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Sonophotocatalytic destruction of 1,4-dioxane in aqueous systems by HF-treated TiO_2 powder

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Abstract

Decomposition efficiency of 1,4-dioxane in water was examined by sonophotocatalytic method through comparison of TiO_2 and HF-treated TiO_2. 1,4-Dioxane is effectively decomposed by combining sonolysis and photocatalysis. This synergistic effect is attributable to effective enhancement of photocatalysis by sonolysis. HF treatment of TiO_2 surface enhances its absorption capabilities for both 1,4-dioxane and ethylene glycol diformate (EGDF), while improving the overall decomposition rate of 1,4-dioxane by sonophotocatalytic treatment.

Keywords: TiO_2; Photocatalysis; Sonolysis; 1,4-Dioxane; HF

1. Introduction

This study addresses 1,4-dioxane, a synthetic organic compound with no known natural source [1]. It has been used widely as a solvent and a stabilizer for chlorinated solvents, particularly 1,1,1-trichloroethane. In addition, 1,4-dioxane is classified as a toxic chemical and hazardous pollutant by the US Environmental Protection Agency [2]; it is viewed with concern because it is a suspected carcinogen [1]. Because of its physical properties, 1,4-dioxane is inferred to migrate swiftly through aquifers to thereby contaminate drinking water resources in various places.

This compound appears to be persistent to degradation in conventional industrial biotreatment processes as well as under aerobic and anaerobic conditions encountered in natural environments [3,4]. A current treatment technology for removing 1,4-dioxane from contaminated water streams is distillation; carbon adsorption and air stripping are insufficient [1]. Chemical treatment should be considered as an alternative for economic reasons; various methods have been tested such as Fenton's reagent [5], γ-ray irradiation [6], sonolysis [7], and so on [8]. However, the efficiency of decomposition engendered by these methods does not meet practical requirements for water treatment. Consequently, development of a treatment method with a higher decomposition rate is still in demand.

Titanium dioxide is well known as a photocatalytic material [9]. When UV light illuminates on TiO_2, electron and hole pairs generate in it; they reduce and oxidize adsorbates on the surface, respectively. Thereby, they produce radical species such as OH radicals and $O_2^{\bullet}$. These radicals can decompose most organic compounds [10–12]. Much research has been conducted on this material from the viewpoint of applications for water and air purification [13].

Decomposition of organic compounds must be carried out in aqueous systems because 1,4-dioxane is difficult to remove from the water as a consequence of its affinity with water. Compared to purification in air, the quantum efficiency of photocatalysis by TiO_2 is drastically lower in water [14,15]. Several researchers have examined photocatalytic decomposition of 1,4-dioxane in water and revealed reaction pathway [16,17]. They have found that ethylene glycol diformate (EGDF) is a main intermediate with a slow decomposition rate during photocatalysis. Therefore, an effective strategy to improve photocatalysis in water is to promote access of 1,4-dioxane and EGDF to the TiO_2 photocatalyst surface.

Very recently, Sun et al. [18] successfully improved adsorption capability of TiO_2 for dibenzofurans by surface modification with fluoric acid solution. Compared with the non-treated TiO_2, HF-treated TiO_2 possessed about three times higher adsorption capability for dibenzofuran at 200 °C. They aimed trapping toxic aromatic carbons at the TiO_2 surface during combustion and succeeded in effective photocatalysis of dioxines; they did not examine this effect in aqueous media.

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Moreover, several researchers [19–23] have also reported synergistic effects of combining sonolysis and photocatalysis for degradation of some organic compounds in water. The mechanism of this effect is attributed to (a) activation of the photocatalyst surface, (b) enhancement of the mass transport of organic compounds, and (c) aggregate breakage. Beckett and Hua [7] examined sonolysis of 1,4-dioxane in water. They revealed reaction pathway by this treatment and found that EGDF is not a main intermediate. Therefore, a proper combination of these two methods may provide a high decomposition rate of 1,4-dioxane. Notwithstanding, no studies have addressed sonophotochemical reaction by TiO_2 for 1,4-dioxane.

The present study investigates sonophotocatalytic destruction of 1,4-dioxane in an aqueous system by comparing TiO_2 and HF-treated TiO_2. It specifically addresses the concentrations of both 1,4-dioxane and EGDF in water.

