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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, zevo-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, NaH_2PO_4 and Na_2HPO_4 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 ($0.1099 \ m^2/g$) 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 μm.

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 Na_2HPO_4 and NaH_2PO_4 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 N_2 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
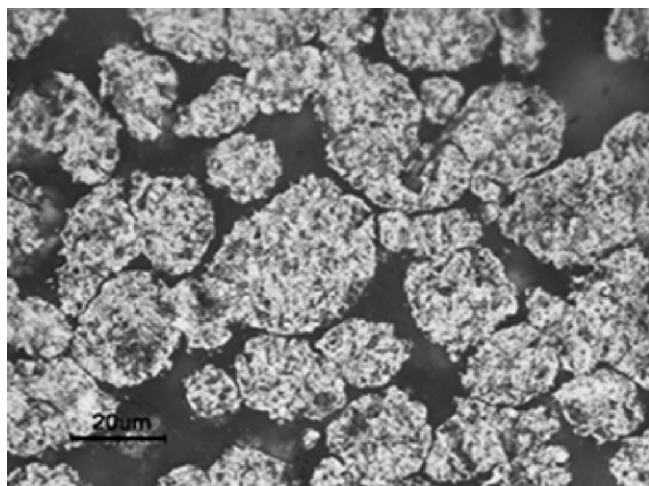
Fig. 1. A typical microphotograph of the metallic zinc under DMR-X microscopy.

amounts of these chemicals in solid forms into volumetric flasks. The 1,2-DCDD stock solution was prepared by transferring an appropriate volume of its toluene solution into a volumetric flask. N_2 gas was used to evaporate the toluene before introducing HPLC-grade acetone. The final concentrations were 34.23, 31.38, 32.53, 44.64, 42.54, 59.76, and 17.45 μM for 1,2,3,4-TCDD, 1,2,3-TrCDD, 1,2,4-TrCDD, 2,3-DCDD, 1,3-DCDD, 1,4-DCDD, and 1,2-DCDD, respectively. All stock solutions were stored in amber bottles with Teflon-lined septa at 5 °C until use.

2.3. Batch experiment

The reductive dechlorination reactions involving each of the seven reactants including a TCDD, two TrCDDs, and four DCDDs were carried out with batch reactors prepared in an anaerobic chamber under an atmosphere of 2.4%H_2 and 97.6%N_2. Amber glass vials (7 ml, SUPELCO, Bellefonte, PA) capped with PTFE lined septa were used as the reactors. In brief, 100 mg (± 0.1 mg) of metallic zinc and 4.8 ml buffer solution were added to each of the prewashed vials. The vials were then spiked with 200 μL of a given acetone stock solution containing a single dioxin congener using a 250 μl-syringe. The initial concentrations of the reactants are listed in Table 1. The vials were capped,

removed from the anaerobic chamber, and placed on a wrist-action shaker for mixing at 22 ± 1 °C and 60 rpm. The reaction times were recorded from the start of mixing. At a designated times between 0−12 h, duplicate reactors were taken out from the shaker, and 1 ml hexane including the internal standard of HCB was added immediately to each reactor. The reactors were capped, and mixed on a mixer for 3 min to extract the reactant and the products from both the aqueous and the solid phases. After mixing, the reactors were centrifuged at 3000 G for 3 min, and a portion of the hexane solution was transferred immediately from each reactor to a GC vial with a disposable glass pipette. It was immediately analyzed for the concentrations of the reactant, intermediate, and final products using a GC-MS with the procedure described below. Our preliminary tests showed that the extraction efficiencies for the target PCDDs exceeded 92%.

2.4. Analytical procedure

The analyses of the hexane extract containing the dioxin congeners were performed using a Hewlett–Packard model 5890 GC with a Hewlett– Packard model 5971 MS. Chromatographic separations were accomplished using a 30 m DB-5MS column with a 0.25 mm i.d. and 0.25 μm film thickness (J&W Scientific, Folsom, CA), with injections in splitless mode. Helium was used as the carrier gas. The injector and detector temperatures were preset at 250 and 280 °C, respectively. Oven temperature was initially isothermal at 70 °C for 2 min, ramped from 70 to 230 °C at a rate of 10 °C/min, then ramped at 20 °C/min to 300 °C. The total run time was 21.5 min. Samples were analyzed in selective ion monitoring mode and the selected ions at m/z ratios of 128.1, 146.0 148.0, 155.1, 180.0, 182.0, 184.0, 186.0, 214.0, 216.0, 218.1, 220.0, 223.0, 252.1, 254.0, 256.0, 286.0, 288.0, 320.0, 322.0 were scanned at a dwelling time of 100 ms per ion. Compounds were identified based on both the retention times of the external standards and the selective ion monitoring described above. Each PCDD congener was quantified with seven-point calibration curves established using external hexane solution standards.

