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Titanium dioxide mediated solar photocatalytic degradation of thiram in aqueous solution: Kinetics and mineralization

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ABSTRACT

The photocatalyzed degradation conditions of thiram in aqueous titanium dioxide-suspended solution were optimized under sunlight illumination. The effect of various factors, such as photocatalyst loading, initial substrate concentration, temperature, pH, sunlight intensity and illumination time on the photocatalytic degradation of thiram was investigated. The primary photocatalytic decomposition reaction followed a pseudo-first-order kinetic law according to the Langmuir–Hinshelwood model. During the photocatalytic degradation, the first-order rate constant k_{obs} was 0.10 min^{-1}, which was approximately 12 times that observed in direct photolysis. The half-lives ($t_{1/2}$) and the activation energy (E_a) were 6.7 min and 33 kJ mol^{-1}, respectively. Carbon dioxide and sulfate, nitrate and ammonium ions were detected as the end products. The stoichiometric transformation of organic sulfur to sulfate ions was observed at relatively shot illumination time (2 h), whereas the complete mineralization of organic carbon and nitrogen atoms took place at delayed illumination time. Dimethylamine and monomethylamine were identified as the intermediate products. The photocatalytic degradation mechanisms were proposed on the basis of the experimental results with molecular orbital (MO) simulation of frontier electron density. The solar photocatalytic degradation treatment for the wastewater including thiram is simple, easy handling and low cost. Therefore, since the artificial lamp devices, for example Hg-Xe lamp, are particularly expensive in the local and poor areas, the proposed technique seems to become a very powerful method for the treatment of wastewater including thiram in those areas.

1. Introduction

Thiram [thiuram (Japan), tetramethylthiuram disulfide (TMTD, former USSR), bis(dimethyldithiocarbamoyl) disulfide, CAS #137-26-8, Fig. 1] is an alkyldithiocarbamate compounds, which has been widely used as fungicides in agriculture. It is also used as an accelerator and vulcanization agent in the rubber industry and has been in commercial use since 1925. Some reports have been described on the mutagenicity and toxicity of thiram. It has been reported that the plate incorporation assays with *Salmonella typhimurium* TA100 and TA98 demonstrated direct mutagenecity of thiram [1,2]. The oral toxicity of thiram was presented in rodents [3]. In tests on human and rat testicular cells, thiram was found to increase possible carcinogenesis [4]. The U.S. Environmental Protection Agency (USEPA) researchers [5] have reported the reference doses (RfDs) in publicly accessible databases such as the Integrated Risk Information System (IRIS), which contained 0.005 mg kg^{-1} day^{-1} of thiram. Smith [6] has established the risk-based concentration of thiuram in tap water at 0.18 mg L^{-1}. The Ministry of the Environment in Japan released the uniform national effluent standards, which included 0.06 mg L^{-1} of thiram [7]. Until 2004, a regulation of the Ministry of Health, Labour and Welfare in Japan required the level of thiram remaining in tap water to be <0.006 mg L^{-1}. Niitsuma et al. [8] have investigated the degradation of thiram by ozone treatment with or without UV radiation. Ohta et al. [9] have found that thiram was degraded immediately during water purification using sodium hypochlorite, and about 30 mol of sodium hypochlorite reacted with one molecule of thiram. Chew and Harpp [10] have reported that the oxidation of thiram using thionyl chloride or chlorine gas in carbon tetrachloride gave *N*,*N*-dimethylthiocarbamyl chloride and diatomic sulfur. Kodama et al. [11] have studied the degradation pathway of thiram in tap water processed by oxidation with sodium hypochlorite. However, very few works related to the use of semiconductors such as TiO_2 in the degradation of thiram have been reported [12,13], although their purification techniques are simple, easy handing, cheap and environmental-benign. Moreover, the limited information concerning the degradation of thiram with TiO_2

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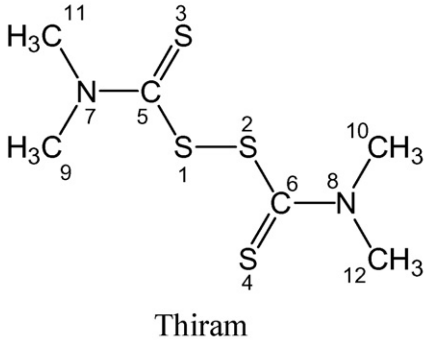

Fig. 1. Chemical structure of thiram.

merely contained the results using the halogen and high-pressure mercury lamp.

Previously, we have investigated the photocatalytic degradation of dibutyl phthalate in aqueous solution under sunlight illumination [14]. In the study, the complete mineralization could not be achieved in the short illumination time (<30 h). In the present work, the solar photocatalytic degradation conditions of thiram in water with TiO_2 were optimized, and the amount of final degradation products was monitored in order to evaluate the complete mineralization of thiram. Furthermore, the photocatalytic degradation pathways were speculated on the base of the evidence of the oxidative intermediate formation.