2. Experimental procedure

2.1. Starting materials and HF treatment

All starting chemicals used in this study were reagent grade. HF treatment was carried out according to ref. [18]. A commercial anatase-type TiO_2 powder (ST-21; Ishihara Sangyo Kaisha, Ltd., Tokyo, Japan) was used in this study. The TiO_2 powder was dispersed into distilled water, then a 47% hydrofluoric acid solution (Wako Pure Chemical Inds. Ltd., Tokyo Japan) was added to the suspension. Weight ratios of the powder and hydrofluoric acid solution to water were 0.1 and 0.0105, respectively. After stirring for 2 h, the suspension was centrifuged; the obtained wet powder was washed by distilled water until the conductivity of the centrifuged water was less than 200 μS/cm. Subsequently, the wet powder was repulped in distilled water and the suspension was controlled to pH 7 by addition of NaOH solution (Wako Pure Chemical Inds. Ltd.). The suspension was centrifuged again and washed by distilled water until the conductivity of the water was less than 50 μS/cm. The wet powder was dried at 110 °C for one night and milled using a mortar and pestle. Specific surface area and surface composition of TiO_2 powders were evaluated by BET method with N_2 (Autosorb-1; Quantachrome Instruments, Boynton Beach, FL, USA) and X-ray photoelectron spectroscopy (XPS) (ESCA model 5500MC; Perkin Elmer Physical Electronics Co., Eden Prairie, MN, USA). Surface acid concentration was evaluated by temperature-programmed desorption (TPD) with NH_3 (Multi-tasc TPD, BEL Japan Inc., Osaka, Japan).

2.2. Sonolysis and photocatalysis of 1,4-dioxane in water

A stock solution of 1,4-dioxane (Wako Pure Chemical Inds. Ltd.) was obtained by dissolving it daily into distilled water. Initial concentration of 1,4-dioxane was fixed as 50 ppm. The commercial TiO_2 powder (ST-21) or HF-treated TiO_2 powder was dispersed into the stock solution and the photocatalyst concentration was adjusted as 200 mg/L. Irradiation experiments were carried out in a pyrex glass vessel (5 cm × 5 cm × 10 cm), containing 100 mL of the aqueous suspensions under stirring, using an Hg–Xe lamp. Schematic illustration of the experimental facility is shown in Fig. 1. The illumination intensity at the inner front surface of the vessel was 144 mw/cm^2 at 365 nm. Ultrasonication was applied to the stock solution or the suspension by an ultrasonicator (20 kHz, 50 W; Sonicator; Ohtake Works, Tokyo, Japan). The vessel was cooled by ice water, and temperature deviation was suppressed within 5 °C during sonolysis.

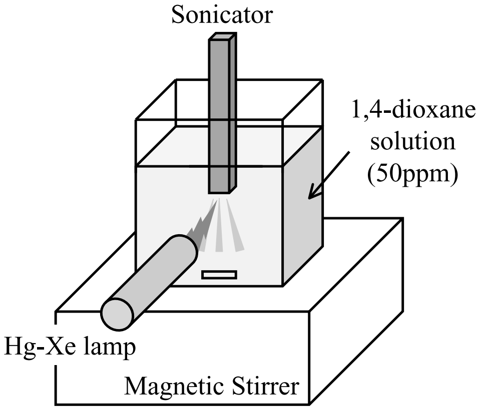

Fig. 1. Schematic illustration of the experimental facility.

After centrifugation and filtration, the concentration of organic compounds in the solution was analyzed by gas chromatography (GC-14A; Shimadzu Corp., Tokyo, Japan). That device was equipped with a flame ionization detector (FID) and a Sunpak-A column (Shimadzu Corp.). The carrier gas was nitrogen; the temperatures for the detector, injection port, and column were 200, 180, and 180 °C, respectively. A reagent grade EGDF (Frinton Laboratories, Inc., Vineland, NJ, USA) was employed to identify the peak.

To evaluate adsorption capability of 1,4-dioxane and EGDF to TiO_2 surface in water, stock solutions of 1,4-dioxane (50 ppm) or EGDF (100 ppm) with 200 mg/L of TiO_2 or HF-treated TiO_2 powder were stored in the dark. They were stirred for 1 h at room temperature. Then the change in concentration of these organic compounds was measured by gas chromatography.

The present study denotes UV illumination, sonolysis, photocatalysis, and sonophotocatalysis as UV, US, UV + TiO_2, and US + UV + TiO_2, respectively. In the case of HF-treated TiO_2, it will be described as HF-TiO_2.

