



Effectiveness and pathways of electrochemical degradation of pretilachlor herbicides

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ABSTRACT

Pretilachlor used as one kind of acetanilide herbicides is potentially dangerous and biorefractory. In this work, electrochemical degradation of lab-synthetic pretilachlor wastewater was carried out with Sb doped Ti/SnO₂ electrode as anode and stainless steel as cathode. The effect of current density on pretilachlor degradation was investigated, and the degradation pathway of pretilachlor was inferred by analyzing its main degradation intermediates. The results showed that the removal of pretilachlor and TOC in treatment time of 60 min were 98.8% and 43.1% under the conditions of current density of 20 mA cm⁻², initial concentration of pretilachlor of 60 mg L⁻¹, Na₂SO₄ dosage of 0.1 mol L⁻¹, pH of 7.2, respectively, while the energy consumption was 15.8 kWh m⁻³. The main reactions for electrochemical degradation of pretilachlor included hydroxylation, oxidation, dechlorination, C–O bond and C–N bond cleavage, resulting in the formation of nine main intermediates.

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1. Introduction

The problem which the pesticides polluted the water body has been widely concerned for a long time. The main contaminated pathway of pesticide in water is that the residues in the soil go into the water body by the way of running water, leakage, washing out and so on [1]. In addition, industrial wastewater containing pesticide discharged into water body is also a pollution way. As a widely used pre-emergence herbicide, acetanilide is accumulated in environment especially in water body due to their constant use and chemical stability, which will bring the potential risk to the aquatic ecosystems and the health of human being. It is reported that the acetanilide herbicide has been detected in the surface and ground water in many countries [2–5].

Pretilachlor [2-chloro-2',6'-diethyl-N-(propyloxyethyl)acetanilide] is widely used to control the annual weeds in rice fields. It is reported that pretilachlor is moderate toxicity, however it is extremely toxic to the aquatic organism, which may

cause the long-term adverse effects to the aquatic environment (Chemblink CAS database 51218-49-6). Currently, the researches on pretilachlor are mainly concentrated on the fate of pretilachlor after it goes into the environment [6–8]. However, there are few reports on removal of pretilachlor from the environment. Kim et al. [9] had reported that the removal of the pretilachlor in solution (60 mg L⁻¹) was only 90% after 24 h reaction by adopted zero-valent iron synthesized in the laboratory. Therefore, it is necessary to find an effective method to removal the pretilachlor in water.

The main common methods to treatment the nonbiodegradable pesticide wastewater are advanced oxidation processes, such as ozonation [10], Fenton oxidation [11], photocatalytic oxidation [12], electrocatalysis oxidation [13] and so on. As one of effective methods for the nonbiodegradable organic compounds, electrocatalysis oxidation can transform the organic components into CO₂ or biodegradable organic ones. Because of its simplicity, easy control and no secondary pollution in the process of electrocatalysis oxidation, it was called “environment friendly technology” [14].

In the paper, we investigated the degradation process of pretilachlor by electrocatalysis oxidation, in which Ti/SnO₂ electrode doped Sb was as anode and stainless steel as cathode. The effect of current density on degradation of pretilachlor was studied in detail. Besides, the degradation pathways of pretilachlor were also studied by analyzing the intermediates from the degradation process. This will provide the basic research data for the practical treatment of the wastewater with pretilachlor.

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2. Materials and methods

2.1. Materials

Pretilachlor (99%) was purchased from J&K chemical Co. Ltd. (Beijing). Na₂SO₄, NaOH and hydrochloric acid (AR) were purchased from Bodi chemical company (Tianjin). Acetic acid, propionic acid, oxalic acid, monochloroacetic acid (AR) were obtained from Tianjin Chemical Reagent Factory. Sb doped Ti/SnO₂ electrode used in the experiments were prepared by ourselves (sol–gel method) [15].

2.2. Methods

2.2.1. Electrochemical degradation of pretilachlor

Electrochemical degradation of pretilachlor was carried out in the electrolysis cell with 100 mL glass beaker. For each cell, a 6 cm² (3 cm × 2 cm) Sb doped Ti/SnO₂ electrode was used as anode and a stainless steel with the same dimension was used as cathode. The electrode gap was set as 2 cm. A DC potentiostat was used as the power supply for organic degradation studies. Pretilachlor sample solution (100 mL, 60 mg L⁻¹) was placed in each cell with supporting electrolyte (Na₂SO₄, 0.1 mol L⁻¹). Electrolysis was performed under galvanostatic control. Solution samples were taken out from the cell after electrolysis for 30 min, 60 min, 90 min, 120 min and 180 min, respectively. Then the concentration of pretilachlor and small organic acids produced in degradation pretilachlor were analyzed by HPLC after samples were filtered through a filter with 0.45 μm. At the same time, total organic carbon (TOC) were also analyzed.

