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Iron-mediated reactions of polychlorinated biphenyls in electrochemical peroxidation process (ECP)

M. Arienzo [a,*], J. Chiarenzelli [b], R. Scrudato [b], J. Pagano [b], L. Falanga [b], B. Connor [b]

[a] *Dipartimento di Scienze Chimico-Agrarie, Università degli Studi di Napoli Federico II, Napoli, Italy*
[b] *Environmental Research Center, 319 Piez Hall, SUNY @ Oswego, Oswego, NY 13126, USA*

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Abstract

A study was conducted to explore some of the basic processes of polychlorinated biphenyl (PCB) destruction by a new technology termed electrochemical peroxidation process (ECP). ECP represents an enhancement of the classic Fenton reaction ($H_2O_2 + Fe^{2+}$) in which iron is electrochemically generated by steel electrodes. Focus was on the extent of adsorption of a mixture of Aroclor 1248 on steel electrodes in comparison to iron filings. Commercially available zero-valent iron filings rapidly adsorbed PCBs from an aqueous solution of Aroclor 1248. Within 4 h, all the PCBs were adsorbed at 1%, 5%, and 10% Fe^0 (w/v) concentrations. Little difference in adsorption was found between acidic (2.3) and unamended solutions (pH 5.5), even though significant differences in iron oxidation state and Fe^{2+} concentrations were measured in solution. PCB adsorption also occurs on steel electrodes regardless of the pH or electric current applied (AC or DC), suggesting the combination of oxidizing (free radical-mediated reactions) and reducing (dechlorination reactions) iron-mediated degradation pathways may be possible. Extraction of the iron powder after 48 h of contact time yielded the progressive recovery of biphenyl with increasing Fe mass(from 0.4% to 3.5%) and changes of the PCB congener-specific pattern as a consequence of dechlorination. A variety of daughter congeners similar to those accumulated during anaerobic microbial dechlorination of Aroclor 1248 in contaminated sediments indicate preferential removal of *meta*- and *para*-chlorines. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Iron, in its zero-valent state (Fe^0), dissolved ferrous form (Fe^{2+}), or as ferric iron (Fe^{3+}) has proven effective in the degradation of contaminants in groundwater, industrial process waters, landfill leachate, soil, sediment, and slurries. The use of iron to address environmental problems involves a variety of oxidative and reductive mechanisms. Contaminant degradation reactions utilizing iron include: light and ultrasound absorption (Pignatello, 1992; Pignatello and Chapa, 1994; Hung and Hoffman, 1998); free radical production via Fenton's reagent (Fenton, 1894; Venkatadri and Peters, 1993) and variants utilizing electrochemically generated ferrous iron (Fe^{2+}) (Sudoh et al., 1986; Tzedakis et al., 1989; Hsiao and Nobe, 1993; Pratap and Lemley, 1994; Chiarenzelli et al., 1997; Roe and Lemley, 1997); dechlorination by electrolytic reduction and in bimetallic systems (Matheson and Tratnyek, 1994; Grittini et al., 1995); soluble iron salts promoting microbial anaerobic dechlorination of

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[*] Corresponding author. Tel.: +39-081-788-5205; fax: +39-081-775-5130.

E-mail address: arienzo@katamail.com (M. Arienzo).

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polychlorinated biphenyls (PCB) (Zwiernik et al., 1998).

Recently, iron-mediated processes, including in situ applications of zero-valent iron 'fences' and Fenton's reagent, have been utilized to address groundwater contamination. Zero-valent iron has proven useful in the dechlorination (Eq. (1)) of a wide variety of organic contaminants including hydrophobic compounds such as PCBs, and DDT and its degradation products (Sayles et al., 1997; Wang and Zhang, 1997; Tratnyek, 1996). Because it produces hydroxyl radicals (Eq. (2)), Fenton's reagent is a widely used and versatile oxidizer capable of degrading a variety of organic compounds (Venkatadri and Peters, 1993). Clearly, remedial processes that can combine both the reductive (Eq. (1)) and oxidative (Eq. (2)) degradation pathways of iron are desired.

$$\mathrm{Fe^0 + RX + H^+ \rightarrow Fe^{2+} + RH} + X^- \tag{1}$$

$$\mathrm{H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^0} \tag{2}$$

Both reactions are possible in the electrochemical peroxidation process (ECP) a recent technology developed to enhance the effectiveness of the Fenton reaction. The ECP utilizes an electric current and sacrificial steel electrodes to supply soluble Fe^{2+} as in Eqs. (3) and (4) (Pratap and Lemley, 1994; Chiarenzelli et al., 1997; Roe and Lemley, 1997; Pratap and Lemley, 1998). Iron dissolution is enhanced by lowering the pH of the solution and thus eliminating the addition of iron sulfate or chloride salts to the treatment system (Chiarenzelli et al., 1997).