In addition, selected sample solutions were analyzed with the GC–MS in a full-scan mode (50−500 m/z) at conditions

Table 1
Identified daughter products, fitted pseudo-first-order rate constants, and the half-lives of the seven PCDDs

Reactants	Daughter products	Initial concentration (μM)	$k_{1,obs}$ (h^{-1})	$t_{1/2}$ (h)	Reaction time (h)
2,3-DCDD	DD, 2-MCDD	1.79	0.0041 ± 0.0004	169	120
1,4-DCDD	DD, 1-MCDD	2.39	0.0074 ± 0.0006	93.7	120
1,3-DCDD	DD, MCDD	1.70	0.0167 ± 0.0012	41.5	120
1,2-DCDD	DD, MCDD	0.70	0.0278 ± 0.0016	24.9	120
1,2,4-TrCDD	MCDDs; 1,2-, 1,3- and 1,4-DCDD	1.30	0.121 ± 0.012	5.71	30
1,2,3-TrCDD	MCDDs; 1,3- and 2,3-DCDD	1.26	0.265 ± 0.036	2.62	30
1,2,3,4-TCDD	MCDDs; 1,2-,1,3-, 1,4-, and 2,3-DCDD, 1,2,3-, and 1,2,4-TrCDD	1.37	1.24 ± 0.02	0.56	8

set similarly to those mentioned above for GC/MS/SIM. Except for the reactants, the less chlorinated and the non-chlorinated dibenzo-p-dioxins, no other compounds were detected.

3. Results and discussion

3.1. Identified products and time-dependent concentration profiles

Table 1 summarizes the results of the seven reaction systems initiated with the seven reactants, including the daughter products detected within the tested time periods, pseudo-first order rate constants and the half lives of the reactants. The MCDDs in the two TrCDD systems and the 1,2- and 1,3-DCDD systems were not further identified as 1-MCDD and/or 2-MCDD because they were not resolved on the chromatographs with our GC–MS method.

Fig. 2 presents the concentration profiles of the reactant and the major daughter products for the TCDD reaction systems within a time frame of 2 h. It shows that 85% of the TCDD disappeared in 1 h and that 1,2,4- and 1,2,3-TrCDD, and 1,3- and 2,3- DCDD were major daughter products whereas 1,2 and 1,4-DCDDs were minor products. MCDDs, which are not shown, were detected at very low concentrations after 6 h of reaction, and DD was not detected within 24 h. The molar balance of the reactant and the products is also shown in the Fig. 2. There was an initial deficiency in the molar balance of up to 50% of the total reactant, however, the molar balance increased to 70−80% of the total reactant added after 55 min of reaction. This indicated that a fraction of the TCDD and the evolved daughter products were not extractable with hexane, which is consistent with prior studies (Kim and Carraway, 2000). A possible explanation is that some PCDD

molecules adsorbed on surfaces might have been encapsulated by Zn(II) phosphate precipitates during reaction. Addition of 1 ml of 12 M HCl to the reactors after incubation for 40 and 90 min were shown to enhance the recovery efficiency up to about 77% and 91%, respectively. As discussed below, the formation of Zn(II) phosphate lowered the reactivity of the metallic zinc surface and inhibited the reaction.

Fig. 3a and b show the concentration profiles of the reactants and the products of 1,2,3-TrCDD and 1,2,4-TrCDD respectively. As shown in Fig. 3a, 1,3-DCDD is the major product of 1,2,4-TrCDD whereas 1,2- and 1,4-TCDDs are the minor products. Fig. 3b showed that the 2,3-DCDD is the dominant product of 1,2,3-TCDD whereas 1,3-DCDD is a minor product. 1,2-TCDD, a theoretically possible product, was not detected in this system. Very low concentrations of MCDDs of 0.13 and 0.07 μM

