

# Photo-Fenton degradation of alachlor in the presence of citrate solution

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## Abstract

The photodegradation of alachlor, which is one of acetanilide herbicides, was carried out in the presence of the Fenton reagent (Fe(II) and H<sub>2</sub>O<sub>2</sub>) and citrate. The degradation rate was strongly influenced by the pH, and initial concentrations of H<sub>2</sub>O<sub>2</sub>, Fe(II) and citrate. An initial alachlor concentration of 10 mg L<sup>-1</sup> was completely degraded after 10 min at pH 5 under the optimum conditions. Therefore, it was possible to extend available pH range of the photo-Fenton reaction by the existence of the citrate. The decrease of total organic carbon (TOC) as a result of mineralization of alachlor was observed during the photo-Fenton process with citrate. The degree of alachlor mineralization was about 100% under UV irradiation after 26 h. The formations of chloride, nitrate and ammonium ions as end-products were observed during the photocatalytic system. The decomposition of alachlor gave seven kinds of intermediate products. The degradation mechanism of alachlor was proposed on the base of the evidence of the identified intermediates. Based on these results, UV/Fe(II)-citrate/H<sub>2</sub>O<sub>2</sub> system could be useful technology for the treatment of wastewater containing alachlor.

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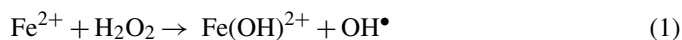
**Keywords:** Alachlor degradation; Photo-Fenton reaction; Citrate; Mineralization; Wastewater treatment

## 1. Introduction

Herbicides represent the largest group of chemicals used as plant protection agents. However, with increasing amounts of chemical herbicides, contaminants in a water stream have become an important issue of worldwide concern. Alachlor, 2-chloro-2',6'-diethyl-N-methoxymethyl acetanilide, is an herbicide widely used in the United States, Europe and Japan, and is commonly used to control most annual grasses and many broadleaf weeds. It has been detected in ground water and surface water [1], despite its rapid microbial and photo-induced decomposition [2,3]. Alachlor has been classified as the carcinogen of B2 group by the EPA [4] and has been known as a highly toxic endocrine disrupting chemical, where the allowed maximum concentration for drinking water is 2 µg L<sup>-1</sup> [5].

A variety of effective treatment techniques for aqueous alachlor have been proposed by using ozonation including the combination with catalyst [6–8], sonication [9], TiO<sub>2</sub> [10–14],

photo-Fenton [15] and anodic Fenton [16] procedures. Recent reports indicate that a combination of H<sub>2</sub>O<sub>2</sub> and UV irradiation with Fe(II), so-called the photo-Fenton process, can significantly enhance decomposition of many refractory organic compounds [17]. Recently, we also reported the degradation of bisphenol A and pesticides in aqueous solution by the photo-Fenton reaction [18–20]. The acceleration for decomposition of organic compounds is believed to be in order to photolysis of iron aquacomplex, Fe(H<sub>2</sub>O)<sub>5</sub>(OH)<sup>2+</sup> (represented hereafter by Fe(OH)<sup>2+</sup>), to providing a new importance source of OH• radicals [21,22]. Further, the photolysis of Fe(OH)<sup>2+</sup> regenerates Fe(II) (Eqs. (1) and (2)), which means that the photo-Fenton reaction would need low Fe(II) concentration compared with the Fenton process.



Furthermore, the Fe(OH)<sup>2+</sup> can absorb light at wavelengths up to ca. 410 nm, while TiO<sub>2</sub> photocatalysis can use photon with wavelength close to 380 nm [23]. Therefore, the photo-Fenton process can be expected to an efficient method for

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wastewater treatment and promotes the rate of degradation of various organic pollutants. However, Fenton systems have a disadvantage in which the applicable pH range is restricted at pH around 3 because of large production of iron sludge. It is expected that the production of iron precipitation can be prevented and the applicable pH of Fenton reaction can be expanded by the presence of suitable ligands. Furthermore, Fe(III) complexes have been known to play an important role in producing oxidants because of its high molar absorptivity and quantum yield. For example, several attempts have been made to apply Fe(III)-oxalate as a photochemical method in the treatment of polluted water, using artificial or solar light [24,25].

In the present study, we have investigated the degradation and mineralization of alachlor in water using of photo-Fenton process in the presence of citrate. The many factors, such as pH value, and initial concentrations of Fe(II), citrate and H<sub>2</sub>O<sub>2</sub>, affected on the degradation were evaluated. The progress of mineralization of alachlor was monitored by total organic carbon (TOC) content and ionic chromatography. Furthermore, the photoproducts of alachlor during this photocatalytic process have been identified by gas chromatography-mass spectrometry (GC/MS). The degradation pathway was proposed on the basis of intermediates formed.

