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Reductive dechlorination of polychlorinated biphenyl compounds in supercritical carbon dioxide

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Polychlorinated biphenyl mixtures (Aroclor 1242 and 1248) are dechlorinated efficiently (but not quantitatively) with heated columns of zero-valent metal or bimetallic mixture in a continuous process. Supercritical carbon dioxide transfers the substrates through the reactor and cumulative ten minute fractions of eluate are trapped in hexane during 1 h of continued operation. The extent of dechlorination is influenced appreciably by the identity of the zero-valent (ZV) metal ($Fe^0 > Ni^0 > Zn^0 > Cu^0$), by the temperature ($400 \gg 300 > 200$ °C) and pressure ($\leqslant$4500 psi) within the reactor column(s) and especially by the composition of the feedstock. Although water is both unnecessary and detrimental to the dechlorination yields, the inclusion of methyl ketone(s) in the feedstock solution appreciably improves the extent of the dechlorination. Two columns (25×1 cm) of Ag^0/Fe^0 or Ag^0/Ni^0 bimetallic mixture result in a virtually quantitative dechlorination of substrate Aroclor 1242 (~ 28 mg min^{-1}). Moreover, during 1 h of continued operation, the dechlorinations are very repeatable. In preliminary treatments of 30% (*v/v*) acetone–hexane extracts (*ca.* 600 ppm PCBs) of a spiked sandy loam soil, no chlorinated organics could be detected in the PCB eluting region by GC-MS.

Introduction

A popular strategy to effect abiotic dehalogenations has been to mediate the reduction in aqueous media in the presence of a sacrificial metal in its elemental form. Zero-valent iron[1–8] and iron–palladium[9–11] bimetallic mixtures have become especially popular for this purpose. In anoxic aqueous media, free metal ions, chloride ion and hydrogen gas were produced by reaction at the surface of metal particles and protons were consumed. The process kinetics were dependent on solution pH, surface area of the metal particle, substrate concentration, buffer selection and solvent composition.[6] Dechlorination approximately followed first-order kinetics and rate coefficients tended to increase with time, an observation that was postulated to have resulted from an increase in reactive metal surface area due to cathodic depolarization and pitting of the iron surface.[3] Dechlorination occurred under oxic conditions as well, although the rates were appreciably slower. A rapid pH increase was synchronous with dissolved oxygen consumption and the pH remained constant after the oxygen had been depleted. This was attributed to the proton and oxygen consuming aerobic corrosion of the Fe^0 surface.[3]

Normalisation of the apparent rate constants for the dechlorination of different halogenated substrates to the iron surface area yielded a specific rate constant (k_{SA}) that varied by only one order of magnitude for individual halocarbons. Surface area normalised rate constants for nanoscale Fe^0 particles (1–100 nm diameter) were 10–100 times higher than for commercial particles.[7] Correlation analysis also revealed that dechlorination is generally more rapid at saturated carbon centres than at unsaturated carbons and that high degrees of halogenation favoured rapid reduction.[6]

Based on the low concentration of chlorinated degradation products in the solution phase it was suggested that most of the substrate remained sorbed to the iron surface until complete dechlorination had been achieved.[5] Prolonged exposure of the Fe or Pd/Fe surface to a saturated solution of aqueous organochlorine compounds resulted in the growth of a hydroxylated iron oxide film that deactivates the Pd/Fe surface. The thick hydroxylated iron oxide film could be removed and the original activity of the Fe (Pd/Fe) surface restored by washing the surface with a dilute acid.[2,9,11,12]

A mechanistic model for the zero-valent metal (Fe^0) mediated dechlorination has suggested a surface mediated process[13] and indicated that rates of decomposition were limited by the sparing solubilities of substrates in the aqueous phase.[8] When iron was used to mediate anoxic dechlorination, the slow adsorption of the target compounds to the iron surface and the desorbtion of hydrocarbon products became the rate-limiting steps that retarded the rate of the overall process appreciably.[14] It is often considered that water is a necessary component of metal-mediated corrosion reactions with chlorinated alicyclics.

