

# EMISSION CONTROL & ABATEMENT

## UV/OZONE/NITROGEN/HYDROGEN-PHOTOLYSIS OF DIOXINS IN WATER

Hirokazu Minami, Yasushi Terao, Yasuo Horii, Teruyuki Nakao<sup>1</sup> and Hideaki Miyata<sup>1</sup>

Environmental Control Plant Consolidated Division, Kubota Corporation, Osaka 556-8601, Japan  
<sup>1</sup>Faculty of Pharmaceutical Sciences, Setsunan University, Osaka 573-0101, Japan

### Introduction

Dioxins are discharged to the environment in gaseous emissions from incinerators, inleachate from dump sites, in accidents, and as contaminants in other products<sup>1</sup>. Although dioxins are characterized by extremely low water solubility, dissolved organic matters and particulate matters enhance solubility of dioxins<sup>1</sup>. Therefore, the diffusion of dioxins in water causes environmental problems. Kubota Corporation has developed the dioxins degradation system using UV/ozone-photolysis. This system reduces dioxins levels in dioxin-polluted water to the background levels without high pressure, high temperature and special chemicals, which is environmentally friendly. For example, this system reduced the dioxins level in actual dioxin-polluted water from 2,600,000pg-TEQ/L to less than 0.1pg-TEQ/L<sup>2</sup>.

In this study, the reaction rate, the mechanism for dioxins degradation, and the effects of UV 185nm were investigated to evaluate UV/ozone-photolysis from lab-scale experiments using commercial standards of octachlorinated dibenzo-p-dioxin (OCDD) and octachlorinated dibenzofuran (OCDF) in distilled water. In addition, UV/nitrogen-photolysis and UV/hydrogen-photolysis were also conducted for the case of UV-photolysis under reducing condition.

### Materials and Methods

#### Chemicals

Standards of OCDD and OCDF used in this study were obtained from Accu Standard Inc. 100µg of OCDD or OCDF was dissolved into 1mL of 1,4-dioxane. Test solutions used for this study were prepared by diluting 10 or 100µL stock solution with 1L distilled water.

#### Apparatus

The schematic flow of the experimental system is shown in Figure 1. The volume and diameter of this reactor unit were 3.0L and 10cm, respectively. A 40W low-pressure mercury lamp (UV-lamp) was placed in the quartz glass tube, and had spectrum of mainly 254nm and 185nm. The ozonizer capacity was 2g-O<sub>3</sub>/hr (PSA type).

Ozone concentrations of input and output gas were measured by ozone monitors (UV method).

#### Experimental Conditions

Batch degradation experiments were conducted by circulating 2.8L test solution at 5 L/min. Ozonated gas was diffused at 0.4 L/min from the bottom of the reactor, and the ozone concentration in the input gas was about 80mg-O<sub>3</sub>/L. The test solution was controlled at 20°C and pH7. After starting of reaction, each 50ml of solution was sampled at 0, 15, 30, 45, 60, 90, 120, 180 and 300 min, respectively. In addition, comparative experiments were also conducted under UV-photolysis,

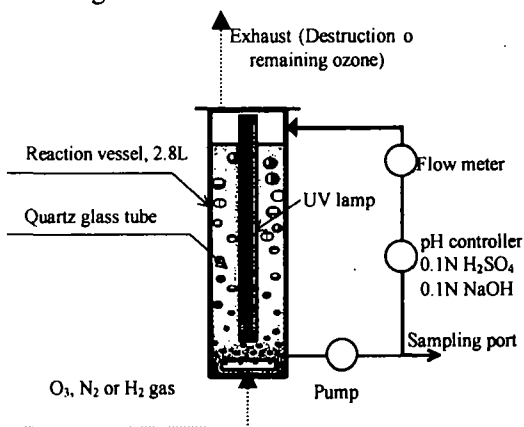


Figure 1. UV/ozone photolysis batch-reactor

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UV/nitrogen-photolysis, UV/hydrogen-photolysis, ozone oxidation.

## Analysis

<sup>13</sup>C-2,3,7,8 chlorine-substituted isomers of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) were spiked into each sample before extraction. The sample was extracted one time with 20mL of hexane, dried by passing through anhydrous sodium sulfate in a glass funnel, and concentrated to 20 $\mu$ L. Detection of PCDDs and PCDFs was carried out at EI-SIM by HRGC/LRMS (HP6890 GC / HP5973 MS, Hewlett Packard, USA). DB 17 (30m length, 0.32mmID, 0.25 $\mu$ m film thickness, J&W SCIENTIFIC, US) was used for HpCDDs and HpCDFs (HpCDD/Fs); and OCDDs and OCDFs (OCDD/Fs). Other conditions were follows; carrier gas: helium 1.2 ml/min, injector: 250°C, splitless: 0.7 min, injection volume: 2 $\mu$ L, column oven: held for 1 min at 140°C, programmed to 280°C at 10°C/min and held for 10min at 280°C, and interface: 260°C.

