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SEOK-YOUNG OH[1], MYONG-KEUN YOON

DEGRADATIONS OF 2,4-DICHLOROPHENOL AND POLYCHLORINATED BIPHENYLS WITH ZERO VALENT IRON UNDER SUBCRITICAL CONDITIONS. IMPORTANCE OF SUBCRITICAL WATER OXIDATION

The abiotic transformations of 2,4-dichlorophenol (DCP) and polychlorinated biphenyls (PCBs) has been examined in the presence and of zero valent iron (Fe(0)) under subcritical conditions. It was found that the degradation of DCP was significantly enhanced, showing complete degradation of DCP in 3 h at 300 °C. Control experiments without Fe(0) indicated that the removal of DCP in the iron–water system was mostly due to subcritical water oxidation and that the enhancement of degradation in the presence of Fe(0) was less significant. Regardless of Fe(0), PCBs were rapidly decomposed, showing 93% destruction in 5 h at 300 °C. Product identification by gas chromatography-mass spectrometry (GC-MS) analysis showed that the reductive transformation of DCP and PCBs w Fe(0) existed under subcritical conditions. Our results suggest that subcritical water degradation may be a possible remediation option to treat DCP and PCBs in water and soil.

1. INTRODUCTION

Halogenated compounds, the most frequently reported contaminants in subsurface environments, are toxic and carcinogenic to human beings. Development of an effective treatment process for the remediation of soils and groundwater contaminated with such compounds has been an issue in recent decades. Among various proposed processes, reductive transformation of halogenated compounds with zero valent iron (Fe(0)) is an attractive option because of its passive nature, ease of operation and potential cost-effectiveness. Since the mid-90s, much research has been conducted to evaluate the feasibility of using Fe(0) to treat halogenated organics [1–3]. As a result,

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[1] Department of Civil and Environmental Engineering, University of Ulsan, Ulsan 680-749, South Korea, corresponding author S.-Y. Oh, e-mail: quartzoh@ulsan.ac.kr

Fe(0) has been installed in field applications as a reactive material in permeable reactive barriers (PRBs) for groundwater remediation [4].

Though Fe(0) has been successfully applied to abiotic dechlorination of chlorinated solvents such as carbon tetrachloride and trichloroethylene in groundwater remediation, the Fe(0) reduction process has not been successfully used for some persistent halogenated compounds such as polychlorinated biphenyl (PCB) and pentachlorophenol (PCP) because their dechlorination rates are too slow. Several attempts were made in the last decade to overcome this kinetic barrier. Nano zero valent iron and bimetals such as Fe/Pd, were evaluated for their abilities to accelerate dechlorination of the persistent compounds [5–7]. Though nano zero valent iron enhanced the dechlorination of PCBs to some extent [5, 6], successful results have not yet been reported. Fe/Pd was shown to significantly enhance the reduction of PCBs [7]. However, the addition of Pd is costly.

Subcritical water is defined as liquid water under pressure at temperatures between the usual boiling point (100 °C) and the critical temperature (374.1 °C) [8]. Under subcritical conditions, the electrical permittivity, surface tension and viscosity of a water molecule are dramatically decreased [9]. For these reasons, in the last decade, attempts have been made to utilize subcritical water to extract or decompose PCBs, polychlorinated diobenzo-*p*-dioxins (PCDDs), polycyclic aromatic hydrocarbons (PAHs), pesticides and other persistent organic contaminants from soils [10–12]. Yang et al. [10] demonstrated that more than 90% of PCBs were extracted from soil in 15 min at 250–300 °C. Hashimoto et al. [11] reported that subcritical water can extract 94.5% and 99.4% of PCDDs from contaminated soil in 4 h at 300 °C and 350 °C, respectively.