Green Context

Dechlorination has become one of the most important reactions in clean technology. The conversion of toxic or in other ways environmentally damaging compounds into useful and more benign molecules is a subject of growing importance. This paper presents the latest results from attempts to develop and optimise the operation of a continuous reactor to dechlorinate polychlorobiphenyls (PCBs). It shows how supercritical carbon dioxide can be used to mobilize PCBs from particulate matter and transport them through the reactor. The advantages of using SCFs in this context include good substrate solubility and enhanced diffusion rates coupled with the general advantages of $scCO_2$ such as zero toxicity, reactivity and flammability. ***JHC***

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However, there are several literature reports[15–18] emphasising that zero-valent iron or aluminium can react directly with these substrates to yield chlorocarbon radicals, metal chlorides and/or chloride ion.

Somewhat less is known about reactions of halogenated aromatics with zero-valent metals. Copper metal has been reported to dechlorinate polychlorodibenzo dioxin (PCDD) and furan (PCDF) derivatives[19] and Fe^0 can mediate the dechlorination of chlorinated benzenes,[20] DDT and derivatives[21] and chlorinated phenols.[22] Although polychlorinated biphenyl compounds (PCBs) are generally considered to be unreactive to Fe^0 at ambient temperature, they have been dechlorinated efficiently with bimetallic iron mixtures. For a methanol–water solution of a commercial mixture of PCBs when contacted for a short time with palladized iron at ambient temperature, the only reaction products were biphenyl and chloride ions.[10] Success has also been achieved using Fe^0 at elevated temperatures. At 400 °C in the absence of solvent, PCB mixtures underwent hydrodehalogenation in the presence of Fe^0 powder that resulted in the complete loss of chlorinated congeners[23] and the efficient recovery of biphenyl. Nanoscale Fe^0 particles have also been demonstrated to mediate PCB dechlorinations efficiently.[7,24] More recently sub-critical water at 250 °C and 10 MPa pressure has been used to mediate PCB dechlorinations by Fe^0.[25]

As a remediation strategy, extractions are limited in that the target toxicant(s) can only be transferred / concentrated from one medium to another but are not detoxified *per se*. A more efficient strategy would be to couple the extraction with an on-line modification of the toxiforic groups. The objectives of current studies were to develop and optimise the operation of a continuous reactor to dechlorinate PCBs. It was anticipated that supercritical carbon dioxide (Sc-CO_2) could be used advantageously to mobilize PCBs from particulate media and transport them through the reactor. Supercritical fluids including sc-CO_2 possesses several advantages that can be exploited in dechlorinations including appreciable substrate solubility[26] and enhanced rates of solute partitioning and diffusion relative to the liquid phase. On the other hand, CO_2 has been reported to cause the gradual deactivation of Pd supported catalyst.[27] PCBs have been purged efficiently from soils with sc-CO_2[28,29] which remains among the least expensive of solvents. It is non-polar yet is readily separated from non-polar solutes, non-explosive, virtually non-toxic, non-flammable, relatively non-reactive, and waste emissions do not directly increase the burden to greenhouse gases.

Experimental

Chemicals

Copper (electrolytic grade, 40–100 mesh, nominally 99.5% purity), iron (40 mesh, nominally 99.5% purity), nickel (50–100 mesh, nominally 99.5% purity), zinc particles (100 mesh, nominally 99.9% purity) and sodium dispersion [40% (*w/v*) in oil were purchased from Alfa Aesar, Ward Hill, MA] and used as received. Acetic anhydride (Ac_2O), ethylene glycol dimethyl ether (1,2-DME), hexane, acid washed sea sand and silver nitrate were purchased from Fisher Scientific, Ottawa, ON and were used as received. Aroclor 1242 and Aroclor 1248 mixtures were kindly donated by Monsanto Company, Sauget, IL.

Ag^0/metal^0 bimetallic mixtures

The general preparations described by Zhang *et al.*[30] were followed. Ag/Fe^0 and Pd^0/Fe^0 were prepared from *ca.* 40-mesh iron that had been washed copiously with 6 M HCl and rinsed with distilled water. Sufficient aqueous $AgNO_3$ or K_2PdCl_6 to result in a 2% (*w/w*) surface coverage of the iron, was added to the aqueous iron suspension that was gently mixed on a rotary evaporator for 12 h. Ag/Ni^0 was prepared in similar fashion by reaction of aqueous $AgNO_3$ [sufficient to provide a 2% (*w/w*) surface coverage] with an aqueous suspension of pre-washed 50-100 mesh nickel granules during 12 h.