3. Results and discussion

Specific surface areas for TiO_2 powder before and after HF treatment are 84 and 66 m^2/g, respectively. Fig. 2 shows

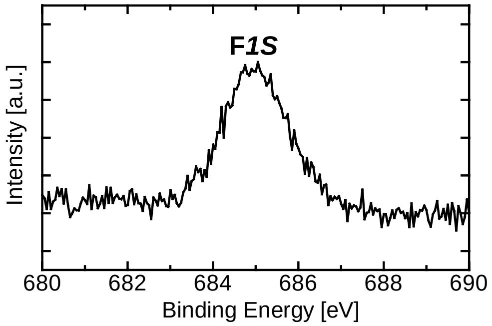

Fig. 2. XPS spectra of TiO_2 powder after HF treatment.

XPS spectra after HF treatment. Fluorine remains on the surface of TiO_2 powder.

Fig. 3 shows decomposition behavior of 1,4-dioxane by US, UV + TiO_2, UV + HF–TiO_2, US + UV + TiO_2, and US + UV + HF–TiO_2. The order of the degradation rate of 1,4-dioxane is US < UV + TiO_2 < UV + HF–TiO_2 < US + UV + TiO_2 < US + UV + HF–TiO_2. These results imply that the combination of sonolysis and photocatalysis is an effective method for degradation of 1,4-dioxane in water under this experimental condition. Further investigation revealed that 1,4-dioxane in water does not decrease as a result of UV, and the result on US was the same when TiO_2 powder was dispersed under the same condition in the dark. A linear relationship was obtained between reaction time and ln[(1,4-dioxane)/$(1,4\text{-dioxane})_0$] (where, $(1,4\text{-dioxane})_0$ means the initial concentration of 1,4-dioxane in water) on UV+TiO_2, indicating that this photocatalytic decomposition is governed by diffusion of 1,4-dioxane [24]. This linearity also concurs well with treatment by US. Although data on US + UV + TiO_2 and US + UV + HF–TiO_2 scatter, it is noteworthy that these two treatments exhibit higher decomposition rates than US or UV+TiO_2. Table 1 shows reaction constants calculated by assuming a first-order reaction. The reaction constant on the decomposition of 1,4-dioxane by US+UV+TiO_2 is three times higher than that by UV+TiO_2. Moreover, the reaction constant on US + UV + HF–TiO_2 is slightly higher than that on US + UV + TiO_2 despite a low specific surface area of HF-TiO_2 powder.

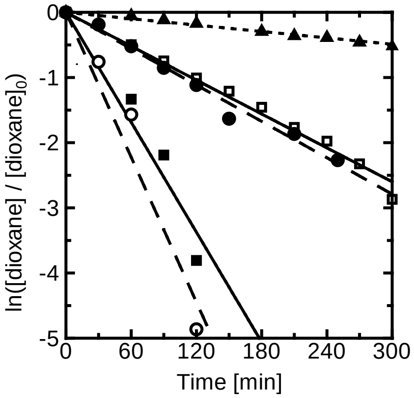

Fig. 3. Decomposition behavior of 1,4-dioxane by each treatments; (▲) US, (□) UV + TiO_2, (●) UV + HF–TiO_2, (■) US + UV + TiO_2, and (○) US + UV + HF–TiO_2.

Table 1
Reaction constants calculated by assuming a first-order reaction

	No TiO_2	UV + TiO_2	UV + HF–TiO_2
No US	–	1.4×10^{-4}	1.6×10^{-4}
US	2.8×10^{-5}	4.7×10^{-4}	5.4×10^{-4}

Fig. 4 shows a comparison of the concentration change of 1,4-dioxane and EGDF by US, UV+TiO_2, UV+HF–TiO_2, US + UV + TiO_2, and US + UV + HF–TiO_2. The initial concentration of EGDF (C_0) in Fig. 4 was set as that of 1,4-dioxane, namely 50 ppm in this experimental condition. Although the decomposition rate of 1,4-dioxane is small by US, no EGDF was identified during treatment. This result agrees with that of Beckett et al. [7]. Besides US, the concentration of EGDF increases while that of 1,4-dioxane decreases, indicating that EGDF is generated as an intermediate by photocatalysis with a slow decomposition rate. The amount of EGDF begins to decrease when 1,4-dioxane is almost decomposed. This trend also agrees with previous investigations [16,17]. A high-decomposition rate was obtained both on 1,4-dioxane and on EGDF by US+UV+TiO_2 and US + UV + HF–TiO_2.

