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Hydrodechlorination/detoxification of PCDDs, PCDFs, and co-PCBs in fly ash by using calcium polysulfide

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ABSTRACT

Dioxins like polychlorinated dibenzo-*p*-dioxins (PCSDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) are mainly emitted from waste incinerators (WIs) and have become an international research focus because of its serious concerns over the adverse health effects. The detoxification of PCCDs/Fs and PCBs is very difficult because of their stable chemical structure. A significant hydrodechlorination/detoxification of polychlorinated 1-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) were achieved in fly ash by using an aqueous mixture of calcium hydroxide and sulfur. Two different fly ashes were studied: originating from municipal waste incinerator (FA1) and industrial waste incinerator (FA2). They were heated with the aqueous mixture at 150 °C for 30 or 60 min with agitation. Higher decomposition (87%) and detoxification (87.7%) of PCDD/Fs and PCBs were achieved at 150 °C with two runs; every run was for 30 min, compared to one run for 60 min. FA2 gave higher decomposition and detoxification as compared to FA1, which might be due to higher metal content that played a catalytic role to decompose and detoxify the PCDDs, PCDFs and PCBs. The decomposition and detoxification of PCDFs in fly ash was higher than PCDDs and was augmented with increasing number of chlorides on aromatic compounds. As the highly significant decomposition and detoxification of higher concentration of PCDD/Fs and PCBs were achieved in 1 hour without additive catalyst and at low temperature of 150 °C, therefore, the developed method is cost effective and most suitable to apply on commercial/industrial level. The detail results of hydrodechlorination/detoxification of PCDD, PCDFs at different conditions are described and its mechanism is discussed.

1. Introduction

Dioxins like polychlorinated dibenzo-p-dioxins (PCSDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) have become an international research focus during the past 20 years because of its serious concerns over the adverse health effects. PCDDs and PCDFs, which are formed and released unintentionally from anthropogenic sources, are 2 of the 12 prior controlled persistent organic pollutants (POPs) by Stockholm Convention (UNEP, 2005). The waste combustion incinerators were considered as the "No. 1" sources in many European countries and Japan in 1990s. The U.S. EPA has set a limit of 0.00003 micrograms of dioxins per liter of drinking water (ug/L). The Food and Drug Administration recommends not eating fish and shell fish with more than 50 parts per trillion (50 ppt) of dioxins (ATSDR, 1999).

Among all of the possible sources of PCDDs, PCDFs and PCBs, waste incinerators (WIs) have been considered as one of the main emission sources since 1977 (Olie et al., 1977). Moreover, these compounds formed from WIs are mainly adsorbed on the fly ash (Hartmut et al., 2001). Consequently, the fly ash was considered as a hazardous solid waste that may cause severe environmental pollution.

Developing an efficient method to degrade the virulent PCCDs/Fs and PCBs is necessary for environmental protection. Much more concern has been focused on identifying suitable disposal methods for PCCDs/Fs to avoid the catastrophic environmental pollution (Dobbs and Grant, 1979; Crosby et al., 1971; Bunge et al., 2003; Hagenmaier et al., 1987; Schetter et al., 1990). However, the detoxification of PCCDs/Fs and PCBs is very difficult because of their stable chemical structure, trace concentration in environmental samples, and interference with other co-existent halogenated pollutants with higher concentrations. In case of biodegradable methods for the detoxification of PCCDs/Fs lower detoxification efficiency and longer periods are the common limitations. Even some chemical detoxification processes can cause severe secondary pollution because of the use of large amounts of organic solvents and metals. Hydrodechlorination is an effective alternative procedure for decomposing chlorinated organic wastes under

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relatively mild conditions without the formation of the toxic by-products (Ishida et al., 1996). Catalytic dechlorination with noble-metal and transition-metal catalysts is an especially simple and efficient method. Molecular hydrogen is often used as a hydrogen source in the catalytic dechlorination, and also hydrogen-transfer reactions using hydrogen donors such as alcohols and formats have been studied extensively (Pekek et al., 1995).

In recent years, catalytic hydrodechlorination methods have been developed including transfer hydrogenation by means of hydrogen donors such as metal hydrides, (Vogg et al., 1987) formic acid and its salts and alcohols, (Schetter et al., 1990; Hagenmaier et al., 1987) which use water or methanol as solvents. The practical application of catalysts to the dechlorination of organic halides is always accompanied by the problem of the deactivation of the catalyst (Alonso et al., 2002).

Researchers demonstrated that, under oxygen deficiency, the destruction of PCCDs/Fs and other chlorinated aromatics is a general property of fly ash from waste incineration processes (Johnstone et al., 1985; Hagenmaier et al., 1987). It is well known that both halogenation and dehalogenation reactions are catalyzed also by fly ash at elevated temperatures and proceed simultaneously on the fly ash surface (Hutchins et al., 1989; Aresta et al., 2005; Tundo et al., 2001; Hitchman et al., 1995; Pekek et al., 1995). The authors have proved that hydrodechlorination/hydrogenation of PCCDs/Fs and other chlorinated aromatic compounds on fly ash are catalyzed under certain conditions (Ishida et al., 1996; Trumpf et al., 1998; Zook and Rappe, 1994). An effective hydrodechlorination method for dioxins with supported palladium catalysts at 82 °C in isopropanol on fly ash has been reported (Ukisu and Miyadera, 2004). A number of methods are reported for the decomposition of PCCDs/Fs (Tundo et al., 2001) and PCBs (Ohno et al., 1997; Noma et al., 2003) in fly ash, especially the catalytic reductive methods with noble-metal catalysts in organic phase. Recently, Mitoma and coworkers reported that the dechlorination of PCCDs/Fs proceeds efficiently at room temperature using calcium in ethanol under atmospheric pressure and that this procedure decreases the toxicity of PCCDs/Fs (Mitoma et al., 2004).

