RAPID DECHLORINATION OF PCDDS USING PALLADIZED ZERO VALENT IRON

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Abstract
1,2,3,4- tetrachlorinateddibenzo-p-dioxins can be completely dechlorinated by palladized zero valent iron. With palladization, first order kinetics of dechlorination reaction was enhanced up to 5 orders of magnitude. 1,2,3,4-TCDD was dechlorinated to dibenzo-p-dioxin within 2 days by palladized nano and micro size iron. The kinetics and pathways of various iron types were compared, and the mechanism of dechlorination reaction of PCDDs was suggested.

Introduction
The detoxification strategy for halogenated organic pollutant through reductive dechlorination using transient metal oxidation is widely studied[1,2]. Thermodynamically, polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs) should be dechlorinated by electron transferring reduction[3]. Because toxicity of PCDD/Fs can be increase by incomplete dechlorination, treatments methods for PCDD/Fs that give the deep dechlorination are needed, should be seriously considered. We reported that PCDDS can be dechlorinated using unaemended zero valent iron (ZVI)[4], however this reaction was very slow and incomplete. In this report, we archived fast and complete dechlorination using palladized micro scale iron and nano scale iron. The kinetics and pathways of various iron type were compared, and the mechanism of dechlorination reaction of PCDDs is suggested.

Materials and Methods
Chemicals
1,2,3,4- (1,2,3,4-TCDD, Accustandard) was used for dechloriantion studies. Standard solutions of 1,2,3,4-TCDD and its dechlorinated PCDDs products were used for qualification and quantification. 1,2,3,4-tetrachloronaphthalene from Accustandard was used for recovery standard in the extraction. Acetone, toluene, hydrochloric acid, (Merk, pesticide grade) and sodium sulfate (Kanto, 98%) were used in the degradation experiments, extraction and analysis.

Preparation of unamended and amended iron
The micro size Fe was an electrolytically-produced 100 mesh iron powder (Fisher) and was used without treatments. The nano size iron was synthesized from adding 0.24M $NaBH_4$ (98%, Aldrich) to 0.15M $Fe{\cdot}Cl_3$ solution (98%, Kanto) solution under argon stream following Zhang's method[5]. The BET surface area was 0.12 and 33.2 m^2/g, respectively. Palladization was archived by adding 5mM Pd(II)-acetate(Aldrich) solution to each iron. By controlling Pd dosage, Pd to Fe ratio was controlled by Pd dosage to Fe and the ratio was confirmed by ICP analysis.

Dechlorination Experiments and analysis
0.4 g of unamended micro size iron (mFe^{Fisher}) and palladized micro size iron ($Pd\text{-}mFe^{Fisher}$), 0.1g of unamended nano size iron ($Pd\text{-}mFe^{BH}$), palladized nano size iron($Pd\text{-}nFe^{BH}$) was transferred to 20 mL glass amber vial(Wheaton). Then 1 μ mol of 1,2,3,4-TCDD solution was spiked to each iron. After removing spiked solution, 20 mL of degassed distilled water was added. The vials were sealed with tefron-coated screw cap. All procedures were performed under the argon stream to keep the anaerobic conditions. All vials were prepared by batch method and shaken on a 15rpm rolling mixer at room temperature in the dark. During incubation periods, the vials were sacrificed for extraction. Solution phase was separated by strong magnet and transferred to test tube. 1,2,3,4-TCDD and its products were extracted by liquid-liquid extraction method using toluene. Acetone was added to vials to extract the remained particles for three times. 1,2,3,4-TCDD and its dechlorinated congener were qualified and quantified by ion trap mass spectrometry (Polaris-Q, Thermo electro) equipped with DB-5MS

column (30m × 0.25 mm, 0.25 ㎛).

Results and Discussion

Kinetics of Dechlorination of 1,2,3,4-TCDD by each iron type

In case of unamended iron, the reactions were very slow (Fig 1). In previous paper, we reported that only 2% of 1,2,3,4-TCDD was dechlorinatied by mFe^{Fisher} by 50 days reaction[4]. Unamened nano size iron shows one order of enhancement compared to micro size iron. Under anaerobic environment, activated life time of micro size iron is almost 40 days and nano scale iron is shorter[6]. Therefore, complete dechlorination can not be archived by unamended iron.