2.2.2. Solid phase extraction of degradation solution of pretilachlor

Before analyzing and identifying the intermediates of pretilachlor degradation, degradation solution was processed with solid phase extraction (SPE) by solid phase extraction column (Agilent, 500 mg/6 mL, C18). SPE column was adjusted by methanol (5 mL) and then followed by distilled water (5 mL). Degradation solution (200 mL) was flowed at 8 mL/min via column, then dried in high vacuum for 30 min. The column was eluted with CH₂Cl₂ (5 mL) and methanol (5 mL) at the flow rate of 1 mL min⁻¹. The eluant was dried over by anhydrous Na₂SO₄ and condensed to 1 mL at 45 °C under nitrogen gas for GC–MS measurement.

2.3. Analyses and measurement

The concentration of pretilachlor in solution was analyzed by HPLC (Agilent 1100, Zorbax SB-C18 column, 5.0 μm, 2.1 × 150 mm, Agilent, USA). The UV detected wavelength was set as 210 nm, CH₃CN/H₂O (90/10, v/v) with 1 mL min⁻¹ was used as flow phase, and amount of sample injection was 20 μL.

GC–MS (Agilent 6890 GC/5973 MSD) coupled with an HP-5MS column (30 m × 0.25 mm × 0.25 μm film thickness) was used to analyze the intermediates during the degradation of pretilachlor. Helium gas was used as carrier gas at a flow rate of 1.0 mL min⁻¹. The oven temperature started at 50 °C and held for 2 min; increased to 300 °C at the heating rate of 8 °C min⁻¹ and held for 1 min. Inlet temperature was 250 °C. Test was progressed by EI as ion source, temperature of 230 °C, electro energy of 70 eV and interface temperature of 280 °C.

The concentration of small organic acids in the degradation solution was analyzed by HPLC (Shimadzu LC-10A, WATO20190 Ion-Exclusion column, 7.8 mm × 300 mm, WATERS, USA). The UV detected wavelength was set as 210 nm, H₃PO₄/H₂O (15/85, v/v) with 0.8 mL min⁻¹ was used flow phase, and amount of sample injection was 10 μL.

UV absorption spectra were obtained on a SHIMADZU UV–visible spectrometer model UV-2550. Degradation solution was diluted to 10 times for absorption measurement.

TOC measurement was obtained on a SHIMADZU TOC instrument ASI-5000A.

3. Results and discussion

3.1. Degradation effect of pretilachlor

The initial pretilachlor (100 mL) concentration was 60 mg L⁻¹, and 0.1 mol L⁻¹ Na₂SO₄ was used as supporting electrolyte. Current density was set as 10, 20 and 30 mA cm⁻² for DC degradation. The degradation effect of pretilachlor at different current densities was shown in Fig. 1.

Decay of pretilachlor was enhanced with the increase of current density as shown in Fig. 1(a). After 60 min, the removal of pretilachlor at the current density of 10, 20 and 30 mA cm⁻² was 78%, 98.8% and 100%, respectively. The concentration of pretilachlor decreased exponentially with reaction time and the degradation rate could be expressed by the following equation:

$$\ln\left(\frac{c_0}{c}\right) = kt \quad (1)$$

where c was the concentration of pretilachlor at the reaction time t , c_0 was the initial concentration and k was the reaction rate constant. The degradation of pretilachlor was in accordance with pseudo-first-order kinetics as shown in Fig. 1(b). The reaction rate constant k is found to be 2.39×10^{-2} , 7.67×10^{-2} and 9.65×10^{-2} min⁻¹ at the current density of 10, 20 and 30 mA cm⁻² with regression coefficient R^2 of 0.9910, 0.9969 and 0.9840, respectively.

On the other hand, the current density remarkably influenced the mineralization of pretilachlor. At current density of 10, 20, 30 mA cm⁻², removal of TOC was 24.0%, 43.1% and 59.2% in 60 min and 56.0%, 85.1% and 100% in 180 min, as shown in Fig. 1(c). The removal of TOC was lower than that of pretilachlor, which indicated the formation of unmineralized products during the degradation of pretilachlor. Moreover, complete mineralization of pretilachlor is possible with the increased current density and reaction time, such as the current density of 30 mA cm⁻² and the treatment time of 180 min.