Hawthorne et al. [12] showed via a pilot-scale demonstration that PAHs could be completely removed from soil with subcritical water at 275 °C. They also observed that chlorinated aliphatic compounds including lindane, dieldrin, tetrachloroethene and trichloroethene could be completely dechlorinated with subcritical water in 1 h at 150–300 °C [13]. In addition, the combination of subcritical water with oxidizing agents such as permanganate, O_2 and air, via so-called subcritical water oxidation (SCWO) can effectively oxidize organic compounds that are normally very difficult to oxidize [14, 15]. Dadkhah and Akgerman [14] showed that more than 99.99% of PAHs could be removed from soil with the combination of extraction and oxidation with air and O_2 at 250 °C. Kronholm et al. [15] reported that more than 99.9% of 4-chloro-3-methylphenol was oxidized by potassium persulfate within 1 min at 250–300 °C under 23.5–31.0 MPa. Under subcritical and supercritical conditions, PCBs were rapidly degraded with oxidants within minutes [16, 17]. Weber et al. [16] showed that PCBs were easily degraded at 300–450 °C in the presence of O_2, and that polychlorinated dibenzofurans (PCDFs) were not produced at higher temperatures and longer retention times. O’Brien et al. [17] also showed that 2-chlorobiphenyl was rapidly oxidized with H_2O_2 at 400–500 °C, and that no PCDDs or PCDFs were observed as products.

In order to overcome this kinetic hindrance in the reduction of persistent chlorinated compounds with Fe(0), attempts were made to combine subcritical and supercritical conditions with the iron reduction process. Chuang et al. [18] showed that Aroclor[2] 1221 and Aroclor 1254 were completely dechlorinated with Fe(0) in 1 h at 400 °C. They also showed that, even at 300 °C, more than 60% of the PCBs were dechlorinated in 1 h with Fe(0). nano Yak et al. [19] showed that 60–100% of Aroclor 1260 was dechlorinated with Fe(0) in 8 h at 250 °C. In a subsequent study, they also found that some reductive positional isomers showed relative resistance during reduction with Fe(0) at 250 °C [20]. Hawthorne et al. [21] showed that the addition of metals including Pb, Al, Cu, Zn and Fe could enhance the dechlorination of Aroclor 1254 in subcritical water in 1 h at 350 °C. The combination of nano zero valent iron and subcritical conditions (300 °C) showed more than 95% PCB destruction in the mixture of PCB-contaminated soil and iron nano particles in water [22].

In this study, the degradation of persistent halogenated compounds with Fe(0) under subcritical conditions was examined. It seems that subcritical conditions may enhance the reductive transformation of persistent halogenated compounds with Fe(0), and that oxidation with subcritical water may also be involved in the transformation of halogenated compounds. PCBs and 2,4-dichlorophenol (DCP) were chosen as persistent halogenated compounds for this study. Similar to PCBs, DCP is known to be persistent in the reductive transformation with Fe(0), and nano materials and bimetals have been applied to enhance the degradation rate [23]. Through a series of batch experiments using a temperature-controlled pressurized reactor, the removals of DCP and PCBs with Fe(0) were investigated. The effects of temperature and addition of Fe(0) on the degradation of DCP and PCBs under subcritical conditions were examined. Possible products formed during degradation in subcritical conditions have also been discussed.

2. MATERIALS AND METHODS

Chemicals. Aroclor 1248 provided by Chem Service (West Chester, PA, USA) was chosen as the PCBs source. 2,4-Dichlorophenol (DCP, >99%), 2-chlorophenol (2CP, >99%), 4-chlorophenol (4CP, >99%) and phenol (~99%) were purchased from Aldrich (Milwaukee, WI, USA). Methanol (>99.9%) was obtained from Fisher Scientific (Pittsburgh, PA, USA). The Fe(0) used for the study was Peerless iron (Peerless Metal Powders and Abrasives, Detroit, MI, USA), widely used in remediation work and laboratory studies [3]. The specific surface area of the Peerless iron was 1.67 m^2/g

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[2] Aroclor is one of the most commonly known trade names for PCB mixtures. There are many types of Aroclors, and each has a distinguishing suffix number that indicates the degree of chlorination. For details, see <http://www.epa.gov/solidwaste/hazard/tsd/pcbs/pubs/aroclor.htm>.

as determined by the Brunauer–Emmett–Teller method with nitrogen. All chemicals were used without further purification, and Peerless iron was used as received. In order to conduct a feasibility test for PCB-contaminated soil, Aroclor 1248-contaminated soil was collected from a site near Seoul, South Korea. The concentration of Aroclor 1248 was determined according to the Korean standard method for soil analysis [24].