$$\mathrm{Fe^0(s) \rightarrow Fe^{2+} + 2e^-} \tag{3}$$

$$\mathrm{2H_2O + 2e^- \rightarrow H_2 + 2OH^-} \tag{4}$$

Batch treatment pilot-scale studies on 200 l of subsurface storage tank water from a New York State Superfund site contaminated with chlorinated solvents and PCBs have shown ECP to achieve high levels of contaminant degradation with reaction times of minutes and minimal peroxide additions (Chiarenzelli et al., 1997; Chiarenzelli et al., 2001). Given the slow flow rate of most natural groundwater systems, implementation of ECP includes both 'fast' hydroxyl radical-mediated reactions and other 'slower' reactions which may occur during the adsorption of contaminants to the steel electrodes of the ECP-technology.

In this paper we report on the extent of adsorption of PCBs on steel electrodes and for comparison on zero-valent iron powder. The effect of pH, induced current and consequently Fe^{2+} concentrations and the nature of degradation products formed at ambient conditions were also investigated.

2. Material and methods

2.1. Reagents

All reagents utilized in these experiments including hexane, sodium sulfate, sodium hydroxide, sulfuric acid (Fisher Scientific), Florisil and tetrabutylammonium (TBA) sulfate (Sigma Chemical Company) were reagent grade. Concentrated Aroclor 1248 standard was obtained from Chemservice Inc. and a stock solution of 322 mg/l in hexane was prepared. Zero-valent (Fe^0) iron metal (40 mesh, 3.3 m^2/g) was obtained from Fisher Scientific and analyzed for PCB content.

2.2. Experimental procedure

An aqueous PCB solution was prepared using the generator column method (Sokol et al., 1992). Aroclor 1248 standard solution (3 mg 1248) was evaporated onto glass beads within a 35 cm glass column through which DDI was pumped at a rate of 2 ml/min. The final PCB concentration of the entire 4 l batch was 61.2 ± 8.3 μg/l ($n = 4$). Adsorption of PCBs on zero-valent iron was determined by placing 1.2 (1% w/v), 6.0 (5% w/v), and 12.0 g (10% w/v) of Fe^0 in 125 ml Erlenmeyer flasks with 120 ml of PCB aqueous solution. Flasks were sealed with lids to minimize evaporative loss and agitated in the dark at 25 ± 1°C using an oscillatory shaker. At 0.25, 1, 4, 24, and 48 h, the iron was allowed to settle and 20 ml aqueous subsamples were taken. After 48 h, the supernatant was removed and the Fe^0 was added to 50 ml of a 1:1 hexane/acetone mixture and stored at 4°C until extracted. To assess the effect of the pH on short-term adsorption of PCBs the experiment with 1% Fe^0 (w/v) was performed beside the pH 5.5 of the stock PCB solution at pH 2.3 and subsampled at 3, 6, and 9 min. All experiments were conducted in duplicate. The average relative percent difference was 17% for aqueous duplicate samples and 6.7% for Fe^0 duplicate samples, which included spiking variability and all analytical errors.

The adsorption of PCBs on iron electrodes was determined by conducting five-minute electrolysis experiments and measuring PCB concentration in the aqueous phase and adsorbed to the electrodes. Two mild steel electrodes were placed 1 cm apart in a 250 ml beaker and 200 ml of PCB stock solution were added, submerging 120 cm^2 of the electrode surface area. In some experiments, before applying current, the pH was adjusted to 2.3 (1 N sulfuric acid). Before use, the electrodes were abraded with sandpaper and then cleaned with successive rinses of water, acetone, ethyl acetate, and hexane. The PCB solution was mixed using a teflon-coated magnetic stir bar. Direct current (DC) and alternating current (AC) (0.2 A) were applied for 5 min and regulated by an EG&G potentiostat/galvanostat. Alternating current was reversed every 5 s. Aqueous Fe^{2+} concentrations were monitored every minute using EM Quant Test Strips (EM Science) and a reflectance meter. Total aqueous iron concentrations were measured using a Perkin Elmer Model 3030 B atomic absorption spectrometer equipped with a deuterium-arc background correction.

2.3. Extraction of aqueous phase and adsorbed PCBs

Decachlorobiphenyl was added to the aqueous subsamples before extraction to monitor extraction recovery. Subsamples (20 ml) were extracted using triplicate hexane shakes (50 ml). The hexane solution was collected in a 250 ml beaker containing 10 g of anhydrous sodium sulfate to absorb any water remaining in the hexane extract. The hexane extract was oxidized with sulfuric acid. Elemental sulfur and polar compounds were removed from the extracts using 1 ml of TBA sulfate and 4% activated Florisil columns, respectively. Final concentration to 2 ml was carried out in a Kuderna-Danish condensor on a steam bath. Condensed samples in hexane were stored at 4°C until analyzed. Iron was extracted by shaking with 120 ml of hexane in a separatory funnel and then back extracted with 120 ml of water. The water was discarded and hexane extract was treated with TBA to remove sulfur. The treated extract was passed through sodium sulfate to absorb any remaining water and then concentrated to 5 ml. PCB spike (1248 solution) recovery from iron averaged 88%. Decachlorobiphenyl recovery from water was $89.3 \pm 8.2\%$ and from iron $91.2 \pm 3.1\%$.