Mixed particle size Pd^0/Fe^0

Prepared by mixing freshly precipitated micron-scale iron particles with 40-mesh iron granules.[30] Aqueous 1.6 M $NaBH_4$ was added dropwise to 1.0 M $FeCl_3 \cdot 6H_2O$ with constant stirring. The precipitated product was mixed with an equal quantity of freshly washed 40-mesh Fe^0 particles and the mixture was treated with sufficient aqueous K_2PdCl_6 to result in a 2% surface deposit of Pd^0.

Reactor

The dechlorination assembly (Fig. 1) consisted of standard HPLC fittings and column assemblies that were rated to 6000 psi. A diaphragm compressor (Newport Scientific, Jessup, MD) delivered liquid carbon dioxide from the eductor tube of the K-type cylinder of CO_2 [bone dry grade ex MEGS, Montréal Que] to a large heated (1.4 L) reservoir (temperature and pressure equilibration vessel, TPEV) that served as both a pressure dampener and as a source of supercritical carbon dioxide (sc-CO_2) for the system. The supercritical solvent [*ca.* 0.8 or 1.5 l min^{-1} of decompressed gas as measured at the exit of the capillary restrictor with a digital flow meter (ADM1000, J and W Scientific, Folsom, CA)] was transferred to a 5 ml saturation vessel (SV, V = 5 ml, Keystone Scientific, Bellefonte, PA) mounted vertically, a pressure transducer (PT, Model PX300, 15–5000 psig capacity, Omega Engineering, Laval, QC) connected to a digital readout meter (Model DP280, Omega Engineering), a mixing tee and a reactor unit. Polychlorinated biphenyl (PCB) substrate, dissolved in a suitable solvent, was delivered at 0.1 ml min^{-1} to the mixing tee (1/16 inch i.d.), merged with the sc-CO_2 stream (*ca.* 4 ml min^{-1}) and fed to one or two stainless steel (ss) HPLC column assemblies [10 mm inner diameter (i.d., 12 mm o.d.) × 25 cm] that were filled with test zero-valent metal (or metal mixture, *ca.* 21 g) encased in an insulating alumina jacket (fashioned from thin walled alumina 12 mm o.d. 10 mm i.d. tube, Alfa Aesar, that had been cut lengthways to provide two semi-cylinders) and mounted in series. The ss column-alumina jacketed assemblies were heated separately with 80-turn coils of high resistance heating wire that were energised from variable transformers. Pressure within the

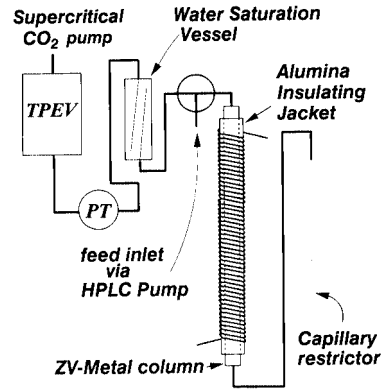

Fig. 1 Dechlorination reactor assembly consisting of a temperature and pressure equilibration vessel (TPEV), a pressure transducer (PT), a saturation vessel (SV), a mixing tee to merge the supercritical carbon dioxide with feedstock solution, one or more columns containing zero valent metal and a capillary restrictor all connected in series.

assembly was maintained at the desired level with a flexible polyamide coated silica capillary restrictor (*ca.* 25 cm × 0.050 mm i.d.), Chromatographic Specialties, Brockville, ON). The components of the extractor (standard HPLC components, tubing and fittings) were pressure rated to 6000 psi.

Reactor operation

After a short delay to purge residues of air from the system (during which time only sc-CO_2 was fed to the reactor), feedstock 0.1 ml min^{-1} of 2–20% (*v/v*), was added continuously *via* the HPLC pump to the sc-CO_2 stream and transported to the reactor. Measurements at the exit of the capillary restrictor indicated a flow rate corresponding to 800–850 ml min^{-1} of decompressed gas. The exit tip of the capillary restrictor was immersed in hexane (25 ml, contained in a 30 × 2 cm test tube) to trap products from the reactor eluate. Each experiment was continued until six successive traps had been collected, each corresponding to 10 min of cumulative trapping of reactor eluate. The course of the dechlorination was monitored by gas chromatography (GC) or occasionally by GC-MS to monitor the spectrum and identities of products and by titration to measure levels of residual organically bound chlorine in the eluate.

