

Photocatalytic degradation of Linuron in aqueous solution with nanosized TiO₂ under sunlight irradiation

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Abstract

The photocatalytic degradation of 3-[3,4-(dichlorophenyl)-1-methoxy-1-methylurea] (Linuron) in aqueous solutions with TiO₂ semiconductors was investigated under sunlight illumination. It was found that the primary photocatalytic decomposition reaction follows a pseudo-first order kinetic law. During the photocatalytic degradation, the first-order rate constant k was 0.12 min⁻¹. The present degradation method will be able to be applied to various chemicals.

Key words

sunlight photocatalytic degradation, Linuron, nanosized TiO₂, herbicide, waste water

1. Introduction

The herbicides are the most widely used chemicals of pesticides in agriculture. These chemicals are generally non biodegradable and toxic. The phenylurea herbicides demonstrate a significant group of herbicides applied to the pre and post emergence control of weeds in many agricultural crops. One of the most significant widely used types of this group, Linuron [3-(3,4-(dichlorophenyl)-1-methoxy-1-methylurea), MW = 248.0 g/mol] is relatively persistent in soil, with half-life ranges from 38 to 67 days (Mechakra et al., 2016). Its persistence in soil is owing to its physicochemical properties such as low solubility in water (estimated as 75 mg L⁻¹ at 25 °C) and stability. Like others phenylurea herbicides, Linuron was also present in polluted natural waters, showing that it is difficult to reduce by a conventional wastewater treatment process.

In the case of toxic or non biodegradable wastewater sources, alternative treatments have to be applied. Advanced oxidation process (AOPs) have been proposed as the effective methods for remediation of wastewaters. The reducing of Linuron has been industrially speculated by different methods, containing homogeneous and heterogeneous AOPs such as the direct photolysis, the UV photolysis of hydrogen peroxide, the photolysis by UV/O₃ process, the combined O₃/H₂O₂ system, and photocatalysis. The AOPs are characterized by production of hydroxyl radicals (OH), a powerful oxidizing agent with oxidation potential of 2.8 V. Photons whose energy is equal to or greater than the band-gap energy (E_g) of the photocatalytic semiconductor (SC), can be absorbed exciting the valence band electrons. Consequently, a positive photoinduced hole (h⁺) in the valence band (VB) and a

photoelectron (e⁻) in the conduction band (CB) are formed (SC + hu → e⁻ + h⁺). The h⁺/e⁻ pairs generated act as the oxidizing and reducing agents, respectively. Simultaneously, a spontaneous adsorption occurs, and according to the redox potential of each adsorbate, an e⁻ transfer proceeds towards acceptor molecules (A_{ads} + e⁻ → A_{ads}⁻), whereas a positive h⁺ is transferred to a donor molecule (D_{ads} + h⁺ → D_{ads}⁺) (Fenoll et al., 2013).

Titanium dioxide, owing to its remarkable activity together with non-toxicity, chemical inertness, robustness to UV irradiation and low cost, is a greatly promising materials. Until now, a number of researches have been reported for the photocatalytic remediation of Linuron in water with TiO₂ using an artificial light source such as a Xe lamp (Laoufi and Bentahar, 2014; Ruggieri et al., 2011). The artificial lamp device is particularly expensive in the local and nonexclusive areas. The photocatalytic remediation of Linuron on TiO₂ in water under sunlight irradiation by using the UV range, that is, a small fraction of solar light, may be possible, although it takes long time for the photocatalytic treatment. However, there is little information on the solar photocatalytic remediation of Linuron with nanosized TiO₂ in water (Fenoll et al., 2013). Therefore, the present work deals mainly with the photocatalytic degradation of Linuron with nanosized TiO₂ in aqueous solution.