Fig. 3. 1,2,3-TrCDD (a) and 1,2,4-TrCDD (b) dechlorination and product formation using zerovalent zinc. Symbols represent mean values of duplicate experimental data. Error bars indicate standard error of duplicate samples. Some error bars are smaller than data symbols. The solid line represents the model fit of the data, while the dashed lines represent the smooth lines of the data. Total (▲), 1,2,3-/1,2,4-TrCDD (○), 2,3-DCDD (□), 1,3-DCDD (△), 1,2-DCDD (×), 1,4-DCDD (+), MCDD (◇).
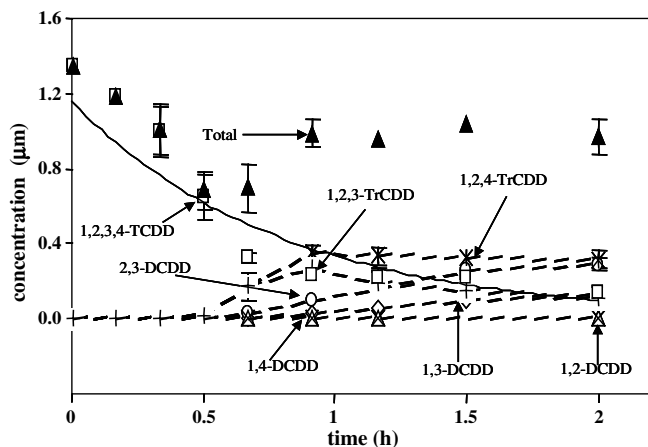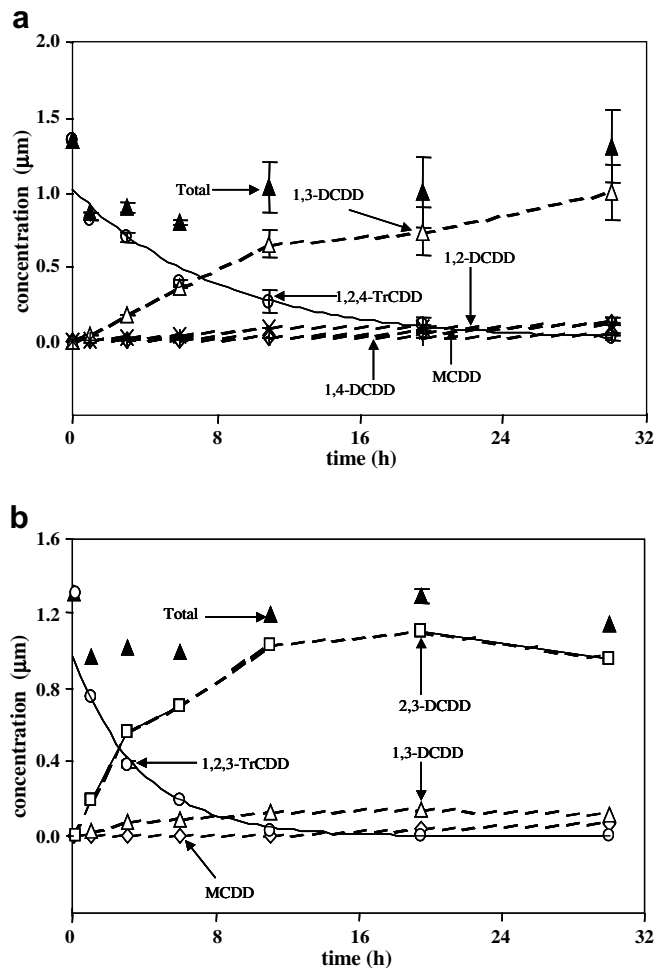
Fig. 2. 1,2,3,4-TCDD dechlorination and product formation using zerovalent zinc. Symbols represent mean values of duplicate experimental data. Error bars indicate standard error of