Reductive Dechlorination of Polychlorinated Biphenyls by Zerovalent Iron in Subcritical Water

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A method for remediation of PCB-contaminated soil and sediments is described that uses zerovalent iron as the dechlorination agent and subcritical water extraction (SWE) as the transporting medium. By using 100-mesh iron powder and SWE conditions of 250 °C and 10 MPa on Aroclor 1260 for 1−8 h, the higher chlorine-substituted homologues were completely reduced to their lower-substituted counterparts. The lower-substituted congeners were subsequently near-completely dechlorinated. The initial findings indicate that this technique may be a viable method for remediation of PCB-contaminated soil and sediments.

Introduction

Polychlorinated biphenyls (PCBs) are a group of chemicals comprising of 209 congeners ranging from mono- to decachlorobiphenyl that are very persistent to degradation and hazardous to the biosphere (*1*). Manufactured by subjecting technical biphenyl to chlorine, commercial PCBs typically come with a mixture of many congeners and are categorized by the amount of chlorine by weight present in the PCB mixture. For instance, Aroclor 1260 marketed by Monsanto contains 60 wt % of chlorine in this product. Between 1929 and 1972, the United States produced about 560 million kg of PCBs, about half the world's total PCB production. Polychlorinated biphenyls were used in transformers, capacitors, inks, and pesticide formulations. It is estimated that about 35% of these productions found their way into the environment. This estimation suggests that about 400 million kg of PCBs are dispersed into the geo-, aqua-, atmo-, and biosphere, with the majority of them being concentrated in the geosphere because of their low volatility, low solubility in water, and high affinity for particulates (*2*). Under the Toxic Substance Control Act (TSCA), the most widely accepted method for remediation of PCBs is by using specialty incinerators that are capable of reaching a temperature of 1200 °C (*3*). Despite its high efficacy, pyrolysis of PCBs is expensive and may produce undesirable byproducts such as polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzodioxins (PCDDs) due to incomplete combustion (*3*). Several new remediation techniques for PCB are currently under development including bioremediation, γ radiolysis, and dechlorination using zerovalent metals and other chemical reagents (*3−6*).

Elemental iron is a reducing agent via the following reaction.

$$\mathrm{Fe(s)} \rightarrow \mathrm{Fe}^{2+} + 2\mathrm{e}^{-} \quad (E^{0} = \text{-}0.44\ \mathrm{V}) \tag{1}$$

By direct contact with iron it was demonstrated that halocarbons such as chloromethanes, trichloroethylene, and DDT [1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane] can be dechlorinated to hydrocarbons and chloride ions at ambient temperatures (*7−10*). The reductive dechlorination process follows as

$$\mathrm{Fe(0)} + \mathrm{R{-}Cl} + \mathrm{H}^{+} \rightarrow \mathrm{Fe}^{2+} + \mathrm{R{-}H} + \mathrm{Cl}^{-} \tag{2}$$

However, for reduction of polychlorinated biphenyls under ambient temperature and pressure (ATP) the reaction was found to be kinetically very slow. Fernando et al. reported that no biphenyl (reduction product) was found 24 h after mixing Aroclor 1254 and Arolocr 1260 in methanol solutions with 10-μm iron particles (*11*). Even with their success in synthesizing nanoscale iron particles for rapid dechlorination, Zhang et al. reported that only less than 25% of 5 mg/L Aroclor 1254 in ethanol/water solution was reduced after 17 h of reaction time (*8*). Nonetheless, the kinetics of PCB dechlorination at ATP can be greatly enhanced by the use of palladized iron (*11, 12*) or other bimetallic systems (*13*).

Recent reports indicate that superheated water is capable of extracting organic pollutants including PCBs from solid matrices (*14−18*). Subcritical water extraction (SWE) refers to extractions that are performed under conditions that are below the critical temperature (T_c) and pressure (P_c) of water ($T_c = 374$ °C, $P_c = 22$ Mpa). The energy content of a subcritical water system may be sufficient to promote chemical reactions such as the dechlorination of PCBs using zerovalent iron besides extraction of these environmental contaminants. A recent publication by Chuang and co-workers indicates that complete reductive dechlorination of PCBs to biphenyl by Fe(0) is possible in the presence of superheated (400 °C) water vapor and that significant dechlorination did not occur below 300 °C (*19*). Their findings also indicated that water is likely to be the hydrogen donor for the reduction of PCB to biphenyl. The impetus of this investigation was to discover if dechlorination of PCBs in subcritical water extraction conditions is efficient. Such possibility would allow for the disposal of PCBs and other halocarbons upon their extraction from solid wastes. This paper summarizes the preliminary findings from our research regarding the efficiency of dechlorination of Aroclor 1260 with zerovalent iron in subcritical water.

