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# Continuous-flow photoreactor packed with titanium dioxide immobilized on large silica gel beads to decompose oxalic acid in excess water

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## Abstract

A tubular continuous-flow photoreactor consisting of a pyrex glass tube 8 mm in diameter packed with titanium dioxide photocatalyst immobilized on 2 mm diameter silica gel beads was constructed to efficiently decompose water contaminants at high-flow rate. To fix titanium dioxide using sol-gel without destroying silica gel beads, the beads were exposed to ethanol vapor and then wetted with ethanol before being dipped into the TiO<sub>2</sub> precursor sol. Photoreactor performance was evaluated for how it decomposed aqueous oxalic acid solution as a model contaminant. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* Photocatalysis; Tubular photoreactor; Titanium dioxide; Silica gel bead; Decomposition; Oxalic acid

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## 1. Introduction

Photoreactors with immobilized TiO<sub>2</sub> photocatalysts have been designed to decompose contaminants in water without photocatalyst separation [1–9]. Of these, a tubular reactor packed with 30–40 mesh silica gel with attached fine TiO<sub>2</sub> powders (Aldrich, 99.9+%, anatase), prepared by mixing a concentrated TiO<sub>2</sub> slurry and calcining, seems superior [8]. Its high photo-efficiency may be due to the effect of platinum loading and also to the large surface area of TiO<sub>2</sub> photocatalysts per unit volume of the reactor, although TiO<sub>2</sub> particles immobilized on silica gel placed inside the reactor were scarcely excited due to the decreasing incident photon flux caused by silica gel scattering and adsorption and by TiO<sub>2</sub> particles themselves. The problem with this reactor is the high resistance to solution flow due to dense packing of small granular silica gel particles. This can be improved without great reduction of photo-efficiency by using larger silica gel beads, because all TiO<sub>2</sub> photocatalysts in the reactor will be excited due to incident photon flux passing through large gaps between silica gel beads and also penetrating through silica gel beads covered with a thin TiO<sub>2</sub> layer. We report the performance of a tubular photoreactor packed with TiO<sub>2</sub> immobilized on silica gel beads 2 mm in diameter to decompose oxalic acid as a model compound under UV-irradiation using fluorescent lamps.

## 2. Experimental

Silica gel beads with a mean diameter of 2.1 mm (Wako) were used to support TiO<sub>2</sub> photocatalysts. Titanium dioxide was deposited by dip coating and heating of a TiO<sub>2</sub> precursor sol prepared by adding 2.7 cm<sup>3</sup> of 2 M (M=mol dm<sup>-3</sup>) HCl into a mixture of 15 cm<sup>3</sup> titanium tetraisopropoxide and 100 cm<sup>3</sup> ethanol. Silica gel bead immersion without pre-treatment in the precursor sol solution destroys beads due to rapid solvent adsorption. To avoid this destruction, silica gel beads were made to absorb gaseous ethanol molecules before sol coating. That is, a 100 ml beaker containing 20 g of silica gel beads was placed in a 300 ml beaker containing ethanol, then this 300 ml beaker was covered with a watch glass and warmed at 80°C for 1 h. Silica gel beads were then washed with ethanol, immersed in the precursor sol solution for 90 min, filtered using suction, and dried at 100°C following drying at room temperature overnight. Silica gel beads were then heated in an electric furnace at a given temperature for 3 h to convert the precursor gel, formed by coated sol gelation with water vapor in air during filtration and drying, to TiO<sub>2</sub>. At this time, the temperature was increased at 10°C min<sup>-1</sup> and the resultant sample cooled naturally in the furnace. To increase the amount of fixed TiO<sub>2</sub>, the above process, starting from ethanol treatment, was repeated. The amount of fixed TiO<sub>2</sub> was determined colorimetrically using diantipyryl-methane after deposited TiO<sub>2</sub> was dissolved with hot

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sulfuric acid. The cross-sectional distribution of fixed TiO<sub>2</sub> on silica gel beads was observed by energy dispersive X-ray spectroscopy.

The best sample showing the optimum heat temperature for converting the precursor gel to TiO<sub>2</sub> and the optimum amount of fixed TiO<sub>2</sub> (the number of coatings) was determined as follows. That is, 2.5 g of TiO<sub>2</sub>-loaded silica gels prepared under different conditions was immersed in a stationary solution of 1 mM oxalic acid (50 cm<sup>3</sup>) in a 100 ml Erlenmeyer flask and the decreases in oxalic acid concentration during 90 min irradiation at 5.6 m W cm<sup>2</sup> were compared. The oxalic acid concentration was determined by liquid chromatography using a UV detector at a wave length of 200 nm.