## 2. Experimental

### 2.1. Reagents

Alachlor was purchased from Wako Pure Chemical Industries (Osaka, Japan) and was used as received (GC grade >98.0%). Analytical grade hydrogen peroxide solution (30%, w/w) and ferrous sulfate heptahydrate (FeSO<sub>4</sub>·7H<sub>2</sub>O) were purchased from Wako Pure Chemical Industries (Osaka) and Nacalai Tesque (Kyoto, Japan), respectively, and were used as received. Ligands used were trisodium citrate dehydrate (Nacalai Tesque), Na<sub>2</sub>EDTA·2H<sub>2</sub>O (Wako Pure Chemicals), and sodium pyrophosphate decahydrate (Wako Pure Chemicals). All other chemicals and solvents were of the purest grade commercially available and were used without further purification. All aqueous solutions were prepared with ultrapure water obtained from an ultrapure water system (Advantec MFS Inc., Tokyo, Japan) resulting in a resistivity > 18 MΩ cm.

### 2.2. Photodegradation procedure

Photodegradation was conducted in a Pyrex glass cell of 30 mL capacity as previously reported [20]. The reaction mixture inside the cell, consisting of 20 mL of alachlor solution and the precise amounts of Fenton reagent and ligand, was continuously stirred with a magnetic bar. The pH of the sample solution was adjusted with H<sub>2</sub>SO<sub>4</sub> and/or NaOH solution. The initial concentration of alachlor in all experiments was 10 mg L<sup>-1</sup> (3.7 × 10<sup>-5</sup> mol L<sup>-1</sup>). Reaction temperature was kept at 25 ± 1 °C with a water bath. The sample solution was illuminated with a Xe lamp (990 W, Ushio Electronics Co.). The beam was parallel and the length between lamp and the reactor wall was 10 cm. The lamp was warmed up for 10 min

to reach constant output. In this case, the short UV radiation (λ < 300 nm) was filtered out by the vessel wall. The intensity of the light was measured by a UV radio meter (UVR-400, Iuchi Co.) with a sensor of 320–410 nm wavelength. The radio meter was set up at the same position as the reactor. In the majority of experiments, degradation of alachlor was examined under a light intensity of 2.0 mW cm<sup>-2</sup>. The degradation reaction was quenched by adding 1 mL of methanol for HPLC and of H<sub>3</sub>PO<sub>4</sub> for TOC analyses [15]. These experiments were conducted in triplicates and the results showed at the mean values. Relative standard deviations were range of 4.3–8.6%.

### 2.3. Analyses

The progress in the degradation of alachlor was followed with a HPLC (JASCO Co., Tokyo, Japan) equipped with a JASCO UVDEC-100-VI UV detector and a RP-18 GP 150 separation column (150 mm × 4.6 mm i.d., Kanto Chemicals, Tokyo, Japan). The elution was monitored at 220 nm. The mobile phase was a mixture of acetonitrile and water (6/4, v/v), and was pumped at a flow rate of 0.7 mL min<sup>-1</sup>.

The progress of mineralization of alachlor was monitored by measuring the TOC. TOC of the sample solution was measured with a Shimadzu TOC analyzer (TOC-V<sub>E</sub>) based on CO<sub>2</sub> quantification by non-dispersive infrared analysis after high-temperature catalytic combustion.

The progress of ammonium ion formation was obtained by ionic chromatography using a Shimadzu LC-10AT VP pump equipped with a Shimadzu COD-6A conductivity detector and a Shodex cationic column (IC YK-421). Similarly, the formations of chloride and nitrate ions were also analyzed by ionic chromatography using a Hitachi L-6000 pump equipped with a Hitachi L-3270 conductivity detector and a Hitachi anionic column (#2710-SK-IC).

The hydroxyl radical concentration was estimated using a deoxyribose method [26]. Deoxyribose (3.5 mM) was reacted with OH• radicals generating by the optimized Fe(II)/citrate/H<sub>2</sub>O<sub>2</sub>/UV system. Total reaction volume was 20 mL. The reaction was stopped by addition of 5 mL thiobarbituric acid (1%, w/v, in 50 mM NaOH) and 5 mL of trichloroacetic acid (2.8%, w/v). The mixture was heated at 80 °C for 30 min. The product of the reaction was quantified at 532 nm using an UVDEC-610 double-beam spectrometer (JASCO Co.). The concentration of OH• radicals was equated with thiobarbituric acid active substances using an extinction coefficient, ε<sub>532 nm</sub>, of 153 mM<sup>-1</sup> cm<sup>-1</sup>. A reaction system containing only Fe(II), H<sub>2</sub>O<sub>2</sub> and citrate at the same concentration was used as control.

The intermediate products during photodegradation of alachlor were extracted with dichloromethane (2 mL × 3). The combined organic fraction was dried by Na<sub>2</sub>SO<sub>4</sub>, and concentrated under N<sub>2</sub> flow. A GC/MS (Shimadzu GC-MS 5050A) was used for separation and detection of the intermediate products. The GC was equipped with a HP-5 capillary column (30 m × 0.25 mm i.d.) in helium carrier gas (1.5 mL min<sup>-1</sup>) and with splitless injection system. The GC oven temperature was programmed to hold 50 °C for initial 1 min, to increase from 50 to 240 °C at a rate of 20 °C min<sup>-1</sup> and to hold at 240 °C

for 10 min. The injector and interface temperatures were kept at 250 °C. Mass spectra were obtained by the electron-impact (EI) mode at 70 eV using the full scan mode.

