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# Photodecomposition Behaviors of Pesticides in the Source for Water Supply Using an Alumina Carrier-Titanium Dioxide Photocatalyst

Seiichi Ishikawa, Bunko Cho,  
Shin Li, Yuji Okumura, Yoshikazu Iida,  
Teiji Tanizaki and Masayuki Higuchi  
*The University of Kitakyushu  
Japan*

## 1. Introduction

The countermeasures against toxic substances or musty odor cause substances in the source for water supply have become a serious subject with the pollution of environmental waters (Coleman et al., 1980; Nakasugi, 1993; Tanada et al., 1995; U. S. EPA, 1993). For the purpose of the utilization of the photodecomposition method for the water purification at a water purification plant or a water purifier, we have investigated on the photodecomposition behaviors of organic pollutants (Matsuda et al., 2002; Okumura et al., 2003), total organic compounds (Tanizaki et al., 2005), formaldehyde (Tanizaki et al., 2005), total organic halides (Tanizaki et al., 2005), trihalomethanes (Tanizaki et al., 1997, 2005), geosmin (Okumura et al., 2004) and 2-methyl-iso-borneol (Okumura et al., 2004) using a titanium dioxide ( $\text{TiO}_2$ ) photocatalyst. Relatively high photodecomposition efficiencies were obtained for these substances.

Pesticide is one of the toxic chemical substances polluting the source for water supply (Tanada et al., 1995), vegetables, fruits, etc (Ishikawa et al., 2004). Then, the residual pesticide in many kinds of food have already been regulated and the aiming standard values of 101 types of pesticide for tap water quality control were set up in 2003 (Ando, 2004). However, only 21 in 117 types of pesticide showed over 80% of removal ratio in the coagulation and sedimentation usually performed at a water purification plant (Ishikawa et al., 2006). Then, we investigated on the photodecomposition behaviors of the 5 types of pesticide which were largely used in Kitakyushu district.

We have ever used silica gel having high decomposition efficiency as a carrier of  $\text{TiO}_2$  photocatalyst. However, a silica gel carrier was fragile. In addition, sufficient endurance of the carrier is demanded when the decomposition of chemicals in water and food or that disinfection using supersonic wave together is performed (Ishikawa et al., 2008). Then, we also investigated on the photodecomposition ability with an alumina carrier, which could stand against ultra violet (UV) light and water, instead of silica gel carrier.

2. Material and methods

2.1 Instruments

Gas chromatograph/mass spectrometer (GC/MS) was a Hewlett Packard HP-5890 series and a JEOL auto mass system. Total nitrogen (T-N) analysis was performed using a Tokyo Kasei Ind. Co. TCI-NOX 1000, GASTORR GT-102, VISIBLE DETECTOR S-3250 and AUTO SAMPLER SS-3600, while other determinations Hitachi Co. U-2000A a spectrophotometer was used.

2.2 Objective pesticides and other reagents

Five pesticides (Table 1) were selected for an objective pesticide. These pesticides were used in the Onga River Basin and their aiming standard values in tap water quality were established (Ando, 2004). Their structural formulas were shown in Fig. 1. Dinitrophenol (DNP) was used as a chemical substance for the capability evaluation of alumina carrier (Okumura et al., 2003). These chemical substances were obtained from Hayashi Pure Chemical Industries, Wako Pure Chemical Industries and Tokyo Kasei Kogyo Co.. Each standard solution was prepared by the dilution with acetone. An alumina carrier was obtained from Sumitomo Chemical Co.. The properties of the alumina and silica gel carriers, comparative carriers, were shown in Table 2. Two types of alumina, NK124 and NKHO24

(Fig. 2), and silica gel carrier-TiO<sub>2</sub> photocatalysts were produced by the Sol-Gel Method (Okumura et al., 2004; Tanizaki et al., 1997). All solvents were the grade reagents for pesticide residue analysis, which were obtained from Kanto Chemical Co. and Wako Pure Chemical Industries. Other reagents were special grade reagents, which were obtained from Wako Pure Chemical Industries. Anhydrous Na<sub>2</sub>SO<sub>4</sub> and NaCl were heated at 800 °C for 3 h after acetone-washing. The water was purified using a Millipore Milli-Q Ultra-pure Water System.

Pesticide	Use	Shipped amount <sup>a</sup> (kg)	Aiming standard value (mg l <sup>-1</sup> )
Chlorthalonil	Disinfectant	185	0.05
Pencycuron	Disinfectant	686	0.04
Cafenstrole	Herbicide	1,946	0.008
Thiobencarb	Herbicide	155	0.02
Trifluralin	Herbicide	5,238	0.06

<sup>a</sup> The values in 2003

Table 1. The shipped amounts and the aiming water qualities of the objective pesticides in the Onga River Basin

