Bull. Environ. Contam. Toxicol. (2002) 68:732–739

DOI: 10.1007/s00128-001-0315-4

Bulletin of Environmental Contamination and Toxicology

Catalytic Photodegradation of Endocrine Disrupting Chemicals Using Titanium Dioxide Photosemiconductor Thin Films

T. Tanizaki,[1] K. Kadokami,[1] R. Shinohara[2]

[1] Kitakyushu City Institute of Environmental Sciences, 1-2-1 Shin-ike, Tobata-ku, Kitakyushu 804-0082, Japan
[2] Faculty of Environmental and Symbiotic Sciences, Prefectural University of Kumamoto, 3-1-100 Tsukide, Kumamoto 862-8502, Japan

Received: 21 July 2001/Accepted: 20 December 2001

According to Nagatomi et al. (1999), over 60 of chemicals were detected in drinking water and more than a total of 100 kinds were detected in river water, which is used as a drinking water source in Kitakyushu City, Japan. Although over 60 different chemicals pass through the purification process, including pesticides, disinfection by-products and endocrine disrupting chemicals, their concentrations are generally in the low μ g/L to sub- μ g/L concentrations.

Recently, the problem of endocrine disrupting chemicals has been discussed in both social and academic circles (Keith 1997; Martin et al. 1998). The issue we are now faced with is that most of these pollutants are considered to be non-toxic or their toxicity is underestimated. Therefore, over several decades large amounts have been used as industrial materials and household products, and they have consequently spread into the environment.

Titanium dioxide (TiO2) photocatalysts utilize activated micro-holes, which are generated on the surface due to irradiation by UV (shorter than 388 nm in wavelength) to decompose organic substances in water or air (Ollis et al. 1984; Shiraishi et al. 1999). There are good features in the photodegradation with TiO2, which is a stable and safe photosemiconductor. Also, TiO2 is not soluble when it is photo-excited, as opposed to other photosemiconductors (Ishizaki et al. 1998).

The oxidation level of holes generated during photoexcitation is 3.2 eV, which is higher than the ozonation process (Bocklemann et al. 1993). Recently, TiO2 under UV irradiation has been applied in environmental cleaning systems for atmospheric and biological environments (Ibusuki et al. 1994; Shiraishi et al. 1999). For water environments, it has been said that it is difficult to apply because of the low quantum coefficient and low phototransmission (Matthews 1993).

With improvement of TiO2 activity, a photoreactor can be classified as a more advanced water purification method. We have tested a TiO2 photocatalyst on toxic chemical compounds, such as pesticides, disinfection by-products and other industrial materials and have shown, with some exceptions, that most of these chemical compounds can be effectively decomposed.

Correspondence to: R. Shinohara

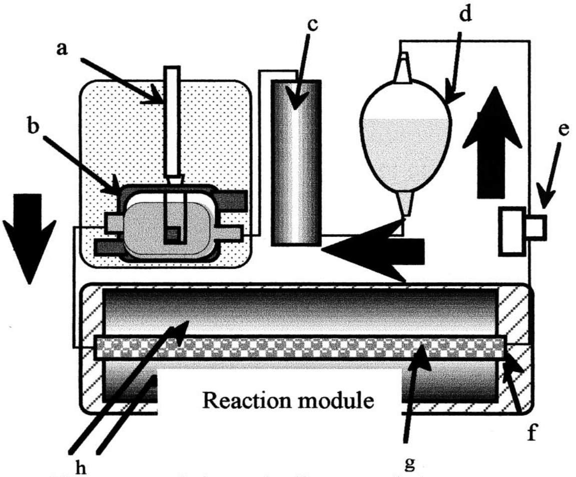

Figure 1. Schematic diagram of photoreactor
a:Thermometer; b:Cooling jacket; c:Constant flow rate pump; d:Reservoir; e:Sampling port; f:quartz tube; g:Ti O2 immobilized quartz beads; h:20 W Black light

In this experiment, we used a porous and nanostructured immobilized TiO2, which was designed for high reactivity. We report on the removal of endocrine disrupting chemicals, including alkylphenols, bisphenol-A, some of persistent organic pollutants (POPs) authorized by Organization for Economic Cooperation and Development (OECD) in 1995 and natural or artificial estrogen using a TiO2 photocatalyst.