Electrodes were extracted by sequential ultrasonication in 200 ml of acetone, acetone/hexane (1:1), and hexane after surrogate spiking. The extracts were combined in a separatory funnel, back extracted with 300 ml of DDI, dried using sodium sulfate, oxidized by sulfuric acid, and cleaned using a Florisil column. Hexane extracts were condensed to 2 ml and stored at 4°C until analyzed. Decachlorobiphenyl recovery ranged from $95.9 \pm 5.7\%$ and mass balance calculations indicated recovery of 89–104% of the original PCB mass.

2.4. PCB gas chromatography

Complete analytical details pertaining to PCB analysis are given in Pagano et al. (1995). Congener-specific PCB analysis was performed on a Hewlett-Packard (HP) HP-5890 gas chromatograph using an electron capture detector and a HP Ultra DB-5 capillary column with a 0.22 nm inner diameter and 0.33 m film thickness. Helium as a carrier gas and argon/methane (P5) as the makeup gas. The system was temperature programmed after 2 min at 100–160°C at 10°C/min and then increased by 3°C/min to 270°C and held for 16 min. The injection port and detector were maintained at 330°C and 270°C, respectively. The gas chromatograph was calibrated using a mixed aroclor standard prepared by the New York State Department of Health Wadsworth Laboratory. Biphenyl was identified in trace amounts in the Aroclor 1248 standard and in larger amounts in hexane extracts of iron particles by GC/EI-MS by comparison with biphenyl standard (Aldrich).

Chromatographic data were computed and processed with use of the HP 3365 Series II ChemStation software and Microsoft Excel 5.0 spreadsheet procedures. The HP software system generated the identity and amount of each PCB congener. Data were used to calculate average chlorination (Cl/biphenyl), and the mole fraction percentage by congener, chlorine number, and steric position. Co-eluting congeners were assumed to be in equal proportions for all spreadsheet calculations.

3. Results and discussion

3.1. Adsorption of PCBs by Fe^0 powder

Exposure of an aqueous solution of Aroclor 1248 (61.2 ± 8.3 μg/l) to 1–10% (w/v) zero-valent iron (henceforth iron) removed more than 90% of PCBs from solution within 4 h of contact (Fig. 1(a)). The rate of adsorption was initially rapid and then decreased with time. Within 15 min ~60% of the PCBs were adsorbed to the iron (1% w/v), compared to 85% when 10 times more iron was used. Under the experimental conditions investigated, the effect of increasing the iron mass and surface area by an order of magnitude on the adsorption rate was minor. These data suggest that PCBs exhibit a high affinity for iron adsorption and that contaminant mass transport to its surface may be the primary factor limiting adsorption rates. Little change in the mole fraction of ortho/meta/para-positioned chlorines or the average chlorine/biphenyl ratio was noted relative to the Aroclor 1248 aqueous solution in longer-term experiments. However, water samples from short-term experiments, (not shown), suggest rapid adsorption of more chlorinated congeners and delayed adsorption of more soluble lower, ortho-chlorinated congeners.

3.2. Effect of pH on adsorption and Fe^{2+} concentrations

The effects of acidifying the solution (pH of unaltered solution was 5.5) on PCB adsorption to iron (1% w/v) were assessed at pH 2.3 by adjustment with 1 N sulfuric acid. Results shown in Fig. 1(b) indicate that PCB adsorption was not affected by pH over every time period investigated. The PCBs recovered from the aqueous solution after 4 h of contact with 1% Fe (w/v) yielded 10% and 8% of the original PCB mass, respectively at pH 2.3 and 5.5, suggesting little, if any, difference in adsorption during longer exposure times (Fig. 1(b)). These data suggest that once iron saturation in solution

