Remediation of Dioxin contaminated soil and Degradation of PCDDs and PCDFs by the Base Catalyzed Decomposition (BCD) Process

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Introduction

The Base Catalyzed Decomposition (BCD) Process is a chemical treatment method which has been successfully applied to the degradation of the persistent organic halogen compounds such as PCBs, PCP and chlorinated pesticides. We have earlier reported the decomposition of PCBs[1,2], and the remediation of PCB contaminated soils[3] by the BCD process.

Recently the soil contaminated by PCDDs and PCDFs found near the municipal incineration facilities in Japan have become a serious concern for the residents. Recently, Sakurai [4] reported that the main sources of PCDDs and PCDFs contaminated soils in Japan can be categorized into the followings: Deposition of airborne contaminants including PCDDs and PCDFs, Chloronitrofene (CNP earlier used herbicide for the rice paddy field), PCPs also used as herbicide and unknown sources. There has been significant progress in the studies on the mechanism of PCDDs and PCDFs formation in incinerators as well as in the technologies for controlling PCDDs and PCDFs emission however, the decomposition technology of PCDDs and PCDFs that have already contaminated the environment has been rarely studied.

In this paper we report the successful application of the BCD process to the remediation of soil contaminated by PCDDs and PCDFs and the decomposition of PCDDs and PCDFs contained in PCB oils and CNP.

The principle of BCD process

The organic halogen compounds are decomposed in the presence of a hydrogen donor, alkali, and a catalyst at 300-350℃ resulting in the nontoxic organic compounds, alkali salt, and water.

Materials and methods

PCBs: Kanechlor KC-300 and KC-400 equivalent. The GC/MS analysis data showed that two kinds of PCB oils collected from the used condensers were very similar to Kanechlor KC-300 and KC-400, respectively.

CNP: Sankei Chemical's MO(EC-20) was provided from the National Institute for Environmental Studies.

Solvents: C-heavy oil, transformer oil and liquid paraffin were available on the market.

Catalyst: A patented carboneous compound was available on the market. The catalyst was crashed in the mortar prior to use.

Alkali: Sodium hydroxide, potassium hydroxide and sodium bicarbonate were guaranteed reagent grade(Wako Pure Chemicals).

XAD -2: The resin was purchased from Supelco, and washed with acetone, and then Soxhlet extracted for 16hrs with toluene prior to use.

Soil contaminated by PCDFs : The sample was collected from a chloroalkali plant site in Sweden, and was homogenized before treatment.

Experimental conditions

Degradation of PCDDs and PCDFs in PCBs

Bench scale:

Figure 1 shows the experimental set-up used for the degradation of PCDDs and PCDFs contained in KC-400. An aliquot of 150 mL of C heavy oil, 1.5 g of carbon catalyst, and sodium hydroxide were placed in the three neck flask and then KC-400 was added to make up a concentration of 57,000ppm in the solvent. The solution was heated at 340°C by a heating mantle for 6hrs under a nitrogen stream. The start was defined as the time when the temperature in a vessel reached 280°C.

Plant scale:

Figure 2 shows a flow chart of the batch type plant, which consisted of a 300 L reactor, supply tanks for hydrogen donors and alkali, and a cooling tank for the treated oils. 80 L of transformer oil, 0.8 L of a hydrocarbon, and potassium hydroxide were placed in the reactor. KC-300 was then added, in an amount that the PCB concentration inside the reactor became 100,000 ppm. The solution was stirred for about 1hr at 60°C and then heated at 320°C for 4hrs by an electrical heater under a nitrogen stream. The start was defined as the time when the temperature reached 280°C.

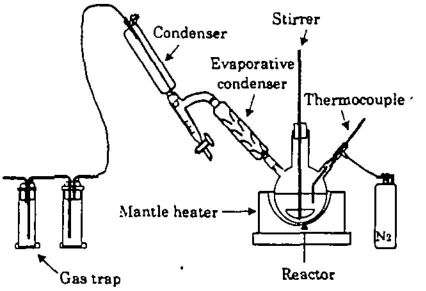

Fig. 1 Bench-scale experimental apparatus

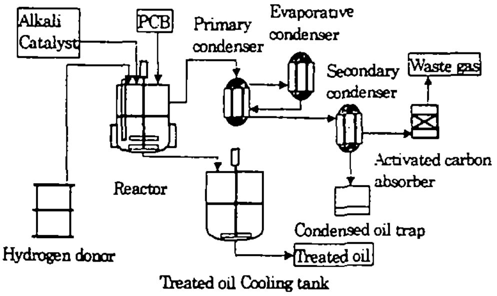

Fig. 2 Outline of batchwise pilot-scale plant

Degradation of PCDDs and PCDFs in CNP

An aliquot of 150mL of liquid paraffin, 1.5 g of carbon catalyst and 2.5 g of sodium hydroxide were placed in a three neck flask. The CNP was then added, in an amount that the CNP concentration inside the reactor became 5,000 µg/mL. The solution was stirred at a temperature 100°C for about 1hr, and then heated at 340°C for 6hrs under a nitrogen stream. The start was defined as the time when the temperature in the vessel reached 280°C.