The photoreactor was constructed as follows: to avoid the destruction of the beads, TiO<sub>2</sub>-loaded silica gel beads prepared under optimum conditions were exposed to ethanol vapor once more and wetted with ethanol as in precursor sol coating, then added up to 45 cm in pyrex glass tubes (8 mm i.d., 10 mm o.d., 47 cm long) filled with distilled water. Both ends of the packed bed were fixed with glass fibers. The porosity of the packed bed, determined by the volume of overflowing water, was 50%. The silica gel beads, which at this point had ethanol molecules adsorbed on the outer surface and penetrating into pores, were washed with flowing water, and irradiated with a UV light source, described below, to decompose residual ethanol molecules photocatalytically.

As a light source, two sets of 10, 20 W fluorescent black-light tubes in flat arrays were placed 20 cm apart from tube center to tube center. Each set was constructed from 10 fluorescent tubes placed vertically 5 cm apart from tube center to tube center on an aluminum plate with brackets. Photoreactors were placed vertically between light sources (Fig. 1). The light intensity was reduced by inserting an insect net between the reactor and fluorescent tubes. Light intensity was measured with a UV-intensity meter (Minolta

UM-36, measurements range: 310–400 nm). Black-light lamps and the aluminum plate placed at the opposite side reflected 20% of the photon flux, so that the light intensity below included reflected photons. The number of photons received by the reactor was calculated from the UV-intensity assuming that the black-light lamp is a monochromatic light of 360 nm, the wave length of the maximum radiation energy for this type of lamp.

The reactant solution (1 mM oxalic acid) was pumped through the irradiated reactors, which were serially connected with silicone and glass tubes from bottom to top, and the concentrations at the inlet and outlet were determined by liquid chromatography using a UV detector in order to monitor the reactor performance.

### 3. Results and discussion

#### 3.1. Optimum preparation conditions for fixing TiO<sub>2</sub> on silica gel beads

Oxalic acid was photocatalytically decomposed on several TiO<sub>2</sub>-loaded silica gel samples prepared at different temperatures and whose precursor sol was coated once. The sample prepared at 500°C shows the highest photocatalytic activity (Fig. 2). The X-ray diffraction patterns of fixed TiO<sub>2</sub> was difficult to measure because the amount of TiO<sub>2</sub> on beads was very small, below 0.1 wt%. So the TiO<sub>2</sub> crystal structure is unknown. However, the TiO<sub>2</sub> structure showing the highest activity may be anatase, because this sample was treated at 500°C and the anatase phase is known to show higher activity than the rutile phase, which forms at temperatures above 600°C.

The optimum number of sol coatings was determined by comparing the decomposition percentage of oxalic acid on different samples during 90 min of irradiation (Fig. 3). As coating is repeated, the amount of fixed TiO<sub>2</sub> increases

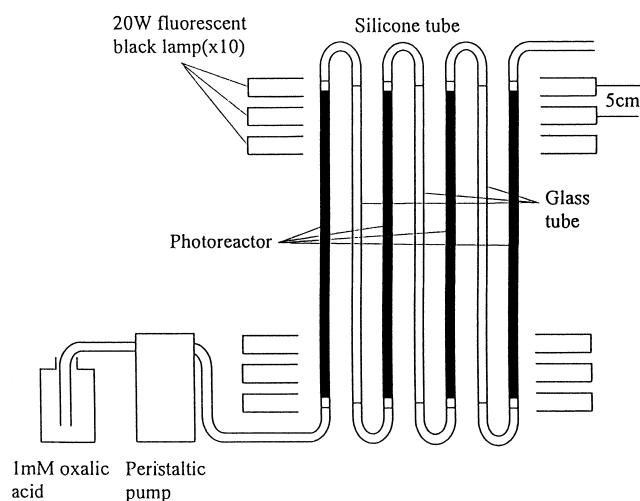


Fig. 1. Experimental apparatus. For details, see text.

