

DEGRADATION OF PCDDs/Fs BY MECHANOCHEMICAL TREATMENT OF FLY ASH FROM A MEDICAL WASTE INCINERATOR

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Abstract

The potential degradation of PCDDs/Fs in fly ash (FA) was investigated by mechanochemical treatment in absence of additional calcium oxide. The original fly ash was sampled from fabric filter of a rotary kiln fluidized bed multi-stage pyrolysis and combustion incinerator. Increasing weight ratio of CaO from 0 to 60% was mixed into FA and grounded in MC reactor. The degradation efficiency of PCDDs/Fs up to 60% in respect with Total concentration and I-TEQ concentration was achieved during MC treatment at a rotating speed of 350 rpm. Increasing ratio of CaO made more contact possibility between PCDDs/Fs and CaO, and higher degradation efficiency appeared. Degrees of chlorination of PCDDs/Fs for MC treated samples and no-treated sample were calculated. It show that the chlorination degree decreased from 6.05 for original FA to 5.82~5.88 for those with CaO addition. Though chlorination degree reduction was not so great, it could be concluded that the dechlorination reaction occurred during MC treatment and the ratio of CaO influenced little on the dechlorination of PCDDs/Fs. The toxicity of 2,3,7,8-substituted PCDDs and PCDFs congener patterns resulting from the MC treatment were very similar. No preference of dechlorination of the toxicological relevant 2,3,7,8-positions was observed in either PCDFs or PCDDs. Consequently, 2,3,7,8-substituted congeners decreased with CaO percentage increasing. Experimental study raised the question about whether destruction and dechlorination of PCDDs/Fs occurred simultaneously or whether PCDDs/Fs were dechlorinated prior to destruction. Our present study could confirm the occurring of dechlorination. But the pathway of destruction of the dibenzodioxin/furan structure is still the focal point in future study.

Introduction

The most of the PCDDs/Fs generated from Waste Incineration processes are mainly adsorbed on fly ash^{1,2}. Consequently, the fly ash was considered as a hazardous waste which should be managed in proper method to avoid the catastrophic environmental pollution. Numerous studies have been carried out to identify suitable disposal methods for PCDDs/Fs in polluted solid ashes¹⁻³⁻⁶. With either biodegradable methods or some chemical detoxification methods, lower detoxification efficiency or longer periods or expensive costs are the common limitations for the detoxification of PCDDs/Fs in fly ashes. Recently, a mechanochemical (MC) method has attracted attention in the destruction of chlorinated aromatic compound, specifically PCDDs/Fs and PCBs. MC Treatment is a non-combustion technology that requires no heating process or off-gas treatment, which is notable advantage over the conventional heating processes. Results from previous study show that many Organochlorinated compounds have been successfully degraded by MC treatment. Further more, Nomura et al. recently demonstrate MC treatment with CaO can degrade OCDD and OCDF⁷. It is reasonable to believe that MC treatment with CaO can destruct PCDD and PCDF in fly ash. However, there is still little information about the application in

degradation of PCDDs and PCDFs in fly ashes.

In this work, fly ash sampled from a medical waste incinerator was chosen as the target material and grounded together with calcium oxide to investigate the MC degradation effects on PCDD/Fs.

Materials and methods

The original fly ash (FA) was selected from fabric filter of a medical waste incinerator for the experiments. As abnormal high dosage of activated carbon (800mg/m^3) injection during flue gas cleaning process, the content of carbon in the sampled fly ash was fairly high. Increasing weight ratio of CaO mixed into FA and was grounded in MC reactor to test the effects of CaO dosage on degradation efficiency, i.e. 6% (S1), 12% (S2), 40% (S3), 60% (S4), and 50% of weight ratio was chosen to mix CaO with FA as a no treated sample for comparison. For experimental tests, the CaO (purity 98%; Lotus Chemicals Co., China) was used as the additive for MC treatment. Prior to use, CaO was treated at 800°C for 2h.

Table 1 Test runs of the fly ashes for MC treatment

Test runs	Weight percentage of CaO addition /%
FA _{original}	0
FA _{no-treatment}	50
S1	6
S2	12
S3	40
S4	60

The MC reactor was a planetary ball mill (XQM-0.4L, Kexi, China) with four stainless steel pots (100 cm³) in which 20 steel balls (10-mm diameter) were arranged. The pots are situated on a rotating disk, which enables the pots and the disk to rotate in opposite directions. Under atmospheric pressure, the planetary ball mill was operated at 350 rpm for 2-min rotation in clockwise proceeding with a 2-min counter clock rotating and repeated the work for 2 hours.

