Degradation of linuron by ultrasound combined with photo-Fenton treatment

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ABSTRACT

Sonochemical photodegradation of linuron, which is one of phenylurea herbicides, was carried out in the presence of Fe(II). The degradation rate was strongly influenced by initial concentration of Fe(II) and solution pH. The optimal Fe(II) concentration and pH were found to be 1.2×10^{-4} mol L^{-1} and 3.0, respectively. An initial linuron concentration of 10 mg L^{-1} was completely degraded by ultrasound/Fe(II)/UV system after 20 min under the optimum conditions while only 79.3% of linuron was decomposed under ultrasonic irradiation. Furthermore, the first-order rate constant in ultrasound//Fe(II)/UV process (0.17 min^{-1}) was about 2 times greater than that in ultrasonic alone (0.08 min^{-1}). The decrease of TOC as a result of mineralization of linuron was observed during the combination process. The complete linuron mineralization was achieved after 120 min. The formations of chloride, nitrite and nitrate ions as end-products were observed during the degradation system. Based on these results, ultrasound/Fe(II)/UV system would be useful technology for the treatment of water samples containing linuron.

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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 times 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], O_3/UV [10], direct photolysis [11], TiO_2/H_2O_2 [12,13], Fenton [14] and photo-Fenton [15,16] procedures. Among these methods, photocatalytic one is highly promising because it can operate at ambient temperature and pressure with low energy photons, does not require expensive catalyst, and utilizes natural sunlight. Over the past several years, there has been an increasing interest in use of ultrasonic irradiation to treat organic contaminants in aqueous solutions [17]. The sonochemical reaction pathways for the degradation of organic compounds involve the reaction with hydroxyl radicals and a thermal reaction. The hydroxyl radicals are produced by the sonolysis of water as the solvent inside the collapsing cavitation bubbles under extremely high temperature and pressure [18]. The hydroxyl radicals generated can react with organic compounds or occur the recombination to H_2O_2 inside the cavitation bubble and at its interfacial region. Alternatively, organic compounds in the vicinity of a collapsing bubble may undergo pyrolytic decomposition due to the high local temperature and pressure [19]. US action can be affected in several ways. Frequency, power, and nature of the dissolved gas(es) have important effects on reaction product distribution and reaction rate [20–22]. Furthermore, previous studies have demonstrated that the addition of chemicals, such as iron ions or ozone, or combination with UV radiation, can amplify ultrasonic action [23,24].

Among these combination methods, photo-Fenton process can be expected to an efficient method for wastewater treatment and promotes the rate of degradation of various organic pollutants. It has been showed that sonication accelerated degradation and

mineralization of bisphenol A [24], malachite green [25], dioxins [26] and phenol [27] in the presence of Fe(II) under UV irradiation.

In the present study, the degradation and mineralization of linuron in water have been investigated by using ultrasound/Fe(II)/UV process. The initial concentrations of Fe(II) and solution pH affected on the degradation were evaluated. The progress of mineralization of linuron was monitored by total organic carbon (TOC) content and ionic chromatography.

## 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 ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) was purchased from Wako Pure Chemical Industries Nacalai Tesque (Kyoto, Japan) and was 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 $M\Omega$ cm.

2.2. Ultrasonic degradation procedure

Ultrasonic frequency of 200 kHz (power: 100 W) was generated using a SRK-200 (Shinka Industries Co. Ltd., Kanagawa, Japan) ultrasonic transducer (70 mm of diameter) with the reaction solution held in a 350 mL jacketed glass reactor. Ultrasound was emitted from the bottom of the reactor. Linuron solution and the precise amount of Fe(II) was placed into the reactor. 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} (4.0×10^{-5} mol L^{-1}). The temperature was controlled at $25 \pm 2\,^{\circ}C$ with a water bath. The mixture solution of linuron and Fe(II) (100 mL) was sonicated under batch mode and was simultaneously irradiated with a black light (Toshiba Lighting & Technology Co.). The beam was parallel and the distance 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.

