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Degradation of linuron in aqueous solution by the photo-Fenton reaction

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Abstract

The photodegradation of linuron, which is one of phenylurea herbicides, was carried out in the presence of Fenton reagent. The degradation rate was strongly influenced by the pH and initial concentrations of H_2O_2 and Fe(II). An initial linuron concentration of 10 mg L^{-1} was completely degraded after 20 min under the optimum conditions. The decrease of TOC as a result of mineralization of linuron was observed during the photo-Fenton process. The degree of linuron mineralization was about 90% under UV irradiation after 25 h. The formations of chloride, nitrate and ammonium ions as end-products were observed during the photocatalytic system. The decomposition of linuron gave eight kinds of intermediate products. The degradation mechanism of linuron was proposed on the base of the evidence of the identified intermediates. Based on these results, the photo-Fenton reaction could be a useful technology for the treatment of wastewater containing linuron.

Keywords: Linuron; Photo-Fenton reaction; Degradation; Mineralization; Wastewater treatment

1. Introduction

Herbicides represent the largest group of chemicals used as plant protection agents. One class of herbicides widely used in pre- and post-emergencies is represented by the substituted phenylureas.

The phenylureas are persistent herbicides. At high rates of application they are useful as total weed killers, but at low rates many can be used for selective weed control in a wide range of crops. Linuron, 3-[3,4-(dichlorophenyl)-1-methoxy-1-methylurea], one of the most important commercial ureas, has good contact activity and it may kill emergent weed seedlings [1]. In addition, linuron is a weak competitive androgen receptor antagonist in vitro, induces a positive response in the immature and adult rat Hershberger assay and suppresses androgen-dependent gene expression [2–4].

Half-life in soil ranges from 38 to 67 days for linuron [5]. Therefore, this compound has been found as contaminants in surface and ground waters [6] and microbial degradation is considered to be the primary mechanism for their dissipation from soil. Many bacterial [7] and fungal isolates [8] that are able to (partially) break down phenylureas have been reported. In general, biological methods commonly require long time for the wastewater containing linuron at high concentration. Therefore, the rapid and simple wastewater treatment of linuron is now required urgently.

A few of treatment techniques for wastewater which contains linuron has been reported by using O_3/H_2O_2 [9], direct photolysis [10] and Fenton [11] procedures. Recent reports indicate that a combination of H_2O_2 and UV irradiation with Fe(II), so-called the photo-Fenton process, can significantly enhance decomposition of many refractory organic compounds. Until now, the photo-Fenton process has been applied to the degradation of pesticides [12,13], nitrobenzene and other organics [14], chlorophenols [15–17], nitrophenols

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[18], dibutyl-phthalate [19], PCBs [20] and bisphenol A [21]. The acceleration for decomposition of organic compounds is believed to be in order to photolysis of iron aquacomplex, $Fe(H_2O)_5(OH)^{2+}$ (represented hereafter by $Fe(OH)^{2+}$), to provide a new importance source of $OH^{\bullet}$ radicals [22,23]. Further, the photolysis of $Fe(OH)^{2+}$ 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.

$$Fe^{2+} + H_2O_2 \rightarrow Fe(OH)^{2+} + OH^{\bullet} \qquad (1)$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + OH^{\bullet} \qquad (2)$$

Furthermore, the $Fe(OH)^{2+}$ can absorb light at wavelengths up to ca. 410 nm, while TiO_2 photocatalysis can use photon with wavelength close to 380 nm [24]. Therefore, the photo-Fenton process can be expected to be an efficient method for wastewater treatment and promotes the rate of degradation of various organic pollutants.

