Available online at www.sciencedirect.com
ScienceDirect
Journal of Hazardous Materials 153 (2008) 551–556
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Decolorization of methylene blue in aqueous suspensions of titanium peroxide

Chiaki Ogino[a], Mahmoud Farshbaf Dadjour[b], Yasuo Iida[c], Nobuaki Shimizu[b,*]

[a] *Division of Material Engineering, Graduate School of Natural Science and Technology, Kanazawa University, Kanazawa 920-1192, Japan*
[b] *Division of Biological Measurement and Applications, Institute of Nature and Environmental Technology, Kanazawa University, Kanazawa 920-1192, Japan*
[c] *National Institute of Advanced Industrial Science and Technology (AIST), Nagoya 463-8560, Japan*

Received 14 December 2006; received in revised form 7 June 2007; accepted 30 August 2007
Available online 2 September 2007

Abstract

The pretreatment of TiO_2-photocatalysts in solutions of H_2O_2 was studied by examining the decolorization of methylene blue in the dark. Incubation of TiO_2 particles in H_2O_2 solutions increased the oxidizing capacity of TiO_2. Methylene blue (0.3 mM) was degraded in the presence of pretreated TiO_2, and a decolorizing ratio of 47% was obtained after a 48-h incubation period in the presence of 5.0 g/L pretreated TiO_2. Titanium peroxide as a stable oxidant, which can be synthesized with the reaction of titanium sulfate and H_2O_2, was studied in the decolorizing process of methylene blue. Concentrations of methylene blue were significantly reduced in the presence of titanium peroxide, and a greater extent of decolorization was obtained with larger amounts of titanium peroxide. A 63% decrease in methylene blue concentration was achieved in 5 h incubation in the presence of 4.0 g/L titanium peroxide. H_2O_2 accelerated the decolorizing process in the presence of titanium peroxide. The addition of 100 mM H_2O_2 to a methylene blue solution containing 2.0 g/L titanium peroxide increased the decolorizing ratio to 85% after 5 h incubation. The addition of a hydroxyl radical scavenger, dimethyl sulfoxide, significantly decreased the decolorizing ratio, indicating the role of hydroxyl radicals in the oxidation process.

Keywords: Titanium peroxide; Titanium dioxide (TiO_2); Hydrogen peroxide; Methylene blue; Decolorization; Hydroxyl radical

1. Introduction

Photocatalysts have been studied extensively as excellent materials for the elimination of hazardous organic compounds in contaminated air or water [1–4]. Titanium dioxide (TiO_2) is undoubtedly the best-studied inorganic photocatalyst, and the degradation of a number of different chemicals by TiO_2 under UV irradiation has been reported in the literature [5–7]. The application of TiO_2 photocatalysts in ultrasonic systems has also been reported to enhance chemical reactions [8–11]. It is known that as a synergistic effect, the addition of TiO_2 particles, together with the oxidative power of the positive holes produced under UV irradiation, can enhance sonochemical reactions [12]. TiO_2 was found to improve the yield of sonochemical reactions under appropriate conditions, not only in the presence but also in the absence of UV irradiation. However, the mode of action that TiO_2 exerts in this system has not been clarified.

Different mechanisms have been studied and proposed to explain the enhancing effect of photocatalysts in ultrasonic systems. It has been hypothesized that this enhancement may be caused by the induction of cavitation nuclei in irradiating solutions, similar to the enhancements obtained in the presence of inert particles such as Al_2O_3 [13,14]. However, the oxidizing power obtained in the presence of TiO_2 was higher than that of materials like Al_2O_3 [11,15]. While it has been reported that the sonoluminescence caused by cavitation may induce the excitation of TiO_2 in an ultrasonic system [16], Tuziuti et al. [17] have introduced another mechanism in this regard, namely, the appearance of titanium peroxide on the surface of TiO_2 during ultrasonic irradiation. It has been recognized that the exposure of air-saturated water to ultrasonic irradiation leads to the formation of hydrogen peroxide (H_2O_2) [18,19]. Further, the formation of a yellowish substance on the surface of TiO_2 particles occurs in H_2O_2 solutions, and the yellow coloration of TiO_2 after

* Corresponding author. Tel.: +81 76 234 4807; fax: +81 76 234 4829.
E-mail address: nshimizu@t.kanazawa-u.ac.jp (N. Shimizu).

0304-3894/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2007.08.090

treatment with H_2O_2 is believed to arise from the presence of a surface titanium peroxide complex [20–22]. Accordingly, the interaction of H_2O_2 in the vicinity of the TiO_2 surface might result in the formation of a stable oxidizing agent, i.e., a titanium peroxide complex, suggesting a mechanism based on the formation of long-lived active species on the surface of TiO_2 by ultrasonic irradiation.

In the present study, pretreatment of a TiO_2 photocatalyst in a solution of H_2O_2 was investigated by examining the decolorization of methylene blue solution. Also, the decolorization of methylene blue in the presence of titanium peroxide was studied kinetically to confirm the high activity of this chemical substance in the color-removal process.