Organically bound chlorine

The general procedure of Ware *et al.*[31] was followed. Residual organically bound chlorine in the hexane trapping solution was determined by titration with standardised $AgNO_3$ (*ca.* 0.01 M). Sodium dispersion, 2 ml, was added to a vigorously stirred 10 ml aliquot of hexane trapping solution that had been further diluted 5-fold with fresh hexane. Methanol, 1 ml, was added dropwise; the reaction was continued for 5 min then quenched by the addition of propan-2-ol (15 ml) followed by 90 ml water. The aqueous phase, after separation from the organic phase, was diluted to 100 ml in a volumetric flask. A 20 ml aliquot of the reaction mixture was acidified to pH 6–7 with nitric acid (7 M), supplemented with 5 drops of potassium chromate indicator solution then titrated with $AgNO_3$. Blank determinations for chloride in reactor eluate consisted of an identical procedure in the absence of added sodium dispersion. The reduction efficiency was calculated as:

$$\text{Percent reduction efficiency} = \frac{W_i - W_f}{W_i} \times 100$$

where W_i and W_f are the initial and final weights of organically-bound chlorine in the sample.

Biphenyl formation from PCB mixtures

Aroclor mixtures were converted quantitatively to biphenyl by reaction with a solid mixture of Mg and K_4PdCl_6 following the procedure of Doyle *et al.*[32]

Gas chromatography

This was performed on a Varian Model 3700 GC fitted with a 0.53 mm i.d. × 25 m megabore DB5 column and a flame ionisation detector. Helium, delivered at 30 ml min^{-1}, served as the carrier gas. A splitless injection of sample (2 μl) was transferred to the column inlet and after an initial temperature hold at 50 °C during 5 min, the temperature was ramped to 250 °C during 30 min then held at the upper temperature for a further 5 min. GC-MS were performed on a Saturn-3400 system. The DB-5 capillary column (30 m × 0.2 mm), eluted with helium at 1 mL min^{-1}, was temperature programmed from 40–300 °C during 45 min then held at the final temperature for a further 5 min. Eluting components were identified tentatively by comparison of experimental mass spectra with spectra catalogued in the data base [National Institute of Standards and Technology (NIST) or Saturn, Varian Associates] and corroborated by co-chromatography and spectral matching with authentic standards. Quantitation was achieved with external standards.

Results and discussion

The dechlorination efficiency (yield) was defined as one minus the ratio of the quantity of organically-bound chlorine in the reactor eluate divided by the chlorine content in an equivalent quantity of feedstock. The extent of dechlorination was influenced appreciably by the identity of the zero-valent (ZV) metal, by the temperature and pressure within the reactor column(s) and especially by the composition of the feedstock. As summarised in Table 1, the replacement of water–ethylene glycol dimethyl ether (1,2-dimethoxyethane, DME) mixture with acetic anhydride (Ac_2O) was beneficial to both the dechlorination yield and the repeatability among the six samples collected sequentially during 1 h of operation. For these and all subsequent trials the saturation vessel was removed from the reactor assembly. The dechlorination efficiency seemed to depend on the content of acetic anhydride in the transporting solvent. Whereas 5% and 10% (*v/v*) of acetic anhydride (Ac_2O) in the DME feedstock provided mean dechlorination efficiencies of 63 ±10 and 74 ± 9% respectively, an increase in the Ac_2O content to greater than 40% (*v/v*) resulted in the virtually complete (*ca.* 99%) dechlorination of feedstock containing 10% PCBs (Fig. 2). The error bars of this Figure reflect one relative standard deviation (RSD) associated with three replicate determinations, by titration, of residual organically bound chlorine in the eluate trap (mean RSD for the ten separate samples was ±1.3%). Fig. 2 also summarises the influence of operating pressure on the mean dechlorination efficiency. An increase of 1500 psi in operating pressure increased the dechlorination yield by approximately twenty percent. Increased operating pressures result in increased densities of the sc-CO_2 and a greater solvating power of the fluid for the substrate PCBs. Because the components of the reactor were standard HPLC fittings that were rated to 6000 psi at ambient temperature, it was decided arbitrarily to limit the operating