In the present study, we have investigated the degradation and mineralization of linuron in water using photo-Fenton process. The many factors, such as pH value and initial concentrations of Fe(II) and H_2O_2, affected on the degradation were evaluated. The progress of mineralization of linuron was monitored by total organic carbon (TOC) content and ionic chromatography. Furthermore, the photoproducts of linuron 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

Linuron was purchased from Wako Pure Chemical Industries (Osaka, Japan) and was used as received (HPLC grade >99.0%). Analytical grade hydrogen peroxide solution (30%, w/w) and ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) were purchased from Wako Pure Chemical Industries (Osaka, Japan) and Nacalai Tesque (Kyoto, Japan), respectively, and were used as received. 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 illustrated in Fig. 1. The reaction mixture inside the cell, consisting of 20 mL of linuron solution and the precise amount of Fenton reagent, was continuously stirred with a magnetic bar. The pH of the sample solution was adjusted with H_2SO_4 and/or NaOH solution. The initial concentration of linuron in all experiments was $10\,mg\,L^{-1}$ ($4.0 \times 10^{-5}\,mol\,L^{-1}$). In majority of the experiments, temperature was kept at $25 \pm 1\,°C$ 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 ($\lambda < 300$ 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. The degradation reaction was quenched by adding 1 mL of methanol for HPLC and of H_3PO_4 for TOC analyses. These experiments were conducted in triplicates and the results showed at the mean values. The relative standard deviations were range of 5–12%.

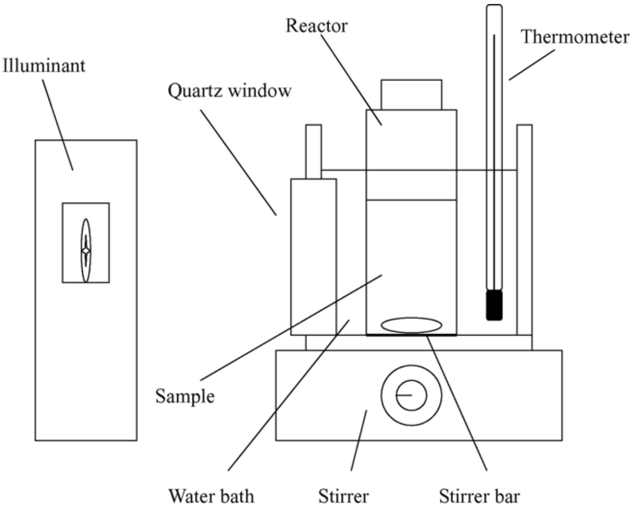


Fig. 1. Schematic illustration of the photochemical reactor.

2.3. Analyses

After illumination, the sample solution was filtered through a 0.45 μm-membrane filter. The decrease of UV absorption was monitored with an UVIDEC-610 double-beam spectrometer (JASCO Co., Tokyo, Japan). The progress in the degradation of linuron was followed with a HPLC (JASCO Co., Tokyo, Japan) equipped with a JASCO UVIDEC-100-VI UV detector and a CHROMSPHER 5POLY C18 REPEAL (150 mm length × 4.5 mm i.d., VARIAN, USA). The elution was monitored at 250 nm. The mobile phase was a mixture of acetonitrile and water (3/7, v/v) and was pumped at a flow rate of $1.0\,mL\,min^{-1}$. Concentration of Fe(II) consumed during the photocatalytic process was determined by the phenanthroline (phen) method. The absorbance of Fe(II)–phen complex was taken at 510 nm ($\varepsilon_{510\,nm} = 1.118 \times 10^{4}\,L\,mol^{-1}\,cm^{-1}$).

The progress of mineralization of linuron was monitored by measuring the TOC. TOC of the sample solution was measured with a Shimadzu TOC analyzer (TOC-V_E) based on

CO_2 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 intermediate products during photodegradation of linuron were extracted by the solid phase extraction (C18 disk, 3M Empore). A mixture of dichloromethane and ethyl acetate (1/1, v/v) was used to elute the intermediate products. This solution was concentrated under nitrogen flow for the analysis of the by-products. 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^{-1}) and with splitless injection system. The GC oven temperature was programmed to hold 50 °C for initial 3 min, to increase from 50 to 250 °C at a rate of 5 °C min^{-1} and to hold at 250 °C for 5 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 linuron

The time courses of the UV absorption spectra of linuron solution in the photocatalytic degradation by the photo-Fenton reaction were observed in the range of 0–60 min. The experimental conditions were: $[Fe(II)]_0 = 1.0 \times 10^{-5}$ mol L^{-1}, $[H_2O_2]_0 = 1.0 \times 10^{4}$ mol L^{-1}, pH 3.0 and light intensity = 2.0 mW cm^{-2} Other conditions were described in Section 2. The UV spectrum of linuron solution before illumination presented one absorption maximum at 250 nm. The disappearance of 250 nm absorption band was observed with increasing reaction time. Consequently, it was confirmed that Fenton reagent was effective photocatalyst for the decomposition of linuron under UV illumination.