Experimental Section

Chemicals and Instruments. Electrolytic iron powder (100 Mesh), HPLC grade acetone, HPLC grade hexanes, and HPLC grade water were obtained from Fisher Scientific (Fair Lawn, NJ). Arochlor 1260 standards (2000 ppm in methanol), BZ no. 54 (2,2′,6,6′-tetrachlorobiphenyl), BZ no. 207 (2,2′,3,3′,4,4′,5,6,6′-nonachlorobiphenyl), and BZ no. 209 (2,2′,3,3′,4,4′,5,5′,6,6′-decachlorobiphenyl), were purchased from ChemService (West Chester, PA) and used without further purification. Aroclor 1260 standards were made by appropriate dilution with HPLC grade hexanes in volumetric glassware. An Isco 260D Syringe Pump was used to pressurize the water,

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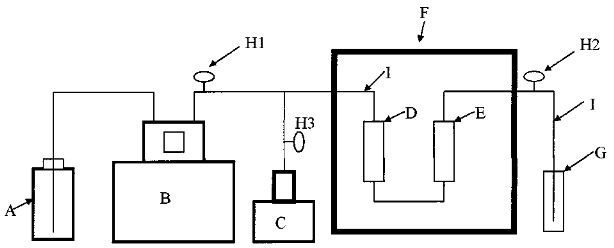


A = HPLC grade H_2O Reservoir
B = Isco 260 Syringe Pump
C = HPLC solvent pump
D = H_2O Preheat Unit
E = Stainless-steel Extraction Cell
F = Thermostated Oven
G = Collection Vessel
H (1,2,3) = High-pressure Valves
I = Stainless-steel tubings

FIGURE 1. Schematic of the subcritical water extraction apparatus.

and a GC oven was used for maintaining the temperature to ±2 °C. A HPLC solvent pump was connected to the system to deliver the hexanes. High temperature and pressure extraction cells were purchased from Keystone Scientific, Inc. (Bellefonte, PA). A Hewlett-Packard 5890A GC-ECD/FID was used for analyses of the PCB standard and samples. The 30-m EC-1 capillary column purchased from Alltech (Deerfield, IL) had a 0.45 mm i.d. and 1.0 μm film thickness. The carrier gas was chromatographic grade He (Oxarc, Spokane, WA). Sample injection volume was 1 μL splitless with the injector temperature set at 300 °C and the detector set at 300 °C. Separation was conducted with a temperature program that held column temperature at 150 °C for 2 min and then ramped at 4 °C/min until it reached 300 °C, where it was held for 10 min.

Procedures. One hundred grams of 100-mesh iron powder was washed once with 100 mL of HPLC grade hexanes followed by 100 mL of acetone to rid any organic substances. The washed iron was then dried by nitrogen sparging and stored. A 3.0-g sample of this iron powder was transferred to a plastic weighing boat, and the desired amount of Arochlor 1260 in methanol solution was spiked directly onto the iron powder and the methanol was allowed to air-dry. The PCB-spiked iron powder was transferred into a 2.2-mL stainless steel extraction cell. The extraction cell was tightened and completely filled with HPLC grade water by using a syringe before it was placed in the oven, connected to the extraction system, and brought to pressure for leak check. The oven was then brought to temperature. Timing began after the temperature readout corresponded with the set temperature. Figure 1 depicts the apparatus. Reduction and extraction were carried out in situ statically (without flow of solvent) for the desired amount of time. The system was then flushed with ca. 10 mL of HPLC grade water, followed by ca. 5 mL of hexanes by using a HPLC solvent pump, and finally with another ca. 5 mL of HPLC grade water, all collected in a 40-mL glass vial. The hexane phase was separated from the aqueous phase with a 60-mL separatory funnel. The aqueous phase was washed twice, each with ca. 3 mL of hexanes, and all three portions were pooled together before nitrogen-sparged to a volume of ca. 6 mL. BZ no. 207 was added as internal standard before each sample was brought to a final volume of 10 mL. Each sample (1.0 mL) was transferred to a 1.5-mL autosampler vial with Teflon-coated stopper for GC analyses. For the studies of temperature effect on dechlorination efficiency using BZ no. 54 and BZ no. 207, the procedure was the same with the exception that BZ no. 209 was added as the internal standard instead. Individual peak areas of the standard solution and the sample solution were normalized by using the peak area of the internal standard after GC analyses. Dechlorination efficiency of a particular PCB congener was calculated by dividing the difference in peak area between the corresponding peak in the standard and the sample by the peak area of this peak in the standard.

TABLE 1. Effect of Temperature on Dechlorination Efficiencies of BZ No. 54 and BZ No. 207 Using the SWE-Fe^0 System[a]

	dechlorination efficiency (%)	
temp (°C)	BZ no. 54	BZ no. 207
150	20	66
200	18	98
250	52	99
300	48	96

[a] P = 10 MPa. Time = 2 h.