### 3. Results and discussion

#### 3.1. Effect of variables on the degradation of alachlor

Effect of ligand on the degradation of alachlor by the photo-Fenton process was examined. Ligands studied were citrate, EDTA and pyrophosphate. These results are shown in Fig. 1. The degradation percentage of alachlor was 60% after 60 min in the absence of ligands because much precipitation of  $\text{Fe}(\text{OH})_3$  observed during the process. Citrate and EDTA gave a positive effect for the degradation of alachlor, that is, alachlor was achieved the complete degradation within 30 min in the presence of the ligands. Especially, UV/Fe(II)–citrate/ $\text{H}_2\text{O}_2$  system provided a most rapid alachlor degradation (15 min). On the contrary, pyrophosphate gave a negative effect. Pyrophosphate ion in water is known to easily form complex with ferric ions [27]. This Fe(III)–pyrophosphate formation can reduce the photo-Fenton system reactivity. This is because of low activity for  $\text{H}_2\text{O}_2$  decomposition [28], low quantum yield for ferrous ion reproduction [29] or working as an  $\text{OH}^\bullet$  radical scavenger. Therefore, the following experiments were conducted in the presence of citrate.

Effect of pH on the degradation of alachlor by use of the photo-Fenton process was investigated over the pH range of 2–8 in the presence of citrate. These results are shown in Fig. 2. The degradation percentages of alachlor were relatively high values over the pH range of 2–5. On the other hand, the degradation efficiencies of alachlor were almost constant (ca. 65%) when pH was even above 6. These results show that the degradation system (UV/Fe(II)–citrate/ $\text{H}_2\text{O}_2$ ) of alachlor can precede at a neutral pH range comparing with conventional photo-Fenton process. It is noteworthy that the degradation percentage of alachlor was about 85% after 5 min at pH 5. Furthermore, pre-

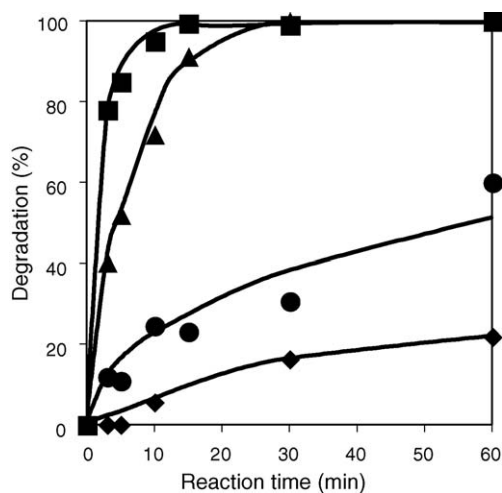


Fig. 1. Effect of ligand kind on the degradation of alachlor by use of the photo-Fenton process. (●) Absence of ligand; (▲) EDTA; (■) citrate; (◆) pyrophosphate ( $[\text{Fe}(\text{II})]_0 = 1 \times 10^{-4} \text{ M}$ ;  $[\text{H}_2\text{O}_2]_0 = 4 \times 10^{-3} \text{ M}$ ;  $[\text{ligand}]_0 = 1 \times 10^{-4} \text{ M}$ ; pH 5.0; light intensity =  $2.0 \text{ mW cm}^{-2}$ ).

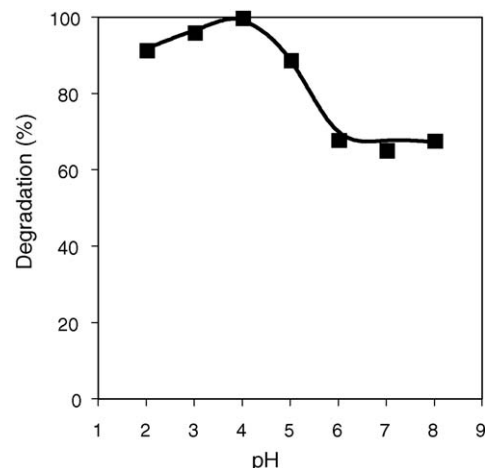


Fig. 2. Effect of pH on the degradation of alachlor by use of the photo-Fenton process in the presence of citrate ( $[\text{Fe}(\text{II})]_0 = 1 \times 10^{-4} \text{ M}$ ;  $[\text{H}_2\text{O}_2]_0 = 4 \times 10^{-3} \text{ M}$ ;  $[\text{citrate}]_0 = 1 \times 10^{-4} \text{ M}$ ; irradiation time = 5 min; light intensity =  $2.0 \text{ mW cm}^{-2}$ ).