Batch experiment procedure. Two types of batch experiments were conducted. At 20–80 °C, experiments were performed in a shaker water bath (HB-205SW, Hanbaek, Korea) whose temperature was controlled at 20, 40, 60, and 80 °C. Duplicate vials (8 cm^3) containing 5 cm^3 of aqueous solution and 1 g of iron were used for each experiment. The initial concentration of the DCP solution was 50 mg/dm^3 (0.307 mM), and the solutions were deoxygenated by purging with N_2 for 30 min. After iron was added, the vials were shaken in a horizontal position in the shaker bath at 150 rpm. At selected time intervals, duplicate vials were sacrificed, and the supernatant was immediately filtered through a 0.22 μm membrane filter (Millipore, MA) for analytic determination of DCP and its reduction daughter products. In order to exclude the aging effect of Peerless iron, acid-washed Fe(0) was tested. Fe(0) was washed with 3% HCl for 10 min using a Vortex shaker. Then the same procedure was repeated three times with deoxygenated deionized water. The iron was dried in the vacuum oven at 100±5 °C for 1.5 h. After the iron cooled down, it was weighed and added to vials for batch experiments under identical conditions.

Under subcritical conditions, experiments were performed using a pre-designed, temperature-controlled, pressurized reactor system, including a 500 cm^3 main reactor, a temperature controller, a shaking speed controller, pressure controllers and gauges and gas sampling ports. The temperature was set to 150, 200, 250 and 300 °C, and the internal pressure of the reactor was maintained at the vapor pressure of steam. Thus, the internal pressures of the reactor at 150, 200, 250, and 300 °C were approximately 0.47, 1.5, 3.9 and 8.5 MPa, respectively. 5 g of Fe(0) and 100 cm^3 of DCP or PCB solution were placed in the reactor and shaken at 180 rpm. The initial concentration of the DCP or PCB solution was approximately 50 mg/dm^3. Due to the extremely low water solubility of PCBs, 20% methanol was added to make 50 mg/ dm^3 PCB solution [6]. The solutions were deoxygenated by purging with N_2 for 30 min. After a selected sampling time, the solution was separated with a 0.22 μm membrane filter (Millipore, MA), and DCP and PCB were analyzed using high performance liquid chromatography (HPLC) and gas chromatography (GC), respectively. Control experiments were also performed without Fe(0) under identical conditions. The acid-washed Fe(0) was also evaluated.

In order to evaluate the feasibility of the Fe(0)–subcritical water system for the remediation of PCB contaminated soil, experiments were performed using the temperature controlled pressurized reactor system at 300 °C. 150 g of PCB contaminated soil, 100 cm^3 of deionized water and approximately 9.5 g of Fe(0) were added into the reactor and shaken at 180 rpm throughout the experiment. The initial concentration of PCBs in the soil was approximately 142 mg/kg. After 5 h, soil and water samples were collected and pre-treated for determination of PCB concentration following the Korean standard method for soil analysis [24]. A control experiment was conducted without Fe(0) under identical conditions.

Chemical analysis. 2,4-Dichlorophenol (DCP) and its reduction products were analyzed using an UltiMate^{TM} 3000 HPLC system (Dionex, Sunnyvale, CA, USA) equipped with an Acclaim$^{®}$ 120 guard column (4.3 × 10 mm, Dionex, Sunnyvale, CA, USA) and an Acclaim$^{®}$ 120 C18 column (4.6 × 250 mm, 5 μm, Dionex, Sunnyvale, CA). A methanol–water mixture (60/40, v/v) was used as the mobile phase at a flow rate of 1.0 cm^3/min. The wavelength of the UV detector was set at 224 nm. Retention times for DCP, 4CP, 2CP and phenol were 18.22, 8.89, 7.25 and 4.83 min, respectively. PCBs were analyzed using a GC (6890N Agilent, Santa Clara, CA, USA) equipped with an electron capture detector (ECD) and a DB5-MS column (60 m × 0.25 mm × 0.25 μm, Agilent JW, Santa Clara, CA, USA). The carrier gas was helium and the flow rate was 1.0 cm^3/min. The temperature of the injection port was 270 °C and the injection type was splitless. The oven temperature program was 100 °C (20 °C/min) → 180 °C (1 min, 8 °C/min) → 220 °C (10 °C/min) → 300 °C (10 min). To determine the products formed during DCP and PCB degradation with Fe(0) under subcritical conditions, qualitative mass spectrometry analyses were performed using a GC-mass spectrometer (GC-MS, Clarus 600 T GC/MS, Perkin Elmer, Waltham, MA, USA) with a DB-5 column (30 m × 0.25 mm × 0.25 μm, Agilent J&W, Santa Clara, CA, USA).