2. Experimental

Linuron used in this study was purchased from FUJIFILM Wako Pure Chemical Corporation, Japan (GC grade > 99.0 %). Aqueous Linuron solutions were prepared with ultrapure water, which was purified by an ultrapure water system (Advantec MFS, Tokyo, Japan) resulting in a resistivity >18 MΩ cm. A 50 mL aqueous solution containing 5 μg/mL (20 μM) Linuron was put into a Pyrex reaction vessel (100 mL capacity). TiO₂

powder (anatase, purity 99.9 %, diameter 230 nm, surface area 8.7 m²/g, FUJIFILM Wako Pure Chemical Corporation, Japan) was added to the solution to produce a concentration of 1.4 mg/mL. The pH of the solution was 6.4. The temperature was kept constant at 30 °C with a water bath. The TiO₂ suspension containing Linuron was irradiated under sunlight illumination. In this case, the short ultraviolet radiation ($\lambda < 300$ nm) was filtered out by the vessel wall. The intensity of light was measured by a UV radio meter (UVR-400, Luchi, Osaka, Japan). The light intensity with wavelengths from 320 to 410 nm was 1.9 mW/cm².

After illumination, the amount of Linuron in the aqueous solution was measured using a high-performance liquid chromatograph (HPLC, JASCO, Tokyo, Japan), equipped with a JASCO UVDEC-100-VI optical detector and a Chromspher 5 Poly C18 column (Chrompack, VARIAN, California, USA). The elution was monitored at 248 nm. The eluent used was a mixed solvent of acetonitrile and water (7/3, v/v). The flow rate of the mobile phase was 1.0 mL/min. The UV absorption measurements were made using a UVDEC-610 double-beam spectrometer (JASCO, Tokyo, Japan). The spectra were measured in 1-cm optical path quartz cells after filtration to remove the suspended TiO₂.

3. Results and discussion

3.1 Absorption spectra

The UV absorption spectra of a Linuron solution is presented in Figure 1. The photocatalytic degradation of Linuron caused the disappearance of the 210 and 248 nm absorption bands of Linuron. From the observed absorbance at $\lambda_{\text{max}} = 248$ nm, ϵ was estimated to be $2.28 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. Consequently, it was found that TiO₂ was an effective photocatalyst

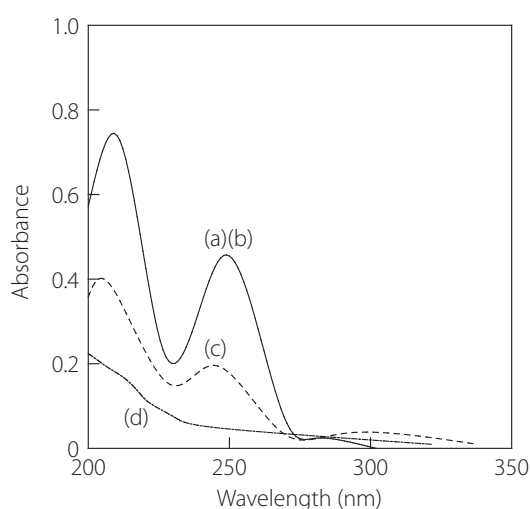


Figure 1: UV absorption spectra of Linuron before and after sunlight illumination in the presence of suspended TiO₂. Notes: TiO₂; 1.4 mg/mL, temperature 30 °C, initial pH 6.4, (a); Linuron 5 µg/mL, (b); photocatalysis for 30 min, (c); after 10 min illumination, (d) after 30 min illumination.

for the degradation of Linuron under sunlight illumination.

3.2 Effect of sunlight illumination time

The effect of sunlight illumination time on the photocatalytic degradation of Linuron in aqueous solutions with TiO₂ semiconductors was investigated. These results are shown in Figure 2. The photocatalytic decomposition process rapidly proceeded up to 20 min. At a 40 min sunlight illumination time, Linuron in the aqueous solutions almost completely disappeared and was degraded.

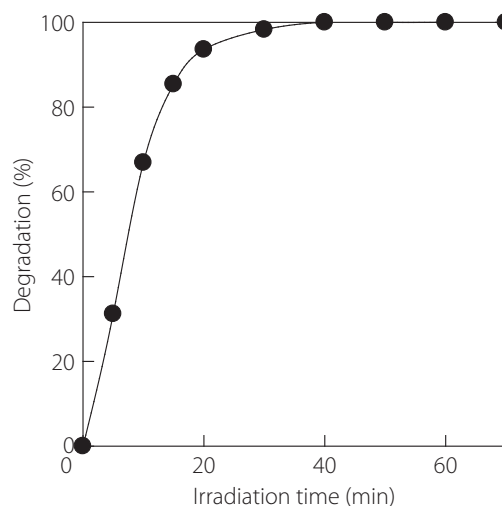


Figure 2: Effect of sunlight illumination time on the photocatalytic degradation of Linuron in water using TiO₂

Notes: Linuron 5 µg/mL, TiO₂; 1.4 mg/mL, temperature 30 °C, initial pH 6.4.