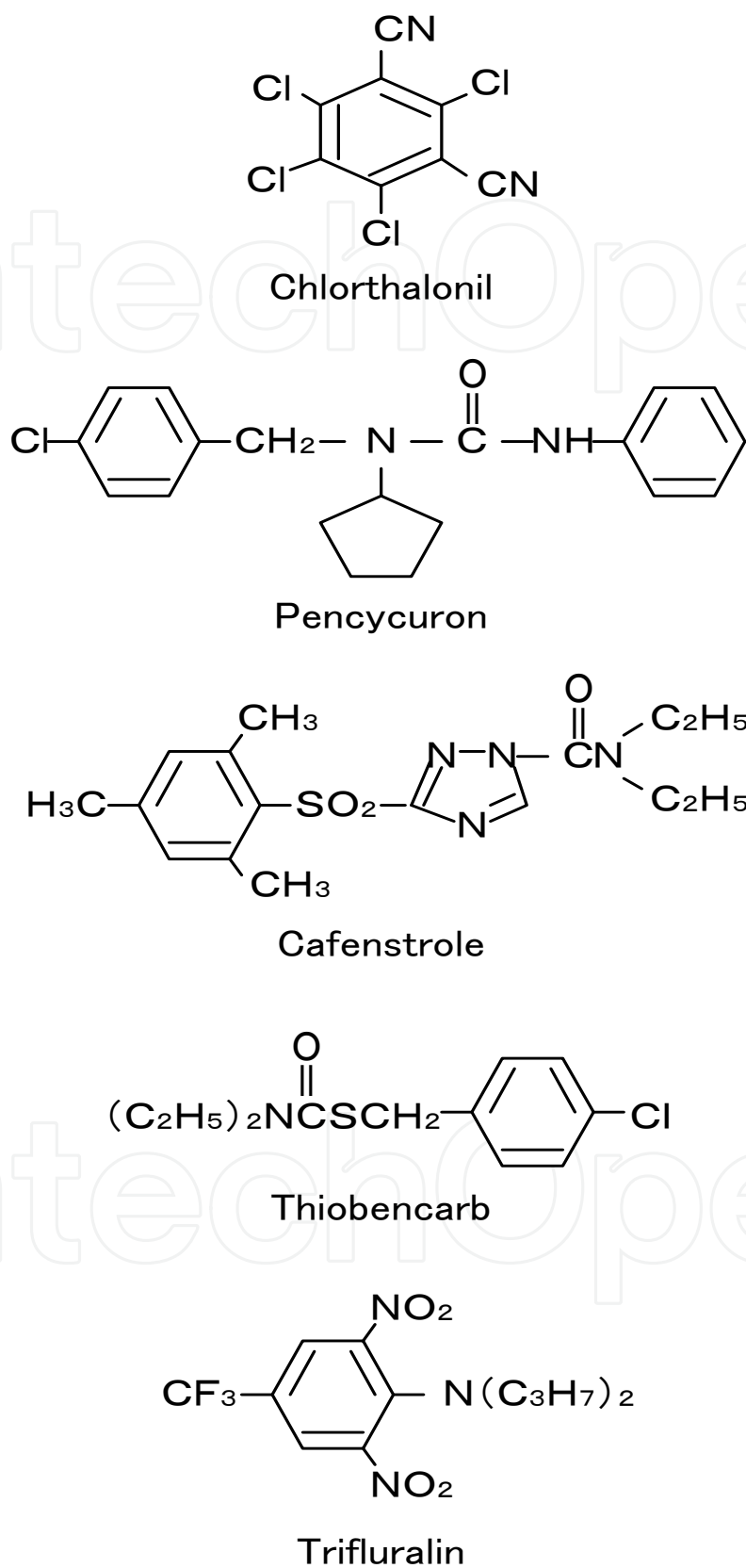


Fig. 1. Structural formulas of the objective pesticides

Item	Carrier		
	NK124	NKHO24	Silica gel
Particle size (mm)	2-4	2-4	1.7-4
Al <sub>2</sub> O <sub>3</sub> contents (%)	99.9	99.7	—
Micropore volume (cm <sup>3</sup> g <sup>-1</sup> )	0.77	0.58	—
Relative surface area (m <sup>2</sup> g <sup>-1</sup> )	130	160	—
Compacting strength (kg)	2	6	—
Supporting ratio (%)	20	17	25

Table 2. Properties of alumina and silica gel carriers



Fig. 2. Prepared alumina carrier-TiO<sub>2</sub> photocatalysts

2.3 Apparatus for the photodecomposition of the pesticides

The apparatus for the photodecomposition experiments of the pesticides and DNP was shown in Fig. 3. The photoreactor (Fig. 4) was made of stainless steel and equipped with a 6 W low pressure mercury lamp (a Matsushita Electric Ind. Co. GL6/Q) and a stabilizer (Nihon Fluorescence Electric Co.). Eighty five milliliters of each photocatalyst was packed in a thickness of about 5 mm. The UV illumination intensity on the surface of catalyst was 10 mW cm<sup>-2</sup>. Sample water was circulated with a roller pump (Furue Science Co.).

