Degradation of PCDD/Fs by mechanochemical treatment of fly ash from medical waste incineration

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Abstract

The potential of mechanochemical treatment (MC) to degrade PCDD/Fs contained in fly ash was tested via grounding with and without calcium oxide (CaO) under atmospheric pressure. Three types of fly ash collected from medical waste incineration were compared, originating either from rotary kiln fluidized bed multi-stage incinerator using activated carbon spray (FA1, FA2), or a simple stoker incinerator without activated carbon spray (FA3). In test I: CaO to FA1 mixed at ratio of 6–60% was milled at rotational speed of 350 rpm; in test II: FA2 and FA3 without CaO were milled at rotational speed of 400 rpm. The duration of the tests was 2 h.

The results from the present study indicate that (1) under two test conditions of with and without CaO, PCDD/Fs contained in real fly ash both can be degraded by mechanochemical treatment, (2) under condition of blending with CaO, the degradation efficiency of PCDD/Fs increased with increasing ratio of CaO, (3) the degradation efficiency of PCDD/Fs may increase with rotational speed increasing and (4) the destruction and dechlorination are major mechanism for PCDD/Fs degradation.

These results show that mechanochemical treatment is a high potential technology for PCDD/Fs degradation in fly ash.
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Keywords: PCDD/Fs; Degradation; Fly ash; Mechanochemical treatment; Dechlorination

1. Introduction

Persistent organic pollutants (POPs) are a well-known threat to the environment, and the Stockholm POPs Convention declared that waste containing POPs such as dioxins and polychlorinated biphenyls (PCBs) should be decomposed in an environmentally sound manner. In particular, countermeasures generally include process of detoxification and decomposition for dioxin contaminated substance. The highest load of PCDD and PCDF released from waste incineration is mainly adsorbed on fly ash, and depending on the air pollution control devices used, it typically amounts to more than 80% of the total PCDD/F outlet from an incinerator [1]. This concern has led to intensive investigations for the complete decomposition of such toxic compounds. Numerous methods [1–6] have been studied for decomposing such toxic compounds, including microbial degradation, homogeneous and heterogeneous catalysis, persul-fate oxidation, UV-irradiation, TiO$_2$-based catalysis, reductive degradation, subcritical and supercritical water degradation.

A mechanochemical (MC) method has recently attracted attention as a simple route for treating chlorinated organic compounds, including 4-chlorobiphenyl, octachlorodibenzo-*p*-dioxin and octachlorodibenzofuran [7], 4-chloroaniline, pentachlorophenol, polychlorinated biphenyls [8], 1,2,3-trichlorobenzene [9], polyvinyl chloride (PVC) [10], 3-chlorobiphenyl [11], hexachlorobenzene [12] and DDT [13]. 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. The chlorinated organic compounds can be destructed by grinding with an excess of metal oxides to give carbon dioxide and metal chlorides as the final decomposition products. In this case, inorganic additives such as CaO and Ca metal play important roles in the dissociating reactions.

Results from previous study show that many organochlorinated compounds have been successfully degraded by MC treatment. Further more, Nomura et al. [7] recently demonstrated MC treatment with CaO can degrade OCDD and OCDF. It is

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reasonable to believe that MC treatment with CaO can destruct PCDD/Fs in fly ash; however, there is still little information about the application in degradation of PCDD and PCDF in fly ash.

In this work, two tests were conducted, i.e. test I: under 350 rpm rotational speed, increasing weight ratio of CaO mixed with fly ash (FA) were grounded to test the effect of CaO dosage on degradation efficiency of PCDD/Fs, test II: FA from medical waste incineration naturally contains high percent of CaO content and some other metal oxides (Tables 2 and 3), which may act as added CaO, so two different types of FA without addition of CaO were grounded at 400 rpm rotational speed to test the feasibility to degrade PCDD/Fs in FA. This experiment could fill the gap that real fly ashes are processed by MC treatment. Additionally a detailed investigation of the congener patterns of PCDD/Fs from the products can further verify the feasibility of this technology.

