

Enhanced Corrosion-Based Pd/Mg Bimetallic Systems for Dechlorination of PCBs

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Polychlorinated biphenyls (PCBs) are toxic pollutants notorious for their aquatic and sedimentary prevalence and recalcitrant nature. Bimetallic systems like Pd/Fe have been widely studied for degrading them. Mg, with oxidation potential higher than Fe, has been reported to dechlorinate PCBs in conjunction with K_2PdCl_6 —systems that are distinct from Pd/Mg bimetallics. This study primarily aims to evaluate Pd/Mg bimetallic systems for dechlorinating 2-chlorobiphenyl (2-CIBP), a model PCB. Candidacy of Mg is based on its unique corrosion properties that afford synthesis and storage under ambient conditions and application-based advantages. A simple wet-chemistry procedure was developed to synthesize Pd/Mg particles with 0.11–1.62% Pd content and nanoscale Pd-islands as determined by X-ray diffraction (XRD) and environmental scanning electron microscopy (ESEM). Aqueous 2-CIBP matrices were effectively degraded using these particles, the dechlorination kinetics showing linear dependence on the total Pd content. The pH profile obtained with varying bimetallic content led to useful insights into the unique behavior of Mg surface. A carbon mole balance showed 85–105% recoveries. Performance of the Pd/Mg particles in PCB spiked clays and sediment suggests that they may work well in such systems. Finally, a mechanism for PCB dechlorination in Pd/Mg systems was proposed.

Introduction

PCBs, a family of 209 compounds that were manufactured until the mid-1970s for use in electrical equipment, were banned in 1979 due to their toxicity and persistence in the environment (1). Over the years, a variety of approaches have been tested for remediating PCB contaminated matrices with limited success (2–4). Dechlorination of PCBs using bimetallic systems is a promising technology wherein enhanced corrosion of a reactive metal is combined with catalytic hydrogenation properties of a noble metal to drive the reduction of PCBs at the bimetallic interface (5). Pd/Fe bimetallic systems have been demonstrated to completely dechlorinate trichloroethylenes (6) and PCBs (7). Numerous

research studies have been conducted since then to understand, optimize, and apply these systems (8–11). However, Fe tends to corrode spontaneously (both in pure and coupled forms) requiring surface pretreatment and synthesis and storage in anaerobic conditions. Mg, on the other hand, is considered better-suited for such purposes, although the factors responsible have not been reported. In addition, it has an oxidation potential of 2.372 V that is significantly higher than 0.44 V of Fe (12), and thus a greater force to drive the hydrodehalogenation reaction (13). These properties of Mg coupled with its natural abundance, low cost, and environmentally friendly nature have led to growing interest in Pd/Mg-based dechlorination systems as in ongoing studies by Gardner and co-workers (14).

Doyle et al. (15) were among the first to use “Pd/Mg bimetallic particles” to dechlorinate PCBs. In their study with Fe and Mg as substrates, Fe was palladized in a separate step before being used for dechlorinating PCBs. However, the two steps were combined by adding PCB solution to a mixture of solid K_2PdCl_6 and Mg to palladize the Mg in-situ and simultaneously dechlorinate PCBs. The two systems were termed Pd/Fe and Pd/Mg bimetallic particles and investigators (13, 16–18) continued to classify and treat the K_2PdCl_6 /Mg system as Pd/Mg bimetallic systems, even though they are distinct. Dechlorination by K_2PdCl_6 /Mg systems is best explained by cementation-induced redox of organics (19). Systems such as Cu^{2+}/Al , Cr^{3+}/Fe undergo spontaneous cementation involving the induction of multiple anodic sites for dissolution of the active metal and cathodic sites for the reductive deposition of the noble metal ions. Side-reactions involving other bulk species which occur simultaneously due to intense cementation have been successfully tested for the treatment of organics (19) and most likely govern the initial and intermediate organic degradation in K_2PdCl_6 /Mg systems. Even though a combination of cementation and bimetallic corrosion-driven degradation at a later stage cannot be excluded, K_2PdCl_6 /Mg and Pd/Mg systems should not be treated as the same.