MATERIALS AND METHODS

A nanostructured TiO2 thin film was immobilized on quartz beads by an advanced sol-gel method (Kato et al. 1995). The TiO2 coating solution was prepared by titanium tetraisopropoxide and diethanolamine in absolute ethanol under dry nitrogen. After addition of H_2O, polyethylene glycol (M.W 2000) was dissolved in the solution.

A moderate amount of 2 mm diameter quartz beads were immersed in the solution, and then dried at 100 ℃ for 1hr. After this process, the dried beads were heated from 100 ℃ to 650 ℃ at an increased rate of 2 ℃/min. The thickness of TiO2 thin film was measured by using a scanning electron microscope (SEM), and an X-ray analyzer to determine the crystal structure of TiO2.

The quartz beads obtained by the method described above were packed into a quartz tube (8 mm in diameter X 600 mm in length). Two 20 W blacklights (1.4 mW/cm^2, 359 nm in wavelength) were attached to both sides of the quartz tube in order to assemble the reactor module. The photoreactor consisted of this reactor module, a 1-L reservoir, a temperature controller, and Teflon and glass tubes for connection. The schematic diagram of the photoreactor is shown in Figure 1.

For this experiment, 13 chemical substances were employed. Namely, 10 suspected endocrine disrupting chemicals and 3 estrogens, which are either natural or artificial estrogens. Chemical substances used in the experiment can be categorized in Table 1. We prepared test solutions by adding 100 μg of each compound to one liter of Mili-Q water.

Table 1. Chemical substances employed for TiO2 photodegradation

Name	Use	Category
Amylphenol	Industrial material	Suspected endocrine disrupting chemicals
Hexylphenol		
Heptylphenol		
Octylphenol		
Nonylphenol		
p-tert-Octylphenol		
Bisphenol-A		
α-HCH	Pesticides	Suspected endocrine disrupting chemicals & POPs
β-HCH		
Hexachlorobenzene (HCB)	Disinfectant	
17-β-Estradiol		Natural estrogens
Estrone		
Ethynylestradiol	Birth control	Artificial estrogen

Each test solution was introduced into the photoreactor and was recirculated while being irradiated by UV light. The temperature of each test solution was maintained at 25 ℃ and the circular flow rate was 100 mL/min. A portion of (10 or 20 mL) of test solution was sampled periodically to determine the time dependence on reactant concentration.

With the exception of estradiols, 10 mL of each test solution was extracted with 1 mL of dichloromethane. In addition, 1 μL of the extract was injected into an ion trap type GC/MS to measure the concentration. Estrone, 17-β-estradiol, and ethynylestradiol were extracted with a PS-2 solid phase extraction cartridge and eluted with 1 mL of methanol. The eluent was derivatized with N-methyl-N-(tert-butyldimethylsilyl)-trifluoroacetamide (MTBSTFA) which is a silylation reagent, for the concentration measurement of 17-β-estradiol by GC/MS. For the measurement of estrone and ethynylestradiol, 25 μl of the eluate was directly injected into a LC/MS.

For the test samples, 2 μg/mL solutions of 4-n-octylphenol and bisphenol-A were prepared. As in the previous experiment, one liter of test solution was put into the photoreactor and circulated. A portion (10 mL) of test solution was sampled periodically and aliquot of it was injected directly into a Total Organic Carbon (TOC) meter to measure non-purgeable organic compounds.

RESULTS AND DISCUSSION

The SEM measurement was carried out to determine the surface structure and thickness of the TiO2 thin film. The thickness of a TiO2 thin film was found to be

