DETOXIFICATION OF DIOXIN-CONTAMINATED FLY ASH BY SOLVENT EXTRACTION AND CATALYTIC DECHLORINATION

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Introduction

Since it was discovered that polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) were contained in fly ash and flue gas from municipal solid waste incinerators (MSWI)[1], the reduction technology has been studied extensively. Catalytic oxidation with V_2O_5-TiO_2 catalysts has been adopted in incineration facilities to decompose PCDD/Fs from exhaust gases in the temperature region of ca. 200ºC[2]. As for disposal of PCDD/Fs in fly ash, dechlorination/destruction of dioxins by Hagenmaier processes is applied in full-scale facilities[3,4].

We previously reported that catalytic dechlorination of PCDD/Fs such as 2,7-DCDD, 2,8-DCDF and 1,2,6,7-TeCDD occurs efficiently in a solution of NaOH in 2-propanol in the presence of supported noble metal catalysts such as Pd/C and Pd/Al_2O_3 under mild conditions (< 35ºC)[5,6]. This method does not use molecular hydrogen, because 2-propanol serves as a hydrogen source. In this study, we examined dechlorination of PCDD/Fs and co-PCBs contained in fly ash by combining the catalytic system with the solvent extraction technique.

Methods and Materials

Materials: The catalysts used in this study were 5 wt% palladium catalysts supported on activated carbon or γ-alumina (Pd/C or Pd/Al_2O_3), which were purchased from N. E. Chemcat Co. (Japan). The specific surface area and metal dispersion were as follows: Pd/C (1088 m^2/g, 27 %), Pd/Al_2O_3 (205 m^2/g, 15 %). Fly ash contaminated by PCDD/Fs and co-PCBs was obtained from a certain MSWI in Japan.

Detoxification method (1): The fly ash was Soxhlet extracted with toluene for 18 h. A part of toluene solution was taken in a flat bottom flask and the solvent was evaporated at room temperature, followed by addition of 2-propanol (20 mL). The TEQ concentration of the 2-propanol solution was 1574 pg-TEQ/mL based on WHO-TEF (1998). To the 2-propanol solution, NaOH (80 mg) was dissolved and a supported Pd catalyst (200 mg) was added under N_2 atmosphere. Then, the mixture was stirred vigorously under refluxing conditions (82 ºC) for 3 h in the flask with a water-cooled condenser. After the reaction, the concentrations of PCDD/Fs and co-PCBs were determined after the inclusion of extracted species adsorbed on the catalyst (Soxhlet

extraction by toluene for 120-140 h) by using a high-resolution GC/MS (GC:HP-6890; MS: Micromass AutoSpec Ultima).

Detoxification method (2): The fly ash was treated with HCl (2 mol/L), washed with distilled water, and dried at 110ºC. Then, the fly ash (1.7 g) was added to a solution of NaOH (0.10 mol/L) in 2-propanol (60 mL) and underwent dechlorination in the presence of Pd/Al_2O_3 (200 mg) at 82ºC for 8 h. After the reaction, fly ash and catalyst underwent the prolonged Soxhlet extraction (120-140 h) with toluene and the amounts of PCDD/Fs and co-PCBs were determined by the GC/MS.

Results and Discussion

Solvent extraction of dioxins from fly ash: ***Soxhlet extraction of fly ash was done for 18 h with toluene or 2-propanol to compare the extraction efficiencies, where toluene is known to be the best solvent for extraction of dioxins from fly ash[7], and 2-propanol is used as solvent in our catalytic system. The effect of pretreatment of fly ash with with HCl (2 mol/L) was examined, since highest extraction efficiencies are found on acid treatment of fly ash prior to extraction[7]. Table 1 shows the amount of extracted PCDD/Fs and co-PCBs per weight of fly ash. Extraction with toluene for the pretreated fly ash gave the best result (32 ng-TEQ/g). 2-Propanol had less extraction efficiency than toluene.***

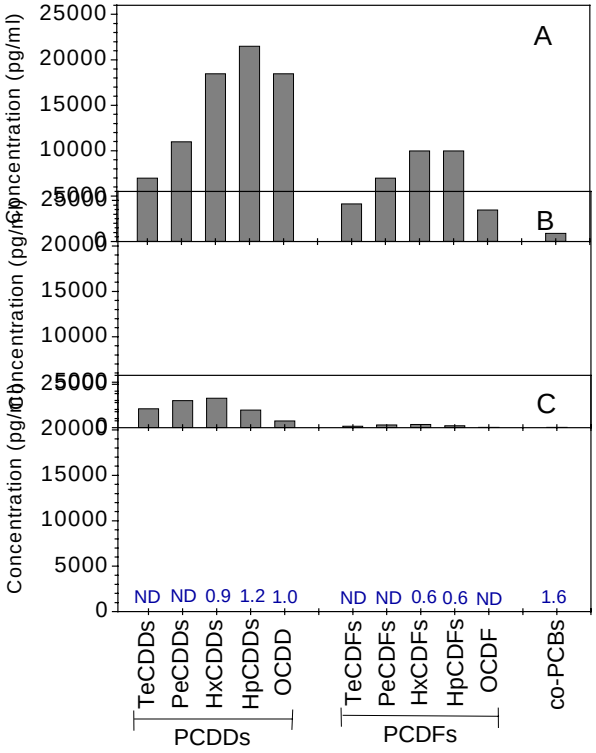
Table 1: Solvent extraction of dioxins from fly ash