3. RESULTS AND DISCUSSION

3.1. DEGRADATION OF DCP WITH Fe(0) AT 20–80 °C

The removal of DCP with Fe(0) at 20, 40, 60 and 80 °C is summarized in Fig. 1. Control experiments without Fe(0) showed that DCP was inert for 14 days regardless of temperature (data not shown). At 20 °C, 27.1% of the DCP was rapidly removed within one day, and the removal was thereafter almost halted until 14 days. No reduction daughter products were observed until ten days. Even at 14 days, only 5 μM of 4CP was observed, less than 2% of the initial mass of DCP. These results indicated that the removal of DCP at the earlier stage was probably due to sorption to the iron surface. At 14 days, 33.3% of DCP was removed from solution with Fe(0). As temperature increased, the removal of DCP slightly increased, showing 37.3, 42.0 and 44.7% removal in 14 days at 40, 60 and 80 °C, respectively. The extent of 4CP formation also gradually increased with temperature until 80 °C, indicating that the reduction of DCP with Fe(0) mostly occurred at the *orto* position.

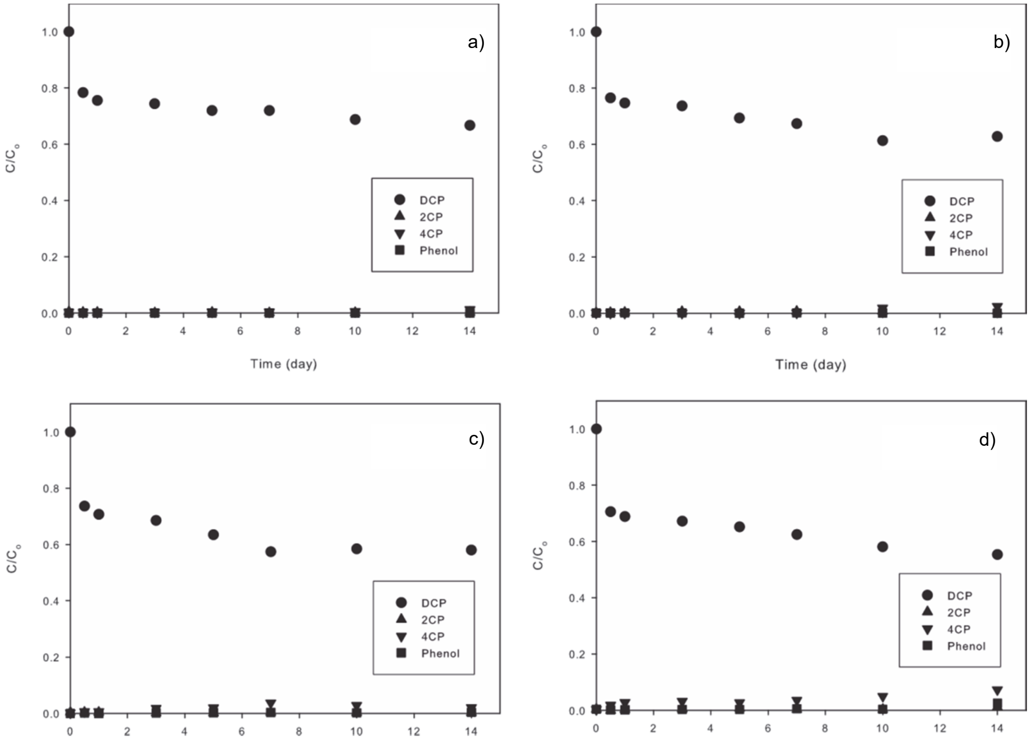

Fig. 1. Removal of DCP in water with Fe(0): a) 20 °C, b) 40 °C, c) 60 °C, d) 80 °C

However, it is likely that the extent of enhancement in DCP reduction with Fe(0) was not significant as temperature increased from 20 ŻC to 80 °C. Even at 80 °C, only 4 μM of phenol was produced, which was 1.3% of the initial mass of DCP. When acid-washed Fe(0) was used, the removal of DCP was not greatly enhanced (Fig. 1). The formation of 4CP and phenol was also limited. It appears that the acid-washed Fe(0) was rapidly passivated by anaerobic corrosion with water molecules. Due to slow kinetics of DCP dechlorination and rapid passivation [2, 23], fresh surface of Fe(0) did not markedly enhance the reductive transformation of DCP.

