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## Dechlorination of chlorinated phenols by catalyzed and uncatalyzed Fe(0) and Mg(0) particles

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### Abstract

Uncatalyzed, and palladium-catalyzed Fe(0) and Mg(0) systems were examined for their efficiencies of dechlorination of 2.86 mM 4-chlorophenol (4-CP), 2.52 mM 2,6-dichlorophenol (2,6-DCP), 3.03 mM 2,4,6-trichlorophenol (2,4,6-TCP), and 2.48 mM pentachlorophenol (PCP) in 50/50 (v/v) 2-propanol/water under room temperature and pressure conditions. Previous investigators have found that PCP is extremely recalcitrant under these conditions. In this investigation, complete dechlorination of 5.0 ml of 2.48 mM PCP was observed for 1.0 g of 2659 ppm Pd/Mg (20 mesh) after 48 h. The only detectable products were cyclohexanol and cyclohexanone at 25% yield. No other chlorinated or otherwise products were observed by mass spectral analysis. It is hypothesized that volatile low molecular weight species were formed from the Pd/Mg dechlorination of PCP. Under conditions of equal surface area (0.0786 m<sup>2</sup>), the approximate order of PCP dechlorination power of these systems followed as 2659 ppm Pd/Mg > 319 ppm Pd/Mg > Mg ≈ 4856 ppm Pd/Fe > Fe. Degradation of the other chlorinated phenols by all metallic systems was more facile than PCP. © 2002 Elsevier Science B.V. All rights reserved

*Keywords:* Pentachlorophenol; Dechlorination; Zero-valent metals; Hydrogenation

### 1. Introduction

Chlorophenols were used extensively as wood preservatives, pesticides, and as intermediates in the manufacture of pesticides. Chlorophenols, especially pentachlorophenol (PCP), are exceptionally recalcitrant in the environment and towards chemical reactions aimed at their destruction. Combustion of PCP releases observable quantities of polychlorodibenzodioxins and polychlorodibenzofurans [1]. Coupled with high costs associated with incineration, there is much interest in alternatives to the destruction of PCP and the chlorophe-

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nols. Previous investigators have studied decomposition by ozonation, Fenton's reagent, UV photolysis, sonication, electrolysis, supercritical water oxidation, and dechlorination [2–12]. However, a universally accepted method has been elusive. Furthermore, conditions for the complete degradation of PCP under mild reaction conditions, i.e. neutral pH, room temperature, and pressure, without exclusion of air, and inexpensive reagents and reactor designs have not yet been described.

In this investigation, the relative dechlorination efficiencies of PCP and other chlorinated phenols in 50/50 (v/v) water/2-propanol solutions of uncatalyzed and palladium-catalyzed Mg(0), and Fe(0) particles were examined. Previous investigators have only mentioned qualitative observations or found incomplete degradation of PCP by zero-valent metals [4,13,14]. The driving force for such reaction is based on the following half reactions:



Reaction 1 represents the spontaneous dissolution of a metal. Reaction 2 is the coupled hydrogenation of the carbon–chlorine bond. Several zero-valent metals are suitable for this reaction, however, two metals, Fe and Mg, stand out from others based on considerations of cost and environmental impact of the spent metal ion. Such examples of dechlorination of halocarbons by unmodified zero-valent iron are numerous, however, there is one feature shared by all, the relatively slow kinetics of dechlorination of halocarbons [4,15–21]. In a previous investigation, it was found that palladized Mg(0) was particularly effective in the degradation of PCB and DDT [22,24]. In principle, zero-valent metal dechlorinations of halocarbon pollutants offer many advantages over incineration, among those include lower costs, and no production of polychlorodibenzodioxins and polychlorodibenzofurans.