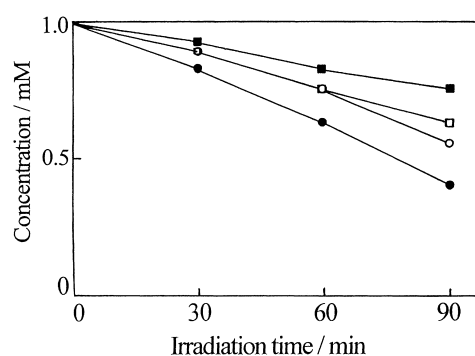


Fig. 2. Photocatalytic decomposition of 1 mM oxalic acid on TiO<sub>2</sub>-loaded silica gel beads as a function for the catalyst preparation temperature. Experiments were conducted using a system in which 2.5 g of the sample was put into a 100 ml Erlenmeyer flask containing 50 cm<sup>3</sup> of reactant solution. Preparation temperature of samples: (○) 400°C; (●) 500°C; (□) 600°C; (■) 700°C.

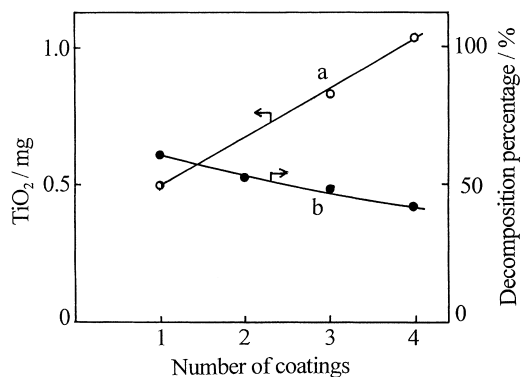


Fig. 3. Relation between (a) number of sol coatings and amount of TiO<sub>2</sub> fixed on 1 g of silica gel beads and (b) oxalic acid decomposition on resultant photocatalysts prepared at 500°C. Experiments were conducted as explained in Fig. 2.

monotonically, whereas the photocatalytic activity of samples decreases. The optimum number of sol coatings was one.

Silica gel beads used as a support have a very large specific surface area of 360 m<sup>2</sup> g<sup>-1</sup> before sol coating, determined by BET method using Monosorb MS-16 (Quantachrome). Energy-dispersive X-ray spectroscopic observation of the cross-section of silica gel beads with fixed TiO<sub>2</sub> showed, however, that TiO<sub>2</sub> deposited only on the surface of beads. The precursor sol does not penetrate micropores because ethanol molecules already occupy these and the precursor sol gels at the bead surface through reaction with water vapor in the air during filtration and drying.

In one coating, TiO<sub>2</sub> was deposited like a film (Fig. 4). Upon repeated coatings, depositing TiO<sub>2</sub> appears as small rectangular pieces as if the film had cracked (Fig. 4(b)). Decreasing activity with repeated coating (Fig. 3) may be due to the scattering of incident light and the decrease in the light fraction arriving at the TiO<sub>2</sub> layer fixed on the back of the silica gel bead by increasing the thickness of TiO<sub>2</sub>.

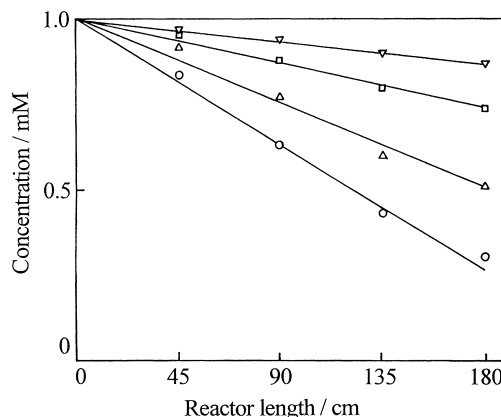


Fig. 5. Oxalic acid decomposition with reactor length at several flow rate at 9 mW cm<sup>-2</sup> (irradiation from one side): (○) 2.5 cm<sup>3</sup> min<sup>-1</sup>; (Δ) 4 cm<sup>3</sup> min<sup>-1</sup>; (□) 8.3 cm<sup>3</sup> min<sup>-1</sup>; (∇) 15 cm<sup>3</sup> min<sup>-1</sup>.

Silica gel beads coated only with the TiO<sub>2</sub> precursor sol and heated at 500°C were used for photoreactors. About 2500 beads prepared as above were packed in all the reactors. If their surface was flat, the TiO<sub>2</sub> photocatalyst surface area in one reactor amounted to 350 cm<sup>2</sup>.