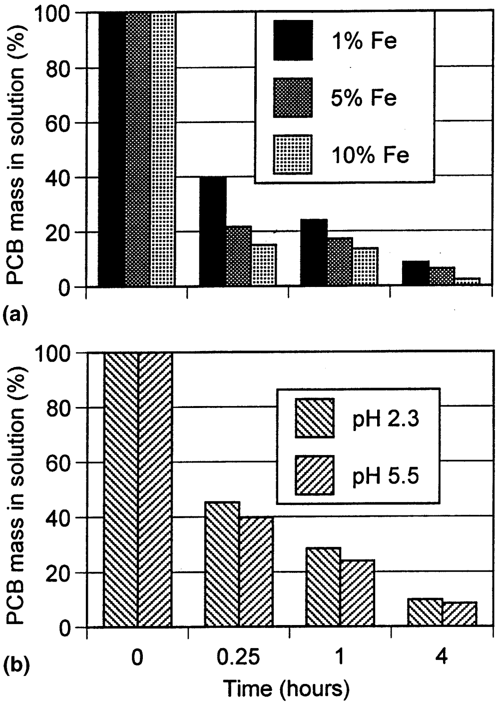

Fig. 1. Adsorption of aqueous phase PCBs on zero-valent iron: (a) percentage of PCB mass remaining in aqueous solution (120 ml, pH = 5.5) at iron concentrations of 1%, 5%, and 10% (w/v); (b) comparison of the percentage of PCB mass remaining in aqueous solution (120 ml, iron 1%) at pH 2.3 and 5.5 (unamended).

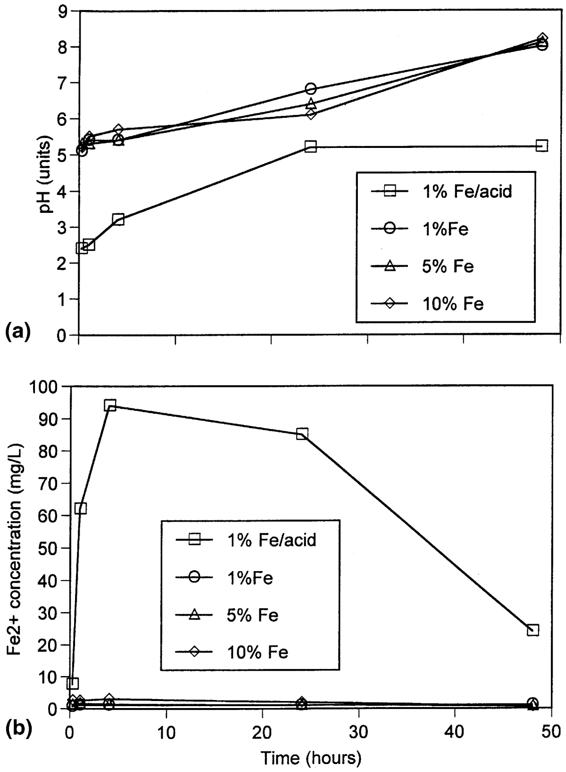

Fig. 2. (a) Variation of pH with time in PCB adsorption experiments (each data point represents the average of two measurements). (b) Variation of Fe^{2+} concentrations with time in PCB adsorption experiments (each data point represents the average of two measurements).

is reached, adsorption can occur uninhibited. At 5% and 10% iron concentrations, 99% and 108% of the PCB mass originally in aqueous solution were recovered from the iron grains, indicating complete adsorption. Figs. 2(a) and (b) depict pH and Fe^{2+} variation in solution between 0 and 48 h, respectively; data show a significant increase of about 3 pH units in both unaltered and acidified samples. The acidified sample containing 1% Fe reached a pH plateau of 5.2 units at 24 h. A maximum concentration of dissolved Fe^{2+} was measured at 4 h (94 mg/l) with a subsequent decrease to 24 mg/l at 48 h (Fig. 2(b)). Elevated concentrations of Fe^{2+} are the consequence of the corrosion of zero-valent iron, an electrochemical process in which Fe^0 is oxidized to Fe^{2+} (Eq. (5)). The associated cathodic reaction may vary with the reactivity of available electron acceptors. In a purely aqueous media, acceptors include H^+, H_2O, and O_2, yielding the reduction of these species to H_2 and OH^- by Eqs. (5)–(7).

$$2Fe^0 + O_2 + 2H_2O \leftrightarrow Fe^{2+} + 4OH^- \quad (5)$$

$$Fe^0 + 2H^+ \leftrightarrow Fe^{2+} + H_2 \quad (6)$$

$$Fe^0 + 2H_2O \leftrightarrow Fe^{2+} + H_2 + 2OH^- \quad (7)$$

Under acidic conditions, dissolution of iron is primarily by Eq. (6). This explains the greater corrosion of the metal at pH 2.3 within the first 4 h of reaction. Increase of OH^- concentration in solution occurs by Eqs. (5) and (7). The concomitant increase in pH (2.3–5.2 at 24 h) causes oxidation of Fe^{2+} to Fe^{3+} thereby reducing the Fe^{2+} concentrations with time. The total Fe dissolved concentration at 48 h was 45 mg/l (Table 1), approximately half of the Fe^{2+} detected in the solution in 4 h. A suspended orange–brown flocculent occurred during the experiments and most likely consists of ferric hydroxides; drying and heating of the separated flocculent yielded hematite (Fe_2O_3).