Remediation of soil contaminated by PCDFs

The soil remediation experiment was conducted using a set-up shown in Figure 3. The soil mixed with $NaHCO_3$ (3% w/w) was placed in a flask and heated at 350°C or 400°C by a heating mantle in nitrogen atmosphere. The upper part of the flask was kept at about 200°C by using a ribbon heater. The steam and gas generated from the soil samples were condensed using a Liebig condenser, and the remaining gaseous constituents were collected in a XAD-2 resin trap. The temperature of the soil was measured by a thermocouple. The reaction start was defined as the time when the temperature reached 350°C or 400°C, respectively.

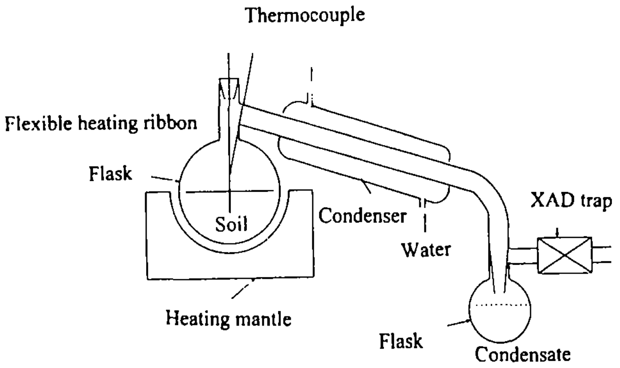

Fig.3 Bench scale set-up for the soil treatment

Analysis

The content of PCDDs and PCDFs contained in PCB oils, CNP and the soil samples before and after treatment were analyzed by means of HRGC/HRMS after the multistep clean-up procedure.

Results and discussion

Degradation of PCDFs in PCB oils

Table 1 shows the concentration of PCDFs in KC-300 and KC-400 before and after treatment by the BCD process in the bench scale reaction and the pilot-scale plant, respectively. T_4CDFs and P_5CDFs were the major congeners in KC-300 and KC-400, respectively. After the treatment by the BCD process, the concentration of PCDFs and PCDDs were below the limit of detection(LOD: 0.2ng/g) in the treated oils, and PCDFs and PCDDs were not detected in the off gas collected from the outlet of the pilot-scale plant. The results showed that PCDDs and PCDFs were decomposed by the BCD process and not formed in the process regardless of the different congener distribution or the different reaction scale.

Table 1. PCDFs in KC-300 and KC-400 and the treated oil

(ng/g)

PCB	KC-300(100000ppm)		KC-400(57000ppm)	
Isomers	initial	treated	initial	treated
T4CDFs	150	N.D.	78	N.D.
P5CDFDs	41	N.D.	120	N.D.
H6CDFs	9.6	N.D.	27	N.D.
H7CDFs	11	N.D.	5.1	N.D.
O8CDFs	N.D.	N.D.	N.D.	N.D.
Total PCDFs	210	N.D.	230	N.D.
Total Dioxins	210	N.D.	230	N.D.

(N.D. <0.1ng/g)

Degradation of PCDDs contained in CNP

CNP was manufactured from 2,4,6-trichlorophenol as a starting material. Yamagishi et al reported that CNP formulations contained T4CDDs, P5CDDs, T4CDFs, at the level of 150 ppm, 30 ppm, and 15 ppm respectively[5].

PCDDs(Cl_1 through Cl_8) were analyzed to see the change of Dioxin degradation(see table 2). The initial concentration, 732ng/g of PCDDs were reduced to 18 ng/g after 1hr, and decomposed below the limit of detection at 6hrs. The decomposition rate was achieved of >99.98%. T4CDDs accounted for 99.7% in total PCDDs while monochloro and dichloro dioxin content was trace in the staring material, and after 1 hr treatment, the amount of these low chlorinated dioxins increased to 18 ng/g however, the amount of T4CDDs decreased to trace levels. This result suggested that chlorines of PCDDs were sequentially dechlorinated as the reaction proceeded.

