



# Linuron decomposition in aqueous semiconductor suspension under visible light irradiation with and without H<sub>2</sub>O<sub>2</sub>

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## ARTICLE INFO

### Article history:

Received 26 May 2009

Received in revised form

11 December 2009

Accepted 21 December 2009

### Keywords:

Photocatalysis

Semiconductor

Hydrogen peroxide

Linuron

Hydroxyl radicals

## ABSTRACT

The degradation of LNR in TiO<sub>2</sub> suspension with and without H<sub>2</sub>O<sub>2</sub> was investigated under the irradiation of visible light at 419 nm. The removal of LNR in TiO<sub>2</sub>-P25 suspension can be increased from 10% to nearly 100% by simply adding H<sub>2</sub>O<sub>2</sub> to the process after 3 h of reaction. Various types of TiO<sub>2</sub> including anatase, rutile and TiO<sub>2</sub>-P25 exhibited different photocatalytic activities on LNR decay, while their performances were strongly dependent on the presence and/or absence of H<sub>2</sub>O<sub>2</sub>. The performance of using other metal oxides (semiconductors) as alternatives for TiO<sub>2</sub> was also studied. Among three selected semiconductor oxides, ZnO was found to be most effective for the reaction without H<sub>2</sub>O<sub>2</sub>, while significant rate enhancement was observed for TiO<sub>2</sub>-P25 and WO<sub>3</sub> as H<sub>2</sub>O<sub>2</sub> was used.

The H<sub>2</sub>O<sub>2</sub>-assisted TiO<sub>2</sub> photocatalysis using visible light could be optimized by adjusting TiO<sub>2</sub> dosage, initial concentration of H<sub>2</sub>O<sub>2</sub> and the initial pH of the system. The LNR decay rate, generally, increased with the increase of TiO<sub>2</sub> dosage, but too high the TiO<sub>2</sub> was not cost-effective due to the light attenuation. The initial H<sub>2</sub>O<sub>2</sub> concentration did not show a significant influence on the reaction rate because the amount of the available electrons on the TiO<sub>2</sub> surface is likely the rate-limiting factor rather than the concentration of H<sub>2</sub>O<sub>2</sub>. A neutral initial pH level was found to be favorable for the H<sub>2</sub>O<sub>2</sub>-assisted photocatalysis under visible light, which made the proposed process more attractive for real application.

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## 1. Introduction

Semiconductor-induced photocatalysis has received intensive attention as an environmental remediation technology over the past decades [1–5]. Among all semiconductors, Titanium dioxide (TiO<sub>2</sub>) is believed to be one of the most appropriate photocatalysts in terms of environmental application owing to its particularly optical properties, innocuity, low cost and enduring stability regarding photo- and chemical corrosion [6,7]. In general, a photon with energy higher than the bandgap energy ( $E_g = 3.2$  eV and 3.0 eV for anatase and rutile phases, respectively) of TiO<sub>2</sub> can initiate the excitation of electron from the valence band (VB) to the conduction band (CB), leaving a hole,  $h_{vb}^+$  behind [8]. These charged species are believed to induce the generation of free radicals such as OH<sup>•</sup> and O<sub>2</sub><sup>•-</sup> which play a major part coupling with  $h_{vb}^+$  in the oxidation of organic compounds [7]. The widespread use of TiO<sub>2</sub> as an effective photocatalyst, however, has been curbed by its poor light absorption in the visible region due to its large band gap. Therefore, efforts have been devoted to improve the utility of TiO<sub>2</sub> by shift-

ing its optical response from the UV to the visible spectral range. Using transition metal and nonmetal doping to lower the threshold energy for the excitation of electron in the valence band plays a big part in these efforts [9–16]. In addition, recently photosensitization via surface adsorbed organic dyes and coordination metal complexes also holds promise for extending TiO<sub>2</sub> absorption into the visible region [17–19]. Whereas doping and photosensitization have demonstrated successful performance in either narrowing the band gap of TiO<sub>2</sub> or sensitizing photocatalytic properties of TiO<sub>2</sub> towards visible light irradiation, the preparation process of photocatalyst is time-consuming and expensive, which may hinder the use of TiO<sub>2</sub> in practical applications. In this study, a novel and cost-efficient process was developed to allow the degradation of organic compounds in TiO<sub>2</sub> suspension under visible light irradiation with the assistant of H<sub>2</sub>O<sub>2</sub>.