PCDDs/PCDFs Co-PCBs	Concentration (ng/g)			
	HCl treated Toluene	-------- Toluene	HCl treated 2-propanol	--------- 2-propanol
TeCDDs	140	67	2.0	0.58
PeCDDs	210	97	2.6	0.91
HxCDDs	370	180	4.7	1.5
HpCDDs	390	210	5.6	1.5
OCDD	320	180	5.5	1.4
TeCDFs	83	36	1.8	0.33
PeCDFs	130	65	2.8	0.58
HxCDFs	190	91	3.5	0.84
HpCDFs	190	100	3.6	0.90
OCDF	88	50	1.4	0.31
Co-PCBs	16	9.1	1.9	0.26
Total TEQ	32	15	0.35	0.075

Dechlorination of dioxins extracted from fly ash: ***Dechlorination of dioxins extracted from fly ash was performed in a solution of NaOH in 2-propanol with Pd/C and Pd/Al_2O_3 at 82 ºC for 3 h (detoxification method (1)). Figure 1 shows***

the concentrations of tetra- to octachlorinated PCDD/F homologues and co-PCBs before and after the reaction. Before the reaction (Fig.1A), the homologues of PCDDs and PCDFs were distributed with a maximum value at heptachlorinated compounds (HpCDDs and HpCDFs), and the concentration of co-PCBs was much lower than the concentrations of PCDD/Fs. From analysis of 29 toxic congeners, the TEQ of the solution was calculated to be 1574 pg-TEQ/mL After the reaction with Pd/C (Fig.1B), the concentration of PCDDs had drastically decreased, the maximum value had shifted toward the lower-chlorinated homologues, and PCDFs and co-PCBs were hardly detected. The TEQ was still high (846 pg-TEQ/mL) after the reaction because of the increase in the concentration of the most toxic congeners, 2,3,7,8-TeCDD and 1,2,3,7,8-PeCDD. When Pd/Al_2O_3 was used as the catalyst, the concentrations of PCDD/Fs and co-PCBs decreased almost to the detection limits (Fig.1C). The TEQ was < 0.6 pg-TEQ/mL, indicating the toxicity reduction was calculated to be >99.96 % in terms of TEQ.

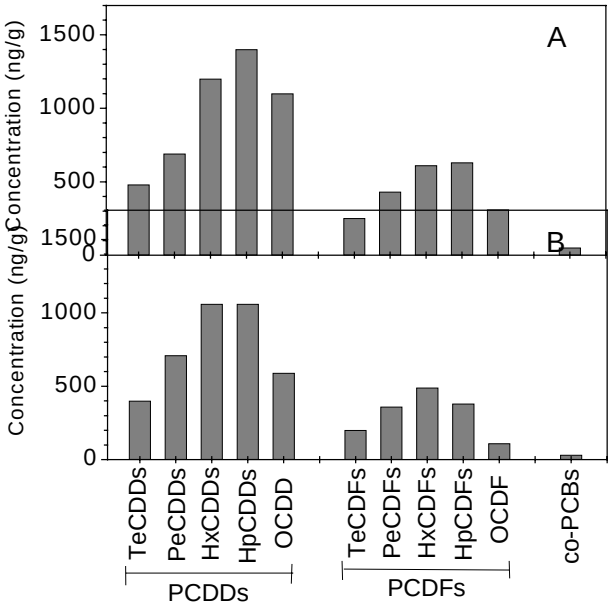
Figure 1: Dechlorination of dioxins extracted from fly ash. (A) before reaction, (B) after reaction with Pd/C, (C) after reaction with Pd/Al_2O_3.



It is known that the sample extracted from fly ash generated in an MSWI is likely to contain various chlorinated organic compounds (highly chlorinated benzenes etc.) as well as PCDD/Fs and co-PCBs[1]. Under these competitive dechlorination conditions, PCDD/Fs and co-PCBs were successfully dechlorinated by using Pd/Al_2O_3. We carried out the dechlorination of PCDD/Fs and co-PCBs with Pd/C and Pd/Al_2O_3 after the organic impurities in the sample had been removed by multilayer silica-gel column chromatography. No enhancement in toxicity reduction was observed in either the reaction with Pd/C or that with Pd/Al_2O_3. This result indicates that the catalytic activities may not be suppressed by the organic impurities.

One-step disposal of dioxin-contaminated fly ash: ***The fly ash treated by HCl was added to the catalytic system and dechlorination of dioxins was performed in the presence of Pd/Al_2O_3 at 82ºC for 8 h (detoxification method (2)). Figure 2 shows the concentration change of PCDD/F homologues and co-PCBs in fly ash, where the concentration was based on the weight of fly ash after the HCl treatment. After the reaction, the concentrations of PCDD/F homologues decreased and the distribution shifted to lower chlorinated side, indicating that dioxins in fly ash undergo dechlorination. The TEQ concentration before the reaction was 102 ng-TEQ/g and that after the reaction was 90 ng-TEQ/g, although dioxins were not detected in the liquid-phase after the reaction. Thus, the detoxification of fly ash was not completed. This is because extraction of dioxins with 2-propanol is less efficient; once dioxins are extracted from fly ash, they are dechlorinated efficiently in the 2-propanol solution by the catalyst.***

Figure 2: Detoxification of dioxin-contaminated fly ash. (A) before reaction, (B) after reaction.



In this study, detoxification of dioxin-contaminated fly ash was examined by combining solvent extraction and catalytic dechlorination. Toluene was effective for the extraction solvent. The dioxins extracted from fly ash were dechlorinated efficiently in a solution of NaOH in 2-propanol in the presence of Pd/Al_2O_3 at 82ºC.

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