EFFECTS OF ZERO-VALENT METALS ON THE MECHANOCHEMICAL DESTRUCTION OF DECHLORANE PLUS WITH QUARTZ SAND

Wang HZ, Huang J*, Zhang KL, Yu G, Deng SB, Wang B

State Key Joint Laboratory of Environment Simulation and Pollution Control (SKJLESPC), School of Environment, POPs Research Center, Tsinghua University, Qinghuayuan, Haidian,Beijing 100084, P.R. China

Introduction

Dechlorane Plus (DP; CAS No. 13560-89-9) is a chlorinated flame retardant used in polymer additives for protective coating of electrical wires and cables, computer connectors, and plastic roofing material in polymeric systems[1]. DP was first detected in the environment by Hoh et al. in 2006[2], they found that the sludge of the North American Great Lakes contained high concentration of DP, indicating DP may possess characteristics of Persistent Organic Pollutants (POPs). This is consistent with the reported property of DP including degradation, easy bioaccumulation, and high toxicity[3, 4]. Later more studies revealed that DP can be found in various media like air, sludge, house dust, tree bark, and gull eggs across North America and Asia[5,6]. These reports further confirmed that DP might be a remarkable potential POPs candidate.Therefore, it's necessary to explore the destruction method of DP.

Considering the possible formation and subsequent release of dioxins from the incineration disposal of chlorinated POPs waste, non-combustion technologies have received wide attention in recent years. Among various strategies investigated, mechanochemical destruction has been identified as a promising technology for the non-combustion disposal of POPs contaminants, due to its advantages in effectiveness and safety in terms of preventing secondary pollution[6].Such as, the mechanochemical destruction has been successfully used to destroy PCNB, TBBPA and Mirex when co-grinding with iron powders and quartz sand in a planetary ball mill due to the high reducing potential[7-9].

Therefore, In the present study, we investigated the feasibility of applying mechanochemical destruction to solid-state DP employing co-grinding strategy. Various zero-valent metal powders (Al, Zn and Fe) were compared for the destruction efficiency of DP coground with quartz sanda planetary ball mill. The most efficient process was then optimized for its operational parameters including charge ratio of materiel and grinding media.

Materials and methods

DechloranePlus 25 (99% in purity) was purchased from Jiangsu Anpon Electrochemical Co., Ltd(China). Aluminum powder, zinc powder, iron powder (Al, Zn, Fe, ≥98% in purity), and quartz sand (SiO_2, ≥99.8% in purity) were obtained from Sinopharm Chemical Reagent Co., Ltd (China). A planetary ball mill (QM-3SP2, Nanjing University Instrument Corporation, China) was used in all experiments. A stainless 80mL vial was filled with stainless balls in diameter of between 5mm and 10mm, which serve as the milling medium. Zero-valent metal (Al, Zn, Fe) and quartz sand were individually screened as reactive chemicals during ball milling of DP. They were mixed with DP with weight ratio of 11:1 (8.25 g $Al+SiO_2$, $Zn+SiO_2$ or $Fe+SiO_2$ and 0.75 g DP). The total mass of powder mixture was 9 g and the balls-to-powder mass ratio was 20:1. The mixture was placed in the covered stainless vial containing balls in ambient air and then milled using a high energy mill. The planetary ball mill was operated at a speed of 275 rpm and the rotation direction changed automatically every 30 min.

One portion (0.01g per batch) of each milled mixture was ultrasonically extracted with hexane, and centrifugalized at 3000 rpm for 15min to remove any solids from the extraction. DP and possible chlorinated degradation products were analyzed using an Aglient 6890 plus gas chromatography equipped with a microelectron capture detector (GC/µECD; Agilent, USA) and a DB-5MS capillary column (30m×0.25mm×0.25µm).Nitrogen (99.999% in purity) was used as carrier gas at a constant flow of 34.5 mL/min.All solvents (methanol, hexane and acetone) used in for extraction and clean-up were of HPLC grade or higher (J.T.Baker Inc., USA).

Another portion (0.05g per batch) was used for the determination of residual chloride content after the mechanochemical dechlorination of DP. The sample was ultrasonically agitated in 50mL deionized water at 60°C for 30 min, and centrifugalized at 3000 rpm for 15 min. The separated solid residue was extracted twice for complete extraction of inorganic contents. The combined solution was concentrated (in nitrogen blow) was analyzed for chloride ions by a DX-1000 ion chromatography (Dionex, USA) equipped with an Ion-Pac AS4A-SC anion exchange column.