In general, K_2PdCl_6 /Mg systems have been poorly understood. Studies involving these systems (13, 15, 16, 18) except by Morales et al. (17) do not report any details on the kinetics of the process. Excessive reactants were used to dechlorinate small amounts of Aroclors developing these systems more as an analytical tool to quantify total PCBs than as a potential method for remediating contaminated matrices. Even though, K_2PdCl_6 /Mg systems may be an effective preparatory tool for PCB analyses, they have major remediation-based limitations.

The primary objective of the study was to evaluate Mg as a substrate in Pd-doped bimetallic particles for dechlorinating PCB matrices. The candidature of Mg was substantiated by its dechlorination performance and by tracing the distinctive advantages it offers in synthesis, storage, and application to its unique corrosion properties. The bimetallic particles were synthesized using a simple wet-chemistry procedure and characterized for the content and morphology of Pd deposits using an inductively coupled plasma-atomic emission spectrometer (ICP-AES), XRD, and ESEM. The effects of Pd-doping and bimetallic loading on dechlorination kinetics were studied in pure aqueous systems. The pH variation with bimetallic content was investigated for plausible effects on the kinetics of these systems. The effectiveness of these particles to dechlorinate PCBs in sediment and clays was also assessed. A carbon mole balance was conducted throughout to minimize unexplained PCB losses. Based on our findings, a mechanism for dechlorination in Pd/Mg

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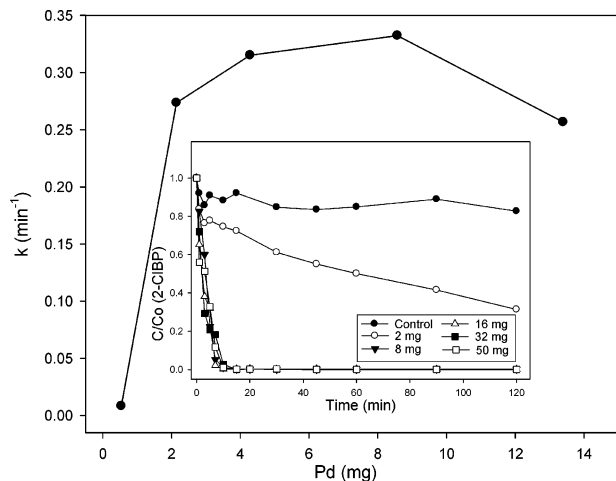


FIGURE 1. First-order dechlorination rate constant k of 2-CIBP in K_2PdCl_6/Mg system. Inset is dechlorination of 2-CIBP over time.

systems was proposed to integrate the unique corrosion behavior of Mg into the established dechlorination pathway in bimetallic systems. In addition, we attempted to verify that K_2PdCl_6/Mg systems as reported in the literature and Pd/Mg systems discussed here are not the same.

Experimental Section

All experiments were done in ambient conditions. 2-CIBP was used since its solubility of 5.9 mg/L is highest among all PCB congeners, and it gives a single dechlorination product which allows us to focus on evaluation of process potential.

K_2PdCl_6/Mg System. Calculated amounts of K_2PdCl_6 (99%, Sigma) and 0.24 g Mg (-40#/+80, Sigma) were weighed out in 60 mL glass vials with septa caps (Fisher). A 3.25 mg/L aqueous solution of 2-CIBP (99%, Accustandard) was added to start the cementation reaction where Pd^{4+} is reductively deposited onto Mg as elemental Pd, inducing dechlorination of 2-CIBP (17). Samples were taken at predetermined time intervals with 1 mL syringes (Hamilton, Fisher) through the septa for closed-system reaction conditions and collected in 3 mL micro-reaction vessels (Supelco) filled with 1.5 mL of 70:30 hexane: acetone cosolvent. They were extracted on a platform shaker (Burnswich Scientific) at 165 rpm and 35 °C for 18 h followed by centrifugation (Centrifac) at 1200 rpm for 10 min. The water-free organic phase (0.5 mL) was pipetted out, spiked with 10 μ L of the internal standard (200 ppm D-8 Naphthalene in dichloromethane) and analyzed in the gas chromatograph (HP 6890)/mass spectrometer (HP 5973). The GC/MS was equipped with a Supelco SPB-5 30 m \times 0.32 μ m \times 0.25 μ m column; the calibration curves had R^2 of greater than 0.999 based on eight-point data; the method detection limit was 50 μ g/L.