## 2. Experimental

### 2.1. Chemicals

Hexanes (Optima grade), iron powder (>99%, electrolytic and finer than 100 mesh), 2-propanol (HPLC grade) and hydrochloric acid (Certified ACS Plus) were obtained from Fisher (Fair Lawn, NJ). Magnesium granules (~20 mesh, 98%), fluoranthene (98%), PCP (98%), cyclohexanol (99%), cyclohexanone and phenol (>99%) were from Aldrich Chemical Co. (Milwaukee, WI). Potassium hexachloropalladate (Pd 26.59%) was obtained from Alfa Aesar (Ward Hill, MA). The 4-chlorophenol (4-CP) (>99%), 2,6-dichlorophenol (2,6-DCP) (99%) and 2,4,6-trichlorophenol (2,4,6-TCP) (98%) were obtained from Acros Organics (New Jersey, USA). Cyclohexanone (99%) was supplied by EM Scientific (Gibbstown, NJ).

#### 2.1.1. Experimental setup

The chlorinated phenols stock solutions used in this experiment were prepared in a 50/50 (% v/v) distilled water/2-propanol (IPA) solvent. PCP was prepared with a total concentration of 2.48 mM in the water/IPA system. The other chlorinated phenols were

prepared as a mixture of 2.86 mM 4-chlorophenol, 2.52 mM 2,4-dichlorophenol and 3.03 mM 2,4,6-trichlorophenol. For the reactions with magnesium metal, 1.000 ( $\pm 0.0001$ ) g of magnesium granules were transferred to a 15 ml glass vial. Reaction time started once 5.00 ml of the chlorinated phenol stock solution was transferred to the vial containing the metal or bimetal. The surface area of magnesium ( $\sim 20$  mesh, 98%) was measured by Brunauer–Emmett–Teller (BET) analysis, resulting in a value of  $0.0786 \text{ m}^2/\text{g}$  (Porous Materials, Inc. Ithaca, NY). In this investigation, we employed a previously reported BET area for the finer than 100 mesh Fisher Fe(0) of  $0.12 \text{ m}^2/\text{g}$  [4]. Using this figure, 0.6552 g of the Fe(0) powder corresponds to the same surface area as 1.000 g of Mg(0). This area was kept constant in all dechlorination runs.

### 2.1.2. Preparation of the bimetallic systems and dechlorination

Each bimetallic system was synthesized in situ in the dechlorination solution itself, followed by its immediate use. This was done by carefully weighing the required quantity of  $\text{K}_2\text{PdCl}_6$  ( $\pm 0.001$  g) in the dechlorination vial followed by addition of the zero-valent metal, and an aliquot of dechlorination solution. Palladium deposits were spontaneously formed on the zero-valent metal surface [24,25]. No attempts were made at keeping  $\text{O}_2$  away from these solutions. Attempts to produce bimetallic systems for long-term storage fails because of rapid oxidation of the surface caused by the galvanic corrosion characteristics of the bimetals.

### 2.1.3. Extraction

At the end of each correspondent reaction time, the supernatant in the reaction vial was transferred to another vial free of metals. Then samples were vigorously shaken with 2.00 ml of hexanes (Fisher Optima grade) along with three drops of concentrated hydrochloric acid (in order to protonate any phenolates left in the solution) [4]. This procedure resulted in an extraction efficiency of  $>97\%$ . Failure to protonate the phenols prior to extraction results in an efficiency of 5–10%. Analysis then took place once both phases achieved complete separation. It was also found that essentially none of the chlorinated phenols or phenol were adsorbed onto the metal particles prior to decanting of the supernatant reaction solution. This was discovered by the comparisons of GC–FID results of runs in which the supernatant was acidified before and those in which acidification took place after decanting. Hexanes were chosen for this particular procedure because ethyl acetate were found to miscible with the 50/50 water/2-propanol solution.