2. Experimental

Thiram used in this study was purchased from Wako Pure Chemical Industries, Ltd., Osaka, Japan (pesticide grade). Thiram aqueous solutions were prepared with ultrapure water, which was purified by an ultrapure water system (Advantec MFS, Inc., Tokyo, Japan) resulting in a resistivity >18 MΩ cm. A 50 mL aqueous solution containing 5 μg mL^{-1} ($\sim$21 μM) thiram was put into a closed columnar Pyrex reaction vessel (100 mL capacity). TiO_2 powder (anatase, purity 99.9%, diameter 230 nm, surface area 8.7 m^2 g^{-1}, Wako Pure Chemical Industries, Ltd.) was added to the solution to produce a given concentration of TiO_2 suspension. The pH of sample solution was adjusted with HCl and NaOH solutions. The temperature was kept constant with a water bath. The detailed typical experimental conditions were shown in Table 1. The TiO_2 suspension containing thiram was allowed to equilibrate for 60 min in the darkness, and then it was irradiated under sunlight illumination. During these treatments, the suspensions were magnetically stirred for the dispersion of TiO_2. In this case, the short ultraviolet radiation ($\lambda < 300$ nm) was filtered out by the vessel wall. The irradiance was measured by a UV radio meter with a sensor of 320–410 nm wavelengths (UVR-400, Iuchi Co., Osaka, Japan). The variations of irradiance for 20 min were less than 10%.

After illumination, TiO_2 was separated through the 0.45 μm Advantec membrane filter. The TiO_2 powders could be almost removed by the filtration. The amount of thiram in the aqueous solution was measured using a high-performance liquid chromatograph. The degradation efficiency of thiram was calculated with the following equation:

$$\text{Degradation efficiency (\%)} = \frac{100 \times (q_0 - q_1 - q_2)}{q_0 - q_1} \qquad (1)$$

where q_0, q_1 and q_2 were the initial amount of thiram, the amount adsorbed onto the catalyst at equilibrium and the residual amount undegraded after the treatment, respectively. The thiram amount adsorbed onto the catalyst was less than 3% of total amount in the solution. The reproducibility of the treatment [relative standard deviation (R.S.D.), for degradation efficiency] was better than R.S.D. 15% for three repeated measurements. The formation of sulfate and nitrate ions was measured by ion chromatography. The evolution of CO_2 was evaluated with a GL Science GC-353B equipped with a methanizer and a flame ionization detector, combined with a Porapack Q using nitrogen carrier gas. The detailed information for the experimental was described in the supplementary data.

Table 1
Typical experimental conditions

Thiram	5 μg mL^{-1} (50 mL)
TiO_2	0–15 mg (0–300 μg mL^{-1})
Temperature	0–60 °C
pH	2.5–11.4
Light source	Sunlight
Irradiance	0–1.8 mW cm^{-2}
Illumination time	20 min

Molecular orbital calculations were carried out at the single determinant (Hartree-Fock) level for optimization of the minimum energy obtained at the AM1 level. All semi-empirical calculations were performed in MOPAC Version 6.01 with a CAChe package (Fujitsu Co. Ltd.). An initial position for a possible $^{\bullet}$OH radical attack was estimated from calculations of frontier electron densities of the thiram structure. The mode by which thiram might adsorb onto the TiO_2 surface was estimated from calculated partial charges of thiram [15].

3. Results and discussion

3.1. UV–vis spectral changes

The temporal absorption spectral changes taking place during the photocatalytic degradation of thiram mediated by TiO_2 particles under sunlight illumination are investigated (supplementary data Fig. S1). Thiram shows a major absorption band at 215 and 276 nm. From the observed absorbance, absorptivity at 215 nm was estimated to be 6.3 cm^2 ng^{-1}. The well-defined absorption bands disappeared after irradiation for 60 min, indicating that thiram had degraded in the presence of TiO_2 particles with sunlight illumination. Therefore, because it was confirmed that TiO_2 was an effective photocatalyst for the decomposition of thiram under sunlight illumination, various factors such as photocatalyst loading, initial substrate concentration, temperature, pH, irradiance and illumination time, were evaluated for the photocatalytic degradation of thiram.

3.2. Effect of photocatalyst loading

In order to optimize the TiO_2 suspension concentration, the effect of photocatalyst loading on the degradation of thiram in aqueous solution was investigated as illustrated in the supplementary data Fig. S2. The degradation efficiency increased with increasing the amounts up to 8 mg, and then the efficiency became nearly flat. When the suspension concentration of TiO_2 increased above the limiting value 8 mg, the number of active sites on the TiO_2 surface may become almost constant because of the decreased light penetration, the increased light scattering and the loss in surface area occasioned by agglomeration (particle–particle interactions) at high solid concentration [16]. Therefore, 8 mg of TiO_2 was selected as the optimal amounts of photocatalyst for the sequential experiment. The TiO_2 amounts corresponded to the suspension concentration of 160 μg mL^{-1}.