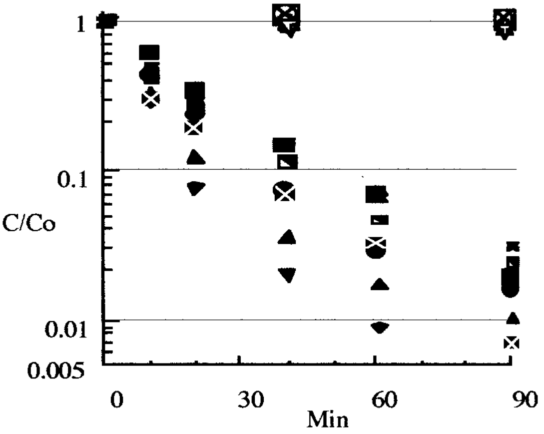

Figure 2. TiO2 photodegradation for alkylphenols and bisphenol-A

■ 4-n-Amylphenol	□ 4-n-Amylphenol (without TiO2)
● 4-n-Hexylphenol	○ 4-n-Hexylphenol (without TiO2)
▲ 4-n-Heptylphenol	△ 4-n-Heptylphenol (without TiO2)
◆ 4-n-Octylphenol	▬ 4-n-Octylphenol (without TiO2)
⊠ 4-n-Nonylphenol	▣ 4-n-Nonylphenol (without TiO2)
▬ Bisphenol-A	▽ Bisphenol-A (without TiO2)
✱ 4-tert-Octylphenol	✚ 4-tert-Octylphenol (without TiO2)

Co=100μg/L,T=298K

about 150 nm. A nanosized porous structure was found to be developed on the surface of the TiO2 thin film, and such a structure is known to be much more effective than a nonporous TiO2 film. By X-ray analysis, moreover, we confirmed that the crystal structure of the TiO2 thin film is a perfect anatase type. The orientation of TiO2 crystal structure was C axis parallel, which is reported to be much more effective than an ordinary orientation (Kato et al. 1995).

Alkylphenols are known as endocrine disrupting chemicals and the influence of 4-n-octylphenol, p-tert-octylphenol and nonylphenol is stronger than other alkylphenols. Their environmental concentrations were reported to be μg/L or sub-μ g/L levels. In environmental water, alkylphenol is generated by biodegradation of alkylphenol ethoxylate. Bisphenol-A used as an industrial raw material of polycarbonate is found at a similar concentration to alkylphenols in environmental water. The results of photodegradation of alkylphenols and bisphenol-A by using a TiO2 are shown in Figure 2.

None of the alkylphenols employed for this experiment were changed in concentration by UV irradiation without the TiO2 photocatalyst. With the photocatalyst about 90 % of their initial concentration are decomposed within 60 min of UV irradiation. Amylphenol has the lowest decomposition rate of the alkylphenols and p-octylphenol was found to be the most unstable compound among the endocrine disrupting chemicals used in this experiment. Over 90 % of its initial concentration was decomposed within less than 20 min of irradiation. The decomposition rate of bisphenol-A is less compared to the alkylphenols, and bisphenol-A is decomposed 90 % of initial concentration within about 50 min of UV irradiation.

From the results, the concentrations of these endocrine-disrupting chemicals decreased by the photodegradation with TiO2, according to the first-order rate law as follows,

$\ln (C/Co)=-kt$ (1)

Co: initial concentration, C: concentration at some time, k: decomposition rate constant, t: irradiation time.

Table 2. Decomposition rate of alkylphenols and bisphenol-A by TiO2 photodegradation

Compounds	Decomposition rate (min^{-1})
Amylphenol	$2.6X10^{-2}$
Hexylphenol	$5.5X10^{-2}$
Heptylphenol	$8.0X10^{-2}$
Octylphenol	$1.4X10^{-1}$
p-tert-Octylphenol	$6.9X10^{-2}$
Nonylphenol	$5.5X10^{-2}$
Bisphenol-A	$1.5X10^{-1}$

Decomposition rate constants calculated by equation (1) for alkylphenols and bisphenol-A are shown in Table 2. The decomposition rate of octylphenol was the highest among the alkylphenols tested and the rate constant was 0.14 min^{-1}. The decomposition rate varied depending on alkylchain length of alkylphenols and the rate of amylphenol was found to be the lowest at 0.026 min^{-1}. The decomposition rate of p-tert-octylphenol was less than that of n-octylphenol. To summarize our finding:

1. The longer the alkylchain length of alkylphenols, the faster the decomposition rate becomes.
2. The decomposition rate of straight-chained alkylphenols is faster than branched alkylphenols. Therefore, we expected the decomposition rate of nonylphenol to be the fastest among the alkylphenols used in this experiment.

However, the decomposition rate of nonylphenol is similar to that of hexylphenol. A reason for this contradiction could be that nonylphenol, which was prepared with a mixture of isomers, contained both branched and straight chained nonylphenols. Thus, the rate obtained here was considered to be the average value of mixed isomers and the rate was slower than the expected rate. The experiment described above only focused on the reduction of concentration of chemical substances. The mineralization of chemical substances by TiO2 photodegradation was confirmed. We show the change of TOC concentration with irradiation time for 4-n-octylphenol and bisphenol-A following the process of photodegradation by TiO2 in Figure 3.