cipitation of  $\text{Fe}(\text{OH})_3$  was not observed at all studied pH range. Generally, the optimal pH of the photo-Fenton reaction is around 3 [30] because the main species at pH 2–3,  $\text{Fe}(\text{OH})^{2+}$ , is the one with the largest light absorption coefficient and quantum yield for  $\text{OH}^\bullet$  radical production, along with Fe(II) regeneration, in the range 280–370 nm [29]. Fukushima et al. [31,32] reported that the degradation of pentachlorophenol (PCP) and aniline was enhanced at pH 5 by the presence of humic acid (HA) in the photo-Fenton system because the complexation of Fe(III) with HA contributed to the stabilization of iron species. In the present study, citrate might react with iron species followed by the formation of iron complexes and these could assist the catalytic cycles of iron in the photo-Fenton system. In addition, the complete degradation of alachlor could be achieved within 10 min by adding  $5 \times 10^{-4} \text{ M}$  of citrate at pH 6 (data not shown). Therefore, it was possible to extend available pH range of the photo-Fenton reaction by the existence of the citrate.

Effect of initial  $\text{H}_2\text{O}_2$  concentration on the degradation of alachlor with the use of UV/Fe(II)–citrate/ $\text{H}_2\text{O}_2$  system was investigated in the range of  $4 \times 10^{-5}$  to  $0.4 \text{ M}$  at pH 5.0. The degradation rate of alachlor increased with increasing the initial concentration of  $\text{H}_2\text{O}_2$  up to  $4 \times 10^{-3} \text{ M}$ . This can be explained by the effect of the additionally produced  $\text{OH}^\bullet$  radicals. Addition of  $\text{H}_2\text{O}_2$  beyond  $4 \times 10^{-3} \text{ M}$  did not drastically improve the maximum degradation percentage. This would be due to self-decomposition of  $\text{H}_2\text{O}_2$  to oxygen and water, and the recombination of  $\text{OH}^\bullet$  radical. Since  $\text{OH}^\bullet$  radical reacts with  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{O}_2$  itself contributes to the  $\text{OH}^\bullet$  radical scavenger [33].

To obtain the optimal initial Fe(II) and citrate concentrations, the investigations were carried out in the ranges of  $0\text{--}2 \times 10^{-4}$  and  $0\text{--}5 \times 10^{-4} \text{ M}$ , respectively, at pH 5.0 ( $[\text{H}_2\text{O}_2]_0 = 4 \times 10^{-3} \text{ M}$ ). As shown in Fig. 3, the degradation rate of alachlor increased with increasing initial Fe(II) and citrate concentrations. The highest degradation was obtained with  $2 \times 10^{-4} \text{ M}$  Fe(II) and  $5 \times 10^{-4} \text{ M}$  citrate.

The UV/Fe(II)–citrate/ $\text{H}_2\text{O}_2$  system produced  $\text{OH}^\bullet$  radical during the reaction. The radical is a strong oxidizing agent that reacts with alachlor and causes its degradation. The concen-

tration of  $\text{OH}^\bullet$  radical in the reaction mixture increased with increasing reaction time up to 4 h, decreasing for reaction time above 4 h and then it reached a relatively stable value that lasted at least 24 h (Fig. 4). The  $\text{OH}^\bullet$  radical was thus produced during the whole reaction time (24 h), which was confirmed by prolonged incubation with deoxyribose. Accordingly, a continuous formation of  $\text{OH}^\bullet$  radical is observed allowing the complete mineralization of alachlor.

Fig. 5 shows a comparison of the degradation of alachlor in both the dark and light. The Fe(II)–citrate/ $\text{H}_2\text{O}_2$  system in the dark was evaluated for the degradation of alachlor. For this case, although the degradation reaction of alachlor was observed at pH 5.0 because of faster generation of  $\text{OH}^\bullet$  radical than the conventional Fenton reaction and inhibition the precipitation of  $\text{Fe}(\text{OH})_3$  [34], it could not be achieved the complete degradation within 60 min (ca. 60% degradation). On the other hand, alachlor could be completely degraded within 10 min under the light condition. These results indicate that the UV/Fe(II)–citrate/ $\text{H}_2\text{O}_2$  system is useful for the treatment of environmental samples containing alachlor.