Effect of pH on the degradation of linuron by use of the photo-Fenton process was investigated over the pH range of 2.0–5.0 because much precipitation of $Fe(OH)_3$ observed during the process above pH 5.0. These results are shown in Fig. 2. The degradation percentage of linuron rapidly increased with increasing pH value up to 4.0, decreasing at pH above 4.0. Therefore, the photo-Fenton reaction is strongly affected by pH of the solution. Generally, the optimal pH of the photo-Fenton reaction is around 3 [25] because the main species at pH 2–3, $Fe(OH)^{2+}(H_2O)_5$, is the one with the largest light absorption coefficient and quantum yield for $OH^{\bullet}$ radical production, along with Fe(II) regeneration, in the range 280–370 nm [26]. However, the optimal pH in this process was obtained as 4.0. A similar result has been obtained in the case of bisphenol A as previously reported [21]. Fukushima et al. [17,27] 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, linuron or its intermediate products 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. Therefore, the degradation efficiency of linuron may be the highest at pH 4.

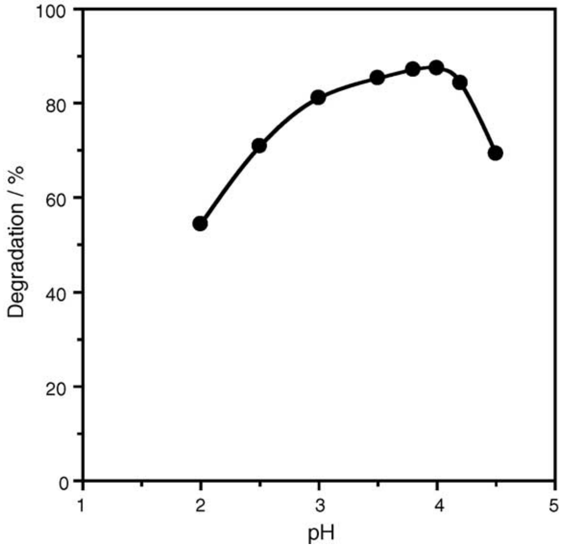


Fig. 2. Effect of pH on the degradation of linuron by use of the photo-Fenton process ($[H_2O_2]_0 = 4 \times 10^{-4}$ mol L^{-1}; $[Fe(II)]_0 = 4 \times 10^{-5}$ mol L^{-1}; irradiation time = 5 min; light intensity = 2.0 mW cm^{-2}).

Effect of temperature on the degradation of linuron by the photo-Fenton system was examined in the range of 10–40 °C. Although the degradation efficiency of linuron gradually increased as the temperature increased, the appreciable change was not observed in the temperature range. This effect is due to an increase in the rate constant of the degradation reaction. The thermal enhancement of the degradation rate can be explained by the increase of $Fe(OH)^{2+}$ concentration and the temperature dependence of quantum yield of photochemical reduction of Fe(III) considering the activation energy [28]. All subsequent experiments were performed at 25 °C, considering practical application and the operating cost for the degradation system.

