

Photocatalytic degradation of PCDDs, PCDFs and Coplanar-PCBs in exhaust fuel gas phase and waste water from waste industrial incinerator

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Introduction

When TiO₂ particles are accepted energies from UV irradiation, a paired electron (e⁻) and positive hole (h⁺), in the conduction band and valence band, are formed on the TiO₂ surface. The positive hole is apparently able to oxidize a water molecule to hydroxyl radical (OH·), while the electron is trapped by O₂ molecule to yield superoxide radical (O₂⁻). The electron/hole pairs, hydroxyl radical and superoxide radical, have strong oxidation activity. The oxidation of organic pollutants seems to be mediated by a series of reactions raised by hydroxyl radical and/or superoxide radical on the TiO₂ surface^{1,2}. Recently, photocatalytic technologies has been applied as useful removal methods of pollutants, because of low cost and simple system. To investigate the destruction mechanism of organic pollutants by TiO₂/UV, we carried out degradation of dioxins [polychlorinated-dibenzo-*p*-dioxins (PCDDs), polychlorinated-dibenzofurans (PCDFs) and coplanar-polybiphenyls (Co-PCBs)] in exhaust fuel gas phase and waste water by photocatalytic systems with TiO₂/UV.

Methods and Materials

The exhaust gases and waste water were collected at industrial waste incineration facility in Tokai district of Japan. Sample gas were collected from inlet and outlet of the photocatalytic reactor which were provided between multi cyclones and stuck. The reactor was designed according to our previous description³. Analysis of dioxins performed only in gas phase. Waste water was collected in wet scrubber, filtrated with glass fiber filter(0.45 μm) and circulated through the photocatalytic systems at flow rate of 16ml/min. This systems, as shown Fig 1., consist of quartz column filled with silica gel/TiO₂ and eight of UV lamps(6w, 254nm). After circulation of 1, 2, 4 and 24 hr, each test solutions were analyzed for dioxins. The analysis of dioxins were carried out according to Japanese standards⁴. Silica gel/TiO₂ were used HQ-C21

(SINTO V CERACS Ltd). GC/MS analysis were performed using a HP6890 gas chromatograph connected to Autospec Ultima mass spectrometer (Micromass Ltd.).

Results and Discussion

Analysis results of dioxins in exhaust fuel gas phase and waste water were shown as table 1. Total dioxins, $240\text{ng}/\text{m}^3\text{N}$ ($4.5\text{ng-TEQ}/\text{m}^3\text{N}$), in fuel gas phase in inlet of the photocatalytic reactor decreased to $13.4\text{ng}/\text{m}^3\text{N}$ ($0.16\text{ng-TEQ}/\text{m}^3\text{N}$) in outlet. As regards waste water, initial concentrations of $195,000\text{pg}/\text{L}$ ($3,100\text{pg-TEQ}/\text{L}$) decreased to $320\text{pg}/\text{L}$ ($20\text{pg-TEQ}/\text{L}$) after 1hr through the circulation systems with TiO_2/UV . Moreover, the concentrations of dioxins in waste water were $170\text{pg}/\text{L}$ ($0.83\text{pg-TEQ}/\text{L}$) after 24hr. The homologue profiles of PCDD/Fs and Co-PCBs of fuel gas phase and waste water were shown as figure 2.1 and 2.2 respectively. In fuel gas, homologue patterns of PCDD/Fs in inlet and outlet of reactor were similar. Although the removal efficiency of many homologue were beyond 90%, that of TeCDFs and OCDD/F were below 90%. Co-PCBs isomer patterns were also same in inlet as in outlet of the reactor. But the removal rates of Co-PCBs were higher than PCDD/Fs, and those of all isomer were beyond 90%. Especially the concentration of PCB #169, #167, #157 and #189 in outlet of the reactor were not detected. The decrease rates with the passage of circulation time in waste water show that Te- and PeCDD/Fs are more than Hx-, Hp- and OCDD/F. Even after 24 hr, the concentrations of Hx-, Hp-, OCDD and HpCDFs in test solutions of waste water were 26, 57, 29 and $14\text{pg}/\text{L}$ respectively. The tendency which the removal ratio of TeCDFs was low in exhaust fuel gas phase was not observed in waste water. The isomer patterns of Co-PCBs were same trend as in the case of fuel gas, which the concentrations of PCB #169, #167, #157 and #189 in the process of photocatalytic oxidation decrease more than other isomer. While, four isomer of Co-PCBs (#77, #126, #123 and #118) remained in test solutions after 24 hr.