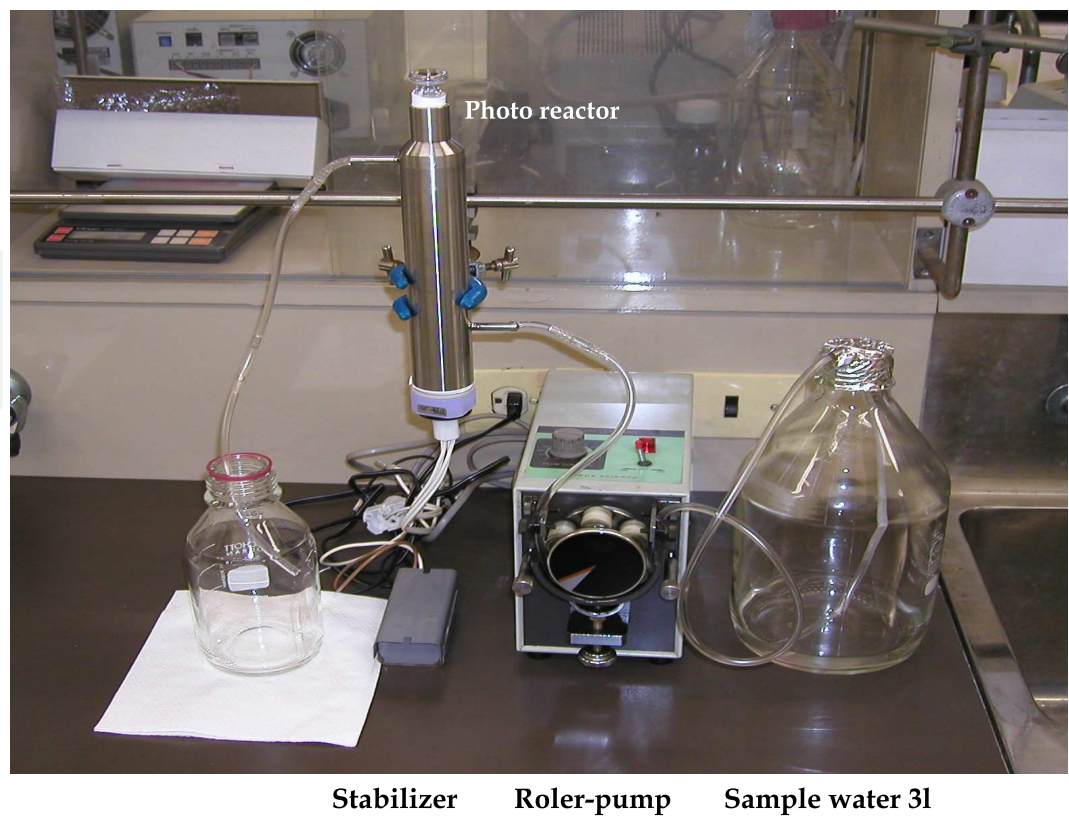


Fig. 3. Apparatus for the photodecomposition of the pesticides

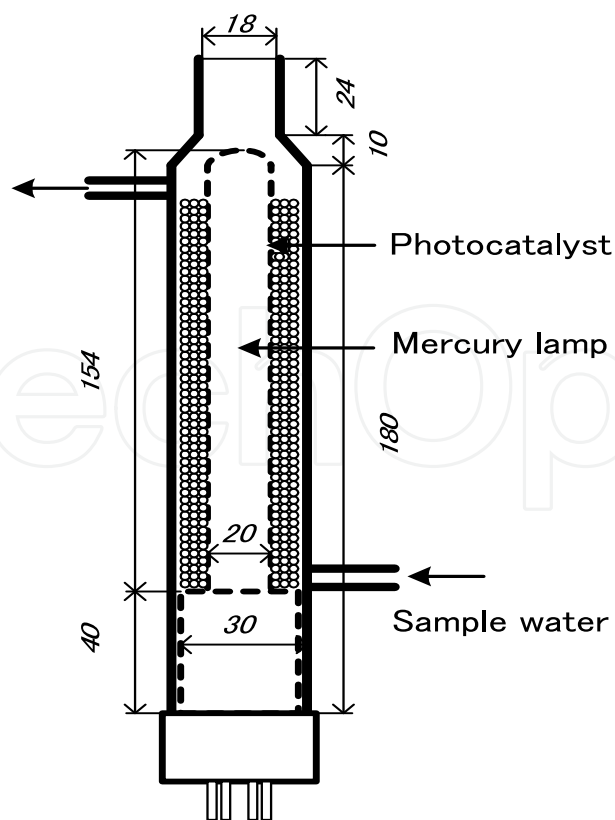


Fig. 4. Structure of photoreactor



2.4 Analyses of pesticides, DNP and other items

The quantification of the pesticides and DNP in UV irradiated solution was performed in the next procedure. About 2 g of NaCl was added in 40 ml of UV irradiated solution and each pesticide or DNP was extracted with 4 ml of dichloromethane. The dichloromethane layer was separated from aqueous layer, dehydrated with anhydrous Na<sub>2</sub>SO<sub>4</sub> and analyzed by the GC/MS method (Nakano et al., 2004; Yamaguchi et al., 1997). The GC/MS conditions were shown in Table 3. Each calibration curve showed good linearity in the quantification range. Their recoveries by the method were over 85%.  
pH, suspended solid matter (SS), BOD, KMnO<sub>4</sub> consumption, total nitrogen (T-N), total phosphorus (T-P) and electric conductivity (EC) were measured by the method of Japanese Industrial Standard K0102 (Japan Industrial Standards Committee, 1995).