Influence of light intensity on the photocatalytic decomposition of linuron was carried out in the range of 0–2.5 mW cm^{-2}. The degradation rate of linuron rapidly increased with increasing light intensity up to 1.5 mW cm^{-2} and then the rate gradually increased. The degradation percentages of linuron were 83, 88 and 90% when the light intensities were 1.5, 2.0 and 2.5 mW cm^{-2}, respectively. There was little effect of light intensity on the degradation of lin-

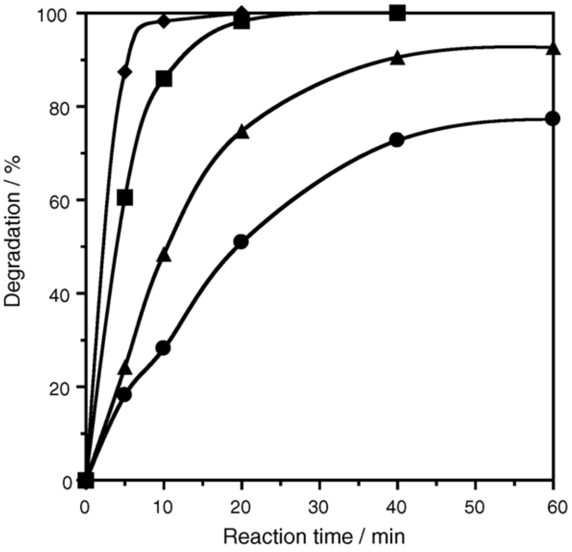


Fig. 3. Degradation of linuron by use of the photo-Fenton process at the different initial concentrations of iron(II): (●) 4×10^{-6} M, (▲) 1×10^{-5} M, (■) 2×10^{-5} M, (♦) 4×10^{-5} M ($[H_2O_2]_0 = 4 \times 10^{-4}$ M; pH 4.0; light intensity = 2.0 mW cm^{-2}).

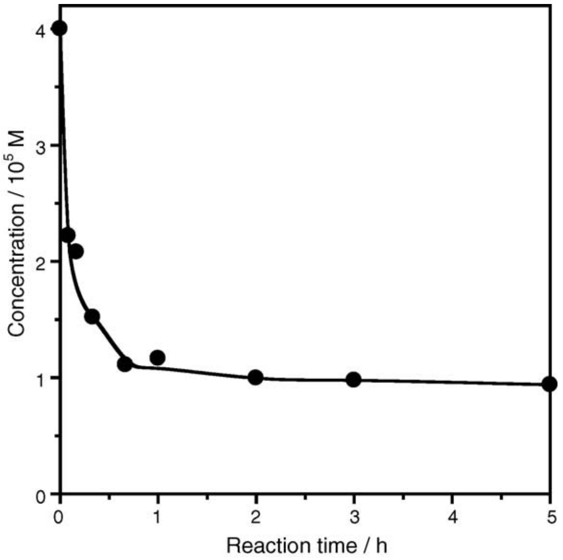


Fig. 4. Time course of Fe(II) concentration changes during the photo-Fenton process ($[Fe(II)]_0 = 4 \times 10^{-5}$ M; $[H_2O_2]_0 = 4 \times 10^{-4}$ M; pH 4.0; light intensity = 2.0 mW cm^{-2}).

uron between 2.0 and 2.5 mW cm^{-2}. Therefore, all subsequent degradation of linuron was carried out under light intensity of 2.0 mW cm^{-2}.

To obtain the optimal initial Fe(II) concentration, the investigation was carried out in the range of 4×10^{-6} to 4×10^{-5} mol L^{-1} at pH 4 ($[H_2O_2]_0 = 4 \times 10^{-4}$ mol L^{-1}). These results are shown in Fig. 3. As it can be seen from Fig. 3, the degradation rate of linuron increased with increasing initial Fe(II) concentration. Complete degradation of linuron under these conditions was reached at Fe(II) concentration of above 2×10^{-5} mol L^{-1} within 60 min, while low concentration of Fe(II) did not allow for complete degradation in photo-Fenton process. When Fe(II) concentration was selected as 4×10^{-5} mol L^{-1}, linuron was completely degraded after 20 min. At the same time, the concentration of Fe(II) (4×10^{-5} mol L^{-1}) consumed during the process was measured using phenanthroline method (Fig. 4). Concentration of Fe(II) decreased until 1.0×10^{-5} mol L^{-1}, a plateau value reached after about 60 min of irradiation while the degradation of linuron and its photoproducts keeps going on. This plateau can be assigned to a photostationary equilibrium between Fe(II) and Fe(III) that regenerates the absorbing species [22,23]. Accordingly, the formation of $OH^\bullet$ radicals can continue allowing the complete mineralization of linuron.