### 2.1.4. GC–FID analysis

Fluoranthene (2.03 mM) was selected as the internal standard for these experiments. It was added to the extraction solvent (hexanes) and kept as a stock solution. An HP5890 GC–FID was used for the separation and analysis of the components. The separation column was an Alltech EC-5 (0.32 mm i.d.,  $0.25 \mu\text{m}$  film). The temperature program used was 1 min at  $50^\circ\text{C}$ , with a temperature ramp of  $20^\circ\text{C}/\text{min}$  up to  $270^\circ\text{C}$  for 2 min. Injection was performed in splitless mode using helium as a carrier gas at a rate of  $3.35 \text{ ml}/\text{min}$  ( $37.5 \text{ ml}/\text{min}$  including makeup gas). Calibration curves for both PCP phenol, and cyclohexanol/cyclohexanone were produced, both showing a linear response in the concentration

range of interest. Cyclohexanol and cyclohexanone were found to co-elute in the temperature program above, and thus, were detected as one peak. The detection limit for these species was 0.19 mM. For phenol, the detection limit was approximately 0.23 mM, while for PCP it was 0.39 mM.

### 2.1.5. GC-MS and direct probe

Mass spectral analysis of reaction solutions were conducted on a Jeol JMS-AX505 HA. Ionization was conducted by electron impact with a current of 100  $\mu$ A. The GC separation conditions were identical to those used in GC-FID above. Direct probe measurements between 50 and 800 amu were conducted using the instrument above. Acceleration voltage was 3.0 kV with a run time of 20 min at 350 °C.

## 3. Results

Fig. 1 illustrates the GC-FID response from the hexane (2.0 ml) extracted PCP from a 50/50 (v/v) H<sub>2</sub>O/IPA dechlorination mixture as a function of reaction time for the single

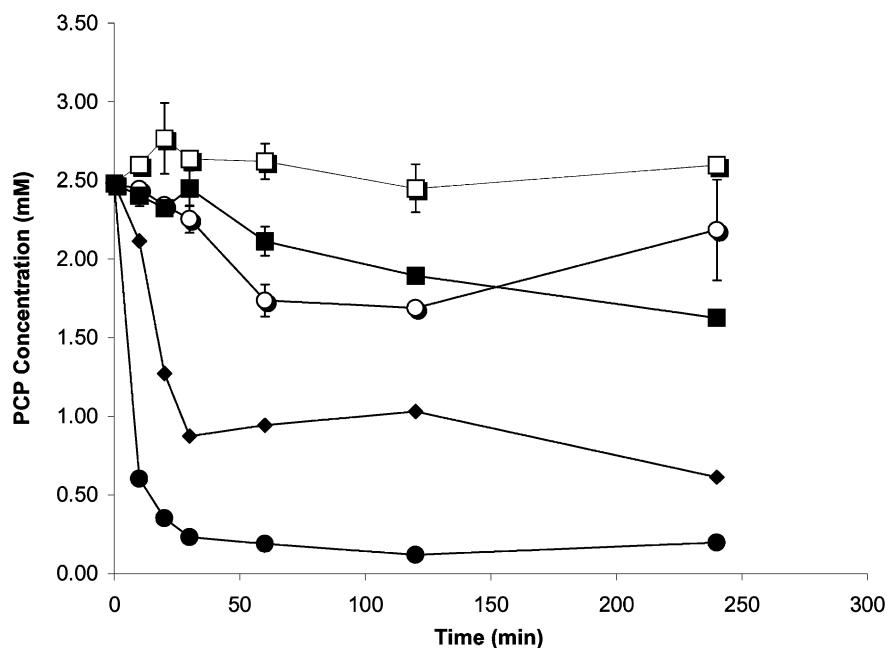


Fig. 1. The points in the graph represent normalized extractable PCP concentrations after different reaction times with the metallic systems. PCP concentrations were obtained from GC-FID data and normalized using fluoranthene as an internal standard. Error bars indicate 1 standard deviation for three measurements, and in some cases the symbols are bigger than the error bars. Each point represents the average of three measurements performed to the same sample. Fe (□), Pd (4856 ppm)/Fe (■), Mg (○), Pd (2659 ppm)/Mg (●), Pd (319 ppm)/Mg (◆).