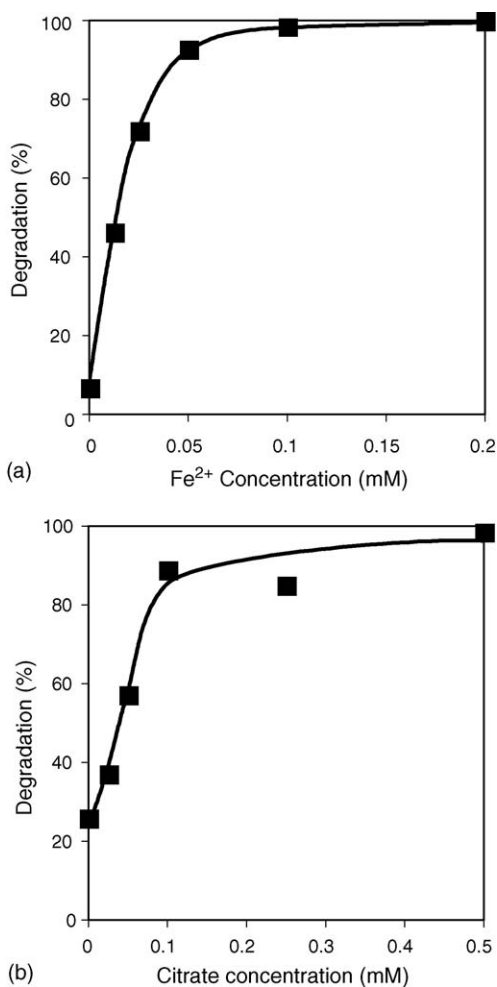


Fig. 3. Degradation of alachlor by the photo-Fenton process after 5 min at different concentrations of (a) Fe(II) ( $[\text{H}_2\text{O}_2]_0 = 4 \times 10^{-3}$  M;  $[\text{citrate}]_0 = 5 \times 10^{-4}$  M) and (b) citrate ( $[\text{H}_2\text{O}_2]_0 = 4 \times 10^{-3}$  M;  $[\text{Fe}(\text{II})]_0 = 1 \times 10^{-4}$  M); pH 5.0; light intensity =  $2.0 \text{ mW cm}^{-2}$ .

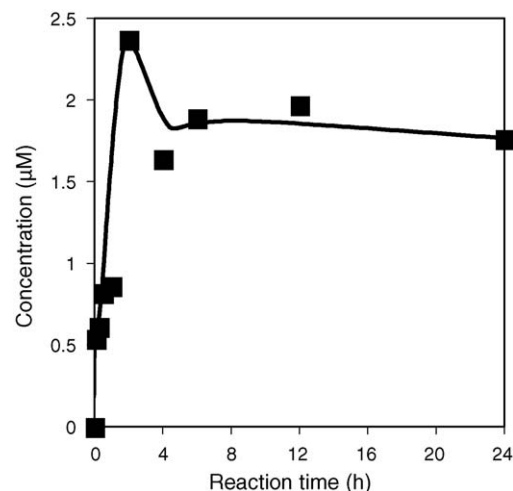
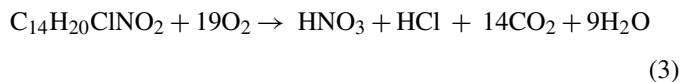


Fig. 4. Concentration of  $\text{OH}^\bullet$  radical during the photo-Fenton process in the presence of citrate ( $[\text{Fe}(\text{II})]_0 = 1 \times 10^{-4}$  M;  $[\text{H}_2\text{O}_2]_0 = 4 \times 10^{-3}$  M;  $[\text{citrate}]_0 = 5 \times 10^{-4}$  M; pH 5.0; light intensity =  $2.0 \text{ mW cm}^{-2}$ ).

### 3.2. Mineralization

When the total mineralization of alachlor proceeds stoichiometrically using oxygen as oxidizing agent, the mineralization reaction can be estimated as follows:



It should be remarked that nitrogen released has been measured as a combination of ammonia and nitrate, but ammonia can be oxidized to nitrate after long irradiation time [35,36].

The formation of chloride ion from alachlor degradation was investigated. The concentration of chloride ion quickly increased with increasing the reaction time, suggesting a very fast degradation/dechlorination stage (Fig. 6). The total amount of chloride ion produced after 1 h of irradiation time was approximately

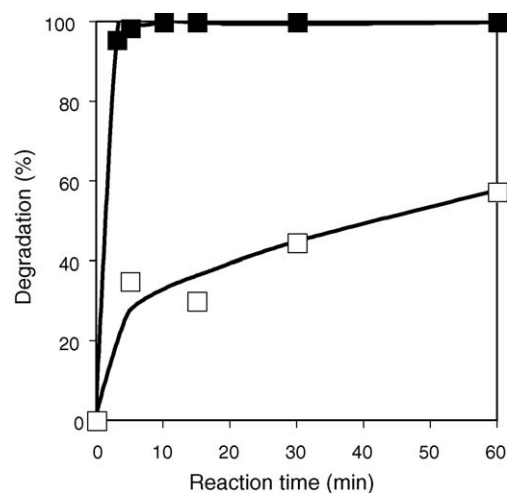


Fig. 5. Degradation characteristics of alachlor under dark and light conditions. (■) Light, Fe(II)–citrate/ $\text{H}_2\text{O}_2$ ; (□) dark, Fe(II)–citrate/ $\text{H}_2\text{O}_2$  ( $[\text{Fe}(\text{II})]_0 = 1 \times 10^{-4}$  M;  $[\text{H}_2\text{O}_2]_0 = 4 \times 10^{-3}$  M;  $[\text{citrate}]_0 = 5 \times 10^{-4}$  M; pH 5.0; light intensity =  $2.0 \text{ mW cm}^{-2}$ ).