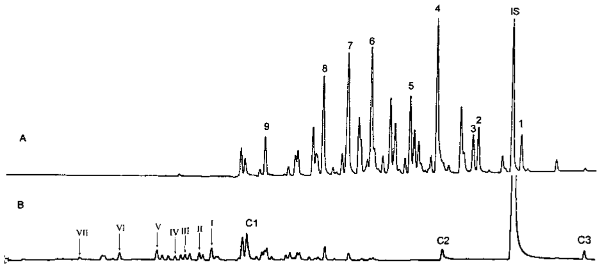
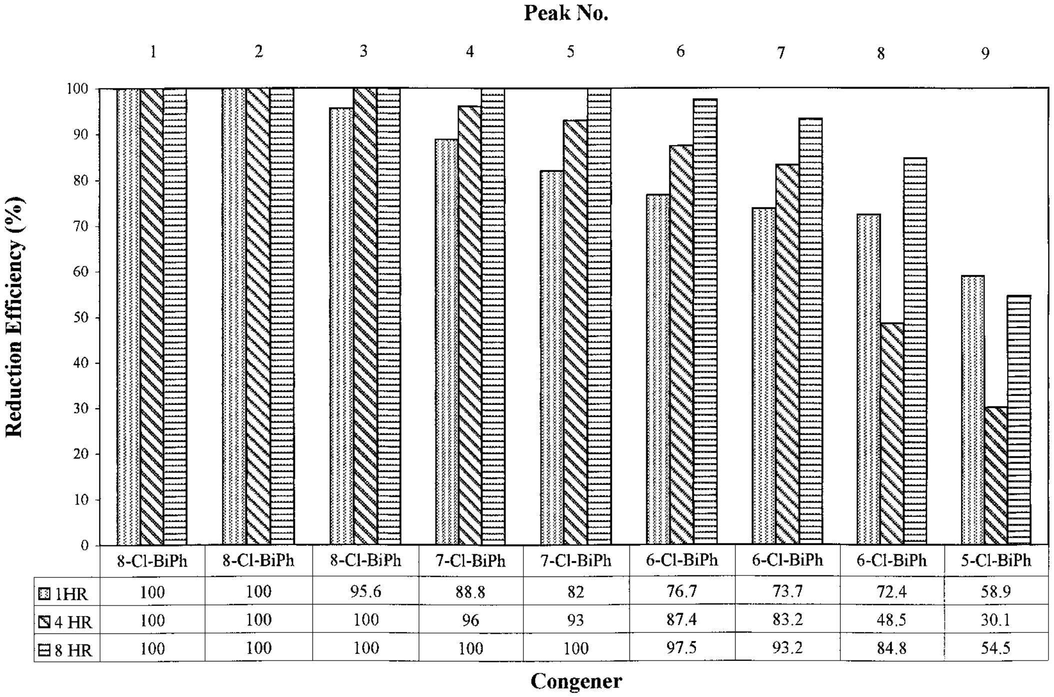


FIGURE 2. GC-ECD chromatograms: (A) Ten ppm Arochlor 1260 standard in HPLC grade hexanes, internal standard (IS) at t_R = 36.9 min is 1 ppm BZ no. 207 (2,2′,3,3′,4,4′,5,6,6′-nonachlorobiphenyl), integration area normalized to 1. (B) One hundred micrograms of Arochlor 1260 after 8-h dechlorination procedure and dissolved in 10 mL hexanes, internal standard (IS) is 5 ppm BZ no. 207, integration area 5.16 of 1-ppm BZ no. 207. Peaks C1 (A: 23.5, B: 23.5 min), C2 (A: 33.7, B: 33.4 min), and C3 (A: 40.6, B: 40.7 min) appear in both chromatograms and were determined to be contaminants, including heptachlor, in the hexanes. Peaks 1−9 correspond to the peaks discussed in Figure 3. Peaks I−VII were identified as follows: peaks I and II = tetrachlorobiphenyl; peaks III, IV, and V = trichlorobiphenyl; peak VI = dichlorobiphenyl; peak VII = monochlorobiphenyl. Identification was done using GC-MS.

Results and Discussions

The congener BZ no. 54 was used for quantitation of mass recovery owing to the complex nature of the Aroclor 1260 chromatogram. By performing recovery experiments at room pressure and temperature and at 10 MPa and 250 °C, mass recovery of BZ no. 54 was found to be close to 95% in both cases. This degree of recovery indicates that PCBs can be fully recovered from this system and the 5% loss may be due to loss of analyte during the spiking and transferring processes. Because the vapor pressure of water at 300 °C is 8.58 MPa, operating pressure of 10 MPa was selected to ensure that the water remain in the liquid state throughout the temperature range used in this study. In the various initial experiments performed by using BZ no. 54 and BZ no. 207 and by varying the reaction temperature it was found that 250 °C was the optimal temperature. These results are shown in Table 1. The presence of zerovalent iron was also found to be imperative for the dechlorination of these congeners to occur at any appreciable rate. No attempt was done to compare the relative efficiency of various sizes of iron particles in this study, and the results reported here are based on the 100-mesh iron particles used. The BZ no. 54 congener (2,2′,6,6′tetrachlorobiphenyl) was found to be especially tenacious with respect to dechlorination under the studied conditions (Table 1) and is an ideal candidate for studies such as recovery and temperature effect. However, it is important to note that this particular congener does not appear in any Arochlor mixture (*20*).