metal and palladium-catalyzed systems. The reaction conditions were 5.0 ml of 2.50 mM PCP in the aqueous 2-propanol solvent system. As evident from the diagram, 0.6552 g of 100 mesh Fe ( $0.079 \text{ m}^2$ ,  $0.12 \text{ m}^2/\text{g}$ ) [4] by itself was unable to achieve any significant dechlorination within 240 min of reaction time. The presence of palladium deposits (4859 ppm, m/m) on 100 mesh Fe increased dechlorination rate so that  $\approx 17\%$  dechlorination was achieved at 240 min. Magnesium (1.000 g, 20 mesh,  $0.0786 \text{ m}^2/\text{g}$ ) dechlorinated PCP with approximately the same efficiency as Pd/Fe. By far the most efficient PCP dechlorination systems were the Pd/Mg series. Both Pd (319 ppm)/Mg (1.000 g) and Pd (2659 ppm)/Mg (1.000 g) bimetallic systems achieved significant PCP dechlorination. Tables 1 and 2 highlight the 30 and 240 min reaction time results for the dechlorination of PCP by the investigated metallic systems. The tables highlight the production of phenol, cyclohexanol/cyclohexanone, and qualitative observation of the production of a partial dechlorination product, trichlorophenol by Pd/Fe. The tables also illustrate the relative degradation of PCP contaminant, tetrachlorophenol. Neither iron systems or unmodified Mg were able to completely remove this chlorinated phenol congener. Both Pd/Mg systems were able to degrade both PCP and the tetrachlorophenol contaminant with no evidence of chlorinated phenol intermediates, however, in both cases the phenol yields are noticeably lower than for Pd/Fe.

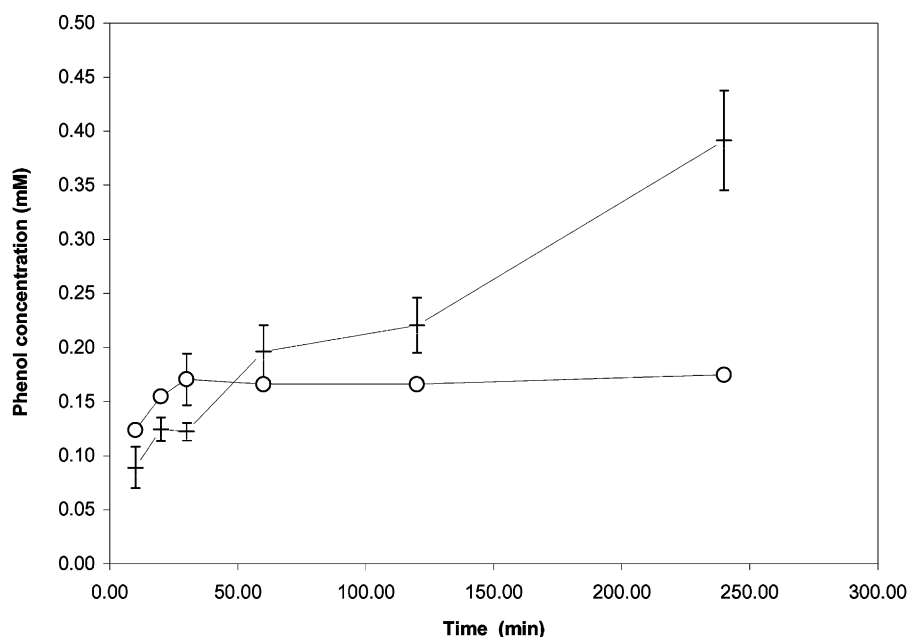


Fig. 2. Production of phenol from PCP degradation as a function of time in the presence of the metallic and bimetallic systems. Error bars indicate 1 standard deviation for three measurements. In some cases the symbols are bigger than the error bars. Each point represents the average of three measurements performed to the same sample. In this graph: (+) Fe/Pd, (O) Pd (2659 ppm)/Mg. No phenol was observed for Fe, Mg and Pd (319 ppm)/Mg.