duplicate samples. Some error bars are smaller than data symbols. The solid line represents the model fit of the data, while the dashed lines represent the smooth lines of the data. Total (▲), 1,2,3,4-TCDD (□), 1,2,3-TrCDD (+), 1,2,4-TrCDD (∗), 2,3-DCDD (○), 1,3-DCDD (◇), 1,2-DCDD (△), 1,4-DCDD (×).
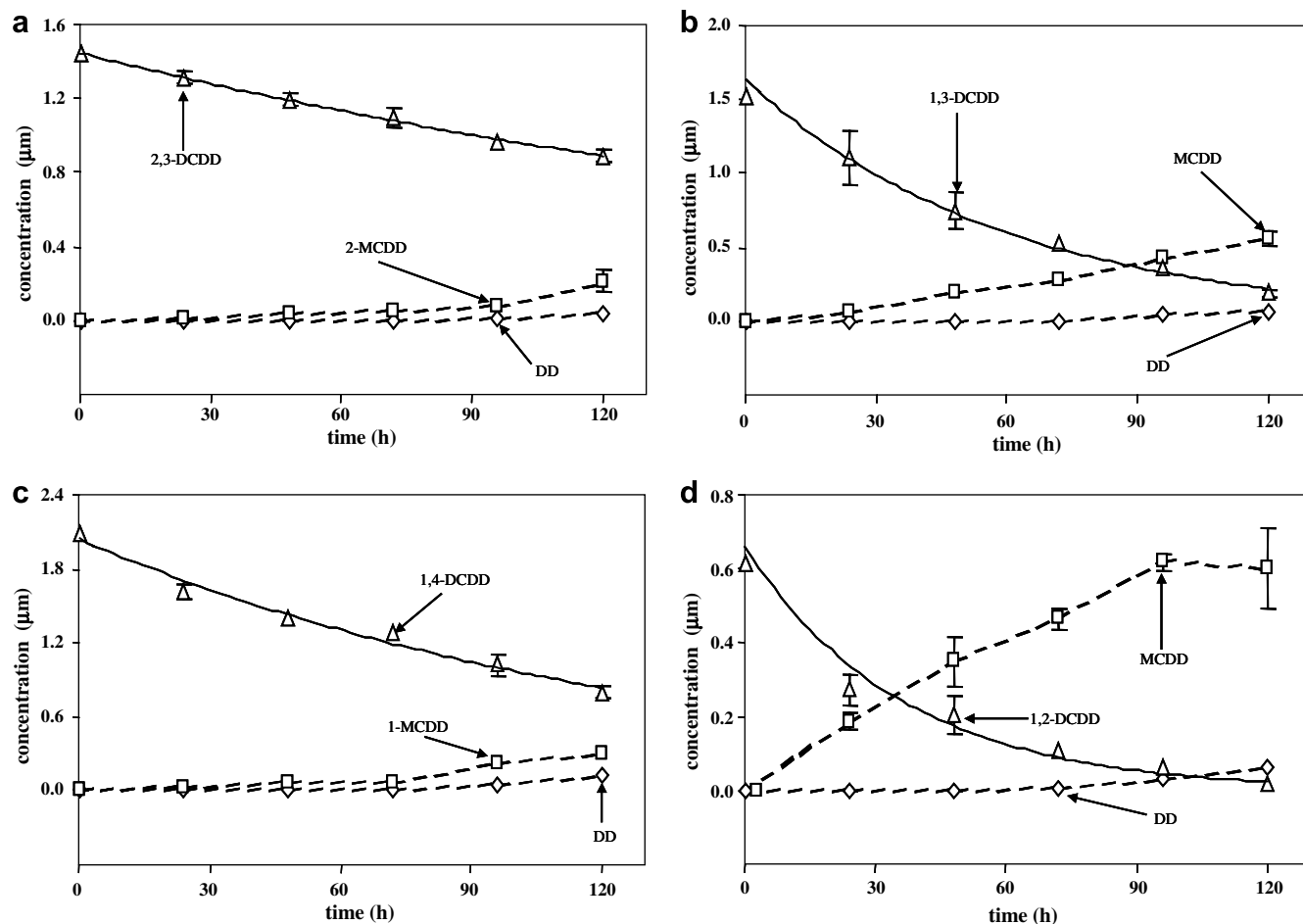
Fig. 4. 2,3-DCDD (a), 1,3-DCDD (b), 1,4-DCDD (c) and 1,2-DCDD (d) dechlorination and product formation using zerovalent zinc. Symbols represent mean values of duplicate experimental data. Error bars indicate standard error of duplicate samples. The solid line represents the model fit of the data, while the dashed lines represent the smoothed lines of the data. 2,3-/1,3-/1,4-/1,2-DCDD (△), MCDD (□), DD (◇).