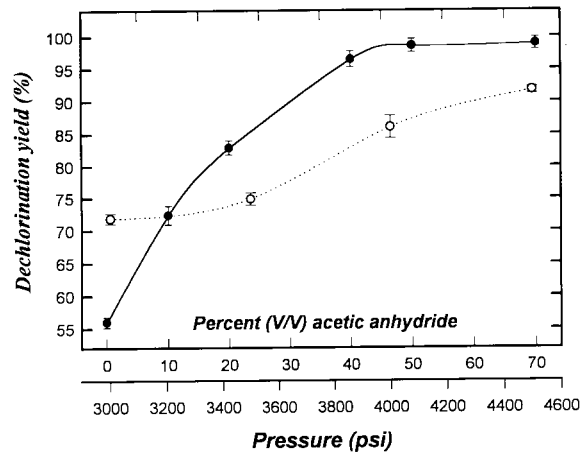

Fig. 2 Variations in the dechlorination efficiency for 10% (*v/v*) solutions of Aroclor 1242 in 1,2-dimethoxyethane with (*a*) increasing percent of acetic anhydride in the solvent mixture (—●—) delivered to two Ag^0/Fe^0 columns at 400 °C and 4500 psi or (*b*) with increasing pressure (----○---) for the same feedstock delivered to two Fe^0 columns at 400 °C.

Table 1 Variations in the mean[a] percent dechlorination (±1 RSD) for 2 successive columns (i) containing various zero-valent metals and (ii) with different solvent compositions to transfer 20% (*v*/*v*) Aroclor 1242 to the reactor

ZV-Metal	Feedstock composition (*v*/*v*) in the presence of 20% (*v*/*v*) Aroclor 1242	Mean % dechlorination for two columns
Cu	5% H_2O, 75% DME	36 ± 11
Cu	70% Ac_2O, 10% DME	86 ± 8
Fe	5% H_2O, 75% DME	36 ± 30
Fe	70% Ac_2O, 10% DME	94 ± 4
Ni	5% H_2O, 75% DME	68 ± 8
Ni	70% Ac_2O, 10% DME	91 ± 6
Zn[b]	5% H_2O, 75% DME	67 ± 11
Zn[b]	70% Ac_2O, 10% DME	90 ± 8

[a] Mean percent dechlorination for six successive traps of reactor eluate. [b] Determined at 200 °C.

pressure of the reactor to 4500 psi or less for reasons of safety.

The presence of water was not necessary for the dechlorination reaction (Table 1). The requirement for at least some water in the reductive dehalogenation at metal surfaces had been suggested by the reported lack of any measurable reaction at ambient temperature of neat chlorinated liquid substrate in contact with reducing metal surfaces. We had anticipated that in the presence of sc-CO_2, the pH of the entrained aqueous phase would be decreased sufficiently [2.8–2.95[33]] to minimise the build-up of an oxide(hydroxide)/carbonate layer on the ZV metal surfaces. In consequence, we had added the saturator vessel (SV, Fig. 1) to the sc-CO_2 inlet line. However, when water was removed from the transporting solvent and the SV was removed from the inlet train no differences in the dechlorination efficiencies were detected. In all subsequent trials no water was added to the mobile phase. When a 20% (*v*/*v*) Aroclor solution in Ac_2O alone or diluted with ethylene glycol dimethyl ether was mixed with sc-CO_2 and fed to a single reactor column containing ZV iron (Fe^0) (400 °C, 4500 psi) no organically bound chlorine was detected in any of the six traps of column eluates. Fourier transform infrared (FTIR) spectroscopy indicated that in addition to residual dissolved carbon dioxide, the product mixture was composed predominantly of methyl ketone(s). A possible source for these compounds would involve the capture of alkyl radicals by a methylated carbon monoxide radical species. sc-CO_2 is known to form short chain (C_1–C_5) alkyl radicals by catalytic reduction at iron surfaces.[34]

The dechlorination process was also temperature dependent. As summarised in Table 2, an increase in the operating temperature as measured by the outer skin temperature of the reactor columns improved both the extent of dechlorination and the repeatability between the six cumulative 10-minute traps that had been collected sequentially during 1 h. The dechlorination efficiency was seen to decrease gradually with increasing trap number. The decrease is reflected in the elevated RSDs at 200 and 300 °C. For ZV-zinc, the metal granules were observed to soften appreciably at reactor skin temperatures above 200 °C, so that dechlorination trials were limited to this temperature. Trials were also conducted with Aroclor 1248 (Table 2). Yields between the 1248 and 1242 are not directly comparable because of differences in density (20 °C) (1.44 *vs.* 1.38[31] respectively) and differences in the spectrum of congener for these mixtures.[32] The 1248 mixture was more highly chlorinated (48 *vs.* 42%). Additionally, for incomplete dechlorinations, identical rates of reaction would have resulted in lower dechlorination yields for 1248 because of the greater chlorine concentrations in this substrate.