Pd/Mg Bimetallic system. A. Synthesis. Calculated amounts of K_2PdCl_6 were added to ethanol (Fisher) and stirred for 1 h. Ethanol, used as the medium here, limits corrosion of Mg, unlike water which corrodes Mg during synthesis, compromising its dechlorination potential. Mg particles (-325#, Sigma) were then added to each of the flasks and the resulting slurry was stirred for 2 h wherein elemental Pd deposited onto Mg to form the bimetallic particles. The slurry was then vacuum filtered (Whatman Ashless, Fisher). The particles were washed with acetone to remove excess Pd-salts, dried for 2 min under vacuum, and stored in an anaerobic chamber.

B. Characterization. The Pd content of bimetallic particles was determined by an ICP-AES (IRIS Intrepid, Thermo Electron Corporation, CA) after microwave-assisted digestion (EPA method 3051). The size of Pd crystallites on the Mg particles was determined by X-ray diffraction (Phillips

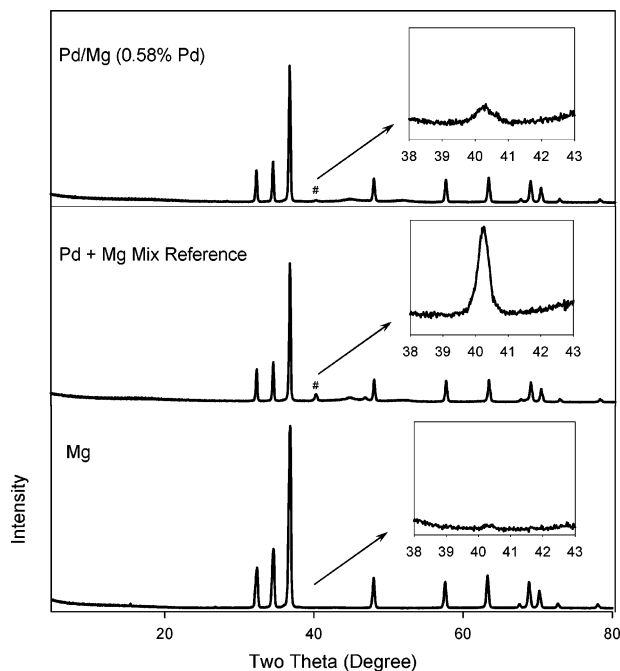


FIGURE 2. XRD patterns for Pd/Mg bimetallic particles, Pd-Mg mixture reference and elemental Mg. The peaks for Pd (#) were of weak intensity due to the small amounts doped.

TABLE 1. Pd Content and Pd-island Size of Pd/Mg Particles

desired Pd doping (%)	actual Pd doping (%)	Pd-crystal size (nm)
0.2	0.11	- ^a
0.5	0.34	45.6
1	0.58	47.8
2	1.62	47.6

^a no peak observed due to low Pd content

PW3040/00 X'Pert-MPD diffractometer system) using Scherrer formula (20). A mechanical mixture of Pd and Mg was used as reference (21). The distribution of Pd-islands on the surface of Mg was determined by an ESEM with field emission gun (Phillips XL 30 ESEM-FEG).

C. Degradation Studies. Aqueous Matrix. Bimetallic particles were weighed out in vials and 60 mL of a 4 mg/L aqueous solution 2-CIBP was added. Sampling and analysis were done as before. The samples were extracted in 4 mL vials (Fisher) with 2 mL hexane by shaking on a vortex mixer for 1 min.

