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Chemosphere

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# Mechanochemical degradation of hexabromocyclododecane and approaches for the remediation of its contaminated soil

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## ARTICLE INFO

### Article history:

Received 26 September 2013  
Received in revised form 3 February 2014  
Accepted 9 February 2014  
Available online xxx

### Keywords:

Hexabromocyclododecane  
Mechanochemistry  
Ball mill  
Degradation  
Soil remediation

## ABSTRACT

Hexabromocyclododecane (HBCD) has been listed in the Stockholm Convention for elimination due to its persistent and accumulative properties. In consideration of its sound disposal, mechanochemical (MC) method was employed using different co-milling reagents. Fe–Quartz was proven to a good reagent for HBCD destruction achieving both good degradation efficiency and high yield of bromide. The absence of organic matters after MC treatment was demonstrated by thermogravimetry and GC–MS analysis, indicating the complete degradation of HBCD and its conversion into inorganic compounds. No obvious intermediates could be detected due to the swift and spontaneous reaction between HBCD and Fe–Quartz. FTIR and Raman spectra further showed that the organic structures in HBCD were broken down while amorphous and graphite carbon were obtained as another final product besides bromide. After the successful destruction of HBCD, approaches to remediate its contaminated soil were also carried out. Fe–Quartz was also proven to be the best reagent for HBCD degradation in Kaolin, while CaO showed better performance for the remediation of HBCD contaminated Krasnozern. For practical application, preliminary experiments are necessary in order to select a suitable co-milling reagent and a proper milling time depending on the differences in soil properties and HBCD concentration.

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## 1. Introduction

Hexabromocyclododecane (HBCD or HBCDD) is a frequently used brominated flame retardant (BFR) and mostly applied in polystyrene-based building materials for thermal insulation, i.e. expanded polystyrene (EPS) and extruded polystyrene (XPS) (de Wit, 2002). It was estimated that the production of HBCDs in 2011 was 28000 tons and the main market share was in Europe and China (UNEP, 2013). With the widespread use, HBCD has been frequently detected in the environment and very high levels have been found near the e-waste dismantling sites (Gao et al., 2011) or producing and using places (Li et al., 2012; Eguchi et al., 2013). Human exposure of HBCD has also been evidenced from its presence in breast milk, adipose tissue and blood (Covaci et al., 2006). Due to its persistent and accumulative properties, HBCD is of particular concern since the increasing levels might lead to toxic effects in human and wildlife (Marvin et al., 2011). It is not surprising that HBCD was identified as a substance “of very high concern” in 2008 and added into the REACH authorization list in 2010 by European Chemicals Agency. Later in May 2013, HBCD

was listed in the Annex A of Stockholm Convention on Persistent Organic Pollutants (POPs) for elimination from the market.

Addressing the ban of HBCD, its stockpiles, highly contaminated wastes and soil need to be disposed soundly. High temperature incineration is the most commonly applied method for the disposal of such chemicals. However, recent studies have shown the release of toxic PBDD/Fs as byproducts from the combustion of BFRs containing wastes (Barontini and Cozzani, 2006; Duan et al., 2011). Comparatively, mechanochemical (MC) destruction has been identified as a promising non-combustion technology for the disposal of solid wastes containing POPs (Rowlands et al., 1994). As a low temperature reaction, it can normally avoid unintentionally produced POPs such as PCDDs/Fs (Guo et al., 2010). There have already been many successful studies on the MC destruction of chlorinated POPs such as DDT (Hall et al., 1996), PCBs (Nah et al., 2008) and PCDD/Fs (Mitoma et al., 2004). Therefore it might also be an alternative method to be applied for HBCD destruction.

In MC treatment, pollutants are first mixed with reactive reagents and placed into a ball mill machine. During milling, marked chemical activation and radicals will be produced by mechanic force (Gilman, 1996), resulting in chemical reactions between the reagents and pollutants. The co-milling reagent is

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one of the most important influencing factors for MC reaction. The first reported co-milling reagent for POPs degradation was CaO (Rowlands et al., 1994) and later it became the mostly used one. Quartz sand was also found to be a good reagent for MC remediation of POPs contaminated soil and used in practical application by a New Zealand company (E.D.L., 2013). Our previous study showed that zero-valent iron also had a good performance in the degradation of pentachloro-nitrobenzene (PCNB) (Zhang et al., 2011). Additionally, Fe–Quartz was recently proven to be even a better reagent compared with CaO when applied for the degradation of tetrabromobisphenol A (TBBPA) and mirex (Zhang et al., 2012; Yu et al., 2013).

In the present work, the MC degradation of industrial HBCD was performed using different co-milling reagents, aiming at the disposal of HBCD stockpiles or highly contaminated solids. The decomposition efficiency was evaluated combined with the identification of the degradation process. Further perspectives on MC remediation of HBCD contaminated soil were also assessed. Kaolin and Krasnozem (red soil) were used and different co-milling reagents were added to evaluate their influences on the remediation effects.