Table 2 The influence of temperature of two reactor columns connected in series on the mean percent dechlorination (±1 RSD) of feedstock containing 20% (*v*/*v*) Aroclor 1242 (or Aroclor 1248), 70% (*v*/*v*) acetic anhydride and 10% (*v*/*v*) dimethoxyethane

	Temperature					
	200 °C		300 °C		400 °C	
ZV-metal	1242	1248	1242	1248	1242	1248
Cu	69 ± 9		71 ± 23		86 ± 8	
Fe	86 ± 7	69 ± 15	88 ± 10	72 ± 14	94 ± 4	92 ± 6
Ni	55 ± 12	42 ± 8	61 ± 14	67 ± 2	91 ± 6	89 ± 2
Zn	69 ± 15					
Ag/Fe	63 ± 17		73 ± 9		97 ± 3	
Pd/Fe	60 ± 22	56 ± 25	74 ± 15	64 ± 19	96 ± 3	93 ± 5

The effect of increased operating temperature can be seen more clearly in Fig. 3 which compares Fe^0 mediated dechlorination efficiencies for sequential traps at different operating temperatures. There was a gradual decrease in dechlorination yield with increasing trap number. The gradual decrease in efficiency was characteristic of all four ZV-metals and the three bimetallic mixtures that were studied. The negative slopes of the spline curves were greater at lower than at higher operating temperatures for different zero-valent (ZV) metal substrates. Other ZV metals (Cu^0, Ni^0 and Zn^0) behaved similarly but the dechlorination was not as extensive.

In addition, three bimetallic mixtures of ZV-metals (Ag^0/Fe^0, Ag^0/Ni^0 and Pd^0/Fe^0) were assessed for dechlorinating efficiency in this system. All three mixtures further improved both the dechlorination yield and the repeatability of the reaction over 1 h (Table 3). For these trials, the reactor temperature was maintained at 400 °C and the substrate composition was varied using two ZV-metal columns. Although efficient, the reactions were not quantitative. For a single reactor column (Table 4), there was no apparent differences between the use of acetic anhydride or methyl isobutyl ketone (MIBK) in the transporting solvent although the use of heptan-2-one depressed dechlorination by approximately 10 percent. Surprisingly, the inclusion of 1,2-DME (10% *v*/*v*) in the solvent increased the yield by 9 and 14 percent over neat acetic anhydride for the Ag^0/Fe^0 and the Ag^0/Ni^0 mixtures respectively. The dechlorinating activities of silver-coated iron and nickel were also more durable as seen in

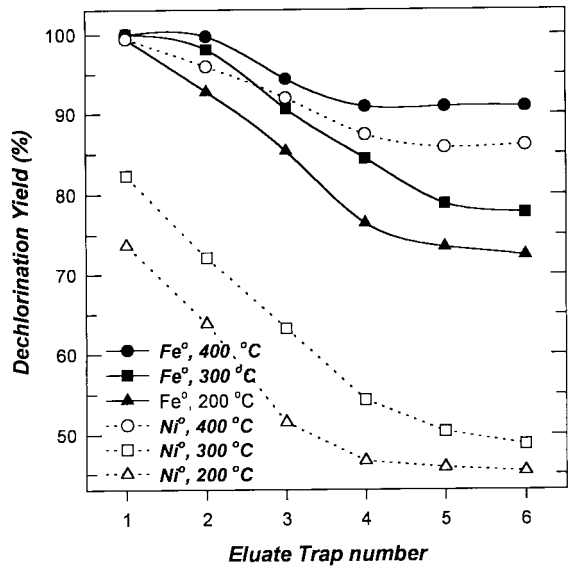

Fig. 3 Efficiencies for Fe^0 mediated (filled symbols) or Ni^0 mediated (open symbols) dechlorinations of 20% (*v*/*v*) Aroclor 1242 solution delivered at 0.1 ml min^{-1} to two reactor columns maintained at 4500 psi and 400 °C [mean dechlorination in six traps that had been trapped successively = 95 ± 4% and 91 ± 6% respectively], or at 300 °C [mean = 88 ± 10% and 67 ± 6% respectively] or at 200 °C [mean = 84 ± 12% and 54 ± 11% for Fe^0 and Ni^0 mediated reactions respectively].