Table 1
Concentration of Fe^{2+} after 48 h of immersion of zero-valent iron (1, 5, and 10 w/v) in an aqueous solution of Aroclor 1248 (pH 2.3 and 5.5)

Experimental parameters	1% Fe^0 pH 2.3	1% Fe^0 pH 5.5	5% Fe^0 pH 5.5	10% Fe^0 pH 5.5
Fe^{2+} concentration (mg/l)	45	0.5	18.3	28.5

3.3. Degradation products

Even though at low concentration, 0.4–1.5–3.5%, biphenyl was identified in the GC/EI-MS chromatogram of the hexane extract of iron grains after 48 h of submersion at all iron concentrations investigated, 1–5–10%, respectively, Fig. 3. Biphenyl was also identified in trace amounts, 0.1%, in the Aroclor 1248 standard. Biphenyl was not identified in the hexane extracts of the PCB aqueous solutions suggesting it was primarily adsorbed on the iron grains. Biphenyl found in experimental samples is interpreted as a product of PCB dechlorination occurring during adsorption to zero-valent iron.

The production of biphenyl during adsorption to zero-valent iron is supported by several observations. Aqueous PCB solutions were exposed to higher iron contained larger concentrations of biphenyl (Fig. 3). In addition, the gas chromatograph trace of iron grain extracts had additional low retention time peaks not present in the original aqueous 1248 solution (Fig. 4) or in extracts of iron alone (iron blanks). These peaks represent PCB congeners and/or degradation products not identifiable by our analytical procedures. Some of the PCB congeners measured show either progressive reduction or increase in peak area with iron mass (Figs. 3–5). In particular, IUPAC# peaks 17 (24/2), and 25 (24/3) showed the greatest reduction, while congeners 1 (2), 4 (2/2), and 7 (24) showed the largest increases (Fig. 5). The 'parent' congeners likely yielded the 'daughter' congeners by dechlorination of *meta*- or *para*-chlorines. Finally, although biphenyl was also found in the Aroclor 1248 standard, its concentration was more than an order of magnitude less than that recovered from the iron after adsorption experiments. The production of biphenyl was confirmed in two additional replicate experiments.

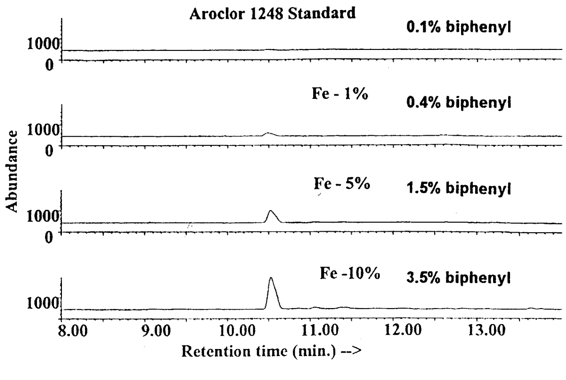

Fig. 3. GC/EI-MS chromatograms showing biphenyl in Aroclor 1248 standard (a) and recovered from zero-valent iron after 48 h adsorption experiments (b) 1%, (c) 5%, and (d) 10% iron (w/v).

The production of small amounts of biphenyl during 48 h experiments at ambient conditions is in agreement with previous studies. Little degradation of PCBs (Aroclors 1254) was in fact also reported by Wang and Zhang (1997) in the presence of commercial iron powders within 17 h and at ambient temperature (22 ± 1°C). Chuang et al. (1995) reported the relatively rapid (10 min) dechlorination of PCBs (Aroclors 1221 and 1254) and production of biphenyl in the presence of zero-valent iron at temperatures in excess of 300°C; well below the 800°C thermodynamic stability limit of PCBs. Similar reaction rates were observed when a bimetallic Pd–Fe system was used to dechlorinate Aroclors 1254 and 1260 in an aqueous acetone/methanol solution at ambient temperatures (Grittini et al., 1995). Zero-valent iron alone promoted the dechlorination of DDT, DDD, and DDE in aqueous solutions and at ambient temperatures during 20 day reaction periods (Sayles et al., 1997) and biphenyl was produced when PCBs were exposed to nanoscale iron for 17 h (Wang and Zhang, 1997). A general consensus suggests that dechlorination takes place as surface reactions on zero-valent iron particles. Here we have demonstrated that PCBs rapidly adsorb to iron filings.

In view of the strong affinity of PCBs to adsorb on the surface of iron, dechlorination probably involves either direct electron transfer or complexation via a product of iron corrosion. The incomplete reactions observed in this study provide evidence of direct dechlorination reactions in which congeners in an aqueous solution adsorb iron to surfaces and are dechlorinated. It is interesting to note that the ortho-chlorinated congeners produced by dechlorination (2, 2/2, 24) are similar to those observed in anaerobically dechlorinated sediments contaminated with Aroclor 1248 (Sokol et al., 1994).