Clays and Sediment Matrix. One gram each of Montmorillonite and Kaolin (clays) and Caesar Creek Sediment (CCS, 3.4% organic matter) were put in 40 mL glass vials (Fisher) and spiked with 1 mg of 2-CIBP in 10 mL acetone. The vials were tumbled at 45 rpm for 1 h followed by evaporation of the acetone in an oven at 60 °C for 4 h to obtain PCB-spiked soils. The 2-CIBP was extracted from the soils into 10 mL of added hexane by vigorous mixing on a vortex shaker for 2 min. 25 μ L of hexane was sampled in triplicates from each of the vials and diluted 20 times before being analyzed as described before. This gave the baseline PCB concentration in each substrate. There were four sets of vials for each substrate thus spiked: acetone-water (1:1)-soil slurry and water-soil slurry, both with and without Pd/Mg bimetallic particles. One gram of soil, 0.25 g of bimetal, and 20 mL of solvents were used in all units. Bimetallic particles and 20 mL of solvents (as applicable) were added to each set of vials, put in the shaker at 180 rpm for 12 h followed by extraction with 10 mL of hexane on the vortex shaker for 2 min. The extracts were analyzed using the same procedure followed for the analysis of the spiked soil stocks.

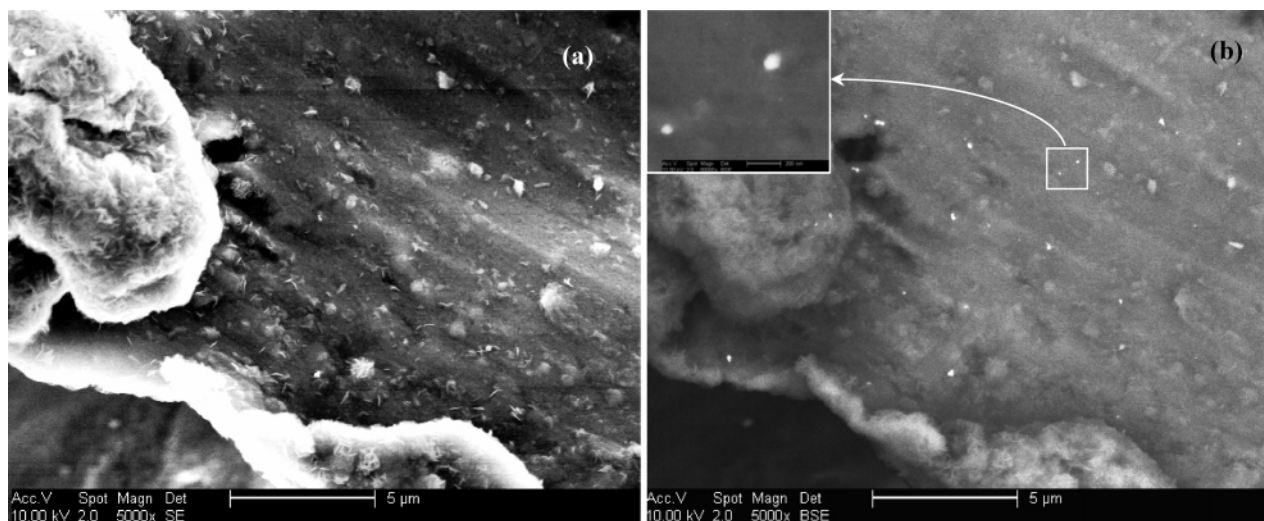


FIGURE 3. ESEM images of a Pd/Mg particle with 0.58% Pd taken by secondary (a) and backscattered (b) electron detectors. Inset shows two Pd-islands magnified at 80 000 \times .

