

Photodegradation of Dioxins in Aqueous TiO₂ Dispersions under Sunlight Irradiation

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Introduction

Dioxins produced in process of waste combustion, manufacture of pesticides, bleaching of pulp, etc. diffuse through the air and water to the environment. Especially, dioxins released into the water are concentrated through multistage food-chains, and the chemicals are incorporated in our body with seafood. Therefore it is important that dioxins are not released into the environmental water by efficient removal and decomposition of them in processes for wastewater treatments. At present the advanced oxidation processes with catalysis or supercritical water is developing as technology which effectively oxidizes and decomposes dioxins in wastewater. In this study, we investigated a possibility of wastewater treatment using titanium dioxide (TiO₂) photocatalyst.

Difficulties in oxidizing and decomposing dioxins effectively in aqueous TiO₂ dispersions are in the photocatalytic reaction system itself. One is that TiO₂ semiconductor particles are excited by near ultraviolet radiation of $\lambda < 385$ nm (less than 5% of solar radiation energy). The other is that strong oxidizers of hole (h⁺) or hydroxyl radical (-OH) are distributed on the TiO₂ surface only. In short, utilization of visible light and efficient contact with the TiO₂ surface are required in order to conduct the wastewater treatment using a TiO₂ photocatalyst. Utilization of visible light is one of the important themes in TiO₂ photocatalyst research. Therefore, research in which TiO₂ is modified with various materials excited by visible light is being conducted¹. In this study, we performed photocatalytic degradation of dioxins (PCDD/Fs) in an aqueous TiO₂ solution under sunlight irradiation (that is natural condition) and also examined coexistence effect of Rhodamine B (RhB) as dye sensitized in the degradation system.

Material and Methods

Chemicals

TiO₂ particles (P25, ca. 80% anatase, 20% rutile; BET area, ca. 50 m² g⁻¹) were kindly supplied by Degussa Co. (Japan). RhB (high-purity grade) was purchased from Tokyo Kasei Co. Ltd. (Japan). Dioxins were extracted from fly ash and dissolved in acetone. Approximately average values of each compounds in the dioxins solution were the following: 3.4 ng/ml for 2,3,7,8-TCDD, 61 ng/ml for 1,2,3,7,8-PeCDD, 96 ng/ml for 1,2,3,4,7,8-HxCDD, 231 ng/ml for 1,2,3,6,7,8-HxCDD, 174 ng/ml for 1,2,3,7,8,9-HxCDD, 832 ng/ml for 1,2,3,4,6,7,8-HpCDD, 564 ng/ml for OCDD, 12 ng/ml for 2,3,7,8-TCDF, 36 ng/ml for 1,2,3,7,8-PeCDF, 48 ng/ml for 2,3,4,7,8-PeCDF, 58 ng/ml for 1,2,3,4,7,8-HxCDF, 62 ng/ml for 1,2,3,6,7,8-HxCDF, 9.9 ng/ml for 1,2,3,7,8,9-HxCDF, 85 ng/ml for 2,3,4,6,7,8-HxCDF, 173 ng/ml for 1,2,3,4,6,7,8-HpCDF, 33 ng/ml for 1,2,3,4,7,8,9-HpCDF, 103 ng/ml for OCDF. PCDD/Fs and ¹³C₁₂-PCDD/Fs were acquired from Wellington Laboratories (Canada). All solvents, Na₂SO₄ anhydrous (Wako Pure Chemical Industries, Ltd., Japan) and active carbon dispersed silica gel (Kanto Chemical Co., Inc., Japan) were of dioxin-analysis grade.

Photoreactor and Light Source

Cylindrical Pyrex vessels were used as photoreactor. Sunlight was used as light source. The flux

energy of sunlight received at the roof of the research main building III of National Institute for Environmental Studies (36°N, 140°E) totaled to ~25 MJ/m² for 10 hours (the total exposure period) between 11:00 and 16:00 on April 23 - 24, 2002.

Procedures and Analyses

1. Photodegradation system

We prepared three systems in aqueous TiO₂ dispersions under sunlight irradiation. The first system (No.1#) was the control system comprised of 100µl of dioxins solution in 200ml water to give a final concentration of ~68 pg-TEQ/ml (~50 pg-TEQ/ml for PCDDs and ~18 pg-TEQ/ml for PCDFs). The second (No.2#) was the photodegradation system which added 100mg of TiO₂ to the control system (No.1#). The third (No.3#) was the dye-sensitized photodegradation system which added 1µmol of RhB to the photodegradation system (No.2#).