2. Materials and methods

2.1. Fly ash

Three types of fly ash (FA) were sampled from two different medical waste incineration systems for the comparison. FA1 and FA2 were sampled from the bag filter of a rotary kiln fluidized bed multi-stage pyrolysis-incineration system with activated carbon (AC) spray for removal of dioxin. The high carbon content of FA1 (80.04%), FA2 (39.61%) was observed, which was due to quite high AC load (300–800 mg/m^3) was sprayed in flue gas. Some other FA samples collected from this incineration system were also tested the carbon content, which varied within the range of 11.40–91.0%. FA1 and FA2 may be sampled in operational condition of high and medium AC load. FA3 was sampled from the cyclone dust collector of a simplified stoker incinerator, in which no AC was sprayed into flue gas. I-TEQ and total PCDD/Fs concentration for the original FA1, FA2, and FA3 were shown in Table 1.

In test I, FA1 and the ground samples were characterized as follows (Table 2). Energy dispersive X-ray analysis (EDXA)

Table 1
I-TEQ and total PCDD/F concentration for the original FA

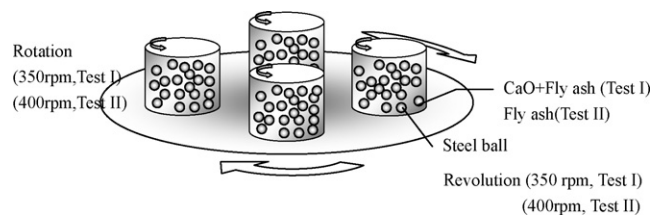|	Total concentration (pg/g)	I-TEQ concentration (pg-TEQ/g)
FA1	67828.93	9547.16
FA2	125305.40	11371.98
FA3	183041.84	15619.12

Fig. 1. Schematic representation of MC treatment.

was used to identify elemental composition for milled sample and original sample. Increasing weight ratio of CaO to FA were chosen to test the effect of CaO dosage on degradation efficiency of PCDD/Fs, 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 (S0) for comparison.

In test II, FA2 and FA3 were characterized as follows (Table 3): loss of weight, Colorimetric methods was used to identify principle composition of fly ash. Ion chromatography was (792basic IC, Metrohm) used to analyze chloride ions content.

2.2. Materials

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 2 h.

2.3. MC reactor

Fig. 1 shows a schematic diagram of the MC treatment process. The MC reactor was a planetary ball mill (XQM-0.4L, Kexi, China) with four stainless steel pots (100 cm^3). In tests I

Table 2
Elemental composition (%) of the fly ashes (FA1, S0) and samples after MC treatment

	C	O	Si	P	S	Cl	Ca	Fe	Cu	Zn	K	Al	Na	Mg
FA1	80.04	8.48	0.56	0.19	0.35	2.35	5.14	0.45	0.65	0.49	0.18	0.36	0.45	0.33
S0	56.50	14.79	0.59	0.37	0.30	1.52	22.92	0.65	0.50	0.76	0.13	0.12	0.56	0.30
S1	80.52	9.16	0.30	0.10	0.29	2.12	6.14	0.44	0.38	–	0.14	0.13	–	0.28
S2	72.11	11.25	0.17	0.31	0.42	1.68	11.15	0.58	0.44	0.16	0.32	0.40	0.30	0.71
S3	61.57	12.00	0.38	0.41	0.60	1.53	19.12	3.01	0.30	0.20	0.48	0.26	0.14	–
S4	55.32	14.43	0.55	0.34	0.28	1.34	25.26	0.91	0.51	0.30	0.17	0.22	0.12	0.24

–: no detect.

Table 3
Main composition (wt%) of the fly ashes applied in test II

	C	K$_2$O	Na$_2$O	Fe$_2$O$_3$	MgO	CaO	TiO$_2$	Al$_2$O$_3$	SiO$_2$	Cl$^-$
FA2	39.61	0.44	1.44	4.28	0.92	23.19	0.66	2.66	9.84	9.18
FA3	18.25	0.52	1.68	1.48	2.27	27.31	3.46	6.01	23.35	8.82

and II, 20 stainless steel balls (10 mm diameter) were arranged in each pot. 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 (test I) and 400 rpm (test II) for 2-min rotation in clockwise proceeding with a 2 min counter clock rotating and repeated the work for 2 h.

2.4. Extraction, clean up and analysis

A portion of each 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 extraction of PCDD/Fs. As a control experiment, a nonmilled fly ash and CaO mixture and pure fly ash was also analyzed to PCDD/Fs. The procedure for clean up was conducted according to USEPA method 1613B.