3.2. DEGRADATION OF DCP WITH Fe(0) UNDER SUBCRITICAL CONDITIONS

Due to the limitation of enhancement in DCP reduction with Fe(0) at 20–80 °C, temperature was further increased under subcritical conditions (150–300 °C) using a temperature-controlled pressurized reactor. As shown in Fig. 2, the removal of DCP was further enhanced as temperature increased to 150–300 °C. At 150 °C, approximately 40% of the initial DCP was removed from solution, producing 4CP in 5 h. Compared with the removal of DCP at 20–80 °C (Fig. 1), the removal rate was clearly enhanced (hours vs. days). However, similar to DCP removal with Fe(0) at 20–80 °C, no significant reduction in the yield of 4CP was observed. Interestingly, control experiments without Fe(0) showed that DCP was transformed at 150 °C. After 5 h, 31% of the DCP was removed, suggesting that thermal decomposition of DCP in addition to reductive transformation might have existed in the DCP-water system under subcritical conditions (Fig. 2).

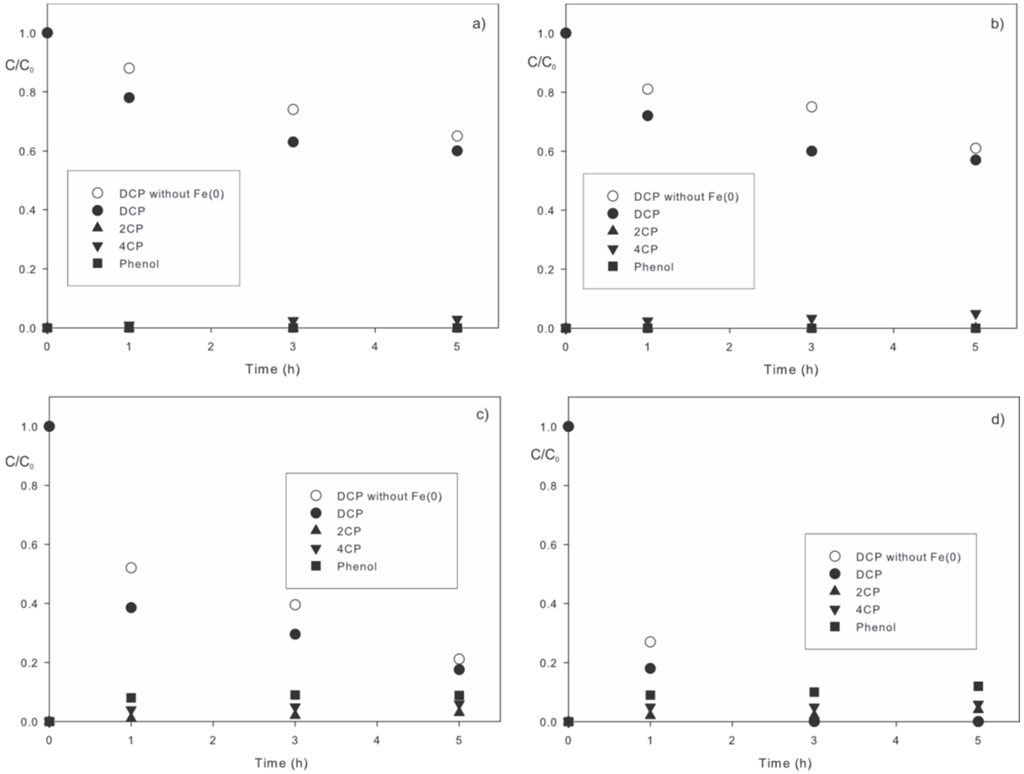

Fig. 2. Removal of DCP in water with Fe(0) under subcritical conditions:
a) 150 °C, b) 200 °C, c) 250 °C d) 300 °C

Experiments for the reduction of DCP with Fe(0) were performed using a 500 cm^3 pressurized reactor including 100 cm^3 of DCP solution and 5 g of Fe(0). When the temperature increased, the internal pressure increased, as determined by the vapor pressure of steam. Under the given conditions, the dissolution of oxygen from air into the solution was markedly increased as the temperature was elevated. When the temperature was elevated from 200 °C to 250 °C, the solubility of oxygen in water increased very abruptly from 0.6–0.7 to 2.6–2.8 cm^3/g [25]. At 300 °C, the solubility of oxygen in water was estimated to be approximately 8–9 cm^3/g, according to extrapolation of the regression curves given by Pray et al. [25]. Therefore, it is plausible that the increased amount of oxygen in subcritical water can enhance the oxidative degradation of DCP at 150–300 °C. To confirm the subcritical water oxidation of DCP, the reactor was purged with Ar for 30 min, and the experiments were conducted without Fe(0) under identical conditions. Due to the limited amount of O_2 in the reactor, a limited amount of DCP (5–10%) was removed from solution after 5 h at 150–300 °C (data not shown). These results indicate that the oxidation under subcritical conditions (SCWO) might be responsible for the removal of DCP in the control experiments.

