



Photodegradation of environmental pollutants using perylene adsorbed on silica gel as a visible-light photocatalyst



Hiroshi Moriwaki^{a,b,*}, Yasutaka Akaishi^a, Michiya Akamine^a, Hisanao Usami^c

^a Shinshu University, Faculty of Textile Science and Technology, Division of Applied Biology, 3-15-1, Tokida, Ueda 386-8567, Japan

^b Shinshu University, Division of Instrumental Analysis (Ueda branch), Research Center for Human and Environmental Sciences, 3-15-1, Tokida, Ueda 386-8567, Japan

^c Shinshu University, Faculty of Textile Science and Technology, Division of Chemistry and Materials, 3-15-1, Tokida, Ueda 386-8567, Japan

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ABSTRACT

Decomposition of several environmental pollutants in water using perylene adsorbed on silica gel (Pe/SiO₂ powder) as a photocatalyst under the visible-light irradiation have been studied. The Pe/SiO₂ powder was prepared by mixing a toluene solution of the perylene with silica gel followed by evaporating the toluene. Irradiation by visible light (>420 nm) of the methyl orange aqueous solution with the Pe/SiO₂ powder in the presence of ascorbic acid resulted in the decomposition of the methyl orange. The rate of decrease of the methyl orange reached 99% by visible light irradiation for 20 min. The reaction also occurred by the irradiation of sunlight. In addition, the irradiation of visible light also led to the decomposition of imidacloprid using Pe/SiO₂ in the presence of ascorbic acid. Furthermore, irradiation by visible light (>420 nm) of a pentachlorophenol aqueous solution with the Pe/SiO₂ powder resulted in the decomposition of the pentachlorophenol. The possible mechanisms of these reactions are discussed.

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1. Introduction

Applications of solar power to environmental water clean-up technology have received much attention because the drain of fossil energy resources is a concern. Since the 1970s, various photocatalysts have been developed, and applied to environmental purification. Titanium oxide (TiO₂), in particular, has been widely used as a photocatalyst to decompose many kinds of organic pollutants [1–6]. However, TiO₂ is not excited by visible light irradiation, and ultraviolet radiation is required to use TiO₂ as a photocatalyst. The ultraviolet portion in the solar spectrum is very small (~6%), while visible light occupies 52% of the spectrum [7]. Therefore, the development of materials, which shows a catalytic activity under visible light, are expected. Recently, the modifications of TiO₂ for the utilization of visible light, such as doping, dye sensitization, and coupling semiconductors, have been extensively studied [8].

In a previous study, we reported that the irradiation of visible light led to the decomposition of methyl orange using C₆₀ fullerene adsorbed on silica gel (C₆₀/SiO₂) as a photocatalyst in the presence

of ascorbic acid [9]. Irradiation by visible light or sunlight of the methyl orange aqueous solution (10 mL, 25 μM) for 30 min in the presence of C₆₀/SiO₂ (20 mg) and ascorbic acid (0.5 mM) resulted in the decomposition of the methyl orange of over 90%. Furthermore, continuous photodecomposition of the methyl orange using the C₆₀/SiO₂ packed column was achieved.

The C₆₀/SiO₂ can be used as a photocatalyst for the degradation of azo dyes, such as methyl orange and methyl red. However, the decomposition of other chemicals using the C₆₀/SiO₂ as a photocatalyst could not be observed. The results would depend on the low reduction ability of the C₆₀/SiO₂. The excited C₆₀/SiO₂ accepts an electron from ascorbic acid during of the photoreaction, and forms a radical anion of C₆₀. The electron transfer from the radical anion of C₆₀ to the compounds other than the azo dyes would not efficiently occur because of the low reduction potential of the C₆₀ fullerene (-0.42 V vs. SCE in benzonitrile) [10]. In addition, C₆₀ fullerene is very expensive, which makes it difficult to use C₆₀ for environmental clean-up technology.

In this report, the photoreactions of environmental pollutants using perylene adsorbed on silica gel (Pe/SiO₂) as a visible light active catalyst are described. The reductive potential of perylene (-2.0V vs. SCE in CH₃CN) is more negative than that of C₆₀ [11]. Therefore, it is expected that the non-metal material could be

* Corresponding author at: Shinshu University, Faculty of Textile Science and Technology, Division of Applied Biology, 3-15-1, Tokida, Ueda 386-8567, Japan.
E-mail address: moriwaki@shinshu-u.ac.jp (H. Moriwaki).

applied to the decomposition of various environmental organic pollutants. SiO₂ was used as a support material in order to disperse perylene in an aqueous solution.

Perylene has an absorption at visible light region. The carcinogenicity of perylene is much lower than those of the other polycyclic aromatic hydrocarbons, such as benzo[*a*]pyrene and benzo[*ghi*]perylene [12]. Furthermore, the water solubility of perylene is very low.

Environmental organic pollutants, methyl orange, imidacloprid, and the pentachlorophenol sodium salt, were selected as substrates for the photoreaction using Pe/SiO₂ as the photocatalyst. Methyl orange is an anionic azo dye, and often used as a model compound for photoreactions. This dye has a mutagenic activity [13]. Imidacloprid is a neonicotinide pesticide, which is possibly the be causative substance for the bee colony collapse disorder [14]. Pentachlorophenol was used as a pesticide, but its toxicity, such as its harmful effects on the liver, kidneys, and nervous system, is so high that the preparation and use of this compound have been restricted in many countries [15]. Pentachlorophenol and its salts and esters were recently listed as new POPs (persistent organic pollutants) under the Stockholm Convention in 2015 [16]. These pollutants are highly-polar compounds and water soluble, and it has been a concern that they widely diffuse in the water environment and exert harmful effects on living creatures [17].