2.3. Analyses

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 degradation 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}) using a Shimadzu UV-1650 PC spectrophotometer. Hydrogen peroxide concentrations were determined by spectrophotometric method with KI and ammonium molybdate as a catalyst [28]. Aliquots taken from the reactor were immediately added in the sample quartz cuvette of the spectrophotometer containing the reagents and absorbance at 352 nm was recorded after 2 min.
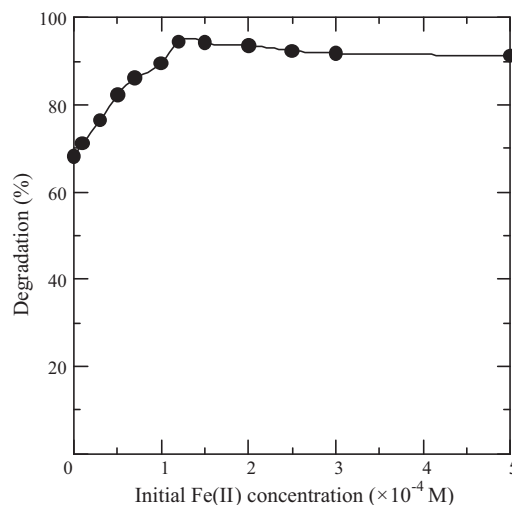
Fig. 1. Effect of Fe(II) initial concentration on linuron degradation by ultrasound/Fe(II)/UV system (reaction time = 15 min; pH 3.0; light intensity = 2.0 mW cm^{-2}).

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 formations of anions and cations were analyzed by ionic chromatography using a Metrohm Compact IC 7611 equipped with a Shodex anionic (IC SI-90 4E) and a Shodex cationic (IC YK-421) column, respectively.

These analyses were conducted in triplicates and the results showed at the mean values. The relative standard deviations for the three determinations were in the range of 3.8–13.2%.

3. Results and discussion

3.1. Effect of variables on the degradation of linuron

Effect of iron(II) concentration on the degradation of linuron was investigated in the range of 0–5 × 10^{-4} mol L^{-1}. The results are shown in Fig. 1. It was found that the degradation of linuron increased with increasing the initial Fe(II) concentration. The highest degradation was obtained with 1.2×10^{-4} mol L^{-1}. However, further increases in Fe(II) initial concentration showed no further activity due to the direct reduction of $^{\bullet}$OH radicals by the metal ions [29]. Therefore, initial concentration of Fe(II) was used as 1.2×10^{-4} mol L^{-1} for the further experiments.

One of important parameter of the degradation is the pH of the aqueous media. Generally, the optimal pH of the photo-Fenton reaction is around 3 [30] because the main species at pH 2–3, Fe(OH)$^{2+}$(H$_2$O)$_5$, is the one with the largest light absorption coefficient and quantum yield for $^{\bullet}$OH radical production, along with Fe(II) regeneration, in the range 280–370 nm [31]. Therefore, the effect of pH of linuron solution was examined. Fig. 2 shows the effect of pH on the degradation of linuron during the sonication coupled with the photo-Fenton process. A maximum degradation efficiency of 80.0% after 5 min was obtained in the combination process at pH 3. As can be seen in Fig. 2, increasing pH value from 3.0 to 5.4 decreased the linuron degradation from 80.1 to 54.1%. Effect of pH by ultrasound alone was also investigated in the same pH range. The highest degradation percentage showed at pH 3.0, and then gradually decreased with increasing pH (data not shown). The degradation of linuron after 5 min at pH 3.0 and 5.4 was 38.0 and 34.3%, respectively.
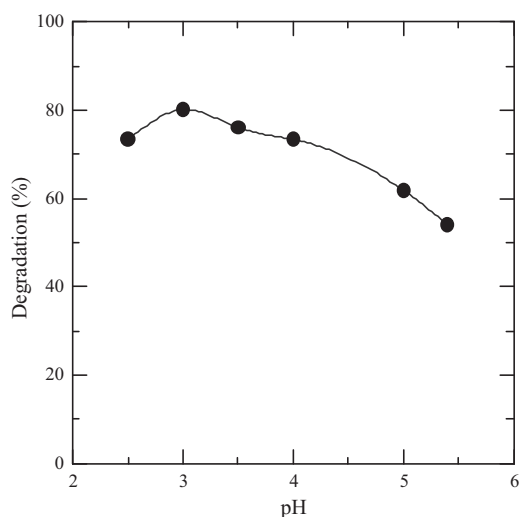
Fig. 2. Effect of pH on linuron degradation by ultrasound/Fe(II)/UV system. ([Fe(II)]$_0$ = 1.2 × 10^{-4} mol L^{-1} (reaction time = 5 min; light intensity = 2.0 mW cm^{-2}).

Fig. 3 shows linuron degradation under ultrasonic irradiation and by the combination of the processes. The degradation rate for ultrasound/UV/Fe(II) process was fastest in all ones. After 20 min, linuron was completely degraded using ultrasound/UV/Fe(II) system, whereas 79.3% was decomposed with ultrasound, 93.3% with ultrasound/Fe(II), and only 28.4% with UV. It took 40 min to degrade linuron completely by ultrasound system. In our previous study, the complete degradation of linuron was also achieved after 20 min using Fe(II)/H$_2$O$_2$/UV process under optimum conditions [15]. Furthermore, the degradation rate constant in ultrasound/UV/Fe(II) process (0.17 min^{-1}) was about 2 times greater than that in ultrasound alone (0.08 min^{-1}). Therefore, ultrasound process combined with Fe(II)/UV system is very useful for the degradation of linuron.