Figure 2A shows the chromatogram of a 10 ppm Aroclor 1260 solution. Close examination of the chromatogram



	8-Cl-BiPh	8-Cl-BiPh	8-Cl-BiPh	7-Cl-BiPh	7-Cl-BiPh	6-Cl-BiPh	6-Cl-BiPh	6-Cl-BiPh	5-Cl-BiPh
░ 1HR	100	100	95.6	88.8	82	76.7	73.7	72.4	58.9
▧ 4 HR	100	100	100	96	93	87.4	83.2	48.5	30.1
▤ 8 HR	100	100	100	100	100	97.5	93.2	84.8	54.5

FIGURE 3. Percent dechlorination efficiency of selected peaks of Aroclor 1260 after 1, 4, and 8 h of reaction time using SWE/Fe^0 (T = 250 °C and P = 10 MPa). Peak area was normalized to area of internal standard (BZ no. 207). Dechlorination efficiency was calculated by dividing the difference in peak area between the corresponding peak in the standard and the sample by the peak area of this particular peak in the standard.

reveals about 40 peaks present in this PCB mixture, hence making quantitation extremely complicated and with large error bars. Alternatively, nine major and well-resolved peaks were chosen from the chromatogram for quantification purpose since they represent the majority and provide accurate quantitation results. These nine major peaks comprise of three octachlorobiphenyl, two heptachlorobiphenyl, three hexachlorobiphenyl, and one pentachlorobiphenyl peaks. Figure 2B shows the chromatogram of the subcritical-water/Fe^0 treated sample after 8 h of reaction with the same attenuation factor on the integrator. Direct comparison of the individual peak area before and after reduction was made by normalizing each peak area with respect to the peak area of the internal standard (BZ no. 207). For Aroclor 1260, the quantitation limit was close to 0.2 ng of Aroclor 1260 per μL hexanes on this particular instrument. Figure 3 summarizes the approximate reduction efficiencies of the selected peaks.

Referring to Figures 2 and 3 for the degree of chlorination of the PCBs, it is evident that the higher chlorinated PCBs are much more easily dechlorinated than the lower homologues. This phenomenon is also evident by contrasting the dechlorination efficiencies of BZ no. 54 and BZ no. 207 in Table 1. The resistance of the lower homologues toward reductive dechlorination may be related to the increase in the lowest unoccupied molecular orbital (LUMO) energy which decreases the probability of the reductive electron to occupy the LUMO, thus decreasing the probability of the formation of the reactive excimer of the PCB molecule (*21*). Figure 2B also shows that many lower congeners below the penta-substituted congener are formed after the reaction. This finding indicates that reductive dechlorination in this SWE-Fe^0 system perhaps occurs stepwise, with the chlorine on the PCB molecule being sequentially substituted by hydrogen. As the PCB molecule becomes less chlorinated, the kinetic barrier for dechlorination becomes larger. Eventually when the energy barrier exceeds the energy barrier for ring opening of the biphenyl, destruction of the biphenyl ring occurs. This postulation is supported by the fact that while some mono-, di-, tri-, and tetrachlorobiphenyls can be identified using GC-MS (see Figure 2 caption), virtually no biphenyl can be observed after reductive dechlorination. Instead, some amount of 5,6-dimethyldecane and other medium-size hydrocarbons are consistently appearing on the chromatograms.

Compositional homologues of various Aroclor mixtures are well studied, and the weight percent of Aroclor 1260 is given as 12% pentachlorobiphenyl, 42% hexachlorobiphenyl, 38% heptachlorobiphenyl, 7% octachlorobiphenyl, and 1% nonachlorobipenyl (*20*). Although dechlorination did not proceed toward completion after the 8-h reaction, it is apparent that the majority of the original PCBs in the mixture, particularly the higher-substituted congeners which are predominant in Aroclor 1260 and typically more toxic (*20*), were completely reduced (Figure 2). The result from this preliminary study indicates that reductive dechlorination using SWE and zerovalent iron may be a promising remediation alternative for PCB-contaminated soils and sediments. Further research such as designing an on-line approach and optimization of the dechlorination efficiency, particularly those of the lower-substituted homologues, is currently being pursued.

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