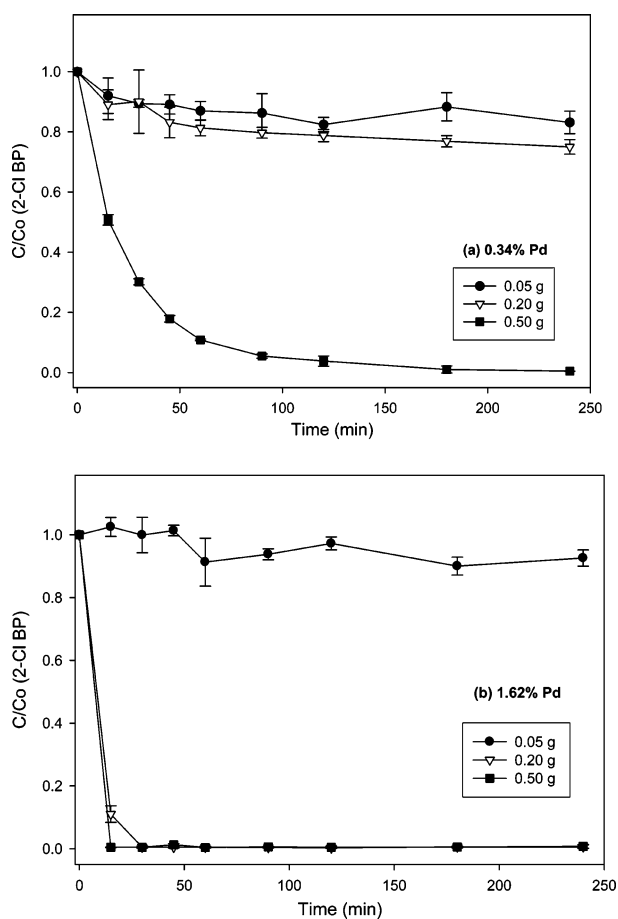


FIGURE 4. Effect of Pd/Mg loading on the kinetics of dechlorination of 2-CIBP at (a) 0.34% Pd and (b) 1.62% Pd.

Results and Discussion

K_2PdCl_6/Mg Systems. As shown in Figure 1, pseudo first-order dechlorination kinetics were observed in K_2PdCl_6/Mg systems. The rate increased, reached a maximum, and then decreased with increasing concentration of Pd^{4+} . First-order kinetics and such trends in the rate as seen are well established in cementation systems (22). They are attributed to the difference in the morphology of noble metal deposits or to the transition of deposition from a migration-limited process to one limited by diffusion (22) or both. Bimetallic

particle-based dechlorination is not known to exhibit such behavior. Support along these lines also comes from detection of cyclohexanone during the destruction of chlorophenols by K_2PdCl_6/Mg systems (17). This is compelling evidence that cementation, which causes parallel redox of secondary species, is a prominent, if not the only, mechanism involved as bimetallic particles dechlorinate reductively and will not oxidize chlorophenols to cyclohexanone. Further, there are practical limitations in the adoption of these systems for treatment purposes. Use of K_2PdCl_6/Mg at contaminated sites implies application of the Pd-salt directly to the ecosystem where they can be potentially hazardous. Also, Mg will have to compete with sediments for capturing the Pd salt, which, apart from adsorbing on unreactive substrates, can get carried away in water currents leading to high wastages, and thus impaired treatment efficiencies. It has been reported that direct treatment of PCB contaminated soil with a K_2PdCl_6/Mg in a small batch system led to little or no dechlorination with this method (18) most probably due to interferences discussed above. Smaller amounts of Pd/Mg particles resulted in complete dechlorination of 2-CIBP in this study. Moreover, Pd/Mg can be applied while contained in a reactive barrier thereby reducing the bioavailability of Pd critical to environmental applications.

Pd/Mg Bimetallic Systems. The XRD patterns obtained for Pd/Mg bimetallic particles (0.58% Pd), a mechanical mixture of Pd–Mg (reference) and elemental Mg are shown in Figure 2. The broadening of the Pd peak in Pd/Mg particles as compared to the Pd–Mg reference mixture was used to calculate the size of Pd crystallites (21). Table 1 lists the amount of Pd doped on each Mg substrate and the corresponding crystallite size which was consistently between 45 and 48 nm. Doping efficiencies of 55–80% are a stark reminder of the potential wastage of Pd and hazards involved in the direct application of its salts for cementation purposes where the contact time may be a small fraction of 2 h used here, depending on uncontrolled site-specific factors.