Column	DB-5MS (5%Diphenyl 95%dimethyl polysiloxane) 0.25 mm x 30 m x 0.25 μm
Column temperature	60 °C (1 min) – 30 °C min <sup>-1</sup> – 130 °C – 5 °C min <sup>-1</sup> – 240 °C – 10 °C min <sup>-1</sup> – 300 °C (10 min)
Injector temperature	250 °C
Carrier gas	He 1.5 ml min <sup>-1</sup>
Transfer line temperature	260 °C
Mode	EI

Table 3. GC/MS conditions

2.5 The photodecomposition capability experiments of alumina carrier-TiO<sub>2</sub> photocatalysts and photodecomposition experiments of pesticides

Each alumina or silica gel carrier-TiO<sub>2</sub> photocatalyst was packed in the photoreactor. The water samples for DNP and pesticides experiments were prepared by adding 3 ml of each 1,000 mg l<sup>-1</sup> DNP or pesticide acetone solution in 3 l of purified water (for the photodecomposition capability experiment of photocatalyst) or the river water (Table 4) (for the photodecomposition experiment of pesticide). The water sample was vigorously shaken for 30 min using a separatory funnel and placed in 5 l glass bottle. The water sample was firstly circulated for 30 min at 1 min<sup>-1</sup> of flow rate by stirring and the system was allowed to reach equilibrium. Then the mercury lamp was switched on. The UV irradiated solution was periodically withdrawn during irradiation and DNP or each pesticide was quantified by the GC/MS method. The photodecomposition experiments of pesticides without a photocatalyst were also performed.

Item	Concentration
pH	7.6
SS (mg l <sup>-1</sup> )	6
BOD (mg l <sup>-1</sup> )	3.5
KMnO <sub>4</sub> consumption (mg l <sup>-1</sup> )	5.8
T-N (mg l <sup>-1</sup> )	1.52
T-P (mg l <sup>-1</sup> )	0.08
EC (μS cm <sup>-1</sup> )	264

Table 4. Quality of the river water used for this experiment

3. Results and discussion

3.1 Comparison of the photodecomposition capability of alumina carrier-TiO<sub>2</sub> photocatalysts

Figure 5 shows the photodecomposition rates of DNP using the alumina and silica gel carrier-TiO<sub>2</sub> photocatalysts. DNP was decreased exponentially with reaction time (t) and the rate of DNP disappearance was nearly represented by a first-order process. The values of pseudo-first-order rate constant ( $k$ :  $C=C_0e^{-kt}$ ) of NK124, NKHO24 and silica gel carrier-TiO<sub>2</sub> photocatalysts determined from the plot of data points ( $C/C_0$  vs. t) were 0.027, 0.016 and 0.030 min<sup>-1</sup>, respectively. The rate constant of NK124 carrier-TiO<sub>2</sub> photocatalyst was near that of silica gel-TiO<sub>2</sub> photocatalyst. The micropore volume of NK124 is larger than that of NKHO24 but its relative surface area is smaller than that of NKHO24. The supporting ratio of NK124 was higher than that of NKHO24. It was supposed that the difference of DNP photodecomposition rate was caused by the difference of supporting ratio. Then, the photodecomposition experiments of the pesticides were performed using a NK124 carrier-TiO<sub>2</sub> photocatalyst.

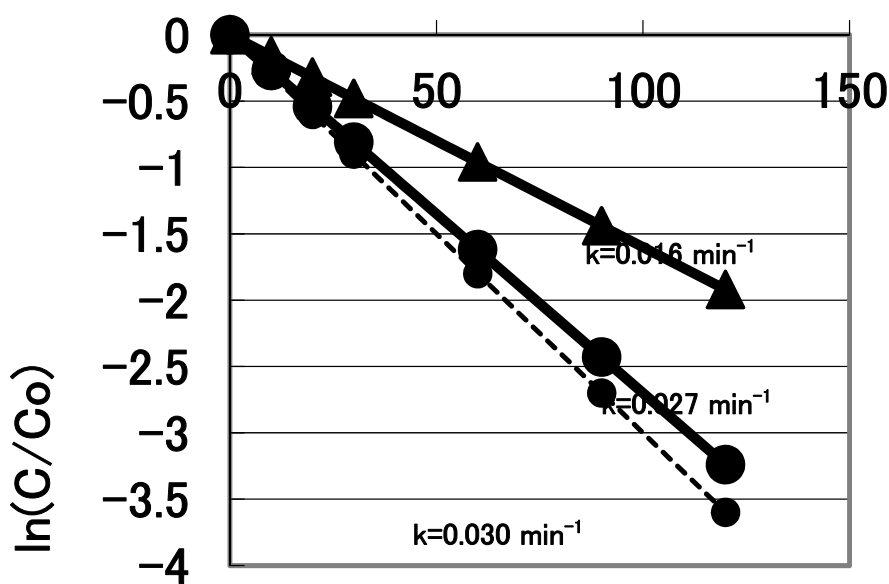


Fig. 5. Photodecomposition rates of DNP

3.2 Photodecomposition behaviors of pesticides

Figure 6-10 show the photodecomposition ratios of the pesticides. These pesticides were decomposed faster than DNP and the removal efficiencies after 3 min UV irradiation were 94% (Cafenstrole), 92% (Chlorthalonil), 75% (Thiobencarb), 67% (Pencycuron), 58% (Trifluralin) and 8% (DNP). After 30 min UV irradiation, the removal efficiencies of Cafenstrole and Chlorthalonil, and Thiobencarb, Pencycuron and Trifluralin, were 98 and 94%, respectively. The UV illumination intensity in the experiments was so strong that the same removal efficiencies as with the photocatalyst were obtained without the