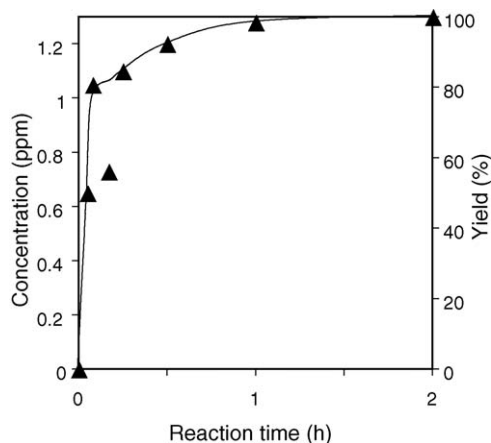


Fig. 6. Time evolution of chloride ion concentration during irradiation of alachlor ( $[\text{Fe(II)}]_0 = 1 \times 10^{-4} \text{ M}$ ;  $[\text{H}_2\text{O}_2]_0 = 4 \times 10^{-3} \text{ M}$ ;  $[\text{citrate}]_0 = 5 \times 10^{-4} \text{ M}$ ; pH 5.0; light intensity =  $2.0 \text{ mW cm}^{-2}$ ).

1.3 ppm (ca. 100% conversion of the alachlor chloride content). The formations of ammonium and nitrate ions during the degradation reaction as a function of reaction time are presented in Fig. 7. Both ammonium and nitrate ions were detected in different relative concentrations. Although only 40% of the initial N was detected as ammonium and nitrate ions after 1 h of irradiation time, 100% conversion of the alachlor nitrogen content was achieved after 6 h. Therefore, nitrogen atoms from alachlor could be completely mineralized by this photocatalytic system. By comparing the formation rates of chloride, nitrate and ammonium ions, it was found that the oxidation of side chain of the alachlor molecular happened more easily than the cleavage of the ring. The results revealed that the first step of alachlor degradation was mainly the dechlorination.

The progress of the mineralization of the alachlor solution was monitored by measuring the TOC. At the same time the decrease of TOC for citrate alone was also investigated because citrate is organic compound and contributes to TOC value. As shown in Fig. 8, TOC for the mixture of alachlor and citrate rapidly decreased with increasing the reaction time up to 6 h, and

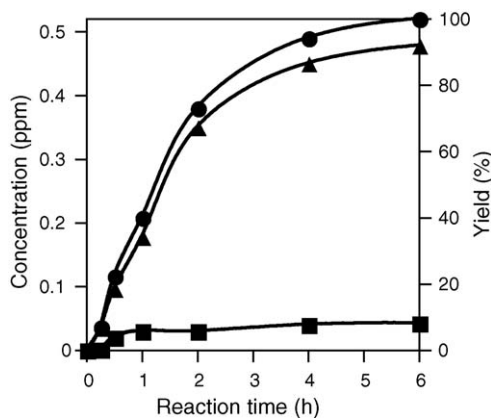


Fig. 7. Time evolution of ammonium and nitrate ions concentrations during irradiation of alachlor: (●) total N; (▲)  $\text{NH}_4^+\text{-N}$ ; (■)  $\text{NO}_3^-\text{-N}$ ; ( $[\text{Fe(II)}]_0 = 1 \times 10^{-4} \text{ M}$ ;  $[\text{H}_2\text{O}_2]_0 = 4 \times 10^{-3} \text{ M}$ ;  $[\text{citrate}]_0 = 5 \times 10^{-4} \text{ M}$ ; pH 5.0; light intensity =  $2.0 \text{ mW cm}^{-2}$ ).

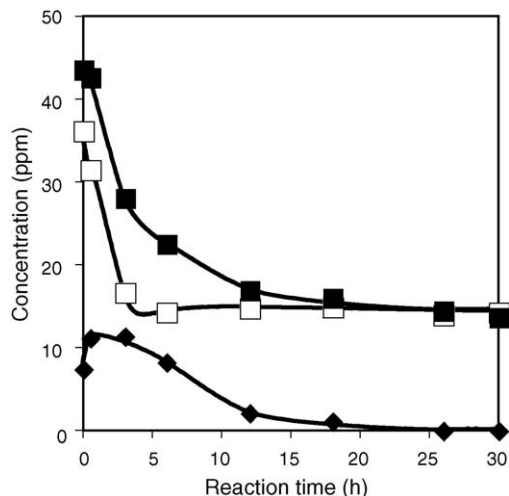
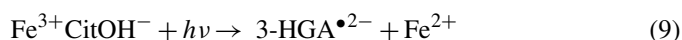
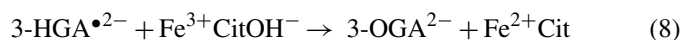
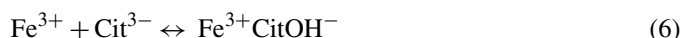
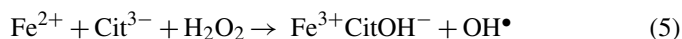
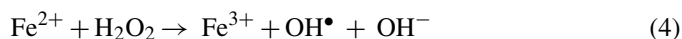