were detected in the 1,2,4-TrCDD and the 1,2,3-TrCDD reaction systems, respectively, at the time point of 30 h, but DD was not detected within 30 h. The molar balance for each reaction system exhibited a similar trend to the TCDD reaction systems, in that a deficiency in the molar balance was noted early in the incubation period.

The concentration profiles for the four DCDDs and their daughter products MCDD and DD are presented in Fig. 4a–d. It is clear that all the four DCDDs were dechlorinated to MCDD as the intermediate and further to DD as the final product. 1- and 2-MCDDs were expected to form from 1,4- and 2,3-DCDD, respectively, but the MCDDs were not differentiated in the other two DCDD systems with our GC–MS technique. The molar balance for each reaction system, which is not shown in Fig. 4, was similar to those shown in Figs. 2 and 3.

3.2. Possible reaction pathways for TCDD

It is generally believed that the reactions of halogenated organic compounds with zero-valent metals (ZVMs) are surface controlled reactions (Matheson and Tratnyek, 1994; Orth and Gillham, 1996; Yak et al., 1999; Hernandez et al., 2004) which involve oxidation of ZVM coupled with reduction of the chlorine–carbon bond on the ZVM surface. These two separate reactions in the case of PCDDs could be represented with two general reactions:

$$M^0 \rightarrow M^{2+} + 2e \tag{1}$$

$$C_{12}H_YCl_Z + zH^+ + 2ze^- \rightarrow C_{12}H_{Y+Z} + zCl^- \tag{2}$$
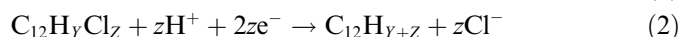
At the metallic zinc surface, the electrons provided by zinc could attack PCDDs to form less chlorinated congeners. Figs. 2–4 show that reductive dechlorination of TCDD by zero-valent zinc occurs stepwise, with the four chlorine atoms on the TCDD molecule being sequentially substituted by hydrogen to form the final DD.

Fig. 5 shows the possible pathways proposed for TCDD dechlorination by zero-valent zinc. The pathways are proposed according to the products identified in the seven tested reaction systems. The first step of the proposed pathways is the formation of 1,2,3-TrCDD and 1,2,4-TrCDD after removal of either a peri or lateral chlorine. Based on the nearly even distribution of the products (TrCDD and DCDD congeners) in the TCDD systems, the chances for elimination of chlorine at 4 and 3 positions are likely
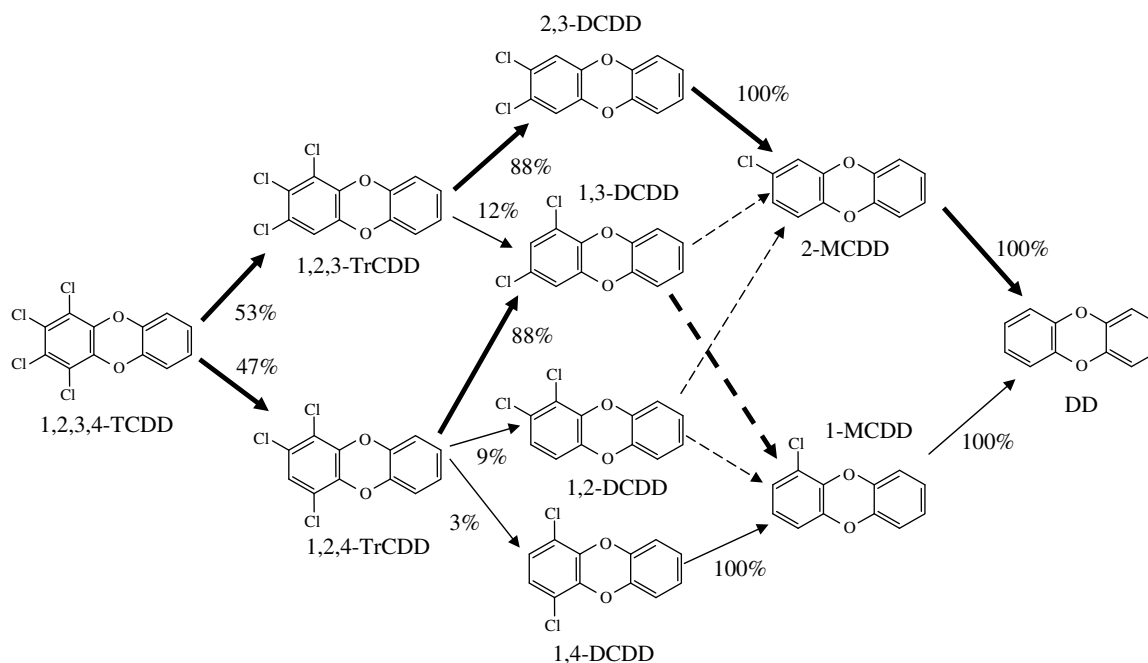
Fig. 5. The reaction pathways proposed for the dechlorination of 1,2,3,4-TCDD. The major routes are marked with bold arrow. The dashed lines are postulated but not verified in this study. The percentages indicate the estimated ratio of the accumulated concentrations of daughter products.

