was observed. The accumulation of acids in the solution was due to the low reactivitiy of small-molecule fatty acids with ozone and ·OH except for formic acid (Hoigne and Bader, 1983). A great number of ·OH were needed to oxide these carboxylic acids. However, in the oxidation of alachlor by ozone alone, the amount of ·OH produced from the decomposition of ozone was not enough to degrade these acids. On the other hand, the reaction of organic hazardous substances with ozone might proceed by following two possible mechanisms:

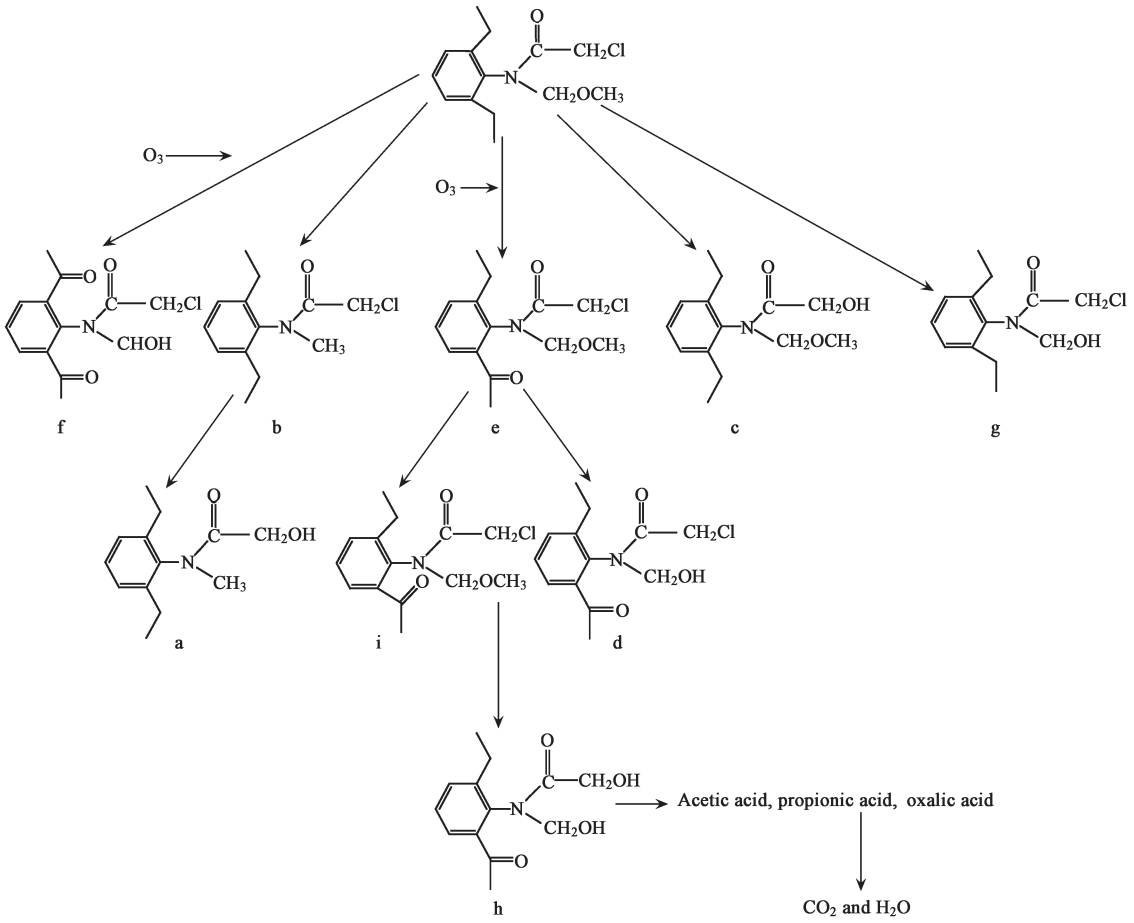

Fig. 6 Deduced ozonation pathway of alachlor in acidic condition.