After stirring in the dark for at least 30 min., the photodegradation experiment was performed by stirring the dispersions magnetically under sunlight irradiation on the roof of the National Institute for Environmental Studies for 10 hours between 11:00 and 16:00 on April 23 - 24, 2002. Eight samples were collected for GC/MS analysis from the systems at each 50ml in term of different exposure periods as follows:

0min (before irradiation): 1# and 2#

20min (when RhB faded out): 1#, 2# and 3#

600min (when 2 days exposure finished): 1#, 2# and 3#

#3 sample at 0min collected for measuring change of the absorbance ($\lambda < 522\text{nm}$) of RhB.

The samples were filtrated through a Millipore filter (pore size, 0.22µm, Millipore Co., Japan) and the TiO₂ particles were separated from the aqueous solution. The filtrates and residuals were stored under cool and dark conditions for 1 to 2 weeks prior to GC/MS analysis.

2. Extraction, Cleanup and GC/MS analysis

After adding 17 internal standards of ¹³C₁₂-PCDD/Fs to each filtrate, the filtrate was passed through a Empore C₁₈ FF extraction disk (Sumitomo 3M Co., Japan) and dioxins in the filtrate were sorbed onto the C₁₈ disk. The dioxins were extracted from the filtrates and residuals into acetone and toluene using an accelerated solvent extraction (ASE-200, Dionex Co., USA) in conforming to the EPA method 3545A².

Each extract was purified and fractionated by treatment with a concentrated sulfuric acid, 10%AgNO₃/44%H₂SO₄ cartridge (Supelco, Sigma-Aldrich Japan Co., Japan) and an active carbon dispersed silica column. ¹³C₁₂-1,2,3,4-TCDD and ¹³C₁₂-1,2,3,4,6,8,9-HpCDF were added to each eluate which concentrated to a final volume of ~100µl under a stream of N₂. The concentration of dioxins in the eluates was determined using HRGC/HRMS.

HRGC/HRMS analysis was performed according to the EPA method 1613³. The HRGC/HRMS analytical system was comprised of an HP 6890 series unit (Hewlett-Packard, Agilent Technologies, USA) equipped with a JMS-700K (JEOL Ltd., Japan), a CP-Sil 88 fused silica capillary column (0.25mm i.d. × 50m, with 0.2µm film thickness, Chrompack, Varian Association, USA) for 4 - 6 PCDD/Fs congeners and a DB-5 fused silica capillary column (0.25mm i.d. × 60m, with 0.25µm film thickness, J&W Scientific, Agilent Technologies, USA) for 7 - 8 PCDD/Fs. Resolution of the mass spectrometer was maintained above 10,000 throughout the work. Recoveries of 2,3,7,8-TCDD were more than 60% and the average (± S.D.) was 96 ± 27% (n=8).

Results and Discussion

Photodegradation system

After sunlight irradiation for 10 hours was completed, ~90% of PCDD/Fs in the photo-

degradation system (No.2# and 3#) by comparison with the control (No.1#) were detoxified by the strong oxidation of TiO₂ photocatalyst (Fig. 1). Toxic half lives of PCDD/Fs were estimated to be ~4 hours in aqueous TiO₂ suspension under sunlight irradiation, assuming that the detoxication of PCDD/Fs followed pseudo-first order reaction. This result is consistent with the fact that dioxins react with h⁺ or ·OH very fast (second order rate constant for TCDD is about ~10⁻¹² cm³s⁻¹, relative to half life less than 10 hours comparing to h⁺ or ·OH average quantum yield ~10⁻² %) ⁴.

Dye-sensitized photodegradation system (Effect on coexistence with dye-pollutants)

Photodegradation of PCDD/Fs in the dye-sensitized system (No.3#) was inhibited in comparison with the simple photodegradation (No.2#). Similarly, in the photocatalytic degradation of polychlorinated biphenyls (PCBs) in aqueous TiO₂ suspension, photodegradation of PCBs in the river water was inhibited in comparison with pure water ⁵. The authors speculated that the inhibition resulted from competitively sunlight absorption by organic pollutants (e.g. colored humic substance) contained in natural waters.

Composition of PCDD/Fs congeners (Implication in the photodegradation mechanism)

PCDDs and PCDFs were reduced at almost the same rate or PCDDs were decreased slightly faster than PCDFs (Fig. 2). This is not inconsistent with the result that experimental rate constants for PCDDs are higher than those for PCDFs ⁴. The proportion of less chlorinated PCDD/Fs in the samples decomposed by ~90% of PCDD/Fs (No.2# and 3# after 10 hours) increased (Fig. 3), although less chlorinated dioxins tend to decompose faster than more chlorinated ones ^{4,5}. This suggests that the photodegradation of PCDD/Fs would be accompanied by dechlorination and PCDD/Fs would be oxidized in a chain reaction involving Cl atoms on the hydrated surface of TiO₂ to produce intermediate products ⁶.