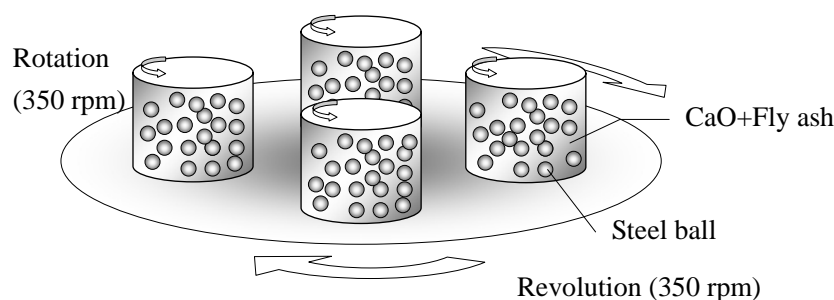


Fig.1. Schematic of MC reactor

After each MC treatment experiment, a portion of milled mixture was sampled from the pots, and spiked with known amounts of ^{13}C isotopically labeled internal standard solution; the sample was then extracted by refluxing with toluene (purity 99.5%; J. T. Baker, USA) for 24 h for analysis of PCDDs/Fs. As a control experiment, PCDDs/Fs in a non-milled fly ash and CaO mixture and original fly ash were also analyzed. The procedures for extraction and clean up were conducted according to USEPA method 1613. All analysis was performed on a high resolution gas chromatograph (HRGC) coupled with a high resolution mass spectrometer (HRMS) (JMS-800D,

JEOL Co, Japan). Chromatographic separation was carried out on a 60m DB-5 quartz capillary column. Degradation products were identified by spike tests and by comparing their mass spectral patterns with patterns stored in the U.S. National Institute of Standards and Technology (NIST) mass spectral library.

Results and Discussion

Results of the degradation efficiency of PCDDs/Fs in respect with Total concentration and I-TEQ concentration during MC treatment were given in Fig.2. The degradation efficiency of PCDD/Fs was calculated by the following two equations.

$$\eta_{s(\text{total-concentration})} = \frac{C_{\text{no-treatment}} - C_s}{C_{\text{no-treatment}}} \times 100\% \quad S=1, 2, 3, 4 \quad (1)$$

$$\eta_{s(\text{ITEQ-concentration})} = \frac{C'_{\text{no-treatment}} - C'_s}{C'_{\text{no-treatment}}} \times 100\% \quad S=1, 2, 3, 4 \quad (2)$$

In both two type of degradation efficiency, similar trends were exhibited that the degradation efficiency of PCDDs/Fs increased with increasing ratio of CaO. Comparing the present result with the study of Nomura et al, the degradation efficiency of PCDDs/Fs in our experiment was much lower than that of theirs. It may due to low rotate speed of 350 rpm applied in our study, whereas 700 rpm was chosen in the experiment of Nomura et al. Nevertheless, Mio et al studied the relation between rotational speeds for the mill and, who demonstrated that de-chlorination rate correlate with rotational speed.

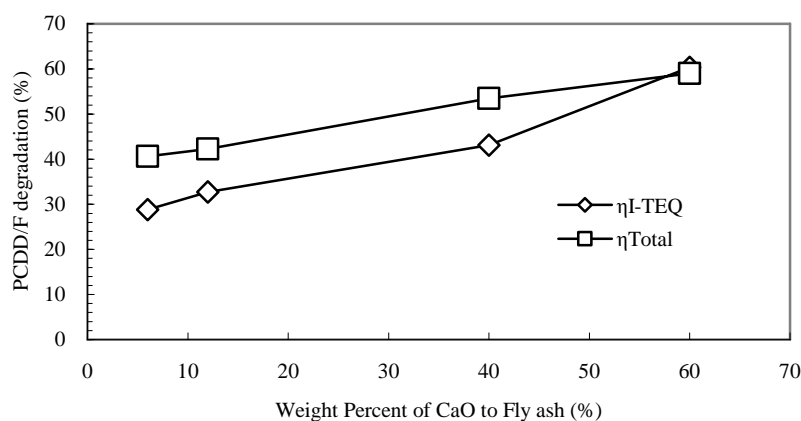


Fig.2. Degradation efficiency dependence of the ratio of CaO during MC treatment

It showed that the curve for I-TEQ curve was steeper than that of total concentration. Some literatures^{7,8} proposed the destruction and dechlorination reaction occurred simultaneously in MC treatment. Since MC reactions occur in the solid phase, it can be concluded that lower ratio of CaO possibly lead to less possibility to contact of PCDDs/Fs with CaO in milling resulting in this phenomenon.