In previous studies carried out by Ghaffar et al., significant hydrodechlorination of di-chlorobenzene (47%), tri-chlorobenzene (60%) hexa-chlorobenzene (74%), p-nitrochlorobenzene (60%) p-chloroanisole (65%), chloronaphthalene (75%), 2,4,5 trichlorobiphenyl (87%) DDT (94%) and TCP (97%) were achieved on fly ash by using mild conditions (Ghaffar and Tabata, 2009–2010; Ghaffar et al., 2012). As the PCDDs, PCDFs and co-PCBs are most persistent and stable pollutants generated in the fly ash and there is a need of an environment friendly technique to treat these pollutants. Therefore, research was extended to hydrodechlorinate/detoxify the PCDDs, PCDFs and co-PCBs in fly ash at low temperature under mild reaction conditions. Fly ashes were taken from municipal waste and industrial waste incinerator. A significant concentration and toxicity of PCDDs, PCDFs and PCBs in studied fly ashes were reduced. The most attractive point of our present studies are achieving of higher dechlorination of PCDDs, PCDFs and PCBs at low temperature without using organic solvent and metals as such in water media.

2. Experimental

Two types of fly ashes were used for our studies. Fly ash (FA1) was taken from municipal waste incinerator and fly ash (FA2) was taken from industrial waste incinerator used for combustion of materials wasted from general industries. The experiments were conducted in a 20 dm^3 reaction vessel (SS) provided with an agitator (150–2000 rpm), pressure gauge and an electric heating jacket provided with a digital temperature controller (200 °C max.).

FA1 (4000 g) containing PCDDs, PCDFs and co-PCBs (conc. 248.6 ng/g and 1.97 ng TEQ/g) was treated with calcium hydroxide (1000 g) and sulfur (1000 g) in water (10 dm^3) used as reaction media and was heated at 150 °C for 30 min (Method A). FA2 (4000 g) containing PCDDs, PCDFs, co-PCBs (conc. 2522 ng/g and 49.43 ng TEQ/g) was treated with same concentration of calcium hydroxide, sulfur in water under same experimental condition as were applied for FA1. But in case of FA2 containing high concentrations of PCDDs, PCDFs and co-PCBs, the reaction mixture was heated with three different methods (Method A, B, and C). Method A: reaction mixture was heated at 150 °C continuously for 30 min and cooled to room temperature. Method B: reaction mixture was heated at 150 °C continuously for 60 min and cooled to room temperature. Method C: reaction mixture was first heated at 150 °C for 30 min, cooled to room temperature and then again heated at 150 °C for 30 min and cooled to room temperature by natural cooling.

The resultant products were extracted through a general procedure applied for cleanup of PCDDs, PCDFs and *co*-PCBs (JISC, 1999; JME, 2003). The reaction mixture was poured into 100 cm^3 of 1 M nitric acid and then was extracted twice with 100 cm^3 of dichloromethane under vigorous shaking. After being separated from the aqueous layer, the combined organic phases were washed with distilled water until the pH of the aqueous layer became 7. The dichloromethane layer was dried by anhydrous $MgSO_4$, then filtered, and concentrated to 10 cm^3.

Hydrodechlorinated products were determined in Saga Environmental Science Inspection Foundation at Saga, Japan by the standard method according to the notification 80 of Ministry of the Environment, Japan (2004) that regulates the analytical method of dioxins in fly ashes in incinerator regarding sampling, pretreatment of samples, identification and quantitative determination, allowable errors (JME, 2004) and calculation of toxicity, etc.

2.1. Analysis of PCDDs and PCDFs

The GC–MS analysis of PCDDs and PCDFs was performed on an HP 6890 series gas chromatograph (Hewlett–Packard) equipped with a 60 m SP-2331 (i.d. 0.25 mm, 0.20 μm film thickness) (Supelco) and JMS-700 series (JEOL). The program and pressure of GC was as follows: the initial temperature of the column was 170 °C and held for 1 min (270 kPa), and then the temperature was increased at a rate of 20 °C/min (14 kPa/min) up to 210 °C (298 kPa). The rate was changed to 2 °C/min (1.4 kPa/min) up to 255 °C (336 kPa), and the temperature was held for 5 min. The temperature of the column was then increased by 40 °C/min (100 kPa/min) up to 260 °C (500 kPa), where the temperature was maintained for 20 min. The injection was performed by a splitless mode. The temperatures of the injection port and the ion source were 265 °C and 250 °C, respectively and the carrier gas was He (99.9999%). The ionization energy and current were 45 eV and 600 μA with the resolution of 10,000. The general procedure for the assignment and quantitative determination and details of the cleanup spikes and syringe spike as internal standards for all isomers of PCDDs and PCDFs by HRGC-HRMS are related to relevant regulations (JISC, 1999; JME, 2003, 2004). Calibration curve was made by using standard solutions (WELLIGTON, USA) of PCDDs or PCDFs at different molar ratio of C12 to C13, and a 500 pg of internal standard involving C13-PCDDs or C13-PCDFs was added to the samples. The difference at clean-up spikes and syringe spikes were 60–98% that is within the range of 50–120% ruled by the notification 80 of Ministry of the Environment, Japan (JME, 2004). The recoveries of PCDD/Fs and PCBs were checked from repeated measurements of same samples and the relative errors are 1% for GC/MS and lower than 20% for all the processes, respectively.