3.4. Reaction of PCBs with steel electrodes

One of the goals of this research was to evaluate the effect of the electric current on PCB adsorption to immersed steel electrodes. Table 2 shows PCB mass balance during immersion of steel electrodes in an aqueous solution of Aroclor 1248 for 5 min. The total PCB mass recovered (Table 2) was calculated by summing the mass of PCBs remaining in solution and the mass captured on the cathode and anode. Control electrodes (no current) and those to which 0.25 A of DC and AC were applied adsorbed similar PCB mass. No difference in the amount or pattern of PCBs adsorbed on the electrodes at pH 2.3 was noted regardless of whether current was applied.

The total submerged surface area of the two electrodes was 120 cm^2/200 ml (72 cm^2/120 ml), approximately corresponding to twice the surface area available in experiments conducted with 1% iron (39.6 cm^2/120 ml). After 5 min ~10% of the PCBs in aqueous solution

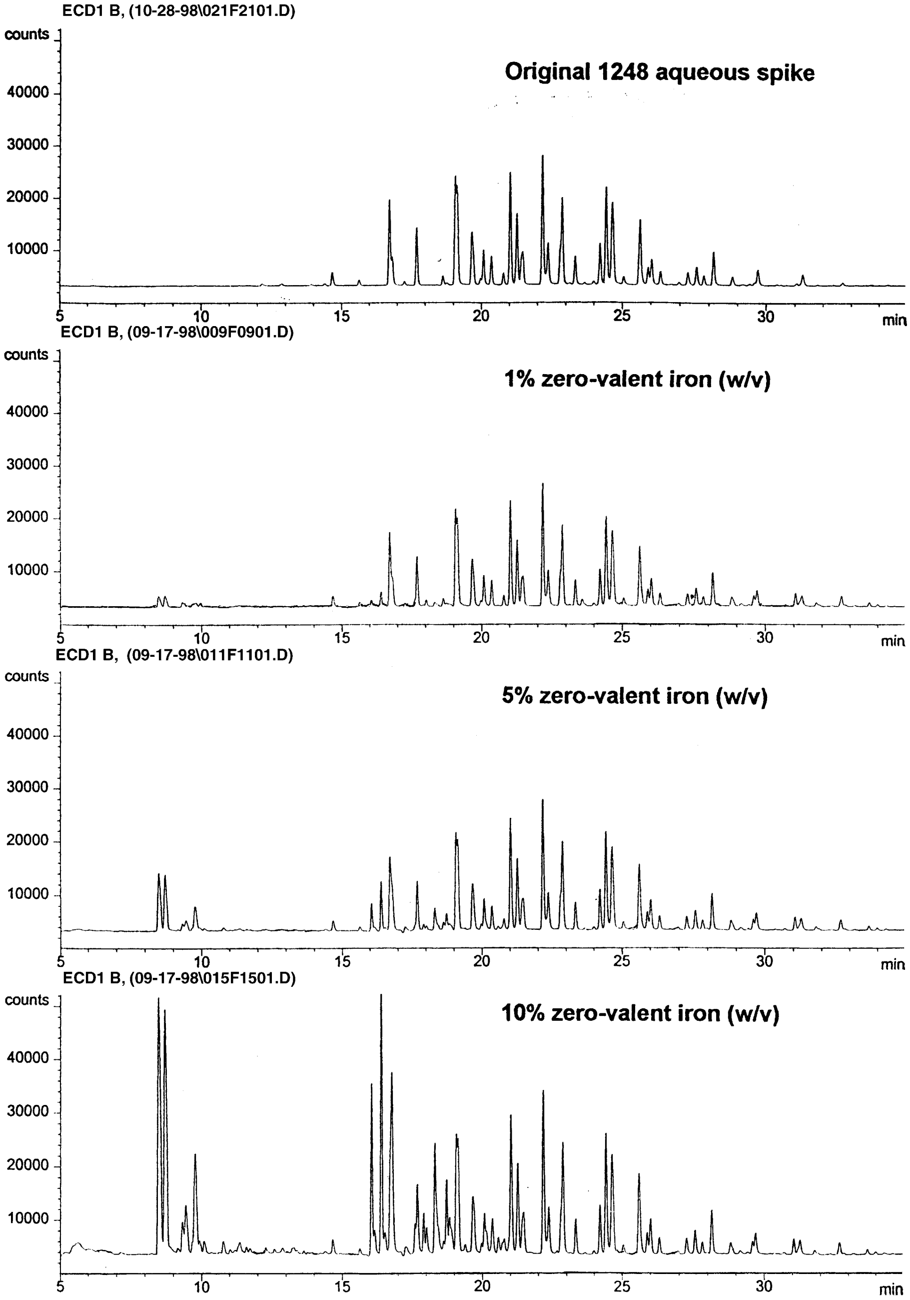

Fig. 4. GC/ECD equal PCB mass chromatograms showing alteration of congener-specific pattern of aqueous Aroclor 1248 with exposure to increasing amounts of zero-valent iron.

were adsorbed on the steel electrodes regardless of the presence of current or its form (DC or AC). In the experiment conducted with 1% iron filings, nearly 65% of the PCBs were adsorbed to the iron after 6 min. The difference in PCB adsorption is attributed to differences in the surface morphology of iron grains and cold-rolled steel electrodes. This suggests that the use of high surface area iron electrodes will enhance adsorption during electrochemical reactions.