Regarding the experimental data for 4-n-octylphenol, the TOC concentration did

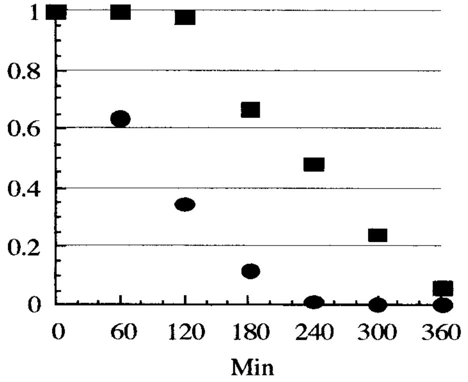

Figure 3. TiO2 photodegradation for TOC of 4-n-octylphenol and bisphenol-A measured by TOC

■ 4-n-Octylphenol ● Bisphenol-A

Co=2.0mg/L, T=298K

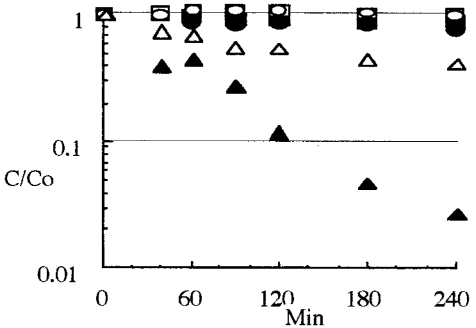

Figure 4. TiO2 photodegradation of α-HCH, ß-HCH and HCB

■ α-HCH □ α-HCH (without TiO2)
● β-HCH ○ β-HCH (without TiO2)
▲ HCB △ HCB (without TiO2)

Co=100μg/L,
T=298K

not decrease in the early stage of the reaction process, i.e., during the first 2 hr of irradiation. After 3 hr of irradiation, the TOC concentration began to decrease and changed to about 20 % of initial concentration within 5 hr after irradiation. The experimental result shows that 4-n-octylphenol was easily converted into the by-product that was identified as 4-n-octylcatechol by GC/MS within 20 to 60 min in the initial stage of the reaction. In all of the reaction systems the by-product was mineralized 3 hr after irradiation. The TOC concentration of bisphenol-A decreased to 10 % of initial concentration within 3 hr after irradiation. The by-product of bisphenol-A is estimated to be rapidly mineralized compared with that of 4-n-octylphenol.

α-HCH, β-HCH and HCB are, as suspected, endocrine disrupting chemicals. Large amounts were used as pesticides or disinfectant 30 years ago.

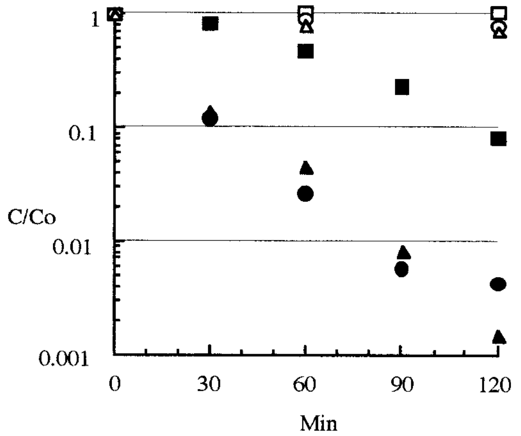

Figure 5. TiO2 photodegradation for 17-β-estradiol, estrone and ethynylestradiol

■ 17-ß-estradiol □ 17-β-estradiol (without TiO2)
● Estorne ○ Estrone (without TiO2)
▲ Ethynylestradiol △ Ethynylestradiol (without TiO2)

Co=100μg/L, T=298K

These compounds have strong residual tendencies and have been detected from some well water in agricultural areas despite their current prohibition. Results of degradation by a TiO2 photocatalyst on these compounds are shown in Figure 4.