Results and discussion

Performance comparison of Al+SiO_2, Zn+SiO_2 and Fe+SiO_2 as reactive chemicals

The ball milling experiments of DP co-ground with Al+SiO_2, Zn+SiO_2 and Fe+SiO_2 respectively were carried out for 1h, the amount of residual DP was measured and summarized in Figure 1. We found that the destruction result of DP was best using Al+SiO_2, with16% and 22%syn- and anti-DP remaining respectively, however, DPs nearly remained intact using Fe+SiO_2. Therefore, the Al+SiO_2 co-grinding process had a better performance for DPs destruction compared with other combinations screened including Zn+SiO_2 and Fe+SiO_2.

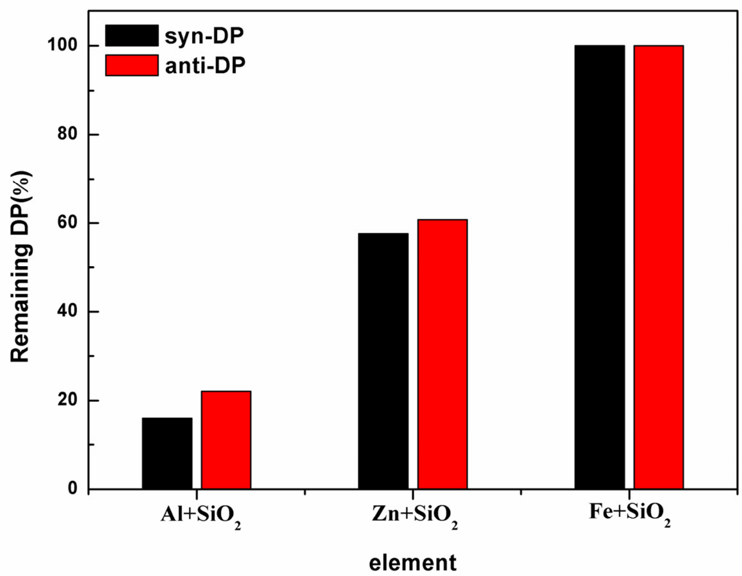

Figure1Different results of remaining DP treated with Al+SiO_2, Zn+SiO_2 and Fe+SiO_2

Effect of charge ratio in mechanochemical reaction

The charge ratio $C_R=m_b/m_p$ is considered to be the determining factor of mechanochemical destruction efficiency, where m_b is the total mass of the balls and m_p is the mass of the added reaction mixture (mass of Al, SiO_2 and DP). The Figure 2 shows the destruction rate of syn-DP with different charge ratio and Al/SiO_2 molar ratio after milled for 1h. The degradation rates increase with the increasing charge ratio. A destruction efficiency of 99% within 1 h grinding is reached for the sample with charge ratio of (40:1). In comparison, samples with the lowest charge ratio (10:1) tested has only reached about 30%syn-DP after same amount of grinding time. However, the effect of different Al/SiO_2 molar ratio was not visible for a charge ratio of 40:1, while it was a significant for charge ratios of 20:1 and 10:1.

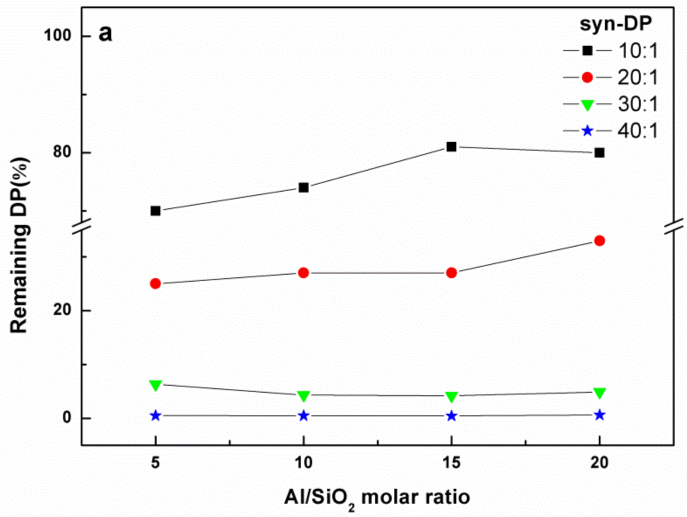

Figure2Change of the remaining syn-DP with different charge ratio in 1h milling time