Enhancement of linuron degradation can be realized by Fe(II) addition in a catalytic amount. These combination processes such as ultrasound/Fe(II) and ultrasound/Fe(II)/UV result in •OH radical generation in Fenton {Fe(II)/H$_2$O$_2$} [32], and Fenton-like {Fe(III)/H$_2$O$_2$} reactions (reactions (1)–(4)) [33,34]

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \tag{1}$$

$$Fe^{3+} + H_2O_2 = Fe^{2+}-OOH + H^+ \tag{2}$$
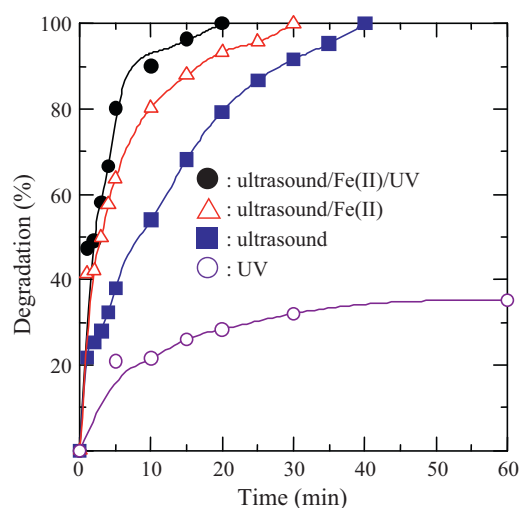
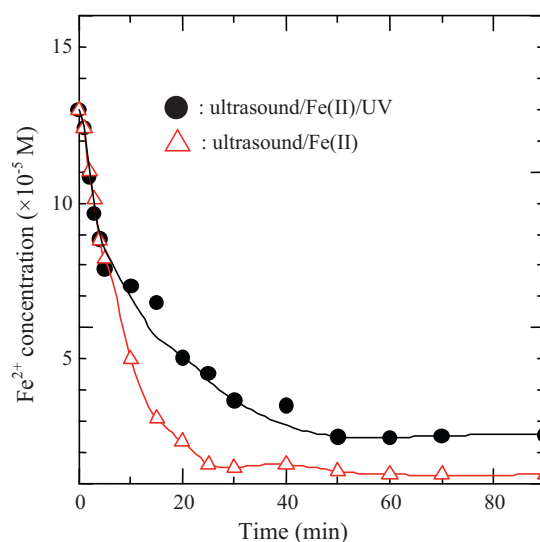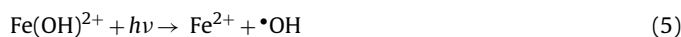

Fig. 3. Effect of reaction time on linuron degradation by the different processes. ([Fe(II)]$_0$ = 1.2 × 10^{-4} mol L^{-1}; pH 3.0; light intensity = 2.0 mW cm^{-2}).
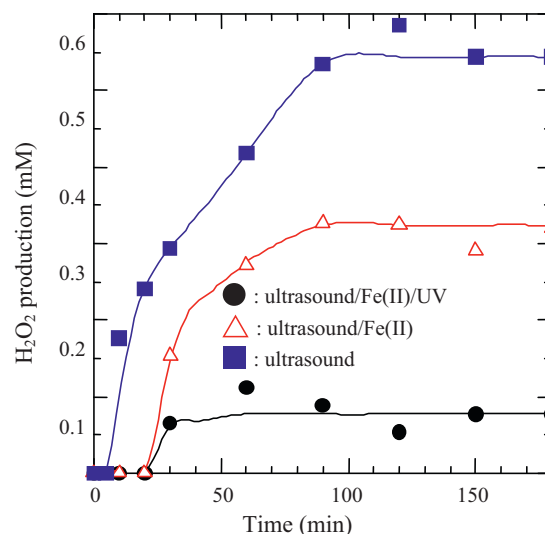

Fig. 4. Time course of Fe(II) concentration as a function of reaction time with different processes. ([Fe(II)]$_0$ = 1.2 × 10^{-4} mol L^{-1}; pH 3.0; light intensity = 2.0 mW cm^{-2}).