The widespread application of herbicides as a regular and effective practice to control weed growth has led to increasing environmental concerns in the past decades because of their low biodegradability and long-term persistence in soil. Most herbicides are diffused into aquatic environment via agricultural runoff or leaching [20], which makes them ubiquitous. Linuron (LNR), one of the most important phenylurea herbicides, has received particular attention in recent years due to the toxicity, being frequently detected in the surface and underground waters, and

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possible endocrine disrupting properties of LNR and/or its metabolites [21,22]. Therefore, various treatment techniques have been developed to remove LNR in the aqueous phase, including biological methods [22,23], direct photolysis [24],  $O_3/H_2O_2$  [25], photo-Fenton procedure [21,26],  $UV/H_2O_2$  [27],  $UV/O_3$  [28] and photocatalysis under UV irradiation [29]. The information regarding the photocatalytic decay of LNR under visible light, however, is very limited.

In view of these, this study sets out to examine the photocatalytic decomposition of LNR under visible range irradiation with and without  $H_2O_2$ . Its objectives are to explore a new and effective approach to utilize visible light to assist the decay of LNR in semiconductor suspension. The performance of the LNR degradation was investigated in this study under different conditions, such as selection of semiconductors, the effects of  $TiO_2$  phase composition,  $TiO_2$  dosage, the concentration of  $H_2O_2$ , and initial pH levels.

## 2. Materials and methods

### 2.1. Reagents

Linuron (3-[3,4-(dichlorophenyl)-1-methoxy-1-methylurea]) (99%) was obtained from SUPELCO. Three different  $TiO_2$  powders used were anatase, rutile (purchased from Shanghai Kexiang Chemical Reagent Company at 98.5% and 98%, respectively), and Degussa P25, The latter containing 80% anatase and 20% rutile was verified and confirmed by X-ray analysis. The analysis of the specific areas of these  $TiO_2$  powders using the Brunauer–Emmett–Teller (BET) isotherms (Micromeritics ASAP 2010) was 11.4, 9.5 and  $55.0\text{ m}^2\text{ g}^{-1}$  for rutile, anatase and Degussa P25, respectively. The powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray diffractometer with  $Cu\ K\alpha$  radiation ( $\lambda = 1.54178\text{ \AA}$ ) at a scan rate of  $0.05^\circ\ 2\theta/s$ . The crystal size of anatase and rutile powders estimated from (1 0 1) and (1 1 0) peaks in XRD spectra is 26.95 and 26.53 nm, respectively (XRD spectra are not shown here). The mean diameters of anatase, rutile and P25 powders were measured to be 265.1, 305, and 211.3 nm, respectively by Zeta Plus/Zeta Potential Analyzer (Brookhaven Instruments Corporation). Nanopowder  $WO_3$  and  $ZnO$  (<100 nm) were purchased from Aldrich as well. The  $H_2O_2$  (35% in solution) and titanium oxide sulfate hydrate ( $TiOSO_4 \cdot xH_2O$ ) was purchased from Riedel-deHaën and International Laboratory, respectively. All other chemicals are analytic purity and all solvents are HPLC grade and used without further purification. For pH adjustment, 0.1 M sulfuric acid and 0.1 M sodium hydroxide were used. The water used in the preparation of all solutions was obtained from a Millipore Waters Milli-Q water purification system.

### 2.2. Procedures and analysis

The photodegradation of LNR was conducted in a Luzchem CCP-4V photochemical reactor controlled by a computer. To ensure a thorough mixing, 150 mL of solution was dispensed into a 300 mL quartz cylinder with mechanical stirring before and during the illumination. Twelve low-pressure mercury lamps at 419 nm (The emission spectra were shown in Fig. 1) were installed in the photoreactor. The diagram of the experimental installation is shown in Fig. 2, in which 1 mL samples were withdrawn at a predetermined interval and were filtered through a  $0.2\ \mu\text{m}$  PTFE membrane to keep the particles free from the solution prior to quantification. All experiments were carried out at room temperature (air-conditioned) at  $23^\circ\text{C}$  in duplicate and the error is less than 5.0%.