## Results and Discussion

### Comparison of degradation rate

In general where the rate of substrate degradation was a first order process with respect to substrate concentration, the rate can be written as the following:

$$-d[S]/dt = k[S]$$

**Table 1. First order rate constants of degradation and dechlorination ratio of OCDD/F in distilled water**

Treatment	OCDD		Time min	Dechlorination ratio		OCDF		Time min	Dechlorination ratio	
	Initial conc. ng/L	k <sup>*1</sup> min <sup>-1</sup> x10 <sup>-3</sup>		1-, 4-, 6- or 9- chlorine substituent f <sub>1</sub> , % <sup>*2</sup>	2-, 3-, 7- or 8- chlorine substituent f <sub>2</sub> , % <sup>*3</sup>	Initial conc. ng/L	k <sup>*1</sup> min <sup>-1</sup> x10 <sup>-3</sup>		1- or 9-, or 4- or 6- chlorine substituent f <sub>3</sub> , % <sup>*4</sup>	2- or 8-, or 3- or 7- chlorine substituent f <sub>4</sub> , % <sup>*5</sup>
	UV/ozone	8,740	18.1	45 300	3.25 0.13	9.84 0.39	18,200	15.3	45 300	1.13 0.18
UV	22,600	16.5	60 300	--- ---	--- ---	9,360	9.2	30 300	3.31 0.37	9.6 1.1
UV/nitrogen	36,580	11.9	20 300	5.19 0.05	18.4 0.13	11,230	14.0	--- ---	--- ---	--- ---
UV/ hydrogen	16,540	12.2	--- ---	--- ---	--- ---	--- ---	--- ---	--- ---	--- ---	--- ---
Ozone oxidation	8,500	6.1	10 240	0.58 0.26	0.66 0.70	16,170	4.7	--- ---	--- ---	--- ---

\*1. k: First order rate constant

\*2. f<sub>1</sub> = ( $\Delta$ 1,2,3,4,6,7,8-HpCDD)/( $\Delta$ OCDD)\*100

\*3. f<sub>2</sub> = ( $\Delta$ 1,2,3,4,6,7,9-HpCDD)/( $\Delta$ OCDD)\*100

\*4. f<sub>3</sub> = [( $\Delta$ 1,2,3,4,6,7,8-HpCDF)+( $\Delta$ 1,2,3,4,7,8,9-HpCDF)]/( $\Delta$ OCDF)\*100

\*5. f<sub>4</sub> = [( $\Delta$ 1,2,3,4,6,7,9-HpCDF)+( $\Delta$ 1,2,3,4,6,8,9-HpCDF)]/( $\Delta$ OCDF)\*100

[S] means the substrate concentration, and k means the first-order rate constant<sup>3</sup>. The first-order rate constant of each experiment was determined from the experimental data by plotting time vs. OCDD/F concentration. Table 1 shows the first-order rate constant and dechlorination ratio of OCDD/F in distilled water. The first-order rate constant was calculated mainly in a range of 0 and 100 min reaction time. By comparing the first-order rate constants, UV/ozone-photolysis was best and ozone treatment was worst in the degradation of OCDD/F. Furthermore, in the case of the actual dioxins-polluted wastewater, UV/ozone-photolysis treatment was more effective than UV-photolysis treatment<sup>4</sup>. This means the ozone oxidation was considered to promote the dioxins degradation rate by UV transmittance increase in the case of the actual dioxins-polluted wastewater.

## ORGANOHALOGEN COMPOUNDS

## Degradation pathways

Table 1 and Figure 3 show about dechlorination. As C-Cl cleavage was one of the main pathways for UV-photolysis of OCDD, some lower chlorinated dioxins, such as HpCDDs, increased temporarily after just beginning of reaction progress. The experimental data showed that the about 3% of degraded OCDD turned into 1,2,3,4,6,7,8-HpCDD by UV/ozone-photolysis at an early stage of 45min and the ratio decreased until about 0.1% at a final experiment time of 300 min. Therefore, the ratio of dechlorination to all degradation of OCDD decreased with the passage of reaction time. Focusing on C-Cl cleavage, 1,2,3,4,6,7,9-HpCDD was produced about 3 times more than 1,2,3,4,6,7,8-HpCDD (see Table1 and Figure3). This suggests that preferential chlorine loss occurred at 2-, 3-, 7, and 8-chlorine substituents rather than 1-, 4-, 6-, and 9-chlorine substituents on the dioxin ring.