Effect of molar ratio of Al and SiO_2 in mechanochemical reaction
As mentioned above, the reaction rate at charge ratio of 30:1 and 40:1 is too fast to investigate the degradation process in detail, thus a reasonable charge ratio of 20:1 was selected for subsequent experiments. The degradation of DPs in the experiments with different Al/SiO_2 molar ratio is shown in Figure 3. The results demonstrate that the remaining DP decreased sharply first and then increased slowly with extended grinding time. The optimal region of molar ratio is between 0.63:1 and 5:1.

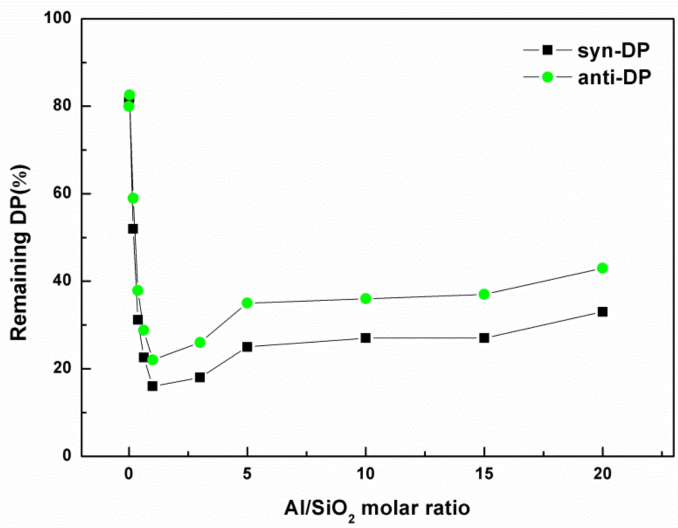

Figure3Change of the remaining DP with different Al/SiO_2 molar ratio in 1h milling time

Effect of dechlorination and syn/anti change in mechanochemical reaction
An important evaluation parameter for verifying the degradation of organochlorine compounds using non-combustion technologies is the amount of chloride generated during destruction process. Both chloride

generation and DP degradation were monitored for a set of experiments with fixed ($Al+SiO_2$)/DP weight ratio of 11:1 and fixed Al/SiO_2 molar ratio of 1:1, and the results are shown in Figure 4. We have shown soluble chloride ions increases with the increase of grinding time and decrease of DP, it reaches 80.6% after 4h milling where the DPs maximum destruction rate of 99.9% has been reached. The high chloride yield verifies that dechlorination is the major degradation mechanism of DP mechanochemical destruction. However the chloride content recovered is lesser than the amount of degraded DP, this is consistent to the observation described by Hall et al. (1996)[11].

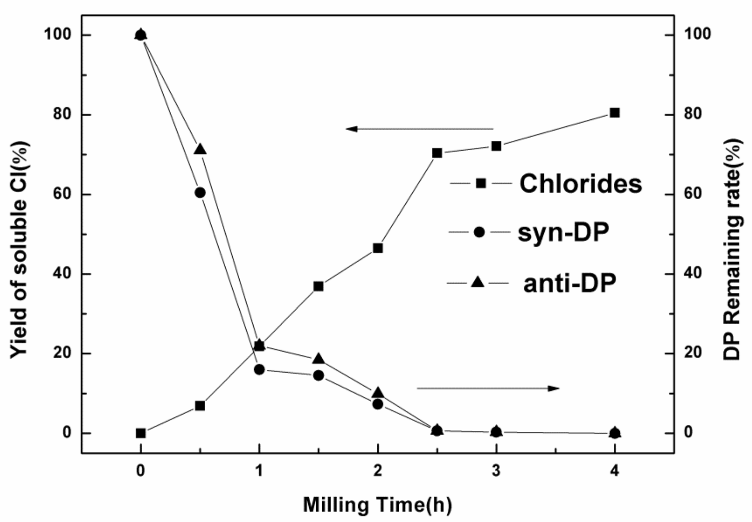

Figure4syn/anti-DP remaining ratio and chlorides change with ball milling time

Acknowledgements
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