INDIRECT HEATING TREATMENT OF DIOXINS-CONTAMINATED SEDIMENT USING A CATALYST TO ACCELERATE DEGRADATION OF DIOXINS

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Abstract

This study aimed at confirming feasibility of remedying dioxins-contaminated sediment by indirect heating treatment (IHT) and searching for catalysts suitable to accelerate degradation of dioxins by IHT. By IHT of the artificial sediment, Al_2O_3 was found to accelerate degradation of dioxins. In IHT of the real dioxins-contaminated sediments, Al_2O_3 demonstrated the accelerated degradation of dioxins, and TEQ of the treated samples met the Japanese environmental standard for sediment. The results confirmed the feasibility of remedying dioxins-contaminated sediment by IHT using Al_2O_3.

Introduction

As a remediation technology of dioxins-contaminated sediment, IHT has attracted growing interest in recent years, because several studies demonstrated the excellent removal of dioxins from soil[1,2,3]. Based on the mechanisms on dioxins removal, IHT may be applicable for remediation of dioxins-contaminated sediment; however its matrices are generally more complex than that of soil. Therefore, much research must be carried out to establish appropriate operation of IHT.

IHT remove dioxins from sediment by desorption and/or degradation of dioxins[1,2,3]; however the desorbed dioxins require further treatment. Since dechlorination of highly chlorinated PCDD/PCDF possibly produces more toxic lower chlorinated congeners[4,5], IHT and other POPs destruction technologies must ensure degradation of dioxins and other POPs without increase the toxicity[5]. Elevation of treatment temperature and prolongation of heating time may accomplish the task; however, for economical reasons, these operation parameters should be minimized.

Metal salts, such as CuO and Fe_2O_3, are known to be catalysts for degradation of organohalogen compounds in fly ashes derived from municipal waste and coal[4]. The fact allowed us to use such catalysts to accelerate degradation of dioxins in sediment for practical IHT. Till now, only limited number of applications has been reported for IHT of dioxin contaminated sediment[3]. Therefore, this study was carried out to confirm the feasibility of remedying dioxins contaminated sediment by IHT and to search for catalysts suitable to accelerate degradation of dioxins.

Materials and Methods

Artificial dioxins-contaminated sediment was used to search for catalysts to accelerate degradation of dioxins by IHT, whereas pentachlorophenol-originated dioxins contaminated sediment F and polychlorinated biphenyl-/combustion-originated dioxins contaminated sediment Y taken in Japan were treated to confirm feasibility of remedying dioxins contaminated sediment by IHT using such catalysts and to investigate effects of catalyst addition on the degradation of dioxins.

0.25 g of each of metal catalysts was added to 5 g of octachlorodibenzo-p-dioxin (OCDD)-sorbed quartz sand (100000 pg/g) and then kept at 450°C for 15 min under 10%oxygen/nitrogen using a laboratory scale IHT apparatus (Figure 1). In IHT of the real dioxins contaminated sediment, the catalyst was added to each sample at

the same ratio (5%). In the control experiments, samples were treated without catalyst addition (w/o catalyst) under the same operating condition to confirm remedial efficiency of IHT. After IHT, polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) remaining in the samples and that collected from the quartz tube reactor and the ice/XAD resin/toluene traps were analyzed.

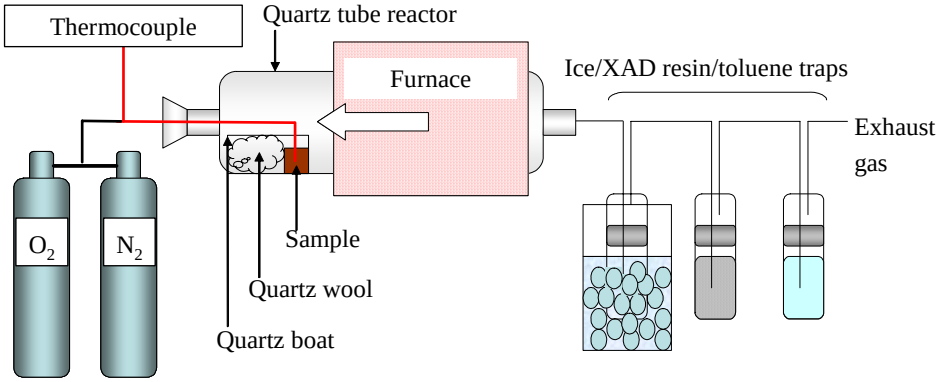

Figure 1 A laboratory scale IHT apparatus.

Results and Discussion

Catalyst application for artificial soil

Figure 2 presents an example of results obtained by the preliminary experiments using the artificial sediment, where the sum of PCDD remaining in the treated sample and that collected from the quartz reactor and traps is presented. OCDD was degraded by IHT without catalyst, while accelerated degradation of PCDDs occurred by addition of Al_2O_3, but not $CuCl_2$. As shown in Fig. 3, Te—HpCDDs did not appear in the Al_2O_3-added system, though OCDD was still major. The results indicate that Al_2O_3 might have potential to cleavage dibenzo-*p*-dioxin-frame rather than promote dechlorination.