Table 1  
 Pentachlorophenol, chlorinated phenol intermediates, phenol, and cyclohexanol/cyclohexanone concentrations (mM) after reaction with the metallic systems after 30 min of reaction time<sup>a</sup>

Metallic system	PCP (mM) (S.D.)	Phenol (mM) (S.D.)	Cyclohexanol/cyclohexanone (mM) (S.D.)	Identified chlorophenols			Carbon balance (%)
				Tri	Tetra	Tetra <sup>b</sup>	
Control	2.48	N.D.	N.D.	–	+	1.00	100
Mg	2.25 ± 0.11	N.D.	N.D.	–	+	0.75	104
Pd (319 ppm)/Mg	0.87 ± 0.02	N.D.	N.D.	–	+	0.43	34
Pd (2659 ppm)/Mg	0.23 ± 0.03	0.17 ± 0.00	0.089 ± 0.002	–	–	0.00	35
Fe	2.64 ± 0.01	N.D.	N.D.	–	+	0.72	115
Pd (4856 ppm)/Fe	2.46 ± 0.11	0.12 ± 0.01	N.D.	–	+	1.38	110

<sup>a</sup> N.D. indicates no detection. Tetrachlorophenol was found to be a contaminant of PCP.

<sup>b</sup> Indicates the ratio of the normalized peak area of the tetrachlorophenol peak in the control with the corresponding peak in the samples. Concentrations were calculated from calibration curves and normalized with an internal standard. The appearance (+) and disappearance (–) of possible intermediates are also indicated. The intermediates were identified by GC–MS.

Table 2

Pentachlorophenol, chlorinated phenol intermediates, phenol, and cyclohexanol/cyclohexanone concentrations after reaction with the metallic systems after 240 min of reaction time<sup>a</sup>

Metallic system	PCP (mM) (S.D.)	Phenol (mM) (S.D.)	Cyclohexanol/cyclohexanone (mM) (S.D.)	Identified chlorophenols			Carbon balance (%)
				Tri	Tetra	Tetra	
Control	2.48	0	0	–	+	1.00	100
Mg	2.22 ± 0.03	N.D.	N.D.	–	+	0.63	104
Pd (319 ppm)/Mg	0.37 ± 0.02	N.D.	0.05 ± 0.04	–	–	0.00	34
Pd (2659 ppm)/Mg	0.25 ± 0.02	0.13 ± 0.00	0.16 ± 0.01	–	–	0.00	35
Fe	2.77 ± 0.08	N.D.	N.D.	–	+	0.83	115
Pd (4856 ppm)/Fe	2.06 ± 0.06	0.16 ± 0.01	0.07 ± 0.00	+	+	0.96	110

<sup>a</sup> See Table 1 for other explanations and reaction conditions.

Table 3  
Chlorinated phenol degradation time at 30 min reaction time<sup>a</sup>

Metallic system	4-CP and 2,6-DCP (mM) (S.D.)	2,4,6-TCP (mM) (S.D.)	Phenol (mM) (S.D.)	Cyclohexanol/ cyclohexanone (mM) (S.D.)	Carbon balance (%)
Control	5.38	3.03	N.D.	N.D.	100
Mg	7.35 ± 0.23	1.92 ± 0.07	N.D.	N.D.	111
Pd (319 ppm)/Mg	0.55 ± 0.01	0.65 ± 0.02	4.20 ± 0.48	0.09 ± 0.00	65
Pd (2659 ppm)/Mg	N.D.	N.D.	6.31 ± 0.22	0.21 ± 0.01	78
Fe	7.84 ± 0.12	2.12 ± 0.03	N.D.	N.D.	118
Pd (4856 ppm)/Fe	6.73 ± 0.13	1.92 ± 0.03	0.90 ± 0.003	N.D.	114

<sup>a</sup> Both 4-chlorophenol and 2,4-dichlorophenol had the same GC retention time and thus, were quantified together. The initial concentrations of 4-chlorophenol, and 2,6-dichlorophenol were 2.86, 2.52 mM, respectively.

Fig. 2 illustrates phenol production from the degradation of 2.48 mM PCP for each system examined in this study. Tables 1 and 2 highlights that phenol production for both Pd/Mg systems was far less than might be expected given the amount of PCP degraded at the 30 and 240 min time intervals. Both Pd/Mg systems were quite efficient at removing the tetrachlorophenol contaminant.