Table 3 Variations in the mean[a] percent dechlorination (±1 RSD) for 2 columns maintained at 400 °C and 4500 psi (i) containing different bimetallic mixtures and (ii) with varying acetic anhydride–dimethoxyethane mixtures to transfer Aroclor 1242 to the reactor

ZV-Bimetallic mixture	% (*v*/*v*) PCB content	Feedstock composition (*v*/*v*) in the presence of 20% (*v*/*v*) Arochlor 1242	Mean % dechlorination[a]
Ag/Fe	2	20% Ac_2O, 78% DME	99.8 ± 0.1
	10	50% Ac_2O, 40% DME	98.3 ± 1.2
	15	50% Ac_2O, 35% DME	98.0 ± 1.3
	20	50% Ac_2O, 35% DME	88.5 ± 5.2
	20	70% Ac_2O, 10% DME	97.0 ± 2.6
	20	80% Ac_2O	88.9 ± 4.5
Ag/Ni	2	20% Ac_2O, 78% DME	99.9 ± 0.2
	10	50% Ac_2O, 40% DME	97.8 ± 1.1
	15	50% Ac_2O, 35% DME	90.9 ± 5.0
	20	50% Ac_2O, 35% DME	83.9 ± 8.9
	20	70% Ac_2O, 10% DME	95.8 ± 2.1
	20	80% Ac_2O	81.1 ± 3.9
Pd/Fe	2	20% Ac_2O, 78% DME	99.9 ± 0.2
	5	20% Ac_2O, 75% DME	99.0 ± 0.8
	10	50% Ac_2O, 40% DME	97.8 ± 2.1
	15	70% Ac_2O, 15% DME	97.0 ± 2.4
	20	70% Ac_2O, 10% DME	96.1 ± 3.1
	20	80% Ac_2O	84.3 ± 4.6

[a] Mean ± 1 relative standard deviation (RSD) of six successive traps of reactor eluate.

Table 4 Variations in mean dechlorination efficiencies (±1 RSD) for one column of silver (2% *w*/*w*) iron bimetallic mixture maintained at 400 °C and 4500 psi for 15 or 20% (*v*/*v*) Aroclor 1242 and different transporting solvent mixtures

% (*v*/*v*) Arochlor 1242	Feedstock composition[a](*v*/*v*)	Mean % dechlorination[b]
15	40% Ac_2O, 45% DME	97 ± 7
20	70% Ac_2O, 10% DME	92 ± 5
15	70% MIBK, 15% DME	92 ± 5
20	80% MIBK	89 ± 3
15	60% heptan-2-one, 25% DME	93 ± 4
20	70% heptan-2-one, 10% DME	80 ± 6
20	80% heptan-2-one	80 ± 6

[a] DME = 1,2 dimethoxyethane, MIBK = methyl isobutyl ketone. [b] Mean in six 10 minute cumulative traps that were collected sequentially during 1 h.

Fig. 4. Although the efficiency of dechlorination appeared to decrease continuously for the Ag^0/Ni^0 bimetallic mixture, it appeared to level off for the Ag^0/Fe^0 support in these short-term trials. The mixed particle size palladium iron mixture proved to be less efficient under these conditions and was not investigated further.

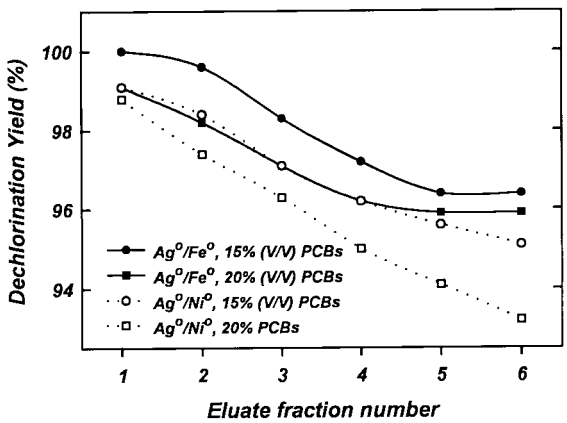

Fig. 4 Dechlorination efficiencies for 15% (●, ○) or 20% (■, □, *v*/*v*) 1242 feedstock delivered to two columns mounted in series of Ag^0/Fe^0 (filled symbol, mean dechlorination for six successive traps = 98 ± 2% and 97 ± 3%) or to Ag^0/Ni^0 (open symbol, mean = 97 ± 2% and 96 ± 2% for 15 and 20% PCB feedstock respectively) at 400 °C and 4500 psi.