SEM images of a bimetallic particle sample with 0.58% Pd taken by secondary and backscattered electron detectors (SE and BSE) are shown in Figure 3a and b respectively. As seen in Figure 3a, the Mg surface is rich in contours making identification of tiny Pd-islands difficult with an SE detector which provides a more detailed surface imagery. The Pd-islands were clearly identifiable as minute bright spots in the BSE image shown in Figure 3(b). This is because elements with higher atomic number (Pd) appear significantly brighter than ones with a lower number in a BSE image (23). Also,

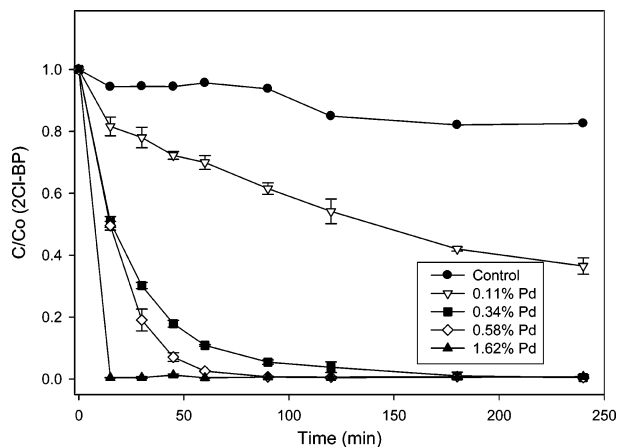


FIGURE 5. Effect of Pd-doping levels on the dechlorination kinetics of 2-CIBP with Pd/Mg loading constant at 0.5 g.

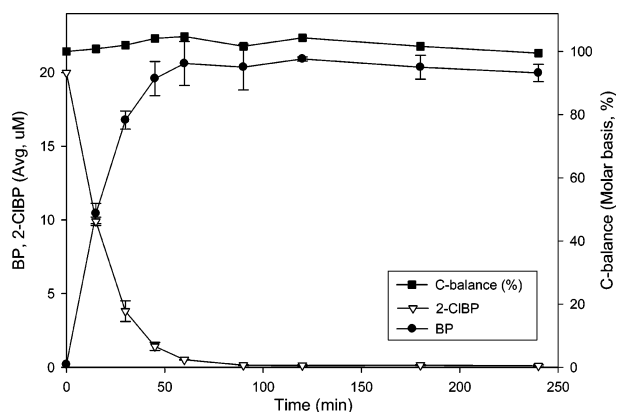


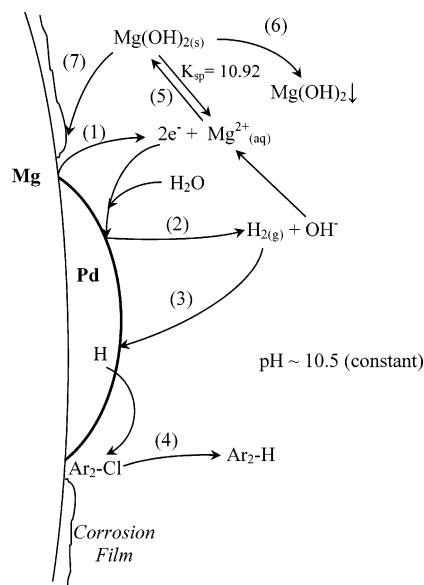
FIGURE 6. Carbon-mole balance for a system with 0.5 g of Pd/Mg particles and 0.58% Pd-doping.

from Figure 3b, it can be said that the Pd-islands have a small size distribution between 50 and 100 nm and are sparsely distributed on the Mg surface. Some agglomeration of Pd crystallites was noted at 1.62% Pd doping.