Conclusion

From the results of this study, we found the method of photocatalytic oxidation with TiO_2/UV is efficiently to reduce dioxins in gas phase and water. Now, to apply widely to various organic environmental pollutants, we are developing lower cost and utility equipment using TiO_2/UV .

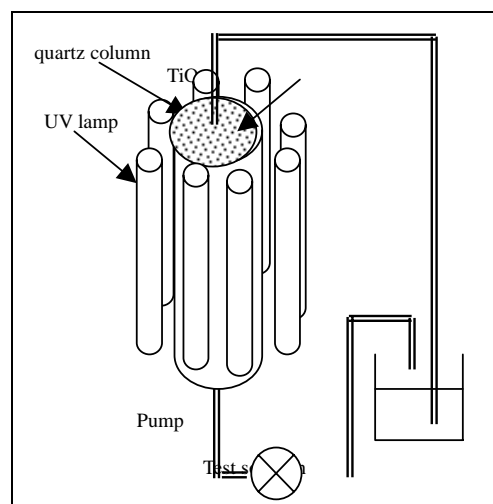


Fig 1. Schematic diagram of photocatalytic circulation systems

Table 1. Results of photocatalytic destruction of PCDD/Fs and Co-PCBs

Compounds	Exhaust gas (gas phase)		Waste water(dissolve)				
	ng/m ³ N		pg/L				
	Inlet	Outlet	Initial	1hr	2hr	4hr	24hr
2,3,7,8-TeCDD	0.22	ND.	60	ND.	ND.	ND.	ND.
1,2,3,7,8-PeCDD	1.1	0.031	390	8.3	ND.	ND.	ND.
1,2,3,4,7,8-HxCDD	1.4	0.062	840	ND.	ND.	8.2	ND.
1,2,3,6,7,8-HxCDD	2.1	0.093	1,500	ND.	ND.	13	ND.
1,2,3,7,8,9-HxCDD	1.3	0.082	760	ND.	ND.	ND.	ND.
1,2,3,4,6,7,8-HpCDD	6.3	0.45	13,000	34	29	31	27
OCDD	4.8	0.61	21,000	27	64	80	29
Σ TeCDDs	19	1.1	5,600	ND.	62	ND.	ND.
Σ PeCDDs	25	0.67	11,000	8.3	ND.	ND.	ND.
Σ HxCDDs	30	1.2	20,000	36	42	64	26
Σ HpCDDs	14	0.93	29,000	75	86	78	57
OCDD	4.8	0.61	21,000	27	64	80	29
Σ PCCDDs	93	4.5	87,000	150	250	220	110
2,3,7,8-TeCDF	0.86	0.17	320	8.1	ND.	ND.	ND.
1,2,3,7,8-PeCDF	2.3	0.085	1,200	14	12	ND.	ND.
2,3,4,7,8-PeCDF	2.5	0.080	1,800	12	7.6	8.1	ND.
1,2,3,4,7,8-HxCDF	2.4	0.093	2,100	9.4	9.8	ND.	ND.
1,2,3,6,7,8-HxCDF	2.3	0.076	2,100	7.9	7.5	ND.	ND.
1,2,3,7,8,9-HxCDF	0.12	ND.	120	ND.	ND.	ND.	ND.
2,3,4,6,7,8-HxCDF	2.8	0.12	4,000	9.1	ND.	12	ND.
1,2,3,4,6,7,8-HpCDF	3.5	0.22	11,000	28	28	35	14
1,2,3,4,7,8,9-HpCDF	0.38	0.031	1,100	ND.	ND.	ND.	ND.
OCDF	0.86	0.10	5,300	11	ND.	21	ND.
Σ TeCDFs	52	5.4	22,000	8.1	ND.	ND.	ND.
Σ PeCDFs	37	1.1	23,000	26	19	8.0	ND.
Σ HxCDFs	24	0.79	25,000	28	19	32	ND.
Σ HpCDFs	5.3	0.34	17,000	32	31	40	16
OCDF	0.86	0.10	5,300	11	ND.	21	ND.
Σ PCDFs	120	7.7	92,000	110	69	100	16
#81	2.7	0.12	760	ND.	ND.	ND.	4.9
#77	5.3	0.42	1,400	8.7	9.8	15	13
#126	3.6	0.069	2,200	5.3	5.6	5.3	3.9
#169	0.86	ND.	1,500	4.1	5.4	4.7	3.1
#123	0.79	0.079	220	ND.	ND.	ND.	ND.
#118	4.7	0.31	1,300	27	21	27	17
#105	3.5	0.10	420	11	10	ND.	ND.
#114	1.3	0.029	1,300	ND.	ND.	ND.	ND.
#167	1.2	ND.	670	ND.	ND.	ND.	ND.
#156	2.8	0.033	2,200	ND.	ND.	ND.	ND.
#157	1.7	ND.	1,200	ND.	ND.	ND.	ND.
#189	1.6	ND.	2,600	ND.	ND.	ND.	ND.
Σ Co-PCBs	30	1.2	16,000	56	52	50	42
Σ (PCDD/Fs/Co-PCBs)	240	13.4	195,000	320	370	370	170
TEQ	4.5	0.16	3,100	20	7.3	8.6	0.83