IHT of real contaminated sediment

Since Al_2O_3 demonstrated the accelerated degradation of dioxins in the artificial sediment, we decided to use Al_2O_3 for further testing. Al_2O_3 was added to the real dioxin contaminated sediment samples, followed by IHT at 450°C for 5 min under 10%oxygen/nitrogen.

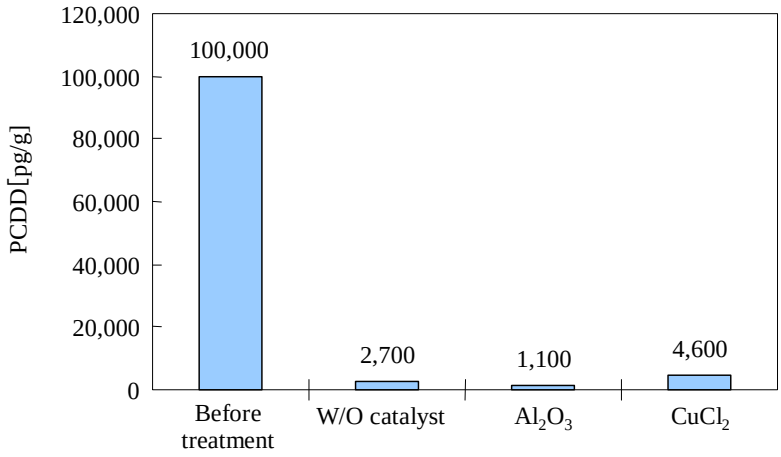

Figure 2 Effect of catalysts addition on degradation of OCDD and the resultant Te—HpCDDs.

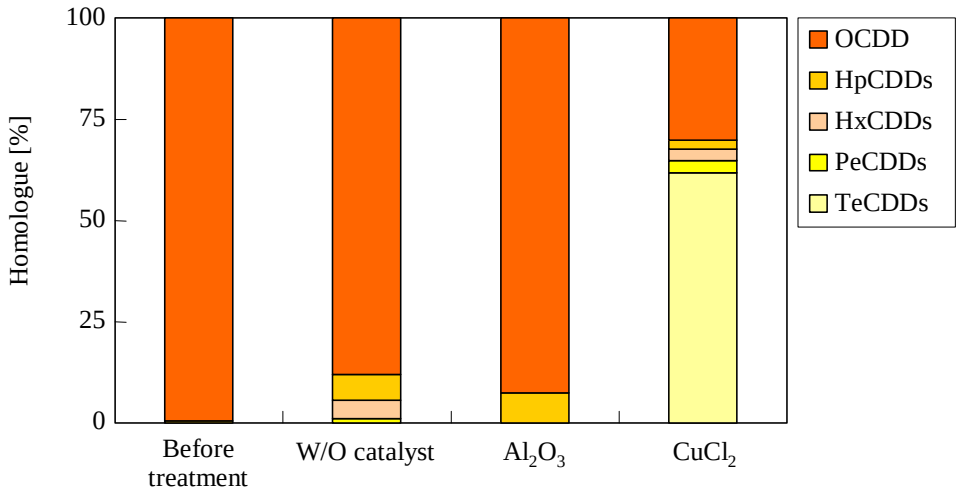

Figure 3 Homologue patterns of PCDDs after IHT of the artificial sediment.

The concentrations of PCDD/DFs remaining in the treated sediment, reactor and traps are summarized in Table 1 for a comparison between the Al_2O_3-added and w/o catalyst systems. The treated sediment F samples in both systems meet the Japanese environmental standard for sediment (150 pg-TEQ/g). As for the TEQ of dioxins in the reactor and traps, that in the w/o catalyst system was twice as that in untreated sediment F, whereas the Al_2O_3-added system showed much lower TEQ. The results confirmed the accelerated degradation of dioxins by Al_2O_3 in IHT of sediment F. The increase of TEQ in the w/o catalyst system was due to the existence of Te—HpCDDs that might be produced by dechlorination of OCDD as shown in Fig. 4, though the total PCDD/DFs concentration was decreased by IHT.

In IHT of sediment Y, the treated sample w/o catalyst showed the increase in TEQ and PCDFs. Since the one of PCDD/DFs origins of sediment Y were PCBs, the increase in PCDFs was probably due to their formation from PCBs[5]. In fact, sediment Y contained PCBs at about 1200 ng/g before IHT, and the concentration was much higher than that of the increased PCDFs. Contrast to IHT w/o catalyst, IHT with Al_2O_3 successfully removed dioxins to meet the Japanese environmental standard for sediment (Table 1), thereby confirming the feasibility of remedying dioxins-contaminated sediment by IHT using Al_2O_3. Furthermore, the total PCDD/DFs and their TEQ concentrations in the Al_2O_3-added system were ever lower than that in the w/o catalyst system (Fig. 5, Table 1). These results showed that Al_2O_3 was a useful catalyst for to accelerate dioxin degradation in IHT of contaminated sediment.