(i) *Dechlorination Studies with Aqueous PCBs. Effect of Bimetallic Loading.* Dechlorination studies were conducted in triplicate with varying bimetallic content and Mg-only controls. Dechlorination of 2-CIBP was found to be rapid and complete with 0.5 g of bimetallic particles as shown in Figure 4. The difference in dechlorination rates between systems with 0.05 and 0.2 g bimetallic particles, though not remarkable, was observed in all sets of constant Pd-doped systems, more so in terms of biphenyl generated. Systems with 1.62% Pd were an exception where rapid dechlorination kinetics, almost as fast as those in 0.5 g systems, were seen with 0.2 g of the bimetals (Figure 4b).

Effect of Pd-Doping Levels. Vastly improved dechlorination kinetics with increased Pd-doping were seen in units with 0.5 g of bimetallic loading (Figure 5). Further, pseudo first-order constants for these units plotted against their total Pd content showed a linear trend ($R^2 = 0.97$) indicating a direct correlation between the two. Increased doping at a given Pd/Mg loading and fairly constant Pd-island size means increased number of Pd-islands. The dechlorination reactions occur at the bimetallic interface (5). Hence, an increased number of Pd-islands implies increased dechlorination sites. The acceleration in kinetics with Pd-doping in systems with 0.2 g Pd/Mg particles, though not very drastic, was clearly observed in 0.34, 0.58, and 1.62% Pd-doped systems.

SCHEME 1. Proposed Scheme for Enhanced Corrosion-based Pd/Mg Bimetallic Systems for Dechlorination of PCBs



Carbon Mole Balance. A carbon balance plot for a system with 0.5 g Pd/Mg loading and 0.58% Pd-doping is shown in Figure 6. The mole balance showed recoveries in the range of 85–105% for all units except for the one with the highest Pd content (~75%). Lower recoveries were seen when experiments were run for 12 h. This may be attributed to (a) the further reduction of BP, 2-CIBP, the only product measured during the study and/or (b) by loss of BP via adsorption on $Mg(OH)_2$, the corrosion product, precipitated in the system.

pH Profiles. Bimetallic corrosion involves consumption of H^+ and generation of OH^- entailing probable influence of pH on the process. However, a pH study on the experimental design yielded unexpected results. The pH increased from near neutral, initially, to ~10.6 within the first sampling event and remained steady throughout in all units, including those with only Mg. The remarkable similarity of pH profiles was traced to the corrosion behavior of Mg surfaces.

The surface of elemental Mg in ambient conditions may show scattered corrosion but otherwise remains largely unaffected as confirmed in our study by SEM analysis. Impure Mg surface forms a partially protective film of crystalline $Mg(OH)_2$ by superficial corrosion. This film is weaker than that formed in Al but much stronger than the flaky, non-adherent film in Fe (24). On being immersed in water, part of the oxide spots or layer dissolves quickly saturating the water with sparingly soluble $Mg(OH)_2$ bringing the pH to a steady 10.5 (24). In Pd/Mg particles, the Pd islands act as cathodes facilitating accelerated localized galvanic corrosion, breaching the metastable film further. Mg starts corroding and generating OH^- , favoring the formation of $Mg(OH)_2$, part of which goes into repairing the protective oxide layer (25). This means that corrosion prompts repair of the film making the system self-regulated (25). These unique corrosion properties of Mg carry powerful practical implications. The largely pristine nature of exposed Mg particles allows it to be doped without surface pretreatment. The quasi-passive hydroxide film formed on thus doping Mg particles enables storage in ambient conditions without compromising dechlorination potential. Breakdown of the partially protective film in water by corrosion at localized cathodes produces dechlorination at the bimetallic interface.

The widely accepted dechlorination mechanism in Pd/Fe particles (5) is being modified by including the self-limiting corrosion behavior of Mg to propose a mechanism for