Each metallic and bimetallic system was studied for their ability to degrade 4-chlorophenol, 2,6-dichlorophenol, and 2,4,6-trichlorophenol. These chlorinated phenols were selected as possible intermediates for PCP dechlorination and because of their own pollution concerns [4,6,23]. Table 3 summarizes the GC–FID analysis results of the hexane extraction of the exposure of a 2.48 mM mixture of these chlorinated phenols to each reductive dechlorination system. At the 30 min time interval only Pd/Mg systems were able to degrade significantly the mixtures of the chlorinated phenols.

It should be noted that on occasion both Fe and Pd/Fe runs gave greater than 100% extraction efficiencies (see Tables 1–4). Such effect has been noted for Fe(0), PCP solutions [4]. This phenomenon may be attributable to the formation of Fe<sup>2+</sup>(aq) species which may improve extraction efficiency.

### 3.1. Complete dechlorination of pentachlorophenol

The complete disappearance of PCP to non-chlorinated products under the reaction conditions described in this investigation was noted for both Pd (319 ppm)/Mg (1.00 g) and Pd (2659 ppm)/Mg (1.00 g) after they were allowed to react with 5.00 ml 2.48 mM PCP for 48 h. A GC–FID analysis of both systems indicated the complete disappearance of PCP with only cyclohexanol/cyclohexanone detected as a product (25% yield) (Table 4). The approximate detection limit (DL) of GC–FID was 0.5 ppm. Analysis of the products of the 319 ppm Pd/Fe and 2659 ppm Pd/Mg systems by GC–MS (100 ppb DL) revealed a small peak, and no peak for PCP, respectively. The latter Pd/Mg system was further examined for low-volatility components by direct probe-MS at 350 °C for masses between 50 and 800 amu. No peaks were observed. Other metal systems are summarized in Table 4.



Table 4

Pentachlorophenol, chlorinated phenol intermediates, phenol, and cyclohexanol/cyclohexanone concentrations (mM) after reaction with the metallic systems after 48 h of reaction time<sup>a</sup>

Metallic system	PCP (mM) (S.D.)	Phenol (mM) (S.D.)	Cyclohexanol/cyclohexanone (mM) (S.D.)	Identified chlorophenols			Carbon balance (%)
				Tri	Tetra	Tetra	
Control	2.48	N.D.	N.D.	–	+	1.00	100
Mg	2.12 ± 0.02	N.D.	N.D.	–	+	0.56	85
Pd (319 ppm)/Mg	0.23 ± 0.01	N.D.	0.23 ± 0.00	–	+	0.04	19
Pd (2659 ppm)/Mg	N.D.	N.D.	0.63 ± 0.01	–	–	0.00	25
Fe	2.52 ± 0.12	N.D.	N.D.	–	+	0.86	102
Pd (4856 ppm)/Fe	0.33 ± 0.01	0.84 ± 0.08	0.11 ± 0.00	+	+	0.71	52

<sup>a</sup> See Table 1 for other explanations and reaction conditions.

#### 4. Discussion

None of the PCP concentration decay curves in Fig. 1 follow pseudo-first-order kinetics. This characteristic is probably attributable to the presence of  $O_2$ , which may cause the formation of insoluble surface oxides. This is consistent with previous studies of Pd-catalyzed zero-valent metal dechlorinations of halocarbon pollutants under aerobic conditions [4,13,24,25]. The greatest significance of Fig. 1 is the demonstration of the greater efficiency of PCP removal for the Mg(0) systems over Fe(0) and Pd/Fe. Such characteristic has been previously observed for the dechlorination of DDT [24]. Perhaps the two most significant reasons for the increased reactivity of Mg(0) over Fe(0) are (i) the redox potential for metal dissolution,  $-2.2$  V, NHE for  $E_{Mg^{2+}/Mg}^0$  versus  $-0.44$  V, NHE for  $E_{Fe^{2+}/Fe}^0$ , and (ii) the relative solubilities for the passivating metal hydroxides,  $pK_{sp}$  Mg(OH) $_2 = 11.2$  versus  $pK_{sp}$  Fe(OH) $_2 = 15.1$ . Equal surface areas of unmodified Mg was observed to dehalogenate the chlorinated phenols with approximately the same efficiency as Pd (4060 ppm)/Fe (see Fig. 1, and Tables 1–4).