Fig. 5 shows the effect of initial H_2O_2 concentration on the degradation of linuron with the use of photo-Fenton process. As expected, the degradation rate of linuron increased with increasing the concentration of H_2O_2 added. This can be explained by the effect of the additionally produced $OH^\bullet$ radicals. When concentration of H_2O_2 was below 2×10^{-4} mol L^{-1}, linuron did not achieve the complete degradation within 60 min.

Fig. 6 shows a comparison of the degradation of linuron in both the dark and light. Only 3.7% of linuron was degraded in the absence of Fe(II) and H_2O_2 for the case of light condition. The Fe(II)/H_2O_2 system in the dark (Fenton reaction) was also evaluated for the degradation of linuron. For this case, although more than 75% of linuron was degraded after 20 min at pH 4.0, it could not achieve the complete degradation within 60 min (ca. 90% degradation). These results indicate that the photo-Fenton reaction is useful for the treatment of wastewater containing linuron.

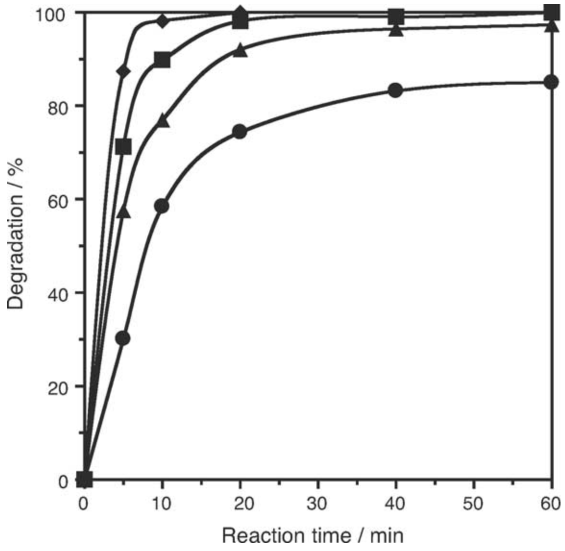


Fig. 5. Degradation of linuron by use of the photo-Fenton process at the different initial concentrations of H_2O_2: (●) 4×10^{-5} M, (▲) 1×10^{-4} M, (■) 2×10^{-4} M, (♦) 4×10^{-4} M ($[Fe(II)]_0 = 4 \times 10^{-5}$ M; pH 4.0; light intensity = 2.0 mW cm^{-2}).

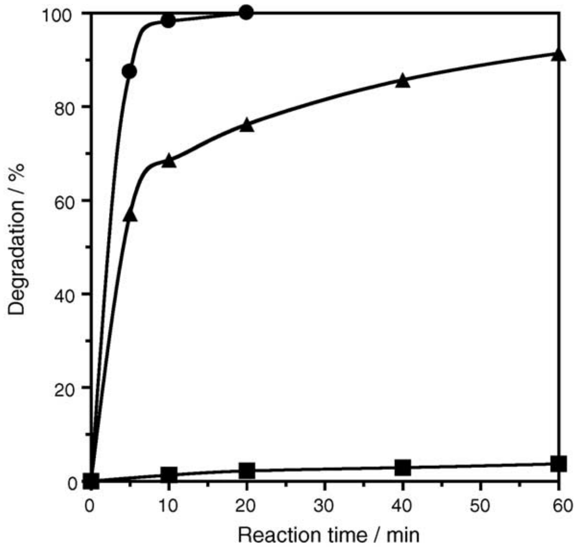


Fig. 6. Degradation characteristics of linuron under dark and light conditions (●) light, Fe(II)/H_2O_2; (▲) dark, Fe(II)/H_2O_2; (■) light ($[Fe(II)]_0 = 4 \times 10^{-5}$ M; $[H_2O_2]_0 = 4 \times 10^{-4}$ M; pH 4.0; light intensity = 2.0 mW cm^{-2}).