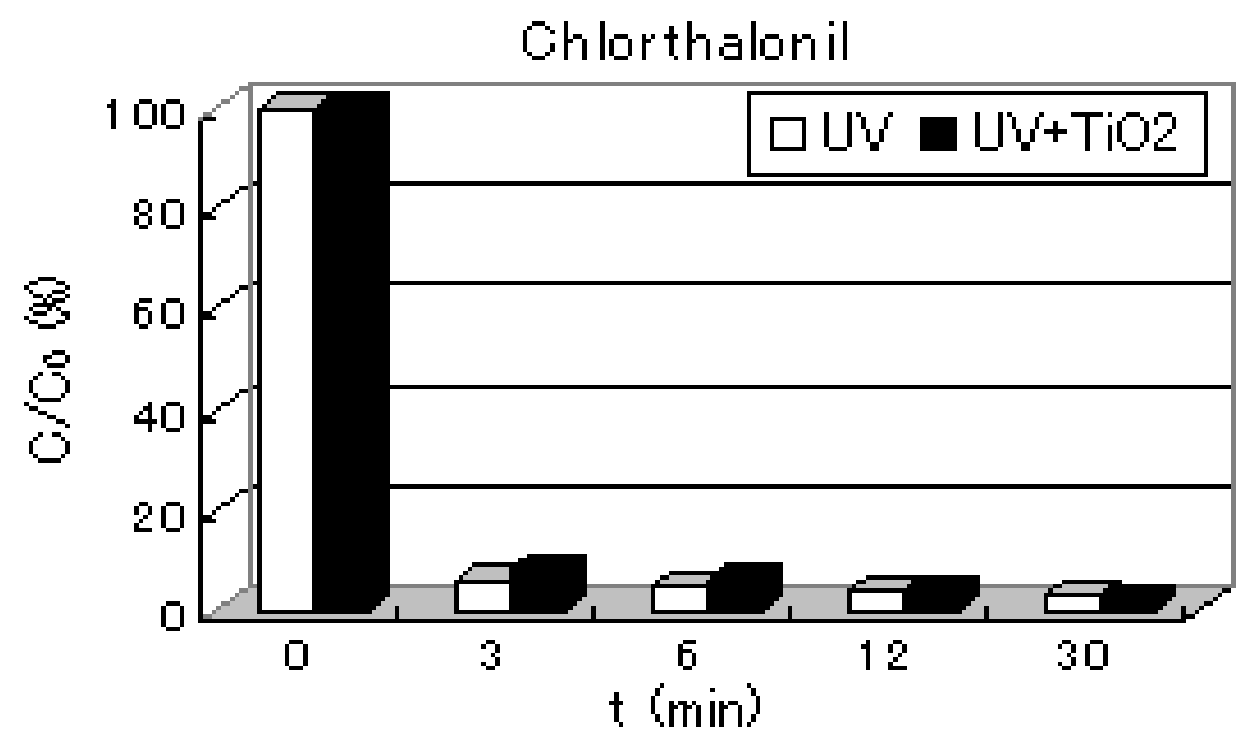


Fig. 6. Photodecomposition of Chlorthalonil

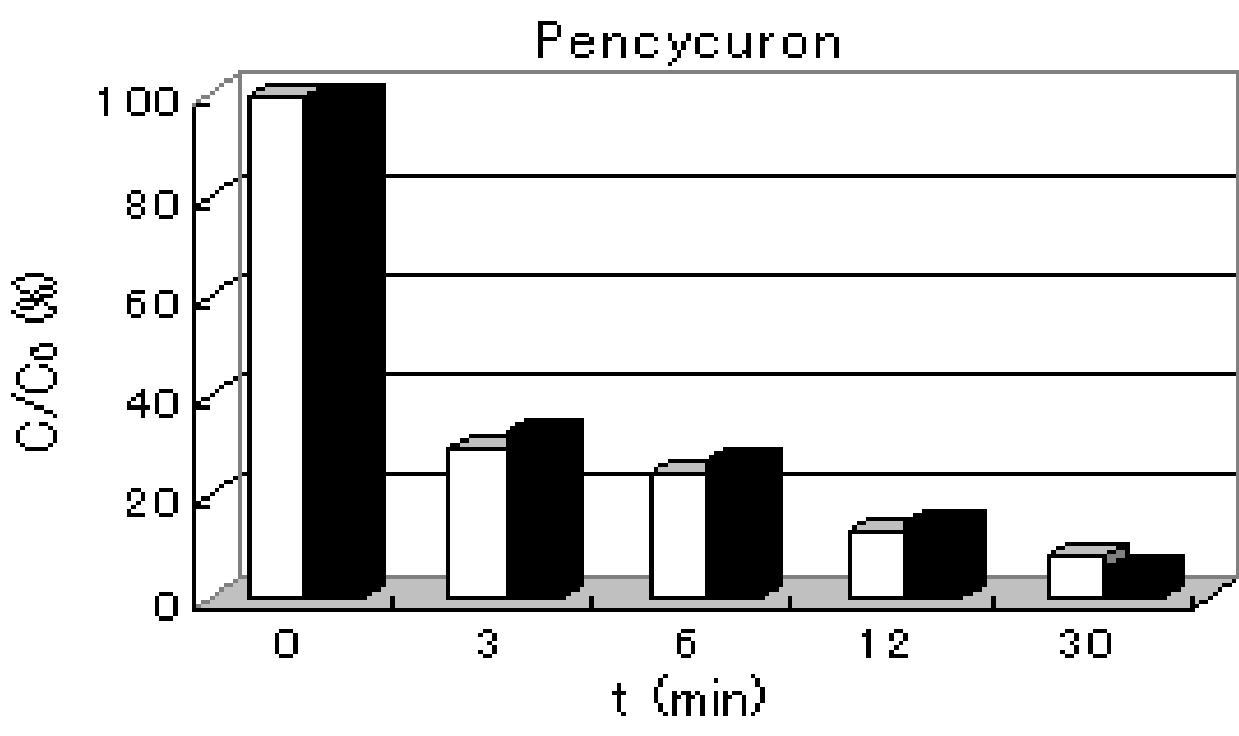


Fig. 7. Photodecomposition of Pencycuron

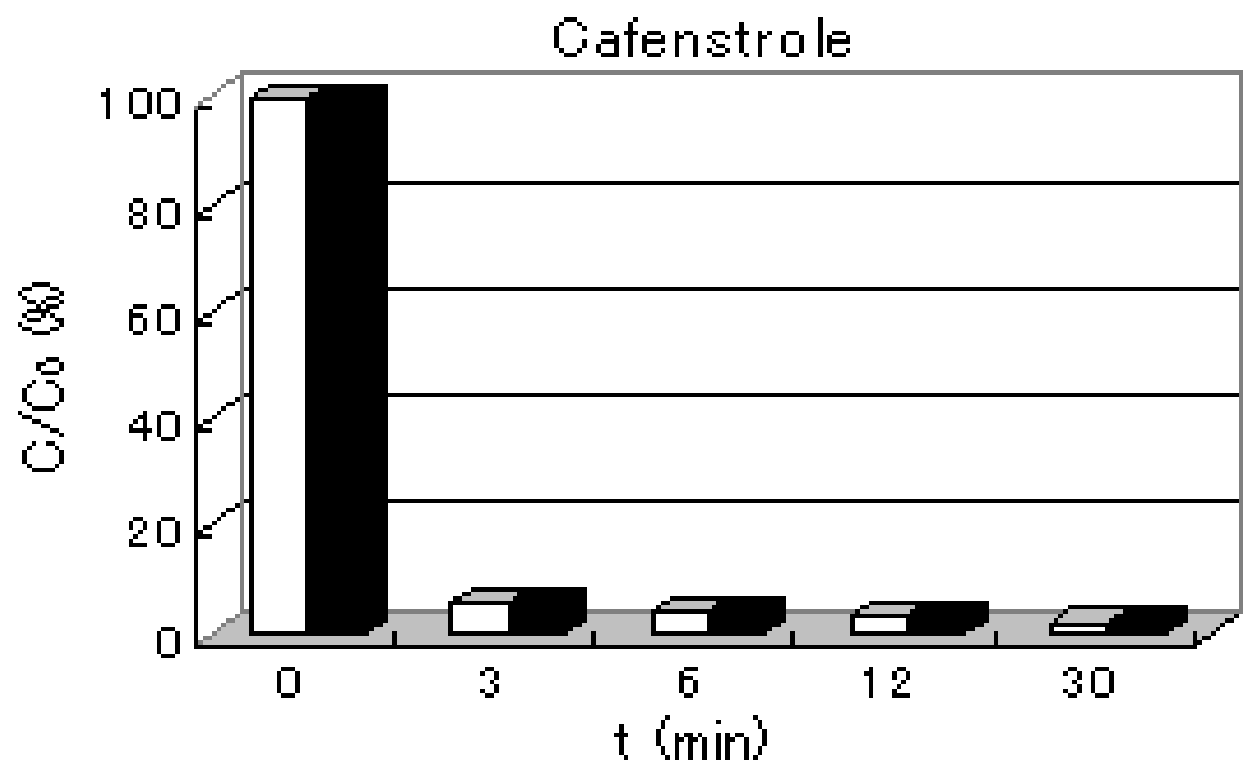


Fig. 8. Photodecomposition of Cafenstrole

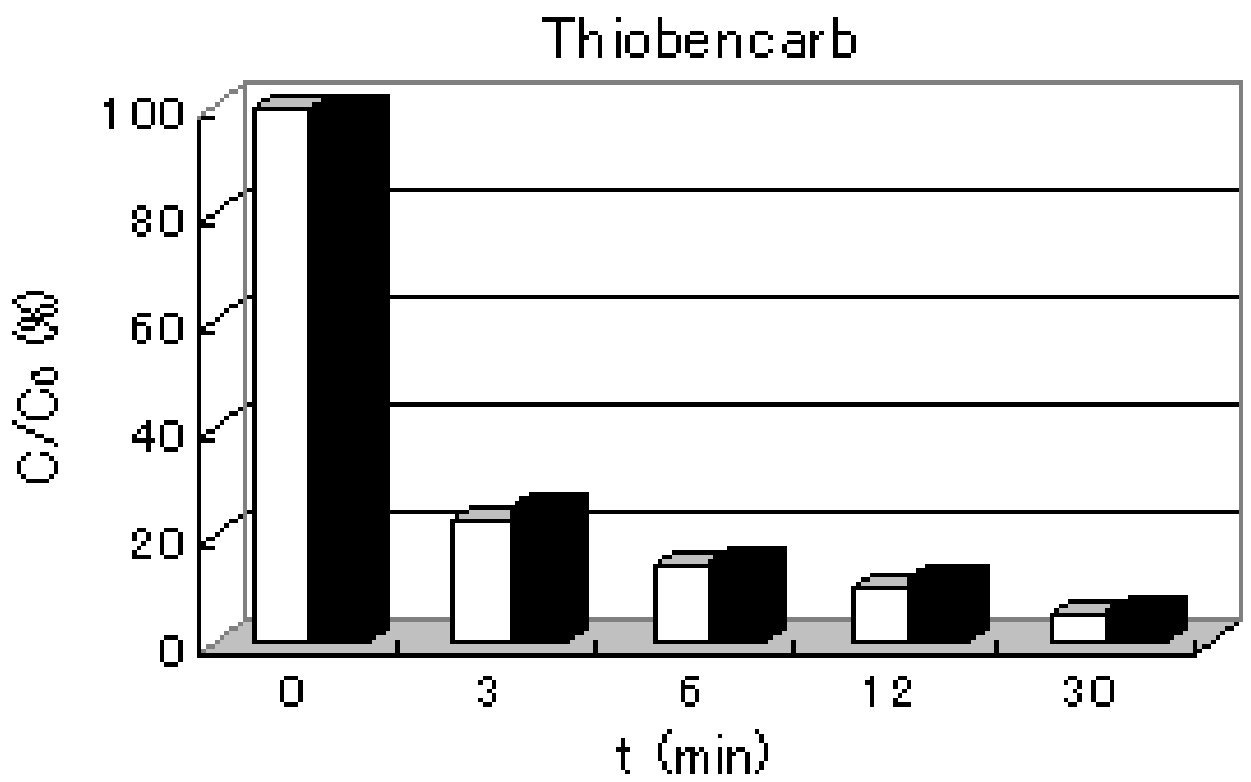


Fig. 9. Photodecomposition of Thiobencarb

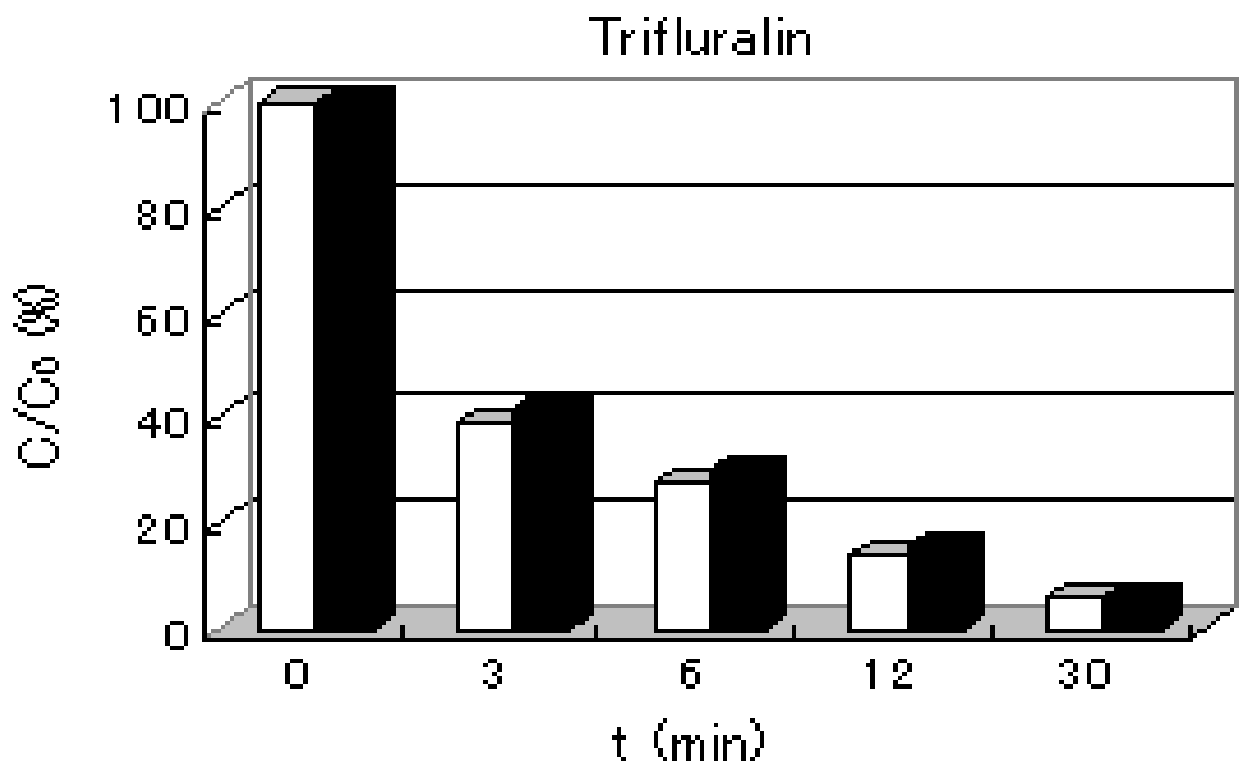


Fig. 10. Photodecomposition of Trifluralin

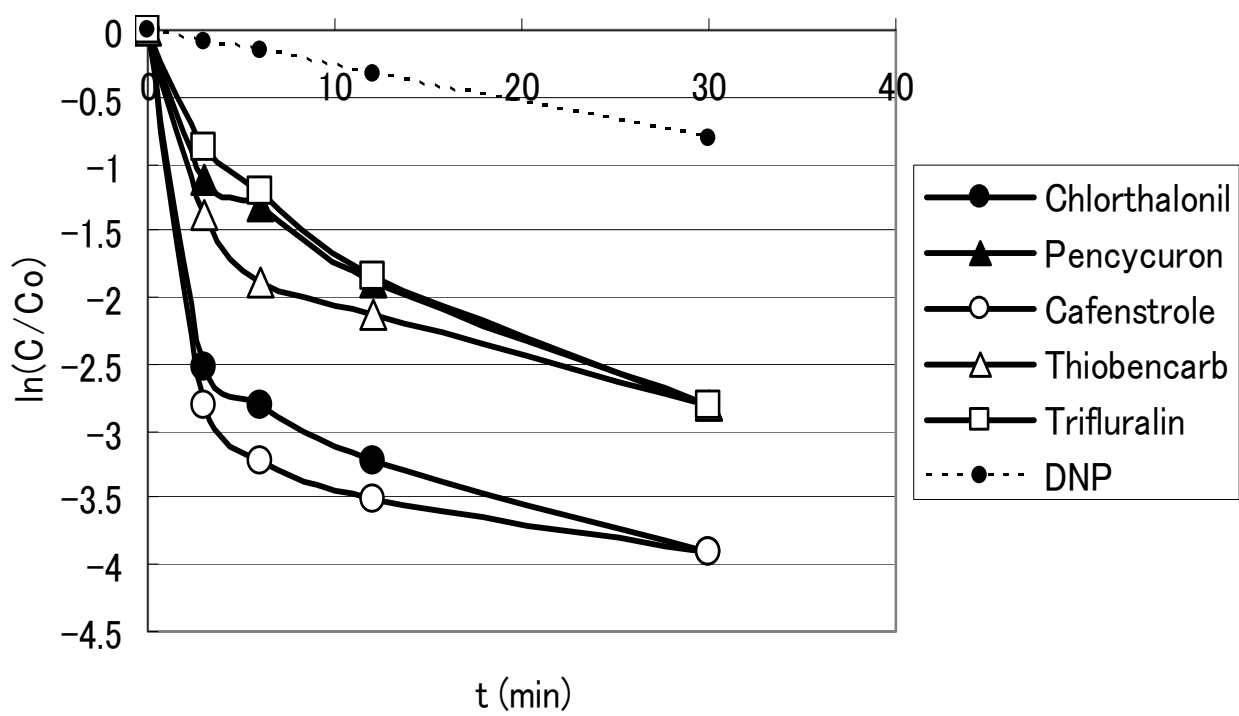


Fig. 11. Relationship between ln(C/C<sub>0</sub>) and t photocatalyst.