2. Experimental

2.1. Materials and chemicals

Perylene, methyl orange, methyl red, imidacloprid, pentachlorophenol sodium salt, ascorbic acid, acetonitrile (HPLC grade), methanol (HPLC grade), chloranil, 2-propanol, acetic acid, ammonium acetate, toluene, triethylamine, chloranil, sodium hydroxide and SiO₂ for column chromatography (particle diameter: 20–40 μm) were obtained from Wako Pure Chemical Industries (Osaka, Japan). All reagents were used without further purification.

Pure water was prepared by an automatic water distillation apparatus (MQ academic A10, Millipore, Billerica, MA, USA). The synthesis of 2,5,6-trichloro-3-hydroxy-1,4-benzoquinone was carried out by a procedure reported in Reference [18].

2.2. Preparation of Pe/SiO₂

The preparation method of Pe/SiO₂ was similar to that of C₆₀/SiO₂ described in our previous report [9]. The SiO₂ powder (1.0 g) was added to the perylene toluene solution (20 mL, 1000 μg mL⁻¹), then the toluene was removed by a rotary evaporator. The obtained pale yellow powder was freeze-dried. The powder was next washed with distilled water in order to remove the perylene, which is not tightly adsorbed on the silica gel. The Pe/SiO₂ powder was mixed with distilled water (40 mL) for 30 min by a stirrer bar followed by filtration and drying.

The quantity of perylene adsorbed on the Pe/SiO₂ powder was determined. The powder (20 mg) was initially extracted by acetonitrile (10 mL). The concentration of perylene in the acetonitrile-extracted solution was determined by HPLC. A liquid chromatography system consisting of a Shimadzu (Kyoto, Japan) LC-20AD constant volume pump and UV absorbance detector (SPD-20A UV-vis, Shimadzu, 254 nm) was used. An L-column ODS (Chemicals Evaluation and Research Institute, Tokyo, Japan: 5 μm particle size, 2.1 mm × 150 mm i.d.) was used for the LC separation of the perylene. The HPLC separation was carried out at 40 °C. The flow rate was 0.20 mL min⁻¹, and the injection volume was 10 μL. As a result, 3.5 mg of perylene was adsorbed onto 1.0 g of the SiO₂ powder. When the powder (50 mg) was stirred in distilled water (10 mL)

for 1 h, there was no perylene separated from the powder onto the liquid. The filtrate of the solution was extracted by toluene, and the concentration of perylene dissolved in the aqueous solution was determined. The perylene concentration was 0.042 mg L⁻¹. This result indicated that the dissolution of perylene from Pe/SiO₂ occurs by mixing in aqueous solution. However, the desorption (in percent) of perylene from Pe/SiO₂ was below 0.2% of the adsorbed perylene on the powder. The Pe/SiO₂ powder was characterized by FT-IR (FT/IR-6700FV, JASCO, Tokyo, Japan). The material was kept in the dark at room temperature, and used within a few weeks of its production. The Pe/SiO₂ powder was stored under a nitrogen atmosphere.

2.3. Photoreactions of environmental pollutants using Pe/SiO₂

The general procedure of the photoreactions of environmental pollutants using Pe/SiO₂ is represented by the reaction of methyl orange. The irradiation of a methyl orange aqueous solution (50 μM, 10 mL) with the Pe/SiO₂ powder (50 mg) in the presence of ascorbic acid (1.0 mM) was carried out using a xenon lamp (300 W cm⁻², RSX-500 and LHX-500, Koken Kogyo, Saitama, Japan) through a filter (>420 nm, L42, Hoya, Tokyo, Japan). The pH value of the solution was 3.5–3.7. The Pe/SiO₂ powder was dispersed in the reaction liquid by a stirrer bar during the irradiation. The temperature of the reaction liquid was maintained at 20 °C by a constant-temperature bath.

The reuse of the Pe/SiO₂ powder was studied. The photodecomposition of methyl orange using the same Pe/SiO₂ powder was repeated. The reaction liquid after the photoreaction was centrifuged (3000 rpm, 3 min), and the supernatant was removed from the tube. The residue was mixed with the methyl orange aqueous solution (25 μM, 10 mL) containing ascorbic acid (1 mM), and irradiated again. The UV spectrum of the obtained supernatant was measured by a UV absorption spectrometer (V-630, JASCO Corporation, Tokyo, Japan). The methyl orange concentration was calculated by the absorbance at 500 nm. After filtration through filter paper (No. 5A, Advantec, Tokyo, Japan), the obtained solution was analyzed by electrospray ionization/mass spectrometry (ESI/MS) in both the positive and negative ion modes for the detection and identification of the products by the photoreactions and liquid chromatography (LC)/MS for their determination. The photoreactions for methyl orange and imidacloprid by sunlight were studied (Ueda City, Nagano, Japan). The solar radiation was monitored for 5 min by a photometer (LM-230, As One, Osaka, Japan), and the solar radiation in this study was approximately 200 W m⁻².

2.4. Photoreactions of methyl orange by the continuous flow system

The Pe/SiO₂ column was prepared by packing 700 mg of Pe/SiO₂ powder into a Pasteur pipette (7 mm inner diameter) stuffed with cotton. The length of the column was 5.5 cm. The methyl orange (25 μM) aqueous solution containing ascorbic acid (2.0 mM) was pumped through the Pe/SiO₂ column by a microtube pump (EYELA, Tokyo, Japan) at 0.40 mL min⁻¹. The solution was held in the column for 180 s. The column was irradiated by a xenon lamp or sunlight. Fractions of the solution through the column were sampled and analyzed by UV absorption, ESI/MS and LC/MS.

2.5. Analysis of the degradation of pollutants by the photoreactions

The obtained sample solutions were filtered using a cellulose acetate filter (pore diameter: 0.45 μm), and analyzed by ESI/MS

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