2. Experimental

2.1. Materials

TiO_2 (MT-150A, rutile) was obtained from Tayca Co. (Osaka, Japan) and was employed as the catalyst. The content of the rutile phase, the particle size and the specific surface area of the TiO_2 powder were 99.9%, 2.27 μm and 110 m^2/g, respectively. Methylene blue [3,7-bis(dimethylamino) phenothiazin-5-ium chloride], dimethyl sulfoxide [DMSO; $(CH_3)_2SO$] and H_2O_2 were obtained from Wako Pure Chemical Industries (Osaka, Japan). Oxo[5,10, 15, 20-tetra(4-pyridyl)-porphinato] titanium (IV) was obtained from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan) for the analysis of H_2O_2. All other chemicals used in this study were of guaranteed reagent grade and were used without further purification. Laboratory-grade water was prepared with a Milli-Q water purification system.

Titanium peroxide was prepared according to the procedures described in the literature [20,22]. Fifty milliliter of H_2O_2 (30%) was added to a solution of 10% titanium sulfate (150 mL) and stirred thoroughly. With the formation of titanium peroxide, a yellow solution was obtained, which was then neutralized (pH 7–8) with a solution of 10% NH_3 to precipitate the titanium peroxide particles. Precipitates were separated and dried in a desiccator containing concentrated sulfuric acid. The particle size, the specific surface area and the pore diameter of the titanium peroxide particles were 6.5 μm, 73.7 m^2/g and 40.4 Å, respectively.

2.2. Methods

A solution of 0.3 mM methylene blue was prepared and used in this study. The decolorization of methylene blue was first examined in the presence of pretreated TiO_2. TiO_2 powder (50 mg) was incubated in a 110-mM H_2O_2 solution (10 mL) in the dark for 24 h. The concentration of H_2O_2 was analyzed during the incubation period by a spectrophotometric method [23]. The suspension was then centrifuged at 8000 rpm for 10 min and the incubated TiO_2 was separated and washed three times with distilled water (10 mL each). After washing and drying, incubated TiO_2 (50 mg) was suspended in 0.3 mM methylene blue solution (10 mL). All solutions were incubated in the dark without agitation to avoid possible complicating effects of illumination or mixing. Samples were taken at designated times and analyzed according to the change in the concentration of methylene blue, which was measured with a spectrophotometer (U-3010, Hitachi, Tokyo, Japan) at 661 nm. The measured absorption was converted to a concentration using a standard calibration curve for methylene blue.

The decolorizing ratio was defined by the following formula:

$$\text{Decolorizing ratio}\,(\%) = \frac{(\text{ABS [Init]} - \text{ABS [Test]})}{\text{ABS [Init]}} \times 100$$

where ABS [Init] and ABS [Test] represent the absorbances of the methylene blue solution for the initial (without treatment) and test samples, respectively; thus, (ABS [Init] − ABS [Test]) indicates the net decrease of the absorbance.

3. Results and discussion

3.1. Pretreatment of TiO_2 by incubation in H_2O_2 solution

Pretreatment of the TiO_2 photocatalyst was carried out by incubation in a solution of H_2O_2. Fig. 1 shows the change in H_2O_2 concentration in the presence of TiO_2 during a 24-h incubation period. The H_2O_2 concentration gradually decreased with increasing incubation time and reached a steady value of about 60 mM after 6 h of incubation. A pale yellowish powder was obtained after 6 h of incubation in the presence of H_2O_2, and this color did not change after washing with distilled water. These results suggested the possibility that H_2O_2 was consumed in a chemical reaction with TiO_2 and that titanium peroxide could have formed on the surfaces of the TiO_2 particles. The formation of titanium peroxide reached its peak at 6 h incubation time under these experimental conditions. This suggestion was supported by the study of Ohno et al. [21] using X-ray photoelectron spectroscopy analysis, indicating the generation of titanium peroxide on the rutile TiO_2 surface after treatment with H_2O_2. After the treatment with H_2O_2, a new band appeared at 533 eV on the X-ray photoelectron spectrum, and this band was considered to

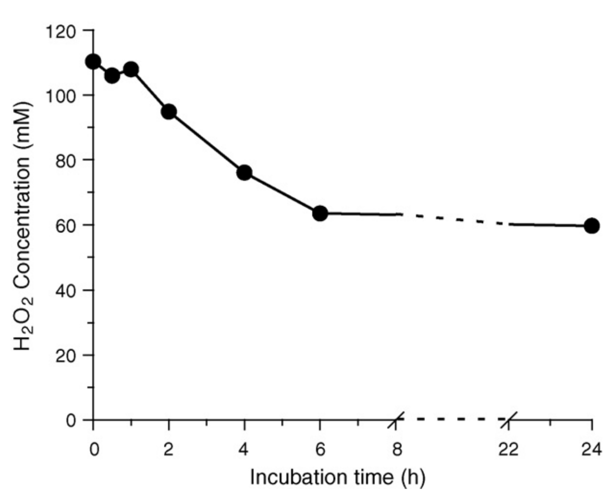

Fig. 1. Reduction of H_2O_2 in the presence of TiO_2 during incubation in the dark. TiO_2 powder (50 mg) was suspended in a 10-mL volume of H_2O_2 solution (concentration, 110 mM). Data are means of three replicate experiments.