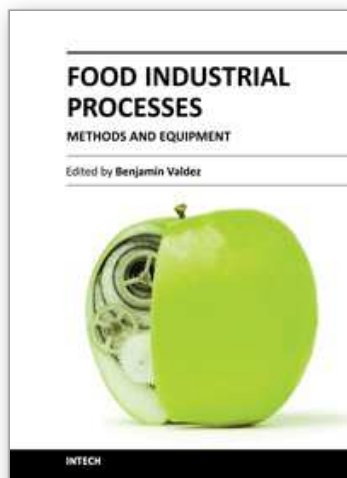
Figure 11 shows the relationship between ln(C/C<sub>0</sub>) and t. As these pesticides were decomposed immediately, the linear relationship between ln(C/C<sub>0</sub>) and t could not be obtained.

Every pesticide has a biologically or chemically changeable structure in molecule. For example, a N-CO-N bond (Pencycuron and Cafenstrole) and a N-CO-S bond (Thiobencarb) are easily hydrolyzed. Cyano group (Chlorthalonil) is easily oxidized. Carbon-Cl bond, benzene ring and alkyl group are biologically hydroxylized (Haque & Freed, 1975; Hutson & Roberts, 1981; Matsumura & Murti, 1982; Uesugi et al., 1997; Yamamoto & Fukami, 1979). On the other hand, the scissions of a C-Cl bond, a C-F bond, a C-NO<sub>2</sub> bond, a C-NR<sub>2</sub> bond and a N-N bond, especially a C-Cl bond and a N-N bond, are easily occurred photochemically (Ishikawa et al., 1989, 1992; Ishikawa & Suetomi, 1993; Ishikawa, 1996; Tanizaki et al., 2005). Moreover, the photochemical scission of a C-Cl bond is faster than the photohydrolyses of organic phosphate esters (Ishikawa et al., 1992). The differences of the photodecomposition rates in these parts would have caused the differences of the photodecomposition rate or the removal efficiency after 30 min UV irradiation of each pesticide. As the photodecomposition products could not be detected by the GC/MS analysis, it was considered that these pesticides converted into the high polar compounds.

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