Table 1 PCDD/DFs remaining in the sediment samples, reactor and traps {upper [pg/g]; lower [pg-TEQ/g]}

	Before treatment	W/O catalyst			Al_2O_3		
		Sediment	Reactor	Total	Sediment	Reactor	Total
Sediment F	70,000,000	24,000	150,000	150,000	2,800	110,000	110,000
	5,900	11	12,000	12,000	1.3	1,100	1,100
Sediment Y	18,000	6,800	7,000	14,000	1,300	2,700	4,000
	420	610	32	640	44	31	75

The homologue pattern of the sediment F sample treated in the Al_2O_3-addition system supports the hypothesis that Al_2O_3 might have potential to cleavage dibenzo-*p*-dioxin-frame rather than promote dechlorination (Fig. 5); the removal efficiency of PCDDs is more than 98%, while that of PCDFs are below 60% in the IHT of sediment Y. As for sediment F, both PCDDs and PCDFs were removed at more than 99%. To reveal the mechanisms of the accelerated degradation of dioxins, degradation products of PCDDs must be identified in future works.

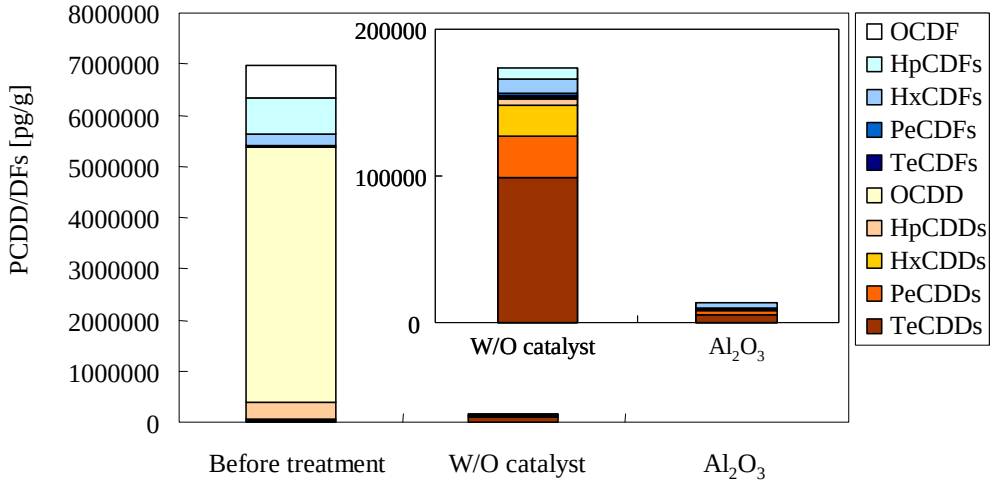

Figure 4 Removal of PCDD/DFs from sediment F by IHT with/without Al_2O_3.

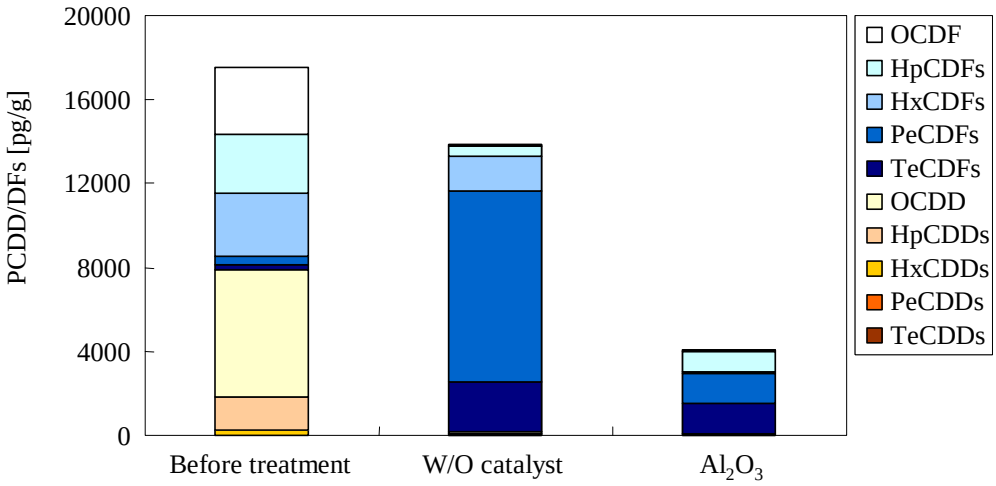

Figure 5 Removal of PCDD/DFs from sediment Y by IHT with/without Al_2O_3.

References

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