Remaining LNR after photoreaction was determined by HPLC (Waters). The system was comprised of a Waters 515 HPLC pump, Waters 2487 Dual  $\lambda$  Absorbance Detector, an Agilent Hypersil

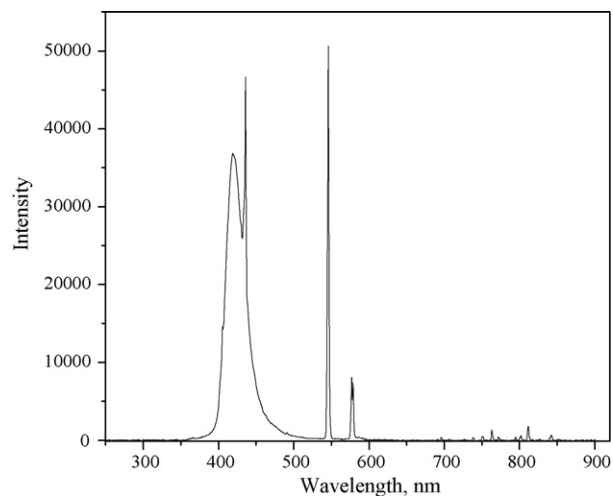


Fig. 1. The emission spectra of 419 nm lamps.

ODS column ( $5\ \mu\text{m}$ ,  $0.46 \times 25\text{ cm}$ ), and Waters 717plus Autosampler. The maximum adsorption wavelength ( $\lambda_{\text{max}}$ ) was selected as 246 nm for LNR. A mixture of 60% acetonitrile and 40% water was used as the mobile phase running at a flow rate of 1 mL/min. The  $H_2O_2$  concentration was measured by means of UV–visible light absorbance spectroscopy at 408 nm [30]. A Varian CARY 300 UV–visible Spectrophotometer were used to obtain the ultraviolet–visible diffuse reflection spectra (UV–vis DRS) of the samples over a range of 200–800 nm. The emission spectra of lamps were recorded by ILT900 Wideband Rapid Portable Spectroradiometer (International Light Technologies).

## 3. Results and discussion

### 3.1. LNR degradation under visible light irradiation in $TiO_2$ – $H_2O_2$ system

Many studies have shown that, under UV irradiation,  $H_2O_2$  play a dual role in enhancing the semiconductor-sensitized photocatalytic degradation of organic compounds by acting either as an electron scavenger to prevent the recombination of  $e^-$  and  $h^+$  or as a direct source of hydroxyl radicals [31–34]. However, under visible light, such information is limited.

In this section, the degradation of LNR was investigated under various conditions including the presence or absence of  $TiO_2$  (P25), the processes with or without  $H_2O_2$ , and the use of visible light irradiation or in the dark. As shown in Fig. 3a, it is interesting to observe that the elimination of LNR is insignificant in the systems of

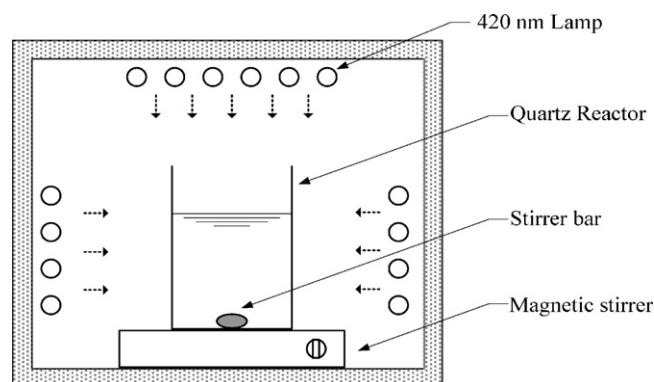


Fig. 2. The diagram of the experimental setup.

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