Many previous literatures⁷⁻⁹ showed that the dechlorination mechanism was mainly engaged in degradation of chlorinated organic compounds. To see how far the chlorination of PCDDs/Fs has proceeded, we calculated the degree of chlorination of PCDDs/Fs.

Table 2 Degrees of chlorination of PCDDs/Fs for MC treated samples and no-treated sample

FA _{original}	FA _{no-treatment}	S1	S2	S3	S4
6.05	6.02	5.88	5.82	5.87	5.85

The results in table 2 show that the degrees of chlorination varies from 6.05 for original FA to 5.82 for CaO%=12%. Note the d_c for FA_{original} and FA_{no-treatment} are exhibited similar value as well as which for the milled products, and the chlorination degree slightly decreased after MC treatment. Though the reduction of chlorination degree was not so great, it still can be concluded from the data that, (1) the dechlorination reaction occurs in the degradation mechanism, (2) the ratio of CaO influence little on the extent of de-chlorination of PCDDs/Fs for MC treatment.

See Fig.3, the toxicity of 2,3,7,8-substituted PCDDs and PCDFs congener patterns resulting from the MC treatment were very similar. No preference of dechlorination of the toxicological relevant 2,3,7,8-positions was observed in either PCDF or PCDD. Consequently, 2,3,7,8-substituted congeners of PCDD and PCDF decreased with CaO percentage increasing in MC mixtures to achieve fly ash detoxification with respect to TEQ concentrations.

The fundamental experiments raised the question about whether destruction and dechlorination of PCDDs/Fs occur simultaneously or if PCDDs/Fs are dechlorinated prior to destruction. In study of MC treatment, Tetra- to Hepta- chlorinated dibenzo-dioxins and -furans produced from OCDD/F were observed to peak at the same time⁷. In our study, similar phenomenon was observed, that the pattern of degradation of each congener for all MC sample exhibited in similar manner.

Another possible degradation pathway of PCDDs/Fs may be cleavage of the dibenzodioxin/furan structure, that is to say, MC treatment of PCDD/F produced intermediates, such as chlorinated phenols and quinines⁷. Experiments from the present study confirm that the dechlorination occurs; the pathway of cleavage of the dibenzodioxin/furan structure is still the focal point in future study.

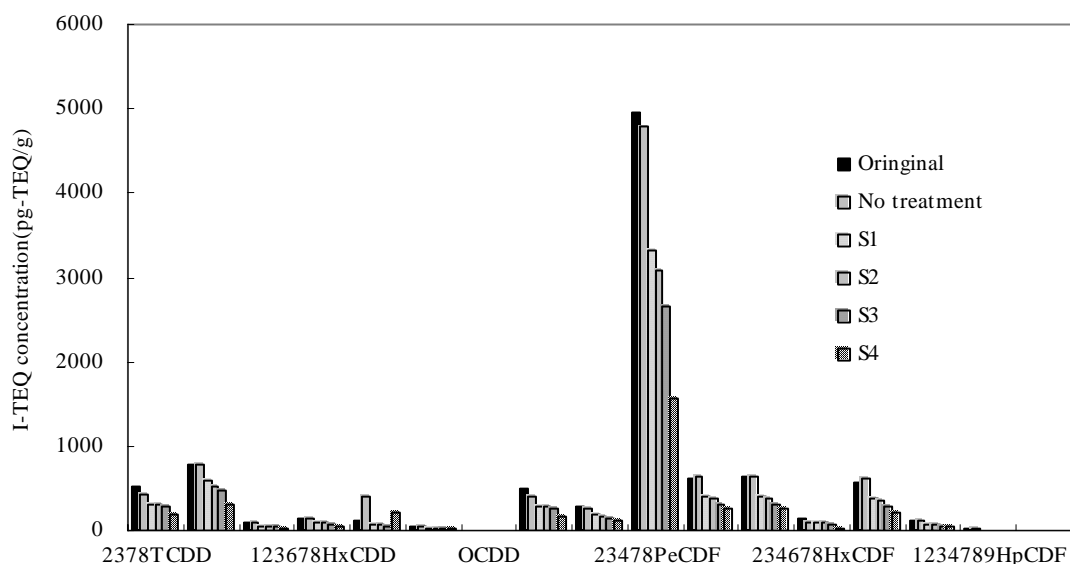


Fig.3 Toxicity of 2,3,7,8-substituted PCDDs and PCDFs congener patterns by the MC treatment

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