Table 3 GC-MS characteristics of major compounds

Compound	Retention time (min)	Molecular weight	Main ions-EI mode (relative abundance)
a	31.007	221	221 (100), 189 (97), 176 (78), 148 (40), 133 (15)
b	37.727	239	239 (5), 224 (9), 190 (100), 162 (35), 148 (47)
c	41.571	251	251 (32), 202 (55), 174 (75), 160 (100), 146 (25)
d	44.551	269	269 (1), 234 (28), 202 (11), 174 (19), 160 (100), 146 (15)
e	44.690	283	283 (4), 238 (15), 224 (4), 188 (100), 160 (75), 146 (36), 118 (28)
f	46.096	283	283 (1), 248 (37), 188 (16), 174 (100), 160 (20), 132 (17)
g	47.197	255	255 (7), 238 (4), 223 (27), 188 (9), 174 (78), 146 (100), 118 (32)
h	48.701	251	251 (4), 238 (51), 223 (29), 188 (64), 174 (100), 146 (21)
i	51.064	265	265 (2), 237 (22), 220 (16), 202 (63), 188 (100), 174 (12), 160 (4), 146 (7)
j	24.269	unknown	220 (29), 205 (100), 189 (4), 145 (15)
k	27.445	unknown	191 (32), 164 (28), 115 (44), 88 (100)
l	29.105	unknown	223 (43), 208 (40), 188 (4), 174 (56), 146 (100)
m	31.618	unknown	259 (10), 227 (50), 214 (100), 150 (76)
n	37.612	unknown	255 (2), 226 (100), 196 (11), 168 (10)

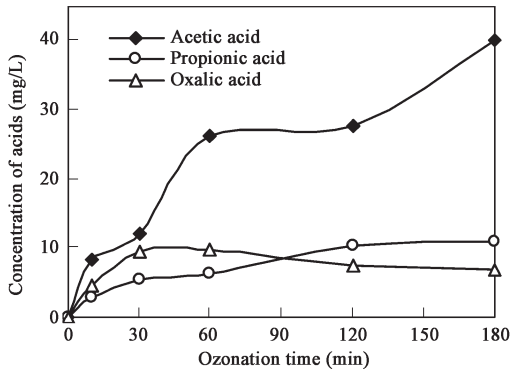

Fig. 7 Variation of organic acids created in the ozonation process. Initial alachlor: 120 mg/L; ozone applied: 1.17 mg/(L·min); ozone flow rate: 30 ml/min; temperature: 20°C.

direct reaction with ozone and indirect reaction with radicals formed during the decomposition of ozone in water. At high pH, radical reaction might be the main reaction mechanism, while at a low pH the selective direct reaction might play the major role. Since the oxidation potential of hydroxyl radicals is 2.80 V, much higher than that of molecule ozone (2.07 V), radical oxidation can be much more favorable than the direct oxidation. Therefore, with the decrease of pH of alachlor solution in the ozonation, the direct reaction between alachlor and ozone became a dominant process. As a result, the intermediate products, especially those acids, tended to accumulate in the ozonation process. These compounds were assumed to contribute to a majority of the residual TOC during ozonation, and the decomposition of these compounds was considered to be the rate-determining step of alachlor mineralization.

3 Conclusions

This study investigated the removal and decomposition mechanism of alachlor, an endocrine disruptor, in water under acidic conditions by ozone. Results showed that ozone could successfully degrade alachlor, but a complete mineralization of alachlor into CO_2 and H_2O under acidic condition was proved to be difficult to achieve. This was due to the formation of intermediate products in the ozonation process. Using UV, HPLC and GC-MS, the molecular weights and structures of several intermediates were obtained. Our results also suggested that de-chlorination might be more likely to occur than the cleavage of the aromatic ring in acidic condition. The earliest intermediates included several aromatic compounds. These compounds underwent further oxidation to more refractory and short-chained mono- or di-carboxylic acids such as acetic acid, propionic acid and oxalic acid, and these acids contributed to the remaining TOC of the reaction solution as major secondary pollutants.

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