Table 2. PCDDs concentration in CNP treatment

(ng/g)

Reaction time(hr) Isomers	0	1	6
M1CDDs	N.D.	8.7	N.D.
D2CDDs	0.65	9.1	N.D.
T3CDDs	1.4	0.34	N.D.
T4CDDs	730	0.14	N.D.
(1,3,6,8-TCDDs)	480	0.1	N.D.
(1,3,7,8-TCDDs)	250	N.D.	N.D.
P5CDDs	0.43	N.D.	N.D.
H6CDDs	N.D.	N.D.	N.D.
H7CDDs	N.D.	N.D.	N.D.
O8CDDs	N.D.	N.D.	N.D.
Total PCDDs	732	18	N.D.

(N.D. <0.1ng/g)

Remediation of soil contaminated by PCDFs

Table 3 shows the concentrations of PCDFs in the soil before and after treatment by the BCD process. As a result, more than 99% of PCDFs was removed from the soils at 350°C as well as 400℃ within 1hr and after the treatment, PCDDs were not observed in the soils, condensates nor XAD-2. From this result, the TEQ value of PCDDs/DFs was less than the proposed German reference value, 5 ng-TEQ/kg soil for the unrestricted use of the soil. Most of PCDFs were decomposed during the treatment while some lower chlorinated PCDFs were steam distilled, and collected in the condensates and XAD-resin.

Table3. PCDFs concentration in the soil

(ng/g)

	Untreated	Treatmen at 350℃		Treatmentat 400℃	
	soil	soil	Condensates/XAD-2	Soil	Condensates/XAD-2
2378-TCDF	21	N.D.	3	N.D.	5
SUM T4CDFs	42	N.D.	9	N.D.	15
12378PeCDF	7.7	N.D.	0.5	N.D.	0.6
23478PeCDF	6.9	N.D.	0.5	N.D.	0.5
SUM P5CDFs	27	N.D.	2.5	N.D.	3
123478HxCDF	6	N.D.	0.2	N.D.	0.2
123678HxCDF	1	N.D.	N.D	N.D.	N.D.
234678HxCDF	0.6	N.D.	N.D	N.D.	N.D.
123789HxCDF	0.1	N.D.	N.D	N.D.	N.D.
SUM H6CDFs	6.6	N.D.	0.4	N.D.	0.5
SUM H7CDFs	3	N.D.	N.D	N.D.	N.D.
O8CDFs	3	N.D.	N.D	N.D.	N.D.
Total PCDFs	82	N.D.	11	N.D.	18
TEQ	7	N.D.	0.6	N.D.	0.8

(N.D. <0.2ng/g)

We reported the remediation of PCB contaminated soils by using the pilot scale-plant depicted in Fig.4 and the decomposition of the collected PCBs in the condensates by the BCD process[3]. The experimental results suggested the plant is applicable to clean the high volume of Dioxin contaminated soils.

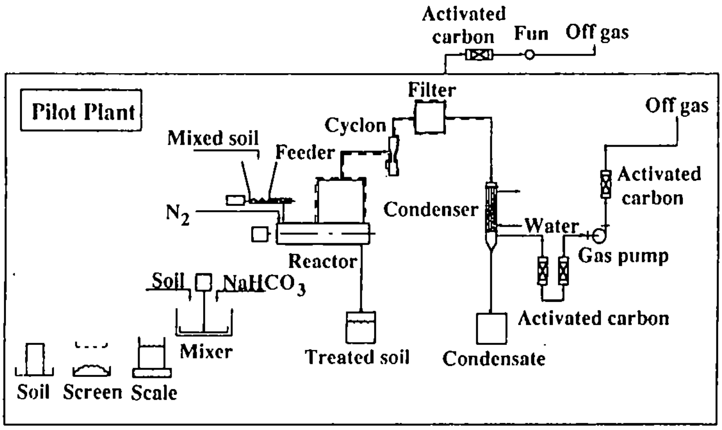

Fig.4 Flow diagram of pilot scale plant for the soil treatment

We have already demonstrated the degradation of PCDDs and PCDFs contained in PCB oils and CNP formulations at about 340℃. Accordingly it is possible to apply the BCD process to completely decompose the collected PCDDs and PCDFs followed by the partial degradation and thermal removal of PCDDs and PCDFs from the soils.

Conclusion

The PCDDs and PCDFs contained in PCB oils and CNP formulations were successfully decomposed and detoxified by the BCD process. Contaminated soils were also successfully decontaminated by this process.

The process can be applied to completely decompose the collected and/or partially dechlorinated PCDDs and PCDFs from the soils contaminated by them which have been found near the municipal incineration facilities in Japan.

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