equal, with the peri-chlorine (4-position) being slightly preferred to be transformed. In the second step, the two TrCDDs are transformed further to DCDDs. 1,2,3-TrCDD is further transformed to 2,3-DCDD (major) via preferred elimination of C1-position chlorine or 1,3-DCDD (minor) via elimination of the lateral-chlorine (C2-position). 1,2-DCDD was not detected in the 1,2,4-TrCDD reaction systems, hence is not considered here as part of the pathway. 1,2,4-TrCDD is further dechlorinated to form the major daughter product of 1,3-DCDD via preferred elimination of the peri-chlorine (C1-position) and two minor products of 1,2- and 1,4-DCDD via elimination of the C2-position or C1-position chlorine, respectively.

The four DCDDs, including 1,3- and 2,3-DCDD as the major intermediates and 1,2- and 1,4-DCDD as the minor intermediates are dechlorinated to MCDDs. 1- and 2-MCDD are formed from 1,4- and 2,3-DCDD, respectively, and either or both MCDDs can be formed from 1,3- and 1,2-DCDDs. In the latter case, 1-MCDD may be preferentially formed according to the standard Gibbs free energy change (Huang et al., 1996). Reductive dechlorination of chlorinated dioxins is a two-electron transfer reaction that involves the release of chloride as a chloride ion and its replacement on the aromatic ring by hydrogen (Huang et al., 1996). Information on Gibbs free energy values for the reductive dechlorination of chlorinated dioxins would make it possible to evaluate the potential of these compounds to serve as electron acceptors in anaerobic environments (Dolfin and Harrison, 1992; Huang et al., 1996). As shown in (Huang et al., 1996), the ΔG_o values for the formation of 2-MCDD from 1,3- and 1,2-DCDD via the above dechlorination mechanisms are -138.7 and

-151.8 kJ/mol, respectively, whereas the ΔG_o values for the formation of 1-MCDD from the same two DCDD congeners are -139.5 or -152 kJ/mol, respectively. Both MCDDs undergo further dechlorination to form DD as the final product of the sequential reactions.

It should be noted that the pathways shown in Fig. 4 are different from those proposed for Pd/C and Pd/Al$_2$O$_3$ catalyzed dechlorination reactions. According to Ukisu and Miyadera (2003), the Pd-catalyzed reactions follows a dominant route from 1,2,3,4-TCDD → 1,2,3-TrCDD → 1,2-DCDD → 1-MCDD → DD. Our finding of two major parallel pathways (Fig. 4) suggests that metal zinc is less selective for the dechlorination reaction probably because it is more reactive and the overall reaction is much faster.

The proposed reaction pathways (Fig. 5) are also very different from the biodechlorination pathways of PCDD (Ballerstedt et al., 1997; Bunge et al., 2003; Fennell et al., 2004). Reductive dechlorination of TCDD by mixed cultures isolated from the Saale River sediments (Ballerstedt et al., 1997) and a pure culture (Dehalococcoides ethenogenes strain 195) (Fennell et al., 2004) follows a major route from TCDD to 1,2,4-TrCDD and to 1,3-DCDD. TCDD dechlorination by Dehalococcoides sp. strain CBDB1 (Bunge et al., 2003) follows a dominant route from TCDD to 1,2,3-TrCDD, 2,3-DCDD, and finally to 2-MCDD. The different dechlorination patterns in different strains may result from activity of different dehalogenase genes that may be responsible for the expression of different dehalogenase enzymes. Individual Dehalococcoides spp. in particular have been found to have multiple dehalogenase genes (Hölscher et al., 2004). The expression and specificity of the genes involved in dechlorination of chlorinated solvents

has been examined (Waller et al., 2005; Rahm et al., 2006), however, there is currently no information on which genes are involved in the dechlorination of PCDDs. Thus for biological dechlorination, the pathway is likely strain and/or dehalogenase specific.