Fig. 8. Time evolution of TOC during irradiation of alachlor: (■) alachlor + citrate (total); (□) citrate alone; (◆) total – citrate alone ( $[\text{Fe(II)}]_0 = 1 \times 10^{-4} \text{ M}$ ;  $[\text{H}_2\text{O}_2]_0 = 4 \times 10^{-3} \text{ M}$ ;  $[\text{citrate}]_0 = 5 \times 10^{-4} \text{ M}$ ; pH 5.0; light intensity =  $2.0 \text{ mW cm}^{-2}$ ).

then gradually decreased although the complete mineralization could not achieve after 26 h. On the other hand, mineralization of citrate quickly proceeded up to 6 h, and then showed a constant TOC value. Hug et al. [34] reported that citrate ligand decomposed to acetone dicarboxylate ( $\text{C}_5\text{H}_4\text{O}_5^{2-}$ ) and further to acetone ( $\text{C}_3\text{H}_6\text{O}$ ). Therefore, subtraction of TOC for the mixture of alachlor and citrate to TOC for citrate alone would show the TOC changes for original alachlor because TOC for citrate alone was almost constant 6 h after. The complete mineralization of alachlor could be achieved by UV/Fe(II)–citrate/ $\text{H}_2\text{O}_2$  system after 26 h if based on the interpretation.

### 3.3. Identification of photoproducts and degradation mechanism

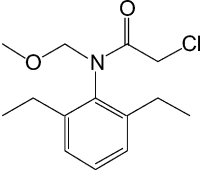
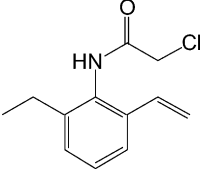
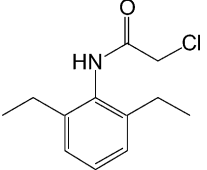
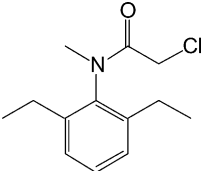
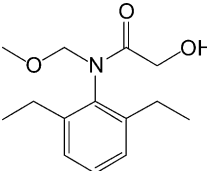
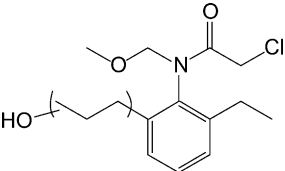
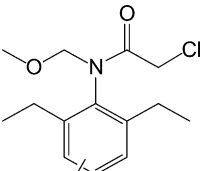
The mechanism of photo-Fenton reaction in the presence of citrate has been proposed by Hug et al. [34] as follows:



where  $\text{Cit}^{3-}$ ,  $3\text{-HGA}^{\bullet 2-}$  and  $3\text{-OGA}^{2-}$  represent citrate ion, 3-hydroxo-glutarate radical and 3-oxo-gulutarate, respectively.  $3\text{-OGA}^{2-}$  is quite unstable and decays into  $\text{CO}_2$  and acetone.

The photoproducts formed in this photocatalytic degradation of alachlor in the aqueous solution after 10 min were investigated by GC/MS analysis. Seven products including isomers were identified by the molecular ion and mass fragment ions, and also through comparison with NIST library data. The structures of the main photoproducts are represented in Table 1. The

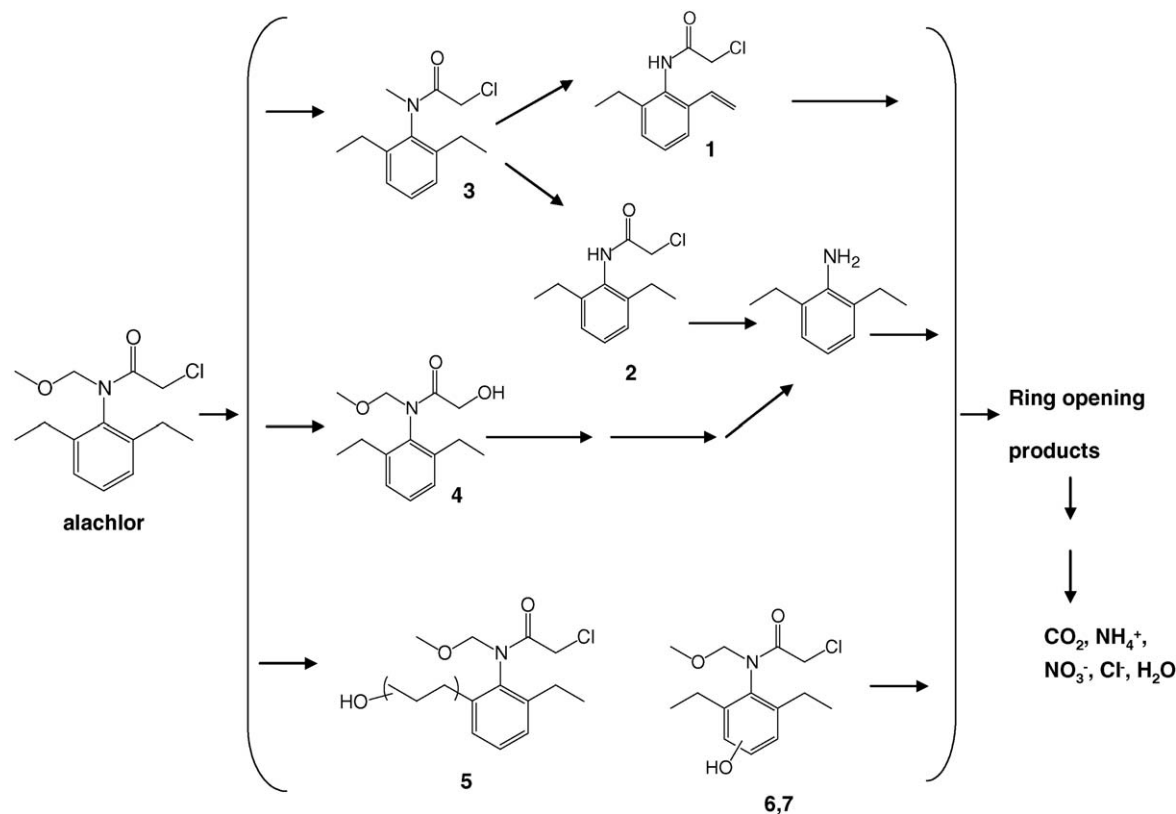
Table 1  
Photoproducts obtained by degradation of alachlor