The lower amount of adsorption of PCBs on the electrodes at 5 min (~10%) relative to iron filings was accompanied by greater chlorine/biphenyl and shifts in steric positioning percentages relative to the aqueous Aroclor 1248 solution. This confirms trends evident in

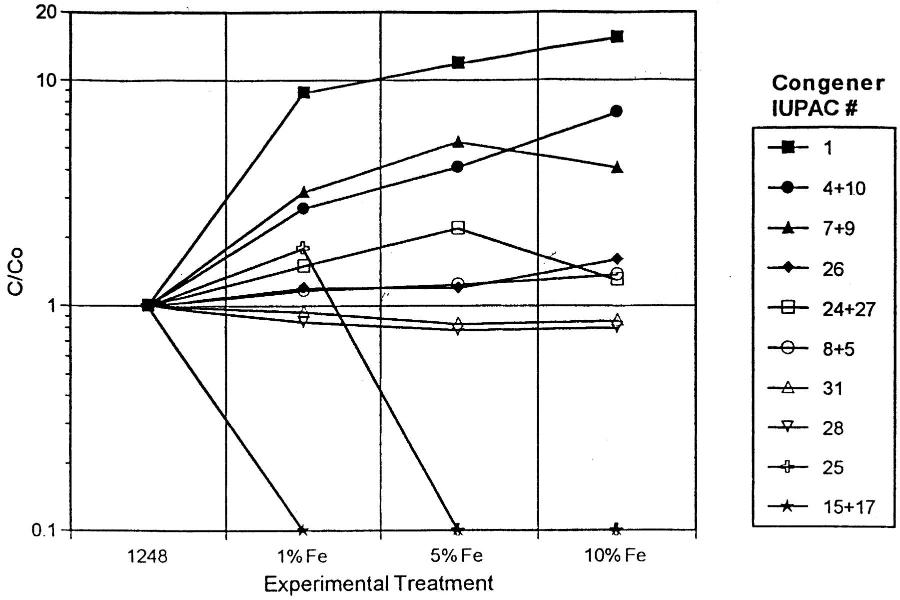

Fig. 5. The relative increase and/or decrease in select congener concentrations in experimental samples compared to the original Aroclor 1248 aqueous spike. Congeners 15 + 17 and 25 were entirely depleted after 48 h exposure to 1% and 5% iron, respectively.

Table 2
Mass balance and partitioning of PCBs between aqueous phase and submerged electrodes after 5 min of 0.25 mA AC, DC, and without current at pH 2.3[a]

Experimental parameters	AC	DC	No applied current
Solution	6.95 (90.7%)	5.74 (87.6%)	6.54 (89.2%)
Cathode/electrode	0.32 (4.2%)	0.36 (5.6%)	0.42 (6.0%)
Anode/electrode	0.39 (5.1%)	0.45 (6.8%)	0.35 (4.8%)
Total	7.66 μg	6.55 μg	7.32 μg
Mass balance	104.4%	89.2%	100.0%

[a] All values are given in μg; % with respect to total recovered given in parentheses.

Table 3
Concentrations of total (Fe_T) and Fe^{2+} during electrolysis of Aroclor 1248 aqueous solution at pH 2.3 and 11.0 with 0.25 mA of AC and DC

Time (min)	Fe_T (mg/l)		Fe^{2+} (mg/l)	
	DC, pH = 11.0	AC, pH = 11.0	DC, pH = 2.3	AC, pH = 2.3
0	0	0	0	0
1	16	7.6	18	38
2	18	6.5	25	55
3	17	8.4	33	74
4	28	11	39	82
5	38	15	47	101

the water samples from short-term experiments suggesting early, preferential adsorption of more highly chlorinated congeners.

Tracking total Fe and Fe^{2+} concentrations during electrolysis (Table 3) revealed that at pH 2.3 iron dissolution is a function of effective surface area of the electrodes. At each monitored time, Fe^{2+} concentration during AC was twice that during DC. That is, if the polarity of the current is periodically reversed, the amount of Fe^{2+} in solution is essentially doubled.

Presumably, during AC, both electrodes undergo cathodic dissolution as displayed by Eqs. (6) and (7), effectively doubling the amount of Fe^{2+} available for Fenton's reagent reactions. Fe^{2+} concentrations over 100 ppm were observed in solution after 5 min of electrolysis with current densities of 1 mA/cm^2 suggesting electrochemistry provides an efficient alternative to the addition of ferrous salts to promote degradation by Fenton's reagent.