It has been reported that the increasing current density would enhance the electron transfer rate of organic compounds on electrode surface and hence accelerated the direct oxidation rate. Meanwhile, the increasing current density also enhanced the generation rate of hydroxy radical as indirect oxidation reagent and hence increased the degradation and mineralization of pretilachlor [16]. However, with the increasing of current density, the probability and reaction rate of side reaction on anode were also greatly increased, resulting in the decreasing of mineralization current efficiency (MCE) and increasing of energy consumption. Under various current densities, mineralization current efficiency of degradation of pretilachlor was shown in Fig. 1(d). MCE was calculated as follows [17]:

$$\text{MCE} = \frac{nFV_s \Delta(\text{TOC})_{\text{exp}}}{4.32 \times 10^7 mlt} \times 100\% \quad (2)$$

Where n was the number of electrons consumed via the theoretical mineralized reaction of pretilachlor (94), F was the Faraday constant (96,487 C mol⁻¹), V_s was the volume of electrolyte (L), $\Delta(\text{TOC})_{\text{exp}}$ was the decreased value of TOC under degradation (mg L⁻¹), 4.32×10^7 was conversion factor (=3600 s h⁻¹ × 12,000 mg of C mol⁻¹), m was the number of carbon atoms of pretilachlor molecule (=17) and I was applied current (A).

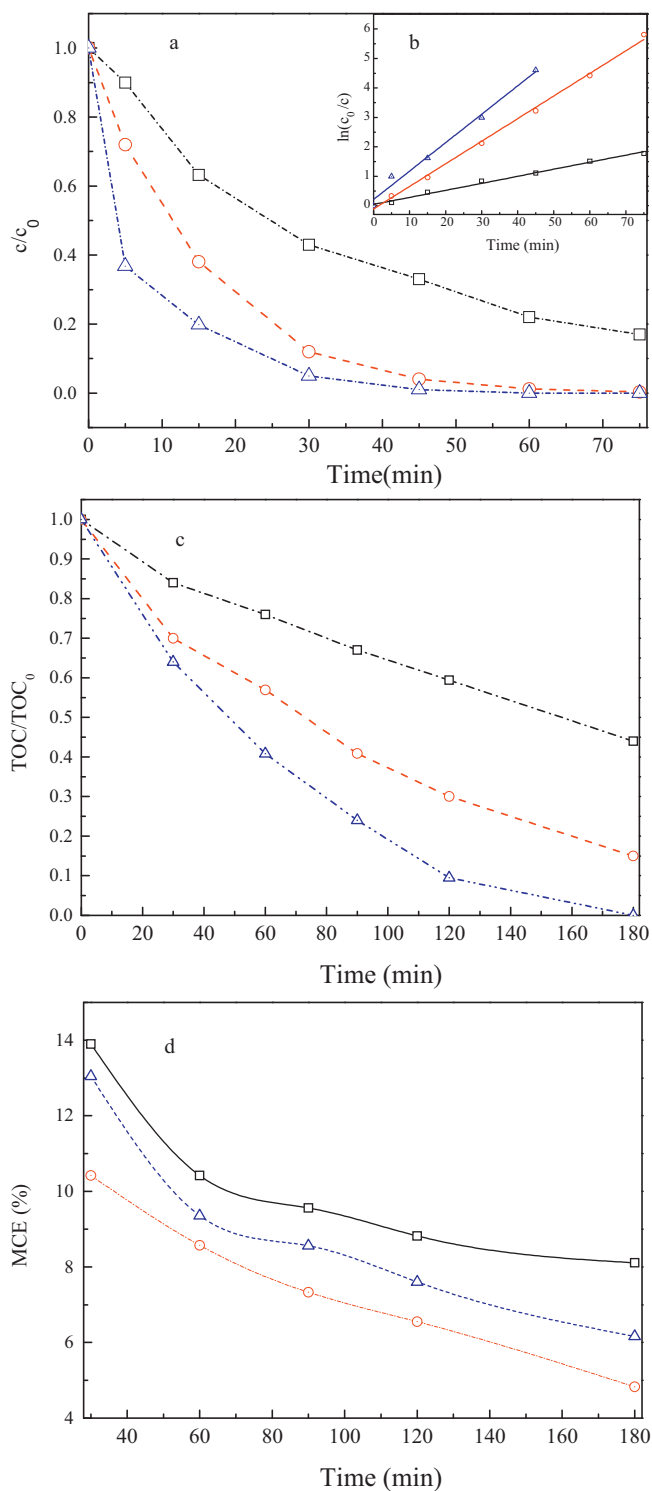
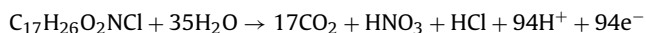


Fig. 1. The current density influence on pretilachlor degradation: (□) 10 mA cm⁻², (○) 20 mA cm⁻², (△) 30 mA cm⁻². (a) The current density influence on the removal rate of pretilachlor. (b) The current density influence on reaction rate of degradation of pretilachlor. (c) The current density influence on mineralization rate of pretilachlor. (d) The current density influence on mineralization current efficiency of pretilachlor.

