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Rapid dechlorination of 1,2,3,4-TCDD by Ag/Fe bimetallic particles

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HIGHLIGHTS

- The bimetallic Ag/Fe is an effective catalyst for transforming PCDD.
- The dechlorination route of 1,2,3,4-TCDD in the Ag/Fe systems is stepwise.
- The efficiency of 1,2,3,4-TCDD dechlorination depends on the silver content.

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ABSTRACT

Polychlorinated dibenzo-*p*-dioxins (PCDDs) are among the most concerned environmental pollutants on the priority list, and their degradation is difficult to achieve. Hence, developing cost-effective technologies for destroying or detoxifying PCDDs are in high demand. This study investigated the reductive dechlorination of 1,2,3,4-TCDD in the presence of bimetallic Ag/Fe catalysts under aqueous solution and mild temperature conditions. It was found that Ag/Fe catalyst can rapidly transform 1,2,3,4-TCDD to less chlorinated PCDDs and the reaction was pseudo-first-order with respect to the reactant concentration. The dechlorination route of 1,2,3,4-TCDD in the Ag/Fe systems was found to be stepwise and the pathway of from 1,2,3,4-TCDD to DD via 1,2,4-TrCDD, 1,2-DCDD and MCDD was the major one. The surface-area-normalized rate constant (k_{SA}) corresponding to the silver bulk loading of 0.0060 mol%, 0.0125 mol% and 0.0228 mol% was 0.0155, 0.0399 and 0.0421 L h^{-1} m^{-2} respectively. Compared to our prior study of reductive dechlorination of 1,2,3,4-TCDD with bimetallic Pd/Fe catalysts as the catalyst, the reactions with bimetallic Ag/Fe particles were faster for TCDD, but much slower for the intermediates of TrCDDs, DCDDs and MCDD. Our results suggest that bimetallic Ag/Fe is a suitable candidate for rapidly reducing highly chlorinated PCDDs to less or non-chlorinated daughter products.

1. Introduction

PCDDs and PCDFs possess great health and environmental concerns due to their high toxicity, widespread occurrence, and persistence in the environment. Among the 210 PCDD/Fs, the 17 PCDD/F congeners with four chlorines in the lateral 2-, 3-, 7-, and 8-positions are most toxic and are currently regulated [1]. They enter the environment mainly through their inadvertent formation during combustion processes and chemical manufacturing. These compounds accumulate in soils and aquatic sediments and their bioaccumulation in fish, meat and dairy products results in deleterious human exposure. So it is of particular importance to develop effective remedial technologies to convert these chemicals to nontoxic forms at contaminated sites.

Prior studies have demonstrated that zero-valent iron (ZVI) is effective for remedy of soils and groundwater contaminated by different pollutants such as chlorinated aliphatics [2], chlorinated aromatics [3], and heavy metals [4], etc. ZVI-based remedial technology has been widely accepted as a cost-effective method for in situ or above-ground treatments [5]. However, it is found that the reduction rates of some contaminants such as aromatic compounds by granular iron were very low under ambient temperature and pressure (ATP), but the rates could be dramatically enhanced with iron coated with noble metal such as Pd, Ni, Pt, or Cu [6]. The coupled iron and noble metal forms galvanic cells in which iron serves as the anode and becomes preferably oxidized and noble metal is protected and may further promote the dechlorination reactions by their catalytic capabilities [7].

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Among those noble metals used for coating iron, palladium is the most commonly used one, and the bimetal of iron and palladium has been proven to be very effective particles for enhancing the reaction generally [8–10]. However, the Pd catalysis is highly expensive, which limited its wide application. So it is of significance to explore lower price and more effective catalysts. Compared to palladium, silver is substantially less expensive [7]. Xu and Zhang [7] reported that HCB was completely dechlorinated to tetra-, tri- and dichlorobenzenes by subcolloidal Ag/Fe particles, but little reduction was observed by microscale ZVI particles, indicating that the bimetal of iron and silver may be also effective particles for enhancing chlorinated aromatics.

In some previous studies on 1,2,3,4-TCDD dechlorination, using microscale [11] and nanoscale bimetallic Pd/Fe [12] as reductant were reported. It was found that 1,2,3,4-TCDD could be significantly reduced by bimetallic Pd/Fe and form the non-chlorinated DD. In the present work, another type of bimetallic particles, microscale Ag/Fe, which has not been reported in literature so far on the dechlorination of PCDD, were synthesized and used to dechlorinate 1,2,3,4-TCDD in aqueous solution. The primary objective of this study is to investigate if the bimetallic particles of Ag/Fe could be used to transform toxic PCDDs to less- or non-toxic forms as bimetallic particles of Pd/Fe do. Furthermore, the specific objectives of this study include the following: (i) examining the rates and extent of dechlorination, and determining the influence of the extent of silverization for the TCDD dechlorination, (ii) identifying reaction intermediates and final products, and then elucidate the main pathways of the dechlorination reaction of 1,2,3,4-TCDD by bimetallic Ag/Fe. Again, a comparison of the dechlorination results of 1,2,3,4-TCDD by different catalysts and microbes were made.