As shown in Table 1, the ratio of dechlorination (C-Cl cleavage) under reducing condition such as and UV-photolysis, UV/nitrogen-photolysis and UV/hydrogen-photolysis was about 1.5~3.5 times greater than that under oxidizing condition such as UV/ozone-photolysis, ozone oxidation. Therefore, UV-photolysis under reducing condition enhanced the reaction

of dechlorination and hydrogen addition, and must be free of the peroxides formation. Taking these results into consideration, the combination of UV/ozone-photolysis and UV/hydrogen-photolysis, which consists of oxidizing and reducing conditions, can take the merits of both treatments.

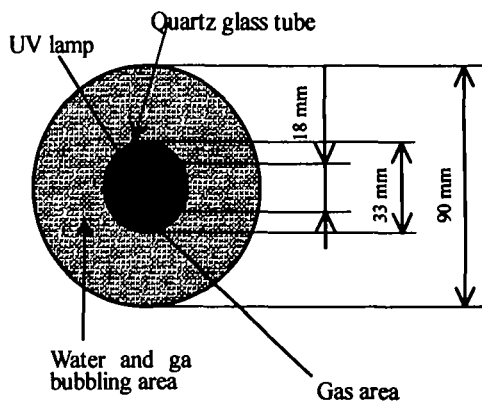


Figure 2. The cross-sectional view of UV/ozone-photolysis reactor

Table 2. Effect of UV185nm for OCDD degradation

Purge gas in quartz glass tube	UV/ozone photolysis		UV/hydrogen-photolysis	
	Initial conc. ng/L	k <sup>*1</sup> min <sup>-1</sup> x10 <sup>-3</sup>	Initial conc. ng/L	k <sup>*1</sup> min <sup>-1</sup> x10 <sup>-3</sup>
Air	1,397	9.5	1,193	9.6
Nitrogen gas	1,059	10.2	993	11.6
Improvement rate, r <sup>*2</sup> %		107		121

\*1 k: First order rate constant

\*2 r = (k of air purge)/(k of nitrogen purge)\*100

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## Effect of UV185nm for OCDD degradation

The UV lamp irradiates mainly UV spectrum of mainly 254nm and 185nm. Oxygen in air has a nature with an absorbance of UV 185nm, but nitrogen does not. As shown in Figure 2, UV lamp is covered with a quartz glass tube for protection, and has gas area around UV lamp. Nitrogen gas was purged instead of air in gas area to check the effects of UV185nm. Then, the experimental data showed the improving rate of degradation to be 107% for UV/ozone-photolysis and 121% for UV/hydrogen-photolysis (see Table 2).

## Conclusion

1. UV/ozone-photolysis was most effective for degradation of OCDD/F in distilled water.
2. The presence of nitrogen gas in gas space surrounding UV lamp promoted the rate of OCDD degradation.
3. Preferential chlorine loss occurred at 2-, 3-, 7, and 8-chlorine substituents rather than 1-, 4-, 6-, and 9-chlorine substituents on the dioxin ring.

## Acknowledgement

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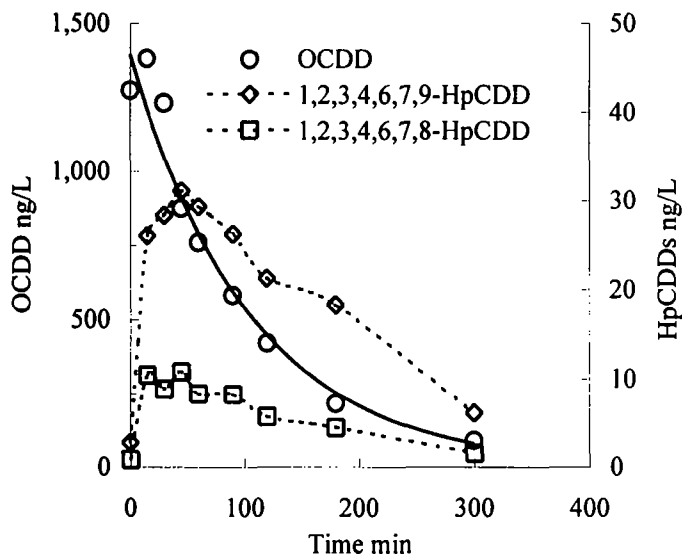


Figure 3. OCDD time-conversion curve by UV/ozone-photolysis