The mineralized reaction of pretilachlor was as follows:



The mineralized current efficiency decreased with increasing current density. After 60 min degradation of pretilachlor, when the

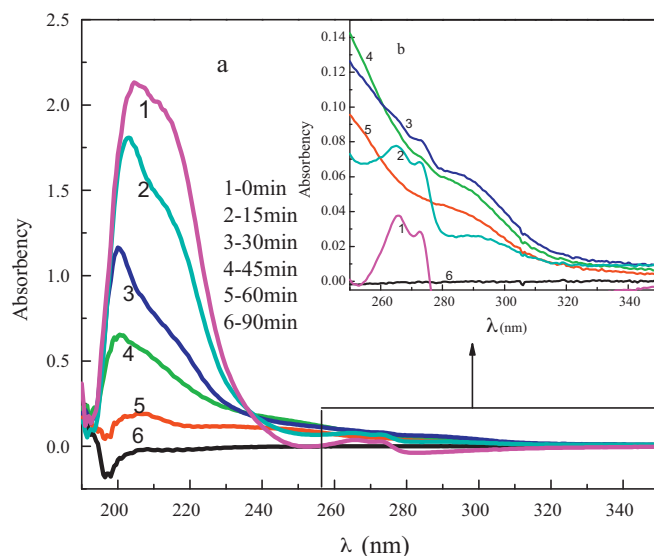


Fig. 2. UV spectra of the degradation solution which was diluted to 10 times at different reaction time at current density of 20 mA cm⁻², pretilachlor concentration of 60 mg L⁻¹, Na₂SO₄ concentration of 0.1 mol L⁻¹.

current density was 10, 20 and 30 mA cm⁻², the MCE was 10.4%, 9.4% and 8.6%, respectively, while the energy consumption was 6.1, 15.8 and 29.9 kWh m⁻³, respectively.

Therefore, we synthetically considered the influence of current density on TOC removal, MCE and energy consumption during degradation of pretilachlor. In order to ensure the effective removal of the pretilachlor and TOC, enhance mineralization current efficiency and reduce energy consumption, the preferable current density is 20 mA cm⁻² under the present experimental conditions.

3.2. Intermediates in the electrocatalysis oxidation process of pretilachlor

3.2.1. UV spectrum during degradation of pretilachlor

Results of UV scans of the solution sample under different degradation time with the concentration diluted by 10 times were shown in Fig. 2. The absorption peaks of pretilachlor were at 210 nm and 270 nm. The peak at 270 nm was weak and the peak at 210 nm was the maximum absorption peak. With the increase of degradation time, the maximum absorption peak at 210 nm rapidly decreased and finally disappeared after 60 min. In addition, an absorption band in the range of 250 nm and 400 nm appeared and its intensity was increased initially and then decreased with the reaction time. The appearance of new peak indicated that some intermediates which were more difficult to degrade than pretilachlor were formed. Therefore, it was more important to analyze the structures and degradability of these intermediates.

3.2.2. Analysis of small organic acids during the electrocatalysis oxidation of pretilachlor

During electrocatalysis oxidation of pretilachlor, the value of pH changed greatly from 8.14 to 4.38 after 60 min, which showed that small organic acids were generated during degradation of pretilachlor. These organic acids were identified and quantitated, which was showed in Fig. 3. It could be found that along with degradation of pretilachlor acetic and propionic acids were immediately generated and then they increased continuously with reaction time, even when pretilachlor was almost removed after 60 min. Therefore it could be presumed that acetic and propionic acids were generated from degradation of pretilachlor and its intermediates. In addition, another part of acetic and propionic acids came from

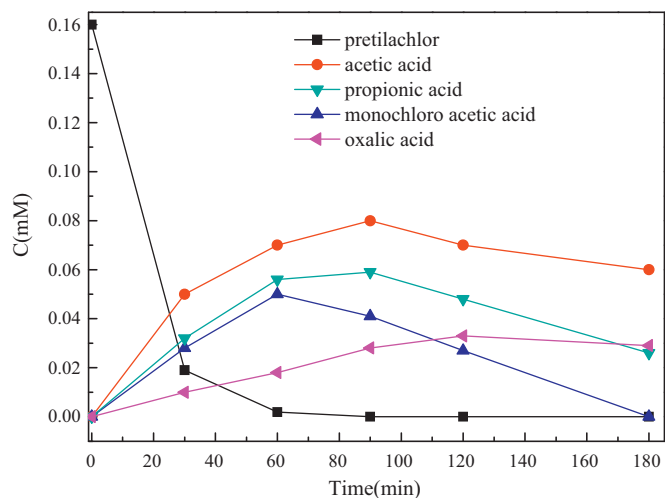


Fig. 3. Formation of organic acids during degradation of pretilachlor at current density of 20 mA cm^{-2} , pretilachlor concentration of 60 mg L^{-1} , Na_2SO_4 concentration of 0.1 mol L^{-1} .

cleavage of benzene ring. Li et al. [18] proposed that the benzene ring cleavage could occur during the degradation of aromatic ring by electrocatalysis oxidation and acetic acid as well as oxalic acid were generated.