However, palladized irons show great enhancement in dechlorination. About 80% of 1,2,3,4-TCDD was dechlorinated to DD in 48 hours by palladized iron. Observed pseudo first kinetics orders (k_{obs}) for $Pd\text{-}mFe^{Fisher}$ and $Pd\text{-}nFe^{BH}$ were 2.90×10^{-2}, 5.43×10^{-2} h^{-1} respectively and palladization process enhanced the reaction up to 5 orders.

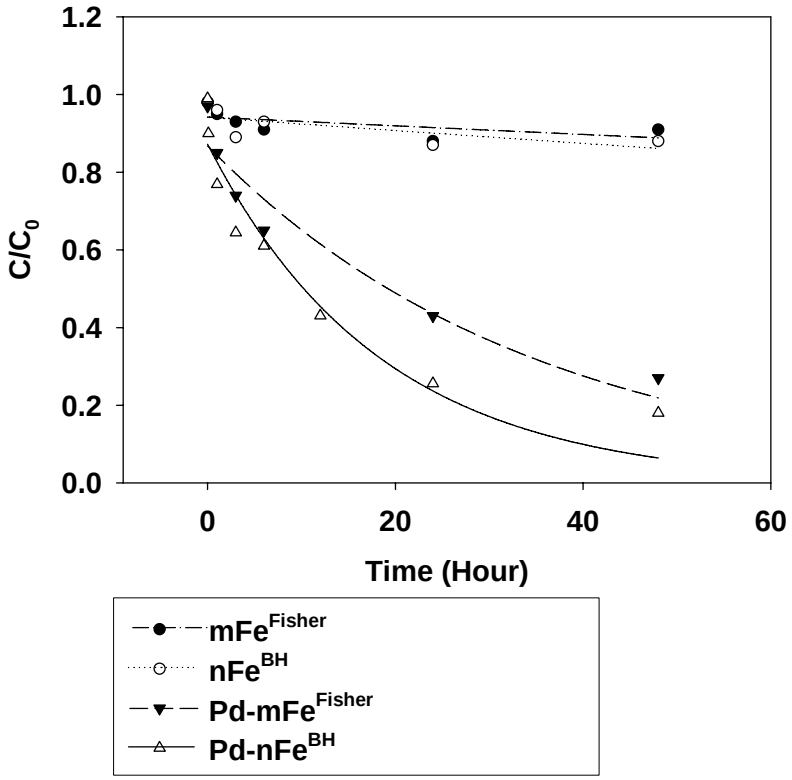

Figure 1. Dechlorination of 1,2,3,4-TCDD using unamended micro size iron (mFe^{Fisher}) and palladized micro size iron ($Pd\text{-}mFe^{Fisher}$), unamended nano size iron ($Pd\text{-}mFe^{BH}$) and palladized nano size iron($Pd\text{-}nFe^{BH}$). Line is fitted by the first order kinetic model.

Figure 2 shows the degradation of 1,2,3,4-TCDD and accumulation of intermediates and final products. During 2 days of reaction, mass balances were 103 ± 12 %. The disappearance pattern of 1,2,3,4-TCDD and accumulation pattern of DD was almost same, however amount of mono- to tri- chlorinated compounds, the intermediates, were lower with micro size iron, possibly from differences in the total dosage of surface area. Total surface area of $Pd\text{-}nFe^{BH}$ was 67 times higher than $Pd\text{-}mFe^{Fisher}$. Adsorption and desorption characteristics between Fisher iron and borohydride iron could be different due to available surface area in the system. However, this phenomenon should be studied further.