At 200 °C, the removal of DCP was slightly enhanced compared to that at 150 °C. However, as the temperature was further increased to 250 °C and 300 °C, the removal of DCP was remarkably enhanced (Figs. 2c, d). At 250 °C, 82.5% of DCP was removed in 5 h, producing 4CP (6.1%), 2CP (3.0%) and phenol (8.8%). At 300 °C, complete removal of DCP was obtained after 3 h, and the reduction intermediates and end product accounted for 22.1% of initial DCP in 5 h. Control experiments without Fe(0) indicated that the extent of DCP removal was also enhanced at higher temperatures, with 78.9% in 5 h at 250 °C and 73.0% in 1 h at 300 °C. The results of the control experiments clearly indicate that the removal of DCP from the iron-water system was mostly due to SCWO under subcritical conditions, and that the reductive dechlorination of DCP with Fe(0) was not dominant even at 300 °C. Acid washed Fe(0) did not show any noticeable difference.

3.3. DEGRADATION OF PCBs WITH FE(0) UNDER SUBCRITICAL CONDITIONS

PCBs were removed with Fe(0) under subcritical conditions by 86% at 250 °C (Fig. 3a). Fe(0) free control experiments showed that PCBs were also transformed under subcritical conditions.

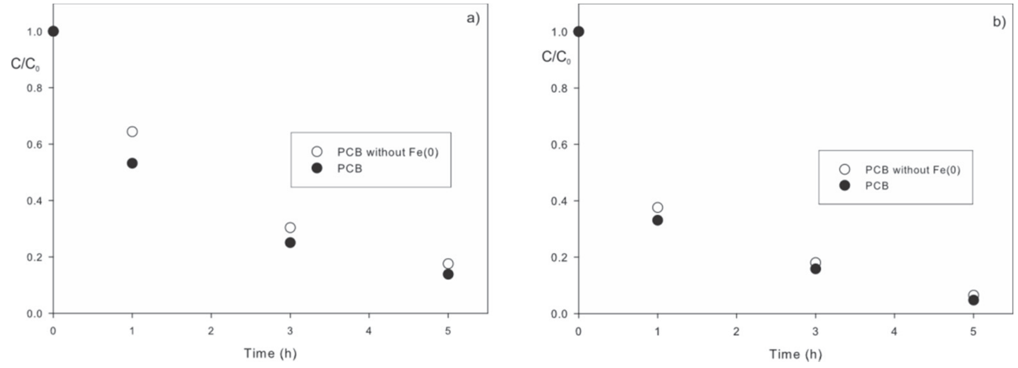

Fig. 3. Removal of PCB (Aroclor 1248) with Fe(0) under subcritical conditions: a) 250 °C, b) 300 °C

Even without Fe(0), 82% of PCBs were removed at 250 °C, indicating that non-reductive thermal decomposition of PCBs occurred at subcritical temperatures, similar to that of DCP. Compared to 250 °C, PCBs were more rapidly removed from solution at 300 °C with or without Fe(0), showing 95% and 93% of removal in 5 h, respectively (Fig. 3b). Therefore, similar to DCP, our results indicate that PCBs in the iron–water system were destroyed mainly via SCWO at 250 °C and 300 °C under the given conditions, consistent with previous results reported by Webber et al. [16]. Considering the difference in PCB removal with or without Fe(0) under subcritical conditions, it appears that the reductive transformation of PCBs with Fe(0) is not significant even at 250 °C or 300 °C.