Monochloroacetic acid might originate from the oxidation of chloroacetyl group coming off from the pretilachlor and its intermediates.

It could be also found that the concentration of oxalic acid increased gradually with the decrease of monochloroacetic acid and acetic acid, which might be due to that monochloroacetic acid and acetic acid were converted into oxalic acid. Therefore oxalic acid was the ultimate carboxylic acid [19].

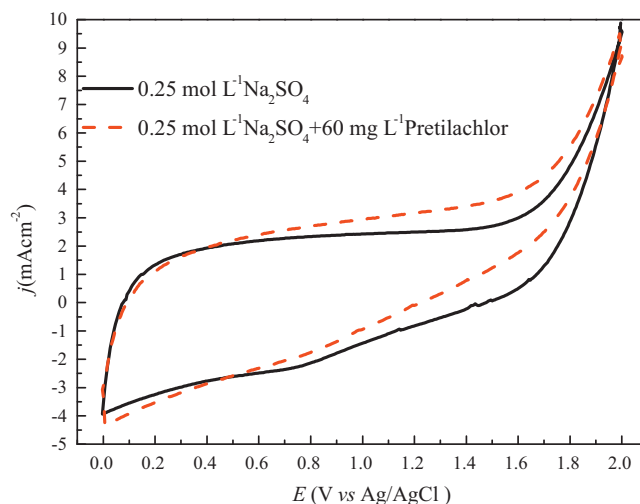


Fig. 5. Cyclic voltammogram on the Sb doped Ti/SnO_2 electrode in 0.25 mol L^{-1} Na_2SO_4 solution with and without pretilachlor obtained at a scan rate of 50 mV/s .

3.2.3. Identification of intermediates during the electrocatalysis oxidation of pretilachlor

The degradation solution of electrocatalysis oxidation of pretilachlor was analyzed by GC–MS, and the total ion chromatograms of pretilachlor and its intermediates at different degradation time were shown in Fig. 4. A number of intermediates were formed during the degradation of pretilachlor. Nine intermediates were identified by comparing the obtained fragments in mass spectra with the data in the other literatures. The mass spectral characterization of pretilachlor and intermediates and also the speculated structures were summarized in Table 1.