$$Fe^{2+}-OOH \rightarrow Fe^{2+} + HOO^{\bullet} \tag{3}$$

$$Fe^{3+} + HOO^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+ \tag{4}$$

in where hydrogen peroxide is produced by ultrasonic irradiation (Fig. 4). Although Fe^{2+}–OOH can be decomposed Fe^{2+} and HOO$^{\bullet}$ spontaneously (Eq. (3)), the decomposition rate is much lower, i.e., the reduction of Fe(III) to Fe(II) occurs at a lower rate in the absence of UV irradiation. Thus, the degradation rate of linuron was higher than that observed in the case of ultrasound alone, but concentration of Fe(II) during the degradation reaction was very low in ultrasound/Fe(II) system (Fig. 5). Further, ultrasound/Fe(II)/UV process also leads to photo-Fenton reaction. The acceleration for decomposition of linuron would be due to the photolysis of iron aquacomplex, Fe(OH)$^{2+}$, providing a new source of •OH radicals [35]. The photoreaction regenerates Fe(II). Therefore, concentration of Fe(II) during this combination process was 20 times higher than that of ultrasound/Fe(II) (Fig. 5).

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH \tag{5}$$

Fig. 5. Evolution of H$_2$O$_2$ concentration as a function of reaction time with different processes. ([Fe(II)]$_0$ = 1.2 × 10^{-4} mol L^{-1}; pH 3.0; light intensity = 2.0 mW cm^{-2}).
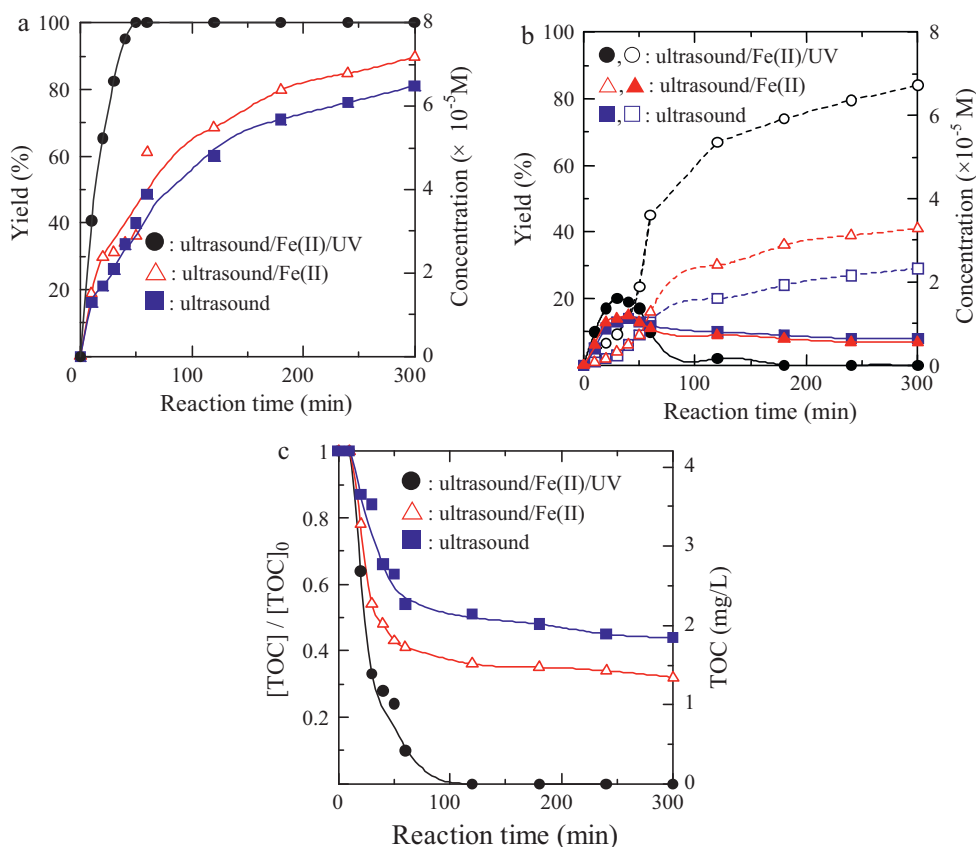
Fig. 6. Time courses of the mineralization during the degradation of linuron by different processes. (a) Chloride ion; (b) nitrite (closed symbols) and nitrate (open symbols) ions; and (c) TOC.

The Fe(II) regenerated reacts with H_2O_2. As a result, almost all H_2O_2 formed by sonication was consumed (Fig. 4). Therefore, ultrasound irradiation combined with photo-Fenton reaction would exhibit considerable enhancement in the degradation of linuron.

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 [36].