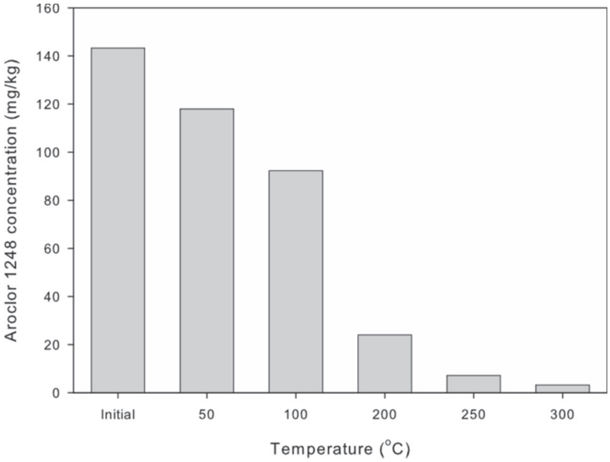

Fig. 4. Results of treatment of PCB (Aroclor 1248) contaminated soil with Fe(0) for 1 h at various temperatures (100 g of contaminated soil, 100 cm^3 of water and 9.5 g of iron)

Using Aroclor 1248 contaminated soil, degradation of PCBs with Fe(0) in the soil–water system at various temperatures was evaluated. The initial concentration of PCBs in the contaminated soil was 143.3 mg/kg. As the temperature increased, the removal of PCBs from the soil was enhanced. At 50 °C and 100 °C, the concentration of PCBs in soil decreased to 117.9 and 92.3 mg/kg, corresponding to 17.8% and 35.6% of PCB removal, respectively (Fig. 4). Because the reductive transformation of PCBs with Fe(0) was not significant even at 300 °C (Fig. 3), the removal of PCBs at 50 °C and 100 °C was probably due to desorption from the soil. As temperature further increased, the removal of PCBs was outstandingly enhanced, showing 95.0% and 97.8% removal at 250 °C and 300 °C, respectively. A control experiment without Fe(0) also showed similar removals under subcritical conditions (data not shown), suggesting that SCWO and desorption may be responsible for the removal of PCBs from the soil.

3.4. IDENTIFICATION OF PRODUCTS USING GC-MS

In order to better understand and obtain insight on the degradation pathways of DCP and PCBs with Fe(0) under subcritical conditions, degradation products were identified through gas chromatography-mass spectrometry (GC-MS) analysis. The identified possible products of DCP degradation under subcritical conditions are summarized in Table 1.

Table 1

Identified compounds after treatment of DCP solution
at 250 °C for 5 h

Retention time [min]	Identified compound	
	without Fe(0)	with Fe(0)
4.41	2-heptanone	–
4.71	heptanal	heptanal
5.99	2-heptanone, 6-methyl	–
6.47	1-heptanol	–
6.83	–	2-chlorophenol
6.94	2-octanone	–
7.31	octanal	octanal
9.33	1-octanol	–
9.84	2-nonanone	–
10.19	nonanal	nonanal
11.88	2,4-dichlorophenol	2,4-dichlorophenol
13.25/13.11	4-chlorophenol	4-chlorophenol

In the absence of Fe(0), aliphatic compounds (C_7–C_9) were formed, including alcohols (1-heptanol and 1-octanol), ketones (2-heptanone, 6-methyl-2-heptanone, 2-octanone, and 2-nonanone) and aldehydes (heptanal, octanal, and nonanal). Though the ring was not cleaved, 4CP, a dechlorinated intermediate, was also identified. Based on the formation of those compounds, it appears that ring cleavage, dechlorination, and polymerization may be involved in the degradation of DCP under subcritical conditions. In the presence of Fe(0), the identified products were different. First, aliphatic compounds (C_7–C_9) were identified. However, unlike the Fe(0) free subcritical system, the only type of aliphatic products were aldehydes, including heptanal, octanal and nonanal. The presence of Fe(0) may thus enhance the oxidation of alcohols and ketones to aldehydes. Further study is needed to clearly elucidate Fe(0) enhanced oxidation. Second, dechlorinated intermediates 4CP and 2CP were also formed, probably due to the enhancement of reductive transformation of DCP with Fe(0) (Fig. 3). Similarly, ring cleavage, dechlorination and polymerization may also have participated in the degradation of DCP with Fe(0) under subcritical conditions.