The GC chromatograms of reaction products from PCB dechlorinations were gradually shifted to more rapidly eluting components as the dechlorination efficiency was increased. Two Fe^0 reactor columns in sequence, that resulted in a 95% reduction in organically-bound chlorine, provided a chromatogram that was reduced approximately 94% in total peak areas in the PCB eluting region indicating that the majority of products were eluted more rapidly. When only biphenyl dissolved in DME comprised the feedstock for the Ag^0/Fe^0 column (operated under optimised dechlorination conditions), a maximum of only 84% could be recovered in the hexane traps indicating further reaction. There were no products that were more retained than biphenyl on the GC column. With Ag^0/Fe^0 bimetallic mixture and 99.5% dechlorination of the 1242 substrate only two chlorinated products (*o*-chlorobiphenyl and 2,4-dichlorobiphenyl and/or 2,6-dichlorobiphenyl (which collectively accounted for appreciably less than 1% of the starting material) were detected by GC-MS. Similarly, for substrate that had been 99.8% dechlorinated, only *o*-chlorobiphenyl was detected among the chlorinated products. Other non-chlorinated products that were identified tentatively included methylbiphenyl(s), dimethylbiphenyl(s), toluene and short chain esters of benzene-1,2-dicarboxylic acids. The latter products (that were observed for 2% loadings of Aroclor 1242 in the mobile phase) are thought to arise *via* carboxylation and reductive catenation of the CO_2.

Having optimized the reaction conditions for virtually complete PCB dechlorination (based on the loss of organically-bound chlorine) a series of further trials were undertaken to corroborate the efficiency of the process. Initially, the temperature of the single Pd^0/Fe^0 column was lowered to 300 °C and 20% (*v*/*v*) PCB feedstock in hexane was delivered to the reactor column at 0.1 mL min^{-1}. The mean recovery of organically-bound chlorine in successive traps of hexane was virtually quantitative at this temperature (Aroclor 1242, 99.0 ± 4.7%; Aroclor 1248, 103.9 ± 6.6%). Further experiments monitored the eluate content of products that could be converted to biphenyl. Aliquots of eluate were reacted with Mg^0 and K_2PdCl_6 to produce biphenyl. With 20% (*v*/*v*) 1242 in acetic anhydride (70% *v*/*v*) dimethoxyethane (10% *v*/*v*) as feedstock, the recovery of biphenyl was virtually quantitative, 99.1 ± 8.7% at 300 °C but was reduced to 84.0 ± 12.9% at 400 °C. For these trials, the reactor column was packed freshly prior to each trial. Despite equilibration with mobile phase in the absence of substrate, the contents of the first trap were converted to biphenyl less efficiently. Mean recoveries were based on traps two to six. These results indicated that at the higher operating temperature a portion of the biphenyl derivatives were further degraded on column. To demonstrate an active role for the zero-valent metal(s) in the dechlorinations, companion experiments were also conducted using silica (sea sand) to fill the reactor column. With the optimized reaction conditions (400 °C/4500 psi, 800 ml min^{-1} of decompressed flow), the mean recovery of substrate(s) in the six trapping solutions that could be converted to biphenyl was virtually quantitative (104 ± 11%). Finally the chloride ion accumulated on the Pd^0/Fe^0 column during 1 h of continued operation (optimal operating conditions) as determined by titration of the wash water accounted for 99.6% of the total chlorine in the feedstock.

In further trials, acetone/hexane extract from a spiked sandy loam soil that had been extracted using a patented SESR (Solvent Extraction Soil Remediation technology)[37] were dechlorinated with a single Ag^0/Fe^0 column maintained at 4500 psi and 400 °C. No chlorine containing materials were detected by GC-MS in the reactor eluate when acetone/hexane extract supplemented with 30% (*v*/*v*) Ac_2O, that had contained approximately 600 ppm PCBs, was fed continuously at 0.1 ml min^{-1} to the reactor. Of equal importance, soil co-extractives in

the PCB solution did not seem to affect either the course of the efficiency of the reaction perceptibly.

Thus, it has been demonstrated that zero-valent metal mediated reactions of Aroclor mixtures at elevated temperature in sc-CO_2 provides an efficient technique for PCB detoxification by dechlorination. The quantities of 1242 or 1248 substrate that were dechlorinated efficiently (but not quantitatively) are considered to far exceed the burdens in concentrated extracts that could be isolated from polluted environmental matrices.

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