It was found that HCH was not decomposed by a TiO2 photocatalyst. After this experiment, we tried to change the light source of the photoreactor from a blacklight to a disinfection lamp (10 mW/cm^2, Max 254 nm in wavelength), which can generate higher energy than a blacklight. However, the concentration of HCH did not decrease. On the other hand, the decomposition rate of HCB was 1.2 X 10^{-2} • min^{-1}. The rate was calculated by subtracting the decomposition rate caused by UV photodegradation from the total rate by UV irradiation with TiO2.

HCB decomposed about 40% under the black light irradiation of 4hr. The rate is similar to other chemical compounds such as pesticides and industrial materials shown in Table 1. However, the rate was found to be slower than that of other chemical compounds.

One of the natural estrogens, 17-β-estradiol, found in sewage, night soil, and environmental water is considered to be one of the leading causes of feminization in river fish. Estrone is a natural estrogen found in urine of pregnant women, mares, pigs and other animals. Ethynylestradiol is an artificial estrogen and is used in birth control pill, which has been sold commercially in Japan since 1999. Screen-test results, using a MCF-7 cell indicate that 17-β-estradiol shows more than 10 times of endocrine disrupting effect by diethylstilbestrol (DES) (Ichikawa et al. 1998), which is known as the cause of DES syndrome in the USA. The results of photodegradation using TiO2 for estradiols are shown in Figure 5 and Table 3.

Table 3 Decomposition rate of TiO2 photodegradation of estrogens

Compounds	Decomposition rate (min^{-1})
17-β-Estradiol	$1.5X10^{-2}$
Estrone	$5.8X10^{-2}$
Ethynylestradiol	$5.0X10^{-2}$

The concentration of 17-β-estradiol did not change by using only UV irradiation, but was reduced to about 90 % of its initial concentration with TiO2 after 2 hr of irradiation. Estrone and ethynylestradiol showed much faster photodegradation rates than 17-β-estradiol. It took 30 min to decrease 90 % of initial concentration and within 60 min of irradiation, the concentration decreased to below 5 % of initial concentration. However, estrone and ethynylestradiol, decomposed 20 % of their initial concentration by only UV irradiation.

REFERENCES

Bockelmann D, Goslich R, Weichgrebe D, Bahnemann D (1993) Solar detoxification of polluted water: Comparing the efficiencies of aparabolic trough reactor and a novel thin-film-fixed-bed reactor, Photocatalytic purification and treatment water and air. Elsevier Sciences Publishers, B.V, Amsterdam, p 771-776

Ibusuki T, Takeuchi K (1994) Removal of low concentration nitrogen oxides through photoassisted heterogeneous catalyst. J Molec Cat 88: 93-102

Ichikawa K, Han KK, Kim SH, Utsumi H (1998) In vitro bioassay for estrogen-like endocrine disrupting chemicals. Proceeding of 7th Japan/Korea Symposium on Water Environment, Fukuoka, Japan, p 44-52

Ishizaki A, Saito T, Sunada K, Takeuchi K, Hashimoto K, Fujishima A, Doumoto T, Miyashita Y, Murasawa S, Watanabe, T (1998) TiO2 photocatalysis (its application to self cleaning, anti-bacterial and air purifying materials), CMC Publishers, Tokyo p 3-23

Kato K, Tsuzuki A, Torii Y, Taoda H, Butsugan Y (1995) Morphology of thin anatase coating prepared from alkoxide solutions containing organic polymer, affecting the photocatalytic decomposition of aqueous acetic acid. J Mat Sci 30: 837-841

Matthews RW (1993) Photocatalysis in water purification: possibilities, problems and prospects. Photocatalytic purification and treatment water and air, Elsevier Sciences Publishers, B.V, Amsterdam, p 121-135

Nagatomi T, Taketomi M, Hashimoto A, Sugishima S, Suzuki M (1999) Behavior of organic micro-pollutants in drinking water purification process. J Japan Wat Works Assoc 68: 2-11

Ollis DF, Hsiao CY, Budiman L, Lee CL (1984) Heterogeneous photoassisted catalysis: conversion of perchloroethylene, dichloroethane, chloroacetic acids, and chlorobenzene. J Cat 88: 89-96

Shiraishi F, Toyoda K, Fukinbara S, Obuchi E, Nakano K (1999) Photolytic and photocatalytic treatment of an aqueous solution containing microbial cells and organic compounds in an annular-flow reactor. Chem Eng Sci 54: 1547-1552