During the primary degradation, the aqueous solutions containing 5 µg/mL of Linuron and 1.4 mg/mL of suspended TiO₂ showed complete disappearance of the substrate after 40 min. It is established that the photocatalytic degradation of organic substances on the aqueous TiO₂ suspension can be expressed by a Langmuir-Hinshelwood kinetics model (Ruggieri et al., 2011)

$$-dc/dt = kKc / (1 + Kc) \quad (1)$$

where c is the concentration of reactant, k the reaction rate constant, K an equilibrium adsorption constant and t the irradiation time. For low concentrations of reactant (millimolar or below), the above equation can be simplified to a pseudo-first order kinetic equation that in the integrated form gives

$$\ln(c/c_0) = Kkt = k_{app}t \quad (2)$$

where c_0 is the initial concentration of reactant, and k_{app} an apparent pseudo-first order kinetic constant.

In order to confirm this speculation, $\ln(c/c_0)$ was plotted as a function of the sunlight illumination time (Figure 3). Since

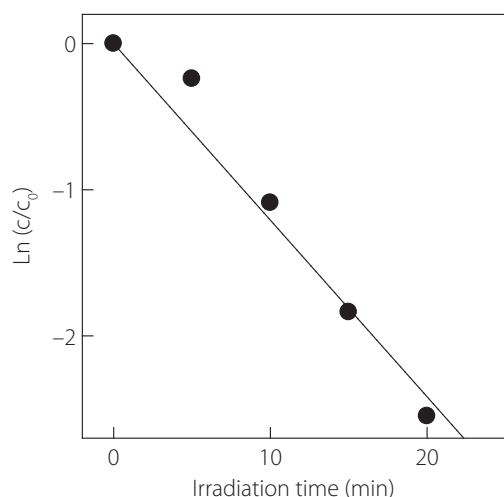


Figure 3: Plot of $\ln(c/c_0)$ versus sunlight illumination time during the photocatalytic degradation of Linuron in water using TiO₂

Note: The experimental conditions are described in Figure 2.

the linear plots were observed in Figure 3 as expected, the primary photocatalytic degradation dynamics of Linuron may be a pseudo-first order kinetics. During the photodegradation experiment, the substrate half-life was 7.3 min. The value k_{app} in Figure 3 was 0.12 min^{-1} and $t_{1/2}$ was calculated to be 5.7 min.

3.3 Photocatalytic degradation mechanism

In the photodegradative process implicating TiO₂ particulates, the absorption of light with an energy greater than 3.2 eV (wavelengths below 387 nm) generates electron/hole pairs that upon separation yield conduction band electrons and valence band holes (Eq. 3) (Kaneco et al., 2004; 2006; 2009; Ruggieri et al., 2011). Migration of these carriers to the surface in competition with a variety of other decay channels leads to trapping of the holes by OH⁻ groups or by H₂O to produce •OH radicals (Eq. 4) and trapping of the electrons by Ti^{IV} and/or by the ubiquitous oxygen molecules at the particle surface to yield the superoxide radical anion, •O₂⁻, which on protonation forms the hydroperoxide radical •OOH (Eq. 5). In addition to the main reactions shown, other processes can also occur. As consequence, the important reaction process is that involving an oxidizing species which can attack and transform the organic molecules through the formation of intermediates.



4. Conclusion

The photocatalytic degradation of Linuron in aqueous solutions with TiO₂ semiconductors was investigated under sunlight illumination. It was found that the primary photocatalytic decomposition reaction follows a pseudo first-order kinetic law. During the photocatalytic degradation, the first-order rate constant k was 0.12 min^{-1} . Since it was found that the sunlight photocatalytic decomposition process for Linuron succeeded, the proposed degradation method could apply the treatment plant in local and nonexclusive area. Further investigations including the effect of pH, temperature and light intensity and intermediate products are in progress for the sunlight photocatalytic degradation of Linuron in water with TiO₂.

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