All analysis was performed on a high resolution gas chromatograph (HRGC)/high resolution mass spectrometer (HRMS) (JMS-800D, JEOL Co., Japan). Chromatographic separation was carried out on a 60 m DB-5 quartz capillary column. The temperature program for GC oven was: initial temperature 150 °C, held for 1 min; 150–190 °C at; 190–280 °C at 3 °C/min held for 20 min. Carrier gas: helium (99.999%), 1.2 ml/min; 2 μl of the extract was automatically injected in splitless mode. Mass spectrum condition: ion source temperature 280 °C; interface temperature 280 °C; SIM (selective ion monitoring mode); the mass spectrometer was operated at the ionization energy of 38 eV with a resolution higher than 10,000. All the isotope standards were obtained from Wellionton Laboratory, Canada. In the analysis of PCDD/Fs, ^{13}C-labeled PCDD/Fs were used as internal standards.

3. Results and discussion

3.1. MC treatment for mixture of FA and CaO

3.1.1. Relationship between degradation efficiency of PCDD/Fs with ratio of CaO

In order to test the factor of CaO on the degradation efficiency of PCDD/Fs in actual FA, the ratio of CaO to FA during the MC experiment covered the range of 6–60%, while it was chosen to 200:1 (CaO:OCDD, CaO:OCDF) for MC treatment of OCDD and OCDF conducted by Nomura et al. [7]. It was reported the removal efficiency from OCDD and OCDF after 2 h of MC treatment respectively reached 99.3% and 99.9% [7].

Results of the degradation efficiency of PCDD/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 Eqs. (1) and (2). $\eta_{S\text{(total-concentration)}}$ (%) and $\eta_{S\text{(ITEQ-concentration)}}$ (%) are respectively degradation efficiency of PCDD/Fs for total concentration and I-TEQ concentration, C (pg/g) and C' (pg-TEQ/g) are respectively PCDD/Fs total (through 4–8 chlorinated PCDD/Fs homologue) and I-TEQ concentration. Both C and C' were calculated on the
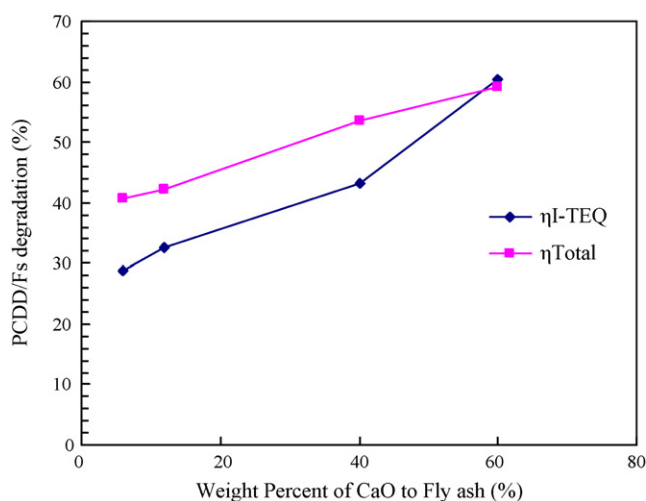

Fig. 2. Degradation efficiency dependence of the ratio of CaO during MC treatment.

basis of actual FA but not for mixture of FA and CaO:

$$\eta_{S\text{(total-concentration)}} = \frac{C_{\text{FA1}} - C_S}{C_{\text{FA1}}} \times 100\%, \qquad S = 1, 2, 3, 4 \tag{1}$$

$$\eta_{S\text{(ITEQ-concentration)}} = \frac{C'_{\text{FA1}} - C'_S}{C'_{\text{FA1}}} \times 100\%, \qquad S = 1, 2, 3, 4 \tag{2}$$

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

It showed that the curve for I-TEQ curve was steeper than that of total concentration. Some literatures [7,9] 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 PCDD/Fs with CaO in milling resulting in this phenomenon.

3.1.2. The degrees of chlorination for PCDD/Fs in MC treated sample and no treated sample

Many previous literatures [7,9,11] shown that the dechlorination mechanism was mainly engaged in degradation of chlorinated organic compounds. To see how far the chlorination of PCDD/Fs has proceeded, we calculated the degree of chlorination of PCDD/Fs d_c by Eq. (3), which is defined as the sum of the products of the mole fraction f_j and the number of

Table 4
Degrees of chlorination of PCDD/Fs for MC treated sample and original sample