### 3.2. Photoreactor performance

The concentration of oxalic acid flowing through the photoreactors decreased linearly as a function of the reactor length, which was adjusted by changing the number of the photoreactor tubes at all the flow rates under fluorescent lamp irradiation from only one side (Fig. 5). Data (Fig. 5) were redrawn for residence time of the reactant in reactors with data obtained for two-side illumination (Fig. 6). Oxalic acid concentration decreases almost linearly with residence time until about 40% of its initial concentration, then deviates slightly from linearity perhaps due to the decrease in contact between oxalic acid and oxygen molecules and TiO<sub>2</sub> photocatalysts. These curves

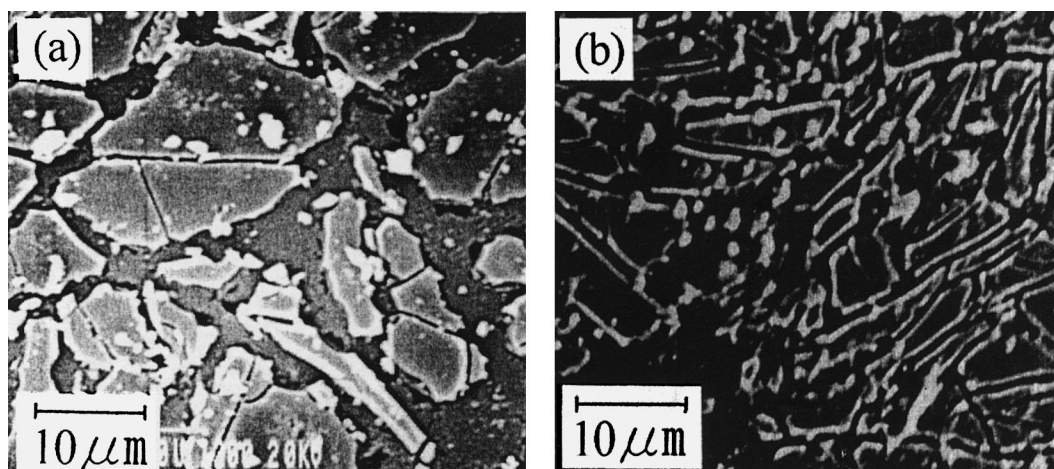


Fig. 4. Surface observation of TiO<sub>2</sub>-loaded silica gels: (a) one TiO<sub>2</sub> coating; (b) four TiO<sub>2</sub> coatings.

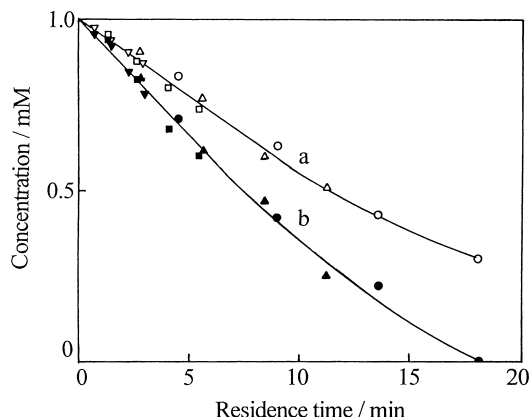
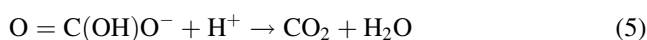
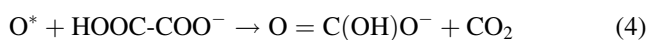
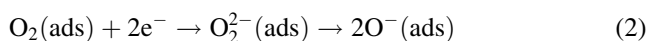


Fig. 6. Oxalic acid decomposition as a function of oxalic acid residence-time in reactors: (a) UV-irradiation from one side; (b) UV-irradiation from both sides.

obeyed first-order kinetics until about 40% of the initial concentration although decomposition was accelerated at lower concentrations.

When reactors were irradiated from both sides, oxalic acid decomposition increased. Complete decomposition was attained by irradiation on both sides of the four inter-connected reactors at  $2.5 \text{ cm}^3 \text{ min}^{-1}$ . However, the increase in the decomposition percentage was not twice of that with a one-side irradiation, so the effect of light intensity on decomposition was investigated and we found that the decomposition percent increases with the square root of incident light intensity. The square root dependence of the decomposition percentage or quantum yield on incident light intensity has been observed at dispersed and also immobilized  $\text{TiO}_2$  photocatalyst system at moderate-to-high light intensity [8,10–15] and is explained by the fact that the recombination rate of photogenerated charge carriers is much higher than hole capture by surface hydroxyl groups and/or reactant(s) [15]. The same explanation applies to our reactor.

For the photocatalytic decomposition of oxalic acid in oxygenated solution, Hermann et al. [16] proposed that decomposition proceeded by activated oxygen ( $\text{O}^*$ ) produced from oxygen molecule, photogenerated electrons ( $\text{e}^-$ ) and holes ( $\text{h}^+$ ).