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References

Chiarenzelli, J., Scrudato, R., Fabrizio, M., Wunderlich, M.L., 1997. Electrochemical peroxidation of PCBs and VOCs in subsurface storage tank water and slurry. In: Proceedings of the Second International Symposium on Environmental Applications of Advanced Oxidation Technologies, vol. 4. San Francisco, CA, pp. 77–89.

Chiarenzelli, J., Scrudato, R., Wunderlich, M.L., Pagano, J., Hong, C.S., 2001. Combined steam distillation and electrochemical peroxidation (ECP) treatment of river sediment contaminated by PCBs. J. Adv. Oxid. Technol., in press.

Chuang, F., Larson, R.A., Wessman, M.S., 1995. Zero-valent iron-promoted dechlorination of polychlorinated biphenyls. Environ. Sci. Technol. 29 (9), 2460–2463.

Fenton, H., 1894. Oxidation of tartaric acid in the presence of iron. J. Chem. Soc. 65, 899.

Grittini, C., Malcomson, M., Fernando, Q., Korte, N., 1995. Rapid dechlorination of polychlorinated biphenyls on the surface of Pd/Fe bimetallic system. Environ. Sci. Technol. 29 (11), 2898–2900.

Hsiao, Y., Nobe, K., 1993. Hydroxylation of chlorobenzene and phenol in a packed bed flow reactor with electrogenerated Fenton's reagent. J. Appl. Electrochem. 23, 943–945.

Hung, H., Hoffman, M., 1998. Kinetics and mechanism of the enhanced reductive degradation of CCl_4 by elemental iron in the presence of ultrasound. Environ. Sci. Technol. 32, 3011–3016.

Matheson, L.J., Tratnyek, P.G., 1994. Reductive dechlorination of chlorinated methanes by iron metal. Environ. Sci. Technol. 28, 2045–2053.

Pagano, J., Scrudato, R., Roberts, R., Bemis, J., 1995. Reductive dechlorination of PCB-contaminated sediments in an anaerobic bioreactor system. Environ. Sci. Technol. 29, 2564–2589.

Pignatello, J., 1992. Dark and photoassisted Fe^{+3}-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. Environ. Sci. Technol. 26, 944–951.

Pignatello, J., Chapa, G., 1994. Degradation of PCBs by ferric iron, hydrogen peroxide and UV light. Environ. Toxicol. Chem. 13, 423–427.

Pratap, K., Lemley, A., 1994. Electrochemical peroxide treatment of aqueous herbicide solutions. J. Agric. Food Chem. 42, 209–215.

Pratap, K., Lemley, A., 1998. Fenton electrochemical treatment of aqueous atrazine and metolachlor. J. Agric. Food Chem. 46, 3285–3291.

Roe, B., Lemley, A., 1997. Treatment of two insecticides in an electrochemical Fenton system. J. Environ. Sci. Health B 32, 261–281.

Sayles, G.D., You, G., Wang, M., Kupferle, M.J., 1997. DDT, DDD, and DDE dechlorination by zero-valent iron. Environ. Sci. Technol. 31, 3448–3454.

Sokol, R., Bush, B., Wood, L., Jahan-Parwar, B., 1992. Production of aqueous PCB solutions for environmental toxicology. Chemosphere 24, 483–495.

Sokol, R., Kwon, O-S., Bethoney, C., Rhee, G-Y., 1994. Reductive dechlorination of polychlorinated biphenyls in St. Lawrence River sediments and variations in dechlorination characteristics.. Environ. Sci. Technol. 28, 2054–2064.

Sudoh, M., Kodera, T., Sakai, K., Zhang, J., Koide, K., 1986. Oxidative degradation of aqueous phenol effluent with electrogenerated Fenton's reagent. J. Chem. Eng. Jpn. 19, 513–518.

Tratnyek, P.G., 1996. Putting corrosion to use: remediating contaminated groundwater with zero-valent metals. Chem. Ind. 13, 499–503.

Tzedakis, T., Savall, A., Clifton, M., 1989. The electrochemical regeneration of Fenton's reagent in hydroxylation of aromatic substrates: batch and continuous processes. J. Appl. Electrochem. 19, 911–921.

Venkatadri, R., Peters, R., 1993. Chemical oxidation technologies: ultraviolet light/hydrogen peroxide, Fenton's reagent and titanium dioxide-assisted photocatalysis. Haz. Waste Haz. Materials 10, 107–141.

Wang, C., Zhang, W-X., 1997. Synthesizing nanoscale iron particles for rapid and complete dechlorination of TCE and PCBs. Environ. Sci. Technol. 31, 2154–2156.

Zwiernik, M., Quensen, J., Boyd, S., 1998. $FeSO_4$ amendments stimulate extensive anaerobic dechlorination. Environ. Sci. Technol. 32, 3360–3365.