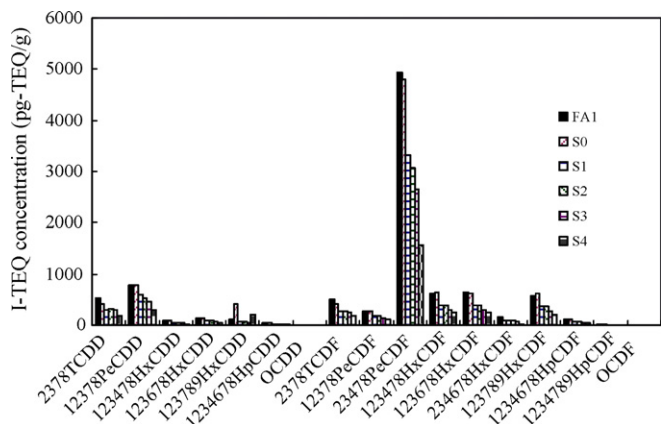|	
FA1	6.05
S0	6.02
S1	5.88
S2	5.82
S3	5.87
S4	5.85

Fig. 3. PCDD/Fs toxic congener pattern of concentration resulting from MC Treatment under desired the CaO dosage in comparison to the original pattern of FA1.

chlorine atoms n_j for each homologue:

$$d_c = \sum_{j=4}^{8} f_j n_j \qquad (3)$$

The results in Table 4 show that the degrees of chlorination vary from 6.05 for original FA to 5.82 for CaO% = 12%. Note the d_c for FA1 and S0 are exhibited similar value as well as which for the milled products, and the d_c slightly decreased after MC treatment. Though the reduction of d_c was not so great, it still can be concluded from the data that (1) the dechlorination reaction occurs in the degradation mechanism and (2) the ratio of CaO influence little on the extent of de-chlorination of PCDD/Fs for MC treatment.

3.1.3. Resulting toxic congener patterns

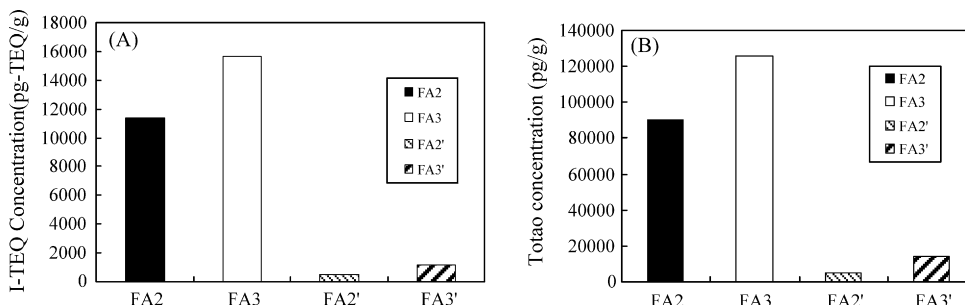See Fig. 3, the 2,3,7,8-substituted PCDD/Fs congener patterns resulting from the MC treatment were very similar.

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.

3.2. MC treatment for FA without addition of CaO

3.2.1. Degradation behavior of the two types of fly ash

The change of total and I-TEQ concentration of PCDD/Fs for the two types of FA were illustrated in Fig. 4. After MC treatment, the 95.33% of total and 94.22% of I-TEQ concentration were reduced for FA2 as well as 92.76% and 88.60% for FA3. Comparing with that of test I, the degradation efficiency for PCDD/Fs of test II was considerably increased. Provided CaO content is an essential factor to influence the degradation reaction, that of FA2 and FA3 are respectively 23.19% and 27.31% which can be equivalent to the Ca content of S3 in test I. However, the degradation efficiency of former two FA was significantly higher than that of the lag one. There should be some other decisive factors to contribute the increase of degradation, such as rotational speed and FA composition.

3.2.2. Effect of rotational speed on degradation

The increase of rotational speed from 350 rpm (test I) to 400 rpm (test II) can be a most important reason to explain why the degradation efficiency for PCDD/Fs greatly increased. It also can be verified by the study of Mio et al. [10], who found the relationship between dechlorination rate of PVC and the impact energy of the colliding balls during milling (Eqs. (4)–(6)), where E is the specific impact energy of the balls (J/(s g)), v_j the relative velocity (m/s) between two colliding balls or a ball colliding against the mill wall, m the mass of a grinding media (g), n the number of collisions within a second (s^{-1}), W the weight of the sample charged into the mill pot (g), C_r is PVC remaining, t is MC treatment time (h), K_d the dechlorination rate of PVC (s^{-1}), E_0 is minimum specific impact energy for dechlorinating PVC (J/(s g)) and A is gradient (g/J) [10]:

$$E = \sum_{j=1}^{n} \frac{1}{2W} m v_j^2 \qquad (4)$$

$$C_r = \exp(-K_d t) \qquad (5)$$

Fig. 4. PCDD/Fs I-TEQ concentration (A) and total concentration (B) resulting from MC treatment on FA2′ and FA3′ without addition of CaO in comparison to that of FA2 and FA3.
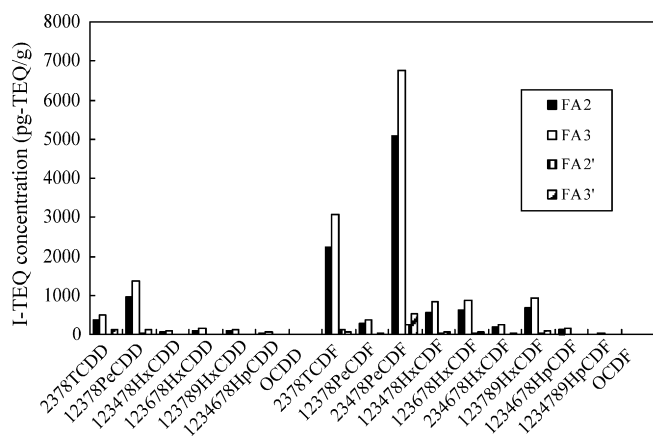
Fig. 5. PCDD/Fs toxic congener pattern of concentration resulting from MC treatment on FA2′ and FA3′ without addition of CaO in comparison to the original pattern of FA2 and FA3.

$$K_d = A(E - E_0) \tag{6}$$

Comparably speaking, the theory proposed by Mio et al. may be introduced to explain the sharp increase in degradation efficiency of test II, namely, the degradation rate of PCDD/Fs was greatly increased as the impact energy of the balls increasing which directly correlates with rotational speed.

3.2.3. Resulting toxic congener patterns for test I

The PCDD/Fs toxic congener patterns resulting from the MC treatment on the two types of fly ashes were very similar (Fig. 5). For specific congeners, the degradation of PCDD/Fs for FA2 was generally higher that of FA3, though both types of FA were MC treated in the same condition. The degradation efficiencies for both FA were not exhibited as expectation based on the CaO content for respective FA. As some other metal oxides and high percent of Carbon contained in FA, all these factors may together influence the MC reaction.

3.2.4. Dechlorination and destruction behavior differences of the two types of fly ash

The degree of chlorination for PCDD/Fs of the two FA after MC treatment was also calculated by Eq. (3), which showed the opposite trend (Table 5). As the degree of chlorination for FA2 increased after MC treatment, therefore the destruction of PCDD/Fs may mainly contribute to the degradation mechanism, while that for FA3 decreased after MC treatment, which demonstrated dechlorination of PCDD/Fs may engage in the degradation mechanism.

Table 5
Degrees of chlorination of PCDD/Fs for MC treated FA and no-treated FA

FA2	4.86
FA2′	6.51
FA3	4.86
FA3′	4.53

3.3. Degradation mechanism

The fundamental experiments by Hagenmaier et al. [14] raised the question about whether destruction and dechlorination of PCDD/F occur simultaneously or if PCDD/F are dechlorinated prior to destruction. In study of MC treatment, tetra-through heptachlorodibenzodioxins and -furans produced from OCDD/Fs were observed to peak at the same time [7]. 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 PCDD/Fs may be cleavage of the dibenzodioxin/furan structure, that is, MC treatment of PCDD/F produced intermediates, such as chlorinated phenols and quinines [7].

Experiments from the present study confirmed that degradation and dechlorination simultaneously occur; the pathway of cleavage of the dibenzo-*p*-dioxin and furan structure is still the further focal point in future study.

4. Conclusions

The results obtained in this study demonstrated that (1) under two test conditions of with and without CaO, PCDD/Fs contained in real fly ash both can be degraded by Mechanochemical treatment, (2) under condition of blending with CaO, the degradation efficiency of PCDD/Fs increased with increasing ratio of CaO, (3) the degradation efficiency of PCDD/Fs may increase with rotational speed increasing and (4) the destruction and dechlorination are major mechanism for PCDD/Fs degradation.

Experiments from the present study confirm that the PCDD/Fs of real fly ash can be directly degraded by MC treatment. The effects of characteristic of fly ash on PCDD/Fs degradation by MC treatment shall be evaluated by future study.

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