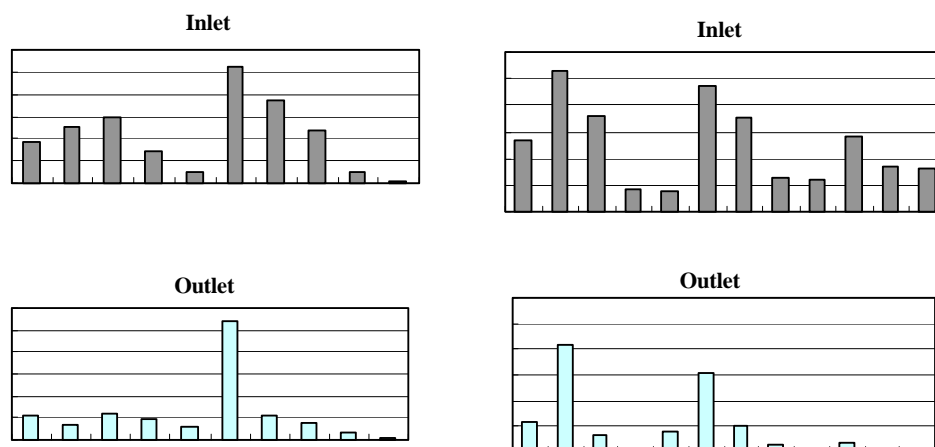


Fig2.1 Homologue profiles of PCDD/Fs and Co-PCBs in exhaust gas phase

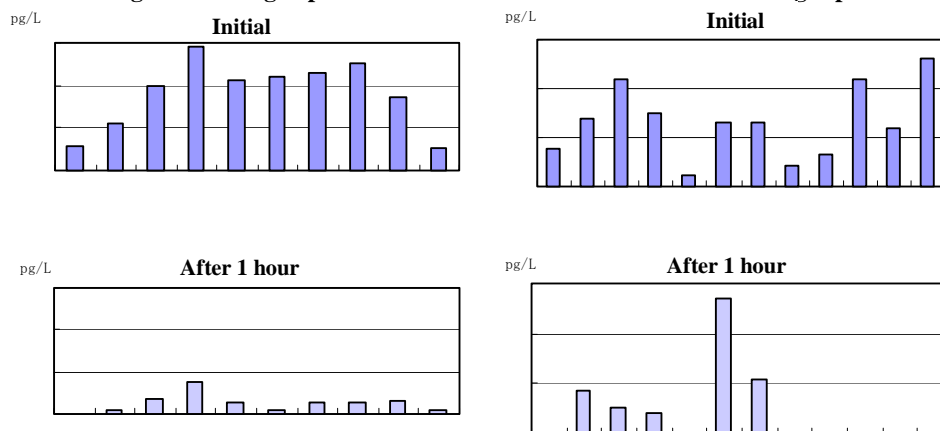


Fig2.2 Homologue profiles of PCDD/Fs and Co-PCBs in waste water

References

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