3.2. Mineralization

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

$$2C_9H_{10}Cl_2N_2O_2 + 25O_2 \rightarrow 4HNO_3 + 4HCl + 18CO_2 + 6H_2O$$

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 [29,30].

The progress of the mineralization of the linuron solution was monitored by measuring the TOC. As shown in Fig. 7, the complete mineralization of linuron was not achieved after 20 min, although linuron was not present in the solution after the irradiation time. This difference indicates that intermediate products were produced during the photo-Fenton process. The generated photoproducts are attacked in their turn by hydroxyl radicals which are formed in a continuous manner via a homogeneous photocatalytic process involving Fe(III, II) [22,23]. TOC rapidly decreased with increasing the reaction time up to 5 h and then decreased gradually. TOC remained about 0.4 mg L^{-1} (90% mineralization) after 25 h of irradiation time. This result indicates the formation of persistent intermediate compounds, which are difficult to be degraded by this photocatalytic system.

The formation of chloride ion from linuron degradation was investigated. The concentration of chloride ion quickly increased with increasing the reaction time, suggesting a very fast degradation/dechlorination stage (Fig. 8). The total amount of chloride ion produced after 2 h of irradiation time was approximately 8×10^{-5} mol L^{-1} (100% conversion of the linuron chloride content). This means that the residual TOC after 25 h of irradiation time did not correspond to any chlorinated compounds.

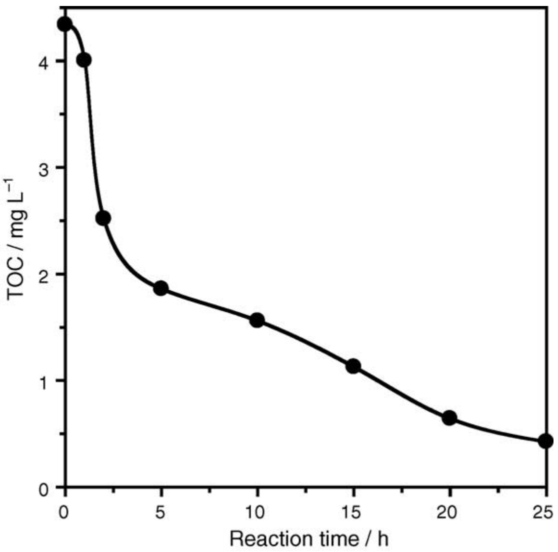


Fig. 7. Time evolution of TOC during irradiation of linuron ($[Fe(II)]_0 = 4 \times 10^{-5}$ M; $[H_2O_2]_0 = 4 \times 10^{-4}$ M; pH 4.0; light intensity = 2.0 mW cm^{-2}).

The formations of ammonium and nitrate ions during the photo-Fenton process as a function of reaction time are presented in Fig. 9. The nitrogen content of diuron having a similar structure to linuron was converted to ammonium and nitrate ions, which has already been described by other authors [31]. This information suggested that this photocatalytic degradation of linuron would also yield these ions as breakdown products. Both ammonium and nitrate ions were detected in different relative concentrations. Only 35% of the

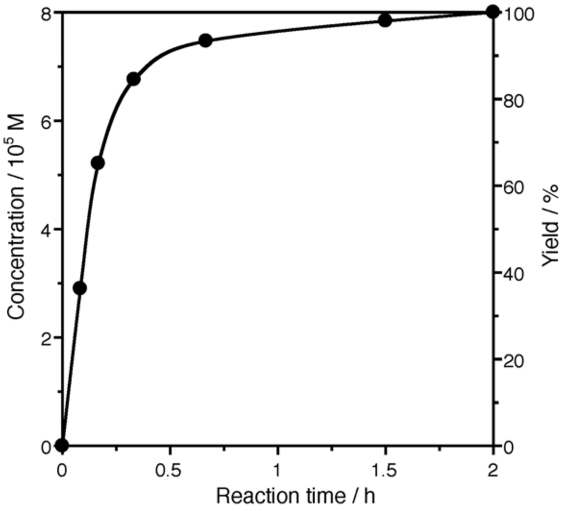


Fig. 8. Time evolution of chloride ion concentration during irradiation of linuron ($[Fe(II)]_0 = 4 \times 10^{-5}$ M; $[H_2O_2]_0 = 4 \times 10^{-4}$ M; pH 4.0; light intensity = 2.0 mW cm^{-2}).