Table 2

Identified compounds after treatment of Aroclor 1248 solution (with 20% methanol) at 250 °C for 5 h

Retention time [min]	Identified compound	
	without Fe(0)	with Fe(0)
4.39	benzene, 1,3-dimethyl	benzene, 1,3-dimethyl
5.10	ethane, 1,1,2,2,-tetrachloro-	ethane, 1,1,2,2,-tetrachloro-
5.24	–	methyl hexanoate (hexanoic acid, methyl ester)
6.59	–	octanoic acid, 2-methyl-, methyl ester
6.79	–	benzene, methoxymethyl
8.05	–	2-propyl-1-pentanol
12.64	2-decanone	–
13.03	decanal	–
14.24	benzoic acid, 4-chloro, methyl ester	–
15.38	1-undecanone	–
15.77	octadecanal	–
17.43	biphenyl	biphenyl
17.53	dodecane, 1,1-dimethoxy	–
17.98	2-dodecanone	–
18.19	2-undecanone,6,10-dimethyl-	–
18.37	hexadecanal	–
19.99	1-tridecanol	–
20.33	–	3-chlorobiphenyl
20.46	2-tridecanone	–
20.84	octadecanal	–
21.17	–	dodecanoic acid, methyl ester
21.96	2-nonadecanone	–
22.53	–	propanoic acid, 2-methyl-, 1-(1,1-dimethylethyl)-2-methyl-1,3-prop
22.96	1,1′-biphenyl, 2,2′-dichloro-	1,1′-biphenyl, 2,2′-dichloro-
24.80	1,1′-biphenyl, 3,5-dichloro-	1,1′-biphenyl, 3,5-dichloro-
25.04	2-nonadecanone	–
25.48	1,1′-biphenyl, 2,3,4-trichloro-	1,1′-biphenyl, 2,3,4-trichloro-
25.64	methyl tetradecanoate (tetradenoic acid, methyl ester)	–
26.00	1-tridecene	–
26.56–34.15	Aroclor 1248 pattern	Aroclor 1248 pattern

In the case of PCBs, the identification of products was somewhat complicated because Aroclor 1248 is a mixture of congeners of chlorinated biphenyl (Table 2). In the absence of Fe(0), it was shown that, similar to DCP, aliphatic compounds (C_{10}–C_{19}) were produced; alcohol (1-tridecanol), ketones (2-decanone, 1-undecanone, 6,10-dimethyl-2-undecanone, 2-dodecanone, 2-tridecanone, 2-nonadecanone), aldehydes (decanal, octadecanal, hexadecanal), alkane (1,1-dimethoxyl dodecane), alkene (1-tridecene) and acid (methyl tetradecanoate). Second, the aromatic compound 1,3-dimethyl benzene was produced. Third, chlorinated aliphatic/aromatic compounds were produced, including 1,1,2,2-tetrachloroethane and 4-chloro-methyl ester benzoic acid. Fourth, possible dechlorination products were produced: 2,2′-dichloro-1,1′-biphenyl, 3,5-dichloro-1,1′-biphenyl, 2,3,4-trichloro-1,1′-biphenyl and biphenyl.

The presence of Fe(0) under otherwise identical conditions showed different byproducts. Aliphatic organic acids were dominantly produced: methyl hexanoate (hexanoic acid, methyl ester), octanoic acid 2-methyl-methyl ester, dodecanoic acid methyl ester and propanoic acid 2-methyl- 1-(1,1-dimethylethyl)-2-methyl-1,3-prop. In contrast, ketones and aldehydes were not formed. Similar to the Fe(0)-free control experiments, aromatic and chlorinated compounds were also formed, including 1,3-dimethyl benzene and 1,1,2,2-tetrachloroethane. In addition to the dechlorination products found in the Fe(0) control experiments, 3-chlorobiphenyl was identified. Therefore, similar to DCP, it is likely that ring cleavage, dechlorination, polymerization and oxidation (to organic acid) were occurring during the degradation of the congeners of chlorinated biphenyl under subcritical conditions with or without Fe(0). No PCDDs or PCDFs were produced in either system under subcritical conditions.

4. CONCLUSIONS

DCP and PCBs were rapidly degraded under subcritical conditions irrespective of the presence of Fe(0). The degradation of DCP and PCBs occurred mainly via subcritical water oxidation (SCWO) and in part through reductive transformation with Fe(0). Real PCB contaminated soil was also effectively treated, showing 97.8% removal efficiency. Product identification using GC-MS suggested that ring cleavage, dechlorination, and polymerization might be involved in the degradation of DCP and PCBs with Fe(0) under subcritical conditions. Our results suggest that treatment under subcritical conditions may be a feasible option for the remediation of persistent organic pollutants such as DCP and PCBs. A pilot-scale SCWO demonstration unit is being designed and fabricated for field verification.

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