3.3. Reaction rates

The following pseudo-first-order reaction model can be used to describe the rate phenomena observed for a given reaction system,

$$\frac{dC_{i,t}}{dt} = -k_{1,obs}t \tag{3}$$

where C_i is the concentration of the reactant at time t, and $k_{1,obs}$ is the apparent first-order rate constant for the disappearance of the reactant. An assumption underlying this model is that the total surface area of the metal Zn and the surface reactivity in each reactor are constant over time.

The unique feature of our study is that the reaction rate data were collected for each reactive species involved in the complex sequential reactions delineated in Fig. 5. This data set makes it possible to obtain the rate parameters for each reaction step using the simple pseudo-first order kinetics model. For data fitting purpose, Eq. (3) is integrated, yielding the following equation,

$$C_{i,t} = C_{i,0}e^{-k_{1,obs}t} \tag{4}$$

or

$$\ln C_{i,t} = \ln C_{i,0} - k_{1,obs}t \tag{5}$$

where $C_i,0$ is the initial concentration of the reactant for a given reaction system. In this study, Eq. (5) was used to fit the experimental data for disappearance of starting compound obtained for each reaction system. The resulting rate constants ($k_{1,obs}$), along with their standard deviations, are listed in Table 1.

For any surface mediated reaction, a sequence of physical and chemical steps is involved: (1) movement of reaction molecules into the interfacial region by convection and diffusion; (2) diffusion of reactant molecules within the interfacial region; (3) surface chemical reaction such as ligand replacement and electron and group transfer reactions; (4) outward movement of product molecules from interfacial region to bulk solution. The overall rates of the reactions depend on one or more of these steps (Deng et al., 1999). According to Table 1, the $k_{1,obs}$ value for TCDD is 1.24 h^{-1}, which is 5 and 10 times the $k_{1,obs}$ values for 1,2,3- and 1,2,4-TrCDD, respectively, and 45 to 303 times the $k_{1,obs}$ values for the four DCDDs. The fact that the more chlorinated dioxin congeners are dechlorinated at faster rates using metallic zinc is similar with photocatalytic degradation of polychlorinated dibenzo-p-dioxins on TiO$_2$ film under UV or solar light irradiation (Choi et al., 2000). The more highly chlorinated dioxin congeners will likely be more susceptible to further reaction due to the smaller HOMO-LUMO gap (Lynam et al., 1998). The trend may be also relative to the redox potential difference between the metallic zinc and the congeners. The higher chlorinated PCBs are also much more easily dechlorinated than the lower homologues by zero-valent iron in subcritical water (Yak et al., 1999). Similar phenomena were also observed in the reductive dechlorination of haloacetic acids (Hozalski et al., 2001), halocarbons (Johnson et al., 1996) by zero-valent iron, for example, the observed reaction rate normalized to surface area (k_{SA}) of tetrachloroethene (PCE), trichloroethene (TCE), 1,1-dichloroethene (11DCE), $trans$-1,2-dichloroethene (t12DCE), cis-1,2-dichloroethene (c12DCE), vinyl chloride (VC) were $(2.1 \pm 2.7) \times 10^{-3}$, $(3.9 \pm 3.6) \times 10^{-4}$, $(6.4 \pm 5.5) \times 10^{-5}$, $(1.2 \pm 0.4) \times 10^{-4}$, $(4.1 \pm 1.7) \times 10^{-5}$, $(5.0 \pm 1.5) \times 10^{-5}$ l m^{-2} h^{-1} respectively; and the pseudo-first-order rate constants (k_{obs}) for tribromoacetic acid (TBAA), dibromoacetic acid (DBAA), bromoacetic acid (BAA) reduction were 1.41 ± 0.28, 0.82 ± 0.24 and 0.14 ± 0.03 h^{-1} respectively.

It should be pointed out that the rates of PCDD dechlorination by metallic zinc under the conditions described here are significantly faster than that of biodechlorination. In mixed culture, $Dehalococcoides\ ethenogenes$ strain 195 dechlorinated 1,2,3,4-TCDD with a half-life of approximately 2.5 months at 28 °C (Fennell et al., 2004), and native dechlorinating bacteria in marine sediments exhibited a minimum half-life for 1,2,3,4-TCDD of about 3.5 months (Ahn et al., 2005). This same congener had a half-life of less than an hour (Table 1) in our reaction systems with metallic zinc as the reducing agent. The much faster reaction rates of dechlorination of PCDDs suggest that zero-valent zinc is a suitable candidate for remedy of PCDD contaminated environmental media.

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