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References

1. Chen C, Li X., Ma W., Zhao J., Hidaka H. and Serpone N. (2002), *J. Phys. Chem.*, 106, 318-324.
2. EPA, USA, Office of Water, Engineering and Analysis Division (1996): Method 3545A: Pressurized Fluid Extraction (PFE), SW-846 Ch 4.2.1.
3. EPA, USA, Office of Water, Engineering and Analysis Division (1994): Method 1613: Tetra through octa-chlorinated dioxins and furans by isotope dilution HRGC/HRMS, EPA82B-94-00-005.
4. Brubaker Jr. W. W. and Hites R. A. (1998), *J. Physical Chem. A*, 102, 915-921.
5. Huang I-W, Hong C-S, Bush B. (1996), *Chemosphere*, 32, 1869-1881.
6. Hoffmann M. R., Martin S.T., Choi W. and Bahnemann D. W. (1995), *Chem. Rev.*, 95, 69-96.

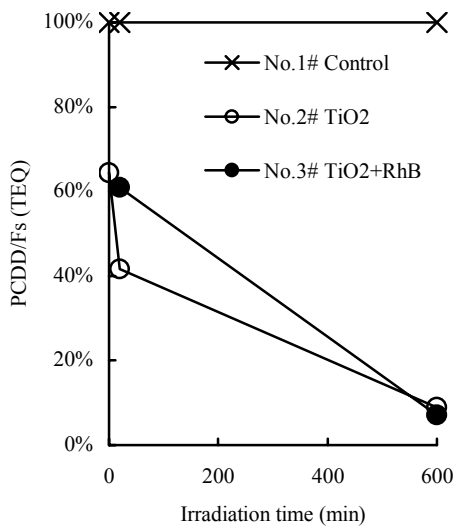


Fig.1 Photodegradation of PCDD/Fs in 3 systems under sunlight irradiation

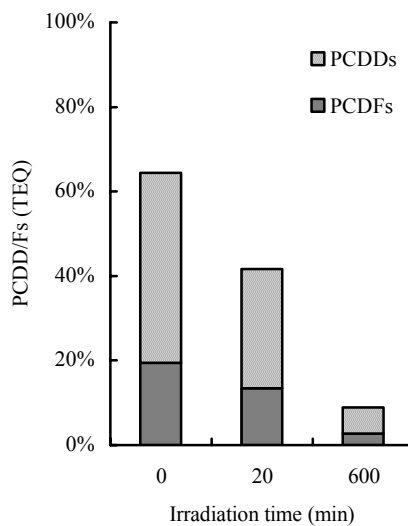


Fig.2 Photodegradation of PCDD/Fs in No.2# system

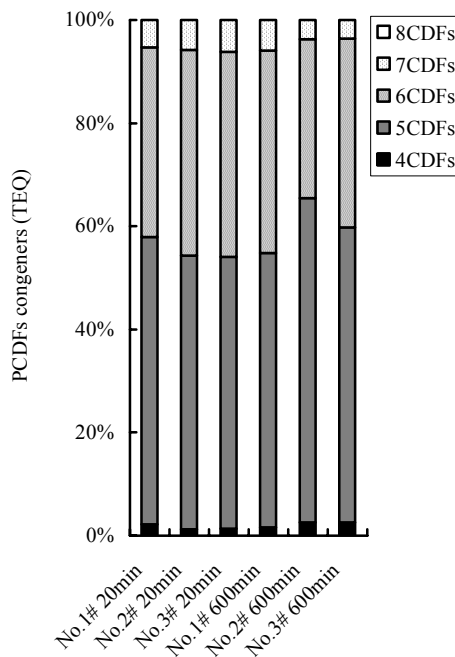
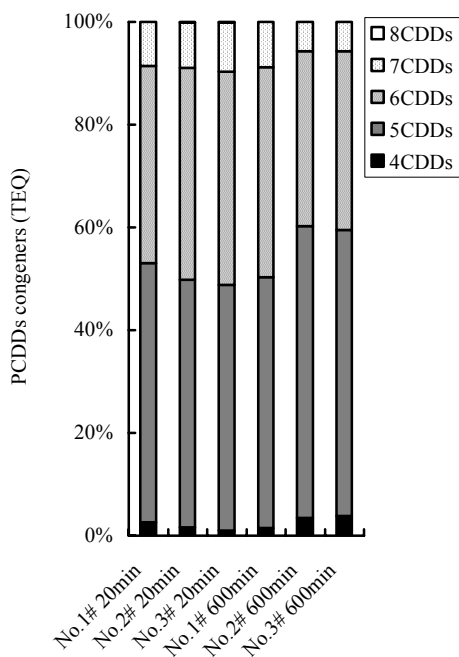


Fig.3 Composition of PCDDs (right) and PCDFs (left) congeners after sunlight irradiation for 20 and 600 min