The formation of chloride ion from linuron degradation was investigated in the three different processes. In all cases, the concentration of chloride ion quickly increased with increasing the reaction time, suggesting a very fast degradation/dechlorination stage (Fig. 6a). The total amount of chloride ion produced after 50 min of reaction time was approximately $8 \times 10^{-5}\, mol\, L^{-1}$ (100% conversion of the linuron chloride content) using ultrasound/Fe(II)/UV treatment while the complete conversion to chloride ion was not achieved after 300 min by other processes. It has been reported that it took 120 min to form chloride ion from linuron completely by the photo-Fenton reaction under the optimum conditions [15].

The formations of ammonium, nitrite and nitrate ions during ultrasound/Fe(II)/UV process as a function of reaction time are presented in Fig. 6b, together with ultrasound alone and

ultrasound/Fe(II) processes. 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 [37]. This information suggested that degradation of linuron in these processes would also yield these ions as breakdown products. Both nitrite and nitrate ions were detected in different relative concentrations while ammonium ion was not obtained during the degradation processes. In all cases, similar tendencies were observed for the formation of N-containing inorganic ions, that is, the formation of nitrite ion was observed at early stage then nitrite ion was readily oxidized to nitrate ion. The yields of initial N from linuron detected as nitrite and nitrate ions after 300 min of the reaction time were 84, 48 and 37% for ultrasound/Fe(II)/UV, ultrasound/Fe(II) and ultrasound alone, respectively. Therefore, a part of nitrogen atoms from linuron could be mineralized by all systems. This incomplete nitrogen mass balance has frequently been observed in similar process [38–40] and indicates that other nitrogen-containing compounds must be present in the solution or evaporated during the processes. The possible existence of alkyl nitrogen, cianno derivatives [41], carbamic acids and amines could explain the residual TOC as described below, except for ultrasound/Fe(II)/UV system, but the analytical procedures applied to the samples have not been able to detect them. Other authors described N_2 [42] and/or hydroxylamine [43] evolving from nitrogen-containing compounds degraded by photocatalysis. Therefore, the remaining initial N may be due to the formation of N_2 gas and/or hydroxylamine in ultrasound/Fe(II)/UV process and the increase of nitrate concentration after 120 min would be from N-containing inorganic species, considering the complete

mineralization of linuron from TOC measurement as mentioned below.

The progress of the mineralization of the linuron solution by ultrasound/Fe(II)/UV system was monitored by measuring the TOC. As shown in Fig. 6c, 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 combination process. Further, TOC was remained after 50 min while chloride ion was completely released from the parent compound (Fig. 6a, the case of ultrasound/Fe(II)/UV system). Therefore, chlorine atoms in linuron would be easily released and the remained intermediates might be dechlorinated compounds at this time. The generated intermediate products are attacked in their turn by hydroxyl radicals which are formed in a continuous manner via a homogeneous photocatalytic process involving Fe(III, II) [35] and ultrasonic irradiation. TOC rapidly decreased with increasing the reaction time and the TOC value of linuron solution was $0\,mg\,L^{-1}$ after 120 min of the reaction time. However, TOC remained about 1.4 and $1.9\,mg\,L^{-1}$ (68 and 56% mineralization) by ultrasound/Fe(II) and ultrasound alone, respectively, after 300 min of the reaction time. Furthermore, TOC value during the photo-Fenton process was about $0.4\,mg\,L^{-1}$ after 25 h of irradiation time [15]. These results indicate that the combination of ultrasound irradiation and photo-Fenton reaction was effective for the degradation and mineralization of linuron in water samples.

4. Conclusions

Sonochemical photodegradation of linuron in aqueous solution was investigated by ultrasound/Fe(II)/UV treatment. The degradation efficiency was strongly affected by experimental factors, such as the pH value and the initial concentration of Fe(II). Linuron achieved complete degradation after 20 min under the optimum conditions. The first-order rate constant for linuron degradation by ultrasound/Fe(II)/UV process was ca. 2 times higher than ultrasound alone.

The disappearance of TOC was observed during the combination process and the complete mineralization was achieved after 120 min. However, TOC remained about 1.4 and $1.9\,mg\,L^{-1}$ (68 and 56% mineralization) by ultrasound/Fe(II) and ultrasound alone, respectively, after 300 min. The formations of chloride, nitrite and nitrate ions were also observed. Therefore, the starting compound could be mineralized during ultrasound/Fe(II)/UV process.

The advantages of the sonication with photo-Fenton process as an oxidative treatment are rapid degradation and simple handling. Therefore, ultrasound/Fe(II)/UV system would be applied to wastewater treatment works as a new developing methodology for reducing levels of other pesticides and endocrine disrupting chemicals.

Acknowledgements

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