In this investigation, palladized iron was incrementally more efficient at the dehalogenation of PCP than unmodified iron (Fig. 1). This result differs from a previous investigation [4]. However, this study used slightly different conditions from the reported literature, thus, the two investigations may be consistent. One major difference between the two studies was the storage of dried bimetallic systems. In this investigation, it was observed that attempts at preparation of air-dried bimetallic systems for long-term storage invariably failed because of rapid oxidation of the substrate metal surfaces. Stored bimetallics, therefore, were much less active in dechlorination efficiency than freshly prepared samples. This is consistent with another investigator's observations [26]. It is expected that long-term storage is feasible if careful precautions are taken to exclude  $O_2$ .

Phenol is the carbon backbone of the chlorinated species used in this study and thus, thought to be the most logical product. Cyclohexanol and cyclohexanone were also detected as products. These species are probably formed as a result of the hydrogenation of phenol. It was found that the Pd/Mg systems were able to hydrogenate phenol to cyclohexanol and cyclohexanone. A previous investigation of the dechlorination of PCP by Fe(0) and Pd (500 ppm)/Fe indicated that complete degradation to phenol was not achieved [4]. In that study 1.00 g of Fisher finer than 100 mesh iron, both unaided and Pd (500 ppm) modified were found to degrade 37.5  $\mu$ M PCP (10.00 ml) to a variety of chlorinated phenols in pure aqueous conditions. Under the conditions described for this investigation, it was observed that Pd (4060 ppm)/Fe (0.6552 g) degraded 2.50 mM to a significant quantity of phenol after 240 min (Fig. 2). However, at the 30 min time interval both Fe(0) and Pd/Fe degraded the investigated chlorinated phenols with approximately the same efficacy (Table 3). Tables 1–4 also demonstrates the greater relative ability of the Mg systems to dehalogenate the examined chlorinated phenols albeit without production of phenol.

The lack of carbon balance evident in Tables 1–4 for the Pd/Mg systems may be attributable to the formation of multi-radical intermediates, which may not be well stabilized by aromatic phenol ring. Fig. 2 demonstrates that phenol production for the Pd/Mg system is much lower than might be expected for the quantity of PCP degraded in Tables 1 and 2. Using the quantity of PCP degraded, total product yields at 30 and 240 min for Pd

(2659 ppm)/Mg are 11.5 and 13%, respectively. The yield for the degradation of the combined 4-CP, 2,6-DCP, and 2,4,6-TCP was 78% (see Table 3). This may indicate that heavier chlorination about the phenol ring increases the chances of the production of multi-radical species, which rapidly degrade to lower molecular weight species. Mass spectral results (detection limit  $\approx$  100 ppb) do not indicate any chlorinated compounds. A variety of low-molecular weight hydrocarbons were detected, but these may be minor components of the extraction solvent. The possibility of high molecular weight species, i.e. products due to radical couplings was ruled out from the lack of any detectable compounds from direct probe mass spectroscopy. We, therefore, hypothesize that Pd/Mg rapidly dechlorinates PCP to non-chlorinated low molecular compounds, which may have significant volatility. It was for this reason that a carbon balance was not possible in this investigation.

The demands of large-scale remediations may require aqueous or mostly aqueous dechlorination conditions. However, pentachlorophenol exhibited limited solubility in pure aqueous solutions. The Pd/Mg dechlorination system requires solvation of PCP, and water as a source of protons in Reaction 2 and for metal corrosion in Reaction 1. Although the use of 50/50 (v/v) 2-propanol/water as a dechlorination medium might seem to preclude the widespread viability of the Pd/Mg system, it is noteworthy to add that at least one pilot scale study proposes to use the water/ethanol solvent for the extraction of PCP from contaminated studies [27]. Such solvent system would be ideal for the Pd/Mg dechlorination system demonstrated in this investigation.

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