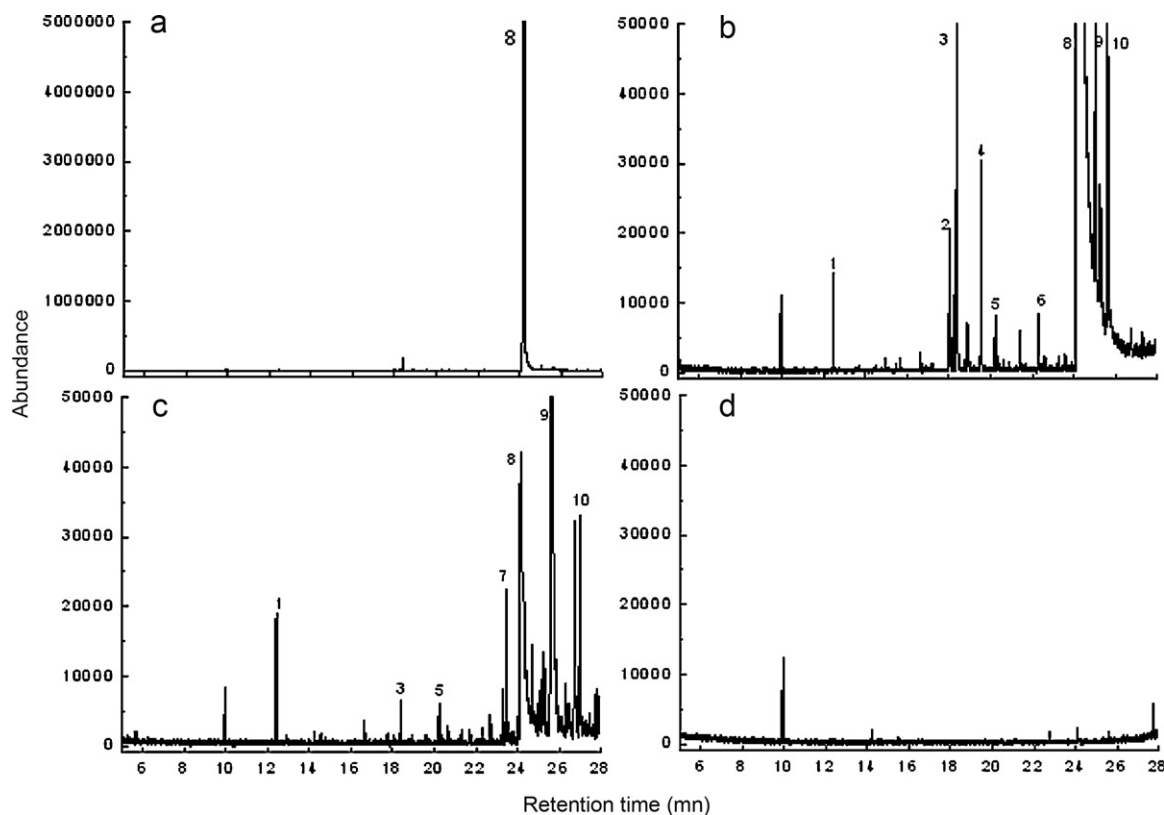


Fig. 4. GC–MS total ion chromatograms of pretilachlor and its intermediates at different degradation time: (a) 0 min, (b) 30 min, (c) 60 min, (d) 120 min at current density of 20 mA cm^{-2} , pretilachlor concentration of 60 mg L^{-1} , Na_2SO_4 concentration of 0.1 mol L^{-1} .

Table 1
Mass spectral characterization of pretilachlor and intermediates and the speculated structures.

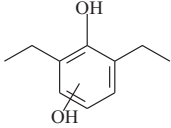
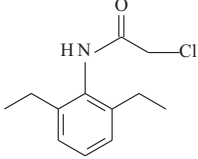
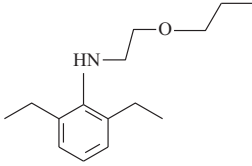
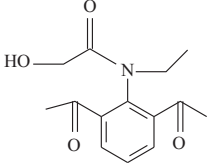
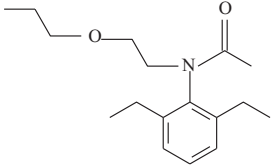
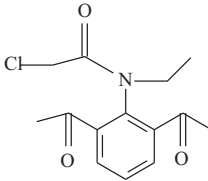
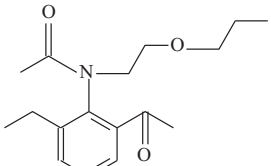
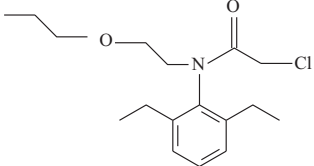
No.	RT (min)	MW	Major daughter ions (relative abundances (%))	Structures
1	12.421	166	166M ⁺ (8) 152[M-CH ₃] ⁺ (42) 109[M-C ₄ H ₉] ⁺ (100)	
2	18.012	225	225 M ⁺ (10) 176[M-CH ₂ Cl] ⁺ (100) 147[M-C ₂ H ₃ OCl] ⁺ (11)	
3	18.382	233	233 M ⁺ (11) 160[M-C ₃ H ₇ O] ⁺ (100) 146[M-C ₄ H ₉ O] ⁺ (10)	
4	19.532	263	263M ⁺ (15) 203[M-C ₃ H ₇ O] ⁺ (12) 175[M-C ₄ H ₇ O ₂] ⁺ (100) 161[M-C ₄ H ₇ O ₂ N] ⁺ (56)	
5	20.223	277	277M ⁺ (5) 204[M-C ₄ H ₉ O] ⁺ (23) 191[M-C ₅ H ₁₀ O] ⁺ (38) 162[M-C ₆ H ₁₁ O ₂] ⁺ (100)	
6	22.253	281	281M ⁺ (1) 216[M-C ₂ H ₅ Cl] ⁺ (51) 188[M-C ₃ H ₅ OCl] ⁺ (100) 174[M-C ₄ H ₇ OCl] ⁺ (98)	
7	23.556	291	291M ⁺ (3) 218[M-C ₄ H ₉ O] ⁺ (25) 205[M-C ₅ H ₁₀ O] ⁺ (37) 190[M-C ₆ H ₁₃ O] ⁺ (29) 160[M-C ₇ H ₁₅ O ₂] ⁺ (100)	
8	24.148	311	311M ⁺ (4) 238[M-C ₄ H ₉ O] ⁺ (87) 176[M-C ₆ H ₁₂ OCl] ⁺ (70) 162[M-C ₆ H ₁₀ O ₂ Cl] ⁺ (100)	

Table 1 (Continued)

No.	RT (min)	MW	Major daughter ions (relative abundances (%))	Structures
9	25.632	325	325M ⁺ (2) 282[M-C ₃ H ₇] ⁺ (13) 252[M-C ₄ H ₉ O] ⁺ (21) 190[M-C ₆ H ₁₁ O ₂ Cl] ⁺ (71) 176[M-C ₇ H ₁₃ O ₂ Cl] ⁺ (100)	
10	26.985	327	327M ⁺ (9) 254[M-C ₅ H ₉ O] ⁺ (100) 218[M-C ₅ H ₁₀ OCl] ⁺ (97) 178[M-C ₆ H ₁₀ O ₂ Cl] ⁺ (99)	