Eqs. (3)–(5) indicate that oxalic acid is decomposed with one hole. The above equations shows that one oxygen molecule is consumed in the photocatalytic decomposition of one oxalic acid molecule. In our photoreactor, oxygen was initially supplied from the air as dissolved oxygen and

not supplied between reactors, and only about 50% sufficient for completely decomposing 1 mM oxalic acid if the reaction proceeded under the above scheme. Despite insufficient dissolved oxygen, 1 mM oxalic acid solution was decomposed entirely (curve b, Fig. 6). Oxalic acid has been reported to be decomposed in an aqueous  $\text{TiO}_2$  suspension in the dark [16]. Dark decomposition did not, however, occur in our reactor because the outlet oxalic acid concentration in the dark equaled that of the stock solution. Oxalic acid was also decomposed negligibly by photochemical reaction without  $\text{TiO}_2$  [16]. Our results may contain only a small amount of photochemical decomposition, because a concentration decrease of a few percent to that obtained using  $\text{TiO}_2$ -fixed silica gel beads was observed when experiments used glass tubes packed with silica gel beads without a  $\text{TiO}_2$  layer. These facts make it necessary to consider whether the photocatalytic oxalic acid decomposition in our reactor involved other photocatalytic decomposition reaction(s) than (1)–(5) or proceeded under an alternative reaction mechanism. We have no clear answers for these questions at present. We evaluate the efficiency of the photoreactor by an apparent quantum yield ( $\Phi_{\text{app}}$ ) defined as

$$\Phi_{\text{app}} = n_s/N \quad (6)$$

where  $n_s$  is the number of oxalic acid molecules decomposed during the reactor residence, and  $N$  is the number of photons received by the photoreactor during oxalic acid residence. The surface area of one reactor is also assumed to be  $1 \text{ cm}^2$ , that is, the o.d., of the glass tube,  $\times 45 \text{ cm}$ , that is the silica gel bed height.

Photoreactor efficiency was compared at an initial stage because oxalic acid in four serially connected reactors decomposed by about 10% at a high oxalic acid solution flow rate or at weak light intensity. The  $\Phi_{\text{app}}$  depended negligibly on the solution flow rate.  $\Phi_{\text{app}}$  at  $5\text{--}15 \text{ cm}^3 \text{ min}^{-1}$  was about 15% larger than that at  $2.5 \text{ cm}^3 \text{ min}^{-1}$ . At a high flow rate, the reactant contacts  $\text{TiO}_2$  photocatalysts much more due to fluidity.

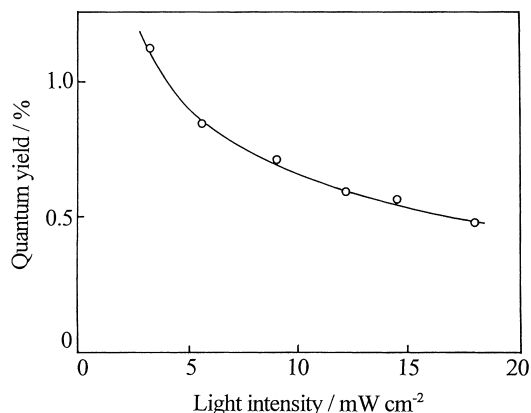


Fig. 7. Apparent quantum yield at  $5.4 \text{ cm}^3 \text{ min}^{-1}$  as a function of light intensity. Yields were compared when oxalic acid was decomposed at 10–30%.

As expected from the fact that the oxalic acid decomposition percentage increases with the square root of incident light intensity,  $\Phi_{\text{app}}$  is inversely proportional to the square root of light intensity (Fig. 7); 1% of  $\Phi_{\text{app}}$  was obtained at  $5.4 \text{ cm}^3 \text{ min}^{-1}$  at  $4 \text{ mW cm}^{-2}$  UV-intensity corresponding to summer solar irradiation.

Our reactor's relatively high efficiency is due to the following factors: (1) A 10 mm thick layer of silica gel beads loaded with  $\text{TiO}_2$  had 2% transmittance from 300 to 400 nm, so the packed bed transmittance in a reactor with an i.d., of 8 mm should exceed 2%. In addition,  $\text{TiO}_2$  catalysts on silica gel beads packed at the back of the reactor were irradiated with reflected light, so that all the  $\text{TiO}_2$  photocatalysts in the reactor are excited and participate in the reaction. (2) The concentration of the reactant by support leading to highly efficient charge transfer [17,18] may contribute of the high photoefficiency.

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