2. Experimental section

2.1. Chemicals

Water used in this study was a product of the Milli-Q Plus water system (Millipore Co.). Ten PCDD congeners used in this study included dibenzo-*p*-dioxin (DD), 1-monochlorodibenzo-*p*-dioxin (1-MCDD), 2-monochlorodibenzo-*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 AccuStandard Inc. (New Haven, CT). Hexachlorobenzene (HCB), HPLC-grade hexane, ethanol, acetone, silver sulfate (Ag_2SO_4), NaCl, NaH_2PO_4, Na_2HPO_4, and metallic iron (<10 μm, >99.9%) were purchased from Aldrich-Sigma Chemical Co. (St. Louis, MO). All the chemicals were used as received without further purification or treatment.

2.2. Bimetals preparation and characterization

The bimetallic ZVIs were prepared in an anaerobic chamber filled with H_2 (2.4%) + N_2 (97.6%) gases following a procedure developed by Wang and Zhang [9] with minor modifications. Prior to silverization, the surfaces of the zero-valent iron were cleaned with 0.4 M HCl for 2 min to remove any surface oxide layers. The acid-washed iron was rinsed 3 times with deoxygenated Milli-Q water. Then a dilute water solution of Ag_2SO_4 was added to 10 g of the acid-washed iron with agitation. The reduction and subsequent deposition of Ag on the Fe surface follow the reaction below:

$$Ag^{2+} + Fe^0 \rightarrow Ag^0 \downarrow + Fe^{2+} \quad (1)$$

After the dilute aqueous Ag_2SO_4 solution was added, the content including metal particles in the reactor was immediately stirred for 20 min. The supernatant within the reactor was then decanted and the iron particles were rinsed 5 times with deoxygenated Milli-Q water.

The Ag-coated iron particles were then taken out from the anaerobic chamber and freeze-dried. The Ag-coated iron particles were dark gray in color with no visual evidence of oxide formation. Three different contents of Ag deposited on the iron particles were 0.0060, 0.0125 and 0.0228 mol% assuming that the added Ag_2SO_4 was completely reduced and entirely precipitated on the ZVI surfaces. The specific surface area of the Ag/Fe materials was measured by employing the N_2-BET adsorption method with an ASAP 2010 surface analyzer (Micromeritics Co., Atlanta, USA). The morphology, size, and size distribution of the Ag/Fe particles were examined under DMR-X microscopy equipped with a Nikon digital camera DXM 1200F (Leica, Germany). The metal oxidation states of freshly prepared bimetallic Ag/Fe particles were obtained by X-ray photoelectron spectroscopy (Thermo VG Scientific ESCALAB 250) using Al Kα X-rays with photon energy of 1486.6 eV.

2.3. Batch experiment

The reductive dechlorination reaction was performed with a completely-mixed batch reactor system 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 Ag/Fe metal particles and 4.8 mL of 0.1 M phosphate buffer solution pH 6.85, autoclaved and sparged in N_2 to remove resolved oxygen before used were added to each of pre-washed reactors. They were then spiked with 200 μL of 27.48 μM 1,2,3,4-TCDD acetone stock solution using a 250-μL syringe. The initial concentration of the given reactant was set at 1.10 μM. The vials were capped, removed from the anaerobic chamber, and placed on a shaker for mixing at 22 ± 1 °C and 200 rpm. The reaction times were recorded since the start of mixing.

At a designated time (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 followed by 1 mL of concentrated HCl. Addition of hydrochloric acid was to enhance dissolution of ZVI surfaces, thereby releasing the absorbed reactant and products to the organic solvent [6]. 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 2 mL 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 method described below.

To assess the extraction efficiencies in the presence of 12 M HCl, a series of reactors that contained 5 mL of 1,2,3,4-TCDD (1.10 μg/L) aqueous solution and 100 mg of bimetallic Ag/Fe and had run for 2 h were run simultaneously. The recovery efficiencies calculated based on triplicates were 72%, 91%, 104% and 102% for the reactors added with 0, 0.5, 1.0 and 2.0 mL of 12 M HCl, respectively. The result suggested that 1 mL of 12 M HCl was sufficient for complete extraction of the PCDD chemicals from the reactor.

2.4. Analytical procedure

The analyses of hexane solution were performed using a Hewlett–Packard model 5890 GC with a Hewlett–Packard model 5971 MS. Chromatographic separations were accomplished using