By analyzing the fragments in mass spectra and comparing with the data in literatures, it was found that compounds 2, 6 and 9 were in accordance with 2-chloro-2',6'-diethyl-N-acetanilide, 2-chloro-2',6'-diacetyl-N-(ethyl) acetanilide and 2-chloro-2'-acetyl-6'-ethyl-N-(propyloxyethyl) acetanilide. Compound 2 were detected during the direct oxidation of alachlor by O₃ [20]. And some intermediates similar to compound 6 and 9 were also detected.

The structures of compound 3 and 5 were in accordance with 2,6-diethyl-N-(propyloxyethyl) aniline and 2,6-diethyl-N-(propyloxyethyl) acetanilide. These compounds had similar structures with some intermediates in the bio-degradation process of acetanilide herbicide [21].

Until now, the intermediates similar to compound 1, 4 and 7 were undetected in degradation of acetanilide herbicide. According to the fragments in mass spectra, we speculated the structures of compound 1, 4 and 7 were 2,6-diethyl-benzenediol, 2-hydroxy-2', 6'-diacetyl-N-(ethyl) acetanilide, and 2-acetyl-6-ethyl-N-(propyloxyethyl) acetanilide.

The retention time of compound 8 was 24.148 min and the MW is 311. It was consistent with the retention time of the standard pretilachlor solution. Therefore the chemical formula of the compound 8 must be the 2-chloro-2',6'-diethyl-N-(propyloxyethyl) acetanilide.

By analyzing the fragment of compound 10 in mass spectra, compound 10 should be hydroxylalachlor, which was similar to the intermediate of photocatalysis degradation of alachlor [22].

3.3. The degradation pathways of pretilachlor

In the present, the common view of electrocatalysis oxidation mechanism for DSA electrode illustrated that two ways were participated in the electrochemical oxidation of organic compounds: the direct electrochemical oxidation degradation at the electrode and the indirect oxidation of organic compounds by using the oxidative •OH produced on the surface of electrode [23]. When •OH as physical adsorbed oxygen was located on the surface of electrode, the electrochemical combustion would be happened and the organic compounds would be completely degraded; whereas, •OH as chemical adsorbed oxygen was located on the surface of electrode,

the electrochemical conversion would be generated, resulting in incomplete degradation of organic compound [24].

Cyclic voltammogram was measured in order to examine the direct oxidation of organism on the Sb doped Ti/SnO₂ electrode. Fig. 5 was the CV curves of Ti/SnO₂ electrode in 0.25 mol L⁻¹ sodium sulfate solution with and without pretilachlor. No oxidized peak or deoxidized peak was observed in the CV curve of solution containing pretilachlor, which proved that direct oxidation of pretilachlor can not occur on the electrode surface.

Taking terephthalic acid as •OH capture agent, fluorescence spectrum technique was employed to examine whether •OH could be produced during the electrochemical degradation process or not in the previous experiment of our research group [25]. The results proved that •OH was produced on the surface of Ti/SnO₂ electrode during the electrolysis process, and •OH caused the indirect oxidation of organism.

Based on the above discussion, we could speculate the degradation process of electrocatalysis oxidation of pretilachlor, which mainly contains hydroxylation, oxidation, dechlorination, C–O bond and C–N bond cleavage, as shown in Fig. 6.

Oxidative •OH generated on the anode surface or in the solution attacks the benzene ring of pretilachlor, leading to the formation of compound 10. Then the electron density in the aromatic ring of compound 10 was increased and the electrophilic substitution of •OH continuously occurred, resulting in the formation of compound 1. Meanwhile, the side chains would be oxidized into propionic acid, acetic acid, monochloroacetic acid and oxalic acid. In addition, •OH also attacked on the side chain of benzene ring, resulting in the cleavage of C–N bond and formation of compound 2 and 3, at the same time propionic acid, acetic acid and monochloroacetic acid were also generated.

•OH as chemical adsorbed oxygen on the surface of electrode attacked on the ethyl side chain of pretilachlor, and formed compound 9 via oxidation reaction. The continuous oxidation of compound 9 and the cleavage of C–O induced the formation of compound 6 and propionic acid. Then compound 4 could be formed via dechlorination and hydroxyl reaction of compound 6.

Compound 5 was formed by dechlorination of pretilachlor on the cathode of electrolysis cell, where chloride atom in pretilachlor was substituted by hydrogen atom [26]. Oxidation of the compound 5 then formed the compound 7.