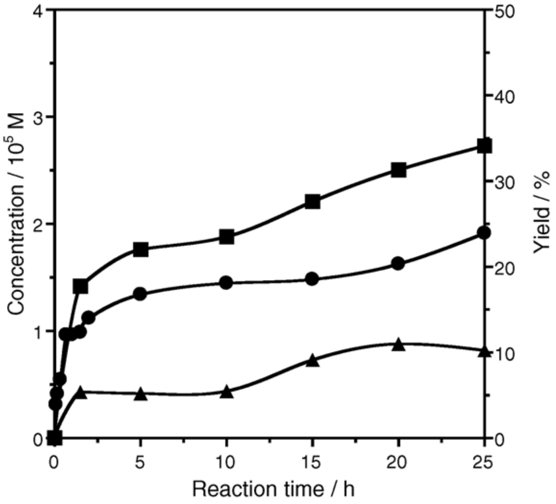
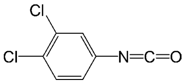
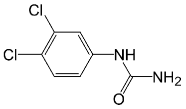
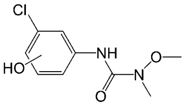
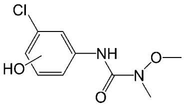
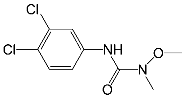
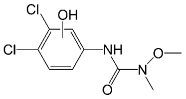
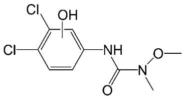
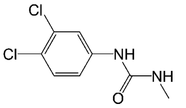
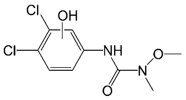


Fig. 9. Time evolution of ammonium and nitrate ions concentrations during irradiation of linuron. (●) ammonium ion; (▲) nitrate ion; (■) total N ($[\mathrm{Fe(II)}]_0 = 4 \times 10^{-5}$ M; $[\mathrm{H_2O_2}]_0 = 4 \times 10^{-4}$ M; pH 4.0; light intensity = 2.0 mW cm^{-2}).

initial N was detected as ammonium and nitrate ions after 25 h of irradiation time. Therefore, a part of nitrogen atoms from linuron could be mineralized by this photocatalytic system. This incomplete nitrogen mass balance has frequently been observed in a similar process [32–34] and indicates that other nitrogen-containing compounds must be present in the solution or evaporated during the process. The possible existence of alkyl nitrogen, cianno derivatives [35], carbamic acids and amines could explain the residual TOC, but the analytical procedures applied to the samples have not been able to detect them. Other authors described N_2 [36] and/or hydroxylamine [37] evolving from nitrogen-containing compounds degraded by photocatalysis.