Further investigation revealed that EGDF is not decomposed under sonolysis of this experimental condition. This result means that the decomposition of 1,4-dioxane by sonolysis does not generate EGDF at all because of its different decomposition pathway from photocatalysis. Since EGDF is generated at higher rate with increasing decomposition rate of 1,4-dioxane by combining sonolysis to photocatalysis, it is deduced that sonolysis effectively enhances the photocatalysis probably due to surface activation, aggregation breakage, or the enhancement of mass transport. Furthermore, this effect is more conspicuous on HF–TiO_2.

In the case of US + UV + HF–TiO_2 (Fig. 4e), the overall decomposition of 1,4-dioxane and EDGF was accomplished in the measurement period. The relationship between the decrease of 1,4-dioxane and the increase of EGDF during treatment ([1,4-dioxane decrease]/[EGDF increase]) was not unity but 0.67. This value was also the same as that in the case of UV + US + TiO_2. Since sonolysis contributes to the decrease of 1,4-dioxane but does not generates EGDF, the reaction does not proceed stoichiometrically. The amount of initial 1,4-dioxane is higher than the total amount of EGDF. This is due to the decomposition of EGDF during the decomposition of 1,4-dioxane. Actually, we have detected the generation of ethylene glycol monoformate (EGMF), which is reported as the product of photocatalysis of EGDF [16,17] during this measurement.

Fig. 5 shows absorption capability on the TiO_2 and HF–TiO_2 powders for 1,4-dioxane and EGDF in water at room temperature. HF–TiO_2 exhibits higher absorp-