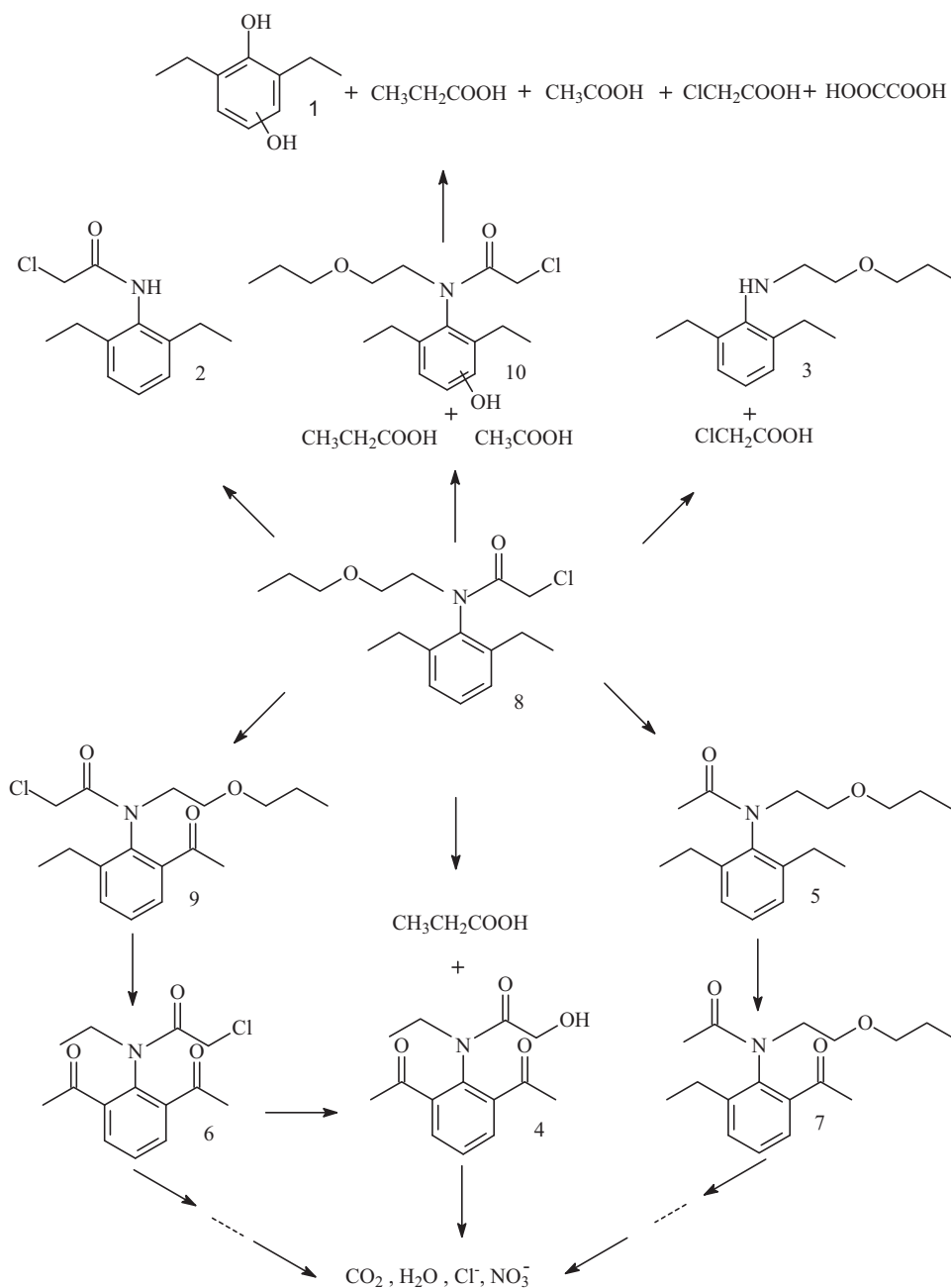


Fig. 6. The degradation pathways of pretilachlor.

These intermediates and small organic acids would be further oxidized on the surface of electrode by electrochemical combustion, and would be completely mineralized with longer reaction time, which could be confirmed from Fig. 1(d).

4. Conclusions

In conclusion, the electro-oxidation process could efficiently degrade pretilachlor in the solution. In these experiments, under the condition of current density of 20 mA cm⁻², pH of 7.2, concentration of electrolyte of 0.1 mol L⁻¹, reaction time of 60 min, and concentration of pretilachlor of 60 mg L⁻¹, removal of pretilachlor and TOC was as high as 98.8% and 43.1%, respectively, and the energy consumption was only 15.8 kWh m⁻³. The results showed that the degradation pathways contained hydroxylation, oxidation,

dechlorination, C–O bond and C–N bond cleavage, resulting in the formation of nine main intermediates. These intermediates could be completely mineralized through the increased current density and reaction time.

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