

Kinetics of reductive dechlorination of 1,2,3,4-TCDD in the presence of zero-valent zinc

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Abstract

Polychlorinated dibenzo-*p*-dioxins (PCDDs) are toxic and widespread persistent organic pollutants (POPs). Cost-effective technologies for destroying or detoxifying PCDDs are in high demand. The overall purpose of this study was to develop a zero-valent zinc based technology for transforming toxic PCDDs to less- or non-toxic forms. We measured the dechlorination rates of 1,2,3,4-tetrachlorodibenzo-*p*-dioxin (1,2,3,4-TCDD) in the presence of zero-valent zinc under aqueous conditions, identified the daughter compounds of the reaction, and constructed possible pathways for the reactions. The reaction rates of daughter compounds with zero-valent zinc were also measured independently. Our results showed that the zero-valent zinc is a suitable candidate for reducing PCDDs. Reductive dechlorination of 1,2,3,4-TCDD was stepwise and complete to dibenzo-*p*-dioxin (DD) mainly via 1,2,4-trichlorodibenzo-*p*-dioxin (1,2,4-TrCDD), 1,3-dichlorodibenzo-*p*-dioxin (1,3-DCDD), 1-chlorodibenzo-*p*-dioxin (1-MCDD) to DD and via 1,2,4-TrCDD, 2,3-dichlorodibenzo-*p*-dioxin (2,3-DCDD), 2-chlorodibenzo-*p*-dioxin (2-MCDD) to DD. In each separate system, the observed half-lives of 1,2,3,4-TCDD, 1,2,3-TrCDD, 1,2,4-TrCDD, 1,2-DCDD, 1,3-DCDD, 1,4-DCDD and 2,3-DCDD are 0.56, 2.62, 5.71, 24.93, 41.53, 93.67 and 169.06 h respectively. The tendency of rate constant follows TCDD > TrCDD > DCDD. Our results suggest that zero-valent zinc is a suitable candidate for rapidly reducing highly chlorinated PCDDs to less or non-chlorinated daughter products.

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1. Introduction

Dioxins and dioxin-like compounds include polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). There are 75 PCDD congeners and 135 PCDF congeners. PCDD/Fs enter the environment mainly through their inadvertent formation during combustion processes and chemical manufacturing. The 17 PCDD/F congeners with chlorines in the lateral 2-, 3-, 7- and 8-positions are the most toxic and regulated of these compounds. Among these, 2,3,7,8-dibenzo-*p*-dioxin (TCDD) is considered the most toxic and, indeed, has been

identified as one of the most toxic compounds on the planet (ATSDR, 1998; Van den Berg et al., 2006). These chemicals are of great health and environmental concern because of their high toxicity, widespread occurrence, and persistence in the environment (ATSDR, 1998). These compounds accumulate in soils and aquatic sediments and their bioaccumulation in fish, meat and dairy products results in deleterious human exposure. It is of particular importance to develop effective remedial technologies to convert these chemicals to non-toxic forms at contaminated sites.

Several remediation technologies have been developed or being developed for treating these chemicals, including incineration and thermal treatment (Gullett et al., 1997; Kasai et al., 2000; Lundin and Marklund, 2005), photolysis (Konstantinov and Bunce, 1996; Konstantinov et al., 2000; Rayne et al., 2002; Choi et al., 2004), photocatalysis

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(Choi et al., 2000), γ -radiolysis (Hilaridles et al., 1994), biodegradation (Ballerstedt et al., 1997; Barkovskii and Adriaens, 1998; Mori and Kondo, 2002; Fennell et al., 2004). Dechlorination using zero-valent metals (Adriaens et al., 1996; Kluyev et al., 2002; Mitoma et al., 2004) has also been reported. Zero-valent metals have been successfully used for the degradation of a variety of chlorinated organic compounds such as chlorinated hydrocarbons (Matheson and Tratnyek, 1994; Johnson et al., 1996; Orth and Gillham, 1996; Roberts et al., 1996; Schlimm and Heitz, 1996; Boronina et al., 1998; Fennelly and Roberts, 1998; Deng et al., 1999; Alessi and Li, 2001), polychlorinated biphenyls (Yak et al., 1999, 2000; Lowry and Johnson, 2004) and chlorinated phenol (Kim and Carraway, 2000). Published research concerning dechlorination of PCDDs using zero-valent metals is also available (Hagenmaier et al., 1987; Adriaens et al., 1996; Kluyev et al., 2002; Weber et al., 2002; Mitoma et al., 2004). An early report by Hagenmaier et al. (1987) indicated that, under oxygen deficient conditions, the octachlorodibenzo-*p*-dioxin (OCDD) was dechlorinated in the presence of copper powder, and the isomer distribution patterns of congeners obtained by the copper-catalyzed dechlorination of OCDD depended upon the temperature and the degree of dechlorination. TCDDs and heptachlorodibenzo-*p*-dioxins (HpCDDs) were formed when the mixture of copper and OCDD was above 150 °C (Weber et al., 2002). Zero-valent zinc was also demonstrated to mediate the reductive dechlorination of PCDDs (Adriaens et al., 1996). In the presence of zero-valent zinc, OCDD was stoichiometrically dechlorinated to hexachlorodibenzo-*p*-dioxins (HeCDD) and pentachlorodibenzo-*p*-dioxins (PeCDDs) under basic and neutral conditions, respectively. Recently, it was found that, under subcritical water condition, zero-valent iron can cause stepwise reductive dechlorination of OCDD and the elimination of chlorine can occur both from 2,3,7,8 and from 1,4,6,9 to less chlorinated congeners (Kluyev et al., 2002). More recently, Mitoma et al. (2004) reported an efficient dechlorination of PCDDs in ethanol using metallic calcium at room temperature under atmospheric pressure. Although all these cited studies provided insight information on the reactions, they were performed under either hot aqueous conditions or in organic solvents. Little is known about the dechlorination of the chlorinated PCDDs by zero-valent metals at ambient temperatures and under aqueous condition. Moreover, the reaction kinetics and detailed pathways of the reactions have not been clearly delineated in the literature.