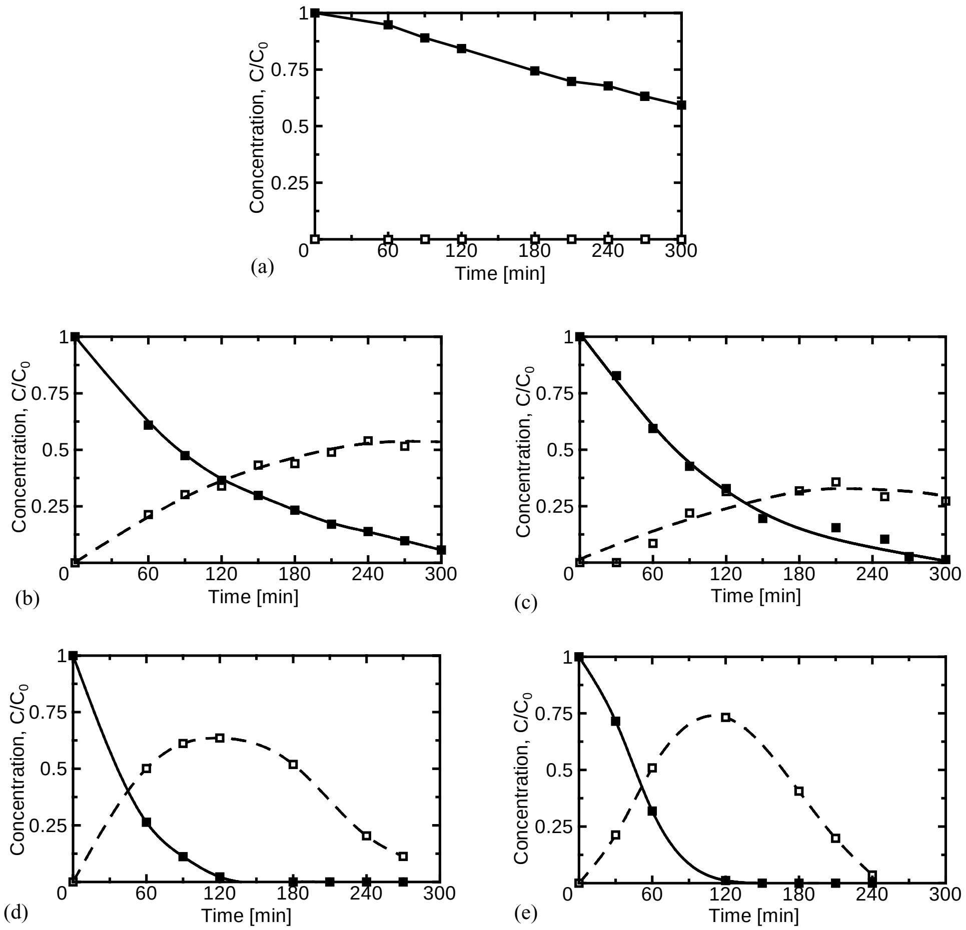

Fig. 4. Comparison of the concentration change of 1,4-dioxane (■) and EGDF (□) by each treatments: (a) US, (b) UV+TiO$_2$, (c) UV + HF–TiO$_2$, (d) US + UV + TiO$_2$, and (e) US + UV + HF–TiO$_2$.

tion capability for both 1,4-dioxane and EGDF than pure TiO$_2$. Because of the increase of absorption capability, both 1,4-dioxane and EGDF are decomposed effectively by photocatalysis. Therefore, US + UV + HF–TiO$_2$ treatment exhibited a higher reaction constant than that on US + UV + TiO$_2$. It is known that the Luis acidity of TiO$_2$ surface is increased by hydrofluoric acid treatment [25], and we confirmed this fact by NH$_3$–TPD (Fig. 6). Sun et al. [18] analyzed surface composition of HF–TiO$_2$ by XPS and confirmed the replacement of surface OH groups with –F. They deduced the enhancement of interaction between the surface acid sites on HF–TiO$_2$ and the π-electrons of the aromatic compounds. Since EGDF has π-electrons in its C=O bonding, HF–TiO$_2$ exhibits higher adsorption capability of EGDF than TiO$_2$. However, 1,4-dioxane does not possess a π-electron in its molecular structure. One plausi-

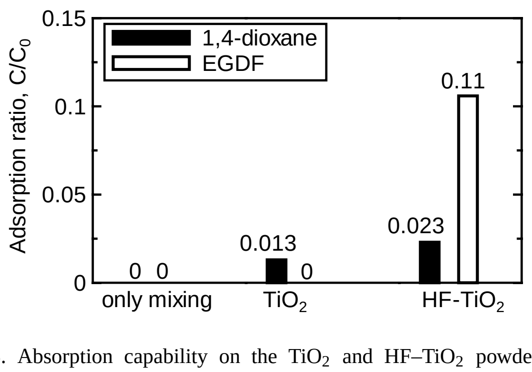

Fig. 5. Absorption capability on the TiO$_2$ and HF–TiO$_2$ powders for 1,4-dioxane and EGDF in water at room temperature.

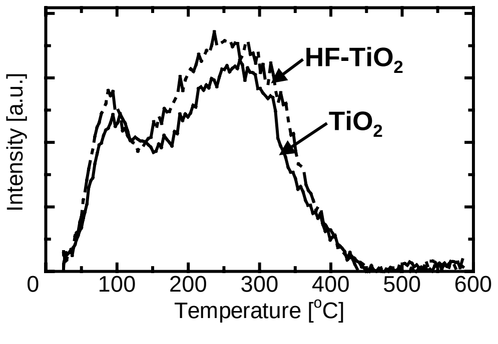

Fig. 6. Results of NH$_3$–TPD on TiO$_2$ (dotted line) and HF–TiO$_2$ (solid line) powder.

ble explanation for the present case is the increase of surface polarization by the replacement of surface OH groups with –F. Peller et al. [19] reported that polar compounds are more suitable for photocatalysis. Further investigation is required to elucidate the effect of HF treatment on improvement of adsorption capability of 1,4-dioxane.

The current work demonstrates the effect of HF treatment and sonophotochemical treatment on degradation of 1,4-dioxane in water. Sonophotocatalysis with HF–TiO_2 is a candidate method for 1,4-dioxane treatment by high efficiency. Further investigations of the dependence of 1,4-dioxane concentration, photointensity, sonication intensity, and HF treatment condition on overall reaction efficiency will provide or at least suggest optimum process conditions and thereby engender higher efficiency.

4. Conclusion

Sonophotochemical treatment decomposes 1,4-dioxane effectively. This synergistic effect is attributable to effective enhancement of photocatalysis by sonolysis. HF treatment of TiO_2 surface enhances absorption capabilities of both 1,4-dioxane and EGDF. It improves the overall decomposition rate of 1,4-dioxane by sonophotocatalytic treatment.

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