Product no.	Retention time (min)	Molecular weight ( <i>m/z</i> )	Photoproduct
Alachlor	8.9	269	
1	7.4	223	
2	7.8	225	
3	8.6	235	
4	9.1	251	
5	9.8	285	
6, 7	10.3, 10.6	285	

similarities of these compounds to the NIST library data were more than 85%. By interpreting the mass spectra, the product no. 4 was formed from alachlor due to the replacement of hydroxyl group to one chlorine atom. Similarly, the product nos. 5–7 were found to be the products in which hydroxyl group added to the benzene ring or alkyl side chain of alachlor. The product nos. 1–3 were identified as the compounds which were

eliminated the alkyl groups. In addition to these seven compounds, other degradation products still possibly would exist in the UV/Fe(II)–citrate/H<sub>2</sub>O<sub>2</sub> system but were not detected because of their low concentration, extraction efficiency and limited sensitivity in GC/MS.

Based on the intermediate products listed in Table 1 and the results of metolachlor degradation, which has similar structure to



Scheme 1. Proposed degradation mechanism of alachlor by use of the photo-Fenton process in the presence of citrate.

alachlor, obtained by other researchers [37], the possible degradation pathway for alachlor is proposed in Scheme 1. One of the degradation steps was initiated by the attack on the aromatic ring or alkyl side chain by  $\text{OH}^\bullet$  radicals without dechlorination or alkyl chains. Another step involved a series of oxidation processes that eliminated alkyl groups and chlorine atoms. The last step involved oxidative opening of the aromatic ring, leading to small organic ions and inorganic species. In any case, aniline derivatives, typical degradation products which have been proposed as the main alachlor chemical degradation intermediates [9,38] were not detected, possibly because they were easily degraded by the  $\text{OH}^\bullet$  radicals, as demonstrated previously [39], and could not be found in a sufficient concentration to be detected. It was reported that the toxicity of aniline derivatives is higher than that of alachlor [8]. However, toxicity of water contaminated by alachlor after the treatment would be lower than that of original one since alachlor could be completely mineralized after 26 h using UV/Fe(II)-citrate/ $\text{H}_2\text{O}_2$  system.

#### 4. Conclusions

The photodegradation of alachlor in aqueous solution was investigated by UV/Fe(II)-citrate/ $\text{H}_2\text{O}_2$  system. The degradation rate was strongly affected by many factors, such as the pH value, and the initial concentrations of  $\text{H}_2\text{O}_2$ , Fe(II) and citrate. Alachlor achieved complete degradation after 10 min even at pH in the vicinity of the neutral region. Therefore, it was possible to extend available pH range of the photo-Fenton reaction by the existence of the citrate.

The disappearance of TOC was observed during the photo-Fenton process in the presence of citrate. The formations of chloride, nitrate and ammonium ions were also observed. Therefore, we could reach the complete mineralization of the starting compound. Furthermore, we identified seven kinds of intermediate products of alachlor during the oxidation process. The degradation pathway of alachlor was proposed based on the identified by-products under a given set of reaction conditions.

The advantages of the photo-Fenton process in the presence of citrate as an oxidative treatment are rapid degradation, simple handling and wide applicable pH range. Therefore, UV/Fe(II)-citrate/ $\text{H}_2\text{O}_2$  system would be applied to wastewater treatment works as a new developing methodology for reducing levels of other pesticides and endocrine disrupting chemicals.

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