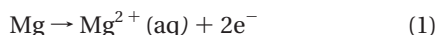
TABLE 2. Dechlorination of 2-chlorobiphenyl in Clays and Sediment (all 2-CIBP, BP Concentrations in $\mu\text{mol/g}$ Sediment)

substrates	20 mL acetone–water (1:1)–soil slurry EUs						20 mL water–soil slurry EUs			
	spiked soil (1 g)		with Pd/Mg (0.8% Pd, 0.25 g)		only–Mg controls		with Pd/Mg (0.8% Pd, 0.25 g)		only–Mg controls	
	2–CIBP	BP	2–CIBP	BP	2–CIBP	BP	2–CIBP	BP	2–CIBP	BP
kaolin	2.28	0.01	0.01	2.46	2.91	0.01	0.00	0.68 ^a	2.68	0.01
KSF	2.75	0.01	0.34	2.60	2.92	0.02	0.01	2.09	2.00	0.01
CCS	2.78	0.00	0.01	3.56	3.75	0.03	0.01	1.67	1.65	0.01

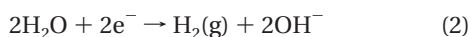
^a A leak resulted in poor recoveries

dechlorination in Pd/Mg systems (schematic 1) based on the following equations:

Corrosion of Mg at the anode, $E^\circ = 2.372 \text{ V}$



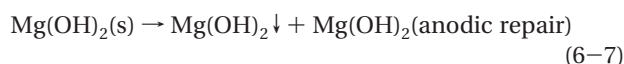
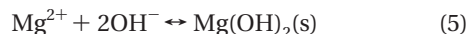
Electrolysis of water, $E^\circ = -0.8277 \text{ V}$ (12) and intercalation of $\text{H}_2(\text{g})$ in Pd lattice at cathode (5)



Hydrodechlorination of organics at the bimetallic interface (8)



Dynamic partitioning of $\text{Mg}(\text{OH})_2$ in the bulk as soluble species, for anodic film repair and precipitate; K_{sp} of $\text{Mg}(\text{OH})_2 = 10.92$ (26)



(ii) *Dechlorination of PCBs in Clays and Sediments.* Results from the batch study to evaluate the ability of the Pd/Mg particles to dechlorinate PCBs in two clays and CCS have been summarized in Table 2. In general, carbon recoveries in acetone–water units were higher than in water-only units due to the nature of the solvent. No 2-CIBP was detected in any units with Pd/Mg particles, an exception being Montmorillonite unit with cosolvent where the dechlorination was 88%. This suggests that Pd/Mg bimetallic particles work well not only in soil–water slurry systems aided by enhanced extraction using organic solvents, but in stand-alone water–slurry systems as well.

Pd/Mg bimetallics can be used in reactive barriers to treat highly chlorinated plumes in groundwater aquifers and submarine matrices where the redox environment often favors reduction. Pd/Mg barriers in sediment beds can deplete the dissolved organics adjacent to the contaminated sediments inducing their desorption into the aqueous phase thereby reducing their concentrations in the sediment. Pd will be contained in such barriers allowing recycling of Pd while ensuring that it is not free to enter the natural waters. Reductive dechlorination by Pd/Mg can also be a primary treatment step before the application of oxidative technologies which may falter with highly chlorinated organics (4).

In natural waters, Pd/Mg particles should experience enhanced corrosion as chloride ions attack and break down the film locally (25). Near neutral pH in water bodies will likely lead to accelerated corrosion and hence dechlorination rates higher than in bench-scale systems where pH is

regulated by Mg^{2+} chemistry. Irrespective of corrosion conditions, the self-limiting nature of process due to corrosion induced oxide-layer repair implies that Pd/Mg bimetallic particles are likely to have a long active lifetime. However, Mg is difficult to synthesize on a nanoscale by the reduction of Mg salts in solution due to its high oxidation potential. Nanoscale Mg and Pd/Mg hold vast promise, when synthesized with procedures that can be adopted for inexpensive large scale production.

Acknowledgments

This paper has not been subjected to internal policy review of the U.S. Environmental Protection Agency. Therefore, the research results presented herein do not, necessarily, reflect the views of the Agency or its policy. Mention of trade names or commercial products does not constitute endorsement or recommendation for use. The authors greatly appreciate Hyeok Choi for insightful feedback on the manuscript, and Aaron Williams, Gautham Jegadeesan, and Scott Korfhagen for help in the XRD, ICP, and SEM analyses.

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