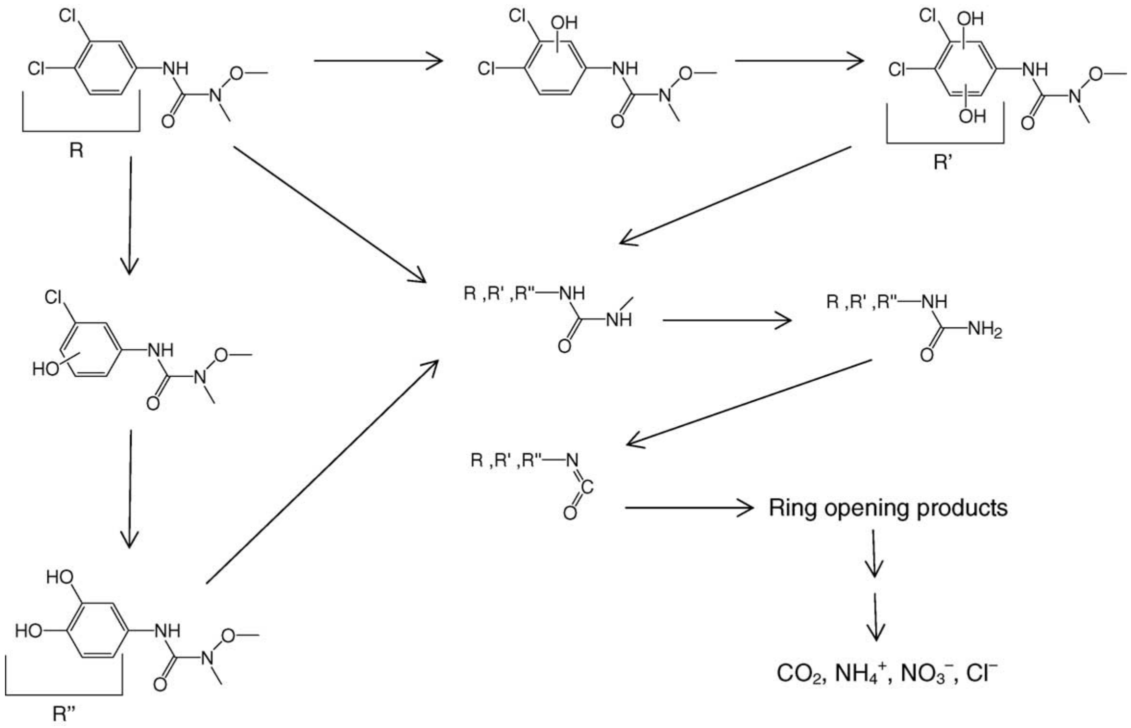
Table 1
Photoproducts obtained by degradation of linuron

Product no.	Retention time (min)	Molecular weight (*m*/*z*)	Photoproduct
1	14.4	187	
2	17.2	204	
3	28.9	230	
4	29.1	230	
Linuron	30.0	248	
5	32.0	264	
6	32.9	264	
7	33.2	218	
8	33.6	264	

3.3. *Identification of photoproducts and degradation mechanism*

The photoproducts formed in this photocatalytic degradation of linuron in the aqueous solution for 5 min were investigated by GC–MS analysis. Eight products 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 similarities of these compounds to the NIST library data were more than 85%. By mass spectrum confirmation and the authentic standard comparison, linuron, the parent compound, was found in the chromatogram. By interpreting the mass spectrum, the product nos. 3 and 4 were formed from linuron due to the replacement of hydroxyl group to one chlorine atom. Similarly, the product nos. 5, 6 and 8 were found to be the products in which hydroxyl group added to the benzene ring of linuron. The product nos. 1, 2 and 7 were identified as the compounds which were eliminated the alkyl groups. In addition to these eight compounds, other degradation products still possibly would exist in the photo-Fenton 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 obtained by other researchers [9,10,34], the possible degradation pathway for linuron is proposed in Scheme 1. The first step was initiated by the attack on the aromatic ring by $\mathrm{OH}^\bullet$ radicals without dechlorination or alkyl chains. The next 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. This proposed degradation pathway was consistent with previous work [37–40]. In any case, aniline and 3,4-dichloroaniline, two typical degradation products which have been proposed as the main phenylurea chemical degradation intermediates [41,42] were not detected, possibly because they were easily degraded by the $\mathrm{OH}^\bullet$ radicals, as demonstrated previously [43] and could not be found in a sufficient concentration to be detected.



Scheme 1. Proposed degradation mechanism of linuron by use of the photo-Fenton process.

4. Conclusions

The photodegradation of linuron in aqueous solution was investigated by the photo-Fenton treatment. The degradation rate was strongly affected by many factors, such as the pH value and the initial concentrations of H_2O_2 and Fe(II). Linuron achieved complete degradation after 20 min under the optimum conditions.

The disappearance of TOC was observed during the photo-Fenton process and the remaining TOC achieved 0.4 mg L^{-1} after 25 h (90% mineralization). 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 eight kinds of intermediate products of linuron during the photo-Fenton process. The degradation pathway of linuron was proposed based on the identified by-products under a given set of reaction conditions.

The advantages of the photo-Fenton process as an oxidative treatment are rapid degradation and simple handling. Therefore, the photo-Fenton reaction 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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