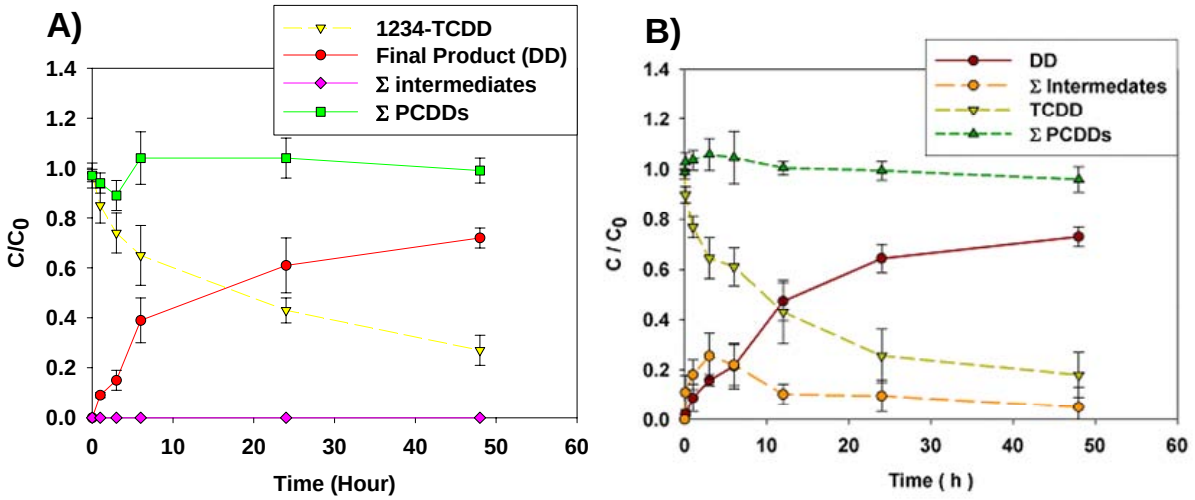

Figure2. Degradation of 1,2,3,4-TCDD and accumulation of its intermediates and final products. A) Pd-mFe[Fisher] , B)Pd-nFe[BH]

Pathway difference in dechlorination of 1,2,3,4-TCDD

In previous paper, we reported that the main dechlorination pathway of 1,2,3,4-TCDD by unamended iron was 1,2,3,4-TCDD→1,2,4-TriCDD→1,3-DiCDD→2-MCDD (Figure3-A)[4]. In the case of palladized iron, the pathway was 1,2,3,4-TCDD→1,2,3-TriCDD→1,2-DiCDD→1-MCDD(Figure 3-B) and more selective than that of unamended iron. The pathway of unamended iron suggests an electron transfer mechanism, which is thermodynamically-flavored, as suggested by Dolfing[2]. However, the pathway of palladized iron did not followed to the thermodynamically favored electron transfer pathways, instead showing of pattern reactivity more consistent with a mechanism involving hydride transfer of catalytic Palladium - iso-propyl alcohol[7]. In Pd-Fe-water system, protons may be transferred to hydrogen radical by electron from oxidation of iron on point of Pd-Fe contact and this hydrogen radical may be participated in TCDD reduction.

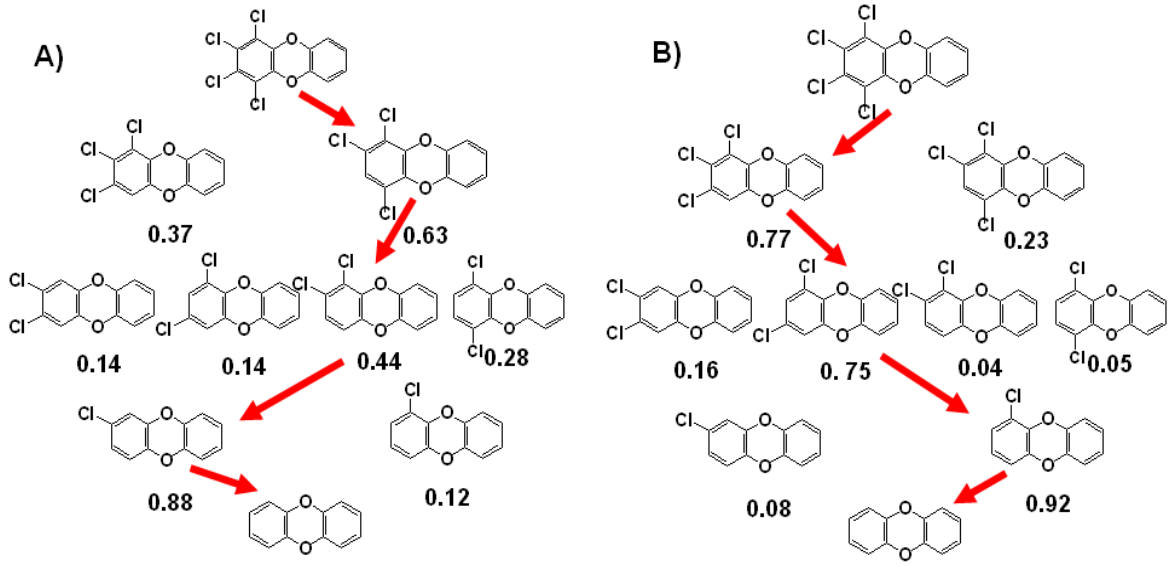

Figure 3. Dechlorination pathway of 1,2,3,4-TCDD. A) Unamended iron B) Palladized iron

Acknowledgements
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