## 2. Materials and methods

### 2.1. Materials

1,2,5,6,9,10-Hexabromocyclododecane (HBCD,  $C_{12}H_{18}Br_6$ , 99%) was purchased from Tokyo Chemical Industry Co. (TCI, Japan). Reactive iron powder (Fe, 98%) and quartz sand (99.8%) was obtained from Sinopharm Chemical Reagent Co. (SCRC, China). Calcium oxide (CaO, 98%) was purchased from Beijing Modern Eastern Fine-Chemical Co. (China) and was heated at 800 °C for 2 h before use. Kaolin and Krasnozem were purchased from the National Information Center for Certified Reference Materials (China). The Krasnozem was composed of 20.1 wt% sand, 43.2 wt% silt and 36.7 wt% clay, with 14.6 g kg<sup>-1</sup> organic carbon, less than 1% water content and 8.35% hematite (Fe<sub>2</sub>O<sub>3</sub>). All solvents (*n*-hexane, acetone) used in the study were of HPLC grade (J.T. Baker Inc., USA) and the ultrapure water was produced by a Milli-Q system (Millipore, USA). The contaminated soils were artificially prepared for a final HBCD concentration of 500 mg kg, during which the HBCD was stepwise mixed with the standard soils in a low speed ball mill to obtain a homogenous contamination.

### 2.2. MC experiments

The MC experiments were carried out using a planetary ball mill (QM-3SP2, Nanjing University Instrument Corporation, China). Four stainless steel pots with the volume of 100 mL and 45 balls with a diameter of 9.60 mm were used in the machine. During the MC destruction of HBCD, 5.5 g different reagents (CaO, Quartz, Fe and Fe–Quartz 10:1) were respectively mixed with 0.5 g HBCD powder and placed into the machine. For the MC experiments on HBCD contaminated soil, 1.0 g different reagents (CaO, quartz, Fe–Quartz or without reagent) were mixed with 3.0 g soil sample and subjected for milling. The revolution speed of the planetary disk was set as 275 rpm for a specific time and the rotation direction was changed automatically every 30 min.

### 2.3. Samples extraction

Although Soxhlet method is considered efficient for the extraction of HBCD from solid phase, given the high concentration of HBCD in the samples, the sonication was used as an alternative for the extraction in this study. For the MC destruction of HBCD,

0.05 g of the milled sample was extracted in 50 mL hexane and acetone (1:1, v/v) with a 15 min ultrasonic treatment. After that, the solution was centrifuged at 3000 rpm while the supernatant was collected and filtered by 0.22 μm polytetrafluoroethylene (PTFE) filter. In the experiments applied on soil, 1.0 g of the milled sample was taken and extracted using the same procedure, followed by an extra clean-up and concentrating process before analysis. In order to show the recoveries of HBCD during analysis, control tests on non-milled samples and spiking experiments on Kaolin and Krasnozem (low concentration – 50 mg kg<sup>-1</sup>, high concentration – 300 mg kg<sup>-1</sup>) were also conducted.

For the extraction of the bromides formed, a similar extraction procedure was applied as for HBCD, but using 50 mL ultrapure water as the extraction solvent.

### 2.4. Sample analysis and characterization

The determination of residual HBCD was carried out using a GC–MS system (Shimadzu GC–MS, QP-2010 Plus, Japan) equipped with a DB-5MS capillary column (15 m × 0.25 mm × 0.1 μm). Helium (99.999% purity) was used as the carrier gas at a flow rate of 1.5 mL min<sup>-1</sup>. The oven temperature was programmed from 60 °C (held for 1 min) to 200 °C at 15 °C min<sup>-1</sup>, and to a final temperature of 300 °C (held for 5 min) at 10 °C min<sup>-1</sup>. The injection temperature was set as 200 °C while the ion source (negative chemical ionization) and interface temperature were set as 230 °C and 280 °C respectively. The water soluble bromide was determined by ion chromatography (IC, DX-2000, DIONEX Co., USA) using an IonPac AS4A-SC anion exchange column (4 × 250 mm).

Besides the instrumental determination described above, the HBCD milled samples were also characterized by multiple approaches to show the changes of the chemical composition. Thermogravimetry (TG) curves were recorded using a simultaneous thermal apparatus (TGA/DSC, Mettler Toledo, Switzerland), with 20 mg sample, 25–800 °C temperature range, 15 °C min<sup>-1</sup> heating rate and nitrogen flow. Microscopic Confocal Raman Spectrometer (RM 2000, Renishaw Co., UK) was used with 514.5 nm Ar-laser beam and scan range from 400 cm<sup>-1</sup> to 2200 cm<sup>-1</sup>. The milled samples were also analyzed by Fourier transform infrared (FTIR) spectrometer (Nicolet 6700, Thermo Fisher Scientific, US) with the KBr disk method from 200 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>.

## 3. Results and discussion

### 3.1. Comparison of different co-milling reagents

For the selection of an appropriate co-milling reagent, the MC destruction of HBCD was performed using CaO, quartz sand, iron powder (Fe) and iron combined with quartz sand (Fe–Quartz) respectively. In each case the residual HBCD and the bromide ions were determined (as shown in Fig. 1).

As shown in Fig. 1a, MC treatment is proven to be an effective method for HBCD destruction, while the co-milling reagent is an important factor that significantly affects the process efficiency. Milling with different reagents, the residual HBCD decreased consistently to almost complete destruction after 4 h except for the case of using quartz sand only. Fe–Quartz was proved to be best reagent while the traditionally used CaO was less effective for HBCD destruction. When using quartz only, the destruction rate of HBCD was high in the first hour but decreased quickly during further milling. However, inverse behavior was noticed when using iron powder: the HBCD destruction rate was quite low during the first hour, while later increased leading to a very fast and efficient degradation.

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