The objectives of this study were to measure the rates and to elucidate the pathways of the dechlorination of 1,2,3,4-tetrachlorodibenzo-*p*-dioxin (1,2,3,4-TCDD) with zero-valent zinc under ambient temperature and aqueous conditions. Zinc was shown to be very effective for reductive dechlorination of organic contaminants and was thermodynamically more favorable and kinetically more reactive than iron, which is commonly utilized in zero-valent metal applications (Orth and Gillham, 1996; Rob-

erts et al., 1996; Schlimm and Heitz, 1996; Boronina et al., 1998; Fennelly and Roberts, 1998). Zinc was selected in the study as the reductant because the successful treatment of PCDDs could be achieved in mild conditions due to its high electrochemical reactivity. Additional experiments were carried out with 1,2,3- and 1,2,4-trichlorodibenzo-*p*-dioxin (1,2,3-TrCDD and 1,2,4-TrCDD) and four dichlorodibenzo-*p*-dioxins (DCDDs) including 1,2-, 1,3-, 1,4- and 2,3-DCDD to verify the pathways of the dechlorination of 1,2,3,4-TCDD using zero-valent zinc.

2. Experimental section

2.1. Chemicals

Water used in this study was a product of the Milli-Q Plus water system (Millipore Co.). Ten dioxin congeners used in this study included dibenzo-*p*-dioxin (DD), 1-chlorodibenzo-*p*-dioxin (1-MCDD), 2-chlorodibenzo-*p*-dioxin (2-MCDD), 1,2-dichlorodibenzo-*p*-dioxin (1,2-DCDD), 1,3-dichlorodibenzo-*p*-dioxin (1,3-DCDD), 1,4-dichlorodibenzo-*p*-dioxin (1,4-DCDD), 2,3-dichlorodibenzo-*p*-dioxin (2,3-DCDD), 1,2,3-trichlorodibenzo-*p*-dioxin (1,2,3-TrCDD), 1,2,4-trichlorodibenzo-*p*-dioxin (1,2,4-TrCDD) and 1,2,3,4-tetrachlorodibenzo-*p*-dioxin (1,2,3,4-TCDD). They were purchased from the AccuStandard, Inc. (New Haven, CT). Except for 1,2-DCDD which was purchased as a stock solution in toluene, all the congeners were purchased in their solid forms. Hexachlorobenzene (HCB), HPLC-grade hexane and acetone, NaCl, NaH₂PO₄ and Na₂HPO₄ were purchased from Sigma Inc. (St. Louis, MO). All the chemicals were used as received without further treatment.

Metallic zinc (dust) was obtained from Fisher Scientific (Pittsburgh, PA). The specific surface area of the zinc particles (0.1099 m²/g) was measured by employing the nitrogen adsorption method with an ASAP 2010 surface analyzer (Micromeritics Co., USA). The morphology of the particles was observed by DMR-X (Leica, Germany) microscopy with Nikon digital camera DXM 1200F to characterize the size and size distribution of the metal particles. A typical microphotograph is shown in Fig. 1. More than 95% of the metal dust had sizes of 5–35 μ m.

2.2. Preparation of buffer solution and stock solutions

Phosphate buffer (0.1 M) at pH 6.85 was used in all the experiments. The buffer solution was prepared by dissolving appropriate amounts of Na₂HPO₄ and NaH₂PO₄ into Milli-Q water and adding NaCl to adjust the ionic strength to 0.1 M. The solution was stored no more than 7 days in a volumetric flask at 5 °C. Before use, the prepared buffer solution was transferred into a 250 ml serum glass, autoclaved at 121 °C for 20 min, cooled, and then sparged with N₂ gas for about 30 min to remove dissolved oxygen. All the PCDD stock solutions except 1,2-DCDD were prepared with HPLC-grade acetone by introducing appropriate

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